Physical Chemistry
Part 2: Quantum Mechanics, Spectroscopy, and Statistical Mechanics:
Answers to Problems

(To accompany the text in Physical Chemistry)

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Thomas W. Shattuck
Colby College
Waterville, Maine

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Chapter

Chapter 23 Problems: Foundations of Quantum Mechanics

1. A typical mid-infrared spectrophotometer for studying molecular vibrations has a wavenumber range from 4000. cm^{-1} to 400. cm^{-1}. (NaCl cell windows have a 460 cm^{-1} long-wavelength cutoff and KBr has a 345 cm^{-1} cutoff.) Calculate the frequency and energy range for the mid-IR. Express the energy units in J, eV, and kJ mol^{-1}.

Answer: The conversions are given by $\nu\lambda = c$ and $\tilde{\nu} = 1/\lambda$ with the energy as:

$E = h\nu = hc/\lambda = hc\tilde{\nu}$ in J
$E = h\nu/e = hc\tilde{\nu}/e$ in eV $1 \text{ eV} = 96.485 \text{ kJ mol}^{-1} = 8065.5 \text{ cm}^{-1}$
$E = N_A h\nu \ (1 \text{ kJ}/1000\text{J})$ in kJ mol^{-1} $1 \text{ cm}^{-1} = 11.962 \text{ J mol}^{-1}$

Wavenumbers can be converted into m^{-1} to match the units of $c = 2.9979 \times 10^8 \text{ m s}^{-1}$:

$\tilde{\nu} = 4000 \text{ cm}^{-1}$ corresponds to $\tilde{\nu} = 4000 \text{ cm}^{-1}(100 \text{ cm}/1 \text{ m}) = 4.000 \times 10^5 \text{ m}^{-1}$:
$\nu = c/\lambda = 2.998 \times 10^8 \text{ m s}^{-1} (4.000 \times 10^5 \text{ m}^{-1}) = 1.199 \times 10^{14} \text{ s}^{-1}$

Alternatively, the wavenumber may be kept in cm^{-1} and then $c = 2.9979 \times 10^{10} \text{ cm s}^{-1}$:

$E = hc\tilde{\nu} = 6.6261 \times 10^{-34} \text{ J s } (2.9979 \times 10^{10} \text{ cm s}^{-1})(4000 \text{ cm}^{-1}) = 7.946 \times 10^{-20} \text{ J}$
$E = hc\tilde{\nu}/e = 7.946 \times 10^{-20} \text{ J}/1.6022 \times 10^{-19} \text{ C} = 0.4959 \text{ eV}$
$E = N_A h\nu \ (1 \text{ kJ}/1000\text{J}) = 6.0221 \times 10^{23} \text{ mol}^{-1}(7.946 \times 10^{-20} \text{ J})(1 \text{ kJ}/1000\text{J}) = 47.85 \text{ kJ mol}^{-1}$

Alternatively, the conversion factors that are listed above may be used.
At 400. cm^{-1} the values are just a factor of ten different:

$\nu = c/\lambda = 2.998 \times 10^8 \text{ m s}^{-1} (4.000 \times 10^4 \text{ m}^{-1}) = 1.20 \times 10^{13} \text{ s}^{-1}$
$E = 7.946 \times 10^{-21} \text{ J} = 0.0496 \text{ eV} = 4.79 \text{ kJ mol}^{-1}$

These energies are not sufficient to break typical covalent bonds. However, if a sample absorbs the infrared light, the energies give the heat effect for the sample.

2. Complete the following table. For the region, choose from radiowave, microwave, infrared, visible, and ultraviolet.

λ (cm)	λ (μm)	λ (nm)	ν (s^{-1})	E (J)	E (eV)	E (kJ mol^{-1})	$\tilde{\nu}$ (cm^{-1})	region
			100 MHz					
			10 GHz					microwave
							1	
	10							
		1000						
					2			
						200		
		500						
		350						
		190						
							100,000	

Answer: The conversions are given by $\nu\lambda = c$ and $\tilde{\nu} = 1/\lambda$ with:

$E = h\nu = hc/\lambda = hc\tilde{\nu}$ in J
$E = h\nu/e = hc\tilde{\nu}/e$ in eV 1 eV = 96.485 kJ mol^{-1} = 8065.5 cm^{-1}
$E = N_A\, h\nu$ (1 kJ/1000J) in kJ mol^{-1} 1 cm^{-1} = 11.962 J mol^{-1}

The following spreadsheet was developed:

λ (cm)	λ (μm)	λ (nM)	ν (s^{-1})	E (J)	E (eV)	E (kJ/mol)	$\bar{\nu}$ (cm^{-1})	region
299.79	3.00E+06	3.00E+09	1.00E+08	6.63E-26	4.14E-07	3.99E-05	0.0033	radiowave
2.9979	29979	3.00E+07	1.00E+10	6.63E-24	4.14E-05	3.99E-03	0.3336	microwave
1	10000	10000000	3.00E+10	1.99E-23	1.24E-04	1.20E-02	1	far-IR
1.00E-03	10	10000	3.00E+13	1.99E-20	0.124	11.96	1000	mid-IR
1.00E-04	1	1000	3.00E+14	1.99E-19	1.240	119.63	10000	near-IR
6.20E-05	0.620	619.92	4.84E+14	3.20E-19	2.000	192.97	16131	red
5.98E-05	0.598	598.13	5.01E+14	3.32E-19	2.073	200.00	16719	red
5.00E-05	0.5	500	6.00E+14	3.97E-19	2.480	239.25	20000	blue-green
3.50E-05	0.35	350	8.57E+14	5.68E-19	3.542	341.79	28571	violet
1.90E-05	0.19	190	1.58E+15	1.05E-18	6.525	629.61	52632	UV
1.00E-05	0.1	100	3.00E+15	1.99E-18	12.398	1196.27	100000	vacuum-UV

The choices have the following correspondences:

100 MHz is a typical NMR frequency (^{13}C)
10 GHz is a typical frequency for microwave-rotational spectroscopy
1000 cm^{-1} is a typical mid-infrared wavenumber (mid-IR range: 4000 cm^{-1} – 400 cm^{-1})
2 eV and 200 kJ mol^{-1} are typical of enthalpies for chemical reactions
500 nm is blue-green visible light
350 nm is the cut-off for glass cuvettes; UV work requires quartz cuvettes
190 nm is the wavelength cut-off for typical UV-Visible spectrophotometers and the approximate beginning of the vacuum UV range.

3. All else being equal, the wavelength of the light in a photoelectric effect experiment is halved. Describe the effect on the photoelectron current and the kinetic energy of the photoelectrons.

Answer: From $\nu\lambda = c$ and $E = h\nu = hc/\lambda$, halving the wavelength doubles the frequency and energy of the exciting light. The photoelectron current remains unchanged, because the number of photons per second remains unchanged. The kinetic energy of the photoelectrons increases, because the energy of the exciting light exceeds the work function by a greater amount:

$$E = \underset{\uparrow}{h\nu} = \underset{\uparrow}{\tfrac{1}{2} m\upsilon^2} + \underset{\text{cst.}}{\Phi}$$

4. Calculate the kinetic energy of a photoelectron emitted by sodium metal when light of wavelength 400.0 nm is incident on it. The work function of sodium is 2.28 eV.

Answer: The energy of the exciting light is:

$$E = h\nu = hc/\lambda = 6.6261\text{x}10^{-34}\text{ J s}(2.9979\text{x}10^{8}\text{ m s}^{-1})/400.0\text{x}10^{-9}\text{ m} = 4.966\text{x}10^{-19}\text{ J}$$

The Einstein photoelectric effect relationship with the work function in eV is:

$$E = \tfrac{1}{2}\, m\upsilon^2 + e\Gamma$$
$$4.966\text{x}10^{-19}\text{ J} = \tfrac{1}{2}\, m\upsilon^2 + 1.6022\text{x}10^{-19}\text{ C}(2.28\text{ V})$$
$$\tfrac{1}{2}\, m\upsilon^2 = 1.31\text{x}10^{-19}\text{ J}$$

or 26% of the excitation energy is released as kinetic energy of the photoelectrons. Alternatively, the problem may be worked in electron-volts with 1 J = 1 C V:

$$E = h\nu/e = 4.966\text{x}10^{-19}\text{ J}/1.6022\text{x}10^{-19}\text{ C} = 3.100\text{ eV}$$

and the photoelectric effect formula becomes:

$$3.100\text{ eV} = \tfrac{1}{2}\, m\upsilon^2 + 2.28\text{ eV} \qquad \text{and} \qquad \tfrac{1}{2}\, m\upsilon^2 = 3.100\text{ eV} - 2.28\text{ eV} = 0.820\text{ eV}$$

5. The work function for cesium metal is 2.10 eV. Cesium is used as a coating for photodetector tubes in some older spectrophotometers. Calculate the long wavelength limit for photoelectron production for a cesium coated phototube.

Answer: The plan is to note that the low wavelength cutoff corresponds to the minimum energy necessary to eject a photoelectron from cesium.

The Einstein photoelectric effect relationship with the work function in eV is:

$$E = \tfrac{1}{2}\, m\upsilon^2 + e\Gamma$$

With no kinetic energy, this last equation gives the minimum energy for photoelectron production:

$$E_{min} = e\Gamma = 1.6022\text{x}10^{-19}\text{ C}(2.10\text{ V}) = 3.36_5\text{x}10^{-19}\text{ J}$$

The corresponding wavelength using $E = hc/\lambda$ is:

$$\lambda = hc/E = 6.6261\text{x}10^{-34}\text{ J s}(2.9979\text{x}10^{8}\text{ m s}^{-1})/\ 3.36_5\text{x}10^{-19}\text{ J}$$
$$\lambda = 5.904\text{x}10^{-7}\text{ m} = 590.\text{ nm}$$

6. Rephrase the four experimental observations for the photoelectric effect assuming light is only wave-like (not particle-like) and the electrons in atoms are harmonically bound.

Answer: Think of a harmonically bound electron as a pendulum. Energy is coupled to a pendulum from a periodic excitation only if the frequency of the excitation matches the frequency of the pendulum. The energy imparted to a pendulum is proportional to the $(\text{amplitude})^2$ of the excitation and builds gradually over time:

1. "Current flows only if light has greater than a minimum frequency" becomes:
    1. Current flows only if light has a specific frequency.
2. "Current is finite and instantaneous even if the light intensity is small" becomes:
    2. Current increases with time up to a steady-state.
3. "Kinetic energy of ejected electrons is not a function of the intensity" becomes:
    3. Kinetic energy of ejected electrons increases with intensity.
4. "Current is proportional to intensity = (amplitude)^2," remains valid in the steady-state.

7. Electron microscopes can be used to determine the electron diffraction pattern of crystalline materials, in a similar fashion to X-ray diffraction. (a). Calculate the de Broglie wavelength for electrons that are accelerated to 10.0 keV. (b). Calculate the wavelength for 8.046 keV X-rays from a Cu X-ray tube. The effective wavelength for the electrons or X-rays determines the limiting spatial resolution for the diffraction study.

Answer: (a). The momentum is given from $E_k = p^2/2m$ by rearrangement and $1\ \text{J} = 1\ \text{V C} = 1\ \text{kg m}^2\ \text{s}^{-2}$:

$$p = \sqrt{2mE} = [2(9.109\text{x}10^{-31}\ \text{kg})(10{,}000\ \text{V})(1.602\text{x}10^{-19}\ \text{C})]^{1/2} = 5.402\text{x}10^{-23}\ \text{kg m s}^{-1}$$

The de Broglie relationship, $p = h/\lambda$, gives the effective wavelength:

$$\lambda = h/p = 6.6261\text{x}10^{-34}\ \text{J s}/5.402\text{x}10^{-23}\ \text{kg m s}^{-1} = 1.227\text{x}10^{-11}\ \text{m} = 0.123\ \text{Å}$$

which is a small fraction, ~ 1/50, of the expected lattice spacing for simple crystalline substances.

(b). The wavelength for the 8.046 keV X-rays from a Cu X-ray tube is given using the units identities:

$$1\ \text{J} = 1\ \text{V C} = 1\ \text{kg m}^2\ \text{s}^{-2} \qquad \text{and} \qquad 1\ \text{eV} = 1.6022\text{x}10^{-19}\ \text{J} = e\ (1\ \text{V})$$

where e is the charge of the electron.

$$E = 8.046\text{x}10^{3}\ \text{eV}(1.6022\text{x}10^{-19}\ \text{J}/1\ \text{eV}) = 1.2891\text{x}10^{-15}\ \text{J}$$
$$\lambda = hc/E = 6.6261\text{x}10^{-34}\ \text{J s}(2.9979\text{x}10^{8}\ \text{m s}^{-1})/1.2891\text{x}10^{-15}\ \text{J} = 1.541\text{x}10^{-10}\ \text{m} = 1.541\ \text{Å}$$

8. Why don't we normally notice the wave behavior of particles in the macroscopic world that we directly experience? (a). Calculate the de Broglie wavelength of a 58.0 g tennis ball traveling at 80.0 km hr^{-1} and a 70.0 kg human traveling at 2 km hr^{-1}. (b). Calculate the de Broglie wavelength of an O_2 molecule based on the overall translational energy at room temperature. The average speed (rms) of an O_2 molecule at room temperature is 482. m s^{-1}.

Answer: (a). The momentum of the tennis ball is:

$$p = m\upsilon = 58.0\text{x}10^{-3}\ \text{kg}(80.0\text{x}10^{3}\ \text{m hr}^{-1})(1\ \text{hr}/3600\ \text{s}) = 1.289\ \text{kg m s}^{-1}$$

The de Broglie relationship, $p = h/\lambda$, gives the effective wavelength:

$$\lambda = h/p = 6.6261\text{x}10^{-34}\text{ J s}/1.289\text{ kg m s}^{-1} = 5.14\text{x}10^{-34}\text{ m}$$

which is too small to give wave-like interactions. A 70.0 kg human gives an even smaller wavelength:

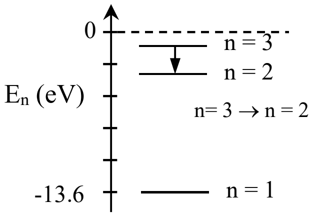
$$p = 70.0\text{ kg}(2.0\text{x}10^{3}\text{ m hr}^{-1})(1\text{ hr}/3600\text{ s}) = 38.89\text{ kg m s}^{-1}$$
$$\lambda = h/p = 6.6261\text{x}10^{-34}\text{ J s}/38.89\text{ kg m s}^{-1} = 1.70\text{x}10^{-35}\text{ m}$$

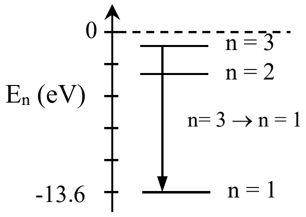
(b). The momentum and de Broglie wavelength of the O_2 molecule is:

$$p = m\upsilon = 32.0\text{ g mol}^{-1}(1\text{ mole}/6.022\text{x}10^{23}\text{ mol}^{-1})(1\text{ kg}/1000\text{ g})(482.\text{ m s}^{-1})$$
$$p = 2.561\text{x}10^{-23}\text{ kg m s}^{-1}$$
$$\lambda = h/p = 6.6261\text{x}10^{-34}\text{ J s}/2.561\text{x}10^{-23}\text{ kg m s}^{-1} = 2.59\text{x}10^{-11}\text{ m} = 0.259\text{ Å}$$

9. Calculate the photon energy, in electron volts and wavenumbers, and the wavelength for the hydrogen atomic emission lines for the transitions: (a) n = 3 to n = 2, (b). n = 3 to n = 1. However, before you do the numerical calculations predict the transition that is "bluer."

Answer: The transitions are shown in the energy level diagram below. The n = 3 → n = 1 has a larger energy difference, longer arrow, and is then "bluer." The n= 3 → n = 2 is part of the Balmer series, which is in the visible region of the spectrum. The energies are given as $E_n = -13.606\text{ eV}(Z^2/n^2)$, where Z is the charge on the nucleus of a one-electron atom or ion.





10. (a). Calculate the energy and wavelength for the lowest energy absorption transition for ground state atomic hydrogen. (b). Calculate the ionization potential and the corresponding wavelength of the transition that ionizes ground state hydrogen atoms. Report the energies in eV and wavenumbers. Report the wavelengths in nm. In what region of the electromagnetic spectrum are these two transitions?

Answer: The plan is to note that the lowest energy absorption transition is from n = 1 to n = 2. The ionization potential corresponds to the onset of the dissociation continuum, which is for the transition from n = 1 to n = ∞.

(a). The Bohr formula for the energies of the different quantum levels of the hydrogen atom is $E_n = -13.606\text{ eV}(Z^2/n^2)$. For the lowest energy absorption, n = 1 to n = 2:

$$\Delta E = E_2 - E_1 = -13.606\text{ eV}(1/2^2 - 1/1^2) = 10.20\text{ eV}$$

$= 10.20\ \text{eV}(8065.5\ \text{cm}^{-1}/1\ \text{eV}) = \ = 82{,}304.\ \text{cm}^{-1}$

and the corresponding wavelength is:

$\lambda = 1/\tilde{\nu} = 1/[82{,}304.\ \text{cm}^{-1}(100\ \text{cm}/1\ \text{m})] = 1.215\text{x}10^{-7}\ \text{m} = 121.5\ \text{nm}$

This transition is in the vacuum ultraviolet, and corresponds to the Lyman-α emission line.
(b). The ionization potential and the wavelength of the transition that ionizes ground state hydrogen atoms is for the transition from n = 1 to n = ∞ and corresponds to $-E_1$:

$\Delta E = E_\infty - E_1 = 0 - E_1 = 13.606\ \text{eV}$
$= 13.606\ \text{eV}(8065.5\ \text{cm}^{-1}/1\ \text{eV}) = \ = 109{,}740.\ \text{cm}^{-1}$

which is in the vacuum ultraviolet.The corresponding wavelength is:

$\lambda = 1/\tilde{\nu} = 1/[109{,}740.\ \text{cm}^{-1}(100\ \text{cm}/1\ \text{m})] = 9.1125\text{x}10^{-8}\ \text{m} = 91.1\ \text{nm}$

which corresponds to the convergence limit of the Lyman emission series.

11. Li^{2+} is a one-electron ion, which is well described using the Bohr formula. Compare the wavelength of the n = 3 to n = 2 emission lines for H-atoms and Li^{2+}. Before you do the numerical calculation, determine qualitatively which transition is "bluer."

Answer: The plan is to note the Bohr formula for the hydrogen atom or any one-electron atomic ion is $E_n = -13.606\ \text{eV}(Z^2/n^2)$, where Z is the nuclear charge.

The lowest energy Balmer transition is at 656.3 nm, in the red region of the spectrum. The factor of Z^2 in the energy will increase the transition energy for Li^{2+}, making the corresponding transition for Li^{2+} bluer. For Li^{2+}, Z = 3 giving:

$\Delta E = E_3 - E_2 = -13.606\ \text{eV}(3^2)(1/2^2 - 1/3^2) = 17.01\ \text{eV}$
$= 17.01\ \text{eV}(1.6022\text{x}10^{-19}\ \text{J}/1\ \text{eV}) = 2.725\text{x}10^{-18}\ \text{J}$

Then since $E = hc/\lambda$:

$\lambda = 6.6261\text{x}10^{-34}\ \text{J s}(2.9979\text{x}10^{8}\ \text{m s}^{-1})/2.725\text{x}10^{-18}\ \text{J} = 7.290\text{x}10^{-8}\ \text{m} = 72.90\ \text{nm}$

in the vacuum UV. Of course, we could have just divided 656.3 nm by 9 to get the final result.

12. The spectrum of the sun incident on the earth is shown in the table below and Figure P23.1.[2] Gases in the atmosphere absorb infrared light through vibrational transitions and ultraviolet light through electronic transitions. Gas molecular absorption and scattering by atmospheric particulates reduce the solar intensity at sea level compared to outside the atmosphere. Using the data in the following table, show that the solar irradiance outside the earth's atmosphere is well modeled by the Planck blackbody expression at 5800 K:

$$H(\lambda) = \frac{2\pi hc^2}{\lambda^5}\left(\frac{1}{e^{hc/kT\lambda} - 1}\right)$$

where k is Boltzmann's constant, $k = R/N_A = 1.3807\text{x}10^{-23}$ J K^{-1}. The irradiance is the energy flux per unit wavelength interval; that is, the energy emitted from a unit area per unit time per unit wavelength interval. A square meter cross section of the earth captures a tiny fraction of the total energy output of the sun, so a small scale factor must applied to match the overall intensity to the experimental data.

λ (nm)	250.	375.	460.	500.	625.	750.	1000.	1250.	1500.	1750.
H_λ (W m^{-2} nm^{-1})	0.034	1.193	2.032	1.929	1.667	1.279	0.742	0.445	0.263	0.166

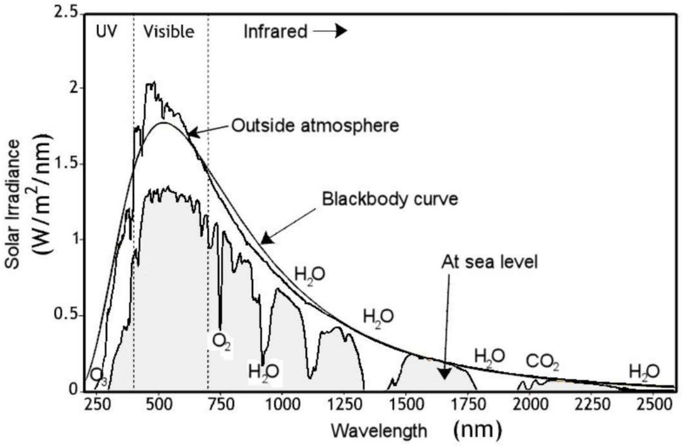
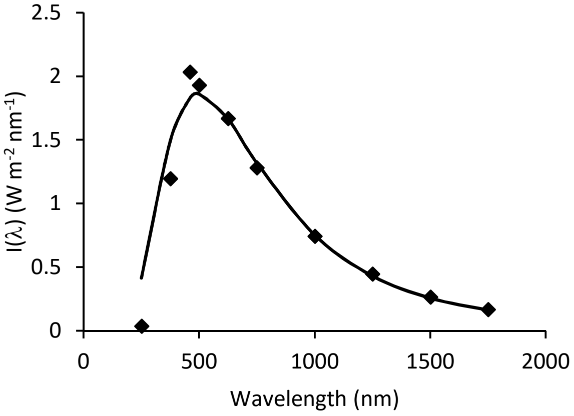


Figure P23.1: The solar irradiance incident on the earth at the top of the atmosphere and at sea level. The irradiance is given in watts for a one-meter surface placed perpendicular to the incident angle of the sun for a 1 nm range in wavelength, λ to $\lambda+d\lambda$, given in nm.

Answer: The wavelengths must be converted to meters to match the units of h, k, and c. For example, $\lambda = 250$ nm ($1\text{x}10^{-9}$ m/1 nm) = $2.50\text{x}10^{-7}$ m. Using the Planck blackbody expression and multiplying by a scale factor to get the best fit gives the following spreadsheet:

		T (K)=	5800
	Experimental	scale =	2.18E-14
λ (nm)	H_λ (W m^{-2} nm^{-1})	ν (s^{-1})	H(λ) (W m^{-2} nm^{-1})
250	0.034	0.410	4.14E-01
375	1.193	1.478	1.49E+00
460	2.032	1.81	1.83E+00
500	1.929	1.844	1.86E+00
625	1.667	1.649	1.66E+00
750	1.279	1.308	1.32E+00
1000	0.742	0.746	7.52E-01
1250	0.445	0.427	4.30E 01
1500	0.263	0.255	2.57E-01
1750	0.166	0.159	1.60E-01



The scale factor of $2.18\text{x}10^{-14}$ can be treated as arbitrary and chosen to fit the long-wavelength portion of the experimental curve. However, the distance of the earth from the sun is $93.\text{x}10^{6}$ miles, giving the surface area of a sphere at that radius of $2.79\text{x}10^{23}$ m^2. The surface area of the sun is $6.09\text{x}10^{18}$ m^2. The energy falling on a unit area at the top of the earth's atmosphere per unit time per nm wavelength interval is given as:

$$\begin{aligned}&\qquad\qquad\qquad\quad \textit{flux}\quad \textit{(area of emitter)}\quad \textit{(fraction absorbed)}\quad \textit{(convert wavelength interval)}\\ \text{solar insolation}(\lambda) &= H(\lambda)\ (6.09\text{x}10^{18}\ \text{m}^2)(1\ \text{m}^2/2.79\text{x}10^{23}\ \text{m}^2)(1\text{x}10^{-9}\ \text{m}/1\ \text{nm})\\ &= 2.18\text{x}10^{-14}\ H(\lambda)\end{aligned}$$

giving an exact value for the scale factor from first principles.

13. The Planck blackbody expression in terms of frequency is:

$$I(\nu) = \frac{2\pi h\nu^3}{c^2}\left(\frac{1}{e^{h\nu/kT} - 1}\right)$$

Show that the total flux radiated by a blackbody is $J = \sigma T^4$, where $\sigma = 5.6704\text{x}10^{-8}$ W m^{-2} K^{-4} (see Section 11.2 and Eq. 11.2.16). [Hint: $\int_0^\infty (x^3/(e^x - 1))\, dx = \pi^4/15$]

Answer: The plan is to integrate the Planck expression over all wavelengths of the emitted radiation.

The total energy per unit area per unit time is given by:

$$J = \frac{2\pi h}{c^2}\int_0^\infty \frac{\nu^3}{e^{h\nu/kT} - 1}\, d\nu$$

Using the substitution $x = h\nu/kT$ gives $dx/d\nu = h/kT$, $d\nu = (kT/h)\, dx$, and $\nu = kTx/h$. The integration limits remain 0 to ∞:

$$J = \frac{2\pi h}{c^2}\left(\frac{kT}{h}\right)^4 \int_0^\infty \frac{x^3}{e^x - 1}\, dx = \left(\frac{2\pi^5 k}{15h^3c^2}\right) T^4 \qquad \text{giving } \sigma = \frac{2\pi^5 k^4}{15h^3c^2}$$

$$\sigma = \frac{2\pi^5(1.380662\text{x}10^{-23}\ \text{J K}^{-1})^4}{15(6.6261\text{x}10^{-34}\ \text{J s})^3(2.9979\text{x}10^8\ \text{m s}^{-1})^2} = 5.6704\text{x}10^{-8}\ \text{J s}^{-1}\ \text{m}^{-2}\ \text{K}^{-4}$$

with 1 W = 1 J s^{-1}. Radiative energy transfer is a very strong function of temperature. The fundamental constant, σ, is called the Stefan-Boltzmann constant. See Section 11.2 for applications of this result to solar energy production.

14. The Planck blackbody expression in terms of frequency is given in the last problem. This expression gives the intensity of radiation in an interval of frequency from ν to $\nu+d\nu$:

$$I(\nu)\, d\nu = \frac{2\pi h\nu^3}{c^2}\left(\frac{1}{e^{h\nu/kT} - 1}\right) d\nu$$

Apply a change in variables to show that the distribution in terms of wavelength is given by:

$$I(\lambda)\, d\lambda = \frac{2\pi hc^2}{\lambda^5}\left(\frac{1}{e^{hc/kT\lambda} - 1}\right) d\lambda$$

Answer: The plan is to do the normal procedure for the change in variable for an integration using $\nu = c/\lambda$.

Using the change in variable $\nu = c/\lambda$ gives $d\nu/d\lambda = -c/\lambda^2$, $d\nu = -c/\lambda^2\, d\lambda$. The integral limits when this distribution is used change from $\int_o^\infty$ over ν to $\int_\infty^o = -\int_o^\infty$ over λ, since ν increases while λ decreases. The negative signs cancel giving:

$$I(\lambda)\, d\lambda = \frac{2\pi hc^3}{c^2\lambda^3}\left(\frac{1}{e^{hc/kT\lambda} - 1}\right)\left(\frac{-c}{\lambda^2}\right) d\lambda = \frac{2\pi hc^2}{\lambda^5}\left(\frac{1}{e^{hc/kT\lambda} - 1}\right) d\lambda$$

15. The total flux radiated by a blackbody is $J = \sigma T^4$, where $\sigma = 5.6704\text{x}10^{-8}$ W m^{-2} K^{-4} (see Section 11.2 and Eq. 11.2.16). This flux is the energy emitted per unit area of the emitter per unit time. The solar constant is the energy from the sun falling on the top of earth's atmosphere per unit area per unit time. The solar constant is 1.37 kW m^{-2}. The surface area of the sun is $6.09\text{x}10^{18}$ m^2. A square meter cross section of the earth captures a tiny fraction of the total energy output of the sun. The average distance of the earth from the sun is $93.\text{x}10^6$ miles, giving the surface area of a sphere at that radius of $2.79\text{x}10^{23}$ m^2. Calculate the effective blackbody temperature of the surface of the sun.

Answer: The emitted power is the flux multiplied by the surface area of the sun, $J\mathcal{A}$. The Stefan-Boltzmann equation, $J = \sigma T^4$, gives the flux at the top of earth's atmosphere as:

$$1370 \text{ W m}^{-2} = (5.6704\text{x}10^{-8} \text{ W m}^{-2} \text{ K}^{-4})\, T^4\, (6.09\text{x}10^{18} \text{ m}^2)(1 \text{ m}^2/2.79\text{x}10^{23} \text{ m}^2)$$

Solving for T gives 5768. K or 5800 K.

16. (This problem expands on material in Chapter 12, using the partition function for vibration.) Planck's treatment of blackbody radiation and Einstein's treatment of the heat capacity of a solid are based on the assumption of quantized energy levels. Assume the energy levels for the electrons in a metal or for the vibration of atoms in a solid are equally spaced with $\varepsilon_j = j\, h\nu$, where ν is a fundamental vibration frequency for the motion and j is an integer. The probability of an electron or atom having energy ε_j is given by the Boltzmann distribution, $n_j/N = e^{-\beta\varepsilon_j}/q$, where $\beta = 1/kT$. The average energy is given by Eq. 12.2.6:

$$<\varepsilon> = \frac{\sum_{j=0}^{\infty} \varepsilon_j\, e^{-\beta\varepsilon_j}}{q} \qquad \text{where q is the partition function: } q = \sum_{j=0}^{\infty} e^{-\beta\varepsilon_j}$$

(a). Show that the average energy can also be expressed as:

$$<\varepsilon> = -\frac{1}{q}\left(\frac{\partial q}{\partial \beta}\right)_V$$

(b). Show that the partition function reduces to: $q = \frac{1}{1 - e^{-\beta h\nu}}$

Note that the infinite power series can be summed as: $\sum_{ji=0}^{\infty} a^j = 1 + a + a^2 + a^3 + \ldots = \frac{1}{1-a}$

(c). Using the partition function, show that the average energy is: $<\varepsilon> = \frac{h\nu}{(e^{\beta h\nu} - 1)}$

Answer: (a). Starting with the partition function in general form, $q = \Sigma\, e^{-\beta\varepsilon_j}$, the derivative with respect to β at constant volume is:

$$\left(\frac{\partial q}{\partial \beta}\right)_V = -\sum_{i=0}^{\infty} \varepsilon_j\, e^{-\beta\varepsilon_j}$$

Dividing this result by –1/q gives the average energy

$$<\varepsilon> = -\frac{1}{q}\left(\frac{\partial q}{\partial \beta}\right)_V = \frac{\sum_{j=0}^{\infty} \varepsilon_j\, e^{-\beta\varepsilon_j}}{q}$$

(b). Equally spaced energy levels with energies $\varepsilon_j = j\, h\nu$ gives the partition function as:

$$q = \sum_{j=0}^{\infty} e^{-\beta\, j\, h\nu}$$

Let $a = e^{-\beta h\nu}$ then $q = \sum_{i=0}^{\infty} a^j = 1 + a + a^2 + a^3 + \ldots = \frac{1}{1-a}$

Substituting back in for a gives the partition function for equally spaced levels as:

$$q = \frac{1}{1 - e^{-\beta h\nu}}$$

(c). The derivative of the partition function with respect to β is:

$$\left(\frac{\partial q}{\partial \beta}\right)_V = \frac{-1}{(1 - e^{-\beta h\nu})^2}\,(h\nu\, e^{-\beta h\nu})$$

Finally, the average energy is then:

$$<\varepsilon> = -\frac{1}{q}\left(\frac{\partial q}{\partial \beta}\right)_V = -\,(1 - e^{-\beta h\nu})\,\frac{-1}{(1 - e^{-\beta h\nu})^2}\,(h\nu\, e^{-\beta h\nu}) = \frac{h\nu\, e^{-\beta h\nu}}{(1 - e^{-\beta h\nu})} = \frac{h\nu}{(e^{\beta h\nu} - 1)}$$

This final result was central in understanding blackbody radiation and the heat capacity of solids.

17. The Wein relationship for the spectral distribution of blackbody radiation is:

$$I(\nu) = \frac{2\pi\nu^2}{c^2} <\varepsilon>$$

where ν is the frequency of the light emitted, and <ε> is the average energy of an electron oscillator in the walls of the cavity of the solid. The radiation in the cavity is assumed to be in thermodynamic equilibrium with the electron oscillators in the cavity walls. Using the equipartition theorem for the average energy of an electron oscillator gives <ε> = RT. However, classical result is found to vastly overestimate the blackbody intensity in the ultraviolet. Show that the assumption of quantized oscillators and the corresponding average energy derived in the previous problem gives the Planck distribution function, which was given in Problems 13 and 14.

Answer: Note that $\beta = 1/kT$. Simply substituting the average energy of a quantized oscillator from the previous problem into $I(\nu) = (2\pi\nu^2/c^2) <\varepsilon>$ gives the Planck blackbody formula:

$$I(\nu) = \frac{2\pi h\nu^3}{c^2}\left(\frac{1}{e^{h\nu/kT} - 1}\right)$$

18. The heat capacity of an oscillator can be determined from the derivative of the average energy versus temperature: $C_v = (\partial U/\partial T)_v = N_A(\partial<\varepsilon>/\partial T)_v$. The average energy of a one-dimensional quantized oscillator was derived in Problem 16:

$$<\varepsilon> = \frac{h\nu}{(e^{\beta h\nu} - 1)}$$

Einstein estimated that the heat capacity of a simple solid is $C_v = 3N_A(\partial<\varepsilon>/\partial T)_v$, where the factor of three results since the atoms in a solid can oscillate in the x, y, and z directions. Derive the Einstein relationship for the heat capacity of an atomic solid. Plot the relationship versus temperature for $\tilde{\nu} = 100.\ \text{cm}^{-1}$.

Answer: $$C_v = 3\,N_A\left(\frac{\partial<\varepsilon>}{\partial T}\right)_V = 3\,N_A\,h\nu\left(\frac{\partial\left(\frac{1}{e^{h\nu/kT} - 1}\right)}{\partial T}\right)_V = 3\,N_A\,h\nu\left[\frac{-\,e^{h\nu/kT}}{(e^{h\nu/kT} - 1)^2}\right]\left(\frac{-\,h\nu}{kT^2}\right)$$

$$= 3N_A\,k\left(\frac{h\nu}{kT}\right)^2\frac{e^{h\nu/kT}}{(e^{h\nu/kT} - 1)^2}$$

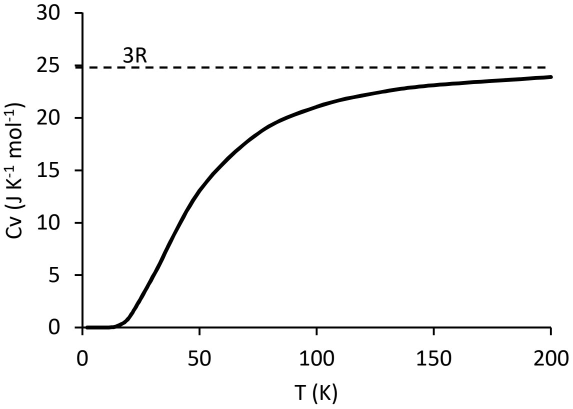
Remember that $N_Ak = R$, giving: $C_v = 3R\left(\frac{h\nu}{kT}\right)^2\frac{e^{h\nu/kT}}{(e^{h\nu/kT} - 1)^2}$

The units are converted to kelvins from wavenumbers using:

$$hc\tilde{\nu}/k = 6.6261\text{x}10^{-34}\text{J s}(2.9979\text{x}10^{10}\text{ cm s}^{-1})(100.\text{ cm}^{-1})/1.3807\text{x}10^{-23}\text{ J K}^{-1}$$
$$= 143.88\text{ K}$$

The plot was done using a spreadsheet:

$\tilde{\nu}$ =	100	cm^{-1}
$hc\tilde{\nu}/k$ =	143.88	K
T (K)	$e^{(h\nu/kT)}$	C_v ($J\ K^{-1}\ mol^{-1}$)
2	1.748E+31	0.000
5	3.141E+12	0.000
10	1.772E+06	0.003
15	1.464E+04	0.157
20	1.331E+03	0.971
30	1.210E+02	4.820
50	1.777E+01	13.050
75	6.810E+00	18.520
100	4.216E+00	21.052
125	3.161E+00	22.363
150	2.610E+00	23.116
200	2.053E+00	23.895



The heat capacity has a limiting high temperature value of 3R, which is the equipartition prediction.

19. (a). Assume the uncertainty for the one-dimensional linear position of an electron is 1.00 Å. Calculate the uncertainty of the momentum using $\delta x\ \delta p_x \geq \hbar/2$. (b). The average momentum for a confined particle, such as the particle in a box, is zero: $\langle p \rangle = 0$. The uncertainty in the momentum, as measured by the standard deviation, then reduces to just the root-mean-squared momentum, $\sigma_{p_x} = (\langle p^2 \rangle - \langle p \rangle^2)^{½} = (\langle p^2 \rangle)^{½} = p_{rms,x}$. The root-mean-squared momentum can be used to estimate the kinetic energy of the particle, $E_{k,x} \approx (p_{rms,x})^2/2m$. Estimate the kinetic energy of a confined electron with a positional uncertainty of 1 Å. (c). The kinetic energy of a particle confined in a cubical box is determined by adding the kinetic energy in each direction, $E_k = E_{k,x} + E_{k,y} + E_{k,z} = 3\ E_{k,x}$, for a cubical box. The diameter of an atom is about 1 Å (the Bohr radius of the H atom is 0.529 Å). Assume the hydrogen atom is approximated by a 1 Å cubical box. Use the kinetic energy from part (b) to estimate an approximate kinetic energy of the ground state of the H atom in eV and kJ mol^{-1}. Is this resulting energy chemically significant? In other words, is the magnitude comparable to or greater than typical enthalpy changes for chemical reactions?

Answer: The plan is to use the Heisenberg uncertainty principle in the form $\delta x\ \delta p_x \geq \hbar/2$ and then $E_k = 3\ (p_{rms,x})^2/2m$ to estimate the ground state energy of the H atom.
(a). Using the Heisenberg uncertainty relationship and 1 Å = $1\text{x}10^{-10}$ m gives:

$$\delta p_x \geq \hbar/(2\delta x) = 1.0546\text{x}10^{-34}\ \text{J s}/2/1.00\text{x}10^{-10}\ \text{m} = 5.273\text{x}10^{-25}\ \text{kg m s}^{-1}$$

(b). The corresponding kinetic energy is:

$$E_{k,x} \approx (p_{rms,x})^2/2m = (5.273\text{x}10^{-25}\ \text{kg m s}^{-1})^2/2/9.109\text{x}10^{-31}\ \text{kg} = 1.526\text{x}10^{-19}\ \text{J}$$
$$E_{k,x} \approx 1.526\text{x}10^{-19}\ \text{J}\ (1\ \text{eV}/1.6022\text{x}10^{-19}\ \text{J}) = 0.953\ \text{eV}$$
$$E_{k,x} \approx 1.526\text{x}10^{-19}\ \text{J}\ (6.022\text{x}10^{23}\ \text{mol}^{-1})(1\ \text{kJ}/1000\ \text{J}) = 91.9\ \text{kJ mol}^{-1}$$

(c). The result for a cubical, 1 Å box is then $E_k = 3\ E_{k,x} = 2.86$ eV = 275. kJ mol^{-1}

The experimental kinetic energy for the ground-state of the H-atom is 13.6 eV; this problem is a rough estimate. An atom is spherical, instead of a cubical box, and has a strong attractive potential energy. However, the kinetic energy corresponding to $\delta p_x \geq 5.273\text{x}10^{-25}$ kg m s^{-1} is definitely chemically significant. Typical enthalpy changes for chemical reactions are on the order of 200 kJ mol^{-1}. Chemical phenomena are most certainly governed by the Heisenberg uncertainty relationship.

<u>20</u>. (a). The momentum of a 10.0 eV electron is known to 10%. Calculate the minimum uncertainty in the position of the electron. (b). The speed of a 58.0 g tennis ball traveling at 80.0 km hr^{-1} is known to 10%. Calculate the uncertainty in the position of the tennis ball. Does this uncertainty contribute to the difficulty in returning an 80.0 km hr^{-1} tennis serve?

Answer: The plan is to use $E_k = p^2/2m$ or $p = m\upsilon$ to find the momentum of each particle. The Heisenberg uncertainty relationship is then used to find the uncertainty in the position.
(a). The momentum of the electron is:

$$p_x = \sqrt{2mE_k} = \sqrt{2(9.109\text{x}10^{-31}\ \text{kg})(10.0\ \text{eV})(1.6022\text{x}10^{-19}\ \text{J/1eV})} = 1.709\text{x}10^{-24}\ \text{kg m s}^{-1}$$
$$\Delta p_x = 0.10\ (1.709\text{x}10^{-24}\ \text{kg m s}^{-1}) = 1.709\text{x}10^{-25}\ \text{kg m s}^{-1}$$

Rearranging the Heisenberg uncertainty relationship, $\delta x\ \delta p_x \geq \hbar/2$, gives:

$$\delta x \geq \hbar/(2\delta p_x) = 1.0546\text{x}10^{-34}\ \text{J s}/2/1.709\text{x}10^{-25}\ \text{kg m s}^{-1} = 3.08\text{x}10^{-10}\ \text{m} = 3.1\ \text{Å}$$

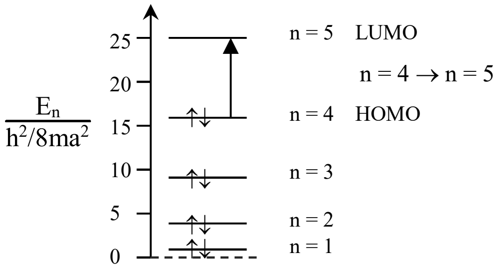
which is a significant uncertainty for the position, on the order of the size of a small molecule.
(b). The momentum of the tennis ball is (see Problem 8):

$$p = m\upsilon = 58.0\text{x}10^{-3}\ \text{kg}(80.0\text{x}10^{3}\ \text{m hr}^{-1})(1\ \text{hr}/3600\ \text{s}) = 1.289\ \text{kg m s}^{-1}$$
$$\delta p_x = 0.10(1.289\ \text{kg m s}^{-1}) = 0.1289\ \text{kg m s}^{-1}$$
$$\delta x \geq \hbar/(2\delta p_x) = 1.0546\text{x}10^{-34}\ \text{J s}/2/0.1289\ \text{kg m s}^{-1} = 4.09\text{x}10^{-34}\ \text{m}$$

Unfortunately, you cannot blame the Heisenberg uncertainty when you fail to return a tennis serve (or strike out).

<u>21</u>. (a). What are the quantum numbers for the energy levels that are involved in the lowest energy electronic transition for the molecule, $H_2C{=}CH{-}CH{=}CH{-}CH{=}CH{-}CH{=}CH_2$? Base your answer on the particle in a box model. (b). Calculate the wavelength of the light absorbed in nm. Calculate the energy change for the transition in wavenumbers, cm^{-1}. The average bond length for a conjugated double bond is 1.39 Å. Lengthen the box by one-half of a bond beyond each terminal C atom to take into account that the π orbital doesn't end exactly at the nucleus of the terminal C atoms.

Answer: The plan is two note that in the conjugated-π system, there are 2(4) electrons, since there are four double bonds and accordingly eight sp^2 hybridized C atoms.
(a). Placing two electrons in each particle in a box orbital gives the highest occupied molecular orbital, the HOMO, as n = 4. The lowest unoccupied molecular orbital, or LUMO, is n = 5. The absorption transition is from n = 4 to n = 5:



(b). The energy of a particle in a box orbital with box length a is: $E_n = \frac{h^2}{8ma^2} n^2$.

The transition energy between initial state n_i and final state n_f is then:

$$\Delta E = E_f - E_i = \frac{h^2}{8ma^2}(n_f^2 - n_i^2)$$

The mass of the electron is $9.109\text{x}10^{-31}$ kg. There are seven conjugated bonds and adding ½ of a bond at each terminus gives the box length as 8(1.39 Å) = 11.12 Å = $1.112\text{x}10^{-9}$ m:

$$\Delta E = \frac{h^2}{8ma^2}(5^2 - 4^2) = \frac{(6.626\text{x}10^{-34}\text{ J s})^2}{8(9.109\text{x}10^{-31}\text{ kg})(1.112\text{x}10^{-9}\text{ m})^2}(9) = 4.872\text{x}10^{-20}\text{ J }(9)$$
$$= 4.385\text{x}10^{-19}\text{ J}$$

Giving the wavelength as : $\lambda = hc/\Delta E = 6.626\text{x}10^{-34}\text{ J s }(2.998\text{x}10^{8}\text{ m s}^{-1})/4.385\text{x}10^{-19}\text{ J}$
$= 4.530\text{x}10^{-7}\text{ m }(1\text{ nm}/1\text{x}10^{-9}\text{ m}) = 453.\text{ nm}$

and energy in cm^{-1} as: $\tilde{\nu} = 1/\lambda = 1/4.530\text{x}10^{-5}\text{ cm} = 22{,}100\text{ cm}^{-1}$

If we don't add half a bond length on each end of the box, the transition is predicted to occur at 28,900 cm^{-1}.

22. Two restrictions are placed on the solutions to the Schrödinger equation that take the form of integrals. Name the two restrictions, the two integrals, and the values that define these restrictions.

Answer: The solutions to the Schrödinger equation should be orthogonal and normalized, or so called orthonormal solutions. For two quantum states, n and m, orthogonality and normalization are respectively:

Orthogonality: $\int \Psi_n^* \Psi_m \, d\tau = 0$ Normalization: $\int \Psi_n^* \Psi_n \, d\tau = 1$

23. Show that the n = 2 and n = 3 wave functions for the particle in the box are orthogonal. Show that the n = 2 wave function is normalized.

Answer: The plan is to show that $\int \Psi_2^* \Psi_3 \, dx = 0$ and $\int \Psi_2^* \Psi_2 \, dx = 1$.

The particle in the box wave functions for quantum number n and box length a are $\Psi(x) = (2/a)^{1/2} \sin(n\pi x/a)$. For n = 2 and n = 3:

$$\int \Psi_2^* \Psi_3 \, dx = (2/a) \int_0^a \sin(2\pi x/a) \sin(3\pi x/a) \, dx$$

Changing variables to $y = \pi x/a$, giving $dy/dx = \pi/a$ or $dx = a/\pi \, dy$, and the range y = 0 to π:

$$\int \Psi_2^* \Psi_3 \, dx = (2/a)(a/\pi) \int_0^\pi \sin(2y) \sin(3y) \, dy$$

Integral tables give this integral equal to zero:[1] $\int_0^\pi \sin(ax) \sin(bx) \, dx = 0$ for $a \neq b$:

$$\int \Psi_2^* \Psi_3 \, dx = 0$$

The solutions are orthogonal. The integral can also be done visually, Figure P23.2. The n = 2 wave function is odd with reference to the center of the box, while the n = 3 wave function is even, so the result over the full interval is zero. Centering the integration range, $x' = x - a/2$, gives:

$$\int \Psi_2^* \Psi_3 \, dx = (2/a) \int_{-a/2}^{a/2} \underset{\uparrow \textit{ odd}}{\sin[2\pi(x'+ a/2)/a]} \; \underset{\uparrow \textit{ even}}{\sin[3\pi(x'+ a/2)/a]} \, dx' = 0$$

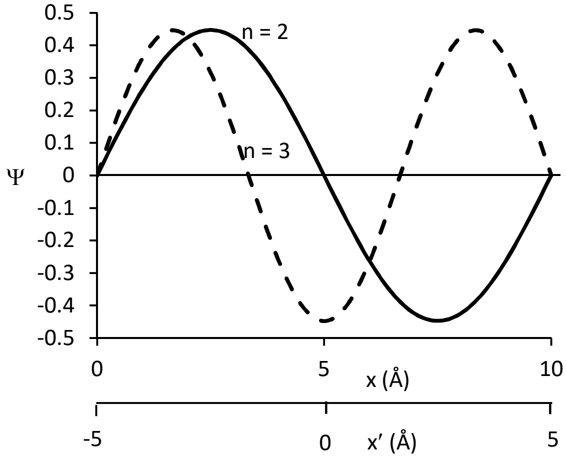


Figure P23.2: Particle in the box wave functions for n = 2 (–) and n = 3 (- - -).

For the normalization, use the substitution $y = 2\pi x/a$, giving $dy/dx = 2\pi/a$ or solving for dx, $dx = a/(2\pi) \, dy$, and the range y = 0 to 2π:

$$\int \Psi_2^* \Psi_2 \, dx = (2/a) \int_0^a \sin^2(2\pi x/a) \, dx = (2/a)(a/(2\pi)) \int_0^{2\pi} \sin^2(y) \, dy$$

Integral tables give this integral as:[1] $\int \sin^2(x)\,dx = -\tfrac{1}{2}\cos x \sin x + \tfrac{1}{2}x$:

$$\int \Psi_2^* \Psi_2\,dx = (1/\pi)\,[-\tfrac{1}{2}\,(\cos y \sin y\,\Big|_0^{2\pi} + \tfrac{1}{2}\,y\,\Big|_0^{2\pi}\,]$$
$$= (1/\pi)\,[-\tfrac{1}{2}\,(\cos 2\pi \sin 2\,\pi - \cos 0 \sin 0) + \tfrac{1}{2}\,2\pi]$$

However, $\sin 0 = 0$ and $\sin 2\pi = 0$, giving that Ψ_2 is normalized:

$$\int \Psi_2^* \Psi_2\,dx = (1/\pi)\,[\tfrac{1}{2}\,2\pi] = 1$$

<u>24</u>. The harmonic oscillator ground state has a Gaussian wave function of the form $\Psi(x) = N\,e^{-x^2/4\sigma_x^2}$. Normalize the wave function over $-\infty \leq x \leq \infty$.

Answer: The normalization integral for a real function is $\int_{-\infty}^{\infty} \Psi^2\,dx = 1$. Substituting in the wave function and using the fact that the integrand is even gives:

$$N^2 \int_{-\infty}^{\infty} e^{-x^2/2\sigma_x^2}\,dx = 2\,N^2 \int_0^{\infty} e^{-x^2/2\sigma_x^2}\,dx = 1$$

Integral tables give: $\int_0^{\infty} e^{-x^2/2\sigma_x^2}\,dx = \frac{1}{2}\,(2\pi)^{1/2}\sigma_x$:

$$N^2 \int_{-\infty}^{\infty} e^{-x^2/2\sigma_x^2}\,dx = 2\,N^2 \frac{1}{2}\,(2\pi)^{1/2}\sigma_x = N^2\,(2\pi)^{1/2}\sigma_x = 1$$

Solving for the normalization constant: $N = \dfrac{1}{(2\pi)^{1/4}\,\sigma_x^{1/2}}$

This result is used in Example 23.4.4.

<u>25</u>. What is the probability that a particle is in the left side of the particle in a box, for a box of length a and quantum number n?

Answer: The probability is given by the integral:

$$\int_0^{a/2} \Psi_n^2\,dx = \left(\frac{2}{a}\right) \int_0^{a/2} \sin^2(n\pi x/a)\,dx$$

Applying the change in variables $y = n\pi x/a$ gives $dy/dx = n\pi/a$ or solving for dx, $dx = a/(n\pi)\,dy$, and the range $y = 0$ to $n\pi/2$:

$$\int_0^{a/2} \Psi_n^2\,dx = \left(\frac{2}{a}\right)\left(\frac{a}{n\pi}\right) \int_0^{n\pi/2} \sin^2(y)\,dy$$

Integral tables give this integral as:[1] $\int \sin^2(x)\,dx = -\tfrac{1}{2}\cos x \sin x + \tfrac{1}{2}x$:

$$\int_0^{a/2} \Psi_n^2\,dx = (2/n\pi)\,[-\tfrac{1}{2}\,(\cos y \sin y\,\Big|_0^{n\pi/2} + \tfrac{1}{2}\,y\,\Big|_0^{n\pi/2}\,]$$
$$= (2/n\pi)\,[-\tfrac{1}{2}\,(\cos(n\pi/2)\sin(n\pi/2) - \cos 0 \sin 0) + \tfrac{1}{2}\,n\pi/2]$$

However, $\cos(n\pi/2) = 0$ and $\sin 0 = 0$, giving:

$$\int_0^{a/2} \Psi_n^2\, dx = (2/n\pi)\ [½\ n\pi/2] = ½$$

As expected, the probability of being found on the left half of the box is 50%.

26. Show that $<x^2>$ for a particle in a box of length a and quantum number n is:

$$<x^2> = a^2\left(\frac{1}{3} - \frac{1}{2n^2\pi^2}\right)$$

Answer: The plan is to note that we must find the expectation value of the displacement squared. Since the particle in a box wave functions are real, $\Psi^* = \Psi$. We will use the normalized form of the wave function, giving $\int_o^a \Psi_n^2\, dx = 1$. The operator, x^2, is a multiplicative function, so the order of operation is not important, giving:

$$<x^2> = \frac{\int_o^a \Psi_n^*\, x^2\, \Psi_n\, dx}{\int_o^a \Psi_n^*\, \Psi_n\, dx} = \int_o^a x^2\, \Psi_n^2\, dx \qquad 1$$

Substituting in the general form of the wave function gives:

$$<x^2> = \left(\frac{2}{a}\right) \int_0^a x^2 \sin^2(n\pi x/a)\, dx \qquad 2$$

Applying the change in variables $y = n\pi x/a$ gives $dy/dx = n\pi/a$ or solving for dx, $dx = a/(n\pi)\, dy$, $x = a/(n\pi)\, y$, and the range $y = 0$ to $n\pi$:

$$<x^2> = \left(\frac{2}{a}\right)\left(\frac{a}{n\pi}\right)^3 \int_0^{n\pi} y^2 \sin^2(y)\, dy \qquad 3$$

Integral tables give this integral as:[1]

$$\int x^2 \sin^2(x)\, dx = \frac{x^3}{6} - \left(\frac{x^2}{4} - \frac{1}{8}\right) \sin 2x - \frac{x \cos 2x}{4} \qquad 4$$

Note that $\sin 2x = \sin(2n\pi) = 0$ at the upper limit and $\sin 0 = 0$ at the lower limit. Similarly, $\cos 2x = \cos(2n\pi) = 1$ at the upper limit:

$$\int_0^{n\pi} x^2 \sin^2(x)\, dx = \left[\frac{x^3}{6} - \left(\frac{x^2}{4} - \frac{1}{8}\right) \sin 2x - \frac{x \cos 2x}{4}\right]_0^{n\pi} = \frac{(n\pi)^3}{6} - \frac{n\pi}{4} \qquad 5$$

Substituting Eq. 5 into Eq. 3 gives:

$$<x^2> = \left(\frac{2}{a}\right)\left(\frac{a}{n\pi}\right)^3\left(\frac{(n\pi)^3}{6} - \frac{n\pi}{4}\right) = a^2\left(\frac{1}{3} - \frac{1}{2n^2\pi^2}\right)$$

27. Using the result from the last problem, find the uncertainty in the position of the particle in box, for box length a and quantum number n. Express the result as the standard deviation, $\sigma_x = (<x^2> - <x>^2)^{½}$.

Answer: The expectation value of the position for a particle in a box is <x> = a/2, giving:

$$\sigma_x^2 = <x^2> - <x>^2 = a^2\left(\frac{1}{3} - \frac{1}{2n^2\pi^2}\right) - \frac{a^2}{4} = \frac{a^2}{12} - \frac{a^2}{2n^2\pi^2} = \frac{a^2}{4n^2\pi^2}\left(\frac{n^2\pi^2}{3} - 2\right)$$

$$\sigma_x = \frac{a}{2n\pi}\left(\frac{n^2\pi^2}{3} - 2\right)^{½}$$

28. Find the average momentum for a particle in a box, with box length a and quantum number n.

Answer: The plan is to note that we must find the expectation value of the momentum operator. Since the particle in a box wave functions are real, $\Psi^* = \Psi$. We will use the normalized form of the wave function, giving $\int_o^a \Psi_n^2\, dx = 1$. The operator, $\hat{p}_x = (\hbar/i)(d/dx)$, involves a derivative, so the order of operation is important, giving:

$$<p_x> = \frac{\int_o^a \Psi_n^* \hat{p}_x \Psi_n\, dx}{\int_o^a \Psi_n^* \Psi_n\, dx} = \int_0^a \Psi_n \frac{\hbar}{i}\left(\frac{d}{dx}\right) \Psi_n\, dx$$

The derivative is:

$$\frac{d}{dx}\Psi_n = \left(\frac{2}{a}\right)^{½} \frac{d}{dx}\sin(n\pi x/a) = \left(\frac{2}{a}\right)^{½}\left(\frac{n\pi}{a}\right)\cos(n\pi x/a)$$

Substituting in the general form of the wave function gives:

$$<p_x> = \frac{\hbar}{i}\left(\frac{2}{a}\right)\int_0^a \sin(n\pi x/a)\frac{d}{dx}\sin(n\pi x/a)\, dx$$

$$= \frac{\hbar}{i}\left(\frac{2}{a}\right)\left(\frac{n\pi}{a}\right)\int_0^a \sin(n\pi x/a)\cos(n\pi x/a)\, dx$$

Applying the change in variables $y = n\pi x/a$ gives $dy/dx = n\pi/a$ or solving for dx,
$dx = a/(n\pi)\, dy$, $x = a/(n\pi)\, y$, and the range $y = 0$ to $n\pi$:

$$<p_x> = \frac{\hbar}{i}\left(\frac{2}{a}\right)\left(\frac{n\pi}{a}\right)\left(\frac{a}{n\pi}\right)\int_0^{n\pi} \sin(y)\cos(y)\, dy$$

This integral is equal to zero, giving <p> = 0. This result is concordant with the classical idea that the particle in a box wave function is the superposition of a wave traveling forward and a wave traveling backward, the net result giving a standing wave confined in the box. The average momentum is then zero.

29. Show that $<p_x^2>$ for a particle in a box of length a and quantum number n is:

$$<p_x^2> = \hbar^2 \left(\frac{n\pi}{a}\right)^2$$

Answer: The plan is to note that we must find the expectation value of the momentum operator squared. Since the particle in a box wave functions are real, $\Psi^* = \Psi$. We will use the normalized form of the wave function, giving $\int_o^a \Psi_n^2\, dx = 1$. The operator, $\hat{p}^2 = \hat{p}\,\hat{p} = -\,\hbar^2\,(d^2/dx^2)$, involves a derivative, so the order of operation is important, giving:

$$<p_x^2> = \frac{\int_o^a \Psi_n^*\, \hat{p}^2\, \Psi_n\, dx}{\int_o^a \Psi_n^*\, \Psi_n\, dx} = -\,\hbar^2 \int_0^a \Psi_n \frac{d^2}{dx^2} \Psi_n\, dx$$

The second derivative is:

$$\frac{d^2}{dx^2}\Psi_n = \left(\frac{2}{a}\right)^{½} \frac{d^2}{dx^2} \sin(n\pi x/a) = \left(\frac{2}{a}\right)^{½}\left(\frac{n\pi}{a}\right)\frac{d}{dx}\cos(n\pi x/a) = -\left(\frac{2}{a}\right)^{½}\left(\frac{n\pi}{a}\right)^2 \sin(n\pi x/a)$$

Substituting in the general form of the wave function gives:

$$<p_x^2> = -\,\hbar^2\left(\frac{2}{a}\right)\int_0^a \sin\,(n\pi x/a)\,\frac{d^2}{dx^2}\sin(n\pi x/a)\,dx = \hbar^2\left(\frac{2}{a}\right)\left(\frac{n\pi}{a}\right)^2\int_0^a \sin^2(n\pi x/a)\,dx$$

However, $\left(\frac{2}{a}\right)\int_0^a \sin^2(n\pi x/a)\,dx = 1$, since this integral is the normalization integral, giving:

$$<p_x^2> = \hbar^2 \left(\frac{n\pi}{a}\right)^2$$

30. Using the results of Problems 28 and 29, find the standard deviation of the momentum for a particle in a box:

$$\sigma_{px} = (<p_x^2> - <p_x>^2)^{½} = \hbar \left(\frac{n\pi}{a}\right)$$

Rationalize the results on the basis of the Heisenberg uncertainty principle.

Answer: (a). The standard deviation of the momentum for a particle in a box is, using Problems 28 and 29:

$$\sigma_{px} = (<p_x^2> - <p_x>^2)^{½} = \left(\hbar^2\left(\frac{n\pi}{a}\right)^2 - 0\right)^{½} = \hbar\left(\frac{n\pi}{a}\right)$$

As the box length increases, the uncertainty in position of the particle increases and the uncertainty in momentum decreases, which is expected on the basis of the Heisenberg uncertainty principle.

31. Using the results of Problems 27 and 30, show that $\sigma_x \, \sigma_p \geq \hbar/2$ for a particle in a box, in concordance with the Heisenberg uncertainty principle.

Answer: Using Problem 27 for σ_x and Problem 30 for σ_{px}:

$$\sigma_x \, \sigma_{px} = \frac{a}{2n\pi}\left(\frac{n^2\pi^2}{3} - 2\right)^{1/2} \hbar \left(\frac{n\pi}{a}\right) = \left(\frac{n^2\pi^2}{3} - 2\right)^{1/2} \frac{\hbar}{2}$$

The numeric factor multiplying $\hbar/2$ is greater than 1. For example, for n = 1:

$$\sigma_x \, \sigma_p = 1.136 \, \frac{\hbar}{2}$$

which is greater than $\hbar/2$ as required by the Heisenberg uncertainty relationship. The numerical factor is greater for greater quantum numbers.

32. Determine the standard deviation of the position, $(<x^2> - <x>^2)^{1/2}$, for the Gaussian wave function:

$$\Psi(x) = \frac{1}{(2\pi)^{1/4} \, \sigma_x^{1/2}} \, e^{-x^2/4\sigma_x^2} \qquad \text{over } -\infty \leq x \leq \infty$$

Answer: The given Gaussian wave function is normalized, $\int_{-\infty}^{\infty} \Psi^2 \, dx = 1$, and real, $\Psi^*\Psi = \Psi^2$. The normalization constant is $N = 1/[(2\pi)^{1/4}\sigma_x^{1/2}]$. The average position is zero for a symmetrical distribution because x is odd and Ψ^2 is even and the integral is taken over all space:

$$<x> = \int_{-\infty}^{\infty} \underset{\textit{normalized}}{\Psi^* \, x \, \Psi} \, dx = \int_{-\infty}^{\infty} \underset{\textit{real}}{x \, \Psi^2} \, dx = N^2 \int_{-\infty}^{\infty} \underset{\textit{odd}}{x} \, \underset{\textit{even}}{e^{-x^2/2\sigma_x^2}} \, dx = 0$$

The expectation value for the squared position is:

$$<x^2> = \int_{-\infty}^{\infty} \Psi^* \, x^2 \, \Psi \, dx = \int_{-\infty}^{\infty} x^2 \, \Psi^2 \, dx = N^2 \int_{-\infty}^{\infty} x^2 \, e^{-x^2/2\sigma_x^2} \, dx$$

The integrand is even so that $\int_{-\infty}^{\infty} = 2 \int_0^{\infty}$ giving: $\quad <x^2> = 2N^2 \int_0^{\infty} x^2 \, e^{-x^2/2\sigma_x^2} \, dx$

Integral tables give $\int_0^{\infty} x^2 \, e^{-x^2/2\sigma_x^2} \, dx = \frac{2\sigma_x^2}{4} (2\pi)^{1/2}\sigma_x$:

$$<x^2> = 2N^2 \, \frac{2\sigma_x^2}{4} (2\pi)^{1/2}\sigma_x = 2 \, \frac{1}{(2\pi)^{1/2} \, \sigma_x} \, \frac{2\sigma_x^2}{4} (2\pi)^{1/2}\sigma_x = \sigma_x^2$$

Finally $(<x^2> - <x>^2)^{1/2} = \sigma_x$, as expected. This result is used in Example 23.4.4.

33. Consider a particle in a box of length a with a potential that goes to infinity at $-a/2$ and $+a/2$. The general form of the wave function is given by Eq. 23.4.5 also applies for $-a/2 \leq x \leq +a/2$. Apply the boundary conditions to determine the wave function for the particle.

Answer: The plan is to follow the procedure used in Eqs. 23.4.5-23.4.8, but at the new end points. We also need to consider Ψ at the center of the box, $x = 0$.

At $x = 0$, in the center of the box: $\Psi(0) = A \sin(0) + B \cos(0) = B$

If $B = 0$ then each wave function will have a node in the center of the box and only half the possible wave functions will be represented. The conclusion is $B \neq 0$.

At $x = -a/2$ the wave function is: $\Psi(-a/2) = A \sin(-ka/2) + B \cos(-ka/2) = 0$ or

$$\Psi(-a/2) = -A \sin(ka/2) + B \cos(ka/2) = 0$$

At $x = + a/2$ the wave function is: $\Psi(a/2) = A \sin(ka/2) + B \cos(ka/2) = 0$

Consulting Figure 23.4.2a, if B is non-zero then at the boundary, $\cos(ka/2) = 0$ gives $ka/2 = n\pi/2$ or $k = n\pi/a$. However, then $\sin kx = \sin(n\pi/2) = 1$, which gives that $A = 0$. The combined result is then $\Psi(x) = B \cos(n\pi x/a)$. To verify our conclusions note that:

$$\Psi(-a/2) = B \cos(n\pi/2) = 0 \qquad \Psi(0) = B \cos(0) = B \qquad \Psi(a/2) = B \cos(n\pi/2) = 0$$

34. Give the wave function and energy for a 3D-particle in a box with quantum numbers (1,1,2) and side lengths a, b, and c for a particle of mass m.

Answer: The wave function and energy using Eqs. 23.6.15 and 23.6.16 are:

$$\Psi(x,y,z) = \left(\frac{8}{abc}\right)^{1/2} \sin\frac{\pi x}{a} \sin\frac{\pi y}{b} \sin\frac{2\pi z}{c} \qquad E = \frac{h^2}{8m}\left(\frac{1}{a^2} + \frac{1}{b^2} + \frac{4}{c^2}\right)$$

35. Why does a confined particle have quantized energy levels?

Answer: The particle in a box is an excellent example of a confined particle. The solution to the Schrödinger equation for a particle in a box is identical to a free particle until the boundary conditions are applied. Then $\sin kx$ is restricted to $\sin(n\pi x/a)$. The boundary conditions force the wave function to approach zero for small and large x. The wave function must then have an integer number of half-cycles to fulfill the required asymptotic behavior.

36. Find the average penetration depth of a particle of mass m and energy E into an infinite barrier of constant potential V. Assume the total energy is less than the potential energy, Figure 23.5.1a. Given the amplitude of the incident wave, a, show that the average penetration depth is:

$$<x> = \left(\frac{4k^2}{k^2 + \kappa^2}\right) \frac{a^2}{4\kappa^2}$$

Answer: The plan is to use Eqs. 23.5.3 with 23.5.6 to find the expectation value for the position of the particle inside the barrier with $\hat{x} = x$.

Inside the barrier $0 \le x \le \infty$ and the average or expectation value of the position for the tunneling particle is:

$$<x> = \int_0^\infty \Psi^* \, x \, \Psi \, dx = c^*c\int_0^\infty x \, e^{-2\kappa x} \, dx \quad \text{with } k = \frac{\sqrt{2mE}}{\hbar} \text{ and } \kappa = \frac{\sqrt{2m(V-E)}}{\hbar}$$

using Eqs. 23.3.6 and 23.5.2 for the constants k and κ.

Integral tables give the integral as: $\int_0^\infty x \, e^{-ax} \, dx = 1/a^2$:

$$<x> = c^*c/4\kappa^2$$

$$\text{with } c^*c = \left(\frac{-2ik}{-ik-\kappa}\right)\left(\frac{2ik}{ik-\kappa}\right) a^2 = \left(\frac{4k^2}{(-ik-\kappa)(ik-\kappa)}\right) a^2 = \left(\frac{4k^2}{k^2+\kappa^2}\right) a^2$$

Substitution of c^*c back into the integral gives:

$$<x> = \left(\frac{4k^2}{k^2+\kappa^2}\right)\frac{a^2}{4\kappa^2}$$

37. Find the tunneling probability for a 1.00 eV electron into a 2.00 eV potential energy barrier of thickness 10.0 Å.

Answer: The plan is to follow Example 23.5.1.

The ratio of the energy to the barrier height is $\varepsilon = 1.00/2.00 = 0.500$. Using Eq. 23.5.2 gives κ; for an electron $m_e = 9.109\text{x}10^{-31}$ kg:

$$\kappa = \frac{\sqrt{2m(V-E)}}{\hbar} = \frac{\sqrt{2(9.109\text{x}10^{-31}\text{ kg})(2.00\text{ eV} - 1.00\text{ eV})(1.602\text{x}10^{-19}\text{ J/1 eV})}}{1.055\text{x}10^{-34}\text{ J s}^{-1}}$$

$$\kappa = 5.121\text{x}10^{9}\text{ m}^{-1}$$

giving for L = 10.0 Å = $10.0\text{x}10^{-10}$ m:

$$e^{-\kappa L} = e^{-5.121\text{x}10^9(10.0\text{x}10^{-10})} = 0.005970 \quad \text{and} \quad \frac{(e^{\kappa L} - e^{-\kappa L})^2}{4} = 7.014\text{x}10^3$$

The tunneling probability is given by Eq. 23.5.7:

$$T = \left[\frac{(e^{\kappa L} - e^{-\kappa L})^2}{16\varepsilon(1-\varepsilon)} + 1\right]^{-1} = \left[\frac{7.014\text{x}10^3}{4(0.500)(1-0.500)} + 1\right]^{-1} = 1.43\text{x}10^{-4} \quad \text{or} \quad 0.0143\%$$

38. Show that $\Psi = N\, e^{-\alpha x}$ is an eigenfunction of the operator d^2/dx^2. What is the eigenvalue? Normalize the wave function for $x \ge 0$.

Answer: The plan is to show that $\hat{o}\Psi = o\Psi$, with o a constant.

Applying the operator to the wave function gives:

$$\frac{d^2}{dx^2}\Psi = \frac{d^2}{dx^2} N\, e^{-\alpha x} = N\, \alpha^2\, e^{-\alpha x}$$

Substituting back in the wave function, $\Psi = N\, e^{-\alpha x}$, gives: $\frac{d^2}{dx^2}\Psi = \alpha^2\, \Psi$

The operator applied to the wave function gives back a constant multiplied by the same wave function. Ψ is an eigenfunction of d^2/dx^2 with eigenvalue α^2. The normalization is given by:

$$\int_0^\infty \Psi^* \Psi\, dx = N^2 \int_0^\infty e^{-2\alpha x}\, dx = 1$$

$$= N^2 \left(\frac{-1}{2\alpha}\right) e^{-2\alpha x}\Big|_0^\infty = N^2 \left(\frac{-1}{2\alpha}\right)(e^{-\infty} - e^0) = \left(\frac{N^2}{2\alpha}\right) = 1$$

giving $N = (2\alpha)^{½}$

39. (a). Show that $\Psi(x) = e^{-ikx}$ is an eigenfunction of the momentum and kinetic energy operators, but not an eigenfunction of the position operator, for motion in one-dimension. (b). Will repeated measurements of the position, momentum, and kinetic energy give the same result or different results?

Answer: The plan is to note that by Postulates III and IV, if the wave function is an eigenfunction of the operator representing the given observable, then repeated measurements will give identical results. The operator for position is just "multiply by x": $\hat{x} = x$. The operator for momentum is $\hat{p}_x = (\hbar/i)(d/dx)$. The operator for kinetic energy in the x-direction is $\hat{E}_k = -(\hbar^2/2m)(d^2/dx^2)$.

If $\hat{o}\Psi = o\Psi$, with o a constant, then Ψ is an eigenfunction. For the momentum:

$$\hat{p}_x\, \Psi = \frac{\hbar}{i}\frac{d}{dx} e^{-ikx} = -\hbar k\, e^{-ikx} = -\hbar k\, \Psi$$

The wave function is an eigenfunction of the momentum operator, so every observation of the momentum will give the same result, $-\hbar k$.

For the kinetic energy:

$$\hat{E}_k\Psi = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\Psi = \frac{\hbar^2 k^2}{2m} e^{-ikx} = \frac{\hbar^2 k^2}{2m}\Psi$$

The wave function is an eigenfunction of the kinetic operator, so every observation of the kinetic energy will give the same result, $\hbar^2 k^2/2m$.

The wave function is not an eigenfunction of the position operator:

$$\hat{x}\, \Psi = x\, e^{-ikx}$$

Repeated observations of the position of the particle will give different results, over the full range allowed for x: $-\infty \le x \le \infty$.

40. What are the restrictions on the wave functions that may represent physical systems? Can the following be valid wave functions? (a). $\Psi(x) = N \ln x$ for $0 \leq x \leq \infty$, (b). $\Psi(x) = N e^{ax^2}$ for $-\infty \leq x \leq \infty$, and (c). $\Psi(x) = N x e^{-ax}$ with $a > 0$ and the range $0 \leq x \leq \infty$.

Answer: By the Born interpretation, $\psi^*(x)\, \psi(x)\, dx$ is the probability of finding the particle in the interval x to x + dx. To be interpreted as a probability, $\psi^*(x)\, \psi(x)$ must be real, non-negative, single-valued, and normalizable. To be normalizable, the function must be square integrable; the product must remain finite across the allowed range.

(a). Considering $\Psi(x) = N \ln x$ for $0 \leq x \leq \infty$: note that $\ln x \to -\infty$ as $x \to 0$, so ln x is not finite over the given range and is therefore not a valid wave function.

(b). Considering $\Psi(x) = N e^{ax^2}$ for $-\infty \leq x \leq \infty$: if a is positive the exponential diverges to infinity for $x \to \pm \infty$. Therefore, for $a > 0$ the function is not acceptable. However, for $a < 0$ the function is finite over the full range, approaches zero asymptotically for $\pm x$, and defining $b = -a$ (see standard integral tables or the back cover over-leaf):[1]

$$\int_{-\infty}^{\infty} \psi^*(x)\, \psi(x)\, dx = 2\, N^2 \int_0^{\infty} e^{-2bx^2}\, dx = 2\, N^2 \frac{1}{2}\left(\frac{\pi}{2b}\right)^{1/2} \qquad (b > 0)$$

and so is normalizable.

(c). Considering $\Psi(x) = N x e^{-ax}$ for $0 \leq x \leq \infty$: as $x \to 0$ then $e^{-ax} \to 1$ and $x e^{-ax} \to 0$, which is acceptable. As $x \to \infty$ then $e^{-ax} \to 0$ but $x \to \infty$. However, as a test, evaluating $x e^{-ax}$ for $a = 1$ and $x = 100$ gives $x e^{-ax} = 4\text{x}10^{-42}$. The function asymptotically approaches zero.

The official method to find the asymptotic behavior of $x e^{-ax}$ is to use L'Hospital's rule. Consider the function as the ratio x/e^{ax}; both numerator and denominator diverge to infinity. The ratio of the derivatives is $1/(ae^{ax})$ and $\lim(1/(ae^{ax}))$ as $x \to \infty$ gives 0. The function asymptotically approaches zero for large x.

The function is also square integrable; the integral is available in standard tables as:

$$\int_0^{\infty} \psi^*(x)\, \psi(x)\, dx = N^2 \int_0^{\infty} x^2 e^{-2ax}\, dx = N^2 \frac{2!}{8a^3}$$

The function would not be acceptable for $x < 0$, because the function would diverge to $-\infty$.

41. Show that a linear combination of two eigenfunctions of the momentum that have the same momentum is also an eigenfunction of the momentum.

Answer: Let two eigenfunctions, Ψ_A and Ψ_B, have the same momentum, p:

$$\hat{p}\Psi_A = p\, \Psi_A \qquad \text{and} \qquad \hat{p}\Psi_B = p\, \Psi_B \qquad 1$$

A linear combination of the two separate solutions is $\Psi = a\, \Psi_A + b\, \Psi_B$, for a and b constants. The momentum is a linear operator. Applying the momentum operator to the linear combination:

$$\hat{p}\Psi = \hat{p}(a\, \Psi_A + b\, \Psi_B) = a\, \hat{p}\Psi_A + b\, \hat{p}\Psi_B$$

However, using Eq. 1 for the individual terms gives:

$$\hat{p}\Psi = a\,p\Psi_A + b\,p\Psi_B$$

Distributing out the common factor of p gives:

$$\hat{p}\Psi = p\,(a\,\Psi_A + b\,\Psi_B) = p\,\Psi$$

which shows that the linear combination is also a valid eigenfunction of the momentum. This result shows that degenerate solutions are not unique; any linear combination of degenerate solutions is also a solution.

42. Determine the value for the commutation relationship between the observation time and total energy of a particle, $[\hat{t},\hat{E}]$. [Hint: apply the commutator as an operator for an arbitrary function, f(t)]

Answer: The plan is to note that $[\hat{t},\hat{E}] = (\hat{t}\,\hat{E} - \hat{E}\,\hat{t})$. The operator for time is just "multiply by t": $\hat{t} = t$. The operator for total energy is $\hat{E} = i\hbar\,(d/dt)$.

With f(t) as an arbitrary function of t:

$$[\hat{t},\hat{E}]\,f = (t\,\hat{E} - \hat{E}\,t)\,f = t\,\hat{E}\,f - \hat{E}\,t\,f = i\hbar\left(t\frac{\partial f}{\partial t} - \frac{\partial (tf)}{\partial x}\right)$$

Using the product rule for the last derivative:

$$[\hat{t},\hat{E}]\,f = i\hbar\left(t\frac{\partial f}{\partial t} - t\frac{\partial f}{\partial t} - f\frac{\partial t}{\partial t}\right) = -\,i\hbar\,f$$

Dividing both sides of this expression by f gives the final result:

$$[\hat{t},\hat{E}] = -\,i\hbar$$

This result holds for any wave function. Since the commutator for time and energy does not vanish, the two observables are governed by the Heisenberg uncertainty principle. Observation time and energy cannot both be defined to high precision, $\Delta E\,\Delta t > \hbar/2$.

43. Consider a two-dimensional problem, such as the two-dimensional particle in a box. Determine the value for the commutation relationship between the position in the x-direction and the momentum in the y-direction, $[\hat{x},\hat{p}_y]$. [Hint: apply the commutator as an operator for an arbitrary function, f(x,y)]

Answer: The plan is to note that $[\hat{x},\hat{p}_y] = (\hat{x}\,\hat{p}_y - \hat{p}_y\,\hat{x})$. The operator for the x-position is just "multiply by x": $\hat{x} = x$. The operator for the momentum in the y-direction is $\hat{p}_y = (\hbar/i)(\partial/\partial y)_x$.

With f(x,y) as an arbitrary function of x and y:

$$[\hat{x},\hat{p}_y]\, f = (\hat{x}\, \hat{p}_y - \hat{p}_y\, \hat{x})\, f = \hat{x}\, \hat{p}_y\, f - \hat{p}_y \hat{x}\, f = (\,\hbar/i) \left(x \left(\frac{\partial f}{\partial y}\right)_x - \left(\frac{\partial (xf)}{\partial y}\right)_x \right)$$

For the last derivative, x is a constant and factors through the derivative with respect to y:

$$[\hat{x},\hat{p}_y]\, f = (\,\hbar/i) \left(x \left(\frac{\partial f}{\partial y}\right)_x - x \left(\frac{\partial f}{\partial y}\right)_x \right) = 0$$

In general, the commutator vanishes and both the x-position and the y-momentum can be simultaneously precisely defined.

44. Determine the value for the commutation relationship between the momentum and kinetic energy of a particle in one-dimension, $[\hat{p}_x, \hat{E}_k]$. [Hint: apply the commutator as an operator for an arbitrary function, f(x)]

Answer: The plan is to note that $[\hat{p}_x,\hat{E}_k] = (\hat{p}_x\, \hat{E}_k - \hat{E}_k\, \hat{p}_x)$. The operator for momentum is $\hat{p}_x = (\,\hbar/i)(d/dx)$. The operator for kinetic energy in the x-direction is $\hat{E}_k = -(\,\hbar^2/2m)(d^2/dx^2)$.
With f(x) as an arbitrary function of x:

$$[\hat{p}_x,\hat{E}_k]\, f = (\hat{p}_x\, \hat{E}_k - \hat{E}_k\, \hat{p}_x)\, f = \hat{p}_x\, \hat{E}_k\, f - \hat{E}_k\, \hat{p}_x\, f = -(\,\hbar^3/2mi) \left(\frac{d}{dx}\frac{d^2 f}{dx^2} - \frac{d^2}{dx^2}\frac{df}{dx} \right) = 0$$

Both terms result in the third derivative, and are then identical. In general, the commutator vanishes and both the momentum and kinetic energy for motion in the x-direction can be simultaneously precisely defined.

45. Find the absolute values for the following:
(a). 2 + i6, (b). $e^{-i\alpha x^2}$, (c). cos(nπx/a) + i sin(nπx/a), (d). $e^{-i\,n\pi x/a}$ and (e). – ħ/i.

Answer: Note that since i·i = -1. For a complex number, $|z| = (z^*z)^{1/2}$, giving:

(a). $|2 + i6\,| = [(2 - i6)(\,2 + i6)]^{1/2} = [4 - i12 + i12 + 36]^{1/2} = [40]^{1/2}$

(b). $|e^{-i\alpha x^2}\,| = [e^{i\alpha x^2}\, e^{-i\alpha x^2}\,]^{1/2} = [e^0]^{1/2} = 1$

(c). $|\cos(n\pi x/a) + i \sin(n\pi x/a)| = [\,(\cos(n\pi x/a) - i \sin(n\pi x/a))\,(\cos(n\pi x/a) + i \sin(n\pi x/a))\,]^{1/2}$
$= [\,\cos^2(n\pi x/a) + i \cos(n\pi x/a) \sin(n\pi x/a) - i \sin(n\pi x/a) \cos(n\pi x/a) + \sin^2(n\pi x/a)]^{1/2}$
$= [\,\cos^2(n\pi x/a) + \sin^2(n\pi x/a)]^{1/2} = 1$

(d). $|e^{-i\,n\pi x/a}| = [e^{i\,n\pi x/a}\, e^{-i\,n\pi x/a}]^{1/2} = [e^0]^{1/2} = 1$

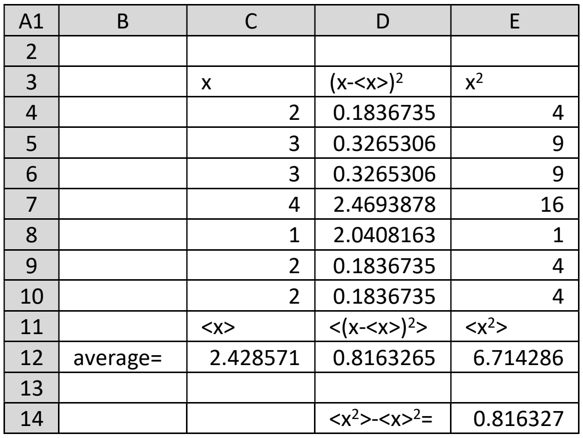
(e). $|-\hbar/i\,| = [(+\,\hbar/i\,)(-\,\hbar/i\,)]^{1/2} = \hbar$

Note that parts (c) and (d) are equivalent, so they should give the same answer:

$$e^{-i\,n\pi x/a} = \cos(n\pi x/a) + i \sin(n\pi x/a)$$

46. Using explicit summations, show that $\sigma_x^2 = <(x - <x>)^2>$ is equivalent to $\sigma_x^2 = <x^2> - <x>^2$. Use the trial data set x = {2,3,3,4,1,2,2}.

Answer: The following spreadsheet was developed to do the necessary averages.



A1	B	C	D	E
2				
3		x	(x-<x>)^2	x^2
4		2	0.1836735	4
5		3	0.3265306	9
6		3	0.3265306	9
7		4	2.4693878	16
8		1	2.0408163	1
9		2	0.1836735	4
10		2	0.1836735	4
11		<x>	<(x-<x>)^2>	<x^2>
12	average=	2.428571	0.8163265	6.714286
13				
14			<x^2>-<x>^{2}=	0.816327

The formula in D4 is: "=(C4-$C$12)^2". The average of each column is in row 12. The final result verifies that $\sigma_x = <(x - <x>)^2> = <x^2> - <x>^2$.

47. Prove that $\sigma_x = <(x - \bar{x})^2>^{½} = (<x^2> - <x>^2)^{½}$ (Eq. 23.4.36).

Answer: The multiplication gives:

$$(x - \bar{x})^2 = x^2 - 2\,x\bar{x} + \bar{x}^2$$

The averages are: $<(x - \bar{x})^2> = <x^2> - 2\,<x>\bar{x} + \bar{x}^2$

However, since $<x> = \bar{x}$, the second and third terms combine to give:

$$<(x - \bar{x})^2> = <x^2> - <x>^2$$

and taking the square root: $\sigma_x = <(x - \bar{x})^2>^{½} = (<x^2> - <x>^2)^{½}$

48. The moments of a probability distribution characterize the distribution. The first moment is the mean, $<x> = \bar{x}$. The second central moment is the standard deviation, $\sigma_x = [<(x - \bar{x})^2>]^{½}$. Central moments are evaluated using the deviations from the mean $(x - \bar{x})$. The third central moment is defined as $[<(x - \bar{x})^3>]^{1/3}$. The third central moment is a measure of the asymmetry about the mean for the distribution. For example, for a Gaussian distribution the third central moment is zero. (a). Prove that the third central moment can be calculated using:

$$<(x - \bar{x})^3> = <x^3> - 3\,\bar{x}\,<x^2> + 2\,\bar{x}^3$$

(b). Verify the formula using explicit summations with the trial data set listed in the previous problem.

Answer: The plan is to parallel the derivation for Problem 47 with $\langle(x-\bar{x})^3\rangle$.
(a). The multiplications are:

$$(x-\bar{x})^3 = (x^2 - 2\,x\bar{x} + \bar{x}^2)(x-\bar{x}) = x^3 - 3\,x^2\bar{x} + 3\,x\,\bar{x}^2 - \bar{x}^3$$

The averages are: $\langle(x-\bar{x})^3\rangle = \langle x^3\rangle - 3\,\langle x^2\rangle\bar{x} + 3\,\langle x\rangle\,\bar{x}^2 - \bar{x}^3$
However, since $\langle x\rangle = \bar{x}$, the third and fourth terms combine to give:

$$\langle(x-\bar{x})^3\rangle = \langle x^3\rangle - 3\,\bar{x}\,\langle x^2\rangle + 2\,\bar{x}^3$$

(b). The following spreadsheet was developed to do the necessary averages to verify the equality.

x	(x-<x>)³	x³	x²
2	-0.07872	8	4
3	0.186589	27	9
3	0.186589	27	9
4	3.880466	64	16
1	-2.91545	1	1
2	-0.07872	8	4
2	-0.07872	8	4
<x>	<(x-<x>)³>	<x³>	<x²>
2.428571	0.157434	20.42857	6.714286
	<x³> –3x̄<x²>	+ 2x̄³ =	0.157434

<u>49</u>. Use Eq. 23.7.35 to determine the product of the uncertainty in the position and momentum for a one-dimensional particle in a box of length a for n = 2.

Answer: The plan is to note that $[x,p_x] = -(\hbar/i)$.

The particle in the box wave function is $\Psi_2(x) = (2/a)^{½} \sin 2\pi x/a$. The product of the uncertainty in the position and momentum, using Eq. 23.7.35, is:

$$\sigma_x\,\sigma_p \geq ½\,\left|\int_0^a \Psi_2^*\,[x,p_x]\,\Psi_2\,dx\right| = (1/a)\,\left|\int_0^a \sin(2\pi x/a)\,(-\hbar/i)\,\sin(2\pi x/a)\,dx\right|$$

$$\sigma_x\,\sigma_p \geq ½\,|-\hbar/i\,|\,(2/a)\int_0^a \sin^2(2\pi x/a)\,dx$$

For a complex number, $|z| = (z^*z)^{½}$, giving $|-\hbar/i\,| = [(+\hbar/i\,)(-\hbar/i\,)]^{½} = \hbar$. The particle in a box wave function is normalized so that:

$$\int_0^a \Psi^*\,\Psi\,dx = (2/a)\int_0^a \sin^2(2\pi x/a)\,dx = 1$$

Using this normalization:

$$\sigma_x\,\sigma_p \geq \hbar/2$$

which corresponds to the Heisenberg uncertainty relationship.

50. Show that the commutator for the position and kinetic energy of a particle, in one-dimension, is:

$$[\hat{x},\hat{E}_k] = -(i\hbar/m)\,\hat{p}$$

Can position and kinetic energy be simultaneously defined to high precision? [Hint: find the result of the commutator operating on an arbitrary function f(x).]

Answer: The plan is to find $[\hat{x},\hat{E}_k]f(x) = (\hat{x}\hat{E}_k - \hat{E}_k\hat{x})f(x)$. The operator for position is just "multiply by x," $\hat{x} = x$. The kinetic energy operator in one linear-dimension is $\hat{E}_k = -(\hbar^2/2m)\, d^2/dx^2$.

Expanding the commutator and applying the operators to f(x) gives:

$$[\hat{x},\hat{E}_k]f = (\hat{x}\hat{E}_k - \hat{E}_k\hat{x})f = \hat{x}\hat{E}_k f - \hat{E}_k\hat{x}f = -(\hbar^2/2m)\left(x\frac{d^2f}{dx^2} - \frac{d^2(xf)}{dx^2}\right)$$

Using the product rule, twice, for the last derivative gives:

$$\frac{d}{dx}\left(\frac{d(xf)}{dx}\right) = \frac{d}{dx}\left(x\frac{df}{dx} + f\frac{dx}{dx}\right) = x\frac{d^2f}{dx^2} + \frac{df}{dx}\frac{dx}{dx} + \frac{df}{dx} = x\frac{d^2f}{dx^2} + 2\frac{df}{dx}$$

Substituting this last result back into the commutation relationship gives:

$$[\hat{x},\hat{E}_k]f = -(\hbar^2/2m)\left(x\frac{d^2f}{dx^2} - x\frac{d^2f}{dx^2} - 2\frac{df}{dx}\right) = 2\,(\hbar^2/2m)\frac{df}{dx}$$

Note that the momentum operator is $\hat{p} = \hbar/i\ d/dx$, which upon substitution into the commutation relationship gives:

$$[\hat{x},\hat{E}_k]f = -(\hbar^2/2m)\left(x\frac{d^2f}{dx^2} - x\frac{d^2f}{dx^2} - 2\frac{df}{dx}\right) = -(i\hbar/m)\,\hat{p}\,f$$

The final result is: $[\hat{x},\hat{E}_k] = -(i\hbar/m)\,\hat{p}$. The position and kinetic energy of a particle cannot be simultaneously specified precisely.

51. Is the operator $\hat{o} = (d/dx)$ Hermitian? [Hint: use integration by parts: $\int u\,dv = uv - \int v\,du$]

Answer: The plan is to follow Example 23.7.4. The goal is to show that:

$$\int \Psi_j^* \left(\frac{d}{dx}\right) \Psi_i\, dx = \int \Psi_i \left(\frac{d}{dx}\right)^* \Psi_j^*\, dx \qquad 1$$

Starting with the left hand integral:

$$\int_{-\infty}^{\infty} \Psi_j^* \left(\frac{d}{dx}\right) \Psi_i\, dx = \int_{-\infty}^{\infty} \Psi_j^*\, d\Psi_i$$

Integration by parts, with $u = \Psi_j^*$ and $dv = d\Psi_i$, gives:

$$\int_{-\infty}^{\infty} \Psi_j^* \, d\Psi_i = \Psi_j^*\Psi_i\Big|_{x=-\infty}^{x=\infty} - \int_{-\infty}^{\infty} \Psi_i \, d\Psi_j^* \qquad 2$$

The product $\Psi_j^*\Psi_i$ goes to zero at each endpoint. Substituting this last equation back into Eq. 1 gives:

$$\int_{-\infty}^{\infty} \Psi_j^* \left(\frac{d}{dx}\right) \Psi_i \, dx = -\int_{-\infty}^{\infty} \Psi_i \, d\Psi_j^* = -\int_{-\infty}^{\infty} \Psi_i \left(\frac{d}{dx}\right) \Psi_j^* \, dx \qquad 3$$

Finally, $(d/dx)^* = (d/dx)$ so that the last equation reduces to:

$$\int_{-\infty}^{\infty} \Psi_j^* \left(\frac{d}{dx}\right) \Psi_i \, dx = -\int_{-\infty}^{\infty} \Psi_i \left(\frac{d}{dx}\right)^* \Psi_j^* \, dx \qquad 4$$

which shows that (d/dx) is <u>not</u> Hermitian. The "i" in the definition, $\hat{p} = -i\hbar\,(d/dx)$, is necessary for the momentum operator to be Hermitian.

<u>52</u>. (*Challenge Problem*) Show that the operator (d^2/dx^2) is Hermitian. Is the kinetic energy operator also Hermitian? Do the problem using the following intermediate steps. (a). Show that: [Hint: use integration by parts, $\int u\, dv = uv - \int v\, du$.]

$$\int_{-\infty}^{\infty} \Psi_j^* \left(\frac{d^2}{dx^2}\right) \Psi_i \, dx = -\int_{-\infty}^{\infty} \left(\frac{d\Psi_i}{dx}\right) d\Psi_j^* = -\int_{-\infty}^{\infty} \left(\frac{d\Psi_i}{dx}\right)\left(\frac{d\Psi_j^*}{dx}\right) dx$$

(b). Show that: [Hint: use integration by parts again.]

$$\int_{-\infty}^{\infty} \Psi_j^* \left(\frac{d^2}{dx^2}\right) \Psi_i \, dx = \int_{-\infty}^{\infty} \Psi_i \left(\frac{d}{dx}\right)\left(\frac{d\Psi_j^*}{dx}\right) dx$$

(c). Finally show that (d^2/dx^2) is Hermitian by proving that:

$$\int \Psi_j^* \left(\frac{d^2}{dx^2}\right) \Psi_i \, dx = \int \Psi_i \left(\frac{d^2}{dx^2}\right)^* \Psi_j^* \, dx$$

(d). Is the kinetic energy operator also Hermitian?

Answer: The plan is to follow Example 23.7.4. The goal is to show that:

$$\int \Psi_j^* \left(\frac{d^2}{dx^2}\right) \Psi_i \, dx = \int \Psi_i \left(\frac{d^2}{dx^2}\right)^* \Psi_j^* \, dx \qquad 1$$

(a). Starting with the left hand integral:

$$\int_{-\infty}^{\infty} \Psi_j^* \left(\frac{d^2}{dx^2}\right) \Psi_i \, dx = \int_{-\infty}^{\infty} \Psi_j^* \left(\frac{d}{dx}\right)\left(\frac{d\Psi_i}{dx}\right) dx = \int_{-\infty}^{\infty} \Psi_j^* \, d\left(\frac{d\Psi_i}{dx}\right)$$

Integration by parts, with $u = \Psi_j^*$ and $dv = d(d\Psi_i/dx)$, gives:

$$\int_{-\infty}^{\infty} \Psi_j^* \, d\left(\frac{d\Psi_i}{dx}\right) = \Psi_j^* \left(\frac{d\Psi_i}{dx}\right)\Big|_{x=-\infty}^{x=\infty} - \int_{-\infty}^{\infty} \left(\frac{d\Psi_i}{dx}\right) d\Psi_j^* \qquad 2$$

The wave function Ψ_j^* and ($d\Psi_i/dx$) go to zero at each endpoint, because the wave functions approach zero asymptotically for large distances. Substituting this last equation back into Eq. 1:

$$\int_{-\infty}^{\infty} \Psi_j^* \left(\frac{d^2}{dx^2}\right) \Psi_i \, dx = -\int_{-\infty}^{\infty} \left(\frac{d\Psi_i}{dx}\right) d\Psi_j^* = -\int_{-\infty}^{\infty} \left(\frac{d\Psi_i}{dx}\right)\left(\frac{d\Psi_j^*}{dx}\right) dx \qquad 3$$

(b). However, the two derivatives in this last expression are functions and can switch places, since the derivatives are completed and the resulting functions commute:

$$\int_{-\infty}^{\infty} \Psi_j^* \left(\frac{d^2}{dx^2}\right) \Psi_i \, dx = -\int_{-\infty}^{\infty} \left(\frac{d\Psi_j^*}{dx}\right)\left(\frac{d\Psi_i}{dx}\right) dx = -\int_{-\infty}^{\infty} \left(\frac{d\Psi_j^*}{dx}\right) d\Psi_i \qquad 4$$

This last integral can also be integrated by parts, with $u = (d\Psi_j^*/dx)$ and $dv = d\Psi_i$, giving:

$$\int_{-\infty}^{\infty} \Psi_j^* \left(\frac{d^2}{dx^2}\right) \Psi_i \, dx = -\left(\frac{d\Psi_j^*}{dx}\right)\Psi_i\Big|_{x=-\infty}^{x=\infty} + \int_{-\infty}^{\infty} \Psi_i \, d\left(\frac{d\Psi_j^*}{dx}\right) \qquad 5$$

The first term again goes to zero at the extremes in x. The last integral expands back giving:

$$\int_{-\infty}^{\infty} \Psi_j^* \left(\frac{d^2}{dx^2}\right) \Psi_i \, dx = \int_{-\infty}^{\infty} \Psi_i \left(\frac{d}{dx}\right)\left(\frac{d\Psi_j^*}{dx}\right) dx \qquad 6$$

(c). Finally, $(d^2/dx^2)^* = (d^2/dx^2)$ so that the last equation reduces to Eq. 1, which shows that $\hat{o} = (d^2/dx^2)$ is Hermitian.
(d). Since the kinetic energy operator is the second derivative multiplied by a constant, $E_k = -(\hbar^2/2m)(d^2/dx^2)$, the kinetic energy operator is also Hermitian.

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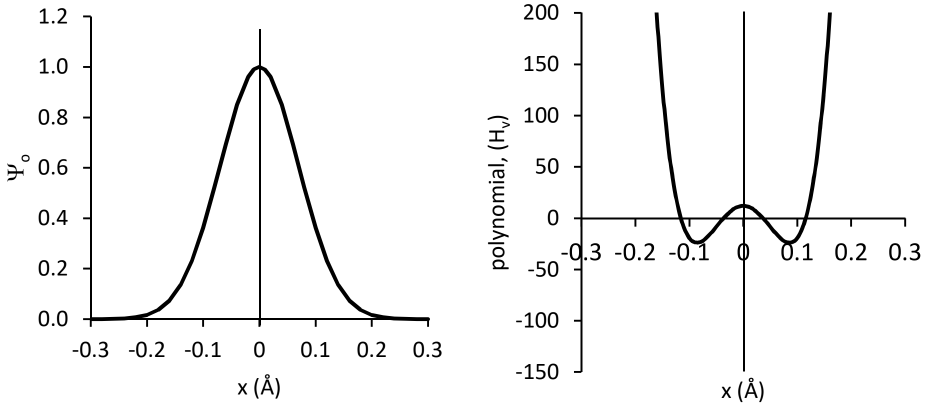
Chapter 24 Problems: The Quantum Mechanics of Rotation and Vibration

1. (a). How many nodes are in the $\upsilon = 3$ wave function for the harmonic oscillator? (b). How many angular nodes are in the $\ell = 3$, $m_\ell = 2$ wave function for the rigid rotor? (c). How many of the angular nodes for the $\ell = 3$, $m_\ell = 2$ rigid rotor include the z-axis? (d). Why are the nodes important?

Answer: (a). The lowest energy state for the harmonic oscillator is for $\upsilon = 0$, which has no nodes. The number of nodes is therefore given by υ. For $\upsilon = 3$ there are three nodes. Reference to Figure 24.2.3b verifies the assignment.
(b). The total number of angular nodes for the rigid rotor is given by ℓ and the number of nodes that include the z-axis is m_ℓ. For $\ell = 3$ there are 3 total nodes.
(c). For $m_\ell = 2$, there are 2 nodes that include the z-axis. The spherical harmonics for this wave function have the same angular distribution as an atomic f-orbital.
(d). Nodes are important because they are a measure of the curvature of the wave function, which in turn determines the kinetic energy. The nodes that include the z-axis also determine the orientation of the angular momentum vector. For $m_\ell = \ell$, all the nodes include the z-axis and the angular momentum vector has its maximum projection on the z-axis. For $m_\ell = 0$, the angular momentum vector is perpendicular to the z-axis. The number of nodes that include the z-axis determines the spatial quantization.

2. Multiply the harmonic oscillator ground state wave function, Figure P24.1a, by the polynomial, Figure P24.1b, to give the excited state wave function. Sketch the excited state wave function. What is the quantum number for this wave function?

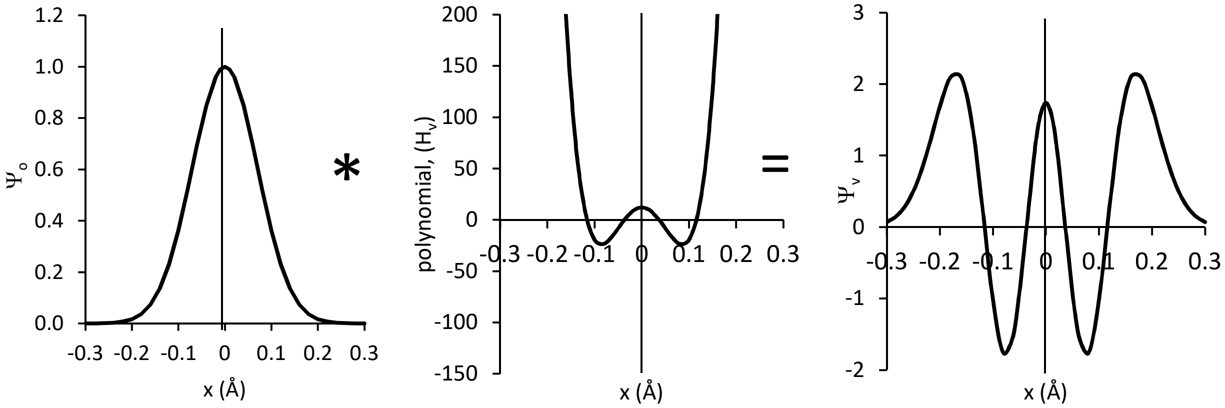


(a). (b).

Figure P24.1: (a) The ground state for the harmonic oscillator. (b). The polynomial used to generate an excited state of the harmonic oscillator. The polynomial is a Hermite polynomial.

Answer: The plan is to note that the excited state is the product of the ground state wave function and a polynomial. Also, note that v for the ground state is zero and there are no nodes for the ground state.

The ground state wave function determines the asymptotic form for the wave function at large r. The number of zeros for the polynomial determines the number of nodes for the excited state wave function. The number of nodes is equal to the quantum number, nodes = v. For this example, there are four nodes giving v = 4.



3. (a). The fundamental vibration frequency for $^1H^{79}Br$ is 2649.67 cm^{-1}. Calculate the force constant. Calculate the energy for the transition in kJ mol^{-1}. (b). The force constant for the vibration in $^1H^{35}Cl$ is 515.90 N m^{-1}. Calculate the vibration frequency in cm^{-1}. Calculate the energy for the transition in kJ mol^{-1}. (c). Which has a stronger bond, and why?

Answer: The plan is to note that the fundamental vibration frequency is given by: $\nu = (1/2\pi)\sqrt{k/\mu}$ with $\mu = [\mathfrak{M}_1\mathfrak{M}_2/(\mathfrak{M}_1 + \mathfrak{M}_2)](1/N_A)(1\ \text{kg}/1000\ \text{g})$. The units for the force constant are N m^{-1} and the reduced mass kg molecule^{-1}, or officially just kg.

(a). The wavenumber is converted to m^{-1} by $\tilde{\nu} = 2649.67\ \text{cm}^{-1}(100\ \text{cm}/1\ \text{m})$. The frequency-wavenumber conversion is given by solving $\nu\lambda = c$:

$$\tilde{\nu} = \frac{1}{\lambda} = \frac{\nu}{c} \qquad \text{and} \qquad \nu = \tilde{\nu}c = 264967.\ \text{m}^{-1}(2.99792458\text{x}10^8\text{m s}^{-1})$$
$$= 7.943511\text{x}10^{13}\ \text{s}^{-1}$$

The reduced mass is given using isotope specific atomic masses:

$$\mu = \left(\frac{\mathfrak{M}_1\mathfrak{M}_2}{\mathfrak{M}_1 + \mathfrak{M}_2}\right)\frac{1}{N_A}(1\ \text{kg}/1000\ \text{g})$$
$$= \frac{1.0078250\ \text{g mol}^{-1}(78.918337\ \text{g mol}^{-1})}{1.0078250\ \text{g mol}^{-1} + 78.918337\ \text{g mol}^{-1}}\left(\frac{1}{6.0221367\text{x}10^{23}\ \text{mol}^{-1}}\right)(1\ \text{kg}/1000\ \text{g})$$
$$= 1.652432\text{x}10^{-27}\text{kg}$$

The force constant and energy change for the transition are:

$$k = 4\pi^2\nu^2\mu = 4\pi^2(7.943511\text{x}10^{13}\ \text{s}^{-1})^2(1.652432\text{x}10^{-27}\text{kg}) = 411.631\ \text{N m}^{-1}$$

$$\Delta E = h\nu(N_A)(1\ \text{kJ}/1000\ \text{J}) = hc\tilde{\nu}\ N_A\ (1\ \text{kJ}/1000\ \text{J})$$
$$= 6.626076\text{x}10^{-34}\ \text{J s}(2.997925\text{x}10^8\text{m s}^{-1})(264967.\ \text{m}^{-1})(6.0221367\text{x}10^{23}\ \text{mol}^{-1})(1\ \text{kJ}/1000\ \text{J})$$
$$= 31.6971\ \text{kJ mol}^{-1}$$

(b). The calculations are summarized in the table, below.

Molecule	ν (cm^{-1})	$\mathfrak{M}_1$ (g mol^{-1})	$\mathfrak{M}_2$ (g mol^{-1})	μ (kg)	k(N m^{-1})	ΔE (J)	ΔE (kJ mol^{-1})
$^{1}H^{79}Br$	2649.67	1.0078250	78.918337	$1.6524\text{x}10^{-27}$	411.631	$5.263\text{x}10^{-20}$	31.6971
$^{1}H^{35}Cl$	2989.74	1.0078250	34.9688527	$1.6267\text{x}10^{-27}$	515.90	$5.939\text{x}10^{-20}$	35.765

(c). Because HCl has the larger force constant, HCl has the stronger bond. The reason is often ascribed to the larger atomic radius for Br atoms compared to Cl, which gives a longer bond for HBr.

4. Normalize the wave function for the ground state of the harmonic oscillator, $\Psi_o = N\, e^{-\frac{1}{2}\alpha^2 x^2}$ (without using Eq. 24.2.22).

Answer: The plan is to use the normalization integral, $\int_{-\infty}^{\infty} \Psi^*\Psi\, dx = 1$, to find the normalization constant N.

Remember that $(e^x)^2 = e^{2x}$. Substitution of the wave function into the normalization integral gives:

$$N^2 \int_{-\infty}^{\infty} e^{-\alpha^2 x^2}\, dx = 1 \qquad\qquad \text{with} \quad \alpha^2 = m\omega_o/\hbar$$

This integrand is even about x = 0. Using the table in the Appendix: $\int_0^{\infty} e^{-ax^2}\, dx = \frac{1}{2}\,(\pi/a)^{\frac{1}{2}}$:

$$N^2\, 2\int_0^{\infty} e^{-\alpha^2 x^2}\, dx = N^2\,(\pi/\alpha^2)^{\frac{1}{2}} = 1$$

Solving for the normalization constant gives: $N = \left(\frac{\alpha^2}{\pi}\right)^{\frac{1}{4}} = \left(\frac{m\omega_o}{\pi\hbar}\right)^{\frac{1}{4}}$

The complete wave function is then: $\Psi_o = \left(\frac{\alpha^2}{\pi}\right)^{\frac{1}{4}} e^{-\frac{1}{2}\alpha^2 x^2} = \left(\frac{m\omega_o}{\pi\hbar}\right)^{\frac{1}{4}} e^{-\frac{m\omega_o}{2\hbar} x^2}$

5. Find the expectation values for the position and momentum of the ground state of the harmonic oscillator.

Answer: The plan is to note that the position operator is just "multiply by x", $\hat{x} = x$, and the momentum operator is $\hat{p} = \hbar/i\,(d/dx)$. The expectation values are then:

$$\langle x\rangle = \frac{\int_{-\infty}^{\infty} \Psi_o^*\, x\, \Psi_o\, dx}{\int_{-\infty}^{\infty} \Psi_o^*\, \Psi_o\, dx} \qquad \text{and} \qquad \langle p\rangle = \frac{\int_{-\infty}^{\infty} \Psi_o^*\, \frac{\hbar}{i}\left(\frac{d}{dx}\right) \Psi_o\, dx}{\int_{-\infty}^{\infty} \Psi_o^*\, \Psi_o\, dx}$$

Since the harmonic oscillator wave functions are real, $\Psi^* = \Psi$. We will use the normalized form of the wave function, $N = (\alpha^2/\pi)^{\frac{1}{4}}$, giving $\int_{-\infty}^{\infty} \Psi_o^2\, dx = 1$.

The expectation value of the position, using a normalized wave function, is:

$$<x> = \int_{-\infty}^{\infty} \Psi_o^* \, x \, \Psi_o \, dx = N^2 \int_{-\infty}^{\infty} e^{-½ \alpha^2 x^2} \, x \, e^{-½ \alpha^2 x^2} \, dx$$

The integrand is a product of functions, so the order is immaterial:

$$<x> = N^2 \int_{-\infty}^{\infty} \underset{\substack{\uparrow \\ \textit{odd}}}{x} \;\; \underset{\substack{\uparrow \\ \textit{even}}}{e^{-\alpha^2 x^2}} \, dx$$

The integrand is the product of an odd and an even function over all space, which gives an integral of zero: <x> = 0.

The expectation value of the momentum, using a normalized wave function, is:

$$<p> = \int_{-\infty}^{\infty} \Psi_o^* \frac{\hbar}{i} \left(\frac{d}{dx}\right) \Psi_o \, dx = \frac{\hbar}{i} N^2 \int_{-\infty}^{\infty} e^{-½ \alpha^2 x^2} \left(\frac{d}{dx}\right) e^{-½ \alpha^2 x^2} \, dx$$

The derivative is:

$$\left(\frac{d}{dx}\right) e^{-½ \alpha^2 x^2} = -\alpha^2 x \, e^{-½ \alpha^2 x^2}$$

Substitution of the derivative into the integral gives:

$$<p> = -\frac{\hbar}{i} N^2 \alpha^2 \int_{-\infty}^{\infty} x \, e^{-\alpha^2 x^2} \, dx$$

Once again, the integrand is the product of an odd and an even function over all space, which gives an integral of zero: <p> = 0.

6. Find the expectation value of the potential energy for the ground state of the harmonic oscillator.

Answer: The plan is to note that we must find the expectation value of the potential energy operator, $\hat{V} = ½ kx^2$. Since the harmonic oscillator wave functions are real, $\Psi^* = \Psi$. We will use the normalized form of the wave function, $N = (\alpha^2/\pi)^{¼}$, giving $\int_{-\infty}^{\infty} \Psi_o^2 \, dx = 1$.

The expectation value of the potential energy is:

$$<V> = \int_{-\infty}^{\infty} \Psi_o^* \, ½ kx^2 \, \Psi_o \, dx = ½ \, k \, N^2 \int_{-\infty}^{\infty} e^{-½ \alpha^2 x^2} \, x^2 \, e^{-½ \alpha^2 x^2} \, dx$$

The integrand is a product of functions, so the order is immaterial. Noting that the integrand is an even function of x gives:

$$<V> = ½ \, k \, N^2 \, 2 \int_{0}^{\infty} x^2 \, e^{-\alpha^2 x^2} \, dx$$

Using the integral table in the Appendix: $\int_0^{\infty} x^2 e^{-ax^2} \, dx = (1/4a) \, (\pi/a)^{½}$:

$$<V> = ½ \, k \, N^2 \, 2 \left(\frac{1}{4\alpha^2}\right) \left(\frac{\pi}{\alpha^2}\right)^{½}$$

Substitution of the normalization constant, $N = (\alpha^2/\pi)^{1/4}$, into the last equation gives:

$$\langle V\rangle = \tfrac{1}{2}\, k \left(\frac{\alpha^2}{\pi}\right)^{1/2} 2 \left(\frac{1}{4\alpha^2}\right)\left(\frac{\pi}{\alpha^2}\right)^{1/2} = k \left(\frac{1}{4\alpha^2}\right)$$

The force constant and α^2 are related through Eq. 24.2.11; with $\alpha^2 = (mk)^{1/2}/\hbar$:

$$\langle V\rangle = \frac{k}{4}\frac{\hbar}{(mk)^{1/2}} = \frac{\hbar}{4}\left(\frac{k}{m}\right)^{1/2} = \frac{\hbar\omega_o}{4}$$

where $\omega_o = (k/m)^{1/2}$. The total energy of the harmonic oscillator in the ground state is $E = \hbar\omega_o/2$. The average potential energy is, then, one-half of the total energy: $\langle E_k\rangle = \tfrac{1}{2} E$. Since $E = \langle E_k\rangle + \langle V\rangle$, the average potential and kinetic energies are equal, $\langle E_k\rangle = \langle V\rangle$. This result is a specific example of the **Virial Theorem**. If the potential is in the form of a power law, $V(x) = k\, x^n$, then the average potential and kinetic energy are related by:

$$2 \langle E_k\rangle = n \langle V\rangle$$

For the harmonic oscillator, $n = 2$, which gives $\langle E_k\rangle = \langle V\rangle$ by the Virial Theorem, as shown by this problem.

7. Find the expectation value of the kinetic energy for the ground state of the harmonic oscillator.

Answer: The plan is to note that we must find the expectation value of the kinetic energy operator, $\hat{E}_k = -(\hbar^2/2m)\, d^2/dx^2$. Since the harmonic oscillator wave functions are real, $\Psi^* = \Psi$. We will use the normalized form of the wave function, $N = (\alpha^2/\pi)^{1/4}$, giving $\int_{-\infty}^{\infty} \Psi_o^2\, dx = 1$.

The expectation value of the kinetic energy is:

$$\langle E_k\rangle = \int_{-\infty}^{\infty} \Psi_o^* \left[-\frac{\hbar^2}{2m}\left(\frac{d^2}{dx^2}\right)\right] \Psi_o\, dx = -\frac{\hbar^2}{2m} N^2 \int_{-\infty}^{\infty} e^{-\frac{1}{2}\alpha^2x^2} \left(\frac{d^2}{dx^2}\right) e^{-\frac{1}{2}\alpha^2x^2}\, dx$$

with: $\left(\frac{d}{dx}\right) e^{-\frac{1}{2}\alpha^2x^2} = -\alpha^2 x\, e^{-\frac{1}{2}\alpha^2x^2}$ and $\left(\frac{d^2}{dx^2}\right) e^{-\frac{1}{2}\alpha^2x^2} = (\alpha^4x^2 - \alpha^2)\, e^{-\frac{1}{2}\alpha^2x^2}$

Substituting in the second derivative gives:

$$\langle E_k\rangle = -\frac{\hbar^2}{2m} N^2 \int_{-\infty}^{\infty} (\alpha^4x^2 - \alpha^2)\, e^{-\alpha^2x^2}\, dx$$

Separating the integral into two terms and noting that the integrand for each integral is even gives:

$$\langle E_k\rangle = -\frac{\hbar^2}{2m} N^2\, 2\left[\alpha^4 \int_0^{\infty} x^2 e^{-\alpha^2x^2}\, dx - \alpha^2 \int_0^{\infty} e^{-\alpha^2x^2}\, dx\right]$$

Using the table in the Appendix: $\int_0^{\infty} e^{-ax^2}\, dx = \tfrac{1}{2}(\pi/a)^{1/2}$ and $\int_0^{\infty} x^2 e^{-ax^2}\, dx = (1/4a)(\pi/a)^{1/2}$:

$$<E_k> = -\frac{\hbar^2}{2m} N^2\, 2\left[\alpha^4\left(\frac{1}{4\alpha^2}\right)\left(\frac{\pi}{\alpha^2}\right)^{½} - \alpha^2\left(\frac{1}{2}\right)\left(\frac{\pi}{\alpha^2}\right)^{½}\right] = -\frac{\hbar^2}{2m} N^2\, 2\alpha^2\left(\frac{\pi}{\alpha^2}\right)^{½}\left[\left(\frac{1}{4}\right)-\left(\frac{1}{2}\right)\right]$$

Substitution of the normalization constant, $N = (\alpha^2/\pi)^{¼}$, Eq. 24.2.13, into the last equation gives:

$$<E_k> = -\frac{\hbar^2}{2m}\left(\frac{\alpha^2}{\pi}\right)^{½} 2\alpha^2\left(\frac{\pi}{\alpha^2}\right)^{½}\left[-\frac{1}{4}\right] = \frac{1}{2}\left(\frac{\hbar^2\alpha^2}{2m}\right)$$

The total energy of the harmonic oscillator in the ground state is $E = \hbar^2\alpha^2/2m$. The average kinetic energy is, then, one-half of the total energy: $<E_k> = ½\, E$. Since $E = <E_k> + <V>$, the potential and kinetic energies are equal, $<E_k> = <V>$. This result is a specific example of the **Virial Theorem**. If the potential is in the form of a power law, $V(x) = k\, x^n$, then the average potential and kinetic energy are related by:

$$2 <E_k> = n <V>$$

For the harmonic oscillator, n = 2, which gives $<E_k> = <V>$, as shown by this problem.

8. Show that the ground state of the harmonic oscillator is consistent with the Heisenberg uncertainty principle. [Hint: Calculate the standard deviations of the position and momentum. However, you don't need to prove that <x> = 0 and <p> = 0, which are established by symmetry.]

Answer: The plan is to note that since $<x> = 0$ and $<p> = 0$, then $\sigma_x = (<x^2> - <x>^2)^{½} = (<x^2>)^{½}$ and $\sigma_p = (<p^2> - <p>^2)^{½} = (<p^2>)^{½}$. Note that the momentum operator is $\hat{p} = \hbar/i\, (d/dx)$.

Since the harmonic oscillator wave functions are real, $\Psi^* = \Psi$. We will use the normalized form of the wave function, $N = (\alpha^2/\pi)^{¼}$, giving $\int_{-\infty}^{\infty} \Psi_o^2\, dx = 1$.The expectation value of x^2 is then (see also Problem 6):

$$<x^2> = \int_{-\infty}^{\infty} \Psi_o^*\, x^2\, \Psi_o\, dx = N^2 \int_{-\infty}^{\infty} e^{-½\,\alpha^2x^2}\, x^2\, e^{-½\,\alpha^2x^2}\, dx$$

The integrand is a product of functions, so the order is immaterial. Noting that the integrand is an even function of x gives:

$$<x^2> = N^2\, 2 \int_0^{\infty} x^2\, e^{-\alpha^2x^2}\, dx$$

Using the integral table in the Appendix: $\int_0^{\infty} x^2 e^{-ax^2}\, dx = (1/4a)\, (\pi/a)^{½}$:

$$<x^2> = N^2\, 2\left(\frac{1}{4\alpha^2}\right)\left(\frac{\pi}{\alpha^2}\right)^{½}$$

Substitution of the normalization constant, $N = (\alpha^2/\pi)^{¼}$, into the last equation gives:

$$<x^2> = \left(\frac{\alpha^2}{\pi}\right)^{½} 2\left(\frac{1}{4\alpha^2}\right)\left(\frac{\pi}{\alpha^2}\right)^{½} = \left(\frac{1}{2\alpha^2}\right)$$

The operator, $\hat{p}^2 = \hat{p}\,\hat{p} = -\,\hbar^2\,(d^2/dx^2)$, involves a derivative, so the order of operation is important, giving for the expectation value of $\hat{p}^2$ (see also Problem 7):

$$<p^2> = \int_{-\infty}^{\infty} \Psi_o^* \left(-\hbar^2 \frac{d^2}{dx^2}\right) \Psi_o \, dx = -\,\hbar^2 N^2 \int_{-\infty}^{\infty} e^{-\frac{1}{2}\alpha^2x^2} \left(\frac{d^2}{dx^2}\right) e^{-\frac{1}{2}\alpha^2x^2}\, dx$$

with: $\left(\frac{d}{dx}\right) e^{-\frac{1}{2}\alpha^2x^2} = -\,\alpha^2 x\, e^{-\frac{1}{2}\alpha^2x^2}$ and $\left(\frac{d^2}{dx^2}\right) e^{-\frac{1}{2}\alpha^2x^2} = (\alpha^4x^2 - \alpha^2)\, e^{-\frac{1}{2}\alpha^2x^2}$

Substituting in the second derivative gives:

$$< p^2> = -\,\hbar^2 N^2 \int_{-\infty}^{\infty} (\alpha^4x^2 - \alpha^2)\, e^{-\alpha^2x^2}\, dx$$

Separating the integral into two terms and noting that the integrand for each integral is even gives:

$$< p^2> = -\,\hbar^2 N^2\, 2 \left[\alpha^4 \int_0^{\infty} x^2\, e^{-\alpha^2x^2}\, dx - \alpha^2 \int_0^{\infty} e^{-\alpha^2x^2}\, dx\right]$$

Using the table in the Appendix: $\int_0^{\infty} e^{-ax^2}\, dx = \frac{1}{2}\,(\pi/a)^{\frac{1}{2}}$ and $\int_0^{\infty} x^2 e^{-ax^2}\, dx = (1/4a)\,(\pi/a)^{\frac{1}{2}}$:

$$< p^2> = -\,\hbar^2 N^2\, 2\left[\alpha^4\left(\frac{1}{4\alpha^2}\right)\left(\frac{\pi}{\alpha^2}\right)^{\frac{1}{2}} - \alpha^2\left(\frac{1}{2}\right)\left(\frac{\pi}{\alpha^2}\right)^{\frac{1}{2}}\right] = -\,\hbar^2 N^2\, 2\alpha^2\left(\frac{\pi}{\alpha^2}\right)^{\frac{1}{2}}\left[\left(\frac{1}{4}\right) - \left(\frac{1}{2}\right)\right]$$

Substitution of the normalization constant, $N = (\alpha^2/\pi)^{\frac{1}{4}}$, into the last equation gives:

$$< p^2> = -\,\hbar^2\left(\frac{\alpha^2}{\pi}\right)^{\frac{1}{2}} 2\alpha^2\left(\frac{\pi}{\alpha^2}\right)^{\frac{1}{2}}\left[-\frac{1}{4}\right] = \frac{1}{2}\,\hbar^2\alpha^2$$

The product of the variances is then: $\sigma_x^2\,\sigma_p^2 = \left(\frac{1}{2\alpha^2}\right)\left(\frac{1}{2}\,\hbar^2\alpha^2\right) = \frac{\hbar^2}{4}$

which is consistent with the Heisenberg uncertainty principle, $\sigma_x\,\sigma_p \geq \hbar/2$.

9. Use the recursion relationship for Hermite polynomials to generate the first four excited state wave functions for the harmonic oscillator (H_1 to H_4).

Answer: The ground state and the general form for the wave functions of the harmonic oscillator are:

$$\Psi_o = \left(\frac{\alpha^2}{\pi}\right)^{\frac{1}{4}} e^{-\frac{1}{2}\alpha^2x^2} \qquad\qquad \Psi_v = N_v\, H_v\, e^{-\frac{1}{2}\alpha^2x^2}$$

The recursion relationship is: $H_{v+1} = 2y\, H_v - 2v\, H_{v-1}$, and the first Hermite polynomial, upon which all the others are based is $H_o = 1$. Building up from H_o gives:

$H_1 = 2y\, H_o = 2y$
$H_2 = 2y\, H_1 - 2(1)\, H_o = 2y\,(2y) - 2(1)(1) = 4y^2 - 2$
$H_3 = 2y\, H_2 - 2(2)\, H_1 = 2y(4y^2 - 2) - 2(2)(2y) = 8y^3 - 12y$
$H_4 = 2y\, H_3 - 2(3)\, H_2 = 2y(8y^3 - 12y) - 2(3)(4y^2 - 2) = 16y^4 - 48y^2 + 12$

The normalization integral, using the change in variables $y = \alpha x$, $dy/dx = \alpha$, and $dx = dy/\alpha$, gives:

$$N_v^2\,(1/\alpha) \int_{-\infty}^{\infty} H_v\, e^{-\frac{1}{2} y^2}\, H_v\, e^{-\frac{1}{2} y^2}\, dy = 1$$

The standard form of the integral, using Eq. 24.2.99% with v' = v, is:

$$\int_{-\infty}^{\infty} H_v\, e^{-\frac{1}{2} y^2}\, H_v\, e^{-\frac{1}{2} y^2}\, dy = \pi^{\frac{1}{2}}\, 2^v\, v! \qquad \text{giving} \qquad N_v^2\,(1/\alpha)(\pi^{\frac{1}{2}}\, 2^v\, v!) = 1$$

The normalization constant is then $N_v = (\alpha/(\pi^{\frac{1}{2}}\, 2^v\, v!))^{\frac{1}{2}}$. Explicitly, the normalization for the first four excited state levels is:

$$N_1 = \left(\frac{\alpha}{\pi^{\frac{1}{2}}\, 2^1\, 1!}\right)^{\frac{1}{2}} = \left(\frac{\alpha^2}{4\pi}\right)^{\frac{1}{4}} \qquad N_2 = \left(\frac{\alpha}{\pi^{\frac{1}{2}}\, 2^2\, 2!}\right)^{\frac{1}{2}} = \frac{1}{2}\left(\frac{\alpha^2}{4\pi}\right)^{\frac{1}{4}}$$

$$N_3 = \left(\frac{\alpha}{\pi^{\frac{1}{2}}\, 2^3\, 3!}\right)^{\frac{1}{2}} = \frac{1}{2}\left(\frac{\alpha^2}{144\pi}\right)^{\frac{1}{4}} \qquad N_4 = \left(\frac{\alpha}{\pi^{\frac{1}{2}}\, 2^4\, 4!}\right)^{\frac{1}{2}} = \frac{1}{8}\left(\frac{\alpha^2}{36\pi}\right)^{\frac{1}{4}}$$

The final wavefunctions are:

$$\Psi_1 = \left(\frac{\alpha^2}{4\pi}\right)^{\frac{1}{4}} (2\alpha x)\, e^{-\frac{1}{2}\alpha^2 x^2}$$

$$\Psi_2 = \frac{1}{2}\left(\frac{\alpha^2}{4\pi}\right)^{\frac{1}{4}} (4\alpha^2 x^2 - 2)\, e^{-\frac{1}{2}\alpha^2 x^2}$$

$$\Psi_3 = \frac{1}{2}\left(\frac{\alpha^2}{144\pi}\right)^{\frac{1}{4}} (8\alpha^3 x^3 - 12\alpha x)\, e^{-\frac{1}{2}\alpha^2 x^2}$$

$$\Psi_4 = \frac{1}{8}\left(\frac{\alpha^2}{36\pi}\right)^{\frac{1}{4}} (16\alpha^4 x^4 - 48\alpha^2 x^2 + 12)\, e^{-\frac{1}{2}\alpha^2 x^2}$$

10. Confirm that wavefunctions for a 2D-rigid rotor (particle-in-a-ring) are orthogonal. [Hint: the wave functions are $\psi(\phi) = a\, e^{i\, m_\ell\, \phi}$ with different m_ℓ.]

Answer: The plan is to show that $\int_0^{2\pi} \Psi_{m_\ell'}^{*}\Psi_{m_\ell}\, d\phi = 0$ with $m_{\ell'} \neq m_\ell$.
The integral to test for orthogonality is:

$$\int_0^{2\pi} \Psi_{m_\ell'}^{*}\Psi_{m_\ell}\, d\phi = a^2 \int_0^{2\pi} e^{-i\, m_{\ell'}\, \phi}\, e^{i\, m_\ell\, \phi}\, d\phi = a^2 \int_0^{2\pi} e^{i\,(m_\ell - m_{\ell'})\phi}\, d\phi$$

with $m_{\ell'} \neq m_\ell$. Using the Euler identity for the complex exponential gives:

$$\int_0^{2\pi} \Psi_{m_\ell'}^{*}\Psi_{m_\ell}\, d\phi = a^2 \int_0^{2\pi} \cos[(m_\ell - m_{\ell'})\phi]\, d\phi + i\, a^2 \int_0^{2\pi} \sin[(m_\ell - m_{\ell'})\phi]\, d\phi$$

However, $(m_\ell - m_{\ell'})$ is an integer. Let $n = (m_\ell - m_{\ell'})$ with $n \neq 0$, which gives:

$$\int_0^{2\pi} \cos n\phi\, d\phi = \sin n\phi\Big|_0^{2\pi} = 0 \qquad \text{and} \qquad \int_0^{2\pi} \sin n\phi\, d\phi = -\cos n\phi\Big|_0^{2\pi} = -[1 - 1] = 0$$

Substitution of these standard integrals into the orthogonality integral gives $\int_0^{2\pi} \Psi_{m_\ell'}^{*}\Psi_{m_\ell}\, d\phi = 0$.

11. Show that the wave function $\Psi(\phi) = a\,e^{im_\ell\phi}$ is an eigenfunction of the Hamiltonian for the rigid-rotor in the x-y plane, where $\hat{\mathcal{H}} = -\hbar^2/2I\,(d^2/d\phi^2)$. What is the energy for this wavefunction?

Answer: The plan is to note that the Hamiltonian for the 2D-rigid rotor is a function of the azimuthal angle ϕ through $\hat{\mathcal{H}} = -\hbar^2/2I\,(d^2/d\phi^2)$.

The derivatives are:

$$\frac{d\,e^{im_\ell\phi}}{d\phi} = i\,m_\ell\,e^{im_\ell\phi} \qquad \text{and} \qquad \frac{d^2e^{im_\ell\phi}}{d\phi^2} = (i\,m_\ell)^2\,e^{im_\ell\phi} = -\,m_\ell^2\,e^{im_\ell\phi}$$

The Schrödinger equation is then: $\hat{\mathcal{H}}\Psi = -\dfrac{\hbar^2}{2I}\dfrac{d^2\,a\,e^{im_\ell\phi}}{d\phi^2} = \dfrac{\hbar^2 m_\ell^2}{2I}\,a\,e^{im_\ell\phi} = \dfrac{\hbar^2 m_\ell^2}{2I}\,\Psi$

This final result shows that the wave function is an eigenfunction of the Hamiltonian. The eigenvalue corresponding to the Hamiltonian is the energy:

$$E = \frac{\hbar^2 m_\ell^2}{2I}$$

12. Show that $\Psi(\theta) = \cos\theta$ is an eigenfunction of the square of the total angular momentum operator, where: (total angular momentum operator)$^2 = \hat{L}^2 = -\,\hbar^2\,\Lambda^2$.

Answer: The plan is to show that $-\,\hbar^2\,\Lambda^2\,\Psi = c\,\Psi$, with c a constant. For multi-step derivatives, order is important; remember to work from right to left. We can anticipate that since $\cos\theta$ is the spherical harmonic $Y_{1,0}$ without normalization, the constant will be $|L|^2 = \hbar^2\,\ell(\ell + 1)$, with $\ell = 1$.

The first step is to note that: $\Lambda^2 = \dfrac{1}{\sin^2\theta}\left(\dfrac{\partial^2}{\partial\phi^2}\right) + \left(\dfrac{1}{\sin\theta}\right)\left(\dfrac{\partial}{\partial\theta}\sin\theta\,\dfrac{\partial}{\partial\theta}\right)$

The wave function is not a function of ϕ, so $(\partial^2\cos\theta/\partial\phi^2)_\theta = 0$. The remaining derivatives are:

$$\begin{aligned}
\Lambda^2\cos\theta &= \left(\frac{1}{\sin\theta}\right)\left(\frac{\partial}{\partial\theta}\sin\theta\,\frac{\partial}{\partial\theta}\right)\cos\theta \\
&= \left(\frac{1}{\sin\theta}\right)\left(\frac{\partial}{\partial\theta}(-\sin^2\theta)\right) \\
&= -\left(\frac{1}{\sin\theta}\right)(2\sin\theta\cos\theta) \\
&= -\,2\cos\theta
\end{aligned}$$

The square of the total angular momentum operating on the wave function is then:

$$-\,\hbar^2\,\Lambda^2\cos\theta = 2\hbar^2\cos\theta$$

This last result shows that cos θ is an eigenfunction. The eigenvalue for the total angular momentum operator squared is then $|L|^2 = 2\hbar^2$. This result agrees with Eq. 24.5.34 since $\ell = 1$ for $Y_{1,0}$ and then $|L|^2 = \hbar^2\, \ell(\ell + 1) = 2\hbar^2$.

13. Normalize $Y_{1,0} = N \cos\theta$.

Answer: The plan is to note that normalization requires $\int \Psi^*\Psi\, d\tau = 1$, where the integral is over all space and the volume element is $d\tau = \sin\theta\, d\theta\, d\phi$ for the rigid-rotor.

Note that $Y_{1,0}$ is real, so that $Y^*_{1,0} = Y_{1,0}$. The normalization integral is given by:

$$\int_0^{\pi}\int_0^{2\pi} Y^2_{1,0} \sin\theta\, d\theta\, d\phi \;= N^2 \int_0^{2\pi} d\phi \int_0^{\pi} \cos^2\theta \sin\theta\, d\theta = 1$$

Integral tables give: $\int_0^{\pi} \cos^2(ax) \sin(ax)\, dx = -(1/3a) \cos^3(ax)$. In this case a = 1:

$$\int_0^{\pi} \cos^2\theta \sin\theta\, d\theta = -(1/3) \cos^3(\theta)\Big|_0^{\pi} = -(1/3) [\cos^3(\pi) - \cos^3(0)] = {}^2/_3$$

The integral over the azimuthal angle is $\int_0^{2\pi} d\phi = 2\pi$:

$$N^2 \int_0^{2\pi} d\phi \int_0^{\pi} \cos^2\theta \sin\theta\, d\theta = N^2 (2\pi)({}^2/_3) = 1 \qquad \text{and } N = \left(\frac{3}{4\pi}\right)^{1/2}$$

The normalized spherical harmonic is then $Y_{1,0} = (3/4\pi)^{1/2} \cos\theta$.

14. Show that the rigid-rotor wave functions $Y_{0,0}$ and $Y_{1,0}$ are orthogonal.

Answer: The plan is to note that $Y_{0,0} = (1/4\pi)^{1/2}$ and $Y_{1,0} = (3/4\pi)^{1/2} \cos\theta$. Orthogonality requires $\int \Psi^*\Psi\, d\tau = 0$, where the integral is over all space and the volume element is $d\tau = \sin\theta\, d\theta\, d\phi$ for the rigid-rotor.

Note that these particular spherical harmonics are real, so that $Y^*_{0,0} = Y_{0,0}$. The orthogonality integral is given by:

$$\int_0^{\pi}\int_0^{2\pi} Y_{0,0}\, Y_{1,0} \sin\theta\, d\theta\, d\phi \;= (1/4\pi)^{1/2}\, (3/4\pi)^{1/2} \int_0^{2\pi} d\phi \int_0^{\pi} \cos\theta \sin\theta\, d\theta = 0$$

because integral tables give $\int_0^{\pi} \cos(ax) \sin(ax)\, dx = (1/2a) \sin^2(ax)\Big|_0^{\pi} = 0$.

15. Show that the rigid-rotor wave functions $Y_{1,0}$ and $Y_{1,1}$ are orthogonal.

Answer: The plan is to note that $Y_{1,0} = (3/4\pi)^{1/2} \cos\theta$ and $Y_{1,1} = (3/8\pi)^{1/2} \sin\theta\, e^{i\phi}$. Orthogonality requires $\int \Psi^*\Psi\, d\tau = 0$, where the integral is over all space and the volume element is $d\tau = \sin\theta\, d\theta\, d\phi$ for the rigid-rotor.

Note that $Y_{1,0}$ is real, so that $Y^*_{1,0} = Y_{1,0}$. The orthogonality integral is given by:

$$\int_0^{\pi}\int_0^{2\pi} Y_{1,0}\, Y_{1,0} \sin\theta \, d\theta \, d\phi = (3/4\pi)^{1/2} (3/8\pi)^{1/2} \int_0^{2\pi} e^{i\phi} \, d\phi \int_0^{\pi} \cos\theta \sin^2\theta \, d\theta = 0$$

because integral tables give $\int_0^{\pi} \cos(ax) \sin^2(ax)\, dx = (1/3a) \sin^3(ax)\big|_0^{\pi} = 0$.

16. Give the magnitude of the total angular momentum and the z-axis projection of the angular momentum for an $\ell = 2$, $m_\ell = 1$ state of a rigid rotor. Give your answers in multiples of ħ.

Answer: For $\ell = 2$ the magnitude of the angular momentum is: $|L| = \hbar\sqrt{\ell(\ell + 1)} = \sqrt{6}\,\hbar$
The z-axis projection of the angular momentum is: $L_z = m_\ell \hbar = \hbar$.

17. Give the transition energy, in wave numbers, for the J = 0 to J = 1 transition in carbon monoxide. Find the transition frequency in GHz. Use the most abundant isotopes, $^{12}C{\equiv}^{16}O$, with the bond length 1.1282 Å.

Answer: The plan is to use Eq. 24.5.43 converted to wave numbers, with J as the quantum number for the lower state: $\Delta E/hc = \tilde{\nu} = 2\,\tilde{B}\,(J + 1)$.
The reduced mass is given using isotope specific atomic masses:

$$\mu = \left(\frac{\mathcal{M}_1\mathcal{M}_2}{\mathcal{M}_1 + \mathcal{M}_2}\right)\frac{1}{N_A}\,(1\text{ kg}/1000\text{ g})$$
$$= \frac{12.000000\text{ g mol}^{-1}(15.994915\text{ g mol}^{-1})}{12.000000\text{ g mol}^{-1} + 15.994915\text{ g mol}^{-1}}\left(\frac{1}{6.0221367\text{x}10^{23}\text{ mol}^{-1}}\right)(1\text{ kg}/1000\text{ g})$$
$$= 1.1385010\text{x}10^{-26}\text{ kg}$$

Note that 1 Å = $1\text{x}10^{-10}$ m. The moment of inertia and rotational constant are:

$$I = \mu r^2 = 1.138501\text{x}10^{-26}\text{ kg}(1.1282\text{x}10^{-10}\text{ m})^2 = 1.44912\text{x}10^{-46}\text{ kg m}^2$$
$$\tilde{B} = \frac{\hbar}{4\pi I c} = \frac{1.054573\text{x}10^{-34}\text{ J s}}{4\pi(1.44912\text{x}10^{-46}\text{ kg m}^2)(2.997925\text{x}10^{8}\text{ m s}^{-1})} = 193.170\text{ m}^{-1}$$
$$\tilde{B} = 193.170\text{ m}^{-1}\ (1\text{ m}/100\text{ cm}) = 1.93170\text{ cm}^{-1}$$

The transition energy using Eq. 24.5.43 is: $\Delta E/hc = \tilde{\nu} = 2\,\tilde{B}\,(J + 1) = 2\tilde{B} = 3.86341\text{ cm}^{-1}$

The transition frequency is given by:

$$\nu = c/\lambda = \tilde{\nu}c = 3.86341\text{ cm}^{-1}(2.997925\text{x}10^{8}\text{ m s}^{-1})(100\text{ cm}/1\text{m}) = 1.15822\text{x}10^{11}\text{ s}^{-1}$$
$$\nu = 1.15822\text{x}10^{11}\text{ s}^{-1}\ (1\text{ GHz}/1\text{x}10^{9}\text{s}^{-1}) = 115.82\text{ GHz}$$

This transition is one of the prominent lines observed in interstellar space using radio telescopes.

18. Show that $[\hat{L}_x, \hat{L}_y] = i\hbar\,\hat{L}_z$. This problem is best done using the operators expressed in Cartesian coordinates.

Answer: The plan is to note that $[\hat{A},\hat{B}] = \hat{A}\hat{B} - \hat{B}\hat{A}$, Eq. 23. 7.10. The operators are given by Eqs. 24.5.19. Note that the partial derivative with respect to x is taken with y and z constant. In addition using the Euler criterion, mixed partials are equal, Eq. 9.1.6. So for example:

$$\frac{\partial}{\partial x}\, z \frac{\partial}{\partial y} = z \frac{\partial}{\partial x}\frac{\partial}{\partial y} \qquad \text{and} \qquad \frac{\partial}{\partial y}\frac{\partial}{\partial x} = \frac{\partial}{\partial x}\frac{\partial}{\partial y}$$

Note also that multiplicative operators commute, yx = xy. The commutator is then:

$$[\hat{L}_x, \hat{L}_y] = \hat{L}_x\hat{L}_y - \hat{L}_y\hat{L}_x$$

$$= -\hbar^2\left[\left(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right)\left(z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z}\right) - \left(z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z}\right)\left(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right)\right]$$

$$= -\hbar^2\left[\left(y\frac{\partial}{\partial z}\, z\frac{\partial}{\partial x} - xy\frac{\partial^2}{\partial z^2} - z^2\frac{\partial}{\partial x}\frac{\partial}{\partial y} + xz\frac{\partial}{\partial y}\frac{\partial}{\partial z}\right) - \left(yz\frac{\partial}{\partial x}\frac{\partial}{\partial z} - z^2\frac{\partial}{\partial x}\frac{\partial}{\partial y} - xy\frac{\partial^2}{\partial z^2} + x\frac{\partial}{\partial z}\, z\frac{\partial}{\partial y}\right)\right]$$

Canceling the common factors, in xy and z^2, and using the product rule for the z-derivative gives:

$$= -\hbar^2\left[\left(yz\frac{\partial}{\partial z}\frac{\partial}{\partial x} + y\frac{\partial}{\partial x}\frac{\partial z}{\partial z} + xz\frac{\partial}{\partial y}\frac{\partial}{\partial z}\right) - \left(yz\frac{\partial}{\partial x}\frac{\partial}{\partial z} + xz\frac{\partial}{\partial z}\frac{\partial}{\partial y} + x\frac{\partial}{\partial y}\frac{\partial z}{\partial z}\right)\right]$$

Then $(\partial z/\partial z) = 1$ and canceling common factors gives:

$$[\hat{L}_x, \hat{L}_y] = \hbar^2\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right) = i\hbar\, \hat{L}_z$$

The x and y components of the angular momentum cannot both be determined simultaneously with arbitrary precision.

<u>19</u>. Show that $[\hat{L}^2,\hat{L}_z] = 0$. This problem is best done using the operators expressed in spherical polar coordinates.

Answer: The plan is to note that $[\hat{A},\hat{B}] = \hat{A}\hat{B} - \hat{B}\hat{A}$, Eq. 23. 7.10. The operators are given by Eqs. 24.5.20-24.5.21. Note that the partial derivative with respect to θ is taken with ϕ constant.

From $[\hat{L}^2,\hat{L}_z] = \hat{L}^2\,\hat{L}_z - \hat{L}_z\,\hat{L}^2$, consider the first term and second term separately. Note that the ϕ derivative is done with θ held constant. The terms in θ are constants for the ϕ derivative and can factor in and out, for example:

$$\frac{\partial}{\partial\phi}\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\,\frac{\partial}{\partial\theta}\right)\right] = \frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\,\frac{\partial}{\partial\theta}\right)\frac{\partial}{\partial\phi} \qquad 1$$

The first term in the commutator is:

$$\hat{L}^2\,\hat{L}_z = -\frac{\hbar^3}{i}\left[\frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2} + \frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\,\frac{\partial}{\partial\theta}\right)\right]\left(\frac{\partial}{\partial\phi}\right) \qquad 2$$

$$= -\frac{\hbar^3}{i}\left[\frac{1}{\sin^2\theta}\frac{\partial^3}{\partial\phi^3} + \frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\,\frac{\partial}{\partial\theta}\right)\frac{\partial}{\partial\phi}\right] \tag{3}$$

The second term in the commutator has the opposite order for the operators:

$$\hat{L}_z\,\hat{L}^2 = -\frac{\hbar^3}{i}\left(\frac{\partial}{\partial\phi}\right)\left[\frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2} + \frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\,\frac{\partial}{\partial\theta}\right)\right] \tag{4}$$

Using Eq. 1 gives:

$$\hat{L}_z\,\hat{L}^2 = -\frac{\hbar^3}{i}\left[\frac{1}{\sin^2\theta}\frac{\partial^3}{\partial\phi^3} + \frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\,\frac{\partial}{\partial\theta}\right)\frac{\partial}{\partial\phi}\right] \tag{5}$$

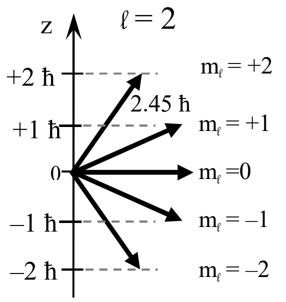
Note that Eqs. 3 and 5 are identical, so that $[\hat{L}^2,\hat{L}_z] = \hat{L}^2\,\hat{L}_z - \hat{L}_z\,\hat{L}^2 = 0$.

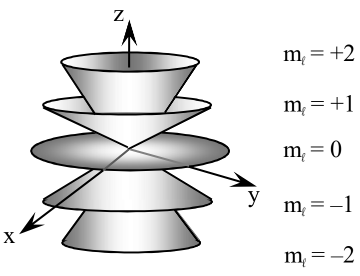
20. Why is $[\hat{L}^2,\hat{L}_z] = 0$ significant?

Answer: The energy of the system is given by $E_\ell = L^2/2I$. The eigenvalue of $\hat{L}^2$ is $L^2 = \hbar^2\,\ell(\ell + 1)$, which upon taking the square root gives the magnitude of the total angular momentum, |L|. The eigenvalue of $\hat{L}_z$ is $\ell_z = \hbar m_\ell$, which determines the orientation of the angular momentum vector. The vanishing commutator means that both L^2 and ℓ_z can be specified simultaneously to arbitrary precision. The total energy, the magnitude of the angular momentum, and the orientation with respect to the z-axis can all be specified exactly at the same time. The energy, angular momentum, and spatial orientation are all quantized. However, the spherical harmonics are not eigenfunctions of the two remaining projections, $\hat{L}_x$ and $\hat{L}_y$. Instead, these components give zero expectation values and the uncertainties span the range of ϕ.

21. Draw the angular momentum vector diagrams for $\ell = 2$ angular momentum states.

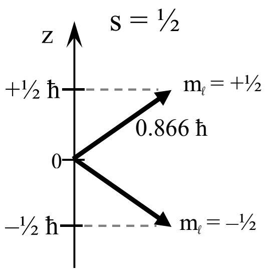
Answer: The magnitude of the angular momentum for $\ell = 2$ is $|L| = \sqrt{6}\,\hbar = 2.45\,\hbar$, Problem 16. For $\ell = 2$ the magnetic quantum number can be m_ℓ = -2, -1, 0, 1, 2, giving five precession cones:

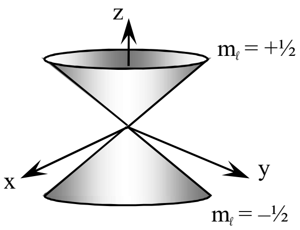




22. Draw the angular momentum vector diagram for a single electron or proton, s = ½.

Answer: The magnitude of the angular momentum for s = ½ is $|S| = \sqrt{3/4}\ \hbar = 0.866\ \hbar$. For s = ½ the magnetic quantum number can be $m_\ell = -½, ½$, giving two precession cones:





23. The spins of the protons and neutrons combine to give the overall spin of a nucleus. The details depend on the quantum structure of the nucleus and can result in half-integer or integer overall spin. The nucleus of ^{35}Cl has a spin of $I = {}^3/_2$. Give the possible values for the quantum number for the z-axis projection of the angular momentum.

Answer: The quantum number for the z-axis projection of the angular momentum is the magnetic quantum number, which for nuclei is called m_I. Starting from $m_I = -{}^3/_2$ in unit steps gives four m_I states: $m_I = (-{}^3/_2, -{}^1/_2, +{}^1/_2, +{}^3/_2)$. The angular momentum vector diagram has four precession cones.

24. The nucleus of ^{105}Pd has a spin of $I = {}^5/_2$. Give the possible values for the quantum number for the z-axis projection of the angular momentum. (The NMR resonance frequency for ^{105}Pd is 22.9 MHz on a 500 MHz NMR.)

Answer: The quantum number for the z-axis projection of the angular momentum is the magnetic quantum number, which for nuclei is called m_I. Starting from $m_I = -{}^5/_2$ in unit steps gives six m_I states: $m_I = (-{}^5/_2, -{}^3/_2, -{}^1/_2, +{}^1/_2, +{}^3/_2, +{}^5/_2)$. The angular momentum vector diagram has six precession cones.

25. Show that the operator $\hat{\mathcal{H}}^- = \left(y + \frac{d}{dy}\right)$ is a lowering operator for the z-axis projection angular momentum quantum states.

Answer: The plan is to follow Example 24.7.2. We need to show that $[\hat{A},\hat{A}^-] = k\,\hat{A}^-$, Eq. 24.7.1.
The harmonic oscillator Hamiltonian is given by eq. 24.7.14: $\hat{\mathcal{H}} = \hat{\mathcal{H}}^-\hat{\mathcal{H}}^+ - 1$. The commutator is then:

$$[\hat{\mathcal{H}},\hat{\mathcal{H}}^-] = (\hat{\mathcal{H}}^-\hat{\mathcal{H}}^+ - 1)\,\hat{\mathcal{H}}^- - \hat{\mathcal{H}}^-(\hat{\mathcal{H}}^-\hat{\mathcal{H}}^+ - 1)$$

$$= \hat{\mathcal{H}}^-\hat{\mathcal{H}}^+\,\hat{\mathcal{H}}^- - \hat{\mathcal{H}}^- - \hat{\mathcal{H}}^-\hat{\mathcal{H}}^-\hat{\mathcal{H}}^+ + \hat{\mathcal{H}}^-$$

Canceling the terms in just $\hat{\mathcal{H}}^-$ and factoring out the common term in $-\hat{\mathcal{H}}^-$ from the left gives:

$$= -\,\hat{\mathcal{H}}^-\,(\hat{\mathcal{H}}^-\hat{\mathcal{H}}^+ - \hat{\mathcal{H}}^+\hat{\mathcal{H}}^-) = -\,\hat{\mathcal{H}}^-\,[\hat{\mathcal{H}}^-,\hat{\mathcal{H}}^+]$$

Substituting for the commutator from Eq. 24.7.13 gives:

$$[\hat{\mathcal{H}},\hat{\mathcal{H}}^-] = -2\,\hat{\mathcal{H}}^- \tag{24.7.14}$$

The final result corresponds to k = -2, so $\hat{\mathcal{H}}^-$ is a lowering operator.

26. Use the raising operator for the harmonic oscillator to find Ψ_3 from $\Psi_2 = (4y^2 - 2)\,e^{-y^2/2}$.

Answer: The plan is to operate on Ψ_2 with $\hat{\mathcal{H}}^+$, which defined by Eq. 24.7.12. See Example 24.7.3.

The next excited state is determined by:

$$\hat{\mathcal{H}}^+\Psi_2 = \left(y - \frac{d}{dy}\right)(4y^2 - 2)\,e^{-y^2/2} = 4y^3\,e^{-y^2/2} - 2y\,e^{-y^2/2} - \frac{d}{dy}\,4y^2\,e^{-y^2/2} + 2\frac{d}{dy}\,e^{-y^2/2}$$

Using the product rule:

$$\begin{aligned}\hat{\mathcal{H}}^+\Psi_2 &= 4y^3\,e^{-y^2/2} - 2y\,e^{-y^2/2} - 4y^2\frac{d}{dy}\,e^{-y^2/2} - e^{-y^2/2}\frac{d}{dy}\,4y^2 + 2(-y)\,e^{-y^2/2}\\ &= 4y^3\,e^{-y^2/2} - 2y\,e^{-y^2/2} - 4y^2(-y)\,e^{-y^2/2} - 8\,y\,e^{-y^2/2} + 2(-y)\,e^{-y^2/2}\\ &= (8y^3 - 12y)\,e^{-y^2/2}\end{aligned}$$

The result is as expected from Table 24.1.1. Even though ladder operators are more abstract than directly solving the Hermite equation, ladder operators are computationally much simpler to use.

27. The lowering operator acting on the lowest energy state gives zero. For the harmonic oscillator $\hat{\mathcal{H}}^-\,\Psi_o = 0$, since there is no state with lower energy. Integrate $\hat{\mathcal{H}}^-\,\Psi_o = 0$ to show that the un-normalized ground state wave function of the harmonic oscillator is $\Psi_o = e^{-\,y^2/2}$.

Answer: The plan is to substitute in the lowering operator, Eq. 24.7.11, separate variables, and complete the integral, just as we did for chemical kinetics problems. This process is straight forward because the lowering operator involves only a first derivative.

Substituting in the definition of the lowering operator gives:

$$\hat{\mathcal{H}}^-\,\Psi_o = \left(y - \frac{d}{dy}\right)\Psi_o = 0$$

Adding $y\Psi_o$ to both sides of the last equation and then multiplying by -1 gives:

$$\frac{d}{dy}\,\Psi_o = -\,y\,\Psi_o$$

Separating variables gives: $\frac{1}{\Psi_o}\, d\Psi_o = -\, y\, dy$

The integrals give: $\int \frac{1}{\Psi_o}\, d\Psi_o = -\int y\, dy$ or $\ln \Psi_o = -\frac{y^2}{2}$

Exponentiation of both sides of the last equation gives: $\Psi_o = e^{-\,y^2/2}$
The result agrees with un-normalized form of Eq. 24.2.18.

28. Show that the z-projection angular momentum raising operator acting on $Y_{1,-1}$ gives $Y_{1,0}$. Use the un-normalized form of the wave functions, $Y_{1,-1} = \sin\theta\, e^{-i\phi}$ and $Y_{1,0} = \cos\theta$. Do this problem in the following steps.

(a). Show that: $\hat{L}^+ Y_{1,-1} = (\hat{L}_x + i\,\hat{L}_y)\sin\theta\, e^{-i\phi}$

(b). Using $\cot\theta = \cos\theta/\sin\theta$, show that: $\hat{L}_x \sin\theta\, e^{-i\phi} = \hbar\cos\theta\,(\cos\phi + i\sin\phi)\, e^{-i\phi}$

(c). Using the Euler Identity, $e^{i\phi} = (\cos\phi + i\sin\phi)$, show that: $\hat{L}_x \sin\theta\, e^{-i\phi} = \hbar\cos\theta$

(d). Show that: $i\,\hat{L}_y \sin\theta\, e^{-i\phi} = \hbar\cos\theta\,(\cos\phi + i\sin\phi)\, e^{-i\phi} = \hbar\cos\theta$

(e). Finally show that: $\hat{L}^+ Y_{1,-1} = (\hat{L}_x + i\,\hat{L}_y)\sin\theta\, e^{-i\phi} = 2\hbar\cos\theta = 2\hbar\, Y_{1,0}$

Answer: The plan is to note that $\hat{L}^+$, $\hat{L}_x$, and $\hat{L}_y$ are given by Eqs. 24.5.20 and 24.7.18.

(a). Making the substitutions in spherical polar coordinates without normalization:

$$\hat{L}^+ Y_{1,-1} = (\hat{L}_x + i\,\hat{L}_y)\sin\theta\, e^{-i\phi} \tag{1}$$

(b). We consider the two terms separately to decrease confusion. Using Eqs. 24.5.20 for $\hat{L}_x$:

$$\hat{L}_x \sin\theta\, e^{-i\phi} = \frac{\hbar}{i}\left(-\sin\phi\,\frac{\partial}{\partial\theta} - \cot\theta\cos\phi\,\frac{\partial}{\partial\phi}\right)\sin\theta\, e^{-i\phi} \tag{2}$$

$$= \frac{\hbar}{i}\big(-\sin\phi\cos\theta - \cot\theta\sin\theta\cos\phi\,(-i)\big)\, e^{-i\phi} \tag{3}$$

However, $\cot\theta = \cos\theta/\sin\theta$ giving:

$$\hat{L}_x \sin\theta\, e^{-i\phi} = \frac{\hbar}{i}(-\sin\phi\cos\theta + i\cos\theta\cos\phi)\, e^{-i\phi} \tag{4}$$

$$= \hbar\cos\theta\,(\cos\phi + i\sin\phi)\, e^{-i\phi} \tag{5}$$

(c). The Euler Identity gives $e^{i\phi} = (\cos\phi + i\sin\phi)$ and $e^{i\phi}\, e^{-i\phi} = 1$:

$$\hat{L}_x \sin\theta\, e^{-i\phi} = \hbar\cos\theta \tag{6}$$

(d). Now for the second term in Eq. 1 for the raising operator:

$$i\,\hat{L}_y \sin\theta\, e^{-i\phi} = i\,\frac{\hbar}{i}\left(\cos\phi\,\frac{\partial}{\partial\theta} - \cot\theta\sin\phi\,\frac{\partial}{\partial\phi}\right)\sin\theta\, e^{-i\phi} \tag{7}$$

$$i\,\hat{L}_y \sin\theta\, e^{-i\phi} = \hbar\,(\cos\theta\cos\phi - \cot\theta\sin\theta\sin\phi\,(-i))\, e^{-i\phi} \tag{8}$$

Once again, $\cot\theta = \cos\theta/\sin\theta$, $e^{i\phi} =$, and $e^{i\phi}\, e^{-i\phi} = 1$, giving:

$$i\,\hat{L}_y \sin\theta\, e^{-i\phi} = \hbar\,(\cos\theta\cos\phi - \cos\theta\sin\phi\,(-i))\,e^{-i\phi} \qquad 9$$

$$= \hbar\cos\theta\,(\cos\phi + i\sin\phi)\,e^{-i\phi} \qquad 10$$

$$= \hbar\cos\theta \qquad 11$$

(e). The sum of the two terms, Eqs. 6 and 11, gives the final result:

$$(\hat{L}_x + i\,\hat{L}_y)\sin\theta\, e^{-i\phi} = 2\hbar\cos\theta \qquad 12$$

where $Y_{1,0} = \cos\theta$, without the normalization:

$$(\hat{L}_x + i\,\hat{L}_y)\sin\theta\, e^{-i\phi} = 2\hbar\, Y_{1,0} \qquad 13$$

The raising operator raises $Y_{1,1}$ to $Y_{1,0}$, multiplied by a constant. The constant is resolved by normalization to give the final form for $Y_{1,0}$.

29. Show that $\hat{L}^-\hat{L}^+ = \hat{L}_x^2 + \hat{L}_y^2 + i[\hat{L}_x, \hat{L}_y] = \hat{L}^2 - \hat{L}_z^2 - \hbar\hat{L}_z$. (This expression is used in the next problem to find the eigenvalue for the total angular momentum.)

Answer: From the defintitions of the lowering and raising operators:

$$\hat{L}^-\hat{L}^+ = (\hat{L}_x - i\,\hat{L}_y)(\hat{L}_x + i\,\hat{L}_y) = \hat{L}_x^2 + i\hat{L}_x\,\hat{L}_y - i\,\hat{L}_y\,\hat{L}_x + \hat{L}_y^2$$

which, with the defintition of the commutator, rearranges to give:

$$\hat{L}^-\hat{L}^+ = \hat{L}_x^2 + \hat{L}_y^2 + i[\hat{L}_x, \hat{L}_y]$$

Using Eqs. 24.6.1 for the commutator gives the final result: $\hat{L}^-\hat{L}^+ = \hat{L}^2 - \hat{L}_z^2 - \hbar\hat{L}_z$

30. Given $\hat{L}_z\Psi_{m_\ell} = m_\ell\hbar\,\Psi_{m_\ell}$, prove that $\hat{L}^2\,\Psi_{m_\ell} = \hbar^2\,\ell(\ell+1)\,\Psi_{m_\ell}$, using the following steps.
(a). Since the z-axis projection of the angular momentum can't be larger than the total angular momentum, there must be a maximum value of m_ℓ for a given total angular momentum. Let that value be m_{max}. The result for the raising operator acting on $\Psi_{m_{max}}$ is zero, since there is no state with higher m_ℓ:

$$\hat{L}^+\,\Psi_{m_{max}} = 0$$

The subsequent application of the lowering operator must also give zero:

$$\hat{L}^-\hat{L}^+\,\Psi_{m_{max}} = 0$$

Given that $\hat{L}^-\hat{L}^+ = \hat{L}^2 - \hat{L}_z^2 - \hbar\hat{L}_z$, which was proved in the last problem, solve for $\hat{L}^2\,\Psi_{m_{max}}$.
(b). Compare with the general eigenvalue equation $\hat{L}^2\,\Psi_{m_{max}} = L^2\,\Psi_{m_{max}}$ to find the eigenvalue L^2 and the magnitude of the angular momentum $|L|$, in terms of m_{max}.
(c). Notice that the total angular momentum is not a function of m_ℓ, but only the maximum value m_{max}. In other words, the total angular momentum is completely determined by m_{max}. Show that renaming $m_{max} = \ell$ gives the final result:

$$\hat{L}^2 \Psi_{m_\ell} = \hbar^2 \ell(\ell + 1) \Psi_{m_\ell}$$

Answer: (a). Substituting $\hat{L}^-\hat{L}^+ = \hat{L}^2 - \hat{L}_z^2 - \hbar\hat{L}_z$ into $\hat{L}^-\hat{L}^+ \Psi_{m_{max}} = 0$ gives:

$$\hat{L}^-\hat{L}^+ \Psi_{m_{max}} = (\hat{L}^2 - \hat{L}_z^2 - \hbar\hat{L}_z) \Psi_{m_{max}} = 0$$

Rearranging the last relationship gives the square of the angular momentum as:

$$\hat{L}^2 \Psi_{m_{max}} = \hat{L}_z^2 \Psi_{m_{max}} + \hbar\hat{L}_z \Psi_{m_{max}}$$

Given that $\hat{L}_z \Psi_{m_\ell} = m_\ell\hbar \Psi_{m_\ell}$:

$$\hat{L}^2 \Psi_{m_{max}} = (m_\ell \hbar)^2 \Psi_{m_{max}} + \hbar(m_\ell\hbar) \Psi_{m_{max}}$$

$$\hat{L}^2 \Psi_{m_{max}} = \hbar^2 (m_{max}^2 + m_{max}) \Psi_{m_{max}} = \hbar^2 m_{max}(m_{max} + 1) \Psi_{m_{max}}$$

(b). Comparison with the general eigenvalue equation $\hat{L}^2 \Psi_{m_{max}} = L^2 \Psi_{m_{max}}$ gives:

$$L^2 = \hbar^2 m_{max}(m_{max} + 1) \qquad \text{and} \qquad |L| = \hbar \sqrt{m_{max}(m_{max} + 1)}$$

(c). We showed in Eq. 24.7.27 that m_ℓ increases in unit steps until the z-axis projection is bigger than the magnitude of the angular momentum, so that $m_\ell\hbar < \hbar \sqrt{m_{max}(m_{max} + 1)}$. The total angular momentum is completely determined by m_{max}, while $m_\ell = 0, \pm1, \ldots, \pm m_{max}$. Renaming $m_{max} = \ell$ gives the final result:

$$\hat{L}^2 \Psi_{m_{max}} = \hbar^2 \ell(\ell + 1) \Psi_{m_{max}} \qquad m_\ell = 0, \pm1, \ldots, \pm \ell$$

Since the raising operator doesn't change the magnitude of the angular momentum, Eq. 24.7.21, the preceding equation must then hold for all values of m_ℓ:

$$\hat{L}^2 \Psi_{m_\ell} = \hbar^2 \ell(\ell + 1) \Psi_{m_\ell}$$

Chapter 25 Problems: Atomic Structure

1. Use node counting rules to argue that ℓ cannot be greater than n–1 and m_ℓ cannot be greater than ℓ for the atomic orbitals of the hydrogen atom.

Answer: The plan is to note that the total number of nodes for an atomic orbital is n – 1. The number of angular nodes is ℓ. The number of angular nodes that include the z-axis is $|m_\ell|$. For positive values of m_ℓ the motion is clockwise around the z-axis and for negative values of m_ℓ the motion is counterclockwise around the z-axis.

The number of angular nodes cannot be greater than the total number of nodes, so $\ell \leq n - 1$. The corresponding range for the angular momentum quantum number is: $\ell = 0,\ldots, n - 1$. The number of angular nodes that include the z-axis cannot be greater than the number of angular nodes, so $|m_\ell| \leq \ell$. The corresponding range for the magnetic quantum number is: $m_\ell = -\ell,\ldots, 0,\ldots,+\ell$.

2. Give the degeneracy, the total number of nodes, the number of radial nodes, the number of angular nodes, and the number of angular nodes that include the z-axis for the following sets of orbitals: (a). 2p, (b). 3p, (c). 3d, (d). 4d, (e). 4f, (f). 5s.

Answer: The plan is to note that the total number of nodes for an atomic orbital is n – 1. The number of angular nodes is ℓ: with allowed values $\ell = 0,\ldots, n - 1$. The number of angular nodes that include the z-axis is $|m_\ell|$: with allowed values $m_\ell = -\ell,\ldots, 0,\ldots,+\ell$. For positive values of m_ℓ the motion is clockwise around the z-axis and for negative values of m_ℓ the motion is counterclockwise around the z-axis.

The number of radial nodes is equal to the difference of total number of nodes and the number of angular nodes: radial nodes = $n - 1 - \ell$. The degeneracy of the sub-level is $g_\ell = 2\ell + 1$ since $m_\ell = -\ell,\ldots, 0,\ldots,+\ell$.

			number of nodes			
sub-level	ℓ	degeneracy $g_\ell = 2\ell + 1$	total $= n - 1$	radial $= n - 1 - \ell$	angular $= \ell$	angular||z-axis $= \|m_\ell\|$
2p	1	3	1	0	1	0, 1
3p	1	3	2	1	1	0, 1
3d	2	5	2	0	2	0, 1, 2
4d	2	5	3	1	2	0, 1, 2
4f	3	7	3	0	3	0, 1, 2, 3
5s	0	1	4	4	0	0

3. Show that $R = A\, e^{-\alpha r}$ is a solution to the ground state radial wave equation for the hydrogen atom, including solving for the value of α:

$$-\frac{\hbar^2}{2m}\left(\frac{1}{r}\frac{d^2}{dr^2}\right) r\, R - \frac{Z e^2}{4\pi\varepsilon_o r} R = E\, R$$

Answer: Substituting in R = A $e^{-\alpha r}$ into the ground state radial wave equation gives:

$$-\frac{\hbar^2}{2m}\left(\frac{1}{r}\frac{d^2}{dr^2}\right) r\,A\,e^{-\alpha r} - \frac{Z\,e^2}{4\pi\varepsilon_o r} A\,e^{-\alpha r} = E\,A\,e^{-\alpha r} \qquad 1$$

Note that r $e^{-\alpha r}$ is a product of two functions, first (r) and second ($e^{-\alpha r}$). The derivatives using the product rule are:

$$\frac{d\,(r\,e^{-\alpha r})}{dr} = r(-\alpha)e^{-\alpha r} + e^{-\alpha r} \qquad 2$$

$$\frac{d^2\,(r\,e^{-\alpha r})}{dr^2} = \frac{d\,(r(-\alpha)e^{-\alpha r})}{dr} + \frac{d\,e^{-\alpha r}}{dr} = r\alpha^2\,e^{-\alpha r} - \alpha e^{-\alpha r} - \alpha e^{-\alpha r} \qquad 3$$

$$= \alpha^2 r\,e^{-\alpha r} - 2\alpha e^{-\alpha r} \qquad 4$$

Gathering terms and substituting back in the definition of the wave function, R = A $e^{-\alpha r}$, into this last equation gives:

$$\left(\frac{1}{r}\frac{d^2}{dr^2}\right) r\,A\,e^{-\alpha r} = \alpha^2\,Ae^{-\alpha r} - \frac{2\alpha}{r}\,Ae^{-\alpha r} = \alpha^2 R - \frac{2\alpha}{r}R \qquad 5$$

Substitution into Eq. 1 gives the ground state radial wave equation as:

$$-\frac{\hbar^2}{2m}\left(\alpha^2\,R - \frac{2\alpha}{r}\,R\right) - \frac{Z\,e^2}{4\pi\varepsilon_o r}\,R = E\,R \qquad 6$$

The derivatives having been completed, only functions remain in the equation. Common factors cancel giving:

$$-\frac{\hbar^2\alpha^2}{2m} + \frac{\hbar^2 2\alpha}{2mr} - \frac{Z\,e^2}{4\pi\varepsilon_o r} = E \qquad 7$$

Since the total energy is a constant, the terms in 1/r must cancel giving:

$$E = -\frac{\hbar^2\alpha^2}{2m} \qquad \text{and} \qquad \frac{\hbar^2\alpha}{mr} - \frac{Z\,e^2}{4\pi\varepsilon_o r} = 0 \qquad 8$$

Solving for α gives:

$$\alpha = \frac{Z\,e^2}{4\pi\varepsilon_o}\frac{m}{\hbar^2} \qquad 9$$

We can simplify this last equation using the definition of the Bohr radius, a_o:

$$a_o = \frac{4\pi\varepsilon_o\,\hbar^2}{me^2} \qquad \text{giving} \qquad \alpha = \frac{Z}{a_o} \qquad 10$$

<u>4</u>. The ground state of the hydrogen atom is: $\Psi_1(r) = R(r) = \frac{1}{\sqrt{\pi}}\left(\frac{Z}{a_o}\right)^{3/2} e^{-Zr/a_o} = \frac{1}{\sqrt{\pi}}\,\alpha^{3/2}\,e^{-\alpha r}$.

(a). Calculate the expectation value of the kinetic energy for the ground state of the hydrogen atom.
(b) From your answer in (a), show that $\langle E_k \rangle = - E_1$, where E_1 is the total energy of the ground state of the hydrogen atom.

Answer: The wave function is real and normalized. The expectation value then reduces to:

$$\langle E_k \rangle = \frac{\int_o^\infty\int_o^\pi\int_o^{2\pi} \Psi_1^* \hat{E}_k \Psi_1 r^2 \sin\theta \, dr \, d\theta d\phi}{\int_o^\infty\int_o^\pi\int_o^{2\pi} \Psi_1^* \Psi_1 r^2 \sin\theta \, dr \, d\theta d\phi} = \int_o^\infty\int_o^\pi\int_o^{2\pi} \Psi_1 \hat{E}_k \Psi_1 r^2 \sin\theta \, dr \, d\theta d\phi$$

Since the wave function only depends on r, $\Psi(r) = R(r)$, the angular integrals give 4π:

$$\langle E_k \rangle = 4\pi \int_o^\infty R(r) \hat{E}_k R(r) r^2 \, dr$$

The kinetic energy operator is: $\hat{E}_k = -\frac{\hbar^2}{2m}\left(\frac{1}{r}\frac{d^2}{dr^2}\right) r$

The result of the operation of the kinetic energy operator is given using Eq. 5 from the last problem:

$$\hat{E}_k R(r) = -\frac{\hbar^2}{2m}\left(\frac{1}{r}\frac{d^2}{dr^2}\right) r R(r) = -\frac{\hbar^2}{2m}\left(\alpha^2 R - \frac{2\alpha}{r} R\right)$$

with $\alpha = Z/a_o$. Substitution of this last result into the integral for the expectation value gives:

$$\langle E_k \rangle = -4\pi \frac{\hbar^2}{2m}\left(\frac{1}{\pi}\right)\alpha^3 \left(\int_0^\infty \alpha^2 r^2 e^{-2\alpha r} dr - \int_0^\infty 2\alpha r \, e^{-2\alpha r} dr\right)$$

The integral table gives: $\int_0^\infty x^n e^{-ax} dx = (n!/a^{n+1})$:

$$\langle E_k \rangle = -4\pi \frac{\hbar^2}{2m}\left(\frac{1}{\pi}\right)\alpha^3 \left[\frac{2\alpha^2}{8\alpha^3} - \frac{2\alpha}{4\alpha^2}\right] = -4\pi \frac{\hbar^2}{2m}\left(\frac{1}{\pi}\right)\alpha^3 \left[-\frac{1}{4\alpha}\right]$$

$$= \frac{\hbar^2}{2m}\alpha^2 = \frac{\hbar^2}{2m}\left(\frac{Z}{a_o}\right)^2$$

The total energy for the ground state of the hydrogen atom is $E_1 = -\frac{Z^2\hbar^2}{2ma_o^2} = -\langle E_k \rangle$.
Since $E = \langle E_k \rangle + \langle V \rangle$, then $\langle V \rangle = -2 \langle E_k \rangle$ for the hydrogen atom. This result is a specific example of the **Virial Theorem**. If the potential is in the form of a power law, $V(x) = k x^n$, then the average potential and kinetic energy are related by:

$$2 \langle E_k \rangle = n \langle V \rangle$$

For the hydrogen atom, n = -1 with x = r, which gives $\langle E_k \rangle = -\frac{1}{2} \langle V \rangle$ by the Virial Theorem, as shown by this problem.

5. The ground state of the hydrogen atom is: $\Psi_1(r) = R(r) = \frac{1}{\sqrt{\pi}}\left(\frac{Z}{a_o}\right)^{3/2} e^{-Zr/a_o}$.

(a). Calculate the expectation value of the potential energy for the ground state of the hydrogen atom.

(b) In your final answer in (a), use the fact that $e^2/4\pi\varepsilon_o = \hbar^2/ma_o$ to show that $<V> = 2E_1$, where E_1 is the total energy of the ground state of the hydrogen atom.

Answer: The plan is to determine the expectation value of $\hat{V}(r) = -\,Ze^2/(4\pi\varepsilon_o\, r)$.
The wave function is real and normalized. The potential energy operator does not involve a derivative, so the integrand for the expectation value is a product of functions of r. The order of the functions is immaterial. The expectation value then reduces to:

$$<V> = \frac{\int_o^\infty\int_o^\pi\int_o^{2\pi} \Psi_1^* \hat{V}\, \Psi_1\, r^2 \sin\theta\, dr\, d\theta d\phi}{\int_o^\infty\int_o^\pi\int_o^{2\pi} \Psi_1^* \Psi_1\, r^2 \sin\theta\, dr\, d\theta d\phi} = -\frac{Ze^2}{4\pi\varepsilon_o}\int_o^\infty\int_o^\pi\int_o^{2\pi} \frac{1}{r}\,\Psi_1^2\, r^2 \sin\theta\, dr\, d\theta d\phi \tag*{1}$$

Since the wave function only depends on r, $\Psi(r) = R(r)$, the angular integrals give 4π:

$$<V> = -\,4\pi\,\frac{Ze^2}{4\pi\varepsilon_o}\, N^2 \int_o^\infty e^{-2Zr/a_o}\, r\, dr \qquad \text{with normalization, } N = 1/\sqrt{\pi}\,(Z/a_o)^{3/2} \tag*{2}$$

The integral table gives: $\int_0^\infty x^n\, e^{-ax}\, dx = (n!/a^{n+1})$ for $n = 1$:

$$<V> = -\,4\pi\,\frac{Ze^2}{4\pi\varepsilon_o}\, N^2 \left(\frac{a_o}{2Z}\right)^2 \tag*{3}$$

Substituting in the normalization constant gives:

$$<V> = -\frac{Ze^2}{\varepsilon_o}\left(\frac{1}{\pi}\right)\left(\frac{Z}{a_o}\right)^3\left(\frac{a_o}{2Z}\right)^2 = -\left(\frac{Z^2}{a_o}\right)\frac{e^2}{4\pi\varepsilon_o} \tag*{4}$$

(b). From the definition of a_o: $a_o = \dfrac{4\pi\varepsilon_o\hbar^2}{me^2}$ or $\dfrac{e^2}{4\pi\varepsilon_o} = \dfrac{\hbar^2}{ma_o}$ $\qquad$ 5

Substitution of Eq. 5 into Eq. 4 gives:

$$<V> = -\frac{Z^2\hbar^2}{ma_o^2} \tag*{6}$$

The total energy for the ground state of the hydrogen atom is $E_1 = -\dfrac{Z^2\hbar^2}{2ma_o^2} = ½ <V>$.
Since $E = <E_k> + <V>$, then $<E_k> = -½ <V>$ for the hydrogen atom. This result is a specific example of the **Virial Theorem**. If the potential is in the form of a power law, $V(x) = k\, x^n$, then the average potential and kinetic energy are related by:

$$2 <E_k> = n <V>$$

For the hydrogen atom, $n = -1$ with $x = r$, which gives $<E_k> = -\,½ <V>$ by the Virial Theorem, as shown by this problem.

<u>6</u>. Find the average radius of an electron in a hydrogen atom in a 2s orbital.

Answer: The normalized 2s orbital is given by:

$$\Psi_{2s} = \frac{1}{4\sqrt{2\pi}} \left(\frac{Z}{a_o}\right)^{3/2} \left(2 - \frac{Zr}{a_o}\right) e^{-Zr/2a_o}$$

The average radius is given by the expectation value of r:

$$<r> = \underbrace{\frac{\int_o^\infty \int_o^\pi \int_o^{2\pi} \Psi_{2s}^* \, r \, \Psi_{2s} \, r^2 \sin\theta \, dr \, d\theta d\phi}{\int_o^\infty \int_o^\pi \int_o^{2\pi} \Psi_{2s}^* \, \Psi_{2s} \, r^2 \sin\theta \, dr \, d\theta d\phi} = \int_o^\infty \int_o^\pi \int_o^{2\pi} r \, \Psi_{2s}^2}_{\text{average r}} \underbrace{r^2 \sin\theta \, dr \, d\theta d\phi}_{\text{volume element}}$$

The integral involves only functions, so the order is immaterial. Since the wave function only depends on r, $\Psi(r) = R(r)$, the angular integrals give 4π:

$$<r> = 4\pi \int_o^\infty r^3 \, \Psi_{2s}^2 \, dr = 4\pi \frac{1}{32\pi} \left(\frac{Z}{a_o}\right)^3 \int_0^\infty r^3 \left(2 - \frac{Zr}{a_o}\right)^2 e^{-Zr/a_o} \, dr$$

$$<r> = 4\pi \frac{1}{32\pi} \left(\frac{Z}{a_o}\right)^3 \int_0^\infty r^3 \left(4 - \frac{4Zr}{a_o} + \frac{Z^2 r^2}{a_o^2}\right) e^{-Zr/a_o} \, dr$$

Splitting the integral gives:

$$<r> = 4\pi \frac{1}{32\pi} \left(\frac{Z}{a_o}\right)^3 \left[4 \int_0^\infty r^3 \, e^{-Zr/a_o} \, dr - \frac{4Z}{a_o} \int_0^\infty r^4 \, e^{-Zr/a_o} \, dr + \frac{Z^2}{a_o^2} \int_0^\infty r^5 \, e^{-Zr/a_o} \, dr \right]$$

Integral tables give: $\int_0^\infty x^n \, e^{-ax} \, dx = (n!/a^{n+1})$ with n = 3, 4 and 5:

$$<r> = \frac{1}{8} \left(\frac{Z}{a_o}\right)^3 \left[\left(\frac{24 \, a_o^4}{Z^4}\right) - \left(\frac{96 \, a_o^4}{Z^4}\right) + \left(\frac{120 \, a_o^4}{Z^4}\right) \right] = \frac{48}{8} \frac{a_o}{Z} = 6 \, \frac{a_o}{Z}$$

The average radius for a $2p_z$ orbital is $5a_o/Z$, which is smaller than the 2s, as shown in the next problem.

7. Find the average radius of an electron in a hydrogen atom in a $2p_z$ orbital.
The normalized $2p_z$ orbital is given by:

$$\Psi_{2pz} = \frac{1}{4\sqrt{2\pi}} \left(\frac{Z}{a_o}\right)^{3/2} \frac{Zr}{a_o} \, e^{-Zr/2a_o} \cos\theta$$

Answer: The average radius is given by the expectation value of r:

$$<r> = \underbrace{\frac{\int_o^\infty \int_o^\pi \int_o^{2\pi} \Psi_{2pz}^* \, r \, \Psi_{2pz} \, r^2 \sin\theta \, dr \, d\theta d\phi}{\int_o^\infty \int_o^\pi \int_o^{2\pi} \Psi_{2pz}^* \, \Psi_{2pz} \, r^2 \sin\theta \, dr \, d\theta d\phi} = \int_o^\infty \int_o^\pi \int_o^{2\pi} r \, \Psi_{2pz}^2}_{\text{average r}} \underbrace{r^2 \sin\theta \, dr \, d\theta d\phi}_{\text{volume element}}$$

The integral involves only functions, so the order is immaterial. Substituting the wave function into the integral gives:

$$<r> = \frac{1}{32\pi}\left(\frac{Z}{a_o}\right)^3 \int_0^\infty \left(\frac{Z}{a_o}\right)^2 r^5\, e^{-Zr/a_o}\, dr \int_0^\pi \cos^2\theta \sin\theta\, d\theta \int_0^{2\pi} d\phi$$

The integral over ϕ is 2π. Integral tables give: $\int_0^\pi \cos^2\theta \sin\theta\, d\theta = -\left.\frac{\cos^3\theta}{3}\right|_0^\pi = \frac{1}{3} - \left(-\frac{1}{3}\right) = \frac{2}{3}$

The expectation value of r reduces to:

$$<r> = \frac{1}{32\pi}\left(\frac{Z}{a_o}\right)^3 \left(\frac{2}{3}\right)(2\pi) \int_0^\infty \left(\frac{Z}{a_o}\right)^2 r^5\, e^{-Zr/a_o}\, dr$$

Integral tables give: $\int_0^\infty x^n\, e^{-ax}\, dx = (n!/a^{n+1})$ with n = 5:

$$<r> = \frac{1}{24}\left(\frac{Z}{a_o}\right)^5 \left(\frac{120\, a_o^6}{Z^6}\right) = 5\,\frac{a_o}{Z}$$

The average radius for a 2s orbital is $6a_o/Z$, as shown in the previous problem, which is larger than the $2p_z$,

8. Find the radius of the 90% contour surface for a 1s orbital in the H-atom. Use the following steps.

(a). Integral tables give $\int x^n\, e^{-ax}\, dx = -\frac{x^n\, e^{-ax}}{a} + \frac{n}{a}\int x^{n-1}\, e^{-ax}\, dx$. Prove that:

$$\int x^2\, e^{-ax}\, dx = -\frac{x^2\, e^{-ax}}{a} - \frac{2x\, e^{-ax}}{a^2} - \frac{2\, e^{-ax}}{a^3}$$

(b). Show that for a given value of the contour radius, r_c, that:

$$\int_0^{r_c} r^2\, e^{-2Zr/a_o}\, dr = \left(-\frac{a_o\, r_c^2}{2Z} - \frac{a_o^2\, r_c}{2Z^2} - \frac{a_o^3}{4Z^3}\right) e^{-2Zr_c/a_o} + \frac{a_o^3}{4Z^3}$$

(c). Show the radius that gives the 90% contour surface is given by:

$$0.90 = \left(-2\,\frac{Z^2\, r_c^2}{a_o^2} - 2\,\frac{Z\, r_c}{a_o} - 1\right) e^{-2Zr_c/a_o} + 1$$

(d). Let $\rho = Zr_c/a_o$. Show that the last equation reduces to: $(-2\rho^2 - 2\rho - 1)\, e^{-2\rho} + 1 = 0.90$. Solve this equation for ρ numerically, to three significant figures, to find the 90% contour radius.

Answer: The plan is to note that the normalized 1s orbital is given by:

$$\Psi_{1s} = \frac{1}{\sqrt{\pi}}\left(\frac{Z}{a_o}\right)^{3/2} e^{-Zr/a_o} \qquad 1$$

The 90% contour radius, r_c, corresponds to an integrated probability of 0.90:

$$0.90 = \int_o^{r_c}\int_o^\pi\int_o^{2\pi} \Psi_{1s}^2\, \underbrace{r^2 \sin\theta\, dr\, d\theta d\phi}_{\textit{volume element}} \qquad 2$$

Since the wave function only depends on r, the angular integrals give 4π:

$$0.90 = 4\pi \int_o^{r_c} \Psi_{1s}^2\, r^2\, dr = 4\left(\frac{Z}{a_o}\right)^3 \int_0^{r_c} r^2\, e^{-2Zr/a_o}\, dr \qquad 3$$

(a). Integral tables give $\int x^n\, e^{-ax}\, dx = -\frac{x^n\, e^{-ax}}{a} + \frac{n}{a}\int x^{n-1}\, e^{-ax}\, dx$. The integral with n = 2 is then:

$$\begin{aligned}\int x^2\, e^{-ax}\, dx &= -\frac{x^2\, e^{-ax}}{a} + \frac{2}{a}\int x\, e^{-ax}\, dx \\ &= -\frac{x^2\, e^{-ax}}{a} - \frac{2x\, e^{-ax}}{a^2} - \frac{2}{a^2}\int e^{-ax}\, dx \\ &= -\frac{x^2\, e^{-ax}}{a} - \frac{2x\, e^{-ax}}{a^2} - \frac{2\, e^{-ax}}{a^3}\end{aligned}$$

(b). Noting that $e^{-ax}\big|_0^{x_o} = e^{-ax_o} - 1$, the definite integral from 0 to x_o is:

$$\int_0^{x_o} x^2\, e^{-ax}\, dx = -\frac{x_o^2\, e^{-ax_o}}{a} - \frac{2x_o\, e^{-ax_o}}{a^2} - \frac{2\, e^{-ax_o}}{a^3} + \frac{2}{a^3}$$

With x = r, a = Zr/a_o, and the integral limit $x_o = r_c$, the needed integral over r^2 is:

$$\int_0^{r_c} r^2\, e^{-2Zr/a_o}\, dr = \left(-\frac{a_o\, r_c^2}{2Z} - \frac{a_o^2\, r_c}{2Z^2} - \frac{a_o^3}{4Z^3}\right) e^{-2Zr_c/a_o} + \frac{a_o^3}{4Z^3}$$

(c). Substituting this last result for the integral into Eq. 3 gives:

$$0.90 = 4\left(\frac{Z}{a_o}\right)^3\left(-\frac{a_o\, r_c^2}{2Z} - \frac{a_o^2\, r_c}{2Z^2} - \frac{a_o^3}{4Z^3}\right) e^{-2Zr_c/a_o} + 4\left(\frac{Z}{a_o}\right)^3 \frac{a_o^3}{4Z^3}$$

$$0.90 = \left(-2\,\frac{Z^2\, r_c^2}{a_o^2} - 2\,\frac{Z\, r_c}{a_o} - 1\right) e^{-2Zr_c/a_o} + 1$$

(d). Letting $\rho = Zr_c/a_o$, the last equation reduces to: $(-2\rho^2 - 2\rho - 1)\, e^{-2\rho} + 1 = 0.90$. Solving for ρ is easily accomplished using a spreadsheet. A quick and efficient search algorithm is to find two values of ρ that bracket the desired result and then "split the difference." That is, divide each interval that brackets the desired value by 2. Using the initial guesses of ρ = 2 and ρ = 3, the next value to try is ρ = 2.5. The second column calculates $(-2\rho^2 - 2\rho - 1)\, e^{-2\rho} + 1$ for the guessed value of ρ in the first column:

$\rho = Zr/a_o$	$4\pi \int \Psi^2\, r^2\, dr$
2	0.7619
3	0.9380
2.5	0.8753
2.75	0.9116
2.625	0.8949
2.6875	0.9036
2.656	0.8993

The final result is ρ ≅ 2.66 or $r_c = 2.66\, a_o/Z$. In comparison, the average radius for a 1s orbital is $\langle r \rangle = 1.5\, a_o/Z$.

9. Show that the 1s and 2s orbitals of the hydrogen atom are orthogonal.

Answer: The plan is to show that the orthogonality integral is equal to zero: $\int \Psi_n^* \Psi_m \, d\tau = 0$. The volume element for a spherical atom is $d\tau = r^2 \sin\theta \, dr \, d\theta \, d\phi$.

The 1s and 2s orbitals are:

$$\Psi_{1s}(r) = \frac{1}{\sqrt{\pi}}\left(\frac{Z}{a_o}\right)^{3/2} e^{-Zr/a_o} \qquad \text{and} \qquad \Psi_{2s}(r) = \frac{1}{4\sqrt{2\pi}}\left(\frac{Z}{a_o}\right)^{3/2}\left(2 - \frac{Zr}{a_o}\right) e^{-Zr/2a_o}$$

For simplicity, let the normalization constants be N_{1s} and N_{2s}, respectively. The wave functions are spherical, so they are independent of θ and ϕ. The angular integrations then give 4π. The orthogonality integral is then:

$$\int_o^\infty \int_o^\pi \int_o^{2\pi} \Psi_{1s}^* \Psi_{2s} \underbrace{r^2 \sin\theta \, dr \, d\theta d\phi}_{\textit{volume element}} = 4\pi N_{1s} N_{2s} \int_0^\infty e^{-Zr/a_o}\left(2 - \frac{Zr}{a_o}\right) e^{-Zr/2a_o} r^2 dr$$

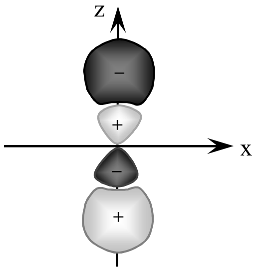
$$= 4\pi N_{1s} N_{2s}\left[2\int_0^\infty r^2 e^{-3Zr/2a_o} dr - \frac{Z}{a_o}\int_0^\infty r^3 e^{-3Zr/2a_o} dr\right]$$

Integral tables give: $\int_0^\infty x^n e^{-ax} dx = (n!/a^{n+1})$ with $n = 2$ and 3:

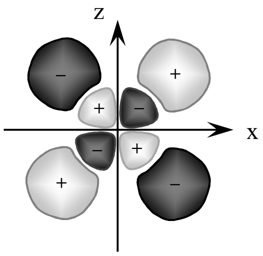
$$\int \Psi_{1s}^* \Psi_{2s} \, d\tau = 4\pi N_{1s} N_{2s}\left[4\left(\frac{2a_o}{3Z}\right)^3 - \left(\frac{Z}{a_o}\right) 6 \left(\frac{2a_o}{3Z}\right)^4\right]$$

$$= 4\pi N_{1s} N_{2s}\left(\frac{a_o}{Z}\right)^3\left[4\left(\frac{8}{27}\right) - 6\left(\frac{16}{81}\right)\right] = 0$$

10. Determine n, ℓ, and $|m_\ell|$ for the following orbitals. Give the orbital designations (e.g. $2p_x$, $3d_{xy}$, etc.).



(a).



(b).

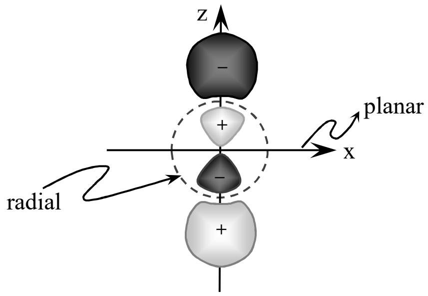
Answer: The plan is to find the number of radial nodes, angular nodes, and angular nodes that include the z-axis. Angular nodes are planes that pass through the nucleus. A radial node is a spherical node that is centered on the nucleus.

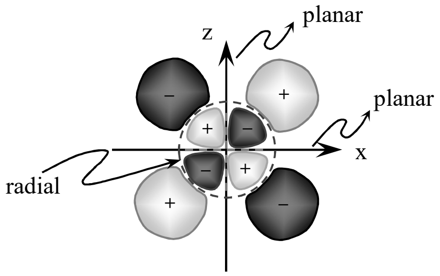
The node counting is:

(a).
total nodes = $n - 1 = 2$
angular nodes = $\ell = 1$
radial nodes = $n - 1 - \ell = 1$
z-axis angular nodes = $|m_\ell| = 0$

(b).
total nodes = $n - 1 = 3$
angular nodes = $\ell = 2$
radial nodes = $n - 1 - \ell = 1$
z-axis angular nodes = $|m_\ell| = 1$

The nodes are shown in the diagrams below. The angular, planar nodes are perpendicular to the plane of the paper.





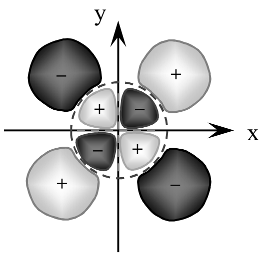
(a). Since $(n - 1) = 2$, $\ell = 1$, and $m_\ell = 0$, the principle quantum number is 3 giving a $3p_z$ orbital.
(b). One of the angular nodes is in the y-z plane, which includes the z-axis. One of the angular nodes is in the x-y plane, so that node does not include the z-axis. Overall then $|m_\ell| = 1$. Since $(n - 1) = 3$ and $\ell = 2$, the principle quantum number is 4 giving a 4d- orbital. Since the lobes of the orbital point between the x- and z- axis, the orbital is a $4d_{xz}$ orbital.

<u>11</u>. Sketch the $4d_{xy}$ orbital. Include the phase for each region.

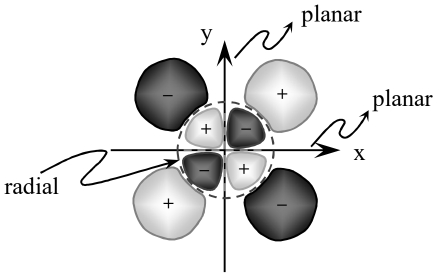
Answer: The plan is to find the number of radial nodes for the $4d_{xy}$ orbital and to note that the orbital points between the x- and y- axes. Angular nodes are planes that pass through the nucleus. A radial node is a spherical node that is centered on the nucleus.

The node counting is:
total nodes = $n - 1 = 3$
angular nodes = $\ell = 2$ (a "d"-orbital)
radial nodes = $n - 1 - \ell = 1$

The angular, planar nodes are perpendicular to the plane of the paper. Since the lobes of the orbital point between the x- and y- axis, both angular nodes include the z-axis, $|m_\ell| = 2$.



$4d_{xy}$



$4d_{xy}$ with nodes labeled

12. The normalized angular portions of the oriented d-orbitals are:

$$d_{xz} = \left(\frac{5}{4\pi}\right)^{1/2} \sqrt{3} \sin\theta \cos\theta \cos\phi$$

$$d_{yz} = \left(\frac{5}{4\pi}\right)^{1/2} \sqrt{3} \sin\theta \cos\theta \sin\phi$$

$$d_{xy} = \left(\frac{5}{4\pi}\right)^{1/2} \sqrt{3} \sin^2\theta \cos\phi \sin\phi$$

$$d_{x2-y2} = \left(\frac{5}{4\pi}\right)^{1/2} \frac{\sqrt{3}}{2} \sin^2\theta\,(\cos^2\phi - \sin^2\phi)$$

$$d_{3z2-r2} = \left(\frac{5}{4\pi}\right)^{1/2} \frac{1}{2} (3\cos^2\theta - 1)$$

Show that $d^2_{xz} + d^2_{yz} + d^2_{xy} + d^2_{x2\text{-}y2} + d^2_{3z2-r2}$ = constant (Eq. 25.2.10). The following trigonometric identities are useful:

$\cos^2 x + \sin^2 x = 1$ and correspondingly $(\cos^2 x + \sin^2 x)^2 = 1$
$\cos^2 x - \sin^2 x = 2\cos^2 x - 1$

Answer: The plan is to work on the ϕ portions first, then the θ portions. The final results must be independent of both ϕ and θ. In addition, expanding $(\cos^2 x + \sin^2 x)^2 = 1$ gives:

$$(\cos^2 x + \sin^2 x)^2 = \cos^4 x + 2\cos^2 x \sin^2 x + \sin^4 x = 1 \qquad 1$$

Let $N = (5/4\pi)^{1/2}$ for convenience. First note that:

$$d^2_{xz} + d^2_{yz} = 3N^2 \sin^2\theta \cos^2\theta\,(\cos^2\phi + \sin^2\phi) = 3N^2 \sin^2\theta \cos^2\theta \qquad 2$$

which is independent of ϕ. Next, note that:

$$\begin{aligned} d^2_{xy} + d^2_{x2\text{-}y2} &= \tfrac{3}{4} N^2 \sin^4\theta\,[4\cos^2\phi \sin^2\phi + (\cos^2\phi - \sin^2\phi)^2] \\ &= \tfrac{3}{4} N^2 \sin^4\theta\,[4\cos^2\phi \sin^2\phi + \cos^4\phi - 2\cos^2\phi \sin^2\phi + \sin^4\phi] \\ &= \tfrac{3}{4} N^2 \sin^4\theta\,[\cos^4\phi + 2\cos^2\phi \sin^2\phi + \sin^4\phi] \qquad 3 \end{aligned}$$

Using identity Eq. 1 gives: $d^2_{xy} + d^2_{x2\text{-}y2} = \tfrac{3}{4} N^2 \sin^4\theta$ 4

We can split $3\cos^2\theta - 1$ into two terms:

$$(3\cos^2\theta - 1) = \cos^2\theta + 2\cos^2\theta - 1 \qquad 5$$

Then using the identity, $\cos^2 x - \sin^2 x = 2\cos^2 x - 1$, gives:

$$(3\cos^2\theta - 1) = \cos^2\theta + \cos^2\theta - \sin^2\theta = 2\cos^2\theta - \sin^2\theta \qquad 6$$

$$\begin{aligned} d^2_{3z2-r2} &= \tfrac{1}{4} N^2 (2\cos^2\theta - \sin^2\theta)^2 = \tfrac{1}{4} N^2 (4\cos^4\theta - 4\cos^2\theta \sin^2\theta + \sin^4\theta) \\ &= N^2(\cos^4\theta - \cos^2\theta \sin^2\theta + \tfrac{1}{4}\sin^4\theta) \qquad 7 \end{aligned}$$

Combining Eqs. 2, 4, and 6 gives:

$$\begin{aligned} & d^2_{xz} + d^2_{yz} + d^2_{xy} + d^2_{x2\text{-}y2} + d^2_{3z2-r2} = \\ & = 3N^2 \sin^2\theta \cos^2\theta + \tfrac{3}{4} N^2 \sin^4\theta + N^2(\cos^4\theta - \cos^2\theta \sin^2\theta + \tfrac{1}{4} \sin^4\theta) \\ & = N^2(\cos^4\theta + 2 \cos^2\theta \sin^2\theta + \sin^4\theta) \qquad 8 \end{aligned}$$

Using the identity Eq. 1 gives the result independent of both θ and ϕ:

$$d^2_{xz} + d^2_{yz} + d^2_{xy} + d^2_{x2\text{-}y2} + d^2_{3z2-r2} = N^2 \qquad 9$$

This result is the d-orbital version of Unsöld's Theorem, and explains why the d_{3z2-r2} has the unique functional form. The problem can also be done using the identities sin 2x = cos x sin x and cos 2x = $\cos^2$x – $\sin^2$x.

<u>13</u>. Normalize the angular portion of the orbital: $d_{yz} = N \sin\theta \cos\theta \sin\phi$. Note that:

$$\int_0^\pi \sin^3 x \cos^2 x \, dx = {}^4\!/_{15}$$

Answer: The plan is to note that the normalization integral is over all θ and ϕ with $d\tau = \sin\theta \, d\theta \, d\phi$.

The normalization integral is:

$$\int_0^\pi \int_0^{2\pi} d^2_{yz} \sin\theta \, d\theta \, d\phi = N^2 \int_0^\pi \int_0^{2\pi} \sin^3\theta \cos^2\theta \sin^2\phi \, d\theta \, d\phi = 1$$

The result is the product of one-dimensional integrals:

$$N^2 \int_0^\pi \sin^3\theta \cos^2\theta \, d\theta \int_0^{2\pi} \sin^2\phi \, d\phi = 1$$

As given in the problem statement: $\int_0^\pi \sin^3 x \cos^2 x \, dx = 4/15$.

Integral tables list: $\int_0^{\pi/2} \sin^2 x \, dx = \pi/4$. Since the integrand is always positive, the integral over the full interval is: $\int_0^{2\pi} \sin^2 x \, dx = \pi$. The normalization integral is then:

$$N^2 \int_0^\pi \sin^3\theta \cos^2\theta \, d\theta \int_0^{2\pi} \sin^2\phi \, d\phi = N^2 \left(\frac{4}{15}\right)(\pi) = 1$$

Giving $N = \left(\frac{15}{4\pi}\right)^{1/2}$

as listed in the last problem. You may wonder how to do the tricky integral. $\int \sin^3 x \cos^2 x \, dx$ is integrated by parts. Integral tables give the indefinite form as:

$$\int \sin^3 x \cos^2 x \, dx = \frac{\cos x \sin^4 x}{5} + \frac{1}{5} \int \sin^3 x \, dx$$

Integral tables give $\int \sin^3 x \, dx = -\,{}^1\!/_3 \cos x \, (\sin^2 x + 2)$:

$$\int_0^\pi \sin^3 x \, dx = -\,{}^1\!/_3[\cos x \, (\sin^2 x + 2)|_0^\pi = -\,{}^1\!/_3 \, [(-1)(0 + 2) - (1)(0 + 2)] = {}^4\!/_3$$

For the definite integral then: $\int_0^\pi \sin^3 x \cos^2 x\, dx = \left[\frac{\cos x \sin^4 x}{5}\right|_0^\pi + \frac{4}{15}$

The first term is zero at both end points giving: $\int_0^\pi \sin^3 x \cos^2 x\, dx = \frac{4}{15}$

14. The oriented forms of the d-orbitals are given as products of the Cartesian coordinates, e.g. d_{xz}. Give the functional form of the $3d_{xz}$ orbital using Cartesian coordinates for the angular portion (e.g. Eqs. 25.2.8) and using spherical polar coordinates (e.g. Eqs. 25.2.6). Just leave the normalization constant as N. Describe the orientation of the lobes of the orbital.

Answer: The plan is to compare to the form of the 2p-orbitals, Eqs. 25.2.6 and 25.2.8. The coordinate transformations are given by Eqs. 24.5.14 resulting in Eqs. 25.2.9.

The asymptotic form has the functional dependence e^{-Zr/na_o}, in this case n = 3, giving:

$$\Psi_{3dxz} = N\, e^{-Zr/3a_o} (Z/a_o)^2\, xz$$

The spherical polar form is given from the transformations in Eqs. 24.5.14:

$$\begin{aligned}\Psi_{3dxz} &= N\, e^{-Zr/3a_o} (Z/a_o)^2 (r \sin\theta \cos\phi)(r \cos\theta) \\ &= N\, e^{-Zr/3a_o} (Zr/a_o)^2 \sin\theta \cos\theta \cos\phi\end{aligned}$$

The factor of $(Z/a_o)^3$ appears because the wave function is overall unitless, so r always appears as Zr/a_o to cancel the units and adjust for contraction caused by the charge on the nucleus. The "rulers" in the atomic world are marked in multiples of Zr/a_o. The lobes of the orbital point between the x- and z-axes. No lobes lie along an axis.

15. The oriented forms of the f-orbitals are given as triple products of the Cartesian coordinates, e.g. f_{xyz}. Give the functional form of the $4f_{xyz}$ orbital using Cartesian coordinates for the angular portion (e.g. Eqs. 25.2.8) and using spherical polar coordinates (e.g. Eqs. 25.2.6). Just leave the normalization constant as N. Describe the orientation of the lobes of the orbital.

Answer: The plan is to compare to the form of the p-orbitals, Eqs. 25.2.6 and 25.2.8. The coordinate transformations are given by Eqs. 24.5.14.

The asymptotic form has the functional dependence e^{-Zr/na_o}, in this case n = 4, giving:

$$\Psi_{4fxyz} = N\, e^{-Zr/4a_o} (Z/a_o)^3\, xyz$$

The spherical polar form is given from the transformations in Eqs. 24.5.14:

$$\begin{aligned}\Psi_{4fxyz} &= N\, e^{-Zr/4a_o} (Z/a_o)^3 (r \sin\theta \cos\phi)(r \sin\theta \sin\phi)(r \cos\theta) \\ &= N\, e^{-Zr/4a_o} (Zr/a_o)^3 \sin^2\theta \cos\theta \cos\phi \sin\phi\end{aligned}$$

The factor of $(Z/a_o)^3$ appears because the wave function is overall unitless, so r always appears as Zr/a_o to cancel the units and adjust for contraction caused by the charge on the nucleus. The "rulers" in the atomic world are marked in multiples of Zr/a_o. The lobes of the orbital point between the x-, y-, and z-axes. No lobes lie along an axis.

16. Hooke's Law is only an approximation of the true vibrational potential energy of a molecule. There are many other possible forms for the potential energy function of a chemical bond. Use perturbation theory to calculate the small change in energy for the harmonic oscillator ground state that is perturbed by the addition of a term = b x^4 to the potential energy function:

$$V(x) = \tfrac{1}{2} k x^2 + b x^4$$

[Hint: Remember that the wave function is $\Psi(x) = \left(\frac{\alpha^2}{\pi}\right)^{1/4} e^{-\frac{1}{2}\alpha^2 x^2}$ where $\alpha^2 = \left(\frac{m\omega_o}{\hbar}\right)$. Just leave α^2 as a parameter until the last step and then substitute in at the last for α^2 to find that the change in energy is $\frac{3b}{4}\left(\frac{\hbar}{m\omega_o}\right)^2$]

Answer: The plan is to note that the perturbation is V' = b x^4.

The first order perturbation correction to the energy is the expectation value of the perturbation using the zeroth-order wave functions, which for the ground state are for v = 0:

$$E^{(1)} = \int_{-\infty}^{\infty} \Psi_0^* (b\, x^4)\, \Psi_0\, dx = b\left(\frac{\alpha^2}{\pi}\right)^{1/2} \int_{-\infty}^{\infty} x^4 e^{-\alpha^2 x^2}\, dx$$

Integral tables give: $\int_0^{\infty} x^4 e^{-ax^2}\, dx = (3/8a^2)\,(\pi/a)^{1/2}$, giving:

$$E^{(1)} = 2b\left(\frac{\alpha^2}{\pi}\right)^{1/2}\left(\frac{3}{8\alpha^4}\right)\left(\frac{\pi}{\alpha^2}\right)^{1/2} = \frac{6b}{8\alpha^4} = \frac{3b}{4}\left(\frac{\hbar}{m\omega_o}\right)^2$$

17. Using the Aufbau Principle predict the ground state electron configuration for: (a). Si, (b). Ti, (c). Ti^{2+}, (d). Cr, (e). Cr^{2+}, and (f). Ag. Show both the condensed configuration (e.g. [Ne] $3s^2$) and the orbital diagram (e.g. 3s: $\boxed{\uparrow\downarrow}$). For which species is the Aufbau prediction expected to differ from the experimental configuration?

Answers:

(a). Si: [Ne] $3s^2\, 3p^2$ 3s: $\boxed{\uparrow\downarrow}$ 3p: $\boxed{\uparrow}\boxed{\uparrow}\boxed{}$

(b). Ti: [Ar] $3d^2\, 4s^2$ 3d: $\boxed{\uparrow}\boxed{\uparrow}\boxed{}\boxed{}\boxed{}$ 4s: $\boxed{\uparrow\downarrow}$

(c). Ti^{2+}: [Ar] $3d^2\, 4s^0$ 3d: $\boxed{\uparrow}\boxed{\uparrow}\boxed{}\boxed{}\boxed{}$ 4s: $\boxed{}$

(d). Cr: [Ar] $3d^4\, 4s^2$ 3d: $\boxed{\uparrow}\boxed{\uparrow}\boxed{\uparrow}\boxed{\uparrow}\boxed{}$ 4s: $\boxed{\uparrow\downarrow}$ (Aufbau)

However, Cr needs only one-electron more to complete a half-filled d sub-orbital, so the experimental configuration is expected to deviate from the Aufbau prediction to give:

Cr: [Ar] $3d^5\, 4s^1$ 3d: $\boxed{\uparrow}\boxed{\uparrow}\boxed{\uparrow}\boxed{\uparrow}\boxed{\uparrow}$ 4s: $\boxed{\uparrow}$ (experimental)

(e). Cr^{2+}: [Ar] $3d^4\, 4s^0$ 3d: $\boxed{\uparrow}\boxed{\uparrow}\boxed{\uparrow}\boxed{\uparrow}\boxed{}$ 4s: $\boxed{}$

(f). Ag: [Kr] $4d^9\ 5s^2$ 4d: $\boxed{\uparrow\downarrow}\boxed{\uparrow\downarrow}\boxed{\uparrow\downarrow}\boxed{\uparrow\downarrow}\boxed{\uparrow}$ 5s: $\boxed{\uparrow\downarrow}$ (Aufbau)

However, Ag needs only one-electron more to complete the d sub-orbital, so the experimental configuration is expected to deviate from the Aufbau prediction to give:

Ag: [Kr] $4d^{10}\ 5s^1$ 4d: $\boxed{\uparrow\downarrow}\boxed{\uparrow\downarrow}\boxed{\uparrow\downarrow}\boxed{\uparrow\downarrow}\boxed{\uparrow\downarrow}$ 5s: $\boxed{\uparrow}$ (experimental)

The completed d sub-shell for Ag is reflected in the lack of reactivity for Ag. Ag is one of the "coinage" metals along with Cu and Au.

18. The following problem explores the Pauli Exclusion Principle and wave function symmetry.[1] Let Ψ_1 and Ψ_2 be the functions for a particle in a one-dimensional particle in a box with n = 1 and n = 2, respectively. If one electron were in each of these orbitals, the space part of the triplet and singlet wave functions would be:

$$\Psi_A = \frac{1}{\sqrt{2}}[\Psi_1(1)\ \Psi_2(2) - \Psi_2(1)\ \Psi_1(2)] \qquad \text{and} \qquad \Psi_S = \frac{1}{\sqrt{2}}[\Psi_1(1)\ \Psi_2(2) + \Psi_2(1)\ \Psi_1(2)]$$

respectively. Suppose that electron 1 is in a small element of length dx at x = 0.250 a and electron 2 is in a small element of length dx at x = 0.255 a. The quantity a is the length of the box. Show that Ψ_A has a very small value under these conditions while Ψ_S is large. What happens to Ψ_A if both electrons are at x = 0.250 a? This problem shows how an anti-symmetric spatial wave function keeps the electrons apart.[1]

A note on nomenclature: for example, $\psi_1(2)$ means wave function 1 (with n = 1) is used for electron 2. Since this wave function is for electron 2 it should be evaluated at x = 0.255 a.

Answer: The single particle wave functions are:

$$\Psi_1(x) = \left(\frac{2}{a}\right)^{1/2} \sin(\pi x/a) \qquad \Psi_2(x) = \left(\frac{2}{a}\right)^{1/2} \sin(2\pi x/a)$$

The values for the single particle wave functions are given in the following table.

electron	x	sin(nπx/a)	
		n = 1	n = 2
electron 1	0.25 a	0.707107	1
electron 2	0.255 a	0.718126	0.999507

Then the anti-symmetric and symmetric two- electron wave function are:

$$\Psi_A = \frac{1}{\sqrt{2}}[\Psi_1(1)\ \Psi_2(2) - \Psi_2(1)\ \Psi_1(2)]$$

$$= \left(\frac{\sqrt{2}}{a}\right)[(0.707107)(0.999507) - (0.718126)(1.00000)] = -0.01608/a$$

$$\Psi_S = \left(\frac{\sqrt{2}}{a}\right)[(0.707107)(0.999507) + (0.718126)(1.00000)] = 2.015091/a$$

Ψ_A has a very small value under these conditions while Ψ_S is large, by comparison. The anti-symmetric spatial wave function gives a much smaller probability, Ψ_A^2, of the particles being close together than the symmetric combination. If both electrons are at x = 0.250 a then $\Psi_A = 0$. There is no probability that both electrons are in the same spot. The anti-symmetric combination keeps the particles at larger distance from each other on average, minimizing electron-electron repulsion between the particles.

19. Two possible wave functions for the ground state of the helium atom are:

$$\Psi_s = {}^1\!/\!\sqrt{2}\ \Psi_{1s}(1)\ \Psi_{1s}(2)\ [\alpha(1)\ \beta(2) + \beta(1)\ \alpha(2)] \qquad (25.4.14)$$

$$\Psi_a = {}^1\!/\!\sqrt{2}\ \Psi_{1s}(1)\ \Psi_{1s}(2)\ [\alpha(1)\ \beta(2) - \beta(1)\ \alpha(2)] \qquad (25.4.15)$$

Show that both transform to give back the original wave function upon exchange of spin labels: $\Psi_s^2 \rightarrow \Psi_s^2$ and $\Psi_a^2 \rightarrow \Psi_a^2$.

Answer: In this case, the transformation properties under exchange of spin labels depend only upon the spin parts. For convenience, we will just look at the spin parts to simplify the nomenclature. The wave functions are one electron functions; $\alpha(1)$ and $\beta(1)$ are only functions of electron 1 while $\alpha(2)$ and $\beta(2)$ are only functions of electron 2. For this reason wave functions with different spin labels commute, for example $\alpha(1)\ \beta(2) = \beta(2)\ \alpha(1)$. Taking the square of Ψ_s gives:

$$[\alpha(1)\ \beta(2) + \beta(1)\ \alpha(2)]^2 = \alpha^2(1)\ \beta^2(2) + 2\ \alpha(1)\ \beta(1)\ \alpha(2)\ \beta(2) + \beta^2(1)\ \alpha^2(2) \qquad 1$$

Exchange of spin labels transforms the probability to:

$$[\alpha(2)\ \beta(1) + \beta(2)\ \alpha(1)]^2 = \alpha^2(2)\ \beta^2(1) + 2\ \alpha(2)\ \beta(2)\ \alpha(1)\ \beta(1) + \beta^2(2)\ \alpha^2(1) \qquad 2$$

Eqs. 1 and 2 are identical, showing $\Psi_s^2 \rightarrow \Psi_s^2$ upon exchange of spin labels.

Taking the square of Ψ_a gives:

$$[\alpha(1)\ \beta(2) - \beta(1)\ \alpha(2)]^2 = \alpha^2(1)\ \beta^2(2) - 2\ \alpha(1)\ \beta(1)\ \alpha(2)\ \beta(2) + \beta^2(1)\ \alpha^2(2) \qquad 3$$

Exchange of spin labels transforms the probability to:

$$[\alpha(2)\ \beta(1) - \beta(2)\ \alpha(1)]^2 = \alpha^2(2)\ \beta^2(1) - 2\ \alpha(2)\ \beta(2)\ \alpha(1)\ \beta(1) + \beta^2(2)\ \alpha^2(1) \qquad 4$$

Eqs. 3 and 4 are identical, showing $\Psi_a^2 \rightarrow \Psi_a^2$ upon exchange of spin labels. An underlying principle in quantum mechanics, in specific, and the theory of differential equations, in general, is that all possible solutions to a given problem must be considered. The Pauli principle shows that only the antisymmetric case is a valid solution for spin ½ particles.

20. Give the spatial and spin parts for the singlet excited state of helium atom that has the configuration, He: $1s^1\ 2p^1$.

Answer: The plan is to note that the singlet wave function is similar to the first excited state, He: $1s^1\ 2s^1$, covered in the chapter.

A singlet spin part is antisymmetric, so the spatial part must be symmetric:

$$^1\Psi^* = {}^1/\sqrt{2}\ \left(\Psi_{1s}(1)\,\Psi_{2px}(2) + \Psi_{1s}(2)\,\Psi_{2px}(1)\right)\,[\alpha(1)\beta(2) - \beta(1)\alpha(2)]$$

21. Give the determinantal wavefunction for the ground state of the beryllium atom (configuration $1s^2 2s^2$).

Answer:

Be: 1s$\boxed{\uparrow\downarrow}$ 2s$\boxed{\uparrow\downarrow}$

$$\Psi_a = {}^1/\sqrt{4!}\begin{vmatrix} 1s(1)\alpha(1) & 1s(1)\beta(1) & 2s(1)\alpha(1) & 2s(1)\beta(1) \\ 1s(2)\alpha(2) & 1s(2)\beta(2) & 2s(2)\alpha(2) & 2s(2)\beta(2) \\ 1s(3)\alpha(3) & 1s(3)\beta(3) & 2s(3)\alpha(3) & 2s(3)\beta(3) \\ 1s(4)\alpha(4) & 1s(4)\beta(4) & 2s(4)\alpha(4) & 2s(4)\beta(4) \end{vmatrix}$$

22. Determine the spin multiplicity of the vanadium ground state.

Answer: The vanadium ground state configuration is: V $\underset{4s}{\boxed{\uparrow\downarrow}}\quad\underset{3d}{\boxed{\uparrow}\boxed{\uparrow}\boxed{\uparrow}\boxed{}\boxed{}}$

Giving three unpaired electrons:

$S = \left(\sum ms\right)_{max} = 3/2$ and $g_S = (2S + 1) = 2\,(3/2) + 1 = 4$

23. Determine the spin multiplicity of the manganese ground state.

Answer: The manganese ground state configuration is: Mn $\underset{4s}{\boxed{\uparrow\downarrow}}\quad\underset{3d}{\boxed{\uparrow}\boxed{\uparrow}\boxed{\uparrow}\boxed{\uparrow}\boxed{\uparrow}}$

Giving five unpaired electrons:

$S = \left(\sum ms\right)_{max} = 5/2$ and $g_S = (2S + 1) = 2\,(5/2) + 1 = 6$

24. Determine the expectation value for the total spin angular momentum squared, that is $<S^2>$ for a triplet state.

Answer: For a triplet state, S = 1. The total spin angular momentum squared is then:

$S(S+1)\,\hbar^2 = 1(1+1)\,\hbar^2 = 2\,\hbar^2$

25. Give the expectation value for the total spin angular momentum squared, that is $<S^2>$ for a quartet state. For example: $\underset{4s}{\boxed{\uparrow\downarrow}}\quad\underset{3d}{\boxed{\uparrow}\boxed{\uparrow}\boxed{\uparrow}\boxed{}\boxed{}}$

Answer: For a quartet, $S = 3/2$. The total spin angular momentum squared is then:

$$S(S+1)\,\hbar^2 = 3/2(3/2+1)\,\hbar^2 = 3.75\,\hbar^2$$

<u>26</u>. (a). Show that the spin-orbit coupling operator, $\vec{\hat{\ell}}\cdot\vec{\hat{s}}$, for a single unpaired electron is:

$$\vec{\hat{\ell}}\cdot\vec{\hat{s}} = \tfrac{1}{2}\,(\hat{j}^2 - \hat{\ell}^2 - \hat{s}^2)$$

(b). Show that $\vec{\hat{\ell}}\cdot\vec{\hat{s}}$ has the eigenvalue:

$$|\,\vec{\ell}\cdot\vec{s}\,| = \tfrac{1}{2}\,\hbar^2\,[\,j(j+1) - \ell(\ell+1) - s(s+1)]$$

Assume that the interaction is weak enough to be treated as a perturbation, which allows ℓ and s to remain separately good quantum numbers. Accordingly, to a good level of approximation, the total angular momentum wave function is the product of orbital and spin angular momentum eigenfunctions: $\Psi_{j,m_j} = \Psi_{\ell,m_\ell}\,\Psi_{s,m_s}$.

Answer: (a). Note that $\vec{\hat{j}} = \vec{\hat{\ell}} + \vec{\hat{s}}$ and following Eq. 25.6.29:

$$\hat{j}^2 = \vec{\hat{j}}\cdot\vec{\hat{j}} = (\vec{\hat{\ell}}+\vec{\hat{s}})\cdot(\vec{\hat{\ell}}+\vec{\hat{s}}) = \vec{\hat{\ell}}\cdot\vec{\hat{\ell}} + \vec{\hat{s}}\cdot\vec{\hat{s}} + 2\,\vec{\hat{\ell}}\cdot\vec{\hat{s}} = \hat{\ell}^2 + \hat{s}^2 + 2\,\vec{\hat{\ell}}\cdot\vec{\hat{s}}$$

Solving this last equation for $\vec{\hat{\ell}}\cdot\vec{\hat{s}}$:

$$\vec{\hat{\ell}}\cdot\vec{\hat{s}} = \tfrac{1}{2}\,(\hat{j}^2 - \hat{\ell}^2 - \hat{s}^2) \tag{1}$$

(b). The general problem for angular momentum has the form: $-\hbar^2\Lambda^2 Y_{\ell,m_\ell} = \hbar^2\,\ell(\ell+1)\,Y_{\ell,m_\ell}$. Assuming that the interaction is weak enough to be treated as a perturbation allows ℓ and s to remain separately good quantum numbers. The problem is then separable in orbital and spin angular momentum and then the general form applies to $\hat{j}^2$, $\hat{\ell}^2$, and $\hat{s}^2$ separately to give:

$$\hat{j}^2\,\Psi_{j,m_j} = \hbar^2\,j(j+1)\,\Psi_{j,m_j} \tag{2}$$

$$\hat{\ell}^2\,\Psi_{\ell,m_\ell} = \hbar^2\,\ell(\ell+1)\,\Psi_{\ell,m_\ell} \tag{3}$$

$$\hat{s}^2\,\Psi_{s,m_s} = \hbar^2\,s(s+1)\,\Psi_{s,m_s} \tag{4}$$

where Ψ_{j,m_j}, Ψ_{ℓ,m_ℓ}, and Ψ_{s,m_s} are the angular momentum wave functions for the total angular momentum, orbital angular momentum, and spin angular momentum, respectively. The explicit functional forms for Ψ_{j,m_j}, Ψ_{ℓ,m_ℓ}, and Ψ_{s,m_s} are not needed. The total angular momentum wave function is then, to a good level of approximation, the product of the orbital and spin angular momentum eigenfunctions:

$$\Psi_{j,m_j} = \Psi_{\ell,m_\ell}\,\Psi_{s,m_s} \tag{5}$$

The orbital angular momentum operator has no effect on the spin wave function and the spin angular momentum operator has no effect on the orbital angular momentum if the problem is separable:

$$\hat{\ell}^2\,\Psi_{\ell,m_\ell}\,\Psi_{s,m_s} = \Psi_{s,m_s}\,\hat{\ell}^2\,\Psi_{\ell,m_\ell} \qquad \text{and} \qquad \hat{s}^2\Psi_{\ell,m_\ell}\,\Psi_{s,m_s} = \Psi_{\ell,m_\ell}\,\hat{s}^2\,\Psi_{s,m_s} \tag{6}$$

Substituting Eqs. 2-6 into Eq. 1 gives:

$$(\vec{\hat{\ell}}\cdot\vec{\hat{s}})\,\Psi_{j,m_j} = \tfrac{1}{2}\,(\hat{j}^2\Psi_{j,m_j} - \hat{\ell}^2\,\Psi_{\ell,m_\ell}\,\Psi_{s,m_s} - \hat{s}^2\Psi_{\ell,m_\ell}\,\Psi_{s,m_s}) \tag{7}$$

$$(\vec{\hat{\ell}}\cdot\vec{\hat{s}})\,\Psi_{j,m_j} = \tfrac{1}{2}\,\hbar^2\,[\,j(j+1)\,\Psi_{j,m_j} - \Psi_{s,m_s}\,\ell(\ell+1)\,\Psi_{\ell,m_\ell} - \Psi_{\ell,m_\ell}\,s(s+1)\,\Psi_{s,m_s}] \tag{8}$$

$$(\vec{\hat{\ell}}\cdot\vec{\hat{s}})\,\Psi_{j,m_j} = \tfrac{1}{2}\,\hbar^2\,[\,j(j+1)\,\Psi_{j,m_j} - \ell(\ell+1)\,\Psi_{j,m_j} - s(s+1)\,\Psi_{j,m_j}] \tag{9}$$

$$(\vec{\hat{\ell}}\cdot\vec{\hat{s}})\,\Psi_{j,m_j} = \tfrac{1}{2}\,\hbar^2\,[\,j(j+1) - \ell(\ell+1) - s(s+1)]\,\Psi_{j,m_j} \tag{10}$$

with the eigenvalue:

$$|\,\vec{\ell}\cdot\vec{s}\,| = \tfrac{1}{2}\,\hbar^2\,[\,j(j+1) - \ell(\ell+1) - s(s+1)] \tag{11}$$

<u>27</u>. Find the spin-orbit splitting of the $^2D_{5/2}$ and $^2D_{3/2}$ terms for the yttrium ground state.

Answer: The plan is to note that L = 1, S= ½, and J is $^5/_2$ or $^3/_2$.

For the d^1 configuration of the group 3 transition metals, the energy of the terms is split by:

$$E_{so}\,(J = {}^5/_2) = \tfrac{1}{2}\,\mathcal{A}hc\,[{}^5/_2({}^5/_2 + 1) - 2(2+1) - \tfrac{1}{2}(\tfrac{1}{2}+1)] = \tfrac{1}{2}\,\mathcal{A}hc\,[{}^{35}/_4 - {}^{24}/_4 - {}^3/_4] = \mathcal{A}hc$$

$$E_{so}\,(J = {}^3/_2) = \tfrac{1}{2}\,\mathcal{A}hc\,[{}^3/_2({}^3/_2 + 1) - 2(2+1) - \tfrac{1}{2}(\tfrac{1}{2}+1)] = \tfrac{1}{2}\,\mathcal{A}hc\,[{}^{15}/_4 - {}^{24}/_4 - {}^3/_4] = -{}^3/_2\,\mathcal{A}hc$$

giving $\Delta E_{so} = {}^5/_2\,\mathcal{A}hc$. Yttrium is used in high power yttrium aluminum garnet, or YAG, lasers and in liquid nitrogen temperature super conductors.

<u>28</u>. Determine the atomic terms that correspond to a d^2 configuration. Specify the total orbital angular momentum and the spin multiplicity. Use the following steps:

(a). Draw all the possible explicit singlet states. For example, two of the explicit singlet states are:

$\boxed{\uparrow\downarrow}\boxed{}\boxed{}\boxed{}\boxed{}$ and $\boxed{\uparrow}\boxed{\downarrow}\boxed{}\boxed{}\boxed{}$

(b). Calculate M_L for each of the states.

(c). Find $L = |M_L|_{max}$. Remove the M_L states from the list from part (b) corresponding to this L.

(d). Find $L = |M_L|_{max}$ for the remaining states. Remove the M_L states from the list corresponding to this L.

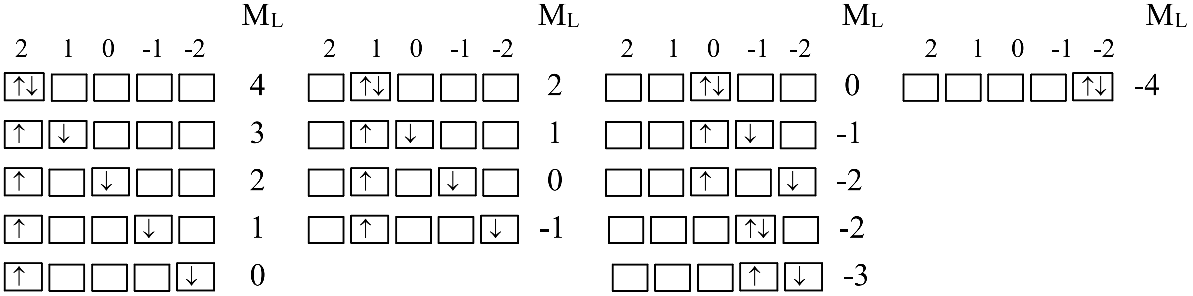
(e). Repeat part (d) until all the M_L states are accounted for. Write the term symbols for each of the different L values that you have found (for example, ^1D or ^3P).

(f). Repeat steps (a) through (e) for all possible explicit triplet states. For example one of the explicit triplet states is:

$\boxed{\uparrow}\boxed{\uparrow}\boxed{}\boxed{}\boxed{}$

(g). Verify that the Clebsch-Gordon series applied to the total orbital angular momentum gives the same results.

Answer: (a). All the possible singlet arrangements are, in no particular order:



(b). The full list is then:

$M_L = \{4,3,2,2,1,1,0,0,0,-1,-1,-2,-2,-3,-4\}$

(c). With $L = |M_L|_{max} = 4$, the first term is a G term based on the definitions of the term symbols:

L:	0	1	2	3	4
Term:	S	P	D	F	G

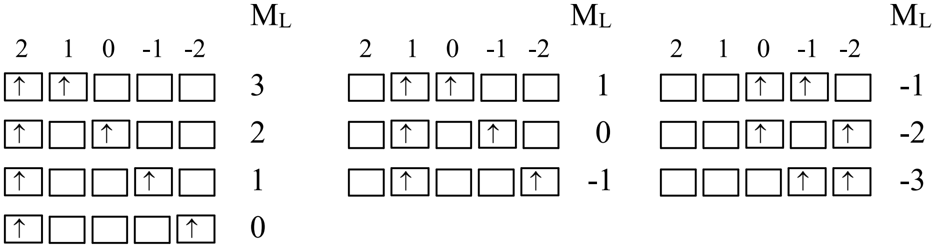
Removing $M_L = \{4,3,2,1,0, -1,-2,-3,-4\}$ from the full list leaves:

$M_L = \{2,1,0,0,-1,-2\}$

(d). Repeating the process, $L = |M_L|_{max} = 2$ and the second term is a D term. Removing $M_L = \{2,1,0, -1,-2\}$ leaves: $M_L = \{0\}$.

(e). The last term is an S term. The final singlet terms are ^{1}G, ^{1}D, ^{1}S.

(f). All the possible triplet arrangements are, in no particular order:



The full list is then: $M_L = \{3,2,1,1,0,0,-1,-1,-2,-3\}$

With $L = |M_L|_{max} = 3$, the first term is an F term. Removing $M_L = \{3,2,1,0,-1,-2,-3\}$ leaves:

$M_L = \{1,0,-1\}$

Repeating the process, $L = |M_L|_{max} = 1$ and the second term is a P term, which corresponds to $M_L = \{1,0,-1\}$. In summary, the resulting triplet terms are then ^{3}F, ^{3}P.

(g). Using the Clebsch-Gordon series for the total orbital angular momentum for a d^2 configuration corresponds to $\ell_1 = 2$ and $\ell_2 = 2$ so that:

$$L = \ell_1 + \ell_2, \ell_1 + \ell_2 - 1, ..., |\ell_1 - \ell_2| = 4, 3, 2, 1, 0$$

giving G, F, D, P, and S terms as listed above.

29. Use the Clebsch-Gordon series and the Russell-Saunders coupling scheme to find the possible total angular momentum J states for the terms that result from the d^2 configuration. See the previous problem for the terms.

Answer: The plan is to use the Clebsch-Gordon series for $\vec{J} = \vec{L} + \vec{S}$ giving:
$J = L + S, L + S - 1, \ldots, |L - S|$. In the previous problem, the Clebsch-Gordon series was applied to the coupling of the orbital angular momenta of the different electrons for the given configuration. In this problem, the Clebsch-Gordon series is applied to the coupling of the total orbital angular momentum and the total spin angular momentum.

Since the total spin quantum number for the singlet states is 0, then J = L and the full singlet terms are $^1G_4$, $^1D_2$, $^1S_0$. Next consider the triplet terms. Applying the Clebsch-Gordon series for the total angular momentum results in the J values:

^3F: L = 3, S = 1: $J = 3 + 1, \ldots, |3 - 1| = 4, 3, 2$ giving $^3F_4$, $^3F_3$, $^3F_2$
^3P: L = 1, S = 1: $J = 1 + 1, \ldots, |1 - 1| = 2, 1, 0$ giving $^3P_2$, $^3P_1$, $^3P_0$

30. Use the Clebsch-Gordon series and the Russell-Saunders coupling scheme to find the possible total angular momentum J states for a ^3P term.

Answer: The plan is to note that a ^3P term corresponds to L = 1 and S = 1.

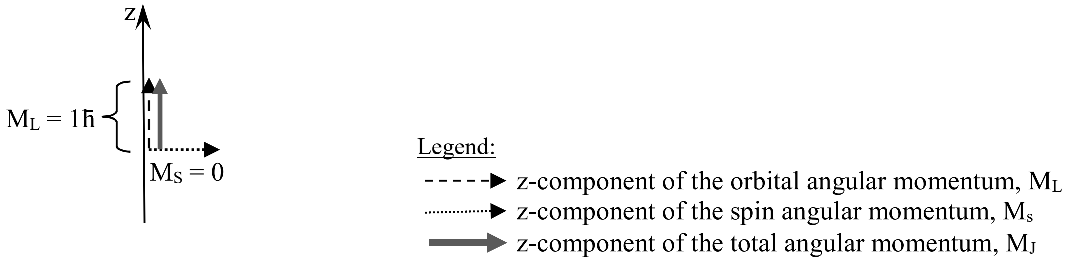
The Clebsch-Gordon series for L = 1 and S = 1 gives:

$$J = L + S, L + S - 1, \ldots, |L - S| = \{2, 1, 0\}.$$

The final terms are $^3P_2$, $^3P_1$, and $^3P_0$.

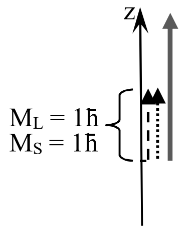
31. The previous problem uses the Clebsch-Gordon series to find the possible values for the total angular momentum for a ^3P term. This problem takes a graphical approach to reach the same conclusion. (a). Draw all the angular momentum diagrams to show the possible total angular momentum M_J states for a ^3P term. (b). Find M_J for each explicit configuration. (c). Determine the possible values for J. Consider only the projections on the z-axis. One example, for $M_L = 1$ and $M_S = 0$ giving $M_J = 1$, is:

$M_J = 1$:

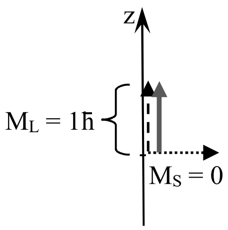


Answer: (a)-(b). The plan is to note that a ^3P term corresponds to L = 1 with $M_L = \{-1,0,1\}$ and S = 1 with $M_S = \{-1,0,1\}$. The Clebsch-Gordon series for L = 1 and S = 1 gives J = {2, 1, 0}.

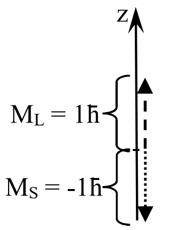
The complete set of explicit states are diagrammed below.



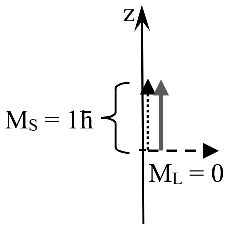
$M_J = 2$



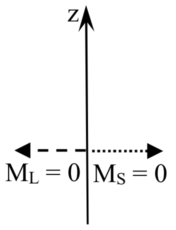
$M_J = 1$



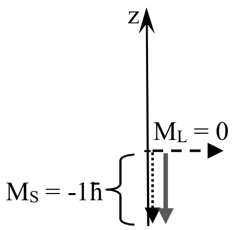
$M_J = 0$



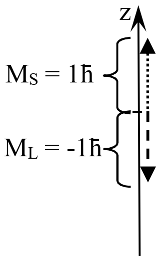
$M_J = 1$



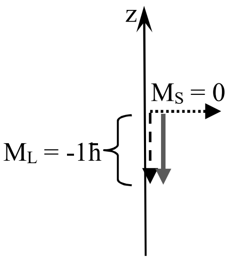
$M_J = 0$



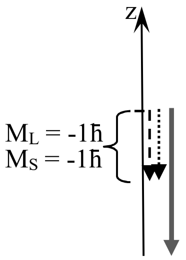
$M_J = -1$



$M_J = 0$



$M_J = -1$



$M_J = -2$

(c). The complete set of M_J values is:

$$M_J = \{2,1,1,0,0,0,-1,-1,-2\}$$

Using $J = |M_J|_{max}$ to extract the first J value gives J = 2. The corresponding degenerate M_J states associated with J = 2 are $M_J = \{2,1,0,-1,-2\}$, which leaves:

$$M_J = \{1,0,0,-1\}$$

Using $J = |M_J|_{max}$ to extract the next J value gives J = 1. The corresponding degenerate M_J states associated with J = 1 are $M_J = \{1,0,-1\}$, which leaves {0}. The final J is J = 0. The final terms are ${}^3P_2$, ${}^3P_1$, and ${}^3P_0$, just as we determined in the last problem using the Clebsch-Gordon series.

<u>32</u>. (a). Use the Clebsch-Gordon series and the Russell-Saunders coupling scheme to find the possible total angular momentum J states for a ${}^3D$ term. (b). Determine the complete set of explicit M_J states for a ${}^3D$ term. Determine the possible total angular momentum J states from the

complete set of M_J values. Compare your results with part (a). For example, two explicit M_J states are tabulated below:

M_L	M_S	M_J
2	1	3
2	0	2

Answer: The plan is to note that a ^3D term corresponds to L = 2 with M_L = {-2,-1,0,1,2} and S = 1 with M_S = {-1,0,1}.

(a). The Clebsch-Gordon series for L = 2 and S = 1 gives:

$$J = L + S, L + S - 1, ..., | L - S| = \{3,2,1\}.$$

The final terms are $^3D_3$, $^3D_2$, and $^3D_1$.

(b). The complete set, in no particular order, is:

M_L	M_S	M_J
2	1	3
2	0	2
2	-1	1
1	1	2
1	0	1
1	-1	0

M_L	M_S	M_J
0	1	1
0	0	0
0	-1	-1
-1	1	0
-1	0	-1
-1	-1	-2

M_L	M_S	M_J
-2	1	-1
-2	0	-2
-2	-1	-3

The complete set of M_J values are:

$$M_J = \{3,2,2,1,1,1,0,0,0,-1,-1,-1,-2,-2,-3\}$$

Using $J = |M_J|_{max}$ to extract the first J value gives J = 3. The corresponding degenerate M_J states associated with J = 3 are M_J = {3,2,1,0,-1,-2,-3}, which leaves:

$$M_J = \{2,1,1,0,0,-1,-1,-2\}$$

Using $J = |M_J|_{max}$ to extract the next J value gives J = 2. The corresponding degenerate M_J states associated with J = 2 are M_J = {2,1,0,-1,-2}, which leaves:

$$M_J = \{1,0,-1\}$$

The final J is J = 1. The final terms are $^3D_3$, $^3D_2$, and $^3D_1$, just as we determined using the Clebsch-Gordon series. [The previous problem provides a graphical interpretation for determining all the possible M_J states, if you are interested.]

33. Using the complete enumeration of explicit configurations, show that the O atom configuration $2s^2 2p^4$ gives rise to ^1D, ^3P, and ^1S terms (just like C: $2s^2 2p^2$). Also verify that the Clebsch-Gordon series based on the holes gives the same terms. The holes are the empty orbitals in the partially filled subshell.

Answer: The configuration is O: $2p^4$. The explicit configurations are:

+1 0 -1	$M_L = \Sigma m_\ell$	+1 0 -1	$M_L = \Sigma m_\ell$	+1 0 -1	$M_L = \Sigma m_\ell$
[↑↓] [↑↓] [ ]	2				
[↑↓] [↑] [↓]	1	[↑↓] [↑] [↑]	1		
[↑] [↑↓] [↓]	0	[↑] [↑↓] [↑]	0	[↑↓] [ ] [↑↓]	0
[↑] [↓] [↑↓]	-1	[↑] [↑] [↑↓]	-1		
[ ] [↑↓] [↑↓]	-2				
^1D		^3P		^1S	

For the first set of singlet configurations, the maximum M_L is 2, giving a ^1D term. For the triplet configurations, the maximum M_L is 1, for a ^3P term. For the remaining singlet configuration, the maximum M_L is 0, giving a ^1S term:

L	0	1	2	3	4	5
Term	S	P	D	F	G	H

The Clebsch Gordon series can also be used to find the total orbital angular momentum with the holes in the p^4 configuration. The holes are both in the p-subshell giving $\ell_1 = 1$ and $\ell_2 = 1$:

Clebsch-Gordan Series: $L = \ell_1 + \ell_2, \ell_1 + \ell_2 - 1, \ldots, |\ell_1 - \ell_2|$ $L = |M_L|$ max

$2p^4$: $1 + 1, \ldots, |1 - 1| = 2, 1, 0$
$2p^4$: D, P, S

34. A p^2 configuration gives ^1S, ^1D, ^3P terms. Give the terms for a p^4 configuration.

Answer: The singlet terms have S = 0, so J = L. The J values for a ^3P term are given by the Clebsch-Gordon series with S = 1 and L = 1:

For ^1D, S = 0 and L = 2 so $^1D_2$.
For ^3P, S = 1 and L = 1 with $J = L + S, L + S - 1, \ldots, |L - S| = 1 + 1, \ldots, |1 - 1| = 2, 1, 0$
or $^3P_2, {}^3P_1, {}^3P_o$.
For ^1S, S = 0 and L = 0 so ^1S_o.

35. A p^2 configuration gives ^1S, ^1D, ^3P terms. Give the terms for a p^4 configuration. Give the lowest energy term for ground state p^2 and p^4 configurations.

Answer: The plan is to note that the p-subshell can hold 6 electrons, so a p^2 and a p^4 configuration are complementary, that is for the p^2 case n = 6, m = 2, and n – m = 4. The energy order of the terms is given by Hund's three rules, Sec. 25.5.

A p^2 and p^4 configuration give the same terms. In other words, the "holes" in the p^4 configuration have the same explicit configurations as the electrons in the p^2 configuration. The triplet terms are lowest in energy by Hund's first rule. The J values for a ^{3}P term are given by the Clebsch-Gordon series with S = 1 and L = 1: J = L + S, …. |L – S| = 2, 1, 0. For a p^2 configuration, the p-subshell is less than half-full, so the term with lowest J is lowest, giving the lowest energy term as ^3P_o. For the p^4 state, the p-subshell is over half-filled giving the lowest energy term as $^3P_2$. Carbon and oxygen are examples, Figure 25.6.3.

36. A d^3 configuration gives ^{2}P, ^{2}D, ^{2}D, ^{2}F, ^{2}G,^{2}H, ^{4}P, ^{4}F terms. Give the terms for a d^7 configuration. Give the lowest energy term for ground state d^3 and d^7 configurations.

Answer: The plan is to note that the d-subshell can hold 10 electrons, so a d^3 and a d^7 configuration are complementary, that is for the d^3 case n = 10, m = 3, and n – m = 7. The energy order of the terms is given by Hund's three rules, Sec. 25.5.

A d^3 and d^7 configuration give the same terms. In other words, the "holes" in the d^7 configuration have the same explicit configurations as the electrons in the d^3 configuration. The quartet terms are lowest in energy by Hund's first rule. The F terms are the lowest quartet terms by Hund's second rule. The J values for a ^{4}F term are given by the Clebsch-Gordon series with S = $^3/_2$ and L = 3: J = L + S, …. |L – S| = $^9/_2$, $^7/_2$, $^5/_2$, $^3/_2$. For a d^3 configuration, the d-subshell is less than half-full, so the term with lowest J is lowest, giving the lowest energy term as $^4F_{3/2}$. For the d^7 state, the d-subshell is over half-filled giving the lowest energy term as $^4F_{9/2}$. Vanadium and cobalt are examples, Figure 25.6.3.

37. Write a spreadsheet to plot the 3-21G Gaussian orbital for a $2p_x$ orbital on carbon, along the x-axis.

Answer: The plan is to note that restricting the plot to the x-axis gives x = r. The plot then is of the wave function amplitude versus x. In other words, along the x-axis θ = 90°, ϕ = 0°, and the conversion from spherical polar coordinates to Cartesian coordinates is x = r sinθ cosϕ = r

The wave function is given by the equations on the handout:

$$\Psi_{2px} = 0.55646\ \Psi_{2px}(\text{inner}) + 0.58708\ \Psi_{2px}(\text{outer})$$

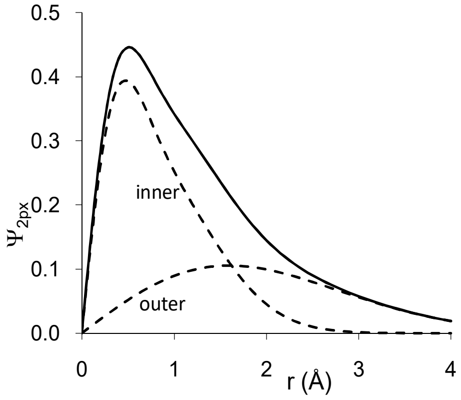
with:
$$\begin{aligned}\Psi_{2px}(\text{inner}) &= 0.2365\ g_x(3.665,r) + 0.8606\ g_x(0.771,r)\\ &= 0.2365\ g_x(3.665,r) + 0.8606\ g_x(0.771,r)\\ &= 0.2365\left(\frac{128(3.665)^5}{\pi^3}\right)^{1/4} x\ e^{-3.665r^2} + 0.8606\left(\frac{128(0.771)^5}{\pi^3}\right)^{1/4} x\ e^{-0.771r^2}\end{aligned}$$

and:
$$\begin{aligned}\Psi_{2px}(\text{outer}) &= 1.000\ g_x(0.196,r)\\ &= 1.000\left(\frac{2(0.196)}{\pi}\right)^{1/4} x\ e^{-0.196r^2}\end{aligned}$$

The first rows of the spreadsheet are given below. The basis set constants are reprinted at left. The normalization constants for each of the Gaussian primitives is listed at the top of each column for the three primitives. Primitives 1 and 2 are for the inner component of the split valence shell. Primitive 3 is for the outer component. The inner and outer portions are calculated separately so that the plot can show the importance of the two components of the split-valence shell.

A1	2	3	4	5	6	7	8	9		11	12	13	14	15
2					3-21G p_x orbital									
3						Primitives:						scaled:		
4	C		Normalization:			7.2282	1.0291	0.1857				0.5565	0.5871	
5	S	3	1		r	g_x1	g_x2	g_x3		$2p_x$ inner	$2p_x$ outer	$2p_x$ inner	$2p_x$ outer	$2p_x$ total
6					0	0.0000	0.0000	0.0000		0.0000	0.0000	0.0000	0.0000	0.0000
7	172.3	0.0618			0.1	0.6968	0.1021	0.0185		0.2526	0.0185	0.1406	0.0109	0.1515
8	25.91	0.3588			0.2	1.2485	0.1996	0.0369		0.4670	0.0369	0.2599	0.0216	0.2815
9	5.533	0.7007			0.3	1.5592	0.2880	0.0547		0.6166	0.0547	0.3431	0.0321	0.3752
10	SP	2	1		0.4	1.6085	0.3639	0.0720		0.6935	0.0720	0.3859	0.0423	0.4282
11	3.665	-0.396	0.2365		0.5	1.4457	0.4244	0.0884		0.7071	0.0884	0.3935	0.0519	0.4454
12	0.771	1.2158	0.8606		0.6	1.1592	0.4679	0.1038		0.6768	0.1038	0.3766	0.0610	0.4376
13	SP				0.7	0.8399	0.4938	0.1181		0.6236	0.1181	0.3470	0.0693	0.4163
14	0.196	1	1		0.8	0.5539	0.5028	0.1311		0.5637	0.1311	0.3137	0.0770	0.3906
15					0.9	0.3342	0.4962	0.1426		0.5060	0.1426	0.2816	0.0837	0.3653
16					1	0.1851	0.4762	0.1527		0.4536	0.1527	0.2524	0.0896	0.3420

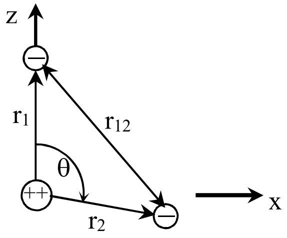
The plot is shown below.



38. In the integral for the expectation value of the electron-electron repulsion in the helium atom, we used the Law of Cosines, $r_{12} = (r_1^2 + r_2^2 - 2\, r_1 r_2 \cos\theta)^{1/2}$. Prove this relationship using the following steps.

(a). The distance between the two electrons is the magnitude of the vector difference: $r_{12} = |\vec{r}_1 - \vec{r}_2|$, where $\vec{r}_1$ is the vector pointing to electron 1 and $\vec{r}_2$ is the vector pointing to electron 2. The length of $\vec{r}_1$ is r_1 and of $\vec{r}_2$ is r_2. The angle between the two vectors is θ. The distance between the two electrons does not dependent on how the coordinate system is oriented, only the difference is important. We orient the coordinate system with $\vec{r}_1$ pointing along the z-axis and $\vec{r}_2$ parallel to the x-axis. The x, y, and z coordinates are then conveniently expressed in terms of r, θ, and ϕ. Show that the coordinates of the two electrons are given as:

$$\vec{r}_1 = (0, 0, r_1)$$
$$\vec{r}_2 = (r_2 \sin\theta, 0, r_2 \cos\theta)$$



(b). From the position vectors in part (a), find $r_{12} = |\vec{r}_1 - \vec{r}_2|$. Remember that $\sin^2\theta + \cos^2\theta = 1$.

Answer: (a). The transformation between Cartesian and spherical polar coordinates is given by Eqs. 24.5.14. With electron 1 lying on the z-axis, θ = 0, giving x = 0, y = 0, and $z = r_1 \cos\theta = r_1$. For electron 2, the electron lies in the x-z plane giving ϕ = 0. Then $x = r_2 \sin\theta \cos\phi = r_2 \sin\theta$. The value of z is $z = r_2 \cos\theta$.

(b). The vector difference is:

$$\vec{r}_1 - \vec{r}_2 = (0 - r_2 \sin\theta)\,\vec{i} + (0 - 0)\,\vec{j} + (r_1 - r_2 \cos\theta)\,\vec{k}$$

were $\vec{i}$, $\vec{j}$, and $\vec{k}$ are the orthogonal unit vectors define the orientations of the x, y, and z-axes, respectively. The magnitude is the square root of the sum of squares:

$$r_{12}^2 = (-\,r_2 \sin\theta)^2 + (r_1 - r_2 \cos\theta)^2 = r_2^2 \sin^2\theta + r_1^2 - 2\, r_1 r_2 \cos\theta + r_2^2 \cos^2\theta$$

Substituting $\sin^2\theta + \cos^2\theta = 1$ into this last equation gives: $r_{12}^2 = r_1^2 + r_2^2 - 2\, r_1 r_2 \cos\theta$

Taking the square root of both sides gives the Law of Cosines:

$$r_{12} = (r_1^2 + r_2^2 - 2\, r_1 r_2 \cos\theta)^{1/2}$$

The next problem continues the determination of the expectation value of the electron-electron repulsion energy.

39. Using the substitution q = cos θ, show that (Eq. 25.7.5):

$$\int_0^{\pi} \frac{1}{(r_1^2 + r_2^2 - 2\, r_1 r_2 \cos\theta)^{½}} \sin\theta \, d\theta = \frac{2}{r_1} \text{ for } r_1 > r_2 \qquad \text{or } = \frac{2}{r_2} \text{ for } r_1 < r_2$$

Answer: The substitution q = cos θ gives dq/dθ = – sin θ so that dq = – sin θ dθ. The integral limits of 0 to π change to cos 0 to cos π, or 1 to – 1. Substitution into the integral gives:

$$\int_0^{\pi} \frac{1}{(r_1^2 + r_2^2 - 2\, r_1 r_2 \cos\theta)^{½}} \sin\theta \, d\theta = -\int_1^{-1} \frac{1}{(r_1^2 + r_2^2 - 2\, r_1 r_2\, q)^{½}} dq = \int_{-1}^{1} \frac{1}{(r_1^2 + r_2^2 - 2\, r_1 r_2\, q)^{½}} dq$$

Switching the integral limits reverses the sign of the integral. The integral is in the form:

$$\int \frac{1}{(a + bx)^{½}} dx = 2\, \frac{(a + bx)^{½}}{b}$$

which can be verified by taking the derivative of the right side. Substitution of the general form into the first equation gives:

$$\int = 2\, \frac{1}{-2\, r_1 r_2} [(r_1^2 + r_2^2 - 2\, r_1 r_2\, q)^{½}|_{-1}^{1} = -\frac{1}{r_1 r_2} [(r_1^2 + r_2^2 - 2\, r_1 r_2)^{½} - (r_1^2 + r_2^2 + 2\, r_1 r_2)^{½}]$$

Note that $(r_1^2 + r_2^2 - 2\, r_1 r_2) = (r_1 - r_2)^2$ and $(r_1^2 + r_2^2 + 2\, r_1 r_2) = (r_1 + r_2)^2$. The square roots each have two roots, one positive and one negative:

$$\int = -\frac{1}{r_1 r_2} \{[\pm(r_1 - r_2)] - [\pm(r_1 + r_2)]\}$$

There are four possibilities for the signs:

[+,+] $\int = -\frac{1}{r_1 r_2} [r_1 - r_2 - r_1 - r_2)] = 2/r_1$

[+,–] $\int = -\frac{1}{r_1 r_2} [r_1 - r_2 + r_1 + r_2)] = -2/r_2$

[–,+] $\int = -\frac{1}{r_1 r_2} [-r_1 + r_2 - r_1 - r_2)] = 2/r_2$

[–,–] $\int = -\frac{1}{r_1 r_2} [-r_1 + r_2 + r_1 + r_2)] = -2/r_1$

The electron-electron repulsion is overall positive, so only the [+,+] roots and the [–,+] roots are valid. However, the integral can only have one result for a given set of circumstances. Both individual contributions at the integral limits of $\int_{-1}^{1}$ should give positive results for the electron-electron repulsion energy. The $(r_1 - r_2)$ term results from the evaluation at the upper limit. If $r_1 > r_2$ then $(r_1 - r_2)$ is positive and the [+,+] roots gives an overall positive contribution for the upper limit for the integral and a final integral value that is also positive. If $r_1 < r_2$ then $(r_1 - r_2)$ is negative and then the [–,+] roots give an overall positive contribution for the upper limit. The two valid results are then:

$$\int_0^{\pi} \frac{1}{(r_1^2 + r_2^2 - 2\, r_1 r_2 \cos\theta)^{½}} \sin\theta \, d\theta = \frac{2}{r_1} \qquad \text{for } r_1 > r_2$$

$$= \frac{2}{r_2} \qquad \text{for } r_1 < r_2$$

The next problem continues the determination of the expectation value of the electron-electron repulsion energy.

40. Evaluate the following integrals, verifying Eqs. 25.7.8 and 25.7.9:

$$\int_{r_1}^{\infty} e^{-2Zr_2/a_o}\, r_2\, dr_2 \qquad \text{and} \qquad \int_0^{r_1} e^{-2Zr_2/a_o}\, r_2^2\, dr_2$$

Answer: The r_2 integrals are derived from the tabulated indefinite integrals:

$$\int e^{-ax}\, x\, dx = -\frac{e^{-ax}}{a^2}(ax + 1) \qquad \text{and} \qquad \int e^{-ax}\, x^2\, dx = -\frac{e^{-ax}}{a^3}(a^2x^2 + 2ax + 2)$$

Note that $\lim_{x\to\infty} e^{-ax}(ax) = 0$ using L'Hospital's Rule. The definite integrals are then:

$$\int_{x_o}^{\infty} e^{-ax}\, x\, dx = \frac{e^{-ax_o}}{a^2}(ax_o + 1) = \frac{x_o}{a}\, e^{-ax_o} + \frac{1}{a^2}\, e^{-ax_o}$$

$$\int_0^{x_o} e^{-ax}\, x^2\, dx = -\frac{e^{-ax_o}}{a^3}(a^2x_o^2 + 2ax_o + 2) + \frac{2}{a^3} = -\frac{x_o^2}{a}\, e^{-ax_o} - \frac{2x_o}{a^2}\, e^{-ax_o} - \frac{2}{a^3}\, e^{-ax_o} + \frac{2}{a^3}$$

Setting $a = 2Z/a_o$, $x = r_2$, and $x_o = r_1$ gives the definite integrals as:

$$\int_{r_1}^{\infty} e^{-2Zr_2/a_o}\, r_2\, dr_2 = \frac{1}{2}\left(\frac{a_o}{Z}\right) r_1\, e^{-2Zr_1/a_o} + \frac{1}{2^2}\left(\frac{a_o}{Z}\right)^2 e^{-2Zr_1/a_o} \qquad (25.7.8)$$

$$\int_0^{r_1} e^{-2Zr_2/a_o}\, r_2^2\, dr_2 = -\frac{1}{2}\left(\frac{a_o}{Z}\right) r_1^2\, e^{-2Zr_1/a_o} - \frac{1}{2}\left(\frac{a_o}{Z}\right)^2 r_1\, e^{-2Zr_1/a_o} - \frac{1}{2^2}\left(\frac{a_o}{Z}\right)^3 e^{-2Zr_1/a_o} + \frac{1}{2^2}\left(\frac{a_o}{Z}\right)^3 \qquad (25.7.9)$$

The next problem continues the determination of the expectation value of the electron-electron repulsion energy.

41. (a). Verify Eq. 25.7.11 starting from Eq. 25.7.10. (b). Verify Eq. 25.7.12 starting from Eqs. 25.7.7 and 25.7.8.

Answer: Integral tabulations list $\int_0^\infty x\, e^{-ax}\, dx = 1/a^2$, $\int_0^\infty x^2\, e^{-ax}\, dx = 2/a^3$, and $\int_0^\infty x^3\, e^{-ax}\, dx = 6/a^4$.
(a). Substituting $a = 4Z/a_o$ for the first three integrals or $a = 2Z/a_o$ into the fourth integral in Eq. 25.7.10 results in:

$$\int_0^{\infty} e^{-2Zr_1/a_o}\, r_1 \left(\int_0^{r_1} e^{-2Zr_2/a_o}\, r_2^2\, dr_2\right) dr_1 =$$

$$= -\frac{1}{2}\left(\frac{a_o}{Z}\right) 6 \left(\frac{a_o}{4Z}\right)^4 - \frac{1}{2}\left(\frac{a_o}{Z}\right)^2 2 \left(\frac{a_o}{4Z}\right)^3 - \frac{1}{2^2}\left(\frac{a_o}{4Z}\right)^2 + \frac{1}{2^2}\left(\frac{a_o}{Z}\right)^3\left(\frac{a_o}{2Z}\right)^2$$

$$= -\frac{6}{2^9}\left(\frac{a_o}{Z}\right)^5 - \frac{1}{2^6}\left(\frac{a_o}{Z}\right)^5 - \frac{1}{2^6}\left(\frac{a_o}{Z}\right)^5 + \frac{1}{2^4}\left(\frac{a_o}{Z}\right)^5$$

(b). Substitution of Eq. 25.7.8 into the second integral in Eq. 25.7.7 gives:

$$\int_0^\infty e^{-2Zr_1/a_o}\, r_1^2 \left(\int_{r_1}^\infty e^{-2Zr_2/a_o}\, r_2\, dr_2\right) dr_1 =$$

$$= \frac{1}{2}\left(\frac{a_o}{Z}\right)\int_0^\infty r_1^3\, e^{-4Zr_1/a_o}\, dr_1 + \frac{1}{2^2}\left(\frac{a_o}{Z}\right)^2\int_0^\infty r_1^2\, e^{-4Zr_1/a_o}\, dr_1$$

Using the tabulated integrals and substituting a = 4Z/a_o into the last equation gives:

$$= \frac{1}{2}\left(\frac{a_o}{Z}\right) 6 \left(\frac{a_o}{4Z}\right)^4 + \frac{1}{2^2}\left(\frac{a_o}{Z}\right)^2 2 \left(\frac{a_o}{4Z}\right)^3$$

$$= \frac{6}{2^9}\left(\frac{a_o}{Z}\right)^5 + \frac{1}{2^7}\left(\frac{a_o}{Z}\right)^5$$

The next problem continues the determination of the expectation value of the electron-electron repulsion energy.

<u>42</u>. Using Eqs. 25.7.7, 25.7.11, and 25.7.12, verify Eq. 25.7.14.

Answer: Adding Eqs. 25.7.11 and 25.7.12 gives:

$$\int_0^\infty e^{-2Zr_1/a_o}\, r_1 \left(\int_0^{r_1} e^{-2Zr_2/a_o}\, r_2^2\, dr_2\right) dr_1 + \int_0^\infty e^{-2Zr_1/a_o}\, r_1^2 \left(\int_{r_1}^\infty e^{-2Zr_2/a_o}\, r_2\, dr_2\right) dr_1 =$$

$$= -\frac{6}{2^9}\left(\frac{a_o}{Z}\right)^5 - \frac{1}{2^6}\left(\frac{a_o}{Z}\right)^5 - \frac{1}{2^6}\left(\frac{a_o}{Z}\right)^5 + \frac{1}{2^4}\left(\frac{a_o}{Z}\right)^5 + \frac{6}{2^9}\left(\frac{a_o}{Z}\right)^5 + \frac{1}{2^7}\left(\frac{a_o}{Z}\right)^5$$

$$= \left[-\frac{1}{2^6} - \frac{1}{2^6} + \frac{1}{2^4} + \frac{1}{2^7}\right]\left(\frac{a_o}{Z}\right)^5 = \left[-\frac{2}{2^7} - \frac{2}{2^7} + \frac{8}{2^7} + \frac{1}{2^7}\right]\left(\frac{a_o}{Z}\right)^5 = \frac{5}{2^7}\left(\frac{a_o}{Z}\right)^5$$

Substituting this last result into Eq. 25.7.7 gives Eq. 25.7.13:

$$E_{gs}^{(1)} = 16\left(\frac{Z}{a_o}\right)^6 \frac{e^2}{4\pi\varepsilon_o} \frac{5}{2^7}\left(\frac{a_o}{Z}\right)^5 = 2^4\left(\frac{Z}{a_o}\right)^6 \frac{e^2}{4\pi\varepsilon_o} \frac{5}{2^7}\left(\frac{a_o}{Z}\right)^5 = = \frac{5Z}{8}\left(\frac{e^2}{4\pi\varepsilon_o\, a_o}\right)$$

The term in parentheses in the last equation is equal to one Hartree, 1H = 27.2116 eV. The full nuclear charge for helium is Z = 2, giving $E_{gs}^{(1)}$ = 34.01 eV.

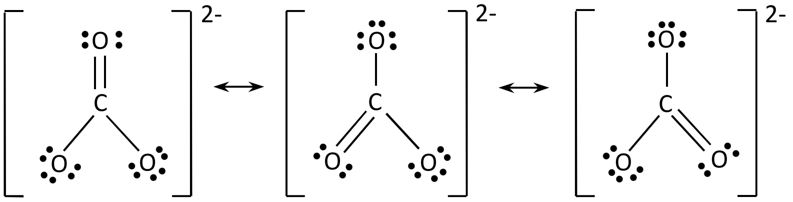
Literature Cited:

1. M. W. Hanna, *Quantum Mechanics in Chemistry, 3rd. ed.*, Benjamin-Cummings, Menlo Park, CA, 1981. Exercise 6-45, p. 176.

Chapter 26 Problems: Molecular Structure

1. Draw the Lewis dot resonance structures for the carbonate ion, CO_3^{2-}. Are the electrons delocalized? Give the average bond order for the bonds. The procedure for the determination of Lewis dot structures is:
(1). Place the nuclei to establish the expected connectivity. In polyatomics, the first listed non-hydrogen atom is assumed to be the central atom, unless otherwise stated. Alternatively, the atom with the smallest electronegativity is often the central atom. (2). Determine the total number of valence electrons. (3). Draw single bonds between the bonded pairs of atoms. (4). Fill in the remaining electrons as lone pairs without exceeding an octet on each heavy atom, or a duet on H or He. (5). If any atoms do not have a completed octet, move lone pairs to complete the octets by forming multiple bonds. (6). If several non-equivalent structures are possible, the predicted lowest energy structure is the structure that minimizes the total formal charges. (7). The bonding pattern that places the largest negative formal charges on the most electronegative atoms is the most important. (8). Use expanded octets on 3rd and 4th period elements only if necessary to accommodate the required total number of electrons. (9). Show the overall ionic charge in the final structures.

Answer: The C-atom is the central atom. The carbonate ion has 4 + 3(6) + 2 = 24 valence electrons. The final two in the sum is added to account for the ionic charge. Following the procedure step 4, one of the atoms does not have a completed octet, which requires one double bond to resolve. Three equivalent structures result, differing only in the C-O pairs that are double bonded. The three resonance structures predict that the carbonate ion has a four-center delocalized π-bond.

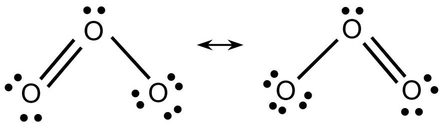


Focusing on the same particular C-O pair in each resonance structure, the total bonds between that particular pair in all the resonance structures is 2+1+1 = 4. On average, over the three resonance structures, the qualitative bond order is $^4/_3 = 1\ ^1/_3$.

2. Draw the Lewis dot resonance structures for (a) ozone, (b) sulfur dioxide, and (c) nitrite ion, NO_2^-. Are the electrons delocalized? Give the average bond order for the bonds. The procedure for the determination of Lewis dot structures is summarized in the previous problem.

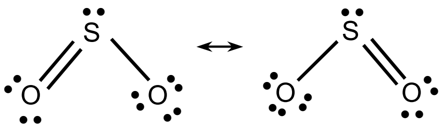
Answers: The plan is to note that ozone, sulfur dioxide, and nitrite ion are isoelectronic; each has 18 valence electrons. The Lewis dot resonance structures are the same for each.
(a). Ozone has 3(6) = 18 valence electrons. With single bonds only one atom does not have an octet, which requires one double bond to resolve. Two equivalent resonance structures result,

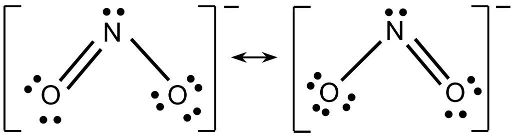
differing only in the O-O pairs that are double bonded. The two resonance structures predict that ozone has a three-center delocalized π-bond.



Focusing on the same particular O-O pair in each resonance structure, the total bonds between that particular pair in all the resonance structures is 2+1 = 3. On average, over the two resonance structures, the qualitative bond order is $^3/_2 = 1\frac{1}{2}$.

(b) and (c). Sulfur dioxide and nitrite ion also have 18 valence electrons, giving delocalized three-center π-bonds with an average qualitative bond order of 1½:





3. For the H_2^+ ion, show that for the bonding orbital $c_A = c_B$ using E_+ and for the anti-bonding orbitals $c_A = -c_B$ using E_- in the secular equations, Eq. 21.1.12.

Answer: The first of the two secular equations, Eqs. 21.1.12 (either one would do), is:

$$c_A(H_{AA} - E) + c_B(H_{AB} - ES) = 0$$

For a homonuclear molecule, $H_{AA} = H_{BB}$ and normalized atomic orbitals give $S_{AA} = S_{BB} = 1$.

(a). Substituting $E_+ = \frac{H_{AA}+H_{AB}}{1+S}$ into the secular equation gives:

$$c_A\left(H_{AA} - \frac{H_{AA}+H_{AB}}{1+S}\right) + c_B\left(H_{AB} - \frac{H_{AA}+H_{AB}}{1+S} S\right) = 0$$

Multiplying the last equation by 1+S gives:

$$c_AH_{AA}(1+S) - c_A H_{AA} - c_AH_{AB} + c_BH_{AB}(1+S) - c_B H_{AA}S - c_B H_{AB}S = 0$$

After cancelling common terms the result is:

$$c_AH_{AA}S - c_AH_{AB} + c_BH_{AB} - c_B H_{AA}S = 0$$

Collecting terms in c_A and c_B:

$$c_A (H_{AA}S - H_{AB}) + c_B (H_{AB} - H_{AA}S) = 0$$

which rearranges to give:

$$c_A (H_{AA}S - H_{AB}) = c_B (H_{AA}S - H_{AB})$$

The common term cancels to give: $c_A = c_B$

(b). Substituting $E_- = \frac{H_{AA} - H_{AB}}{1-S}$ into the secular equation gives:

$$c_A\,(H_{AA}-\frac{H_{AA}-H_{AB}}{1-S})+c_B\,(H_{AB}-\frac{H_{AA}-H_{AB}}{1-S}S)=0$$

Multiplying the last equation by 1+S gives:

$$c_AH_{AA}(1-S)-c_A\,H_{AA}+c_AH_{AB}+c_BH_{AB}(1-S)-c_B\,H_{AA}S+c_B\,H_{AB}S=0$$

After cancelling common terms the result is:

$$-\,c_AH_{AA}S+c_AH_{AB}+c_BH_{AB}-c_B\,H_{AA}S=0$$

Collecting terms in c_A and c_B:

$$c_A\,(-\,H_{AA}S+H_{AB})+c_B\,(H_{AB}-H_{AA}S)=0$$

which rearranges to give:

$$c_A\,(-\,H_{AA}S+H_{AB})=c_B\,(H_{AA}S-H_{AB})$$

The common term cancels to give $c_A = -\,c_B$.

4. Show that the atomic integral for the H_2^+ molecule, $H_{AA} \equiv \int \Psi_A^* \hat{\mathcal{H}} \Psi_A \, d\tau$, reduces to:

$$H_{AA} \cong E_A + \frac{e^2}{4\pi\varepsilon_o R}$$

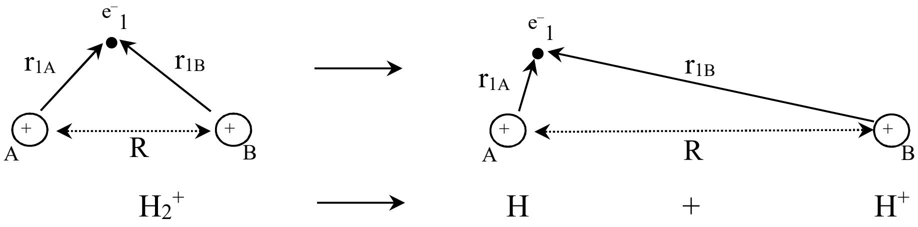
at large internuclear separation, Eq. 26.1.6. Then argue that at large R the atomic integral is approximately equal to the atomic energy of the H-atom. The bond dissociation at large R gives $H_2 \rightarrow H + H^+$.

Answer: The plan is to write the exact Hamiltonian for the H_2^+ ion and then determine the limit of the Hamiltonian for bond dissociation at large R.

The Schrödinger equation for H_2^+ is given by Eq. 26.1.1:

$$-\frac{\hbar^2}{2m}\nabla_1^2\Psi+\frac{e^2}{4\pi\varepsilon_o}\left(-\frac{1}{r_{1A}}-\frac{1}{r_{1B}}+\frac{1}{R}\right)\Psi=E\,\Psi$$

Assume that the molecule dissociates at large R to give a H-atom on nucleus A and a H^+ ion on nucleus B:



In the limit of large R, the Coulomb attraction of the electron for nucleus B is negligible, $e^2/(4\pi\varepsilon_o r_{1B}) \rightarrow 0$. The remaining terms in the Hamiltonian are then the one-electron Hamiltonian for the H-atom on nucleus A, $\mathcal{H}_A$, and the nuclear-nuclear repulsion. The Hamiltonian acting on the one-electron H-atom orbital on nucleus A then simplifies to:

$$\mathcal{H}\Psi_A \cong \left(-\frac{\hbar^2}{2m}\nabla_1^2\Psi - \frac{e^2}{4\pi\varepsilon_o\, r_{1A}}\right)\Psi_A + \frac{e^2}{4\pi\varepsilon_o R}\Psi_A = \mathcal{H}_A\,\Psi_A + \frac{e^2}{4\pi\varepsilon_o R}\Psi_A \cong E\,\Psi_A$$

The first term gives the one-electron atomic energy of the H-atom, $\mathcal{H}_A\,\Psi_A = E_A\,\Psi_A$:

$$E_A\,\Psi_A + \frac{e^2}{4\pi\varepsilon_o R}\Psi_A \cong E\,\Psi_A \quad \text{dividing by } \Psi \text{ gives: } \quad \mathcal{H}\Psi_A \cong E_A + \frac{e^2}{4\pi\varepsilon_o R} \cong E$$

Then $H_{AA} = \int \Psi_A^*\,\mathcal{H}\Psi_A\,d\tau \cong \int \Psi_A^*\,E\,\Psi_A\,d\tau \cong E_A + \frac{e^2}{4\pi\varepsilon_o R}$

As $R \to \infty$, the nuclear-nuclear repulsion term becomes negligible and $H_{AA} \cong E_A$.

5. Determine the Pauling electronegativity of Br. The experimental bond dissociation energies are D_o(H–H) = 432.0 kJ mol^{-1}, D_o(Br–Br) = 190. kJ mol^{-1}, and D_o(H–Br) = 363. kJ mol^{-1}. The electronegativity of H is 2.2.

Answer: The plan is to use the deviation from equal sharing, Eq. 26.3.13, with the bond energies converted to electron volts.

Given 1 eV = 96.4853 kJ mol^{-1}, the experimental bond dissociation energies are D_o(H–H) = 4.477 eV, D_o(Br–Br) = 1.97 eV, and D_o(H–Br) = 3.76 eV. The "*Energy Units Converter*" on the text Web page or companion CD is also useful for easy energy conversions. Using Eq. 26.3.13:

$$(\chi_{Br} - \chi_H)^2 = \left(3.76 - [(4.477)(1.97)]^{1/2}\right)\text{ eV} = 0.790\text{ eV}$$

Solving for the electronegativity of Br, taking the positive root: $\chi_{Br} = 2.2 + \sqrt{0.791} = 3.09$
The accepted value is 2.96, which is an average over several compounds.

6. Determine the Pauling electronegativity of Ge. The experimental bond dissociation energies are D_o(Ge-Ge) = 272. kJ mol^{-1}, D_o(F-F) = 154.8 kJ mol^{-1}, and D_o(Ge-F) = 484. kJ mol^{-1}.[1,2] The electronegativity of F is 3.98, in current revised scales.

Answer: The plan is to use the deviation from equal sharing, Eq. 26.3.13, with the bond energies converted to electron volts.

Given 1 eV = 96.4853 kJ mol^{-1}, the experimental bond dissociation energies are D_o(Ge–Ge) = 0.2.82 eV, D_o(F–F) = 1.604 eV, and D_o(Ge–F) = 5.02 eV. The "*Energy Units Converter*" on the course Web page or companion CD is useful for easy energy conversions. Using Eq. 26.3.13 gives:

$$(\chi_{Ge} - \chi_F)^2 = \left(5.02 - [(2.82)(1.604)]^{1/2}\right)\text{ eV} = 2.89\text{ eV}$$

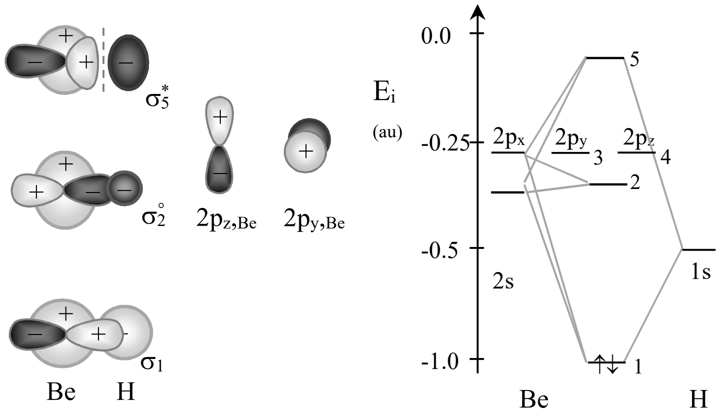
Solving for the electronegativity of Ge, taking the negative root: $\chi_{Ge} = 3.98 - \sqrt{2.89} = 2.28$
The negative root is used because the electronegativity of Ge is expected to be less than the electronegativity of F, based on the corresponding positions in the periodic table and the

direction of the dipole moment of GeF. The accepted value is 2.01, which is an average over several compounds. The experimental uncertainties for the D_o values for Ge_2 and GeF are ~8%.

7. Sketch the qualitative molecular orbital diagram for BeH^+. Calculate the qualitative bond order. Is the bond completely covalent, partially ionic, or strongly ionic?

Answer: The plan is to note the similarity of the molecular orbital diagram for BeH^+ with LiH. The ionic character of the bond is given by the difference in the electronegativities of Be and H.

The difference in electronegativity of Be and H is less than that for LiH, $\Delta\chi = \chi(\text{H}) - \chi(\text{Be}) = 0.63$. This decrease suggests that the bond between Be and H is less ionic than in LiH, which is ~27% ionic, Eq. 26.3.7. So the BeH bond is partially ionic. The decrease in $\Delta\chi$ also suggests that the Be(2s) and H(1s) are closer in energy than the Li(2s) and H(1s), giving greater covalent character. The valence atomic orbital ionization energies, Table 26.8.1, place the separated atom atomic orbital energies at Be(2s) -9.30 eV, Be(2p) -3.50 eV, and H(1s) -13.6 ev. The orbitals are otherwise similar in character to LiH in relative order and symmetry, Figure 26.3.4. The x-axis is chosen as the internuclear axis. Combining four atomic orbitals on Be with one atomic orbital on H gives five final molecular orbitals. The valence atomic orbitals are Be(2s), Be($2p_x$), Be($2p_y$), Be($2p_z$) and H(1s). The Be($2p_y$) and Be($2p_z$) orbitals are non-interacting atomic non-bonding orbitals, because the overlap with H(1s) is zero. The lowest energy molecular orbital has more Be(2s) character than Be($2p_x$) because of better energy matching with H(1s). The Be(2s), Be($2p_x$), and H(1s) create a bonding, non-bonding, anti-bonding triple. These three orbitals added to the Be($2p_y$) and Be($2p_z$) atomic non-bonding orbitals gives five total molecular orbitals:



BeH^+ has 2 valence electrons, filling only the lowest energy σ_1 orbital. The qualitative bond order is 1. While this problem was meant to be qualitative, you might try the CNDO level calculation at the experimental bond length of 1.342 Å, to verify your diagram.

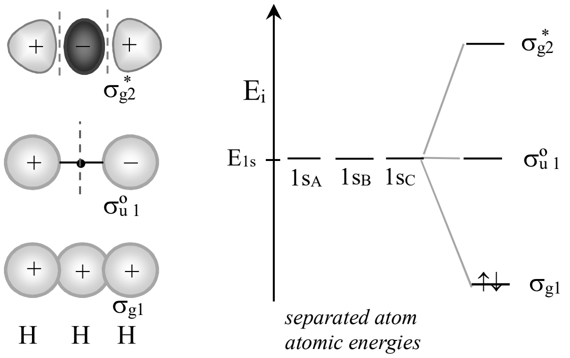
8. Sketch the qualitative molecular orbital diagram for linear H_3^+. The H_3^+ ion is symmetrical about the center H-atom. Show that the odd number of atomic orbitals results in a bonding, non-bonding, anti-bonding trio of molecular orbitals. Calculate the qualitative bond order. Is the ion stable?

Answer: The plan is to note that since we are combining three atomic orbitals, three molecular orbitals result that must be symmetrical about the center H-atom.

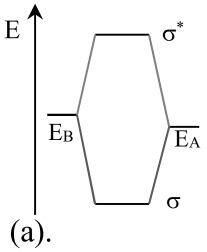
The atomic orbitals are three H(1s) orbitals. The ion has two electrons. The symmetric combination of the three 1s-orbitals gives the most bonding orbital as: ○○○. The anti-bonding complement is generated by reversing the phase of the central orbital: ○●○. The trick to generate other possible molecular orbitals is to reverse the phase of an outer orbital: ○ · ●. However, this new orbital must be a non-bonding orbital, since neither ○●● nor ○○● are symmetrical about the center H-atom. For example, ○●● is anti-bonding on the left and bonding on the right. The molecular orbital diagram is shown below, with the two electrons in the bonding σ_{g1} orbital. The qualitative bond order is:

qualitative BO = (bonding electrons – anti-bonding electrons)/2 = 1

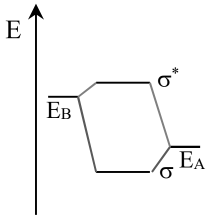
Since we combined an odd number of atomic orbitals, an odd number of molecular orbitals necessarily result. Given the symmetry of the molecule, with one bonding and one-anti-bonding molecular orbital the intermediate molecular orbital must be intermediate in character. In this case the middle orbital is rigorously non-bonding. The ion is predicted to be stable, but not necessarily the lowest energy geometry.



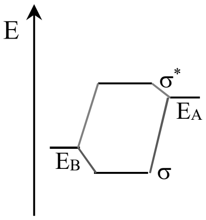
9. Consider the bond between atoms A and B with bonding wave function: $\Psi_1 = 0.800\ \Psi_A + 0.360\ \Psi_B$. (a). Calculate the % ionic character. (b). Choose the corresponding molecular energy diagram from below. (c). Find the corresponding anti-bonding orbital. Assume the atomic orbitals are normalized and the overlap integral is S = 0.400.



(a).



(b).



(c).

Answer: The plan to find the anti-bonding complement to the given bonding orbital is to use orthogonality and normalization.

(a). The % ionic character is given by Eq. 26.3.4:

$$\text{fraction ionic} = \frac{(0.800)^2 - (0.360)^2}{(0.800)^2 + (0.360)^2} = 0.663 \quad \text{or } 66.3\% \text{ ionic}$$

(b). Molecular orbital diagram (b) shows the atomic orbital for A as more electronegative than B, giving the bonding orbital with a larger coefficient for the A-atomic orbital than for the B-atomic orbital. Diagram (a) shows little ionic character, since the atomic orbitals are so similar in energy, so is not applicable.

(c). Assume the anti-bonding complement has coefficients $\Psi_2 = a\,\Psi_A + b\,\Psi_B$. Orthogonality gives the ratio of the orbital coefficients. Assuming the atomic orbitals are real, and normalized gives $\int \Psi_A{}^2\, d\tau = \int \Psi_B{}^2\, d\tau = 1$:

$$\begin{aligned}\int \Psi_1\Psi_2\, d\tau &= \int (0.800\,\Psi_A + 0.360\,\Psi_B)\,(a\Psi_A + b\Psi_B)\, d\tau = 0\\ &= 0.800\,a \int \Psi_A{}^2\, d\tau + 0.360\,b \int \Psi_B{}^2\, d\tau + 0.800\,b \int \Psi_A\Psi_B\, d\tau + 0.360\,a \int \Psi_B\Psi_A\, d\tau\\ &= 0.800\,a + 0.360\,b + 0.800\,b\,S\, d\tau + 0.360\,a\,S\, d\tau = 0\end{aligned}$$

The order of the orbitals doesn't matter, since they are just functions, giving $\int \Psi_A\Psi_B\, d\tau = \int \Psi_B\Psi_A\, d\tau = S$ from the definition of the overlap integral. Orthogonality then gives:

$a(0.80 + 0.360\,S) + b(0.360 + 0.80\,S) = 0$

$a/b = -(0.360 + 0.80\,S)/(0.80 + 0.360\,S)$ with $S = 0.400$ given:

$a/b = -0.7203$

giving: $a^2 = 0.5189\,b^2$ and $ab = -0.7203\,b^2$

The normalization gives the final coefficients:

$$\begin{aligned}\int \Psi_2{}^2\, d\tau &= \int (a\Psi_A + b\Psi_B)^2\, d\tau = 1\\ &= a^2 \int \Psi_A{}^2\, d\tau + b^2 \int \Psi_B{}^2\, d\tau + 2ab \int \Psi_A\Psi_B\, d\tau = 1\\ &= a^2 + b^2 + 2abS = 1\end{aligned}$$

Substituting in for a^2 and ab using the ratio from orthogonality gives:

$0.5189\,b^2 + b^2 + 2(-0.7203)b^2(0.400) = 1$

$b^2 = 1.0609$ or $b = 1.0300$ and $a = -0.7420$

The final anti-bonding orbital is then $\Psi_2 = -0.742\,\Psi_A + 1.030\,\Psi_B$

10. Calculate the bond order and atom charges for BH at the CNDO level at the experimental bond length, 1.236 Å. Calculate the charges and bond order using the molecular orbital coefficients and the overlap integrals (in effect, verifying the listed bond order in the CNDO printout). [Use the online CNDO applet on the textbook Web site.]

Answer: The charge is zero with singlet spin multiplicity. The simplified listing is given below.

```
   ___Atomic Coordinates (Å)__
   Atom      x        y        z
   1  B    0.0      0.0      0.0
   2  H    1.236    0.0      0.0
```

```
   Coulombic repulsion integrals (bottom triangle)(a.u.)
____and internuclear distances (top triangle)(a.u.)_________
Atoms:  1 B    2 H
1 B   0.4723   2.3357
2 H   0.3808   0.75

____________Overlap Matrix_______________________________________
            1 B2s    1 B2px   1 B2py   1 B2pz   2 H1s
1  B2s     1.0      0.0      0.0      0.0      0.4984
1  B2px    0.0      1.0      0.0      0.0      0.5241
1  B2py    0.0      0.0      1.0      0.0      0.0
1  B2pz    0.0      0.0      0.0      1.0      0.0
2  H1s     0.4984   0.5241   0.0      0.0      1.0

          SCF eigenvalues (a.u.) and eigenvectors
______________(eigenvectors listed in columns)____________
E(i)     -0.8084   -0.4892    0.0817    0.0817    0.3019
vector      1         2         3         4         5
1  B2s     0.6739   -0.6534    0.0       0.0      -0.3449
1  B2px    0.3319    0.6848    0.0       0.0      -0.6487
1  B2py    0.0       0.0       0.0       1.0       0.0
1  B2pz    0.0       0.0       1.0       0.0       0.0
2  H1s     0.6601    0.3227    0.0       0.0       0.6784

_____Total Bond Order (Mulliken overlap population)_____
Atoms:  1 B
2  H   1.389

Electronic energy =  -5.2668 a.u.
Total energy =    -3.9824 a.u. includes nuclear-nuclear repulsion
Total bond dissociation energy, Do = 12.9941 eV = 1253.735 kJ/mol

Total atom electron densities and atomic charges
atom  density   charge
1 B   2.9204    0.08
2 H   1.0796   -0.08
```

The atomic orbitals on B in MO 1 and 2 are the 2s and $2p_x$. Using Eq. 26.3.9, the orbital coefficients, and noting that there are two occupied molecular orbitals give the atom density on the B-atom as:

$$d_B = \sum_{j \text{ on B}} (n_1 c_{1j}^2 + n_2 c_{2j}^2) = 2(0.6739)^2 + 2(-0.6534)^2 + 2(0.3319)^2 + 2(0.6848)^2 = 2.9204$$

$$\uparrow\ \uparrow \qquad \uparrow\ \uparrow \qquad \uparrow\ \uparrow \qquad \uparrow\ \uparrow$$

$$n_1\,(c_{1,B(2s)})^2 + n_2\,(c_{2,B(2s)})^2 + n_1\,(c_{1,B(2px)})^2 + n_2\,(c_{2,B(2px)})^2$$

The atomic charge, with three valence electrons for the B-atom: charge = 3 – 2.9204 = 0.0796. Alternately, the atom electron density on B is the sum of the diagonal population matrix elements for B. The charge on H is easier to calculate, and gives the same result.

The Mulliken overlap population is given by Eq. 26.3.10 for m molecular orbitals:

$$P_{BH} = \sum_{j \text{ on B}} \sum_{k \text{ on H}} \sum_{i=1,m} n_i\, 2\, c_{ij}\, c_{ik}\, S_{jk} \qquad \text{(Mulliken)}$$

$$= 4(0.674)(0.660)(0.498)+4(-0.653)(0.323)(0.498)+4(0.332)(0.660)(0.524)+ 4(0.685)(0.323)(0.524)$$

$$\uparrow\ \uparrow\ \ \uparrow\ \ \uparrow \qquad \uparrow\ \uparrow\ \ \uparrow\ \ \uparrow \qquad \uparrow\ \uparrow\ \ \uparrow\ \ \uparrow \qquad \uparrow\ \uparrow\ \ \uparrow\ \ \uparrow$$

$$2n_1c_{1,B(2s)}c_{1,H1(1s)}S_{2s,1s} + 2n_2c_{2,B(2s)}c_{2,H1(1s)}S_{2s,1s} + 2n_1c_{1,B(2px)}c_{1,H(1s)}S_{2px,1s} + 2n_2\, c_{2,B(2px)}\, c_{2,H(1s)}S_{2px,1s}$$

$$= 0.8868 - 0.4204 + 0.4592 + 0.4632 = 1.389$$

The results are within round-off error of the values given in the listing. The bond is 8% ionic. For comparison purposes, the Coulson bond order is given by the sum of the population matrix elements over the atomi orbitals on B and the atomic orbitals on H:

$$BO_{BH} = \sum_{j \text{ on B}} \sum_{k \text{ on H}} \Big(\sum_{i=1,m} n_i\, c_{ij}\, c_{ik} \Big) = \sum_{j \text{ on B}} \sum_{k \text{ on H}} p_{jk} \qquad \text{(Coulson)}$$

$$= 2(0.6739)(0.6601) + 2(-0.6534)(0.3227) + 2(0.3319)(0.6601) + 2(0.6848)(0.3227)$$

$$\uparrow\ \uparrow\ \ \uparrow \qquad \uparrow\ \uparrow\ \ \uparrow \qquad \uparrow\ \uparrow\ \ \uparrow \qquad \uparrow\ \uparrow\ \ \uparrow$$

$$n_1c_{1,B(2s)}c_{1,H1(1s)} + n_2c_{2,B(2s)}c_{2,H1(1s)} + n_1c_{1,B(2px)}c_{1,H(1s)} + n_2\, c_{2,B(2px)}\, c_{2,H(1s)}$$

$$= 0.8897 - 0.4217 + 0.4382 + 0.4420 = 0.4680 + 0.8802 = 1.348$$

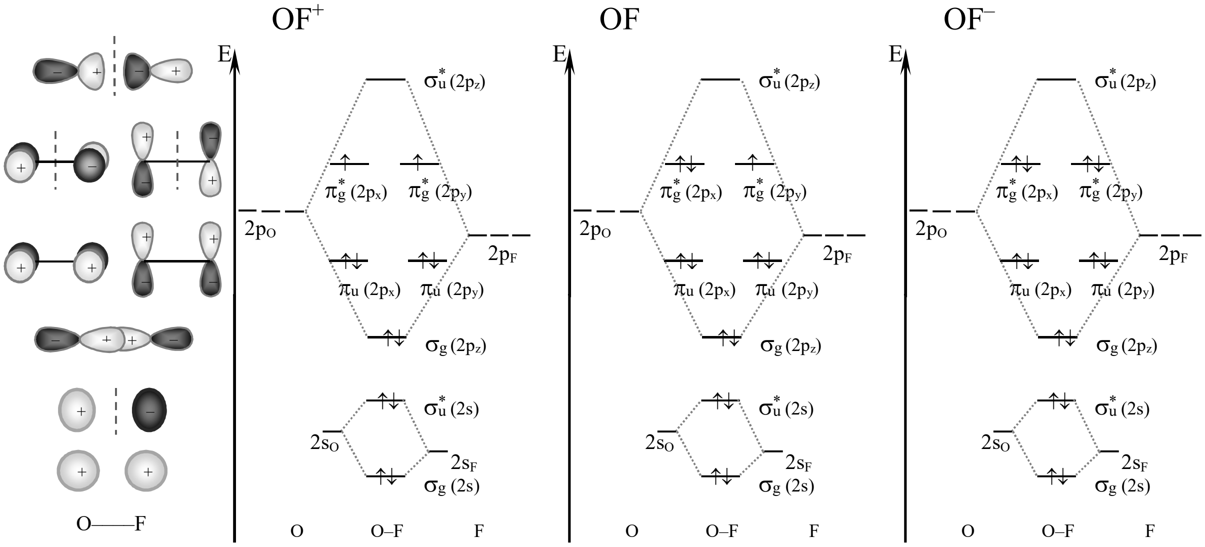
or taken directly from the population matrix listing: $BO_{BH} = 0.4679 + 0.8802 = 1.348$

You should locate the corresponding matrix elements in the CNDO listing for practice. The Coulson and Mulliken bond orders are usually quite similar. For comparison with more advanced methods, the atomic charge on B at the HF/6-31G** level is 0.126 and the Mulliken bond order is 0.927.

11. Using molecular orbital theory, decide if OF is more likely to form an OF^+ ion or an OF^- ion.

Answer: The plan is to assume the molecular orbital diagram is similar to O_2. Note that O_2 and OF^+ are isoelectronic.

The OF molecule has 6+7 = 13 valence electrons. The MOs fill with three electrons in the π_g^* orbitals. Removing an electron from OF to form OF^+ removes an anti-bonding electron, strengthening the bond. Adding an electron to OF to form OF^- adds an anti-bonding electron, weakening the bond. The required approach is to calculate the qualitative bond order, Eq. 26.4.1. As shown below, OF^+ has the largest bond order, giving the strongest bond, and is more likely to form from OF.

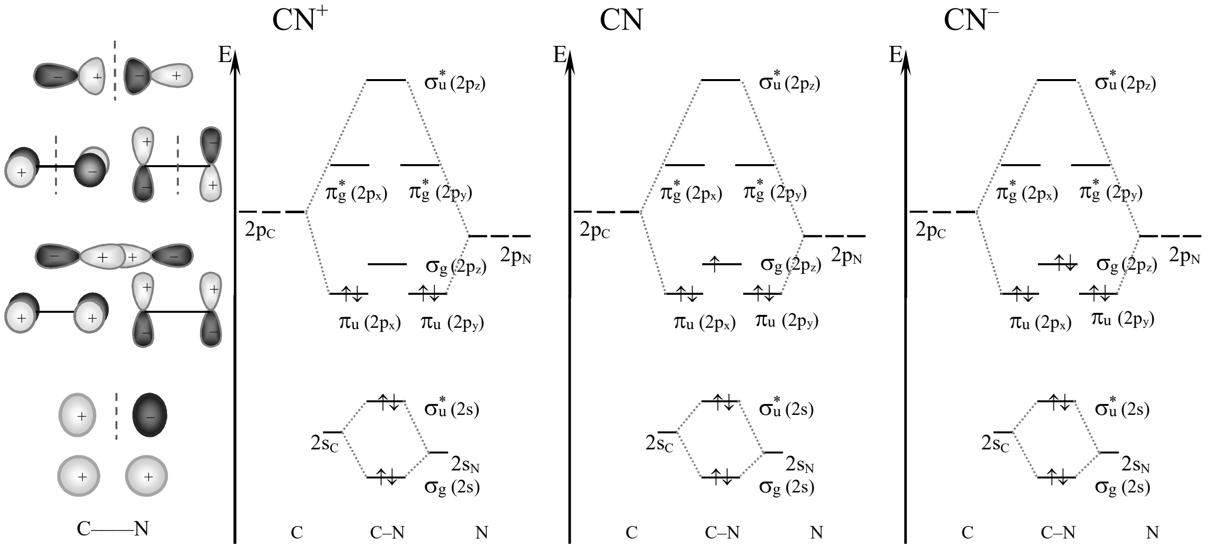


Bond order: $BO = \frac{8-4}{2} = 2$ $BO = \frac{8-5}{2} = 1\frac{1}{2}$ $BO = \frac{8-6}{2} = 1$

12. Using molecular orbital theory, which of CN, CN^+, or CN^- has the strongest bond?

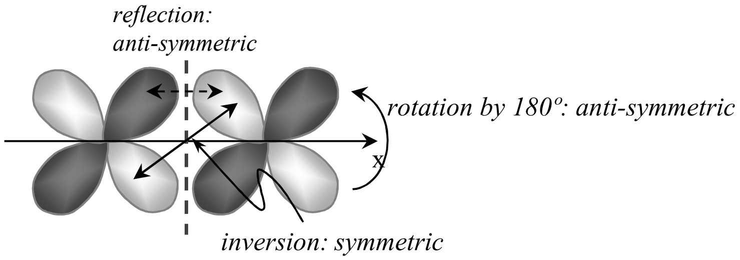
Answer: The plan is to note that the sum of the atomic numbers of CN is 13, which is less than the sum for N_2 of 14. The molecular orbital diagram is expected to have the same molecular orbital ordering as N_2. The bond strengths are expected to correlate with the qualitative bond order.

There are 9 valence electrons. The MOs fill with one electron in the $\sigma_g(2p_z)$-orbital. Removing an electron from CN to form CN^+ removes a bonding electron, weakening the bond. Adding an electron to CN to form CN^- adds a bonding electron, strengthening the bond. The required approach is to calculate the qualitative bond order, Eq. 26.4.1. As shown below, CN^- has the largest bond order, giving the strongest bond. Note that CN^- is isoelectronic with N_2.



Bond order: $\text{BO} = \frac{6-2}{2} = 2$ $\text{BO} = \frac{7-2}{2} = 2\tfrac{1}{2}$ $\text{BO} = \frac{8-2}{2} = 3$

13. What is the symmetry of the orbital formed from the side-on overlap of two d orbitals as shown below (σ,π, or δ; bonding or anti-bonding; g or u)? The lobes of both orbitals lie in the plane of the paper. The x-axis is the internuclear axis.



Answer: The orbital changes sign under rotation by 180°, giving a π-orbital (see above). Reflection across the plane perpendicular to the internuclear axis and positioned midway between the nuclei gives a change in sign. The orbital is anti-symmetric with respect to reflection, giving an anti-bonding orbital. The reflection plane is coincident with the node that is perpendicular to the internuclear axis. Inversion through the center of mass gives the same orbital phase. The orbital is symmetric with respect to inversion, giving a "g" orbital. All together, the orbital is π_g^*.

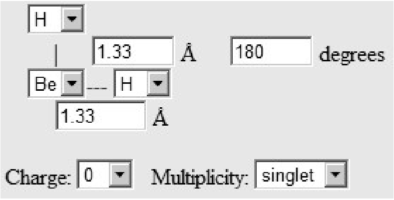
14. Calculate the bond order in linear BeH_2 in the CNDO approximation. Characterize the highest occupied molecular orbital (σ or π, bonding, non-bonding, or anti-bonding). The bond length is 1.330 Å. Calculate the Mulliken bond order using the molecular orbital coefficients and the overlap integrals (in effect, verifying the listed bond order in the CNDO printout).

Answer: The plan is to use the "*cndo*" applet, on the text book Web site and on the companion CD, to obtain the overlap matrix and the eigenvectors. The eigenvectors are the molecular orbital coefficients. The bond order is calculated using Eq. 26.3.10:

$$P_{ab} = \sum_{j\ \mathrm{on}\ a} \sum_{k\ \mathrm{on}\ b} \sum_{i=1}^{m} n_i\, 2c_{ij}\, c_{ik}\, S_{jk} \qquad \text{(Mulliken)}$$

for atoms a and b and MO i with n_i electrons. In this problem atom a is 1-Be and atom b is 2-H. The two Be-H bonds are equivalent, so either may be used.

The input was set-up as:



H
1.33 Å 180 degrees
Be --- H
1.33 Å
Charge: 0 Multiplicity: singlet

There are four valence electrons, filling through the second molecular orbital, giving the HOMO as σ-bonding. The Atomic Coordinates show that the x-axis is chosen as the intermolecular axis. Only the Be(2s) and Be(2p_x) contribute to the bonding with H(1s). Be(2p_y) and (2p_z) are atomic non-bonding. The overlap integrals, eigenvectors, and population analysis from the output are:

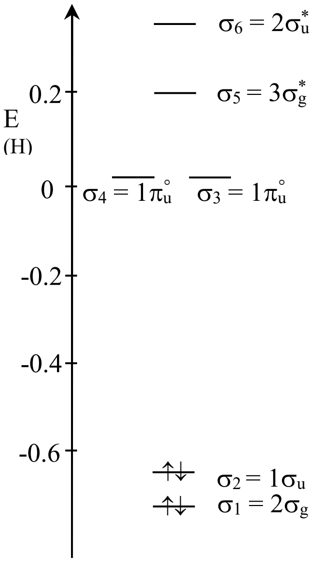
```
___________________ Overlap Matrix __________________________
         1 Be2s   1 Be2px  1 Be2py  1 Be2pz  2  H1s   3  H1s
 1 Be2s   1.0      0.0      0.0      0.0      0.4908   0.4908
 1 Be2px  0.0      1.0      0.0      0.0      0.5593  -0.5593
 1 Be2py  0.0      0.0      1.0      0.0      0.0     -0.0
 1 Be2pz  0.0      0.0      0.0      1.0      0.0      0.0
 2  H1s   0.4908   0.5593   0.0      0.0      1.0      0.046
 3  H1s   0.4908  -0.5593  -0.0      0.0      0.046    1.0
______________________________________________________________

             SCF eigenvalues (a.u.) and eigenvectors
_________________(eigenvectors listed in columns)____________

E(i)    -0.6963  -0.6594   0.0767   0.0767   0.2004   0.3277
vector    1        2        3        4        5        6
atom:
 1 Be2s   0.6759   0.0      0.0      0.0      0.737   -0.0
 1 Be2px  0.0     -0.6294   0.0      0.0      0.0      0.7771
 1 Be2py  0.0      0.0      0.0      1.0      0.0      0.0
 1 Be2pz  0.0      0.0      1.0      0.0      0.0      0.0
 2  H1s   0.5212  -0.5495   0.0      0.0     -0.4779  -0.4451
 3  H1s   0.5212   0.5495   0.0      0.0     -0.4779   0.4451
_______________________________________________________________

__________________SCF Population matrix______________________
         1 Be2s   1 Be2px  1 Be2py  1 Be2pz  2  H1s   3  H1s
 1 Be2s   0.9136   0.0      0.0      0.0      0.7045   0.7045
 1 Be2px  0.0      0.7923   0.0      0.0      0.6917  -0.6917
 1 Be2py  0.0      0.0      0.0      0.0      0.0      0.0
 1 Be2pz  0.0      0.0      0.0      0.0      0.0      0.0
 2  H1s   0.7045   0.6917   0.0      0.0      1.147   -0.0606
 3  H1s   0.7045  -0.6917   0.0      0.0     -0.0606   1.147
_______________________________________________________________

______Total Bond Order (Mulliken overlap population)_____
Atoms:  1 Be   2  H
 2  H   1.465
 3  H   1.465 -0.006
```



The molecular orbital energy diagram is shown at right, with the symmetry designations, for comparison with Figure 26.6.4. The Mulliken overlap population for the (1-Be)-(2-H) bond is:

$$\begin{array}{lcccccccccl}
P_{BeH} = & 4 & (0.6759) & (0.5212) & (0.4908) & + & 4 & (-0.6294) & (-0.5495) & (0.5593) & \qquad \text{(Mulliken)} \\
& \uparrow & \uparrow & \uparrow & \uparrow & & \uparrow & \uparrow & \uparrow & \uparrow & \\
& 2n_1 & c_{1,Be(2s)} & c_{1,H1(1s)} & S_{2s,1s} & + & 2n_2 & c_{2,Be(2p_x)} & c_{2,H(1s)} & S_{2p_x,1s} & \\
& \multicolumn{4}{c}{\textit{molecular orbital 1}} & & \multicolumn{4}{c}{\textit{molecular orbital 2}} &
\end{array}$$

$$= 0.6916 – 0.7737 = 1.465$$

as listed in the *cndo* printout. The Be($2p_x$)-H(1s) term for molecular orbital 1 and the Be(2s)-H(1s) term for molecular orbital 2 vanish because of the zero coefficients for the corresponding Be atomic orbitals.

For comparison purposes, the Coulson bond order is given by the sum of the Population Matrix elements:

$$BO_{BH} = \sum_{j \text{ on } B} \sum_{k \text{ on } H} \Big(\sum_{i=1,m} n_i\, c_{ij}\, c_{ik} \Big) \qquad \text{(Coulson)}$$

$$\begin{array}{lccccccc}
= & 2 & (0.6759) & (0.5212) & + & 2 & (-0.6294) & (-0.5495) \\
& \uparrow & \uparrow & \uparrow & & \uparrow & \uparrow & \uparrow \\
& n_1 & c_{1,B(2s)} & c_{1,H1(1s)} & + & n_2 & c_{2,B(2p_x)} & c_{2,H(1s)}
\end{array}$$

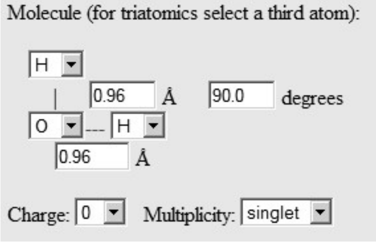
$$= 0.7046 + 0.6917 = 1.396$$

The population matrix is also called the density matrix. You should locate the corresponding matrix elements in the CNDO listing for practice. The Coulson and Mulliken bond orders are usually quite similar. For comparison with more advanced methods, the atomic charge on Be at the HF/6-31G** level is 0.216 as compared to 0.294 at the CNDO level. The Mulliken bond order at HF/6-31G** is 0.988 and taking into account electron-electron correlation using B3LYP/6-311G** is 0.971.

15. Determine the bond order for the O-H bond in H_2O assuming a 90° bond angle and an O-H bond length of 0.96 Å, in the CNDO approximation. Calculate the bond order using the molecular orbital coefficients and the overlap integrals (in effect, verifying the listed bond order in the CNDO printout).

Answer: The plan is to use the "*cndo*" applet, on the text book Web site and on the companion CD, to obtain the overlap matrix and the eigenvectors. The eigenvectors are the molecular orbital coefficients. The bond order is calculated using Eq. 26.3.10. In this problem atom a is 1-O and atom b is 2-H. The two O-H bonds are equivalent, so either may be used.

The input was set up as:



Molecule (for triatomics select a third atom):

H

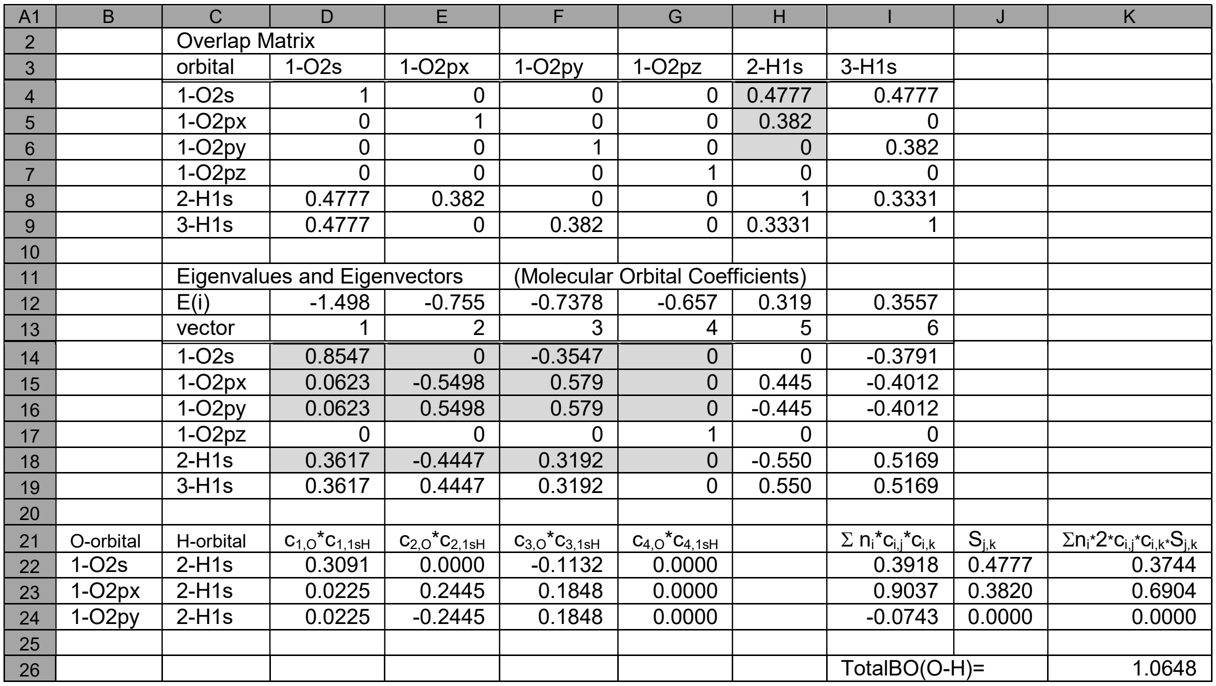
0.96 Å 90.0 degrees

O --- H

0.96 Å

Charge: 0 Multiplicity: singlet

The overlap matrix and eigenvectors were copied and pasted into a text document and then imported in Excel to make the calculation easier. The highlighted areas are the coefficients of interest:



A1	B	C	D	E	F	G	H	I	J	K
2		Overlap Matrix								
3		orbital	1-O2s	1-O2px	1-O2py	1-O2pz	2-H1s	3-H1s		
4		1-O2s	1	0	0	0	0.4777	0.4777		
5		1-O2px	0	1	0	0	0.382	0		
6		1-O2py	0	0	1	0	0	0.382		
7		1-O2pz	0	0	0	1	0	0		
8		2-H1s	0.4777	0.382	0	0	1	0.3331		
9		3-H1s	0.4777	0	0.382	0	0.3331	1		
10										
11		Eigenvalues and Eigenvectors			(Molecular Orbital Coefficients)					
12		E(i)	-1.498	-0.755	-0.7378	-0.657	0.319	0.3557		
13		vector	1	2	3	4	5	6		
14		1-O2s	0.8547	0	-0.3547	0	0	-0.3791		
15		1-O2px	0.0623	-0.5498	0.579	0	0.445	-0.4012		
16		1-O2py	0.0623	0.5498	0.579	0	-0.445	-0.4012		
17		1-O2pz	0	0	0	1	0	0		
18		2-H1s	0.3617	-0.4447	0.3192	0	-0.550	0.5169		
19		3-H1s	0.3617	0.4447	0.3192	0	0.550	0.5169		
20										
21	O-orbital	H-orbital	$c_{1,O}*c_{1,1sH}$	$c_{2,O}*c_{2,1sH}$	$c_{3,O}*c_{3,1sH}$	$c_{4,O}*c_{4,1sH}$		$\Sigma\ n_i*c_{i,j}*c_{i,k}$	$S_{j,k}$	$\Sigma n_i*2*c_{i,j}*c_{i,k}*S_{j,k}$
22	1-O2s	2-H1s	0.3091	0.0000	-0.1132	0.0000		0.3918	0.4777	0.3744
23	1-O2px	2-H1s	0.0225	0.2445	0.1848	0.0000		0.9037	0.3820	0.6904
24	1-O2py	2-H1s	0.0225	-0.2445	0.1848	0.0000		-0.0743	0.0000	0.0000
25										
26								TotalBO(O-H)=		1.0648

Since there are 6+1+1 valence electrons, the highest occupied molecular orbital is orbital 4. Therefore, for the sum, only orbitals 1-4 are required, each with $n_i = 2$. Cells I22:I24 are the sums over the molecular orbitals for each pair of atomic orbitals. For example, cell D22 is given by $c_{1,O2S}\ c_{1,H1s} = (0.8547)(0.3617)$ = D14*D18 and the sum for the coefficients for the O 2s orbital with the H 1s orbital is given in cell I22=SUM(D22:F22)*2:

$$p_{O2s,H1s} = \sum_{i=1}^{4} 2\ c_{i,O2s}\ c_{i,H1s}$$
$$= 2(0.8547)(0.3617)+2(0)(-0.4447)+2(-0.3547)(0.3192)+2(0)(0) = 0.3918$$

where p is the population matrix entry. The population matrix is also called the density matrix. The O $2p_z$ orbital shows no interaction with the H 1s, so these sums are not calculated. These values are listed in the SCF Population matrix in the CNDO printout. Each sum is then multiplied by two and the corresponding overlap integral for the pair of orbitals and the overall sum gives the bond order:

$$P_{O,H} = \sum_{j\text{ on O}} \sum_{k\text{ on H}} \sum_{i=1}^{m} n_i\ 2\ c_{ij}\ c_{ik}\ S_{jk} = = \sum_{j\text{ on a}} \sum_{k\text{ on b}} 2\ p_{jk}\ S_{jk}$$
$$= 2p_{O2s,H1s}\ S_{O2s,H1s} + 2p_{O2px,H1s}\ S_{O2px,H1s} + 2p_{O2py,H1s}\ S_{O2py,H1s} + 2p_{O2pz,H1s}\ S_{O2pz,H1s}$$
$$= 2(0.3918)(0.4777) + 2(0.9037)(0.3820) + 2(-0.0743)(0.0) + 2(0)(0) = 1.065$$

The bond orders at higher levels of approximation are: AM1 (0.967), PM3 (0.969), HF/6-31G** (0.892), and B3LYP/6-311G** (0.981). The larger value for the bond order is typical of the CNDO level. Because the bond order is not an experimentally measureable property, there is no method which is accepted as best for bond order estimations. Comparisons between molecules at the same level of approximation are useful for building chemical intuition.

16. Calculate the % ionic character in the lowest energy molecular orbital, for the valence electrons, of one of the O-H bonds in H_2O assuming a 90° bond angle and an O-H bond length of 0.96 Å, in the CNDO approximation (the same geometry as the previous problem).

Answer: The % ionic character from the CNDO calculation, considering only the H atom in the x-direction, is given by:

$$\%\text{ ionic character} = \frac{(0.8547)^2 + (0.0623)^2 - (0.3617)^2}{(0.8547)^2 + (0.0623)^2 + (0.3617)^2} = 69.8\%$$

The % ionic character is even higher at the AM1 level of approximation (see the following problem).

17. Characterize the highest occupied molecular orbital for H_2O as bonding, non-bonding, or anti-bonding. Is the orbital σ or π type, or is the orbital better characterized as purely atomic? Compare this result to the prediction from hybridization theory. You may use semi-empirical or HF/STO-3G methods.

Answer: The plan is to use any semi-empirical calculation to find the molecular orbital coefficients for the HOMO.

The CNDO level eigenvectors are given in Problem 12. Alternately at a better level of approximation, the MOPAC input file with the O atom at the origin is:

```
1SCF AM1 GEO-OK VECTORS
H2O 90 deg.

O                                        atom 1   [atom 1 is at the origin]
H 0.96 0   0.000 0   0.000 0   1 0 0     atom 2   [the 2-1 distance is 0.96 Å]
H 0.96 0   90.00 0   0.000 0   1 2 0     atom 3   [the 3-1 distance is 0.96 Å, the 3-1-2 angle is 90°]
       ↑         ↑         ↑
            Don't optimize
```

A portion of the MOPAC output file at the AM1 level is:

```
              INTERATOMIC  DISTANCES
                    O  1      H  2      H  3
    ----------------------------------
    O    1    .0000
    H    2    .9600    .0000
    H    3    .9600   1.3576    .0000

                         EIGENVECTORS
        ROOT NO.    1           2           3           4           5           6
              -36.71064   -17.47187   -15.72093   -12.54516     4.80212     5.55102

      S  O   1     .88709      .00000      .38922      .00000      .24816      .00000
     PX  O   1     .11967      .55249     -.54759      .00000      .43107      .44131
     PY  O   1     .11967     -.55249     -.54759      .00000      .43107     -.44131
     PZ  O   1     .00000      .00000      .00000     1.00000      .00000      .00000

      S  H   2     .30367      .44131     -.35270      .00000     -.53234     -.55249

      S  H   3     .30367     -.44131     -.35270      .00000     -.53234      .55249
```

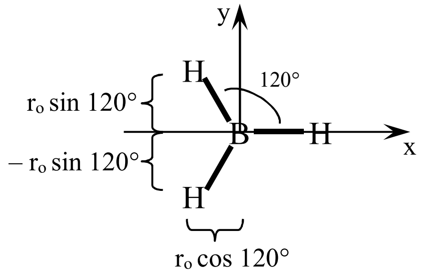
In either the CNDO or AM1 case, the highest occupied molecular orbital is orbital 4, since there are 6+1+1 valence electrons, requiring 4 orbitals. The molecular orbital coefficients on the H atoms are zero in the HOMO. Molecular orbital 4 is just an isolated $2p_z$ orbital on the O atom. The HOMO is then non-bonding. The HOMO can be considered as π-type since π-bonds would form perpendicular to the x-y plane of the molecule, if they were possible. Alternately, the HOMO can be described as an atomic non-bonding $2p_z$ orbital.

The prediction using hybridization is that there should be two equivalent lone pairs in sp^3 hybridized orbitals. The more accurate molecular orbital results give one lone pair as the HOMO, which is an atomic non-bonding $2p_z$ orbital. The other lone pair is approximately described as a core 2s orbital on oxygen, since the lowest energy molecular orbital is predominantly 2s in character with roughly 70% (CNDO) to 80% (AM1) ionic character. The % ionic character from the CNDO calculation is determined in the previous problem.

From an energetic perspective, the hybridization treatment is misleading. However, the electrostatic distribution is well approximated by both molecular orbital and hybridization approaches.

18. Using geometrical considerations, find the Cartesian coordinates for the planar molecule BH_3. Place the B atom at the origin and use a bond length of 1.19 Å. Orient one of the H atoms along the x-axis. Obtain the overlap matrix and the molecular orbital coefficients using the version of the "*cndo*" applet that has Cartesian coordinate input, which is on the text book Web site and on the companion CD. Example input files are shown at the bottom of the applet. The first line of the input file is the number of atoms, the second line is a comment, and the remaining lines are the atom and the x, y, z coordinates. (a). Give the molecular orbital energy diagram and indicate the electron occupancy. (b). Draw orbital 3. (c). Write orbital 3 in terms of the molecular orbital coefficients and the atomic orbitals: $2s_B$, $2p_{x,B}$, $2p_{y,B}$, $2p_{z,B}$, $1s_{H2}$, $1s_{H3}$, and $1s_{H4}$, where the H atoms are atoms 2, 3, and 4. (d). Characterize orbital 3 as bonding, non-bonding, or anti-bonding. (e). Characterize the LUMO as bonding, non-bonding, or anti-bonding. (f). Show the lowest energy electronic transition on the energy level diagram. (g) Referring to the H atom along the x-axis, which atomic orbital on the central B atom has better overlap with the H atom 1s-atomic orbital?

Answer: The plan is to note that the bond angle in a symmetrical triatomic is 120°. If the B atom is at the origin and one H atom is along the x-axis at (r_o, 0, 0), then the remaining two H atoms are at ($r_o \cos 120°$, $r_o \sin 120°$, 0) and ($r_o \cos 120°$, $– r_o \sin 120°$, 0):



The corresponding input file in XYZ format is:

```
 4                                                    number of atoms
 BH3                                                  comment
 B     0.0      0.0      0.0                          Cartesian coordinates for each atom
 H     1.19     0.0      0.0
 H    -0.595    1.031    0.0
 H    -0.595   -1.031    0.0
```

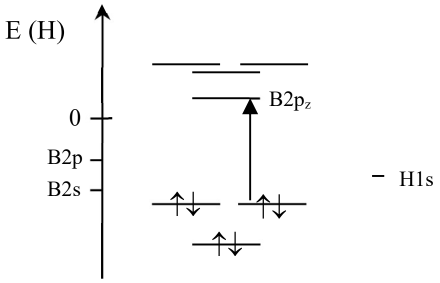
Notice that no information is given about the bonding partners, nor the types of bonds present, as would be required for a molecular mechanics input file. The results are:

```
________________________________ Overlap Matrix _________________________________
          1  B2s     1  B2px    1  B2py    1  B2pz    2  H1s     3  H1s     4  H1s
 1  B2s    1.0        0.0        0.0        0.0        0.5198     0.5196     0.5196
 1  B2px   0.0        1.0        0.0        0.0        0.5366    -0.2681    -0.2681
 1  B2py   0.0        0.0        1.0        0.0        0.0        0.4646    -0.4646
 1  B2pz   0.0        0.0        0.0        1.0        0.0        0.0        0.0
 2  H1s    0.5198     0.5366     0.0        0.0        1.0        0.1209     0.1209
 3  H1s    0.5196    -0.2681     0.4646     0.0        0.1209     1.0        0.1208
 4  H1s    0.5196    -0.2681    -0.4646     0.0        0.1209     0.1208     1.0
___________________________________________________________________________________
```

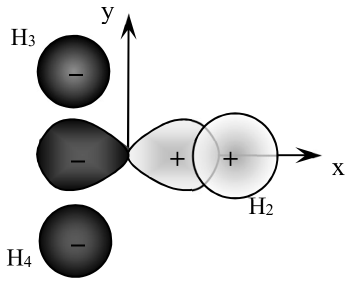
```
                        SCF eigenvalues (a.u.) and eigenvectors
________________________(eigenvectors listed in columns)_________________________
E(i)    -0.9874   -0.7035   -0.7035    0.0726    0.2625    0.3176    0.3176
vector     1         2         3         4          5         6         7
atom:
 1  B2s    0.7131   -0.0       -0.0003    0.0       -0.7011    0.0        0.001
 1  B2px   0.0002    0.0        0.6679    0.0        0.001     0.0        0.7442
 1  B2py   0.0       0.6679    -0.0       0.0       -0.0       0.7442    -0.0
 1  B2pz   0.0       0.0        0.0       1.0        0.0       0.0        0.0
 2  H1s    0.405     0.0        0.6075    0.0        0.4109   -0.0       -0.546
 3  H1s    0.4047    0.5262    -0.304     0.0        0.4121   -0.4723     0.2721
 4  H1s    0.4047   -0.5263    -0.3039    0.0        0.4121    0.4723     0.2721
_________________________________________________________________________________

_______Total Bond Order  (Mulliken overlap population)_______
Atoms:  1  B   2  H   3  H
 2  H   1.471
 3  H   1.471 -0.01
 4  H   1.471 -0.01  -0.01
```

(a). Semi-empirical methods include only valence electrons, while *ab initio* include all electrons. The total number of valence electrons is 3+1+1+1 = 6. Given double occupancy, the highest occupied molecular orbitals are 2 and 3. The HOMO is doubly degenerate in this molecule. The orbital energies are in Hartrees. The molecular orbital energy diagram and the electron occupancy are shown below. The energies of occupied atomic orbitals on B and H at the CNDO level are shown for comparison.



(b). By convention, the positive lobe of the $2p_x$ orbital faces to the right along the positive x-direction. The overlap of the positive lobe of the $2p_x$ orbital with the $1s_{H,2}$ orbital is bonding, since both have positive phases. The overlap of the negative lobe of the $2p_x$ orbital with H atoms 3 and 4 is also bonding, because each orbital or lobe has negative phase. Orbital 3 has three direct bonding interactions:



The overlap matrix shows that the overlap integral for the $2p_x$ orbital with $1s_{H,2}$ is about twice that for $1s_{H,3}$ and $1s_{H,4}$. The $1s_{H,3}$ and $1s_{H,4}$ orbitals are shown smaller than the $1s_{H,2}$ because the corresponding molecular orbital coefficients for $1s_{H,3}$ and $1s_{H,4}$ are smaller (0.304). Each interaction is in the bonding plane, resulting in σ bonds to the three H atoms.

(c). Molecular orbital 3 is given by:

$$\Psi_3 = 0.668\ 2p_{x,B} + 0.608\ 1s_{H2} - 0.304\ 1s_{H3} - 0.304\ 1s_{H4}$$

(d). Orbital 3 has three direct bonding interactions and no anti-bonding interactions making the orbital overall bonding.

(e). The LUMO is orbital 4, which is a pure B $2p_z$ orbital with zero coefficients on the three H atoms. No net overlap is possible between the $2p_z$ orbital and 1s orbitals that are in the nodal plane of the $2p_z$ orbital. The LUMO is non-bonding and can be considered as a π_{nb} orbital or just an atomic $2p_z$ orbital on the central B atom.

(f). The lowest energy electronic transition is shown on the energy level diagram. This transition is a sigma to non-bonding transition, nb←σ, which is expected to have a strong transition dipole moment.

(g) The overlap integral of the B $2p_x$ orbital with $1s_{H,2}$ is larger, at 0.5366, than the B 2s orbital overlap with$1s_{H,2}$, which is 0.5198. The $2p_x$orbital is better directed in space to overlap with H atom 1. However, the B $2p_z$ orbital is higher in energy than the 2s, so energy matching with the $1s_H$ orbital is comparable.

19. Consider the B-H bond using the CNDO level calculation for BH_3 in the previous problem. Focus on the Mulliken overlap population between the B atom and H atom 2, which is along the

x-axis. Does the $2s_B$-$1s_{H,2}$ or the $2p_{x,B}$-$1s_{H,2}$ overlap make a stronger contribution to the bond strength?

Answer: The plan is to note that the overall bond strength includes contributions from both $2s_B$-$1s_{H,2}$ and the $2p_{x,B}$-$1s_{H,2}$ overlap. The total bond order is given by Eq. 26.3.10:

$$P_{ab} = \sum_{j\text{ on }a}\ \sum_{k\text{ on }b}\ \sum_{i=1}^{m} n_i\, 2c_{ij}\, c_{ik}\, S_{jk}$$

There are three filled molecular orbitals, m = 3. The specific terms for the $2s$-$1s_{H,2}$ and the $2p_x$-$1s_{H,2}$ coefficients must be evaluated.

The contribution of the $2s$-$1s_{H,2}$ overlap is:

$$2\,p_{B2s,H1s}\,S_{B2s,H1s} = \sum_{i=1}^{3} 2\,[2\,c_{i,B2s}\,c_{i,H1s}\,S_{B2s,H1s}] \tag{1}$$

The contribution of the $2p_x$-$1s_{H,2}$ overlap is:

$$2\,p_{B2px,H1s}\,S_{B2px,H1s} = \sum_{i=1}^{3} 2\,[2\,c_{i,B2px}\,c_{i,H1s}\,S_{B2px,H1s}] \tag{2}$$

From Eqs. 1and 2 and the eigenvectors listed in the previous problem:

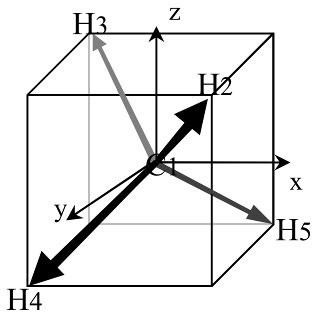
$$\begin{aligned} p_{B2s,H1s}\,S_{B2s,H1s} &= 2[2(0.7131)(0.4050) + 2(-0.0003)(0.6075)]\ 0.5198 \\ &= 2[0.5772(0.5198)] = 0.6002 \end{aligned}$$

$$\begin{aligned} p_{B2px,H1s}\,S_{B2px,H1s} &= 2[2(0.0002)(0.4050) + (2(0.6679)(0.6075)]\ 0.5366 \\ &= 2[0.8117(0.5366)] = 0.8710 \end{aligned}$$

The $2p_{x,B}$-$1s_{H,2}$ overlap has the stronger contribution. The total Mulliken bond order is then 0.6002 + 0.8710 = 1.4712, which agrees with the CNDO printout. The overlap integral for $2p_{x,B}$ - $1s_{H,2}$ is larger than $2s_B$ - $1s_{H,2}$. However, the $2p_{x,B}$ orbital is higher in energy than the $2s_{,B}$, so energy matching with the $1s_H$ orbital is comparable. In this particular case, the central atom orbital with the better overlap provides the stronger contribution to the bonding.

<u>20</u>. (a). Compare the molecular orbital and hybridization models of methane. (b). Find the C-H bond order and the charge on the C-atom in methane. Obtain the molecular orbital coefficients, atom electron distribution and bond order matrices using the version of the "*cndo*" applet that has Cartesian coordinate input, which is on the text book Web site and on the companion CD. The atomic coordinates for methane with a C-H bond length of 1.084 Å are:

Atom	x	y	z
1 C	0.0	0.0	0.0
2 H	0.62565	0.62565	0.62565
3 H	-0.62565	-0.62565	0.62565
4 H	-0.62565	0.62565	-0.62565
5 H	0.62565	-0.62565	-0.62565



Answer: The plan is to compare the CNDO results with the expected sp^3 hybridization.
The “*cndo*” applet input file for methane is:

```
5                                                       number of atoms
CH4                                                     comment
C    0.0     0.0     0.0                                x, y, z coordinates
H    0.62565        0.62565        0.62565
H   -0.62565       -0.62565        0.62565
H   -0.62565        0.62565       -0.62565
H    0.62565       -0.62565       -0.62565
```

The charge is zero and the multiplicity is singlet, all electrons are paired. The condensed “*cndo*” applet output is shown below:

```
                      SCF eigenvalues (a.u.) and eigenvectors
___________________________(eigenvectors listed in columns)__________________________

E(i)    -1.2755   -0.7268   -0.7268   -0.7268    0.3142    0.3334    0.3334    0.3334
vector     1         2         3         4         5         6         7         8
atom:
 1  C2s    0.7261    0.0       0.0       0.0      -0.6876   -0.0       0.0       0.0
 1  C2px  -0.0       0.2083   -0.1454    0.6596    0.0       0.5322    0.2732   -0.3774
 1  C2py  -0.0       0.1873    0.6756    0.0898   -0.0       0.4659   -0.3139    0.4298
 1  C2pz  -0.0       0.649    -0.1483   -0.2377    0.0       0.0015    0.572     0.4161
 2  H1s    0.3438    0.5227    0.1911    0.2561    0.3631   -0.4995   -0.2655   -0.2341
 3  H1s    0.3438    0.1268   -0.3395   -0.4939    0.3631    0.498    -0.3062   -0.1817
 4  H1s    0.3438   -0.3352    0.485    -0.1662    0.3631    0.0339    0.5791   -0.1954
 5  H1s    0.3438   -0.3142   -0.3366    0.404     0.3631   -0.0324   -0.0075    0.6113
_______________________________________________________________________________________

______________________________SCF Population matrix____________________________________
          1  C2s    1  C2px   1  C2py   1  C2pz   2  H1s    3  H1s    4  H1s    5  H1s
 1  C2s    1.0545    0.0       0.0      -0.0       0.4993    0.4993    0.4993    0.4993
 1  C2px   0.0       0.9993    0.0      -0.0       0.5      -0.5      -0.5       0.5
 1  C2py   0.0       0.0       0.9993    0.0       0.5      -0.5       0.5      -0.5
 1  C2pz  -0.0      -0.0       0.0       0.9993    0.5       0.5      -0.5      -0.5
 2  H1s    0.4993    0.5       0.5       0.5       0.9869   -0.0138   -0.0138   -0.0138
 3  H1s    0.4993   -0.5      -0.5       0.5      -0.0138    0.9869   -0.0138   -0.0138
 4  H1s    0.4993   -0.5       0.5      -0.5      -0.0138   -0.0138    0.9869   -0.0138
 5  H1s    0.4993    0.5      -0.5      -0.5      -0.0138   -0.0138   -0.0138    0.9869
_____________________________________________________________________________________

_________Total Bond Order  (Mulliken overlap population)_________
Atoms:  1  C   2  H   3  H   4  H
 2  H   1.371
 3  H   1.371 -0.005
 4  H   1.371 -0.005 -0.005
 5  H   1.371 -0.005 -0.005 -0.005

Total atom electron densities and atomic charges
atom   density   charge
 1  C  4.0524   -0.052
 2  H  0.9869    0.013
 3  H  0.9869    0.013
 4  H  0.9869    0.013
 5  H  0.9869    0.013
```

(a). Notice that the MOs involve C(2s) character or C(2p) character, but not both, in contradiction to hybridization arguments. The hybridization picture emerges when the average of MOs 1-4 is taken, giving s- and p-character. However, the CNDO s-character is greater than the canonical 25% expected for sp^3 hybridization. The hybridization has $(0.73)^2$ s-character. The SCF population matrix shows that the three p-orbital based bonding MOs, 2-4, are equivalent. Using MO 2 as representative gives $[(0.21)^2+(0.19)^2+(0.65)^2]$ p-character per MO. Taking MOs 1-4 into account corresponds to $s^{0.53}p^{1.51}$ overall hybridization. [Compare with the extended Hückel approach in Problem 39.]

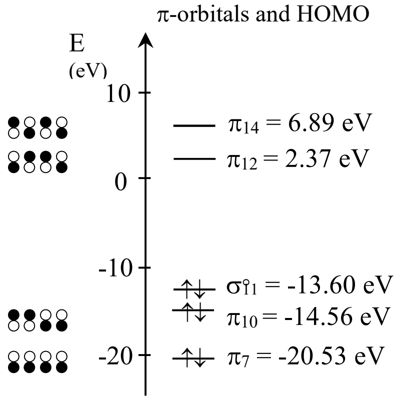
(b). Using the total atom electron densities, the C-atom charge is -0.052. This small charge is consistent with the marginally larger electronegativity of carbon compared to hydrogen. Using the total bond order matrix, the bond order is 1.371. CNDO generally overestimates bond orders. However, bond order is an artificial, but useful, construct. Different calculation methods give strikingly different values for bond orders. No one method can be chosen as "best," because the bond order between two atoms is not directly experimentally observable. Instead, we rely on correlations with bond strength properties to infer the bond order. Bond dissociation energy, bond force constant, and bond length are useful bond strength parameters.

21. Acrolein is the unsaturated aldehyde: H_2C=CH–CH=O. (a). Characterize the HOMO and LUMO of acrolein (σ or π, bonding, non-bonding, or anti-bonding). (b). Draw the molecular orbital energy diagram for the π-orbitals, only. (c) Find the charge on the O-atom of acrolein and the C-O and C-C bond orders. Base your answers on a molecular orbital calculation at the CNDO level. [You need not do any calculations by hand; just interpret the output of the MO program.] The input file for the "*cndo*" Web applet is given below in xyz format. The molecule is oriented in the x-y plane with the O-atom at the origin and the C=O bond along the x-axis.

```
8
Acrolein
 O        0         0      0
 C    1.230         0      0
 C    2.058     1.229      0
 C    3.404     1.150      0
 H    4.039     2.042      0
 H    3.911     0.175      0
 H    1.521     2.187      0
 H    1.810    -0.961      0
```

Answer: The plan is to use the "*cndo*" applet, on the text book Web site and on the companion CD, to obtain the eigenvectors, the "Total Bond Order," and "Total Atom Electron Densities." (a). There are, in the order CHO, 3(4)+4(1)+(6) = 22 valence electrons, giving the HOMO as orbital 11 and the LUMO as orbital 12. The π-orbitals are recognized by having only coefficients for the $2p_z$-orbitals. Omitting the H-atom coefficients, the condensed output for the eigenvectors, including only the π-orbitals, the HOMO, and LUMO is:

```
        SCF eigenvalues (a.u.) and eigenvectors
__________(eigenvectors listed in columns)___________
E(i)      -0.7544  -0.535   -0.4997   0.0872   0.2532
vector      7        10       11       12       14
atom:
 1  O2s     0.0      0.0      0.005    0.0      0.0
 1  O2px    0.0      0.0     -0.012    0.0      0.0
 1  O2py    0.0      0.0     -0.697    0.0      0.0
 1  O2pz    0.508   -0.586    0.0      0.508   -0.376
 2  C2s     0.0      0.0      0.040    0.0      0.0
 2  C2px    0.0      0.0      0.034    0.0      0.0
 2  C2py    0.0      0.0      0.325    0.0      0.0
 2  C2pz    0.572   -0.304    0.0     -0.488    0.586
 3  C2s     0.0      0.0      0.106    0.0      0.0
 3  C2px    0.0      0.0     -0.141    0.0      0.0
 3  C2py    0.0      0.0     -0.332    0.0      0.0
 3  C2pz    0.520    0.485    0.0     -0.392   -0.583
 4  C2s     0.0      0.0      0.001    0.0      0.0
 4  C2px    0.0      0.0      0.051    0.0      0.0
 4  C2py    0.0      0.0      0.119    0.0      0.0
 4  C2pz    0.380    0.574    0.0      0.592    0.419
```



The HOMO is in the x-y plane, corresponding to a σ-type orbital. The biggest coefficient is on the O-atom. The moderate energy of the orbital and the large ionic character between the O-atom and the adjacent C-atom, $(0.697^2 - 0.325^2)/(0.697^2 + 0.325^2)\text{x}100\% = 64\%$, suggest non-bonding character. The HOMO of acrolein is predominantly a non-bonding $2p_y$-orbital localized on the O-atom. The LUMO is an anti-bonding π-orbital, with two nodes: .

(b). The molecular orbital diagram for the π-orbitals and also including the HOMO is shown above. The MO energies are converted to eV, to provide a better feel for the energies and for comparison with subsequent problems.

(c). The bond order and atom densities matrices are reproduced below. The charge on the O-atom is a modest -0.223.

```
_______________Total Bond Order  (Mulliken overlap population) ___________
Atoms:  1  O   2  C   3  C   4  C   5  H   6  H   7  H
 2  C   1.828
 3  C  -0.016  1.584
 4  C   0.001  0.022  2.198
 5  H  -0.0    0.005 -0.006  1.359
 6  H   0.0   -0.01  -0.003  1.356 -0.023
 7  H  -0.003 -0.005  1.342 -0.004 -0.011  0.006
 8  H  -0.021  1.31  -0.022 -0.006  0.0    0.003  0.004

Total atom electron densities and atomic charges
atom   density   charge
 1  O  6.2225   -0.223
 2  C  3.7646    0.235
 3  C  4.0408   -0.041
 4  C  3.9942    0.006
 5  H  0.9842    0.016
 6  H  0.9813    0.019
 7  H  0.9722    0.028
 8  H  1.0402   -0.04
```

The bond orders are diagrammed below, showing the four-center, delocalized nature of the bonding:

1.828 1.584 2.198
O == C $\overset{\cdots\cdots}{-\,-}$ C == C

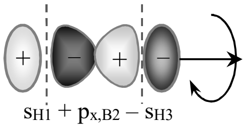
The bond orders from CNDO calculations are generally overestimated. For that reason, some authors prefer to use alternate bond order methods with *ab initio* calculations, instead. Every MO method has its strengths and weaknesses.

22. Consider the molecular orbital for linear BH_2: $\Psi_{MO} = N(s_{H1} + p_{x,B2} - s_{H3})$
with N a normalization constant and the atom numbering H_1— B_2 — H_3 $\rightarrow_x$. The internuclear axis is the x-axis. (a). Determine the symmetry designation of the molecular orbital under the symmetry operations for a linear molecule (σ, π, g, u, and also overall bonding, non-bonding, anti-bonding). (b) Determine the symmetry designation of the molecular orbital under the symmetry operations appropriate to a bent molecule (a, b, 1, 2, and also overall bonding, non-bonding, anti-bonding, Figure 26.6.4).

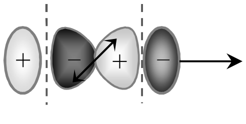
Answer: The plan is to draw the orbital to determine the symmetry with respect to rotation, reflection, and inversion. Refer to Figures 26.6.1 and 26.6.4.

The given orbital is the $2\sigma_u^*$ (b_2^*) orbital. The given orbital is the same as the most anti-bonding orbital for BeH_2 in Figures 26.6.1 and 26.6.4, except with the opposite overall sign. The reasoning follows.

Linear symmetry operations: The internuclear axis is the x-axis. Rotation around the internuclear axis of any angle retains the same phase, giving a σ-orbital. In other words, the orbital is symmetric with respect to rotation of arbitrary angle (wrt = with respect to). The center of mass is coincident with the B-atom nucleus. Inversion through the center of mass gives a change in sign. There are nodes on either side of the central atom, resulting in net anti-bonding character, giving the orbital as σ_u^*.



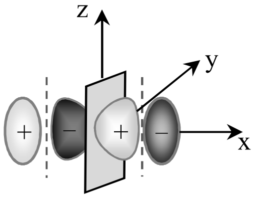
symmetric wrt rotation

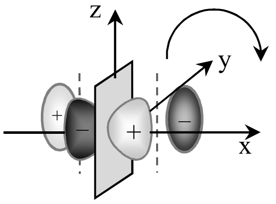


antisymmetric wrt inversion

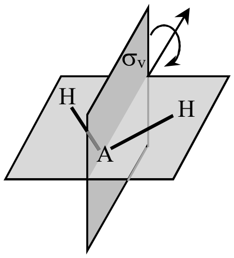
and overall anti-bonding gives σ_u^*

Bent symmetry operations: Picture the molecule as it bends in the x-y plane, as shown below. The rotation axis, or symmetry axis, is the y-axis for this original orientation. Rotation around the y-axis of 180° inverts the phase of the molecular orbital, giving a b-orbital. See the symmetry table in Figure 26.6.4. In other words, the orbital is antisymmetric with respect to rotation by 180°.





antisymmetric wrt rotation and reflection



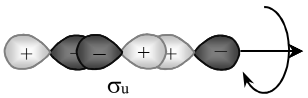
Reflection across the plane passing through the B-nucleus and bisecting the internuclear axes is antisymmetric, giving the final symmetry as b_2^*.

Molecules are assigned to symmetry groups on the basis of their symmetry operations. The symmetry group of a symmetrical bent molecule is called C_2v. The symmetry operations are rotation about the symmetry axis of 180° and reflection across the vertical plane that bisects the molecule. You might wonder about the inversion operation for a bent molecule. A C_{2v} molecule does not have an inversion center: the molecule is not centro-symmetric. An inversion operation does not apply to the C_{2v} case. The symmetry group for a symmetric linear triatomic is $D_{\infty h}$.

23. Consider the molecular orbital for linear BF_2: $\Psi_{MO} = N(-p_{x,F1} + p_{x,B2} - p_{x,F3})$ with N a normalization constant and the atom numbering $F_1 — B_2 — F_3 \rightarrow_x$. The internuclear axis is the x-axis. (a). Determine the symmetry designation of the molecular orbital under the symmetry operations for a linear molecule (σ, π, g, u, and also overall bonding, non-bonding, anti-bonding). (b) Determine the symmetry designation of the molecular orbital under the symmetry operations appropriate to a bent molecule (a, b, 1, 2, and also overall bonding, non-bonding, anti-bonding, Figure 26.6.4).

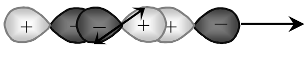
Answer: The plan is to draw the orbital to determine the symmetry with respect to rotation, reflection, and inversion. Refer to Figures 26.6.1 and 26.6.4.

The given orbital is the $3\sigma_u$ (b_2) orbital in Figures 26.6.7 and 26.6.8. The reasoning follows. *Linear symmetry operations*: The internuclear axis is the x-axis. Rotation around the internuclear axis of any angle retains the same phase, giving a σ-orbital. In other words, the orbital is symmetric with respect to rotation of arbitrary angle (wrt = with respect to). The center of mass is coincident with the B-atom nucleus. Inversion through the center of mass gives a change in sign. There are nodes on either side of the central atom, resulting in net anti-bonding character, giving the orbital as σ_u.



$-p_{xF1} + p_{x,B2} - p_{xF3}$

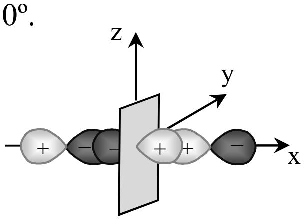
symmetric wrt rotation

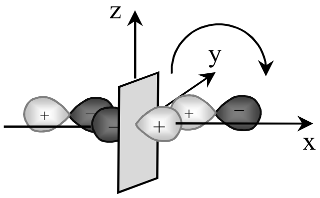


antisymmetric wrt inversion

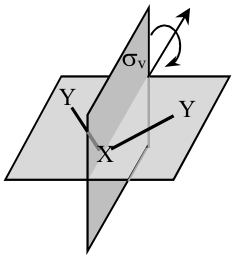
and overall bonding gives σ_u

Bent symmetry operations: Picture the molecule as it bends in the x-y plane, as shown below. The rotation axis, or symmetry axis, is the y-axis for this original orientation. Rotation around the y-axis of 180° inverts the phase of the molecular orbital, giving a b-orbital. See the symmetry table in Figure 26.6.4. In other words, the orbital is antisymmetric with respect to rotation by 180°.





antisymmetric wrt rotation and reflection



Reflection across the plane passing through the B-nucleus and bisecting the internuclear axes is antisymmetric, giving the final symmetry as b_2.

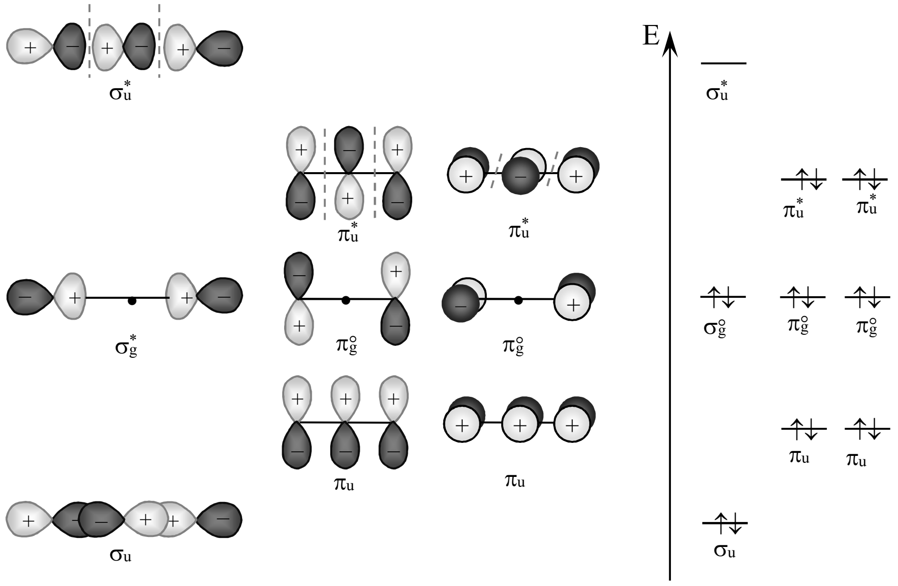
Molecules are assigned to symmetry groups on the basis of their symmetry operations. The symmetry group of a symmetrical bent molecule is called C_2v. The symmetry operations are rotation about the symmetry axis by 180° and reflection across the vertical plane that bisects the molecule. You might wonder about the inversion operation for a bent molecule. A C_{2v} molecule does not have an inversion center: the molecule is not centro-symmetric. An inversion operation does not apply to the C_{2v} case. The symmetry group for a symmetric linear triatomic is $D_{\infty h}$.

24. Sketch the qualitative molecular orbital diagram for I_3^-. The ion is linear and symmetric. Assume the valence 5s-orbitals are sufficiently lower in energy than the valence 5p-orbitals that the valence 5s-orbitals form an inner core set. Combine the valence p-orbitals to give the MO diagram. Characterize the molecular orbitals as σ or π, g or u. Characterize the molecular orbitals as overall bonding, non-bonding, or anti-bonding. Determine the electron filling and calculate the overall bond order. Characterize the bond order of each separate I–I bond. Halogens rarely form double bonds, especially as the atom radius increases. Does your MO diagram agree with this expectation? Determine the primary MOs that determine the bond order. Compare your MO

diagram to the MO diagram for [F–H–F]$^-$; explain the stability of I_3^- in terms of the pattern of MO formation.

Answer: The plan is to combine the $5p_x$, $5p_y$, and $5p_z$-orbitals on each atom to give 12 molecular orbitals that follow the symmetry of the molecule; that is, have the same character, bonding or anti-bonding, on either side of the central I-atom.

The tri-iodide ion, I_3^-, is an electron excess ion. You can think of the ion as the complex between I^- and I_2, both of which are closed shell. The 5s-orbitals on each atom give a completely filled, low energy, net non-bonding set of molecular orbitals: a bonding, non-bonding, and anti-bonding set: ○○○, ○–●, and ○●○. As a consequence the 5s-orbitals do not contribute to the bonding and we omit these MOs from the diagram. Counting only p-electrons and including the negative charge gives 3(5) + 1 = 16 electrons. We align the nuclei along the x-axis. The p_x-orbitals on each atom give a σ-set of molecular orbitals: a bonding, non-bonding, and anti-bonding set: ○● ●○○●, ●○–●○, and ○●○●○●. The most bonding π_u-orbital results from the constructive all-in-phase overlap of the p_z-orbitals, $\overset{\circ}{\bullet}\overset{\circ}{\bullet}\overset{\circ}{\bullet}$. The most anti-bonding π_u^*-orbital results from alternating phases for the p_z orbitals, $\overset{\circ}{\bullet}\overset{\bullet}{\circ}\overset{\circ}{\bullet}$.



[I——I——I]$^-$

Flipping the phase of the outer orbital gives a π_g° non-bonding orbital along the z-axis. The p_y-orbitals overlap to give a corresponding π bonding, non-bonding, and anti-bonding set, which is perpendicular to the p_z-set. The eight pairs of electrons fill through the π-anti-bonding orbitals.

The overall bond order is (6 – 4)/2 = 1. The bond order of each separate I–I bond is ½. However, the net π-bond order is zero. There are as many π-bonding as π-anti-bonding electrons. Tri-iodide ion follows the expectation that halogens don't π-bond. The reason is that since the halogens are in group seven, the seven valence electrons are usually sufficient to fill the π-bonding and π-anti-bonding orbitals, giving a net π-bond order of zero. The primary MOs that determine the bond order are the σ-orbitals, just as in [F-H-F]$^-$, Figure 26.9.1. The stability of I_3^-

is determined by the ability to put electrons in a non-bonding σ-orbital, which while not adding to the stability does not detract from the stability.

Note that we could have simply used Figure 26.6.9, but building the molecular orbitals from scratch using only p-orbitals is instructive. The σ_g° in this model will not end up being degenerate with the π_g° non-bonding orbitals in careful calculations. However, because of the low energy of the 5s-orbital compared to the 5p-orbital for I-atoms, the σ_g° orbital will remain rather non-bonding in character, instead of the predominately anti-bonding character of $5\sigma_g^*$ in carbon dioxide or linear ozone.

25. Bent's Rule states that an atom directs hybrids of greater p character toward more electronegative atoms.[3,4] Consider linear HCN. The C atom sp hybrid that overlaps with the N is expected to have higher p character than the C atom hybrid that overlaps with the H. The hybrid orbital on C that overlaps with the orbital on N is given by $\Psi_{sp,1} = 0.698\ s_C + 0.716\ p_{x,C}$, which is a $sp^{1.05}$ hybrid. Find the second hybrid orbital on carbon, $\Psi_{sp,2}$, which also forms from the s orbital and the p_x orbital. Is the second hybrid $s^{1.05}p$?

Answer: The plan is to note that the set of hybrids for an atom are normalized and orthogonal:

$$\int \Psi^*_{sp,1}\Psi_{sp,1}\, d\tau = \int \Psi^2_{sp,1}\, d\tau = 1 \qquad \text{and} \qquad \int \Psi^*_{sp,1}\Psi_{sp,2}\, d\tau = \int \Psi_{sp,1}\Psi_{sp,2}\, d\tau = 0 \qquad 1$$

For hybrids, $\Psi_{sp,1} = c_{s,1}\ s + c_{p,1}\ p_x$ and $\Psi_{sp,2} = c_{s,2}\ s + c_{p,2}\ p_x$, normalization gives:

$$\begin{aligned}\int \Psi^2_{sp,2}\, d\tau &= \int (c_{s,2}\ s + c_{p,2}\ p_x)^2\, d\tau = c^2_{s,2} \int s^2\, d\tau + c^2_{p,2} \int p^2_x\, d\tau + 2\ c_{s,2}\ c_{p,2} \int s\ p_x\, d\tau \\ &= c^2_{s,2} + c^2_{p,2} = 1 \qquad 2\end{aligned}$$

because the atomic orbitals are normalized and orthogonal, $\int s^2\, d\tau = 1$, $\int p^2_x\, d\tau = 1$, $\int s\ p_x\, d\tau = 0$. Orthogonality requires:

$$\begin{aligned}\int \Psi_{sp,1}\Psi_{sp,2}\, d\tau &= \int (c_{s,1}\ s + c_{p,1}\ p_x)\ (c_{s,2}\ s + c_{p,2}\ p_x)\, d\tau \\ &= c_{s,1}\ c_{s,2} \int s^2\, d\tau + c_{p,1}\ c_{p,2} \int p^2_x\, d\tau + c_{s,1}\ c_{p,2} \int s\ p_x\, d\tau + c_{p,1}\ c_{s,2} \int s\ p_x\, d\tau \\ &= c_{s,1}\ c_{s,2} + c_{p,1}\ c_{p,2} = 0 \qquad 3\end{aligned}$$

Solving Eq. 3 for $c_{p,2}$ gives:

$$c_{p,2} = -\frac{c_{s,1}\ c_{s,2}}{c_{p,1}} \qquad 4$$

Substituting Eq. 4 into Eq. 2 and solving for $c_{s,2}$ gives:

$$c^2_{s,2} = \frac{1}{1 + \dfrac{c^2_{s,1}}{c^2_{p,1}}} = \frac{c^2_{p,1}}{c^2_{s,1} + c^2_{p,1}} \qquad 5$$

Eq. 4 is then used to solve for $c_{p,2}$ or alternately, normality Eq. 2 gives: $c^2_{p,2} = 1 - c^2_{s,2}$. From Eq. 5:

$$c^2_{s,2} = \frac{c^2_{p,1}}{c^2_{s,1} + c^2_{p,1}} = \frac{0.716^2}{0.698^2 + 0.716^2} = 0.512 \qquad \text{or} \quad c_{s,2} = 0.716$$

and normality gives: $c^2_{p,2} = 1 - c^2_{s,2} = 1 - 0.512$ or $c_{p,2} = \sqrt{0.488} = \pm 0.698$

The negative root is necessary to fulfill orthogonality giving: $\Psi_{sp,2} = 0.716\ s_C - 0.698\ p_{x,C}$. The corresponding s character in the hybrid is determined by the ratio of the squared coefficients:

$$\text{relative s-character} = c^2_{s,2}/c^2_{p,2} = 0.512/0.488 = 1.05$$

which corresponds to $s^{1.05}p$ hybridization as expected.

26. Give the hybridization, in the form sp^α, and show that the orbital is normalized for the hybrid orbital:

$$\Psi_{sp\alpha,a} = 0.563\ s + 0.826\ p_x$$

Answer: The plan is to note that the corresponding p-character in the hybrid is determined by the ratio of the squared coefficients, $c^2_{px,a}/c^2_{s,a}$, with the hybrid represented as $\Psi_{sp\alpha,i} = c_{s,i}\ s + c_{px,i}\ p_x$.

A few examples are useful at first.

An sp-hybridized orbital is $\Psi_{sp,a} = {}^1/\sqrt{2}\ (s + p_x)$ giving:

$$c^2_{px,a}/c^2_{s,a} = 1$$

An sp^2-hybridized orbital is $\Psi_{sp^2,a} = \frac{1}{\sqrt{3}}\ s + \frac{\sqrt{2}}{\sqrt{3}}\ p_x$ giving:

$$c^2_{px,a}/c^2_{s,a} = 0.6666/0.3333 = 2$$

For the second sp^2-hybrid $\Psi_{sp^2,b} = \frac{1}{\sqrt{3}}\ s - \frac{1}{\sqrt{6}}\ p_x + \frac{1}{\sqrt{2}}\ p_y$, we need to sum over the p-coefficients:

$$\sum c^2_{p,b}/c^2_{s,b} = (c^2_{px,b} + c^2_{py,b})/c^2_{s,b} = [.1667+0.5000]/0.3333 = 0.6667/0.3333 = 2$$

An sp^3-hybridized orbital is $\Psi_{sp^3,a} = \frac{1}{2}\ (s + p_x + p_y + p_z)$ giving:

$$\sum c^2_{p,a}/c^2_{s,a} = (c^2_{px,a} + c^2_{py,a} + c^2_{pz,a})/c^2_{s,a} = [(\tfrac{1}{2})^2+(\tfrac{1}{2})^2+(\tfrac{1}{2})^2]/(\tfrac{1}{2})^2 = 0.75/0.25 = 3$$

The ratio for this problem is: $c^2_{px,a}/c^2_{s,a} = (0.826)^2/(0.563)^2 = 2.15$

The hybridization is $sp^{2.15}$.

The normalization is:

$$\begin{aligned}\int \Psi^2_{sp\alpha,a}\ d\tau &= \int (0.563\ s + 0.826\ p_x)^2\ d\tau \\ &= (0.563)^2 \int s^2\ d\tau + (0.826)^2 \int p_x^2\ d\tau + 2\ (0.563)\ (0.826) \int s\ p_x\ d\tau \\ &= (0.563)^2 + (0.826)^2 = 1\end{aligned}$$

where $\int s^2\ d\tau = \int p_x^2\ d\tau = 1$ and $\int s\ p_x\ d\tau = 0$ because the original atomic orbitals are orthonormal.

27. Calculate the bond angle in sp^3 hybridization.

Answer: The plan to follow Example 26.7.1.

The dot-product of two vectors is related to the angle between the two vectors by:

$\vec{u} \cdot \vec{v} = |u|\,|v| \cos\theta$. The direction-vectors representing $\Psi_{sp^3,a}$ and $\Psi_{sp^3,b}$ are (½,½,½) and (-½,½,-½), respectively. The lengths are equal: $|½,½,½| = \sqrt{(½)^2 + (½)^2 + (½)^2} = 0.8660$, and the dot-product is:

$$\begin{aligned}
&(½,½,½) \cdot (-½,½,-½) = |0.8660|\,|0.8660| \cos\theta \\
&-0.25 + 0.25 - 0.25 = 0.7500 \cos\theta \\
&-0.25 = 0.75 \cos\theta
\end{aligned}$$

giving: $\cos\theta = -0.3333$ or 109.471°.

28. An sp^2 hybrid orbital oriented along the y-axis is given below. Find the two remaining sp^2 hybrids in the x-y plane. [Hint: Represent the hybrids $\Psi_{sp^2,i} = c_{s,i}\, s + c_{px,i}\, p_x + c_{py,i}\, p_y$. Solve for the ratio of the coefficients $r_{k,i} = c_{k,i}/c_{s,i}$ using orthogonality and then use normalization to find the final values.]

$$\Psi_{sp^2,1} = \frac{1}{\sqrt{3}}\, s + \frac{\sqrt{2}}{\sqrt{3}}\, p_y$$

Answer: The plan is to note that the set of hybrids for an atom are normalized and orthogonal:

$$\int \Psi^*_{sp^2,i}\Psi_{sp^2,i}\, d\tau = \int \Psi^2_{sp,i}\, d\tau = 1 \qquad \text{and} \qquad \int \Psi^*_{sp^2,i}\Psi_{sp^2,j}\, d\tau = \int \Psi_{sp^2,i}\Psi_{sp^2,j}\, d\tau = 0 \qquad 1$$

For the hybrids, $\Psi_{sp^2,i} = c_{s,i}\, s + c_{px,i}\, p_x + c_{py,i}\, p_y$, normalization gives:

$$\begin{aligned}
\int \Psi^2_{sp^2,i}\, d\tau &= \int (c_{s,i}\, s + c_{px,i}\, p_x + c_{py,i}\, p_y)^2\, d\tau \\
&= c^2_{s,i} \int s^2\, d\tau + c^2_{px,i} \int p_x^2\, d\tau + c^2_{py,i} \int p_y^2\, d\tau + \\
&\qquad 2\, c_{s,i}\, c_{px,i} \int s\, p_x\, d\tau + 2\, c_{s,i}\, c_{py,i} \int s\, p_y\, d\tau + 2\, c_{px,i}\, c_{py,i} \int p_x\, p_y\, d\tau \\
&= c^2_{s,i} + c^2_{px,i} + c^2_{py,i} = 1 \qquad 2
\end{aligned}$$

because the atomic orbitals are normalized and orthogonal, $\int s^2\, d\tau = \int p_x^2\, d\tau = \int p_y^2\, d\tau = 1$ and $\int s\, p_x\, d\tau = \int s\, p_y\, d\tau = \int p_x\, p_y\, d\tau = 0$. Orthogonality requires for each pair of orbitals:

$$\begin{aligned}
\int \Psi_{sp^2,i}\Psi_{sp^2,j}\, d\tau &= \int (c_{s,i}\, s + c_{px,i}\, p_x + c_{py,i}\, p_y)\,(c_{s,j}\, s + c_{px,j}\, p_x + c_{py,j}\, p_y)\, d\tau \\
&= c_{s,i}\, c_{s,j} \int s^2\, d\tau + c_{px,i}\, c_{px,j} \int p_x^2\, d\tau + c_{py,i}\, c_{py,j} \int p_x^2\, d\tau + \\
&\quad c_{s,i}\, c_{px,j} \int s\, p_x\, d\tau + c_{s,i}\, c_{py,j} \int s\, p_x\, d\tau + c_{px,i}\, c_{s,j} \int s\, p_x\, d\tau + c_{px,i}\, c_{py,j} \int s\, p_x\, d\tau + \\
&\quad c_{py,i}\, c_{s,j} \int s\, p_x\, d\tau + c_{py,i}\, c_{px,j} \int s\, p_x\, d\tau \\
&= c_{s,i}\, c_{s,j} + c_{px,i}\, c_{px,j} + c_{py,i}\, c_{py,j} = 0 \qquad 3
\end{aligned}$$

The cross terms for different atomic orbitals vanish from orthogonality. Eq. 3 is most easily solved by finding the ratio of the coefficients. Defining the ratio as $r_{k,i} = c_{k,i}/c_{s,i}$ Eqs. 2 and 3 become:

$$c^2_{s,i}\,(1 + r^2_{px,i} + r^2_{py,i}) = 1 \qquad 4$$

$$c_{s,i}\, c_{s,j}\,(1 + r_{px,i}\, r_{px,j} + r_{py,i}\, r_{py,j}) = 0 \qquad 5$$

and then dividing Eq. 5 by $c_{s,i}\, c_{s,j}$ gives the orthogonality relationships as:

$$1 + r_{px,i}\, r_{px,j} + r_{py,i}\, r_{py,j} = 0 \tag{6}$$

For the complete set of three hybrids:

$$\begin{aligned} 1 + r_{px,1}\, r_{px,2} + r_{py,1}\, r_{py,2} &= 0 \\ 1 + r_{px,1}\, r_{px,3} + r_{py,1}\, r_{py,3} &= 0 \\ 1 + r_{px,2}\, r_{px,3} + r_{py,2}\, r_{py,3} &= 0 \end{aligned} \tag{7}$$

For the first hybrid as given in the problem statement:

$$r_{2px,1} = c_{2px,1}/c_{s,1} = 0 \quad \text{and} \quad r_{2py,1} = c_{2py,1}/c_{s,1} = \sqrt{2} \qquad \text{giving:} \tag{8}$$

$$1 + \sqrt{2}\, r_{py,2} = 0 \qquad \text{or} \qquad r_{py,2} = -\,1/\sqrt{2} \tag{9}$$

$$1 + \sqrt{2}\, r_{py,3} = 0 \qquad \text{or} \qquad r_{py,3} = -\,1/\sqrt{2} \tag{10}$$

$$1 + r_{px,2}\, r_{px,3} + r_{py,2}\, r_{py,3} = 1 + r_{px,2}\, r_{px,3} + \frac{1}{2} = r_{px,2}\, r_{px,3} + \frac{3}{2} = 0 \tag{11}$$

From Eqs. 9 and 10, hybrid orbitals 2 and 3 have the same percentage s and p_y character, so they should also have equal p_x character. The hybrids are equivalent in the amount of p character and differ only in the orientation, which gives $r_{px,2}\, r_{px,3} = \pm\, r_{px,2}^2$ and then Eq. 11 can be solved for $r_{px,2}$:

$$r_{px,2}\, r_{px,3} + \frac{3}{2} = \pm\, r_{px,2}^2 + \frac{3}{2} = 0 \qquad \text{or} \quad r_{px,2} = \frac{\sqrt{3}}{\sqrt{2}} \tag{12}$$

Only the negative choice for $\pm\, r_{px,2}^2$ gives a valid solution, with the result that $r_{px,2}$ and $r_{px,3}$ are opposite in sign, $r_{px,3} = -\, r_{px,2} = -\,\sqrt{3}/\sqrt{2}$. The final coefficients are then obtained by normalization using Eq. 4:

$$c_{s,i}^2 + c_{px,i}^2 + c_{py,i}^2 = c_{s,i}^2\,(1 + r_{px,i}^2 + r_{py,i}^2) = 1 \tag{13}$$

for each hybrid:

$$\begin{aligned} &c_{s,2}^2\,(1 + r_{px,2}^2 + r_{py,2}^2) = 1 \qquad \text{giving } c_{s,2}^2\,(1 + {}^3\!/_2 + {}^1\!/_2) = 1 \\ &c_{s,3}^2\,(1 + r_{px,3}^2 + r_{py,3}^2) = 1 \qquad \text{giving } c_{s,3}^2\,(1 + {}^3\!/_2 + {}^1\!/_2) = 1 \qquad \text{or} \quad c_{s,2} = c_{s,3} = 1/\sqrt{3} \end{aligned}$$

Finally from the coefficient ratios: $c_{2px,2} = c_{s,2}\, r_{px,2} = \dfrac{1}{\sqrt{3}}\dfrac{\sqrt{3}}{\sqrt{2}} = \dfrac{1}{\sqrt{2}}$ 14

$$c_{2py,2} = c_{s,2}\, r_{py,2} = -\frac{1}{\sqrt{3}}\frac{1}{\sqrt{2}} = -\frac{1}{\sqrt{6}} \tag{15}$$

The final set of hybrids is:

$$\Psi_{sp^2,1} = \frac{1}{\sqrt{3}}\, s + \frac{\sqrt{2}}{\sqrt{3}}\, p_y \tag{16}$$

$$\Psi_{sp^2,2} = \frac{1}{\sqrt{3}}\, s + \frac{1}{\sqrt{2}}\, p_x - \frac{1}{\sqrt{6}}\, p_y \tag{17}$$

$$\Psi_{sp^2,3} = \frac{1}{\sqrt{3}}\, s - \frac{1}{\sqrt{2}}\, p_x - \frac{1}{\sqrt{6}}\, p_y \tag{18}$$

29. One model for $Zn(CN)_4$ is to use sd^3 hybridization. Use VSEPR rules to determine the shape of $Zn(CN)_4$. Which d-orbitals on Zn are used to form sd^3 hybrids.

Answer: The d-orbital based sd^3 hybridization is tetrahedral, just as in sp^3 hybridization. In other words, mixing four atomic orbitals on the central atom results in four hybrid atomic orbitals that are equivalent in energy, shape, and size. The orbitals differ only in direction. VSEPR rules give the relative orientation of the four hybrids that minimizes electron-electron repulsions as tetrahedral. The molecular geometry of $Zn(CN)_4$ is then tetrahedral. The d-orbitals that combine to give sd^3 hybrids are the d_{xy}, d_{yz}, and d_{xz} orbitals.

30. (a). Use the enthalpies of vaporization and formation in Tables 8.1.1 and 8.4.2 for benzene and cyclohexene to calculate the value of the Hückel $C(2p_z)–C(2p_z)$ resonance integral, β. (b). Repeat the calculation with 1,3-butadiene. Compare the two values for β.

Answer: Using historical values, the π-delocalization energy of benzene is given by comparison of enthalpy of hydrogenation of benzene to the hydrogenation of three moles of cyclohexene (Eq. 26.8.20):

$$\pi\text{-DE} = \underbrace{[-206.0 \text{ kJ mol}^{-1}]}_{\textit{benzene}} - \underbrace{[3(-118.4 \text{ kJ mol}^{-1})]}_{\textit{3(cyclohexene)}} = 149.2 \text{ kJ mol}^{-1} = |2\beta|$$

giving $\beta \cong -75 \text{ kJ mol}^{-1}$.

(a). Using Tables 8.1.1 and 8.4.2 at 298.15 K, the enthalpy of formation of gaseous cyclohexane is: $\Delta_f H^o(g) = \Delta_f H^o(l) + \Delta_{vap} H^o = -156.4 + 33.01 \text{ kJ mol}^{-1} = -123.4 \text{ kJ mol}^{-1}$. The current values for the enthalpies of formation of gaseous benzene and cyclohexene give the enthalpies of hydrogenation as:

$$\begin{array}{llll} & C_6H_6\,(g) + & 3\,H_2\,(g) \rightarrow & C_6H_{12}\,(g) \\ \Delta_f H^o & 82.6 & 0 & -123.4 \text{ kJ mol}^{-1} \end{array}$$

$$\Delta_{hyd} H^o(\text{benzene}) = [-123.4 \text{ kJ mol}^{-1}] - [82.6 \text{ kJ mol}^{-1}] = -206.0 \text{ kJ mol}^{-1}$$

$$\begin{array}{llll} & C_6H_{10}\,(g) + & H_2\,(g) \rightarrow & C_6H_{12}\,(g) \\ \Delta_f H^o & -38.5 & 0 & -123.4 \text{ kJ mol}^{-1} \end{array}$$

$$\Delta_{hyd} H^o(\text{cyclohexene}) = [-123.4 \text{ kJ mol}^{-1}] - [-38.5 \text{ kJ mol}^{-1}] = -84.9 \text{ kJ mol}^{-1}$$

and the corresponding value of the π-delocalization energy and β as:

$$\pi\text{-DE} = [-206.0 \text{ kJ mol}^{-1}] - [3(-84.9 \text{ kJ mol}^{-1})] = 48.7 \text{ kJ mol}^{-1} \text{ and } \beta \cong -24.4 \text{ kJ mol}^{-1}$$

(b). Using Table 8.4.2, at 298.15 K, the enthalpies of formation of gaseous 1,3-butadiene and 1-butene give the enthalpies of hydrogenation as:

$$\begin{array}{llll} & C_4H_6\,(g) + & 2\,H_2\,(g) \rightarrow & C_4H_{10}\,(g) \\ \Delta_f H^o & 108.8 & 0 & -125.6 \text{ kJ mol}^{-1} \end{array}$$

$$\Delta_{hyd} H^o(\text{butadiene}) = [-125.6 \text{ kJ mol}^{-1}] - [108.8 \text{ kJ mol}^{-1}] = -234.4 \text{ kJ mol}^{-1}$$

$$\begin{array}{llll} & C_4H_8\,(g) + & H_2\,(g) \rightarrow & C_4H_{10}\,(g) \\ \Delta_f H^\circ & 0.1 & 0 & -125.6\ \text{kJ mol}^{-1} \end{array}$$

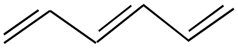
$$\Delta_{hyd}H^\circ(\text{butene}) = [-125.6\ \text{kJ mol}^{-1}] - [0.1\ \text{kJ mol}^{-1}] = -125.7\ \text{kJ mol}^{-1}$$

and the corresponding value of the π-delocalization energy and β as:

$$\pi\text{-DE} = [-234.4\ \text{kJ mol}^{-1}] - [2(-125.7\ \text{kJ mol}^{-1})] = 17.0\ \text{kJ mol}^{-1} \quad \text{and} \quad \beta \cong -8.5\ \text{kJ mol}^{-1}$$

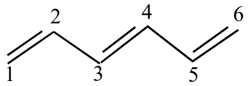
Both values for β are considerably smaller than the commonly quoted value. The discrepancy is in many ways immaterial, since more accurate methods are easily implemented. The usefulness of Hückel molecular orbital theory is to build chemical intuition.

31. Use Hückel molecular orbital theory to determine the molecular orbitals and energies for 1,3,5-hexatriene:



(a). Give the Hückel determinant in terms of x's and 1's:
(b). Determine the energies and the orbital coefficients using a matrix diagonalization program. The "eigen" applet to diagonalize a matrix is available on the text book Web site or companion CD. MatLab or Mathematica are also useful.
(c). Sketch the orbitals with the appropriate phase for each p_z orbital.
(d). Give the number of nodes in each wave function. Classify each orbital as bonding or anti-bonding.
(e). Draw the energy level diagram. Give the electron filling.
(f). Calculate the π-bond order for each unique bond in the molecule (Eq. 26.8.6).
(g). Calculate the π-bond delocalization energy.
(h). Calculate the π-electron density on any two atoms of your choosing (Eq. 26.8.7).
(i). On the energy level in part (e), indicate the lowest energy electronic transition with a vertical arrow. Label the HOMO and LUMO.

Answer: The atom numbering is arbitrary. The atom assignments chosen are:



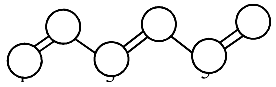
(1).The Hückel determinant in terms of x's and 1's is:

$$\begin{array}{c|cccccc} \textit{Atom} & 1 & 2 & 3 & 4 & 5 & 6 \\ 1 & -x & 1 & 0 & 0 & 0 & 0 \\ 2 & 1 & -x & 1 & 0 & 0 & 0 \\ 3 & 0 & 1 & -x & 1 & 0 & 0 \\ 4 & 0 & 0 & 1 & -x & 1 & 0 \\ 5 & 0 & 0 & 0 & 1 & -x & 1 \\ 6 & 0 & 0 & 0 & 0 & 1 & -x \end{array} = 0 \qquad E_i = \alpha + x_i\,\beta \quad \text{with } x_i \text{ the eigenvalues}$$

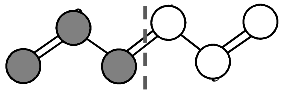
(2). The energies and the orbital coefficients using a matrix diagonalization program are:

```
Eigenvector 1: Eigenvalue=1.80194
0.231921
0.417907
0.521121
0.521121
0.417907
0.231921
-------------
Eigenvector 2: Eigenvalue=1.24698
-0.417907
-0.521121
-0.231921
0.231921
0.521121
0.417907
-------------
Eigenvector 3: Eigenvalue=0.445042
0.521121
0.231921
-0.417907
-0.417907
0.231921
0.521121
-------------
Eigenvector 4: Eigenvalue=-0.445042
-0.521121
0.231921
0.417907
-0.417907
-0.231921
0.521121
-------------
Eigenvector 5: Eigenvalue=-1.24698
-0.417907
0.521121
-0.231921
-0.231921
0.521121
-0.417907
-------------
Eigenvector 6: Eigenvalue=-1.80194
0.231921
-0.417907
0.521121
-0.521121
0.417907
-0.231921
```

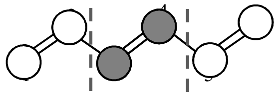
(3). Sketches of the orbitals with the appropriate phase for each p orbital are:



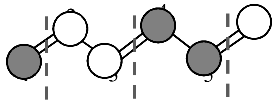
MO1.



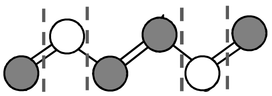
MO2.



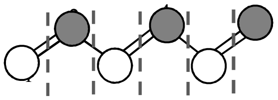
MO3.



MO4.



MO5.

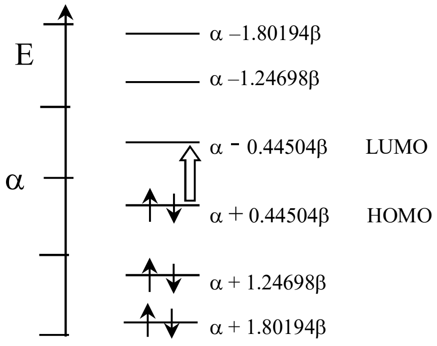


MO6.

(4). The nodes in the wavefunctions are shown by dotted lines in the sketches, above. The number of nodes in each wave function and the overall bonding or anti-bonding character are:

MO1: 0 nodes-bonding; MO2: 1 node-bonding; MO3: 2 nodes-three bonding interactions and two anti-bonding interactions, so net bonding; MO4: 3 nodes-two bonding interactions and three anti-bonding interactions, so net anti-bonding; MO5: 4-anti-bonding; MO6: 5 nodes-completely anti-bonding

(5). The energy level diagram, electron filling, HOMO, LUMO, and lowest energy electronic transition are:



(6). The π-bond order for each unique bond in the molecule is: $P_{ij} = \sum_k n_k\, c_{ki}\, c_{kj}$

$$P_{12} = 2(0.231921)(0.417907) + 2(-0.417907)(-0.521121) + 2(0.521121)(0.231921) = 0.871$$

$$P_{23} = 2(0.\,417907)(0.521121) + 2(-0.521121)(-0.231921) + 2(0.231921)(-0.417907) = 0.483$$

$$P_{34} = 2(0.521121)(0.521121) + 2(-0.231921)(0.231921) + 2(-0.417907)(-0.417907) = 0.785$$

The total π-bond order is 2(0.871) + 2(0.483) + 0.785 = 3.493 showing the effect of conjugation.

(7). The total π-bond energy is:

$$E_{tot} = 2(\alpha + 1.80194\beta) + 2(\alpha + 1.24698\beta) + 2(\alpha + 0.445042\beta) = 6\alpha + 6.9879\beta$$

As the localized reference, each isolated double bond with two electrons has an energy of $E = 2\alpha + 2\beta$. There are three isolated double bond equivalents, so the localized reference energy is $3(2\alpha + 2\beta)$, giving the pi bond delocalization energy as:

$$\pi DE = (6\alpha + 6.9879\beta) - (6\alpha + 6\beta) = 0.9879\ \beta.$$

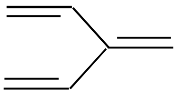
The α part always cancels out.

(8). The π-electron density on each unique atom is: $d_i = \sum_k n_k\, c_{ki}^2$

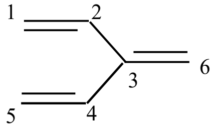
$$d_1 = 2(0.231921)^2 + 2(-0.417907)^2 + 2(0.521121)^2 = 1$$
$$d_2 = 2(0.417907)^2 + 2(-0.521121)^2 + 2(0.231921)^2 = 1$$
$$d_3 = 2(0.521121)^2 + 2(-0.231921)^2 + 2(-0.417907)^2 = 1$$

(9). The HOMO, LUMO, and lowest energy electronic transition are shown in the energy level diagram in part (5).

32. Answer the questions listed in Problem 31 for 3-vinyl-1,3-butadiene:



Answer: The atom numbering is arbitrary. The atom assignments chosen are:



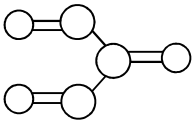
(1). The Hückel determinant in terms of x's and 1's is:

$$\begin{array}{cc} \text{Atom} & \begin{array}{cccccc} 1 & 2 & 3 & 4 & 5 & 6 \end{array} \\ \begin{array}{c} 1 \\ 2 \\ 3 \\ 4 \\ 5 \\ 6 \end{array} & \begin{pmatrix} -x & 1 & 0 & 0 & 0 & 0 \\ 1 & -x & 1 & 0 & 0 & 0 \\ 0 & 1 & -x & 1 & 0 & 1 \\ 0 & 0 & 1 & -x & 1 & 0 \\ 0 & 0 & 0 & 1 & -x & 0 \\ 0 & 0 & 1 & 0 & 0 & -x \end{pmatrix} = 0 \end{array} \qquad E_i = \alpha + x_i\,\beta \quad \text{with } x_i \text{ the eigenvalues}$$

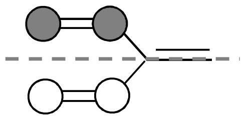
(2). The energies and the orbital coefficients using a matrix diagonalization program are:

```
Eigenvector 1: Eigenvalue=1.93185
0.22985
0.444037
0.627963
0.444037
0.22985
0.325058
-------------
Eigenvector 2: Eigenvalue=1
-0.5
-0.5
0
0.5
0.5
0
-------------
Eigenvector 3: Eigenvalue=0.517638
0.444037
0.22985
-0.325058
0.22985
0.444037
-0.627963
-------------
Eigenvector 4: Eigenvalue=-0.517638
0.444037
-0.22985
-0.325058
-0.22985
0.444037
0.627963
-------------
Eigenvector 5: Eigenvalue=-1
-0.5
0.5
0
-0.5
0.5
0
-------------
Eigenvector 6: Eigenvalue=-1.93185
0.22985
-0.444037
0.627963
-0.444037
0.22985
-0.325058
```

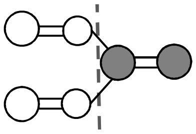
(3). Sketches of the orbitals with the appropriate phase for each p orbital are:



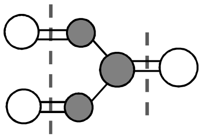
MO1.



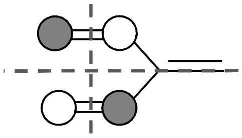
MO2.



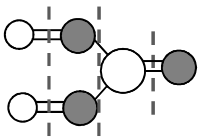
MO3.



MO4.



MO5.

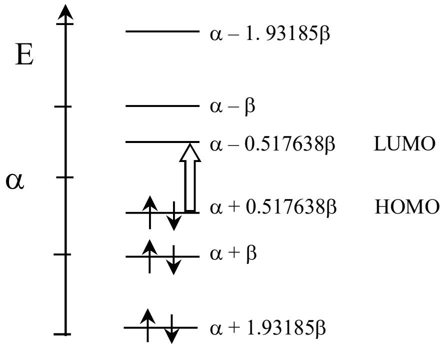


MO6.

(4). The nodes in the wavefunctions are shown by dotted lines in the sketches, above. The number of nodes in each wave function and the overall bonding or anti-bonding character are:

See diagrams above for the nodes: MO1: 0 nodes-bonding; MO2: 1 node-two bonding interactions and no anti-bonding interactions, so net bonding; MO3: 1 node-three bonding interactions and two anti-bonding interactions, so net bonding; MO4: 2 nodes-two bonding interactions and three anti-bonding interactions, so net anti-bonding; MO5: 2 nodes-anti-bonding; MO6: 3 nodes-completely anti-bonding

(5). The energy level diagram, electron filling, HOMO, LUMO, and lowest energy electronic transition are:



(6). The π-bond order for each unique bond in the molecule is: $P_{ij} = \sum_k n_k\, c_{ki}\, c_{kj}$

$P_{12} = 2(0.22985)(0.444037) + 2(-0.50000)(-0.50000) + 2(0.444037)(0.22985) = 0.908$

$P_{23} = 2(0.444037)(0.627962) + 2(-0.50000)(0) + 2(0.22985)(-0.325058) = 0.408$

$P_{36} = 2(0.627962)(0.325058) + 2(0)(0) + 2(-0.325058)(-0.627963) = 0.816$

The total π-bond order is 2(0.907) + 2(0.354) + 0.816 = 3.338 showing the effect of conjugation.

(7). The total π-bond energy is:

$$E_{tot} = 2(\alpha + 1.93185\beta) + 2(\alpha + 1.00000\beta) + 2(\alpha + 0.517638\beta) = 6\alpha + 6.8990\beta$$

As the localized reference, each isolated double bond with two electrons has an energy of $E = 2\alpha + 2\beta$. There are three isolated double bond equivalents, so the localized reference energy is $3(2\alpha + 2\beta)$, giving the pi bond delocalization energy as:

$$\pi DE = (6\alpha + 6.8990\beta) - (6\alpha + 6\beta) = 0.8990\ \beta.$$

The α part always cancels out.

(8). The π-electron density on each unique atom is: $d_i = \sum_k n_k\ c_{ki}^2$

$$d_1 = 2(0.22985)^2 + 2(-0.50000)^2 + 2(0.444037)^2 = 1$$
$$d_2 = 2(0.444037)^2 + 2(-0.50000)^2 + 2(0.22985)^2 = 1$$
$$d_3 = 2(0.627963)^2 + 2(0)^2 + 2(-0.325058)^2 = 1$$
$$d_6 = 2(0.325058)^2 + 2(0)^2 + 2(-0.627963)^2 = 1$$

(9). The HOMO, LUMO, and lowest energy electronic transition are shown in the energy level diagram in part (5).

33. Heteroatoms are introduced into the HMO matrix using two parameters, h and k. The diagonal element is the Coulomb integral, which for carbon is α. The off-diagonal elements are the resonance integrals, which for directly bonded carbon atoms are β. The diagonal element for a heteroatom is changed to $\alpha + h\ \beta$ and the off-diagonal element for directly bonded atoms is changed to $k\beta$. A table of h and k is given below.

Table P26.1: Hückel Parameters for Heteroatoms.

Atom	Bond Type	π electrons for atom	h	k
C	-C=C-	1	0	1
N	-C=N- (pyridine)	1	0.5	1.0
N	=C-N< (pyrrole)	2	1.5	0.8
N	-N=N- (azo)	1	1.0	1.0
O	-C=O (carbonyl)	1	1.0	1.0
O	=C-O- (furan)	2	2.0	0.8
F	=C-F	2	3.0	0.7
Cl	=C-Cl	2	2.0	0.4
Br	=C-Br	2	1.5	0.3
S	=C-S- (thiophene)	2	1.5	0.8

For example, acrolein, C_A=C_B-C_C=O_D, has four total π-electrons and the lower diagonal elements of the Hückel matrix in the form of Eq. 26.8.16 is:

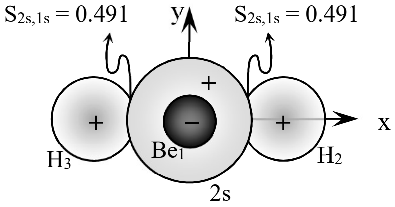
$$\begin{array}{llll} \boxed{0} & & & \\ \boxed{1} & \boxed{0} & & \\ \boxed{0} & \boxed{1} & \boxed{0} & \\ \boxed{0} & \boxed{0} & \boxed{1} & \boxed{\mathbf{1}} \end{array}$$

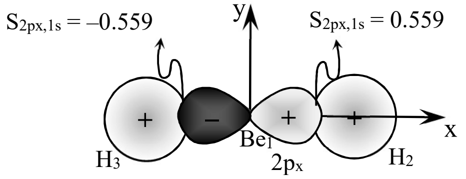
For acrolein:

(a). Give the Hückel determinant in terms of x's and 1's:
(b). Determine the energies and the orbital coefficients using a matrix diagonalization program. The "eigen" applet to diagonalize a matrix is available on the text book Web site or companion CD. MatLab or Mathematica are also useful.
(c). Sketch the orbitals with the appropriate phase for each p_z orbital.
(d). Give the number of nodes in each wave function. Classify each orbital as bonding or anti-bonding.
(e). Draw the energy level diagram. Give the electron filling.
(f). Calculate the π-bond order for each unique bond in the molecule (Eq. 26.8.6).
(g). Calculate the π-bond delocalization energy.
(h). Calculate the π-electron density on any two atoms of your choosing (Eq. 26.8.7).
(i). On the energy level in part (e), indicate the lowest energy electronic transition with a vertical arrow. Label the HOMO and LUMO.

34. Use Hückel molecular orbital theory and the parameters in Table P26.1 to determine the HOMO for vinyl fluoride, CH_2=CH-F. Draw the molecular orbital diagram and show the electron filling. Characterize the HOMO as σ or π, bonding, non-bonding, or anti-bonding. Does the HOMO have predominant character on any one particular atom?

35. Characterize the highest occupied molecular orbital in liner BeH_2. Use extended Hückel theory. Draw the molecular orbital energy diagram and sketch the molecular orbitals. Orient the molecule along the x-axis. Number the Be as atom 1 and the two hydrogens as 2 and 3.The bond length in BeH_2 is 1.330 Å giving the Be(2s)-H(1s) overlap integrals of 0.491 and the Be($2p_x$)-H$(1s)_2$ overlap as 0.559. Notice the change in sign for the H$(1s)_3$-Be($2p_x$) overlap:



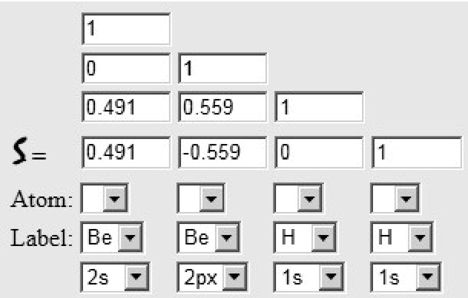


Answer: The plan is to use the "*Secular*" equation applet on the text Web site or companion CD. The VOIEs are Be(2s) -32.3 eV, O($2p_x$, $2p_y$, $2p_z$) -15.9 eV, and H(1s) -13.6. Once the overlap integrals are specified, the resonance integrals are completely determined using Eq. 26.8.22.

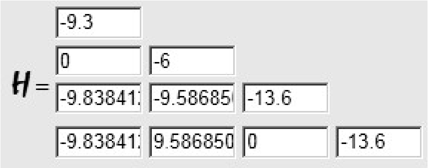
For example, the resonance integral for H(1s)-Be($2p_x$) is given using $K = 1.75$ as:

$$\text{H}(1s)_2\text{- Be}(2p_x)_1: \quad H_{1s,2px} = KS_{ij}\frac{(H_{ii} + H_{jj})}{2} = 1.75(0.559)\frac{(-6.00 + (-13.60))}{2}\ \text{eV} = -9.59\ \text{eV}$$

However, for this problem, we'll cheat and click on the "Generate H" button to have the applet fill in the Hamiltonian matrix automatically, based on the orbital labels. The Be($2p_y$) and Be($2p_z$) orbitals are non-bonding, because the overlap integral with the H-atoms is zero by symmetry. At this low level of approximation, the energies of the $2p_y$ and $2p_z$ are unaffected by the electrons in the σ-molecular orbitals. Because the Be($2p_y$) and Be($2p_z$)–orbitals are non-interacting, we don't need to include them in the secular equations. The input is set-up as follows, using the overlap integrals given in the problem:



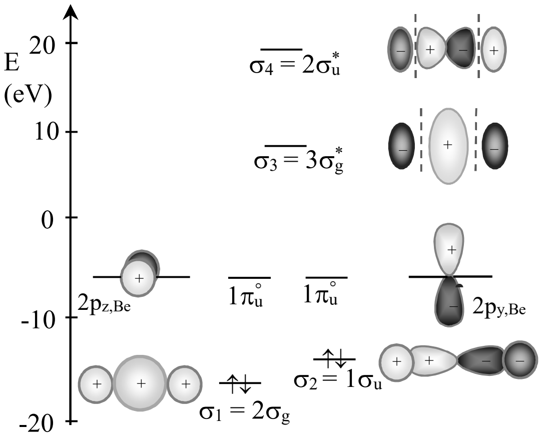
	1			
	0	1		
	0.491	0.559	1	
S =	0.491	-0.559	0	1
Atom:				
Label:	Be	Be	H	H
	2s	2px	1s	1s



	-9.3			
	0	-6		
H =	-9.83841	-9.58685	-13.6	
	-9.83841	9.586850	0	-13.6

The output and corresponding molecular orbital energy diagram are:

```
        Eigenvalues and eigenvectors
_____(eigenvectors listed in columns)_______
E(i)    -15.350   -14.242    8.416   19.208
vector      1         2         3        4
atom:
   Be2s     0.474     0.0       0.744    0.0
   Be2px    0.0      -0.269    -0.0     -0.752
    H1s     0.623    -0.681    -0.472    0.466
    H1s     0.623     0.681    -0.472   -0.466
```



With four valence electrons, the HOMO is orbital 2, which is a σ-bonding orbital ($1\sigma_u$) constructed from the overlap of the H(1s) and Be($2p_x$) orbitals. We added in the non-bonding $2p_y$ and $2p_z$ orbitals on Be to complete the energy level diagram; their energies are given by the unperturbed VOIEs, -6.00 eV. The symmetry designations correspond to Figure 26.6.1. The overall signs of orbitals 2 and 3 are opposite to Figure 26.6.1. However, the change in overall sign of a molecular orbital is immaterial; Ψ^2 and $(-\Psi)^2$ give the same electron distribution. Compare this calculation with Problem 11, which is at the CNDO level.

36. Calculate the Be-H bond order in BeH_2 using the results in the previous problem, at the extended Hückel level of approximation.

Answer: The plan is to note that since BeH_2 is symmetrical, both Be-H bonds are equivalent. Use the Be_1-H_2 bond. The bond order is given by Eq. 26.3.10. The answer is compared to Problem 11%%%.

Using Eq. 26.3.10, there are only two occupied molecular orbitals and each orbital only involves one orbital on the central Be-atom:

$$P_{12} = \sum_{j \text{ on a}} \sum_{k \text{ on b}} \sum_{i=1}^{m} n_i\, 2c_{ij}\, c_{ik}\, S_{jk}$$

$$= 4\, \underbrace{c_{1,2sBe}\, c_{1,1sH}\, S_{2sBe,1sH}}_{MO\ 1} + 4\, \underbrace{c_{2,2pxBe}\, c_{2,1sH}\, S_{2pxBe,1sH}}_{MO2}$$

$$= 4(0.4737)(0.6228)(0.4908) + 4(-0.2688)(-0.68811)(0.5593)$$

$$= 0.5792 + 0.4138 = 0.9930$$

The extended Hückel Mulliken bond order of 0.9930 is significantly smaller than the CNDO bond order of 1.465 from Problem 11. However, the bond order at HF/6-31G** is 0.988 and at B3LYP/6-311G** is 0.971, giving reasonable agreement between the extended Hückel method and the more advanced methods. However, little should be inferred about the accuracy of the extended Hückel method from this rather fortuitous agreement. For extended Hückel calculations the bond order is often approximated, instead, by the Coulson bond order, which is given by:

$$BO_{12} = \sum_{j \text{ on a}} \sum_{k \text{ on b}} \sum_{i=1}^{m} n_i\, c_{ij}\, c_{ik}$$

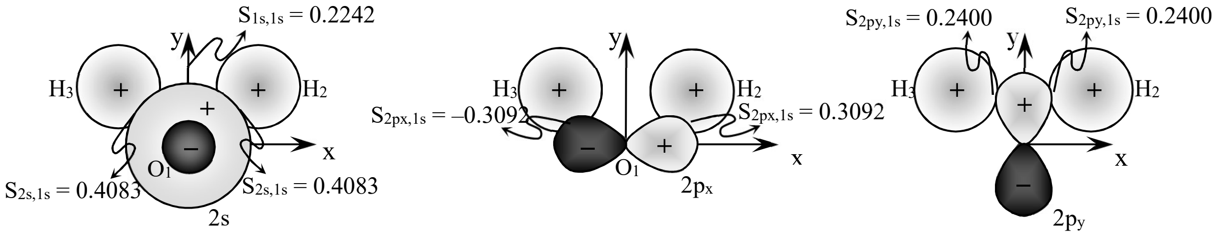
$$= 2\, \underbrace{c_{1,2sBe}\, c_{1,1sH}}_{MO\ 1} + 2\, \underbrace{c_{2,2pxBe}\, c_{2,1sH}}_{MO2}$$

$$= 2(0.4737)(0.6228) + 2(-0.2688)(-0.68811)$$

$$= 0.5900 + 0.3699 = 0.9599$$

The Mulliken overlap population of 0.993 and the Coulson estimate of the bond order both agree with the semi-empirical MNDO bond order of 0.911. While very approximate, the extended Hückel method is easy to apply and tenable for very large systems. Every approximation method has its strengths and weaknesses.

<u>37</u>. Use extended Hückel theory to find the molecular orbital energy diagram for water. Number the oxygen as atom 1 and the two hydrogens as 2 and 3. Orient the molecule in the x-y plane. The overlap integrals for a bond angle and 105° and bond lengths of 0.962 Å are shown below (the overlap between the two hydrogens is $S_{1s,1s} = 0.2242$):

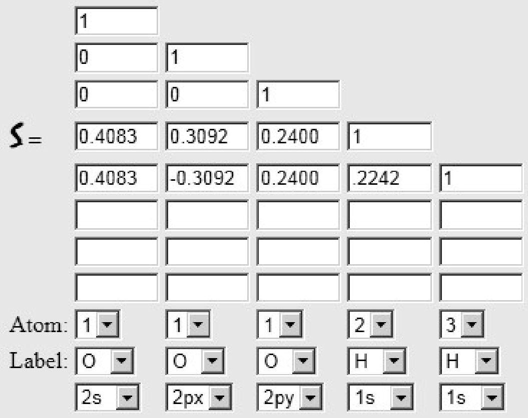


Answer: The plan is to use the "*Secular*" equation applet on the text Web site or companion CD. The VOIEs are O(2s) -32.3 eV, O($2p_x$, $2p_y$, $2p_z$) -15.9 eV, and H(1s) -13.6. Once the overlap integrals are specified, the resonance integrals are completely determined using Eq. 26.8.22.

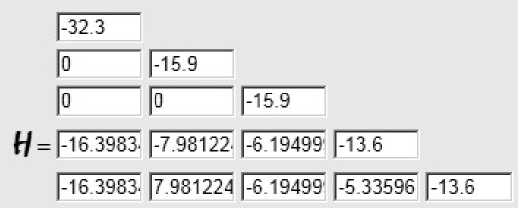
For example, the resonance integral for H(1s)-O($2p_x$) is given using $\kappa = 1.75$ as:

$$H(1s)_2\text{- }O(2p_x)_1: \quad H_{1s,2px} = \kappa S_{ij} \frac{(H_{ii} + H_{jj})}{2} = 1.75(0.3092)\ \frac{(-15.9 + (-13.6))}{2}\ \text{eV} = -7.98\ \text{eV}$$

However, for this problem, we'll cheat and click on the "Generate H" button to have the applet fill in the Hamiltonian matrix automatically, based on the orbital labels. The O($2p_z$) orbital is non-bonding, because the overlap integral with the H-atoms is zero by symmetry. At this low level of approximation, the energy of the $2p_z$ is unaffected by the presence of the electrons in the σ-molecular orbitals. Because the O($2p_z$) –orbital is non-interacting, we don't need to include the $2p_z$ in the secular equations. The input is set-up as follows, using the overlap integrals given in the problem:



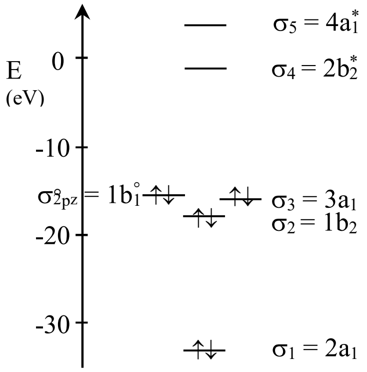
S =	1				
	0	1			
	0	0	1		
	0.4083	0.3092	0.2400	1	
	0.4083	-0.3092	0.2400	.2242	1
Atom:	1	1	1	2	3
Label:	O	O	O	H	H
	2s	2px	2py	1s	1s



H =	-32.3				
	0	-15.9			
	0	0	-15.9		
	-16.3983	-7.98122	-6.19499	-13.6	
	-16.3983	7.981224	-6.19499	-5.33596	-13.6

In terms of looking up the VOIEs, the distinction between $2p_x$, $2p_y$, and $2p_z$ is immaterial. The x, y, and z subscripts are just used to label the output, to make the results easier to read. The results are listed below with the molecular orbital diagram:

```
                   Eigenvalues and eigenvectors
_____________(eigenvectors listed in columns)______________
E(i)   -33.0869  -17.9708  -16.6346   -0.3806    3.0583
vector     1         2         3          4         5
atom:
1  O2s    0.9816   -0.0       0.1952    0.0       0.5312
1  O2px  -0.0       0.856    -0.0       0.5825    0.0
1  O2py  -0.0272   -0.0      -0.9546   -0.0       0.389
2  H1s    0.1337    0.3656   -0.1592   -0.5748   -0.5322
3  H1s    0.1337   -0.3656   -0.1592    0.5748   -0.5322
```



In the MO diagram, we added in the $2p_z$ non-bonding orbital at -15.9 eV, between $\sigma_3$and σ_4. With eight valence electrons, the HOMO is the O($2p_z$) non-bonding orbital. The correspondence of the MOs with the symmetry designations are given in the plot for comparison with Figure 26.6.4. The switch in order of the anti-bonding orbitals is seen in other semi-empirical and HF calculations, depending on bond length and angle. CNDO calculations are more realistic than extended Hückel calculations, but the extended Hückel result is easy to calculate and determines the proper molecular orbital ordering and nodal patterns for this case. Several improvements in the extended Hückel approach are also in common use. We hope that you find the extended Hückel method informative about the inner workings of molecular orbital calculations.

38. Calculate the O-H bond order in water from the extended Hückel calculation in the previous problem.

Answer: Use the O_1-H_2 bond. The bond order is given by Eq. 26.3.10:

$$P_{12} = \sum_{j \text{ on } a}\ \sum_{k \text{ on } b}\ \sum_{i=1}^{m} n_i\, 2c_{ij}\, c_{ik}\, S_{jk}$$

$$= 4\,\underbrace{c_{1,2sO}\, c_{1,1sH}}_{MO\ 1}\, S_{2sO,1sH} + 4\,\underbrace{c_{1,2pyO}\, c_{1,1sH}}_{MO\ 1}\, S_{2py,1sH} + 4\,\underbrace{c_{2,2pxO}\, c_{2,1sH}}_{MO2}\, S_{2pxO,1sH}$$

$$+ 4\,\underbrace{c_{3,2sO}\, c_{3,1sH}}_{MO3}\, S_{2sO,1sH} + 4\,\underbrace{c_{3,2spy}\, c_{3,1sH}}_{MO\ 3}\, S_{2py,1sH}$$

$$= 4(0.982)(0.134)(0.408) + 4(-0.027)(0.134)(0.240) + 4(0.856)(0.366)(0.309)$$
$$+ 4(0.195)(-0.159)(0.408) + 4(-0.955)(-0.159)(0.240)$$

$$= 0.2148 - 0.0035 + 0.3872 - 0.0506 + 0.1458 = 0.6937$$

The extended Hückel bond order of 0.694 is significantly smaller than the CNDO bond order of 1.085. For extended Hückel calculations the bond order is often approximated, instead, by the Coulson bond order:

$$BO_{12} = \sum_{j \text{ on } a}\ \sum_{k \text{ on } b}\ \sum_{i=1}^{m} n_i\, c_{ij}\, c_{ik}$$

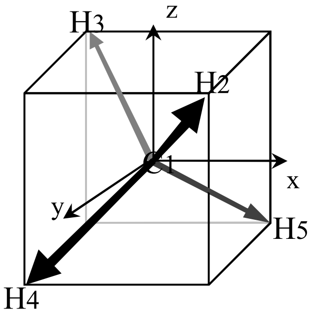
$$= 2\,\underbrace{c_{1,2sO}\, c_{1,1sH}}_{MO\ 1} + 2\,\underbrace{c_{1,2pyO}\, c_{1,1sH}}_{MO\ 1} + 2\,\underbrace{c_{2,2pxO}\, c_{2,1sH}}_{MO2} + 2\,\underbrace{c_{3,2sO}\, c_{3,1sH}}_{MO3} + 2\,\underbrace{c_{3,2spy}\, c_{3,1sH}}_{MO\ 3}$$

$$= 2(0.982)(0.134) + 2(-0.027)(0.134) + 2(0.856)(0.366)$$
$$+ 2(0.195)(-0.159) + 2(-0.955)(-0.159)$$
$$= 0.2632 - 0.0072 + 0.6266 - 0.0620 + 0.3037 = 1.1243$$

This case is unusual; Mulliken and Coulson bond orders are usually similar. For comparison, the HF/6-31G** Mulliken bond order is 0.881 and the B3LYP/6-311G** bond order is 0.967.

39. Calculate the charge on the C-atom in methane. Use the extended Hückel method. The atomic coordinates for methane with a C-H bond length of 1.084 Å are:

Atom	x	y	z
1 C	0.0	0.0	0.0
2 H	0.62565	0.62565	0.62565
3 H	-0.62565	-0.62565	0.62565
4 H	-0.62565	0.62565	-0.62565
5 H	0.62565	-0.62565	-0.62565

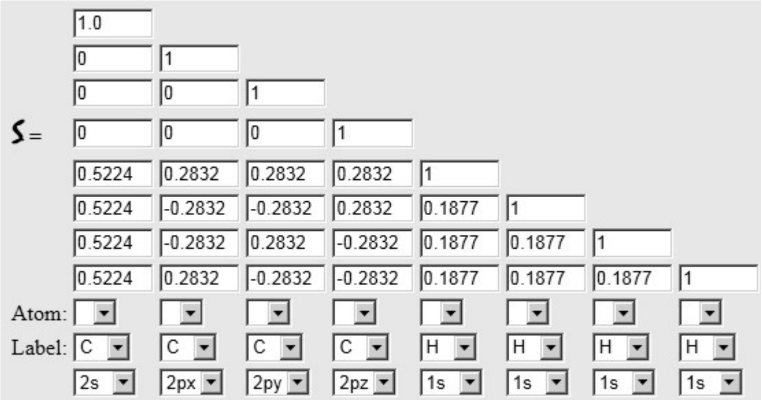


For this orientation, the overlap matrix is:

	1 C2s	1 $C2p_x$	1 $C2p_y$	1 $C2p_z$	2 H1s	3 H1s	4 H1s	5 H1s
1 C2s	1.0	0.0	0.0	0.0	0.5224	0.5224	0.5224	0.5224
1 $C2p_x$	0.0	1.0	0.0	0.0	0.2832	-0.2832	-0.2832	0.2832
1 $C2p_y$	0.0	0.0	1.0	0.0	0.2832	-0.2832	0.2832	-0.2832
1 $C2p_z$	0.0	0.0	0.0	1.0	0.2832	0.2832	-0.2832	-0.2832
2 H1s	0.5224	0.2832	0.2832	0.2832	1.0	0.1877	0.1877	0.1877
3 H1s	0.5224	-0.2832	-0.2832	0.2832	0.1877	1.0	0.1877	0.1877
4 H1s	0.5224	-0.2832	0.2832	-0.2832	0.1877	0.1877	1.0	0.1877
5 H1s	0.5224	0.2832	-0.2832	-0.2832	0.1877	0.1877	0.1877	1.0

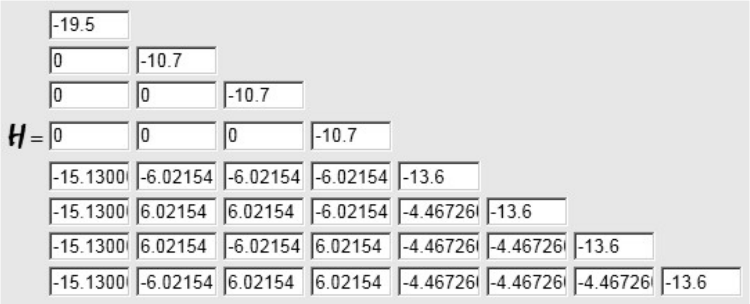
Answer: The plan is to use the "*Secular"* applet and Eqs. 26.3.9.

The hydrogen atoms are placed at the opposing corners of a cube that has faces oriented perpendicular to the axes. To quickly determine the overlap integrals as listed, we used the atomic coordinates as input for the "*cndo*" applet. The "*cndo*" applet lists overlap integrals. Yes, we know that using a more advanced level of approximation to get the overlap integrals for a lower-level extended Hückel calculation is cheating, but the instructional value of the extended Hückel calculation is undiminished. Notice that the C(2s)-H(1s) overlaps are all identical, as expected, while the C(2p)-H(1s) differ only in sign. Adjacent pairs of H-atoms have a significant overlap, 0.1877, as expected from VSEPR theory. Entering these overlap integrals into the "*Secular"* applet gives:



	1.0							
	0	1						
	0	0	1					
S =	0	0	0	1				
	0.5224	0.2832	0.2832	0.2832	1			
	0.5224	-0.2832	-0.2832	0.2832	0.1877	1		
	0.5224	-0.2832	0.2832	-0.2832	0.1877	0.1877	1	
	0.5224	0.2832	-0.2832	-0.2832	0.1877	0.1877	0.1877	1
Atom:								
Label:	C	C	C	C	H	H	H	H
	2s	2px	2py	2pz	1s	1s	1s	1s

Using the Generate H option, the Hamiltonian matrix is:



	-19.5							
	0	-10.7						
	0	0	-10.7					
H =	0	0	0	-10.7				
	-15.1300	-6.02154	-6.02154	-6.02154	-13.6			
	-15.1300	6.02154	6.02154	-6.02154	-4.46726	-13.6		
	-15.1300	6.02154	-6.02154	6.02154	-4.46726	-4.46726	-13.6	
	-15.1300	-6.02154	6.02154	6.02154	-4.46726	-4.46726	-4.46726	-13.6

The final output is:

```
                      Eigenvalues and eigenvectors
___________________________(eigenvectors listed in columns)___________________________
E(i)   -23.2715  -14.9487  -14.9487  -14.9487    6.44       6.44       6.44     35.4649
vector     1         2         3         4         5          6          7         8
atom:
    C2s    0.8444    0.0       0.0      -0.0       0.0       -0.0        0.0       0.7746
    C2px  -0.0      -0.0623    0.6373    0.0684   -0.5167     0.0307     0.4336    0.0
    C2py  -0.0      -0.6387   -0.0561   -0.0595    0.2014    -0.58       0.2811   -0.0
    C2pz  -0.0       0.053     0.0736   -0.6375    0.3852     0.3444     0.4347    0.0
    H1s    0.2678   -0.385     0.389    -0.3734   -0.0381     0.1119    -0.6277   -0.3162
    H1s    0.2678    0.4479   -0.3015   -0.384    -0.3826    -0.4881     0.1529   -0.3162
    H1s    0.2678   -0.3739   -0.4556    0.3027   -0.1819     0.5216     0.3207   -0.3162
    H1s    0.2678    0.3109    0.3681    0.4547    0.6026    -0.1454     0.1541   -0.3162
_______________________________________________________________________________________
```

Notice that the MOs involve C(2s) character or C(2p) character, but not both, in contradiction to hybridization arguments. The hybridization picture emerges when the average of MOs 1-4 is taken, giving s- and p-character. However, the s-character is greater than the canonical 25% expected for sp^3 hybridization. The hybridization has $(0.84)^2$ s-character and approximately $3(0.64)^2$ p-character for $s^{0.71}p^{1.23}$ overall.

The atom electron density for atom-a is calculated as the sum over all atomic orbitals j on atom-a and the sum over all molecular orbitals i:

$$d_a = \sum_{j \text{ on } a} \sum_{i=1}^{m} n_i c_{ij}^2 \qquad j = \text{all atomic orbitals on atom-a} \qquad (9)$$

With 8 valence electrons, the HOMO is orbital 4. The atom electron density on the C-atom is:

$$\begin{aligned} d_C &= 2(0.8444)^2 && \textit{contribution from } C(2s) \\ &+ 2(-0.0623)^2 + 2(\ 0.6373)^2 + 2(\ 0.0684)^2 && \textit{contribution from } C(2p_x) \\ &+ 2(-0.6387)^2 + 2(-0.0561)^2 + 2(-0.0595)^2 && \textit{contribution from } C(2p_y) \\ &+ 2\ (0.0530)^2 + 2(\ 0.0736)^2 + 2(-0.6375)^2 && \textit{contribution from } C(2p_z) \\ &= 3.9137 \end{aligned}$$

The contributions from the $C(2p_x)$, $C(2p_y)$, and $C(2p_z)$ are identical, as expected by symmetry. Since carbon has four valence electrons, the charge on the C-atom is 4 – 3.9137 = +0.0862. For comparison, the charge at the CNDO level is -0.052. The charge on an atom is an artificial, but useful, construct. Different calculation methods give strikingly different values for the charges on atoms. No one method can be chosen as "best," because the charge on an atom is not experimentally observable.

The bond length chosen for this example is the HF/6-31G(d) minimized structure.

40. Place the following electronic structure methods in order of typical energy accuracy: HF, CNDO, MNDO, AM1, PM3, CISD or CCSD, CISDT or CCSDT, CCSD(T), LSDA, B3LYP.

Answer: The general order is: advanced correlated better than density functional better than Hartree Fock better than semi empirical better than Extended Hückel better than Hückel. However, for some circumstances this ordering is arguable (open shell transition states). For the specific methods, in the following list when there is a tie, the more general method is ranked higher than the more specific method:

CNDO, MNDO, AM1~PM3, HF, LSDA, B3LYP~CISD/CCSD, CCSD(T), CISDT/CCSDT

The assumption is that correlation consistent basis sets are used (i.e. 6-311G** or cc-pVTZ). Many might question the indicated rough tie between B3LYP and CISD/CCSD, but in support, B3LYP methods are run with more complete basis sets than CCSD in comparable time. Note that CCSD(T) isn't listed in Figure 26.2.2 because with two electrons triple excitations aren't possible.

Literature Cited:

1. B. deB. Darwent, "Bond Dissociation Energies in Simple Molecules," *Nat. Stand. Ref. Data Ser.*, 1970, NSRDS-NBS 31.
2. K. S. Pitzer, *Quantum Chemistry*, Prentice-Hall, Englewood Cliffs, NJ, 1953. Table 8.4.
3. H. A. Bent, *Chem. Revs.*, **1961**, *61*, 275-311.
4. J. P. Foster, F. Weinhold, *J. Am. Chem. Soc.*, **1980**, *102*, 7211-7218.

Chapter 27 Problems: Rotational and Vibrational Spectroscopy

1. Calculate the ratio, N_1/N_o, of molecules in the $\upsilon = 1$ and $\upsilon = 0$ vibrational states for carbon monoxide, CO, at 25.0 °C. Assume a harmonic oscillator with $\tilde{\nu}_e = 2169.8\ \text{cm}^{-1}$ [Hint: at 25.0 °C, $kT = 207.2\ \text{cm}^{-1}$]

Answer: The plan is to use the Boltzmann population ratio, Eq. 8.10.8, for a harmonic oscillator with energy $\tilde{G}_\upsilon = \tilde{\nu}_e(\upsilon + ½)$, Eq. 27.5.2.

The energy difference in wave numbers is, $\Delta\varepsilon = \tilde{G}_1 - \tilde{G}_o = \tilde{\nu}_e(1 + ½) - \tilde{\nu}_e(0 + ½) = \tilde{\nu}_e$. The Boltzmann population ratio, Eq. 8.10.8, gives:

$$\frac{N_1}{N_o} = e^{-\Delta\varepsilon/kT} = e^{-2169.8\ \text{cm}^{-1}/207.2\ \text{cm}^{-1}} = 2.83\text{x}10^{-5}$$

A negligible number of CO molecules are in upper vibrational states, giving a large population difference. As a result, IR absorbance is a sensitive method compared to NMR and microwave spectroscopy.

2. Calculate the ratio, N_1/N_o, of molecules in the $J = 1$ and $J = 0$ rotational levels for carbon monoxide, CO, at 25.0 °C. Assume a rigid rotor with $\tilde{B}_e = 1.932\ \text{cm}^{-1}$ [Hint: at 25.0 °C, $kT = 207.2\ \text{cm}^{-1}$]

Answer: The plan is to use the Boltzmann distribution, taking into account the $2J + 1$ degeneracy of the rotational states.

The energy in wave numbers of a rigid rotor is $\tilde{F}_J = \tilde{B}_e[J(J + 1)]$. Since the $J = 0$ state of a rigid rotor is at zero in energy, $\Delta\varepsilon = \tilde{F}_1 - \tilde{F}_o = \tilde{B}_e[J(J + 1)]$, in wave numbers. The Boltzmann population ratio, Eq. 8.10.8, gives for any single rotational state with $J = 1$:

$$\frac{N_1}{N_o} = e^{-\Delta\varepsilon/kT} = e^{-2(1.932\ \text{cm}^{-1})/207.2\ \text{cm}^{-1}} = 0.9815 \qquad \text{for } m_J = -1, 0, \underline{\text{or}} +1$$

The degeneracy of the $J = 1$ level is $g_J = 2J + 1 = 3$, giving the final ratio as:

$$\frac{N_1}{N_o} = g_J\ e^{-\Delta\varepsilon/kT} = 3\ e^{-2(1.932\ \text{cm}^{-1})/207.2\ \text{cm}^{-1}} = 2.945$$

In other words, there are more CO molecules in the $J = 1$ level than the $J = 0$ level, because of the degeneracy. However, the probability of a radiative transition is proportional to the state to state population difference.

3. How does the Doppler width of a transition depend on temperature and the mass of the molecule?

Answer: As the temperature increases the root-mean-squared speed of gas molecules increases, thus increasing Doppler broadening. As the mass of the molecule increases the root mean squared speed decreases, thus decreasing the Doppler broadening.

4. Calculate the Doppler line width of the 83305. cm^{-1} electronic transition of HF at 500.0 K. This temperature is on the order of the temperature in the ionosphere.

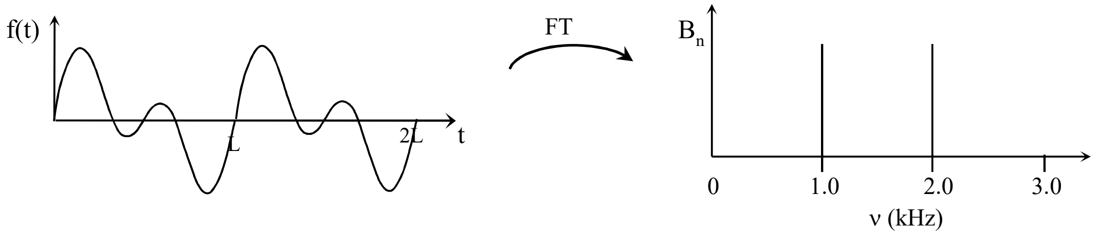
Answer: The plan is to refer to Example 27.2.1.
The mass of HF is $m = (20.00 \text{ g mol}^{-1}/N_A)(1 \text{ kg}/1000 \text{ g}) = 3.321\text{x}10^{-26}$ kg:

$$\Delta\tilde{\nu}_D = 2\left(\frac{\tilde{\nu}_o}{c}\right)\sqrt{\frac{2kT\ln(2)}{m}} = 2\left(\frac{83305.\ \text{cm}^{-1}}{2.998\text{x}10^{8}\ \text{m s}^{-1}}\right)\sqrt{\frac{2(1.381\text{x}10^{-23}\ \text{J K}^{-1})(500.0\ \text{K})\ln(2)}{3.321\text{x}10^{-26}\ \text{kg}}}$$
$$= 0.298\ \text{cm}^{-1} = 8.94\text{x}10^{9}\ \text{s}^{-1} = 8.94\ \text{GHz}$$

See example 27.2.1 for a note about the proper units of the speed of light. The broadening is much greater than some interesting interactions involving the nuclei and is also significant relative to rotational fine-structure spacing. Collisional broadening in the ionosphere is negligible, since the pressure is so low.

5. (a). Draw the Fourier transformed spectrum of the function f(t) in Figure 27.3.2 as a histogram, in the same style as the Fourier transforms shown in Figure 27.3.1b for the three Fourier coefficients. (b). The period of the function, L, is $1.00\text{x}10^{-3}$ s. Calculate the lowest frequency Fourier component.

Answer: (a). From Figure 27.3.2, the Fourier coefficients are large for 1 kHz and 2 KHz and zero for 3 kHz:



(b). The fundamental Fourier frequency is $\nu_o = 1/L = 1/1.00\text{x}10^{-3}\ \text{s} = 1000\ \text{s}^{-1} = 1.00$ kHz. The Fourier components then occur at frequencies $n\nu_o$ = 1 KHz, 2 kHz, 3 KHz, 4 kHz, ….

6. Many experiments give a time response that decays exponentially in time: $f(t) = e^{-t/\tau}$, where τ is the time constant for the decay. (a). Show that the Fourier transform, using Eq. 27.3.8, is:

$$g(\nu) = \frac{2\tau}{1 + i2\pi\tau\nu}$$

(b). The square of the magnitude of a complex function is given using Eq. 23.9.7. Show that:

$$g(\nu)^* g(\nu) = \frac{4\tau^2}{1 + 4\pi^2\tau^2\nu^2}$$

(c). The result of experiments is often given as a magnitude spectrum, $A^2(\nu) = g(\nu)^* g(\nu)$. Do a quick plot of the magnitude spectrum assuming $\tau = 1$ s.

Answer: (a). The Fourier transform using Eq. 27.3.8 is:

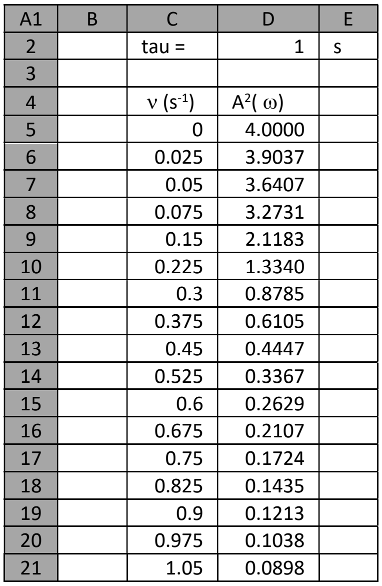
$$g(\nu) = 2\int_0^\infty e^{-t/\tau}\, e^{-i2\pi\nu t}\, dt = 2\int_0^\infty e^{-(1/\tau + i2\pi\nu)t}\, dt = -2\, \frac{e^{-(1/\tau + i2\pi\nu)t}}{1/\tau + i2\pi\nu}\Big|_0^\infty$$

$$= -2\left[\frac{e^{-\infty}}{1/\tau + i2\pi\nu} - \frac{e^0}{1/\tau + i2\pi\nu}\right] = \frac{2}{1/\tau + i2\pi\nu} = \frac{2\tau}{1 + i2\pi\tau\nu}$$

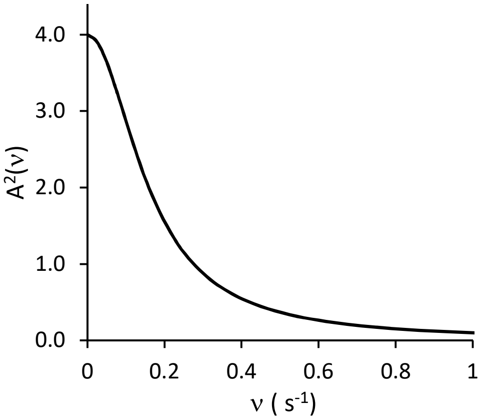
(b). The squared magnitude is given by the complex conjugate multiplied by the original function:

$$A^2(\nu) = g(\nu)^* g(\nu) = \left(\frac{2\tau}{1 - i2\pi\tau\nu}\right)\left(\frac{2\tau}{1 + i2\pi\tau\nu}\right) = \frac{4\tau^2}{(1 - i2\pi\tau\nu)(1 + i2\pi\tau\nu)} = \frac{4\tau^2}{1 + 4\pi^2\tau^2\nu^2}$$

(c). The spreadsheet and plot are given below. The value of $A^2(\nu)$ is given in cell D5 as:
“=4*$D$2/(4*PI()^2*C5^2*$D$2^2 +1)”



A1	B	C	D	E
2		tau =	1	s
3				
4		ν (s^{-1})	$A^2(\omega)$	
5		0	4.0000	
6		0.025	3.9037	
7		0.05	3.6407	
8		0.075	3.2731	
9		0.15	2.1183	
10		0.225	1.3340	
11		0.3	0.8785	
12		0.375	0.6105	
13		0.45	0.4447	
14		0.525	0.3367	
15		0.6	0.2629	
16		0.675	0.2107	
17		0.75	0.1724	
18		0.825	0.1435	
19		0.9	0.1213	
20		0.975	0.1038	
21		1.05	0.0898	



7. Which of the following molecules give pure-rotational absorption spectra? N_2, O_2, NO, CH, CO, CO_2, N_2O, SO_2, C_2H_4, CH_4, and $H_2C{=}O$ (formaldehyde).

Answer: The gross selection rule for rotational absorption is that the molecule must possess a permanent dipole moment. As a result only NO, CH, CO, N_2O, SO_2, and $H_2C{=}O$ are microwave active.

8. Which of the following molecules give vibrational absorption spectra? N_2, O_2, NO, CH, CO, CO_2, N_2O, and SO_2.

Answer: The gross selection rule for vibrational absorption is that the molecule must give a changing dipole moment during the vibration. For the diatomics, only NO, CH, and CO are infrared active. The symmetric stretch of linear triatomics is IR forbidden, but the asymmetric stretch and bending modes are IR active, see Table 27.7.1. As a result, the asymmetric stretch and the two degenerate bending modes of CO_2 are IR active. All normal modes of bent triatomics are IR active; so SO_2 is IR active. All normal modes for asymmetric linear triatomics are IR active, so N_2O is IR active; the symmetric stretch, the asymmetric stretch, and bending modes all present an oscillating dipole moment.

9. Which of the following molecules give vibrational Raman spectra? N_2, O_2, NO, CH, CO, CO_2, N_2O, and SO_2.

Answer: The plan is to note the molecules that have a center of symmetry, that is have an inversion center. Molecules with a center of symmetry are centrosymmetric. The exclusion rule is then applied.

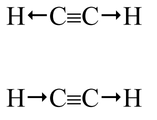
The short answer is only the asymmetric stretch and the bending vibrations of CO_2 are Raman forbidden. All the other molecules and the symmetric stretch of CO_2 are Raman active.

The molecules with a center of symmetry are N_2, O_2, and CO_2. No normal mode of a centrosymmetric molecule is both Raman and IR active. Since the homonuclear diatomics and the symmetric stretch of CO_2 are IR forbidden, the stretches must be Raman active.

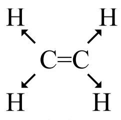
For the heteronuclear diatomics, the stretch is both Raman and IR active. Remember that the polarizability is a function of the volume of the molecule. As a result for the heteronuclear diatomics, the polarizability and dipole moment both change during the vibration. Therefore, NO, CH, and CO are Raman active.

All normal modes for asymmetric linear triatomics and bent triatomics are Raman active, so N_2O and SO_2 are Raman active, see Table 27.7.1.

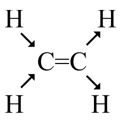
10. Which of the following normal modes are infrared active and which are Raman active? The arrows indicate the movement of the exterior atoms. In the asymmetric stretches, the central atoms also move to maintain a fixed center of mass, but that movement is not shown. [Formal group theory is not required for this problem.]



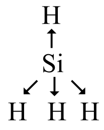
acetylene



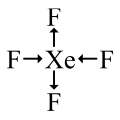
ethylene



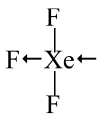
ethylene



silane



XeF_4

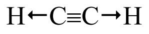


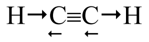
XeF_4

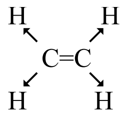
Answer: The plan is to use the volume change during the vibration to judge the change in polarizability and the asymmetry of the vibration to judge the change in dipole moment. No normal mode of a centrosymmetric molecule is both Raman and IR active.

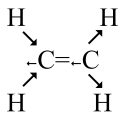
None of the molecules has a permanent dipole moment. We need to look for a changing dipole moment during the vibration. Each molecule is centrosymmetric, so if the mode is IR active, then it must be Raman forbidden. For the totally symmetric stretches, all the exterior atom movements are outward, away from the center of mass. The symmetric stretches are all IR forbidden and Raman active, which includes the symmetric modes for acetylene, ethylene, and silane. The asymmetric stretches, where some exterior atoms move inward and some move outward, are all IR allowed and Raman forbidden, which include the asymmetric stretches for acetylene, ethylene, and the second mode for XeF_4. The symmetric stretches all change the volume of the molecule without a net shift of the electron density, relative to the center of mass.

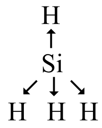
The difficult case is the first mode for XeF_4. The motion of the F-atoms is symmetrical with respect to the center of mass for the opposite pairs. The mode does not change the dipole moment, so the mode must be IR forbidden and correspondingly Raman active. The mode is symmetric, but not totally symmetric. The question remains as to whether the mode changes the volume of the molecule. Luckily the lack of a dipole moment and the center of symmetry give the Raman activity using the Exclusion Rule. In the table below, *IR* is for IR active and *R* is for Raman active.

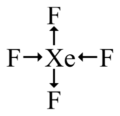

symm R

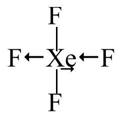

asymm IR


symm R


asymm IR


symm R


symm R


asymm IR

11. The lowest energy transitions in the rotational spectrum of HF are 41.105 and 82.211 cm^{-1}. Calculate the equilibrium bond length of HF, R_o.

Answer: The plan is to note that the spacing between adjacent lines in the rotational absorption spectrum of a diatomic molecule is $2\tilde{B}$, following Example 27.4.1.

The spacing between rotational transitions for HF is 41.106 cm^{-1}. The rotational constant is $\tilde{B}$ = 41.106 cm^{-1}/2 = 20.553 cm^{-1}. The reduced mass for HF is:

$$\mu_{HF} = \frac{(1.007825)(18.998403)}{1.007825+18.998403}\ (\text{g mol}^{-1})\ \frac{1}{N_A}\ (1\text{kg}/1000\text{ g}) = 1.589229\text{x}10^{-27}\text{ kg}$$

For units, the $\tilde{B}$ value can be converted to m^{-1} and then c = 2.99792x10^{8} m s^{-1}:

$$\tilde{B} = 20.553\text{ cm}^{-1}\ (100\text{ cm}/1\text{ m}) = 2055.3\text{ m}^{-1}$$

with Eq. 27.4.2: $I = \hbar/(4\pi\tilde{B}c) = 1.05457266\text{x}10^{-34}\text{ J s}/[4\pi(2055.3\text{ m}^{-1})(2.997925\text{x}10^{8}\text{ m s}^{-1})]$
$= 1.36198\text{x}10^{-47}\text{ kg m}^2$

Alternatively, keeping $\tilde{B}$ in cm^{-1} and the speed of light in cm s^{-1} for the $\tilde{B}c$ product:

with Eq. 27.4.2: $I = \hbar/(4\pi\tilde{B}c) = 1.05457266\text{x}10^{-34}$ J s/[$4\pi(20.553\ \text{cm}^{-1})(2.997925\text{x}10^{10}\ \text{cm s}^{-1})$]
$= 1.36198\text{x}10^{-47}\ \text{kg m}^2$

with Eq. 27.4.2: $R_o = (I/\mu)^{½} = 9.2574\text{x}10^{-11}\ \text{m} = 0.9257$ Å

12. Two adjacent lines in the rotational absorption spectrum of $^{14}N^1H$ are at 98.036 and 130.714 cm^{-1}. Calculate the equilibrium bond length of HF, R_o, and the rotational quantum numbers of the lower states of the two transitions.

Answer: The plan is to note that the spacing between adjacent lines in the rotational absorption spectrum of a diatomic molecule is $2\tilde{B}$, with the transitions at $\Delta\tilde{F} = \tilde{F}_{J''+1} - \tilde{F}_{J''} = 2\tilde{B}(J''+ 1)$.

The spacing between rotational transitions for $^{14}N^1H$ is 32.678 cm^{-1}. The rotational constant is $\tilde{B} = 32.678\ \text{cm}^{-1}/2 = 16.339\ \text{cm}^{-1}$. The reduced mass for $^{14}N^1H$ is:

$$\mu_{NH} = \frac{(1.007825)(14.003074)}{1.007825+14.003074}\,(\text{g mol}^{-1})\,\frac{1}{N_A}\,(1\text{kg}/1000\ \text{g}) = 1.561174\text{x}10^{-27}\ \text{kg}$$

For units, the $\tilde{B}$ value can be converted to m^{-1} and then $c = 2.99792\text{x}10^8\ \text{m s}^{-1}$:

$$\tilde{B} = 16.339\ \text{cm}^{-1}\ (100\ \text{cm}/1\ \text{m}) = 1633.9\ \text{m}^{-1}$$

with Eq. 27.4.2: $I = \hbar/(4\pi\tilde{B}c) = 1.05457266\text{x}10^{-34}$ J s/[$4\pi(1633.9\ \text{m}^{-1})(2.997925\text{x}10^8\ \text{m s}^{-1})$]
$= 1.71325\text{x}10^{-47}\ \text{kg m}^2$

Alternatively, keeping $\tilde{B}$ in cm^{-1} and the speed of light in cm s^{-1} for the $\tilde{B}c$ product:

with Eq. 27.4.2: $I = \hbar/(4\pi\tilde{B}c) = 1.05457266\text{x}10^{-34}$ J s/[$4\pi(16.339\ \text{cm}^{-1})(2.997925\text{x}10^{10}\ \text{cm s}^{-1})$]
$= 1.71325\text{x}10^{-47}\ \text{kg m}^2$

with Eq. 27.4.2: $R_o = (I/\mu)^{½} = 1.04757\text{x}10^{-10}\ \text{m} = 1.0476$ Å

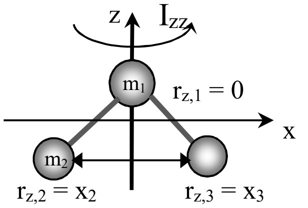
Given Eq. 27.4.3 and the transitions at 98.036 and 130.714 cm^{-1}, the quantum numbers for the lower state, J", are:

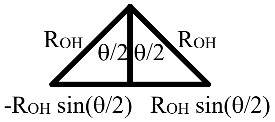
$\Delta\tilde{F} = 98.036\ \text{cm}^{-1} = 2\tilde{B}(J''+ 1) = 2(16.339\ \text{cm}^{-1})(J''+ 1)$ giving J" = 2 i.e. 3←2
and $130.714\ \text{cm}^{-1} = 2\tilde{B}(J''+ 1)$ giving J" = 3 i.e. 4←3

13. Calculate the moment of inertia of water about the z-axis, which is the figure axis. The rotational constant about the z-axis is $\tilde{A} = 14.512\ \text{cm}^{-1}$. Assume the bond angle is 104.48°.[1] Calculate the O–H bond length.

Answer: The plan is to follow Figure 27.4.2 and Example 27.4.2.

The geometry is illustrated below with the water molecule in the x-z plane.





Reference to figure, above, shows that $x_2 = -x_3 = R_{OH}\sin(\theta/2)$, where θ is the H-O-H bond angle and R_{OH} is the O–H bond length. The O-atom does not contribute to the moment of inertia about the z-axis, because it lies on the z-axis. Since all the y_i coordinates are zero, the moment of inertia of water about the z-axis is, as in Equation 27.4.25:

$$I_{zz} = \Sigma\, m_i(x_i^2 + y_i^2) = \Sigma\, m_i\, x_i^2 = 2\, m_H\, [R_{OH}\sin(\theta/2)]^2$$

The mass of the H-atom is $1.67353\text{x}10^{-27}$ kg. The moment of inertia is given by Eq. 27.4.2:

$$I_{zz} = \hbar/(4\pi\tilde{A}c) = 1.05457266\text{x}10^{-34}\text{ J s}/[4\pi(9.285\text{ cm}^{-1})(2.997925\text{x}10^{10}\text{ cm s}^{-1})]$$
$$I_{zz} = 1.9289\text{x}10^{-47}\text{ kg m}^2 = 2\, m_H\, [R_{OH}\sin(104.48/2)]^2$$
$$= 2(1.67353\text{x}10^{-27}\text{ kg})[R_{OH}\,(0.79058)]^2$$

Solving for the bond angle gives $R_{OH} = 9.6024\text{x}10^{-11}$ m or 0.96024 Å.

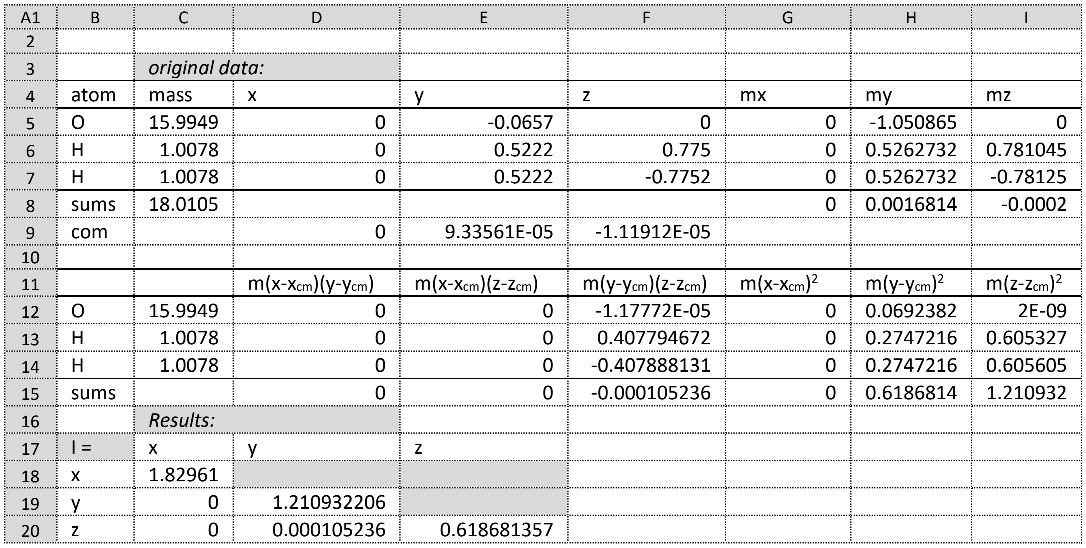
14. Use Eqs. 27.4.11 to calculate the three moments of inertia of H_2O. Use units of g mol^{-1} for the masses and Å for the distances. The coordinates of water, aligned with the O-atom at the origin and one O–H bond extending along the x-axis, are:

Atom	x	y	z
O	0	0	0
H	0.9728	0	0
H	-0.2623	-0.9369	0

The coordinates of the center of mass are:

$$x_{cm} = {}^1/_m\, \Sigma\, m_i x_i \qquad y_{cm} = {}^1/_m\, \Sigma\, m_i y_i \qquad z_{cm} = {}^1/_m\, \Sigma\, m_i z_i$$

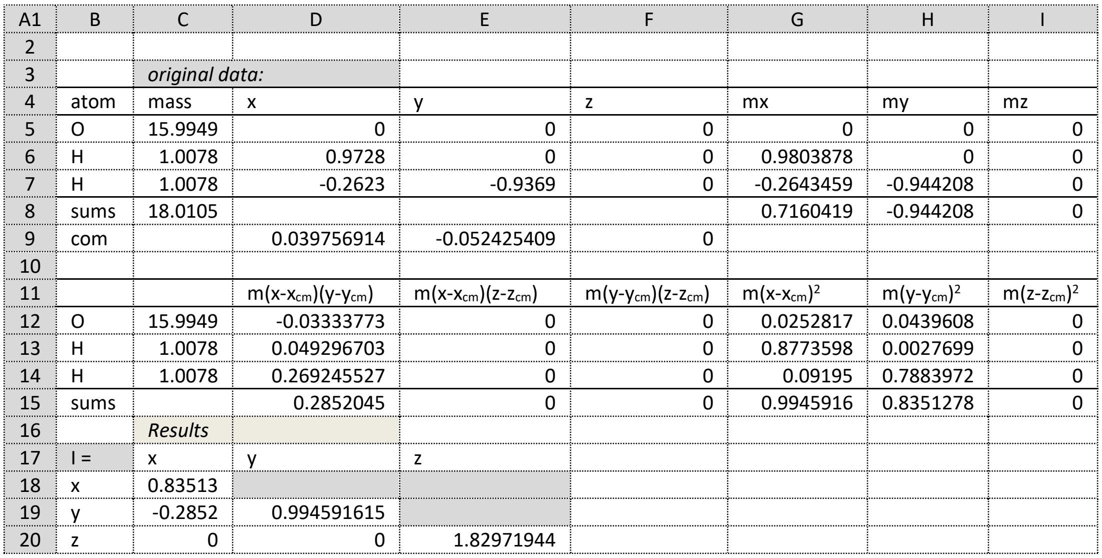
where m_i is the isotope specific mass of atom-i, with coordinates x_i, y_i, z_i, and total molecular mass $m = \Sigma\, m_i$. First, build a spreadsheet to calculate the moment of inertia matrix with the input orientation.[2] Second, the eigenvalues of this matrix are the three moments of inertia. To calculate the eigenvalues use MatLab, Maple, Mathematica, or the "Eigen" matrix diagonalization applet that is on the textbook Web site or on the companion CD. [Hint: The example spreadsheet shown below uses the same geometry for water as given above, but the orientation is chosen as already aligned with the principal axes. For this aligned example, the off-diagonal elements of the moment of inertia matrix should be zero, within round-off error. You should use these values to test your spreadsheet. Your final eigenvalues, starting from the orientation listed above, should give the same results; the final moments of inertia should not depend on the input orientation. The spreadsheet was designed to make the addition of atoms easy for larger molecules.]



A1	B	C	D	E	F	G	H	I
2								
3		*original data:*						
4	atom	mass	x	y	z	mx	my	mz
5	O	15.9949	0	-0.0657	0	0	-1.050865	0
6	H	1.0078	0	0.5222	0.775	0	0.5262732	0.781045
7	H	1.0078	0	0.5222	-0.7752	0	0.5262732	-0.78125
8	sums	18.0105				0	0.0016814	-0.0002
9	com		0	9.33561E-05	-1.11912E-05			
10								
11			$m(x-x_{cm})(y-y_{cm})$	$m(x-x_{cm})(z-z_{cm})$	$m(y-y_{cm})(z-z_{cm})$	$m(x-x_{cm})^2$	$m(y-y_{cm})^2$	$m(z-z_{cm})^2$
12	O	15.9949	0	0	-1.17772E-05	0	0.0692382	2E-09
13	H	1.0078	0	0	0.407794672	0	0.2747216	0.605327
14	H	1.0078	0	0	-0.407888131	0	0.2747216	0.605605
15	sums		0	0	-0.000105236	0	0.6186814	1.210932
16		*Results:*						
17	I =	x	y	z				
18	x	1.82961						
19	y	0	1.210932206					
20	z	0	0.000105236	0.618681357				

The input atomic coordinates are placed in cells D5:F7. The calculated center of mass coordinates, "com", are listed in cells D9:F9, which are then used to form the sums for Eqs. 27.4.11. The resulting moment of inertia matrix is listed in cells C18:E20. The moment of inertia matrix is symmetric, so that only the lower triangular matrix need be listed. In the general case, the moment of inertia matrix will not be a diagonal matrix. The final moment of inertia elements are then input into the "eigen" applet to determine the eigenvalues.

Answer: The spreadsheet with the new orientation is shown below.



A1	B	C	D	E	F	G	H	I
2								
3		*original data:*						
4	atom	mass	x	y	z	mx	my	mz
5	O	15.9949	0	0	0	0	0	0
6	H	1.0078	0.9728	0	0	0.9803878	0	0
7	H	1.0078	-0.2623	-0.9369	0	-0.2643459	-0.944208	0
8	sums	18.0105				0.7160419	-0.944208	0
9	com		0.039756914	-0.052425409	0			
10								
11			$m(x-x_{cm})(y-y_{cm})$	$m(x-x_{cm})(z-z_{cm})$	$m(y-y_{cm})(z-z_{cm})$	$m(x-x_{cm})^2$	$m(y-y_{cm})^2$	$m(z-z_{cm})^2$
12	O	15.9949	-0.03333773	0	0	0.0252817	0.0439608	0
13	H	1.0078	0.049296703	0	0	0.8773598	0.0027699	0
14	H	1.0078	0.269245527	0	0	0.09195	0.7883972	0
15	sums		0.2852045	0	0	0.9945916	0.8351278	0
16		*Results*						
17	I =	x	y	z				
18	x	0.83513						
19	y	-0.2852	0.994591615					
20	z	0	0	1.82971944				

The input to the "eigen" matrix diagonalization applet appears as below:

0.83513		
-0.2852	0.994592	
0	0	1.829719

The output agrees with the moments of inertia given in the pre-aligned example and appears as:

```
Eigenvector 1: Eigenvalue=1.829719
0
0
1
-------------
Eigenvector 2: Eigenvalue=1.21095
-0.604517
0.796593
0
-------------
Eigenvector 3: Eigenvalue=0.618698
0.796593
0.604517
0
-------------
```

An on-line applet is available that automatically determines the moments of inertia, spectroscopic rotational constants, symmetry point group, and the contributions of rotation to the entropy and Gibbs energy of a molecule. The “ABC Rotational Constant Calculator” applet is available on the textbook Web site or on the companion CD. The pre-aligned orientation of H_2O is available through the applet as an example, in addition to other examples of larger molecules.

15. Calculate the bond force constant, k, for $H^{35}Cl$. The fundamental vibration frequency is $\tilde{\nu}_e = 2990.9\ \text{cm}^{-1}$.

Answer: The plan is to use Eq. 27.5.4 to calculate the bond force constant. Remember to use isotope specific masses to calculate the reduced mass.

The reduced mass for $H^{35}Cl$ is: $\mu = \left(\dfrac{\mathcal{M}_1\mathcal{M}_2}{\mathcal{M}_1 + \mathcal{M}_2}\right)\dfrac{1}{N_A}$ (1 kg/1000 g)

$$\mu = \left(\frac{(1.007825)(34.968853)}{(1.007825 + 34.968853)}\right)(\text{g mol}^{-1})\frac{1}{6.022137\text{x}10^{23}}\ (1\ \text{kg}/1000\ \text{g})$$

$$= 1.6266526\text{x}10^{-27}\ \text{kg}$$

The bond force constant is given by rearranging Eq. 24.2.1:

$$k = 4\pi^2\tilde{\nu}_e^2c^2\mu = 4\pi^2(2990.9\ \text{cm}^{-1})^2(2.997925\text{x}10^{10}\ \text{cm s}^{-1})^2(1.62665\text{x}10^{-27}\ \text{kg}) = 516.30\ \text{N m}^{-1}$$

16. Does CH or CO have the greater bond strength? Base your answer on the fundamental vibration frequency for ^{12}CH, which is $\tilde{\nu}_e = 2860.75\ \text{cm}^{-1}$, and for $^{12}C^{16}O$, which is $2169.76\ \text{cm}^{-1}$, Table 27.6.1.

Answer: The plan is to calculate the bonds force constants and then compare. Fundamental vibration frequencies cannot be compared directly, especially when the reduced masses are so different.

For ^{12}CH, the reduced mass is: $\mu = \left(\dfrac{\mathcal{M}_1\mathcal{M}_2}{\mathcal{M}_1 + \mathcal{M}_2}\right)\dfrac{1}{N_A}$ (1 kg/1000 g)

$$\mu = \left(\frac{(1.007825)(12.00000)}{(1.007825 + 12.00000)}\right) (\text{g mol}^{-1}) \frac{1}{6.022137\text{x}10^{23}} (1 \text{ kg}/1000 \text{ g})$$
$$= 1.5438711\text{x}10^{-27} \text{ kg}$$

The bond force constant for CH is given by rearranging Eq. 24.2.1:

$$k = 4\pi^2\tilde{\nu}_e^2c^2\mu = 4\pi^2(2860.75 \text{ cm}^{-1})^2(2.997925\text{x}10^{10} \text{ cm s}^{-1})^2(1.5438711^{-27} \text{ kg}) = 448.30 \text{ N m}^{-1}$$

For $^{12}C^{16}O$, the reduced mass is:

$$\mu = \left(\frac{(12.000000)(15.994915)}{(12.000000 + 15.994915)}\right) (\text{g mol}^{-1}) \frac{1}{6.022137\text{x}10^{23}} (1 \text{ kg}/1000 \text{ g})$$
$$= 1.138500\text{x}10^{-27} \text{ kg}$$

The bond force constant for CO is:

$$k = 4\pi^2\tilde{\nu}_e^2c^2\mu = 4\pi^2(2169.76 \text{ cm}^{-1})^2(2.997925\text{x}10^{10} \text{ cm s}^{-1})^2(1.138500\text{x}10^{-27} \text{ kg}) = 1901.8 \text{ N m}^{-1}$$

The larger force constant corresponds to the stronger bond. Even though CH has a higher vibration frequency, CO has a stronger bond. The reversal in order results because the reduced mass of the CH bond is small, which in g mol^{-1} is:

for C–H $\mu = 0.9297$ g mol^{-1} versus for C≡O $\mu = 6.856$ g mol^{-1}

This result is expected since the qualitative bond order in C–H is one and the qualitative bond order in C≡O is three. The molecular orbital filling for CH is given by Figure 26.3.4 with three valence electrons. The correlation of bond strength with force constant is displayed in Figure 26.4.12.

<u>17</u>. The force constant is defined as the second derivative of the vibrational potential function, Eq. 8.11.2. For a non-harmonic potential, such as the Morse potential in Eq. 27.5.8, we must add the stipulation that the second derivative is evaluated at the equilibrium internuclear distance:

$$\left(\frac{d^2V}{dR^2}\right)_{R\,=\,R_e} \equiv k$$

Derive the relationship that determines the Morse *a*-parameter, Eq. 27.5.8, using the following steps: (a). Show that the second derivative of the Morse potential function, Eq. 27.5.7, is:

$$\frac{d^2V}{dR^2} = -2a^2D_e e^{-a(R\,-\,Re)} + 4a^2D_e\, e^{-2a(R\,-\,Re)}$$

(b). Evaluate the second derivative at the equilibrium internuclear distance, $R = R_e$, and use the definition of the force constant to give:

$$a = \left(\frac{k}{2\,D_e}\right)^{1/2}$$

(c). Use the relationship between the fundamental vibration frequency and the force constant, $\omega_e = 2\pi\nu_e = \sqrt{k/\mu}$, to give Eq. 27.5.8.

Answer: The Morse potential is given by Eq. 27.5.7: $V(R) = D_e\,(1 - e^{-a(R\,-\,Re)})^2$ with first derivative using the chain rule twice:

$$\frac{dV}{dR} = D_e\,2(1 - e^{-a(R-Re)})\,(-\,e^{-a(R-Re)})(-a) = -2aD_e(-\,e^{-a(R-Re)} + e^{-2a(R-Re)})$$

The second derivative is: $\frac{d^2V}{dR^2} = -2aD_e[-\,e^{-a(R-Re)}(-a) + e^{-2a(R-Re)}(-2a)]$

Gathering terms: $\frac{d^2V}{dR^2} = -2a^2D_e e^{-a(R-Re)} + 4a^2D_e\,e^{-2a(R-Re)}$

Evaluating the second derivative at the equilibrium internuclear separation, $R = R_e$, gives:

$$\frac{d^2V}{dR^2} = -2a^2D_e\,e^0 + 4a^2D_e\,e^0 = 2a^2D_e$$

Setting this result equal to the force constant gives $2a^2D_e = k$ and solving for a:

$$a = \left(\frac{k}{2\,D_e}\right)^{½}$$

(b). Using $\omega_e = \sqrt{k/\mu}$ gives the force constant as $k = \omega_e^2\,\mu$, which upon substitution into the previous result gives Eq. Eq. 27.5.8.

18. The bond strength parameters for NF are important in validating bond order-bond strength correlations as displayed in Figure 26.4.12. However, the literature bond dissociation energy for NF varies widely depending on the experimental method used. The bond energy from thermochemical measurements is 297±42 kJ mol^{-1} or 3.08±0.44 eV.[3] Determine $\tilde{\nu}_e$, the force constant, zero point energy, and bond dissociation energies $\tilde{D}_e$ and $\tilde{D}_o$, for ^{14}NF based on the fundamental vibration frequency $\tilde{\nu}_o = 1123.4$ cm^{-1} and anharmonicity $\chi_e\tilde{\nu}_e = 9.0$ cm^{-1}. Report the bond dissociation energies in cm^{-1}, eV, and kJ mol^{-1}. Compare the spectroscopic bond dissociation energy, as D_o, with the thermochemical value. What effect does using the spectroscopic value have on the bond order-bond strength correlation in Figure 26.4.12?

Answer: The plan is to use Eqs. 27.5.4, 27.5.8, 27.5.11, 27.5.18, and 27.5.12 to "correct for anharmonicity."

For ^{14}NF, the reduced mass is: $\mu = \left(\frac{\mathfrak{M}_1\mathfrak{M}_2}{\mathfrak{M}_1 + \mathfrak{M}_2}\right)\frac{1}{N_A}\,(1\text{ kg}/1000\text{ g})$

$$\mu = \left(\frac{(14.003074)(18.998403)}{(1.007825 + 12.00000)}\right)(\text{g mol}^{-1})\,\frac{1}{6.022137\text{x}10^{23}}\,(1\text{ kg}/1000\text{ g})$$
$$= 1.338617\text{x}10^{-26}\text{ kg}$$

Based on $\tilde{\nu}_o = 1123.4$ cm^{-1} and $\chi_e\tilde{\nu}_e = 9.0$ cm^{-1}

with Eq. 27.5.11: $\tilde{\nu}_e = \nu_o + 2\chi_e\nu_e = 1123.4\text{ cm}^{-1} + 2(9.0)\text{ cm}^{-1} = 1141.4\text{ cm}^{-1}$

with Eq. 27.5.4: $k = 4\pi^2c^2\tilde{\nu}_e{}^2\mu = 4\pi^2(2.99792\text{x}10^{10}\text{ cm s}^{-1})^2(1141.4\text{ cm}^{-1})^2(1.62668\text{x}10^{-27}\text{ kg})$

$k = 618.7\text{ N m}^{-1}$

with Eq. 27.5.8: $\text{ZPE} = \tilde{G}_o = ½\,\tilde{\nu}_e - ¼\,\tilde{\nu}_e\,\chi_e = ½(1141.4\text{ cm}^{-1}) - ¼(9.0\text{ cm}^{-1}) = 568.44\text{ cm}^{-1}$

with Eq. 27.5.18: $\tilde{D}_e = \tilde{\nu}_e^2/4\chi_e\tilde{\nu}_e = (1141.4\text{ cm}^{-1})^2/(4(9.0\text{ cm}^{-1}))$

$\tilde{D}_e = 36{,}187\text{ cm}^{-1} = 4.49\text{ eV} = 433\text{ kJ mol}^{-1}$

with Eq. 27.5.12: $\tilde{D}_o = \tilde{D}_e - \text{ZPE} = 36{,}187\ \text{cm}^{-1} - 568.44\ \text{cm}^{-1} = 35618.\ \text{cm}^{-1}$

$\tilde{D}_o = 4.42\ \text{eV} = 426\ \text{kJ mol}^{-1}$ (spectroscopic)

The spectroscopic and thermochemical dissociation energies differ by 43%. The spectroscopic dissociation energy for NF is in better agreement than the thermochemical value with the dissociation energy for O_2 and falls closer to the extrapolated curve on the plot in Figure 26.4.12.

19. Bond order-bond strength correlations as displayed in Figure 26.4.12 play an important role in understanding the chemical bond. Figure 26.4.12 is based on second period elements. Do the same quantitative correlations hold for third period elements? Consider NCl as an example. Determine $\tilde{\nu}_e$, the force constant, zero point energy, and bond dissociation energies $\tilde{D}_e$ and $\tilde{D}_o$, for $^{14}N^{35}Cl$ based on the fundamental vibration frequency $\tilde{\nu}_o = 817.358\ \text{cm}^{-1}$ and anharmonicity $\chi_e\tilde{\nu}_e = 5.300\ \text{cm}^{-1}$. Report the bond dissociation energies in cm^{-1}, eV, and kJ mol^{-1}. How well do the force constant and bond dissociation energy of NCl agree with the bond order-bond strength correlation in Figure 26.4.12?

Answer: The plan is to use Eqs. 27.5.4, 27.5.8, 27.5.11, 27.5.18, and 27.5.12 to "correct for anharmonicity."

For $^{14}N^{35}Cl$, the reduced mass is: $\mu = \left(\frac{\mathfrak{M}_1\mathfrak{M}_2}{\mathfrak{M}_1 + \mathfrak{M}_2}\right)\frac{1}{N_A}(1\ \text{kg}/1000\ \text{g})$

$$\mu = \left(\frac{(14.003074)(34.968853)}{(1.007825 + 12.00000)}\right)(\text{g mol}^{-1})\frac{1}{6.022137\text{x}10^{23}}(1\ \text{kg}/1000\ \text{g})$$

$= 1.660378\text{x}10^{-26}\ \text{kg}$

Based on $\tilde{\nu}_o = 817.358\ \text{cm}^{-1}$ and $\chi_e\tilde{\nu}_e = 5.300\ \text{cm}^{-1}$

with Eq. 27.5.11: $\tilde{\nu}_e = \nu_o + 2\chi_e\nu_e = 817.358\ \text{cm}^{-1} + 2(5.300)\ \text{cm}^{-1} = 827.958\ \text{cm}^{-1}$

with Eq. 27.5.4: $k = 4\pi^2c^2\tilde{\nu}_e^2\mu = 4\pi^2(2.99792\text{x}10^{10}\ \text{cm s}^{-1})^2(827.958\ \text{cm}^{-1})^2(1.62668\text{x}10^{-27}\ \text{kg})$

$k = 403.85\ \text{N m}^{-1}$

with Eq. 27.5.8: $\text{ZPE} = \tilde{G}_o = ½\ \tilde{\nu}_e - ¼\ \tilde{\nu}_e\ \chi_e = ½(827.958\ \text{cm}^{-1}) - ¼(5.300\ \text{cm}^{-1}) = 412.654\ \text{cm}^{-1}$

with Eq. 27.5.18: $\tilde{D}_e = \tilde{\nu}_e^2/4\chi_e\tilde{\nu}_e = (827.958\ \text{cm}^{-1})^2/(4(5.300\ \text{cm}^{-1}))$

$\tilde{D}_e = 32340\ \text{cm}^{-1} = 4.009\ \text{eV} = 386.8\ \text{kJ mol}^{-1}$

with Eq. 27.5.12: $\tilde{D}_o = \tilde{D}_e - \text{ZPE} = 32340\ \text{cm}^{-1} - 412.654\ \text{cm}^{-1} = 31923.\ \text{cm}^{-1}$

$\tilde{D}_o = 3.958\ \text{eV} = 381.9\ \text{kJ mol}^{-1}$ (spectroscopic)

The often listed literature D_o value is the spectroscopic value. The dissociation energy of NCl is in good agreement with the extrapolated curve on the plot in Figure 26.4.12, assuming a doubly-bonded species. However, the NCl force constant, at 404 N m^{-1}, is closer to the force constant for singly-bonded F_2 at 450 N m^{-1} and B_2 at 350 N m^{-1}. Quantitatively, the correlation is poor based on the force constants. However, third period diatomics do show an excellent correlation with qualitative MO bond order, but with weaker bonds overall for a given bond order, compared to the second period diatomics.

20. Determine $\tilde{\nu}_e$, the force constant, anharmonicity, zero point energy, and the bond dissociation energies $\tilde{D}_e$ and $\tilde{D}_o$, for H_2. The fundamental and overtones for H_2 are listed below.

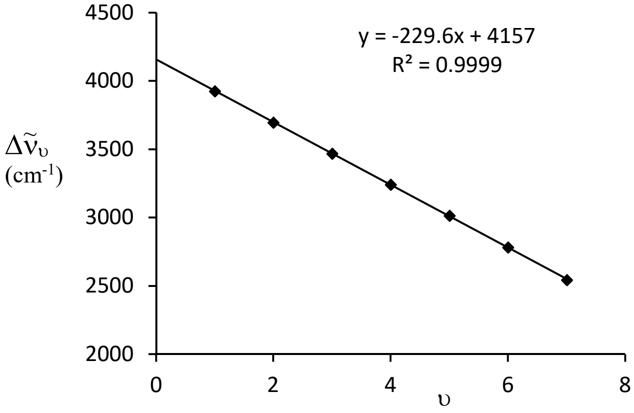
υ	1	2	3	4	5	6	7	8
$\tilde{\nu}_{\upsilon\leftarrow 0}$ (cm^{-1})	4161.14	8087.11	11782.35	15250.36	18491.92	21505.65	24287.83	26830.97

Answer: The plan is to follow Example 27.5.1 by doing a Birge-Sponer plot, Eq.27.5.20, and using the relationship between the anharmonicity and the bond dissociation energy based on the Morse potential, Eq. 27.5.18.

A Birge-Sponer plot based on Eq. 27.5.20 is implemented in the following spreadsheet.

υ	$\tilde{\nu}_{\upsilon\leftarrow 0}$ (cm^{-1})	$\Delta\tilde{\nu}_\upsilon$ (cm^{-1})
1	4161.14	3925.97
2	8087.11	3695.24
3	11782.35	3468.01
4	15250.36	3241.56
5	18491.92	3013.73
6	21505.65	2782.18
7	24287.83	2543.14
8	26830.97	

slope	-229.603	4156.96	intercept
±	0.809909	3.622021	±
r^2	0.999938	4.285633	s(y)
F	80368.15	5	df
ss$_{reg}$	1476094	91.83325	ss$_{resid}$



The curve fit gives the anharmonicity as $\chi_e\tilde{\nu}_e = 229.603/2 = 114.80 \pm 0.40$ cm^{-1}. The difference between the intercept and the experimental fundamental of 4161.14 cm^{-1} is caused by deviations from the Morse potential form and experimental error. The final spectroscopic constants are:

with Eq. 27.5.11: $\tilde{\nu}_e = \nu_o + 2\chi_e\nu_e = 4161.14\text{ cm}^{-1} + 2(114.80)\text{ cm}^{-1} = 4390.74\text{ cm}^{-1}$

with Eq. 27.5.4: $k = 4\pi^2c^2\tilde{\nu}_e^2\mu = 4\pi^2(2.99792\text{x}10^{10}\text{ cm s}^{-1})^2(4390.74\text{ cm}^{-1})^2(1.62668\text{x}10^{-27}\text{ kg})$
$k = 1113.\text{ N m}^{-1}$

with Eq. 27.5.8: $\text{ZPE} = \tilde{G}_o = \tfrac{1}{2}\,\tilde{\nu}_e - \tfrac{1}{4}\,\tilde{\nu}_e\,\chi_e = \tfrac{1}{2}(4390.74\text{ cm}^{-1}) - \tfrac{1}{4}(114.80\text{ cm}^{-1}) = 2166.7\text{ cm}^{-1}$

with Eq. 27.5.18: $\tilde{D}_e = \tilde{\nu}_e^2/4\chi_e\tilde{\nu}_e = (4390.74\text{ cm}^{-1})^2/(4(114.80\text{ cm}^{-1}))$

$\tilde{D}_e = 41{,}982\text{ cm}^{-1} = 5.205\text{ eV} = 502.2\text{ kJ mol}^{-1}$

with Eq. 27.5.12: $\tilde{D}_o = \tilde{D}_e - \text{ZPE} = 41{,}982\text{ cm}^{-1} - 2166.7\text{ cm}^{-1} = 39816.\text{ cm}^{-1}$

$\tilde{D}_o = 4.937\text{ eV} = 476.3\text{ kJ mol}^{-1}$

The literature values are $\tilde{\nu}_e = 4401.2$ cm^{-1}, $\chi_e\tilde{\nu}_e = 121.34$ cm^{-1} and $\tilde{D}_o = 4.4774 \pm 0.0004$ eV = 432.00 ± 0.04 kJ mol^{-1}, Table 27.6.1. The literature values include the second anharmonicity correction giving greater accuracy. The need for accuracy in the bond dissociation energy of H_2 is nicely exemplified by Figure 26.2.2.

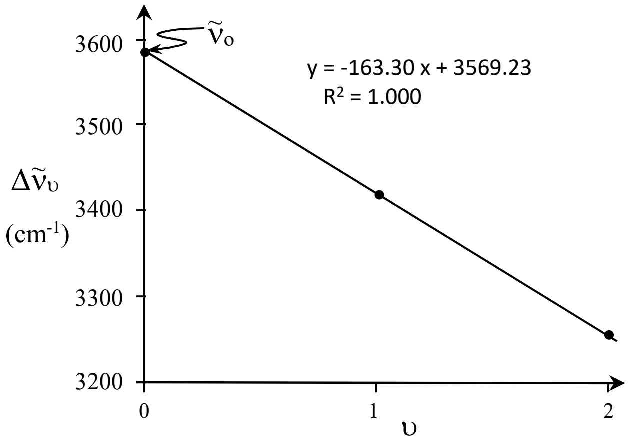
21. The fundamental and first two overtones in the vibrational spectrum of the OH radical are 3569.8, 6974.6, and 10217.8 cm^{-1}, respectively. Determine $\tilde{\nu}_e$, the force constant, anharmonicity, zero point energy, and the bond dissociation energies, $\tilde{D}_e$ and $\tilde{D}_o$.

Answer: The plan is to follow Example 27.5.1 by doing a Birge-Sponer plot, Eq.27.5.20, and using the relationship between the anharmonicity and the bond dissociation energy based on the Morse potential, Eq. 27.5.18.

The successive differences between the transitions is plotted as a function of the overtone. The fundamental transition is included as the value for υ = 0 in the following spreadsheet.

υ	$\tilde{\nu}_{\upsilon\leftarrow 0}$ (cm^{-1})	$\Delta\tilde{\nu}_\upsilon$ (cm^{-1})
0	3569.8	3569.8
1	6974.6	3404.8
2	10217.8	3243.2

slope	-163.30	3569.233	intercept
⍰	0.981495	1.267105	⍰
r2	0.999964	1.388044	s(y)
F	27681.89	1	df
ss_{reg}	53333.78	1.926667	ss_{resid}



The curve fit gives the anharmonicity as $\chi_e\tilde{\nu}_e = 81.65 \pm 0.5\ cm^{-1}$. The final spectroscopic constants are:

with Eq. 27.5.11: $\tilde{\nu}_e = \nu_o + 2\chi_e\tilde{\nu}_e = 3569.8\ cm^{-1} + 2(81.65)\ cm^{-1} = 3733.1\ cm^{-1}$

with Eq. 27.5.4: $k = 4\pi^2c^2\tilde{\nu}_e^2\mu = 4\pi^2(2.99792\text{x}10^{10}\ cm\ s^{-1})^2(3733.1\ cm^{-1})^2(1.62668\text{x}10^{-27}\ kg)$

$k = 804.3\ N\ m^{-1}$

with Eq. 27.5.8: $ZPE = \tilde{G}_o = \frac{1}{2}\,\tilde{\nu}_e - \frac{1}{4}\,\tilde{\nu}_e\,\chi_e = \frac{1}{2}(3733.1\ cm^{-1}) - \frac{1}{4}(81.65\ cm^{-1}) = 1846.14\ cm^{-1}$

with Eq. 27.5.18: $\tilde{D}_e = \tilde{\nu}_e^2/4\chi_e\tilde{\nu}_e = (3733.1\ cm^{-1})^2/(4(81.65\ cm^{-1}))$

$\tilde{D}_e = 42{,}670\ cm^{-1} = 5.29\ eV = 510.4\ kJ\ mol^{-1}$

with Eq. 27.5.12: $\tilde{D}_o = \tilde{D}_e - ZPE = 42{,}670\ cm^{-1} - 1846.14\ cm^{-1} = 40824.\ cm^{-1}$

$\tilde{D}_o = 5.06\ eV = 488.4\ kJ\ mol^{-1}$

The literature values are $\tilde{\nu}_e = 3737.76\ cm^{-1}$, $\chi_e\tilde{\nu}_e = 84.88\ cm^{-1}$ and $\tilde{D}_o = 4.40\ eV = 424.\ kJ\ mol^{-1}$, Table 27.6.1. The literature values include the second anharmonicity correction giving greater accuracy and averaging with thermochemically derived values.

<u>22</u>. Calculate the Morse *a*-parameter for the diatomic molecule Na_2. The fundamental vibration frequency is $\tilde{\nu}_e = 159.13\ \text{cm}^{-1}$ and the dissociation energy from the bottom of the potential energy well is $\tilde{D}_e = 5886.54\ \text{cm}^{-1}$. The most useful final units for *a* are Å^{-1}. [Hint: the units of $(\mu/(2D_e))^{½}$ are (s m^{-1}), so you will need to convert to Å^{-1} using 1 Å = $1\text{x}10^{-10}$ m. Typical values of *a* are in the range of ~ 0.5-3 Å^{-1}.]

Answer: The plan is to convert $\tilde{\nu}_e$ to the corresponding radial frequency and $\tilde{D}_e$ into joules.
In s^{-1}: $\omega_e = 2\pi\tilde{\nu}_e c = 2\pi(159.13\ \text{cm}^{-1})(2.99792\text{x}10^{10}\ \text{cm s}^{-1}) = 2.99736\text{x}10^{13}\ \text{s}^{-1}$

The reduced mass is: $\mu = \left(\frac{\mathfrak{M}_1\mathfrak{M}_2}{\mathfrak{M}_1 + \mathfrak{M}_2}\right)\frac{1}{N_A}(1\ \text{kg}/1000\ \text{g})$

$= (22.98977\ \text{g mol}^{-1}/2)/6.022137\text{x}10^{23}(1\ \text{kg}/1000\ \text{g}) = 1.908772\text{x}10^{-26}\ \text{kg}$

The dissociation energy in joules is:

$$D_e = \tilde{D}_e hc = 5886.54\ \text{cm}^{-1}(6.626076\text{x}10^{-34}\ \text{J s})(2.997925\text{x}10^{10}\ \text{cm s}^{-1}) = 1.169330\text{x}10^{-19}\ \text{J}$$

Using Eq. 27.5.8, the Morse *a*-parameter is:

$$a = \omega_e\left(\frac{\mu}{2D_e}\right)^{½} = 2.99736\text{x}10^{13}\ \text{s}^{-1}\left(\frac{1.908772\text{x}10^{-26}\ \text{kg}}{2(1.169329\text{x}10^{-19}\ \text{J})}\right)^{½} = 8.56313\text{x}10^{9}\ \text{m}^{-1}$$
$$= 8.56313\text{x}10^{9}\ \text{m}^{-1}(1\text{x}10^{-10}\ \text{m}/1\ \text{Å}) = 0.856313\ \text{Å}^{-1}$$

<u>A note about units</u>: In the ratio $\mu/(2D_e)$, you can use the reduced mass in kg mol^{-1} and the dissociation in J mol^{-1}, since the per mol units cancel. Then the conversion factor 1 cm^{-1} = 11.962658 J mol^{-1} is handy. Once again:

$$a = 2\pi\tilde{\nu}_e c\left(\frac{\mu}{2D_e}\right)^{½}$$
$$= 2\pi(159.13\ \text{cm}^{-1})(2.99792\text{x}10^{10}\ \text{cm s}^{-1})\left[\frac{11.49489\ \text{g mol}^{-1}(1\ \text{kg}/1000\ \text{g})}{2(5886.54\ \text{cm}^{-1})(11.962658\ \text{J mol}^{-1})}\right]^{½}$$
$$= 8.56313\text{x}10^{9}\ \text{m}^{-1}(1\text{x}10^{-10}\ \text{m}/1\ \text{Å}) = 0.856313\ \text{Å}^{-1}$$

<u>23</u>. Calculate the Morse *a*-parameter for $H^{35}Cl$ in Å^{-1}. The fundamental vibration frequency is $\tilde{\nu}_e$ = 2990.925 cm^{-1} and the dissociation energy from the bottom of the potential energy well is $\tilde{D}_e$ = 37270. cm^{-1}. [Hint: The conversion 1 cm^{-1} = 11.96266 J mol^{-1} is handy. The units of $(\mu/(2D_e))^{½}$ are (s m^{-1}), so you will need to convert to Å^{-1} using 1 Å = $1\text{x}10^{-10}$ m. Typical values of *a* are in the range of ~ 0.5-3 Å^{-1}.]

Answer: The plan is to convert $\tilde{\nu}_e$ to the corresponding radial frequency and $\tilde{D}_e$ into J mol^{-1}. See the previous problem for comments on the units.
The reduced mass is:

$$\mu = \frac{\mathfrak{M}_1\mathfrak{M}_2}{\mathfrak{M}_1 + \mathfrak{M}_2} = \frac{(1.007825)(34.968853)}{1.007825 + 34.968853} = 0.979593\ \text{g mol}^{-1}$$

Using Eq. 27.5.8 and $\omega_e = 2\pi\tilde{\nu}_e c$, the Morse a-parameter is:

$$a = 2\pi\tilde{\nu}_e c \left(\frac{\mu}{2D_e}\right)^{1/2}$$

$$= 2\pi(2990.925\ \text{cm}^{-1})(2.99792\text{x}10^{10}\ \text{cm s}^{-1})\left[\frac{0.979593\ \text{g mol}^{-1}(1\ \text{kg}/1000\ \text{g})}{2(37270\ \text{cm}^{-1})(11.962658\ \text{J mol}^{-1})}\right]^{1/2}$$

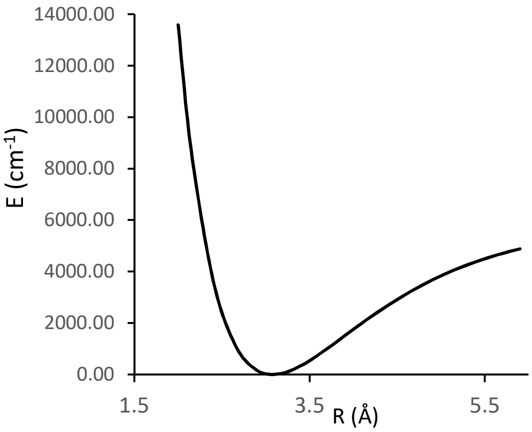
$$= 1.867\text{x}10^{10}\ \text{m}^{-1}(1\text{x}10^{-10}\ \text{m}/1\ \text{Å}) = 1.867\ \text{Å}^{-1}$$

24. Plot the vibrational potential energy function for Na_2. Assume a Morse potential function. The dissociation energy from the bottom of the potential energy well is $\tilde{D}_e = 5886.54\ \text{cm}^{-1}$, the Morse a-parameter is $a = 0.8563\ \text{Å}^{-1}$, and the equilibrium bond length is $R_e = 3.079$ Å. [See Problem 22 for the calculation of a.]

Answer: The plan is to write a spreadsheet based on Eqs. 27.5.7-27.5.8.

The Morse function in cell D11 is given as: "=D$7*(1-EXP(-D$8*($C11-D$6)))^2".

A1	B	C	D	E
5	vibration freq.	n_e	159.1245	cm^{-1}
6	bond length	R_e	3.07887	Å
7	dissociation energy	D_e	5886.54	cm^{-1}
8	Morse *a*	*a*	0.8563	
10		R (Å)	V(R) cm^{-1}	
11		2	13581.22	
12		2.15	8694.26	
13		2.4	3658.84	
14		2.65	1159.12	
15		2.9	161.27	
16		3.15	20.55	
17		3.4	340.24	
18		3.65	880.69	
19		3.9	1501.03	
20		4.15	2121.75	
21		4.4	2701.01	
22		4.65	3219.58	
23		4.9	3671.42	
24		5.15	4057.81	
25		5.4	4383.85	
26		5.65	4656.24	
27		5.9	4882.13	



25. Plot the Morse and harmonic vibrational potential energy functions for $H^{35}Cl$. Assume the fundamental vibration frequency $\tilde{\nu}_e = 2990.9\ \text{cm}^{-1}$, dissociation energy from the bottom of the potential energy well is $\tilde{D}_e = 37270\ \text{cm}^{-1}$, the Morse a-parameter is $a = 1.867\ \text{Å}^{-1}$, and the equilibrium bond length is $R_e = 1.275$ Å. [See Problem 23 for the calculation of a.]

Answer: The plan is to use Eq. 27.5.4 to calculate the bond force constant and then write a spreadsheet based on Eqs. 24.2.1 and 27.5.7-27.5.8.

The reduced mas for $H^{35}Cl$ is: $\mu = \left(\frac{\mathfrak{M}_1 \mathfrak{M}_2}{\mathfrak{M}_1 + \mathfrak{M}_2}\right)\frac{1}{N_A}(1 \text{ kg}/1000 \text{ g})$

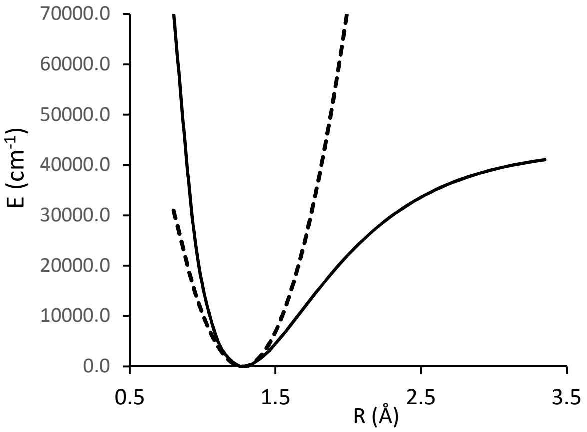
$$\mu = \left(\frac{(1.007825)(34.968853)}{(1.007825 + 34.968853)}\right)\frac{1}{6.022137\text{x}10^{23}}(1 \text{ kg}/1000 \text{ g}) = 1.6266526\text{x}10^{-27} \text{ kg}$$

The bond force constant is given by rearranging Eq. 24.2.1:

$$k = 4\pi^2\tilde{\nu}_e^2c^2\mu = 4\pi^2(2990.9 \text{ cm}^{-1})^2(2.997925\text{x}10^{10} \text{ cm s}^{-1})^2(1.62665\text{x}10^{-27} \text{ kg}) = 516.30 \text{ N m}^{-1}$$

The cell D4 gives this calculation: “=4*PI()^2*D3^2*(2.99792E+10)^2*D2”

A1	B	C	D	E
2	reduced mass	μ	1.627E-27	kg
3	vibration freq.	ν_e	2990.9	cm^{-1}
4	force constant	k	516.29563	$N\ m^{-1}$
5	bond length	R_e	1.275	Å
6	dissociation energy	D_e	37270	cm^{-1}
7	Morse *a*	*a*	1.867	$Å^{-1}$
8				
9		R (Å)	V(R) cm^{-1}	V(Harm)
10		0.8	75937.6	31031.7
11		0.95	25954.8	14527.3
12		1.1	5565.2	4212.1
13		1.25	85.1	86.0
14		1.4	1614.7	2149.0
15		1.55	6009.7	10401.2
16		1.7	11181.3	24842.6
17		1.85	16146.3	45473.1
18		2	20502.1	72292.7
19		2.15	24138.7	105301.5
20		2.3	27083.8	144499.5
21		2.45	29422.1	189886.6
22		2.6	31253.4	241462.9
23		2.75	32674.2	299228.3
24		2.9	33768.8	363182.8
25		3.05	34608.1	433326.5
26		3.2	35249.1	509659.4
27		3.35	35737.5	592181.4



The Morse function in cell D10 is:
“=D$6*(1-EXP(-D$7*($C10-D$5)))^2”.

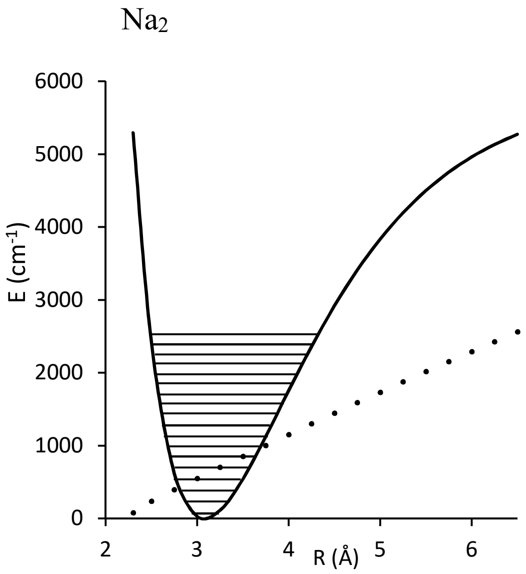
The harmonic potential is $V(R) = ½\ k(R – R_e)^2$, however to convert from joules to wave numbers is given by $\tilde{V}(R) = V(R)/(hc)$ where R is in meters, as given in cell E10:
“=$D$4*((C10-$D$5)/1E10)^2/2/6.2608E-34/2.99792E10”

<u>26</u>. Plot the Morse potential energy function for ^7LiH. See Table 27.6.1 for the spectroscopic constants. Superimpose on the potential energy surface the 15 lowest vibrational energy levels, including the effects of anharmonicity. [Hints: See Problem 22 for hints on calculating the Morse *a*-parameter. A few rows of an example spreadsheet for Na_2 are given below. The calculation of the Morse potential, rows B and C, is independent of the calculation of the vibrational energy

levels, rows D and E. However, you can use the R values as a dummy variable to superimpose the vibrational energy levels on top of the potential energy curve. In other words, use columns B, C, and E to construct your scatter plot. Join the potential energy data points with a curve, but leave the vibrational levels as dots. The horizontal position of the vibrational level data points will be meaningless, but the vertical position gives the vibrational energies. You can draw in the horizontal lines representing the vibrational levels by hand.]

For Na_2:

A1	B	C	D	E
2	reduced mass	μ	11.495	g mol^{-1}
3	vibration freq.	ν_e	159.125	cm^{-1}
4	anharmonicity	$\nu_e\chi_e$	0.725	cm^{-1}
5	bond length	R_e	3.079	Å
6	dissociation E	D_o	0.720	eV
7	dissociation E	D_e	5887	cm^{-1}
8	Morse *a*	*a*	0.856	$Å^{-1}$
9				
10	R (Å)	V(R) cm^{-1}	υ	G(υ) cm^{-1}
11	2.3	5293.9	0	79.4
12	2.5	2423.6	1	237.1
13	2.75	622.8	2	393.3
14	3	28.7	3	548.0
15	3.25	109.4	4	701.4
16	3.5	539.6	5	853.2
17	3.75	1124.8	6	1003.7
18	4	1752.3	7	1152.6
19	4.25	2360.0	8	1300.1
20	4.5	2916.4	9	1446.2



Answer: The plan is to use Eq. 27.5.8 to calculate the Morse *a*-parameter and then write a spreadsheet based on Eqs. 27.5.7 and 27.5.9. The units work out if the reduced mass is given in kg mol^{-1} and the dissociation energy is converted to J mol^{-1} using 1 cm^{-1} = 11.9627 J mol^{-1}.

The reduced mas for ^{7}LiH is: $\mu = \left(\frac{\mathcal{M}_1\mathcal{M}_2}{\mathcal{M}_1 + \mathcal{M}_2}\right) = \left(\frac{(1.007825)(6.015122)}{(1.007825 + 6.015122)}\right) = 0.8632 \text{ g mol}^{-1}$

Using constants from Table 27.6.1 the dissociation energy from the bottom of the potential energy well using Eq. 27.5.12 is:

$$\tilde{D}_e = \tilde{D}_o + \tfrac{1}{2}\,\tilde{\nu}_e - \tfrac{1}{4}\,\tilde{\nu}_e\,\chi_e$$
$$= 2.429 \text{ ev}(8065.5 \text{ cm}^{-1}/1 \text{ eV}) + \tfrac{1}{2}(1405.498 \text{ cm}^{-1}) - \tfrac{1}{4}(23.168 \text{ cm}^{-1}) = 20288. \text{ cm}^{-1}$$

Using the discussion in Problem 22, the Morse *a*-parameter is:

$$a = 2\pi\tilde{\nu}_e c \left(\frac{\mu}{2D_e}\right)^{1/2}$$
$$= 2\pi(1405.498 \text{ cm}^{-1})(2.99792\text{x}10^{10} \text{ cm s}^{-1})\left[\frac{0.8632 \text{ g mol}^{-1}(1 \text{ kg}/1000 \text{ g})}{2(20288. \text{ cm}^{-1})(11.9627 \text{ J mol}^{-1})}\right]^{1/2}$$
$$= 8.56313\text{x}10^9 \text{ m}^{-1}(1\text{x}10^{-10} \text{ m}/1 \text{ Å}) = 1.116 \text{ Å}^{-1}$$

Spreadsheet cell D8 does this calculation for the *a*-parameter:

```
=2*PI()*D3*2.998E10*SQRT(D2/1000/2/(D7*11.9627))*1E-10
```

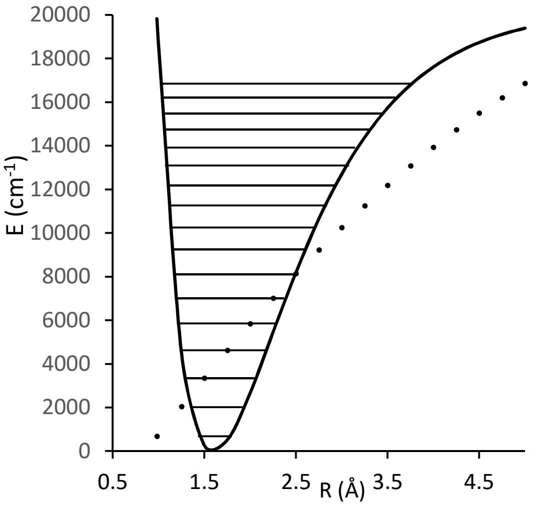
The spreadsheet to generate the potential energy surface and the vibrational energies and the corresponding plot are listed below. Cell C11 for the Morse function is:

=D$7*(1-EXP(-D$8*($B11-D$5)))^2

Cell E11 for the anharmonicity correscted vibrational energy levels is:

=$D$3*(D11+0.5)-$D$4*(D11+0.5)^2

A1	B	C	D	E
2	reduced mass	μ	0.863	g mol^{-1}
3	vibration freq.	ν_e	1405.498	cm^{-1}
4	anharmonicity	$\nu_e\chi_e$	23.168	cm^{-1}
5	bond length	R_e	1.596	Å
6	dissociation E	D_o	2.429	eV
7	dissociation E	D_e	20288	cm^{-1}
8	Morse *a*	*a*	1.116	$Å^{-1}$
9				
10	R (Å)	V(R) cm^{-1}	υ	G(υ) cm^{-1}
11	0.98	19826.5	0	697.0
12	1.25	4501.3	1	2056.1
13	1.5	258.0	2	3368.9
14	1.75	508.1	3	4635.4
15	2	2677.1	4	5855.6
16	2.25	5450.8	5	7029.4
17	2.5	8197.3	6	8156.9
18	2.75	10645.8	7	9238.0
19	3	12710.2	8	10272.8
20	3.25	14393.3	9	11261.3
21	3.5	15736.0	10	12203.5
22	3.75	16791.4	11	13099.3
23	4	17612.6	12	13948.7
24	4.25	18246.8	13	14751.9
25	4.5	18734.0	14	15508.6
26	4.75	19106.8	15	16219.1
27	5	19391.2	16	16883.2



The conclusion is that the illustrations in text books usually overemphasize the effects of anharmonicity. There are typically many more vibrational levels before the dissociation limit than are often depicted, for example Figure 27.5.2.

27. The overtone wave numbers are given directly by Eq. 27.5.8 for the transition $\upsilon'\leftarrow 0$:

$$\tilde{\nu}_{\upsilon'\leftarrow 0} = \tilde{G}_{\upsilon'} - \tilde{G}_o = \tilde{\nu}_e(\upsilon'+½) - \chi_e\tilde{\nu}_e(\upsilon'+½)^2 - \tilde{\nu}_e(0+½) + \chi_e\tilde{\nu}_e(0+½)^2$$

$$= \tilde{\nu}_e\,\upsilon' - \chi_e\tilde{\nu}_e(\upsilon'^2 + \upsilon' + ¼) + ¼\,\chi_e\tilde{\nu}_e$$

$$= -\,\chi_e\tilde{\nu}_e\,\upsilon'^2 + (\tilde{\nu}_e - \chi_e\tilde{\nu}_e)\upsilon' \qquad \text{(Morse, } \upsilon'\text{:upper)}$$

Rather than plotting adjacent differences in a Birge-Sponer plot, this last equation can be used in least squares curve fitting. The result is essentially equivalent, but the process and the associated uncertainties are more direct. Use the data in Example 27.5.1 and a quadratic fit to determine $\tilde{\nu}_e$ and $\chi_e\tilde{\nu}_e$ for $H^{35}Cl$. Compare to the results in the example.

Answer: The overtone data can be directly input into the "Nonlinear Least Squares Curve Fitting" applet on the textbook Web site or companion CD. The result using the fit function "ax^2 + bx + c" with c fixed at c = 0 is shown below:

```
====================  Results  =======================
 a= -51.568 +- 0.0528
 b= 2937.055 +- 0.22
______________________ Output Data ________________________
   x              y           y(fit)           residual
  1.0          2885.98   2885.48658           0.49342
  2.0          5667.98   5667.83714           0.14286
  3.0          8346.78    8347.05168          -0.27168
  4.0          10922.83 10923.13019           -0.30019
  5.0          13396.32 13396.07267           0.24733
---------------------------------------------------------
 sum of squared residuals= 0.489
 stand. dev. y values= 0.4037
 correlation between a & b= -0.9696
```

The fit anharmonicity, $\chi_e\tilde{\nu}_e = 51.568 \pm 0.053\ \text{cm}^{-1}$, differs by 0.3% from the Birge-Sponer value in Example 27.5.1, which is certainly not significant. The fundamental vibration frequency is given by:

$$b = (\tilde{\nu}_e - \chi_e\tilde{\nu}_e)$$

or $$\tilde{\nu}_e = b + \chi_e\tilde{\nu}_e = (2937.055 \pm 0.22) + (51.568 \pm 0.053)\ \text{cm}^{-1} = 2988.62 \pm 0.23\ \text{cm}^{-1}$$

which also differs from the result in Example 27.5.1 by an insignificant amount. One advantage of this direct method is that we can see that the between-parameter correlation coefficient is unacceptably large at -0.9696. This warning suggests that the second anharmonicity correction needs to be taken into account for an accurate representation of the data. The same conclusion can be drawn by noticing that there is some systematic curvature in the final curve fit results, rather than a random scatter of points about the curve fit polynomial. The choice of using the Birge-Sponer method or the quadratic curve fit is a matter of preference.

<u>28</u>. Often only the fundamental and first overtone vibration frequencies are observable in infrared spectra. The experimental values for the fundamental and the first overtone are sufficient to obtain a rough estimate of the anharmonicity and the bond dissociation energy. We can use $H^{35}Cl$ as a good test case. Determine $\tilde{\nu}_e$, the force constant, anharmonicity, zero point energy, and the bond dissociation energies $\tilde{D}_e$ and $\tilde{D}_o$, for $H^{35}Cl$. The fundamental and first overtone for $H^{35}Cl$ are 2885.98 and 5667.98 cm^{-1}.

Answer: The first-overtone adjacent difference is $\Delta\tilde{\nu}_1 = 2782.10\ \text{cm}^{-1}$. Using just the fundamental and first overtone with Eq. 27.5.21 gives:

$$\chi_e\tilde{\nu}_e = (\tilde{\nu}_o - \Delta\tilde{\nu}_1)/2 = (2885.98 - 2782.10)/2\ \text{cm}^{-1} = 51.90\ \text{cm}^{-1}$$

The final spectroscopic constants are:

with Eq. 27.5.11: $\tilde{\nu}_e = \nu_o + 2\chi_e\nu_e = 2885.98\ \text{cm}^{-1} + 2(51.90)\ \text{cm}^{-1} = 2989.78\ \text{cm}^{-1}$

with Eq. 27.5.4: $\underset{\sim}{k} = 4\pi^2c^2\tilde{\nu}_e^2\mu = 4\pi^2(2.99792\text{x}10^{10}\ \text{cm s}^{-1})^2(2989.78\ \text{cm}^{-1})^2(1.62668\text{x}10^{-27}\ \text{kg})$

$\underset{\sim}{k} = 515.9\ \text{N m}^{-1}$

with Eq. 27.5.8: $\text{ZPE} = \tilde{G}_o = \tfrac{1}{2}\,\tilde{\nu}_e - \tfrac{1}{4}\,\tilde{\nu}_e\,\chi_e = \tfrac{1}{2}(2989.78\ \text{cm}^{-1}) - \tfrac{1}{4}(51.90\ \text{cm}^{-1}) = 1481.92\ \text{cm}^{-1}$

with Eq. 27.5.18: $\tilde{D}_e = \tilde{\nu}_e^2/4\chi_e\tilde{\nu}_e = (2989.78\ \text{cm}^{-1})^2/(4(51.90\ \text{cm}^{-1}))$

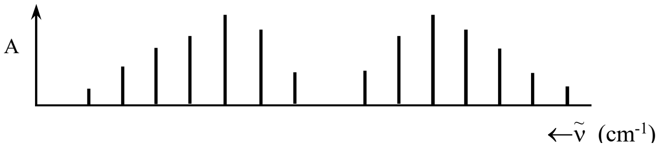
$\tilde{D}_e = 43{,}058\ \text{cm}^{-1} = 5.339\ \text{eV} = 515.1\ \text{kJ mol}^{-1}$

with Eq. 27.5.12: $\tilde{D}_o = \tilde{D}_e - \text{ZPE} = 43{,}058\ \text{cm}^{-1} - 1481.92\ \text{cm}^{-1} = 41576.\ \text{cm}^{-1}$

$\tilde{D}_o = 5.155\ \text{eV} = 497.3\ \text{kJ mol}^{-1}$

In this case the results are remarkably close to the Birge-Sponer extrapolated value in Example 27.5.1. In all honesty, the agreement with only a single observed overtone and more carefully obtained values is rarely so close. Factor of two errors can occur between values obtained using different extrapolation methods and between methods based on other experimental techniques (e.g. thermochemical values or values from mass spectrometry appearance potentials).

29. A schematic rotational-vibrational absorption spectrum of a diatomic molecule is shown below. The bond length is assumed to be the same in the two vibrational states. Sketch the resulting spectrum if, in the absence of any other changes, (a) the bond length of both vibrational states is increased, (b) the bond force constant is increased, (c) the temperature is increased, and (d) the bond length of just the upper vibrational state is increased.



Answer: The plan is to note that the missing, forbidden transition is at $\tilde{\nu}_o = {}^1/_{2\pi}\sqrt{k/\mu}$ and the peak-to-peak spacing, assuming equal bond lengths in the two vibrational states, is $2\tilde{B}$.

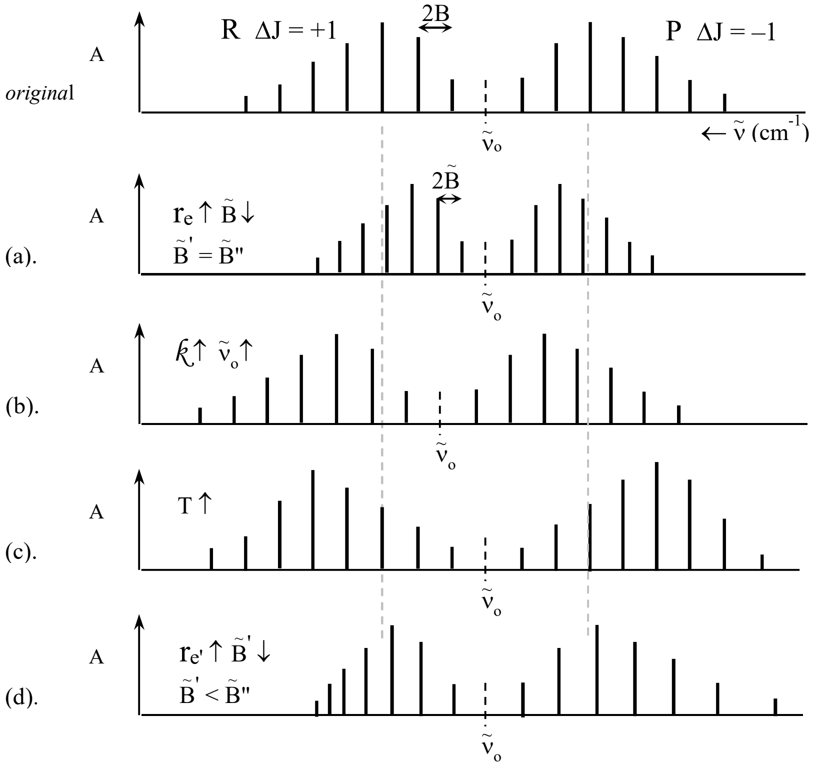
(a). Increasing the bond length decreases the rotational constant $\tilde{B}$, moving the peaks closer together.

(b). Increasing the bond force constant increases the fundamental vibration frequency, $\tilde{\nu}_o$, which shifts all the transitions to higher frequency. Higher wave number, higher energy, higher frequency, and bluer are all towards the left.

(c). Increasing temperature has no effect on the spectroscopic constants. However, increasing temperature does increase the population of higher rotational states, Figure 27.6.7. As a consequence the rotational transition of maximum intensity is a higher J state.

(d). Increasing the bond length of just the upper vibrational state decreases the $\tilde{B}'$ value. With $\tilde{B}' < \tilde{B}''$, each line moves to lower wave number in proportion to the J''^2 value, Eqs. 27.6.8-27.6.9. In other words, lines further away from $\tilde{\nu}_o$ move more than lines closer to $\tilde{\nu}_o$. The R-branch lines get closer together and the P-branch lines get further apart.

The effects are diagrammed below.



30. Write a spreadsheet to simulate the rotational-vibrational infrared spectrum of ^{12}CH for the $1 \leftarrow 0$ fundamental vibrational transition at 25°C. Use the spectroscopic constants in Table 27.6.1. Include six R-branch and six P-branch transitions. The relative intensity of the transitions is proportional to the Boltzmann weighting factors of the initial rotational levels for the $\upsilon = 0$ vibrational state: $p(J'') \propto (2J'' + 1)\, e^{-\tilde{B}'' J''(J''+1)/kT}$. To emphasize the differences caused by $\tilde{B}' < \tilde{B}''$, compare the appearance for α_e equal to zero, the literature value, and three times the literature value. [Hints: Display your results as an unconnected scatter plot of relative intensity, p(J"), versus the transition wave number. You won't get a "stick" spectrum as in the previous problem, but you can draw lines by hand from each data point to the horizontal axis to sketch the spectrum. Remember that $kT = 207.2\ \text{cm}^{-1}$ at 25°C.]

Answer: The plan is to use Eqs. 27.5.12, 27.6.5, and 27.6.6 to calculate the wave number of each transition. The intensity is proportional to the Boltzmann probability of occupation of each of the ground vibrational state energy levels. The ground state of CH is a doublet, so spectra of CH include Q-branches, which we neglect in this problem.

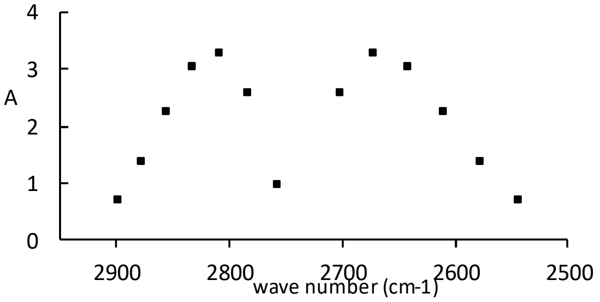
Using Eq. 27.5.12, the center of the rotational-vibrational band, which is the observed fundamental vibration frequency, is at:

$$\tilde{\nu}_o = \tilde{\nu}_e - 2\chi_e\tilde{\nu}_e = 2731.87\ \text{cm}^{-1}$$

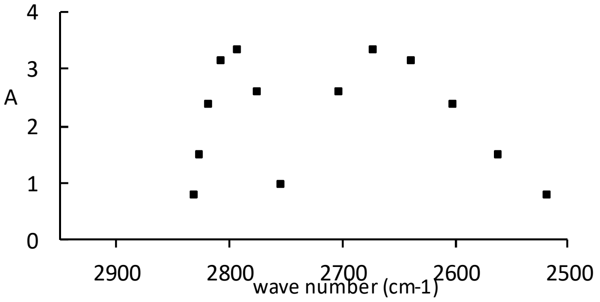
The rotational constants for the $\upsilon'' = 0$ and $\upsilon' = 1$ states are calculated from α_e using Eq. 27.6.5. The spreadsheet is reproduced below.

A1	B	C	D	E	F
2					
3	ν_o	2731.87	cm^{-1}		
4	B_e	14.46	cm^{-1}		
5	α_e	0.536	cm^{-1}		
6	B"	14.192	cm^{-1}	υ=0	
7	B'	13.656	cm^{-1}	υ=1	
8					
9	J"	J'	F(J") cm^{-1}	ν cm^{-1}	p(J")
10	6	7	168.672	2900.542	0.732
11	5	6	147.792	2879.662	1.409
12	4	5	125.84	2857.71	2.287
13	3	4	102.816	2834.686	3.077
14	2	3	78.72	2810.59	3.315
15	1	2	53.552	2785.422	2.616
16	0	1	27.312	2759.182	1.000
17	1	0	-28.384	2703.486	2.616
18	2	1	-57.84	2674.03	3.315
19	3	2	-88.368	2643.502	3.077
20	4	3	-119.968	2611.902	2.287
21	5	4	-152.64	2579.23	1.409
22	6	5	-186.384	2545.486	0.732

With $\alpha_e = 0.536\ \text{cm}^{-1}$:



With $\alpha_e = 3(0.536\ \text{cm}^{-1})$:



Cell C3 to calculate the observed fundamental frequency is: "=2860.75-2*64.44"
Cell C6 to calculate the rotational constant in the υ" = 0 vibrational state is: "=C4-C5/2"
Cell C7 to calculate the rotational constant in the υ' = 1 vibrational state is: "=C4-3*C5/2"
Cell D10 for the first rotational term value is: "=\$C\$7*(C10)*(C10+1)-\$C\$6*B10*(B10+1)"
Cell F10 to find the Boltzmann weighting factor for the J" state is:

=(2*B10+1)*EXP(-\$C\$6*B10*(B10+1)/207.2)

The first transition wave number in cell E10 just adds the observed fundamental vibration wave number to the rotational term value: "=\$C\$3+D10"

Note that $\tilde{B}' < \tilde{B}''$ as expected, since the vibration-averaged bond length increases with vibrational quantum number thus decreasing the corresponding rotational constant. The effect of $\tilde{B}' < \tilde{B}''$ is that all transitions move to smaller wave number, but the transitions for high J" shift more than low J" transitions. As a result the R-branch transitions are closer together and the P-branch transitions are further apart. Only when $\tilde{B}' = \tilde{B}''$ is the adjacent peak spacing $2\tilde{B}_o$.

31. The experimental fundamental vibration frequencies in infrared absorption for N_2O are 2224 cm^{-1}, 1285 cm^{-1}, and 588 cm^{-1}. Assuming N_2O is linear, determine if the bonding configuration is NNO or NON.

Answer: The plan is to use the three observed fundamentals and the expected number of IR active normal modes for a linear diatomic, symmetric or asymmetric, to determine the symmetry.

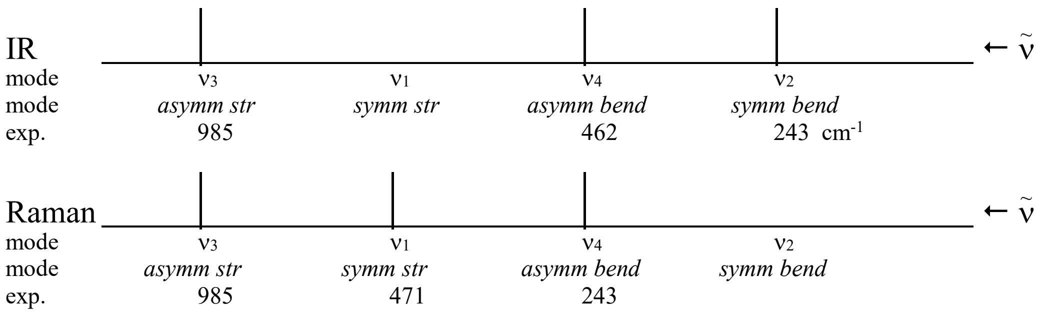
A linear triatomic has 3N – 5 = 3(3) – 5 = 4 normal modes. In order of expected decreasing wave number, the normal modes are an asymmetric stretch, a symmetric stretch, and a degenerate bend. For a symmetric linear triatomic, such as CO_2, the symmetric stretch is IR forbidden, giving two distinct fundamental frequencies. For an asymmetric linear triatomic, such as H–C≡N, the symmetric stretch gives a changing dipole moment, resulting in three distinct fundamental frequencies. Since N_2O has three observed frequencies, the molecule must be asymmetric, arranged as NNO.

32. The experimental fundamental vibration frequencies in infrared absorption for BCl_3 are 985 cm^{-1}, 462 cm^{-1}, and 243 cm^{-1}. The experimental Raman frequencies are 985 cm^{-1}, 471 cm^{-1}, and 243 cm^{-1}. With reference to Table 27.7.1, determine if BCl_3 is planar or trigonal pyramidal. Assign the observed frequencies to the distinct frequencies, ν_1 - ν_4.[4,5]

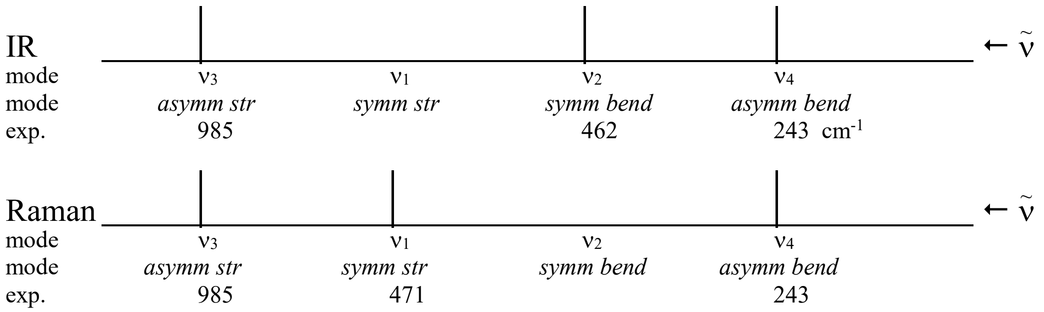
Answer: The plan is to count the number of distinct vibration frequencies that are expected for the two different geometries, based on Table 27.7.1.

The asymmetric stretches and asymmetric bends are doubly degenerate in both planar and trigonal pyramidal XY_3 molecules. Doubly degenerate normal modes have the same vibration frequency. For a planar XY_3 molecule, there are three distinct IR vibration frequencies and three distinct Raman frequencies. For a trigonal pyramidal XY_3 molecule, all modes are IR and Raman active giving four distinct IR and four distinct Raman frequencies. Given the three observed IR and three observed Raman frequencies in BCl_3, the molecule must be planar.

We can take the analysis a step further to confirm our conclusion. Assuming the asymmetric stretches occur at higher wave number than the symmetric stretches and the asymmetric bends occur at higher wave number than the symmetric bends, using the IR and Raman activities listed in Table 27.7.1 gives the following schematic appearance in the spectra. The sticks are the predictions using symmetry arguments and the experimental wave numbers are then assigned to the expected pattern based on IR or Raman activity:



The two repeated transitions didn't match up as expected. However, the pattern of three present and one missing is apparent. Consider the following assignments, which give consistent results for the two repeated frequencies:



The similar wave number of the symmetric stretch and symmetric bend is surprising. Molecular orbital calculations at the Hartree-Fock and B3LYP levels with a 6-311+G(2d,p) basis set give ~11.5 cm^{-1} difference between these two modes. The difference at HF/6-31G* and HF/6-311G* is ~14 cm^{-1}. The agreement between theory and experiment helps to validate the assignment.

33. The carbonyl stretch for ketones is active in both IR and Raman spectroscopy. Assume a carbonyl stretch occurs at 1800. cm^{-1}. Calculate the wave lengths of the Stokes and anti-Stokes transitions in the Raman spectrum assuming laser excitation using a helium-neon laser at 632.8 nm.

Answer: The plan is to convert to wave numbers to find the transitions and then finally to convert back to wave lengths.

The laser excitation is at: $\tilde{\nu} = 1/\lambda = \dfrac{1}{632.8 \text{ nm } (1\text{x}10^{-9} \text{ m/1nm})(100 \text{ cm/1 m})} = 15803. \text{ cm}^{-1}$

The Stokes transition is at 15803. cm^{-1} – 1800. cm^{-1} = 14003 cm^{-1}
Converting to meters and then inverting gives the wave length of the transition:

$$\lambda = 1/\tilde{\nu} = \frac{1}{14003 \text{ cm}^{-1}(100 \text{ cm/1 m})} = 7.141\text{x}10^{-9} \text{ m} = 714.1 \text{ nm} \qquad \text{(Stokes)}$$

The anti-Stokes transition is at 15803. cm^{-1} + 1800. cm^{-1} = 17603 cm^{-1}
Converting to meters and then inverting gives the wave length of the transition:

$$\lambda = 1/\tilde{\nu} = \frac{1}{17603 \text{ cm}^{-1}(100 \text{ cm/1 m})} = 5.6808\text{x}10^{-9} \text{ m} = 568.1 \text{ nm} \qquad \text{(anti-Stokes)}$$

34. Name three advantages of Raman spectroscopy over infrared absorption. Name a disadvantage.

Answer: (1). Raman spectra occur in the near-infrared or visible region, depending on the laser used for excitation, which allows the use of glass or plastic cell windows. Raman spectra can be acquired through the containers of personal care products. Mid-infrared cell windows are usually hygroscopic and fragile. Expensive NaCl and KBr salt crystals are typically used for infrared cell windows. (2). Water is a poor Raman scatterer, so Raman spectra in aqueous solvents is common. Special techniques are required for aqueous infrared spectra, such as attenuated total reflection, ATR. (3). Raman is complementary to IR, which allows the determination of normal modes that are forbidden in the infrared. (4). Raman spectrometers can be easily configured as battery powered hand held devices. (5). Raman microscopes are more easily designed with higher spatial resolution than infrared microscopes, since the wave length for Raman scattering is bluer making the optics easier and giving a smaller diffraction limit.

The main disadvantage of Raman is poor sensitivity compared to infrared absorption.

35. Identifying the point group of a molecule is done using Table 27.8.1 or using a flow chart such as Figure P27.1.

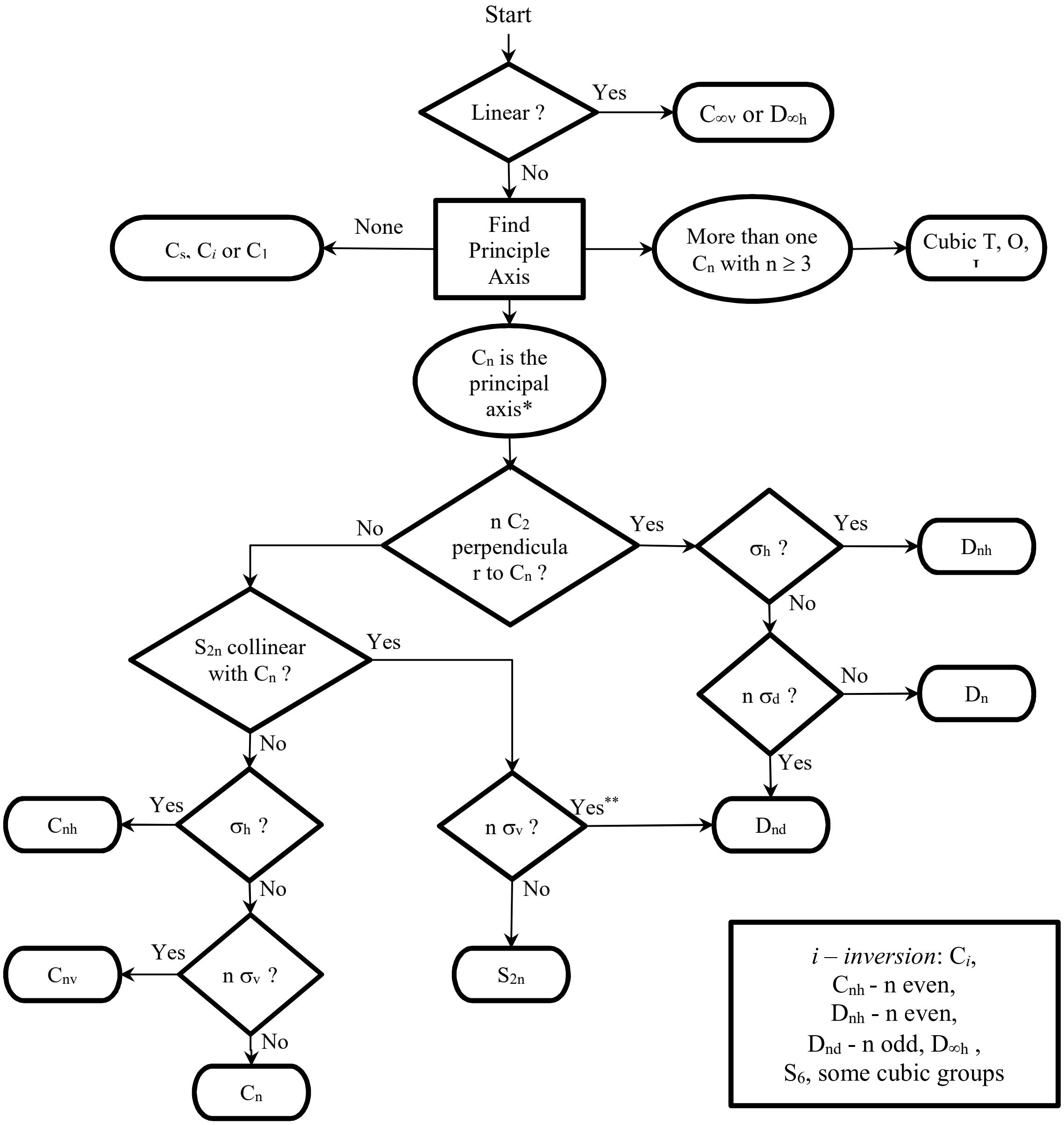
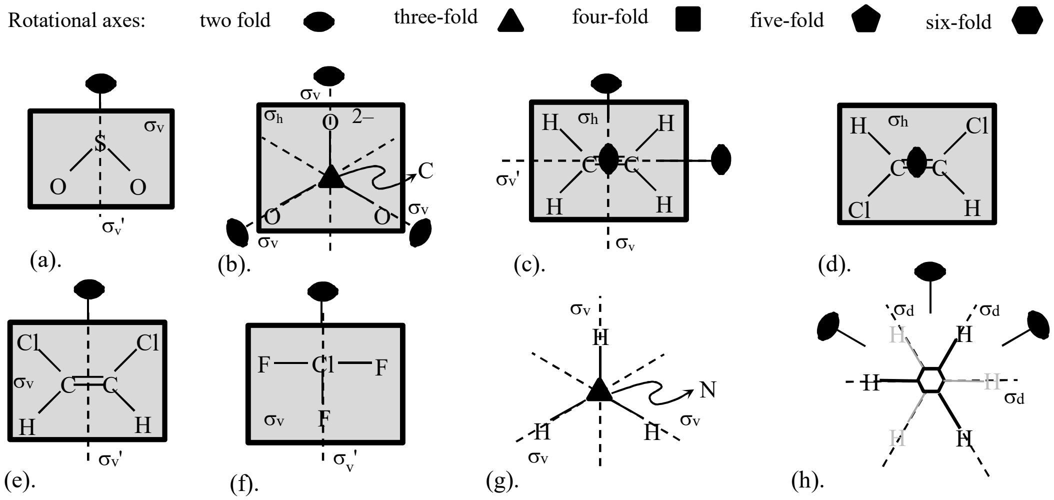


Figure P27. 1: Flow chart to identify the point group of a molecule. * If there are three mutually perpendicular axes, choose the principal axis perpendicular to the axis that passes through the most atoms or the heaviest atoms. ** There are n perpendicular C_2 axes, but they may not be obvious.[6]

Determine the point group for the following species: (a) SO_2; (b) CO_3^{2-}; (c) C_2H_4, ethylene; (d) *trans*-1,2-$C_2H_2Cl_2$, *trans*-1,2-dichloroethylene; (e) *cis*-1,2-$C_2H_2Cl_2$, *cis*-1,2-dichloroethylene; (f) ClF_3 (T-shaped); (g) NH_3; and (h) C_2H_6, staggered ethane.

Answers: The plan is to note that for nonlinear molecules the first step is to find the highest-fold rotational axis. If the highest-fold rotational axis is unique, then that axis is the principal axis, which gives the value of n, for example in C_{nv} or D_{nh}.

In displaying the symmetry elements of molecules, several standard symbols are used. Reflection planes are depicted as dotted lines or shaded planes and rotational axes are depicted as listed below. Solid symbols depict C_n axes and hollow symbols are for S_n axes. For molecules with higher symmetry, finding all the symmetry elements is usually not necessary. Instead, the characteristic symmetry operations as listed in Table 27.8.1 are sufficient.



(a). SO_2 is bent: The highest-fold axis is the C_2 axis, with no perpendicular C_2 axes, no collinear S_{2n} [see Part (h) for an example], no σ_h (which would be perpendicular to the principal axis), but with two σ_v planes: giving C_{2v}.

(b). CO_3^{2-} is trigonal planar: The highest-fold axis is the C_3 axis perpendicular to the plane of the atoms, with three perpendicular C_2 axes, and a σ_h: giving D_{3h}. Note that atoms are not required to lie above and below the σ_h plane; all atoms can lie in the σ_h plane.

(c) C_2H_4, ethylene is planar: The highest-fold axis is a C_2 axis, with two perpendicular C_2 axes, and a σ_h: giving D_{2h}. Since there are three mutually perpendicular C_2 axes, the principal axis is chosen as the C_2 that is perpendicular to the C_2 axis that includes the C-atoms. However, there are two such C_2-axes; the C_2 that is perpendicular to the plane that contains the most atoms is chosen as the principal axis.

(d) *trans*-1,2-$C_2H_2Cl_2$ is planar: The highest-fold axis is the C_2 axis, with no perpendicular C_2 axes, no collinear S_{2n}, but with a σ_h: giving C_{2h}.

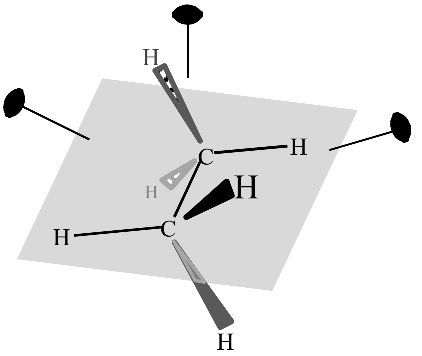
(e) *cis*-1,2-$C_2H_2Cl_2$ is planar: The highest-fold axis is the C_2 axis, with no perpendicular C_2 axes, no collinear S_{2n}, no σ_h, but with two σ_v planes: giving C_{2v}.

(f) ClF_3 is T-shaped: The highest-fold axis is the C_2 axis, with no perpendicular C_2 axes, no collinear S_{2n}, no σ_h, but with two σ_v planes: giving C_{2v}.

(g). NH_3 is trigonal pyramidal: The highest-fold axis is the C_3 axis, with no perpendicular C_2 axes, no S_{2n} , no σ_h, but with three σ_v planes: giving C_{3v}.

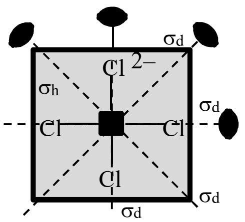
(h). Staggered C_2H_6 has two tetrahedral centers: The drawing, above, is a Newman projection looking down the C-C axis. A hand-held model is really useful for this discussion. The S_6

improper axis requires some explanation. Rotation about the C–C bond by 360/6 = 60° brings a H-atom on the front face of the molecule above a H-atom on the back face. These front-face and back-face atoms are related by a reflection across a plane perpendicular to the S_6 axis. Next considering the vertical planes, the vertical reflection planes bisect the C_2 axes, so they are officially σ_d-dihedral planes. Following the chart then, the highest-fold pure rotational axis is the C_3 axis, with three perpendicular C_2 axes, an S_6 improper axis, and three vertical σ_d-planes: giving D_{3d}. The perspective drawing, below, shows another view of the C_2-axes.

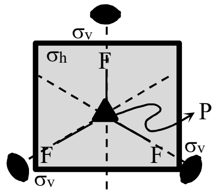


36. Determine the point group for the following species: (a) $PtCl_4^{2-}$ (square planar); (b) PF_5 (trigonal bipyramidal).

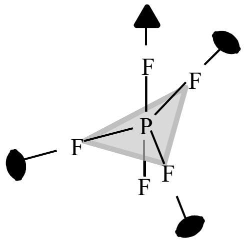
Answer: The plan is to follow Table 27.8.1 or the flow chart, Figure P27.1.



(a).



(b). Projection on σ_h



perspective drawing

(a). $PtCl_4^{2-}$: The highest-fold axis is the C_4 axis perpendicular to the plane of the atoms, with four perpendicular C_2 axes, and a σ_h-plane: giving D_{4h}.

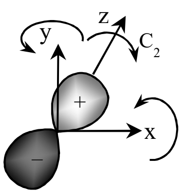
(b) PF_5: The highest-fold axis is the C_3 axis perpendicular to the trigonal-plane of atoms, with three perpendicular C_2 axes, and a σ_h-plane: giving D_{4h}.

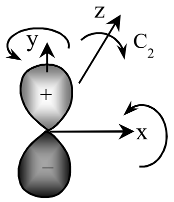
37. Determine the irreducible representations for the x, y, and z-components of the transition electric dipole moment in the point group whose character table is given below. The symmetry operations are three mutually perpendicular C_2-axes, which are aligned along the x, y, and z-axes.

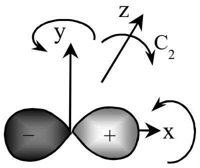
	E	$C_2(z)$	$C_2(y)$	$C_2(z)$
A	1	1	1	1
B_1	1	1	-1	-1
B_2	1	-1	1	-1
B_3	1	-1	-1	1

Answer: The plan is to use atomic p_x, p_y, and p_z orbitals as a visual expedient for determining the symmetry relationships for the three C_2-rotations. The components of the transition dipole transform in the same ways as the corresponding atomic orbitals.

The p_z, p_y, and p_x atomic orbitals are shown below aligned along the z, y, and x-axes, which correspond to the rotational axes in this point group. The identity operation, E, is included for completeness. If the orbital changes phase the "character under rotation" is listed as "–". For no change in phase the listing is "+".



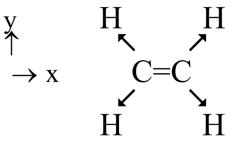




	p_z	p_y	p_x
E	+	+	+
$C_2(z)$	+	–	–
$C_2(y)$	–	+	–
$C_2(x)$	–	–	+
	B_1	B_2	B_3

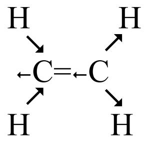
Reading down the columns of the table reproduces the characters (read across) for the corresponding irreducible representation. The p_z-orbital and the z-component of the transition electric dipole moment transform as B_1. The p_y-orbital and the y-component of the transition electric dipole moment transform as B_2. The p_x-orbital and the x-component of the transition electric dipole moment transform as B_3. Any normal mode that transforms according to B_1, B_2, or B_3 is allowed in infrared absorption. As a check, notice that the given character table is for the D_2 point group, data section Table 27.8.2.

38. (a). Determine the symmetry species, which is the irreducible representation, of the following normal modes of ethylene, C_2H_4. (b). Determine the IR and Raman activity of each mode.



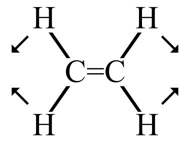
stretch

(a).



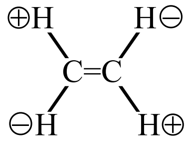
stretch

(b).



bend

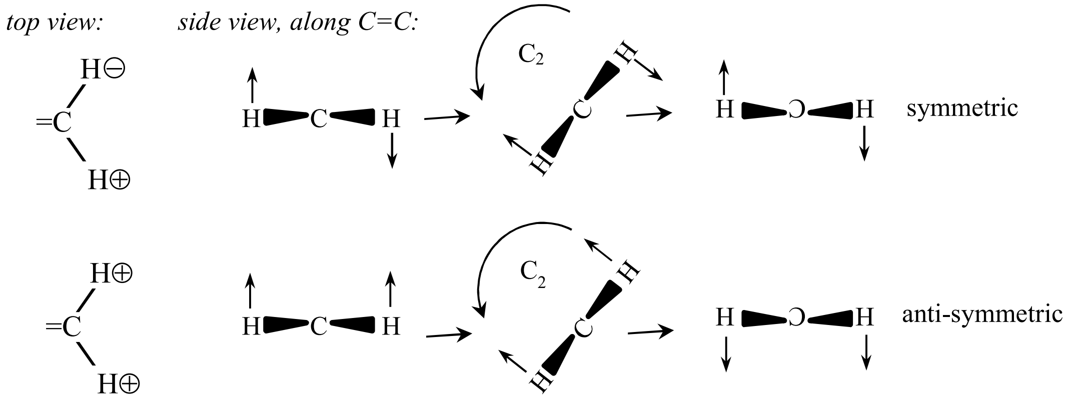
(c).



twist

(d).

The transformation properties of out-of-plane motions might require some clarification. The progress of the $C_2(x)$ rotation, viewed from the top and along the C=C bond is shown below.



Answer: The plan is to determine the symmetric or anti-symmetric behavior of the normal modes under the symmetry operations of the point group for ethylene, D_{2h}.

The D_{2h} character table is given below.

D_{2h}	E	$C_2(z)$	$C_2(y)$	$C_2(x)$	*i*	$\sigma_v(xy)$	$\sigma_v(xz)$	$\sigma_v(yz)$	
A_g	1	1	1	1	1	1	1	1	x^2, y^2, z^2
B_{1g}	1	1	-1	-1	1	1	-1	-1	xy
B_{2g}	1	-1	1	-1	1	-1	1	-1	xz
B_{3g}	1	-1	-1	1	1	-1	-1	1	yz
A_u	1	1	1	1	-1	-1	-1	-1	
B_{1u}	1	1	-1	-1	-1	-1	1	1	z
B_{2u}	1	-1	1	-1	-1	1	-1	1	y
B_{3u}	1	-1	-1	1	-1	1	1	-1	x

The symmetry under the operations of the point group and the corresponding irreducible representations are:

D_{2h}	E	$C_2(z)$	$C_2(y)$	$C_2(x)$	*i*	$\sigma_v(xy)$	$\sigma_v(xz)$	$\sigma_v(yz)$	χ	activity
(a)	1	1	1	1	1	1	1	1	a_g	R
(b)	1	-1	-1	1	-1	1	1	-1	b_{3u}	IR
(c)	1	1	1	1	1	1	1	1	a_g	R
(d)	1	1	1	1	-1	-1	-1	-1	a_u	

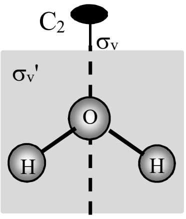
The character table lists the IR active modes as transforming according to the B_{1u}, B_{2u}, and B_{3u} point groups. As a result only mode-b is IR allowed. The character table lists the Raman active modes as transforming according to the A_g, B_{1g}, B_{2g}, and B_{3g} point groups. As a result mode-a and mode-c are Raman allowed. The Exclusion Rule applies because the group includes the inversion operation; as a result no mode is active in both in IR absorption and Raman scattering. Note that mode-d is not active in either form of vibrational spectroscopy. However, this mode is observable in electronic absorption and emission, since there are no symmetry restrictions on vibrational modes in electronic spectroscopy.

<u>39</u>. (a). Use group theory to determine the symmetry species of the normal modes of H_2O, using the corresponding approach to the all-mode vibrational analysis in Figure 27.8.10. The symmetry species are the irreducible representations of the normal modes. (b). Determine which irreducible

representations correspond to stretches and which to bending vibrations. (c). Determine the modes that are IR and Raman active.

Answer: The plan is to use the C_{2v} character table to decompose the reducible representation of the normal modes. We will find 3N – 6 = 3 normal modes and expect two stretching vibrations, since there are two bonds.

The geometry and character table for C_{2v} are shown below. The σ_v-plane is perpendicular to the plane of the paper; see also Figure 27.8.7. The characters of the representations of the translations, $\Gamma_{trans} = \Gamma_x+\Gamma_y+\Gamma_z = A_1+B_1+B_2$, and the rotations, $\Gamma_{rot} = A_2+B_1+B_2$, are appended to the end of the character table.



C_{2v}	E	C_2	σ_v	σ_v'	h = 4	
A_1	1	1	1	1	z, z^2, x^2, y^2	
A_2	1	1	-1	-1	xy	R_z
B_1	1	-1	1	-1	y, yz	R_x
B_2	1	-1	-1	1	x, xz	R_y
Γ_{trans}	3	-1	1	1	$\Gamma_{trans} = A_1+B_1+B_2$	
Γ_{rot}	3	-1	-1	-1	$\Gamma_{rot} = A_2+B_1+B_2$	

(a). The number of stationary atoms is multiplied by the corresponding character of the translations and then the characters of the translations and rotations are subtracted to give the total reducible representation of the vibrations. The complete decomposition is shown below.

C_{2v}	E	C_2	σ_v	σ_v'	Γ	a_i
station. atoms	3	1	1	3		
Γ_{trans}	3	-1	1	1	product	
Γ_{tot}	9	-1	1	3		
Γ_{trans}	3	-1	1	1	subtract	
Γ_{rot}	3	-1	-1	-1	subtract	
Γ_{vib}	3	1	1	3	Γ_{tot}-Γ_{trans}-Γ_{rot}	
A_1	1	1	1	1		$1/h(\Gamma_{vib}\cdot A_1) = 8/4 \rightarrow 2A_1$
A_2	1	1	-1	-1		$1/h(\Gamma_{vib}\cdot A_2) = 0$
B_1	1	-1	1	-1		$1/h(\Gamma_{vib}\cdot B_1) = 0$
B_2	1	-1	-1	1		$1/h(\Gamma_{vib}\cdot B_2) = 4/4 \rightarrow B_2$

For example, the decomposition for the A_1 irreducible representation is based on Eq. 27.8.2:

$$a_1 = {}^1/_h \sum_{j=1}^{4} \chi_j^{vib}\chi_{i,j}^{irr}\, C_{i,j}^{irr} = \tfrac{1}{4}\,[3(1)(1) + 1(1)(1) + 1(1)(1) + 3(1)(1)]$$

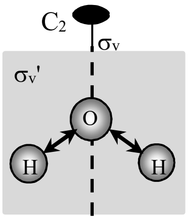
$$= 8/4 \qquad \text{giving that } A_1 \text{ appears twice in } \Gamma_{vib}$$

The decomposition for the A_2 irreducible representation is:

$$a_2 = \tfrac{1}{4}\,[3(1)(1) + 1(1)(1) + 1(-1)(1) + 3(1)(-1)]$$
$$= 0 \qquad \text{giving that } A_2 \text{ does not appear in } \Gamma_{vib}$$

The normal modes decompose as $\Gamma_{vib} = 2A_1 + B_2$, giving three modes with three distinct vibration frequencies (no degeneracies). All the normal modes are both IR and Raman active, which confirms Table 27.1.1. The next step is to determine the stretching modes. The bending modes are then obtained by difference with the overall total.

(b). The molecule is redrawn with double-headed arrows replacing each bond. The number of arrows that are stationary under the transformation operations of the classes of the point group are determined. The stretching analysis for H_2O is listed below.



D_{3h}	E	C_2	σ_v	σ_v'	a_i
stationary arrows: Γ_{str}	2	0	0	2	
A_1	1	1	1	1	$1/h(\Gamma_{str}\cdot A_1) = 4/4 \rightarrow A_1$
A_2	1	1	-1	-1	$1/h(\Gamma_{str}\cdot A_2) = 0$
B_1	1	-1	1	-1	$1/h(\Gamma_{str}\cdot B_1) = 0$
B_2	1	-1	-1	1	$1/h(\Gamma_{str}\cdot B_2) = 4/4 \rightarrow B_2$

The decomposition for the A_1 irreducible representation is:

$$a_1 = {}^1/_h \sum_{j=1}^{4} \chi_j^{str}\chi_{i,j}^{irr}\, C_{i,j}^{irr} = \tfrac{1}{4}\,[2(1)(1) + 0(1)(1) + 0(1)(1) + 2(1)(1)]$$
$$= 4/4 \qquad \text{giving that } A_1 \text{ appears once in } \Gamma_{str}$$

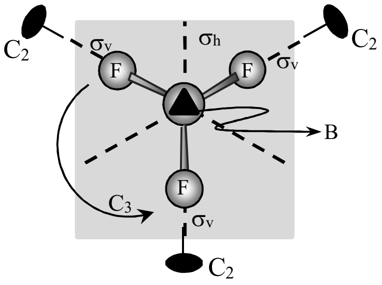
The stretching normal modes are $\Gamma_{str} = A_1 + B_2$, giving two stretching modes with two distinct vibration frequencies. Since all the modes include $\Gamma_{vib} = 2A_1 + B_2$, the remaining is a bending mode of A_1 symmetry. These results agree with Figure 27.8.7.

(c). Referring to the C_{2v} character table, the x, y, and z-components of the transition dipole moment transform as B_2, B_1, and A_1, respectively. The quadratic products, such as z^2 and xy, cover all four irreducible representations, giving all the normal modes as possibly Raman active. As consequence, all the normal modes are both IR and Raman active, which confirms Table 27.1.1.

40. Use group theory to determine the symmetry species of the normal modes of BF_3, using the corresponding approach to the all-mode vibrational analysis in Figure 27.8.10. The symmetry species are the irreducible representations of the normal modes. Determine which irreducible representations correspond to stretches and which to bending vibrations. [Hint: for determining the symmetry of a trigonal planar molecule, the S_3 improper rotations act just like C_3 proper rotations, since all atoms lie in the σ_h-plane.]

Answer: The plan is to use the D_{3h} character table to decompose the reducible representation of the normal modes. We will find 3N – 6 = 6 normal and expect three stretching vibrations, since there are three bonds.

The geometry and character table for D_{3h} are shown below. The characters of the representations of the translations, $\Gamma_{trans} = \Gamma_x+\Gamma_y+\Gamma_z = A_2''+E'$, and the rotations, $\Gamma_{rot} = A_2'+E''$, are appended to the end of the character table.



D_{3h}	E	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_v$	h = 12	
A_1'	1	1	1	1	1	1	x^2+y^2, z^2	
A_2'	1	1	-1	1	1	-1		R_z
E'	2	-1	0	2	-1	0	(x, y),(xy, $x^2–y^2$)	
A_1''	1	1	1	-1	-1	-1		
A_2''	1	1	-1	-1	-1	1	z	
E''	2	-1	0	-2	1	0	(xz, yz)	(R_x,R_y)
Γ_{trans}	3	0	-1	1	-2	1	$\Gamma_{trans} = A_2''+E'$	
Γ_{rot}	3	0	-1	-1	2	-1	$\Gamma_{rot} = A_2'+E''$	

The number of stationary atoms is multiplied by the corresponding character of the translations and then the characters of the translations and rotations are subtracted to give the total reducible representation of the vibrations. The complete decomposition is shown below. Note that once you reach six total modes, you can stop. So the decomposition for E" is not necessary, but we included it for practice.

D_{3h}	E	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_v$	Γ	a_i
station. atoms	4	1	2	4	1	2		
Γ_{trans}	3	0	-1	1	-2	1	product	
Γ_{tot}	12	0	-2	4	-2	2		
Γ_{trans}	3	0	-1	1	-2	1	subtract	
Γ_{rot}	3	0	-1	-1	2	-1	subtract	
Γ_{vib}	6	0	-4	4	-2	2	Γ_{tot}-Γ_{trans}-Γ_{rot}	
A_1'	1	1	1	1	1	1		$1/h(\Gamma_{vib}\cdot A_1') = 12/12 \rightarrow A_1'$
A_2'	1	1	-1	1	1	-1		$1/h(\Gamma_{vib}\cdot A_2') = 0$
E'	2	-1	0	2	-1	0		$1/h(\Gamma_{vib}\cdot E') = 24/12 \rightarrow 2E'$
A_1''	1	1	1	-1	-1	-1		$1/h(\Gamma_{vib}\cdot A_1'') = 0$
A_2''	1	1	-1	-1	-1	1		$1/h(\Gamma_{vib}\cdot A_2'') = 12/12 \rightarrow A_2''$
E''	2	-1	0	-2	1	0		$1/h(\Gamma_{vib}\cdot E'') = 0$

For example, the decomposition for the A_1' irreducible representation is based on Eq. 27.8.2:

$$a_1 = {}^1/_h \sum_{j=1}^{6} \chi_j^{vib}\chi_{i,j}^{irr}\, C_{i,j}^{irr} = {}^1/_{12}\,[6(1)(1) + 0(1)(2) + (-4)(1)(3) + 4(1)(1) + (-2)(1)(2) + 2(1)(3)]$$

$= 12/12$ giving that A_1' appears once in Γ_{vib}

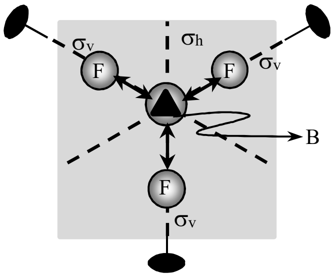
The decomposition for the A_2' irreducible representation is:

$$a_2 = {}^1/_{12}\,[6(1)(1) + 0(1)(2) + (-4)(-1)(3) + 4(1)(1) + (-2)(1)(2) + 2(-1)(3)]$$

$= 0$ giving that A_2' does not appear in Γ_{vib}

The normal modes decompose as $\Gamma_{vib} = A_1' + 2E' + A_2''$, giving six modes with four vibration frequencies, as listed in Table 27.7.1. Because E normal modes are doubly degenerate, the two different A_1-modes and the two different sets of E'-modes give six total normal modes as expected from the 3N-6 rule. The A_1' mode is Raman active, the E' modes are both IR and Raman active, and the A_2'' mode is IR active. The next step is to determine the stretching modes. The bending modes are then obtained by difference with the overall total.

The molecule is redrawn with double-headed arrows replacing each bond. The number of arrows that are stationary under the transformation operations of the classes of the point group are determined. The stretching analysis for BF_3 is listed below.



D_{3h}	E	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_v$	a_i
stationary arrows: Γ_{str}	3	0	1	3	0	1	
A_1'	1	1	1	1	1	1	$1/h(\Gamma_{str}\cdot A_1') = 12/12 \rightarrow A_1'$
A_2'	1	1	-1	1	1	-1	$1/h(\Gamma_{str}\cdot A_2') = 0$
E'	2	-1	0	2	-1	0	$1/h(\Gamma_{str}\cdot E') = 12/12 \rightarrow E'$
A_1''	1	1	1	-1	-1	-1	$1/h(\Gamma_{str}\cdot A_1'') = 0$
A_2''	1	1	-1	-1	-1	1	$1/h(\Gamma_{str}\cdot A_2'') = 0$
E''	2	-1	0	-2	1	0	$1/h(\Gamma_{str}\cdot E'') = 0$

The decomposition for the A_1' irreducible representation is:

$$a_1 = {}^1/_h \sum_{j=1}^{6} \chi_j^{str}\chi_{i,j}^{irr}\, C_{i,j}^{irr} = {}^1/_{12}\,[3(1)(1) + 0(1)(2) + (1)(1)(3) + 3(1)(1) + (0)(1)(2) + 1(1)(3)]$$

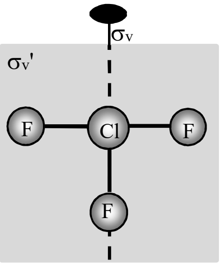
$= 12/12$ giving that A_1' appears once in Γ_{str}

The stretching normal modes are $\Gamma_{str} = A_1' + E'$, giving three stretching modes with two vibration frequencies. Since all the modes include $\Gamma_{vib} = A_1' + 2E' + A_2''$, the remaining bending modes are $E' + A_2''$. This result verifies the listing in Table 27.7.1.

41. (a). Use group theory to determine the symmetry species of the normal modes of T-shaped ClF_3, using the corresponding approach to the all-mode vibrational analysis in Figure 27.8.10. The symmetry species are the irreducible representations of the normal modes. (b). Determine which irreducible representations correspond to stretches and which to bending vibrations. (c). Can the number of IR and Raman active bands distinguish between trigonal-planar and T-shaped geometries for ClF_3? [Hint: Use Table 27.7.1 for the symmetry species of a trigonal planar XY_3 moleucle.]

Answer: The plan is to use the C_{2v} character table to decompose the reducible representation of the normal modes. We will find 3N – 6 = 6 normal and expect three stretching vibrations, since there are three bonds.

The geometry and character table for C_{2v} are shown below. The characters of the representations of the translations, $\Gamma_{trans} = \Gamma_x + \Gamma_y + \Gamma_z = A_1 + B_1 + B_2$, and the rotations $\Gamma_{rot} = A_2 + B_1 + B_2$, are appended to the end of the character table.



C_{2v}	E	C_2	σ_v	σ_v'	h = 4	
A_1	1	1	1	1	z, z^2, x^2, y^2	
A_2	1	1	-1	-1	xy	R_z
B_1	1	-1	1	-1	y, yz	R_x
B_2	1	-1	-1	1	x, xz	R_y
Γ_{trans}	3	-1	1	1	$\Gamma_{trans} = A_1 + B_1 + B_2$	
Γ_{rot}	3	-1	-1	-1	$\Gamma_{rot} = A_2 + B_1 + B_2$	

(a). The number of stationary atoms is multiplied by the corresponding character of the translations and then the characters of the translations and rotations are subtracted to give the total reducible representation of the vibrations. The complete decomposition is shown below.

C_{2v}	E	C_2	σ_v	σ_v'	Γ	a_i
stationary atoms	4	2	2	4		
Γ_{trans}	3	-1	1	1	product	
Γ_{tot}	12	-2	2	4		
Γ_{trans}	3	-1	1	1	subtract	
Γ_{rot}	3	-1	-1	-1	subtract	
Γ_{vib}	6	0	4	2	$\Gamma_{tot} - \Gamma_{trans} - \Gamma_{rot}$	
A_1	1	1	1	1		$1/h(\Gamma_{vib} \cdot A_1) = 12/4 \rightarrow 3A_1$
A_2	1	1	-1	-1		$1/h(\Gamma_{vib} \cdot A_2) = 0$
B_1	1	-1	1	-1		$1/h(\Gamma_{vib} \cdot B_1) = 8/4 \rightarrow 2B_1$
B_2	1	-1	-1	1		$1/h(\Gamma_{vib} \cdot B_2) = 4/4 \rightarrow B_2$

For example, the decomposition for the A_1 irreducible representation is based on Eq. 27.8.2:

$$a_1 = {}^1/_h \sum_{j=1}^{4} \chi_j^{vib} \chi_{i,j}^{irr} C_{i,j}^{irr} = {}^1/_4[6(1)(1) + 0(1)(1) + 4(1)(1) + 2(1)(1)]$$

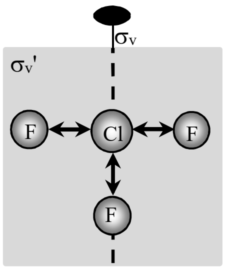
$= 12/4$ giving that A_1 appears three times in Γ_{vib}

The decomposition for the A_2 irreducible representation is:

$$a_2 = {}^1/_4[6(1)(1) + 0(1)(1) + 4(-1)(1) + 2(1)(-1)]$$

$= 0$ giving that A_2 does not appear in Γ_{vib}

The normal modes decompose as $\Gamma_{vib} = 3A_1 + 2B_1 + B_2$, giving six modes with six vibration frequencies. All the normal modes are both IR and Raman active. The next step is to determine the stretching modes. The bending modes are then obtained by difference with the overall total.
(b). The molecule is redrawn with double-headed arrows replacing each bond. The number of arrows that are stationary under the transformation operations of the classes of the point group are determined. The stretching analysis for ClF_3 is listed below.



C_{2v}	E	C_2	σ_v	σ_v'	a_i
stationary arrows: Γ_{str}	3	1	1	3	
A_1	1	1	1	1	$1/h(\Gamma_{str} \cdot A_1) = 8/4 \rightarrow 2A_1$
A_2	1	1	-1	-1	$1/h(\Gamma_{str} \cdot A_2) = 0$
B_1	1	-1	1	-1	$1/h(\Gamma_{str} \cdot B_1) = 0$
B_2	1	-1	-1	1	$1/h(\Gamma_{str} \cdot B_2) = 4/4 \rightarrow B_2$

The decomposition for the A_1 irreducible representation is:

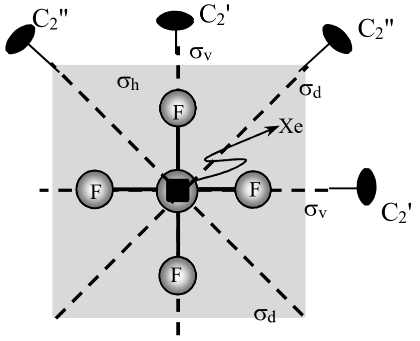
$$a_1 = {}^1/_h \sum_{j=1}^{4} \chi_j^{str} \chi_{i,j}^{irr} C_{i,j}^{irr} = {}^1/_4[3(1)(1) + 1(1)(1) + 1(1)(1) + 3(1)(1)]$$

$= 8/4$ giving that A_1 appears twice in Γ_{str}

The stretching normal modes are $\Gamma_{str} = 2A_1 + B_2$, giving three stretching modes with three vibration frequencies. Since all the modes include $\Gamma_{vib} = 3A_1 + 2B_1 + B_2$, the remaining bending modes are $A_1 + B_1 + B_2$. Note that formaldehyde, $CH_2{=}O$, is also planar tetra-atomic C_{2v} and therefore gives the same normal mode results.
(c). Referring to the C_{2v} character table, the x, y, and z-components of the transition dipole moment transform as B_2, B_1, and A_1, respectively. The quadratic products, such as z^2 and xy, cover all four irreducible representations, giving all normal modes as possibly Raman active. As a consequence, all the normal modes are both IR and Raman active.

Yes, the number of IR and Raman active bands does distinguish between trigonal-planar and T-shaped geometries for ClF_3. From Table 27.7.1, for trigonal-planar D_{3h} XY_3 molecules there are three IR and three Raman transitions. From the analysis above, all normal modes of C_{2v} XY_3 molecules are both IR and Raman active.

<u>42</u>. (a). Use group theory to determine the symmetry species of the normal modes of square-planar XeF_4, using the corresponding approach to the all-mode vibrational analysis in Figure 27.8.10. The symmetry species are the irreducible representations of the normal modes. (b). Determine which irreducible representations correspond to stretches and which to bending vibrations. (c). Determine the IR and Raman activity of the modes. The projection of the symmetry operations of the D_{4h} point group upon XeF_4 is shown below. [Hints: There are two C_4 axes, one for clockwise and one for counterclockwise rotation. The C_2 axis is coincident with the C_4 axis, while the C_2' and C_2'' are perpendicular to the C_4 axes. The C_2 axis is required for mathematical completeness and is equivalent to two successive C_4 rotations in the same direction. For determining the symmetry of a square-planar molecule, the S_4 improper rotations act just like C_4 proper rotations, since all atoms lie in the σ_h-plane.]



Answer: The plan is to use the D_{4h} character table to decompose the reducible representation of the normal modes. We will find 3N – 6 = 9 normal modes and expect four stretching vibrations, since there are four bonds.

(a). The character table for D_{4h} is shown below. The characters of the representations of the translations, $\Gamma_{trans} = \Gamma_x+\Gamma_y+\Gamma_z = A_{2u}+E_u$, and the rotations, $\Gamma_{rot} = A_{2g}+E_g$, are appended to the end of the character table.

D_{4h}	E	$2C_4$	C_2	$2C_2'$	$2C_2''$	*i*	$2S_4$	σ_h	$2\sigma_v$	$2\sigma_d$	h = 16	
A_{1g}	1	1	1	1	1	1	1	1	1	1	x^2+y^2, z^2	
A_{2g}	1	1	1	-1	-1	1	1	1	-1	-1		R_z
B_{1g}	1	-1	1	1	-1	1	-1	1	1	-1	$(x^2–y^2)$	
B_{2g}	1	-1	1	-1	1	1	-1	1	-1	1	xy	
E_g	2	0	-2	0	0	2	0	-2	0	0	(xz, yz)	(R_x,R_y)
A_{1u}	1	1	1	1	1	-1	-1	-1	-1	-1		
A_{2u}	1	1	1	-1	-1	-1	-1	-1	1	1	z	
B_{1u}	1	-1	1	1	-1	-1	1	-1	-1	1		
B_{2u}	1	-1	1	-1	1	-1	1	-1	1	-1		
E_u	2	0	-2	0	0	-2	0	2	0	0	(x,y)	
Γ_{trans}	3	1	-1	-1	-1	-3	-1	1	1	1	$\Gamma_{trans} = A_{2u}+E_u$	
Γ_{rot}	3	1	-1	-1	-1	3	1	-1	-1	-1	$\Gamma_{rot} = A_{2g}+E_g$	

The number of stationary atoms is multiplied by the corresponding character of the translations and then the characters of the translations and rotations are subtracted to give the total reducible representation of the vibrations. The complete decomposition is shown below.

D_{4h}	E	$2C_4$	C_2	$2C_2'$	$2C_2''$	*i*	$2S_4$	σ_h	$2\sigma_v$	$2\sigma_d$	a_i
stat. atms	5	1	1	3	1	1	1	5	3	1	
Γ_{trans}	3	1	-1	-1	-1	-3	-1	1	1	1	←product
Γ_{tot}	15	1	-1	-3	-1	-3	-1	5	3	1	
Γ_{trans}	3	1	-1	-1	-1	-3	-1	1	1	1	←subtract
Γ_{rot}	3	1	-1	-1	-1	3	1	-1	-1	-1	←subtract
Γ_{vib}	9	-1	1	-1	1	-3	-1	5	3	1	
A_{1g}	1	1	1	1	1	1	1	1	1	1	$1/h(\Gamma_{vib}\cdot A_{1g}) = 16/16 \rightarrow A_{1g}$
A_{2g}	1	1	1	-1	-1	1	1	1	-1	-1	$1/h(\Gamma_{vib}\cdot A_{2g}) = 0$
B_{1g}	1	-1	1	1	-1	1	-1	1	1	-1	$1/h(\Gamma_{vib}\cdot B_{1g}) = 16/16 \rightarrow B_{1g}$
B_{2g}	1	-1	1	-1	1	1	-1	1	-1	1	$1/h(\Gamma_{vib}\cdot B_{2g}) = 16/16 \rightarrow B_{2g}$
E_g	2	0	-2	0	0	2	0	-2	0	0	$1/h(\Gamma_{vib}\cdot E_g) = 0$
A_{1u}	1	1	1	1	1	-1	-1	-1	-1	-1	$1/h(\Gamma_{vib}\cdot A_{1u}) = 0$
A_{2u}	1	1	1	-1	-1	-1	-1	-1	1	1	$1/h(\Gamma_{vib}\cdot A_{2u}) = 16/16 \rightarrow A_{2u}$
B_{1u}	1	-1	1	1	-1	-1	1	-1	-1	1	$1/h(\Gamma_{vib}\cdot B_{1u}) = 0$
B_{2u}	1	-1	1	-1	1	-1	1	-1	1	-1	$1/h(\Gamma_{vib}\cdot B_{2u}) = 16/16 \rightarrow B_{2u}$
E_u	2	0	-2	0	0	-2	0	2	0	0	$1/h(\Gamma_{vib}\cdot E_u) = 32/16 \rightarrow 2E_u$

For example, the decomposition for the A_{1g} irreducible representation is based on Eq. 27.8.2:

$$a_1 = {}^1\!/_h \sum_{j=1}^{10} \chi_j^{vib}\chi_{1,j}^{irr}\, C_{1,j}^{irr}$$

$$= {}^1\!/_{16}\,[9(1)(1) + (-1)(1)(2) + 1(1)(1) + (-1)(1)(2) + 1(1)(2) + (-3)(1)(1) + (-1)(1)(2) + 5(1)(1) + 3(1)(2) + 1(1)(2)]$$

$= 16/16$ giving that A_{1g} appears once in Γ_{vib}

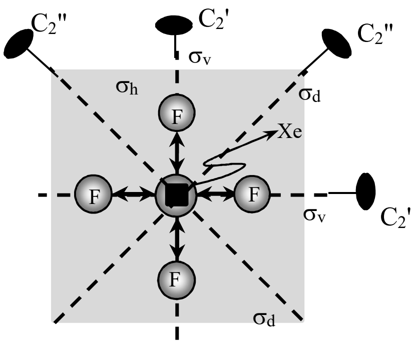
The decomposition for the A_{2g} irreducible representation is:

$$a_2 = {}^1\!/_{16}\,[9(1)(1) + (-1)(1)(2) + 1(1)(1) + (-1)(-1)(2) + 1(-1)(2) + (-3)(1)(1) + (-1)(1)(2) + 5(1)(1) + 3(-1)(2) + 1(-1)(2)]$$

$= 0$ giving that A_{2g} does not appear in Γ_{vib}

The normal modes decompose as $\Gamma_{vib} = A_{1g} + B_{1g} + B_{2g} + A_{2u} + B_{2u} + 2E_u$, giving nine vibration frequencies. Because the E_u normal modes are doubly degenerate, the two different sets of E_u-modes give nine total normal modes as expected from the 3N-6 rule. The next step is to determine the stretching modes. The bending modes are then obtained by difference with the overall total.

(b). The molecule is redrawn with double-headed arrows replacing each bond. The number of arrows that are stationary under the transformation operations of the classes of the point group are determined. The stretching analysis for XeF_4 is listed below.



D_{4h}	E	$2C_4$	C_2	$2C_2'$	$2C_2''$	*i*	$2S_4$	σ_h	$2\sigma_v$	$2\sigma_d$	*a*i
stationary arrows	4	0	0	2	0	0	0	4	2	0	← Γ_{str}
A_{1g}	1	1	1	1	1	1	1	1	1	1	$1/h(\Gamma_{vib}\cdot A_{1g}) = 16/16 \rightarrow A_{1g}$
A_{2g}	1	1	1	-1	-1	1	1	1	-1	-1	$1/h(\Gamma_{vib}\cdot A_{2g}) = 0$
B_{1g}	1	-1	1	1	-1	1	-1	1	1	-1	$1/h(\Gamma_{vib}\cdot B_{1g}) = 16/16 \rightarrow B_{1g}$
B_{2g}	1	-1	1	-1	1	1	-1	1	-1	1	$1/h(\Gamma_{vib}\cdot B_{2g}) = 0$
E_g	2	0	-2	0	0	2	0	-2	0	0	$1/h(\Gamma_{vib}\cdot E_g) = 0$
A_{1u}	1	1	1	1	1	-1	-1	-1	-1	-1	$1/h(\Gamma_{vib}\cdot A_{1u}) = 0$
A_{2u}	1	1	1	-1	-1	-1	-1	-1	1	1	$1/h(\Gamma_{vib}\cdot A_{2u}) = 0$
B_{1u}	1	-1	1	1	-1	-1	1	-1	-1	1	$1/h(\Gamma_{vib}\cdot B_{1u}) = 0$
B_{2u}	1	-1	1	-1	1	-1	1	-1	1	-1	$1/h(\Gamma_{vib}\cdot B_{2u}) = 0$
E_u	2	0	-2	0	0	-2	0	2	0	0	$1/h(\Gamma_{vib}\cdot E_u) = 16/16 \rightarrow E_u$

The decomposition for the A_{1g} irreducible representation is:

$$a_1 = {}^1/_h \sum_{j=1}^{10} \chi_j^{str}\chi_{i,j}^{irr} C_{i,j}^{irr} = {}^1/_{16}\,[4(1)(1) + 0(1)(2) + 0(1)(1) + 2(1)(2) + 0(1)(2) + 0(1)(1) + 0(1)(2) + 4(1)(1) + 2(1)(2) + 0(1)(2)]$$

$$= 16/16 \qquad \text{giving that } A_{1u} \text{ appears once in } \Gamma_{str}$$

The stretching normal modes are $\Gamma_{str} = A_{1g} + B_{1g} + E_u$, giving four stretching modes with three vibration frequencies. Since all the modes include $\Gamma_{vib} = A_{1g} + B_{1g} + B_{2g} + A_{2u} + B_{2u} + 2E_u$, the remaining bending modes are $B_{2g} + A_{2u} + B_{2u} + E_u$.

(c). The x, y, and z-components of the transition dipole moment transform as E_u, E_u, and A_{2u} respectively. The quadratic products, such as z^2 and $(x^2 - y^2)$, transform as A_{1g}, B_{1g}, B_{2g}, and E_g. Note that for a molecule with a center of symmetry, the x, y, z-components of the transition dipole all transform as “u” irreducible representations while the polarizability components transform as “g” irreducible representations, verifying the Exclusion rule. As a consequence, the A_{2u} and both E_u normal modes are possibly infrared active, while the A_{1g}, B_{1g}, and B_{2g} are possibly Raman active. The B_{2u} is forbidden in both infrared absorption and Raman scattering.

43. The normal mode vibrations of a square-planar XY_4 molecule transform as $\Gamma_{vib} = A_{1g} + B_{1g} + B_{2g} + A_{2u} + B_{2u} + 2E_u$. The normal mode vibrations of a tetrahedral XY_4 transform as $\Gamma_{vib} = A_1 + E + 2T_2$. For molecules such as CH_4 or XeF_4, are square-planar XY_4 and tetrahedral XY_4 geometries distinguishable on the basis of the number of IR and Raman active modes?

Answer: The plan is to use the D_{4h} and T_d character tables, Table 27.8.2 in the data section, to determine if each normal mode is IR or Raman active. This decision is based on the transformation properties of alternatively: the x, y, z-components of the electric transition dipole moment for IR and the quadratic components of the polarizability for the Raman transitions.

Note that E-modes are doubly degenerate, while T-modes are triply degenerate. Each mode within the degenerate set have the same transition frequency.

For square-planar D_{4h} molecules, the x, y, and z-components of the transition dipole moment transform as E_u, E_u, and A_{2u} respectively. The quadratic products, such as z^2 and $(x^2 - y^2)$, transform as A_{1g}, B_{1g}, B_{2g}, and E_g. With overall $\Gamma_{vib} = A_{1g} + B_{1g} + B_{2g} + A_{2u} + B_{2u} + 2E_u$, the A_{2u} and both doubly-degenerate E_u normal modes are possibly infrared active, while the A_{1g}, B_{1g}, and B_{2g} are possibly Raman active. The B_{2u} is forbidden in both infrared absorption and Raman scattering.

For tetrahedral T_d molecules, the x, y, and z-components of the transition dipole moment transform as T_2. The quadratic products, such as xy and $(x^2 - y^2)$, transform as A_1, E, and T_2. With overall $\Gamma_{vib} = A_1 + E + 2T_2$, both triply-degenerate T_2 normal modes are possibly infrared active, while all nine modes are possibly Raman active. The B_{2u} is forbidden in both infrared absorption and Raman scattering.

The results for a square-planar XY_4 and a tetrahedral XY_4 are distinguishable on the basis of the number of IR and Raman active modes and the corresponding distinct frequencies:

Geometry XY_4	IR active (possibly)	Raman active (possibly)	IR & Raman forbidden
square-planar	5 modes / 3 $\tilde{\nu}$s	3 modes / 3 $\tilde{\nu}$s	1
tetrahedral	6 modes / 2 $\tilde{\nu}$s	9 modes / 4 $\tilde{\nu}$s	0

Since square-planar molecules have a center of symmetry, no normal mode is both IR and Raman active, the transition frequencies are mutually exclusive. However, for tetrahedral molecules the T_2-modes are both IR and Raman active. For tetrahedral molecules two different frequencies can possibly occur in both the IR and Raman.

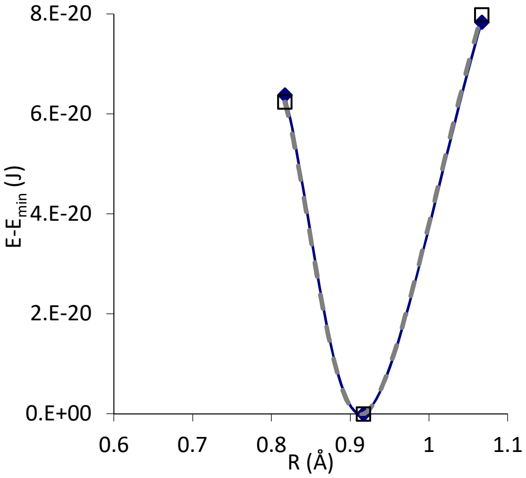
<u>44</u>. *Challenge Problem*: Determine the equilibrium bond length R_e, dissociation energy $\tilde{D}_e$, Morse *a*-parameter, fundamental vibration frequency $\tilde{\nu}_e$, and anharmonicity for HF using molecular structure calculations at the CCSD(T)/cc-pVTZ level. Assume the potential energy surface is in the Morse form with Eq. 27.5.7 giving the fundamental vibration frequency and Eq. 27.5.19 giving the anharmonicity. Calculate the dissociation energy, $\tilde{D}_e$, using separate calculations of the atomic energies of H- and F-atoms. Compare the theoretical spectroscopic constants with experimental literature values. [Hint: you will need to do calculations for HF at the geometry optimized bond length and two other values of the internuclear separation, use R_e – 0.10 Å and R_e + 0.15 Å. Then fit your three data points to a Morse potential in a spreadsheet.]

Answer: The plan to note that the bond dissociation energy is for the process $HF \rightarrow H\,(^2S) + F(^2P)$ with the $\tilde{D}_e$ calculated as the difference in energy of the products and reactants.

The minimized bond length for HF was 0.917 Å with the energy -100.3383563 H. The values for the two additional bond lengths and the H- and F-atoms are listed in the spreadsheet, below. The spreadsheet was developed to compare the electronic structure energy values to Morse potential values based on the calculated $\tilde{D}_e$, R_e, and a guessed value for the Morse *a*-parameter. The Morse *a*-parameter, cell G3, is varied to minimize the sum of squared residuals, cell H11, between the electronic structure calculation data points, cells F7:F9, and the fit Morse curve, cells G7:G9. Goal search can be used, but because of convergence problems, we had to finish by hand to achieve four significant figures in *a*. The final fit curve is shown in the plot below. The electronic structure values are the solid black triangles and the Morse curve values are in hollow squares. The derived fit is not perfect because the potential energy curve is not exactly a Morse potential.

A1	B	C	D	E	F	G	H	I	J
2		*Atoms*	E (H)		D_e	9.51E-19	J	5.937132	eV
3		H	-0.499809811		*a*	2.2804	$Å^{-1}$	2.280E+10	m^{-1}
4		F	-99.62036076		R_e	0.917	Å		
5		*Molecule*							
6		HF R (Å)	E (H)	$E-E_{min}$ (H)	$E-E_{min}$ (J)	Morse (J)	$residual^2$		
7		0.817	-100.323722	0.01463	6.38E-20	6.24E-20	1.95E-42		
8		0.917	-100.3383563	0	0.00E+00	0	0		
9		1.067	-100.3203793	0.01798	7.84E-20	7.98E-20	2.12E-42		
10									
11						ssr*1E40 =	0.040649		

12				
13		$\mathcal{M}_1$	1.007825	g mol^{-1}
14		$\mathcal{M}_2$	18.998403	g mol^{-1}
15		μ	1.59E-27	kg
16		ν_e	1.26E+14	s^{-1}
17		ν_e	4187.455392	cm^{-1}
18		$\mathcal{k}$	989.3258205	N m^{-1}
19		$\chi_e\ \nu_e$	91.57056	cm^{-1}
20				
21		1H =	2625.4974	kJ mol^{-1}
22		N_A=	6.02E+23	
23		c=	3.00E+10	cm s^{-1}
24		h=	6.63E-34	J s



Cell G2 for the dissociation energy is: “=(D3+D4-D8)*D21/D22*1000”
Cell G7 for the Morse curve is: “=$G$2*(1-EXP(-$G$3*(C7-$G$4)))^2”
Cell H7 for the first squared residual is: “=(F7-G7)^2”
Cell H11 sums the squared residuals and multiplies by a fixed factor of 10^{40} to provide a convenient scale for the fit evaluation: “=SUM(H7:H10)*1E40”
Cell G3 is adjusted to minimize cell H11, which at the same time provides a better fit in the plot.

Once the Morse a-parameter is obtained by manual curve fitting the remaining spectroscopic parameters are calculated. The reduced mass for HF is:

$$\mu_{HF} = \frac{(1.007825)(18.998403)}{1.007825+18.998403}\,(\text{g mol}^{-1})\,\frac{1}{N_A}\,(1\text{kg}/1000\text{ g}) = 1.589229\text{x}10^{-27}\text{ kg}$$

With Eq. 27.5.7, *a* must be converted to m^{-1} from $Å^{-1}$ to match joule units for D_e:

rearranging $a = \omega_e\left(\frac{\mu}{2D_e}\right)^{1/2}$ gives:

$$\nu_e = \frac{a}{2\pi}\left(\frac{2D_e}{\mu}\right)^{1/2} = \frac{2.2804\text{x}10^{10}\ \text{m}^{-1}}{2\pi}\left(\frac{2(9.51234\text{x}10^{-19}\text{J})}{1.589229\text{x}10^{-27}\ \text{kg}}\right)^{1/2} = 1.25573\text{x}10^{14}\ \text{s}^{-1}$$

$$\tilde{\nu}_e = \nu_e/c = 4187.5\ \text{cm}^{-1}$$

With Eq. 27.5.18, rearranging gives:

$$\chi_e\tilde{\nu}_e = \frac{a^2\text{h}}{8\pi^2\mu\text{c}} = \frac{(2.2804\text{x}10^{10}\ \text{m}^{-1})^2\ 6.6260755\text{x}10^{-34}\ \text{J s}}{8\pi^2(1.589229\text{x}10^{-27}\ \text{kg})(2.99879246\text{x}10^{10}\ \text{cm s}^{-1})} = 91.571\ \text{cm}^{-1}$$

Comparison with the experimental literature values shows gratifying agreement. Using Eq. 27.5.12, in the form $\tilde{D}_o = \tilde{D}_e - \frac{1}{2}\,\tilde{\nu}_e + \frac{1}{4}\,\chi_e\tilde{\nu}_e$, to put the calculated and experimental dissociation energies on the same basis:

Parameter	CCSD(T)/cc-pVTZ	Experimental
R_e	0.917 Å	0.91681 Å
D_o	5.680 eV	5.86 eV
$\tilde{\nu}_e$	4187.5 cm^{-1}	4138.385 cm^{-1}
$\chi_e\tilde{\nu}_e$	91.571 cm^{-1}	89.943 cm^{-1}

45. Determine if the following statements are true or false. If the statement is false, describe the changes that are necessary to make the statement true, if possible. If the statement is true but too restrictive, give the more general statement.

(a). Doppler line broadening for UV transitions is greater than for microwave transitions.
(b). As molecules increase in size, rotational constants decrease.
(c). The wave number for vibrational transitions increases with temperature.
(d). In Raman scattering, the anti-Stokes lines are more intense than the Stokes lines.
(e). Two states with the same energy always mix and transitions to the two states can share intensity even if otherwise forbidden.

Answers:

(a). True: The Doppler broadening in wave numbers or frequency is given as a fraction of the transition frequency, Eq. 27.2.2.

(b). True: For example, for a diatomic molecule the $\tilde{B}$ value is inversely proportional to the bond length. In general the moment of inertia increases with increasing size, which decreases the rotational constant.

(c). False: Vibrational frequencies depend only on the quantum spacing of the energy levels, which does not depend on temperature. The Boltzmann population of excited states increases with temperature giving a change in transition intensity. As a result hot bands are more intense with increasing temperature. Doppler and collisional broadening increase with temperature.

(d). False: Anti-Stokes lines originate in an excited vibrational state, which by the Boltzmann distribution have a much smaller population than the ground state.

(e). Not quite true: To interact the two states must have the same symmetry. For example, anti-symmetric stretches can only interact with overtones or combinations that are also antisymmetric. As a consequence Fermi resonances aren't as common as they would be without the symmetry restriction. However, the remainder of the statement is correct; with an interaction, transitions to the two states can share intensity even if otherwise forbidden.

46. The selection rule Δυ = ± 1 for harmonic vibrations can also be motivated by using the odd or even symmetry of the integrand in the transition dipole moment integrals, Eqs. 27.9.13. Note that the harmonic oscillator wave functions alternate between even or odd for increasing υ, Table 24.1.1 and Figure 24.2.3b. (a). Assume υ" for the lower level is even, use the overall even/odd symmetry of the integrand to note if the transition dipole vanishes for Δυ = –2, –1, 0, +1, +2. (b). Assume υ" for the lower level is odd, use the overall even/odd symmetry of the integrand to note if the transition dipole vanishes for Δυ = –2, –1, 0, +1, +2.

Answer: The plan is to note that the harmonic oscillator wave functions are purely odd or even, while the x, y, or z-component of the extension operator is odd.

The harmonic oscillator wave functions alternate between even and odd for increasing υ. The transition electric dipole moment is proportional to the integral given by Eqs. 27.9.13:

$$\int \chi_{\upsilon'}\,(R - R_e)\,\chi_{\upsilon''}\;dR$$

The integrand factors into three functions: the final harmonic oscillator wave function, the extension operator (R – R$_e$), and the initial harmonic oscillator wave function. The extension operator is purely odd around the equilibrium position.

(a). With υ" even, the final state is υ' as given by the following table:

υ'	parity	integrand	overall parity	transition dipole
υ"– 2	even	even odd even	odd	forbidden
υ"– 1	odd	odd odd even	even	allowed
υ"	even	even odd even	odd	forbidden
υ" +1	odd	odd odd even	even	allowed
υ" +2	even	even odd even	odd	forbidden

(b). With υ" odd, the final state is υ' as given by the following table:

υ'	parity	integrand	overall parity	transition dipole
υ"– 2	odd	odd odd odd	odd	forbidden
υ"– 1	even	even odd odd	even	allowed
υ"	odd	odd odd odd	odd	forbidden
υ" +1	even	even odd odd	even	allowed
υ" +2	odd	odd odd odd	odd	forbidden

This method doesn't work for odd Δυ greater than +3 or less than –3. The general integral result in Eq. 27.9.15 resolves those cases.

47. The “ABC Rotational Constant Calculator” applet determines the moments of inertia, spectroscopic rotational constants, symmetry point group, and the contributions of rotation to the entropy and Gibbs energy of a molecule. The applet is available on the textbook Web site or on the companion CD. Extensive collections of molecular coordinates are available on-line and from molecular mechanics or electronic structure calculations. While many electronic structure packages determine the point group of an input molecule, the “ABC” applet has an adjustable tolerance that allows the point group to be determined in cases where other programs fail. Use the following coordinates to determine the point group and rotational constants for ethane:

```
8
ethane
C      -0.7704   0.0003  -0.0010
C       0.7707  -0.0002  -0.0001
H      -1.1734   1.0280  -0.0004
H      -1.1725  -0.5129  -0.8919
H      -1.1740  -0.5148   0.8883
H       1.1736  -1.0279  -0.0013
H       1.1742   0.5154  -0.8891
H       1.1728   0.5124   0.8911
```

The list is in xyz-format. The first line is the atom count. The second line is a comment. The subsequent lines list the atom and the coordinates.

Answer: The given coordinates are from a density functional minimized structure with the cc-pTZP basis set. The above data was entered into the “ABC” applet (you need to know your ABC’s, afterall). The output appears as shown below.

```
Moments of Inertia
Ix =   25.7705 g mol-1 Ang2  or 0.42793e-45 kg m2
Iy =   25.7693 g mol-1 Ang2  or 0.42791e-45 kg m2
Iz =    6.3882 g mol-1 Ang2  or 0.10608e-45 kg m2
___________________________________________
 Rotational constants
Ae = 0.65414 cm-1 or 19.611 GHz or 0.94117 K
Be = 0.65418 cm-1 or 19.612 GHz or 0.94121 K
Ce = 2.6389 cm-1 or 79.111 GHz or 3.7968 K
Point group D3d
___________________________________________
 Thermodynamics
qr=829.26 with sigma=6
Rotational Entropy=68.35 J mol-1 K-1
Translational Entropy=151.2944 J mol-1 K-1
Trans+Rotation Gibbs Free Energy=-55.571 kJ mol-1
=============================================

 Coordinates in Principal Coordinates Frame
___________________________________________
8
ethane (pBP/TZVP in pcf
C     0.0000    0.0000   -0.7705
C     0.0000   -0.0000    0.7705
H     0.5134    0.8902   -1.1738
H    -1.0279   -0.0004   -1.1730
H     0.5139   -0.8902   -1.1734
H    -0.5138   -0.8898    1.1737
H    -0.5133    0.8905    1.1734
H     1.0279   -0.0001    1.1730
```

The point group is correctly recognized as D_{3d} with the default tolerance; see Problem 35h. The moment of inertia calculations are presented in Problem 14. We will have much more to say about the thermodynamic values, which are for an ideal gas, in the statistical mechanics chapter. Translation and rotation make a significant contribution to the Gibbs energy of formation of a molecule.

48. Bending vibrations are characterized as one of four basic types of movements, Figure P27.2.

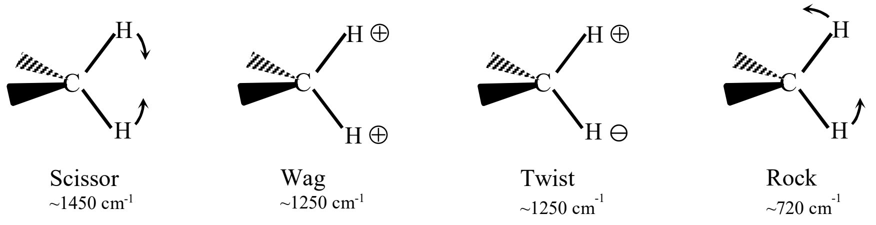


Figure P27.2: Bending vibrations of methylene. Typical frequencies for small hydrocarbons of normal modes dominated by the given type of bend are given.

Determine the normal modes of formaldehyde using an electronic structure calculation at the HF/6-31G* level (or equivalently HF/6-31G(d)). Display the "raw" numerical output files to find the symmetry designations. The experimental frequencies are given in Table P27.1.[7] Formaldehyde has C_{2v} symmetry, the symmetry properties for which are given in Figure 26.6.4. The totally symmetric group, a_1, contains the most symmetrical vibrations. The b_1 and b_2-groups are less symmetrical in the atom movements, b_1 is symmetrical with respect to reflection across the vertical plane that runs through the C=O bond. The b_1 and b_2 designations may be switched in the calculation listing; some authors switch the symmetry labels. Compare the calculated and experimental frequencies, Table P27.1. Animate the normal modes to help compare the modes. Frequencies from *ab initio* calculations are normally multiplied by 0.9 to compare with experimental frequencies. This factor adjusts for anharmonicity. Multiply your frequencies by 0.9; does the scaling improve the agreement with the experimental values?

Table P27.1. Experimental Frequencies of the Normal Modes of Formaldehyde.7

Symmetry of mode	Type of mode	Frequency (cm^{-1})
a_1	CH_2 symmetric stretch	2783 strong
	CO stretch	1746 very strong
	CH_2 scissor	1500 strong
b_1	CH_2 wag	1167 strong
b_2	CH_2 asymmetric stretch	2843 very strong
	CH_2 rock	1249 strong

Answer: The Spartan results are given below. The b_1 and b_2 symmetry labels are switched from the given data. The output also lists the thermodynamic parameters from the calculation. We will discuss these thermodynamic calculations in the statistical mechanics chapter.

```
Standard Thermodynamic quantities at 298.15 K and 1.00 atm

           Term      ZPE     Enthalpy   Entropy     Cv      % in
           cm-1    kJ/mol    kJ/mol    J/mol.K   J/mol.K  Ground IR Int.
  --   ----------   -------   -------   -------    ----
 1  B2    1335.821    7.9900    0.0254    0.0984    0.5498   99.84   0.37
 2  B1    1383.128    8.2729    0.0209    0.0807    0.4689   99.87  23.15
 3  A1    1679.553   10.0460    0.0061    0.0229    0.1651   99.97   8.67
 4  A1    2027.134   12.1250    0.0014    0.0051    0.0449   99.99 150.10
 5  A1    3159.409   18.8975    0.0000    0.0000    0.0005  100.00  49.69
 6  B1    3230.997   19.3257    0.0000    0.0000    0.0003  100.00 135.93
  --   ----------   -------   -------   -------    ----
 Total Vibrations   76.6569    0.0538    0.2070    1.2295

        Ideal Gas              2.4789
      Translation              3.7184  151.1751   12.4716
         Rotation              3.7184   66.6145   12.4716
       ----------             -------   -------   -------
           Totals             86.6265  217.9967   26.1727

 Vibrational(v) Corrections:
   Temp. Correction    Hv     86.6265
 Entropy Correction (Hv-TSv)  21.6308
```

The results from the full Gaussian output are shown below. The normal mode displacements are listed below each normal mode. These displacements are the basis of the normal mode animation, see Sec. . The IR and Raman relative intensities and the extent of Raman polarization are also listed. Notice that the non-totally symmetric normal modes are depolarized.

```
 Harmonic frequencies (cm**-1), IR intensities (KM/Mole), Raman scattering
  activities (A**4/AMU), depolarization ratios for plane and unpolarized
  incident light, reduced masses (AMU), force constants (mDyne/A),
  and normal coordinates:
                     1                      2                      3
                    B1                     B2                     A1
 Frequencies --  1335.9812              1383.2798              1679.6943
 Red. masses --     1.3690                 1.3442                 1.1042
 Frc consts  --     1.4396                 1.5154                 1.8355
 IR Inten    --     0.3667                23.1572                 8.6538
 Raman Activ --     0.7661                 4.5093                12.8713
 Depolar (P) --     0.7500                 0.7500                 0.5902
 Depolar (U) --     0.8571                 0.8571                 0.7423
 Atom AN      X      Y      Z        X      Y      Z        X      Y      Z
   1   6     0.17   0.00   0.00     0.00   0.15   0.00     0.00   0.00   0.00
   2   8    -0.04   0.00   0.00     0.00  -0.08   0.00     0.00   0.00   0.08
   3   1    -0.70   0.00   0.00     0.00  -0.25  -0.65     0.00  -0.35  -0.61
   4   1    -0.70   0.00   0.00     0.00  -0.25   0.65     0.00   0.35  -0.61
                     4                      5                      6
                    A1                     A1                     B2
 Frequencies --  2027.9363              3160.0193              3231.6842
 Red. masses --     7.2382                 1.0491                 1.1206
 Frc consts  --    17.5385                 6.1721                 6.8951
 IR Inten    --   150.1652                49.7347               135.9693
 Raman Activ --     8.0997               137.6328                58.3200
 Depolar (P) --     0.3279                 0.1828                 0.7500
 Depolar (U) --     0.4938                 0.3090                 0.8571
 Atom AN      X      Y      Z        X      Y      Z        X      Y      Z
   1   6     0.00   0.00   0.58     0.00   0.00   0.06     0.00   0.10   0.00
   2   8     0.00   0.00  -0.41     0.00   0.00   0.00     0.00   0.00   0.00
   3   1     0.00  -0.46  -0.19     0.00   0.61  -0.35     0.00  -0.60   0.37
   4   1     0.00   0.46  -0.19     0.00  -0.61  -0.35     0.00  -0.60  -0.37
```

The frequencies as wave numbers are compared with and without scaling by 0.9 below:

Symm.	Type	Experiment (cm^{-1})	HF/6-31G*	0.9*HF/6-31G*	% difference
a1	CH_2 symm. Str.	2783	3160.0	2844.0	2.2
	CO stretch	1746	2027.9	1825.1	4.5
	CH_2 scissor	1500	1679.7	1511.7	0.8
b1	CH_2 wag	1167	1336.0	1202.4	3.0
b2	CH_2 asymm. Str.	2843	3231.7	2908.5	2.3
	CH_2 rock	1249	1383.3	1245.0	-0.3

The factor of 0.9 scaling, which takes into account anharmonicity, improves the agreement. More precise scaling factors are available for specific *ab initio* levels. If you have covered the group theory section, notice that all the modes are both IR and Raman active as expected from the C_{2v} symmetry. However, the predicted intensity of the 1167 cm^{-1} wag is smaller than expected compared to the experimental spectrum.

Literature Cited:

1. Computational Chemistry Comparison and Benchmark Database, National Institute Of Standards and Technology, *NIST Standard Reference Database 101,* **2013**, http://cccbdb.nist.gov/, Table II.A.1.(XV.A.).
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3. B. deB. Darwent, “Bond Dissociation Energies in Simple Molecules,” *Nat. Stand. Ref. Data Ser.*, NSRDS-NBS 31, Washington, DC, 1970.
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Chapter 28 Problems: Electronic Spectroscopy

1. Why all the interest in diatomic molecules?

Answer: For diatomics and polyatomics, spectroscopic parameters are used to calculate thermodynamic equilibrium constants and kinetic rate constants. Reasons for all the fuss about diatomics include:
(a). Diatomics play a direct role in many chemical reactions, O_2 being a primary example. Atmospheric chemistry requires detailed knowledge of many diatomics including OH, O_2, N_2, NO, CO, Cl_2, Br_2, I_2, ClO, BrO, HCl, and the corresponding ions. Diatomics act as ligands in metal complexes, including CO and NO. H_2 is a commonly used reducing agent in the synthetic laboratory. CO blocks O_2 transport in hemoglobin and is a major industrial reducing agent in metallurgical applications. The halogens are used as gas phase disinfection agents. Chemical vapor deposition of thin films involves diatomics, including H_2 and F_2. Hydride epitaxial growth of thin films using HCl and H_2 is used in the semiconductor industry. Industrial high power ultraviolet excimer lasers are based on stimulated emission from excited state diatomics, including ArF, XeBr, XeCl, XeF, and KrF. Combustion engineering is based on chemical kinetics of gas phase free radical species, many of which are diatomics or derived from reactions with neutral diatomics, such as CO, N_2, C_2, and O_2.
(b). Our basic understanding of bonding, through bond strength measures, is based on diatomics. The correlations displayed in Figure 26.4.12 are central in this regard. For example, bond strength increases with increasing bond order and as bond strength increases equilibrium bond length decreases. These fundamental relationships are based on dissociation energies, force constants, and bond lengths that result from spectroscopic studies of diatomics.
(c). To a first level of approximation, chemical bonding is a pairwise interaction. Knowing the coarseness of the approximation, we often think of chemical bond strength as being a function of just the two atoms involved in each bond. For example, bond enthalpy tables are based on atom pairs, Table 8.8.1. Pauling electronegativities are based on diatomic bond dissociation energies. Eq. 26.3.13. Of course bonding is extensively delocalized, but pair-wise interactions are still an important viewpoint. In this regard, diatomics are the fundamental reference point for pair-wise bonding interactions.[1]
(d). Diatomics are a good point of reference. When we determine the bonding in a complicated molecule, diatomics provide a useful comparison that allows us to identify unusual bonding interactions. These comparisons are often based on bond strength correlations and changes in effective electronegativity as previewed in part (c).
(e). Diatomics are useful for validating electronic structure methods. If an electronic structure method can't reproduce bond dissociation energies for diatomics, then there is little hope of accurately predicting the properties of polyatomics. Excited electronic states are a particular challenge for electronic structure calculations. "Ground-truthing" with data from diatomics is necessary to help develop new excited state methods.
(f). Diatomics often have resolved rotational and vibrational fine-structure, while polyatomics often do not. Rotational fine-structure is necessary for the determination of bond lengths in excited state species. Vibrational fine-structure is necessary for determination of the shape of potential energy surfaces.
(g). Non-adiabatic kinetic processes are difficult to model, so keeping things simple by studying reactions of diatomics is often necessary.

2. Calculate the transition wave number for the ground electronic state to first excited singlet state transition in carbon monoxide. Assume the ground state vibrational-rotational and quantum numbers are $\upsilon'' = 0$, $J'' = 3$ and the excited state quantum numbers are $\upsilon' = 3$, $J' = 4$. The spectroscopic constants are given below.[2,3]

State	$\tilde{T}_e$ (cm^{-1})	$\tilde{\nu}_e$ (cm^{-1})	$\chi_e\tilde{\nu}_e$ (cm^{-1})	$\tilde{B}_e$ (cm^{-1})	$\tilde{\alpha}_e$ (cm^{-1})	$\tilde{D}_e$ (cm^{-1})
$A\ ^1\Pi$	65075.7	1518.2	19.4	1.6115	0.02325	$7.33\text{x}10^{-6}$
$X\ ^1\Sigma^+$	0	2169.814	13.288	1.93128	0.017504	$6.12\text{x}10^{-6}$

Answer: The plan is to use Eqs. 27.6.5 and 28.1.3.

With Eq. 27.6.5, the rotational constant for the ground electronic state with $\upsilon = 0$ is:

$$\tilde{B}_\upsilon^{gs} = \tilde{B}_e^{gs} - \tilde{\alpha}_e^{gs}(\upsilon + ½) = 1.93128\ \text{cm}^{-1} - 0.017504\ \text{cm}^{-1}(0 + ½) = 1.92253\ \text{cm}^{-1}$$

For the excited electronic state with $\upsilon = 3$ the rotational constant is:

$$\tilde{B}_\upsilon^{ex} = \tilde{B}_e^{ex} - \tilde{\alpha}_e^{ex}(\upsilon + ½) = 1.6115\ \text{cm}^{-1} - 0.02325\ \text{cm}^{-1}(3 + ½) = 1.53013\ \text{cm}^{-1}$$

With Eq. 28.1.3, the energy of the ground state for $\upsilon'' = 0$, $J'' = 3$ is:

$$\tilde{E}_{i,\upsilon,J} = \tilde{T}_{e,i} + \tilde{\nu}_{e.i}(\upsilon + ½) - \chi_{e,i}\tilde{\nu}_{e,i}(\upsilon + ½)^2 + \tilde{B}_{\upsilon,i}J(J + 1) - \tilde{D}_{e,i}[J(J + 1)]^2$$

$$\begin{aligned}\tilde{E}_{gs,0,3} &= \tilde{T}_e^{gs} + \tilde{\nu}_e^{gs}(0 + ½) - \chi_e^{gs}\tilde{\nu}_e^{gs}(0 + ½)^2 + \tilde{B}_o^{gs}3(3 + 1) - \tilde{D}_e[3(3 + 1)]^2 \\ &= 0 + 2169.814(0 + ½) - 13.288(0 + ½)^2 + 1.92253[3(3 + 1)] - 6.12\text{x}10^{-6}[3(3 + 1)]^2 \\ &= 1104.65\ \text{cm}^{-1}\end{aligned}$$

The excited state energy for $\upsilon' = 3$, $J' = 4$ is:

$$\begin{aligned}\tilde{E}_{gs,0,3} &= \tilde{T}_e^{ex} + \tilde{\nu}_e^{ex}(0 + ½) - \chi_e^{ex}\tilde{\nu}_e^{ex}(0 + ½)^2 + \tilde{B}_o^{ex}3(3 + 1) - \tilde{D}_e^{ex}[3(3 + 1)]^2 \\ &= 65075.7 + 1518.2(0 + ½) - 19.4(0 + ½)^2 + 1.5301[3(3 + 1)] - 7.33\text{x}10^{-6}[3(3 + 1)]^2 \\ &= 70182.35\ \text{cm}^{-1}\end{aligned}$$

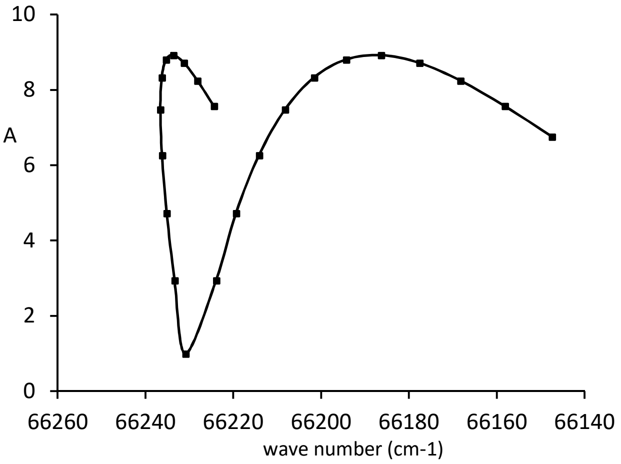
The transition wave number is given by the difference: $\tilde{\nu} = 69077.70\ \text{cm}^{-1}$.

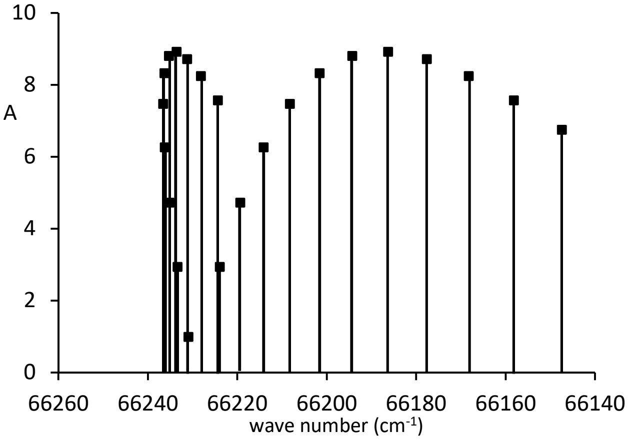
3. In rotation-vibration absorption, with $\tilde{B}' < \tilde{B}''$, each line moves to lower wave number in proportion to the J''^2 value, Eqs. 27.6.8-27.6.9. The R-branch lines get closer together and the P-branch lines get further apart. Please review Problem 27.30. In electronic absorption, the rotational constant in the upper electronic states often differs markedly from the ground electronic state. Write a spreadsheet to simulate the electronic absorption spectrum of carbon monoxide for the $\upsilon'' = 0$ to $\upsilon' = 1$ vibrational transition. The spectroscopic constants are listed in the previous problem. Neglect centrifugal distortion. [Hints: Refer to the hint for Problem 27.30, however this time your plot will be clearer if you choose a scatter plot with marker symbols and a connecting line. Include transitions for $J'' = 0$ to 10 for the R- and P-branches. To start with, to make the plot clearer you may want to use $\tilde{B}_e = 1.93128\ \text{cm}^{-1}$ for both electronic states. Then switch to $\tilde{B}_e = 1.6115\ \text{cm}^{-1}$ for the excited state.]

Answer: The plan is to modify the spreadsheet for Problem 27.30 to calculate the $\widetilde{B}_\upsilon$ value for the ground and excited electronic state and specific vibrational quantum numbers $\upsilon'' = 0$ to $\upsilon' = 1$. The previous problem discusses the necessary calculations.

Using the data and calculations from the previous problem, the spreadsheet appears as follows. The number of rows were increased to plot a wider range of transitions, from J" = 0 to 10 for the R- and P-branches. The "stick" spectrum is also shown for this problem. The R-branch lines move far enough to lower wave number that the transitions for high J" decrease in wave number even though J" is increasing. The rotational fine-structure lines "fall back" on each other. This effect is common in electronic spectroscopy.

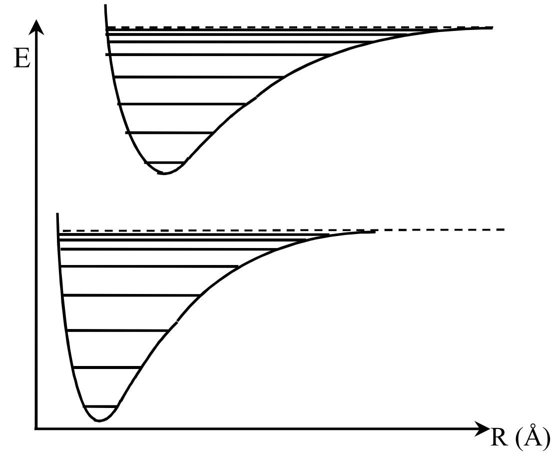
A 1	B	C	D	E	F
2	T_e	0	65075.7	cm^{-1}	
3	ν_e	2169.81	1518.2	cm^{-1}	
4	$\chi_e\nu_e$	13.288	19.4	cm^{-1}	
5	υ	0	1		
6	ν_υ	1081.58	2233.65	cm^{-1}	
7	B_e	1.93128	1.6115	cm^{-1}	
8	α_e	0.01750	0.02325	cm^{-1}	
9	B_υ	1.92253	1.576625	cm^{-1}	
10					
11	J"	J'	F(J") (cm^{-1})	ν (cm^{-1})	p(J")
12	10	11	-3.36358	66224.401	7.568
13	9	10	0.40123	66228.166	8.243
14	8	9	3.474234	66231.239	8.716
15	7	8	5.855432	66233.620	8.921
16	6	7	7.544824	66235.310	8.804
17	5	6	8.54241	66236.307	8.327
18	4	5	8.84819	66236.613	7.476
19	3	4	8.462164	66236.227	6.262
20	2	3	7.384332	66235.149	4.729
21	1	2	5.614694	66233.380	2.945
22	0	1	3.15325	66230.918	1.000
23	1	0	-3.84506	66223.920	2.945
24	2	1	-8.38192	66219.383	4.729
25	3	2	-13.6106	66214.154	6.262
26	4	3	-19.5311	66208.234	7.476
27	5	4	-26.1433	66201.622	8.327
28	6	5	-33.4474	66194.318	8.804
29	7	6	-41.4433	66186.322	8.921
30	8	7	-50.131	66177.634	8.716
31	9	8	-59.5105	66168.255	8.243
32	10	9	-69.5818	66158.183	7.568
33	11	10	-80.3449	66147.420	6.758

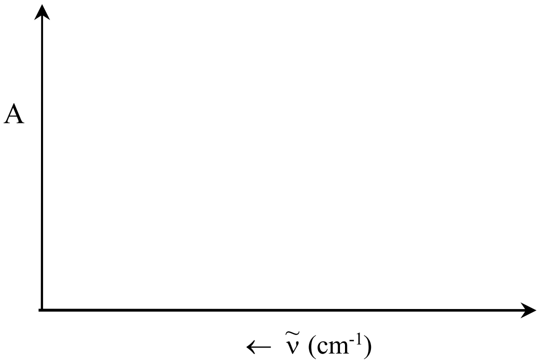




The maximum wave number is called the **band head**. The 0 ← 0 transition is called the **band origin**. In this problem the band origin is obscured, because of the extensive overlap of the R- and P-branches.

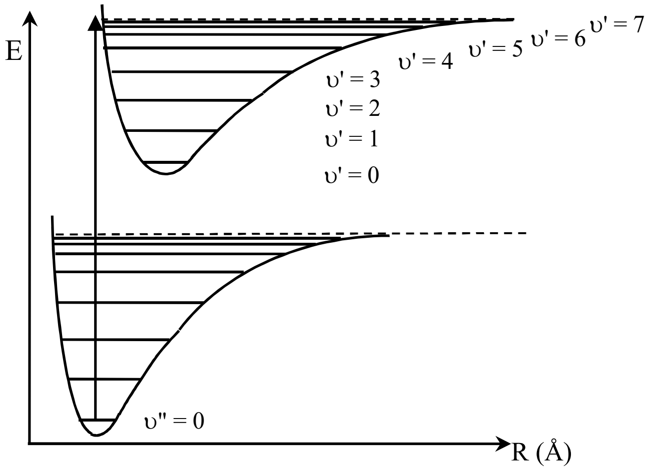
4. Predict the intensities of the different vibrational transitions in the electronic absorption spectrum of the following system. Show at least four peaks. Label each transition in the energy level diagram with the vibrational quantum numbers for the transition and each corresponding peak in the spectrum (e.g. 4←0).

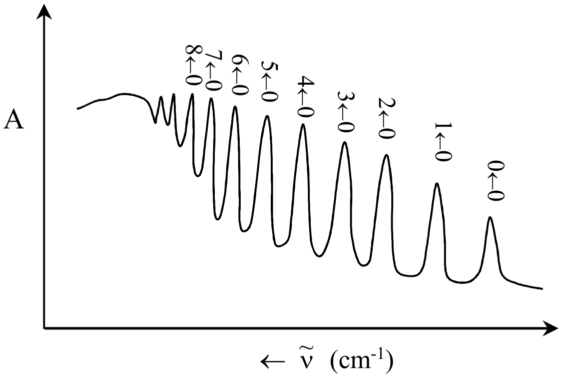




Answer: The plan is to draw in the vertical transition to predict the vibrational fine-structure transition with the largest Franck-Condon factor.

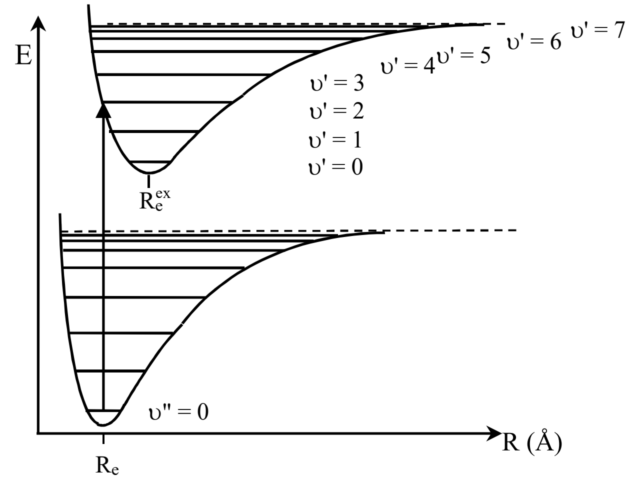
The vertical transition intersects the excited state potential energy curve above the dissociation limit. The highest intensity transitions are to vibrational levels near the convergence limit and to the translational continuum. The peak spacing goes to zero at the convergence limit

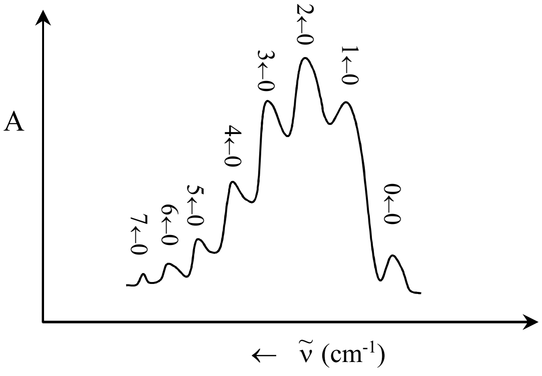




5. Show the relationship between the ground state and excited state potential energy curves for an electronic transition that has a maximum probability for the 2←0 vibrational fine-structure transition. Draw the corresponding absorption spectrum. Label each transition in the energy level diagram with the vibrational quantum numbers for the transition and each corresponding peak in the spectrum (e.g. 4←0). (Use the potential energy curves shown in the previous question for the style of your sketch).

Answer: The plan is to position the equilibrium internuclear separations of the ground and excited state potential energy curves to give the vertical transition with 2←0 as the largest Franck-Condon factor.

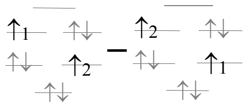




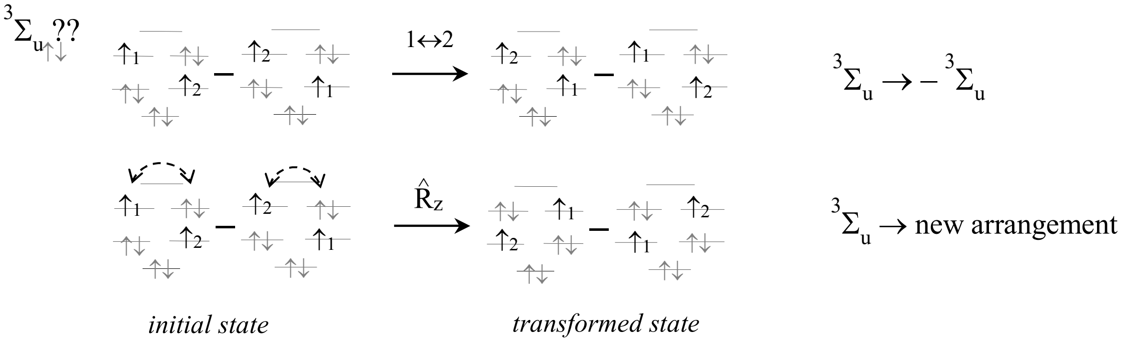
Intense excitations into low lying vibrational levels of the excited state correspond to small changes in equilibrium internuclear separation, as shown in the figure above. Transitions of other adjacent vibrational levels typically have comparable intensities. The vertical transition just predicts the most intense. The absorption spectrum resembles that for benzene, Figure 28.1.12.

6. (a). In Figure 28.1.9b we needed to take the linear combination of four specific assignments to generate a state that satisfies both the Pauli Exclusion Principle and reflection symmetry. Why four states instead of two? Show that the following state does not properly account for electron indistinguishability and reflection symmetry:

$^3\Sigma_u$??



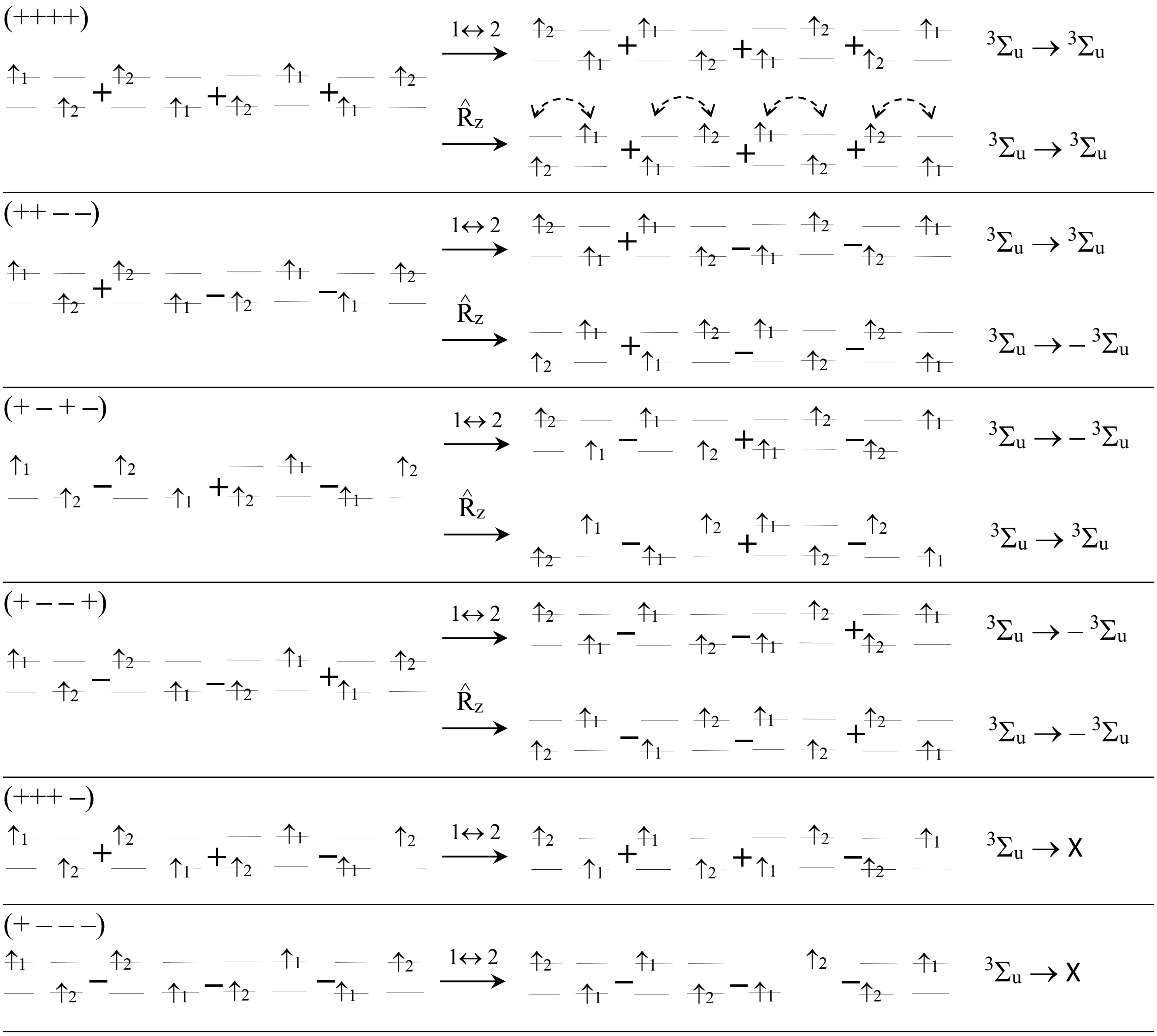
Answer: Consider transformation of the state with respect to exchange of spin labels and reflection:



The given linear combination is anti-symmetric with respect to exchange of spin labels, as required for the spatial part of a triplet state, but reflection symmetry results in a different set of singly occupied orbitals than the initial state. This linear combination is neither symmetric nor anti-symmetric with respect to reflection, it transforms to give a different state. The linear combinations that transform as symmetric or anti-symmetric with respect to exchange of spin labels and reflection are given in Figure 28.1.9.

7. In Figure 28.1.10 we needed to take the linear combination of four specific assignments to generate a state that satisfies both the Pauli Exclusion Principle and reflection symmetry. However, there are eight possible combinations of the coefficients that give equal weight to each assignment: (++++), (++ – –), (+ – + –), (+ – – +), (+++ –), (+ – – –), (+ – ++), (++ – +). Show that only the two linear combinations listed in Figure 28.1.10 properly account for electron indistinguishability and reflection symmetry for the Σ_u triplet terms and two more for the singlet terms.

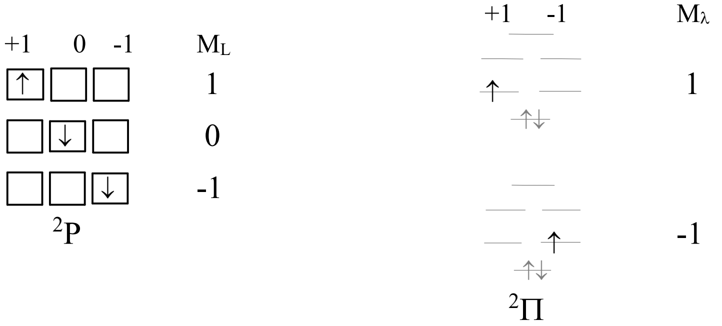
Answer: To make the states easier to compare, show only the singly occupied states. Then determine the symmetry with respect to exchange of spin labels and reflection:



Similarly (+ – ++) and (++ – +) don't transform to give either the original state or its negative. Summarizing, the eight possible states give two states that are anti-symmetric with respect to exchange of spin labels and are either symmetric or anti-symmetric with respect to reflection. These states have the spatial symmetry appropriate to match the symmetric spin parts of the triplet terms. In addition there are two states that are symmetric with respect to exchange of spin labels and are either symmetric or anti-symmetric with respect to reflection. This second pair has the spatial symmetry appropriate to match the anti-symmetric spin part of the singlet terms:

Linear combination	Label exchange	Reflection	Term
(++++)	+	+	$^1\Sigma_u^+$
(++ – –)	+	–	$^1\Sigma_u^-$
(+ – + –)	–	+	$^3\Sigma_u^+$
(+ – – +)	–	–	$^3\Sigma_u^-$
(+++ –)	X		
(+ – – –)	X		
(+ – ++)	X		
(++ – +)	X		

8. In Chapter 25, we determined the complete set of atomic terms for a given electronic configuration by exhaustively enumerating all the possible explicit orbital assignments. In this chapter we took a bit of a short-cut. However, it is still informative to determine all possible molecular terms by exhaustive enumeration. Luckily, diatomic electronic states are simpler, because the π levels are only doubly degenerate. For example, the p^1 atomic configuration gives a ^2P term with $M_L = \{1,0,-1\}$. However, the $(\sigma_{g,2pz})^2 (\pi_{u,2p})^1$ molecular configuration corresponds to only $M_\lambda = \{1,-1\}$, because there are only two degenerate π-molecular orbitals:



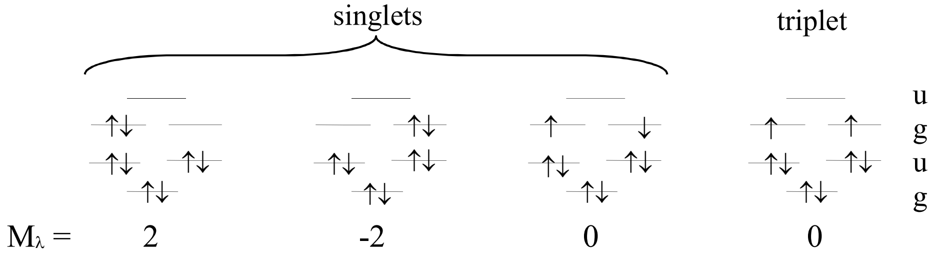
(a). atomic (b). diatomic molecular

Figure P28.8.1: (a). The p^1 atomic configuration is triply degenerate with $M_L = \{1,0,-1\}$. (b). The $(\sigma_{g,2pz})^2 (\pi_{u,2p})^1$ molecular configuration corresponds to only $M_\lambda = \{1,-1\}$, since the π orbitals are doubly degenerate.

Similarly, a Δ term is also doubly degenerate, $M_\lambda = \{2,-2\}$. Show that the molecular terms for the configuration KK $(\sigma_{g,2s})^2(\sigma^*_{u,2s})^2(\sigma_{g,2pz})^2(\pi_{u,2p})^4(\pi^*_{g,2p})^2$ are $^3\Sigma_g + {}^1\Delta_g + {}^1\Sigma_g$, by exhaustive enumeration of explicit molecular orbital assignments. Include the parity, g or u (you don't need to find the reflection symmetry).

Answer: The explicit orbital assignments are:

$$\mathrm{KK}\ (\sigma_{g,2s})^2(\sigma^*_{u,2s})^2(\sigma_{g,2pz})^2(\pi_{u,2p})^4(\pi^*_{g,2p})^2$$



Using the same procedure that we used for atomic term symbols, we first list all the M_λ values for the singlet states:

$$M_\lambda = \{2,0,-2\}$$

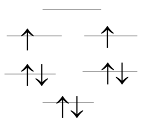
With $\Lambda = 2$, the first term is a ${}^1\Delta$ term. Removing $M_\lambda = \{2,-2\}$ leaves:

$$M_\lambda = \{0\}$$

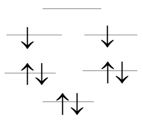
The final singlet term is ${}^1\Sigma$. The only triplet gives $\Lambda = 0$ for a ${}^3\Sigma$ term. The parity of all the states is gguuuugg = g. The final terms are ${}^1\Delta_g + {}^1\Sigma_g + {}^3\Sigma_g$, in agreement with Figure 28.1.5a.

You may wonder why we don't consider assignments like the two below as distinct:

from above:

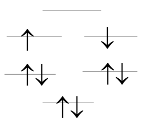


then consider:

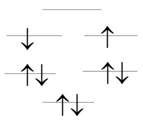


The assignment on the right is the same triplet assignment as on the left with all the spins flipped. Therefore, right-hand assignment doesn't represent a unique explicit orbital assignment. Instead, the two assignments are components of the same triplet state, with spin states $\{\alpha\alpha, \alpha\beta + \beta\alpha, \beta\beta\}$. For another example, the two states below are the same explicit assignment with all the spins flipped. So they aren't unique:

from above:



then consider:

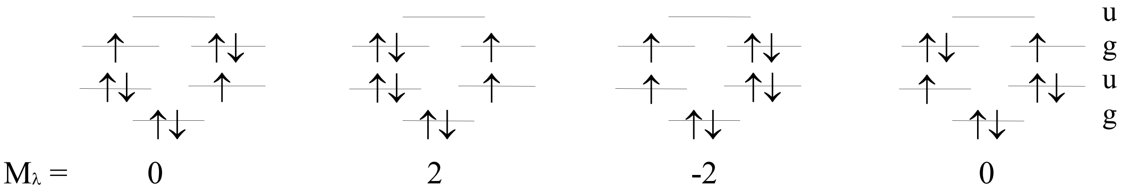


These two assignments are degenerate and combine in symmetry adapted linear combination to form the final ${}^1\Sigma_g^+$ state, as shown in Figure 28.1.9b. In general, two states that are related by flipping all the spins are not unique for the purposes of determining the possible values of M_L for atoms or M_λ for molecules.

9. Find the molecular terms for the configuration KK $(\sigma_{g,2s})^2(\sigma^*_{u,2s})^2(\sigma_{g,2pz})^2(\pi_{u,2p})^3(\pi^*_{g,2p})^3$ by exhaustive enumeration of explicit molecular orbital assignments. Include the parity, g or u (you don't need to find the reflection symmetry).

Answer: There are two degenerate $\pi_{u,2p}$ orbitals for placement of one unpaired electron and two degenerate $\pi^*_{g,2p}$ orbitals for placement of the second unpaired electron, so we expect $2 \cdot 2 = 4$ explicit orbital assignments for triplet states and another 4 for singlet states. The explicit orbital assignments for the triplet states are:

KK $(\sigma_{g,2s})^2(\sigma^*_{u,2s})^2(\sigma_{g,2pz})^2(\pi_{u,2p})^3(\pi^*_{g,2p})^3$ triplets:



Using the same procedure that we used for atomic term symbols, we first list all the M_λ values for the triplet states:

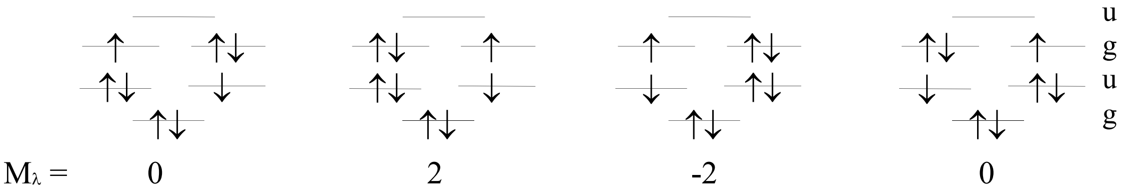
$M_\lambda = \{2,0,0,-2\}$

With $\Lambda = 2$, the first term is a $^3\Delta$ term. Removing $M_\lambda = \{2,-2\}$ leaves:

$M_\lambda = \{0,0\}$

The remaining terms are two $^3\Sigma$ terms. The parity of all the states is gguuuggg = u. The singlet states are obtained by flipping one of the unpaired spins in the previous set:

KK $(\sigma_{g,2s})^2(\sigma^*_{u,2s})^2(\sigma_{g,2pz})^2(\pi_{u,2p})^3(\pi^*_{g,2p})^3$ singlets:



The resulting M_λ set is the same as for the triplet states and the parity also remains the same. The final terms are $^3\Delta_u + {}^3\Sigma_u + {}^3\Sigma_u$ and $^1\Delta_u + {}^1\Sigma_u + {}^1\Sigma_u$ in agreement with Figure 28.1.5b. The repeat $^3\Sigma$ and $^1\Sigma$ terms show the necessity of considering the reflection symmetry.

10. For a homonuclear diatomic molecule, determine which of the following transitions is allowed or forbidden, assuming weakly coupled spin and orbital angular momenta.[4] [Note: identical term symbols can result from two different configurations; term symbols are unique within a given configuration.]

${}^2\Sigma_g^- \leftarrow {}^2\Pi_u$ ${}^1\Sigma_g^- \leftarrow {}^1\Sigma_g^-$ ${}^1\Delta_g \leftarrow {}^1\Pi_u$ ${}^1\Delta_u \leftarrow {}^1\Sigma_g^+$ ${}^1\Sigma_g^- \leftarrow {}^3\Sigma_u^-$ ${}^3\Sigma_u^- \leftarrow {}^3\Sigma_g^-$

Answer: The plan is to note the selection rules, Eq. 28.1.12, for weakly coupled spin and orbital angular momenta.

The allowed transitions are $^2\Sigma_g^- \leftarrow {}^2\Pi_u$, $^1\Delta_g \leftarrow {}^1\Pi_u$, and $^3\Sigma_u^- \leftarrow {}^3\Sigma_g^-$ (the Schumann-Runge band is $^3\Sigma_u^- \leftarrow {}^3\Sigma_g^-$). The forbidden terms and the offended selection rule are:

Transition	Rule broken
$^1\Sigma_g^- \nleftarrow {}^1\Sigma_g^-$	$g \rightarrow u$ or $u \rightarrow g$
$^1\Delta_u \nleftarrow {}^1\Sigma_g^+$	$\Delta\Lambda = 0, \pm 1$
$^1\Sigma_g^- \nleftarrow {}^3\Sigma_u^-$	$\Delta S = 0$

11. (a). Determine the possible values of the projection of the total angular momentum, $\Omega = |\Lambda + \Sigma_s|$, for a $^3\Delta$ term. (b). Determine if the transition to each of these $^3\Delta$ terms from a $^3\Pi_o$ state is allowed or forbidden.

Answer: The plan is to note that the projection of the spin angular momentum along the internuclear axis is from –S to +S in integer steps.[4]

For a Δ-state, $\Lambda = 2$. For a triplet state, $S = 1$ and then the projections are $\Sigma_s = -1, 0, +1$. The possible projection of the total angular momentum are then:

$$\Omega = |\Lambda + \Sigma_s| = 2 - 1,\ 2 + 0,\ 2 + 1 = 1, 2, 3 \quad \text{giving } {}^3\Delta_1, {}^3\Delta_2, \text{ and } {}^3\Delta_3 \text{ terms}$$

The selection rules, $\Delta\Lambda = 0, \pm 1$; $\Delta S = 0$; and $\Delta\Omega = 0, \pm 1$ give:

Allowed: $^3\Delta_1 \leftarrow {}^3\Pi_o$
Forbidden: $^3\Delta_2 \nleftarrow {}^3\Pi_o$, $^3\Delta_3 \nleftarrow {}^3\Pi_o$ ($\Delta\Omega$ too large)

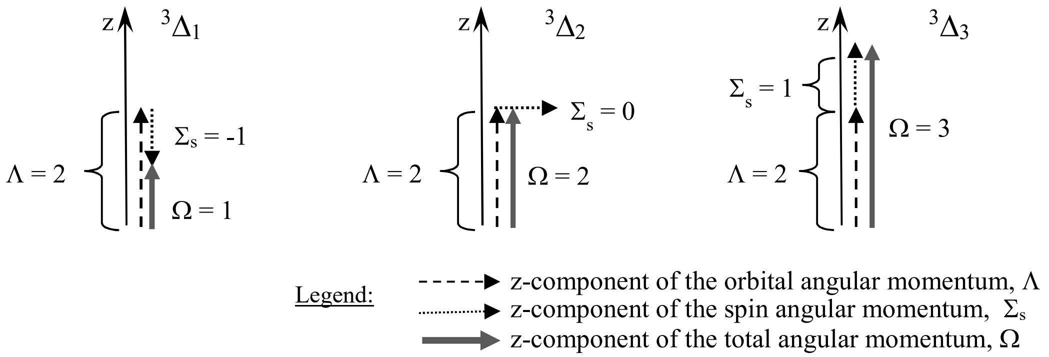
The $\Delta\Omega = 0, \pm 1$ selection rule holds even in cases with strong spin-orbital coupling, when the $\Delta\Lambda = 0, \pm 1$ and $\Delta S = 0$ selections rules no longer apply.

Note: Most authors use the symbol Σ and not Σ_s for the projection of the spin angular momentum. Unfortunately then, the two uses of the symbol Σ, which are the term symbol and the projection of the spin, must be distinguished by context.

12. In Problem 25.31 we illustrated an angular momentum component diagram to help explain the occurrence of multiple total angular momentum states, given the projections of the orbital and spin angular momenta. Give the corresponding molecular diagram showing that the projections of the total angular momentum resolve $^3\Delta$ terms into three states: $^3\Delta_1$, $^3\Delta_2$, and $^3\Delta_3$. [Hint: simply replace M_L, M_S, and M_J with Λ, Σ_s, and Ω. Note that Λ is always positive.[4] Use the S and Λ values corresponding to a $^3\Delta$ term.]

Answer: The plan is to follow the diagram given in Problem 25.31, noting that $\Lambda = 2$ and $S = 1$.

See the previous problem for the derivation of the three total angular momentum states. The diagrams are:



13. Describe in words the purpose of the Birge-Sponer extrapolation in the analysis of electronic absorption spectra.

Answer: The dissociation energy of the ground state is given by the wave number at the convergence limit as:

$$\tilde{D}_o = \tilde{\nu}_{\infty o} - \Delta\tilde{E}_{atomic} \qquad (28.2.6)$$

This equation is not necessarily dependent on the Birge-Sponer extrapolation. If the convergence limit is obvious from the spectrum, the Birge-Sponer extrapolation is not necessary. Such cases include ClF, IBr, and ICl.[5] The purpose of the Birge-Sponer extrapolation is to determine the dissociation limit if the limit is obscured by noise or if vibrational fine-structure transitions near the dissociation limit are not observed.

Hertha Sponer (1895-1968) was a German physicist and physical chemist. The Birge-Sponer extrapolation was developed when she was on a Rockefeller Foundation fellowship with R. T. Birge at the University of California at Berkeley in 1925. In 1934, she was forced from her faculty position at the University of Göttingen by the Nazis, because she was a woman. In 1936 she was appointed as the first woman on the physics faculty at Duke University, where she remained active until 1966.

14. Describe in words the meaning and purpose of the Franck-Condon factors in the interpretation of electronic absorption spectra.

Answer: Franck-Condon factors determine the intensity of vibrational fine-structure transitions in absorption and emission spectroscopy as well as the rate of non-radiative energy transfer in internal conversion, intersystem crossing, and intermolecular energy transfer. Franck-Condon factors are given by the square of the overlap integral of the vibrational wave functions of the two coupled states. Franck-Condon integrals have a significant value only if the two vibrational wave functions have high probability at a common internuclear separation.

For absorption and emission spectra, we often use the approximation of determining the intersection of a vertical transition with the final state potential energy surface to estimate the largest Franck-Condon factor. This short-cut is good for transitions to highly excited vibrational states, but is poor for low lying vibrational states. Of course it is always best to calculate the Franck-Condon integrals directly, using the vibrational wave functions (if the potential energy surfaces are known)

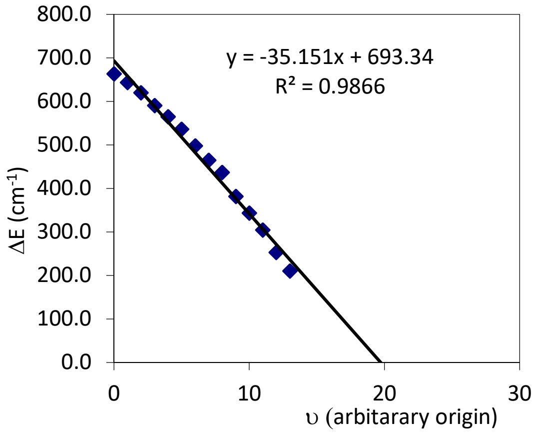
15. The Schumann-Runge band for molecular oxygen is in the UV-region of the spectrum. The wave numbers for the ${}^3\Sigma_u^- \leftarrow {}^3\Sigma_g^-$ transitions are given in the table below. The corresponding vibrational quantum numbers are not known. The ground state dissociates into two ground state ${}^3P$ oxygen atoms, and the ${}^3\Sigma_u^-$ excited state dissociates into a ${}^3P$ and a ${}^1D$ oxygen atom. Calculate (a) the dissociation energy of the ground state (the bond strength). (b). Estimate the dissociation energy of the excited state by assuming the first observed transition is for $\upsilon \cong 0$. The atomic excitation energy, ${}^3P \rightarrow {}^1D$ is 1.9674 eV, 15867.9 cm^{-1}, or 189.82 kJ/mol.

$\tilde{\nu}$ (cm^{-1})	50062.6	50725.4	51369.0	51988.6	52579.0	53143.4	53679.6	54177.0
continued	54641.8	55078.2	55460.0	55803.1	56107.3	56360.3	56570.6	

Answer: The plan is to use a Birge-Sponer extrapolation following Example 28.2.2 and then Eq. 28.2.6 to determine the dissociation energies.

The adjacent differences are calculated in the following spreadsheet with the corresponding Birge-Sponer extrapolation. An arbitrary quantum number of zero is assigned to the first transition, since the vibrational quantum numbers are not known.

υ	$\tilde{\nu}_\upsilon$ cm^{-1}	$\Delta\tilde{\nu}_\upsilon$ (cm^{-1})
0	50062.6	662.8
1	50725.4	643.6
2	51369.0	619.6
3	51988.6	590.4
4	52579.0	564.4
5	53143.4	536.2
6	53679.6	497.4
7	54177.0	464.8
8	54641.8	436.4
9	55078.2	381.8
10	55460.0	343.1
11	55803.1	304.2
12	56107.3	253.0
13	56360.3	210.3
	56570.6	



slope	-35.15121	693.34	b
±	1.1829486	9.0478167	±
r^2	0.9865918	17.842535	s(y)
F	882.97582	12	df
SS$_{reg}$	281100.7	3820.2727	SS$_{residual}$

(a). Using Eq. 28.2.17, the slope gives the anharmonicity: $\chi_e^{ex}\,\tilde{\nu}_e^{ex} = -\tfrac{1}{2}$ slope = 17.58 ± 0.59 cm^{-1}

Using Eq. 28.2.18: $\upsilon_{cl} = \dfrac{\Delta\tilde{\nu}_o}{2\chi_e^{ex}\,\tilde{\nu}_e^{ex}} = \dfrac{693.34}{35.1512} = 19.73 \pm 0.71$

Using Eq. 28.2.19: area = ½ $\Delta\tilde{\nu}_o\,\upsilon_{cl}$ = ½ (693.34)(19.73) = 6839.8 ± 262 cm^{-1}

Using Eq. 28.2.20, the transition wave number at the convergence limit is:

$$\tilde{\nu}_{\infty o} = \tilde{\nu}_{oo} + \text{area} = 50062.6\ \text{cm}^{-1} + 6839.8\ \text{cm}^{-1}$$
$$= 56902.4 \pm 262\ \text{cm}^{-1} = 7.055 \pm 0.032\ \text{eV}$$

Using Eq. 28.2.6, the bond energy of the ground state is:

in cm^{-1}: $\tilde{D}_o = \tilde{\nu}_{\infty o} - \Delta\tilde{E}_{\text{atomic}} = (56902.4 \pm 262\ \text{cm}^{-1}) - 15867.9\ \text{cm}^{-1} = 41035 \pm 262\ \text{cm}^{-1}$
in eV: $D_o = \Delta E(j,\infty\leftarrow i,0) - \Delta E_{\text{atomic}} = (7.055 \pm 0.032\ \text{eV}) - 1.9674\ \text{eV} = 5.0876 \pm 0.032\ \text{eV}$
in kJ mol^{-1}: $= 490.9 \pm 3.1\ \text{kJ mol}^{-1}$

Notice that the Birge-Sponer plot has significant systematic curvature, and the convergence limit by visual extrapolation appears to be less than $\upsilon = 19$, which decreases the calculated ground and excited state dissociation energies. The literature ground state dissociation energy is 5.126 eV.

(b). If $\upsilon \cong 0$ for the first transition, then the excited state dissociation energy is the area under the Birge-Sponer curve, Eq. 28.2.19:

$$\tilde{D}_o^{ex} \cong \text{area} = 6840\ \text{cm}^{-1} = 0.85\ \text{eV}$$

which suffices as a lower limit of the true excited state dissociation energy. The error is within a few multiples of $\tilde{\nu}_o^{ex}$, which is 0.082 eV. If $\tilde{\nu}_o^{ex}$ is 662.8 cm^{-1} as we have assumed, then using Eq. 27.5.11, $\tilde{\nu}_e^{ex} \cong \tilde{\nu}_o^{ex} + 2\chi_e^{ex}\,\tilde{\nu}_e^{ex} = 662.8\ \text{cm}^{-1} + 35.15\ \text{cm}^{-1} = 698.0\ \text{cm}^{-1}$. The literature value of $\tilde{\nu}_e^{ex}$ is 799.1 cm^{-1}, which suggests that the first observed transition is actually for $\upsilon = 3$.

16. For SiS the wave numbers for the $E^1\Sigma^+ \leftarrow X^1\Sigma^+$ transitions are given in the table below.[6] The ground state is labeled as the X-state and this excited state, which has the same symmetry, is the E-state. Assume that the corresponding vibrational quantum numbers are not known. The ground and excited states dissociate into two ground-state ^3P atoms. Calculate the dissociation energy of the ground state (the bond strength).

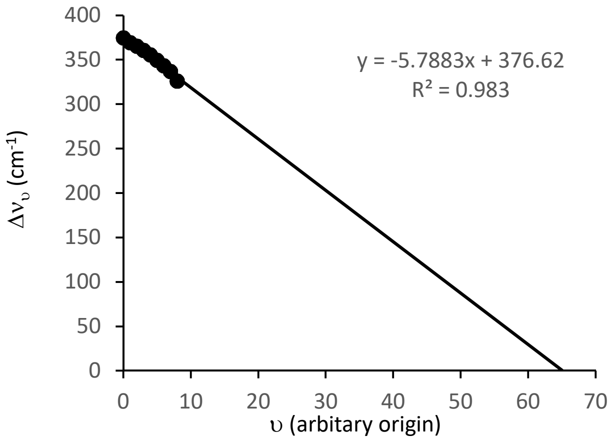
$\tilde{\nu}$ (cm^{-1})	44482.8	44857.6	45227.0	45592.2	45952.8	46308.3	46657.7	47001.0	47337.9	47664.0

Answer: The plan is to use a Birge-Sponer extrapolation following Example 28.2.2 and then Eq. 28.2.6 to determine the dissociation energies. The first transition is assigned an arbitrary vibrational quantum number of zero for the purposes of the extrapolation.

The adjacent differences are calculated in the following spreadsheet with the corresponding Birge-Sponer extrapolation. An arbitrary quantum number of zero is assigned to the first transition, since the vibrational quantum numbers are not known. Because we are assigning an arbitrary vibrational quantum number, the intercept is not the fundamental vibration frequency. The extrapolation to the convergence limit works out just fine, however.

υ	ν_υ (cm^{-1})	$\Delta\nu_\upsilon$ (cm^{-1})
0	44482.8	374.8
1	44857.6	369.4
2	45227	365.2
3	45592.2	360.6
4	45952.8	355.5
5	46308.3	349.4
6	46657.7	343.3
7	47001	336.9
8	47337.9	326.1
9	47664	

slope	-5.7883	376.62	b
±	0.2873	1.3679	±
r^2	0.9830	2.2256	s(y)
F	405.8631	7	df
ss$_{reg}$	2010.2882	34.6718	ss$_{residual}$



(a). Using Eq. 28.2.17, the slope gives the anharmonicity: $\chi_e^{ex}\,\tilde{\nu}_e^{ex} = -\tfrac{1}{2}\,\text{slope} = 2.894 \pm 0.14\ \text{cm}^{-1}$

Using Eq. 28.2.18: $\upsilon_{cl} = \dfrac{\Delta\tilde{\nu}_o}{2\chi_e^{ex}\,\tilde{\nu}_e^{ex}} = \dfrac{376.62}{5.7883} = 65.07 \pm 3.24$

Using Eq. 28.2.19: area = $\tfrac{1}{2}\,\Delta\tilde{\nu}_o\,\upsilon_{cl} = \tfrac{1}{2}\,(376.62)(65.07) = 12250 \pm 612\ \text{cm}^{-1}$

Using Eq. 28.2.20, the transition wave number at the convergence limit is:

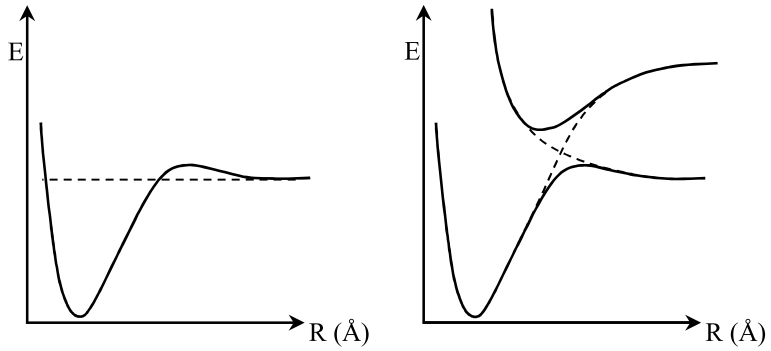
$$\begin{aligned}\tilde{\nu}_{\infty o} &= \tilde{\nu}_{oo} + \text{area} = 44482.8\ \text{cm}^{-1} + 12250\ \text{cm}^{-1}\\ &= 56732.8 \pm 612\ \text{cm}^{-1} = 7.034 \pm 0.076\ \text{eV}\end{aligned}$$

Since the excited state gives ground state atoms, $\Delta\tilde{E}_{atomic}$ is zero for this transition. Using Eq. 28.2.6, the bond energy of the ground state is:

in cm^{-1}: $\tilde{D}_o = \tilde{\nu}_{\infty o} - \Delta\tilde{E}_{atomic} = 56732.8 \pm 612\ \text{cm}^{-1}$
in eV: $D_o = \Delta E(j,\infty \leftarrow i,0) - \Delta E_{atomic} = 7.034 \pm 0.076\ \text{eV}$
in kJ mol^{-1}: $= 678.7 \pm 7.3\ \text{kJ mol}^{-1}$

Notice that the convergence limit is a long extrapolation on the Birge-Sponer plot, giving large uncertainties. The last data point also shows some downward curvature, which would decrease the convergence limit and corresponding dissociation energies. The literature ground state dissociation energy, which is based on the same data is 6.72 eV, which takes into account some of the observed curvature through a second anharmonicity correction.

17. Vibrational potential functions commonly deviate from Morse behavior. One possibility is the appearance of a maximum, Figure P28.17.1a. One cause of a maximum is a strong Van der Waals repulsion at large distances, but strong bonding interactions at short distances.[5] Referring to Figure 26.2.4, strong electron-electron repulsion increases the potential energy at large R, possibly giving a maximum. A second cause, especially for excited states, is an avoided crossing between a bound-state potential energy curve and a repulsive state, Figure P28.17.1b. An example is a state of an alkali halide that tends to dissociate to ions, but because of the curve crossing dissociates to atoms instead.[5] Discuss the effect of a potential maximum on the spectroscopic determination of the dissociation energy of the bound state.

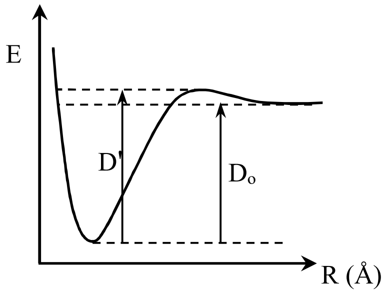


(a). (b).

Figure P28.17.1: (a). Some vibrational potential energy curves have a maximum. (b). One cause is an avoided crossing.

Answer: The plan is to consider what the results of a Birge-Sponer extrapolation would yield for the dissociation energy.

Birge Sponer extrapolation yields the dissociation energy D', which is greater than the true dissociation energy D_o. The relationship is diagrammed below. Such circumstances are not uncommon, especially upon comparisons of spectroscopic and thermodynamically obtained values.[1]



18. The electronic absorption spectrum of water has a Rydberg series that start with the configuration …$(3a_1)^2(1b_1{}^{\circ})^1(3p)^1$ for a 3p-orbital on the O-atom. See Figure 26.6.4 for the molecular orbital diagram. Is the Rydberg series consistent with the ultraviolet photoelectron spectrum, UPS, of water shown in Figure 28.5.4b? The series has transitions:

$$\tilde{\nu}_n = 101786\ \text{cm}^{-1} - \frac{\Re_H}{(n-0.7)^2} \qquad n = 3, 4, 5, \ldots\ldots$$

Answer: The plan is to note that the Rydberg ionization limit corresponds to the formation of the molecular ion.

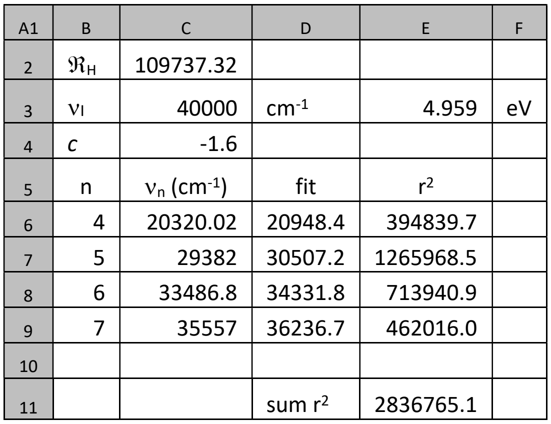
The ionization limit converted to eV is: $\tilde{\nu}_n = 101786\ \text{cm}^{-1}(1\ \text{eV}/8065.5\ \text{cm}^{-1}) = 12.62$ eV which agrees exactly with the first ionization potential from the UPS spectrum in Figure 28.5.4b. Rydberg series don't necessarily give the ground state of the molecular ion, but such is the case in this example.

19. The diatomic molecule Na_2 has a Rydberg series in the electronic absorption spectrum. The ionization limit gives the ground state of the molecular ion, Na_2^+. The ionization limit from the Rydberg series and the ionization potential measured using UPS should be identical for the specific excited state of the molecular ion. The quantum numbers of the Rydberg transitions and the wave numbers are given in the table below. Determine the ionization potential to form Na_2^+. Compare the value to the ionization potential determined using UPS, which is 4.90 eV (see Problem 37 for the reference to the literature value).

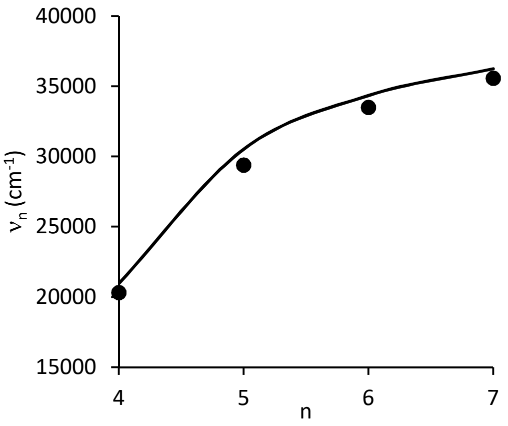
n	4	5	6	7
$\tilde{\nu}_n$	20320.02	29382	33486.8	35557

Answer: The plan is to fit the data to the Rydberg series expression, Eq. 28.2.22. We first write a spreadsheet to approximate the fit coefficients and then use non-linear least squares curve fitting.

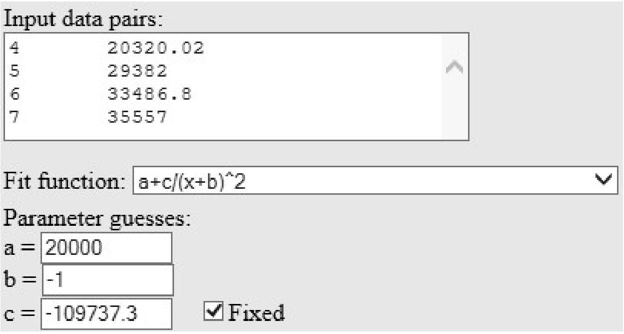
A spreadsheet to do an approximate curve fit is shown below. As usual the goal is to minimize the sum of squared residuals, which is calculated in cell E11. The fit parameters, which are the wave number of the ionization limit $\tilde{\nu}_I$ in cell C3 and the quantum defect c in cell C4, are varied to achieve an approximate fit. With patience, or using Goal Seek, this guessing procedure is sufficient to complete the fit, but we only need to derive approximate fit values at this point.



A1	B	C	D	E	F
2	$\Re_H$	109737.32			
3	ν_I	40000	cm^{-1}	4.959	eV
4	c	-1.6			
5	n	ν_n (cm^{-1})	fit	r^2	
6	4	20320.02	20948.4	394839.7	
7	5	29382	30507.2	1265968.5	
8	6	33486.8	34331.8	713940.9	
9	7	35557	36236.7	462016.0	
10					
11			sum r^2	2836765.1	



Using approximate values close to those from the spreadsheet, a curve fit using the "Nonlinear Least Squares Curve Fitting" applet on the textbook Web site or companion CD is done using the functional form "a+c/(x+b)^2" as set up below with a constant c value for the Rydberg constant.



Input data pairs:

```
4       20320.02
5       29382
6       33486.8
7       35557
```

Fit function: a+c/(x+b)^2

Parameter guesses:

a = 20000

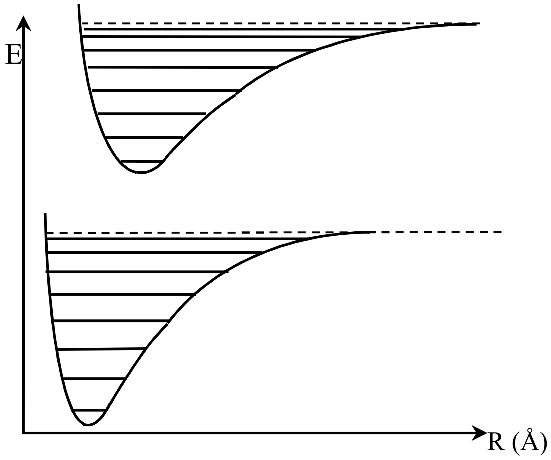
b = -1

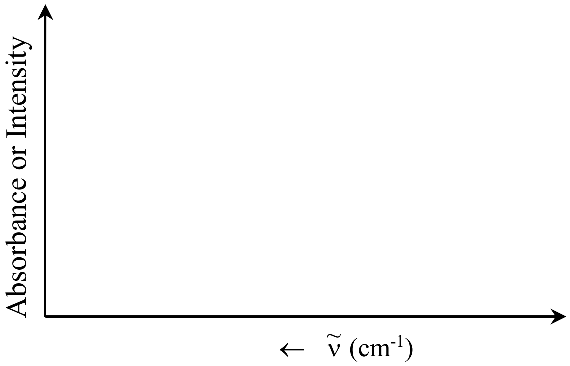
c = -109737.3 ☑ Fixed

```
============    Results    ============
 a= 39107 +- 194
 b= -1.5887 +- 0.023
____________ Output Data ____________
  x       y       y(fit)    residual
 4.0   20320.02  20233.351   86.6684
 5.0   29382.0   29676.904  -294.904
 6.0   33486.8   33467.758   19.0413
 7.0   35557.0   35359.440   197.559
-------------------------------------
 sum of squared residuals= 133900
 stand. dev. y values= 258.7
 correlation between a & b= -0.7453
```

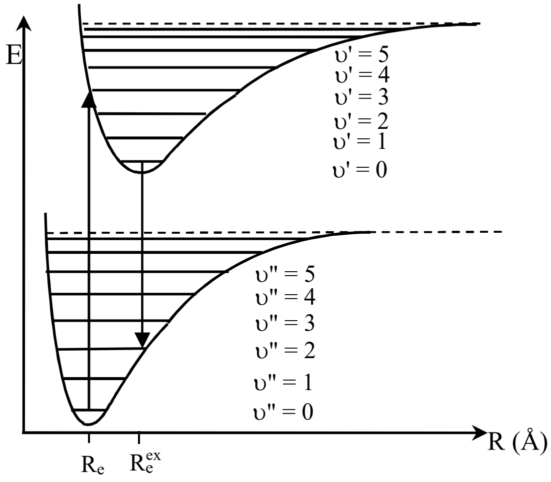
Notice that the guesses don't need to be very close to the final values; we just used the spreadsheet to get a reasonable estimate for *c* (small negative). The curve fit results give the ionization limit, $\tilde{\nu}_I = 39107 \pm 194\ \text{cm}^{-1} = 4.849 \pm 0.024$ eV, which is in excellent agreement with the UPS derived ionization potential.

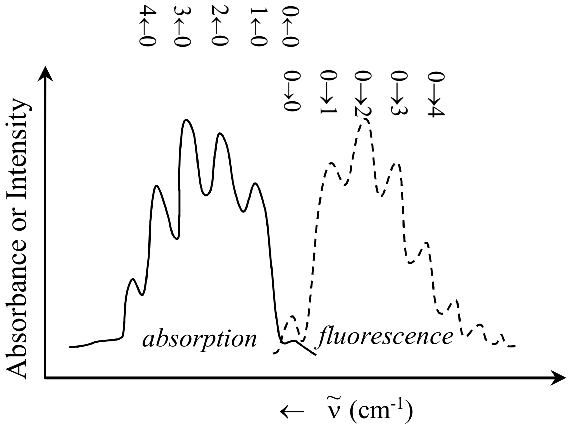
20. Using the potential energy curves shown below, predict the most intense vibrational fine-structure transitions in the absorption and fluorescence spectra. Draw the corresponding absorption and fluorescence spectra. Show four of the intense transitions in each of the spectra. Label each transition in the energy level diagram with the vibrational quantum numbers for the transition and each corresponding peak in the spectrum (e.g. 4←0).





Answer: The plan is to draw in the vertical transitions to predict the vibrational fine-structure transition with the largest Franck-Condon factors.





The most probable internuclear separation in the υ" = 0 vibrational state of the electronic ground state is the middle of the potential energy well, giving the starting point for the vertical transition in absorption as R_e. The most intense transition in absorption is to υ' = 3, as shown in the figure above. Transitions to other adjacent vibrational levels typically have comparable intensities. The vertical transition just predicts the most intense. The most probable internuclear separation in the $\upsilon' = 0$ vibrational state of the first excited electronic state is also in the middle of the potential energy well, giving the starting point for the vertical transition in absorption as R_e^{ex}. The most intense transition in fluorescence is to $\upsilon'' = 2$, as shown in the figure above.

21. We took a short cut in the derivation of Eq. 28.2.13 by working in analogy with Eq. 27.5.12. In this problem we derive Eq. 28.2.13 directly from the term values of the adjacent transitions. The energy of the $\upsilon'' = 0$ level of the ground electronic state is $\tilde{E}_o$. The energy difference from the minimum energy of the ground state potential energy curve to the minimum energy of the excited state potential energy curve, that is the energy without vibration, is $\tilde{T}_e^{ex}$. The energy of the υ' vibrational level of the excited state is $\tilde{E}^{ex}_{\upsilon'}$, neglecting rotation:

$$\tilde{E}^{ex}_{\upsilon'} = \tilde{T}_e^{ex} + \tilde{\nu}_e^{ex}(\upsilon' + \tfrac{1}{2}) - \chi_e^{ex}\tilde{\nu}_e^{ex}(\upsilon' + \tfrac{1}{2})^2 \qquad \text{P28.14.1}$$

The energy of an electronic transition from the $\upsilon'' = 0$ level of the ground electronic state to the υ' vibrational level of the excited state is:

$$\Delta\tilde{E}(j,\upsilon'\leftarrow i,0) = \tilde{E}^{ex}_{\upsilon'} - \tilde{E}_o = \tilde{T}_e^{ex} + \tilde{\nu}_e^{ex}(\upsilon' + \tfrac{1}{2}) - \chi_e^{ex}\tilde{\nu}_e^{ex}(\upsilon' + \tfrac{1}{2})^2 - \tilde{E}_o \qquad \text{P28.14.2}$$

where the fundamental vibration frequency $\tilde{\nu}_e^{ex}$ and anharmonicity $\chi_e^{ex}\tilde{\nu}_e^{ex}$ are for the excited state. Consider two adjacent transitions: $j,\upsilon+1\leftarrow i,0$ and $j,\upsilon\leftarrow i,0$. The adjacent energy difference is:

$$\Delta\tilde{\nu}_\upsilon = \Delta\tilde{E}(j,\upsilon+1\leftarrow i,0) - \Delta\tilde{E}(j,\upsilon\leftarrow i,0) \qquad \text{P28.14.3}$$

(a). Prove that: $\Delta\tilde{\nu}_\upsilon = = \tilde{\nu}_e^{ex} - \chi_e^{ex}\tilde{\nu}_e^{ex}[(\upsilon + \tfrac{1}{2}) + 1)]^2 + \chi_e^{ex}\tilde{\nu}_e^{ex}(\upsilon + \tfrac{1}{2})^2$ P28.14.4

(b). Using $((\upsilon+\tfrac{1}{2})+1)^2 = (\upsilon+\tfrac{1}{2})^2 + 2(\upsilon+\tfrac{1}{2}) + 1$, starting with Eq. P28.14.4 prove that:

$$\Delta\tilde{\nu}_\upsilon = (h\tilde{\nu}_e^{ex} - 2\chi_e^{ex}\tilde{\nu}_e^{ex}) - 2\chi_e^{ex}\tilde{\nu}_e^{ex}\upsilon \qquad (28.2.13)$$

(c). Label $\tilde{E}_o$, $\tilde{E}^{ex}_{\upsilon}$, $\tilde{T}_e^{ex}$, $\Delta\tilde{E}(j,\upsilon+1\leftarrow i,0)$, $\Delta\tilde{E}(j,\upsilon\leftarrow i,0)$, and $\Delta\tilde{\nu}_\upsilon$ on a plot of the ground and excited state potential energy curves. Pick a convenient arbitrary υ for your plot.

Answer: (a). The adjacent energy difference is:

$$\Delta\tilde{\nu}_\upsilon = \Delta\tilde{E}(j,\upsilon+1\leftarrow i,0) - \Delta\tilde{E}(j,\upsilon\leftarrow i,0) = [\tilde{E}^{ex}_{\upsilon+1} - \tilde{E}_o] - [\tilde{E}^{ex}_{\upsilon} - \tilde{E}_o] = \tilde{E}^{ex}_{\upsilon+1} - \tilde{E}^{ex}_{\upsilon} \qquad \text{P28.14.5}$$

Substitution of Eq. P28.14.1 evaluated at $\upsilon+1$ and υ into Eq. P28.14.5 and cancelling the common $\tilde{T}_e^{ex}$ terms gives the adjacent energy difference as:

$$\Delta\tilde{\nu}_\upsilon = \tilde{\nu}_e^{ex}(\upsilon + 1 + \tfrac{1}{2}) - \chi_e^{ex}\tilde{\nu}_e^{ex}(\upsilon + 1 + \tfrac{1}{2})^2 - \tilde{\nu}_e^{ex}(\upsilon + \tfrac{1}{2}) + \chi_e^{ex}\tilde{\nu}_e^{ex}(\upsilon + \tfrac{1}{2})^2$$

Cancelling common terms and rearranging $(\upsilon+1+\tfrac{1}{2})$ to give $((\upsilon+\tfrac{1}{2})+1)$ gives Eq. P28.14.4:

$$\Delta\tilde{\nu}_\upsilon = \tilde{\nu}_e^{ex} - \chi_e^{ex}\tilde{\nu}_e^{ex}[(\upsilon + \tfrac{1}{2}) + 1)]^2 + \chi_e^{ex}\tilde{\nu}_e^{ex}(\upsilon + \tfrac{1}{2})^2 \qquad (\text{P28.14.4})$$

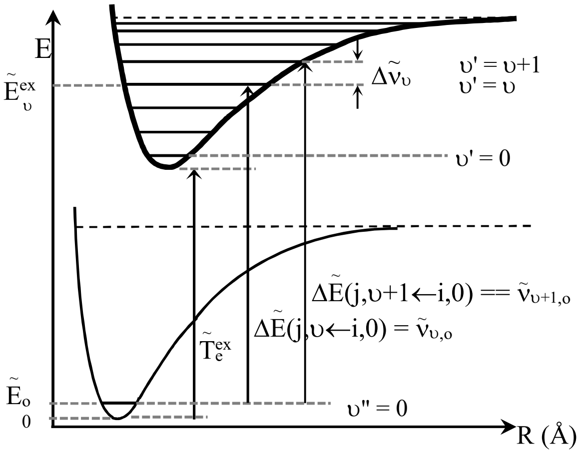
(b). As in Eq. 27.5.9, using $((\upsilon+\tfrac{1}{2})+1)^2 = (\upsilon+\tfrac{1}{2})^2 + 2(\upsilon+\tfrac{1}{2}) + 1$ and cancelling the resulting common terms gives:

$$\Delta\tilde{\nu}_\upsilon = \nu_e^{ex} - \chi_e^{ex}\tilde{\nu}_e^{ex}[(\upsilon + \tfrac{1}{2})^2 + 2(\upsilon + \tfrac{1}{2}) + 1)] + \chi_e^{ex}\tilde{\nu}_e^{ex}(\upsilon + \tfrac{1}{2})^2 = \tilde{\nu}_e^{ex} - \chi_e^{ex}\tilde{\nu}_e^{ex}(2\upsilon + 2)$$

Rearranging the last equation into the form of a straight line gives Eq. 28.2.13:

$$\Delta\tilde{\nu}_\upsilon = (h\tilde{\nu}_e^{ex} - 2\chi_e^{ex}\,\tilde{\nu}_e^{ex}) - 2\chi_e^{ex}\,\tilde{\nu}_e^{ex}\upsilon \tag{28.2.13}$$

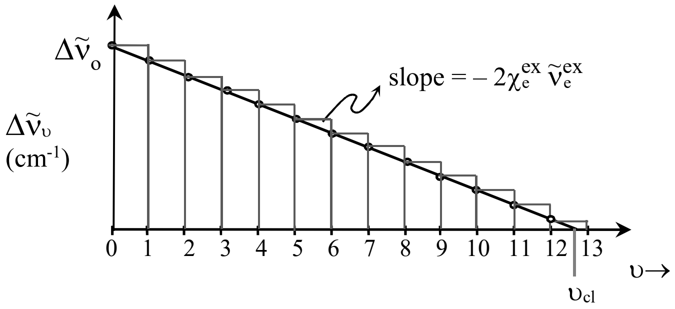
(c).



22. The next three problems discuss errors in the Birge-Sponer extrapolation procedure and why different authors chose different variables to plot along the horizontal axis, υ, υ + ½, or υ + 1. The vibrational fine-structure in an electronic absorption spectrum converges to a limit that is the sum of the dissociation energy of the ground state of the molecule and the atomic excitation energy. The convergence limit is equivalent to the sum of $\tilde{\nu}_{oo}$ and the excited state dissociation energy, Eq. 28.2.8. Reference to Figure 28.2.5 shows that the excited state dissociation energy is the sum of all the adjacent wave number differences up to the convergence limit:

$$\Delta\tilde{E}(j,\infty\leftarrow i,0) = \tilde{D}_o + \Delta\tilde{E}_{atomic} = \tilde{\nu}_{oo} + \tilde{D}_o^{ex} = \tilde{\nu}_{oo} + \sum_{\upsilon=0}^{\infty}\Delta\tilde{\nu}_\upsilon \tag{P28.22.1}$$

Based on the sum of adjacent differences, the Birge-Sponer extrapolation may be viewed from a different perspective. A graphical interpretation of Figure 28.1.20 allows a convenient calculation of the sum in Eq. P28.22.1. Consider a rectangle of unit width drawn at each data point, Figure P28.22.1.



width of each rectangle = 1

height of each rectangle = $\Delta\tilde{\nu}_\upsilon$

area of each rectangle = $\Delta\tilde{\nu}_\upsilon$

area = ½ base height

Figure P28.22.1: The excited state dissociation energy $\tilde{D}_o^{ex}$ is given by the sum of adjacent energy differences, which is conveniently calculated as the triangular area under the plot of $\Delta\tilde{\nu}_\upsilon$ versus υ.

The area of each rectangle is the height multiplied by the width. The sum of all the successive differences is then equal to the total area of all the rectangles. The total area is approximated as the triangle with the area given by ½ base ·height:

$$\sum_{\upsilon=0}^{\infty}\Delta\tilde{\nu}_\upsilon = \text{area} = ½\ \Delta\tilde{\nu}_o\ \upsilon_{cl} \qquad (28.2.19)$$

Compare this approximate result, which we also gave as Eq. 28.2.19, to the exact result using Eq. 28.2.15. Express your answer in terms of the anharmonicity, $\chi_e^{ex}\,\tilde{\nu}_e^{ex}$.

Answer: The plan is to compare $\Delta\tilde{\nu}_o$ to $\tilde{\nu}_e^{ex}$ using Eq. 28.2.16.

The exact result is given by Eq. 28.2.15: $\tilde{D}_o^{ex} = ½\ \tilde{\nu}_e^{ex}\ \upsilon_{cl}$. Substituting Eq. 28.2.16:

$$\Delta\tilde{\nu}_o = \tilde{\nu}_e^{ex} - 2\chi_e^{ex}\,\tilde{\nu}_e^{ex}$$

into Eq. 28.2.16 gives:

$$\tilde{D}_o^{ex} = ½\ \tilde{\nu}_e^{ex}\ \upsilon_{cl} = ½\ (\Delta\tilde{\nu}_o + 2\chi_e^{ex}\,\tilde{\nu}_e^{ex})\ \upsilon_{cl} = ½\ \Delta\tilde{\nu}_o\ \upsilon_{cl} + \chi_e^{ex}\,\tilde{\nu}_e^{ex}\ \upsilon_{cl}$$

The error in using Eq. 28.2.19 is then $\chi_e^{ex}\,\tilde{\nu}_e^{ex}\ \upsilon_{cl}$, which is typically small since the anharmonicity is usually a small fraction of the fundamental vibration frequency.

23. Birge-Sponer extrapolations are plotted as a function of the vibrational quantum number υ based on the following the linear forms:

$$\Delta\tilde{\nu}_\upsilon = (\tilde{\nu}_e^{ex} - 2\chi_e^{ex}\,\tilde{\nu}_e^{ex}) - 2\chi_e^{ex}\,\tilde{\nu}_e^{ex}\ \upsilon \qquad (28.2.13)$$

or equivalently $\quad \Delta\tilde{\nu}_\upsilon = \Delta\tilde{\nu}_o - 2\chi_e^{ex}\,\tilde{\nu}_e^{ex}\ \upsilon \qquad (28.2.17)$

In the previous problem we discuss a graphical interpretation that leads to the use of the triangular area under the Birge-Sponer curve to estimate the dissociation energy of the excited state. This graphical interpretation in Figure P28.22.1 shows a problem in associating the area of each rectangle with the overall area; each rectangle has a small portion above the curve-fit line. Some authors suggest doing the curve fit versus $\upsilon+½$ to limit the error in this area calculation, Figure P28.23.1.

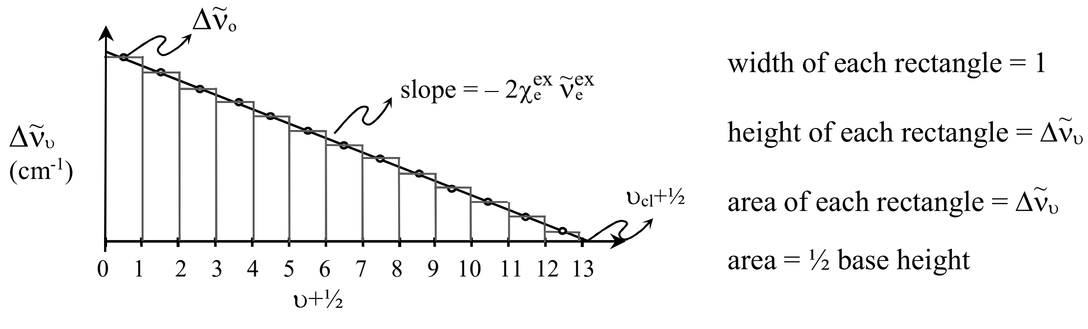


Figure P28.23.1: The excited state dissociation energy $\tilde{D}_o^{ex}$ is given by the sum of adjacent energy differences, which is conveniently calculated as the triangular area under the plot of $\Delta\tilde{\nu}_\upsilon$ versus $\upsilon+½$.

The dissociation energy of the excited state is given approximately by area $\tilde{D}_o^{ex} = ½\, \Delta\tilde{\nu}_o\, \upsilon_{cl}$, where $\Delta\tilde{\nu}_o$ is taken as the first data point and υ_{cl} = (x-intercept) – ½. This result is identical to the result taken from the plot versus υ discussed in the Example 28.2.2. However, some authors instead use:

$$\tilde{D}_o^{ex} \cong \text{area} = ½(\text{y-intercept})(\text{x-intercept})$$

Evaluate the error in the corresponding calculation of $\tilde{D}_o^{ex}$ by showing that:

$$\tilde{D}_o^{ex} = ½\,(\text{y-intercept})(\text{x-intercept}) - ¼\, \tilde{\nu}_e^{ex} + ½\, \chi_e^{ex}\, \tilde{\nu}_e^{ex}\, \upsilon_{cl} + ¼\, \chi_e^{ex}\, \tilde{\nu}_e^{ex}$$

Answer: The plan is to compare the y-intercept to $\tilde{\nu}_e^{ex}$ using Eq. 28.2.13. Make the substitution $x = \upsilon + ½$, where x is the variable plotted along the horizontal axis.

The basis of the Birge-Sponer plot is Eq. 28.2.13: $\Delta\tilde{\nu}_\upsilon = (\tilde{\nu}_e^{ex} - 2\chi_e^{ex}\, \tilde{\nu}_e^{ex}) - 2\chi_e^{ex}\, \tilde{\nu}_e^{ex}\, \upsilon$

To switch variables, rearrange to give $\upsilon = x - ½$ and substitute into the previous equation:

$$\Delta\tilde{\nu}_\upsilon = (\tilde{\nu}_e^{ex} - 2\chi_e^{ex}\, \tilde{\nu}_e^{ex}) - 2\chi_e^{ex}\, \tilde{\nu}_e^{ex}\,(x - ½) = (\tilde{\nu}_e^{ex} - \chi_e^{ex}\, \tilde{\nu}_e^{ex}) - 2\chi_e^{ex}\, \tilde{\nu}_e^{ex}\, x$$

with the y-intercept = $(\tilde{\nu}_e^{ex} - \chi_e^{ex}\, \tilde{\nu}_e^{ex})$ and the x-intercept = $\upsilon_{cl} + ½$.

The exact result for the dissociation energy of the excited state is given by Eq. 28.2.15: $\tilde{D}_o^{ex} = ½\, \tilde{\nu}_e^{ex}\, \upsilon_{cl}$. Solving the y- and x-intercepts for $\tilde{\nu}_e^{ex}$ and υ_{cl} gives:

$$\tilde{D}_o^{ex} = ½\, \tilde{\nu}_e^{ex}\, \upsilon_{cl} = ½\,(\text{y-intercept} + \chi_e^{ex}\, \tilde{\nu}_e^{ex})(\text{x-intercept} - ½)$$

$$= ½\,(\text{y-intercept})(\text{x-intercept}) - ¼\,(\text{y-intercept}) + ½\, \chi_e^{ex}\, \tilde{\nu}_e^{ex}(\text{x-intercept}) - ¼\, \chi_e^{ex}\, \tilde{\nu}_e^{ex}$$

$$= ½\,(\text{y-intercept})(\text{x-intercept}) - ¼\,(\tilde{\nu}_e^{ex} - \chi_e^{ex}\, \tilde{\nu}_e^{ex}) + ½\, \chi_e^{ex}\, \tilde{\nu}_e^{ex}(\upsilon_{cl} + ½) - ¼\, \chi_e^{ex}\, \tilde{\nu}_e^{ex}$$

$$= ½\,(\text{y-intercept})(\text{x-intercept}) - ¼\, \tilde{\nu}_e^{ex} + ½\, \chi_e^{ex}\, \tilde{\nu}_e^{ex}\, \upsilon_{cl} + ¼\, \chi_e^{ex}\, \tilde{\nu}_e^{ex}$$

The last term is negligible. The error in the term $½\, \chi_e^{ex}\, \tilde{\nu}_e^{ex}\, \upsilon_{cl}$ is typically small since the anharmonicity is usually a small fraction of the fundamental vibration frequency. The error in using the y- and x-intercepts directly is dominated by the term $-¼\, \tilde{\nu}_e^{ex}$. Assuming $\tilde{\nu}_e^{ex}$ is typically on the order of ~2000 cm^{-1}:

$$\text{error} = -¼\, \tilde{\nu}_e^{ex} = -¼\,(2000\ \text{cm}^{-1})(1\ \text{eV}/8065.5\ \text{cm}^{-1}) = -0.06\ \text{eV}$$

which is often smaller than other sources of error. In summary, using $\tilde{D}_o^{ex} = ½\, \tilde{\nu}_e^{ex}\, \upsilon_{cl}$ is best, but using $½\, \Delta\tilde{\nu}_o\, \upsilon_{cl}$ introduces small amounts of error. Using ½ (y-intercept)(x-intercept) from the plot versus $\upsilon+½$ introduces small but significant error.

24. As an alternate to the Birge-Sponer plot where $\Delta\tilde{\nu}_\upsilon$ is plotted versus υ, show that a plot of $\Delta\tilde{\nu}_\upsilon$ versus $\upsilon + 1$ gives $\tilde{\nu}_e^{ex}$ directly from the intercept.

Answer: The plan is to compare the y-intercept to $\tilde{\nu}_e^{ex}$ using Eq. 28.2.13. Make the substitution $x = \upsilon + 1$, where x is the variable plotted along the horizontal axis.

The basis of the Birge-Sponer plot is Eq. 28.2.13: $\Delta\tilde{\nu}_\upsilon = (\tilde{\nu}_e^{ex} - 2\chi_e^{ex}\,\tilde{\nu}_e^{ex}) - 2\chi_e^{ex}\,\tilde{\nu}_e^{ex}\,\upsilon$

To switch variables, rearrange to give $\upsilon = x - 1$ and substitute into the previous equation:

$$\Delta\tilde{\nu}_\upsilon = (\tilde{\nu}_e^{ex} - 2\chi_e^{ex}\,\tilde{\nu}_e^{ex}) - 2\chi_e^{ex}\,\tilde{\nu}_e^{ex}\,(x - 1) = \tilde{\nu}_e^{ex} - 2\chi_e^{ex}\,\tilde{\nu}_e^{ex}\,x$$

with the y-intercept = $\tilde{\nu}_e^{ex}$ and the x-intercept = $\upsilon_{cl} + 1$.

The exact result for the dissociation energy of the excited state is given by Eq. 28.2.15: $\tilde{D}_o^{ex} = \tfrac{1}{2}\,\tilde{\nu}_e^{ex}\,\upsilon_{cl}$. The dissociation energy is easily calculated exactly from the y-intercept and then υ_{cl} = x-intercept – 1. This plot type is not commonly used, so we didn't cover it in the body of the chapter.

25. The ultra-violet photoelectron spectrum of HCl taken with He discharge excitation at 21.21 eV is shown below.[7,8] The doublet peaks at 12.74-12.82 and at 13.04-13.12 occur for the $^2\Pi_{3/2}$ and $^2\Pi_{1/2}$ states. The doublet spacing is determined by spin-orbit coupling. The peak spacings listed on the spectrum are vibrational spacings. The ground state spectroscopic constants for HCl are listed in Table 27.6.1. (a). For each band, is the molecular ion stretching frequency greater, roughly equal, or less than that of the ground state HCl? Predict the type of orbital, bonding, non-bonding, or anti-bonding, of the corresponding ionized electron. Include observations on the length of the vibrational progression of each band. (b). The molecular orbital diagram for HI is given in Figure 28.2.7. Is the molecular orbital ordering for HCl consistent with the molecular orbital ordering for HI?

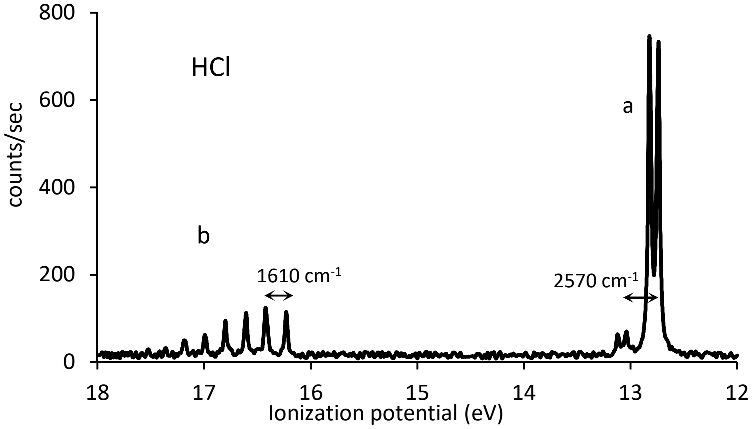


Figure 28.25.1: UPS spectrum of HCl using He discharge excitation at 21.21 eV.

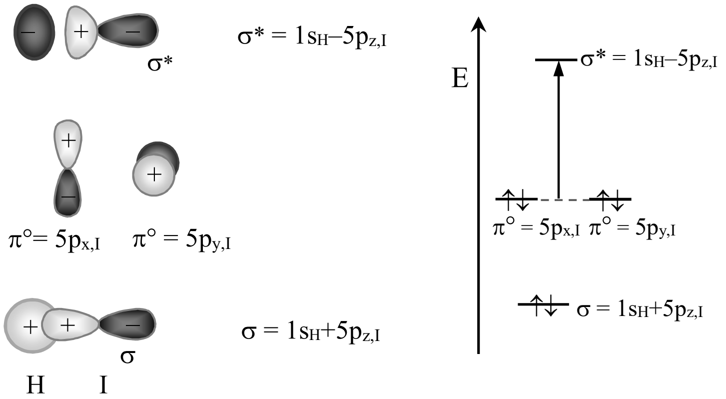
Answer: The plan is to note that, for comparison, the observed fundamental vibration frequency for HCl is $\tilde{\nu}_o = \tilde{\nu}_e - 2\chi_e\tilde{\nu}_e = 2990.925 - 2(52.800)\ \text{cm}^{-1} = 2885.325\ \text{cm}^{-1}$, using Eq. 27.5.11.

(a). The fundamental vibration frequency for the ground state of the molecular ion given for the a-band is only slightly smaller than the ground state, suggesting the removal of a non-bonding orbital. The removal of a high energy non-bonding electron is not surprising for halogens. The fundamental vibration frequency for the excited state of the molecular ion given for the b-band is significantly less than the ground state, suggesting the removal of a bonding electron.

The length of each vibrational progression is consistent with these observations. The vibrational fine-structure includes only two transitions for the a-band, suggesting a small change in bond length between the neutral molecule and the molecular ion. The removal of the corresponding electron makes a small difference in the bond strength. The removal of a non-bonding electron produces no change in the qualitative bond order. The vibrational fine-structure includes seven or eight transitions for the b-band, suggesting a large change in bond length between the neutral molecule and the molecular ion. The removal of the corresponding electron makes a large difference in the bond strength. This result suggests that the electron is removed from a bonding orbital resulting in a smaller qualitative bond order.
(b). The lowest ionization energy for the molecular orbital ordering in Figure 28.2.7 for HI corresponds to the removal of a non-bonding atomic p-electron. The next ionization energy corresponds to the removal of a σ-bonding electron. This order is identical to the character of the transitions in the UPS spectrum. So even though the valence shell for Cl-atoms is 3s-3p the character of the molecular orbital diagram is similar.

26. The molecular orbital diagram for HI is given in Figure 28.2.7. (a). Sketch the four molecular orbitals. (b). Compare the molecular orbitals to the molecular orbitals for LiH, Figure 26.3.4. Suggest the reason why the 5s-orbital on the I-atom doesn't participate in the molecular orbitals to a significant extent (at least at a qualitative level). (c). The molecular orbital ordering in Figure 28.2.7 is verified using UPS. Describe the vibrational fine-structure in the UPS spectrum that is expected for HI. That is for each of the three bands, is the molecular ion stretching frequency greater, roughly equal, or less than that of the ground state HI? Also, is each vibrational progression short or long? (d). Show the "box diagrams" for the $^2P_{½}$ and $^2P_{3/2}$ states of I-atoms. (e). Find the term symbols for the excited states of HI with configuration $\sigma^2(\pi^o)^3(\sigma^*)^1$. (f). Determine the possible projections of the total angular momentum for each term: $\Omega = |\Lambda + \Sigma_s|$.

Answer: (a). The four molecular orbitals are diagrammed below, based on the listed molecular orbitals: bonding $\sigma = 1s_H + 5p_{z,I}$, non-bonding pure atomic $\pi° = 5p_{x,I}$ and $\pi° = 5p_{x,I}$, and anti-bonding $\sigma^* = 1s_H - 5p_{z,I}$.



(b). For HI, the difference is the absence of the predominately non-bonding σ-orbital just below the purely non-bonding atomic p-orbitals. This non-bonding σ-orbital does not exist because the

5s orbital on the I-atom is so low in energy, relative to the 1s(H), that the 5s is core non-bonding. The unavailablility of the 5s(I) leaves only two valence orbitals, the 1s(H) and the 2p(I) that points along the internuclear axis, to form the bonding and anti-bonding molecular orbitals.
(c). The UPS spectrum for HI has an appearance very similar to the spectrum of HCl, which is illustrated in the previous problem. Ionization from the HOMO, which is a non-bonding $5p_x$ or $5p_y$, has little effect on the bond strength. The small change in bond strength predicts the lowest energy band to have a short vibrational progression and a molecular ion vibration frequency little changed from the neutral molecule. The next transition, transition-b in the previous problem, removes an electron from the strongly bonding σ-orbital, giving a large decrease in bond strength. As a result, the fundamental vibration frequency in the molecular ion is predicted to have a large decrease and a long vibrational progression.
(d). Schematically, representing each state with a single box diagram for the configuration $[Kr]4d^{10}5s^25p^7$:

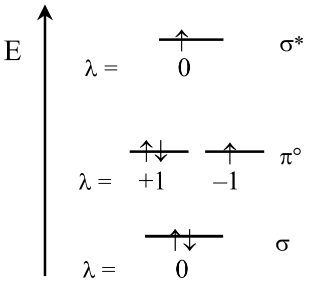
$$ {}^2P_{1/2} \quad \underset{5s}{\boxed{\uparrow\downarrow}} \quad \underset{5p}{\overset{+1}{\boxed{\uparrow\downarrow}}\overset{0}{\boxed{\uparrow}}\overset{+1}{\boxed{\uparrow\downarrow}}} \qquad \text{and} \qquad {}^2P_{3/2} \quad \underset{5s}{\boxed{\uparrow\downarrow}} \quad \underset{5p}{\overset{+1}{\boxed{\uparrow}}\overset{0}{\boxed{\uparrow\downarrow}}\overset{-1}{\boxed{\uparrow\downarrow}}} $$

which represent the total angular momentum states given by the Clebsch-Gordon series:

with $S = \frac{1}{2}$, $L = 1$ then J: $L–S, \ldots, |L+S| = 1–\frac{1}{2}, 1+\frac{1}{2}$

The atomic states have the overall degeneracies: $g_J = 2$ for ${}^2P_{1/2}$ and $g_J = 2J+1 = 4$ for ${}^2P_{3/2}$

(e). The term symbols for the molecular configuration $\sigma^2(\pi^o)^3(\sigma^*)^1$ are given by adding the orbital angular momenta. The explicit configuration with maximum S and Λ is shown below, giving the total orbital angular momentum as $\Lambda = 1$ for a ${}^3\Pi$ term. The spin multiplicity can also be a singlet with paired spins giving a ${}^1\Pi$ terms.



(f). For a Π state, $\Lambda = 1$. For the singlet $S = \frac{1}{2}$ and for the triplet $S = 1$. The projection of the total angular momentum is given by the series.

For the singlet, $S = \frac{1}{2}$, $\Sigma_s = -\frac{1}{2}, +\frac{1}{2}$, $\Lambda = 1$ with $\Omega = |\Lambda+\Sigma_s| = \frac{1}{2}, {}^3/_2$
giving ${}^1\Pi_{1/2}$ and ${}^1\Pi_{3/2}$ molecular terms.

For the triplet, $S = 1$, $\Sigma_s = -1, 0, +1$, $\Lambda = 1$ with $\Omega = |\Lambda+\Sigma_s| = 0, 1, 2$
giving ${}^3\Pi_o$, ${}^3\Pi_1$, and ${}^3\Pi_2$ molecular terms.

Substates of the ${}^1\Pi$ and the ${}^3\Pi$ terms give the repulsive states diagramed in Figure 28.2.7b. The total angular momentum states for the transitions in HI are given in parentheses. The ${}^3\Pi(0^+)$ state has $\Omega = 0$ with the projection of the orbital angular momentum $+\Lambda$, rather than $-\Lambda$ ($\pm\Lambda$ states are degenerate).[4] Note: Most authors use the symbol Σ and not Σ_s for the projection of the spin angular momentum. Unfortunately then, the two uses of the symbol Σ, which are the term symbol and the projection of the spin, must be distinguished by context.

27. Determine the density of states of a one-dimensional particle in a box. Determine the density of states near the state with quantum number n = 100, for CO_2 molecules in a 10.0 cm "box". Express the units as states per wave number.

Answer: The plan is to determine the derivative corresponding to Eq. 28.3.3, which is the derivative of the translational quantum number n with respect to the energy. The energy of the particle in a box states is given by given by Eq. 23.4.9.

The energy of a state with quantum number n is: $E_n = \dfrac{h^2 n^2}{8ma^2}$ with a the box length.

$$\rho(\varepsilon) = \frac{dn}{d\varepsilon} = \left(\frac{d\varepsilon}{dn}\right)^{-1} \qquad \text{with} \qquad \frac{d\varepsilon}{dn} = \left(\frac{h^2}{8ma^2}\right)\frac{d\,n^2}{dn} = \left(\frac{h^2 n}{4ma^2}\right)$$

Substituting the derivative into the density of states gives:

$$\rho(\varepsilon) = \frac{4ma^2}{h^2 n} \qquad \text{states per joule}$$

For CO_2 in a 10.0 cm box, for which m = 44.0 g $mol^{-1}/N_A/(1000\ g/1\ kg) = 7.31\text{x}10^{-26}$ kg:

$$\rho(\varepsilon) = \frac{4ma^2}{h^2 n} = \frac{4(7.31\text{x}10^{-26}\ \text{kg})(0.100\ \text{m})^2}{(6.626\text{xc}10^{-34}\ \text{J s})^2(100)} = 6.66\text{x}10^{37}\ \text{J}^{-1}$$

Remember that $\tilde{E} = E/hc$ to convert to cm^{-1}. The density of states is <u>per</u> unit energy giving the conversion to wave numbers as:

$$\rho(\varepsilon) = 6.66\text{x}10^{37}\ \text{J}^{-1}(hc) = 6.66\text{x}10^{37}\ \text{J}^{-1}(6.626\text{x}10^{-34}\ \text{J s})(2.99792\text{x}10^{10}\ \text{cm s}^{-1})$$
$$= 1.32\text{x}10^{15}\ \text{cm} = 1.32\text{x}10^{15}\,\frac{1}{\text{cm}^{-1}} \qquad \text{that is } 1.32\text{x}10^{15} \text{ states per wave number}$$

The density of states <u>decreases</u> with increasing energy because the spacing between particle in a box energy levels increases with increasing n. However, even at n = 100, the density of states is amazingly high. We will find that for a 3-dimensional particle in a box, the density of states <u>increases</u> with increasing energy, because of degeneracy.

28. Determine the density of states of a linear rigid rotor. Rotational energy levels have a degeneracy of (2J + 1), which we must take into account. The degeneracy is the number of states at a given energy level. The density of states is the product of the number of states at the given energy level with the number of levels per unit energy. The rotational constant for H–C≡N is 1.4782 cm^{-1}.[9] Calculate the density of states for H–C≡N.

Answer: The plan is to determine the derivative corresponding to Eq. 28.3.3, which is the derivative of the rotational quantum numbers J with respect to the energy, which is then multiplied by the degeneracy. The energy of the rotational states is given by given by Eq. 27.4.1.

The energy of a state with quantum number J is $\varepsilon_J = \tilde{B}hc\, J(J + 1)$:

$$\rho(\varepsilon) = (2J + 1)\frac{dJ}{d\varepsilon} = (2J + 1)\left(\frac{d\varepsilon}{dJ}\right)^{-1} \qquad \text{with} \qquad \frac{d\varepsilon}{dJ} = \frac{d\,[\tilde{B}hc\, J(J + 1)]}{dJ} = \tilde{B}hc\,(2J + 1)$$

Substituting the derivative into the density of states gives:

$$\rho(\varepsilon) = (2J + 1)[\tilde{B}hc\,(2J + 1)]^{-1} = \frac{1}{\tilde{B}hc} \text{ per joule} \quad \text{or} \quad \rho(\varepsilon) = \frac{1}{\tilde{B}} \text{ per cm}^{-1}$$

The energy spacing between rotational levels increases with J, so we might expect the density of states decrease to increase with energy. However, the degeneracy increases with J. As a result the rotational density of states is constant with increasing energy. The rotational constant for H–C≡N is 1.4782 cm^{-1}.[9] The density of rotational states is $\rho(\varepsilon) = 1/1.4782\ cm^{-1} = 0.676$ states per wave number.

29. The UV-visible absorption spectrum of SO_2 is given in Figure 28.1.1. The band origin of the visible transition is roughly 340 nm. The band origin corresponds to the $\upsilon' \leftarrow \upsilon''$ vibrational fine-structure transition of $0 \leftarrow 0$. Consider non-radiative energy transfer by internal conversion from this excited electronic state into the ground electronic state. The three normal modes of SO_2 in the ground electronic state are at wave numbers 1151 cm^{-1}, 518 cm^{-1}, and 1362 cm^{-1}, Figure 28.3.2. (a) Assuming all the vibrational energy is in the asymmetric stretch-ν_3, that is $\upsilon_1 = \upsilon_2 = 0$, calculate the vibrational quantum number of the ground state that is isoenergetic with the lowest energy vibrational level of the excited state. (b). Assuming the vibrational quantum numbers are all equal, that is $\upsilon_1 = \upsilon_2 = \upsilon_3$, calculate the approximate vibrational quantum numbers of the ground state that is isoenergetic with the lowest energy vibrational level of the excited state.

Answer: The plan is to convert the band origin to wave numbers and then compare with the harmonic oscillator energy levels.

In wave numbers, $\tilde{\nu}_{oo} = [1/(340\text{x}10^{-9}\ m)]\ (1\ m/100\ cm) = 29400\ cm^{-1}$. This energy is referenced to the zero-point energy of the ground state at $\tilde{G}(0) = \frac{1}{2}\tilde{\nu}_o$.

(a). Using the energy of a harmonic oscillator as $\tilde{G}(\upsilon) = \tilde{\nu}_o(\upsilon + \frac{1}{2})$ gives: $\upsilon = \tilde{\nu}_{oo}/\tilde{\nu}_o = 29400\ cm^{-1}/1362\ cm^{-1} = 21.6 \cong 22$. This is a highly excited vibrational level, which may be near the dissociation limit.

(b). What happens if we don't put all our eggs in one basket and consider vibrational excitation into each of the normal modes?

$$\upsilon = \frac{\tilde{\nu}_{oo}}{(\tilde{\nu}_{1,o} + \tilde{\nu}_{2,o} + \tilde{\nu}_{3,o})} = \frac{29400\ cm^{-1}}{1151\ cm^{-1} + 518\ cm^{-1} + 1362\ cm^{-1}} = 9.70 \cong 10$$

This vibrational level is very difficult to access using absorption directly from the ground electronic state (by infrared absorption spectroscopy for example). However, internal conversion is seen to be mediated through such highly excited vibrational states. We assumed that all the vibrational quantum numbers were equal. However, a given molecular system may prefer to have more quanta in the modes with higher fundamental vibration frequency. For example, very high frequency C–H stretching vibrations play an important role in internal conversion processes in aromatic systems.

30. Avoided-crossings of degenerate states follow a common pattern. Consider two states represented by the wave functions Ψ_A and Ψ_B. The strength of the interaction between the two states is determined by the integral $c = \int \Psi_A \,\hat{o}\, \Psi_B \, d\tau$. Possibilities for the $\hat{o}$ operator include spin-orbit coupling for electronic interactions in intersystem crossing or $(\partial^2/\partial R^2)$ for vibronically coupled states. Vibronic coupling is important in internal conversion and pre-dissociation. We consider the interaction as a perturbation on the unperturbed wave functions Ψ_A and Ψ_B. We assume that there is no net interaction without the perturbation, giving an overlap-type integral:

$$\int \Psi_A \Psi_B \, d\tau = S_{AB} = 0$$

A zero overlap integral is often the result of orthogonality. Any two different electronic states of the same molecule are orthogonal. The unperturbed energies of the two states are:

$$a = \int \Psi_A \hat{\mathcal{H}}' \Psi_A \, d\tau \qquad \text{and} \qquad b = \int \Psi_B \hat{\mathcal{H}}' \Psi_B \, d\tau$$

with $\hat{\mathcal{H}}'$ given by the unperturbed Hamiltonian ($\hat{o}$ is not present). The energies of the two states with the interaction present are the eigenvalues of the secular equations, λ_i, as in Eq. 26.1.13:

$$\begin{vmatrix} a - \lambda & c \\ c & b - \lambda \end{vmatrix} = 0$$

with the eigenvalues given by Eq. 6.3.23. Recasting Eq. 6.3.23 into the terms used in this problem gives:

$$\lambda_i = \frac{(a + b) \pm \sqrt{(a - b)^2 + 4\,c^2}}{2} \qquad \text{P28.32.1}$$

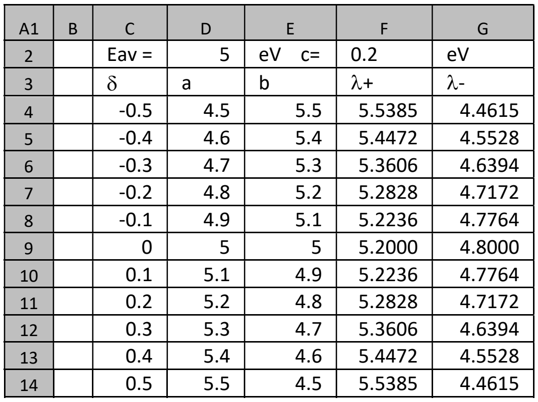
(a). In pre-dissociation, a and b scale with the distance, with a = b at the avoided-crossing. Assume the two states are nearly degenerate and have energies: $a = 5.00 \text{ eV} + \delta$ and $b = 5.00 \text{ ev} - \delta$. The energy gap, δ, has units of eV. Plot the energies of the two states with the interaction present for c = 0.2 eV for δ in the range of $-0.5 < \delta < 0.5$. Determine the energy gap at $\delta = 0$.

(b). Compare the previous plot to Figure 28.2.8. How can you tell that the crossing is avoided?

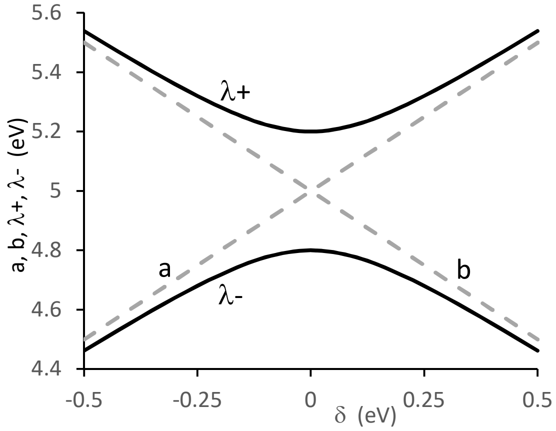
(c). Decrease the interaction parameter to c = 0.01 eV. Is the interaction still avoided? RT at room temperature is 0.0257 eV. Predict the behavior of the system at room temperature at the avoided-crossing.

Answer: The plan is to solve for the eigenvalues as a function of the energy gap, δ. For large positive energy gaps, $\lambda_+ \cong a$ and $\lambda_- \cong b$.

A spreadsheet was developed that solves P28.32.1 as a function of the energy gap parameter.

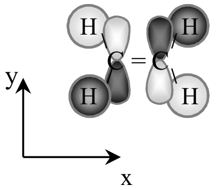


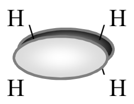
A1	B	C	D	E	F	G
2		Eav =	5	eV c=	0.2	eV
3		δ	a	b	λ+	λ-
4		-0.5	4.5	5.5	5.5385	4.4615
5		-0.4	4.6	5.4	5.4472	4.5528
6		-0.3	4.7	5.3	5.3606	4.6394
7		-0.2	4.8	5.2	5.2828	4.7172
8		-0.1	4.9	5.1	5.2236	4.7764
9		0	5	5	5.2000	4.8000
10		0.1	5.1	4.9	5.2236	4.7764
11		0.2	5.2	4.8	5.2828	4.7172
12		0.3	5.3	4.7	5.3606	4.6394
13		0.4	5.4	4.6	5.4472	4.5528
14		0.5	5.5	4.5	5.5385	4.4615

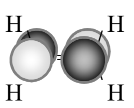


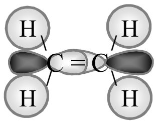
(a). The energy gap at the curve-crossing is 0.4 eV = 2c.
(b). The curve is analogous to pre-dissociation assuming a linear change in unperturbed energy with distance, near the curve-crossing. You can tell that the crossing is avoided because the λ_+ curve approaches curve-b for negative energy gaps, but approaches curve-a for positive energy gaps. If the system starts in the a-state, for increasing δ the system progresses to the b-state for large δ.
(c). Decreasing the interaction parameter decreases the gap at the curve-crossing. If c = 0.01 eV, the gap is only 0.02 eV at the avoided-crossing. This gap is smaller than the available thermal kinetic energy, which easily allows the system to jump across the gap. As a consequence if the system starts in the a-state, for increasing δ at the curve crossing the system can jump to the upper curve. Then instead of progressing to the b-state for large δ, the system stays in the a-state. The result is a mixture of products, some in the a-state and some in the b-state.

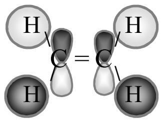
31. Determine the symmetry species of the following molecular orbitals of ethylene. The symmetry species are the irreducible representations. In addition, classify the molecular orbitals as σ or π, non-bonding or bonding.





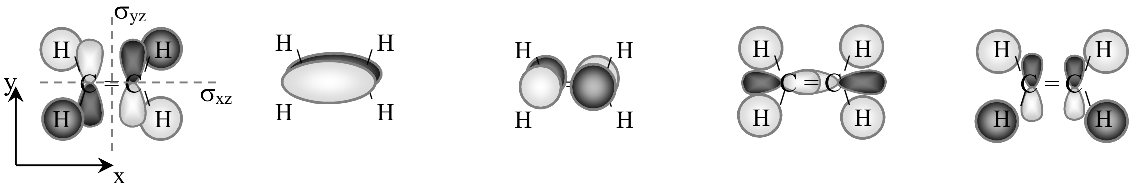






Answer: The plan is to note that the point group is D_{2h} for ethylene. The sufficient characteristic symmetries are the transformation properties under σ(xy), σ(xz), and σ(yz).

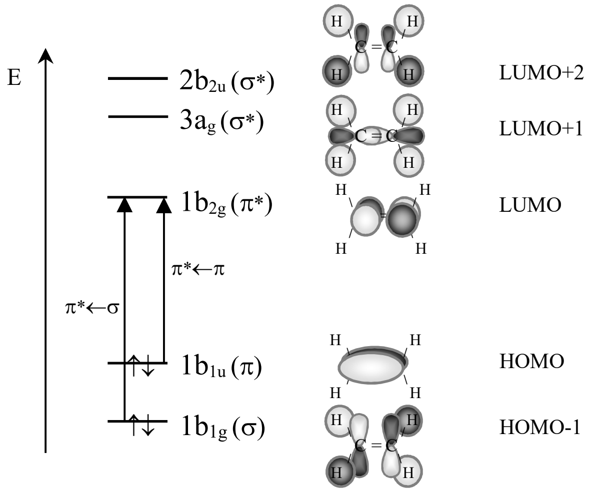
We don't need to consider every symmetry operation of the point group. Such a complete enumeration could drive you crazy with some of the more symmetrical point groups. We can use just σ(xy), σ(xz), and σ(yz) since the results are unique and easy to see. The σ(xy)-plane contains all the atoms. For example, the first molecular orbital is symmetric with respect to the σ(xy)-plane, antisymmetric with respect to σ(xz), and antisymmetric with respect to σ(yz). Symbolizing symmetric with +1 and antisymmetric with -1, the results in the order [σ(xy),σ(xz),σ(yz)] are [1,-1,-1]. Comparison with the D_{2h} character table shows these characters correspond to B_{1g}. The orbital overlaps are all in-plane and correspond to C–H bonds, giving a σ-type orbital. The molecular orbital has four bonding C–H interactions and one anti-bonding C–C interaction, which is net bonding. The other results are given below.



[1,-1,-1] b_{1g} (σ) [-1,1,1] b_{1u} (π) [-1,1,-1] b_{2g} (π*) [1,1,1] a_g (σ*) [1,-1,1] b_{2u} (σ*)

We can check our results by noting the transformation properties under inversion. The symmetric orbitals under inversion are g and the anti-symmetric orbitals are u, which agrees with our assignments. The choice of the σ(xy), σ(xz), and σ(yz) planes is in some ways arbitrary; other combinations of transformations also work. However, usually reflection planes are often the most convenient as long as the results give a unique one-to-one relationship with the irreducible representations of the point group.

32. Use electronic selection rules to determine if the LUMO+1 ← HOMO and LUMO+2 ← HOMO transition are allowed in absorption spectra. The corresponding molecular orbital diagram for the $1b_{1g}$, $1b_{1u}$, $1b_{2g}$, a_g, and b_{2g} levels is given below.



Answer: The plan is to determine the direct products $A_{1g} \otimes B_{1u}$ and $B_{2u} \otimes B_{1u}$.

The ground electronic state for ethylene is A_{1g}, since all occupied orbitals are doubly filled. As a result we need only consider the symmetry of the excited state and the electric dipole operator. In D_{2h} the x, y, and z components of the electric dipole transform as B_3, B_2, and B_1, respectively. The LUMO+1 ← HOMO transition gives an excited state with configuration $\ldots(1b_{1g})^2(1b_{1u})^1(1b_{2g})^0(a_g)^1$ with direct product: $A_{1g} \otimes B_{1u}$. The A_{1g} irreducible representation is the totally symmetric representation. Multiplication by the totally symmetric representation is the unity operation for direct products, since all the characters are +1. As a result $A_{1g} \otimes B_{1u} = B_{1u}$. The z-component of the dipole moment transforms as B_{1u}, which gives the transition as allowed for the singlet states: $^1B_{1u} \leftarrow {}^1A_{1g}$.

The LUMO+2 ← HOMO transition gives an excited state with configuration $\ldots(1b_{1g})^2(1b_{1u})^1(1b_{2g})^0(a_g)^1(2b_{2u})^1$ with direct product: $B_{2u} \otimes B_{1u}$. We can save ourselves some time by noting that the direct product will have g-parity. The x, y, and z-components of the dipole moment transform as u-parity, which gives the transition as forbidden. However, for practice, the direct product $B_{2u} \otimes B_{1u}$ is:

D_{2h}	E	$C_2(z)$	$C_2(y)$	$C_2(x)$	*i*	σ(xy)	σ(xz)	σ(yz)
B_{1u}	1	1	-1	-1	-1	-1	1	1
B_{2u}	1	-1	1	-1	-1	1	-1	1
$B_{2u} \otimes B_{1u}$	1	-1	-1	1	1	-1	-1	1 = B_{3g}

The result has g-parity as predicted giving a forbidden transition. The next problem gives the result from an electronic structure calculation using CIS/6-311G*, which agrees with the results in this problem. However, it is found that the LUMO+1←HOMO transition, which is $^1B_{1u} \leftarrow {}^1A_{1g}$, while allowed is significantly less intense than the LUMO←HOMO transition.

33. In Example 28.8.1 we used group theory based electronic selection rules to determine if the low energy $\pi^* \leftarrow \sigma$ and $\pi^* \leftarrow \pi$ transitions of ethylene are allowed or forbidden. Configuration interaction calculations are used to find excited states, electronic transition energies, and intensities within the Hartree-Fock formalism. Single excitations don't contribute to ground state stability, however single excitations generate many possible excited states. As a consequence configuration interaction with single excitations, CIS, is used to simulate UV-visible spectra. First, do a geometry optimization for ethylene at HF/6-311G* (equivalent to HF/6-311G(d)). Then do a CIS/6-311G* single point calculation to compare to the intensity predictions in Example 28.8.1. [Hints: To do a CIS calculation: Using the Spartan visualization environment select an Energy calculation and check "UV/Vis" and "Orbitals & Energies". Using the WebMo visualization environment for Gaussian choose the Calculation type as "Excited States and UV-Vis". Use the Basis Set "Other" option to specify 6-311G(d). Using the GaussView visualization environment for Gaussian set the Method as CIS and check "Solve for More States, N = 6".]

Answer: We give the Spartan version first and then the Gaussian version. The Spartan/Q-Chem results are shown below with transition wavelengths in nm:

```
UV/Vis Allowed Transitions:
nm    strength MO Component
115.69 0.0000 HOMO-2 -> LUMO 92%
125.52 0.0000 HOMO -> LUMO+3 95%
128.17 0.0000 HOMO-1 -> LUMO 92%
135.48 0.0000 HOMO -> LUMO+2 89%
142.34 0.0443 HOMO -> LUMO+1 99%
146.10 0.6127 HOMO -> LUMO 94%
```

In Example 28.8.1, we predicted the LUMO←HOMO transition to be fully allowed with B_{3u} symmetry and the LUMO←HOMO-1 transition to be forbidden with B_{3g} symmetry. The CIS results agree with the group theory predictions. The calculation places the LUMO+1←HOMO

transition that is weakly allowed and the LUMO+2←HOMO forbidden transition in between the transitions in Example 28.8.1.
The Gaussian results at CIS(NStates=10)/6-311G(d), as displayed by the WebMo "front-end" visualization environment, are shown below with transition wavelengths in nm.

State	Symmetry	Energy (nm)
1	B1U	146.05
2	B3U	142.28
3	B1G	135.45
4	B1G	128.18
5	B2G	125.49
6	B2G	115.61
7	AU	106.02
8	B3G	104.97
9	B2U	96.32
10	AU	95.40

A plot of the electronic spectrum shows only the first transition, B1U at 146.05 nm, has significant intensity. We need to view the "raw" numerical data file to determine the molecular orbitals involved in the transition. Ethylene has 16 electrons, so that the HOMO is orbital 8. The orbitals are listed with the molecular orbital symmetry designations as:

```
Occupied  (AG) (B1U) (AG) (B1U) (B2U) (AG) (B3G) (B3U)
Virtual   (B2G) (AG) (B2U) (B1U) (B3G) (B1U) (AG) (B2U)
          (AG) (B3U) (B1U) (B2G) (B2U) (B3G) (AG) (B1U)
          (B3G) (B1U) (B1G) (B3U) (B2U) (AG) (AU) (B1U)
          (AG) (B3G) (B2G) (AG) (B1U) (B2U) (B1U) (B3U)
          (B3G) (B2G) (B2U) (AG) (B3G) (B1U) (AG) (B1U)
```

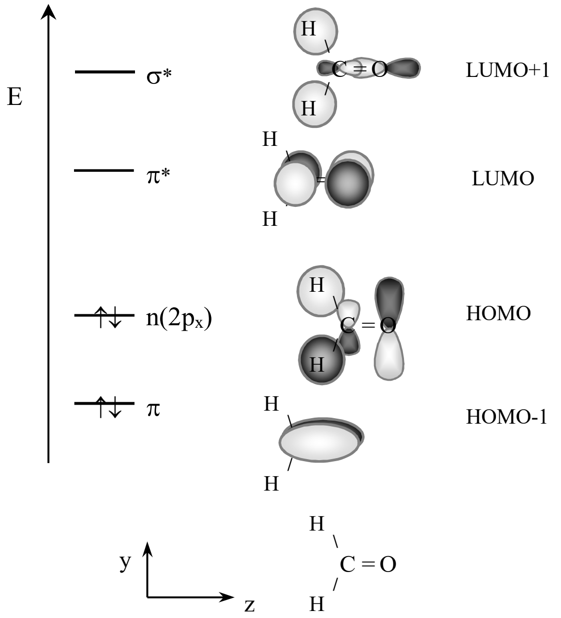
Comparison of the assigned molecular orbital symmetries to Figure 28.8.2 shows the designations of the B_1 and B_3 molecular orbital labels to be switched. Unfortunately there is no definitive choice of symmetry labels for B_1, B_2, and B_3; different authors use different labels. We just need to remember the switch when comparing to our original molecular orbital diagram.

The spectroscopic transitions are listed below.

```
Excitation energies and oscillator strengths:

 Excited State   1:   Singlet-B1U    8.4892 eV  146.05 nm  f=0.6131
       8 ->  9         0.68385
 This state for optimization and/or second-order correction.
 Copying the excited state density for this state as the 1-particle RhoCI density.

 Excited State   2:   Singlet-B3U    8.7144 eV  142.28 nm  f=0.0444
       8 -> 10         0.70271

 Excited State   3:   Singlet-B1G    9.1537 eV  135.45 nm  f=0.0000
       7 ->  9         0.18364
       8 -> 11         0.66646
       8 -> 16         0.11486

Excited State   4:   Singlet-B1G    9.6728 eV  128.18 nm  f=0.0000
       7 ->  9         0.67617
       8 -> 11        -0.18519
```

The LUMO←HOMO transition corresponds to orbitals `8 -> 9` in the listings, below. The LUMO+2←HOMO transition corresponds to `8 -> 11`, which is the largest contributor to transition 3. In Example 28.8.1, we predicted the LUMO←HOMO transition to be fully allowed with $B_{2g} \otimes B_{1u} = B_{3u}$ symmetry and the LUMO←HOMO-1 transition to be forbidden with $B_{2g} \otimes B_{1g} = B_{3g}$ symmetry. Given the switch in labels, the CIS results agree as listed below for transitions 1 and 4. The calculation interposes transition 2, the LUMO+1←HOMO transition as weakly allowed, and transition 3, the LUMO+2←HOMO transition as forbidden.

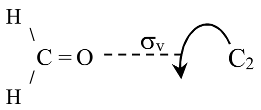
34. Determine the symmetry species of the following molecular orbitals of formaldehyde. The geometry is shown at bottom. The x-direction is the π-bonding direction for these plots. The HOMO has a small contribution from the $2p_y$ orbital on the C-atom. As a result the HOMO is primarily a non-bonding $2p_y$ atomic orbital on the O-atom. [Hint: Use the symmetry operations given in Figure 26.6.4. Formal group theory is not required for this problem.]



Answer: The plan is to orient the C_2 axis along z and the σ_v-plane along the z- and x-axes. The atoms then lie on the z-y plane, which is called the σ_v'-plane.

The symmetry operations are given in Figure 26.6.4 and reproduced below:

symmetry	rotate 180° (C_2)	reflect across σ_v
symmetric	a	1
antisymmetric	b	2



The HOMO–1 is antisymmetric with respect to 180° rotation and symmetric with respect to reflection across σ_v. The HOMO–1 has b_1 symmetry.

The HOMO is antisymmetric with respect to 180° rotation and antisymmetric with respect to reflection across σ_v. The HOMO–1 has b_2 symmetry.

The LUMO is antisymmetric with respect to 180° rotation and symmetric with respect to reflection across σ_v. The LUMO has b_1 symmetry.

The LUMO+1 is symmetric with respect to 180° rotation and symmetric with respect to reflection across σ_v. The LUMO has a_1 symmetry.

These symmetry designations are applied in the next problem.

35. Use electronic selection rules to determine if the LUMO←HOMO, LUMO←HOMO-1, and LUMO+1←HOMO electronic transitions of formaldehyde are allowed or forbidden. The symmetries of the molecular orbitals are:

Orbital	7	8	9	10
MO	HOMO-1	HOMO	LUMO	LUMO+1
Symmetry	b_1	b_2	b_1	a_1
Type	π	n	π^*	σ^*

Answer: The plan is to follow Example 28.8.1 under the C_{2v} point group.

The ground electronic state for formaldehyde is A_1, since all occupied orbitals are doubly filled. As a result we need only consider the symmetry of the excited state and the electric dipole operator. In C_{2v} the x, y, and z components of the electric dipole transform as B_2, B_1 and A_1. The required direct products of the upper and lower singly occupied molecular orbitals in the excited state are:

LUMO←HOMO with orbital types $\pi^*\leftarrow n$ gives excited electronic state configuration $\ldots(b_1)^2(b_2)^1(b_1)^1$ with symmetry $B_1\otimes B_2$:

MO Symmetry	E	C_2	σ_v	σ_v'	Result
B_1	1	-1	1	-1	
B_2	1	-1	-1	1	
$B_1\otimes B_2$	1	1	-1	-1	= A_2 **forbidden**

The A_2 symmetry of the excited state does not match a component of the electric dipole moment, giving a forbidden transition.

LUMO←HOMO-1 with orbital types $\pi^*\leftarrow\sigma$ gives excited electronic state configuration $\ldots(b_1)^1(b_2)^2(b_1)^1$ symmetry $B_1\otimes B_1$:

MO Symmetry	E	C_2	σ_v	σ_v'	Result
B_1	1	-1	1	-1	
B_2	1	-1	1	-1	
$B_1\otimes B_2$	1	1	1	1	= A_1 **allowed**

The A_1 symmetry of the excited state matches the z-component of the electric dipole moment, giving an allowed transition. We could have saved ourselves some work since the product of any non-degenerate irreducible representation with itself is always the totally symmetric group.

LUMO+1←HOMO with orbital types $\sigma^*\leftarrow\sigma$ gives excited electronic state configuration $\ldots(b_1)^2(b_2)^2(b_1)^0(a_1)^1$ symmetry $A_1\otimes B_2 = B_2$. The A_1 irreducible representation is the totally symmetric representation. Multiplication by the totally symmetric representation is the unity operation for direct products, since all the characters are +1. As a result $A_1\otimes B_2 = B_2$. The B_2 symmetry of the excited state matches the y-component of the electric dipole moment, giving an **allowed** transition. The next problem gives the result from an electronic structure calculation using CIS/6-311G*, which agrees with the results in this problem.

36. Use a configuration interaction-singles calculation to determine the predicted intensity of the LUMO←HOMO, LUMO←HOMO-1, and LUMO+1←HOMO electronic transitions of formaldehyde. First, do a geometry optimization for formaldehyde at HF/6-311G** (equivalent to HF/6-311G(d,p)). Then do a CIS/6-311G** single point calculation to compare to the intensity predictions in Problem 35. See Problem 33 for a discussion of the use of CIS calculations for predicting electronic spectra and for hints on doing the calculations.

Answer: All spin allowed transitions are for the singlet states, since the ground state of formaldehyde is a singlet, $^1A_1$. We give the Spartan version first and then the Gaussian version. The Spartan/Q-Chem results are:

```
UV/Vis Allowed Transitions:
nm strength MO Component
103.83 0.0000 HOMO-3 -> LUMO 95%
104.28 0.3556 HOMO -> LUMO+2 90%
117.65 0.1685 HOMO-1 -> LUMO 83%
120.16 0.0006 HOMO-2 -> LUMO 96%
125.60 0.1762 HOMO -> LUMO+1 97%
261.24 0.0000 HOMO -> LUMO 96%
```

The Gaussian results at CIS/6-311G(d), as displayed by the WebMo "front-end" visualization environment, are shown below with transition wavelengths in nm.

State	Symmetry	Energy (nm)
1	A2	261.26
2	B2	125.58
3	B1	120.17
4	A1	117.65
5	A1	104.28
6	A2	103.82
7	B2	99.65
8	B1	95.52
9	A2	86.78
10	B1	80.14

We need to view the "raw" Gaussian numerical data file to determine the molecular orbitals involved in the transition. Formaldehyde has 16 electrons, so that the HOMO is orbital 8. The orbitals are listed with the molecular orbital symmetry designations as:

```
Orbital symmetries:
    Occupied  (A1) (A1) (A1) (A1) (B2) (A1) (B1) (B2)
    Virtual   (B1) (A1) (B2) (A1) (A1) (B2) (B1) (B2) (A1) (A1)
              (A1) (B1) (B2) (A2) (B1) (A1) (A1) (B2) (B2) (A1)
              (B1) (A2) (A1) (B2) (B2) (A1) (A1) (B1) (A2) (A1)
              (B1) (A1) (B2) (B2) (A1) (B1) (B2) (A1) (A1) (A1)
```

The orbital symmetry labels, that is B_1 versus B_2, match those given in Problem 35. The B_1 and B_2 designations are arbitrary and don't necessarily match.

The spectroscopic transitions are listed below.

```
Excitation energies and oscillator strengths:

 Excited State   1:   Singlet-A2     4.7456 eV  261.26 nm  f=0.0000
       8 ->  9         0.69294
 This state for optimization and/or second-order correction.
 Copying the excited state density for this state as the 1-particle RhoCI density.
```

```
 Excited State   2:   Singlet-B2     9.8726 eV  125.58 nm  f=0.1760
       8 -> 10         0.69548


 Excited State   3:   Singlet-B1    10.3177 eV  120.17 nm  f=0.0006
       6 ->  9         0.69272

 Excited State   4:   Singlet-A1    10.5388 eV  117.65 nm  f=0.1688
       7 ->  9         0.64570
       8 -> 11         0.19390
       8 -> 14        -0.13077

 Excited State   5:   Singlet-A1    11.8893 eV  104.28 nm  f=0.3552
       7 ->  9        -0.17516
       8 -> 11         0.67138
```

The LUMO←HOMO transition is for orbitals `8 -> 9`, which has zero oscillator strength corresponding to a forbidden transition. The LUMO←HOMO–1 transition is for orbitals `7 -> 9`, which is the largest contributor to transition 4. Transition 4 is allowed. The LUMO+1←HOMO transition corresponds to `8 -> 10`, which is transition 2. Transition 2 is allowed. The CIS results agree as listed below for transitions 1 and 4. The calculation interposes transition 3, `6 -> 9` LUMO←HOMO–2 transition, as very weakly allowed.

Comparison with experimental spectra don't work out well for formaldehyde. The LUMO+1←HOMO, LUMO←HOMO–1, and LUMO←HOMO–2 transitions are not observed. A series of O-atom centered Rydberg transitions is prominent in the spectrum. One reason for the disagreement is that the $^1A_2$ and $^3A_2$ excited states are not planar, which these calculations do not take into account. The point group of these excited states is C_s.[10] Careful geometry optimized calculations on the excited states at higher levels than CIS are required to completely understand the spectra of many molecules, formaldehyde included. However, CIS calculations are a reasonable starting point, at least as a point of comparison.

37. K. P. Huber and G. Herzberg have produced a comprehensive reference on the spectroscopic data of diatomic molecules.[3] This reference has been transcribed by the National Institute of Standards and Technology, NIST, as an on-line database.[2] The entry for Na_2 is listed as an example below. The spectroscopic constants are presented in wave numbers and the equilibrium bond length in Å. The book tables start with a listing of the reduced mass, μ, in g mol^{-1}. Next the dissociation energy at absolute zero, D_o^o, which we have been referencing as just D_o, and the ionization energy to form the ground state of the molecular ion, I.P. The on-line version excludes μ, D_o^o, and I.P. By convention, the ground state is labeled as X, which for Na_2 is explicitly X $^1\Sigma_g^+$. Excited electronic states are labeled as states A, B, C, D … in order of increasing energy if the states have the same spin multiplicity, or a, b, c, d … if the excited states have a different multiplicity. Many literature references and many notes are included in the tables, which we have omitted in this example for brevity. For this homework problem (a) find the Na_2 reference in the book or on-line, http://webbook.nist.gov/chemistry, and (b) write a spreadsheet to plot the potential energy surfaces as a function of R for the X ground state, and A and B excited states. Use the Morse function for the potential energy surfaces. The A and B excited states dissociate to a ground and excited state Na atom: $Na_2 \rightarrow Na\,(^2S) + Na\,(^2P)$. The atomic excitation energy, ΔE_{atomic} is 16961 cm^{-1} to the $^2P_{1/2}$ state. From Figure 28.2.5, note that $\tilde{T}_e + \tilde{D}_e^{ex} = \tilde{D}_e + \Delta E_{atomic}$.

State (1)	T_e	ω_e	$\omega_e\chi_e$	$\omega_e y_e$	B_e (2)	α_e	D_e (3)	r_e	Trans.	ν_{oo}
$^{23}Na_2$	$\mu = 11.4948852$		$D_0^0 = 0.720$ eV[a]		I.P. = 4.90 eV[b]					
	Diffuse bands of Na_2 Van der Waals molecules close to the lines of principal series of Na. Several fragments of other UV emission and absorption band systems.[c]									
E ($^1\Pi_u$)	35557	106.2 ^{H}	0.65						E←X R	35530.6 ^{H}
D $^1\Pi_u$	33486.8	111.3 ^{H}	0.48		d				D↔X R	33462.9 ^{H}
$^1\Sigma_g^+$	(33000)	Fragment observed in two-photon excited Na_2 fluorescence								
C $^1\Pi_u$	29382	119.33 ^{H}	0.53		d				C↔X R	29362 ^{H}
B $^1\Pi_u$	20320.02	124.090 ^{Z}	0.6999		0.125277	7.237E-4	3.248E-7	3.4228	B↔X R	20302.49 ^{Z}
A $^1\Sigma_u^+$	14680.58	117.323 ^{Z}	0.3576		0.110784	5.488E-4	3.882E-7	3.6384	A↔X R	14659.80 ^{Z}
a $^3\Pi_\upsilon$	<14680	(145)			(0.140)					
X $^1\Sigma_g^+$	0	159.1245 ^{Z}	0.72547		0.154707	8.736E-4	5.811E-7	3.07887		

a. From $D_e^0 = 5890 \pm 70$ cm^{-1} based on RKR potential curve for the ground state. The thermochemical value obtained by a molecular beam technique is 0.732 eV.

b. From photoionization. A similar value is obtained by extrapolation of the Rydberg series B, C, D, E.

c. Molecular absorption cross sections 27000 – 625000 cm^{-1}.

d. Barrow, Travis, et al., 1960 report the following rotational constants for D: $B_e = 0.1185$, $\alpha_e = 0.001$, C: $B_e = 0.12815$, $\alpha_e = 0.00084$. Considerably different constants, however, are quoted by Richards in Rosen, 1970. D: $B_e = 0.1152$, $\alpha_e = 0.00110$, C: $B_e = 0.1185$, $\alpha_e = 0.00096$.

Footnotes:

1. Units: T_e, ω_e, $\omega_e\chi_e$, $\omega_e y_e$, B_e, α_e, D_e, and ν_{oo} in cm^{-1}, with $\omega_e = \tilde{\nu}_e$ and $r_e = R_e$ in Å as given in this text.
2. On-line NIST tables list the vibration-rotation interaction constant, γ_e, for the expansion: $B_\upsilon = B_e - \alpha_e(\upsilon + ½) + \gamma_e(\upsilon + ½)^2$
3. On-line NIST tables list β_e for the centrifugal distortion expansion: $D_\upsilon = D_e + \beta_e(\upsilon + ½)$.

Table Legend

H Data obtained from band head measurements (see Problem 3)

Z Data obtained from, or referring to, band origins (see Problem 3)

R Shaded towards longer wavelengths (appearance of the rotational fine-structure, $B'_e < B''_e$)

V Shaded towards shorter wavelengths (appearance of the rotational fine-structure, $B'_e > B''_e$)

( ) Uncertain data

[ ] Data refer to $\upsilon = 0$ or lowest observed level. T_e values in square brackets give the energy of this level relative to the minimum of the ground-state potential energy curve. Vibrational frequencies in square brackets correspond to $\Delta G(½)$ or the lowest observed interval.

Answer: The spectroscopic constants for the electronic term values, $\tilde{T}_e$, fundamental vibration frequencies, $\omega_e = \tilde{\nu}_e$, anharmonicities, $\omega_e\chi_e = \chi_e\tilde{\nu}_e$, and equilibrium bond lengths, $r_e = R_e$, are transcribed into cells D8:F11. The dissociation energy, $\tilde{D}_e$, and Morse *a*-parameter are calculated from the spectroscopic constants, Eqs. 27.5.6, 27.5.7, 27.5.12, and 27.5.17, allowing the potential energy curves to be calculated as columns in the spreadsheet.

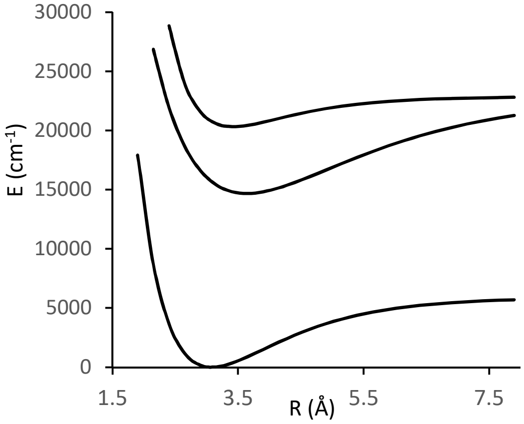
Cell D13 for the dissociation energy of the ground state is: "=D12*C4+D9/2-D10/4"
Cell E13 for the dissociation energy of the first excited state is: "=$D$13+$C$3-E8"
Cell D14 for the Morse *a*-parameter for the ground state is:

```
=2*PI()*D9*2.998E10*SQRT($C$2/1000/2/(D13*11.962))*1E-10
```

Cell D17 for the first cell of the Morse potential energy curve for the ground state is:

```
=D$8+D$13*(1-EXP(-D$14*($C17-D$11)))^2
```

A1	B	C	D	E	F	G
2	reduced mass	11.4949	g/mol			
3	DE$_{atomic}$ =	16961	cm^{-1}			
4	1 eV =	8065.5	cm^{-1}			
5	1 cm^{-1} =	11.962	J/mol			
6						
7	State		X	A	B	
8	electronic	T_e	0	14680.6	20320.0	cm^{-1}
9	vib. freq.	ν_e	159.125	117.323	124.09	cm^{-1}
10	anharmonic.	$\chi_e\nu_e$	0.7254	0.3576	0.6999	cm^{-1}
11	bond length	R_e	3.07887	3.6384	3.4228	Å
12	dissoc. energy	D_o	0.720			eV
13	dissoc. energy	D_e	5886.54	8166.96	2527.52	cm^{-1}
14	Morse a	a	0.85636	0.53604	1.01915	
15	R step	0.25	Å			
16		R (Å)	V(X) cm^{-1}	V(A) cm^{-1}	V(B) cm^{-1}	
17		1.9	17910.6			
18		2.15	8695.89	26851.3		
19		2.4	3659.46	21931.2	28839.7	
20		2.65	1159.30	18666.8	23948.2	
21		2.9	161.29	16606.4	21571.7	
22		3.15	20.56	15412.0	20579.7	
23		3.4	340.28	14832.3	20321.4	
24		3.65	880.78	14680.9	20428.0	
25		3.9	1501.16	14820.4	20694.9	
26		4.15	2121.91	15150.4	21012.5	
27		4.4	2701.20	15598.1	21325.1	
28		4.65	3219.78	16111.4	21607.4	
29		4.9	3671.61	16653.4	21850.2	
30		5.15	4058.00	17198.6	22052.8	
31		5.4	4384.03	17729.9	22218.6	
32		5.65	4656.40	18236.3	22352.2	
33		5.9	4882.28	18710.9	22458.9	
34		6.15	5068.52	19150.5	22543.5	
35		6.4	5221.41	19553.5	22610.2	
36		6.65	5346.50	19920.2	22662.6	
37		6.9	5448.56	20251.9	22703.5	
38		7.15	5531.65	20550.3	22735.6	
39		7.4	5599.19	20817.7	22760.5	
40		7.65	5654.01	21056.4	22780.0	
41		7.9	5698.46	21268.9	22795.1	



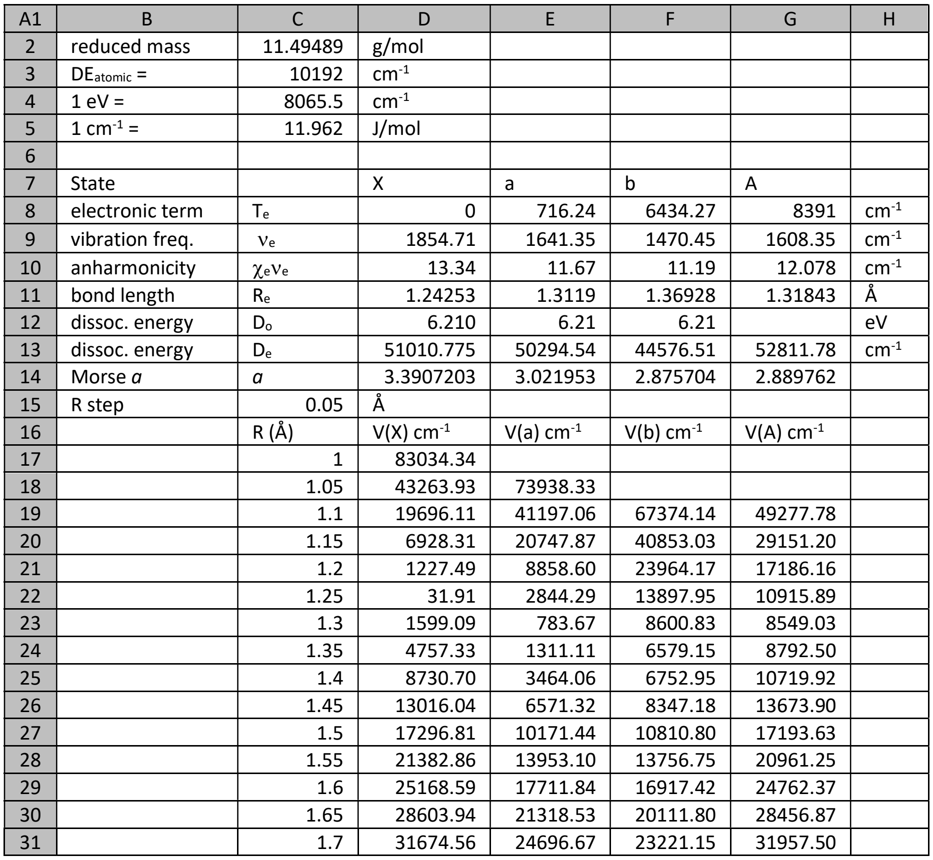
Potential energy surfaces are the necessary starting point for molecular dynamics calculations of chemical kinetics rate constants.

38. The Huber-Herzberg tables of diatomic spectroscopic constants are introduced in the previous problem. Refer to the previous problem for interpretation and footnotes. (a) Find the $^{12}C_2$ reference in the book or on-line, http://webbook.nist.gov/chemistry, and (b) write a spreadsheet to plot the potential energy surfaces as a function of R for the X $^1\Sigma_g^+$ ground state, and a $^3\Pi_u$, b $^3\Sigma_g^-$, and A $^1\Pi_u$ excited states. Use the Morse function for the potential energy surfaces. The ground state dissociation energy is 6.21 eV. The a and b excited states dissociate to ground state atoms: $C_2 \rightarrow C\ (^3P) + C\ (^3P)$. The A excited state dissociates to a ground state and an excited state atom: $C_2 \rightarrow C\ (^3P) + C\ (^1D)$. The atomic excitation energy, ΔE_{atomic}, is 10192 cm^{-1} to the ^1D state. From Figure 28.2.5, note that $\tilde{T}_e + \tilde{D}_e^{ex} = \tilde{D}_e + \Delta E_{atomic}$.

Answer: The data table for C_2 is reproduced below. The low lying $a^3\Pi_u$ excited state is remarkable. Molecules don't typically have such low lying excited states. C_2 is generated at high temperature is carbon arc sources and lighting strikes. At 2000 K, the occupancy of all excited $^3\Pi$ states is roughly 82%.

State	T_e	ω_e	$\omega_e\chi_e$	$\omega_e y_e$	B_e	α_e	D_e	r_e	Trans.	ν_{00}
$^{12}C_2$	$\mu = 6.000000$	$D_0^0 = 6.21$ eV			I.P. = 12.15 eV					
F $^1\Pi_u$	[75456.9]	[1557.5] ^{Z}			1.645	0.019	6.E-6	1.307	F←X R	74532.9 ^{Z}
g $^3\Delta_g$	[73183.6]	[1458.06]^Z			1.5238	0.17	6.60E-6	1.3579	g←a R	71649.6 ^{Z}
f $^3\Sigma_g^-$	71045.8	1360.5 ^{Z}	14.8		1.448	0.04	1.0E-5	1.393	f←a R	70188.4 ^{Z}
E $^1\Sigma_g^+$	55034.7	1671.50 ^{Z}	40.02	0.248	1.7897	0.0387	8.3E-6	1.2529	E→A V	46668.3 ^{Z}
d $^1\Sigma_u^+$	43239.44	1829.57 ^{Z}	13.94		1.8332	0.0196	7.32E-6	1.238	D↔X	43226.74 ^{Z}
e $^3\Pi_g$	40796.65	1106.56 ^{Z}	39.26	2.805	1.1922	0.0242	6.3E-6	1.5351	e→a R	39806.46 ^{Z}
C $^1\Pi_g$	34261.3	1809.1 ^{Z}	15.81		1.7834	0.018	6.8E-6	1.2552	C→A VR	25969.19 ^{Z}
d $^3\Pi_g$	20022.5	1788.22 ^{Z}	16.44	-0.5067	1.7527	0.01608	6.74E-6	1.2661	d↔a VR	19378.44 ^{Z}
c $^3\Sigma_u^+$	13312.1	1961.6	13.7		1.87			1.23		
A $^1\Pi_u$	8391	1608.35 Z	12.078	-0.01	1.6134	0.01686	6.44E-6	1.31843	A↔X R	8268.16 ^{Z}
b $^3\Sigma_g^-$	6434.27	1470.45 ^{Z}	11.19	0.028	1.49852	0.01634	6.22E-6	1.36928	b→a R	5632.7 ^{Z}
a $^3\Pi_u$	716.24	1641.35 ^{Z}	11.67		1.63246	0.01661	6.44E-6	1.31190		
X $^1\Sigma_g^+$	0	1854.71 ^{Z}	13.340	-0.172	1.81984	0.01765	6.92E-6	1.24253		

The spreadsheet from the previous problem was used after adding an additional column. For the triplet a- and b-states, $\Delta E_{atomic} = 0$ since the states dissociate to ground state C-atoms. The cells through the first half of the plot are reproduced below.



A1	B	C	D	E	F	G	H
2	reduced mass	11.49489	g/mol				
3	DE_{atomic} =	10192	cm^{-1}				
4	1 eV =	8065.5	cm^{-1}				
5	1 cm^{-1} =	11.962	J/mol				
6							
7	State		X	a	b	A	
8	electronic term	T_e	0	716.24	6434.27	8391	cm^{-1}
9	vibration freq.	ν_e	1854.71	1641.35	1470.45	1608.35	cm^{-1}
10	anharmonicity	$\chi_e\nu_e$	13.34	11.67	11.19	12.078	cm^{-1}
11	bond length	R_e	1.24253	1.3119	1.36928	1.31843	Å
12	dissoc. energy	D_o	6.210	6.21	6.21		eV
13	dissoc. energy	D_e	51010.775	50294.54	44576.51	52811.78	cm^{-1}
14	Morse *a*	*a*	3.3907203	3.021953	2.875704	2.889762	
15	R step	0.05	Å				
16		R (Å)	V(X) cm^{-1}	V(a) cm^{-1}	V(b) cm^{-1}	V(A) cm^{-1}	
17		1	83034.34				
18		1.05	43263.93	73938.33			
19		1.1	19696.11	41197.06	67374.14	49277.78	
20		1.15	6928.31	20747.87	40853.03	29151.20	
21		1.2	1227.49	8858.60	23964.17	17186.16	
22		1.25	31.91	2844.29	13897.95	10915.89	
23		1.3	1599.09	783.67	8600.83	8549.03	
24		1.35	4757.33	1311.11	6579.15	8792.50	
25		1.4	8730.70	3464.06	6752.95	10719.92	
26		1.45	13016.04	6571.32	8347.18	13673.90	
27		1.5	17296.81	10171.44	10810.80	17193.63	
28		1.55	21382.86	13953.10	13756.75	20961.25	
29		1.6	25168.59	17711.84	16917.42	24762.37	
30		1.65	28603.94	21318.53	20111.80	28456.87	
31		1.7	31674.56	24696.67	23221.15	31957.50	

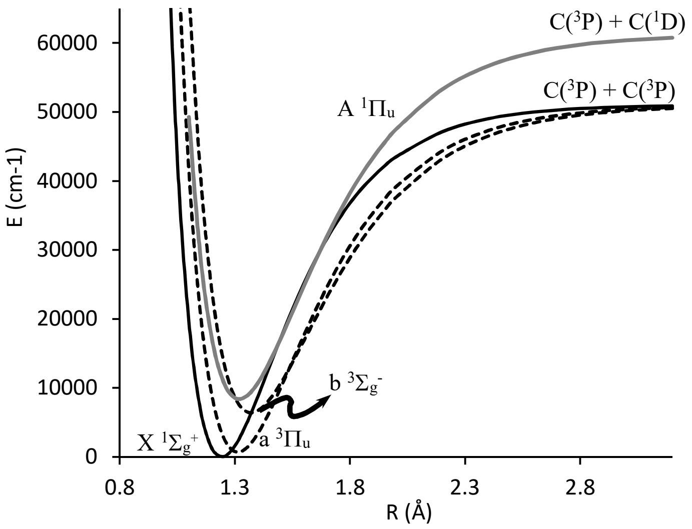


Figure P28.38.1: Potential energy surfaces for the four lowest electronic states of C_2. The singlet states are shown as solid lines and the triplet states are shown as dotted.

C_2 is the source of blue light from flames and the glow from some comets.[1] Synthesis with reactive carbon species is an established area in organic chemistry. The reactive carbon species are typically generated in high current carbon arc discharges.[11] C_2 undoubtedly plays a role in some of these systems. The relevance of this work extends to the formation of organic compounds in interstellar space and in pre-biotic environments in lightning strikes.

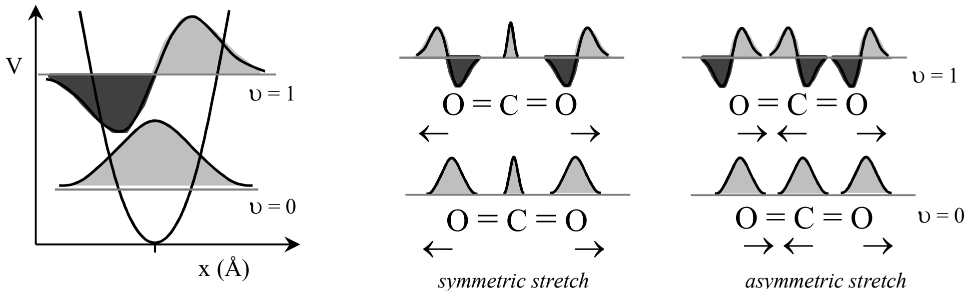
39. In Chapter 27, we did not justify the vibrational selection rule that in absorption, the transition dipole moment vanishes unless the normal mode transforms according to the same representation as the x, y, or z-component of the electric dipole moment. The transition electric dipole moment is proportional to the integral given by Eqs. 27.9.13. For a diatomic molecule aligned along the x-axis, the harmonic oscillator wave functions are functions of the displacement along the x-axis, $x = R - R_o$. The electric dipole operator along the internuclear axis is also a function of the x-axis position of the nuclei and the partial charge on the atoms. The transition dipole moment is then proportional to:

$$\mu_{tr,x} \propto \int_{-\infty}^{\infty} \chi_{\upsilon'}\, x\, \chi_{\upsilon''}\ dx$$

The integrand contains three functions, the final harmonic oscillator wave function with quantum number υ', the x-operator, and the initial harmonic oscillator wave function with quantum number υ". The x-operator is purely odd. The integral is over all space, so that the integral vanishes for an odd integrand. As a consequence the product of the three functions must be overall even for the transition moment integral to be non-zero.

For polyatomics, we must consider the x, y, and z-components of the transition dipole. The symmetry of each vibrational wave function is represented by an irreducible representation of the point group of the molecule. Consider the case for the fundamental transition 1←0. The ground state vibrational wave function, $\upsilon = 0$, always transforms according to the totally symmetric irreducible representation. As a result, to give a non-vanishing integral the product of the excited state vibrational wave function and the x-operator must contain the totally symmetric irreducible representation. The normal mode must transform according to the same representation as the x, y, or z-component of the electric dipole moment.

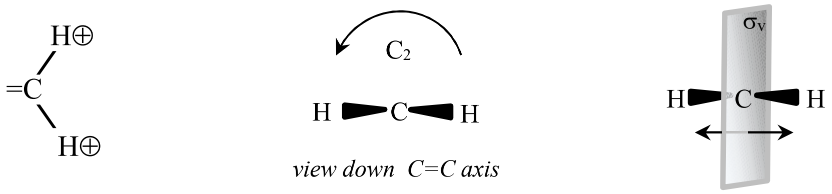
How can we illustrate that the ground vibrational state is totally symmetric under the operations of the point group? Consider a simple polyatomic such as CO_2 as compared to a diatomic molecule. The diatomic harmonic oscillator wave functions for $\upsilon = 0$ and 1 are shown at left and the corresponding wave functions are illustrated for CO_2 at right, Figure P28.39.1. The ground state, $\upsilon = 0$, wave function of any normal mode necessarily retains the same sign upon any symmetry operation of the point group, since the wave function is always positive. Now, consider the action of the reflection operator on the excited state wave function. For the $\upsilon = 1$ state, the inversion operation is symmetric for the symmetric stretch and anti-symmetric for the asymmetric stretch. As a result, the symmetric stretch is IR-inactive and the asymmetric stretch is IR-active.



(a). Diatomic vibrational wave functions (b). Polyatomic normal modes

Figure 28.39.1: Symmetry of harmonic oscillator wave functions for (a) diatomics and (b) the symmetric and asymmetric stretch of CO_2. The CO_2 symmetric stretch is symmetric with respect to a plane perpendicular to the internuclear axis, passing through the center of mass (a σ_v-plane). The asymmetric stretch is anti-symmetric with respect to reflection.

The symmetry of bending vibrations is possibly confusing, based on displacement arrows. Please review Problem 27.38. For this problem, using depictions of the quantum mechanical wave function of the type shown in Figure 28.39.1b, determine the symmetry of the wag-bending vibration with respect to C_2-rotation and reflection across σ_v, Figure 28.39.2:

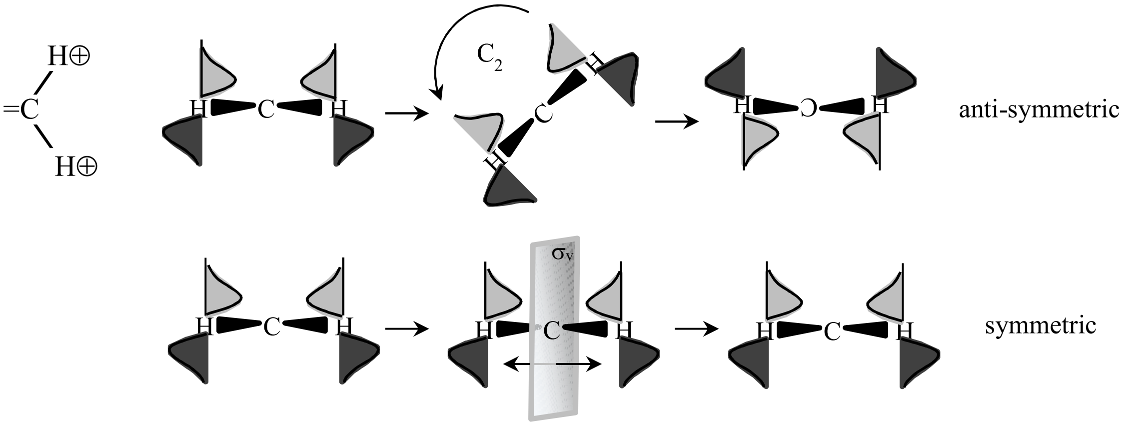


(a). (b).

Figure 28.39.2: (a). Top down view of the wag-mode of a CH_2 group. (b). End-on view, down the C=C internuclear axis, showing the C_2-rotation and σ_v-reflection operations.

Answer: The plan is to note that the wag-bending vibration will have in-phase "blobs" of probability above and below the plane of the equilibrium atom positions.

A schematic depiction of the harmonic oscillator wave function that roughly applies to a bending vibration is shown below. The phase of the lobes is that the positive lobe is in the positive direction for motion of both H-atoms. C_2-rotation inverts the sign of the wave function while reflection maintains the phase of the wave function. The wag transforms as the B_1 irreducible representation of the C_2v-point group, for example. The rock, which is the other bending vibration depicted in Problem 27.38, transforms as B_2 under C_{2v}.



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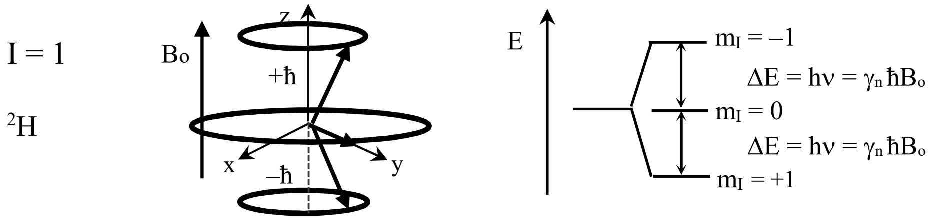
Chapter 29 Problems: Magnetic Resonance

1. Deuterium NMR, ^2H, is quite common. High field instruments have a channel for protons, one or two channels for ^{13}C or other nucleus, and an additional channel for deuterium. The deuterium channel is used for acquiring the resonance frequency of a peak from the deuterated solvent and using that frequency in maintaining a constant magnetic field. This process is called field-locking. The deuterium channel is also used for magnetic field shimming, which adjusts the uniformity of the magnetic field to achieve the narrowest, and hence most intense, transitions. Shimming enhances the resolution of the spectrum. Draw the energy level diagram for deuterium in an applied magnetic field and calculate the resonance frequency of protons and deuterium at a magnetic field of 7.046 T.

Answer: Table 29.1.1 gives the spin quantum number of deuterium as I = 1 and the magnetogyric ratio as $41.066\times10^6\ s^{-1}\ T^{-1}$ or equivalently $41.066\ MHz\ T^{-1}$. As a result in an applied magnetic field the nuclear energy levels are split into three levels, $m_I = -1, 0, +1$, with equal spacing. The magnetic dipole allowed transitions are for $\Delta m_I = \pm1$ with the same transition frequency for both $-1 \rightarrow 0$ and $0 \rightarrow 1$ transitions:

$$\nu = \Delta E/h = \gamma_N\,(2\pi)^{-1}\,B_o = 41.006\ MHz\ T^{-1}\,(2\pi)^{-1}\,7.046\ T = 45.98\ MHz$$



Protons at the same field strength resonate at:

$$\nu = \Delta E/h = \gamma_N\,(2\pi)^{-1}\,B_o = 267.522\ MHz\ T^{-1}\,(2\pi)^{-1}\,7.046\ T = 300.0\ MHz$$

2. The spin quantum number of ^{35}Cl is I = 3/2. For a single ^{35}Cl, assuming no spin-spin coupling, how many transitions are observed for ^{35}Cl?

Answer: One transition is observed because the three transitions all have the same frequency. The magnetic dipole allowed transitions are for $\Delta m_I = \pm1$ giving the three transitions $-3/2 \rightarrow -1/2$, $-1/2 \rightarrow +1/2$, and $+1/2 \rightarrow +3/2$.

3. A spectral width of at least 10 ppm is required to cover the ^1H-NMR spectra of many compounds. (a). Calculate the spectral width in Hz if the resonance frequency of protons is 60 MHz and if the resonance frequency is 500 MHz. (b). The resonance frequency of ^{13}C is ¼ the resonance frequency of protons at the same field strength. A spectral width of 160 ppm is required to cover the ^{13}C-spectra of many compounds. Calculate the spectral width in Hz if the

resonance frequency of ^{13}C is 75 MHz (300 MHz for protons) and if the resonance frequency is 125 MHz (500 MHz for protons).

Answer: The shift in ppm is defined by Eq. 29.1.8: $\delta = [(\nu - \nu_{ref})/\nu_{ref}]$ ($1\text{x}10^6$ ppm). The spectral width corresponds to the maximum plotted value of $\nu - \nu_{ref}$.
(a). At 60 MHz, a 10 ppm spectral width corresponds to 10 ppm($60\text{x}10^6$ Hz)/$1\text{x}10^6$ ppm =600 Hz and at 500 MHz the spectral width is 5000 Hz.
(b). At 75 MHz, 160 ppm corresponds to 160 ppm($75\text{x}10^6$ Hz)/$1\text{x}10^6$ ppm = 11,520 Hz and at 125 MHz the spectral width is 20,000 Hz.

Note that aldehyde protons resonate at 9-10 ppm and carboxylic acid protons resonate in the 10-13 ppm range, so a 10 ppm spectral width is not necessarily sufficient to cover a complete spectrum. We chose a 10 ppm spectral width for this problem to keep the numbers easy to calculate in your head. For ^{13}C spectra carbonyl carbons (C=O) resonate roughly from 150-220 ppm so once again, 160 ppm is not necessarily sufficient to cover a complete spectrum, even though ~160 ppm is a common option for the spectral width in NMR software.

4. In a given instrument, the NMR resonance frequency of a proton in a methyl group is centered at 399,095,832 Hz. The resonance frequency of TMS at the same field strength is 399,095,432 Hz. (a). Calculate the chemical shift of the methyl group. (b). The methyl group is split into a triplet by an adjacent methylene with a spin-spin coupling constant of 7.0 Hz. Calculate the spin-spin splitting in ppm assuming the same resonance frequency as part (a).

Answer: The shift in ppm is defined by Eq. 29.1.8: $\delta = [(\nu - \nu_{ref})/\nu_{ref}]$ ($1\text{x}10^6$ ppm). (a). The chemical shift of the methyl group is:

$$\delta = (399{,}095{,}842 - 399{,}095{,}432)/399{,}095{,}432\ (1\text{x}10^6\ \text{ppm}) = 1.03\ \text{ppm}$$

(b). At a resonance frequency of 400 MHz, a J of 7.0 Hz corresponds to 7.0/400 = 0.0175 ppm

The precise ^1H resonance frequency of a given instrument is essentially never exactly the "name-plate" frequency.

5. The NMR chemical shift of a methyl group is centered at 1.240 ppm at a 60 MHz resonance frequency and the spin-spin splitting constant with an adjacent methylene is 7.0 Hz. (a). Calculate the multiplet peak positions in ppm assuming TMS at 60 MHz. (b). Calculate the multiplet peak positions in ppm with TMS at 500 MHz. (c). Describe the difference in appearance between the spectrum at 60 MHz and 500 MHz.

Answer: An adjacent methylene has two equivalent spins giving the methyl resonance as a triplet. The triplet peak positions are at $\nu_A + J$, ν_A, and $\nu_A - J$ giving the multiplet spacing between the transitions as J.
(a). At 60 MHz, the spin-spin coupling constant of 7.0 Hz corresponds to:

$$J = 7.0\text{ Hz}/60\text{x}10^6\text{ Hz }(1\text{x}10^6\text{ ppm}) = 0.117\text{ ppm}$$

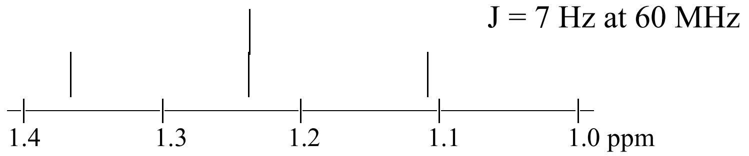
Giving the triplet transitions as: 1.240 + 0.117 ppm = 1.357 ppm, 1.240 ppm, and 1.240 – 0.117 ppm = 1.123 ppm.

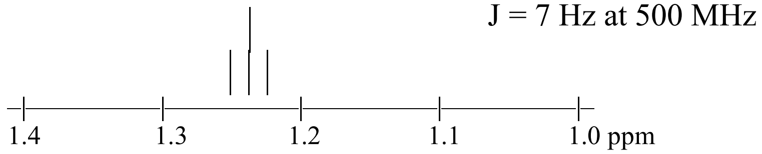
(b). At 500 MHz, the spin-spin coupling constant of 7.0 Hz corresponds to:

$$J = 7.0\text{ Hz}/500\text{x}10^6\text{ Hz }(1\text{x}10^6\text{ ppm}) = 0.014\text{ ppm}$$

Giving the triplet transitions as: 1.240 + 0.014 ppm = 1.254 ppm, 1.240 ppm, and 1.240 – 0.014 ppm = 1.226 ppm.

(c). Using the same ppm spectral width, the component transitions of the triplet are closer together at 500 MHz than at 60 MHz, even though the J in Hz is the same, as shown below:





6. (a). Derive Eq. 29.1.7 for the population difference of the spins states of a spin-½ nucleus. (b). Determine the number of spins in the upper and the lower spin states for protons at 400 MHz at 298.2 K. Assume 10^6 total spins. (c). Table-top, permanent magnet NMR spectrometers commonly operate at 60 MHz. Determine the number of spins in the upper and the lower spin states for protons at 60.0 MHz at 298.2 K. Assume 10^6 total spins.

Answer: (a). Given the Boltzmann population ratio, Eq. 29.1.7 and Eq. 29.1.6:

$$\frac{n_-}{n_+} = e^{-\Delta E/kT} = e^{-\gamma\hbar B_o/kT} = e^{-\nu/(kT/h)} \tag{1}$$

The population difference and sum using Eq. 1 to solve for n_- gives:

$$n_+ - n_- = n_+ - n_+ \left(e^{-\nu/(kT/h)}\right) = n_+ \left(1 - e^{-\nu/(kT/h)}\right)$$

$$n_+ + n_- = n_+ + n_+ \left(e^{-\nu/(kT/h)}\right) = n_+ \left(1 + e^{-\nu/(kT/h)}\right)$$

with $n_{tot} = n_+ + n_-$ as the total number of spins. The ratio is:

$$\frac{n_+ - n_-}{n_+ + n_-} = \frac{1 - e^{-\nu/(kT/h)}}{1 + e^{-\nu/(kT/h)}} \qquad \text{giving} \qquad \Delta n = n_+ - n_- = n_{tot}\left(\frac{1 - e^{-\nu/(kT/h)}}{1 + e^{-\nu/(kT/h)}}\right) \tag{29.1.7}$$

The resulting populations are determined using $n_- = n_{tot} - n_+$:

$$\Delta n = n_+ - n_- = n_+ - (n_{tot} - n_+) \qquad \text{or} \qquad n_+ = ½\,(n_{tot} + \Delta n)$$

(b). At 400 MHz and 298.2 K with Eq. 1, the population ratio is $n_-/n_+ = 0.999936$.
Eq. 29.1.7 with $n_{tot} = 10^6$ spins gives the population difference:

$$\Delta n = n_+ - n_- = n_{tot}\left(\frac{1 - 0.999936}{1 + 0.999936}\right) = 32$$

The populations are: $n_+ = ½(10^6 + 32) = 500016$ and $n_- = 1000000 - 500016 = 499984$.
As a check the population ratio is: $n_-/n_+ = 499984/500016 = 0.999936$ as required.
(c). At the commonly used frequency of 60 MHz, the population ratio is much smaller, Eq. 29.1.7:

$$\frac{n_-}{n_+} = e^{-\nu/(kT/h)} = e^{-(60\text{x}10^6\ s^{-1}/6.2124\text{x}10^{12}\ s^{-1})} = 0.9999903$$

$$\text{or}\qquad n_+ - n_- = (n_+ + n_-)\left(\frac{1 - 0.9999903}{1 + 0.9999903}\right) = 4.83$$

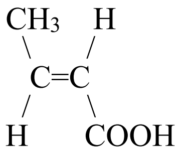
Out of one million spins there ~5 more spin-ups than spin-downs. No wonder NMR has such poor sensitivity. At 60 MHz, samples are often run as pure liquids to gain sensitivity. Typical concentrations in UV/Visible absorption studies are in the 10^{-5} M range. The populations are: $n_+ = ½(10^6 + 4.83) \cong 500002$ and $n_- = 10^6 - 500002 = 499998$.

7. (a). Give the peak intensities in a sextet that result from coupling to equivalent spins. (b). Give the peak intensities in a doublet of triplets. (Don't worry about the transition frequencies.) (c). How many spins are coupled to the observed resonance if the multiplet is a doublet of quartets? Assume each quartet has intensity ratios: 1:3:3:1.

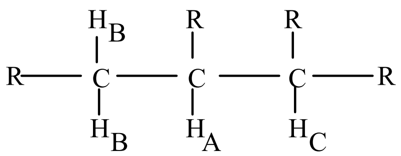
Answer: (a). Using Pascal's triangle, Table 29.1.5, the intensity ratios of a sextet resulting from coupling to five equivalent spins are:

1 : 5 : 10 : 10 : 5 : 1

(b). A doublet of triplets has the intensity ratio of 1:2:1—1:2:1, although the transitions may not arise in that order, see Figure 29.1.10b.
(c). A 1:3:3:1 quartet results from coupling to three equivalent neighbors. A doublet results from coupling to one near neighbor. In total four spins are coupled to the observed spin. An example is *trans*-2-butenoic acid (*trans*-crotonic acid). The *trans*-olefinic coupling constant is typically large: 12-18 Hz:

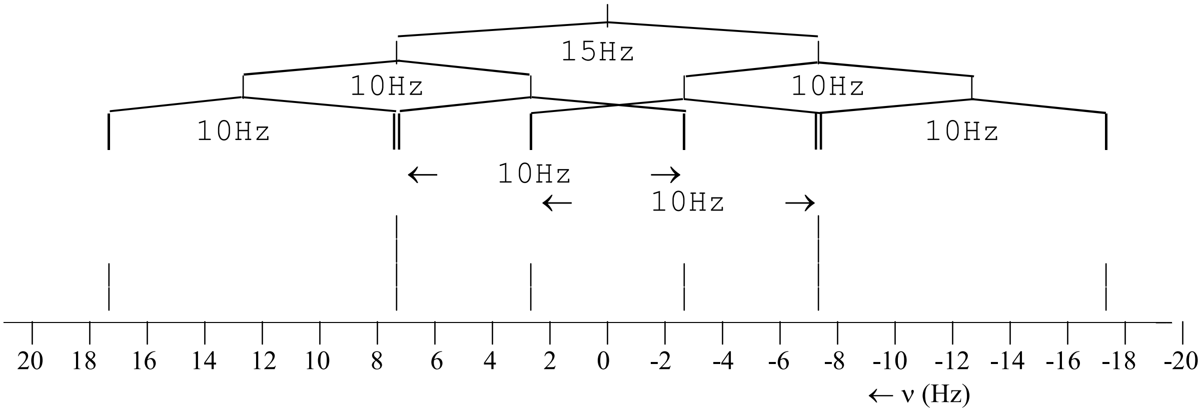


8. Show the spin-spin splitting pattern for nucleus A in the following molecular fragment. Assume $J_{AB} = 10$ Hz and $J_{AC} = 15$ Hz. Indicate the relative intensities. Assume first-order behavior.



$R\text{—}C(H_B)(H_B)\text{—}C(R)(H_A)\text{—}C(R)(H_C)\text{—}R$

Answer: Construct the coupling tree starting with the largest spin-spin splitting constant. With J_{AC} = 15 Hz the resonance is initially split into a doublet with the transitions at +7.5 and –7.5 Hz. With J_{AB} = 10 Hz, the previous transitions are split into 1:2:1 triplets: +17.5, 7.5, -2.5, and +2.5, –7.5, –17.5 Hz.

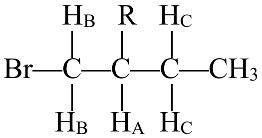


ν: +17.5, 7.5, -2.5
and +2.5, –7.5, –17.5 Hz

intensities
1 2 1 1 2 1

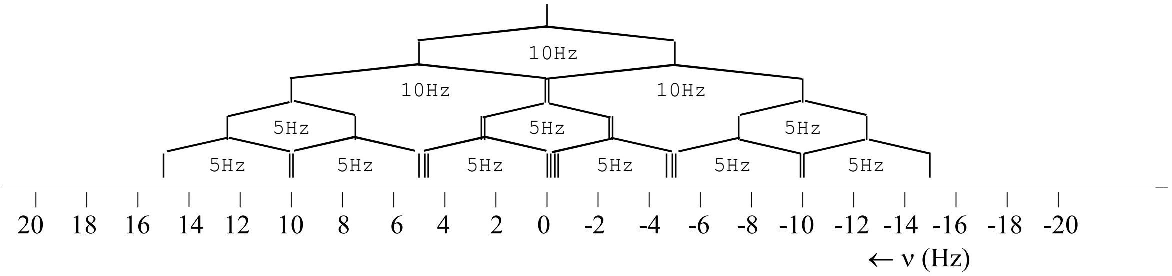
The pattern is a doublet of triplets, or just abbreviated "dt".

9. Show the spin-spin splitting pattern for nucleus A in the following molecular fragment with J_{AB} = 5 Hz and J_{AC} = 10 Hz. Indicate the relative intensities. Assume first-order behavior.



$Br\text{—}C(H_B)(H_B)\text{—}C(R)(H_A)\text{—}C(H_C)(H_C)\text{—}CH_3$

Answer: Construct the coupling tree starting with the largest spin-spin splitting constant. With J_{AC} = 10 Hz the resonance is initially split into a 1:2:1 triplet with the transitions at +10, 0, and –10 Hz. With J_{AB} = 5 Hz, the previous transitions are split into a 1:2:1 triplets: +15, 10, 5; 5, 0, -5; and -5, –10, –15 Hz. Because of the coincidences, two pairs of transitions overlap giving a septet with unusual intensities 1:2:3:4:3:2:1. (Note that a septet from six equivalent neighbors gives an intensity ratio of 1:6:15:20:15:6:1, Table 29.1.5.)



ν: 15 10 5 -5 -10 -15
and 5 0 -5 Hz

Intensities
1 2 3 4 3 2 1

The "JMM: First-Order Multiplet Maker" on the course Web site or companion CD (jmmset.html) calculates the first-order multiplet for a given set of neighbors and spin-spin coupling constants. The applet can be used to make suggestions for the values of coupling constants for different bonding environments. The following input, with the specific values of the J-constants entered for this problem, produces the same multiplet as predicted above.

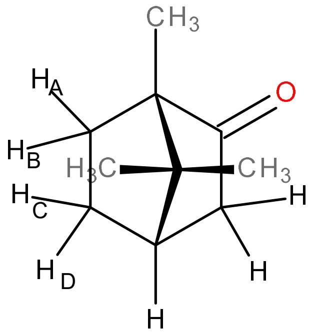
^{2}J geminal				^{3}J vicinal			
n	type	phi	J/Hz	n	type	phi	J/Hz
0	alkyl			2	alkyl		10
^{4}J long range				2	alkyl		5
0	allyl			0	alkyl		
0	allyl			0	alkyl		

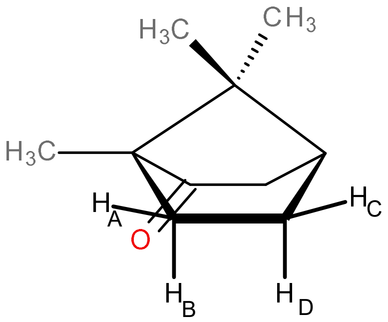
10. In an isolated ethyl group, -CH_2CH_3, there is no spin-spin coupling through the attachment point. Examples include ethyl alcohol, ethylbromide, diethylether, and ethylacetate. An isolated ethyl gives characteristic spin-spin splitting patterns of a quartet and triplet, in the order -CH_2CH_3. Give the characteristic splitting patterns of isolated *n*-propyl, *iso*-propyl, *n*-butyl, *sec*-butyl, *iso*-butyl, *tert*-butyl, and *iso*-amyl. Assume the vicinal spin-spin coupling constants are approximately equal, with no longer range coupling, and free rotation about the bonds. (Note: *iso*-propyl = 1-methylethyl, *sec*-butyl = 1-methylpropyl, *iso*-butyl = 2-methylpropyl, *tert*-butyl = 1,1-dimethylethane, *iso*-amyl = 3-methylbutyl)

Answer: Assuming all the vicinal, ^{3}J coupling constants are the same, we use the n+1 rule, counting all the neighbors three bonds away from the given proton. Consider *n*-propyl: the terminal methyl has two near-neighbors giving a triplet, the central methylene has five near-neighbors giving a sextet, and the terminal methylene has two near-neighbors giving a triplet. The following table gives the remaining results.

Isolated Group	Structure	Multiplets	
ethyl	$-CH_2CH_3$	quartet,triplet	
n-propyl	$-CH_2CH_2CH_3$	triplet,sextet,triplet	
iso-propyl	$-CH(CH_3)CH_3$	septet,doublet	(equiv. methyls)
n-butyl	$-CH_2CH_2CH_2CH_3$	triplet,quintet,sextet,triplet	
sec-butyl	$-CH(CH_3)CH_2CH_3$	sextet,quintet,doublet,triplet	
iso-butyl	$-CH_2CH(CH_3)CH_3$	doublet,nonet,doublet	(equiv. methyls)
tert-butyl	$-C(CH_3)(CH_3)CH_3$	singlet	(equiv. methyls)
iso-amyl	$-CH_2CH_2CH(CH_3)CH_3$	triplet,quartet,nonet,doublet	(equiv. methyls)

11. The geminal coupling constant between inequivalent methylene protons on sp^3-hybridized carbons is often large, ~12 Hz. (a). Use the Karplus relationship to estimate the J_{AC} and J_{AD} spin-spin coupling constants of the labeled protons in camphor, below. (b). Sketch the expected multiplet pattern of proton-A based on your estimated geminal and vicinal coupling constants. Note that proton-B will also give a similar multiplet that will likely overlap with the multiplet of proton-A. We don't consider the proton-B multiplet in this problem for simplicity. (In practice the appearance of the spectrum is sensitive to the exact values of all the parameters. The purpose of this exercise is to give just one reasonable prediction of the appearance of the spectrum.)





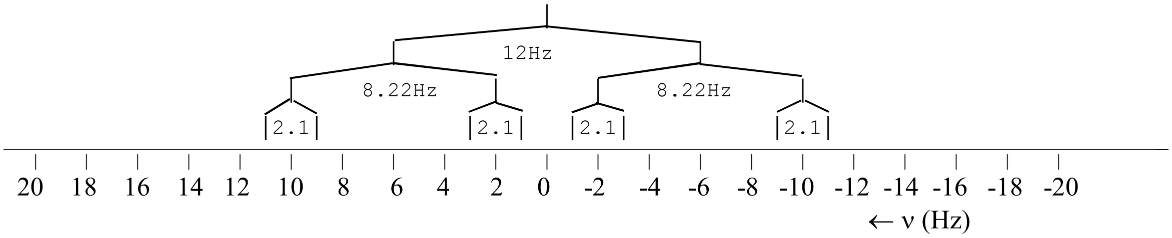
Dihedral angles: $\phi_{AC} = 0°$ and $\phi_{AC} = 120°$

Answer: (a). The Karplus relationship is given by Eqs. 29.1.16:

$$J_{HH} = 8.5 \cos^2\phi - 0.28 \qquad 0° \le \phi \le 90°$$
$$J_{HH} = 9.5 \cos^2\phi - 0.28 \qquad 90° \le \phi \le 180°$$

For $\phi_{AC} = 0°$: $J_{AC} = 8.22$ Hz and $\phi_{AD} = 120°$: $J_{AD} = 2.095$ Hz.

(b). Given that J_{AB} , J_{AC}, and J_{AD} are all different, the spectrum is predicted to have $2^3 = 8$ transitions all of equal intensity (no overlapping of transitions). Start the coupling tree with the largest coupling constant. With $J_{AB} = 12$ Hz the resonance is initially split into a doublet with the transitions at +6 and –6 Hz. With $J_{AC} = 8.22$ Hz, the previous transitions are split into doublets: 10.11, 1.89; and -1.80, -10.11 Hz. With J_{AD} =2.095 Hz, the final doublets are: 11,16, 9.06; 2.94, 0.84; -0.84, -2.94; and -9.06, -11.16 Hz.



Another commonly quoted form of the Karplus relationship is:

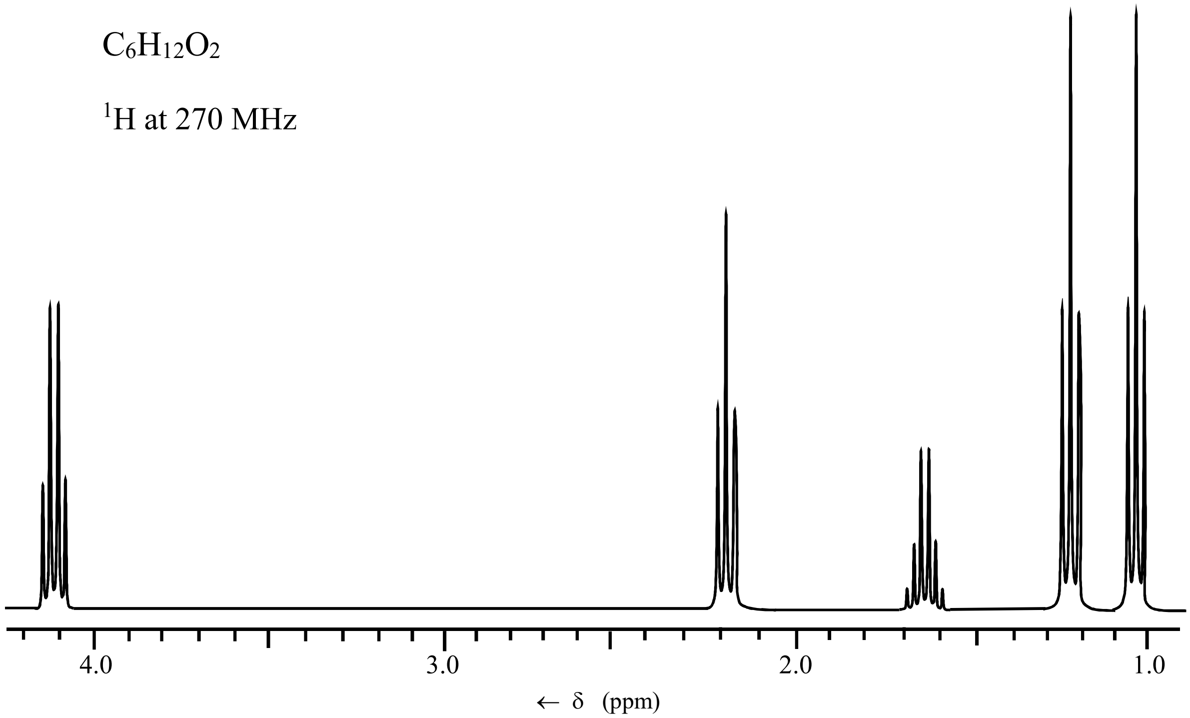
$$^{3}J = 7.8 - 1.0 \cos \phi + 5.6 \cos 2\phi$$

This form is implemented in the "*Vicinal Spin-Spin Coupling Constant Prediction*" applet (altona.html) on the textbook Web site or companion CD. The predicted values based on this version of the Karplus equation are $\phi_{AC} = 0°$: J_{HH} = 8.06 Hz and $\phi_{AD} = 120°$: 3.89 Hz. This applet also implements several more accurate prediction equations that allow for the electron withdrawing effects of neighboring substituents. You should use molecular mechanics to verify the dihedral angles that were given in this problem.

The "*JMM: First-Order Multiplet Maker*" on the course Web site or companion CD (jmmset.html) calculates the first-order multiplet for a given set of neighbors and spin-spin coupling constants. The applet can additionally be used to make suggestions for the values of coupling constants of different bonding environments including dihedral angles. The following input, with the specific values of the J-constants entered for this problem, produces the same multiplet as predicted above.

^{2}J geminal				^{3}J vicinal			
n	type	phi	J/Hz	n	type	phi	J/Hz
1	alkyl			1	alkyl		8.22
^{4}J long range				1	alkyl		2.95
0	allyl			0	alkyl		
0	allyl			0	alkyl		

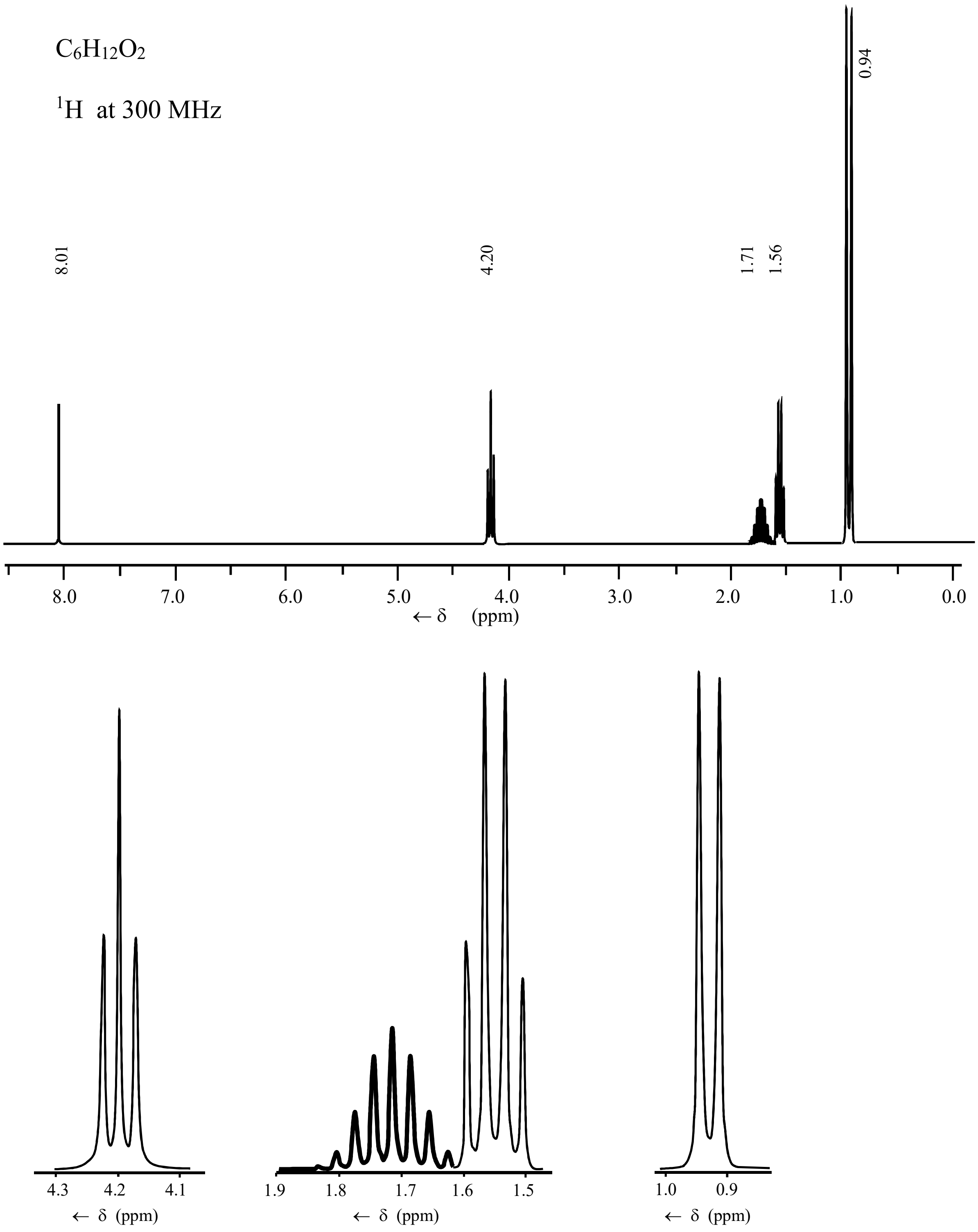
12. Determine the structure of the following compound. The spectrum was acquired at 270 MHz. The degree of unsaturation is a useful starting point if the formula of the compound is known. The degree of unsaturation is equal to the sum of the number of double bonds and rings: dbr = (2c – h + 2 + n – x)/2, where c is the number of carbons, h the number of hydrogens, n the number of nitrogens, and x the number of monovalent atoms, which includes F, Cl, and I.



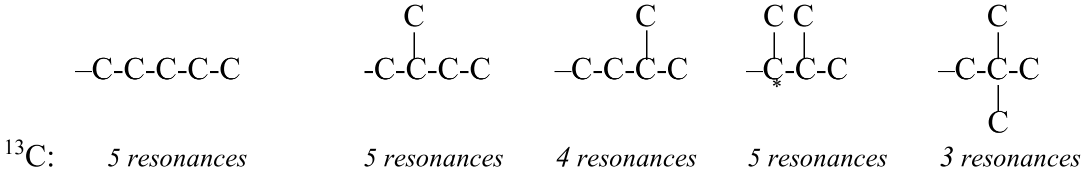
Answer: The number of double bonds and rings is: dbr = $(2\cdot6 - 12 + 2 + 0 - 0)/2 = 1$. An alkene, aldehyde, carboxylic acid, or ester are possible functional groups or a single saturated ring. The typical approach is to begin with the largest chemical shifts. The triplet at 4.1 ppm requires interaction with a nearby heteroatom or that the proton is on a C=C, Table 29.1.3. The chemical shift agrees with the 4.1 ppm entry on Table 29.1.2 for a methylene that is the –O– linked portion of an ester: "R-CH_2-O-C(=O)-R". The appearance of a quartet and a triplet in a spectrum is often a strong indication of an ethyl group. The triplet at 1.23 ppm agrees with the 1.3 ppm entry on Table 29.1.2 for a methyl that is beta to an –O–: "CH_3–C-O-". As a result we suspect that the compound is an ethyl ester. The triplet near 2.2 ppm agrees with the 2.2 ppm entry on Table 29.1.2 for a methylene that is the –C(=O)–OR linked portion of an ester: "R–CH_2-CO–OR". The sextet at 1.63 ppm requires coupling to five similar neighbors, which in this case results from $CH_3CH_2CH_2$–. The terminal position of this three-carbon substituent produces the remaining triplet. The spectrum is then consistent with ethyl butyrate: $CH_3CH_2CH_2C(=O)OCH_2CH_3$.

Note that an aldehyde or carboxylic acid would have a resonance at 9 ppm or below. Protons attached to a double bond are typically down field of 4.1 ppm, Table 29.1.3, although "–HC=C–O–" is a possibility to consider in this example.

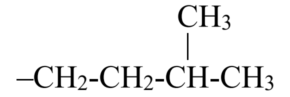
13. Determine the structure of the following compound. The spectrum was acquired at 300 MHz. The down field resonance at 8.01 ppm is a singlet. Expanded spectra of the multiplets are shown below the full spectrum. The ^{13}C spectrum has five peaks with the most downfield peak at 161.2 ppm. [Hint: see the comments about the degree of unsaturation in the previous problem.]



Answer: The ^{13}C spectrum has five peaks, which shows that the compound has two magnetically equivalent carbons. The proton spectrum also has five resonances, which again shows that there are two magnetically equivalent groups. As in the previous problem, the number of double bonds and rings, is dbr = (2·6 – 12 + 2 + 0 – 0)/2 = 1. An alkene, aldehyde, carboxylic acid, or ester are possible functional groups or a single saturated ring. The typical approach is to begin with the largest chemical shifts. The proton singlet at 8.01 ppm is consistent with a formate proton, which are expected in the range of 8.0-8.2, Table 29.1.3. Similarly, the down field ^{13}C shift of 161.2 ppm matches the shift of ethyl formate at 161.4 ppm, Table 29.1.4. We now must account for five carbons, two of which are equivalent, with 11 attached protons. Of the possible five-carbon fragments:



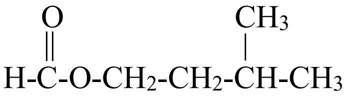
only the third possibility, the *iso*-pentyl group, has two and only two equivalent carbons. The 2,3-dimethylpropyl fragment has a chiral center, *, so the terminal $-CH_3$ groups are inequivalent. The proton spin-spin multiplicities expected for the *iso*-pentyl group are indicated below and are also consistent with the spectrum:



$$-\mathrm{CH_2{-}CH_2{-}}\overset{\overset{\mathrm{CH_3}}{|}}{\mathrm{CH}}\mathrm{{-}CH_3}$$

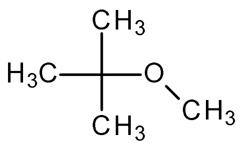
multiplicity: *(3) (4) (9) (2)*

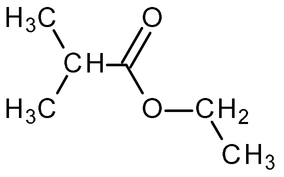
The outer peaks of a nonet are often difficult to see, as they are often obscured by noise. The intensity ratio is unfavorable for detecting the outer transitions: 1:8:28:56:70:56:28:8:1. In this case the ninth transition overlaps with an outer peak of the quartet. However, given that a multiplet from n-equivalent neighbors is always symmetrical, you can determine the multiplicity just from the left side of the multiplet. From Table 29.1.2 the expected chemical shift of the methylene protons adjacent to the HC(=O)-O– of the formate group is 4.1 ppm, as listed for "$R–CH_2–O–C(=O)–R$". The tabulated value is sufficiently close to the observed 4.2 ppm to have confidence in the assignment. The compound is *iso*-pentyl formate:

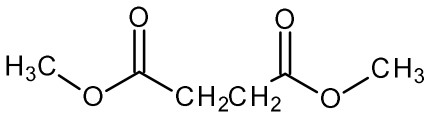


$$\mathrm{H{-}}\overset{\overset{\mathrm{O}}{\|}}{\mathrm{C}}\mathrm{{-}O{-}CH_2{-}CH_2{-}}\overset{\overset{\mathrm{CH_3}}{|}}{\mathrm{CH}}\mathrm{{-}CH_3}$$

14. Determine the number of proton and carbon resonances that are observed for the following compounds. Determine the corresponding multiplicities of the spin-spin coupling multiplets.







Answer: For methyl-*tert*-butylether the three *tert*-butyl groups are magnetically equivalent giving two proton chemical shifts and three ^{13}C chemical shifts. The two proton environments result in singlets.

For ethyl *iso*-butyrate the two methyls in the *iso*-butyrate side of the molecule are magnetically equivalent giving four proton chemical shifts and five ^{13}C chemical shifts (don't forget the carbonyl carbon). The ethyl group gives a quartet and triplet. An isolated *iso*-butyrate group gives a doublet and septet.

Dimethyl succinate has a mirror plane giving two proton chemical shifts and three ^{13}C chemical shifts. Both proton resonances are singlets (magnetically equivalent protons don't split).

15. *Equivalent Spins Don't Split*: Derive the energy levels and transition frequencies of a system with two equivalent protons. This problem fills in the details of the energy level diagram in Figure 29.1.13. Because the chemical shift differences are not greater than the spin-spin coupling constant, the full spin-spin coupling Hamiltonian must be used for this problem:

$$\hat{\mathcal{H}} = -\nu_A \hat{I}_{zA} - \nu_B \hat{I}_{zB} + J_{AB}\, \vec{I}_A \cdot \vec{I}_B \qquad (29.1.13)$$

where $\vec{I}_A \cdot \vec{I}_B = \hat{I}_{xA}\, \hat{I}_{xB} + \hat{I}_{yA}\, \hat{I}_{yB} + \hat{I}_{zA}\, \hat{I}_{zB}$

The allowable spin states for two equivalent spins are the symmetric combinations: $\alpha\alpha$, $1/\sqrt{2}\,(\alpha\beta + \beta\alpha)$, and $\beta\beta$, while the fourth spin state is antisymmetric: $1/\sqrt{2}\,(\alpha\beta - \beta\alpha)$. In Ch. 24.7 we found the relationship between the angular momentum raising and lowering operators and the x and y-components of the angular momentum, Eq. 24.7.18. Expressed explicitly in terms of nuclear angular momentum operators, Eqs. 24.7.18 are recast as:

$$\hat{I}^- = \hat{I}_x - i\, \hat{I}_y \quad \text{(lowering)} \qquad \text{and} \qquad \hat{I}^+ = \hat{I}_x + i\, \hat{I}_y \quad \text{(raising)} \qquad (24.7.18)$$

which have the following effects on the spin wave functions:

$$\hat{I}^+ \alpha = 0 \qquad \hat{I}^+ \beta = \alpha$$
$$\hat{I}^- \alpha = \beta \qquad \hat{I}^+ \beta = 0$$

Solving for $\hat{I}_x$ and $\hat{I}_y$ gives for both A and B spins:

$$\hat{I}_x = ½(\hat{I}^+ + \hat{I}^-) \qquad \text{and} \qquad \hat{I}_y = ½\, i(\hat{I}^+ - \hat{I}^-)$$

In a subsequent problem we will prove that the spin-spin interaction can be written as:

$$J_{AB}\, \vec{I}_A \cdot \vec{I}_B = J_{AB}\, [\, \hat{I}_{zA}\, \hat{I}_{zB} + ½(\hat{I}_A^+\, \hat{I}_B^- + \hat{I}_A^-\, \hat{I}_B^+)]$$

(a). For simplicity of notation set $J = J_{AB}$. Show that:

$$J\, \vec{I}_A \cdot \vec{I}_B\, \alpha\alpha = J/4\; \alpha\alpha$$
$$J\, \vec{I}_A \cdot \vec{I}_B\, \alpha\beta = -J/4\; \alpha\beta + J/2\; \beta\alpha$$
$$J\, \vec{I}_A \cdot \vec{I}_B\, \beta\alpha = -J/4\; \beta\alpha + J/2\; \alpha\beta$$
$$J\, \vec{I}_A \cdot \vec{I}_B\, \beta\beta = J/4\; \beta\beta$$

Answer: The eigenfunctions are the spin-A spin-B products: $\alpha\alpha$, $1/\sqrt{2}(\alpha\beta+\beta\alpha)$, $1/\sqrt{2}(\alpha\beta-\beta\alpha)$, $\beta\beta$. $\hat{I}_A^+$ and $\hat{I}_A^-$ only operate on the coordinates of spin-A and $\hat{I}_B^+$ and $\hat{I}_B^-$ only operate on the coordinates of spin-B. For example, using for a moment explicit A and B designations, the action of the raising and lowering operators on $\alpha\beta = \alpha_A\beta_B$ are:

$$\hat{I}_A^+ \hat{I}_B^- \alpha_A\beta_B = (\hat{I}_A^+ \alpha_A)(\hat{I}_B^- \beta_B) = 0 \cdot 0 \qquad \hat{I}_A^- \hat{I}_B^+ \alpha_A\beta_B = (\hat{I}_A^- \alpha_A)(\hat{I}_B^+ \beta_B) = \beta_A\alpha_B$$

The results of the raising and lowering operators on the products are:

Ψ	$\hat{I}_A^+ \hat{I}_B^-$	$\hat{I}_A^- \hat{I}_B^+$
$\alpha\alpha$	0	0
$\alpha\beta$	0	$\beta\alpha$
$\beta\alpha$	$\alpha\beta$	0
$\beta\beta$	0	0
$^1/\sqrt{2}(\alpha\beta+\beta\alpha)$	$^1/\sqrt{2}\ \alpha\beta$	$^1/\sqrt{2}\ \alpha\beta$
$^1/\sqrt{2}(\alpha\beta-\beta\alpha)$	$^1/\sqrt{2}\ \alpha\beta$	$-\ ^1/\sqrt{2}\ \alpha\beta$

Expanding the terms in the spin-spin interaction, $J_{AB}\,[\,\hat{I}_{zA}\hat{I}_{zB} + \tfrac{1}{2}(\hat{I}_A^+ \hat{I}_B^- + \hat{I}_A^- \hat{I}_B^+)]$, gives:

$$J\,\vec{I}_A\cdot\vec{I}_B\,\alpha\alpha = J\,\hat{I}_{zA}\hat{I}_{zB}\,\alpha\alpha + \tfrac{1}{2}J\,\hat{I}_A^+\hat{I}_B^-\,\alpha\alpha + \tfrac{1}{2}J\,\hat{I}_A^-\hat{I}_B^+\,\alpha\alpha = \ ^J/_4\ \alpha\alpha$$
$$J\,\vec{I}_A\cdot\vec{I}_B\,\alpha\beta = J\,\hat{I}_{zA}\hat{I}_{zB}\,\alpha\beta + \tfrac{1}{2}J\,\hat{I}_A^+\hat{I}_B^-\,\alpha\beta + \tfrac{1}{2}J\,\hat{I}_A^-\hat{I}_B^+\,\alpha\beta = -\,^J/_4\ \alpha\beta + \,^J/_2\ \beta\alpha$$
$$J\,\vec{I}_A\cdot\vec{I}_B\,\beta\alpha = J\,\hat{I}_{zA}\hat{I}_{zB}\,\beta\alpha + \tfrac{1}{2}J\,\hat{I}_A^+\hat{I}_B^-\,\beta\alpha + \tfrac{1}{2}J\,\hat{I}_A^-\hat{I}_B^+\,\beta\alpha = -\,^J/_4\ \beta\alpha + \,^J/_2\ \alpha\beta$$
$$J\,\vec{I}_A\cdot\vec{I}_B\,\beta\beta = J\,\hat{I}_{zA}\hat{I}_{zB}\,\beta\beta + \tfrac{1}{2}J\,\hat{I}_A^+\hat{I}_B^-\,\beta\beta + \tfrac{1}{2}J\,\hat{I}_A^-\hat{I}_B^+\,\beta\beta = \ ^J/_4\ \beta\beta$$

(b). Combine these results to show that:

$$J\,\vec{I}_A\cdot\vec{I}_B\,[^1/\sqrt{2}(\alpha\beta+\beta\alpha)] = \ ^J/_4\,[^1/\sqrt{2}\,(\alpha\beta + \beta\alpha)]$$
$$J\,\vec{I}_A\cdot\vec{I}_B\,[^1/\sqrt{2}(\alpha\beta-\beta\alpha)] = -^{3J}/_4\,[^1/\sqrt{2}\,(\alpha\beta - \beta\alpha)]$$

Answer: Combining the previous results gives:

$$J\,\vec{I}_A\cdot\vec{I}_B\,[^1/\sqrt{2}(\alpha\beta+\beta\alpha)] = \ ^1/\sqrt{2}\,(-\,^J/_4\,\alpha\beta + \,^J/_2\,\beta\alpha\ -\,^J/_4\,\beta\alpha + \,^J/_2\,\alpha\beta) = \ ^J/_4\,[^1/\sqrt{2}\,(\alpha\beta + \beta\alpha)]$$
$$J\,\vec{I}_A\cdot\vec{I}_B\,[^1/\sqrt{2}(\alpha\beta-\beta\alpha)] = \ ^1/\sqrt{2}\,(-\,^J/_4\,\alpha\beta + \,^J/_2\,\beta\alpha\ +\,^J/_4\,\beta\alpha - \,^J/_2\,\alpha\beta) = -^{3J}/_4\,[^1/\sqrt{2}\,(\alpha\beta - \beta\alpha)]$$

(c). Use these results to verify the energies of the levels shown in Figure 29.1.13.

Answer: Using the results of part (b), the symmetric and antisymmetric combinations are seen to be eigenfunctions of the spin-spin coupling operator. In other words, the same wave function appears on both sides of each expression. The eigenvalues are $+\,^J/_4$ for the symmetric combination and $-^{3J}/_4$ for the antisymmetric combination, verifying Figure 29.1.13.

<u>16</u>. Using the relationships given in the introduction to the last problem to prove that the spin-spin interaction can be written as:

$$J_{AB}\,\vec{I}_A\cdot\vec{I}_B = J_{AB}\,[\,\hat{I}_{zA}\,\hat{I}_{zB} + \tfrac{1}{2}(\hat{I}_A^+\,\hat{I}_B^- + \hat{I}_A^-\,\hat{I}_B^+)]$$

Answer: Expanding the dot product into separate components:

$$J_{AB}\,\vec{I}_A\cdot\vec{I}_B = J_{AB}\,(\,\hat{I}_{xA}\,\hat{I}_{xB} + \hat{I}_{yA}\,\hat{I}_{yB} + \hat{I}_{zA}\,\hat{I}_{zB}) \qquad 1$$

The z-component remains unchanged. However we note from the previous problem that $\hat{I}_x = \tfrac{1}{2}(\hat{I}^+ + \hat{I}^-)$ and $\hat{I}_y = \tfrac{1}{2}\,i(\hat{I}^+ - \hat{I}^-)$ and:

$$\begin{aligned}\hat{I}_{xA}\,\hat{I}_{xB} + \hat{I}_{yA}\,\hat{I}_{yB} &= \tfrac{1}{2}(\hat{I}_A^+ + \hat{I}_A^-)\tfrac{1}{2}(\hat{I}_B^+ + \hat{I}_B^-) + \tfrac{1}{2}\,i(\hat{I}_A^+ - \hat{I}_A^-)\tfrac{1}{2}\,i(\hat{I}_B^+ - \hat{I}_B^-)\\ &= \tfrac{1}{4}(\hat{I}_A^+ + \hat{I}_A^-)\,(\hat{I}_B^+ + \hat{I}_B^-) - \tfrac{1}{4}\,(\hat{I}_A^+ - \hat{I}_A^-)\,(\hat{I}_B^+ - \hat{I}_B^-)\\ &= \tfrac{1}{4}(\hat{I}_A^+\hat{I}_B^+ + \hat{I}_A^+\hat{I}_B^- + \hat{I}_A^-\hat{I}_B^+ + \hat{I}_A^-\hat{I}_B^-) - \tfrac{1}{4}\,(\hat{I}_A^+\hat{I}_B^+ - \hat{I}_A^+\hat{I}_B^- - \hat{I}_A^-\hat{I}_B^+ + \hat{I}_A^-\hat{I}_B^-) \qquad 2\end{aligned}$$

Cancelling terms gives:

$$\hat{I}_{xA}\,\hat{I}_{xB} + \hat{I}_{yA}\,\hat{I}_{yB} = \tfrac{1}{4}(\hat{I}_A^+\hat{I}_B^- + \hat{I}_A^-\hat{I}_B^+) - \tfrac{1}{4}\,(-\hat{I}_A^+\hat{I}_B^- - \hat{I}_A^-\hat{I}_B^+) = \tfrac{1}{2}(\hat{I}_A^+\,\hat{I}_B^- + \hat{I}_A^-\,\hat{I}_B^+) \qquad 3$$

Substituting Eq. 3 into Eq. 1 gives the final result: $J_{AB}\,\vec{I}_A\cdot\vec{I}_B = J_{AB}\,[\,\hat{I}_{zA}\,\hat{I}_{zB} + \tfrac{1}{2}(\hat{I}_A^+\,\hat{I}_B^- + \hat{I}_A^-\,\hat{I}_B^+)]$

17. Consider the spin-spin coupling of two inequivalent spins. If the difference in chemical shift is much larger than the spin-spin coupling constant then Eq. 29.1.14 is a good approximation. As seen in Figure 29.1.11, the wave functions αα, αβ, βα, and ββ are then good eigenfunctions of the approximate Hamiltonian, Eq. 29.1.14. If the chemical shift difference is comparable to the spin-spin coupling constant, then the exact Hamiltonian must be used, Eq. 29.1.13. Use the results of Problem 15(b) to determine if αα, αβ, βα, and ββ are eigenfunctions of the exact Hamiltonian. If αα, αβ, βα, and ββ are eigenfunctions of the exact Hamiltonian, then they may be used to determine the energies of the final spin levels directly from the eigenvalues, as we did in Figure 29.1.11. If αα, αβ, βα, and ββ are not eigenfunctions of the exact Hamiltonian, then the exact wave functions will be linear combinations of αα, αβ, βα, and ββ. The wave functions must be determined from the secular equation that is based on the exact Hamiltonian.

Answer: The wave functions αα, αβ, βα, and ββ are eigenfunctions of the portion of the Hamiltonian that describes the interaction of the spins with the external magnetic field, which is called the Zeeman interaction:

$$\hat{\mathcal{H}}(\mathit{Zeeman}) = -\,\nu_A\,\hat{I}_{zA} - \nu_B\,\hat{I}_{zB}$$

However, the results of Problem 15(b) show that αβ and βα are not eigenfunctions of the exact spin-spin Hamiltonian:

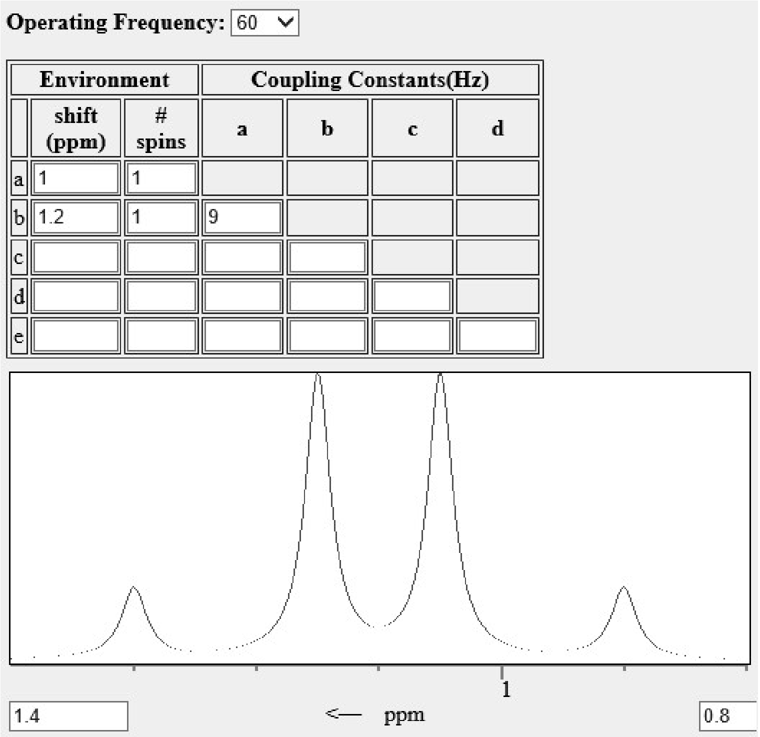
$$J\,\vec{I}_A\cdot\vec{I}_B\,\alpha\beta = -J/4\,\alpha\beta + J/2\,\beta\alpha$$

$$J\,\vec{I}_A\cdot\vec{I}_B\,\beta\alpha = -J/4\,\beta\alpha + J/2\,\alpha\beta$$

In other words just αβ alone does not appear on each side of the first expression and just βα alone does not appear on each side of the second expression. As a result, αβ and βα mix in linear combination to form the eigenfunctions of the exact Hamiltonian in the final results. Computer applications are available to do these exact calculations. The "*JD: Spin-Spin Splitting Simulation*" applet on the course Web site or companion CD is available to do these calculations.

18. Use the "*JD: Spin-Spin Splitting Simulation*" applet (jdplot.html) on the course Web site or companion CD to determine the spectrum of an ^{1}H AB-system. An AB-system is comprised of two inequivalent spin-spin coupled protons, with the difference in chemical shifts between the two protons comparable to the spin-spin coupling constant. Assume the two chemical shifts are 1.00 ppm and 1.20 ppm, with the resonance frequency at 60.000 MHz. Use a spin-spin coupling constant of J = 9.0 Hz. Compare the results to the first-order predictions based on the energy levels derived in Figure 29.1.11 and 29.1.12.

Answer: The input and output from the jdplot.html applet are shown below. The results are summarized in the table, below.



Operating Frequency: 60

	Environment		**Coupling Constants(Hz)**			
	shift (ppm)	**# spins**	**a**	**b**	**c**	**d**
a	1	1				
b	1.2	1	9			
c						
d						
e						

1.4

0.8

```
Transitions (ppm) and Intensities:
  1.05   :      1.6
  1.3    :      0.4
  1.15   :      1.6
  0.9    :      0.4
```

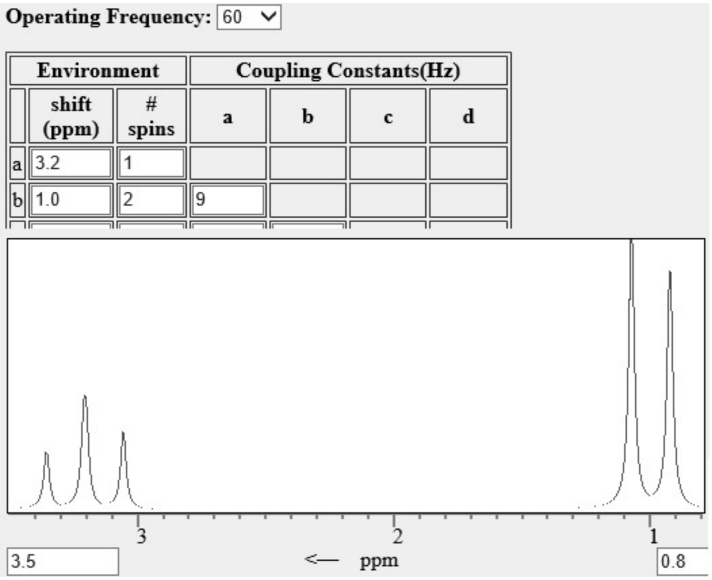
The first-order prediction corresponds to two doublets, the first centered at 1.00 ppm and the second centered at 1.2 ppm. The spin-spin coupling constant of 9.00 Hz at a resonance frequency of 60.000 MHz corresponds to 9.00/60.000x10^6 (1x10^6 ppm) = 0.15 ppm. The first-order transitions are at $\nu_A \pm J_{AB}/2$ and $\nu_B \pm J_{AB}/2$, as given in the table, below. The first-order transition intensities are all the same, 1:1:1:1.

Proton	First Order	1st order (ppm)	Exact (ppm)	Exact – 1st order	Intensity
A	$\nu_A + J_{AB}/2$	1.275	1.3	0.025	0.4
	$\nu_A - J_{AB}/2$	1.125	1.15	0.025	1.6
B	$\nu_A + J_{AB}/2$	1.075	1.05	-0.025	1.6
	$\nu_A - J_{AB}/2$	0.925	0.9	-0.25	0.4

The differences between the exact spin-spin splitting pattern and the first-order prediction are called second-order effects. One second-order effect for an AB-spectrum is that the doublets are no longer centered on the chemical shift values. This effect is shown by the differences shown in the table with the heading: Exact – 1st order. The A-doublet transitions move down-field relative to the chemical shift, which is 1.20 ppm. The B-doublet transitions move up-field relative to the chemical shift, which is 1.00 ppm. The other second-order effect is that the "inner" transitions are higher in intensity than the "outer" transitions. The stronger the second-order effect the larger the difference in intensity of the inner and outer transitions in each doublet. This shift in intensity is commonly observed with multiplets of all kinds, not just doublets.

19. A surprising result of strong second-order effects in spin-spin splitting is that more transitions appear than expected based on first-order analysis. Consider a ^{1}H AB_2 pattern as an example. An AB_2 pattern corresponds to two chemical environments, A with one proton and B with two protons, with the difference in chemical shifts between the two environments comparable to the spin-spin coupling constant. In comparison, an AX_2 pattern corresponds to the same proton distribution but with the difference in chemical shifts between the two environments much larger than the spin-spin coupling constant. (a). Use the "*JD: Spin-Spin Splitting Simulation*" applet (jdplot.html) on the course Web site or companion CD to determine the spectrum of an ^{1}H AX_2-system. Assume the two chemical shifts are 3.20 ppm and 1.00 ppm, with the resonance frequency at 60.000 MHz. Use a spin-spin coupling constant of J = 9.0 Hz. Does the resulting spectrum agree with the first-order prediction? (b). Determine the spectrum of an ^{1}H AB_2-system. Assume the two chemical shifts are 1.20 ppm and 1.00 ppm, with the resonance frequency at 60.000 MHz. Once again, use a spin-spin coupling constant of J = 9.0 Hz. Decrease the line width to 0.75 Hz to better observe the number of transitions. How many transitions are evident?

Answer: (a). The input and output from the jdplot.html applet for the AX_2 case are shown below.

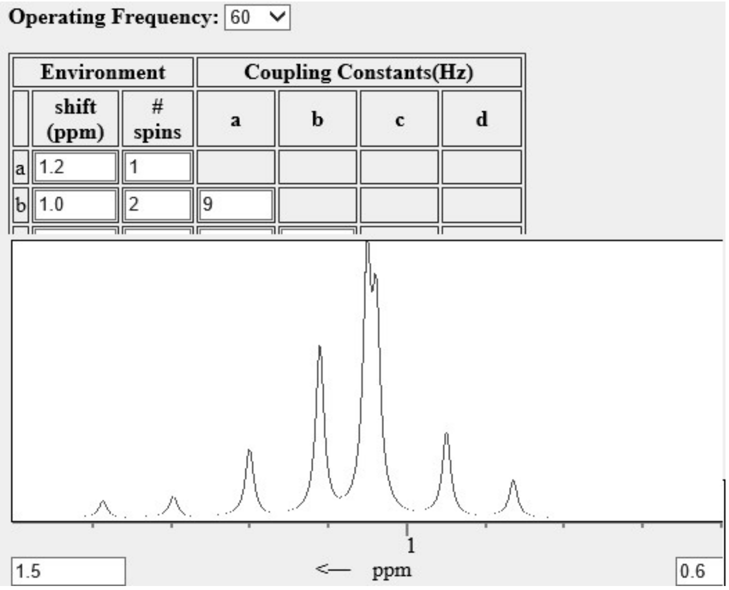


Operating Frequency: 60

	Environment		Coupling Constants(Hz)			
	shift (ppm)	# spins	a	b	c	d
a	3.2	1				
b	1.0	2	9			

The first-order prediction is an A-triplet and B-doublet, based on the n + 1 near-neighbor rule. This expectation is observed giving a total of <u>five</u> observed transitions. [Replotting the spectrum at 0.25 Hz line width shows that the middle two peaks in the triplet don't quite overlap, giving six transitions at very high resolution. However, a resolution of 0.25 Hz is hard to achieve because 0.25 Hz resolution requires very good magnet homogeneity.]

(b). The input and output from the jdplot.html applet for the AB_2 case are shown below.



Operating Frequency: 60

	Environment		Coupling Constants(Hz)			
	shift (ppm)	# spins	a	b	c	d
a	1.2	1				
b	1.0	2	9			

For the AB_2 case <u>eight</u> transitions are apparent. The numerical listing has nine transitions, however. The transition at 0.703 ppm has low intensity. This weak transition is likely to be lost in the baseline noise in practical spectra.

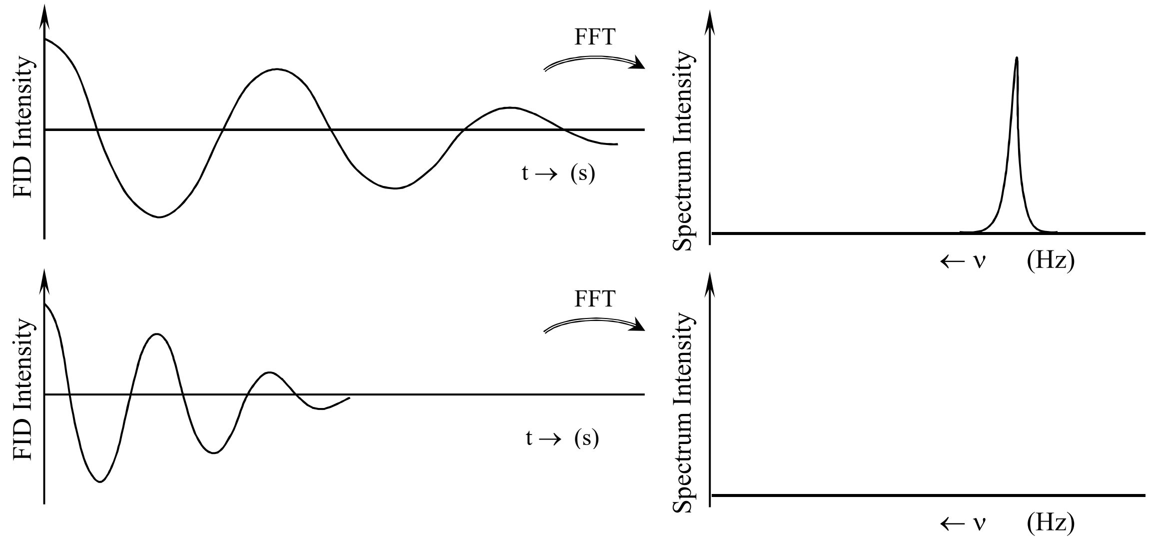
The spectra of aromatic compounds is often complicated by second-order effects, because the chemical shift differences among aromatic chemical environments is often small and the spin-spin coupling constants can be large. Second-order effects are lessened by high-field instruments.

20. In pulsed NMR, the free induction decay of all the chemical shifts in the spectrum are excited by a short pulse at a single frequency. For example, the proton chemical shift range is ~5000 Hz at a resonance frequency of 400.00 MHz, while the pulse is at a single frequency of 400.000 MHz. Explain how all the chemical shifts in the spectrum can be excited by a short pulse at a single frequency. Assume the pulse length is 15.0 μs.

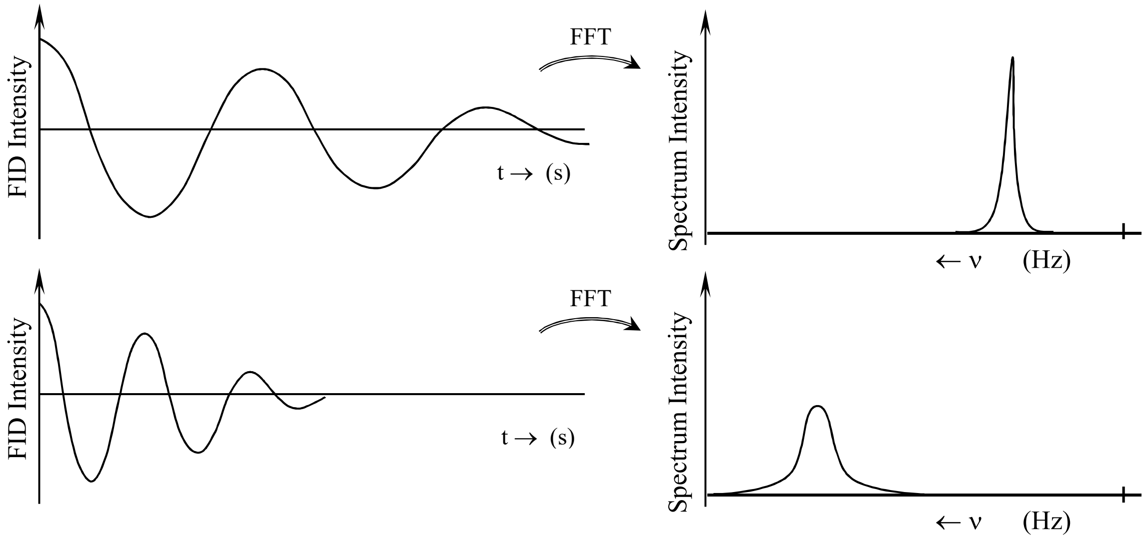
Answer: The Fourier transform of a short pulse has a wide range of component frequencies, even though the pulse itself is constructed by chopping a sine or cosine wave of a single central frequency. In other words, to reconstruct the rectangular pulse, the superposition of a wide range of frequencies is necessary to reproduce the time dependence of the pulse. The range of frequencies is approximately characterized by the width of the pulse in Hz to the first nulls of the Fourier transform, Figure 27.3.3, $\Delta\nu = 1/t_p$ where t_p is the duration of the rectangular pulse. If the pulse length is 15.0 μs, the frequency range to the first nulls is $1/15.0\text{x}10^{-6}$ s = $6.67\text{x}10^{4}$ Hz, which is roughly a factor of ten larger than the expected ^{1}H-chemical shift range.

Note that the chemical shift range of ^{13}C is roughly 20-fold larger than the range of ^{1}H shifts. As a result, care must be taken in ^{13}C experiments to maintain short pulse widths. To minimize the effects of the bandwidth of the excitation pulse, the frequency of the NMR transmitter is usually set to the middle of the chemical shift range, rather than near the TMS resonance frequency.

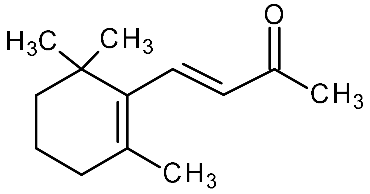
21. Qualitatively sketch the relative changes in the spectra obtained by Fourier transformation of the second FID as compared to the first:



Answer: The frequency of the second FID is higher than the first (by about a factor of two). The spectrum then has the transition at higher frequency, or to the left since the frequency increases to the left. The decay envelope of the second peak is shorter than the first; the second FID decays to zero faster than the first. As a result the FFT requires a broader range of frequencies to reproduce the time dependence. Assuming the envelopes of the FIDs are approximately exponential, e^{-t/T_2}, then the transition full width at half height in the spectrum is $^1/_{\pi T_2}$. The inverse relationship shows that quicker decays in the time domain correspond to broader transitions in the frequency spectrum. Both FIDs are initially equally intense, so to compensate for the broader transition, the second FID gives a peak with lower maximum intensity. The integral remains the same. In fact, the initial intensity of the FID gives the integrated intensity of the frequency spectrum (including multiple peaks if present).



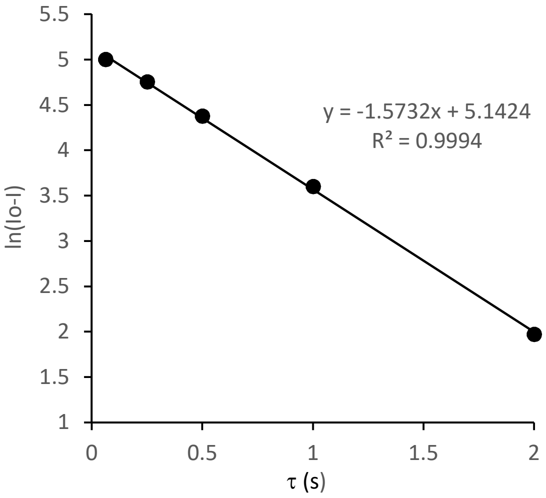
22. The inversion recovery sequence was used to determine the ^1H spin-lattice relaxation time of the geminal-dimethyl groups of β-ionone. The data is reproduced below. Determine the T_1. (Don't bother to get the uncertainty using linest(), just use a linear trendline.)



τ (s)	0.0625	0.2500	0.5000	1.000	2.000	8.000
intensity	-64.8	-32.2	4.43	47.4	76.9	84.1

Answer: The linearized form, Eq. 29.5.13, gives the slope as $-1/T_1$ of the plot of $\ln(I_o - I)$ vs. τ, where the measured transition intensity is directly proportional to the magnetization. A spreadsheet was set up to do the linear curve fit.

I_o =	84.1	
τ (s)	I	$\ln(I_o\text{-}I)$
0.0625	-64.8	5.003275
0.2500	-32.2	4.756173
0.5000	4.43	4.377893
1.0000	47.4	3.602777
2.0000	76.9	1.974081



The T_1 is then 1/1.573 s^{-1} = 0.636 s

23. Derive Eq. 29.5.3 by integrating Eq. 29.5.2.

Answer: Spin-lattice relaxation is a first order kinetic process, Eq. 29.5.2:

$$\frac{dM_z}{dt} = -\frac{1}{T_1}(M_z - M_o)$$

Separating variables (*General Pattern* ℘1: *Simple Exponential Processes*):

$$\int_0^{M_z} \frac{dM_z}{(M_z - M_o)} = -\int_0^t \frac{1}{T_1}\,dt$$

The integrals give: $\ln(M_z - M_o)\Big|_0^{M_z} = -\frac{t}{T_1}$

$$\ln(M_z - M_o) - \ln(-M_o) = -{}^{t}/_{T_1}$$

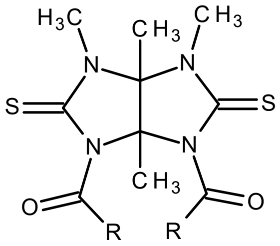
Combining the logarithmic terms gives: $\ln\left(\frac{M_z - M_o}{-M_o}\right) = -{}^{t}/_{T_1}$

Exponentiation of both sides of the relationships gives: $\left(\frac{M_z - M_o}{-M_o}\right) = e^{-{}^{t}/_{T_1}}$

Cross multiplication results in: $M_z - M_o = -M_o\, e^{-{}^{t}/_{T_1}}$

while solving for the magnetization gives: $M_z = M_o - M_o\, e^{-{}^{t}/_{T_1}} = M_o\,(1 - e^{-{}^{t}/_{T_1}})$

24. Consider the following molecule with *tert*-butyl groups as the R-groups:

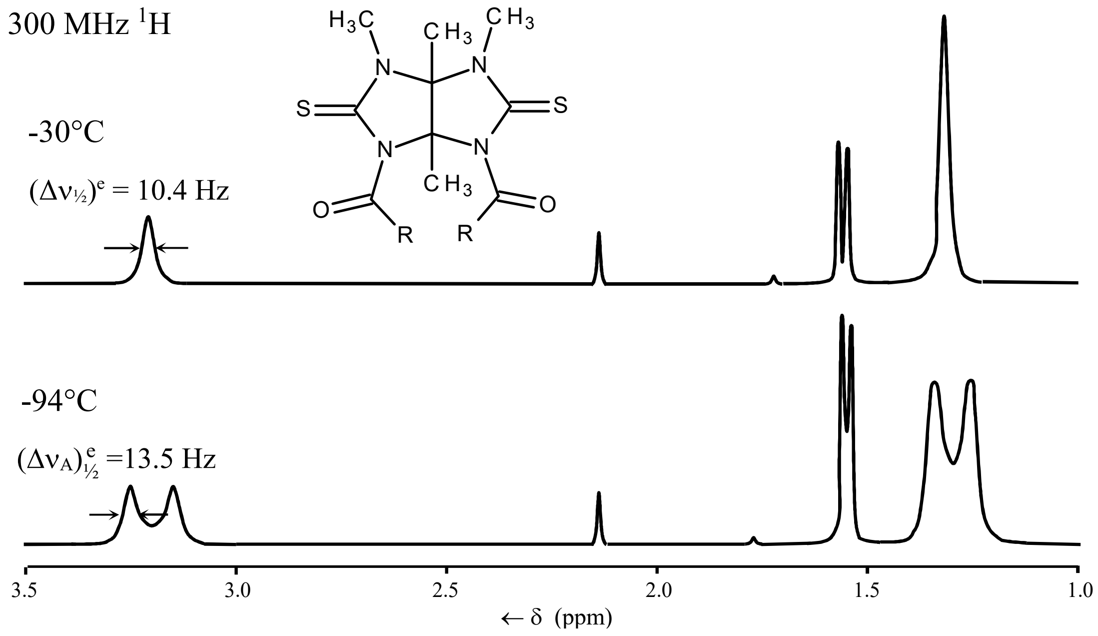


Steric interactions of the *tert*-butyl groups prevent the amide bonds from being planar with each respective ring. The N-methyl groups are not equivalent, because the amide groups are twisted out of plane.[2,3] Rotation about the amide C-N bonds exchanges the chemical environment of the N-methyl resonances. Outline the experimental and data analysis steps necessary to find the activation energy of the chemical exchange process for twisting about the amide bonds.

Answer: (1). The ^{1}H-spectra of the compound are acquired as a function of temperature.
(2). Two transitions that correspond to the same proton in the two different chemical environments are determined by assigning the peaks in the spectrum. As an aid to assigning the peaks, the assumption is that at low temperature these two peaks will be equally broadened, that the peak positions approach each other with an increase in temperature, and that two peaks coalesce at high temperature.
(3). A low temperature that causes no additional peak separation and narrow transitions is used to determine the chemical shift difference between the two environments giving $\Delta\nu_o = \nu_A - \nu_B$. The width of the peaks is used to find the effective spin-spin relaxation time, T_{2A}', using Eq. 29.6.4.
(4). Eqs. 29.6.4, 29.6.6, 29.6.7, 29.6.8, and 29.6.10 are used to estimate the exchange rate constant. See Example 29.6.1
(5). Based on Eq. 3.5.3, a plot of ln k vs. 1/T is constructed giving the activation energy from the slope as: slope = $-E_A/R$.

Curve fitting to the exact line shape is a preferable approach to using the approximate formulas for k. Many computer programs are available for this purpose including the "Chemical Exchange Lineshapes" applet (exchpl.html) on the course Web site or companion CD.

25. The ^{1}H-NMR spectra of the N-methyl compound shown below are plotted at -94°C and -30°C at 300 MHz. The R-groups are *tert*-butyl groups, which force the amide groups to be twisted out of plane, which makes the two N-methyl groups inequivalent. The spectra are taken in deuterated methylene chloride solution. The resonances near 3.2 ppm are the N-methyl groups. The difference in chemical shift at low temperature for the N-methyl groups is 35.0 Hz. Assume that the effective T_2' is 1.5 s. At -94°C, the full-width at half-height of one of the two N-methyl transitions in the exchanging doublet is 13.5 Hz. The coalescence temperature is -70.5°C (spectrum not shown). The width of the coalesced N-methyl peak at -30°C is 10.4 Hz. Calculate the activation energy for the twisting motion of the amide groups.[2,3]



Answer: The effective T_2' of 1.5 s gives the line-width in the absence of exchange, Eq. 29.6.4:

$$(\Delta\nu_A)^\circ_{½} = \frac{1}{\pi T_{2A}'} = \frac{1}{\pi\ 1.5\ \mathrm{s}} = 0.21\ \mathrm{Hz}$$

In intermediate exchange, at -94°C, the line width is 13.5 s^{-1}, so that Eq. 29.6.6 gives:

$$k \cong \frac{\pi}{\sqrt{2}}\left[(\Delta\nu_A)^e_{½} - (\Delta\nu_A)^\circ_{½}\right] = \frac{\pi}{\sqrt{2}}[13.5\ \mathrm{s^{-1}} - 0.21\ \mathrm{s^{-1}}] = 29.5\ \mathrm{s^{-1}}$$

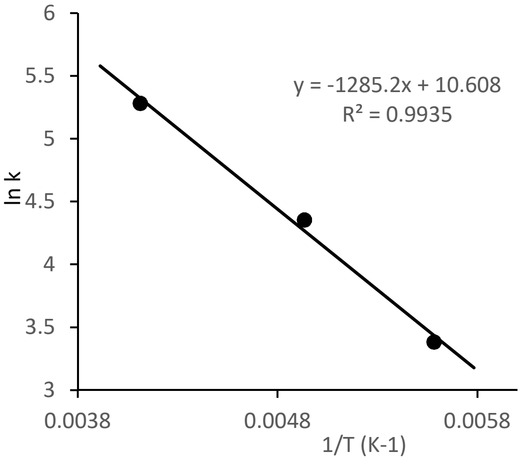
At coalescence, -70.5°C, using Eq. 29.6.8: $k \cong \frac{\pi\Delta\nu_o}{\sqrt{2}} = \frac{\pi\ 35.0\ \mathrm{s^{-1}}}{\sqrt{2}} = 77.8\ \mathrm{s^{-1}}$

In fast exchange, at -30°C, the line width is 10.0 Hz, so that Eq. 29.6.10 gives:

$$k \cong \frac{\pi\Delta\nu_o^2}{2}\ \frac{1}{\left[(\Delta\nu_{½})^e - (\Delta\nu_A)^\circ_{½}\right]} = \frac{\pi(35.0\ \mathrm{s^{-1}})^2}{2}\ \frac{1}{(10.0\ \mathrm{s^{-1}} - 0.21\ \mathrm{s^{-1}})} = 197\ \mathrm{s^{-1}}$$

Assuming Arrhenius temperature dependence, Eq. 3.5.3, a plot of ln k vs. 1/T is constructed giving the activation energy from the slope as: slope = – E_A/R as shown in the following spread sheet:

T (°C)	T (K)	k (s^{-1})	1/T (K^{-1})	lnk
-94	179.15	29.5	0.00558	3.3844
-70.5	202.65	77.8	0.00493	4.3541
-30	243.15	197	0.00411	5.2832
slope	-1285.2	10.61	intercept	
±	104.19	0.512	±	
R^2	0.9935	0.108	s(y)	
F	152.18	1	dof	
ss_{reg}	1.7913	0.012	ss_{res}	



The activation energy is $E_A = -R$ slope = 10.7 kJ mol^{-1}.

26. Create an Excel spreadsheet to do the time averages to determine the correlation function for a random signal. Generate the random signal at equal time increments, of length Δt, with varying persistence, p:

$$f(t + \Delta t) = f(t) + (1 - p)[(2^{*}RND() - 1) - f(t)]$$

where RND() is the built-in random number generator in Excel and (2*RND() – 1) generates a random number between -1 and +1. Plot $f(t)$ and the corresponding correlation function. Hints for setting up the spreadsheet are given below. Use four different values of the persistence: p = 0, 0.2, 0.5, and 0.8. With p = 0, the signal is purely random with no correlation, $f(t + \Delta t) = (2^{*}RND() - 1)$. Increasing p gives a signal that is increasingly slowly varying. For each value of p, generate several different plots. The results will be different in each plot; you can estimate the equivalent of the ensemble average by "averaging" the successive plots by eye. To generate each new set of random numbers, change the value in any arbitrary unused cell in the spreadsheet. Any unused cell will do, the cell chosen for generating updates shouldn't be used in the main part of the spreadsheet. From your comparison of the results for the different values of p, discuss the relationship among the persistence, the appearance of $f(t)$, and the observed approximate correlation time. You don't need to find a numerical value of the correlation time, discuss the results qualitatively.

An example spreadsheet is shown below. Only the first few rows and the final three rows are shown, to save space. Rows 2-5 and column B are input directly, that is with no formulas. The main time variable t in column B runs in 5 ns increments up to 200 ns in row 46. Seven values of the time delay, τ, are specified in row 3. The number of rows that correspond to the chosen τ value are entered in row 4. For example, 3 rows are required to give a τ delay of 15 ns.

A1	B	C	D	E	F	G	H	I	J
2	persistence=	0.5							
3		τ = (ns)	0	5	10	15	20	25	30
4		offset	0	1	2	3	4	5	6
5	t (ns)	f(t)	f(t+τ)f(t)	f(t+τ)f(t)	f(t+τ)f(t)	f(t+τ)f(t)	f(t+τ)f(t)	f(t+τ)f(t)	f(t+τ)f(t)
6	0	-0.8037	0.6459	-0.0719	-0.3803	-0.0622	-0.1562	0.2355	0.3560
7	5	0.0895	0.0080	0.0423	0.0069	0.0174	-0.0262	-0.0396	-0.0567
8	10	0.4731	0.2238	0.0366	0.0919	-0.1386	-0.2096	-0.2997	-0.3480
	⋮								
46	200	0.0258	0.0007						
47									
48		average=	0.1326	0.0539	0.0126	0.0180	-0.0133	-0.0164	0.0163

The starting random value of the signal, $f(t)$, at time zero is in cell C6: =(2*RND()-1)

The subsequent value of $f(t)$ in cell C7 is: = C6 + (1-\$C\$2)*((2*RND()–1)–C6)

This formula is “filled down” to fill in the values for the remaining rows in column C. The product $f(t+\tau)\,f(t)$ is created using the Excel OFFSET function. The formula in cell D6 is:

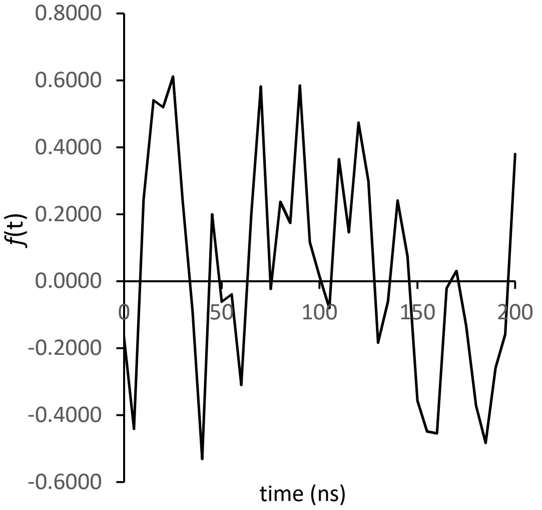
=OFFSET(\$C6:\$C\$46,D\$4,0,1,1)*\$C6

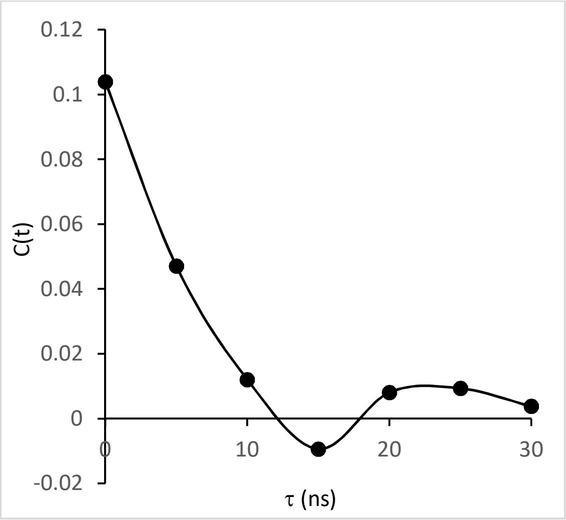
The offset is specified in row 4. Make sure to set up the absolute references exactly as shown. This formula is “filled right” for columns E-J and then “filled down” for all the rows up to 46. Some cells near the bottom of the table will read “0” after filling, because there is insufficient data to complete the required calculation for long τ-values. Delete the contents of these zero cells. The averages of each column are calculated in row 48 giving $\overline{f(t+\tau)\,f(t)}$. The formula in cell D48 is: =AVERAGE(D6:D46)

This cell is “filled right” for the remaining columns E-J. Construct a plot of column C versus column B to see the time-varying random signal. Construct a plot of the averages from row 48 on the vertical axis against the τ-values on the horizontal axis.

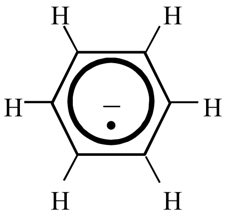
Answer: The spreadsheet gives a different result each time. Changing the number in any cell starts the random number generator anew. You need to do several plots and then average the results by eye. In the correlation plot shown below, the solid line is added to guide the eye from point to point. With a persistence of 0.0, no correlation exists beyond the initial $C(0) = \overline{f(t)^2}$ value. In other words successive plots give results that cancel for $C(\tau)$ with $\tau > 0$. One result for a persistence of 0.5 is shown below. The $f(t)$ signal varies more slowly than with $p = 0$. Successive correlation function plots show an approximately exponential decay. With the persistence of 0.8, $f(t)$ varies slowly and the exponential decay of the correlation function is slow and obvious from plot to plot. Bigger persistence gives a slower decay of the correlation function and a correspondingly longer correlation time for the exponential decay.

The method that we have chosen to generate the random signal is a poor approximation to generate a truly stationary, zero mean, random time-varying signal. However, the simple formula that we have used is sufficient for short correlation times for this simple demonstration.





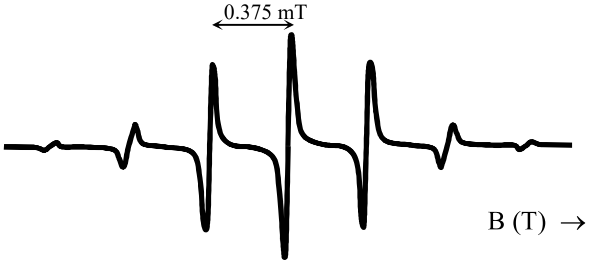
27. The benzene radical anion, $C_6H_6^-$, is produced at low temperature by reduction of benzene with an alkali metal. Predict the multiplicity of the ESR transition of the benzene radical anion and the corresponding transition intensities of the components of the multiplet.



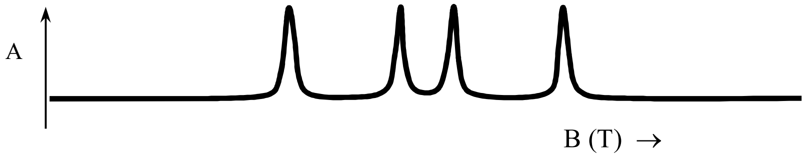
Answer: The π-system of the benzene radical anion is completely delocalized. As a result the six protons are magnetically equivalent giving a hyperfine structure multiplicity of n+1 = 7. The hyperfine coupling constant is 0.375 mT or 3.75 Gauss.[1] Using Pascal's triangle, the line intensities are 1:6:15:20:15:6:1:

n	n+1	Multiplet	Intensity ratios
0	1	Singlet	1
1	2	Doublet	1 1
2	3	Triplet	1 2 1
3	4	Quartet	1 3 3 1
4	5	Quintet	1 4 6 4 1
5	6	Sextet	1 5 10 10 5 1
6	7	Septet	1 6 15 20 15 6 1

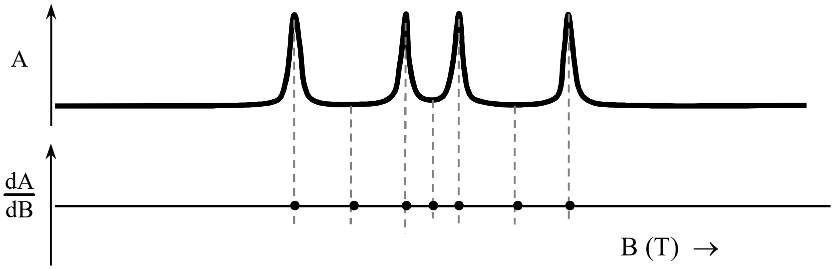
The derivative ESR spectrum is shown below.[1]



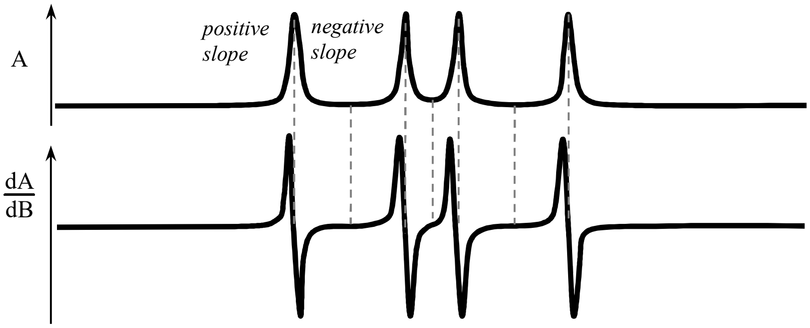
28. Sketch by hand the ESR derivative spectrum of a doublet of doublets. (Note the positions of the maxima in the absorption spectrum as a basis for the zero-derivative points on the plot.)



Answer: The derivative crosses zero at the maximum of each transition. Between each transition the spectrum also has a region of zero slope. Note these zero-slope points on your initial sketch. The derivative spectrum must pass through these points:



Consider starting at low field, on the left side of the spectrum. Scanning to higher field, the absorbance first increases giving a positive slope. After the maximum, the slope is negative and then zero until the next transition begins.

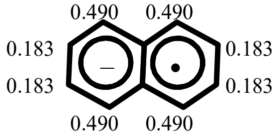


29. The π-systems of the aromatic radicals are extensively delocalized. If the nuclei of the aromatic radical lie in the x-y plane, then the π-orbitals are constructed from the overlap of $2p_z$-

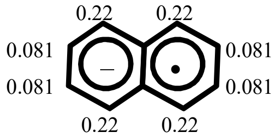
orbitals. The hyperfine interaction, a_H, is then approximately proportional to the unpaired electron density in the $2p_z$-orbital at each C-H, which is denoted ρ_π:

$$a_H = Q\rho_\pi \qquad \text{(aromatic hydrocarbons)}$$

where Q is a proportionality constant derived from model compounds. The hyperfine interaction in the benzene radical anion is 0.375 mT, or 3.75 G; assuming a π-electron density of $^1/_6$ gives Q = 2.25 mT = 22.5 Gauss. The hyperfine coupling constants for the naphthalene radical anion are given below. Calculate the π-electron density on the two types of ring positions.

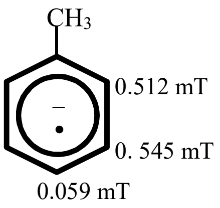


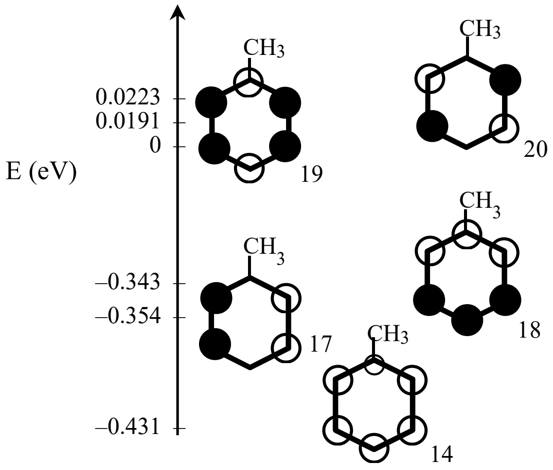
Answer: Assuming the value of Q derived from the benzene radical anion, the π-electron densities are given by $\rho_\pi = a_H/Q$:



As a result the reactivity of the two types of ring positions is expected to differ. This expression is called the McConnell relationship.

<u>30.</u> The hyperfine coupling constants from the ESR spectra of the radical anion of toluene are shown below. The AM1 level π-molecular orbitals for toluene as a neutral molecule are also diagrammed below. Are the hyperfine constants consistent with the π-molecular orbitals? Orbital 18 is the HOMO and orbital 19 is the LUMO. (In benzene, MO 17 and 18 are degenerate and MO 19 and 20 are degenerate.)

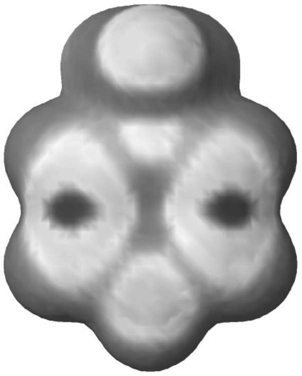




Answer: The extra electron in the anion goes into the LUMO, MO-19. MO-19 has large coefficients of the same sign on the *ortho*- and *meta*- positions. With regard to the orbital signs and coefficients, the *ortho*- and *meta*- positions are equivalent and distinct from the para-position, in agreement with the hyperfine coupling constants. You should do the AM1 calculations (we used MOPAC) for yourself to verify the molecular orbitals listed here.

31. The ESR hyperfine coupling constants and low-lying π-molecular orbitals of the toluene anion radical are given in the previous problem. Using Spartan or Gaussian, build and geometry minimize the toluene radical anion (doublet state) at the HF 3-21G level or higher. Request the molecular orbital coefficients and then generate the "radical density" or "spin density" surface for the toluene radical anion. Does this unpaired electron density surface agree with the hyperfine coupling constants and molecular orbitals listed in the previous problem? (Note that the π-molecular orbital energies depicted in the previous problem are for neutral toluene.)

Answer: The "radical density" plot generated at the HF 3-21G level using the WebMo visualization environment is shown below. Enhanced unpaired spin density resides between the *ortho*- and *meta*- positions. In other words, the largest unpaired electron spin density agrees with MO-19 shown above and the experimental hyperfine constants.



The spin density map using Spartan is even clearer, essentially reproducing the LUMO shown in the previous problem. These predictions are validated at higher theory levels including B3LYP.

32. Determine if the following statements are true or false. If the statement is false, describe the changes that are necessary to make the statement true, if possible. If the statement is true but too restrictive, give the more general statement.

(a). The spacing in ppm between the component transitions of a spin-spin splitting multiplet is constant with increasing field strength.

Answer: *False*. The spacing in Hz between the component transitions of spin-spin splitting multiplets is constant with increasing field strength. However, as the field strength increases, the resonance frequency increases, and the spacing between transitions in a multiplet decrease when expressed in ppm. A J of 9 Hz corresponds to 0.15 ppm at a 60 MHz resonance frequency and only 0.018 ppm at 500 MHz. In other words, the multiplet looks narrower at higher field when compared to the chemical shift differences. Another way of rationalizing this effect is to note that a 10 ppm sweep width at 60 MHz is 600 Hz and the same sweep width at 500 MHz is 5000 Hz. If the spectra at 60 MHz and 500 MHz are plotted on the same size paper, then a J of 9 Hz gives transitions that appear closer together at the higher sweep width. See Problems 2 and 3 for numerical examples.

(b). In ^{1}H NMR spectroscopy, for a given spin with n-coupled neighboring protons the minimum number of transitions in the multiplet is n+1 and the maximum number of transitions in the multiplet is 2^n. Assume the given spin has a unique chemical shift.

Answer: *True*. If the n-neighbors are equivalent then an n+1 multiplet arises. If the n-neighbors are all inequivalent then the given resonance is split into a doublet by each of the n-neighbors giving 2^n transitions in the multiplet. For the n-equivalent case the multiplet transition intensities are given by Pascal's triangle. For the inequivalent case, all transitions are equally intense.

(c). The differences between the exact spin-spin splitting pattern and the first-order prediction are called second-order effects. The exact spin-spin splitting pattern is based on $J_{AB}\,\vec{I}_A\cdot\vec{I}_B$ while the first-order prediction is based on $J_{AB}\,\hat{I}_{zA}\,\hat{I}_{zB}$. Second-order effects are more important at high field (e.g. 500 MHz) than at low field (e.g. 60 MHz).

Answer: *False*. Even though chemical shifts in ppm are identical with increasing resonance frequency, the chemical shifts in Hz are directly proportional to field strength. As a result the difference in resonance frequency, $\nu_A - \nu_B$ in Hz, increases with resonance frequency (field strength). The important comparison for the extent of second-order effects is $\nu_A - \nu_B$ as compared to J. First-order predictions are sufficient if $|\nu_A - \nu_B| >> J$. As a result, second-order effects are less important at high field than at low field. In fact, the simplification of spin-spin splitting patterns at high field is one of the most important advantages of high field instruments.

(d). The spin-lattice relaxation time of a given chemical environment in a ^{1}H-spectrum increases with an increase in temperature. Assume that the motion of the molecule that is most important for relaxation is faster than the resonance frequency at the starting temperature.

Answer: *True*. An increase in temperature increases the motions of the molecule, shortening the correlation time. However, a decrease in correlation time can either increase or decrease the relaxation rate, Figure 29.5.6. If the motion at the original temperature is faster than the resonance frequency, the correlation time is shorter than $1/2\pi\nu_o$. The initial state is to the left of the minimum in the figure. Further shortening of the correlation time moves the system further to the left, increasing the relaxation time. In other words, if motions are too fast to begin with, further increases won't improve the efficiency of the relaxation, thus increasing T_1.

(e). Consider chemical exchange between two inequivalent chemical environments. The line widths decrease with an increase in temperature if the system is initially at a temperature that is below the coalescence temperature.

Answer: *False*. As temperature increases, the exchange rate constant increases. The line widths increase with an increase in temperature if the system is starting at a temperature that is below the coalescence temperature. The two lines broaden until they strongly overlap with increasing exchange rate constant. At temperatures higher than the coalescence temperature, increases in temperature again increase the exchange rate. As the exchange rate increases the lines collapse to the average chemical shift and the line width decreases to the extreme narrowing limit.

Literature Cited:

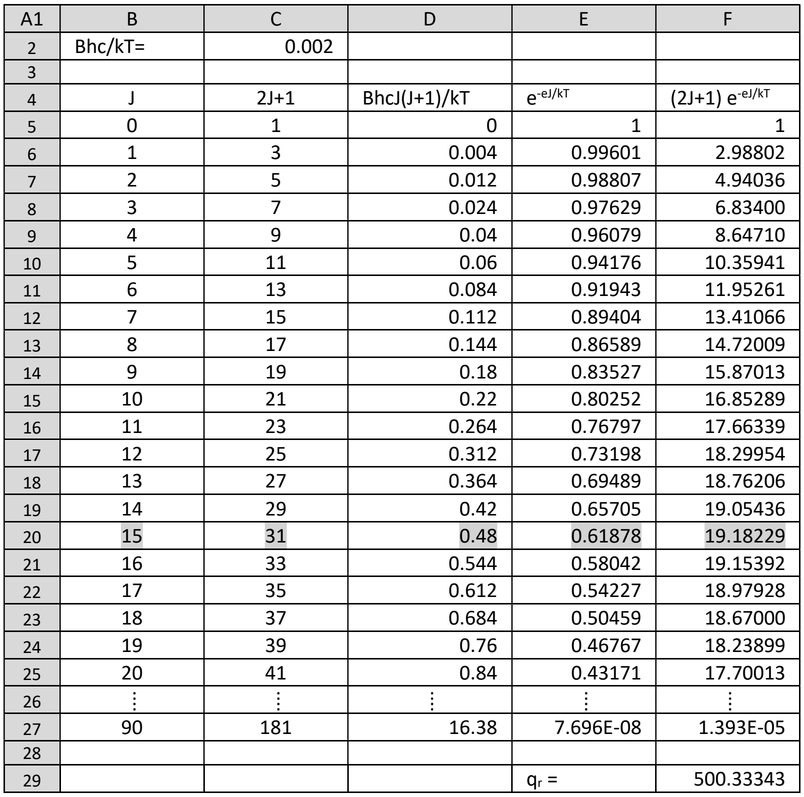
1. A. Carrington, A. D. McLachlan, *Introduction to Magnetic Resonance*, Harper & Row, New York, NY, 1967. pp. 182-194.
2. A. D. Bain, "Chemical Exchange NMR," *Prog. in N.M.R.*, **2003**, *43*, 67-71.
3. P. A. Duspara, C. F. Matta, S. I. Jenkins, P. H. M. Harrison, "Twisted Amides: Synthesis and Structure of 1,6-Dipivaloyl-3,4,7,8- tetramethyl-2,5-dithioglycoluril," *Org. Lett.*, **2001**, *3(4)*, 495–498.

Chapter 30 Problems: Statistical Mechanics

1. For a diatomic molecule, the rotational energy is $\varepsilon_J = \tilde{B}hc\ J(J+1)$. (a.) Evaluate the rotational partition function of a heteronuclear diatomic molecule at 298.15 K by numerically summing the Boltzmann weighting factors over many energy levels in a spreadsheet. Take $\tilde{B}hc/kT = 0.00200$. The degeneracy of each level is $g_J = 2J + 1$. (b.) Compare your numerical answer to the partition function using the high temperature approximation: $q_r = kT/(\sigma\tilde{B}hc)$. (c). Which rotational level has the maximum population of molecules? Why?

Answer: The plan is to note that summing over energy levels, the Boltzmann weighting factors are in the form $(2J + 1)e^{-\varepsilon J/kT}$, with $\varepsilon_J = \tilde{B}hc\ J(J+1)$.

(a). The Excel spreadsheet to accomplish the sums is given below. The sum from J = 0 to J =90 is required to find a five-significant figure value for the partition function. Not all rows are shown.



A1	B	C	D	E	F
2	Bhc/kT=	0.002			
3					
4	J	2J+1	BhcJ(J+1)/kT	$e^{-eJ/kT}$	$(2J+1)\ e^{-eJ/kT}$
5	0	1	0	1	1
6	1	3	0.004	0.99601	2.98802
7	2	5	0.012	0.98807	4.94036
8	3	7	0.024	0.97629	6.83400
9	4	9	0.04	0.96079	8.64710
10	5	11	0.06	0.94176	10.35941
11	6	13	0.084	0.91943	11.95261
12	7	15	0.112	0.89404	13.41066
13	8	17	0.144	0.86589	14.72009
14	9	19	0.18	0.83527	15.87013
15	10	21	0.22	0.80252	16.85289
16	11	23	0.264	0.76797	17.66339
17	12	25	0.312	0.73198	18.29954
18	13	27	0.364	0.69489	18.76206
19	14	29	0.42	0.65705	19.05436
20	15	31	0.48	0.61878	19.18229
21	16	33	0.544	0.58042	19.15392
22	17	35	0.612	0.54227	18.97928
23	18	37	0.684	0.50459	18.67000
24	19	39	0.76	0.46767	18.23899
25	20	41	0.84	0.43171	17.70013
26	⋮	⋮	⋮	⋮	⋮
27	90	181	16.38	7.696E-08	1.393E-05
28					
29				q_r =	500.33343

Cell D5 is “=$C$2*B5*(B5+1)”. Cell E5 is “=EXP(-D5)”. Cell F5 is “=C5*E5”.

(b). For a heteronuclear diatomic, the symmetry number is one, $\sigma = 1$, since rotation by 180° gives a distinguishable state. The high temperature approximation then gives the rotational partition function as $q_r = kT/(\sigma\tilde{B}hc) = 1/0.00200 = 500.0$. The exact result is slightly higher at 500.333.

(c). The level with the maximum population is J = 15. While the Boltzmann distribution gives an exponentially decreasing probability of occupation of a given <u>state</u> with increasing J, the degeneracy increases with increasing J. The product of a decreasing function and an increasing function has a maximum at intermediate value.

2. The fundamental vibration frequency for $H^{35}Cl$ is 2885.3 cm^{-1}. Calculate the ratio of the number of molecules in the first excited vibrational state to the number in the ground vibrational state at 298.2 K.

Answer: The plan is to note that the ratio is given by Eq. 8.10.8 and that at 298.2 K kT/hc = 207.224 cm^{-1}.

The Boltzmann probability of being in state i is: $p_i = n_i/N = e^{-\varepsilon_i/kT}/q$. The ratio of the number of molecules in states j and i is given by the ratio of the Boltzmann probabilities:

$$\frac{n_j}{n_i} = \frac{e^{-\varepsilon_j/kT}/q}{e^{-\varepsilon_i/kT}/q} = e^{-(\varepsilon_j - \varepsilon_i)/kT} = e^{-\Delta\varepsilon/kT} \qquad \text{with } \Delta\varepsilon = \varepsilon_j - \varepsilon_i$$

For the first two vibrational states, $\Delta\varepsilon = h\nu_o$, giving:

$$\frac{n_1}{n_o} = e^{-hc\tilde{\nu}_o/kT} = e^{-2885.3\ \text{cm}^{-1}/207.224\ \text{cm}^{-1}} = 8.976\text{x}10^{-7}$$

In other words, about one in a million are in the first excited vibrational state at room temperature.

3. The rotational constant for the linear molecule H–C≡N is 1.4782 cm^{-1}.[2] Calculate the ratio of the number of molecules in excited rotational level J = 3 to the number in the ground rotational level J = 0 at 298.2 K. [Hint: take the rotational degeneracy 2J + 1 into account.]

Answer: The plan is to note that the degeneracy is 2J + 1 and that at 298.2 K the effective temperature is kT/hc = 207.224 cm^{-1}. The ratio without taking degeneracy into account is given by Eq. 8.10.8

The Boltzmann probability of being in level i is: $p_i = n_i/N = g_i\, e^{-\varepsilon_i/kT}/q$, with g_i the degeneracy of level i. The ratio of the number of molecules in levels j and i is given by the ratio of the Boltzmann probabilities:

$$\frac{n_j}{n_i} = \frac{g_j\, e^{-\varepsilon_j/kT}/q}{g_i\, e^{-\varepsilon_i/kT}/q} = \left(\frac{g_j}{g_i}\right) e^{-(\varepsilon_j - \varepsilon_i)/kT} = \left(\frac{g_j}{g_i}\right) e^{-\Delta\varepsilon/kT} \qquad \text{with } \Delta\varepsilon = \varepsilon_j - \varepsilon_i$$

The rotational energy is $\varepsilon_J = \tilde{B}hc\, J(J + 1)$. For rotational levels J = 3 and 0:

$$\Delta\varepsilon = \tilde{B}hc\,[3(3 + 1) - 0(0 + 1)] = 12\,\tilde{B}hc$$

For H–C≡N the rotational constant is $\tilde{B}$ = 1.4782 cm^{-1}, giving:

$$\frac{n_3}{n_o} = \left(\frac{2\cdot 3 + 1}{2\cdot 0 + 1}\right) e^{-12\ \tilde{B}hc/kT} = \left(\frac{7}{1}\right) e^{-12(1.4782\ \mathrm{cm^{-1}})/207.224\ \mathrm{cm^{-1}}} = \left(\frac{7}{1}\right) 0.9180 = 6.425$$

Even though the probability of being in a <u>single</u> rotational state with J = 3 is less than J = 0, the degeneracy gives roughly 6.5 times more molecules in J = 3 than J = 0 at room temperature.

<u>4</u>. Verify the units conversion factor, Γ = 0.0259467, for the translational partition function in Eqs. 30.3.1-30.3.2 for a P° = 1 bar standard state.

Answer: The units conversion factor Γ is defined with R = 8.3145 J K^{-1} mol and P° = 1 bar = $1\mathrm{x}10^5$ N m^{-2}. Moving the factor of h^3 into the first term and using $R/N_A = k$ gives:

$$\Gamma = \left(\frac{2\pi k}{N_A\ 1000\ \mathrm{g\ kg^{-1}}}\right)^{3/2} \frac{R}{N_A P^\circ\ h^3} = \left(\frac{2\pi k}{N_A\ h^2\ 1000\ \mathrm{g\ kg^{-1}}}\right)^{3/2} \left(\frac{k}{P^\circ}\right)$$

$$= \left(\frac{2\pi(1.3806488\mathrm{x}10^{-23}\ \mathrm{J\ K^{-1}})}{6.0221367\mathrm{x}10^{23}\ \mathrm{mol^{-1}}(6.6260755\mathrm{x}10^{-34}\ \mathrm{J\ s})^2(1000\ \mathrm{g/kg})}\right)^{3/2} \left(\frac{1.3806488\mathrm{x}10^{-23}\ \mathrm{J\ K^{-1}}}{1\mathrm{x}10^5\ \mathrm{N\ m^{-2}}}\right)$$

$$= 0.02594674 \pm 8\mathrm{x}10^{-8} = 0.02594674(8)$$

We estimated the uncertainty using the "*Uncertainty Calculator*" applet that is available on the text book Web site and companion CD. The input formula was:

"(2*pi*k/Na/h^2/1000)^1.5*k/1e5".

For the units note that for energy 1 J = 1 kg m^2 s^{-2} and for pressure 1 N m^{-2} = 1 J m^{-3}. The units of k/h^2 are 1/(J s^2 K). The units of k/P° are m^3 K^{-1}:

$$\Gamma \sim \left(\frac{1}{\mathrm{J\ kg^{-1} s^2}}\right)^{3/2} \left(\frac{1}{\mathrm{g\ mol^{-1}\ K}}\right)^{3/2} (\mathrm{m^3\ K^{-1}})$$

The units of J kg^{-1} s^2 are (kg m^2 s^{-2})(kg^{-1} s^2) = m^2.

$$\Gamma \sim (\mathrm{m^{-3}}) \left(\frac{1}{\mathrm{g\ mol^{-1}\ K}}\right)^{3/2} (\mathrm{m^3\ K^{-1}}) \sim \left(\frac{1}{\mathrm{g\ mol^{-1}}}\right)^{3/2} \left(\frac{1}{\mathrm{K}}\right)^{5/2}$$

These final units are grouped with the factors of $(\mathcal{M}/_{\mathrm{g\ mol^{-1}}})^{3/2}$ and $(T/_{K})^{5/2}$ to give an overall unitless result. Note that the factor of N_A in q°_t/N_A is the molecule count and in this context is unitless, giving q°_t/N_A as overall unitless.

<u>5</u>. (a). Calculate the translational partition function in the form $q^\circ_{t,m}/N_A$ for hydrocyanic acid, H–C≡N, at 298.2 K. (b). Calculate the rotational partition function of H–C≡N at 298.2 K. Hydrocyanic acid is linear with rotational constant 1.4782 cm^{-1}.[2]

Answer: (a). Using isotope averaged atomic masses from the periodic table, the molar mass of H–C≡N is 27.03 g mol^{-1}. The standard state translational partition function is:

$$\frac{q^\circ_{t,m}}{N_A} = \Gamma\ (\mathcal{M}/_{\mathrm{g\ mol^{-1}}})^{3/2}\ (T/_{K})^{5/2} = 0.0259467\ (27.03)^{3/2}(298.15)^{5/2} = 5.597\mathrm{x}10^6$$

or lots and lots of accessible translational states per molecule: $q^\circ_{t,m} = N_A(5.597\text{x}10^6)$.

(b). The rotational symmetry number is $\sigma = 1$, since H–C≡N is unsymmetrical. The rotational partition function at 298.2 K is given using Eqs. 30.1.39 and 30.1.40:

$$q_r = \frac{kT}{\sigma\tilde{B}hc} = \frac{207.224\ \text{cm}^{-1}}{1.4782\ \text{cm}^{-1}} = 140.187$$

Once again, there are a large number of accessible rotational states.

6. Does anharmonicity have a significant effect on the vibrational partition function? The vibrational constants for diatomic Mg_2 are $\tilde{\nu}_e = 51.12\ \text{cm}^{-1}$, $\chi_e\tilde{\nu}_e = 1.64\ \text{cm}^{-1}$, and $\mathcal{Y}_e\tilde{\nu}_e = 0.0162\ \text{cm}^{-1}$. Using the zero-point energy as the zero in energy, determine the vibrational partition function at 298.2 K by explicit summation for three cases. (a). Assume a harmonic oscillator with the observed vibrational frequency $\tilde{\nu}_o$. Calculate $\tilde{\nu}_o$ using the first and second anharmonicity corrections, extending Eq. 27.5.11 as: $\tilde{\nu}_o = \tilde{\nu}_e - 2\chi_e\tilde{\nu}_e + {}^{13}/_4\ \mathcal{Y}_e\tilde{\nu}_e$. (b). Assume an anharmonic oscillator including only the first anharmonicity correction, Eq. 27.5.8. (c). Assume an anharmonic oscillator including the first and second anharmonicity corrections, Eq. 27.5.5. [Hint: for the anharmonic oscillator cases, extend the sums until the vibrational energy reaches a maximum, which corresponds to the dissociation limit.]

Answer: The plan is to determine the vibrational energies in reference to the energy of the $\upsilon = 0$ level at the required levels of approximation.

The observed harmonic oscillator fundamental is at:

$$\tilde{\nu}_o = \tilde{\nu}_e - 2\chi_e\tilde{\nu}_e + {}^{13}/_4\ \mathcal{Y}_e\tilde{\nu}_e = 51.12\ \text{cm}^{-1} - 2(1.64\ \text{cm}^{-1}) + {}^{13}/_4\ (0.0162\ \text{cm}^{-1}) = 47.893\ \text{cm}^{-1}$$

The energy levels are: harmonic $\tilde{G}_\upsilon = \tilde{\nu}_o(\upsilon + ½)$

first-anharmonicity $\tilde{G}_\upsilon = \tilde{\nu}_e(\upsilon + ½) - \chi_e\tilde{\nu}_e(\upsilon + ½)^2$

first and second-anharmonicity $\tilde{G}_\upsilon = \tilde{\nu}_e(\upsilon + ½) - \chi_e\tilde{\nu}_e(\upsilon + ½)^2 + \mathcal{Y}_e\tilde{\nu}_e(\upsilon + ½)^3$

The zero point energies are: harmonic $\text{ZPE} = \tilde{G}_o = \tilde{\nu}_o/2$

first-anharmonicity $\text{ZPE} = \tilde{G}_o = \tilde{\nu}_e/2 - \chi_e\tilde{\nu}_e/4$

first and second-anharmonicity $\text{ZPE} = \tilde{G}_o = \tilde{\nu}_e/2 - \chi_e\tilde{\nu}_e/4 + \mathcal{Y}_e\tilde{\nu}_e/8$

The spreadsheet implementing these calculations and the corresponding Boltzmann weighting factors is given below. The vibrational partition function is the sum of the Boltzmann weighting factors. For the harmonic case, states up to $\upsilon = 40$ are necessary to obtain a good estimate of the sum. For the harmonic calculation not all rows are shown to save space. Summing through $\upsilon = 40$ gives $q_v = 4.846$. Using the first-anharmonicity correction, the vibrational energy is maximum at $\upsilon = 15$, which corresponds to the dissociation energy. Summing through $\upsilon = 15$ gives $q_v = 5.898$. The first-anharmonicity correction increases the number of accessible states by 22% over the harmonic approximation. For the full expression, using the first and second-anharmonicity corrections, the vibrational energy is maximum at $\upsilon = 24$. Summing through $\upsilon = 24$ gives the best estimate of the partition function as $q_v = 6.613$. Using only the first-anharmonicity correction underestimates the partition function by 11%.

ν_e	51.12	cm^{-1}				
$\chi_e\nu_e$	1.64	cm^{-1}				
$y_e\nu_e$	0.0162	cm^{-1}				
ν_o	47.89265	cm^{-1}				
	harmonic: ν_o		$\nu_e(\upsilon+½)-\chi_e\nu_e(\upsilon+½)^2$		full	
ZPE	23.946325		25.15		25.152025	cm^{-1}
υ	ε_υ	$e^{-\varepsilon\upsilon/kT}$	ε_υ	$e^{-\varepsilon\upsilon/kT}$	ε_υ	$e^{-\varepsilon\upsilon/kT}$
0	0	1	0	1	0	1
1	47.89265	0.793647903	47.84	0.793849573	47.89265	0.793647903
2	95.7853	0.629876994	92.4	0.640251444	92.6511	0.639476101
3	143.67795	0.499900556	133.68	0.524610591	134.37255	0.52286025
4	191.5706	0.396745028	171.68	0.436714565	173.1542	0.433618785
5	239.46325	0.314875859	206.4	0.369345179	209.09325	0.364575932
6	287.3559	0.249900565	237.84	0.317352066	242.2869	0.310614436
7	335.24855	0.19833306	266	0.277028442	272.83235	0.268043515
8	383.1412	0.157406617	290.88	0.245686631	300.8268	0.234172175
9	431.03385	0.124925431	312.48	0.221366973	326.36745	0.207017892
10	478.9265	0.099146807	330.8	0.202636774	349.5515	0.185105522
11	526.81915	0.078687655	345.84	0.188450735	370.47615	0.167327012
12	574.7118	0.062450293	357.6	0.178053922	389.2386	0.15284253
13	622.60445	0.049563544	366.08	0.170914689	405.93605	0.141010078
14	670.4971	0.039336003	371.28	0.166679185	420.6657	0.1313349
15	718.38975	0.031218936	373.2	0.165141979	433.52475	0.123432776
16	766.2824	0.024776843	371.84	0.166229361	444.6104	0.117003133
17	814.17505	0.01966409			454.01985	0.111809169
18	862.0677	0.015606363			461.8503	0.107663023
19	909.96035	0.012385958			468.19895	0.104414603
20	957.853	0.009830089			473.163	0.101943073
21	1005.74565	0.00780163			476.83965	0.100150309
22	1053.6383	0.006191747			479.3261	0.098955801
23	1101.53095	0.004914067			480.71955	0.098292619
24	1149.4236	0.003900039			481.1172	0.098104182
25	1197.31625	0.003095258			480.61625	0.098341629
26	1245.2089	0.002456545				
⋮	⋮	⋮				
40	1915.706	9.66307E-05				
q_v =	sum =	4.845714312		5.898082748		6.613415718

The vibrational partition function in the harmonic approximation using Eq. 30.1.31 is slightly larger than we obtained stopping the sum at $\upsilon = 40$:

$$q_v = \frac{1}{1 - e^{\tilde{\nu}/207.224\ \mathrm{cm}^{-1}}} = \frac{1}{1 - e^{47.893/207.224}} = 4.8465$$

Mg_2 is atypical. The bond strength in Mg_2 is small and the vibration is unusually anharmonic. For most stable common diatomics, such as O_2, N_2, CO, and HF, anharmonicity makes a negligible contribution to the vibrational partition functions, because there are so few accessible states.

7. Calculate the electronic partition function of atomic carbon at 298.2 K. The spectroscopic constants for the low-lying electronic states are given in Table 30.1.2.

Answer: The plan is to follow Example 30.1.3 to determine the electronic partition function.

Consider a general three level system with energies ε_o, ε_1, and ε_2 with corresponding degeneracies g_o, g_1, and g_2, respectively. The general form of the partition function of a three-level system is given by the sum of the Boltzmann weighting factors over the three-levels:

$$q_e = \Sigma\, g_i\, e^{-\varepsilon_i/kT} = g_o + g_1\, e^{-\varepsilon_1/kT} + g_2\, e^{-\varepsilon_2/kT}$$

Using the spectroscopic constants for C-atoms gives the partition function at room temperature:

$$q_e = 1 + 3\, e^{-16.40/207.22} + 5\, e^{-43.40/207.22} = 7.827 = 1 + 3(0.9239) + 5(0.8110) = 7.827$$

The low-energy electronic terms of the C-atom are closely spaced in energy compared to kT. C-atoms are an excellent example of a case that gives a significant error by assuming the electronic partition function is the ground state degeneracy.

8. Calculate the contribution of translation to the molar standard state entropy of H–C≡N at 298.2 K. Compare this translation-only result to the literature value of the thermodynamic standard state absolute entropy.

Answer: The plan is to use the Sackur-Tetrode equation.

Using isotope averaged atomic masses from the periodic table, the molar mass of H–C≡N is 27.026 g mol^{-1}. For standard state at 298.2 K, using Eq. 30.2.35°:

$$\begin{aligned} S^\circ_{m,298.15\,K} &= 26.6929 + 71.0587 + {}^{3}\!/_{2}\, R \ln(\mathcal{M}/_{g\ mol^{-1}}) + 11.1037\ J\ K^{-1}\ mol^{-1} \\ &= 26.6929 + 71.0587 + {}^{3}\!/_{2}\, R \ln(27.026) + 11.1037\ J\ K^{-1}\ mol^{-1} \\ &= 149.972\ J\ K^{-1}\ mol^{-1} \end{aligned}$$

Using Table 8.4.1 in the Data Section, $S^\circ_{298\,K} = 201.78\ J\ K^{-1}\ mol^{-1}$. The difference is primarily the contribution of rotation.

9. Calculate the contribution of rotation to the molar entropy of H–C≡N at 298.2 K. Combine the translational contribution from the previous problem with the rotational contribution. Compare this translation-rotation only result to the literature value of the thermodynamic standard state absolute entropy. Hydrocyanic acid is linear with rotational constant 1.4782 cm^{-1}.[9]

Answer: The plan is to use the Sackur-Tetrode equation for the translational contribution, kT/hc = 207.224 cm^{-1}, the high temperature approximation or Equipartition rotational contribution of a diatomic molecule of U – U(0) = RT, and Eq. 30.2.27°.

The translational contribution is determined in the previous problem using the Sackur-Tetrode equation, $S^\circ_{m,298.15\,K} = 149.972\ J\ K^{-1}\ mol^{-1}$. The rotational symmetry number is $\sigma = 1$, since

H–C≡N is unsymmetrical. The rotational partition function at 298.2 K is given using Eqs. 30.1.39 and 30.1.40: (see also Problem 5b.)

$$q_r = \frac{kT}{\sigma\tilde{B}hc} = \frac{207.224\ \text{cm}^{-1}}{1.4782\ \text{cm}^{-1}} = 140.186$$

The contribution of rotation of a linear molecule to the internal energy is U – U(0) = RT, as based on the high temperature approximation, Table 30.3.3, or correspondingly from Equipartition. Using Eq. 30.2.27° the molar rotational entropy is:

$$S_r = R \ln q_r + R = 8.31446\ \text{J K}^{-1}\ \text{mol}^{-1}(\ln 140.186 + 1) = 49.413\ \text{J K}^{-1}\ \text{mol}^{-1}$$

Neglecting vibration, the predicted molar standard state entropy is:

$$S^\circ_{m,298.15\ K} = 149.972\ \text{J K}^{-1} + 49.413\ \text{J K}^{-1}\ \text{mol}^{-1} = 199.38\ \text{J K}^{-1}\ \text{mol}^{-1}$$

Using Table 8.4.1 in the Data Section, $S^\circ_{298\ K} = 201.78\ \text{J K}^{-1}\ \text{mol}^{-1}$ giving a 1.2% difference. The difference is primarily a small contribution from the doubly degenerate bending vibration.

<u>10</u>. Determine the contribution of a vibration to the internal energy of a substance. Use the zero-point vibrational level, υ = 0, as the zero in energy. Repeat the derivation giving Eq. 30.3.13. However, this result was derived using Eq. 30.2.15°; use Eq. 30.2.6° as the basis of your derivation, instead.

Answer: The plan is to use Eq. 30.1.31, written in terms of β instead of kT with Eq. 30.2.6°.
The partition function for the vibration of a diatomic molecule or a single vibrational mode of a polyatomic in the harmonic approximation is given by Eq. 30.1.31. The version of this equation written in terms of β is the most convenient form:

$$q_v = \frac{1}{(1 - e^{-\beta h\nu_o})}$$

The internal energy is given by Eq. 30.2.6°. Using the chain rule, the required derivative is:

$$\left(\frac{\partial q}{\partial \beta}\right)_V = \frac{-1}{(1 - e^{-\beta h\nu_o})^2}\ (h\nu_o\, e^{-\beta h\nu_o})$$

Substitution of the derivative and the vibrational partition function into Eq. 30.2.6° gives:

$$U - U(0) = -\frac{N}{q}\left(\frac{\partial q}{\partial \beta}\right)_V = -\frac{N}{\left(\frac{1}{1 - e^{-\beta h\nu_o}}\right)}\ \frac{-h\nu_o\, e^{-\beta h\nu_o}}{(1 - e^{-\beta h\nu_o})^2}$$

Cancelling the common factors gives the final result:

$$U - U(0) = \frac{Nh\nu_o\, e^{-\beta h\nu_o}}{1 - e^{-\beta h\nu_o}} \qquad (30.3.13)$$

11. Find the contribution of a vibration to the enthalpy, $H_v - H_v(0)$. Assume the energy zero is at the bottom of the vibrational potential, giving the zero-point $\upsilon = 0$ vibrational level at $\varepsilon_o = ½\, h\nu_o$. For vibrations $H_v - H_v(0) = U_v - U_v(0)$. The reason vibrational enthalpy and internal energy are equal is that even though $H \equiv U + PV$, the PV correction term is included in calculating the translational enthalpy. [Hint: Eq. 30.2.15° is most convenient for this problem. Note that Eq. 30.3.13 was derived with the $\upsilon = 0$, zero-point vibrational level as the reference energy.]

Answer: The plan is to take the derivative with respect to β based on Eq. 30.1.29 instead of Eq. 30.1.31 using Eq. 30.2.15° for the internal energy.

Based on Eq. 30.1.29, the logarithm of the partition function is:

$$q_v = \frac{e^{-\beta h\nu_o/2}}{1 - e^{-\beta h\nu_o}} \qquad \ln q_v = -½\beta h\nu_o - \ln(1 - e^{-\beta h\nu_o})$$

The derivative with respect to β is: $\left(\frac{\partial \ln q_v}{\partial \beta}\right)_V = -½h\nu_o - \frac{h\nu_o\, e^{-\beta h\nu_o}}{1 - e^{-\beta h\nu_o}}$

$$H_v - H_v\,(0) = U_v - U_v(0) = -N\left(\frac{\partial \ln q_v}{\partial \beta}\right)_V = ½Nh\nu_o + \frac{Nh\nu_o\, e^{-\beta h\nu_o}}{1 - e^{-\beta h\nu_o}}$$

The first term in the sum is the zero-point vibrational energy, ZPE. The second term is identical to Eq. 30.3.13. In other words, the difference caused by shifting the energy zero to the zero-point vibrational level is just an additive term in the ZPE. This result is used in correcting SCF total electronic energies from *ab initio* electronic structure calculations to the spectroscopic reference energy.

12. For one mole of an ideal gas at 25°C and constant volume, the number of accessible states increases by 10% with a temperature increase of 20°C. Estimate to a single significant figure (don't use a calculator) the internal energy of the substance. Based on Equipartition neglecting vibration, the value of $U_m - U_m(0)$ for a monatomic ideal gas is $^3/_2$ RT, for a diatomic ideal gas is $^5/_2$ RT, for a linear triatomic is $^5/_2$ RT, and for a bent triatomic is $^6/_2$ RT. To which case does this result most closely correspond?

Answer: The plan is to use the estimate given by Eq. 30.2.13°.

For a 10% increase in the partition function, $^{\delta q}/_{q} = 0.10$. For the change in temperature of 10°C:

$$U_m - U_m(0) \approx 1000 \text{ kJ K mol}^{-1}\left(\frac{0.10}{20 \text{ K}}\right) \approx 5 \text{ kJ mol}^{-1}$$

As a factor of R: $[U_m - U_m(0)]/RT \approx 5 \text{ kJ mol}^{-1}/RT \approx 2$

This factor of 2RT is in rough neighborhood of the values for diatomics and linear triatomics.

13. We can find an approximate formula for the internal energy based on the order of magnitude of the change in accessible states by converting Eq. 30.2.16° to base-ten log: ln x = 2.303 log x:

$$U - U(0) = 2.303\ nRT^2 \left(\frac{\partial \log q}{\partial T}\right)_V$$

and at 298.2 K: $U_m - U_m(0) = 1702\ \text{kJ K mol}^{-1}\left(\frac{\partial \log q}{\partial T}\right)_V \approx 2000\ \text{kJ K mol}^{-1}\left(\frac{\partial \log q}{\partial T}\right)_V$

For one mole of an ideal gas at 298 K and constant volume, the number of accessible states increases by a factor of ten for a temperature increase of 20 K. Estimate to a single significant figure (don't use a calculator) the internal energy of the substance.

Answer: The plan is to let the initial partition function, before the temperature increase be q_o. For a factor of ten increase $\partial \log q = \log 10q_o - \log q_o = \log 10 = 1$.

For the change in temperature of 10 K:

$$U_m - U_m(0) \approx 2000\ \text{kJ K mol}^{-1}\left(\frac{1}{20\ \text{K}}\right) \approx 100\ \text{kJ mol}^{-1}$$

14. A quick estimate of the rotational contribution to the Gibbs energy of a linear molecule at room temperature is available by converting ln x to log x and using 2.303RT = 5.71 kJ mol^{-1}:

$$G_m - G_m(0) = -2.303\ RT \log\left(\frac{207.2\ \text{cm}^{-1}}{\sigma\tilde{B}}\right) \cong -6\ \text{kJ mol}^{-1} \log\left(\frac{207.2\ \text{cm}^{-1}}{\sigma\tilde{B}}\right)$$

Without using a calculator estimate the contribution of rotation to the molar Gibbs energy of CO_2. The rotational constant for CO_2 is 0.379 cm^{-1}. [Hint: use $\log 10^n = n$]

Answer: The plan is to note that the symmetry number for CO_2 is $\sigma = 2$ since rotation by 180° gives an indistinguishable state.

The ratio of the available thermal kinetic energy to the molecular constants is roughly:

$$\left(\frac{207.2\ \text{cm}^{-1}}{\sigma\tilde{B}}\right) = \frac{207.2\ \text{cm}^{-1}}{2(0.379\ \text{cm}^{-1})} \cong \frac{100}{0.4} \cong 250$$

By course estimation: log 250 ≈ log 100 = 2. The estimate of the molar Gibbs energy of rotation is then:

$$G_m - G_m(0) \cong -6\ \text{kJ mol}^{-1} \log 250 \cong -6\ \text{kJ mol}^{-1}\ (2) = -12\ \text{kJ mol}^{-1}$$

We will spend a lot of time on very careful calculations in this chapter. However, rough, approximate calculations are very helpful in building insight. The precise result for this problem is given in Example 30.3.1 as -13.9 kJ mol^{-1}.

15. The atomic energy levels for low-lying states of atomic oxygen are given in Figure 30.1.7. These low-lying states are an example of a three-level system. Consider a three level system with energies ε_o, ε_1, and ε_2 with corresponding degeneracies g_o, g_1, and g_2, respectively. The lowest energy level is defined as the energy zero, $\varepsilon_o = 0$. (a). Show that the contribution of the electronic degree of freedom of a three-level system to the molar internal energy is given by:

$$U_m - U_m(0) = N_A \frac{g_1\, \varepsilon_1\, e^{-\varepsilon_1/kT} + g_2\, \varepsilon_2\, e^{-\varepsilon_2/kT}}{g_o + g_1\, e^{-\varepsilon_1/kT} + g_2\, e^{-\varepsilon_2/kT}}$$

(b). Plot the electronic contribution to the molar internal energy of O-atoms as a function of temperature, in the range 10 K to 800 K.

Answer: The plan is to note that the electronic partition function for O-atoms, as a specific case, is given in Example 30.1.2; however, the necessary derivative is easier in terms of β rather than T.

(a). The partition function is the sum over the three levels, taking degeneracy into account:

$$q_e = g_o + g_1\, e^{-\beta\varepsilon_1} + g_2\, e^{-\beta\varepsilon_2}$$

with $\beta = {}^1\!/_{kT}$. The required derivative is: $\left(\frac{\partial q_e}{\partial \beta}\right)_V = -g_1\, \varepsilon_1\, e^{-\beta\varepsilon_1} - g_2\, \varepsilon_2\, e^{-\beta\varepsilon_2}$

Using this derivative, the partition function, and $\beta = {}^1\!/kT$, the contribution to the molar internal energy is given by Eq. 30.2.6°:

$$U_m - U_m(0) = -\frac{N_A}{q}\left(\frac{\partial q}{\partial \beta}\right)_V = N_A \frac{g_1\, \varepsilon_1\, e^{-\varepsilon_1/kT} + g_2\, \varepsilon_2\, e^{-\varepsilon_2/kT}}{g_o + g_1\, e^{-\varepsilon_1/kT} + g_2\, e^{-\varepsilon_2/kT}}$$

This result is identical to the result using Eqs 30.1.1 and 30.1.2 for molecular partition functions: $U - U(0) = N \sum \varepsilon_i\, e^{-\varepsilon_i/kT}/q$. Using the spectroscopic constants for O-atoms, from Example 30.1.2, at room temperature:

$$q_e = 5 + 3\, e^{-158.265/207.22} + 1\, e^{-226.977/207.22} = 6.7322$$

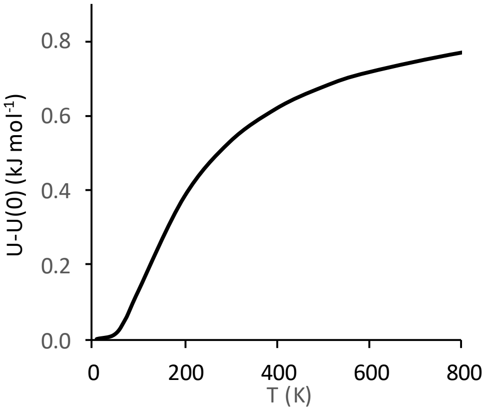
and
$$\begin{aligned} U_m - U_m(0) &= \frac{N_A}{6.7322}\,[3(158.265\ \text{cm}^{-1})\, e^{-158.265/207.22} + 1(226.977\ \text{cm}^{-1})\, e^{-226.977/207.22}] \\ &= \frac{N_A}{6.7322}\,[3(158.265\ \text{cm}^{-1})(0.4659) + 1(226.977\ \text{cm}^{-1})(0.3344)] \\ &= N_A(44.14\ \text{cm}^{-1}) = (44.14\ \text{cm}^{-1})(11.96266\ \text{J mol}^{-1})(1\ \text{kJ}/1000\ \text{J}) \\ &= 0.528\ \text{kJ mol}^{-1} \end{aligned}$$

where we used the conversion $1\text{cm}^{-1} = 11.96266\ \text{J mol}^{-1}$ (from the inside front cover).

(b). The spreadsheet based on the preceding calculation at the given range of temperatures and the corresponding plot are shown below.

$g_o =$	5	$\varepsilon_o = 0$				
$g_1 =$	3	$\varepsilon_1 =$	158.265	cm^{-1}		
$g_2 =$	1	$\varepsilon_2 =$	226.977	cm^{-1}		

T (K)	kT/hc (cm^{-1})	$e^{-\varepsilon 1/kT}$	$e^{-\varepsilon 2/kT}$	q_e	U-U(0) (cm^{-1})	U-U(0) (kJ mol^{-1})
10	6.95	0.0000	0.0000	5	0.00	0.0000
50	34.8	0.0105	0.0015	5.033	1.06	0.0127
75	52.1	0.0480	0.0129	5.157	4.99	0.0597
100	69.5	0.1026	0.0382	5.346	10.73	0.1284
200	139	0.3203	0.1954	6.156	31.91	0.3817
298	207	0.4659	0.3344	6.732	44.14	0.5280
400	278	0.5659	0.4420	7.140	51.69	0.6183
500	348	0.6342	0.5204	7.423	56.48	0.6756
600	417	0.6842	0.5803	7.633	59.81	0.7155
800	556	0.7523	0.6648	7.922	64.14	0.7673
hc/k	=	1.4388	cm K			
1	cm^{-1}=	11.963	J mol^{-1}			



16. Calculate the contribution of the electronic degree of freedom to the molar internal energy of atomic carbon at 298.2 K. The spectroscopic constants for the low-lying electronic states are given in Table 30.1.2.

Answer: The plan is to use Eq. 30.2.6° after following Example 30.1.2 to determine the electronic partition function.

Consider a general three level system with energies ε_o, ε_1, and ε_2 with corresponding degeneracies g_o, g_1, and g_2, respectively. The derivation of the contribution of a three-level system to the molar internal energy is given in the previous problem. Using the spectroscopic constants for C-atoms gives the partition function at room temperature:

$$q_e = g_o + g_1\, e^{-\beta\varepsilon_1} + g_2\, e^{-\beta\varepsilon_2} = 1 + 3\, e^{-16.40/207.22} + 5\, e^{-43.40/207.22} = 7.827$$

The electronic contribution to the molar internal energy is:

$$\begin{aligned} U_m - U_m(0) &= N_A \frac{g_1\, \varepsilon_1\, e^{-\varepsilon_1/kT} + g_2\, \varepsilon_2\, e^{-\varepsilon_2/kT}}{g_o + g_1\, e^{-\varepsilon_1/kT} + g_2\, e^{-\varepsilon_2/kT}} \\ &= \frac{N_A}{7.827}\,[3(16.40\text{ cm}^{-1})\, e^{-16.40/207.22} + 5(43.40\text{ cm}^{-1})\, e^{-43.40/207.22}] \\ &= \frac{N_A}{7.827}\,[3(16.40\text{ cm}^{-1})(0.9239) + 5(43.40\text{ cm}^{-1})(0.8110)] \\ &= N_A(28.29\text{ cm}^{-1}) = (28.29\text{ cm}^{-1})(11.96266\text{ J mol}^{-1})(1\text{ kJ}/1000\text{ J}) \\ &= 0.3385\text{ kJ mol}^{-1} \end{aligned}$$

where we used the conversion $1\text{cm}^{-1} = 11.96266\text{ J mol}^{-1}$ (from the inside front cover). The low-energy electronic terms of the C-atom are closely spaced in energy. C-atoms are an excellent example of a case that gives a significant error by assuming the electronic partition function is the ground state degeneracy.

17. Calculate the contribution of the electronic degree of freedom to the molar Gibbs energy of atomic oxygen at 298.2 K. The spectroscopic constants for the low-lying electronic states are given in Table 30.1.2.

Answer: The plan is to note that the electronic partition function for O-atoms is given in Example 30.3.1; the contribution to the Gibbs energy is given by Eq. 30.2.53.

The explicit sum over the Boltzmann weighting factors gives, using Figure 30.1.7 as shown in Example 30.1.2:

$$q_e = 5 + 3\ e^{-158.265/207.22} + 1\ e^{-226.977/207.22} = 5 + 1.39776 + 0.33443 = 6.7322$$

The electronic contribution to the molar Gibbs energy is:

$$G_e - G_e(0) = -RT \ln q_e$$

$$= -8.3145\ \text{J K}^{-1}\ \text{mol}^{-1}(1\ \text{kJ}/1000\ \text{J})(298.15\ \text{K}) \ln 6.7322 = -4.727\ \text{kJ mol}^{-1}$$

18. The nucleus of a deuterium atom has a spin of one, I = 1. In a magnetic field of strength B_o, a deuterium nucleus has energy levels $\varepsilon = \gamma\hbar B_o\, m_I$, with $m_I = +1, 0, -1$. The magnetogyric ratio, γ, is a constant that is different for each isotope of each element. For deuterium, $\gamma = 41.065$ radians $s^{-1}\ T^{-1}$, with the magnetic field strength given in tesla, T. For thermodynamic calculations, setting the lowest energy level at $\varepsilon = 0$ is most convenient. With the shifted zero in energy, the deuterium nuclear energies are at $\varepsilon = 0$ for $m_I = +1$, $\varepsilon = \gamma\hbar B_o$ for $m_I = 0$, and $\varepsilon = 2\gamma\hbar B_o$ for $m_I = -1$. Find the partition function and the contribution of the nuclear energy to the internal energy. [This three-level system is the basis of deuterium NMR spectroscopy. Deuterium NMR is common, especially for locking and shimming operations while doing conventional proton and ^{13}C NMR.]

Answer: The plan is to find the partition function as the sum of the three Boltzmann weighting factors. The derivative to determine the internal energy is easier with the Boltzmann weighting factors expressed in terms of β instead of kT.

The partition function is the sum of the Boltzmann weighting factors:

$$q_n = \Sigma\ e^{-\beta\varepsilon_i} = e^0 + e^{-\beta\gamma\hbar B_o} + e^{-2\beta\gamma\hbar B_o} = 1 + e^{-\beta\gamma\hbar B_o} + e^{-2\beta\gamma\hbar B_o}$$

The derivative with respect to β is: $\left(\frac{\partial q}{\partial \beta}\right)_V = -\gamma\hbar B_o\, e^{-\beta\gamma\hbar B_o} - 2\gamma\hbar B_o\, e^{-2\beta\gamma\hbar B_o}$

The contribution of the nuclear degree of freedom to the internal energy is given by Eq. 30.2.6°:

$$U - U(0) = -\frac{N}{q}\left(\frac{\partial q}{\partial \beta}\right)_V = N\,\frac{\gamma\hbar B_o\, e^{-\beta\gamma\hbar B_o} + 2\gamma\hbar B_o\, e^{-2\beta\gamma\hbar B_o}}{1 + e^{-\beta\gamma\hbar B_o} + e^{-2\beta\gamma\hbar B_o}}$$

$$= N\,\frac{\gamma\hbar B_o\, e^{-\gamma\hbar B_o/kT} + 2\gamma\hbar B_o\, e^{-2\gamma\hbar B_o/kT}}{1 + e^{-\gamma\hbar B_o/kT} + e^{-2\gamma\hbar B_o/kT}} = N\gamma\hbar B_o\,\frac{e^{-\gamma\hbar B_o/kT} + 2\ e^{-2\gamma\hbar B_o/kT}}{1 + e^{-\gamma\hbar B_o/kT} + e^{-2\gamma\hbar B_o/kT}}$$

A magnetic field strength of 11.74 T gives a deuterium NMR transition frequency of 76.73 MHz and a proton NMR frequency of 500 MHz. At 76.73 MHz or $\nu = 76.73\ \mathrm{s^{-1}}$, for one mole of deuterium nuclei:

$$N_A\, \gamma\hbar B_o = N_A\, h\nu = 6.022\text{x}10^{23}\ \mathrm{mol^{-1}}(6.6261\text{x}10^{-34}\ \mathrm{J\ s})(76.73\text{x}10^{6}\ \mathrm{s^{-1}}) = 0.03062\ \mathrm{J\ mol^{-1}}$$

The small size of this energy explains why we don't normally bother considering nuclear degrees of freedom in thermodynamic problems. At 76.73 MHz the corresponding transition in wave numbers is:

$$\tilde{\nu} = \nu/c = 76.73\text{x}10^{6}\ \mathrm{s^{-1}}/2.9979\text{x}10^{10}\ \mathrm{cm\ s^{-1}} = 0.002559\ \mathrm{cm^{-1}}$$

NMR transitions are very low energy transitions. The ratio to the thermal kinetic energy at room temperature is:

$$\gamma\hbar B_o/kT = 0.002559\ \mathrm{cm^{-1}}/207.224\ \mathrm{cm^{-1}} = 1.235\text{x}10^{-5} \quad \text{giving} \quad e^{-\gamma\hbar B_o/kT} = 0.9999877$$

The average molar internal energy at 298.2 K is:

$$U - U(0) = 0.03062\ \mathrm{J\ mol^{-1}}\ \frac{0.999988 + 2\,(0.999988)^2}{1 + 0.999988 + (0.999988)^2} = 0.03062\ \mathrm{cm^{-1}}$$

In other words, the populations of the three levels are almost identical, so that the internal energy is near the maximum.

<u>19</u>. The translational partition function of a mobile species on a surface is:

$$q_t = \frac{2\pi mkT}{h^2}\,\sigma$$

where σ is the surface area (not to be confused with the rotational symmetry number). Find the contribution of translation to the molar internal energy of the species, $U_t - U_t(0)$.

Answer: The plan is to use Eq. 30.2.16° and $\ln q_t = \ln(2\pi mk\sigma/h^2) + \ln T$.

Substitution of the partition function into Eq. 30.2.16° with n = 1 mol gives:

$$U_t - U_t(0) = RT^2\left(\frac{\partial \ln q}{\partial T}\right)_V = RT^2\left(\frac{\partial(\ln(2\pi mk\sigma/h^2) + \ln T)}{\partial T}\right)_V = RT^2\left(\frac{\partial \ln T}{\partial T}\right)_V$$

The derivative of the first term in the sum is zero, since the values are all constants. Then completing the derivative gives:

$$U_t - U_t(0) = RT^2\left(\frac{1}{T}\right) = RT$$

This value is predicted by Equipartition, since there are two translational degrees of freedom on the surface with each degree of freedom contributing ½ RT to the internal energy.

Alternately, the derivation can also be based on Eq. 30.2.12°:

$$U_t - U_t(0) = \frac{RT^2}{q}\left(\frac{\partial q}{\partial T}\right)_V = \frac{RT^2}{q}\left(\frac{\partial(2\pi mkT\sigma/h^2)}{\partial T}\right)_V = \frac{RT^2}{q}(2\pi mk\sigma/h^2)$$

$$= \frac{RT^2\,(2\pi mk\sigma/h^2)}{(2\pi mkT\sigma/h^2)} = \frac{RT^2}{T} = RT$$

20. Find the relationship between the Helmholtz energy and the molecular partition function. Start with A – A(0) = –kT ln Q, Eq. 30.2.40. Find the relationship between the Helmholtz energy and the molecular partition functions of rotation, vibration, and electronic degrees of freedom (just in the form $q_r\, q_v\, q_e$).

Answer: The plan is to parallel the derivation of Eq. 30.2.25° for the entropy.

The Helmholtz energy in terms of the ensemble partition function is A – A(0) = –kT ln Q. For independent molecules the ensemble partition function is given by Eq. 30.1.13°. For very large numbers of systems, the factor of N! can be expressed using Sterling's approximation, Eq. 30.2.24°:

$$Q \cong \left(\frac{qe}{N}\right)^N$$

Substitution into Eq. 30.2.40 gives: $A - A(0) = -NkT \ln\left(\frac{qe}{N}\right) = -nRT \ln\left(\frac{qe}{N}\right)$

To find the relationships to the molecular degrees of freedom, we parallel the process we used for the entropy and Gibbs energy, Eqs. 30.2.26° and 30.2.52°. The molecular partition function factors as $q = q_t\, q_{int}$ with $q_{int} = q_r\, q_v\, q_e$, Eq. 30.1.16°. The factors that arise from the correction for indistinguishability are grouped with the translational partition function:

$$A - A(0) = -nRT \ln\left(\frac{q_t e}{N}\right) - nRT \ln q_{int} = -nRT \ln\left(\frac{q_t e}{N}\right) - nRT \ln q_r\, q_v\, q_e$$

In other words, the contribution of internal degrees of freedom to the Helmholtz and Gibbs energies are identical. The Helmholtz energy is particularly useful in molecular dynamics simulations at constant volume. See the next problem to explore the relationship between Helmholtz and Gibbs energy.

21. Find the relationship between the Helmholtz energy and the molecular partition function. Start with A – A(0) = –kT ln Q, Eq. 30.2.40. (See also Problem 30.20). From the resulting equation, derive Eq. 30.2.51°.

Answer: The plan is to parallel the derivation of Eq. 30.2.25° for the entropy.

The derivation of the relationship between the Helmholtz energy and the molecular partition function is given in the previous problem:

$$A - A(0) = -nRT \ln\left(\frac{qe}{N}\right)$$

This result can be expanded to separate the factor of "e":

$$A - A(0) = -nRT \ln\left(\frac{qe}{N}\right) = -nRT \ln\left(\frac{q}{N}\right) - nRT \ln e = -nRT \ln\left(\frac{q}{N}\right) - nRT$$

Using the definition of Gibbs energy with PV = nRT for an ideal gas, this last result gives:

$$G \equiv A + PV \quad \text{or} \quad G - G(0) = A - A(0) + PV = -nRT \ln\left(\frac{q}{N}\right) - nRT + nRT = -nRT \ln\left(\frac{q}{N}\right)$$

Remember that e is just a number e = 2.7183.

<u>22</u>. Calculate the rotational partition function for HF at 298.15 K. Calculate the contribution of rotation to the molar entropy and molar Gibbs energy of HF.

Answer: The plan is to use the spectroscopic constants from Table 27.6.1, $kT/hc = 207.224\ \text{cm}^{-1}$, and the high temperature approximation or Equipartition rotational contribution of a diatomic molecule of U – U(0) = RT.

Table 27.6.1 lists $\tilde{B}_e = 20.9537\ \text{cm}^{-1}$. Using Eq. 30.1.39 with $\sigma = 1$, the rotational partition function is:

$$q_r = \frac{kT}{\sigma\tilde{B}hc} = \frac{207.224\ \text{cm}^{-1}}{\sigma\tilde{B}} = \frac{207.224\ \text{cm}^{-1}}{20.9537\ \text{cm}^{-1}} = 9.88961$$

The contribution of rotation of a linear molecule to the internal energy is U – U(0) = RT, from the high temperature approximation, Table 30.3.3, or correspondingly from Equipartition. Using Eq. 30.2.26° the molar rotational entropy is:

$$S_r = R \ln q_r + R = 8.31446\ \text{J K}^{-1}\ \text{mol}^{-1}(\ln 9.88961 + 1) = 27.3669\ \text{J K}^{-1}\ \text{mol}^{-1}$$

Using Eq. 30.2.52°, the contribution to the molar Gibbs energy is:

$$\begin{aligned} G_r - G_r(0) &= -RT \ln q_r = -\ 8.31446\ \text{J K}^{-1}\ \text{mol}^{-1}(1\ \text{kJ}/1000\ \text{J})(298.15\ \text{K}) \ln 9.88964 \\ &= -5.6805\ \text{kJ mol}^{-1} \end{aligned}$$

As a check, note that for the rotational contribution, $H_r - H_r(0) = U_r - U_r(0)$; the factor of nRT in the conversion of the overall internal energy to enthalpy, H = U + nRT, is combined with the translational contribution. Then using the definition of Gibbs energy, G ≡ H – TS, and the entropy result, above:

$$\begin{aligned} G_r - G_r(0) &= H_r - H_r(0) - T\,S_r = U_r - U_r(0) - T\,S_r \\ &= 2.47896\ \text{kJ mol}^{-1} - 298.15\ \text{K}(27.3669\ \text{J K}^{-1}\ \text{mol}^{-1})(1\ \text{kJ}/1000\ \text{J}) \\ &= 2.47896\ \text{kJ mol}^{-1} - 8.15944\ \text{kJ mol}^{-1} = -5.6805\ \text{kJ mol}^{-1} \end{aligned}$$

Even though you might expect six significant figures given $\tilde{B}_e$, our treatment neglects centrifugal distortion and vibration-rotation interaction, which limits the accuracy of the statistical mechanical result. In addition, the statistical mechanical and thermodynamic values have limited precision and accuracy caused by experimental error. See Problem 30.24 for a spreadsheet that implements these calculations.

23. Calculate the rotational spectroscopic temperature and partition function for HF at 298.15 K. Calculate the contribution of rotation to the molar entropy and molar Gibbs energy of HF.

Answer: The plan is to use the spectroscopic constants from Table 27.6.1 and the conversion factor hc/k = 1.438778 cm K.

Table 27.6.1 lists $\tilde{B}_e = 20.9537\ \text{cm}^{-1}$, giving the spectroscopic temperature:

$$\Theta_r = \frac{\tilde{B}hc}{k} = 20.9537\ \text{cm}^{-1}(1.438778\ \text{cm K}) = 30.1477\ \text{K}$$

Using Eq. 30.3.3 with $\sigma = 1$, the rotational partition function is:

$$q_r = \frac{T}{\sigma\Theta_r} = \frac{298.15\ \text{K}}{30.1477\ \text{K}} = 9.88964$$

The preceding problem gives the corresponding contribution of rotation to the molar entropy and Gibbs energy.

24. Calculate the rotational partition function for $^{24}Mg_2$ at 298.15 K. The bond length is R_e = 3.07859 Å. Calculate the contribution of rotation to the molar entropy and molar Gibbs energy of Mg_2.

Answer: The plan is to use $kT/hc = 207.224\ \text{cm}^{-1}$, and the high temperature approximation or Equipartition rotational contribution of a diatomic molecule of U – U(0) = RT.

The molar mass of ^{24}Mg is 23.98504 g mol^{-1}. The reduced mass of $^{24}Mg_2$ is:

$$\mu = \frac{m_1\, m_2}{m_1 + m_2} = \frac{\mathfrak{M}_{Mg}/2}{N_A}\ (1\ \text{kg}/1000\ \text{g}) = 1.991406\text{x}10^{-26}\ \text{kg}.$$

With Eqs. 24.4.10 and 24.5.41, the rotational constant is: $\tilde{B}_e = \dfrac{\hbar}{4\pi\,\mu R_e^2\, c}$

$$\tilde{B}_e = \frac{1.05457266\text{x}10^{-34}\ \text{J s}}{4\pi(1.991406\text{x}10^{-26}\ \text{kg})(3.8905\text{x}10^{-10}\ \text{m})^2(2.99792458\text{x}10^{10}\ \text{cm s}^{-1})} = 0.09287\ \text{cm}^{-1}$$

Using Eq. 30.1.39 with $\sigma = 2$, the rotational partition function is:

$$q_r = \frac{kT}{\sigma\tilde{B}hc} = \frac{207.224\ \text{cm}^{-1}}{\sigma\tilde{B}} = \frac{207.224\ \text{cm}^{-1}}{2(0.09287\ \text{cm}^{-1})} = 1115.7$$

The contribution of rotation of a linear molecule to the internal energy is U – U(0) = RT, from the high temperature approximation, Table 30.3.3, or correspondingly from Equipartition. Using Eq. 30.2.26° the molar rotational entropy is:

$$S_r = R \ln q_r + R = 8.31446\ \text{J K}^{-1}\ \text{mol}^{-1}(\ln 1115.7 + 1) = 66.659\ \text{J K}^{-1}\ \text{mol}^{-1}$$

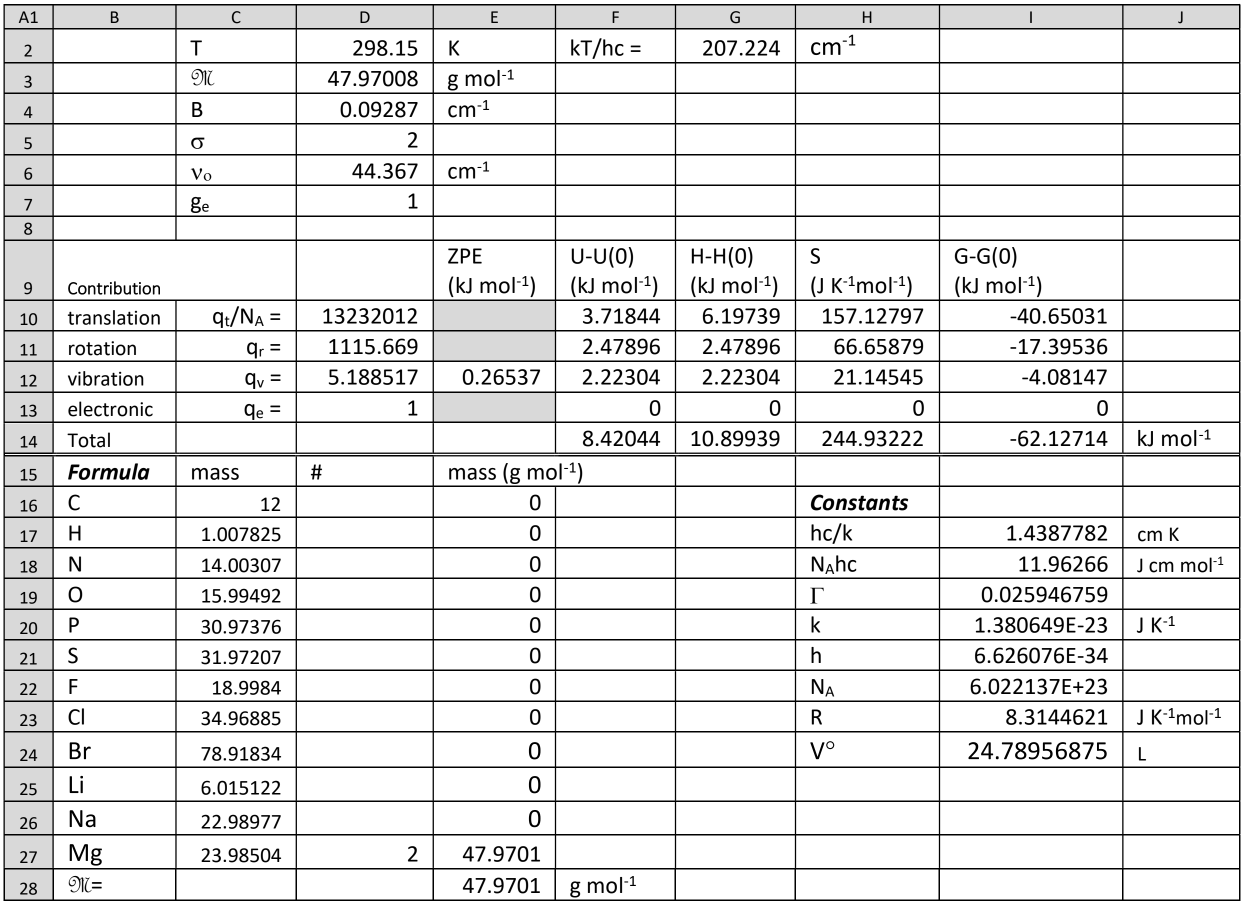
Using Eq. 30.2.52°, the contribution to the molar Gibbs energy is:

$$\begin{aligned} G_r - G_r(0) &= -RT \ln q_r = -\,8.31446\ \text{J K}^{-1}\ \text{mol}^{-1}(1\ \text{kJ}/1000\ \text{J})(298.15\ \text{K}) \ln 1115.7 \\ &= -17.395\ \text{kJ mol}^{-1} \end{aligned}$$

As a check, note that for the rotational contribution, $H_r - H_r(0) = U_r - U_r(0)$; the factor of nRT in the conversion of the overall internal energy to enthalpy, $H = U + nRT$, is combined with the translational contribution. Then using the definition of Gibbs energy, $G \equiv H - TS$, and the entropy result, above:

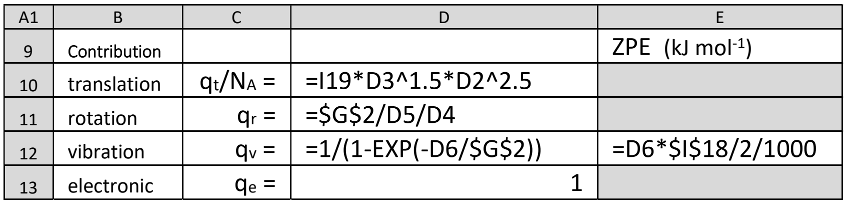
$$\begin{aligned} G_r - G_r(0) &= H_r - H_r(0) - T\,S_r = U_r - U_r(0) - T\,S_r \\ &= 2.47896 \text{ kJ mol}^{-1} - 298.15 \text{ K}(66.659 \text{ J K}^{-1} \text{ mol}^{-1})(1 \text{ kJ}/1000 \text{ J}) \\ &= 2.47896 \text{ kJ mol}^{-1} - 8.15944 \text{ kJ mol}^{-1} = -17.395 \text{ kJ mol}^{-1} \end{aligned}$$

The spreadsheet format is particularly convenient for statistical mechanical calculations. A spreadsheet that implements these calculations for translation, rotation, and vibration in diatomics is shown below. We are so lazy that we even included a section that calculates the molar mass from the molecular formula. The most abundant isotope specific masses are used. This spreadsheet applies to several problems:



A1	B	C	D	E	F	G	H	I	J
2		T	298.15	K	kT/hc =	207.224	cm^{-1}		
3		$\mathfrak{M}$	47.97008	$g\ mol^{-1}$					
4		B	0.09287	cm^{-1}					
5		σ	2						
6		ν_o	44.367	cm^{-1}					
7		g_e	1						
8									
9	Contribution			ZPE ($kJ\ mol^{-1}$)	U-U(0) ($kJ\ mol^{-1}$)	H-H(0) ($kJ\ mol^{-1}$)	S ($J\ K^{-1} mol^{-1}$)	G-G(0) ($kJ\ mol^{-1}$)	
10	translation	q_t/N_A =	13232012		3.71844	6.19739	157.12797	-40.65031	
11	rotation	q_r =	1115.669		2.47896	2.47896	66.65879	-17.39536	
12	vibration	q_v =	5.188517	0.26537	2.22304	2.22304	21.14545	-4.08147	
13	electronic	q_e =	1		0	0	0	0	
14	Total				8.42044	10.89939	244.93222	-62.12714	$kJ\ mol^{-1}$
15	***Formula***	mass	#	mass ($g\ mol^{-1}$)					
16	C	12		0			***Constants***		
17	H	1.007825		0			hc/k	1.4387782	cm K
18	N	14.00307		0			$N_A hc$	11.96266	$J\ cm\ mol^{-1}$
19	O	15.99492		0			Γ	0.025946759	
20	P	30.97376		0			k	1.380649E-23	$J\ K^{-1}$
21	S	31.97207		0			h	6.626076E-34	
22	F	18.9984		0			N_A	6.022137E+23	
23	Cl	34.96885		0			R	8.3144621	$J\ K^{-1} mol^{-1}$
24	Br	78.91834		0			V°	24.78956875	L
25	Li	6.015122		0					
26	Na	22.98977		0					
27	Mg	23.98504	2	47.9701					
28	$\mathfrak{M}$=			47.9701	$g\ mol^{-1}$				

Cell G2 is: “=D2/I17”
Cells D10:E12 are:



A1	B	C	D	E
9	Contribution			ZPE ($kJ\ mol^{-1}$)
10	translation	q_t/N_A =	=I19*D3^1.5*D2^2.5	
11	rotation	q_r =	=$G$2/D5/D4	
12	vibration	q_v =	=1/(1-EXP(-D6/$G$2))	=D6*$I$18/2/1000
13	electronic	q_e =	1	

Cell F10 is: "=3*$I$23*$D$2/2/1000"
Cell G10 is: "=F10+I23*$D$2/1000"
Cell H10 is: "=$I$23*(LN($I$24)+3*LN($D$2)/2+3*LN(D3)/2)+11.1037"
Cell I10 is: "=-I23*D2*LN(D10)/1000"

25. Calculate the contribution of vibration to the molar entropy at 298.15 K for HCN, given the literature value of the observed bending vibration frequency at $\tilde{\nu}_o = 711.98\ \text{cm}^{-1}$ and the two stretching vibrations at 2096.85 cm^{-1} and 3311.47 cm^{-1}.[3] The bending vibration is doubly degenerate. (See also Problems 8 and 9 for the contributions of translation and rotation.)

Answer: The plan is to use Eqs. 30.3.15 and 30.2.26 for the degenerate bending vibrations; the overall vibrational entropy is the sum of the entropy of each normal mode.

The Boltzmann weighting factor for the bending vibration is:

$$e^{-711.98\ \text{cm}^{-1}/207.224\ \text{cm}^{-1}} = 0.032200$$

Using Eq. 30.1.31, the vibrational partition function for each bending vibration is:

$$q_v = \frac{1}{1 - e^{-\tilde{\nu}_o/207.224\ \text{cm}^{-1}}} = \frac{1}{1 - e^{-711.98/207.224}} = 1.033270$$

The vibrational partition functions for the two stretches are 1.000035 and 1.000000115, respectively, which are too close to one to contribute significantly to the final entropy. The constant N_Ahc is given as (see inside front cover of the text):

$$N_Ahc = 6.0221367\text{x}10^{23}\ \text{mol}^{-1}(6.6260755\text{x}10^{-34}\ \text{J s})(2.99792458\text{x}10^{10}\ \text{cm s}^{-1})$$
$$= 11.962658 \pm 1.0\text{x}10^{-5}\ \text{J cm mol}^{-1} = 11.962658(10)\ \text{J cm mol}^{-1}$$

giving: $N_Ahc\tilde{\nu}_o = 11.96266\ \text{J cm mol}^{-1}(1\ \text{kJ}/1000\ \text{J})(711.98\ \text{cm}^{-1}) = 8.51729\ \text{kJ mol}^{-1}$

The zero-point energy is: $\tfrac{1}{2}N_Ahc\tilde{\nu}_o = \tfrac{1}{2}(8.51717\ \text{kJ mol}^{-1}) = 4.259\ \text{kJ mol}^{-1}$

Using Eq. 30.3.15, the contribution of each bending vibration to the molar internal energy is:

$$U_{m,v} - U_{m,v}(0) = \frac{N_Ah\nu_o\, e^{-h\nu_o/kT}}{1 - e^{-h\nu_o/kT}} = 8.51729\ \text{kJ mol}^{-1}\,\frac{0.032200}{1 - 0.032200} = 0.283377\ \text{kJ mol}^{-1}$$

Using Eq. 30.2.26° the molar vibrational entropy of each bending vibration is:

$$S_v = R \ln q_v + \frac{U_v - U_v(0)}{T}$$
$$= 8.31446\ \text{J K}^{-1}\ \text{mol}^{-1}(\ln 1.03327) + \frac{0.283377\text{x}10^3\ \text{J mol}^{-1}}{298.15\ \text{K}}$$
$$= 0.27212\ \text{J K}^{-1}\ \text{mol}^{-1} + 0.95045\ \text{J K}^{-1}\ \text{mol}^{-1} = 1.22253\ \text{J K}^{-1}\ \text{mol}^{-1}$$

For both bending vibrations the total is: $S_v = 2.4451\ \text{J K}^{-1}\ \text{mol}^{-1}$

In Problem 9, we worked out the translational and rotational contributions to the molar standard state entropy: $S^\circ_{m,298.15\ K} = 199.38\ \text{J K}^{-1}\ \text{mol}^{-1}$. Adding in the vibrational contribution gives:

$$S^{\circ}_{m,298.15\text{ K}} = 199.38\text{ J K}^{-1}\text{ mol}^{-1} + 2.4451\text{ J K}^{-1}\text{ mol}^{-1} = 201.83\text{ J K}^{-1}\text{ mol}^{-1}$$

Using Table 8.4.1 in the Data Section, $S^{\circ}_{298\text{ K}} = 201.78\text{ J K}^{-1}\text{ mol}^{-1}$ giving only a 0.02% difference.

26. Calculate the vibrational partition function at 298.15 K for Mg_2, given the literature value of the fundamental vibration frequency, $\tilde{\nu}_o = 47.89\text{ cm}^{-1}$. Calculate the contribution of vibration to the zero point energy, and molar internal energy, entropy, and Gibbs energy of Mg_2.

Answer: The plan is to use Table 30.3.3 and Eq. 30.3.15. (See Problem 6 for the calculation of $\tilde{\nu}_o = 47.89\text{ cm}^{-1}$ for Mg_2).

Using Eq. 30.1.31, the vibrational partition function is:

$$q_V = \frac{1}{1 - e^{-\tilde{\nu}_o/207.224\text{ cm}^{-1}}} = \frac{1}{1 - e^{-47.89/207.224}} = 4.8463$$

The zero-point energy is $½N_Ahc\tilde{\nu}_o$. The constant N_Ahc is given as (see inside front cover of the text):

$$N_Ahc = 6.0221367\text{x}10^{23}\text{ mol}^{-1}(6.6260755\text{x}10^{-34}\text{ J s})(2.99792458\text{x}10^{10}\text{ cm s}^{-1})$$
$$= 11.962658 \pm 1.0\text{x}10^{-5}\text{ J cm mol}^{-1} = 11.962658(10)\text{ J cm mol}^{-1}$$

giving: $N_Ahc\tilde{\nu}_o = 11.96266\text{ J cm mol}^{-1}(1\text{ kJ}/1000\text{ J})(47.89\text{ cm}^{-1}) = 0.57289\text{ kJ mol}^{-1}$

The zero-point energy is: $½N_Ahc\tilde{\nu}_o = ½(0.57289\text{ kJ mol}^{-1}) = 0.28645\text{ kJ mol}^{-1}$

The Boltzmann weighting factor is: $e^{-47.89\text{ cm}^{-1}/207.224\text{ cm}^{-1}} = 0.79366$

Using Eq. 30.3.15, the contribution of a vibration to the molar internal energy is:

$$U_{m,v} - U_{m,v}(0) = \frac{N_Ah\nu_o\, e^{-h\nu_o/kT}}{1 - e^{-h\nu_o/kT}} = 0.57289\text{ kJ mol}^{-1}\,\frac{0.79366}{1 - 0.79366} = 2.2035\text{ kJ mol}^{-1}$$

Using Eq. 30.2.26° the molar vibrational entropy is:

$$S_v = R\ln q_v + \frac{U_v - U_v(0)}{T}$$
$$= 8.31446\text{ J K}^{-1}\text{ mol}^{-1}(\ln 4.8463) + \frac{2.2035\text{x}10^{3}\text{ J mol}^{-1}}{298.15\text{ K}} = 20.511\text{ J K}^{-1}\text{ mol}^{-1}$$

Using Eq. 30.2.52°, the contribution to the molar Gibbs energy is:

$$G_v - G_v(0) = -RT\ln q_v = -\,8.31446\text{ J K}^{-1}\text{ mol}^{-1}(1\text{ kJ}/1000\text{ J})(298.15\text{ K})\ln 4.8463$$
$$= -3.912\text{ kJ mol}^{-1}$$

As a check, note that for the rotational contribution, $H_r - H_r(0) = U_r - U_r(0)$; the factor of nRT in the conversion of the overall internal energy to enthalpy, $H = U + nRT$, is combined with the translational contribution. Then using the definition of Gibbs energy, $G \equiv H - TS$, and the entropy result, above:

$$
\begin{aligned}
G_v - G_v(0) &= H_v - H_v(0) - T\,S_v = U_v - U_v(0) - T\,S_v \\
&= 2.2035 \text{ kJ mol}^{-1} - 298.15 \text{ K}(20.511 \text{ J K}^{-1} \text{ mol}^{-1})(1 \text{ kJ}/1000 \text{ J}) \\
&= 2.2035 \text{ kJ mol}^{-1} - 6.1154 \text{ kJ mol}^{-1} = -3.912 \text{ kJ mol}^{-1}
\end{aligned}
$$

See Problem 30.24 for a spreadsheet that implements these calculations.

27. The symmetry number, σ, in the rotational partition function may seem arbitrary at first. This problem is designed to explore the effects of the symmetry number on the properties of molecules. A good test case is to consider N_2 and CO. We will look at the contribution of rotation to the entropy of these two very similar diatomic molecules. The mass of N_2 is 28.02 g mol^{-1} and the mass of CO is 28.01 g mol^{-1}, so the contribution of translation to the entropy is essentially identical. The fundamental vibration frequencies of the two are very similar, $\tilde{\nu}_o$ for N_2 is 2359.6 cm^{-1} and for CO is 2170.2 cm^{-1}. The vibrational contribution to the entropy is essentially identical. Both molecules have singlet ground states. The rotational constants are also very similar, $\tilde{B}_e$ for N_2 is 2.010 cm^{-1} and for CO is 1.9314 cm^{-1}. So, the only major difference is the symmetry.

(a). Using the result of part a, prove that the contribution of rotation to the molar entropy of a diatomic gas is:

$$S_m = R \ln\left(\frac{kT}{\tilde{B}_e hc}\right) + R - R \ln \sigma$$

(b). Using the result from part a, and assuming that the differences in $\tilde{B}_e$ of N_2 and CO are negligible, calculate the theoretical difference in entropy of N_2 and CO. The experimental entropies are 191.61 J K^{-1} mol^{-1} for N_2 and 197.67 J K^{-1} mol^{-1} for CO. Compare theory and experiment.

(c). Evaluate the contribution of just the symmetry part of the rotational partition function to the equilibrium constant for the reaction: $N_2 + CO_2 \rightleftarrows CO + N_2O$

Answer: The plan is to use Eq. 30.3.7 as the basis for this problem.

(a). Splitting out the symmetry number term from Eq. 30.3.7 for one mole gives:

$$S_{r,m} = R \ln\left(\frac{kT}{\sigma\tilde{B}hc}\right) + R = R \ln\left(\frac{kT}{\tilde{B}hc}\right) + R - R \ln \sigma$$

(b). The difference assuming equal rotational constants with $\sigma_{N2} = 2$ and $\sigma_{CO} = 1$ is then:

$$
\begin{aligned}
S_r(N_2) - S_r(CO) &= -R \ln \sigma_{N2} - (-R \ln \sigma_{CO}) \\
&= 8.3145 \text{ J K}^{-1} \text{ mol}^{-1}(\ln \sigma_{CO} - \ln \sigma_{N2}) \\
&= 8.3145 \text{ J K}^{-1} \text{ mol}^{-1}(\ln 1 - \ln 2) = -5.763 \text{ J K}^{-1} \text{ mol}^{-1}
\end{aligned}
$$

with the experimental difference: $S_r(N_2) - S_r(CO) = 191.61 \text{ J K}^{-1} \text{ mol}^{-1} - 197.67 \text{ J K}^{-1} \text{ mol}^{-1} = -6.06 \text{ J K}^{-1} \text{ mol}^{-1}$. The difference in entropy is primarily given by symmetry.

(c). The contribution of the symmetry part of the rotational partition function to the equilibrium constant for the reaction using $\sigma_{N2} = 2$, $\sigma_{CO2} = 2$, $\sigma_{CO} = 1$, and $\sigma_{N2O} = 1$ is
$K_p = (1)(1)/(2)(2) = 0.25$

28. Write your own spreadsheet that reproduces Example 30.4.1.

Answer: The cells C11:C18 are:

A	B	C
11	q_t/N_A	=$C$24*$C$20^2.5*C6^1.5
12	q_r	=$C$21/C8/C5
13	q_v	=1/(1-EXP(-C4/$C$21))
14	q_e	=C7
15	G-G(0) internal	=-$C$22*$C$20*LN(C12*C13*C14)/1000
16	G-G(0) (kJ mol^{-1})	=-$C$22*$C$20*LN(C11*C12*C13*C14)/1000
17	G(0) (kJ mol^{-1})	=-C9*$C$27
18	G (kJ mol^{-1})	=C17+C16

Cell G20 is "=(2*G18-C18-E18)" and Cell G21 is "=G20/2".

29. The equilibrium constant expression in Eq 30.4.24° can be related directly to the bond length of the diatomic molecules: R_{AB} for the product and R_{BC} for the reactant. (a). Express Eq. 30.4.24° directly in terms of the bond lengths of the diatomic species. The result clearly shows the relationship between molecular structure and the position of equilibrium. (b). For atom-diatom exchange on the basis of rotation alone, if $R_{AB} > R_{BC}$ are products or reactants favored?

Answer: The plan is to use the definition of the rotational constant in terms of the moment of inertia of a diatomic molecule, Eqs. 24.4.10 and 24.5.41, to find the relationship to the bond lengths.

(a). Given the moment of inertia of a diatomic molecule is $I = \mu R^2$ with the rotational constant:

$$\tilde{B} = \frac{\hbar}{4\pi\, I\, c} = \frac{\hbar}{4\pi\, \mu R^2\, c} \qquad (24.4.10,\ 24.5.41)$$

The ratio for the rotational partition functions simplifies to:

$$\left(\frac{1/\tilde{B}_{AB}}{1/\tilde{B}_{BC}}\right) = \frac{\mu_{AB} R_{AB}^2}{\mu_{BC} R_{BC}^2}$$

From Eq. 30.4.24°, the equilibrium expression is:

$$K_p = \left(\frac{m_{AB}\, m_C}{m_A\, m_{BC}}\right)^{3/2} \frac{\mu_{AB} R_{AB}^2}{\mu_{BC} R_{BC}^2} \left(\frac{\dfrac{1}{1-e^{-h\tilde{\nu}_o(AB)\, c/kT}}}{\dfrac{1}{1-e^{-h\tilde{\nu}_o(BC)\, c/kT}}}\right) \left(\frac{g_{AB}\, g_C}{g_A\, g_{BC}}\right) e^{-\Delta E_o/RT}$$

translation rotation vibration electronic zero-point energy shift (b). From this final expression, if $R_{AB} > R_{BC}$ the numerator is larger than the denominator, which favors products. Alternatively, thinking of the string of relationships, if R_{AB} increases compared to R_{BC}:

If $R_{AB}\uparrow$ then:
$I_{AB}\uparrow$, $\tilde{B}_{AB}\downarrow$, rotational level spacing$\downarrow$, accessible rotational states of products$\uparrow$, $K_p\uparrow$

The flow of the logic provides a concise summary of the relationships of fundamental quantum mechanics, spectroscopy, and thermodynamics. The progression is from the structural properties of individual molecules to the many-body phenomena of macroscopic equilibrium.

30. Use typical values of the partition functions, Eq. 30.3.5°, to estimate the equilibrium constant of the ideal gas reaction: $O_2 + F \rightleftarrows OF + O$ at 298 K. This reaction is a possible reaction in ozone depletion in the stratosphere. Use $q_t/N_A = 1\text{x}10^7$, $q_r = 100$, and $q_v = 1$. Since OF has an odd number of electrons, assume the ground state of OF is a doublet, $^2\Pi$. The bond dissociation energies are: $D_o(O_2) = 5.126$ eV = 494.6 kJ mol^{-1} and $D_o(OF) = 1.61$ eV = 155 kJ mol^{-1}.

Answer: The zero point energy shift term is simplified by using the equivalent temperature in eV from Table 30.3.1, kT/e = 0.02569 eV at 298.15 K.

The equilibrium constant for $O_2 + F \rightarrow OF + O$ is:

$$K_p = \left(\frac{q_{OF}/N_A\ q_O/N_A}{q_{O_2}/N_A\ q_F/N_A}\right) e^{-\Delta E_o/RT}$$

with $\Delta E_o = [-D_o(OF)] - [-D_o(O_2)] = [-1.61 \text{ eV}] - [-5.126 \text{ eV}] = 3.52 \text{ eV} = 340.\ \text{kJ mol}^{-1}$

The zero point shift term in eV is: $e^{-\Delta E_o/RT} = e^{-3.53 \text{ eV}/0.02569 \text{ eV}} = e^{-137} = 3.2\text{x}10^{-60}$

Alternatively, the zero point shift term in kJ mol^{-1} is:

$$e^{-\Delta E_o/RT} = e^{-340\text{x}10^3 \text{ J mol}^{-1}/(8.314 \text{ J K}^{-1}\text{mol}^{-1}\ 298.2 \text{ K})} = e^{-137} = 3.2\text{x}10^{-60}$$

The rotational symmetry numbers are $\sigma_{O_2} = 2$ and $\sigma_{OF} = 1$. The vibrations are too high in frequency to make a contribution (> 500 cm^{-1}). At a low level of approximation we can take the electronic partition functions as the ground state degeneracies, which for atoms are given in Table 30.1.2. The ground state degeneracies are $g_{O_2} = 3$, $g_F = 4$, $g_{OF} = 2$, and $g_O = 5$. The equilibrium constant is roughly approximated:

$$K_p \cong \underbrace{\left(\frac{10^7\ 10^7}{10^7\ 10^7}\right)}_{\textit{translation}} \underbrace{\left(\frac{100}{100/2}\right)}_{\textit{rotation}} \underbrace{\left(\frac{1}{1}\right)}_{\textit{vibration}} \underbrace{\left(\frac{2\cdot 5}{3\cdot 4}\right)}_{\textit{electronic}} \underbrace{e^{-137}}_{\textit{zero point shift}} \cong 5\text{x}10^{-60}$$

Products are favored by rotation and reactants are favored by electronic degeneracy. However, the order of magnitude of the equilibrium constant is dominated by the bond dissociation energies. Diatomic O_2 has the stronger bond, strongly favoring reactants.

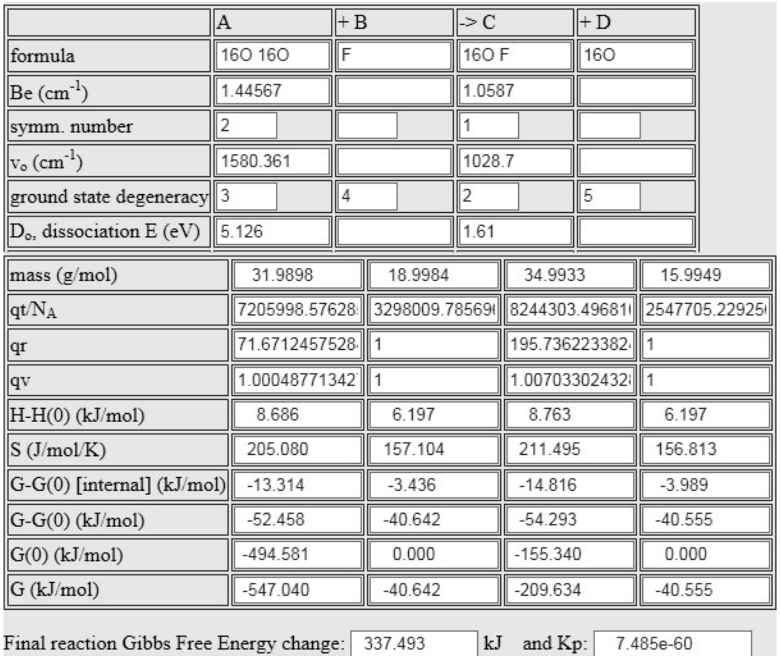
One of the possible large errors in using "garden variety" estimates is in the rotational contribution. The rotational constants are $\tilde{B}_e(OF) = 1.0587$ cm^{-1} and $\tilde{B}_e(O_2) = 1.446$ cm^{-1}, giving more precise values of the rotational partition functions:

$$q_r(\text{OF}) = \frac{207.224\ \text{cm}^{-1}}{1.0587\ \text{cm}^{-1}} = 196.7 \qquad \text{and} \qquad q_r(\text{O}_2) = \frac{207.224\ \text{cm}^{-1}}{2(1.446\ \text{cm}^{-1})} = 71.65$$

with $q_r(\text{OF})/q_r(\text{O}_2) = 196.7/71.65 = 2.75$ rather than the "garden variety" estimate of 2.

31. Use the "*Equilibrium Constants from Molecular Structure*" applet, "efs.html," on the textbook Web site and companion CD to calculate the equilibrium constant for the reaction in the previous problem: $O_2 + F \rightleftarrows OF + O$ at 298 K. The spectroscopic parameters are available as examples, or the values given in the previous problem can be input by hand. Compare with the approximate results from the previous problem.

Answer: The parameters were input using the "Examples" buttons to give the following results:



	A	+ B	-> C	+ D
formula	16O 16O	F	16O F	16O
Be (cm^{-1})	1.44567		1.0587	
symm. number	2		1	
ν_o (cm^{-1})	1580.361		1028.7	
ground state degeneracy	3	4	2	5
D_o, dissociation E (eV)	5.126		1.61	

mass (g/mol)	31.9898	18.9984	34.9933	15.9949
qt/N_A	7205998.57628	3298009.78569	8244303.49681	2547705.22925
qr	71.6712457528	1	195.736223382	1
qv	1.00048771342	1	1.00703302432	1
H-H(0) (kJ/mol)	8.686	6.197	8.763	6.197
S (J/mol/K)	205.080	157.104	211.495	156.813
G-G(0) [internal] (kJ/mol)	-13.314	-3.436	-14.816	-3.989
G-G(0) (kJ/mol)	-52.458	-40.642	-54.293	-40.555
G(0) (kJ/mol)	-494.581	0.000	-155.340	0.000
G (kJ/mol)	-547.040	-40.642	-209.634	-40.555

Final reaction Gibbs Free Energy change: 337.493 kJ and Kp: 7.485e-60

These accurate calculations agree favorably with the "garden variety" estimates used in the previous problem. See also Problem 30.24 for a similar spreadsheet for a single species.

32. Consider the reaction $AB \rightarrow A + B$, where A and B are atoms. Predict the effect on the equilibrium constant if the following changes are made. (a). The AB molecule is a ground state triplet (like O_2) instead of a singlet. (b). The AB bond length is increased. (c). The AB force constant is increased. (d). The AB bond dissociation energy is increased. [In reality changing just one molecular parameter is impossible, bond strength changes have multiple effects. However, for the purposes of this exercise assume that the given change is done without changes in other parameters.]

Answer: The plan is to note if the change increases or decreases the number of accessible states and if the change is for a reactant or product.

The equilibrium constant is given in terms of the partition functions as:

$$K_p = \left(\frac{q_A/N_A\; q_B/N_A}{q_{AB}/N_A}\right) e^{-\Delta E_o/RT} = \left(\frac{q_A/N_A\; q_B/N_A}{q_{AB}/N_A}\right)\left(\frac{1}{q_r(AB)}\right)\left(\frac{1}{q_v(AB)}\right)\left(\frac{q_e(A)\; q_e(B)}{q_e(AB)}\right) e^{-\Delta E_o/RT}$$

with $\Delta E_o = -\varepsilon_o(AB) = -\,[-D_o(AB)]$

(a). If the AB molecule is a ground state triplet (like O_2) instead of a singlet, the ground state degeneracy increases from one to three, and the number of accessible electronic states increases. Since AB is a reactant, increasing the number of accessible states shifts the equilibrium towards reactants.

(b). The rotational constant of a diatomic molecule is given by Eq.30.1.34 with moment of inertia $I = \mu R^2$ for a diatomic molecule : $\tilde{B} = \dfrac{\hbar}{4\pi\, \mu R^2\, c}$

If the bond length of AB is increased, the moment of inertia is increased, the rotational constant is decreased, the rotational energy level spacing is decreased, and the number of accessible states is increased for AB. Since AB is a reactant, increasing the number of accessible states shifts the equilibrium towards reactants. In summary:

If $R_{AB}\uparrow$ then:
 $I_{AB}\uparrow$, $\tilde{B}_{AB}\downarrow$, rotational level spacing↓, accessible rotational states of reactants↑, $K_p\downarrow$

(c). If the bond force constant of AB is increased, the fundamental vibration frequency of AB is increased, the vibrational energy level spacing is increased, and the number of accessible states is decreased. Since AB is a reactant, decreasing the number of accessible states shifts the equilibrium towards products. In summary:

If $k_{AB}\uparrow$ then:
 $\tilde{\nu}_o(AB)\uparrow$, vibrational level spacing↑, accessible vibrational states of reactants↓, $K_p\uparrow$

(d). If the bond dissociation energy of AB is increased, the zero-point energy shift is increased, the overall energy states of AB are lowered, and the number of accessible AB states are increased. Since AB is a reactant, increasing the number of accessible states shifts the equilibrium towards reactants. AB becomes more stable and so is favored in the equilibrium state.

<u>33</u>. Calculate the equilibrium constant of the ideal gas dissociation $Mg_2 \rightleftarrows Mg + Mg$ at 298.15 K. Assume the isotope is ^{24}Mg. The spectroscopic constants for Mg_2 are $R_e = 3.8905$ Å, $\tilde{\nu}_o = 47.89\ cm^{-1}$, and $D_e = 0.04979(4)$ eV.[1] The ground state of Mg_2 is $^1\Sigma_u^+$ and the ground state of Mg-atoms is ^1S_o.

Answer: The molar mass of ^{24}Mg is 23.98504 g mol^{-1}. The mass of Mg_2 is 47.97954 g mol^{-1} and with Eqs. 30.3.1° and 30.3.2°:

$$\frac{q^{\circ}_{t,Mg2}}{N_A} = \Gamma\,(\mathfrak{M}/g\ mol^{-1})^{3/2}(T/K)^{5/2} = 0.0259472\ (47.97954)^{3/2}\ (298.15)^{5/2} = 1.32320x10^{7}$$

For Mg-atoms: $\frac{q^{\circ}_{t,Mg}}{N_A} = 0.0259472\ (23.98504)^{3/2}\ (298.15)^{5/2} = 4.678223\text{x}10^{6}$

The reduced mass of Mg_2 is: $\mu = \frac{m_1\, m_2}{m_1 + m_2} = \frac{\mathfrak{M}_{Mg}/2}{N_A}\ (1\ \text{kg}/1000\ \text{g}) = 1.991406\text{x}10^{-26}\ \text{kg}$.

With Eqs. 24.4.10 and 24.5.41: $\tilde{B}_e = \frac{\hbar}{4\pi\ \mu R_e^2\ c}$

$$\tilde{B}_e = \frac{1.05457266\text{x}10^{-34}\ \text{J s}}{4\pi(1.991406\text{x}10^{-26}\ \text{kg})(3.8905\text{x}10^{-10}\ \text{m})^2(2.99792458\text{x}10^{10}\ \text{cm s}^{-1})} = 0.09287\ \text{cm}^{-1}$$

Using Eq. 30.1.39 with $\sigma = 2$, the rotational partition function is:

$$q_r = \frac{kT}{\sigma\tilde{B}hc} = \frac{207.224\ \text{cm}^{-1}}{\sigma\tilde{B}} = \frac{207.224\ \text{cm}^{-1}}{2(0.09287\ \text{cm}^{-1})} = 1115.7$$

Using Eq. 30.1.31, the vibrational partition function is:

$$q_v = \frac{1}{1 - e^{-\tilde{\nu}_o/207.224\ \text{cm}^{-1}}} = \frac{1}{1 - e^{-47.89/207.224}} = 4.8463$$

See Problem 30.24 for a spreadsheet that implements these calculations. The reaction products are atoms, while the reference point is for totally dissociated atoms. The zero-point energy shift is then just $\Delta E_o = -\varepsilon_o(Mg_2) = -\ [-D_o(Mg_2)] = 0.04979(4)$ eV. In terms of bond energy, the reactions runs uphill from Mg_2. Using Table 30.3.1, kT/e = 0.025693 eV at 298.15 K, the zero-point energy sift term is:

$$e^{-\Delta E_o/RT} = e^{-0.04979\ \text{eV}/0.025693\ \text{eV}} = e^{-1.938} = 0.1440 \pm 0.0023$$

Even though the bond dissociation energy is unusually small, the zero-point energy shift term is still unfavorable. Considering each degree of freedom separately, the overall equilibrium constant is:

$$K_p = \frac{q^{\circ}_{Mg}\, q^{\circ}_{Mg}}{q^{\circ}_{Mg_2}}\ e^{-\Delta E_o/RT}$$

$$= \left(\frac{(4.678223\text{x}10^{6})^2}{1.32320\text{x}10^{7}}\right)\left(\frac{1}{1115.7}\right)\left(\frac{1}{4.8463}\right)\ \left(\frac{1\cdot 1}{1}\right)\quad 0.1440$$

$$= \quad \underset{translation}{1.65400\text{x}10^{6}}\quad \underset{rotation}{0.0008963}\quad \underset{vibration}{0.20634}\quad \underset{electronic}{1}\quad \underset{zero\text{-}point\ energy\ shift}{0.1440}\quad = 44.05 \pm 0.70$$

Mg_2 is 99% dissociated at 298.2 K and 1 bar, Eq. 20.2.8. Our expectation based on Lewis structures is that Mg_2 is not stable, since Mg atoms are closed shell.

34. Heat capacities are the fundamental building blocks of all thermodynamic properties. For example, Third Law absolute entropies are based entirely on the temperature dependence of the heat capacity of the pure substance and enthalpies of the phase transitions, which in turn require heat capacities for their measurement. (a). Prove that the constant volume heat capacity of a pure substance is given by:

$$C_v = \left(\frac{\partial U}{\partial T}\right)_v = 2nRT\left(\frac{\partial \ln q}{\partial T}\right)_v + nRT^2\left(\frac{\partial^2 \ln q}{\partial T^2}\right)_v$$

(b). Show that the constant volume heat capacity of rotation of a linear molecule is nR.

Answer: The plan is to note that the constant volume heat capacity is the temperature derivative of the internal energy, $C_v = (\partial U/\partial T)_v$.

(a). Using Eq. 30.2.16° and the product rule:

$$U - U(0) = nRT^2\left(\frac{\partial \ln q}{\partial T}\right)_v \qquad 1$$

$$C_v = \left(\frac{\partial U}{\partial T}\right)_v = 2nRT\left(\frac{\partial \ln q}{\partial T}\right)_v + nRT^2\left(\frac{\partial^2 \ln q}{\partial T^2}\right)_v \qquad 2$$

(b). For rotations using Eq. 30.1.39: $q_r = \frac{kT}{\sigma\tilde{B}hc}$ or $\ln q_r = \ln\left(\frac{k}{\sigma\tilde{B}hc}\right) + \ln T$ 3

The derivatives are: $\left(\frac{\partial \ln q}{\partial T}\right)_v = \left(\frac{\partial \ln T}{\partial T}\right)_v = \frac{1}{T}\left(\frac{\partial T}{\partial T}\right)_v = 1/T$ and $\left(\frac{\partial^2 \ln q}{\partial T^2}\right)_v = -1/T^2$ 4

Substituting the derivatives into Eq. 2 gives:

$$C_v = \left(\frac{\partial U}{\partial T}\right)_v = 2nRT(1/T) + nRT^2(-1/T^2) = nR$$

as expected from Equipartition.

35. The Equipartition prediction of the contribution of a vibration to the molar heat capacity of a diatomic molecule is $C_v = R$, which is the maximum contribution at high temperatures. More accurately, the contribution of vibration to the internal energy of a diatomic molecule, in the harmonic approximation, is given by Eq. 30.3.13. (a). Determine the heat capacity of a diatomic molecule, in the harmonic oscillator approximation, usng the following steps. (a). To make the derivation easier, start by showing that the vibrational contribution is given by:

$$U - U(0) = \frac{Nh\nu_o\, e^{-\beta h\nu_o}}{1 - e^{-\beta h\nu_o}} = \frac{Nh\nu_o}{e^{\beta h\nu_o} - 1}$$

(b). Then, convert the heat capacity derivative to one written in terms of β:

$$C_v = \left(\frac{\partial U}{\partial T}\right)_v = \left(\frac{\partial U}{\partial \beta}\right)_v\left(\frac{\partial \beta}{\partial T}\right)_v = -\frac{1}{kT^2}\left(\frac{\partial U}{\partial \beta}\right)_v$$

(c). Show that: $C_v = \frac{N(h\nu_o)^2}{kT^2}\left(\frac{e^{\beta h\nu_o}}{(e^{\beta h\nu_o} - 1)^2}\right)$

(d). Finally show that: $C_v = \frac{N(h\nu_o)^2}{kT^2}\left[\frac{e^{-h\nu_o/kT}}{(1 - e^{-h\nu_o/kT})^2}\right]$

(e). Plot the molar heat capacity from T = 10 to 1000 K for a vibration frequency of 200.0 cm^{-1}. At what temperature, compared to $\tilde{\nu}_o$, does the vibration begin to make a significant contribution to the heat capacity?

Answer: The plan is to note that the constant volume heat capacity is the temperature derivative of the internal energy, $C_v = (\partial U/\partial T)_v$.

(a). Eq. 30.3.13 gives the contribution of a vibration to the internal energy as:

$$U - U(0) = \frac{Nh\nu_o\, e^{-\beta h\nu_o}}{1 - e^{-\beta h\nu_o}} \tag{1}$$

This relationship is simplified by multiplying numerator and denominator by $e^{\beta h\nu_o}$:

$$\frac{Nh\nu_o\, e^{-\beta h\nu_o}}{1 - e^{-\beta h\nu_o}}\left(\frac{e^{\beta h\nu_o}}{e^{\beta h\nu_o}}\right) = \frac{Nh\nu_o}{e^{\beta h\nu_o} - 1} \tag{2}$$

(b). To make the derivative easier, using the product rule and Eq. 30.2.8:

$$C_v = \left(\frac{\partial U}{\partial T}\right)_v = \left(\frac{\partial U}{\partial \beta}\right)_v\left(\frac{\partial \beta}{\partial T}\right)_v = -\frac{1}{kT^2}\left(\frac{\partial U}{\partial \beta}\right)_v \tag{3}$$

(c). Using the chain rule, the derivative is:

$$\left(\frac{\partial U}{\partial \beta}\right)_v = -\frac{Nh\nu_o}{(e^{\beta h\nu_o} - 1)^2}\left(\frac{\partial(e^{\beta h\nu_o} - 1)}{\partial \beta}\right)_v = -\frac{Nh\nu_o}{(e^{\beta h\nu_o} - 1)^2}\, e^{\beta h\nu_o}\,(h\nu_o) = -\frac{N(h\nu_o)^2\, e^{\beta h\nu_o}}{(e^{\beta h\nu_o} - 1)^2} \tag{4}$$

Substituting Eq. 4 into Eq. 3, the constant volume heat capacity is:

$$C_v = -\frac{1}{kT^2}\left(\frac{\partial U}{\partial \beta}\right)_v = \frac{N(h\nu_o)^2}{kT^2}\left(\frac{e^{\beta h\nu_o}}{(e^{\beta h\nu_o} - 1)^2}\right) \tag{5}$$

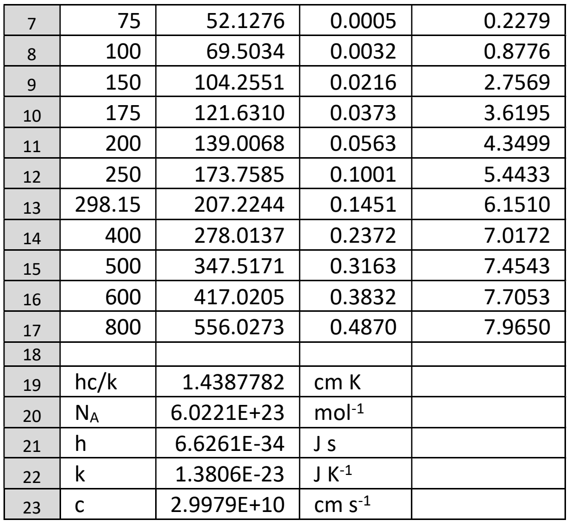
Now, we do the reverse of step 2:

$$C_v = \frac{N(h\nu_o)^2}{kT^2}\left(\frac{e^{\beta h\nu_o}}{(e^{\beta h\nu_o} - 1)^2}\right)\left(\frac{e^{-\beta h\nu_o}}{e^{-\beta h\nu_o}}\right)^2 \tag{6}$$

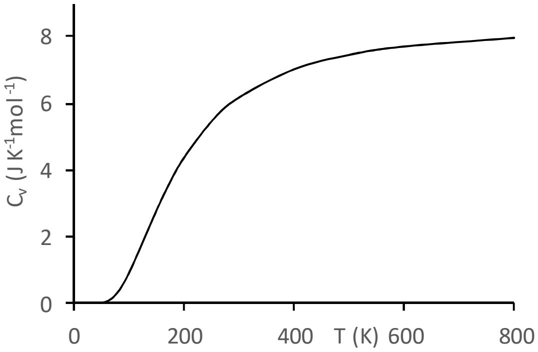
$$C_v = \frac{N(h\nu_o)^2}{kT^2}\left[\frac{e^{-\beta h\nu_o}}{(1 - e^{-\beta h\nu_o})^2}\right] = \frac{N(h\nu_o)^2}{kT^2}\left[\frac{e^{-h\nu_o/kT}}{(1 - e^{-h\nu_o/kT})^2}\right] \tag{7}$$

(d). The spreadsheet and plot are shown below.

A1	B	C	D	E
2	ν_o =	400	cm^{-1}	
3				
4	T (K)	kT/hc (cm^{-1})	$e^{-h\nu oc/kT}$	C_v (J K^{-1}mol^{-1})
5	10	6.9503	0.0000	0.0000
6	50	34.7517	0.0000	0.0110



7	75	52.1276	0.0005	0.2279
8	100	69.5034	0.0032	0.8776
9	150	104.2551	0.0216	2.7569
10	175	121.6310	0.0373	3.6195
11	200	139.0068	0.0563	4.3499
12	250	173.7585	0.1001	5.4433
13	298.15	207.2244	0.1451	6.1510
14	400	278.0137	0.2372	7.0172
15	500	347.5171	0.3163	7.4543
16	600	417.0205	0.3832	7.7053
17	800	556.0273	0.4870	7.9650
18				
19	hc/k	1.4387782	cm K	
20	N_A	6.0221E+23	mol^{-1}	
21	h	6.6261E-34	J s	
22	k	1.3806E-23	$J K^{-1}$	
23	c	2.9979E+10	$cm s^{-1}$	



Cell C5 is "=B5/$C$19". Cell D5 is "=EXP(-$C$2/C5)". Cell E5 is:

=$C$20*($C$21*$C$23*$C$2)^2/$C$22/$B5^2*$D5/(1-$D5)^2

The heat capacity "begins to thaw" near a wave number equivalent temperature of $\tilde{\nu}_o/10$. The heat capacity approaches 10% of the full value at $\tilde{\nu}_o/4$ or equivalently at a temperature of $\Theta_v/4$, where Θ_v is the spectroscopic temperature of the transition. The high temperature limiting value is R, or 8.314 J K^{-1} mol^{-1}, as expected from Equipartition.

Literature Cited:

1. J. G. Speight, *Lange's Handbook of Chemistry, 16th Ed.*, McGraw-Hill, New York, NY, 2005. Table 4.11
2. M. S. Lojko, Y. Beers, "A Table of Rotational Constants of Symmetric Top Molecules Giving Rise to Microwave Spectra," *J. Research National Bureau of Standards – A. Physics and Chemistry*, **1969**, *73A(2)*, 233-239. Available online at (last accessed 4/8/2015):
3. T. Shimanouchi, "Tables of Molecular Vibrational Frequencies, Consolidated Volume I, NSRDS-NBS 39," *Nat. Stand. Ref. Data Ser.*, **1972**, *39*, 1-164.

Chapter 31 Problems: Kinetic Molecular Theory

1. Calculate the average translational kinetic energy in J, cm^{-1}, and kJ mol^{-1} and the rms-speed of CO_2 at 298.2 K, assuming ideal gas behavior.

Answer: The plan is to use Eqs. 31.1.16 and 31.1.18 and note that the rms-speed depends on the molar mass but the average translational kinetic energy does not.

The average translational kinetic energy of any ideal gas at 298.2 K is:

$$\overline{\varepsilon_t} = {}^3/_2\, kT = {}^3/_2\, 1.38065\text{x}10^{-23}\ \text{J K}^{-1}(298.2\ \text{K}) = 6.175\text{x}10^{-21}\ \text{J}$$

$$\overline{\varepsilon_t} = {}^3/_2\, RT = 3.718\ \text{kJ mol}^{-1} \qquad \text{and with: } 1\ \text{cm}^{-1}/11.9627\ \text{J mol}^{-1}$$

$$\overline{\varepsilon_t} = 3.718\ \text{kJ mol}^{-1}\ (1000\ \text{J}/1\ \text{kJ})(1\ \text{cm}^{-1}/11.9627\ \text{J mol}^{-1}) = 310.8\ \text{cm}^{-1}$$

The values in kJ mol^{-1} and cm^{-1} are useful for comparisons, since we have often noted that the available thermal kinetic energy at room temperature is: RT = 2.48 kJ mol^{-1} or 207.2 cm^{-1}.

The molar mass for CO_2 is 44.01 g mol^{-1} or 0.04401 kg mol^{-1}. The rms-speed, using Eq. 31.1.18 is:

$$u = \sqrt{\frac{3\ RT}{\mathfrak{M}}} = \sqrt{\frac{3\ (8.3145\ \text{J K}^{-1}\ \text{mol}^{-1})(298.2\ \text{K})}{0.04401\ \text{kg mol}^{-1}}} = 411.1\ \text{m s}^{-1}$$

To verify the units note that 1 J = 1 kg m^2 s^{-2}, which is the reason that the molar mass must be in kg mol^{-1}.

2. Calculate the rate of molecular collisions in a balloon filled with N_2 at 298.2 K given the balloon has a 1.00 L volume at 1.00 bar. The hard-core collision diameter is $d_{N2} = (2r_{N2}) =$ 3.75 Å.

Answer: The plan is to use Eq. 31.3.8 to calculate the collision cross section.

The collision cross-section, using Eq. 31.3.8:

$$\sigma_{HC} = \pi\ (2r_{N2})^2 = \pi\ [3.75\text{x}10^{-10}\ \text{m}]^2 = 4.418\text{x}10^{-19}\ \text{m}^2 = 0.4418\ \text{nm}^2 = 44.18\ \text{Å}^2$$

The mass of N_2 is: $m = 28.02\ \text{g mol}^{-1}\ (1\ \text{kg}/1000\ \text{g})/6.0221\text{x}10^{23}\ \text{mol}^{-1} = 4.653\text{x}10^{-26}\ \text{kg}$

With Eq. 31.2.31 the average speed of N_2 molecules at 298.2 K is:

$$\overline{c} = \left(\frac{8(1.381\text{x}10^{-23}\ \text{J K}^{-1})(298.2\ \text{K})}{\pi\ 4.653\text{x}10^{-26}\ \text{kg}}\right)^{½} = 474.6\ \text{m s}^{-1}$$

The number density is given by the ideal gas law with 1 bar = $1\text{x}10^5$ Pa = $1\text{x}10^5$ N m^{-2} as:

$$N/V = N_AP/RT = \frac{6.0221\text{x}10^{23}\ \text{mol}^{-1}(1.00\text{x}10^5\ \text{N m}^{-2})}{8.3145\ \text{J K}^{-1}\ \text{mol}^{-1}(298.2\ \text{K})} = 2.429\text{x}10^{25}\ \text{m}^{-3}$$

Concerning the units, remember that 1 J = 1 N m. Using Eq.31.3.18 gives the collision rate per cubic meters as:

$$\begin{aligned} Z_{AA} &= \tfrac{1}{2}\, \sigma_{HC} \sqrt{2}\, \bar{c}\, (\mathcal{N}/V)^2 = \tfrac{1}{2}\, 4.418\text{x}10^{-19}\ \text{m}^2 \sqrt{2}\, (474.6\ \text{m s}^{-1})(2.429\text{x}10^{25}\ \text{m}^{-3})^2 \\ &= 8.75\text{x}10^{34}\ \text{s}^{-1}\ \text{m}^{-3} \end{aligned}$$

For the 1.00 L volume:

$$\text{collision rate} = Z_{AA}\, V = 8.75\text{x}10^{34}\ \text{s}^{-1}\ \text{m}^{-3}(1\ \text{m}^3/1000\ \text{L})(1.00\ \text{L}) = 8.75\text{x}10^{31}\ \text{s}^{-1}.$$

As mentioned in Example 31.3.1, the total collision rate for a 1 L balloon filled with ambient air is the almost the same.

3. Derive a relationship for the rate of a unimolecular surface-catalyzed reaction of an ideal gas. Assume every collision with the surface gives products and that the rate law is expressed in terms of the gas phase concentration of the reactant in mol L^{-1}.

Answer: The plan is to follow the derivation of the bimolecular rate law, Eqs. 31.3.20-31.3.24 for this specific case.

The rate of collisions per unit area of an ideal gas with a wall is, Eq. 31.3.4:

$$Z_{wall} = \frac{1}{4}\frac{\mathcal{N}}{V}\left(\frac{8RT}{\pi\mathcal{M}}\right)^{1/2} = \frac{1}{4}\frac{\mathcal{N}}{V}\,\bar{c} \qquad (31.2.4)$$

for $\mathcal{N}$ molecules in total volume V. Given that every collision is successful, for a surface with area A, the rate of the reaction in molecules per second per unit total volume of reactant A is:

$$-\frac{d(\mathcal{N}_A/V)}{dt} = Z_{wall}\frac{A}{V} = \left(\frac{\bar{c}A}{4V}\right)\frac{\mathcal{N}_A}{V}$$

The rate is given in molecules per unit volume per unit time. To convert to the rate in mol $m^{-3}\ s^{-1}$, we divide the last equation by Avogadro's number:

$$-\frac{d(\mathcal{N}_A/N_A V)}{dt} = Z_{wall}\frac{A}{N_A V} = \left(\frac{\bar{c}A}{4V}\right)\left(\frac{\mathcal{N}_A}{N_A V}\right)$$

Using Eq. 31.3.21 for the concentration A:

$$-\frac{d[A]}{dt} = Z_{wall}\frac{A}{N_A V} = \left(\frac{\bar{c}A}{4V}\right)[A]$$

Expressing the classical rate law as $-\,d[A]/dt = k_1[A]$ gives the unimolecular rate constant as:

$$k_1 = \left(\frac{\bar{c}A}{4V}\right) = \tfrac{1}{4}\left(\frac{8RT}{\pi\mathcal{M}}\right)^{1/2}\left(\frac{A}{V}\right)$$

The V in this last equation is in m^3 to match the units of $\bar{c}A$. The catalyst surface does not need to be wall-like. This expression, assuming 100% successful collisions, pertains to suspended aerosol particles and liquid droplets as long as the products do not accumulate on the surface and decrease the surface activity.

4. Find the most probable molecular speed using the Maxwell distribution of molecular speeds.

Answer: The plan is to set the derivative of the Maxwell distribution function equal to zero to find the maximum.

The Maxwell distribution of molecular speeds is: $p(c)\,dc = 4\pi \left(\frac{m}{2\pi kT}\right)^{3/2} e^{-mc^2/2kT}\, c^2\, dc$

Let the normalization constant be $\mathcal{A} = 4\pi\,(m/2\pi kT)^{3/2}$. Taking the derivative with respect to c using the product rule with the product as $[e^{-mc^2/2kT}][c^2]$ gives:

$$\frac{d\,p(c)}{dc} = -\mathcal{A}\left(\frac{m}{kT}\right) c\, e^{-mc^2/2kT}\, c^2 + 2\mathcal{A}\, c\, e^{-mc^2/2kT} = 0$$

Canceling common terms gives: $-\left(\frac{m}{kT}\right) c^2 + 2 = 0$ or $\left(\frac{m}{kT}\right) c^2 = 2$ with $c = c_{mp}$

Solving for c_{mp} gives Eq. 31.2.27: $c_{mp} = \left(\frac{2kT}{m}\right)^{1/2} = \sqrt{\frac{2kT}{m}}$

5. (a). Find the standard deviation of the molecular speed of an ideal gas at temperature T in terms of the molar mass. (b). Find the most probable, average, and rms-speeds and standard deviation of the speed of CO_2 at 298.2 K.

Answer: The plan is to note that $\sigma^2 = \overline{(c - \bar{c})^2} = \overline{c^2} - (\bar{c})^2$, Eq. 23.4.36. See also Problem 1.

(a). First, in case you haven't done it before, we derive $\sigma^2 = \overline{(c - \bar{c})^2} = \overline{c^2} - (\bar{c})^2$. Starting with the squared deviation from the mean:

$$(c - \bar{c})^2 = c^2 - 2c\,\bar{c} + (\bar{c})^2$$

Next we need to take the average. Because the average speed is a constant, the average of a constant is just that constant:

$$\overline{(\bar{c})} = \bar{c} \qquad \text{and} \qquad \overline{(\bar{c})^2} = (\bar{c})^2$$

Taking the averages of each term: $\sigma^2 = \overline{(c - \bar{c})^2} = \overline{c^2} - 2\,\bar{c}\,\bar{c} + (\bar{c})^2 = \overline{c^2} - (\bar{c})^2$

Now from Eqs. 31.1.18 and 31.2.31 and $8/\pi = 2.546$:

$$\sigma^2 = \overline{c^2} - (\bar{c})^2 = \frac{3RT}{\mathfrak{M}} - \frac{8RT}{\pi\mathfrak{M}} = 0.4535\,\frac{RT}{\mathfrak{M}} \quad \text{or} \quad \sigma = \sqrt{\frac{0.4535\,RT}{\mathfrak{M}}} = 0.673\sqrt{\frac{RT}{\mathfrak{M}}}$$

(b). The molar mass for CO_2 is 44.01 g mol^{-1} or 0.04401 kg mol^{-1}.
The most probable speed, using Eq. 31.2.27 is:

$$c_{mp} = \sqrt{\frac{2\,RT}{\mathfrak{M}}} = \sqrt{\frac{2\,(8.3145\text{ J K}^{-1}\text{ mol}^{-1})(298.2\text{ K})}{0.04401\text{ kg mol}^{-1}}} = 335.6\text{ m s}^{-1}$$

The average speed, using Eq. 32.2.31 is:

$$\bar{c} = \sqrt{\frac{8\,RT}{\pi\mathfrak{M}}} = \sqrt{\frac{8\,(8.3145\text{ J K}^{-1}\text{ mol}^{-1})(298.2\text{ K})}{\pi\;0.04401\text{ kg mol}^{-1}}} = 378.7\text{ m s}^{-1}$$

The rms-speed, using Eq. 32.1.18 is:

$$u = \sqrt{\frac{3\,RT}{\mathfrak{M}}} = \sqrt{\frac{3\,(8.3145\text{ J K}^{-1}\text{ mol}^{-1})(298.2\text{ K})}{0.04401\text{ kg mol}^{-1}}} = 411.1\text{ m s}^{-1}$$

The standard deviation is : $\sigma = \sqrt{\frac{0.4535\,RT}{\mathfrak{M}}} = 0.673\sqrt{\frac{RT}{\mathfrak{M}}} = 159.7\text{ m s}^{-1}$

In conventional notation we can state: $\bar{c} = 378.7 \pm 159.7\text{ m s}^{-1}$, which is a considerable spread in velocities.

Note that for a symmetrical, purely-Gaussian distribution, the rms-speed is equal to the standard deviation. For the Maxwell distribution of molecular speeds the final distribution is unsymmetrical with a long tail at high velocity.

6. (a). Show that the rms-speed is given by the pressure P and mass density d by : $u = \sqrt{3P/d}$. (b). At 1.01325 bar and 373.2 K the density of water vapor is 598 g m^{-3}. Calculate the rms-speed of water molecules in water vapor.

Answer: The plan is to note that the mass and number density are related by $d = \mathcal{N}\mathfrak{M}/(N_A V)$.

First we need to verify that $d = \mathcal{N}\mathfrak{M}/(N_A V)$, which we can do by checking the units:

$$d = \mathcal{N}\mathfrak{M}/(N_A V) \sim (\text{molecules})(\text{g mol}^{-1})/[(\text{molecules mol}^{-1})(\text{m}^3)] = \text{g m}^{-3}$$

Then solving for the number density gives: $\mathcal{N}/V = \mathcal{N}_A d/\mathfrak{M}$. The pressure is given by Eq. 31.1.14:

$$P = \frac{\mathcal{N} m u^2}{3V} \qquad (31.1.14)$$

Substituting in $\mathcal{N}/V = \mathcal{N}_A d/\mathfrak{M}$ for the number density gives: $P = \frac{mu^2}{3}\frac{\mathcal{N}_A d}{\mathfrak{M}} = \frac{u^2\,d}{3}$

noting that $\mathcal{N}_A\,m = \mathfrak{M}$. Then solving for the rms-speed gives: $u = \sqrt{3P/d}$

(b). For unit agreement the pressure is $P = 1.01325\text{x}10^5$ Pa $= 1.01235\text{x}10^5\text{ N m}^{-2}$ and the density is $d = 0.598\text{ kg m}^{-3}$, giving:

$$u = \sqrt{3P/d} = \sqrt{3(1.01325\text{x}10^5\text{ N m}^{-2})/(0.598\text{ kg m}^{-3})} = 713\text{ m s}^{-1}$$

With $\mathfrak{M} = 18.02\text{ g mol}^{-1} = 0.01802\text{ kg mol}^{-1}$ and using Eq. 31.1.18, the value is:

$$u = \sqrt{\frac{3\,RT}{\mathfrak{M}}} = \sqrt{\frac{3\,(8.3145\text{ J K}^{-1}\text{ mol}^{-1})(373.2\text{ K})}{0.01802\text{ kg mol}^{-1}}} = 718.7\text{ m s}^{-1}$$

The difference is caused by experimental error in the gas phase density and non-ideality.

<u>7</u>. A compound with molar mass of 255.2 g mol^{-1} is placed in a small container that has a hole of radius 0.0500 mm. In 30.0 min at 50.0°C, 0.872 g of the substance effuses from the container. Calculate the vapor pressure of the substance.

Answer: The plan is to use the effusion rate from Eq. 31.3.6.

The effusion rate is: $\dfrac{dn}{dt} = \dfrac{0.872\text{ g}}{(255.2\text{ g mol}^{-1})(30.0\text{ min})(60\text{ s/1 min})} = 1.898\text{x}10^{-6}\text{ mol s}^{-1}$

The hole area is $A = \pi(0.050\text{x}10^{-3}\text{ m})^2 = 7.854\text{x}10^{-9}\text{ m}^2$. The molar mass is 0.2552 kg mol^{-1}.

The effusion rate, Eq. 31.3.6, is: $\dfrac{dn}{dt} = PA\left(\dfrac{1}{2\pi\mathcal{M}RT}\right)^{½}$

Solving for the pressure gives: $P = \dfrac{(2\pi\mathcal{M}RT)^{½}}{A}\dfrac{dn}{dt}$

$$= \frac{[2\pi\ 0.2552\text{ kg mol}^{-1}(8.3145\text{ J K}^{-1}\text{ mol}^{-1})(323.2\text{ K})]^{½}}{7.854\text{x}10^{-9}\text{ m}^2}(1.898\text{x}10^{-6}\text{ mol s}^{-1})$$

$$= 1.586\text{x}10^4\text{ N m}^{-2} = 0.1586\text{ bar} = 15.86\text{ kPa}$$

In alternate units: $P = 0.1586$ bar (1 atm/1.01325 bar) = 0.1566 atm = 119. torr

<u>8</u>. A compound with a vapor pressure of 1.680 kPa is placed in a small container closed by a metal membrane with a 0.0500 mm radius hole. The initial mass is 123.5 mg. After 30.0 min at 35.0°C the mass decreases to 39.9 mg. Calculate the molar mass of the substance.

Answer: The plan is to convert the effusion rate in Eq. 31.3.6 to the rate in kg s^{-1} by multiplying by the molar mass.

The effusion rate in kg s^{-1} is obtained by multiplying Eq. 31.3.6 by the molar mass in kg mol^{-1}:

$$r = \frac{d(n\mathcal{M})}{dt} = PA\mathcal{M}\left(\frac{1}{2\pi\mathcal{M}RT}\right)^{½} = PA\mathcal{M}^{½}\left(\frac{1}{2\pi RT}\right)^{½} \tag*{1}$$

Solving this expression for the molar mass in kg mol^{-1} gives: $\mathcal{M} = \dfrac{2\pi RT}{P^2A^2}\,r^2$ 2

$$\text{The effusion rate is: } r = \frac{d(n\mathcal{M})}{dt} = \frac{0.0836\text{ g}(1\text{ kg/1000 g})}{(30.0\text{ min})(60\text{ s/1 min})} = 4.644\text{x}10^{-8}\text{ kg s}^{-1} \tag*{3}$$

The area of the hole is $A = \pi(0.050\text{x}10^{-3}\text{ m})^2 = 7.854\text{x}10^{-9}\text{ m}^2$.
With Eq. 2 the molar mass is:

$$\mathcal{M} = \frac{2\pi RT}{P^2A^2}\,r^2 = \frac{2\pi\ 8.3145\text{ J K}^{-1}\text{ mol}^{-1}(308.2\text{ K})}{(1.680\text{x}10^3\text{ N m}^{-2})^2(7.854\text{x}10^{-9}\text{ m}^2)^2}(4.644\text{x}10^{-8}\text{ kg s}^{-1}) = 0.1994\text{ kg mol}^{-1}$$

or $\mathcal{M} = 199.4$ kg mol^{-1}. Concerning the units, 1 N = 1 J m^{-1} = 1 kg m s^{-2} and 1 N m^{-2} = 1 J m^{-3}.

$$\frac{2\pi RT}{P^2A^2}\, r^2 \sim \frac{\mathrm{J\,K^{-1}\,mol^{-1}(K)}}{\mathrm{(J\,m^{-3})^2(m^2)^2}}\,\mathrm{(kg\,s^{-1})^2} \sim \frac{\mathrm{mol^{-1}}}{\mathrm{J\,m^{-2}}}\,\mathrm{(kg^2\,s^{-2})} \sim \frac{\mathrm{mol^{-1}}}{\mathrm{(kg\,m^2\,s^{-2})\,m^{-2}}}\,\mathrm{(kg^2\,s^{-2})} \sim \mathrm{kg\,mol^{-1}}$$

9. Integrals of the form $\int_o^{x_c} e^{-ax^2}\,dx$ are common in determining the probability of occurrence of speeds or energies within a given range. The integral has no closed form solution and must be integrated numerically. The numerical integrals in dimensionless form are tabulated as the error function, erf( ), where the error function is defined by:

$$\frac{2}{\sqrt{\pi}}\int_o^t e^{-y^2}\,dy = \mathrm{erf}(t)$$

The error function is used extensively in statistics and probability. The inside back cover lists a short table. Extensive tables are available in standard reference sources and Excel has an erf( ) function. In this regard erf( ) is similar to the more familiar functions sin( ), cos( ), exp( ) and ln( ), which are all evaluated as power series expansions.

(a). Show that: $\int_o^{x_c} e^{-ax^2}\,dx = \tfrac{1}{2}\left(\frac{\pi}{a}\right)^{1/2} \mathrm{erf}(\sqrt{a}\,x_c)$

(b). Verify the result in part (a) by showing that $\int_o^{\infty} e^{-ax^2}\,dx$ gives the result listed in standard integral tables.

(c). Show the probability of a molecule having a velocity in the x-direction in the range ±v^* is:

$$\int_{-v^*}^{v^*} p(v_x)\,dv_x = 2\int_o^{v^*}\left(\frac{m}{2\pi kT}\right)^{1/2} e^{-mv_x^2/2kT}\,dv_x = \mathrm{erf}\left(\sqrt{mv^{*2}/2kT}\right)$$

(d). Show that the probability of a molecule having a kinetic energy in the x-direction less than or equal to kT is 84.3%. [Hint: note that erf(1) = 0.8427]

Answer: For part (a) the plan is to do a change of variables. For part (c) the plan is to use the integral in part (a) with $a = m/2kT$. The plan for part (d) is to note that $\varepsilon_t = \tfrac{1}{2} mv^2$

(a). Comparing the definition of the error function to $\int_o^{x_c} e^{-ax^2}\,dx$ requires the change of variables $y^2 = ax^2$ or equivalently $y = \sqrt{a}\,x$ with derivative and corresponding differential:

$$\frac{dy}{dx} = \sqrt{a} \qquad \text{with } dx = \frac{1}{\sqrt{a}}\,dy \qquad \text{and upper limit } t = \sqrt{a}\,x_c$$

then substituting for ax^2 and dx gives:

$$\int_o^{x_c} e^{-ax^2}\,dx = \frac{1}{\sqrt{a}}\int_o^t e^{-y^2}\,dy = \frac{1}{\sqrt{a}}\,\frac{\sqrt{\pi}}{2}\,\mathrm{erf}(t) = \tfrac{1}{2}\left(\frac{\pi}{a}\right)^{1/2}\mathrm{erf}(\sqrt{a}\,x_c)$$

(b). Tables of erf(t) show that the function approaches one for large values of t. In other words, $(2/\sqrt{\pi})\int_o^t e^{-y^2}\,dy$ is normalized. Setting $x_c = \infty$ gives $\int_o^{\infty} e^{-ax^2}\,dx = \tfrac{1}{2}(\pi/a)^{1/2}$ as listed in standard definite integral tables.

(c). The distribution function is even so that $\int_{-v^*}^{v^*} = 2\int_o^{v^*}$. For the one-dimensional velocity distribution with $a = m/2kT$ and $x_c = v^*$ using the integral in part (a) gives:

$$\int_{-v^*}^{v^*} p(v_x)\, dv_x = 2\left(\frac{m}{2\pi kT}\right)^{1/2} \int_o^{v^*} e^{-mv_x^2/2kT}\, dv_x = \left(\frac{m}{2\pi kT}\right)^{1/2} \left(\frac{2\pi kT}{m}\right)^{1/2} \mathrm{erf}\left(\sqrt{mv^{*2}/2kT}\right)$$
$$= \mathrm{erf}\left(\sqrt{mv^{*2}/2kT}\right)$$

(d). Note that $\varepsilon_t = kT$ gives $\frac{1}{2}\, mv^{*2} = kT$ and $mv^{*2}/2kT = 1$ with erf(1) = 0.8427.
Note that erf(1) = 0.8427 is the area under a Gaussian distribution within $x = \pm\sqrt{2}\,\sigma$.

<u>10</u>. Derive the integration by parts formula using the following steps: (a). Let u and v be two functions. Using the product rule for the differential d(uv), show that $\int d(uv) = \int v\, du + \int u\, dv$.
(b). Finally show that for the integral limits u_1v_1 to u_2v_2 :

$$\int u\, dv = uv\Big|_{u_1v_1}^{u_2v_2} - \int v\, du$$

Answer: (a). Using the product rule $d(uv) = vdu + udv$. Integrating both sides of the equation gives: $\int d(uv) = \int v\, du + \int u\, dv$.
(b). Solving for $\int u\, dv$ gives: $\int u\, dv = \int d(uv) - \int v\, du$
The integral of $\int d(uv)$ is just uv evaluated at the limits of the integral: $\int_{u_1v_1}^{u_2v_2} d(uv) = uv\Big|_{u_1v_1}^{u_2v_2}$.
Substituting this result for the integral gives the final result: $\int u\, dv = uv\Big|_{u_1v_1}^{u_2v_2} - \int v\, du$.

<u>11</u>. Integrals over the Maxwell distribution of molecular speeds are in the general form $\int_o^t y^2 e^{-y^2}\, dy$. Use integration by parts, $\int u\, dv = uv\Big|_{u_1v_1}^{u_2v_2} - \int v\, du$, with u = y and $dv = (y\, e^{-y^2}\, dy)$ to show that: [See the next problem for an application of this relationship.]

$$\frac{4}{\sqrt{\pi}} \int_o^t y^2 e^{-y^2}\, dy = \mathrm{erf}(t) - \frac{2}{\sqrt{\pi}}\, t\, e^{-t^2}$$

Answer: The plan is to start by integrating dv to give v in terms of y.
With u = y and $dv = (y\, e^{-y^2}\, dy)$ then: $du = dy$ and $v = \int dv = \int y\, e^{-y^2}\, dy = -\frac{1}{2}\, e^{-y^2}$
Integration by parts gives: $\int u\, dv = uv\Big|_{u_1v_1}^{u_2v_2} - \int v\, du$

$$\int_o^t y^2 e^{-y^2}\, dy = -\tfrac{1}{2}\, y\, e^{-y^2}\Big|_o^t - (-\tfrac{1}{2}) \int_o^t e^{-y^2}\, dy$$

The integral is given by the error function: $(2/\sqrt{\pi}) \int_o^t e^{-y^2}\, dy = \mathrm{erf}(t)$. The first term is evaluated at the limits and substituting in the error function gives:

$$\int_o^t y^2 e^{-y^2}\, dy = -\tfrac{1}{2}\, t\, e^{-t^2} + \frac{\sqrt{\pi}}{4}\, \mathrm{erf}(t)$$

The required integral is then: $\frac{4}{\sqrt{\pi}} \int_o^t y^2 e^{-y^2}\, dy = \mathrm{erf}(t) - \frac{2}{\sqrt{\pi}}\, t\, e^{-t^2}$

See the next problem for an application of this relationship.

12. The probability of occurrence of molecular speeds over a range of values is determined by an integral over the distribution function. (a).Show that the integral of the Maxwell distribution of molecular speeds over the range from c = 0 to c^* is:

$$\int_o^{c^*} p(c)\,dc = 4\pi\left(\frac{m}{2\pi kT}\right)^{3/2}\int_o^{c^*} e^{-mc^2/2kT}\,c^2\,dc = \mathrm{erf}\left(\sqrt{mc^{*2}/2kT}\right) - \frac{1}{\sqrt{\pi}}\sqrt{\frac{mc^{*2}}{2kT}}\;e^{-mc^{*2}/2kT}$$

(b). The kinetic energy at the upper limit is $\varepsilon_t^* = ½mc^{*2}$. Show that the total probability is:

$$\int_o^{c^*} p(c)\,dc = 4\pi\left(\frac{m}{2\pi kT}\right)^{3/2}\int_o^{c^*} e^{-mc^2/2kT}\,c^2\,dc = \mathrm{erf}\left(\sqrt{\varepsilon_t^*/kT}\right) - \frac{2}{\sqrt{\pi}}\left(\frac{\varepsilon_t^*}{kT}\right)^{½} e^{-\varepsilon_t^*/kT}$$

[Hint: use the relationship in the previous problem with the change in variables $y^2 = mc^2/2kT$]

Answer: (a). With the substitution $y^2 = mc^2/2kT$ then $y = (m/2kT)^{½}\,c$ and the derivative is:

$$\frac{dy}{dc} = (m/2kT)^{½} \qquad \text{giving} \quad dc = \left(\frac{2kT}{m}\right)^{½} dy \qquad \text{with} \quad c^2 = \left(\frac{2kT}{m}\right) y^2$$

and upper limit $t = (m/2kT)^{½}\,c^*$. The integral over the Maxwell distribution is:

$$\int_o^{c^*} p(c)\,dc = 4\pi\left(\frac{m}{2\pi kT}\right)^{3/2}\int_o^{c^*} e^{-mc^2/2kT}\,c^2\,dc = 4\pi\left(\frac{m}{2\pi kT}\right)^{3/2}\left(\frac{2kT}{m}\right)\left(\frac{2kT}{m}\right)^{½}\int_o^t y^2\,e^{-y^2}\,dy$$
$$= \frac{4}{\sqrt{\pi}}\int_o^t y^2\,e^{-y^2}\,dy$$

Using the relationship derived in the previous problem gives:

$$\int_o^{c^*} p(c)\,dc = \mathrm{erf}(t) - \frac{2}{\sqrt{\pi}}\,t\,e^{-t^2}$$

The substitution variable is conveniently regrouped as $y = (m/2kT)^{½}\,c = (mc^2/2kT)^{½}$
Reversing the original substitution then gives:

$$\int_o^{c^*} p(c)\,dc = \mathrm{erf}\left(\sqrt{mc^{*2}/2kT}\right) - \frac{2}{\sqrt{\pi}}\sqrt{\frac{mc^{*2}}{2kT}}\;e^{-mc^{*2}/2kT}$$

Or given that the kinetic energy at the upper limit of the speed is $\varepsilon_t^* = ½mc^{*2}$:

$$\int_o^{c^*} p(c)\,dc = \mathrm{erf}\left(\sqrt{\varepsilon_t^*/kT}\right) - \frac{2}{\sqrt{\pi}}\left(\frac{\varepsilon_t^*}{kT}\right)^{½} e^{-\varepsilon_t^*/kT}$$

13. Determine the probability that a molecule has a speed equal to or less than the most probable speed. [Hint: Use the relationship in the previous problem, note that erf(1) = 0.8427]

Answer: The plan is to note that the most probable speed is given by Eq. 31.2.27.
The upper limit on the integral is $c^* = c_{mp}$. With Eq. 31.2.27 the most probable speed is:

$$c_{mp} = \left(\frac{2kT}{m}\right)^{½} = \sqrt{\frac{2kT}{m}}$$

The corresponding translational kinetic energy is: $\varepsilon_t^* = ½\, mc_{mp}^2 = kT$.

As a result the factor appearing in the result is: $\sqrt{\varepsilon_t^*/kT} = 1$

The probability that a molecule has a speed equal to or less than the most probable speed is then:[1]

$$\int_o^{c^*} p(c)\, dc = 4\pi \left(\frac{m}{2\pi kT}\right)^{3/2} \int_o^{c^*} e^{-mc^2/2kT}\, c^2\, dc = \text{erf}(1) - \frac{2}{\sqrt{\pi}}\; 1^{½}\, e^{-1}$$

$$= 0.8427 - \frac{2}{\sqrt{\pi}}\; 0.3679 = 0.8427 - 0.4151 = 0.4276 \quad \text{or} \quad 42.8\%$$

The fraction above the most probable speed is 1 – 0.4276 = 0.572 or 57.2%

14. The fraction of molecules with translational kinetic energy exceeding ε^* is:[1,2]

$$p(\varepsilon_t > \varepsilon^*) = \int_{\varepsilon^*}^{\infty} p(\varepsilon_t)\, d\varepsilon_t = 2\pi \left(\frac{1}{\pi kT}\right)^{3/2} \int_{\varepsilon^*}^{\infty} \varepsilon_t^{½}\, e^{-\varepsilon_t/kT}\, d\varepsilon_t$$

(a). Use the change of variable $x^2 = \varepsilon_t/kT$ to show: [Hint: see Eq. 31.4.5 for a similar change in variables.]

$$p(\varepsilon_t > \varepsilon^*) = \frac{4}{\sqrt{\pi}} \int_{x^*}^{\infty} x^2\, e^{-x^2}\, dx$$

(b). Use integration by parts to show: [Hint: let u = x and $dv = x\, e^{-x^2}\, dx$]

$$\int_{x^*}^{\infty} x^2\, e^{-x^2}\, dx = -½\, x\, e^{-x^2}\Big|_{x^*}^{\infty} - (-½) \int_{x^*}^{\infty} e^{-x^2}\, dx$$

(c). Show that: $\displaystyle\int_{x^*}^{\infty} e^{-x^2}\, dx = \int_o^{\infty} e^{-x^2}\, dx - \int_o^{x^*} e^{-x^2}\, dx$

(d). Use integral tables and the definition of the error function: $\displaystyle\frac{2}{\pi^{½}} \int_o^{t} e^{-x^2}\, dx = \text{erf}(t)$ to show that:

$$\int_{x^*}^{\infty} e^{-x^2}\, dx = \frac{\sqrt{\pi}}{2} - \frac{\sqrt{\pi}}{2}\, \text{erf}(x^*)$$

(e). Using the previous expressions, derive the final result:

$$p(\varepsilon_t > \varepsilon^*) = \frac{4}{\sqrt{\pi}} \int_{x^*}^{\infty} x^2\, e^{-x^2} = \frac{2}{\sqrt{\pi}} \left(\frac{\varepsilon^*}{kT}\right)^{½} e^{-\varepsilon^*/kT} + 1 - \text{erf}\left(\left[\frac{\varepsilon^*}{kT}\right]^{½}\right)$$

(f). Show that for large threshold energies, $\varepsilon^* >> kT$: $\displaystyle p(\varepsilon_t > \varepsilon^*) \cong \frac{2}{\sqrt{\pi}} \left(\frac{\varepsilon^*}{kT}\right)^{½} e^{-\varepsilon^*/kT}$

Answer: (a). We can simplify the integral with the change in variables $x^2 = \varepsilon_t/kT$ or $\varepsilon_t = kTx^2$:

$$\frac{d\varepsilon_t}{dx} = kT \frac{dx^2}{dx} = 2kTx \qquad \text{giving } d\varepsilon_t = 2kTx\, dx \quad \text{and} \quad \varepsilon_t^{½} = (kT)^{½}\, x \qquad 1$$

with the limits from $x^* = (\varepsilon^*/kT)^{\frac{1}{2}}$ to ∞:

$$p(\varepsilon_t > \varepsilon^*) = 2\pi \left(\frac{1}{\pi kT}\right)^{3/2} (2kT)(kT)^{\frac{1}{2}} \int_{x^*}^{\infty} x^2\, e^{-x^2}\, dx$$

$$p(\varepsilon_t > \varepsilon^*) = \frac{4}{\sqrt{\pi}} \int_{x^*}^{\infty} x^2\, e^{-x^2}\, dx \tag{2}$$

(b). There is no closed-form solution to the integral, so we need to relate the integrals to the error function. To integrate by parts, let $u = x$ and $dv = x\, e^{-x^2}\, dx$ giving:

$$du = dx \quad \text{and} \quad v = \int dv = \int x\, e^{-x^2}\, dx = -\tfrac{1}{2}\, e^{-x^2} \tag{3}$$

so that: $\int u\, dv = uv\Big|_{u_1v_1}^{u_2v_2} - \int v\, du$ is:

$$\int_{x^*}^{\infty} x^2\, e^{-x^2}\, dx = -\tfrac{1}{2}\, x\, e^{-x^2}\Big|_{x^*}^{\infty} - (-\tfrac{1}{2}) \int_{x^*}^{\infty} e^{-x^2}\, dx \tag{4}$$

(c). The first term evaluated at the limits is $\tfrac{1}{2}\, x^*\, e^{-x^{*2}}$. For the second integral note that:

$$\int_{o}^{\infty} e^{-x^2}\, dx = \int_{o}^{x^*} e^{-x^2}\, dx + \int_{x^*}^{\infty} e^{-x^2}\, dx \tag{5}$$

which gives the integral we want by difference:

$$\int_{x^*}^{\infty} e^{-x^2}\, dx = \int_{o}^{\infty} e^{-x^2}\, dx - \int_{o}^{x^*} e^{-x^2}\, dx \tag{6}$$

(d). Standard integral tables give $\int_{o}^{\infty} e^{-ax^2}\, dx = \frac{1}{2}\left(\frac{\pi}{a}\right)^{\frac{1}{2}}$, giving: $\int_{o}^{\infty} e^{-x^2}\, dx = \frac{\sqrt{\pi}}{2}$ (7)

The $\int_{o}^{x^*} e^{-x^2}\, dx$ integral is given by the error function: $\frac{2}{\pi^{\frac{1}{2}}} \int_{o}^{t} e^{-x^2}\, dx = \operatorname{erf}(t)$ with $t = x^*$ or:

As a result: $\int_{o}^{x^*} e^{-x^2}\, dx = \frac{\sqrt{\pi}}{2} \operatorname{erf}(x^*)$ (8)

Substituting Eqs. 7 and 8 into Eq. 6 gives:

$$\int_{x^*}^{\infty} e^{-x^2}\, dx = \frac{\sqrt{\pi}}{2} - \frac{\sqrt{\pi}}{2} \operatorname{erf}(x^*) \tag{9}$$

(e). Substituting the last equation into Eq. 4 gives:

$$\int_{x^*}^{\infty} x^2\, e^{-x^2}\, dx = \tfrac{1}{2}\, x^*\, e^{-x^2} + \frac{\sqrt{\pi}}{4} - \frac{\sqrt{\pi}}{4} \operatorname{erf}(x^*) \tag{10}$$

Substituting this last result into Eq. 2 with $x^2 = \varepsilon_t/kT$ gives:

$$p(\varepsilon_t > \varepsilon^*) = \frac{4}{\sqrt{\pi}} \int_{x^*}^{\infty} x^2\, e^{-x^2} = \frac{2}{\sqrt{\pi}} \left(\frac{\varepsilon^*}{kT}\right)^{\frac{1}{2}} e^{-\varepsilon^*/kT} + 1 - \operatorname{erf}\left(\left[\frac{\varepsilon^*}{kT}\right]^{\frac{1}{2}}\right) \tag{11}$$

(f). As ε^* increases, the error function approaches 1, so that for large threshold energies.

$$p(\varepsilon_t > \varepsilon^*) \cong \frac{2}{\sqrt{\pi}} \left(\frac{\varepsilon^*}{kT}\right)^{\frac{1}{2}} e^{-\varepsilon^*/kT} \tag{32.4.9}$$

The $(\varepsilon^*/kT)^{1/2}$ temperature dependence is weaker than the exponential term so that the fraction of translational-energy rich molecules increases roughly as $e^{-\varepsilon^*/kT}$ with increases in temperature.

<u>15</u>. Find the most probable translational kinetic energy of an ideal gas using the Maxwell distribution of translational kinetic energy.

Answer: The plan is to set the derivative of the Maxwell distribution of translational kinetic energy equal to zero to find the maximum.

The Maxwell distribution of translational kinetic energy, Eq. 31.4.3, is:

$$p(\varepsilon_t)\, d\varepsilon_t = 2\pi \left(\frac{1}{\pi kT}\right)^{3/2} e^{-\varepsilon_t/kT}\, \varepsilon_t^{1/2}\, d\varepsilon_t$$

Let the normalization constant be $\mathcal{A} = 2\pi\, (1/\pi kT)^{3/2}$. Taking the derivative with respect to ε_t using the product rule with the product as $[e^{-\varepsilon_t/kT}][\varepsilon_t^{1/2}]$ gives:

$$\frac{d\, p(\varepsilon_t)}{d\varepsilon_t} = -\mathcal{A}\left(\frac{1}{kT}\right) e^{-\varepsilon_t/kT}\, \varepsilon_t^{1/2} + \tfrac{1}{2}\mathcal{A}\, \varepsilon_t^{-1/2}\, e^{-\varepsilon_t/kT} = 0$$

Canceling common terms gives: $-\left(\frac{1}{kT}\right) \varepsilon_t^{1/2} + \frac{1}{2}\, \varepsilon_t^{-1/2} = 0$ or $\left(\frac{1}{kT}\right) \varepsilon_t = \frac{1}{2}$ with $\varepsilon_t = \varepsilon_{mp}$

Solving for ε_{mp} gives: $\varepsilon_{mp} = \frac{1}{2}\, kT$

<u>16</u>. The rate constant for the recombination of methyl radicals is $4.5\text{x}10^{10}$ L mol^{-1} s^{-1} at 398.2 K.

$$H_3C\bullet + \bullet CH_3 \rightarrow H_3C{-}CH_3$$

The reaction has no activation energy. Assuming the hard-core collision radii of the methyl radicals are one-half the normal C–C bond length, $r_{CH_3} = 0.77$ Å, calculate the bimolecular rate constant assuming hard-core collision theory at 398.2 K.[3]

Answer: The plan is to follow Example 31.3.2.

The collision cross-section, using Eq. 31.3.8, is:

$$\sigma_{HC} = \pi\, (2r_{CH_3})^2 = \pi\, [2(0.77\text{x}10^{-10}\text{ m})]^2 = 7.45\text{x}10^{-20}\text{ m}^2 = 0.0745\text{ nm}^2 = 7.45\text{ Å}^2$$

The molar mass of $\bullet CH_3$ is 15.03 g mol^{-1}. The reduced mass of the collision is:

$$\mu = \left(\frac{\mathcal{M}_A\, \mathcal{M}_B}{\mathcal{M}_A + \mathcal{M}_B}\right) \frac{1}{N_A}\, (1\text{ kg}/1000\text{ g}) = \frac{15.03\text{ g mol}^{-1}}{2}\, \frac{1}{N_A}\, (1\text{ kg}/1000\text{ g}) = 1.248\text{x}10^{-26}\text{ kg}$$

With Eq. 31.3.14 the relative speed is:

$$\bar{c}_{rel} = \left(\frac{8(1.3806\text{x}10^{-23}\text{ J K}^{-1})(398.2\text{ K})}{\pi\ 1.248\text{x}10^{-26}\text{ kg}}\right)^{1/2} = 1059.1\text{ m s}^{-1}$$

Assuming each collision is successful, the rate constant is predicted to be, Eq. 31.3.25:

$$k_2 = \sigma_{HC}\,\bar{c}_{rel}\,(1000\ \text{L/m}^3)\,N_A = 7.45\text{x}10^{-20}\ \text{m}^2\,(1059.1\ \text{m s}^{-1})(1000\ \text{L/m}^3)\,6.022\text{x}10^{23}\ \text{mol}^{-1}$$
$$= 4.75\text{x}10^{10}\ \text{L mol}^{-1}\ \text{s}^{-1}$$

This result suggests that roughly each collision is successful (or that the estimate of the collision cross section is too small). The rough agreement of the experimental rate constant and the hard-core prediction indicates that the steric requirements of the reaction are minimal; the orientation of the methyl radicals upon collision is largely immaterial.

17. (a). Show that the density of states of a one-dimensional particle in a box is:

$$\rho(\varepsilon_x)\,d\varepsilon_x = (8m)^{½}\,\frac{a}{h}\,(\varepsilon_x)^{-½}\,d\varepsilon_x$$

[Hint: you don't need to use the graphical approach that we used for three-dimensions.]
(b). Compare the behavior of the one-dimensional and three-dimensional particle in a box as a function of energy. Why the difference with the change in dimensionality?

Answer: The plan is to determine the derivative of the energy with respect to the quantum number n_x; the final relationship should be written in terms of the energy (and not the quantum number).

(a). The one-dimensional particle in a box energy, Eq. 23.4.9, is: $\varepsilon_x = \frac{h^2}{8ma^2}\,n_x^2$ 1

The density of states is given by the derivative, Eq. 31.6.5: $\rho(\varepsilon_x)\,d\varepsilon_x = \frac{dn_x}{d\varepsilon_x}\,d\varepsilon_x$ 2

The derivative is much easier as the inverse: $\frac{dn_x}{d\varepsilon_x} = \left(\frac{d\varepsilon_x}{dn_x}\right)^{-1}$ with $\frac{d\varepsilon_x}{dn_x} = \frac{h^2}{8ma^2}\,(2\,n_x)$ 3

However, we need to eliminate the dependence on the quantum number. Solving Eq. 1 for the quantum number gives: $n_x = (8m\varepsilon_x)^{½}\,\frac{a}{h}$ 4

Substituting Eq. 4 into Eq. 3 gives: $\frac{d\varepsilon_x}{dn_x} = \frac{h^2}{8ma^2}\,(8m\varepsilon_x)^{½}\,\frac{a}{h} = \frac{\varepsilon_x^{½}}{(8m)^{½}}\,\frac{h}{a}$ 5

Inverting this last equation gives the density of states as: $\rho(\varepsilon_x)\,d\varepsilon_x = (8m)^{½}\,\frac{a}{h}\,(\varepsilon_x)^{-½}\,d\varepsilon_x$

(b). The density of states decreases as $(\varepsilon_x)^{-½}$ with increasing energy, as shown in Figures 23.4.2 and 23.4.4.. The density of states of the three-dimensional particle in a box increases with energy as $\varepsilon_t^{½}$. The difference is the result of degeneracy. The one-dimensional problem is not degenerate but Figure 31.6.1 shows the 3D-problem to be highly degenerate, which increases the density of states.

18. Calculate the number of translational energy states at 298.2 K for O_2 in a box of volume 1.00 m^3 with energies from kT to 1.001 kT (i.e. a 0.1% change in energy).

Answer: The plan is to use the density of states in three-dimensions, Eq. 31.6.8.

The mass of O_2 is $m = \mathfrak{M}/N_A$ (1 kg/1000 g) $= 5.314\text{x}10^{-26}$ kg. Using Eq. 31.6.8 with $\varepsilon_t = kT$:

$$\varepsilon_t = kT = 4.116\text{x}10^{-21}\text{ J}$$

$$\rho(kT) = \frac{\pi}{4}(8m)^{3/2}\frac{V}{h^3}(kT)^{½}$$

$$= \frac{\pi}{4}[8(5.314\text{x}10^{-26}\text{ kg})]^{3/2}\frac{1\text{ m}^3}{(6.6261\text{x}10^{-34}\text{ J s})^3}[(1.3806\text{x}10^{-23}\text{ J K}^{-1})(298.15\text{ K})]^{½}$$

$$= 4.801\text{x}10^{52}\text{ J}^{-1}$$

With the energy range as $\delta\varepsilon_t = 0.001\ kT = 4.116\text{x}10^{-24}$ J giving the number of states as:

$$\rho(\varepsilon_t)\ \delta\varepsilon_t = 4.801\text{x}10^{52}\ (4.116\text{x}10^{-24}\text{ J}) = 1.98\text{x}10^{29}$$

In other words, lots of available states. Concerning the units: 1 J s = kg m^2 s^{-1} and then:

$$\rho(\varepsilon_t) = \frac{\pi}{4}(8m)^{3/2}\frac{V}{h^3}\varepsilon_t^{½} \sim \text{kg}^{3/2}\frac{\text{m}^3}{(\text{kg m}^2\text{ s}^{-1})^3}(\text{kg m}^2\text{ s}^{-2})^{½} \sim \frac{1}{\text{kg m}^2\text{ s}^{-2}} \sim \text{J}^{-1}$$

<u>19</u>. (a). For a square box with side length a and area $A = a^2$, show that the density of states of a two-dimensional particle in a box is:

$$\rho(\varepsilon_t)\ d\varepsilon_t = 2\pi m\frac{A}{h^2}\ d\varepsilon_t$$

The two-dimensional case has some applicability to free translational motion on a surface and electrical conduction in restricted geometries. (b). The density of states of a one-dimensional particle in a box is given in the previous problem. Compare the one, two, and three-dimensional cases in terms of the behavior with respect to increasing energy. (c). Find the two-dimensional Maxwell distribution of translational kinetic energy.

Answer: The plan is to note that this derivation is similar to Eqs. 31.6.4-31.6.8, with graphical areas instead of volumes.

(a). The quantum numbers of the two-dimensional particle in a box are combined as $n^2 = n_x^2 + n_y^2$.

The energy is:

$$\varepsilon_t = \frac{h^2}{8ma^2}(n_x^2 + n_y^2) = \frac{h^2}{8ma^2}n^2 \tag{1}$$

The density of states is required, Eq. 31.6.5:

$$\rho(\varepsilon_t) = \frac{dN(\varepsilon_t)}{d\varepsilon_t} \tag{2}$$

The number of quantum states up to energy ε_t can be determined using a graphical analogy. Each choice of quantum numbers, n_x , n_y is represented as a point in an x-y coordinate plot. Each unit change of n_x, and n_y corresponds to a unit area square. Each unit of area corresponds to one specific value of n_x, and n_y. The maximum value of n for states with energy less than or equal to ε_t is calculated by solving Eq. 1 for n:

$$n_{max} = (8m)^{½}\left(\frac{a}{h}\right)\varepsilon_t^{½} \qquad (31.6.6) \qquad 3$$

The total number of states with energies between zero and ε_t is given by 1/4 of the area of the circle with radius n_{max}. The factor of 1/4 is necessary because a circle centered on the origin is divided into quarters, but only one-quarter has both positive x and y values. The area of a circle is πr^2, which gives the number of states with energy from zero to ε_t as:

$$N(\varepsilon_t) = \frac{1}{4}\pi\, n_{max}^2 = \left(\frac{\pi}{4}\right)(8m)\left(\frac{a}{h}\right)^2 \varepsilon_t = 2\pi m \frac{A}{h^2}\varepsilon_t \qquad 4$$

The density of states is the derivative with respect to ε_t, Eq. 31.6.5:

$$\rho(\varepsilon_t) = \frac{dN(\varepsilon_t)}{d\varepsilon_t} = 2\pi m\frac{A}{h^2} \qquad \text{or finally} \quad \rho(\varepsilon_t)\, d\varepsilon_t = 2\pi m \frac{A}{h^2} d\varepsilon_t \qquad 5$$

(b). The density of states is constant with increasing kinetic energy. For one-dimension the density decreases as $(\varepsilon_x)^{-½}$, for two-dimensions the density is constant as $(\varepsilon_t)^0$, and for three-dimensions the density increases as $\varepsilon_t^{½}$. The density of states of a one-dimensional system decreases because the non-degenerate energy states of a one-dimensional box diverge with increasing quantum number. The density of states of a three-dimensional system increases because of the large degeneracy of high energy translational levels.

(c). Given the area A, the two dimensional distribution function, in analogy with Eq. 32.6.3, is:

$$p(\varepsilon_t)\, dn = \frac{n_i}{N} = \frac{e^{-\varepsilon_t/kT}}{(2\pi mkT)\, A/h^2}\, dn \qquad n^2 = n_x^2 + n_y^2 \qquad 6$$

Substituting the density of states into Eq. 6 to complete the change in variables from dn to $d\varepsilon_t$ gives:

$$p(\varepsilon_t)\, d\varepsilon_t = \frac{e^{-\varepsilon_t/kT}}{(2\pi mkT)\, A/h^2}\,\rho(\varepsilon_t)\, d\varepsilon_t = \frac{e^{-\varepsilon_t/kT}}{(2\pi mkT)\, A/h^2}\, 2\pi m\frac{A}{h^2}\, d\varepsilon_t \qquad 7$$

Canceling common terms gives the two-dimensional Maxwell distribution of translational kinetic energy:

$$p(\varepsilon_t)\, d\varepsilon_t = \left(\frac{1}{kT}\right) e^{-\varepsilon_t/kT}\, d\varepsilon_t \qquad 8$$

As a check, if we did things correctly, the final result should automatically be normalized:

$$\int_o^\infty p(\varepsilon_t)\, d\varepsilon_t = \left(\frac{1}{kT}\right)\int_o^\infty e^{-\varepsilon_t/kT}\, d\varepsilon_t \qquad 9$$

Integral tables list $\int_o^\infty e^{-ax}\, dx = 1/a$ and since $a = 1/kT$, the integral is equal to one.

Literature Cited:

1. W. Kauzmann, *Thermal Properties of Matter Vol. I: Kinetic Theory of Gases*, Benjamin, New York, NY, 1966. Sec. 4.4
2. P. L. Houston, *Chemical Kinetics and Reaction Dynamics*, McGraw Hill, New York, NY, 2001; reprinted by Dover, Mineola, NY, 2006. Chap. 1.
3. G. M. Barrow, *Physical Chemistry, 6th Ed.*, McGraw-Hill, New York, NY, 1996, p. 822 Problem 16-7.

Chapter 32: Reaction Dynamics Problems

1. One possible geometry of the activated complex for the 2 ClO → $Cl_2 + O_2$ reaction is shown in Table 32.1.1. Is this square geometry consistent with the expectation that the reaction coordinate is an unstable asymmetric stretch?

Answer: The plan is to follow the motion of the atoms during the collision.
The reaction coordinate is:

$$\begin{array}{ccccccccccc}
 & & & & & & & & \uparrow & & \uparrow \\
\mathrm{Cl} & \rightarrow\ \leftarrow & \mathrm{Cl} & & \mathrm{Cl} & \rightarrow\leftarrow & \mathrm{Cl} & & \mathrm{Cl} & \text{—} & \mathrm{Cl} \\
| & & | & \rightarrow & \updownarrow & & \updownarrow & \rightarrow & & & \\
\mathrm{O} & \rightarrow\ \leftarrow & \mathrm{O} & & \mathrm{O} & \rightarrow\leftarrow & \mathrm{O} & & \mathrm{O} & \text{—} & \mathrm{O} \\
 & & & & & & & & \downarrow & & \downarrow
\end{array}$$

This motion is exactly what you would expect for the asymmetric stretch of a square planar molecule.

2. The lifetime of the transition state is typically on the order of a single vibration period. Calculate the period of a vibration of wave number 500 cm^{-1}.

Answer: The period is the inverse of the frequency:

$$L = 1/\tilde{\nu}c = (500\ \mathrm{cm}^{-1}\ 2.997\mathrm{x}10^{10}\ \mathrm{cm\ s}^{-1})^{-1} = 6.7\mathrm{x}10^{-14}\ \mathrm{s} = 67\ \mathrm{fs}$$

3. Use Activated Complex Theory to discuss the reaction:

$$\mathrm{H} + \mathrm{F{-}F} \rightleftarrows [\ \mathrm{H{-}{-}F{-}{-}F}\ ]^{\dagger} \rightarrow \mathrm{H{-}F} + \mathrm{F}$$

(a). Do the translational partition functions favor or hinder the rate of the reaction? Why?
(b). Do the rotational partition functions favor or hinder the rate of the reaction? Why?

Answer: The plan is to focus on the formation of the activated complex. The products are irrelevant in this analysis. As a result, the plan is to use statistical mechanical arguments to determine factors that favor the formation of the activated complex through the reaction $\mathrm{H} + \mathrm{F{-}F} \rightleftarrows [\ \mathrm{H{-}{-}F{-}{-}F}\ ]^{\dagger}$. The larger the concentration of the activated complex, the faster the formation of products.

(a). The translational degree of freedom hinders the overall reaction rate. The translational part has only one translational partition function in the numerator and two translational partition functions in the denominator: specifically from Eq. 32.1.14°:

$$\frac{q_t^{\circ\neq}/N_A}{q_t^{\circ}(H)/N_A\ q_t^{\circ}(F_2)/N_A} \qquad \text{(translation only)}$$

Each partition function is on the order of $q_t/N_A \cong 10^6 – 10^7$, see Eq. 30.4.5°. The translational partition functions dominate the unfavorable entropy of formation of the activated complex: two collision partners combine to form one activated complex.

(b). The rotational partition functions favor the rate of the reaction. The rotational part has one rotational partition function in the numerator and one rotational partition function in the denominator, since one of the reactants is atomic: specifically from Eq. 32.1.14°:

$$\frac{q_r^{o\neq}}{q_r^{o}(F_2)} = \frac{1/\sigma^{\neq}\tilde{B}^{\neq}}{1/\sigma(F_2)\tilde{B}(F_2)} \qquad \text{with} \quad \tilde{B} = \frac{\hbar}{4\pi Ic} \tag{24.5.41}$$

where $\sigma^{\neq}$ and $\tilde{B}^{\neq}$ are the rotational symmetry number and rotational constant of the activated complex and $\sigma(F_2)$ and $\tilde{B}(F_2)$ are the rotational symmetry number and rotational constant of the diatomic reactant. The symmetry number of F_2 is $\sigma = 2$, which decreases the number of accessible states of the reactants, which increases the ratio of rotational partition functions, favoring the formation of the activated complex. More importantly, even for more complex reactions, the activated complex is larger than either of the reactants individually and larger because of the loose association in the activated complex. In other words, the reactive asymmetric stretch is "loose and floppy" in the activated complex, [H--F--F]†. Both effects make the moment of inertia of the activated complex larger than the reactants, giving smaller rotational constants for the activated complex, and therefore larger number of accessible states for the activated complex, compared to the reactants.

4. Use Activated Complex Theory to discuss the reaction:

$$\text{H} + \text{F–F} \rightleftarrows [\text{ H--F--F }]^{\dagger} \rightarrow \text{H–F} + \text{F}$$

Consider the shift in reaction rate, faster or slower, after making the following changes. (a). The bond length of F_2 is increased. (b). F_2 is changed from a homonuclear to a heteronuclear diatomic. (c). The symmetric stretch force constant of the activated complex is increased. (d). The bond dissociation energy of F_2 is increased. (e). The ^{1}H-atom is changed to deuterium, ^{2}H, considering translation only. [In reality changing just one molecular parameter is impossible, bond strength changes have multiple effects. However, for the purposes of this exercise assume that the given change is done without changes in other parameters.]

Answer: The plan is to focus on the formation of the activated complex. The products are irrelevant in this analysis. As a result, the plan is to consider the change in number of accessible states as we did for the calculation of the equilibrium constant in Example 30.5.5, but this time in the context of activated complex theory, as based on Eq. 32.1.14°:

$$k_2 = \frac{kT}{h}\left(\frac{q^{\neq o'}/N_A}{q^{o}(H)/N_A \; q^{o}(F_2)/N_A}\right)\left(\frac{RT}{P^{o}}\right) e^{-\Delta E_o^{\neq}/kT} \tag{32.1.14°}$$

Each change makes the reaction *slower*:
(a). The rotational partition function of a diatomic is $q_r = kT/\sigma\tilde{B}hc$, Eq. 30.2.33. If the bond length of F_2 is increased, the rotational constant of F_2 is decreased: $\tilde{B} = \hbar/4\pi\mu R_o^2 c$. If the

rotational constant is decreased, the number of accessible rotational states of the reactants is increased, and the rate of formation of the activated complex is decreased.

(b). The rotational symmetry number of a homonuclear diatomic is $\sigma = 2$, but for a heteronuclear diatomic is $\sigma = 1$. If F_2 is changed from a homonuclear to a heteronuclear diatomic, the symmetry number decreases, increasing the number of accessible rotational states of the reactants, and decreasing the rate of formation of the activated complex.

(c). If the symmetric stretch force constant of the activated complex is increased, the number of accessible vibrational states of the activated complex decreases, and the rate of formation of the activated complex decreases. See Eq. 30.2.27.

(d). If the bond dissociation energy, D_o, of F_2 is increased, the zero point energy shift term increases:

$$\Delta E_o^{\ddagger} = [-D_o(HFF^{\neq})] - [-D_o(F_2)] \qquad \textit{increases, so that } e^{-\Delta E_o^{\ddagger}/kT} \textit{ decreases}$$

In other words, if the bond dissociation energy of F_2 increases, the reactant becomes more stable, giving more accessible states to the reactants, and decreasing the rate of formation of the activated complex.

(e). The translational partition function is $q_t = (2\pi mkT)^{3/2}V/h^3$, Eq. 30.2.19°. The effect of the change in isotope is an increase in the mass, m. With increasing mass, the energy spacing of the particle in a box translational energy levels decreases. If the ^{1}H-atom is changed to deuterium, considering translation only, the number of accessible translational states of both the reactants and activated complex increases. The translational partition function factor in activated complex theory for ^{1}H is:

$$\frac{q_t^{\circ\neq}/N_A}{q_t^{\circ}(H)/N_A\; q_t^{\circ}(F_2)/N_A} = \left[\frac{\mathfrak{M}(HFF)}{\mathfrak{M}(H)\mathfrak{M}(F_2)}\right]^{3/2} \frac{N_A}{(2\pi kT/1000\text{ g kg}^{-1}N_A)^{3/2}\; RT/P^\circ h^3}$$

Changing the ^{1}H atom to ^{2}H effects only the mass ratio; the second factor remains unchanged. Changing the ^{1}H atom to ^{2}H doubles the denominator in the mass ratio, but has a smaller fractional change in the numerator, which decreases the rate of formation of the activated complex for ^{2}H. Numerically these factors are:

$$\left[\frac{\mathfrak{M}(HFF)}{\mathfrak{M}(H)\mathfrak{M}(F_2)}\right]^{3/2} = \left[\frac{39}{(1)\,(38)}\right]^{3/2} = 1.039 \qquad \left[\frac{\mathfrak{M}(DFF)}{\mathfrak{M}(D)\mathfrak{M}(F_2)}\right]^{3/2} = \left[\frac{40}{(2)\,(38)}\right]^{3/2} = 0.526^{3/2} = 0.381$$

The change from ^{1}H to ^{2}H increases the number of accessible states of the reactants more than the activated complex, decreasing the reaction rate. This translation-only approximation neglects any changes to the vibrational zero point energies of the activated complex. This problem's approach to the isotope effect is specific to this particular reaction, with atomic hydrogen as a reactant. The **primary isotope effect** for H-atom transfer is more commonly referenced and is developed in a subsequent problem.

5. In the derivation of the Eyring equation, Eq. 32.1.24°, what is the source of the kT/h term?

Answer: The kT/h term relates back to the vibrational partition function of the reactive asymmetric stretch, which gives the reaction coordinate. An increase in temperature partitions more energy into the reactive asymmetric stretch thereby increasing the rate of formation of the activated complex. The explicit form as kT/h results from the use of the high temperature approximation to give the vibrational partition function as $kT/h\nu^{\neq}$, Eq. 30.4.20.

6. (a). Find the activation enthalpy, entropy, and Gibbs energy of the reaction:

$$2\ NO_2\ (g) \rightarrow 2\ NO\ (g) + O_2\ (g)$$

at 600.0 K. The Arrhenius pre-exponential factor is $3.06\text{x}10^{12}\ s^{-1}$. The activation energy is $110.9\ kJ\ mol^{-1}$. (b). The reaction does not necessarily proceed by a single step mechanism. Is the activation entropy consistent with a bimolecular transition state for the rate limiting step?

Answer: The plan is to follow Example 32.1.2 and then compare the activation entropy to the value of $-80\ J\ K^{-1}\ mol^{-1}$ that is typical for a bimolecular process.

At 600.0 K, the transmission factor and standard state molar volume are:

$$\frac{kT}{h} = 1.2502\text{x}10^{13}\ s^{-1} \quad \text{and} \quad \left(\frac{RT}{P°}\right) = \frac{0.0831446\ L\ bar\ K^{-1}\ mol^{-1}(600.0\ K)}{1.000\ bar} = 49.887\ L\ mol^{-1}$$

Using Eq. 32.1.30° for the bimolecular pre-exponential factor with the given experimental value, $A = 3.06\text{x}10^{12}\ M^{-1}\ s^{-1}$, results in:

$$A = \frac{kT}{h}\left(\frac{RT}{P°}\right) e^2\ e^{\Delta_r S^{\circ\neq}/R}$$

$$= 1.2502\text{x}10^{13}\ s^{-1}\ (49.887\ L\ mol^{-1})(2.7183)^2\ e^{\Delta_r S^{\circ\neq}/R} = 3.06\text{x}10^{12}\ L\ mol^{-1}\ s^{-1}$$

or $e^{\Delta_r S^{\circ\neq}/R} = 6.640\text{x}10^{-4}$

Solving for the activation entropy:

$$\Delta_r S^{\circ\neq} = 8.3145\ J\ K^{-1}\ mol^{-1}\ \ln(4.043\text{x}10^{-3}) = -60.84\ J\ K^{-1}\ mol^{-1}$$

With Eq. 32.1.28°: $\Delta_r H^{\circ\neq} = E_a - 2RT$

$$\Delta_r H^{\circ\neq} = 110.9\ kJ\ mol^{-1} - 2(8.3145\ J\ K^{-1}\ mol^{-1})(600.0\ K)(1\ kJ/1000\ J)$$

$$= 110.9\ kJ\ mol^{-1} - 9.9774\ kJ\ mol^{-1} = 100.92\ kJ\ mol^{-1}$$

With Eq. 32.1.23: $\Delta_r G^{\circ\neq} \equiv \Delta_r H^{\circ\neq} - T\Delta_r S^{\circ\neq}$

$$\Delta_r G^{\circ\neq} = 100.92\ kJ\ mol^{-1} - (600.0\ K)(-60.84\ J\ K^{-1}\ mol^{-1})(1\ kJ/1000\ J) = 137.4\ kJ\ mol^{-1}$$

For pre-exponential factors in the range $A \sim 10^{10} - 10^{11}$ the entropy of activation is in the range:

$$e^{\Delta_r S^{\circ\neq}/R} = 8.79\text{x}10^{-6} \text{ to } 8.79\text{x}10^{-5} \quad \text{giving} \quad \Delta_r S^{\circ\neq} = -96.8 \text{ to } -77.7\ J\ K^{-1}\ mol^{-1}$$

or in round numbers ~ $-80\ J\ K^{-1}\ mol^{-1}$. The value for this reaction is likewise strongly negative, but not as negative as expected. The value is much more negative than expected for a unimolecular process. The activation entropy of $-60.8\ J\ K^{-1}\ mol^{-1}$ provides support for a bimolecular transition state, but one that has relaxed steric requirements. The relaxed steric requirements might result from orientation independence, long range forces that increase the effective collision cross section, or relaxed collision timing requirements for the reactive asymmetric stretch.

7. The pre-exponential factor for the reaction $CH_3Br + Cl^- \rightarrow CH_3Cl + Br^-$ in acetone solution is $2.0\text{x}10^9$ L mol^{-1} s^{-1} and the activation energy is 65.7 kJ mol^{-1}. What are the Gibbs energy, entropy, and enthalpy of activation at 298.15 K?

Answer: The plan is to follow Example 32.1.2, but based on Eqs. 32.1.31°-32.1.34°, since the reaction is in solution.

At 298.15 K, the transmission factor is: $\frac{kT}{h} = \frac{1.38064\text{x}10^{-23}\text{ J K}^{-1}(298.15\text{ K})}{6.62608\text{x}10^{-34}\text{ J s}} = 6.2124\text{x}10^{12}\text{ s}^{-1}$

Using Eq. 32.1.34° for the solution phase pre-exponential factor with the given experimental value, $A = 2.0\text{x}10^9$ L mol^{-1} s^{-1}, results in:

$$A = \frac{kT}{h}\, e\, e^{\Delta_r S^{\circ\neq}/R}$$

$$= 6.2124\text{x}10^{12}\text{ s}^{-1}\ (2.7183)\ e^{\Delta_r S^{\circ\neq}/R} = 2.0\text{x}10^{9}\text{ L mol}^{-1}\text{ s}^{-1}$$

or $e^{\Delta_r S^{\circ\neq}/R} = 1.184\text{x}10^{-4}$

Solving for the activation entropy:

$$\Delta_r S^{\circ\neq} = 8.3145\text{ J K}^{-1}\text{ mol}^{-1}\ \ln(1.184\text{x}10^{-4}) = -75.2\text{ J K}^{-1}\text{ mol}^{-1}$$

Since $\Delta_r n_g = 0$, Eq. 32.1.32, $\Delta_r H^{\circ\neq} = E_a - RT$

$$\Delta_r H^{\circ\neq} = 65.7\text{ kJ mol}^{-1} - 8.3145\text{ J K}^{-1}\text{ mol}^{-1}(298.15\text{ K})(1\text{ kJ}/1000\text{ J})$$

$$= 65.7\text{ kJ mol}^{-1} - 2.4790\text{ kJ mol}^{-1} = 63.22\text{ kJ mol}^{-1}$$

With Eq. 32.1.23: $\Delta_r G^{\circ\neq} \equiv \Delta_r H^{\circ\neq} - T\Delta_r S^{\circ\neq}$

$$\Delta_r G^{\circ\neq} = 63.22\text{ kJ mol}^{-1} - (298.15\text{ K})(-75.2\text{ J K}^{-1}\text{ mol}^{-1})(1\text{ kJ}/1000\text{ J}) = 85.6\text{ kJ mol}^{-1}$$

For pre-exponential factors in the range $A \sim 10^{10} - 10^{11}$ the entropy of activation is in the range:

$$e^{\Delta_r S^{\circ\neq}/R} = 8.79\text{x}10^{-6}\text{ to }8.79\text{x}10^{-5}\quad\text{giving}\quad \Delta_r S^{\circ\neq} = -96.8\text{ to }-77.7\text{ J K}^{-1}\text{ mol}^{-1}$$

or in round numbers ~ -80 J K^{-1} mol^{-1}. The value for this reaction is a little below typical, indicating a little more forgiving steric constraints than normal for a bimolecular gas phase reaction. Collision timing constraints are often relaxed because of the cage effect in solution.

8. Find the activation enthalpy, entropy, and Gibbs energy of the gas phase isomerization:

trans-CHCl=CHCl → *cis*-CHCl=CHCl

at 800.0 K. The Arrhenius pre-exponential factor is $5.0\text{x}10^{12}$ s^{-1}. The activation energy is 27.8 kJ mol^{-1}:

Answer: The plan is to follow Example 32.1.2, noting that the reaction is unimolecular, giving $\Delta_r n_g = 0$ for the formation of the transition state.

At 800.0 K, the transmission factor is: $\frac{kT}{h} = 1.6669\text{x}10^{13}\text{ s}^{-1}$

Using Eq. 32.1.35° for the unimolecular pre-exponential factor with the given experimental pre-exponential factor of $A = 5.0\text{x}10^{12}$ s^{-1} results in:

$$A = \frac{kT}{h}\, e\, e^{\Delta_r S^{\circ\neq}/R} \tag{1}$$

$$= 1.6669\text{x}10^{13}\ \text{s}^{-1}\ (2.7183)\ e^{\Delta_r S^{\circ\neq}/R} = 5.0\text{x}10^{12}\ \text{s}^{-1}$$

$$\text{or} \quad e^{\Delta_r S^{\circ\neq}/R} = 0.11035 \tag{2}$$

Solving for the activation entropy: $\Delta_r S^{\circ\neq} = 8.3145\ \text{J K}^{-1}\ \text{mol}^{-1}\ \ln(0.11035) = -18.33\ \text{J K}^{-1}\ \text{mol}^{-1}$

The entropy of activation is seen to be a moderate value, compared to the "garden variety" -80 J K^{-1} mol^{-1} that is expected for a bimolecular gas phase reaction.

With $\Delta_r n_g = 0$, $\Delta_r H^{\circ\neq} = \Delta_r U^{\circ\neq}$ and then $\Delta_r H^{\circ\neq} = E_a - RT$, from Eq. 32.1.32:

$$\Delta_r H^{\circ\neq} = 27.8\ \text{kJ mol}^{-1} - 8.3145\ \text{J K}^{-1}\ \text{mol}^{-1}(800.0\ \text{K})(1\ \text{kJ}/1000\ \text{J})$$

$$= 27.8\ \text{kJ mol}^{-1} - 6.652\ \text{kJ mol}^{-1} = 21.15\ \text{kJ mol}^{-1} \tag{3}$$

With Eq. 32.1.23, $\Delta_r G^{\circ\neq} \equiv \Delta_r H^{\circ\neq} - T\Delta_r S^{\circ\neq}$:

$$\Delta_r G^{\circ\neq} = 21.15\ \text{kJ mol}^{-1} - (800.0\ \text{K})(-18.33\ \text{J K}^{-1}\ \text{mol}^{-1})(1\ \text{kJ}/1000\ \text{J}) = 35.8\ \text{kJ mol}^{-1} \tag{4}$$

Alternatively for $\Delta_r G^{\circ\neq}$ we can use the corresponding equation to Eqs. 32.1.20 and 32.1.22°,which for $\Delta_r n_g = 0$ gives $K_p^{\neq} = K_c^{\neq}$ and:

$$k_1 = \frac{kT}{h}\, e^{-\Delta_r G^{\circ\neq}/RT} \tag{5}$$

To use this approach, we require the value of the unimolecular rate constant at 800.0 K:

$$k_1 = A\ e^{-E_a/RT} = 5.0\text{x}10^{12}\ \text{s}^{-1}\ e^{-27800\ \text{J}/8.3145\ \text{J K}^{-1}\text{mol}^{-1}(800.0\ \text{K})} = 7.653\text{x}10^{10}\ \text{s}^{-1} \tag{6}$$

Substituting this value for k_1 into Eq. 5 gives:

$$e^{-\Delta_r G^{\circ\neq}/RT} = 7.653\text{x}10^{10}\ \text{s}^{-1}/1.6669\text{x}10^{13}\ \text{s}^{-1} = 4.591\text{x}10^{-3} \tag{7}$$

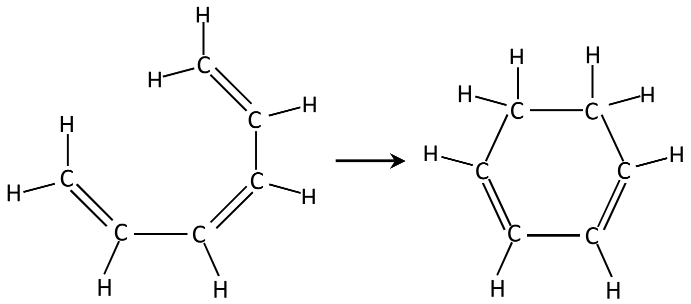
and $\Delta_r G^{\circ\neq} = -\ 8.3145\ \text{J K}^{-1}\ \text{mol}^{-1}\ (800.0\ \text{K})\ \ln(4.591\text{x}10^{-3})\ (1\ \text{kJ}/1000\ \text{J}) = 35.8\ \text{kJ mol}^{-1}$

which matches Eq. 4.

9. The gas phase reaction: *cis*-1,3,5-hexatriene → 1,3-cyclohexadiene has an activation enthalpy of 121.5 kJ mol^{-1} and an entropy of activation of -30.4 J K^{-1} mol^{-1}. Comment on the ease of formation of the transition state.

Answer: The plan is to compare the activation parameters to the values in Table 32.1.1, the "garden variety" activation energy of ~ 50 kJ mol^{-1} given in Sec. 3.5, and the typical bimolecular activation entropy of -80 J K^{-1} mol^{-1} given in Sec. 32.1.

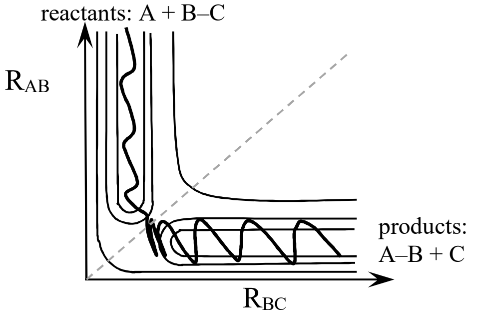
The reaction is diagrammed below:



The activation enthalpy is related to the activation energy through $\Delta_r H^{\circ\neq} = E_a - RT$. In other words, the activation energy and enthalpy differ by only 2.5 kJ mol^{-1} at 298.15 K. The large activation energy suggests the approach to the transition state is dominated by a bond cleavage. The activation entropy is intermediate between "loose and floppy" unimolecular transition states and typical bimolecular transition states. As a result we expect some considerable steric restraints in the formation of the transition state. These results seem reasonable because the process is more complicated than a simple ring closure. The relatively large activation entropy (for a unimolecular process) suggests that the formation of the transition state involves a concerted ring closure and hydride transfer.

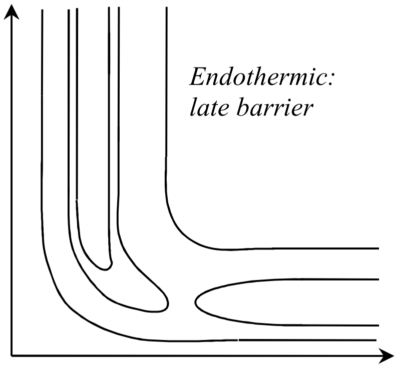
10. Draw the trajectory, on the potential energy surface below, of a reactive atom-diatom collision that experiences multiple crossings and produces a product in a highly excited vibrational state. Label the side of the graph that corresponds to the reactants and specify the corresponding reaction, choosing from either A + B–C → A–B + C or A–B + C → A + B–C.

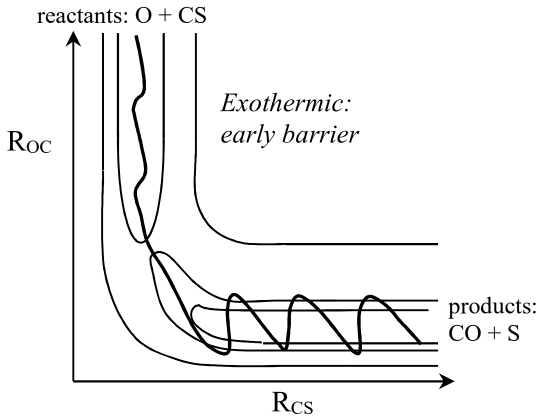
Answer: Choosing the reaction A + B–C → A–B + C and the given axis labels, the reactant well is at the top of the potential energy surface. The trajectory crosses the 45° line more than once and the amplitude of the product vibrations is large.



11. Consider the exothermic gas phase reaction: $O(^3P) + CS \rightarrow CO + S(^3P)$. Is the reaction likely to have an early or late barrier? Does translational or vibrational energy in the collision favor the formation of products? Choose the corresponding energy surface, below. Label the axes with either R_{OC} or R_{CS}. Label the reactant and product valleys. Draw an example of a trajectory that has the favorable combination of translational and vibrational energy for the collision. (You will use only one of the surfaces).

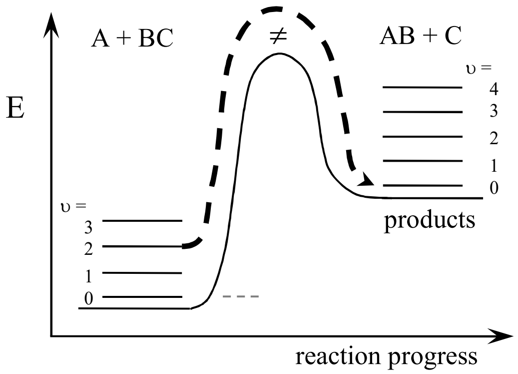
Answer: Exothermic reactions often have early barriers, as in the potential energy surface at right. Initial translational energy favors the formation of products. To explain why, consider standing in the reactant valley looking towards the transition state barrier. The barrier is straight ahead, instead of being a bit around the corner to the left. The best approach to the transition state is then to go straight ahead. Translational energy moves you straight ahead, but vibrational energy moves you to the left and right, perpendicular to the minimum energy path. The amplitude of the initial vibration is small, showing that the energy is primarily in translation. Exothermic reactions are more likely to give products in excited vibrational states than endothermic reactions. Consistent with this expectation, the trajectory in the product valley is shown with a large amplitude, but this choice is not necessary for this problem.

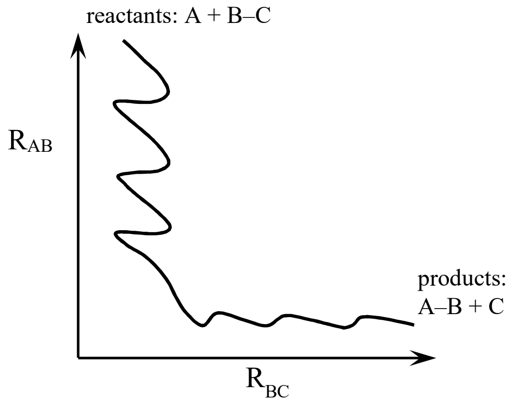




12. The reaction profile of an atom-diatom collision is shown below, including the vibrational levels. Draw a corresponding trajectory for the collision. Label the reactant and product sides.

Answer: Given the reaction A + B–C → A–B + C and the given axis labels, the reactant well is at the top of the potential energy surface. The reaction begins in an excited vibrational state and ends in the ground vibrational state. The amplitude of the vibrations in the reactant well is then large and in the product well is small (at the minimum amplitude given $\upsilon = 0$).





13. Use collision theory to calculate the theoretical value of the bimolecular rate constant of the reaction $H_2\,(g) + I_2\,(g) \rightarrow 2\,HI\,(g)$ at 650 K. The collision cross-section is 0.36 nm^2, the reduced mass is $3.32\text{x}10^{-27}$ kg, and the activation energy is 171. kJ mol^{-1}

Answer: The plan is to use Eq. 32.7.18 with the given cross-section: $\sigma = \pi b_{max}^2 = 0.36\ \text{nm}^2$. The relative collision speed is, Eq. 31.3.14:

$$\bar{c}_{rel} = \left(\frac{8kT}{\pi\mu}\right)^{\frac{1}{2}} = \left(\frac{8(1.38065\text{x}10^{-23}\ \text{J K}^{-1})(650\ \text{K})}{\pi\ 3.32\text{x}10^{-27}\ \text{kg}}\right)^{\frac{1}{2}} = 2624.\ \text{m s}^{-1}$$

The pre-exponential factor is using Eq. 32.7.18 and converting σ to m^2:

$$A = \pi b_{max}^2\ \bar{c}_{rel}\ (1000\ \text{L/m}^3)N_A$$
$$A = 0.36\ \text{nm}^2\ (1\text{x}10^{-9}\ \text{m/ 1nm})^2(2624.\ \text{m s}^{-1})\ (1000\ \text{L/m}^3)\ 6.022\text{x}10^{23}\ \text{mol}^{-1}$$
$$= 5.7\text{x}10^{11}\ \text{L mol}^{-1}\ \text{s}^{-1}$$

14. The rate constant of an aqueous ionic reaction with $z_A = 2$ and $z_B = -1$ at zero ionic strength is $k_{(I=0)}$. Calculate the ratio of the rate constant of the reaction done in 0.1 M NaCl, k, to the rate constant at zero ionic strength: $k/k_{(I=0)}$ at 298 K.

Answer: The plan is to use Eq. 32.6.6 to estimate the kinetic salt effect. The difference of the logs cancels the leading term in Eq. 32.6.6:

$$\log k_2 - \log k_{(I=0)} = \log\left(\frac{kT}{h} K_c^{\neq\prime}\ c^{o-1}\right) + 0.509\ (2z_Az_B)\ I^{\frac{1}{2}} - \log\left(\frac{kT}{h} K_c^{\neq\prime}\ c^{o-1}\right)$$
$$= 0.509\ (2z_Az_B)\ I^{\frac{1}{2}}$$

Solving for the ratio gives:

$$k/k_{(I=0)} = 10^{0.509\ (2z_Az_B)\ I^{\frac{1}{2}}}$$

The ionic strength is given by Eq. 19.4.22. Assume that the ionic strength is dominated by the NaCl. For 0.1 M NaCl, because NaCl is a 1:1 electrolyte, $I = m/m^o = 0.1$. Given $z_A = +2$ and $z_B = -1$ for the reacting ions gives:

$$k/k_{(I=0)} = 10^{0.509\ (2(+2)(-1))(0.1)^{\frac{1}{2}}} = 0.227$$

The reaction is slower at higher ionic strength because the ionic atmosphere decreases the attraction of the two reactant ions.

15. Use Eq. 32.7.13 to prove that the hard-core collision cross section is $\sigma_{HC} = \pi d_{HC}^2$, where d_{HC} is the hard-core collision diameter.

Answer: The plan is to assume the reaction probability is a function of the impact parameter only, $P(\varepsilon_{rel},b) = P(b)$, which in turn is defined as unity for an impact parameter less than the hard-core collision diameter in Eq. 32.7.13.

The probability that a collision with relative kinetic energy ε_{rel} and impact parameter b gives products is $P(\varepsilon_{rel},b)$. The reaction cross-section is then the integral of the reaction probability over the impact parameter, Eq. 32.7.13:

$$\sigma(\varepsilon_{rel}) = 2\pi \int_0^\infty P(\varepsilon_{rel},b)\, b\, db \qquad (32.7.13)$$

Assuming that the reaction probability is unity for every collision with impact parameter $b \leq d_{HC}$, $P(\varepsilon_{rel},b) = 1$, and zero for any greater impact parameter gives the cross-section as:

$$\sigma(\varepsilon_{rel}) = 2\pi \int_0^{d_{HC}} b\, db = \pi b^2\Big|_0^{d_{HC}} = \pi d_{HC}^2$$

This result shows that the more general definition in Eq. 32.7.13 is consistent with the KMT model.

16. Determine if the following statements are true or false. If the statement is false, describe the changes that are necessary to make the statement true, if possible. If the statement is true but too restrictive, give the more general statement.

(a). In atom-diatom collisions, $A + BC \rightarrow AB + C$, the reaction coordinate is an unstable asymmetric stretch.

(b). Once the transition state surface is crossed, the activated complex does not return to reactants.

(c). Activated Complex Theory assumes a Boltzmann distribution among vibrations and rotations in the reactants and the activated complex.

(d). Excluding the reactive asymmetric stretch, the vibrations and rotations of the activated complex do not have an effect on the reaction rate.

(e). Reactions are more likely with excess energy in translation rather than vibration.

(f). Exothermic reactions are more likely to give products in excited vibrational states than endothermic reactions.

(g). The common existence of chemical reactions that are much slower than the corresponding kinetic molecular theory hard-core collision rate is evidence of long-lived transition states.

(h). In the RRKM theory of unimolecular processes, the vibrational and rotational states of the reactants are treated as a continuum while the vibrational and rotational states of the critical configuration are treated as discrete and countable.

(i). In the RRKM theory of unimolecular processes, the critical configuration never returns to the activated reactant.

(j). Non-adiabatic transitions occur by avoided curve crossing.

(k). The Born-Oppenheimer approximation is valid for the progression of the transition state to give products.

(l). Experimental reaction cross-sections are never larger than the hard-core collision cross-sections, although the experimental reaction cross-sections is often smaller than the hard-core collision cross-section.

(m). In collision theory, the line of centers velocity and kinetic energy increase with decreasing impact parameter.

(n). In collision theory, the reaction cross section is independent of the collision relative kinetic energy.

(o). In solution, equilibrium constants are functions of the activities of the reactants and products, rather than the concentrations. Reaction rates are functions of the solution concentrations, and not the activities.

Answers: (a). *True*.

(b). *False*, multiple crossings can occur, which increase the probability of the return to reactants.

(c). *True, but too restrictive*. Activated Complex Theory also assumes a Boltzmann distribution of the available energy into the reactive asymmetric stretch, which is represented by the kT/h factor. We also must consider the electronic degrees of freedom in the reactants and the activated complex. For many reactions the electronic partition functions are equal to the ground state degeneracies, and the ground state degeneracies are often singlets. However, this simplification is not always true, especially if a reactant is atomic, Table 30.2.2.

(d). *False*. The bimolecular rate constant is the number of accessible states in the activated complex divided by the product of the number of accessible states in the reactants. The vibrations and rotations of the activated complex increase the number of accessible states of the activated complex.

(e). *Sometimes true and sometimes false*. Endothermic reactions with late barriers are more likely with excess energy in vibration rather than translation. Exothermic reactions with early barriers are more likely with excess energy in translation rather than vibration.

(f). *True*. Exothermic reactions are more likely to give products in excited vibrational states than endothermic reactions.

(g). *False*: The traversal of the transition state region is typically very fast – tens of femtoseconds. The sluggishness of many reactions is a reflection of the improbability of collisions with sufficient relative kinetic energy, proper orientation, and timing with respect to the progress of the vibrations of the reactants.

(h). *True*.

(i). *False*: The critical configuration is considered to be in equilibrium with the reactants, Eq. 32.5.3, which can only occur if the formation of the critical configuration is reversible from the perspective of the reactants.

(j). *True*.

(k). *False*: Classical trajectory calculations do calculate the potential energy surface of a collision within the Born-Oppenheimer approximation. Never-the-less, the Born-Oppenheimer approximation is violated from the perspective of the bound-vibrational potential energy wells of the reactants and products. The unstable transition state maximum in energy cannot be represented in the bound-state product potential energy functions. The Born-Oppenheimer approximation is violated for the progression of the transition state to give products.

(l). *False*: Attractive intermolecular potentials can result in reaction cross-sections that are larger than the hard-core collision cross-sections. Reactions that have little or no activation energy are commonly in this category. However, it is *true* that the experimental reaction cross-section is often smaller than the hard-core collision cross-section.

(m). *True*, see Eq. 32.7.11.

(n). *False*: In collision theory, the reaction cross section can be strongly dependent on the collision relative kinetic energy, Figure 32.7.4.

(o). *False*: Reaction rates in real gases and in solution are functions of the gas phase fugacities or solution activities and not the concentrations. The thermodynamic activity of a solute differs from the concentration because of intermolecular forces. Intermolecular forces play an important role in molecular dynamics.