1. \textbf{9.9(b)} Calculate the average kinetic and potential energies of a 2s electron in a hydrogenic atom of atomic number \(Z\).

The average kinetic energy is

\[ \langle \hat{E}_K \rangle = \int \psi^* \hat{H} \psi \, d\tau \]

where \(\psi = N(2 - \rho) e^{-\rho/2}\) with \(N = \frac{1}{4} \left( \frac{Z^3}{2\pi a_0^3} \right)^{1/2}\) and \(\rho = \frac{Zr}{a_0}\) here.

\[ \hat{E}_K = -\frac{\hbar^2}{2m} \nabla^2 \psi \, d\tau = r^2 \sin \theta \, \frac{d}{dr} \rho \, d\rho \, d\phi = \frac{a_0^2 \rho^2 \sin \theta \, d\rho \, d\theta \, d\phi}{Z^3} \]

In spherical polar coordinates, three of the derivatives in \(\nabla^2\) are derivatives with respect to angles, so those parts of \(\nabla^2 \psi\) vanish. Thus

\[ \nabla^2 \psi = \frac{\partial^2 \psi}{\partial r^2} + \frac{2}{r} \frac{\partial \psi}{\partial r} = \frac{\partial^2 \psi}{\partial \rho^2} \left( \frac{\partial \rho}{\partial r} \right)^2 + \frac{2Z}{\rho a_0} \frac{\partial \psi}{\partial \rho} \frac{\partial \rho}{\partial r} = \left( \frac{Z}{a_0} \right)^2 \frac{\partial^2 \psi}{\partial \rho^2} + \frac{2Z}{\rho a_0} \frac{\partial \psi}{\partial \rho} \frac{\partial \rho}{\partial r} \]

\[ \frac{\partial \rho}{\partial r} = N(2 - \rho) \times \left( -\frac{1}{2} \right) e^{-\rho/2} - N e^{-\rho/2} = N \left( \frac{1}{2} \rho - 2 \right) e^{-\rho/2} \]

\[ \frac{\partial^2 \psi}{\partial \rho^2} = N \left( \frac{1}{2} \rho - 2 \right) \times \left( -\frac{1}{2} \right) e^{-\rho/2} + \frac{1}{2} N e^{-\rho/2} = N \left( \frac{1}{2} \rho - 2 \right) e^{-\rho/2} \]

\[ \nabla^2 \psi = \left( \frac{Z}{a_0} \right)^2 N e^{-\rho/2} \left( -4/\rho + 5/2 - \rho/4 \right) \]

and

\[ \langle \hat{E}_K \rangle = \int_0^\infty \int_0^\pi \int_0^{2\pi} N(2 - \rho) e^{-\rho/2} \left( \frac{Z}{a_0} \right)^2 \left( -\frac{\hbar^2}{2m} \right) \times \frac{a_0^2 \rho^2 \sin \theta \, d\rho \, d\theta \, d\phi}{Z^3} \times N e^{-\rho/2} \left( -4/\rho + 5/2 - \rho/4 \right) \]

The integrals over angles give a factor of \(4\pi\), so

\[ \langle \hat{E}_K \rangle = 4\pi N^2 \left( \frac{a_0}{Z} \right) \times \left( -\frac{\hbar^2}{2m} \right) \int_0^\infty (2 - \rho) \times \left( -4 + \frac{5}{2} \rho - \frac{1}{4} \rho^2 \right) \rho e^{-\rho} \, d\rho \]

The integral in this last expression works out to \(2\), using \(\int_0^\infty e^{-\rho} \rho^n \, d\rho = n!\) for \(n = 1, 2, 3\). So

\[ \langle \hat{E}_K \rangle = 4\pi \left( \frac{Z^3}{32\pi a_0^3} \right) \times \left( \frac{a_0}{Z} \right) \times \left( \frac{\hbar^2}{m} \right) = \frac{\hbar^2 Z^2}{8m a_0^2} \]

The average potential energy is

\[ \langle V \rangle = \int \psi^* V \psi \, d\tau \] where \(V = -\frac{Z^2 e^2}{4\pi \epsilon_0 r} = -\frac{Z^2 e^2}{4\pi \epsilon_0 a_0 \rho} \)

and \(\langle V \rangle = \int_0^\infty \int_0^\pi \int_0^{2\pi} N(2 - \rho) e^{-\rho/2} \left( -\frac{Z^2 e^2}{4\pi \epsilon_0 a_0 \rho} \right) N(2 - \rho) e^{-\rho/2} \left( \frac{a_0^2 \rho^2 \sin \theta \, d\rho \, d\theta \, d\phi}{Z^3} \right) \)

The integrals over angles give a factor of \(4\pi\), so

\[ \langle V \rangle = 4\pi N^2 \left( \frac{Z^2 e^2}{4\pi \epsilon_0 a_0} \right) \times \left( \frac{a_0}{Z} \right) \int_0^\infty (2 - \rho) e^{-\rho} \, d\rho \]

The integral in this last expression works out to \(2\), using \(\int_0^\infty e^{-\rho} \rho^n \, d\rho = n!\) for \(n = 1, 2, 3, 4\). So

\[ \langle V \rangle = 4\pi \left( \frac{Z^3}{32\pi a_0^3} \right) \times \left( -\frac{Z^2 e^2}{4\pi \epsilon_0 a_0} \right) \times \left( \frac{a_0}{Z} \right) \times (2) = \frac{Z^2 e^2}{16\pi \epsilon_0 a_0} \]
2. **9.10(b)** Write down the expression for the radial distribution function of a 3s electron in a hydrogenic atom and determine the radius at which the electron is most likely to be found.

The radial distribution function is defined as

\[ P = 4\pi r^2 \rho^2 \] so \( P_{3s} = 4\pi r^2 (Y_{00} R_{3s})^2 \),

\[
P_{3s} = 4\pi r^2 \left( \frac{1}{4\pi} \right) \times \left( \frac{1}{243} \right) \times \left( \frac{Z}{a_0} \right) \times (6 - 6\rho + \rho^2)^2 e^{-\rho}
\]

where \( \rho = \frac{22r}{na_0} = \frac{22r}{3a_0} \) here.

But we want to find the most likely radius, so it would help to simplify the function by expressing it in terms either of \( r \) or \( \rho \), but not both. To find the most likely radius, we could set the derivative of \( P_{3s} \) equal to zero; therefore, we can collect all multiplicative constants together (including the factors of \( a_0/Z \) needed to turn the initial \( r^2 \) into \( \rho^2 \)) since they will eventually be divided into zero

\[ P_{3s} = C^2 \rho^2 (6 - 6\rho + \rho^2)^2 e^{-\rho} \]

Note that not all the extrema of \( P \) are maxima; some are minima. But all the extrema of \( (P_{3s})^{1/2} \) correspond to maxima of \( P_{3s} \). So let us find the extrema of \( (P_{3s})^{1/2} \)

\[
\frac{d}{d\rho} (P_{3s})^{1/2} = 0
\]

\[
= C \rho (6 - 6\rho + \rho^2) e^{-\rho/2} \left( -\frac{1}{2} \right) + (6 - 12\rho + 3\rho^2) e^{-\rho/2} = 0
\]

\[
0 = C \left( 6 - 15\rho + 6\rho^2 - \frac{1}{2} \rho^3 \right) e^{-\rho/2} \text{ so } 12 - 30\rho + 12\rho^2 - \rho^3 = 0
\]

Numerical solution of this cubic equation yields

\( \rho = 0.49, \ 2.79, \ \text{and} \ 8.72 \)

corresponding to

\[ r = \frac{0.74a_0/Z}{Z}, \frac{4.19a_0/Z}{Z}, \text{ and } \frac{13.08a_0/Z}{Z} \]

**COMMENT**: If numerical methods are to be used to locate the roots of the equation which locates the extrema, then graphical-numerical methods might as well be used to locate the maxima directly. That is, the student may simply have a spreadsheet compute \( P_{3s} \) and examine or manipulate the spreadsheet to locate the maxima.

3. **9.19(b)** (a) Write the electronic configuration of the \( V^{2+} \) ion. (b) What are the possible values of the total spin quantum numbers \( S \) and \( M_S \) for this ion?

\( V^{2+} : 1s^2 2s^2 2p^6 3s^2 3p^6 3d^3 = [Ar] 3d^3 \)

The only unpaired electrons are those in the 3d subshell. There are three.

\[ S = \frac{3}{2}, \text{ and } \frac{3}{2} - 1 = \frac{1}{2} \]

For \( S = \frac{3}{2}, \) \( M_S = \pm \frac{1}{2} \) and \( \pm \frac{3}{2} \)

for \( S = \frac{1}{2}, \) \( M_S = \pm \frac{1}{2} \)
4. 9.23(b) Suppose that an atom has (a) 4, (b) 5, electrons in different orbitals. What are the possible values of the total spin quantum number $S$? What is the multiplicity in each case?

(a) Possible values of $S$ for four electrons in different orbitals are $2, 1, 0, 1/2$, the multiplicity is $2S + 1$, so multiplicities are $3, 5, 6, 4$ respectively.

(b) Possible values of $S$ for five electrons in different orbitals are $5/2, 3/2, 1/2$, the multiplicity is $2S + 1$, so multiplicities are $6, 4, 2$ respectively.

5. 9.24(b) What atomic terms are possible for the electron configuration $np^4nd^1$? Which term is likely to lie lowest in energy?

The coupling of a $p$ electron ($l = 1$) and a $d$ electron ($l = 2$) gives rise to $L = 3$ (F), $2$ (P), and $1$ (S) terms. Possible values of $S$ include 0 and 1. Possible values of $J$ (using Russell-Saunders coupling) are 3, 2, 1 ($S = 0$) and 4, 3, 2, 1, and 0 ($S = 1$). The term symbols are $1F_{4}, 1F_{3}, 1F_{2}, 1D_{3}, 1D_{2}, 1D_{1}, 1P_{2}, 1P_{1}$. 

Hund's rules state that the lowest energy level has maximum multiplicity. Consideration of spin–orbit coupling says the lowest energy level has the lowest value of $J(J+1) - L(L+1) - S(S+1)$. So the lowest energy level is $1D_{2}$.

Since electrons are in different orbitals any combination is possible paired or unpaired spins

6. 9.27(b) Which of the following transitions between terms are allowed in the normal electronic emission spectrum of a many-electron atom:

(a) $^{3}P_{3/2} \rightarrow ^{3}S_{1/2}$, (b) $^{3}P_{0} \rightarrow ^{3}S_{1}$, (c) $^{3}D_{3} \rightarrow ^{3}P_{1}$?

$\Delta S = 0$, $\Delta L = 0$, $\pm 1$, $\Delta J = 0, \pm 1$.

But $J = 0 \leftrightarrow J = 0$.

a. Allowed, b. Allowed, $\Delta S = 0$ & $\Delta J = 1$, c. Forbidden by spin, $\Delta S = 1$

7. 9.2 A series of lines in the spectrum of atomic hydrogen lies at 656.46 nm, 486.27 nm, 343.17 nm, and 410.29 nm. What is the wavelength of the next line in the series? What is the ionization energy of the atom when it is in the lower state of the transitions?

All lines in the hydrogen spectrum fit the Rydberg formula:

$$\frac{1}{\lambda} = R_{n} \left( \frac{1}{n_{1}^{2}} - \frac{1}{n_{2}^{2}} \right)$$

with $R_{n} = 109677 \text{ cm}^{-1}$.

Find $n_{2}$ from the value of $\lambda_{max}$, which arises from the transition $n_{1} + 1 \rightarrow n_{2}$.

$$\lambda_{max} R_{n} = \frac{n_{2}^2(n_{2}^2 - 1)}{2n_{1} + 1} = \frac{656.46 \times 10^{-9} \text{ m}}{109677 \times 10^{3} \text{ m}^{-1}} = 7.20$$

and hence $n_{2} = 2$, as determined by trial and error substitution. Therefore, the transitions are given by $n_{2} = 3, 4, 5, 6$.

The next line has $n_{2} = 7$, and occurs at

$$\lambda = \frac{1}{(109677 \text{ cm}^{-1}) \times \left( \frac{1}{4} - \frac{1}{6} \right)} = 397.13 \text{ nm}$$

The energy required to ionize the atom is obtained by letting $n_{2} \rightarrow \infty$. Then,

$$\varepsilon = \frac{1}{\lambda} = \frac{1}{(109677 \text{ cm}^{-1}) \times (1 - 0)} = 27.419 \text{ cm}^{-1}$$

or $3.40 \text{ eV}$

(The answer, $3.40 \text{ eV}$, is the ionization energy of an H atom that is already in an excited state, with $n = 2$.)

COMMENT: The series with $n_{2} = 2$ is the Balmer series.
8. **9.8** Positronium consists of an electron and a positron (same mass, opposite charge) orbiting round their common centre of mass. The broad features of the spectrum are therefore expected to be hydrogen-like, the differences arising largely from the mass differences. Predict the wavenumbers of the first three lines of the Balmer series of positronium. What is the binding energy of the ground state of positronium?

The Rydberg constant for positronium \((R_\infty)\) is given by

\[
R_\infty = \frac{1}{2} \frac{R_n}{1 + \frac{1}{n^2}} = \frac{1}{2} \frac{R_n}{1 + \frac{1}{n^2}}
\]

\[\text{[9.15; also Problem 9.7; } m(\text{positron}) = m_e]\]

\[= 54,869 \text{ cm}^{-1} \quad \{R = 109,737 \text{ cm}^{-1}\}\]

Hence,

\[
\nu = \frac{1}{\lambda} = \frac{1}{(54,869 \text{ cm}^{-1})} \times \left(\frac{1}{4} \times \frac{1}{n^2}\right) \quad n = 3, 4, \ldots
\]

\[= [5621 \text{ cm}^{-1}, 10,288 \text{ cm}^{-1}, 17,522 \text{ cm}^{-1}], \ldots\]

The binding energy of \(\text{Ps}\) is

\[E = -\frac{\hbar c}{R_\infty}, \text{ corresponding to } (\sim)54,869 \text{ cm}^{-1}\]

The ionization energy is therefore 54,869 cm\(^{-1}\), or 0.80 eV.

9. **9.32** Thallium, a neurotoxin, is the heaviest member of Group 13 of the periodic table and is found most usually in the +1 oxidation state. Aluminium, which causes anaemia and dementia, is also a member of the group but its chemical properties are dominated by the +3 oxidation state. Examine this issue by plotting the first, second, and third ionization energies for the Group 13 elements against atomic number. Explain the trends you observe. Hints. The third ionization energy, \(I_3\), is the minimum energy needed to remove an electron from the doubly charged cation: 

\[E^{3+}(g) \rightarrow E^{3+}(g) + e^-(g), \quad I_3 = E(E^{3+}) - E(E^{2+})\]

For data, see the links to databases of atomic properties provided in the text’s web site.

See Figure 10.3.

Trends:

(i) \(I_1 < I_2 < I_3\) because of decreased nuclear shielding as each successive electron is removed.

![First three ionization energies of group 13](image)

(ii) The ionization energies of boron are much larger than those of the remaining group elements because the valence shell of boron is very small and compact with little nuclear shielding. The boron atom is much smaller than the aluminum atom.

(iii) The ionization energies of Al, Ga, In, and Tl are comparable even though successive valence shells are further from the nucleus because the ionization energy decrease expected from large atomic radii is balanced by an increase in effective nuclear charge.
10. P15.6) Show that the total energy eigenfunctions $\psi_{210}(r, \theta, \phi)$ and $\psi_{211}(r, \theta, \phi)$ are orthogonal. Do you have to integrate over all three variables to show that the functions are orthogonal?

$$
\int \psi_{210}^* \psi_{211} dr = \frac{1}{32\sqrt{\pi}a_0^3} \int_0^{2\pi} e^{i\phi} d\phi \int_0^\pi \cos \theta \sin^2 \theta d\theta \int_0^\infty r^2 e^{-\frac{r}{a_0}} dr
$$

This integral is zero because \( \int_0^\pi \cos \theta \sin^2 \theta d\theta = \left[ \frac{\sin^3 \theta}{3} \right]_0^\pi = 0 - 0 = 0. \)

It is sufficient to evaluate the integral over $\theta$

11. P15.17) Ions with a single electron such as He$^+$, Li$^{2+}$, and Be$^{3+}$ are described by the H atom wave functions with $Z/a_0$ substituted for $1/a_0$, where $Z$ is the nuclear charge. The 1s wave function becomes $\psi(r) = 1/\sqrt{\pi} (Z/a_0)^{3/2} e^{-Zr/a_0}$. Using this result, compare the mean value of the radius $\langle r \rangle$ at which you would find the 1s electron in H, He$^+$, Li$^{2+}$, and Be$^{3+}$.

$$
\langle r \rangle = \frac{\int_0^\infty r^3 e^{-2Zr/a_0} dr}{\int_0^\infty r^2 e^{-2Zr/a_0} dr}
$$

Using the standard integral: $\int_0^\infty r^n e^{-\alpha r} dr = \frac{n!}{\alpha^{n+1}}$

$$
\langle r \rangle = \frac{4Z^3}{\pi a_0^3} \int_0^\infty r^3 e^{-2Zr/a_0} dr = \frac{3}{2} a_0
$$

$$
\langle r \rangle_H = \frac{3}{2} a_0; \quad \langle r \rangle_{He^+} = \frac{3}{4} a_0; \quad \langle r \rangle_{Li^{2+}} = \frac{1}{2} a_0; \quad \langle r \rangle_{Be^{3+}} = \frac{3}{8} a_0
$$

12. P15.20) Core electrons shield valence electrons so that they experience an effective nuclear charge $Z_{\text{eff}}$ rather than the full nuclear charge. Given that the first ionization energy of Li is 5.39 eV, use the formula in Problem P15.18 to estimate the effective nuclear charge experienced by the 2s electron in Li.

From the previous problem,

$$
I = 13.60 \frac{Z^2}{n^2} \text{eV}; \quad Z_{\text{eff}} = \sqrt{\frac{n^2 I}{13.60 \text{ eV}}} = \sqrt{\frac{4 \times 5.39 \text{eV}}{13.60 \text{ eV}}} = 1.26
$$
13. P15.24) The force acting between the electron and the proton in the H atom is given by \( F = -\frac{e^2}{4\pi\varepsilon_0 r^2} \). Calculate the average value \( \langle F \rangle \) for the 1s and 2p\(_z\) states of the H atom in terms of \( e, \varepsilon_0, \) and \( a_0 \).

\[
\langle F \rangle_{1s} = -\frac{e^2}{4\pi\varepsilon_0} \int \psi^* (\tau) \frac{1}{r^2} \psi (\tau) d\tau
\]

\[
\langle F \rangle_{1s} = -\frac{e^2}{4\pi\varepsilon_0} \frac{1}{\pi a_0^2} \int_0^{2\pi} d\phi \int_0^\pi \sin \theta d\theta \left[ \int_0^\infty \left( \frac{1}{r^3} \right) e^{-r/\alpha_0} r^2 d\tau \right] = -e^2/2\pi\varepsilon_0 a_0^2
\]

\[
\langle F \rangle_{1s} = -\frac{e^2}{4\pi\varepsilon_0} \int \psi^* (\tau) \frac{1}{r^2} \psi (\tau) d\tau
\]

\[
\langle F \rangle_{2p_z} = -\frac{e^2}{4\pi\varepsilon_0} \frac{1}{32\pi a_0^3} \int_0^{2\pi} d\phi \int_0^\pi \cos^2 \theta \sin \theta d\theta \left[ \int_0^\infty \left( \frac{r}{a_0} \right)^2 e^{-r/\alpha_0} \right] r^2 d\tau
\]

\[
\langle F \rangle_{2p_z} = -\frac{e^2}{4\pi\varepsilon_0} \frac{1}{24 a_0^3} \int_0^\infty r^2 e^{-r/\alpha_0} dr
\]

Using the standard integral \( \int_0^\infty r^n e^{-ar} = \frac{n!}{a^{n+1}} \)

\[
\langle F \rangle_{2p_z} = -\frac{e^2}{4\pi\varepsilon_0} \frac{1}{24 a_0^3} \times 2a_0^3 = -\frac{e^2}{48\pi\varepsilon_0 a_0^2}
\]

14. P15.30) You have commissioned a measurement of the second ionization energy from two independent research teams. You find that they do not agree and decide to plot the data together with known values of the first ionization energy. The results are shown here:

The lowest curve is for the first ionization energy and the upper two curves are the results for the second ionization energy from the two research teams. The uppermost curve has been shifted vertically to avoid an overlap with the other new data set. On the basis of your knowledge of the periodic table, you suddenly know which of the two sets of data is correct and the error that one of the teams of researchers made. Which data set is correct? Explain your reasoning.

The data set shown by the dashed (purple) line is correct, the red one is incorrect. Although the alkali atoms have
the lowest ionization energies, they must have the highest ionization energy for the second ionization potential because the singly charged positive ions have the rare gas filled shell configuration. The experimenters that produced the data set shown by the gray (red) line had assigned atomic numbers that were too low by one.

15. P15.33) An approximate formula for the energy levels in a multielectron atom is

\[ E_n \approx -Z_{\text{eff}}^2 \frac{e^2}{8\pi \varepsilon_0 a_0 n^2}, \quad n = 1, 2, 3, \ldots, \]

where \( Z_{\text{eff}} \) is the effective nuclear charge felt by an electron in a given orbital. Calculate values for \( Z_{\text{eff}} \) from the first ionization energies for the elements Li through Ne (SEE www.webelements.com). Compare these values for \( Z_{\text{eff}} \) with those listed in TABLE 15.1. How well do they compare?

Using:

\[ Z_{\text{eff}} = \sqrt{\frac{8\pi E_{\text{ion}} n^2 \varepsilon_0 a_0}{e^2 N_A}} = \sqrt{\frac{8\pi E_{\text{ion}} \frac{1}{2} (8.854187810^{-12} \, \text{C}^2 \, \text{J}^{-1} \, \text{m}^{-1}) \times (5.291772 \times 10^{-11} \, \text{m})}{(1.602177 \times 10^{-19} \, \text{C})^2 \times (6.02210^{23} \, \text{mol}^{-1})}}, \]

the effective charges based on the first ionization energies for the elements Li to Ne are calculated as:

<table>
<thead>
<tr>
<th>Element</th>
<th>Li</th>
<th>Be</th>
<th>B</th>
<th>C</th>
<th>N</th>
<th>O</th>
<th>F</th>
<th>Ne</th>
</tr>
</thead>
<tbody>
<tr>
<td>( E_{\text{ionization}} ) in kJ mol(^{-1})</td>
<td>520.2</td>
<td>899.5</td>
<td>800.6</td>
<td>1086.5</td>
<td>1402.3</td>
<td>1313.9</td>
<td>1681.0</td>
<td>2080.7</td>
</tr>
<tr>
<td>( Z_{\text{eff}} )</td>
<td>1.26</td>
<td>1.66</td>
<td>1.56</td>
<td>1.82</td>
<td>2.07</td>
<td>2.00</td>
<td>2.26</td>
<td>2.52</td>
</tr>
</tbody>
</table>

A comparison with the data in Table 15.1 shows that the approximation reproduces the effective charges reasonably well for the second-row elements with only 2s electrons, however, fails to predict the charges for elements with 2p electrons.

**Extra Problems**

1. **9.13(b)** Locate the angular nodes and nodal planes of each of the 3d orbitals of a hydrogenic atom of atomic number \( Z \). To locate the angular nodes, give the angle that the plane makes with the z-axis.

See Figures 8.35 and 9.16 as well as Table 8.2 of the text. The number of angular nodes is the value of the quantum number \( \ell \), which for d orbitals is 2. Hence, each of the five d-orbitals has two angular nodes. To locate the angular nodes look for the values of \( \theta \) that make the wavefunction zero.

- \( d_{x^2} \) orbital: see eqn 9.23, Table 8.2, and Figures 8.35 and 9.16. The nodal planes are difficult to picture. \( \theta = 0.95532 \) is the angular node for both planes.

- \( d_{yz} \) orbital: see eqn 9.23, Table 8.2, and Figures 8.35 and 9.16. The two nodal planes are the \( yz \) and \( xy \) planes, and \( \theta = 0 \) is the angular node for both planes.

- \( d_{xz} \) orbital: see eqn 9.23, Table 8.2, and Figures 8.35 and 9.16. The two nodal planes are the \( xz \) and \( xy \) planes, respectively, are the angular nodes of these planes.

- \( d_{xy} \) orbital: see eqn 9.23, Table 8.2, and Figures 8.35 and 9.16. The two nodal planes are the \( yx \) and \( xy \) planes, respectively, are the angular nodes of these planes.

- \( d_{3z^2-r^2} \) orbital: see eqn 9.23, Table 8.2, and Figures 8.35 and 9.16. The two nodal planes at \( \phi = \pi/4 \) and \( \phi = 3\pi/4 \), respectively, and \( \theta = 0 \) is the angular node of both of these planes.
2. \textbf{9.14(b)} Which of the following transitions are allowed in the normal electronic emission spectrum of an atom: (a) $5d \rightarrow 2s$, (b) $5p \rightarrow 3s$, (c) $6p \rightarrow 4f$?

(a) $5d \rightarrow 2s$ is \underline{not} an allowed transition, for $\Delta l = -2$ ($\Delta l$ must equal $\pm 1$).

(b) $5p \rightarrow 3s$ is \underline{allowed}, since $\Delta l = -1$.

(c) $5p \rightarrow 3f$ is \underline{not} allowed, for $\Delta l = +2$ ($\Delta l$ must equal $\pm 1$).

(d) $6s : l = 5$; maximum occupancy = 22

3. \textbf{9.16(b)} Estimate the lifetime of a state that gives rise to a line of width

(a) 200 MHz, (b) 2.45 cm$^{-1}$.

The finewidth is related to the lifetime $\tau$ by

$$\delta \nu = \frac{5.31 \text{ cm}^{-1}}{\tau \text{ ps}} \quad \text{[equation in Brief Illustration in Section 9.6(b)] so } \tau = \frac{5.31 \text{ cm}^{-1}}{\delta \nu} \text{ ps}$$

(a) We are given a frequency rather than a wavenumber

$$\nu = \frac{v}{c}, \quad \text{so } \tau = \frac{(5.31 \text{ cm}^{-1}) \times (2.998 \times 10^{10} \text{ cm s}^{-1})}{200 \times 10^{6} \text{ s}^{-1}} \text{ ps} = \frac{7.96 \times 10^{2}}{2.14 \text{ ps}}$$

(b) \( \tau = \frac{5.31 \text{ cm}^{-1}}{2.45 \text{ cm}^{-1}} \text{ ps} = \frac{2.14}{2.14 \text{ ps}} \)

4. \textbf{9.22(b)} What information does the term symbol $^3F_4$ provide about the angular momentum of an atom?

The letter $F$ indicates that the total orbital angular momentum quantum number $L$ is 3; the superscript 3 is the multiplicity of the term, $2S + 1$; related to the spin quantum number $S = 1$; and the subscript 4 indicates the total angular momentum quantum number $J$.

5. \textbf{9.26(b)} Give the possible term symbols for (a) Sc [Ar]3d$^1$4s$^2$, (b) Br [Ar]3d$^{10}$4s$^2$4p$^5$.

Closed shells and subshells do not contribute to either $L$ or $S$ and thus are ignored in what follows.

(a) Se [Ar]3d$^1$4s$^2$; $S = \frac{1}{2}, L = 2; J = \frac{3}{2}, \frac{1}{2}$, so the terms are $^2D_{3/2}$ and $^2D_{5/2}$.

(b) Br [Ar]3d$^{10}$4s$^2$4p$^5$. We treat the missing electron in the 4p subshell as equivalent to a single “electron” with $l = 1, s = \frac{1}{2}$. Hence $L = 1, S = \frac{1}{2}$, and $J = \frac{3}{2}, \frac{1}{2}$, so the terms are $^2P_{3/2}$ and $^2P_{1/2}$.

6. \textbf{9.27(b)} Which of the following transitions between terms are allowed in the normal electronic emission spectrum of a many-electron atom:

(a) $^2P_{3/2} \rightarrow ^2S_{1/2}$, (b) $^3P_0 \rightarrow ^3S_1$, (c) $^3D_3 \rightarrow ^1P_1$?

a. Allowed, b. Allowed, c. Forbidden

\[ \Delta S = 0 \quad \Delta L = 0, \pm 1 \quad \Delta J = \pm 1, \Delta J = 0, \pm 1. \]

\[ \text{but } J = 0 \leftrightarrow J = 0 \]
7. **P15.8)** How many radial and angular nodes are there in the following H orbitals?
   
   a. \( \psi_{2p_x}(r, \theta, \phi) \) 0 radial node and 1 angular nodes
   
   b. \( \psi_{2s}(r) \) 1 radial node and 0 angular node
   
   c. \( \psi_{3d_{x^2-y^2}}(r, \theta, \phi) \) 0 radial node and 2 angular nodes
   
   d. \( \psi_{3d_{x^2-y^2}}(r, \theta, \phi) \) 0 radial node and 2 angular nodes

8. **P15.16)** Calculate the mean value of the radius \( \langle r \rangle \) at which you would find the electron if the H atom wave function is \( \psi_{2l0}(r, \theta, \phi) \).

\[
\langle r \rangle = \frac{1}{32 \pi a_0^5} \int_0^{2\pi} d\phi \int_0^\pi \cos^2 \theta \sin \theta d\theta \int_0^\infty r^5 e^{-\frac{r}{a_0}} dr
\]

\[
\langle r \rangle = \frac{2\pi}{32 \pi a_0^5} \left[ -\frac{\cos^3 \theta}{3} \right]_0^\pi \int_0^\infty r^5 e^{-\frac{r}{a_0}} dr = \frac{2\pi}{32 \pi a_0^5} \frac{2}{3} \int_0^\infty r^5 e^{-\frac{r}{a_0}} dr = \frac{1}{24 a_0^5} \int_0^\infty r^5 e^{-\frac{r}{a_0}} dr
\]

Using the standard integral: \( \int_0^\infty r^n e^{-ar} dr = \frac{n!}{a^{n+1}} \)

\[
\langle r \rangle = \frac{1}{24 a_0^5} 5! a_0^5 = 5a_0
\]

9. **P15.18)** The energy levels for ions with a single electron such as \( \text{He}^+ \), \( \text{Li}^{2+} \), and \( \text{Be}^{3+} \) are given by \( E_n = -\frac{Z^2 e^2}{2n^2} \), \( n = 1, 2, 3, ... \). Calculate the ionization energies of \( \text{H} \), \( \text{He}^+ \), \( \text{Li}^{2+} \), and \( \text{Be}^{3+} \) in their ground states in units of electron-volts (eV).

The ionization potential is the negative of the orbital energy.

\[
I = \frac{Z^2 e^2}{8\pi \varepsilon_0 a_0 n^2} = \frac{Z^2}{n^2} \times \left( \frac{1.602 \times 10^{-19} \text{C}}{1 \text{eV}} \right)^2 = \frac{Z^2}{n^2} \times \frac{\text{eV}}{1 \text{J}}
\]

\[
I = 13.60 \frac{Z^2}{n^2} \text{eV}
\]

\[
I_{\text{H}} = 13.60 \text{eV}; \quad I_{\text{He}^+} = 54.42 \text{eV}; \quad I_{\text{Li}^{2+}} = 122.4 \text{eV}; \quad I_{\text{Be}^{3+}} = 217.7 \text{eV}
\]