

## Chapter 23: Foundations of Quantum Mechanics Problems

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

*Answer:* The conversions are given by  $v\lambda = c$  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	$1 \text{ eV} = 96.485 \text{ kJ mol}^{-1} = 8065.5 \text{ cm}^{-1}$
$E = N_A h\nu \text{ (1 kJ/1000J)}$	in $\text{kJ mol}^{-1}$	$1 \text{ cm}^{-1} = 11.962 \text{ J mol}^{-1}$

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

$$\tilde{\nu} = 4000 \text{ cm}^{-1} \text{ corresponds to } \tilde{\nu} = 4000 \text{ cm}^{-1}(100 \text{ cm}/1 \text{ m}) = 4.000 \times 10^5 \text{ m}^{-1}:$$

$$\nu = c/\lambda = 2.998 \times 10^8 \text{ m s}^{-1} (4.000 \times 10^5 \text{ m}^{-1}) = 1.199 \times 10^{14} \text{ s}^{-1}$$

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

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

Alternatively, the conversion factors that are listed above may be used.

At  $400. \text{ cm}^{-1}$  the values are just a factor of ten different:

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

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.

[illegible]

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

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

The following spreadsheet was developed:

$\lambda$ (cm)	$\lambda$ ( $\mu\text{m}$ )	$\lambda$ (nm)	$\nu$ ( $\text{s}^{-1}$ )	E (J)	E (eV)	E (kJ/mol)	$\tilde{\nu}$ ( $\text{cm}^{-1}$ )	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 ( $^{13}\text{C}$ )

10 GHz is a typical frequency for microwave-rotational spectroscopy

1000  $\text{cm}^{-1}$  is a typical mid-infrared wavenumber (mid-IR range: 4000  $\text{cm}^{-1}$  – 400  $\text{cm}^{-1}$ )

2 eV and 200  $\text{kJ mol}^{-1}$  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:

$$E = h\nu = \frac{1}{2} m v^2 + \Phi$$

$\uparrow$        $\uparrow$       cst.

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:

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

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

$$\begin{aligned} E &= \frac{1}{2} m v^2 + e\Gamma \\ 4.966 \times 10^{-19} \text{ J} &= \frac{1}{2} m v^2 + 1.6022 \times 10^{-19} \text{ C} (2.28 \text{ V}) \\ \frac{1}{2} m v^2 &= 1.31 \times 10^{-19} \text{ J} \end{aligned}$$

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

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

and the photoelectric effect formula becomes:

$$3.100 \text{ eV} = \frac{1}{2} m v^2 + 2.28 \text{ eV} \quad \text{and} \quad \frac{1}{2} m v^2 = 3.100 \text{ eV} - 2.28 \text{ eV} = 0.820 \text{ eV}$$

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:

$$E = \frac{1}{2} m v^2 + e\Gamma$$

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

$$E_{\min} = e\Gamma = 1.6022 \times 10^{-19} \text{ C} (2.10 \text{ V}) = 3.365 \times 10^{-19} \text{ J}$$

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

$$\begin{aligned} \lambda &= hc/E = 6.6261 \times 10^{-34} \text{ J s} (2.9979 \times 10^8 \text{ m s}^{-1}) / 3.365 \times 10^{-19} \text{ J} \\ \lambda &= 5.904 \times 10^{-7} \text{ m} = 590. \text{ nm} \end{aligned}$$

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 (amplitude)<sup>2</sup> 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)<sup>2</sup>,” 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  $1 \text{ J} = 1 \text{ V C} = 1 \text{ kg m}^2 \text{ s}^{-2}$ :

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

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

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

which is a small fraction,  $\sim 1/50$ , 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:

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

where  $e$  is the charge of the electron.

$$E = 8.046 \times 10^3 \text{ eV} (1.6022 \times 10^{-19} \text{ J} / 1 \text{ eV}) = 1.2891 \times 10^{-15} \text{ J}$$

$$\lambda = hc/E = 6.6261 \times 10^{-34} \text{ J s} (2.9979 \times 10^8 \text{ m s}^{-1}) / 1.2891 \times 10^{-15} \text{ J} = 1.541 \times 10^{-10} \text{ m} = 1.541 \text{ Å}$$

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<sup>-1</sup> and a 70.0 kg human traveling at 2 km hr<sup>-1</sup>. (b). Calculate the de Broglie wavelength of an O<sub>2</sub> molecule based on the overall translational energy at room temperature. The average speed (rms) of an O<sub>2</sub> molecule at room temperature is 482. m s<sup>-1</sup>.

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

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

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

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

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

$$p = 70.0 \text{ kg} (2.0 \times 10^3 \text{ m hr}^{-1}) (1 \text{ hr} / 3600 \text{ s}) = 38.89 \text{ kg m s}^{-1}$$

$$\lambda = h/p = 6.6261 \times 10^{-34} \text{ J s} / 38.89 \text{ kg m s}^{-1} = 1.70 \times 10^{-35} \text{ m}$$

(b). The momentum and de Broglie wavelength of the  $\text{O}_2$  molecule is:

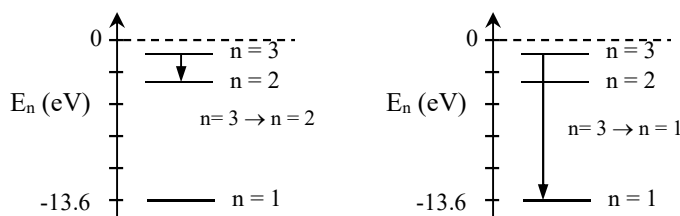
$$p = mv = 32.0 \text{ g mol}^{-1} (1 \text{ mole} / 6.022 \times 10^{23} \text{ mol}^{-1}) (1 \text{ kg} / 1000 \text{ g}) (482. \text{ m s}^{-1})$$

$$p = 2.561 \times 10^{-23} \text{ kg m s}^{-1}$$

$$\lambda = h/p = 6.6261 \times 10^{-34} \text{ J s} / 2.561 \times 10^{-23} \text{ kg m s}^{-1} = 2.59 \times 10^{-11} \text{ m} = 0.259 \text{ \AA}$$

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  $n = 3 \rightarrow n = 1$  has a larger energy difference, longer arrow, and is then “bluer.” The  $n = 3 \rightarrow n = 2$  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  $n = \infty$ .

(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:

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

This transition is in the vacuum ultraviolet, and corresponds to the Lyman- $\alpha$  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  $n = \infty$  and corresponds to  $-E_1$ :

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

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

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

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

11.  $\text{Li}^{2+}$  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  $\text{Li}^{2+}$ . 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  $\text{Li}^{2+}$ , making the corresponding transition for  $\text{Li}^{2+}$  bluer. For  $\text{Li}^{2+}$ ,  $Z = 3$  giving:

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

Then since  $E = hc/\lambda$ :

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

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.<sup>2</sup> 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,  $k = R/N_A = 1.3807 \times 10^{-23} \text{ J K}^{-1}$ . 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 be applied to match the overall intensity to the experimental data.

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

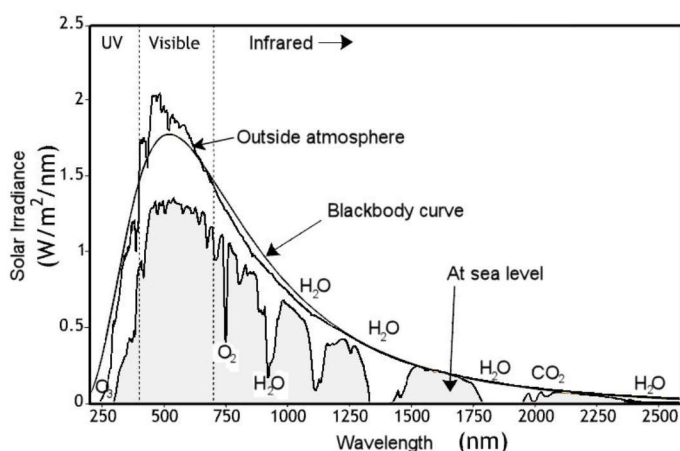
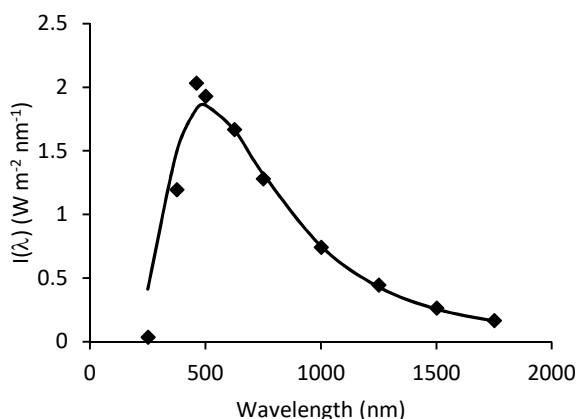


Figure P23.1: The solar irradiance incident on the earth at the top of the atmosphere and at sea level. The irradiance is given in watts for a one-meter surface placed perpendicular to the incident angle of the sun for a 1 nm range in wavelength,  $\lambda$  to  $\lambda + d\lambda$ , given in nm.

*Answer:* The wavelengths must be converted to meters to match the units of  $h$ ,  $k$ , and  $c$ . For example,  $\lambda = 250 \text{ nm} (1 \times 10^{-9} \text{ m/1 nm}) = 2.50 \times 10^{-7} \text{ m}$ . 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 =	$2.18\text{E-}14$
$\lambda$ (nm)	$H_\lambda$ ( $\text{W m}^{-2} \text{ nm}^{-1}$ )	$\nu$ ( $\text{s}^{-1}$ )	$H(\lambda)$ ( $\text{W m}^{-2} \text{ nm}^{-1}$ )
250	0.034	0.410	$4.14\text{E-}01$
375	1.193	1.478	$1.49\text{E+}00$
460	2.032	1.81	$1.83\text{E+}00$
500	1.929	1.844	$1.86\text{E+}00$
625	1.667	1.649	$1.66\text{E+}00$
750	1.279	1.308	$1.32\text{E+}00$
1000	0.742	0.746	$7.52\text{E-}01$
1250	0.445	0.427	$4.30\text{E-}01$
1500	0.263	0.255	$2.57\text{E-}01$
1750	0.166	0.159	$1.60\text{E-}01$



The scale factor of  $2.18 \times 10^{-14}$  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  $93 \times 10^6$  miles, giving the surface area of a sphere at that radius of  $2.79 \times 10^{23} \text{ m}^2$ . The surface area of the

sun is  $6.09 \times 10^{18} \text{ m}^2$ . 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:

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

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  $\sigma = 5.6704 \times 10^{-8} \text{ W m}^{-2} \text{ K}^{-4}$  (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  $\infty$ :

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

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

with  $1 \text{ W} = 1 \text{ J s}^{-1}$ . Radiative energy transfer is a very strong function of temperature. The fundamental constant,  $\sigma$ , 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  $\nu$  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:

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



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

Using the change in variable  $v = c/\lambda$  gives  $dv/d\lambda = -c/\lambda^2$ ,  $dv = -c/\lambda^2 d\lambda$ . The integral limits when this distribution is used change from  $\int_0^\infty$  over  $v$  to  $\int_\infty^0 = -\int_0^\infty$  over  $\lambda$ , since  $v$  increases while  $\lambda$  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  $\sigma = 5.6704 \times 10^{-8} \text{ W m}^{-2} \text{ K}^{-4}$  (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  $1.37 \text{ kW m}^{-2}$ . The surface area of the sun is  $6.09 \times 10^{18} \text{ m}^2$ . 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  $93 \times 10^6$  miles, giving the surface area of a sphere at that radius of  $2.79 \times 10^{23} \text{ m}^2$ . 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:

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

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  $\epsilon_j = j h\nu$ , where  $\nu$  is a fundamental vibration frequency for the motion and  $j$  is an integer. The probability of an electron or atom having energy  $\epsilon_j$  is given by the Boltzmann distribution,  $n_j/N = e^{-\beta\epsilon_j}/q$ , where  $\beta = 1/kT$ . The average energy is given by Eq. 12.2.6:

$$\langle \epsilon \rangle = \frac{\sum_{j=0}^{\infty} \epsilon_j e^{-\beta\epsilon_j}}{q} \quad \text{where } q \text{ is the partition function: } q = \sum_{j=0}^{\infty} e^{-\beta\epsilon_j}$$

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

$$\langle \epsilon \rangle = -\frac{1}{q} \left( \frac{\partial q}{\partial \beta} \right)_V$$

(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:  $\sum_{j=0}^{\infty} a^j = 1 + a + a^2 + a^3 + \dots = \frac{1}{1 - a}$

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

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

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

Dividing this result by  $-1/q$  gives the average energy

$$\langle \epsilon \rangle = - \frac{1}{q} \left( \frac{\partial q}{\partial \beta} \right)_V = \frac{\sum_{j=0}^{\infty} \epsilon_j e^{-\beta \epsilon_j}}{q}$$

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

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

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

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  $\beta$  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:

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

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:

$$I(\nu) = \frac{2\pi\nu^2}{c^2} \langle \epsilon \rangle$$

where  $\nu$  is the frequency of the light emitted, and  $\langle \epsilon \rangle$  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  $\langle \epsilon \rangle = RT$ . 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  $I(\nu) = (2\pi\nu^2/c^2) \langle \epsilon \rangle$  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:  $C_v = (\partial U / \partial T)_v = N_A (\partial \langle \epsilon \rangle / \partial T)_v$ . The average energy of a one-dimensional quantized oscillator was derived in Problem 16:

$$\langle \epsilon \rangle = \frac{h\nu}{(e^{\beta h\nu} - 1)}$$

Einstein estimated that the heat capacity of a simple solid is  $C_v = 3N_A (\partial \langle \epsilon \rangle / \partial T)_v$ , 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  $\tilde{\nu} = 100. \text{ cm}^{-1}$ .

$$\begin{aligned} \text{Answer: } C_v &= 3 N_A \left( \frac{\partial \langle \epsilon \rangle}{\partial T} \right)_v = 3 N_A h\nu \left( \frac{\partial \left( \frac{1}{e^{h\nu/kT} - 1} \right)}{\partial T} \right)_v = 3 N_A h\nu \left[ \frac{-e^{h\nu/kT}}{(e^{h\nu/kT} - 1)^2} \right] \left( \frac{-h\nu}{kT^2} \right) \\ &= 3 N_A k \left( \frac{h\nu}{kT} \right)^2 \frac{e^{h\nu/kT}}{(e^{h\nu/kT} - 1)^2} \end{aligned}$$

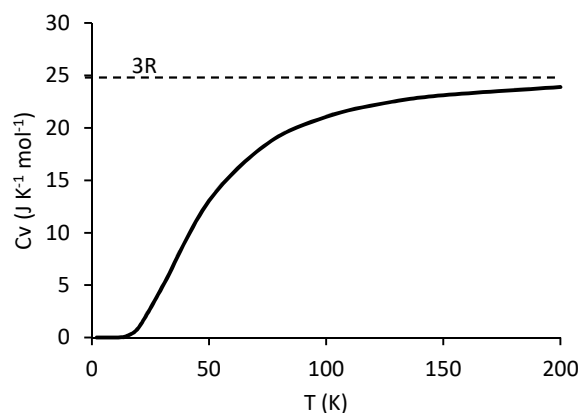
$$\text{Remember that } N_A k = R, \text{ giving: } C_v = 3R \left( \frac{h\nu}{kT} \right)^2 \frac{e^{h\nu/kT}}{(e^{h\nu/kT} - 1)^2}$$

The units are converted to kelvins from wavenumbers using:

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

The plot was done using a spreadsheet:

$\tilde{\nu} =$	100	$\text{cm}^{-1}$
$hc\tilde{\nu}/k =$	143.88	K
$T \text{ (K)}$	$e^{(h\nu/kT)}$	$C_v \text{ (J K}^{-1} \text{ mol}^{-1})$
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  $1.00 \text{ \AA}$ . 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,  $\sigma_{p_x} = (\langle p^2 \rangle - \langle p \rangle^2)^{1/2} = (\langle p^2 \rangle)^{1/2} = p_{\text{rms},x}$ . The root-mean-squared momentum can be used to estimate the kinetic energy of the particle,  $E_{k,x} \approx (p_{\text{rms},x})^2/2m$ . Estimate the kinetic energy of a confined electron with a positional uncertainty of  $1 \text{ \AA}$ . (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  $1 \text{ \AA}$  (the Bohr radius of the H atom is  $0.529 \text{ \AA}$ ). Assume the hydrogen atom is approximated by a  $1 \text{ \AA}$  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  $\text{kJ mol}^{-1}$ . 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  $E_k = 3 (p_{\text{rms},x})^2/2m$  to estimate the ground state energy of the H atom.

(a). Using the Heisenberg uncertainty relationship and  $1 \text{ \AA} = 1 \times 10^{-10} \text{ m}$  gives:

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

(b). The corresponding kinetic energy is:

$$E_{k,x} \approx (p_{\text{rms},x})^2/2m = (5.273 \times 10^{-25} \text{ kg m s}^{-1})^2 / (2 \times 9.109 \times 10^{-31} \text{ kg}) = 1.526 \times 10^{-19} \text{ J}$$

$$E_{k,x} \approx 1.526 \times 10^{-19} \text{ J} (1 \text{ eV} / 1.6022 \times 10^{-19} \text{ J}) = 0.953 \text{ eV}$$

$$E_{k,x} \approx 1.526 \times 10^{-19} \text{ J} (6.022 \times 10^{23} \text{ mol}^{-1}) (1 \text{ kJ} / 1000 \text{ J}) = 91.9 \text{ kJ mol}^{-1}$$

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

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  $\delta p_x \geq 5.273 \times 10^{-25} \text{ kg m s}^{-1}$  is definitely chemically significant. Typical enthalpy changes for chemical reactions are on the order of  $200 \text{ kJ mol}^{-1}$ . Chemical phenomena are most certainly governed by the Heisenberg uncertainty relationship.

20. (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  $80.0 \text{ km hr}^{-1}$  is known to 10%. Calculate the uncertainty in the position of the tennis ball. Does this uncertainty contribute to the difficulty in returning an  $80.0 \text{ km hr}^{-1}$  tennis serve?

*Answer:* The plan is to use  $E_k = p^2/2m$  or  $p = mv$  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:

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

$$\Delta p_x = 0.10 (1.709 \times 10^{-24} \text{ kg m s}^{-1}) = 1.709 \times 10^{-25} \text{ kg m s}^{-1}$$

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

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

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):

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

$$\delta p_x = 0.10(1.289 \text{ kg m s}^{-1}) = 0.1289 \text{ kg m s}^{-1}$$

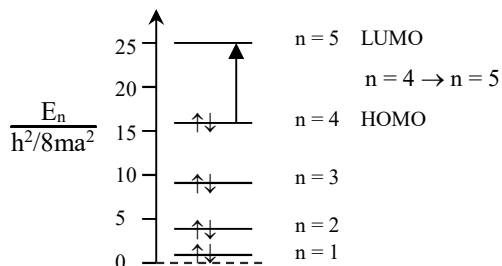
$$\delta x \geq \hbar/(2\delta p_x) = 1.0546 \times 10^{-34} \text{ J s} / 2 / 0.1289 \text{ kg m s}^{-1} = 4.09 \times 10^{-34} \text{ m}$$

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

21. (a). What are the quantum numbers for the energy levels that are involved in the lowest energy electronic transition for the molecule,  $\text{H}_2\text{C}=\text{CH}-\text{CH}=\text{CH}-\text{CH}=\text{CH}-\text{CH}=\text{CH}_2$ ? 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,  $\text{cm}^{-1}$ . 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  $\pi$  orbital doesn't end exactly at the nucleus of the terminal C atoms.

*Answer:* The plan is to note that in the conjugated- $\pi$  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  $9.109 \times 10^{-31}$  kg. There are seven conjugated bonds and adding  $\frac{1}{2}$  of a bond at each terminus gives the box length as  $8(1.39 \text{ \AA}) = 11.12 \text{ \AA} = 1.112 \times 10^{-9} \text{ m}$ :

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

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

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

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

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  $\pi$ :

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

Integral tables give this integral equal to zero:<sup>1</sup>  $\int_0^\pi \sin(ax) \sin(bx) dx = 0$  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:

$$\int \Psi_2^* \Psi_3 dx = (2/a) \int_{-a/2}^{a/2} \sin[2\pi(x' + a/2)/a] \sin[3\pi(x' + a/2)/a] dx' = 0$$

$\uparrow$  odd                       $\uparrow$  even

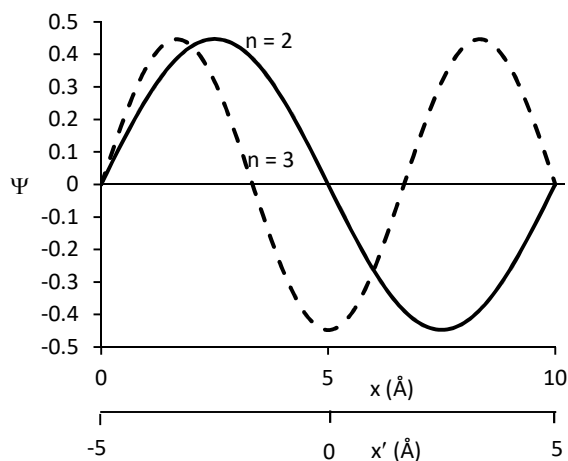


Figure P23.2: Particle in the box wave functions for  $n = 2$  (—) and  $n = 3$  (- - -).

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  $2\pi$ :

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

Integral tables give this integral as:<sup>1</sup>  $\int \sin^2(x) dx = -\frac{1}{2} \cos x \sin x + \frac{1}{2} x$ :

$$\begin{aligned} \int \Psi_2^* \Psi_2 dx &= (1/\pi) \left[ -\frac{1}{2} (\cos y \sin y) \Big|_0^{2\pi} + \frac{1}{2} y \Big|_0^{2\pi} \right] \\ &= (1/\pi) \left[ -\frac{1}{2} (\cos 2\pi \sin 2\pi - \cos 0 \sin 0) + \frac{1}{2} 2\pi \right] \end{aligned}$$

However,  $\sin 0 = 0$  and  $\sin 2\pi = 0$ , giving that  $\Psi_2$  is normalized:

$$\int \Psi_2^* \Psi_2 dx = (1/\pi) \left[ \frac{1}{2} 2\pi \right] = 1$$

24. 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:  $N = \frac{1}{(2\pi)^{1/4} \sigma_x^{1/2}}$

This result is used in Example 23.4.4.

25. 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:<sup>1</sup>  $\int \sin^2(x) dx = -\frac{1}{2} \cos x \sin x + \frac{1}{2} x$ :

$$\begin{aligned} \int_0^{a/2} \Psi_n^2 dx &= (2/n\pi) \left[ -\frac{1}{2} (\cos y \sin y) \Big|_0^{n\pi/2} + \frac{1}{2} y \Big|_0^{n\pi/2} \right] \\ &= (2/n\pi) \left[ -\frac{1}{2} (\cos(n\pi/2) \sin(n\pi/2) - \cos 0 \sin 0) + \frac{1}{2} n\pi/2 \right] \end{aligned}$$

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



$$\int_0^{a/2} \Psi_n^2 dx = (2/n\pi) [1/2 n\pi/2] = 1/2$$

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

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

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

*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  $\int_0^a \Psi_n^2 dx = 1$ . The operator,  $x^2$ , is a multiplicative function, so the order of operation is not important, giving:

$$\langle x^2 \rangle = \frac{\int_0^a \Psi_n^* x^2 \Psi_n dx}{\int_0^a \Psi_n^* \Psi_n dx} = \int_0^a x^2 \Psi_n^2 dx \quad 1$$

Substituting in the general form of the wave function gives:

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

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  $n\pi$ :

$$\langle x^2 \rangle = \left( \frac{2}{a} \right) \left( \frac{a}{n\pi} \right)^3 \int_0^{n\pi} y^2 \sin^2(y) dy \quad 3$$

Integral tables give this integral as:<sup>1</sup>

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

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:

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

Substituting Eq. 5 into Eq. 3 gives:

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

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,  $\sigma_x = (\langle x^2 \rangle - \langle x \rangle^2)^{1/2}$ .

Answer: The expectation value of the position for a particle in a box is  $\langle x \rangle = a/2$ , giving:

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

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

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  $\int_0^a \Psi_n^2 dx = 1$ . The operator,  $\hat{p}_x = (\hbar/i)(d/dx)$ , involves a derivative, so the order of operation is important, giving:

$$\langle p_x \rangle = \frac{\int_0^a \Psi_n^* \hat{p}_x \Psi_n dx}{\int_0^a \Psi_n^* \Psi_n dx} = \int_0^a \Psi_n \frac{\hbar}{i} \left( \frac{d}{dx} \right) \Psi_n dx$$

The derivative is:

$$\frac{d}{dx} \Psi_n = \left( \frac{2}{a} \right)^{1/2} \frac{d}{dx} \sin(n\pi x/a) = \left( \frac{2}{a} \right)^{1/2} \left( \frac{n\pi}{a} \right) \cos(n\pi x/a)$$

Substituting in the general form of the wave function gives:

$$\begin{aligned} \langle p_x \rangle &= \frac{\hbar}{i} \left( \frac{2}{a} \right) \int_0^a \sin(n\pi x/a) \frac{d}{dx} \sin(n\pi x/a) dx \\ &= \frac{\hbar}{i} \left( \frac{2}{a} \right) \left( \frac{n\pi}{a} \right) \int_0^a \sin(n\pi x/a) \cos(n\pi x/a) dx \end{aligned}$$

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  $n\pi$ :

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

This integral is equal to zero, giving  $\langle p \rangle = 0$ . 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  $\langle p_x^2 \rangle$  for a particle in a box of length  $a$  and quantum number  $n$  is:

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

*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  $\int_0^a \Psi_n^2 dx = 1$ . 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:

$$\langle p_x^2 \rangle = \frac{\int_0^a \Psi_n^* \hat{p}^2 \Psi_n dx}{\int_0^a \Psi_n^* \Psi_n dx} = -\hbar^2 \int_0^a \Psi_n \frac{d^2}{dx^2} \Psi_n dx$$

The second derivative is:

$$\frac{d^2}{dx^2} \Psi_n = \left( \frac{2}{a} \right)^{1/2} \frac{d^2}{dx^2} \sin(n\pi x/a) = \left( \frac{2}{a} \right)^{1/2} \left( \frac{n\pi}{a} \right) \frac{d}{dx} \cos(n\pi x/a) = -\left( \frac{2}{a} \right)^{1/2} \left( \frac{n\pi}{a} \right)^2 \sin(n\pi x/a)$$

Substituting in the general form of the wave function gives:

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

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:

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

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

$$\sigma_{px} = (\langle p_x^2 \rangle - \langle p_x \rangle^2)^{1/2} = \hbar \left( \frac{n\pi}{a} \right)$$

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:

$$\sigma_{px} = (\langle p_x^2 \rangle - \langle p_x \rangle^2)^{1/2} = \left( \hbar^2 \left( \frac{n\pi}{a} \right)^2 - 0 \right)^{1/2} = \hbar \left( \frac{n\pi}{a} \right)$$

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  $\sigma_x$  and Problem 30 for  $\sigma_{px}$ :

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

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,  $(\langle x^2 \rangle - \langle x \rangle^2)^{1/2}$ , for the Gaussian wave function:

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

*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  $\Psi^2$  is even and the integral is taken over all space:

$$\langle x \rangle = \int_{-\infty}^{\infty} \underbrace{\Psi^*}_{\text{normalized}} x \underbrace{\Psi}_{\text{real}} dx = \int_{-\infty}^{\infty} x \underbrace{\Psi^2}_{\text{real}} dx = N^2 \int_{-\infty}^{\infty} x \underbrace{e^{-x^2/2\sigma_x^2}}_{\text{odd even}} dx = 0$$

The expectation value for the squared position is:

$$\langle x^2 \rangle = \int_{-\infty}^{\infty} \Psi^* x^2 \Psi dx = \int_{-\infty}^{\infty} x^2 \Psi^2 dx = N^2 \int_{-\infty}^{\infty} x^2 e^{-x^2/2\sigma_x^2} dx$$

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

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

$$\langle x^2 \rangle = 2N^2 \frac{2\sigma_x^2}{4} (2\pi)^{1/2} \sigma_x = 2 \frac{1}{(2\pi)^{1/2} \sigma_x} \frac{2\sigma_x^2}{4} (2\pi)^{1/2} \sigma_x = \sigma_x^2$$

Finally  $(\langle x^2 \rangle - \langle x \rangle^2)^{1/2} = \sigma_x$ , 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  $\Psi$  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:

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

**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:

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

**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:

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

*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  $0 \leq x \leq \infty$  and the average or expectation value of the position for the tunneling particle is:

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

using Eqs. 23.3.6 and 23.5.2 for the constants  $k$  and  $\kappa$ .

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

$$\langle x \rangle = c^* c / 4\kappa^2$$

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

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

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

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  $\kappa$ ; for an electron  $m_e = 9.109 \times 10^{-31}$  kg:

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

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

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

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

The tunneling probability is given by Eq. 23.5.7:

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

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  $x \geq 0$ .

*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.  $\Psi$  is an eigenfunction of  $d^2/dx^2$  with eigenvalue  $\alpha^2$ . The normalization is given by:

$$\begin{aligned} \int_0^\infty \Psi^* \Psi dx &= N^2 \int_0^\infty e^{-2\alpha x} dx = 1 \\ &= N^2 \left( \frac{-1}{2\alpha} \right) e^{-2\alpha x} \Big|_0^\infty = N^2 \left( \frac{-1}{2\alpha} \right) (e^{-\infty} - e^0) = \left( \frac{N^2}{2\alpha} \right) = 1 \end{aligned}$$

giving  $N = (2\alpha)^{1/2}$

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  $\Psi$  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  $x$ :  $-\infty \leq x \leq \infty$ .

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  $\ln x \rightarrow -\infty$  as  $x \rightarrow 0$ , 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  $x \rightarrow \pm \infty$ . 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):<sup>1</sup>

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

and so is normalizable.

(c). Considering  $\Psi(x) = N x e^{-ax}$  for  $0 \leq x \leq \infty$ : as  $x \rightarrow 0$  then  $e^{-ax} \rightarrow 1$  and  $x e^{-ax} \rightarrow 0$ , which is acceptable. As  $x \rightarrow \infty$  then  $e^{-ax} \rightarrow 0$  but  $x \rightarrow \infty$ . However, as a test, evaluating  $x e^{-ax}$  for  $a = 1$  and  $x = 100$  gives  $x e^{-ax} = 4 \times 10^{-42}$ . 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  $x \rightarrow \infty$  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,  $\Psi_A$  and  $\Psi_B$ , have the same momentum,  $p$ :

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

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  $t$ :

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

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).  $\cos(n\pi x/a) + i \sin(n\pi x/a)$ , (d).  $e^{-i n\pi x/a}$  and (e).  $-\hbar/i$ .

*Answer:* Note that since  $i \cdot i = -1$ . 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  $\sigma_x^2 = \langle (x - \langle x \rangle)^2 \rangle$  is equivalent to  $\sigma_x^2 = \langle x^2 \rangle - \langle x \rangle^2$ . 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	$(x - \langle x \rangle)^2$	$x^2$
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		$\langle x \rangle$	$\langle (x - \langle x \rangle)^2 \rangle$	$\langle x^2 \rangle$
12	average=	2.428571	0.8163265	6.714286
13				
14			$\langle x^2 \rangle - \langle x \rangle^2 =$	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  $\sigma_x = \langle (x - \langle x \rangle)^2 \rangle = \langle x^2 \rangle - \langle x \rangle^2$ .

47. Prove that  $\sigma_x = \langle (x - \bar{x})^2 \rangle^{1/2} = (\langle x^2 \rangle - \langle x \rangle^2)^{1/2}$  (Eq. 23.4.36).

*Answer:* The multiplication gives:

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

The averages are:  $\langle (x - \bar{x})^2 \rangle = \langle x^2 \rangle - 2\langle x \rangle \bar{x} + \bar{x}^2$

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

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

and taking the square root:  $\sigma_x = \langle (x - \bar{x})^2 \rangle^{1/2} = (\langle x^2 \rangle - \langle x \rangle^2)^{1/2}$

48. The moments of a probability distribution characterize the distribution. The first moment is the mean,  $\langle x \rangle = \bar{x}$ . The second central moment is the standard deviation,  $\sigma_x = [\langle (x - \bar{x})^2 \rangle]^{1/2}$ . Central moments are evaluated using the deviations from the mean  $(x - \bar{x})$ . The third central moment is defined as  $[\langle (x - \bar{x})^3 \rangle]^{1/3}$ . 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:

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

(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:

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

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	$(x - \langle x \rangle)^3$	$x^3$	$x^2$
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
$\langle x \rangle$	$\langle (x - \langle x \rangle)^3 \rangle$	$\langle x^3 \rangle$	$\langle x^2 \rangle$
2.428571	0.157434	20.42857	6.714286
	$\langle x^3 \rangle - 3\bar{x}\langle x^2 \rangle + 2\bar{x}^3 =$		0.157434

49. 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  $\Psi_2(x) = (2/a)^{1/2} \sin 2\pi x/a$ . The product of the uncertainty in the position and momentum, using Eq. 23.7.35, is:

$$\begin{aligned} \sigma_x \sigma_p &\geq \frac{1}{2} \left| \int_0^a \Psi_2^* [x, p_x] \Psi_2 dx \right| = (1/a) \left| \int_0^a \sin(2\pi x/a) (-\hbar/i) \sin(2\pi x/a) dx \right| \\ \sigma_x \sigma_p &\geq \frac{1}{2} \left| -\hbar/i \right| (2/a) \int_0^a \sin^2(2\pi x/a) dx \end{aligned}$$

For a complex number,  $|z| = (z^* z)^{1/2}$ , giving  $|\hbar/i| = [(+\hbar/i)(-\hbar/i)]^{1/2} = \hbar$ . 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:

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

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:

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

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:

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

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

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

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

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

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

**52. (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:

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

(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:

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

The wave function  $\Psi_j^*$  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:

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

(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:

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

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

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

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

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

(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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