

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: $\ell = 0, \dots, n - 1$. 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: $m_\ell = -\ell, \dots, 0, \dots, +\ell$.

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 $\ell = 0, \dots, n - 1$. The number of angular nodes that include the z-axis is $|m_\ell|$: with allowed values $m_\ell = -\ell, \dots, 0, \dots, +\ell$. 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 $m_\ell = -\ell, \dots, 0, \dots, +\ell$.

sub-level	ℓ	degeneracy $g_\ell = 2\ell + 1$	number of nodes			
			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 :

$$-\frac{\hbar^2}{2m} \left(\frac{1}{r} \frac{d^2}{dr^2} \right) r R - \frac{Z e^2}{4\pi\epsilon_0 r} R = E R$$

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

$$-\frac{\hbar^2}{2m} \left(\frac{1}{r} \frac{d^2}{dr^2} \right) r A e^{-\alpha r} - \frac{Z e^2}{4\pi\epsilon_0 r} A e^{-\alpha r} = E A e^{-\alpha r} \quad 1$$

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:

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

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

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

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

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

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

$$-\frac{\hbar^2}{2m} \left(\alpha^2 R - \frac{2\alpha}{r} R \right) - \frac{Z e^2}{4\pi\epsilon_0 r} R = E R \quad 6$$

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

$$-\frac{\hbar^2 \alpha^2}{2m} + \frac{\hbar^2 2\alpha}{2mr} - \frac{Z e^2}{4\pi\epsilon_0 r} = E \quad 7$$

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

$$E = -\frac{\hbar^2 \alpha^2}{2m} \quad \text{and} \quad \frac{\hbar^2 \alpha}{mr} - \frac{Z e^2}{4\pi\epsilon_0 r} = 0 \quad 8$$

Solving for α gives:

$$\alpha = \frac{Z e^2 m}{4\pi\epsilon_0 \hbar^2} \quad 9$$

We can simplify this last equation using the definition of the Bohr radius, a_0 :

$$a_0 = \frac{4\pi\epsilon_0 \hbar^2}{m e^2} \quad \text{giving} \quad \alpha = \frac{Z}{a_0} \quad 10$$

4. The ground state of the hydrogen atom is: $\Psi_1(r) = R(r) = \frac{1}{\sqrt{\pi}} \left(\frac{Z}{a_0} \right)^{3/2} e^{-Zr/a_0} = \frac{1}{\sqrt{\pi}} \alpha^{3/2} e^{-\alpha r}$.

- (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:

$$\langle E_k \rangle = \frac{\int_0^\infty \int_0^\pi \int_0^{2\pi} \Psi_1^* \hat{E}_k \Psi_1 r^2 \sin\theta \, dr \, d\theta \, d\phi}{\int_0^\infty \int_0^\pi \int_0^{2\pi} \Psi_1^* \Psi_1 r^2 \sin\theta \, dr \, d\theta \, d\phi} = \int_0^\infty \int_0^\pi \int_0^{2\pi} \Psi_1 \hat{E}_k \Psi_1 r^2 \sin\theta \, dr \, d\theta \, d\phi$$

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

$$\langle E_k \rangle = 4\pi \int_0^\infty R(r) \hat{E}_k R(r) r^2 \, dr$$

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 $\alpha = Z/a_0$. 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: $\int_0^\infty x^n e^{-ax} \, dx = (n!/a^{n+1})$:

$$\begin{aligned} \langle E_k \rangle &= -4\pi \frac{\hbar^2}{2m} \left(\frac{1}{\pi} \right) \alpha^3 \left[\frac{2\alpha^2}{8\alpha^3} - \frac{2\alpha}{4\alpha^2} \right] = -4\pi \frac{\hbar^2}{2m} \left(\frac{1}{\pi} \right) \alpha^3 \left[-\frac{1}{4\alpha} \right] \\ &= \frac{\hbar^2}{2m} \alpha^2 = \frac{\hbar^2}{2m} \left(\frac{Z}{a_0} \right)^2 \end{aligned}$$

The total energy for the ground state of the hydrogen atom is $E_1 = -\frac{Z^2 \hbar^2}{2ma_0^2} = -\langle E_k \rangle$.

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: $\Psi_1(r) = R(r) = \frac{1}{\sqrt{\pi}} \left(\frac{Z}{a_0} \right)^{3/2} e^{-Zr/a_0}$.

(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 $e^2/4\pi\epsilon_0 = \hbar^2/ma_0$ to show that $\langle V \rangle = 2E_1$, 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 $\hat{V}(r) = -Ze^2/(4\pi\epsilon_0 r)$.

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:

$$\langle V \rangle = \frac{\int_0^\infty \int_0^\pi \int_0^{2\pi} \Psi_1^* \hat{V} \Psi_1 r^2 \sin\theta \, dr \, d\theta \, d\phi}{\int_0^\infty \int_0^\pi \int_0^{2\pi} \Psi_1^* \Psi_1 r^2 \sin\theta \, dr \, d\theta \, d\phi} = -\frac{Ze^2}{4\pi\epsilon_0} \int_0^\infty \int_0^\pi \int_0^{2\pi} \frac{1}{r} \Psi_1^2 r^2 \sin\theta \, dr \, d\theta \, d\phi \quad 1$$

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

$$\langle V \rangle = -4\pi \frac{Ze^2}{4\pi\epsilon_0} N^2 \int_0^\infty e^{-2Zr/a_0} r \, dr \quad \text{with normalization, } N = 1/\sqrt{\pi} (Z/a_0)^{3/2} \quad 2$$

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

$$\langle V \rangle = -4\pi \frac{Ze^2}{4\pi\epsilon_0} N^2 \left(\frac{a_0}{2Z}\right)^2 \quad 3$$

Substituting in the normalization constant gives:

$$\langle V \rangle = -\frac{Ze^2}{\epsilon_0} \left(\frac{1}{\pi}\right) \left(\frac{Z}{a_0}\right)^3 \left(\frac{a_0}{2Z}\right)^2 = -\left(\frac{Z^2}{a_0}\right) \frac{e^2}{4\pi\epsilon_0} \quad 4$$

$$(b). \text{ From the definition of } a_0: a_0 = \frac{4\pi\epsilon_0\hbar^2}{me^2} \quad \text{or} \quad \frac{e^2}{4\pi\epsilon_0} = \frac{\hbar^2}{ma_0} \quad 5$$

Substitution of Eq. 5 into Eq. 4 gives:

$$\langle V \rangle = -\frac{Z^2\hbar^2}{ma_0^2} \quad 6$$

The total energy for the ground state of the hydrogen atom is $E_1 = -\frac{Z^2\hbar^2}{2ma_0^2} = \frac{1}{2} \langle V \rangle$.

Since $E = \langle E_k \rangle + \langle V \rangle$, then $\langle E_k \rangle = -\frac{1}{2} \langle V \rangle$ 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.

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

Answer: The normalized 2s orbital is given by:

$$\Psi_{2s} = \frac{1}{4\sqrt{2\pi}} \left(\frac{Z}{a_0}\right)^{3/2} \left(2 - \frac{Zr}{a_0}\right) e^{-Zr/2a_0}$$

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

$$\langle r \rangle = \frac{\int_0^\infty \int_0^\pi \int_0^{2\pi} \Psi_{2s}^* r \Psi_{2s} r^2 \sin\theta \, dr \, d\theta \, d\phi}{\int_0^\infty \int_0^\pi \int_0^{2\pi} \Psi_{2s}^* \Psi_{2s} r^2 \sin\theta \, dr \, d\theta \, d\phi} = \int_0^\infty \int_0^\pi \int_0^{2\pi} r \Psi_{2s}^2 r^2 \sin\theta \, dr \, d\theta \, d\phi$$

\uparrow \uparrow $\underbrace{\hspace{10em}}$
average r *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 :

$$\langle r \rangle = 4\pi \int_0^\infty r^3 \Psi_{2s}^2 \, dr = 4\pi \frac{1}{32\pi} \left(\frac{Z}{a_0}\right)^3 \int_0^\infty r^3 \left(2 - \frac{Zr}{a_0}\right)^2 e^{-Zr/a_0} \, dr$$

$$\langle r \rangle = 4\pi \frac{1}{32\pi} \left(\frac{Z}{a_0}\right)^3 \int_0^\infty r^3 \left(4 - \frac{4Zr}{a_0} + \frac{Z^2 r^2}{a_0^2}\right) e^{-Zr/a_0} \, dr$$

Splitting the integral gives:

$$\langle r \rangle = 4\pi \frac{1}{32\pi} \left(\frac{Z}{a_0}\right)^3 \left[4 \int_0^\infty r^3 e^{-Zr/a_0} \, dr - \frac{4Z}{a_0} \int_0^\infty r^4 e^{-Zr/a_0} \, dr + \frac{Z^2}{a_0^2} \int_0^\infty r^5 e^{-Zr/a_0} \, dr \right]$$

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

$$\langle r \rangle = \frac{1}{8} \left(\frac{Z}{a_0}\right)^3 \left[\left(\frac{24 a_0^4}{Z^4}\right) - \left(\frac{96 a_0^4}{Z^4}\right) + \left(\frac{120 a_0^4}{Z^4}\right) \right] = \frac{48}{8} \frac{a_0}{Z} = 6 \frac{a_0}{Z}$$

The average radius for a $2p_z$ orbital is $5a_0/Z$, 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:

$$\Psi_{2p_z} = \frac{1}{4\sqrt{2\pi}} \left(\frac{Z}{a_0}\right)^{3/2} \frac{Zr}{a_0} e^{-Zr/2a_0} \cos\theta$$

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

$$\langle r \rangle = \frac{\int_0^\infty \int_0^\pi \int_0^{2\pi} \Psi_{2p_z}^* r \Psi_{2p_z} r^2 \sin\theta \, dr \, d\theta \, d\phi}{\int_0^\infty \int_0^\pi \int_0^{2\pi} \Psi_{2p_z}^* \Psi_{2p_z} r^2 \sin\theta \, dr \, d\theta \, d\phi} = \int_0^\infty \int_0^\pi \int_0^{2\pi} r \Psi_{2p_z}^2 r^2 \sin\theta \, dr \, d\theta \, d\phi$$

\uparrow \uparrow $\underbrace{\hspace{10em}}$
average r *volume element*

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

$$\langle r \rangle = \frac{1}{32\pi} \left(\frac{Z}{a_0}\right)^3 \int_0^\infty \left(\frac{Z}{a_0}\right)^2 r^5 e^{-Zr/a_0} dr \int_0^\pi \cos^2\theta \sin\theta d\theta \int_0^{2\pi} d\phi$$

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

The expectation value of r reduces to:

$$\langle r \rangle = \frac{1}{32\pi} \left(\frac{Z}{a_0}\right)^3 \left(\frac{2}{3}\right) (2\pi) \int_0^\infty \left(\frac{Z}{a_0}\right)^2 r^5 e^{-Zr/a_0} dr$$

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

$$\langle r \rangle = \frac{1}{24} \left(\frac{Z}{a_0}\right)^5 \left(\frac{120 a_0^6}{Z^6}\right) = 5 \frac{a_0}{Z}$$

The average radius for a 2s orbital is $6a_0/Z$, 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:

$$\int_0^{r_c} r^2 e^{-2Zr/a_0} dr = \left(-\frac{a_0 r_c^2}{2Z} - \frac{a_0^2 r_c}{2Z^2} - \frac{a_0^3}{4Z^3}\right) e^{-2Zr_c/a_0} + \frac{a_0^3}{4Z^3}$$

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

$$0.90 = \left(-2 \frac{Z^2 r_c^2}{a_0^2} - 2 \frac{Z r_c}{a_0} - 1\right) e^{-2Zr_c/a_0} + 1$$

(d). Let $\rho = Zr/a_0$. 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:

$$\Psi_{1s} = \frac{1}{\sqrt{\pi}} \left(\frac{Z}{a_0}\right)^{3/2} e^{-Zr/a_0} \quad 1$$

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

$$0.90 = \int_0^{r_c} \int_0^\pi \int_0^{2\pi} \underbrace{\Psi_{1s}^2 r^2 \sin\theta}_{\text{volume element}} dr d\theta d\phi \quad 2$$

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

$$0.90 = 4\pi \int_0^{r_c} \Psi_{1s}^2 r^2 dr = 4 \left(\frac{Z}{a_0} \right)^3 \int_0^{r_c} r^2 e^{-2Zr/a_0} dr \quad 3$$

(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 $e^{-ax}|_0^{x_0} = e^{-ax_0} - 1$, the definite integral from 0 to x_0 is:

$$\int_0^{x_0} x^2 e^{-ax} dx = -\frac{x_0^2 e^{-ax_0}}{a} - \frac{2x_0 e^{-ax_0}}{a^2} - \frac{2 e^{-ax_0}}{a^3} + \frac{2}{a^3}$$

With $x = r$, $a = Zr/a_0$, and the integral limit $x_0 = r_c$, the needed integral over r^2 is:

$$\int_0^{r_c} r^2 e^{-2Zr/a_0} dr = \left(-\frac{a_0 r_c^2}{2Z} - \frac{a_0^2 r_c}{2Z^2} - \frac{a_0^3}{4Z^3} \right) e^{-2Zr_c/a_0} + \frac{a_0^3}{4Z^3}$$

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

$$\begin{aligned} 0.90 &= 4 \left(\frac{Z}{a_0} \right)^3 \left(-\frac{a_0 r_c^2}{2Z} - \frac{a_0^2 r_c}{2Z^2} - \frac{a_0^3}{4Z^3} \right) e^{-2Zr_c/a_0} + 4 \left(\frac{Z}{a_0} \right)^3 \frac{a_0^3}{4Z^3} \\ 0.90 &= \left(-2 \frac{Z^2 r_c^2}{a_0^2} - 2 \frac{Z r_c}{a_0} - 1 \right) e^{-2Zr_c/a_0} + 1 \end{aligned}$$

(d). Letting $\rho = Zr_c/a_0$, 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 $\rho = 2$ and $\rho = 3$, the next value to try is $\rho = 2.5$. The second column calculates $(-2\rho^2 - 2\rho - 1) e^{-2\rho} + 1$ for the guessed value of ρ in the first column:

$\rho = Zr/a_0$	$4\pi \int \Psi^2 r^2 dr$
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 $\rho \cong 2.66$ or $r_c = 2.66 a_0/Z$. In comparison, the average radius for a 1s orbital is $\langle r \rangle = 1.5 a_0/Z$.

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:

$$\Psi_{1s}(r) = \frac{1}{\sqrt{\pi}} \left(\frac{Z}{a_0}\right)^{3/2} e^{-Zr/a_0} \quad \text{and} \quad \Psi_{2s}(r) = \frac{1}{4\sqrt{2\pi}} \left(\frac{Z}{a_0}\right)^{3/2} \left(2 - \frac{Zr}{a_0}\right) e^{-Zr/2a_0}$$

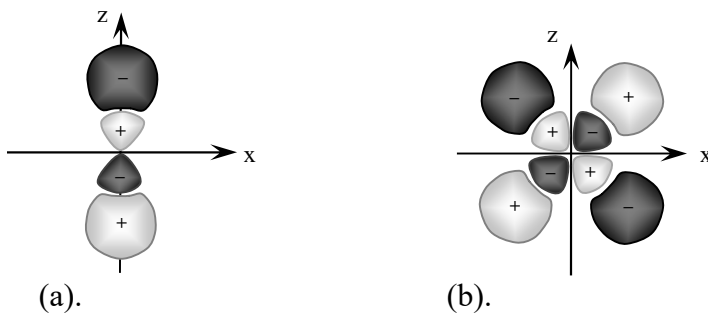
For simplicity, let the normalization constants be N_{1s} and N_{2s} , respectively. The wave functions are spherical, so they are independent of θ and ϕ . The angular integrations then give 4π . The orthogonality integral is then:

$$\begin{aligned} \int_0^\infty \int_0^\pi \int_0^{2\pi} \Psi_{1s}^* \Psi_{2s} \underbrace{r^2 \sin\theta dr d\theta d\phi}_{\text{volume element}} &= 4\pi N_{1s} N_{2s} \int_0^\infty e^{-Zr/a_0} \left(2 - \frac{Zr}{a_0}\right) e^{-Zr/2a_0} r^2 dr \\ &= 4\pi N_{1s} N_{2s} \left[2 \int_0^\infty r^2 e^{-3Zr/2a_0} dr - \frac{Z}{a_0} \int_0^\infty r^3 e^{-3Zr/2a_0} dr \right] \end{aligned}$$

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

$$\begin{aligned} \int \Psi_{1s}^* \Psi_{2s} d\tau &= 4\pi N_{1s} N_{2s} \left[4 \left(\frac{2a_0}{3Z}\right)^3 - \left(\frac{Z}{a_0}\right) 6 \left(\frac{2a_0}{3Z}\right)^4 \right] \\ &= 4\pi N_{1s} N_{2s} \left(\frac{a_0}{Z}\right)^3 \left[4 \left(\frac{8}{27}\right) - 6 \left(\frac{16}{81}\right) \right] = 0 \end{aligned}$$

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



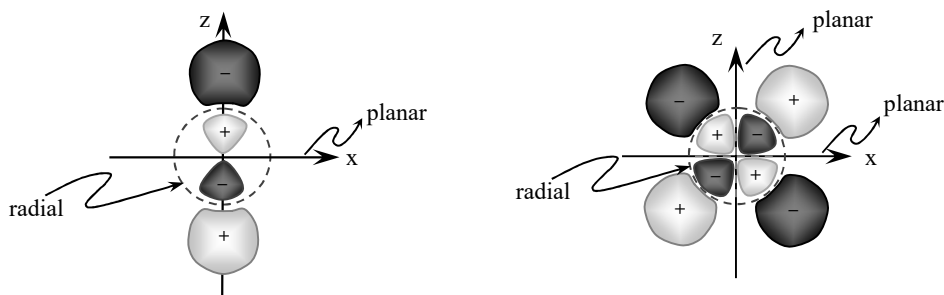
Answer: The plan is to find the number of radial nodes, angular nodes, and angular nodes that include the z -axis. Angular nodes are planes that pass through the nucleus. A radial node is a spherical node that is centered on the nucleus.

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.

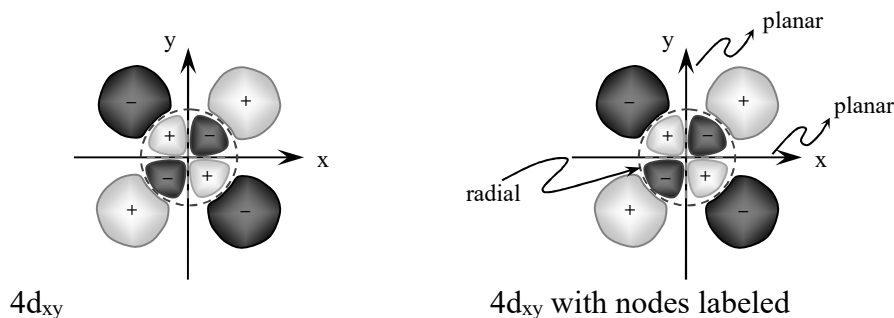
11. Sketch the $4d_{xy}$ orbital. Include the phase for each region.

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, $|m_\ell| = 2$.



12. The normalized angular portions of the oriented d-orbitals are:

$$d_{xz} = \left(\frac{5}{4\pi}\right)^{1/2} \sqrt{3} \sin \theta \cos \theta \cos \phi$$

$$d_{yz} = \left(\frac{5}{4\pi}\right)^{1/2} \sqrt{3} \sin \theta \cos \theta \sin \phi$$

$$d_{xy} = \left(\frac{5}{4\pi}\right)^{1/2} \sqrt{3} \sin^2 \theta \cos \phi \sin \phi$$

$$d_{x^2-y^2} = \left(\frac{5}{4\pi}\right)^{1/2} \frac{\sqrt{3}}{2} \sin^2 \theta (\cos^2 \phi - \sin^2 \phi)$$

$$d_{3z^2-r^2} = \left(\frac{5}{4\pi}\right)^{1/2} \frac{1}{2} (3\cos^2 \theta - 1)$$

Show that $d_{xz}^2 + d_{yz}^2 + d_{xy}^2 + d_{x^2-y^2}^2 + d_{3z^2-r^2}^2 = \text{constant}$ (Eq. 25.2.10). The following trigonometric identities are useful:

$$\begin{aligned} \cos^2 x + \sin^2 x &= 1 & \text{and correspondingly } (\cos^2 x + \sin^2 x)^2 &= 1 \\ \cos^2 x - \sin^2 x &= 2 \cos^2 x - 1 \end{aligned}$$

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:

$$(\cos^2 x + \sin^2 x)^2 = \cos^4 x + 2 \cos^2 x \sin^2 x + \sin^4 x = 1 \quad 1$$

Let $N = (5/4\pi)^{1/2}$ for convenience. First note that:

$$d_{xz}^2 + d_{yz}^2 = 3N^2 \sin^2 \theta \cos^2 \theta (\cos^2 \phi + \sin^2 \phi) = 3N^2 \sin^2 \theta \cos^2 \theta \quad 2$$

which is independent of ϕ . Next, note that:

$$\begin{aligned} d_{xy}^2 + d_{x^2-y^2}^2 &= \frac{3}{4} N^2 \sin^4 \theta [4 \cos^2 \phi \sin^2 \phi + (\cos^2 \phi - \sin^2 \phi)^2] \\ &= \frac{3}{4} N^2 \sin^4 \theta [4 \cos^2 \phi \sin^2 \phi + \cos^4 \phi - 2\cos^2 \phi \sin^2 \phi + \sin^4 \phi] \\ &= \frac{3}{4} N^2 \sin^4 \theta [\cos^4 \phi + 2\cos^2 \phi \sin^2 \phi + \sin^4 \phi] \end{aligned} \quad 3$$

$$\text{Using identity Eq. 1 gives: } d_{xy}^2 + d_{x^2-y^2}^2 = \frac{3}{4} N^2 \sin^4 \theta \quad 4$$

We can split $3 \cos^2 \theta - 1$ into two terms:

$$(3\cos^2 \theta - 1) = \cos^2 \theta + 2 \cos^2 \theta - 1 \quad 5$$

Then using the identity, $\cos^2 x - \sin^2 x = 2 \cos^2 x - 1$, gives:

$$(3\cos^2 \theta - 1) = \cos^2 \theta + \cos^2 \theta - \sin^2 \theta = 2 \cos^2 \theta - \sin^2 \theta \quad 6$$

$$\begin{aligned} d_{3z^2-r^2}^2 &= \frac{1}{4} N^2 (2 \cos^2 \theta - \sin^2 \theta)^2 = \frac{1}{4} N^2 (4 \cos^4 \theta - 4 \cos^2 \theta \sin^2 \theta + \sin^4 \theta) \\ &= N^2 (\cos^4 \theta - \cos^2 \theta \sin^2 \theta + \frac{1}{4} \sin^4 \theta) \end{aligned} \quad 7$$

Combining Eqs. 2, 4, and 6 gives:

$$\begin{aligned}
 & d_{xz}^2 + d_{yz}^2 + d_{xy}^2 + d_{x^2-y^2}^2 + d_{3z^2-r^2}^2 = \\
 & = 3N^2 \sin^2 \theta \cos^2 \theta + \frac{3}{4} N^2 \sin^4 \theta + N^2 (\cos^4 \theta - \cos^2 \theta \sin^2 \theta + \frac{1}{4} \sin^4 \theta) \\
 & = N^2 (\cos^4 \theta + 2 \cos^2 \theta \sin^2 \theta + \sin^4 \theta)
 \end{aligned} \tag{8}$$

Using the identity Eq. 1 gives the result independent of both θ and ϕ :

$$d_{xz}^2 + d_{yz}^2 + d_{xy}^2 + d_{x^2-y^2}^2 + d_{3z^2-r^2}^2 = N^2 \tag{9}$$

This result is the d-orbital version of Unsöld's Theorem, and explains why the $d_{3z^2-r^2}$ has the unique functional form. The problem can also be done using the identities $\sin 2x = 2 \cos x \sin x$ and $\cos 2x = \cos^2 x - \sin^2 x$.

13. 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:

$$\int_0^\pi \int_0^{2\pi} d_{yz}^2 \sin \theta \, d\theta \, d\phi = N^2 \int_0^\pi \int_0^{2\pi} \sin^3 \theta \cos^2 \theta \sin^2 \phi \, d\theta \, d\phi = 1$$

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 $\int \sin^3 x \, dx = -\frac{1}{3} \cos x (\sin^2 x + 2)$:

$$\int_0^\pi \sin^3 x \, dx = -\frac{1}{3} [\cos x (\sin^2 x + 2)]_0^\pi = -\frac{1}{3} [(-1)(0 + 2) - (1)(0 + 2)] = 4/3$$

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_0} , in this case $n = 3$, giving:

$$\Psi_{3d_{xz}} = N e^{-Zr/3a_0} (Z/a_0)^2 xz$$

The spherical polar form is given from the transformations in Eqs. 24.5.14:

$$\begin{aligned} \Psi_{3d_{xz}} &= N e^{-Zr/3a_0} (Z/a_0)^2 (r \sin \theta \cos \phi) (r \cos \theta) \\ &= N e^{-Zr/3a_0} (Zr/a_0)^2 \sin \theta \cos \theta \cos \phi \end{aligned}$$

The factor of $(Z/a_0)^3$ appears because the wave function is overall unitless, so r always appears as Zr/a_0 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_0 . 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_0} , in this case $n = 4$, giving:

$$\Psi_{4f_{xyz}} = N e^{-Zr/4a_0} (Z/a_0)^3 xyz$$

The spherical polar form is given from the transformations in Eqs. 24.5.14:

$$\begin{aligned} \Psi_{4f_{xyz}} &= N e^{-Zr/4a_0} (Z/a_0)^3 (r \sin \theta \cos \phi)(r \sin \theta \sin \phi)(r \cos \theta) \\ &= N e^{-Zr/4a_0} (Zr/a_0)^3 \sin^2 \theta \cos \theta \cos \phi \sin \phi \end{aligned}$$

The factor of $(Z/a_0)^3$ appears because the wave function is overall unitless, so r always appears as Zr/a_0 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_0 . 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:

$$V(x) = \frac{1}{2} k x^2 + b x^4$$

[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 $\alpha^2 = \left(\frac{m\omega_0}{\hbar}\right)$. 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 $\frac{3b}{4} \left(\frac{\hbar}{m\omega_0}\right)^2$]

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:

$$E^{(1)} = 2b \left(\frac{\alpha^2}{\pi}\right)^{1/2} \left(\frac{3}{8\alpha^4}\right) \left(\frac{\pi}{\alpha^2}\right)^{1/2} = \frac{6b}{8\alpha^4} = \frac{3b}{4} \left(\frac{\hbar}{m\omega_0}\right)^2$$

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. $3s: \uparrow\downarrow$). For which species is the Aufbau prediction expected to differ from the experimental configuration?

Answers:

(a). Si: [Ne] $3s^2 3p^2$ $3s: \uparrow\downarrow$ $3p: \uparrow\uparrow\ \square$

(b). Ti: [Ar] $3d^2 4s^2$ $3d: \uparrow\uparrow\ \square\square\square$ $4s: \uparrow\downarrow$

(c). Ti^{2+} : [Ar] $3d^2 4s^0$ $3d: \uparrow\uparrow\ \square\square\square$ $4s: \square$

(d). Cr: [Ar] $3d^4 4s^1$ $3d: \uparrow\uparrow\uparrow\uparrow\ \square$ $4s: \uparrow\downarrow$ (Aufbau)

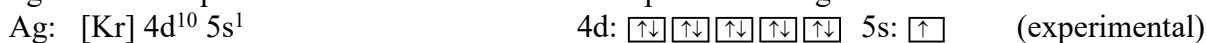
However, Cr needs only one-electron more to complete a half-filled d sub-orbital, so the experimental configuration is expected to deviate from the Aufbau prediction to give:

Cr: [Ar] $3d^5 4s^1$ $3d: \uparrow\uparrow\uparrow\uparrow\uparrow$ $4s: \uparrow$ (experimental)

(e). Cr^{2+} : [Ar] $3d^4 4s^0$ $3d: \uparrow\uparrow\uparrow\uparrow\ \square$ $4s: \square$

(f). Ag: [Kr] $4d^9 5s^2$ $4d: \uparrow\downarrow\uparrow\downarrow\uparrow\downarrow\uparrow\downarrow\uparrow$ $5s: \uparrow\downarrow$ (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:



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:

$$\Psi_A = \frac{1}{\sqrt{2}} [\Psi_1(1) \Psi_2(2) - \Psi_2(1) \Psi_1(2)] \quad \text{and} \quad \Psi_S = \frac{1}{\sqrt{2}} [\Psi_1(1) \Psi_2(2) + \Psi_2(1) \Psi_1(2)]$$

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:

$$\Psi_1(x) = \left(\frac{2}{a}\right)^{1/2} \sin(\pi x/a) \quad \Psi_2(x) = \left(\frac{2}{a}\right)^{1/2} \sin(2\pi x/a)$$

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:

$$\begin{aligned} \Psi_A &= \frac{1}{\sqrt{2}} [\Psi_1(1) \Psi_2(2) - \Psi_2(1) \Psi_1(2)] \\ &= \left(\frac{\sqrt{2}}{a}\right) [(0.707107)(0.999507) - (0.718126)(1.00000)] = -0.01608/a \\ \Psi_S &= \left(\frac{\sqrt{2}}{a}\right) [(0.707107)(0.999507) + (0.718126)(1.00000)] = 2.015091/a \end{aligned}$$

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:

$$\Psi_s = 1/\sqrt{2} \Psi_{1s}(1) \Psi_{1s}(2) [\alpha(1) \beta(2) + \beta(1) \alpha(2)] \quad (25.4.14)$$

$$\Psi_a = 1/\sqrt{2} \Psi_{1s}(1) \Psi_{1s}(2) [\alpha(1) \beta(2) - \beta(1) \alpha(2)] \quad (25.4.15)$$

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:

$$[\alpha(1) \beta(2) + \beta(1) \alpha(2)]^2 = \alpha^2(1) \beta^2(2) + 2 \alpha(1) \beta(1) \alpha(2) \beta(2) + \beta^2(1) \alpha^2(2) \quad 1$$

Exchange of spin labels transforms the probability to:

$$[\alpha(2) \beta(1) + \beta(2) \alpha(1)]^2 = \alpha^2(2) \beta^2(1) + 2 \alpha(2) \beta(2) \alpha(1) \beta(1) + \beta^2(2) \alpha^2(1) \quad 2$$

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:

$$[\alpha(1) \beta(2) - \beta(1) \alpha(2)]^2 = \alpha^2(1) \beta^2(2) - 2 \alpha(1) \beta(1) \alpha(2) \beta(2) + \beta^2(1) \alpha^2(2) \quad 3$$

Exchange of spin labels transforms the probability to:

$$[\alpha(2) \beta(1) - \beta(2) \alpha(1)]^2 = \alpha^2(2) \beta^2(1) - 2 \alpha(2) \beta(2) \alpha(1) \beta(1) + \beta^2(2) \alpha^2(1) \quad 4$$

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 $1/2$ 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:

$${}^1\Psi^* = 1/\sqrt{2} (\Psi_{1s}(1) \Psi_{2px}(2) + \Psi_{1s}(2) \Psi_{2px}(1)) [\alpha(1)\beta(2) - \beta(1)\alpha(2)]$$

21. Give the determinantal wavefunction for the ground state of the beryllium atom (configuration $1s^2 2s^2$).

Answer:

$$\text{Be: } 1s \begin{array}{|c|} \hline \uparrow\downarrow \\ \hline \end{array} 2s \begin{array}{|c|} \hline \uparrow\downarrow \\ \hline \end{array} \quad \Psi_a = 1/\sqrt{4!} \begin{vmatrix} 1s(1)\alpha(1) & 1s(1)\beta(1) & 2s(1)\alpha(1) & 2s(1)\beta(1) \\ 1s(2)\alpha(2) & 1s(2)\beta(2) & 2s(2)\alpha(2) & 2s(2)\beta(2) \\ 1s(3)\alpha(3) & 1s(3)\beta(3) & 2s(3)\alpha(3) & 2s(3)\beta(3) \\ 1s(4)\alpha(4) & 1s(4)\beta(4) & 2s(4)\alpha(4) & 2s(4)\beta(4) \end{vmatrix}$$

22. Determine the spin multiplicity of the vanadium ground state.

Answer: The vanadium ground state configuration is: V $\begin{array}{|c|} \hline \uparrow\downarrow \\ \hline \end{array}$ $\begin{array}{|c|c|c|c|c|} \hline \uparrow & \uparrow & \uparrow & \square & \square \\ \hline \end{array}$
4s 3d

Giving three unpaired electrons:

$$S = (\sum m_s)_{\max} = 3/2 \quad \text{and} \quad g_s = (2S + 1) = 2(3/2) + 1 = 4$$

23. Determine the spin multiplicity of the manganese ground state.

Answer: The manganese ground state configuration is: Mn $\begin{array}{|c|} \hline \uparrow\downarrow \\ \hline \end{array}$ $\begin{array}{|c|c|c|c|c|} \hline \uparrow & \uparrow & \uparrow & \uparrow & \uparrow \\ \hline \end{array}$
4s 3d

Giving five unpaired electrons:

$$S = (\sum m_s)_{\max} = 5/2 \quad \text{and} \quad g_s = (2S + 1) = 2(5/2) + 1 = 6$$

24. Determine the expectation value for the total spin angular momentum squared, that is $\langle S^2 \rangle$ 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 $\langle S^2 \rangle$ for a quartet state. For example: $\begin{array}{|c|} \hline \uparrow\downarrow \\ \hline \end{array}$ $\begin{array}{|c|c|c|c|c|} \hline \uparrow & \uparrow & \uparrow & \square & \square \\ \hline \end{array}$

4s

3d

Answer: For a quartet, $S = 3/2$. The total spin angular momentum squared is then:

$$S(S+1) \hbar^2 = 3/2(3/2+1) \hbar^2 = 3.75 \hbar^2$$

26. (a). Show that the spin-orbit coupling operator, $\vec{\ell} \cdot \vec{s}$, for a single unpaired electron is:

$$\vec{\ell} \cdot \vec{s} = \frac{1}{2} (\hat{j}^2 - \hat{\ell}^2 - \hat{s}^2)$$

(b). Show that $\vec{\ell} \cdot \vec{s}$ has the eigenvalue:

$$|\vec{\ell} \cdot \vec{s}| = \frac{1}{2} \hbar^2 [j(j+1) - \ell(\ell+1) - s(s+1)]$$

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 $\vec{j} = \vec{\ell} + \vec{s}$ and following Eq. 25.6.29:

$$\hat{j}^2 = \vec{j} \cdot \vec{j} = (\vec{\ell} + \vec{s}) \cdot (\vec{\ell} + \vec{s}) = \vec{\ell} \cdot \vec{\ell} + \vec{s} \cdot \vec{s} + 2 \vec{\ell} \cdot \vec{s} = \hat{\ell}^2 + \hat{s}^2 + 2 \vec{\ell} \cdot \vec{s}$$

Solving this last equation for $\vec{\ell} \cdot \vec{s}$:

$$\vec{\ell} \cdot \vec{s} = \frac{1}{2} (\hat{j}^2 - \hat{\ell}^2 - \hat{s}^2) \quad 1$$

(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:

$$\hat{j}^2 \Psi_{j,m_j} = \hbar^2 j(j+1) \Psi_{j,m_j} \quad 2$$

$$\hat{\ell}^2 \Psi_{\ell,m_\ell} = \hbar^2 \ell(\ell+1) \Psi_{\ell,m_\ell} \quad 3$$

$$\hat{s}^2 \Psi_{s,m_s} = \hbar^2 s(s+1) \Psi_{s,m_s} \quad 4$$

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:

$$\Psi_{j,m_j} = \Psi_{\ell,m_\ell} \Psi_{s,m_s} \quad 5$$

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:

$$\hat{\ell}^2 \Psi_{\ell,m_\ell} \Psi_{s,m_s} = \Psi_{s,m_s} \hat{\ell}^2 \Psi_{\ell,m_\ell} \quad \text{and} \quad \hat{s}^2 \Psi_{\ell,m_\ell} \Psi_{s,m_s} = \Psi_{\ell,m_\ell} \hat{s}^2 \Psi_{s,m_s} \quad 6$$

Substituting Eqs. 2-6 into Eq. 1 gives:

$$(\vec{\ell} \cdot \vec{s}) \Psi_{j,m_j} = \frac{1}{2} (\hat{j}^2 \Psi_{j,m_j} - \hat{\ell}^2 \Psi_{\ell,m_\ell} \Psi_{s,m_s} - \hat{s}^2 \Psi_{\ell,m_\ell} \Psi_{s,m_s}) \quad 7$$

$$(\vec{\ell} \cdot \vec{s}) \Psi_{j,m_j} = \frac{1}{2} \hbar^2 [j(j+1) \Psi_{j,m_j} - \Psi_{s,m_s} \ell(\ell+1) \Psi_{\ell,m_\ell} - \Psi_{\ell,m_\ell} s(s+1) \Psi_{s,m_s}] \quad 8$$

$$(\vec{\ell} \cdot \vec{s}) \Psi_{j,m_j} = \frac{1}{2} \hbar^2 [j(j+1) \Psi_{j,m_j} - \ell(\ell+1) \Psi_{j,m_j} - s(s+1) \Psi_{j,m_j}] \quad 9$$

$$(\vec{\ell} \cdot \vec{s}) \Psi_{j,m_j} = \frac{1}{2} \hbar^2 [j(j+1) - \ell(\ell+1) - s(s+1)] \Psi_{j,m_j} \quad 10$$

with the eigenvalue:

$$|\vec{\ell} \cdot \vec{s}| = \frac{1}{2} \hbar^2 [j(j+1) - \ell(\ell+1) - s(s+1)] \quad 11$$

27. 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 $L = 1$, $S = 1/2$, 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:

$$E_{so} (J = 5/2) = \frac{1}{2} \mathcal{A}hc [5/2(5/2 + 1) - 2(2+1) - 1/2(1/2+1)] = \frac{1}{2} \mathcal{A}hc [35/4 - 24/4 - 3/4] = \mathcal{A}hc$$

$$E_{so} (J = 3/2) = \frac{1}{2} \mathcal{A}hc [3/2(3/2 + 1) - 2(2+1) - 1/2(1/2+1)] = \frac{1}{2} \mathcal{A}hc [15/4 - 24/4 - 3/4] = -3/2 \mathcal{A}hc$$

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.

28. 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:

$$\boxed{\uparrow\downarrow}\boxed{}\boxed{}\boxed{} \quad \text{and} \quad \boxed{\uparrow}\boxed{\downarrow}\boxed{}\boxed{}\boxed{}$$

(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-Gordan series applied to the total orbital angular momentum gives the same results.

Answer: (a). All the possible singlet arrangements are, in no particular order:

2	1	0	-1	-2	M_L	2	1	0	-1	-2	M_L	2	1	0	-1	-2	M_L	2	1	0	-1	-2	M_L
↑↓	□	□	□	□	4	□	↑↓	□	□	□	2	□	□	↑↓	□	□	0	□	□	□	□	↑↓	-4
↑	↓	□	□	□	3	□	↑	↓	□	□	1	□	□	↑	↓	□	-1						
↑	□	↓	□	□	2	□	↑	□	↓	□	0	□	□	↑	□	↓	-2						
↑	□	□	↓	□	1	□	↑	□	□	↓	-1	□	□	□	↑↓	□	-2						
↑	□	□	□	↓	0							□	□	□	↑	↓	-3						

(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 1G , 1D , 1S .

(f). All the possible triplet arrangements are, in no particular order:

2	1	0	-1	-2	M_L	2	1	0	-1	-2	M_L	2	1	0	-1	-2	M_L
↑	↑	□	□	□	3	□	↑	↑	□	□	1	□	□	↑	↑	□	-1
↑	□	↑	□	□	2	□	↑	□	↑	□	0	□	□	↑	□	↑	-2
↑	□	□	↑	□	1	□	↑	□	□	↑	-1	□	□	□	↑	↑	-3
↑	□	□	□	↑	0												

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 3F , 3P .

(g). Using the Clebsch-Gordan series for the total orbital angular momentum for a d^2 configuration corresponds to $l_1 = 2$ and $l_2 = 2$ so that:

$$L = l_1 + l_2, l_1 + l_2 - 1, \dots, |l_1 - l_2| = 4, 3, 2, 1, 0$$

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:

$J = L + S, L + S - 1, \dots, |L - S|$. 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:

$$\begin{array}{ll} ^3F: L = 3, S = 1: & J = 3 + 1, \dots, |3 - 1| = 4, 3, 2 \quad \text{giving } ^3F_4, ^3F_3, ^3F_2 \\ ^3P: L = 1, S = 1: & J = 1 + 1, \dots, |1 - 1| = 2, 1, 0 \quad \text{giving } ^3P_2, ^3P_1, ^3P_0 \end{array}$$

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.

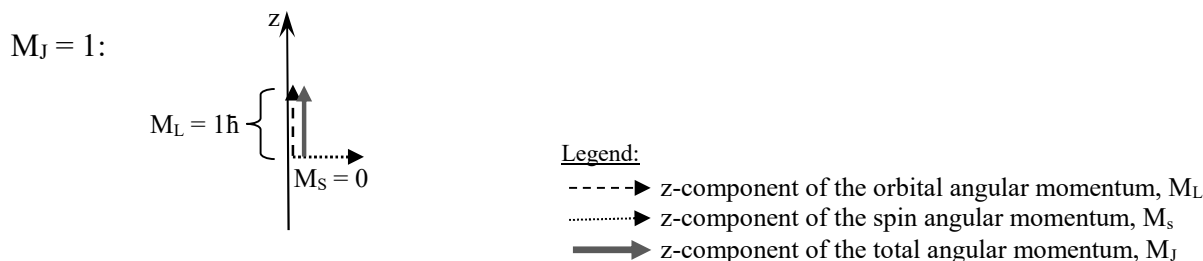
Answer: The plan is to note that a 3P term corresponds to $L = 1$ and $S = 1$.

The Clebsch-Gordon series for $L = 1$ and $S = 1$ gives:

$$J = L + S, L + S - 1, \dots, |L - S| = \{2, 1, 0\}.$$

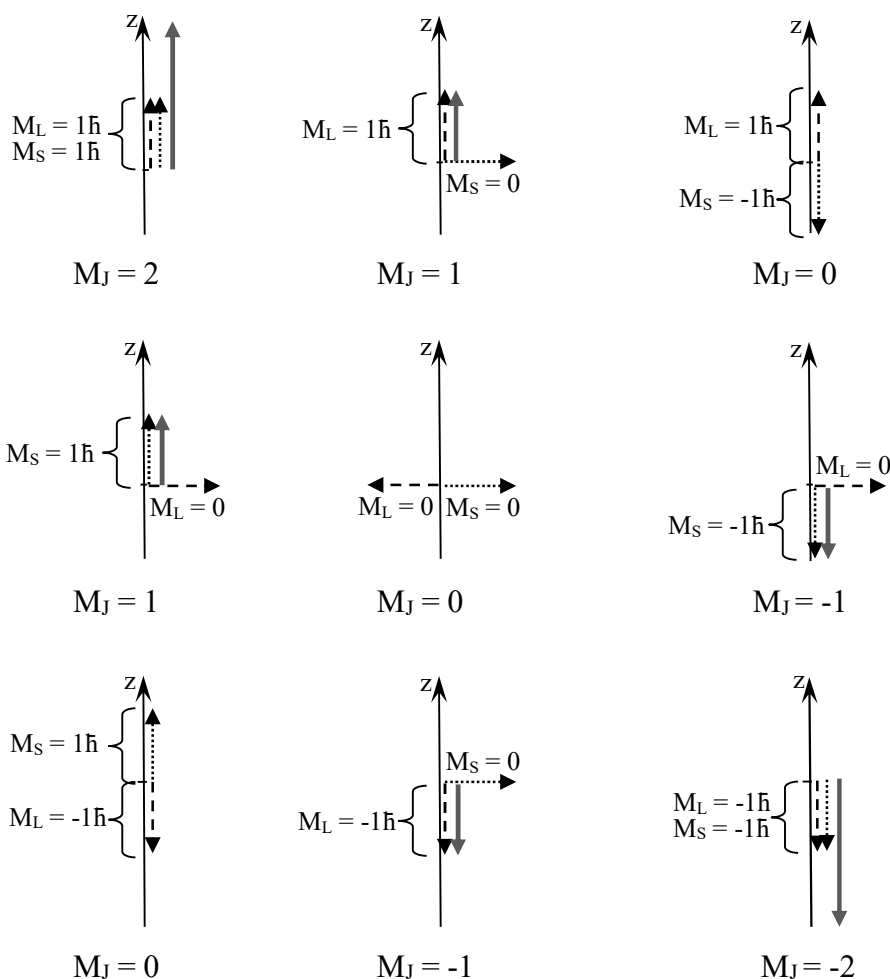
The final terms are $^3P_2, ^3P_1$, and 3P_0 .

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:



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.



(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-Gordan series.

32. (a). Use the Clebsch-Gordan 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:

$$J = L + S, L + S - 1, \dots, |L - S| = \{3, 2, 1\}.$$

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	M_L	M_S	M_J	M_L	M_S	M_J
2	1	3	0	1	1	-2	1	-1
2	0	2	0	0	0	-2	0	-2
2	-1	1	0	-1	-1	-2	-1	-3
1	1	2	-1	1	0			
1	0	1	-1	0	-1			
1	-1	0	-1	-1	-2			

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:

$M_L = \sum m_l$		$M_L = \sum m_l$		$M_L = \sum m_l$
+1 0 -1	$\boxed{\uparrow\downarrow}\boxed{\uparrow\downarrow}\boxed{}$	2	+1 0 -1	
	$\boxed{\uparrow\downarrow}\boxed{\uparrow}\boxed{\downarrow}$	1	$\boxed{\uparrow\downarrow}\boxed{\uparrow}\boxed{\uparrow}$	1
	$\boxed{\uparrow}\boxed{\uparrow\downarrow}\boxed{\downarrow}$	0	$\boxed{\uparrow}\boxed{\uparrow\downarrow}\boxed{\uparrow}$	0
	$\boxed{\uparrow}\boxed{\downarrow}\boxed{\uparrow\downarrow}$	-1	$\boxed{\uparrow}\boxed{\uparrow}\boxed{\uparrow\downarrow}$	-1
	$\boxed{}\boxed{\uparrow\downarrow}\boxed{\uparrow\downarrow}$	-2		
1D			3P	
				+1 0 -1
				$\boxed{\uparrow\downarrow}\boxed{}\boxed{\uparrow\downarrow}$
				0
				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 $l_1 = 1$ and $l_2 = 1$:

Clebsch-Gordan Series: $L = l_1 + l_2, l_1 + l_2 - 1, \dots, |l_1 - l_2|$ $L = |M_L| \text{ max}$

$2p^4$: $1 + 1, \dots, |1 - 1| = 2, 1, 0$

$2p^4$: 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-Gordan 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 $J = L + S, L + S - 1, \dots, |L - S| = 1 + 1, \dots, |1 - 1| = 2, 1, 0$
or ${}^3P_2, {}^3P_1, {}^3P_0$.

For 1S , $S = 0$ and $L = 0$ so 1S_0 .

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 3P term are given by the Clebsch-Gordon series with $S = 1$ and $L = 1$: $J = L + S, \dots |L - S| = 2, 1, 0$. 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_0 . 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 $^2P, ^2D, ^2D, ^2F, ^2G, ^2H, ^4P, ^4F$ 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 4F term are given by the Clebsch-Gordon series with $S = 3/2$ and $L = 3$: $J = L + S, \dots |L - S| = 9/2, 7/2, 5/2, 3/2$. 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 $\theta = 90^\circ, \phi = 0^\circ$, and the conversion from spherical polar coordinates to Cartesian coordinates is $x = r \sin\theta \cos\phi = r$

The wave function is given by the equations on the handout:

$$\Psi_{2p_x} = 0.55646 \Psi_{2p_x(\text{inner})} + 0.58708 \Psi_{2p_x(\text{outer})}$$

$$\begin{aligned} \text{with: } \Psi_{2p_x(\text{inner})} &= 0.2365 g_x(3.665, r) + 0.8606 g_x(0.771, r) \\ &= 0.2365 g_x(3.665, r) + 0.8606 g_x(0.771, r) \\ &= 0.2365 \left(\frac{128(3.665)^5}{\pi^3} \right)^{1/4} x e^{-3.665r^2} + 0.8606 \left(\frac{128(0.771)^5}{\pi^3} \right)^{1/4} x e^{-0.771r^2} \end{aligned}$$

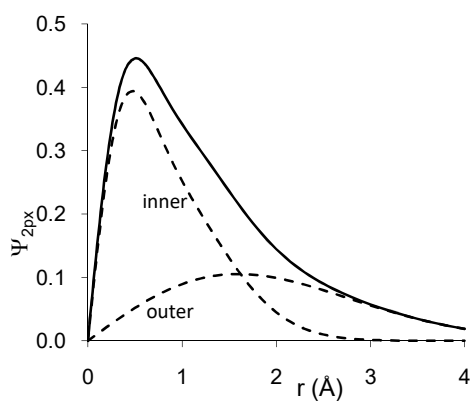
$$\begin{aligned} \text{and: } \Psi_{2p_x(\text{outer})} &= 1.000 g_x(0.196, r) \\ &= 1.000 \left(\frac{2(0.196)}{\pi} \right)^{1/4} x e^{-0.196r^2} \end{aligned}$$

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	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.

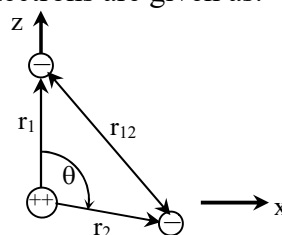


38. In the integral for the expectation value of the electron-electron repulsion in the helium atom, we used the Law of Cosines, $r_{12} = (r_1^2 + r_2^2 - 2 r_1 r_2 \cos \theta)^{1/2}$. Prove this relationship using the following steps.

(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 depend 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, $\theta = 0$, 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 $\phi = 0$. 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:

$$\vec{r}_1 - \vec{r}_2 = (0 - r_2 \sin \theta) \vec{i} + (0 - 0) \vec{j} + (r_1 - r_2 \cos \theta) \vec{k}$$

where \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 $q = \cos \theta$, show that (Eq. 25.7.5):

$$\int_0^\pi \frac{1}{(r_1^2 + r_2^2 - 2 r_1 r_2 \cos \theta)^{1/2}} \sin \theta \, d\theta = \frac{2}{r_1} \quad \text{for } r_1 > r_2 \quad \text{or} \quad = \frac{2}{r_2} \quad \text{for } r_1 < r_2$$

Answer: The substitution $q = \cos \theta$ gives $dq/d\theta = -\sin \theta$ so that $dq = -\sin \theta d\theta$. The integral limits of 0 to π change to $\cos 0$ to $\cos \pi$, or 1 to -1 . Substitution into the integral gives:

$$\int_0^\pi \frac{1}{(r_1^2 + r_2^2 - 2 r_1 r_2 \cos \theta)^{3/2}} \sin \theta d\theta = -\int_1^{-1} \frac{1}{(r_1^2 + r_2^2 - 2 r_1 r_2 q)^{3/2}} dq = \int_{-1}^1 \frac{1}{(r_1^2 + r_2^2 - 2 r_1 r_2 q)^{3/2}} dq$$

Switching the integral limits reverses the sign of the integral. The integral is in the form:

$$\int \frac{1}{(a + bx)^{3/2}} dx = 2 \frac{(a + bx)^{1/2}}{b}$$

which can be verified by taking the derivative of the right side. Substitution of the general form into the first equation gives:

$$\int = 2 \frac{1}{-2 r_1 r_2} [(r_1^2 + r_2^2 - 2 r_1 r_2 q)^{1/2}]_{-1}^1 = -\frac{1}{r_1 r_2} [(r_1^2 + r_2^2 - 2 r_1 r_2)^{1/2} - (r_1^2 + r_2^2 + 2 r_1 r_2)^{1/2}]$$

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:

$$\begin{aligned} [+ , +] & \quad \int = -\frac{1}{r_1 r_2} [r_1 - r_2 - r_1 - r_2] = 2/r_1 \\ [+ , -] & \quad \int = -\frac{1}{r_1 r_2} [r_1 - r_2 + r_1 + r_2] = -2/r_2 \\ [- , +] & \quad \int = -\frac{1}{r_1 r_2} [-r_1 + r_2 - r_1 - r_2] = 2/r_2 \\ [- , -] & \quad \int = -\frac{1}{r_1 r_2} [-r_1 + r_2 + r_1 + r_2] = -2/r_1 \end{aligned}$$

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:

$$\begin{aligned} \int_0^\pi \frac{1}{(r_1^2 + r_2^2 - 2 r_1 r_2 \cos \theta)^{3/2}} \sin \theta d\theta &= \frac{2}{r_1} && \text{for } r_1 > r_2 \\ &= \frac{2}{r_2} && \text{for } r_1 < r_2 \end{aligned}$$

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:

$$\int_{r_1}^{\infty} e^{-2Zr_2/a_0} r_2 dr_2 \quad \text{and} \quad \int_0^{r_1} e^{-2Zr_2/a_0} r_2^2 dr_2$$

Answer: The r_2 integrals are derived from the tabulated indefinite integrals:

$$\int e^{-ax} x dx = -\frac{e^{-ax}}{a^2} (ax + 1) \quad \text{and} \quad \int e^{-ax} x^2 dx = -\frac{e^{-ax}}{a^3} (a^2x^2 + 2ax + 2)$$

Note that $\lim_{x \rightarrow \infty} e^{-ax}(ax) = 0$ using L'Hospital's Rule. The definite integrals are then:

$$\begin{aligned} \int_{x_0}^{\infty} e^{-ax} x dx &= \frac{e^{-ax_0}}{a^2} (ax_0 + 1) = \frac{x_0}{a} e^{-ax_0} + \frac{1}{a^2} e^{-ax_0} \\ \int_0^{x_0} e^{-ax} x^2 dx &= -\frac{e^{-ax_0}}{a^3} (a^2x_0^2 + 2ax_0 + 2) + \frac{2}{a^3} = -\frac{x_0^2}{a} e^{-ax_0} - \frac{2x_0}{a^2} e^{-ax_0} - \frac{2}{a^3} e^{-ax_0} + \frac{2}{a^3} \end{aligned}$$

Setting $a = 2Z/a_0$, $x = r_2$, and $x_0 = r_1$ gives the definite integrals as:

$$\int_{r_1}^{\infty} e^{-2Zr_2/a_0} r_2 dr_2 = \frac{1}{2} \left(\frac{a_0}{Z} \right) r_1 e^{-2Zr_1/a_0} + \frac{1}{2^2} \left(\frac{a_0}{Z} \right)^2 e^{-2Zr_1/a_0} \quad (25.7.8)$$

$$\int_0^{r_1} e^{-2Zr_2/a_0} r_2^2 dr_2 = -\frac{1}{2} \left(\frac{a_0}{Z} \right) r_1^2 e^{-2Zr_1/a_0} - \frac{1}{2} \left(\frac{a_0}{Z} \right)^2 r_1 e^{-2Zr_1/a_0} - \frac{1}{2^2} \left(\frac{a_0}{Z} \right)^3 e^{-2Zr_1/a_0} + \frac{1}{2^2} \left(\frac{a_0}{Z} \right)^3 \quad (25.7.9)$$

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 $a = 4Z/a_0$ for the first three integrals or $a = 2Z/a_0$ into the fourth integral in Eq. 25.7.10 results in:

$$\begin{aligned} \int_0^{\infty} e^{-2Zr_1/a_0} r_1 \left(\int_0^{r_1} e^{-2Zr_2/a_0} r_2^2 dr_2 \right) dr_1 &= \\ &= -\frac{1}{2} \left(\frac{a_0}{Z} \right) 6 \left(\frac{a_0}{4Z} \right)^4 - \frac{1}{2} \left(\frac{a_0}{Z} \right)^2 2 \left(\frac{a_0}{4Z} \right)^3 - \frac{1}{2^2} \left(\frac{a_0}{4Z} \right)^2 + \frac{1}{2^2} \left(\frac{a_0}{Z} \right)^3 \left(\frac{a_0}{2Z} \right)^2 \\ &= -\frac{6}{2^9} \left(\frac{a_0}{Z} \right)^5 - \frac{1}{2^6} \left(\frac{a_0}{Z} \right)^5 - \frac{1}{2^6} \left(\frac{a_0}{Z} \right)^5 + \frac{1}{2^4} \left(\frac{a_0}{Z} \right)^5 \end{aligned}$$

(b). Substitution of Eq. 25.7.8 into the second integral in Eq. 25.7.7 gives:

$$\begin{aligned} \int_0^\infty e^{-2Zr_1/a_0} r_1^2 \left(\int_{r_1}^\infty e^{-2Zr_2/a_0} r_2 \, dr_2 \right) dr_1 &= \\ &= \frac{1}{2} \left(\frac{a_0}{Z} \right) \int_0^\infty r_1^3 e^{-4Zr_1/a_0} \, dr_1 + \frac{1}{2^2} \left(\frac{a_0}{Z} \right)^2 \int_0^\infty r_1^2 e^{-4Zr_1/a_0} \, dr_1 \end{aligned}$$

Using the tabulated integrals and substituting $a = 4Z/a_0$ into the last equation gives:

$$\begin{aligned} &= \frac{1}{2} \left(\frac{a_0}{Z} \right) 6 \left(\frac{a_0}{4Z} \right)^4 + \frac{1}{2^2} \left(\frac{a_0}{Z} \right)^2 2 \left(\frac{a_0}{4Z} \right)^3 \\ &= \frac{6}{2^9} \left(\frac{a_0}{Z} \right)^5 + \frac{1}{2^7} \left(\frac{a_0}{Z} \right)^5 \end{aligned}$$

The next problem continues the determination of the expectation value of the electron-electron repulsion energy.

42. 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:

$$\begin{aligned} \int_0^\infty e^{-2Zr_1/a_0} r_1 \left(\int_0^{r_1} e^{-2Zr_2/a_0} r_2^2 \, dr_2 \right) dr_1 + \int_0^\infty e^{-2Zr_1/a_0} r_1^2 \left(\int_{r_1}^\infty e^{-2Zr_2/a_0} r_2 \, dr_2 \right) dr_1 &= \\ &= -\frac{6}{2^9} \left(\frac{a_0}{Z} \right)^5 - \frac{1}{2^6} \left(\frac{a_0}{Z} \right)^5 - \frac{1}{2^6} \left(\frac{a_0}{Z} \right)^5 + \frac{1}{2^4} \left(\frac{a_0}{Z} \right)^5 + \frac{6}{2^9} \left(\frac{a_0}{Z} \right)^5 + \frac{1}{2^7} \left(\frac{a_0}{Z} \right)^5 \\ &= \left[-\frac{1}{2^6} - \frac{1}{2^6} + \frac{1}{2^4} + \frac{1}{2^7} \right] \left(\frac{a_0}{Z} \right)^5 = \left[-\frac{2}{2^7} - \frac{2}{2^7} + \frac{8}{2^7} + \frac{1}{2^7} \right] \left(\frac{a_0}{Z} \right)^5 = \frac{5}{2^7} \left(\frac{a_0}{Z} \right)^5 \end{aligned}$$

Substituting this last result into Eq. 25.7.7 gives Eq. 25.7.13:

$$E_{\text{gs}}^{(1)} = 16 \left(\frac{Z}{a_0} \right)^6 \frac{e^2}{4\pi\epsilon_0} \frac{5}{2^7} \left(\frac{a_0}{Z} \right)^5 = 2^4 \left(\frac{Z}{a_0} \right)^6 \frac{e^2}{4\pi\epsilon_0} \frac{5}{2^7} \left(\frac{a_0}{Z} \right)^5 = \frac{5Z}{8} \left(\frac{e^2}{4\pi\epsilon_0 a_0} \right)$$

The term in parentheses in the last equation is equal to one Hartree, $1H = 27.2116 \text{ eV}$. The full nuclear charge for helium is $Z = 2$, giving $E_{\text{gs}}^{(1)} = 34.01 \text{ eV}$.

Literature Cited:

1. M. W. Hanna, *Quantum Mechanics in Chemistry, 3rd. ed.*, Benjamin-Cummings, Menlo Park, CA, 1981. Exercise 6-45, p. 176.