Chapter 25: Atomic Structure

Why can only two electrons occupy each atomic orbital?

The electronic structure of an atom or monatomic ion is determined by the energies and spatial distribution of the atomic orbitals. The electronic structure of atoms and atomic ions is the foundation of chemical bonding theories. Chemical bonding is a small perturbation on the structure of an atom. The atoms in chemical bonds maintain much of the electronic structure of the corresponding free atom. Our understanding of chemical reactivity is often explained using the periodic properties of the elements. The periodic properties of size, ionization energy, electron affinity, and electronegativity are the results of the electronic structure of the elements and the monoatomic ions.

The energies and degeneracies of the atomic orbitals determine the accessible oxidation states of the elements. An understanding of the speciation of the different oxidation states of the elements is an important aspect of biogeoenvironmental chemistry and inorganic chemistry. For example, descriptions of metal ion complexes start with an understanding of the electron configuration of the free metal ion. The ease of conversion of the elements among their accessible oxidation states influences the fate and transport of compounds in the environment.

Angular momentum is an important property of atoms and atomic ions. Electrons move around the nucleus and take on quantized amounts of orbital angular momentum. The quantum behavior of angular momentum determines the overall shape of the periodic table and the accessible oxidation states for the elements. The orbital angular momentum of an electron determines the shape of its orbital. The interaction of the intrinsic angular momentum of the electron and orbital angular momentum is called spin-orbit coupling. Spin-orbit coupling is an important factor in chemical reactivity and atomic spectroscopy, especially of heavy elements.

Atomic spectroscopy encompasses a commonly used group of analytical techniques for the determination of elemental composition. Atomic spectroscopic techniques include atomic absorption and inductively coupled plasma-optical emission, absorption, and fluorescence. X-ray based spectroscopies use core level transitions for elemental analysis. Finally, the magnetic properties of the elements are critical in diverse areas, including medical diagnostics, the magnets used in wind turbine electrical generators, and magnetic media for data storage.

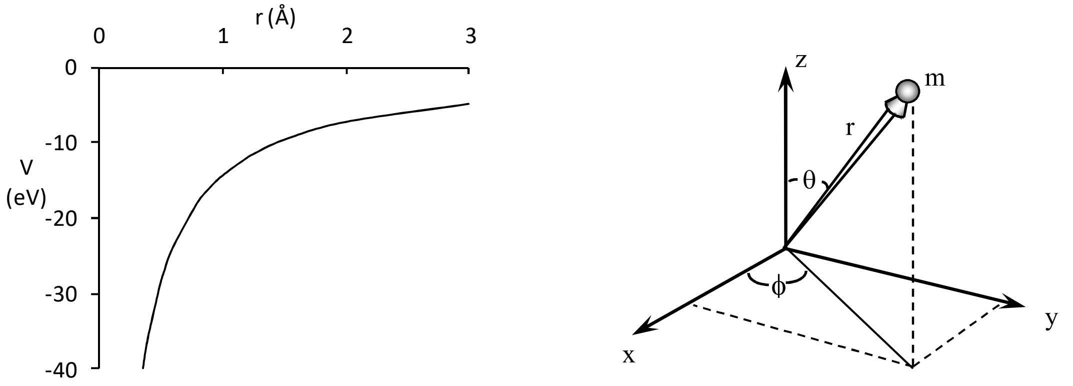
In this chapter we study the energies, spatial distribution, and angular momentum interactions in atoms and atomic ions. The Schrödinger equation for multi-electron atoms cannot be solved exactly. The approximation techniques that are used for atomic structure are also the basis of electronic structure methods for molecules. The approximation methods include perturbation theory, variation theory, and self-consistent field theory.

25.1 Hydrogen Atom

To determine the electronic structure of atoms, it is best to start with the hydrogen atom, which consists of a single proton as the nucleus and a single electron. We will use the hydrogen atom as the basis for building-up the electronic structure of multi-electron atoms. In determining the electronic structure of the hydrogen atom, we will begin by determining the lowest energy, ground state. We used the same approach for the harmonic oscillator. Excited states of the hydrogen atom are likewise constructed by multiplying the ground state with a polynomial to introduce nodes. The presence of nodes indicates higher curvature, which in turn indicates higher kinetic energy than the ground state.

The Ground State of the Hydrogen Atom: The Schrödinger equation for the hydrogen atom is in the same general form as any quantum mechanical system:

$$-\frac{\hbar^2}{2m}\nabla^2\Psi + \hat{V}\Psi = E\,\Psi \qquad 25.1.1$$



(a). Coulomb potential (b). spherical polar coordinates

Figure 25.1.1: (a). The Coulomb attraction of an electron and nucleus with Z = 1. (b). The Coulomb potential is a function only of the radial distance of the electron from the nucleus, r.

As a first approach, we will assume the nucleus is stationary, and then m is the mass of the electron. The wave functions are eigenfunctions of the Hamiltonian and are called atomic **orbitals**. The Coulomb potential governs the attraction of the electron for the nucleus:

$$\hat{V}(r) = \frac{-Z\,e^2}{4\pi\varepsilon_o r} \qquad e = 1.60218\text{x}10^{-19}\text{C} \qquad \varepsilon_o = 8.85419 \text{ x } 10^{-12}\ \text{J}^{-1}\ \text{c}^2\ \text{m}^{-1} \qquad 25.1.2$$

where Z is the charge on the nucleus and r is the radial distance of the electron from the nucleus, Figure 25.1.1a. The permittivity of free space, ε_o, determines the strength of electrostatic interactions in vacuum. We will leave the nuclear charge as a parameter; Eq. 25.1.2 holds for all one-electron atoms and ions. For hydrogen and deuterium, Z = 1. For the one-electron ions, He^+ has Z = 2, Li^{2+} has Z = 3, and Be^{3+} has Z = 4. In much of the following, we will mention only the hydrogen atom, but keep in mind the applicability to one-electron ions. Because the Coulomb potential is only a function of r, the Schrödinger equation for the hydrogen atom is best expressed in spherical polar coordinates:

$$-\frac{\hbar^2}{2m}\nabla^2\Psi + \frac{-Z\,e^2}{4\pi\varepsilon_o r}\Psi = E\,\Psi \qquad 25.1.3$$

with $\nabla^2 = \frac{1}{r}\left(\frac{\partial^2}{\partial r^2}\right) r + \left(\frac{1}{r^2}\right)\Lambda^2$ (24.5.23) $\Lambda^2 = \frac{1}{\sin^2\theta}\left(\frac{\partial^2}{\partial\phi^2}\right) + \left(\frac{1}{\sin\theta}\right)\left(\frac{\partial}{\partial\theta}\sin\theta\,\frac{\partial}{\partial\theta}\right)$ (24.5.25)

The angular operator, Λ^2, is the general curvature for 3D-rotation, which in this case describes the motion in θ and ϕ of the electron about the nucleus. The Schrödinger equation is separable in r, θ, and ϕ. As a result, the full wave function is the product of one-dimensional wave functions, $\Psi = R(r)\,\Theta(\theta)\,\Phi(\phi)$. The R(r) wave function is called the **radial** part of the atomic orbital. We have already solved the ϕ part of the wave function. The $\Phi(\phi)$ wave function gives the angular momentum of the electron in the x-y plane with eigenvalue m_ℓ, Eqs. 24.5.1-24.5.12:

$$-\frac{\hbar^2}{2mr^2}\frac{\partial^2\Phi}{\partial\phi^2} = -\frac{\hbar^2 m_\ell^2}{2mr^2}\Phi \qquad L_z = \hbar\, m_\ell \qquad \Phi(\phi) = \left(\frac{1}{2\pi}\right)^{1/2} e^{im_\ell\phi} \qquad 25.1.4$$

The θ and ϕ wave functions, taken together, are the spherical harmonics, $\Theta(\theta)\,\Phi(\phi) = Y_{\ell,m_\ell}$, Eq. 24.5.32:

$$\Psi = R(r)\,\Theta(\theta)\,\Phi(\phi) = R(r)\,Y_{\ell,m_\ell} \qquad 25.1.5$$

For full 3D-rotation, the spherical harmonics are the eigenfunctions of the square of the total angular momentum, with eigenvalues ℓ and m_ℓ:

$$-\hbar^2\Lambda^2\, Y_{\ell,m_\ell} = \hbar^2\, \ell(\ell+1)\, Y_{\ell,m_\ell} \qquad (24.5.32)\ \ 25.1.6$$

Substitution of Eqs. 24.5.23, 24.5.25, and 25.1.5 into Eq. 25.1.3 gives the Schrödinger equation for the hydrogen atom:

$$-\frac{\hbar^2}{2m}\left(\frac{1}{r}\frac{\partial^2}{\partial r^2}\, r\, R(r)\, Y_{\ell,m_\ell} + \frac{\Lambda^2}{r^2} R(r)\, Y_{\ell,m_\ell}\right) - \frac{Z\,e^2}{4\pi\varepsilon_o r} R(r)\, Y_{\ell,m_\ell} = E\, R(r)\, Y_{\ell,m_\ell} \qquad 25.1.7$$

The Λ^2 operator only acts on θ and ϕ, giving:

$$\Lambda^2 R(r)\, Y_{\ell,m_\ell} = R(r)\, \Lambda^2 Y_{\ell,m_\ell} \qquad 25.1.8$$

The spherical harmonics are eigenfunctions of Λ^2. Solving Eq. 25.1.6 for $\Lambda^2\, Y_{\ell,m_\ell}$ and substitution into Eq. 25.1.7 gives:

$$-\frac{\hbar^2}{2m}\left(Y_{\ell,m_\ell}\frac{1}{r}\frac{\partial^2}{\partial r^2}\, r\, R(r) - R(r)\frac{\ell(\ell+1)}{r^2}\, Y_{\ell,m_\ell}\right) - \frac{Z\,e^2}{4\pi\varepsilon_o r} R(r)\, Y_{\ell,m_\ell} = E\, R(r)\, Y_{\ell,m_\ell} \qquad 25.1.9$$

The partial derivative can be replaced by a one-dimensional derivative, because the radial wave function is only a function of r. Dividing both sides of the last equation by Y_{ℓ,m_ℓ} gives:

$$-\frac{\hbar^2}{2m}\left(\frac{1}{r}\frac{d^2}{dr^2}\, r\, R - \frac{\ell(\ell+1)}{r^2} R\right) - \frac{Z\,e^2}{4\pi\varepsilon_o r} R = E\, R \qquad 25.1.10$$

The ground state has the lowest possible energy, E_{gs}, which from the last equation requires $\ell = 0$. The ground state has no angular momentum; the curvature in the wave function is only in the radial direction. The result is the radial Schrödinger equation for spherically symmetric orbitals:

$$-\frac{\hbar^2}{2m}\left(\frac{1}{r}\frac{d^2}{dr^2}\, r\, R\right) - \frac{Z\,e^2}{4\pi\varepsilon_o r} R = E_{gs}\, R \qquad (\text{spherically symmetric, } \ell = 0)\ 25.1.11$$

The most general approach to solving the radial part of the Schrödinger equation is to assume the wave function is in the form of a power series. For our purposes, we will make a guess at the form of the solution and then verify that the guess is an eigenfunction of the Hamiltonian. The probability of finding the electron should approach zero for large r. An exponential function has the appropriate asymptotic form and is a good guess:

$$R(r) = A\ e^{-\alpha r} \tag{25.1.12}$$

where A is the normalization constant and α is a constant that determines the extent, that is size, of the orbital. Using the product rule, the first and second derivatives are:

$$\frac{d}{dr} r\,R = r\frac{dR}{dr} + R \tag{25.1.13}$$

$$\frac{d^2}{dr^2} r\,R = \frac{d}{dr}\left(r\frac{dR}{dr}\right) + \frac{dR}{dr} = r\frac{d^2R}{dr^2} + \frac{dR}{dr} + \frac{dR}{dr} = r\frac{d^2R}{dr^2} + 2\frac{dR}{dr} \tag{25.1.14}$$

Substitution of the second derivative into the radial Schrödinger equation, Eq. 25.1.11, gives:

$$-\frac{\hbar^2}{2m}\left(\alpha^2 R - \frac{2\alpha}{r} R\right) - \frac{Z\,e^2}{4\pi\varepsilon_o r} R = E_{gs}\,R \qquad \text{(ground state, } \ell = 0) \tag{25.1.15}$$

All the derivatives have been completed, only multiplicative functions remain, so we can divide through by the common factors to give:

$$-\frac{\hbar^2\alpha^2}{2m} + \frac{\hbar^2 2\alpha}{2mr} - \frac{Z\,e^2}{4\pi\varepsilon_o r} = E_{gs} \qquad \text{(ground state, } \ell = 0) \tag{25.1.16}$$

The total energy, E_{gs}, is a constant, but terms in r remain on the left side. The guessed wave function can only be an eigenfunction if the terms in r cancel to give:

$$\frac{\hbar^2\alpha}{mr} - \frac{Z\,e^2}{4\pi\varepsilon_o r} = 0 \qquad \text{(ground state, } \ell = 0) \tag{25.1.17}$$

The remaining constant term in Eq. 25.1.16 gives the energy as:

$$E_{gs} = -\frac{\hbar^2\alpha^2}{2m} \qquad \text{(ground state, } \ell = 0) \tag{25.1.18}$$

This result is promising; the energy is in the same form as a free particle, a particle in a box (Eq. 23.4.4), and the harmonic oscillator (Eq. 24.2.9). Eq. 25.1.17 determines the value of α:

$$\alpha = \frac{Z\,e^2}{4\pi\varepsilon_o}\frac{m}{\hbar^2} \tag{25.1.19}$$

Substituting α back into the equation for the energy, Eq. 25.1.18, gives the final result:

$$E_{gs} = -\left(\frac{Z^2e^4m}{32\pi^2\varepsilon_o{}^2\,\hbar^2}\right) \qquad \text{(ground state, } \ell = 0) \tag{25.1.20}$$

So far we have only considered the ground state. The complete solution to the Schrödinger equation, including excited states, gives the energy as:

$$E_n = -\left(\frac{m\,e^4}{32\pi^2\varepsilon_o{}^2\hbar^2}\right)\frac{Z^2}{n^2} \tag{25.1.21}$$

where n is the **principle quantum number.** The ground state corresponds to n = 1. The total energy is only a function of the principle quantum number and is independent of the angular momentum quantum number, ℓ. All atomic orbitals with the same principle quantum number are degenerate in single-electron atoms and ions. The combination of fundamental constants in the total energy and in α can be simplified by using the definition of the Bohr radius from Eq. 23.2.15:

$$a_o = \frac{4\pi\varepsilon_o \hbar^2}{me^2} \qquad \text{giving} \qquad E_n = -\frac{\hbar^2}{2ma_o^2}\frac{Z^2}{n^2} \qquad \alpha = \frac{Z}{a_o} \qquad 25.1.22$$

where $a_o = 0.052918$ nm = 52.918 pm = 0.52918 Å. The energy of the hydrogen-like atomic orbitals can be expressed in several useful units:

$$E_n = -13.606 \text{ eV} \frac{Z^2}{n^2} = -109{,}678 \text{ cm}^{-1} \frac{Z^2}{n^2} = -1312.7 \text{ kJ mol}^{-1} \frac{Z^2}{n^2} \qquad 25.1.23$$

This result is consistent with the Rydberg formula, Eq. 23.2.10, verifying the quantum mechanical approach. For convenience, the Schrödinger equation for hydrogen-like atoms can also be expressed in dimensionless form, just as we did for the harmonic oscillator, Eq. 24.3.6. In dimensionless form the energy is given as:

$$E_n = -\frac{H}{2}\frac{Z^2}{n^2} \qquad 25.1.24$$

where the effective unit of energy is the **Hartree**, H:

$$1 \text{ H} \equiv 27.211384 \text{ eV} = 219{,}474.6 \text{ cm}^{-1} = 2625.4996 \text{ kJ mol}^{-1} \qquad 25.1.25$$

Hartrees are also commonly called **atomic units**, **au**. Many molecular orbital computer programs give energies in Hartrees.

The constant in Eq. 25.1.23 differs slightly from the empirical Rydberg constant, $\mathfrak{R}_h$ = 109677.5 cm^{-1}. The difference is resolved if the reduced mass of the hydrogen atom is substituted for the electron mass in Eq. 25.1.1 and the resulting total energy, Eq. 25.1.19. The reduced mass of the hydrogen atom is $\mu = m_p m_e/(m_p + m_e)$ where m_p is the mass of the hydrogen nucleus and m_e the mass of the electron.

To complete the solution of the ground state, the wave function must be normalized. Using the wave function with $\alpha = Z/a_o$, Eqs. 25.1.12 and 25.1.22, gives the normalization integral as:

$$\int_0^\infty \int_0^\pi \int_0^{2\pi} \Psi^2 \, r^2 \sin\theta \, dr \, d\theta \, d\phi = A^2 \int_0^\infty \int_0^\pi \int_0^{2\pi} e^{-2Zr/a_o} r^2 \sin\theta \, dr \, d\theta \, d\phi = 1 \qquad 25.1.26$$

The ground state wave function is spherically symmetric, so the integral factors into a product of one-dimensional integrals. The angular integrals give 4π:

$$A^2 \int_0^{2\pi} d\phi \int_0^\pi \sin\theta \, d\theta \int_0^\infty e^{-2Zr/a_o} r^2 \, dr = A^2 \, 4\pi \int_0^\infty e^{-2Zr/a_o} r^2 \, dr = 1 \qquad 25.1.27$$

Integral tables list $\int_0^\infty x^n \, e^{-ax} \, dx = n!/a^{n+1}$ giving the normalization constant as:

$$A^2 \, 4\pi \left(\frac{2}{(2Z/a_o)^3}\right) = 1 \qquad 25.1.28$$

$$A = \frac{1}{\sqrt{\pi}}\left(\frac{Z}{a_o}\right)^{3/2} \qquad 25.1.29$$

The ground state wave function is spherically symmetric, because the wave function is not a function of θ and ϕ. This result is anticipated since the ground state requires $\ell = 0$, giving no angular momentum. Since $\ell = 0$, then m_ℓ must also be zero. The spherically symmetric $\ell = 0$ wave functions are called s-orbitals (the spectroscopic transitions involving these orbitals are "sharp"). The ground state can be labeled with the quantum numbers, $\Psi_{n,\ell,m_\ell} = \Psi_{100}$, or using spectroscopic notation as a 1s-orbital, Ψ_{1s}. Substitution of the normalization constant back into the wave function, Eq. 25.1.12, gives the ground state:

$$\Psi_{1s}(r) = \Psi_{100}(r) = R(r) = \frac{1}{\sqrt{\pi}}\left(\frac{Z}{a_o}\right)^{3/2} e^{-Zr/a_o} \qquad 25.1.30$$

For the hydrogen atom, the charge on the nucleus is $Z = 1$. For the one-electron ions, $Z > 1$. The effect of the increased nuclear charge is to decrease the extent of the orbital, Figure 25.2.1a. The decrease in size of an orbital with increasing nuclear charge is called **orbital contraction**. Now that we have the ground state wave function of the hydrogen atom, we can answer some important questions about the electronic distribution in the atom.

How Big is an Atom? Expectation Values and Most Probable Values: The hydrogen atom 1s orbital approaches zero amplitude asymptotically. So the size of the atom is somewhat arbitrary. There is a finite, though small, probability of the electron being centimeters away from the nucleus. There are several useful measures of the size of an atom. The most direct is the average radius as determined by the expectation value of r:

$$<r> = \frac{\int \Psi_{1s}^* \, r \, \Psi_{1s} \, d\tau}{\int \Psi_{1s}^* \, \Psi_{1s} \, d\tau} = \int_0^\infty \int_0^\pi \int_0^{2\pi} r \, \Psi_{1s}^2 \, r^2 \sin\theta \, dr \, d\theta \, d\phi \qquad 25.1.31$$

The wave function as given by Eq. 25.1.30 is normalized, giving $\int \Psi_{1s}^* \Psi_{1s} \, d\tau = 1$. The squared wave function is spherically symmetric, so the integral over all angles is 4π, Eq. 24.5.17:

$$<r> = \frac{1}{\pi}\left(\frac{Z}{a_o}\right)^3 (4\pi) \int_0^\infty e^{-2Zr/a_o} \, r^3 \, dr \qquad 25.1.32$$

Integral tables list $\int_0^\infty x^n \, e^{-ax} \, dx = n!/a^{n+1}$ giving the integral as:

$$<r> = \frac{1}{\pi}\left(\frac{Z}{a_o}\right)^3 (4\pi) \frac{6}{(2Z/a_o)^4} = \frac{3}{2}\frac{a_o}{Z} \qquad 25.1.33$$

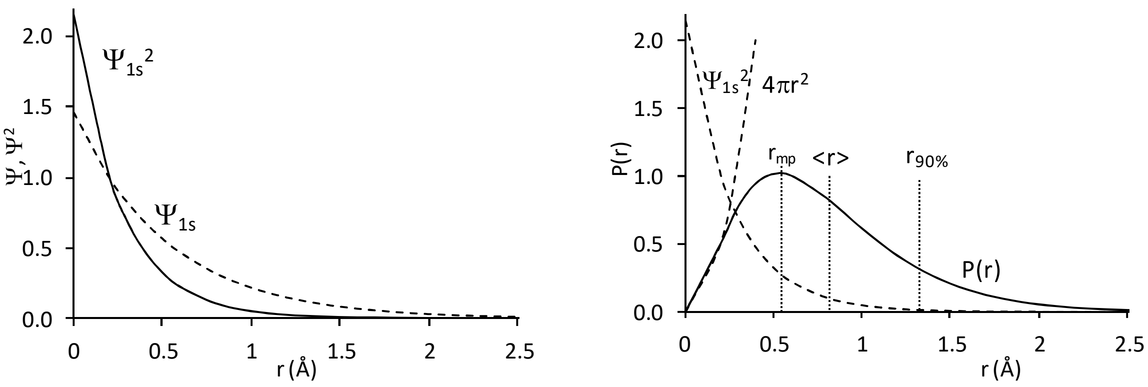
Since a_o is 0.529 Å, the average "size" of a hydrogen atom corresponds to a diameter of 1.56 Å. However, for a specific r, θ, and ϕ, the most probable spot for finding the electron is at $r = 0$, inside the nucleus. The atomic orbital is delocalized, so it is not surprising that the electron can be inside the nucleus. Consider throwing two rocks into a pond; the two waves generated pass through each other. The electron and the nucleus are both waves, so they should be able to pass through each other. However, it is surprising that the most probable spot for the electron is inside the nucleus. An equivalent approach based on the radial probability resolves this issue.

The **radial probability distribution, P(r),** is the integral of Ψ^2 over all angles θ and ϕ:

$$P(r) \, dr = \int_0^\pi \int_0^{2\pi} \Psi^2 \, r^2 \sin\theta \, dr \, d\theta \, d\phi = \int_0^\pi \sin\theta \, d\theta \int_0^{2\pi} d\phi \, \Psi^2 \, r^2 \, dr \qquad 25.1.34$$

The hydrogen 1s-orbital is spherically symmetric, so the angular integral is just 4π:

$$P(r) \, dr = \Psi^2 \, 4\pi r^2 \, dr \qquad \text{(spherically symmetric)} \qquad 25.1.35$$



(a).at a specific spot, r, θ, and ϕ (b). at radius r

Figure 25.1.2: (a). The probability of finding the electron in a 1s-orbital in a narrow range around (r, θ, ϕ) is proportional to Ψ^2. (b). The probability of finding an electron at a radius r, irrespective of angles, is given by $P(r)\,dr = \Psi^2\, 4\pi r^2\, dr$.

Ψ^2 is probability of finding the electron at a specific r, θ, and ϕ. P(r) is the probability of finding the electron at radius r, irrespective of θ and ϕ, Figure 25.1.2. The $4\pi r^2 dr$ factor is the volume of the annular region from r to r + dr, Eq. 24.8.6. The radial probability is then the product of Ψ^2, which is a decreasing function of r, and $4\pi r^2$, which is an increasing function of r. The product of a decreasing factor with an increasing factor gives a function with a maximum, Figure 25.1.2b. Even though the wave function amplitude decreases with distance, the radial probability increases to a maximum because more room is available at large r than small r. However, for very large r, the small value of Ψ^2 forces the radial probability to approach zero. The **most probable radius**, r_{mp}, is a measure of the "size" of an atom. The most probable radius is the maximum of the radial probability distribution:

$$\frac{dP(r)}{dr} = \frac{d}{dr}\left(4\pi r_{mp}^2\, \Psi^2\right) = 4\pi\left(r_{mp}^2 \frac{d\Psi^2}{dr} + 2r_{mp}\,\Psi^2\right) = 0 \qquad \text{with } \frac{d\Psi^2}{dr} = \left(\frac{-2Z}{a_o}\right)\Psi^2 \tag{25.1.36}$$

$$\frac{dP(r)}{dr} = 4\pi\left(r^2 \frac{-2Z}{a_o}\Psi^2 + 2r\,\Psi^2\right) = 0 \tag{25.1.37}$$

Dividing by the common factors gives:

$$\left(-\frac{Zr_{mp}}{a_o} + 1\right) = 0 \qquad \text{or} \quad r_{mp} = a_o/Z \tag{25.1.38}$$

Based on the most probable radius, the "size" of the hydrogen atom is a diameter of ~ 1 Å. The radial probability is particularly useful for spherically symmetric orbitals.

The average radius can also be calculated from P(r), by the integral over all r:

$$\langle r\rangle = \int_0^\infty r\,P(r)\,dr = 4\pi\int_0^\infty \Psi^2\, r^3\, dr \qquad \text{(spherically symmetric)} \tag{25.1.39}$$

This integral is identical to Eq. 25.1.32, we just did the integrals in a different order. Knowing that the angular integral for a spherical distribution is 4π, to find P(r) we just do the angular integrals first and do the r integral later.

Another method for determining the size of an atom is useful for graphical representations of orbitals. Orbitals are often drawn as "balloon" type shapes that are based on fixed probability contour surfaces (Figure 25.2.2). For example, the 90% contour surface for the hydrogen 1s-orbital is defined by the radius that encloses 90% of the probability for finding the electron, $r_{90\%}$:

$$\int_0^{r_{90\%}} \int_0^{\pi} \int_0^{2\pi} \Psi^2\, r^2 \sin\theta\, dr\, d\theta\, d\phi = 0.90 \qquad \text{(spherically symmetric)} \qquad 25.1.40$$

where the wave function is assumed to be normalized. You will show in the Problems that $r_{90\%} = 2.66\ a_o/Z$. How big is the hydrogen atom? The answer depends on the particular experiment that you are doing; $<r>$, r_{mp}, and $r_{90\%}$ are all useful. A ball of cotton candy is a better mental image of an atom than is a billiard ball. We are now ready to consider excited state atomic orbitals for hydrogen.

25.2 Excited States are Built from the Ground State Wave Function

In Sec. 24.2, we showed that the excited states of the harmonic oscillator are obtained by multiplying the ground state wave function by a polynomial. The ground state acts as the asymptotic form that describes how the wave function approaches zero for large distances. The excited states for the hydrogen atom are constructed using the same method. The wave functions for the $\ell = 0$ spherical orbitals with principle quantum numbers n = 2 and 3 are called the 2s- and 3s-orbitals, Figures 25.2.1:

$$\Psi_{2s} = \underbrace{\frac{1}{4\sqrt{2\pi}}\left(\frac{Z}{a_o}\right)^{3/2}}_{\text{normalization}} \underbrace{\left(2 - \frac{Zr}{a_o}\right)}_{\text{polynomial}} \underbrace{e^{-Zr/2a_o}}_{\text{asymptotic}} \qquad \Psi_{3s} = \underbrace{\frac{1}{18\sqrt{3\pi}}\left(\frac{Z}{a_o}\right)^{3/2}}_{\text{normalization}} \underbrace{\left(6 - \frac{4Zr}{a_o} + \frac{4Z^2r^2}{9a_o^2}\right)}_{\text{polynomial}} \underbrace{e^{-Zr/3a_o}}_{\text{asymptotic}} \qquad 25.2.1$$

The asymptotic form is taken from Eq. 25.1.30 with the exponential argument given by $-Zr/na_o$. The appearance of the principle quantum number in the denominator increases the spatial extent for the higher energy orbitals. The average distance of the electron to the nucleus increases with n. The polynomial in r introduces **radial nodes** into the wave function. A radial node corresponds to zero wave function amplitude on the surface of a sphere centered on the nucleus. The order of the polynomial gives the number of zeros and hence the number of radial nodes. The radial node for the 2s-orbital occurs when the 2s-orbital amplitude is zero. Setting $\Psi_{2s} = 0$ and dividing both sides of the equation by the multiplicative factors gives:

$$\left(2 - \frac{Zr}{a_o}\right) = 0 \qquad \text{or} \qquad r = 2\ {}^{a_o}/_{Z} \qquad \text{(2s-node)} \qquad 25.2.2$$

The 2s-orbital has one radial node at $r = 2a_o = 1.06$ Å. The total number of nodes in general is $n - 1$. For the s-orbitals all the nodes are radial nodes. The 3s-orbital has two radial nodes, Figure 25.2.1c. The sign of the wave function changes across each node. The sign of the wave function is often called the **phase**. The change in phase across each node is often depicted as a change in color or gray value in 3D-graphical models of the orbitals.

The radial distribution functions are also plotted in Figure 25.2.1. As the number of radial nodes increases, the curvature increases, and the orbital kinetic energy increases. The radial nodes are a measure of the "wiggliness" of the wave function as the electron moves radially from the nucleus. The orbitals with angular momentum are constructed in an analogous fashion, where the polynomials are represented by the spherical harmonics.

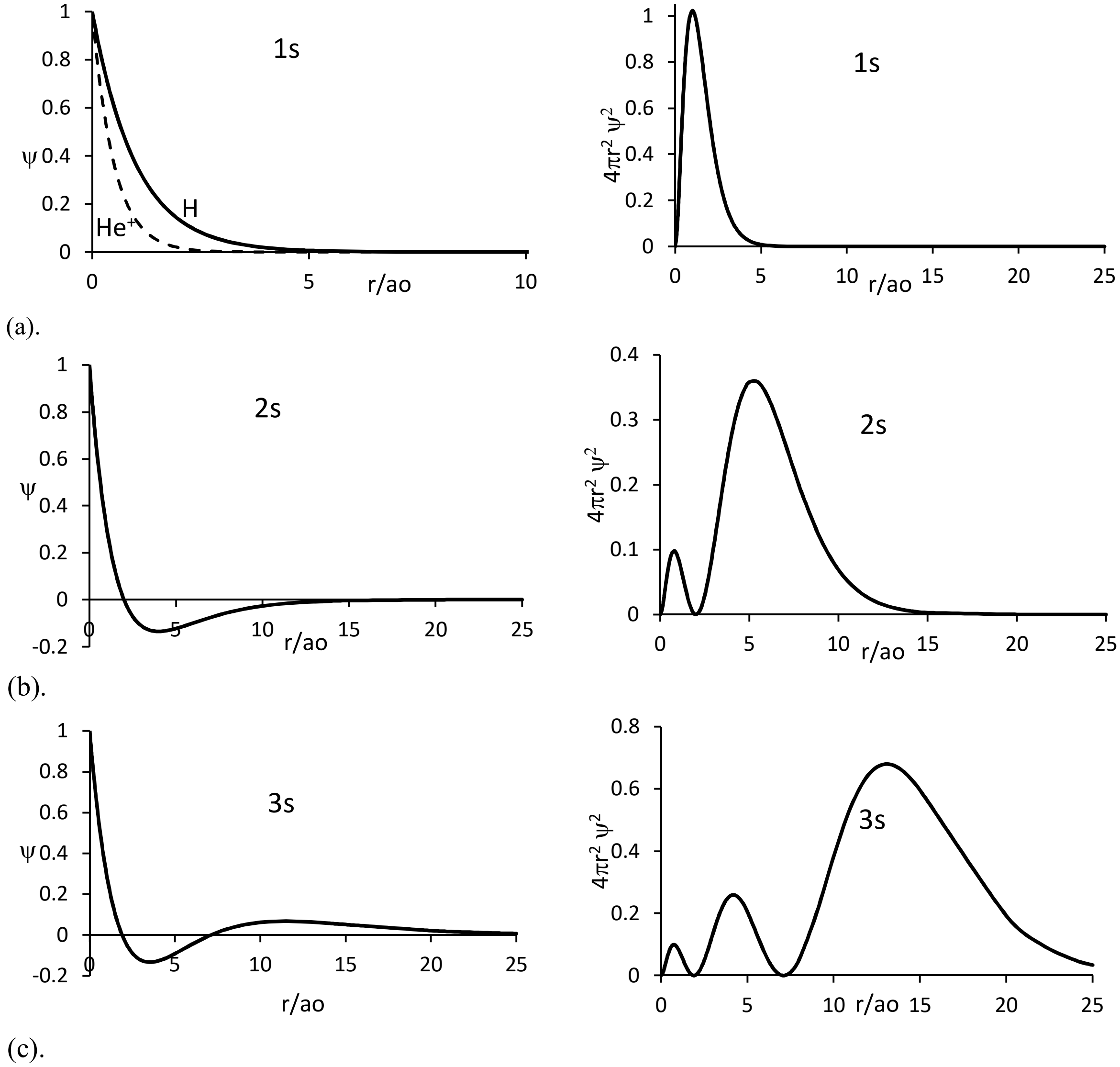


Figure 25.2.1: Hydrogen atom spherical orbitals. (a). Increased nuclear charge contracts the orbitals. (b).-(c). The number of radial nodes is n – 1.

The n = 2 orbitals with angular momentum quantum number $\ell = 1$ and $m_\ell = -1, 0, +1$ are:

$$\Psi_{2pz} = \frac{1}{4\sqrt{2\pi}}\left(\frac{Z}{a_o}\right)^{3/2} e^{-Zr/2ao}\,\frac{Zr}{a_o}\cos\theta \qquad m_\ell = 0 \qquad L_z = 0$$

$$\Psi_{211} = \frac{1}{4\sqrt{2\pi}}\left(\frac{Z}{a_o}\right)^{3/2} e^{-Zr/2ao}\,\frac{Zr}{a_o}\sin\theta\, e^{i\phi} \qquad m_\ell = +1 \qquad L_z = +\hbar$$

$$\Psi_{21-1} = \frac{1}{4\sqrt{2\pi}}\left(\frac{Z}{a_o}\right)^{3/2} e^{-Zr/2ao}\,\frac{Zr}{a_o}\sin\theta\, e^{-i\phi} \qquad m_\ell = -1 \qquad L_z = -\hbar \qquad 25.2.3$$

The spherical harmonics $Y_{1,-1}$, $Y_{1,0}$, and $Y_{1,1}$ used in these equations are taken from Table 24.5.1. The spherical harmonics generate a planar node that passes through the nucleus at either $\theta = 90°$

for $Y_{1,0}$ or $\theta = 0°$ for $Y_{1,-1}$ and $Y_{1,1}$. The angular nodes with $\theta = 0°$ include the z-axis. The node counting is given by:

$$\begin{aligned} &\text{total nodes} = n - 1 \\ &\text{total angular nodes} = \ell \\ &\text{angular nodes that include the z-axis} = m_\ell \\ &\text{radial nodes} = \text{total nodes} - \text{angular nodes} = n - 1 - \ell \qquad 25.2.4 \end{aligned}$$

The number of radial nodes is simply determined by difference; there are only two types of nodes, radial and angular. The angular momentum quantum number, ℓ, may not exceed $n - 1$, since the number of angular nodes may not exceed the total number of nodes. The absolute value of the magnetic quantum number, $|m_\ell|$, may not exceed the angular momentum quantum number, since the number of angular nodes that include the z-axis may not exceed the number of angular nodes. These restrictions are summarized as:

$$n = 0, \ldots, \infty \qquad \ell = 0, \ldots, n - 1 \qquad m_\ell = -\ell, \ldots, 0, \ldots, +\ell \qquad 25.2.5$$

The orbitals with the same principle quantum number form a **shell** of orbitals that are degenerate and have similar average radii. As n increases the average radius of each shell increases. The angular momentum quantum number determines the shape. Orbitals with $\ell = 0$ are "s-type," $\ell = 1$ are "p-type," $\ell = 2$ are "d-type," $\ell = 3$ are "f-type," and alphabetically thereafter skipping the letter j. The magnetic quantum number determines the orientation, relative to the z-axis.

Example 25.2.1: *Orbital Degeneracy*
Find the degeneracy of the n = 1, 2, 3, and 4 principal quantum shells.

Answer: For $n = 1$, ℓ can only be 0 and m_ℓ only 0, giving a degeneracy $g = 1$. The orbitals with the same n and ℓ form a subshell. From Eq. 24.5.39, the degeneracy of the subshell is $2\ell + 1$. For the second principle quantum shell, the orbitals can be s- and p- type, $\ell = 0$ and 1. The shells are listed in Table 25.2.1. The degeneracy is seen to mirror the number of groups in each period of the periodic table. The p-block is $2 \cdot 3$ elements across, the d-block is $2 \cdot 5$ elements across, and the f-block is $2 \cdot 7$ elements across.

The form of the p-orbitals given in Eqs. 25.2.3 is for a non-interacting atom in free space. These orbitals are symmetric about the z-axis. The probability of finding the electron as a function of the ϕ angle is $\Phi^*\Phi = e^{-im_\ell\phi} e^{im_\ell\phi} = 1$. The electron can be found with equal probability at any ϕ around the z-axis. Atoms have no directional preference in free space. When an atom is interacting with other atoms in chemical bonds an alternate form is appropriate. The identities in Eqs. 23.9.11 show that linear combinations of $e^{i\phi}$ and $e^{-i\phi}$ give the real and imaginary parts of a complex number:

$$\frac{e^{i\phi} + e^{-i\phi}}{2} = \frac{(\cos\phi + i\sin\phi) + (\cos\phi - i\sin\phi)}{2} = \cos\phi$$

$$\frac{e^{i\phi} - e^{-i\phi}}{2i} = \frac{(\cos\phi + i\sin\phi) - (\cos\phi - i\sin\phi)}{2i} = \sin\phi \tag{23.9.11}$$

Table 25.2.1. The Orbitals in each Quantum Shell and the Degeneracy.

n	l	m_l	type	subshell degeneracy	shell degeneracy
1	0	0	s	1	g = 1
2	0	0	s	1	
	1	-1, 0, 1	p	3	g = 4
3	0	0	s	1	
	1	-1, 0, 1	p	3	
	2	-2, -1, 0, 1, 2	d	5	g = 9
4	0	0	s	1	
	1	-1, 0, 1	p	3	
	2	-2, -1, 0, 1, 2	d	5	
	3	-3, -2, -1, 0, 1, 2, 3	f	7	g = 16

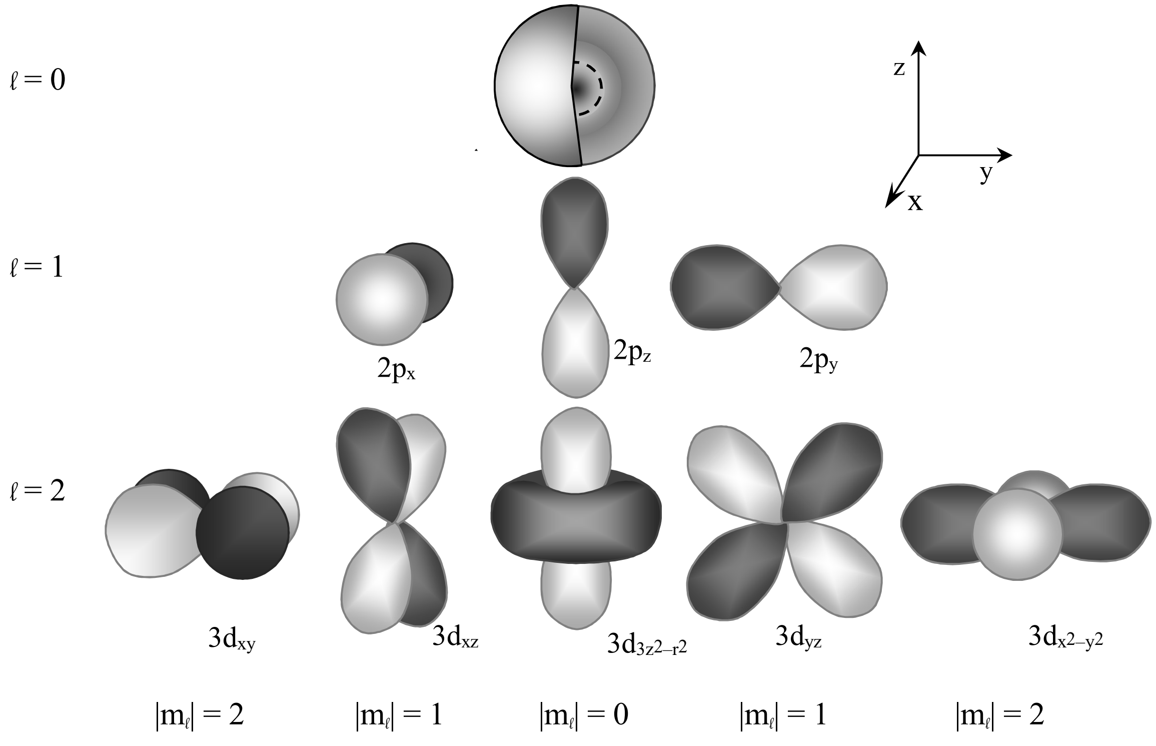


Figure 25.2.2: Oriented forms of the atomic orbitals rendered as probability contour surfaces. The 2s orbital is cut-away to show the radial node.

Real wave functions are generated using linear combinations of the "pure angular momentum" wave functions Ψ_{211} and Ψ_{21-1} using Eqs. 23.9.11. The results are p-orbitals that are oriented along the x- and y-axes, Figure 25.2.2:

$$\Psi_{2px} = \frac{\Psi_{211} + \Psi_{21-1}}{2} = \frac{1}{4\sqrt{2\pi}}\left(\frac{Z}{a_o}\right)^{3/2} e^{-Zr/2ao}\,\frac{Zr}{a_o}\sin\theta\cos\phi$$

$$\Psi_{2py} = \frac{\Psi_{211} - \Psi_{21-1}}{2i} = \frac{1}{4\sqrt{2\pi}}\left(\frac{Z}{a_o}\right)^{3/2} e^{-Zr/2ao}\,\frac{Zr}{a_o}\sin\theta\sin\phi \qquad 25.2.6$$

These linear combinations correspond to a superposition of orbitals with the electron rotating clockwise and counter-clockwise. These "oriented" forms of the orbitals, along with Ψ_{2pz}, are better disposed for constructive overlap with other atoms to form chemical bonds. Ψ_{2px}, Ψ_{2py}, and Ψ_{2pz} are the angular forms of the atomic orbitals that are depicted in General and Organic Chemistry texts, where the principle goal is to understand chemical bonding. Applications in atomic spectroscopy use the "pure angular momentum" forms in Eqs. 25.2.3. The angular portion for the "oriented" forms of atomic orbitals are easy to specify.

Spherical Polar Coordinate Transforms Specify the Angular Portion of "Oriented" Atomic Orbitals: The transformations from spherical polar coordinates to Cartesian coordinates are specified in Eqs. 24.5.14. Comparing to Eqs. 25.2.3, notice that the angular portion of the $2p_z$ orbital is r cos θ, which is equivalent to the z-coordinate. Comparing transformations, Eqs. 24.5.14, and orbitals, Eqs. 25.2.6, also shows correspondences between the angular portions of the $2p_x$ and $2p_y$ orbitals and the x- and y-coordinates:

$$2p_z \Rightarrow r\cos\theta = z \qquad 2p_x \Rightarrow r\sin\theta\cos\phi = x \qquad 2p_y \Rightarrow r\sin\theta\sin\phi = y \qquad 25.2.7$$

We now see why the oriented orbitals are called Ψ_{2px}, Ψ_{2py}, and Ψ_{2pz}. Using the transformations defined in Eqs. 24.5.14, we can rewrite the 2p-orbitals as:

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

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

$$\Psi_{2py} = \frac{1}{4\sqrt{2\pi}}\left(\frac{Z}{a_o}\right)^{3/2} e^{-Zr/2ao}\,\frac{Z}{a_o}\,y \qquad 25.2.8$$

Eqs. 25.2.6 and 25.2.8 can be used interchangeably, as convenience dictates.

We can use the same procedure for specifying the angular portions of the oriented forms of the d-orbitals. The Φ portion of the pure angular momentum forms of the d-orbitals are: $e^{-i2\phi}$, $e^{-i\phi}$, 1, $e^{i\phi}$, $e^{i2\phi}$. The oriented forms are given as products of the Cartesian coordinates, Figure 25.2.2:

$$d_{xz} \Rightarrow xz = r^2 \sin\theta\cos\phi\cos\theta$$

$$d_{yz} \Rightarrow yz = r^2 \sin\theta\sin\phi\cos\theta$$

$$d_{xy} \Rightarrow xy = r^2 \sin\theta\cos\phi\sin\theta\sin\phi = r^2 \sin\theta^2 \cos\phi\sin\phi$$

$$d_{x2\text{-}y2} \Rightarrow x^2 - y^2 = r^2 (\sin^2\theta\cos^2\phi - \sin^2\theta\sin^2\phi)$$

$$d_{z2} = d_{3z2\text{-}r2} \Rightarrow r^2 (3\cos^2\theta - 1) \qquad 25.2.9$$

The d_{xz}, d_{yz}, and d_{xy} orbitals are oriented between the x-z, y-z, and x-y axes, respectively. The lobes of the $d_{x^2-y^2}$ orbital point along the x and y axis. The d_{z^2} orbital points along the z-axis. The d_{z^2} orbital has a unique shape, why? Closed shell atoms are spherical. The functional form of the d_{z^2} orbital is needed to make a sphere from the superposition of all the d-orbitals (Unsöld's Theorem[1]):

$$d_{xz}^2 + d_{yz}^2 + d_{xy}^2 + d_{x^2-y^2}^2 + d_{z^2}^2 = \text{constant} \qquad 25.2.10$$

Assuming the given forms for d_{xz}, d_{yz}, d_{xy} and $d_{x^2-y^2}$, solving for the form of the d_{z^2} angular term gives $r^2 (3 \cos^2\theta - 1)$, as listed in Eqs. 25.2.9. The unique shape of the d_{z^2} orbital is required by symmetry. However, the d_{z^2} is degenerate with the other d-orbitals and has the same average radius. A better symbol for the d_{z^2} orbital might be d_{z^2-1} or $d_{3z^2-r^2}$ to better highlight the geometric relationship.

The d-orbitals each have 2 angular nodes, since $\ell = 2$. Angular nodes are planar nodes passing through the nucleus. The angular nodes for the d_{z^2} orbital are often pictured as planes that have been folded into cones. The magnetic quantum number for d_{z^2} is $m_\ell = 0$; no angular nodes include the z-axis. The other oriented d-orbitals do not have pure m_ℓ quantum numbers; each is a linear combination of pure angular momentum orbitals with $\pm m_\ell$. The absolute value of m_ℓ in the superposition can be specified and is equal to the number of angular nodes that include the z-axis. The d_{xz} and d_{yz} orbitals are for $|m_\ell| = 1$ and have one node that includes the z-axis. The d_{xy} and $d_{x^2-y^2}$ orbitals are for $|m_\ell| = 2$ and have two nodes that include the z-axis, which is the maximum possible. The nodal relationships reinforce the importance of angular momentum in determining the overall properties of the atom.

The Atom can have Orbital Angular Momentum: The angular momentum of an electron in an orbtial is given by Eq. 25.1.6 with magnitude:

$$|L| = \hbar \sqrt{\ell(\ell + 1)} \qquad (24.5.34) \quad 25.2.11$$

Atomic orbitals can correspondingly be depicted using angular momentum vector diagrams. The vector diagram for the 2p-orbitals is shown in Figure 24.6.1b. The m_ℓ quantum number is called the magnetic quantum number because the degeneracy of the m_ℓ levels is lifted in the presence of a magnetic field. The different m_ℓ sub-levels are at different energies in an external magnetic field. In summary, the angular momentum quantum numbers have energetic consequences in addition to determining the shape and orientation of the orbitals through the disposition of the nodes. Table 25.1.1 shows that the shape of the periodic table results from the quantum properties of angular momentum. In single-electron atoms and ions, the sub-shells with different ℓ values are degenerate. In multi-electron atoms the influence of electron-electron repulsions breaks this degeneracy. We now proceed to discuss the rest of the periodic table.

The Intrinsic Angular Momentum of the Electron gives the Fourth Quantum Number: The intrinsic angular momentum quantum number of the electron is s = ½, Sec. 24.5. Accordingly, the hydrogen atom has two different types of angular momentum, orbital angular momentum and the intrinsic spin of the electron. The complete specification of the electronic state of the hydrogen atom requires the specification of the z-axis projection of the intrinsic angular momentum of the electron, with $m_s = \pm\frac{1}{2}$:

$$S_z = \hbar m_s \qquad 25.2.12$$

In the absence of an external magnetic field, the two spin states for the ground state of the hydrogen atom are degenerate. The overall degeneracy of the principle quantum shells is then 2, 8, 18, and 32 for n = 1, 2, 3, and 4, respectively, Table 25.2.1. In summary, four quantum numbers are required to specify the electronic state of the hydrogen atom, one for each spatial coordinate and one for the intrinsic spin of the electron. The spin angular momentum of the electron and the orbital angular momentum can interact; this coupling is discussed in Sec. 25.6.

25.3 Multi-Electron Atoms

The next atom in the periodic table is helium, with two protons and two electrons. The electronic structure of helium sets the stage for understanding the rest of the periodic table. The potential energy function for the helium atom includes the attraction of electron 1 for the nucleus, the attraction of electron 2 for the nucleus, and the electron-electron repulsion between the two electrons, Figure 25.3.1:

$$\hat{V}(r) = \frac{1}{4\pi\varepsilon_o}\left(-\frac{2e^2}{r_1} - \frac{2e^2}{r_2} + \frac{e^2}{r_{12}}\right) \qquad 25.3.1$$

where r_1 is the distance from electron 1 to the nucleus, r_2 is the distance from electron 2 to the nucleus, and r_{12} is the distance between the two electrons.

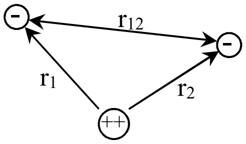


Figure 25.3.1: The two electrons in the helium atom experience electron-electron repulsion.

The Schrödinger equation for the helium atom is:

$$\frac{-\hbar^2}{2m}\left(\nabla_1^2 + \nabla_2^2\right)\Psi + \frac{1}{4\pi\varepsilon_o}\left(-\frac{2e^2}{r_1} - \frac{2e^2}{r_2} + \frac{e^2}{r_{12}}\right)\Psi = E\Psi \qquad 25.3.2$$

This Schrödinger equation cannot be solved exactly; no three-body problem has yet been solved exactly. The electron-electron repulsion term is the cause of the problem. We must develop approximation techniques to solve for the electronic structure of multi-electron atoms. We will progress from the simplest approximation to the most common approximation techniques used in electronic structure methods. The simplest approach is to ignore the electron-electron repulsion. The results are not quantitatively useful, but the neglect of electron-electron repulsion acts as the basis for more exact approaches.

Independent Electron Approximation: The neglect of the electron-electron repulsion, the "e^--e^-" term, allows the approximate Schrödinger equation to be solved exactly to find the atomic orbitals for the helium atom. The motion of the two electrons is uncorrelated in the absence of the interaction and the two electrons act independently. The result is called the **independent electron approximation**. The Hamiltonian then rearranges into a term only in the coordinates of electron 1 and a term only in the coordinates of electron 2:

$$\left(-\frac{\hbar^2}{2m}\nabla_1^2 - \frac{2e^2}{4\pi\varepsilon_o r_1}\right)\Psi + \left(-\frac{\hbar^2}{2m}\nabla_2^2 - \frac{2e^2}{4\pi\varepsilon_o r_2}\right)\Psi(r_1,r_2) = E\Psi(r_1,r_2) \qquad 25.3.3$$

The term for electron 1 is identical to the Hamiltonian for the hydrogen atom written in terms of r_1, but with the charge on the nucleus of $Z = 2$. The term for electron 2 is identical to the Hamiltonian for the hydrogen atom written in terms of r_2, but with the charge on the nucleus of $Z = 2$. The Schrödinger equation is separable in the coordinates for the two electrons, giving the wave function as the product of two one-electron hydrogen-like atomic orbitals:

$$\Psi(r_1,r_2) = \Psi_1(r_1)\,\Psi_2(r_2) \qquad 25.3.4$$

The one-electron wave functions are solutions to the one-electron Schrödinger equations:

$$\left(-\frac{\hbar^2}{2m}\nabla_1^2 - \frac{2e^2}{4\pi\varepsilon_o r_1}\right)\Psi_1(r_1) = E_1\Psi_1(r_1) \qquad 25.3.5$$

$$\left(-\frac{\hbar^2}{2m}\nabla_2^2 - \frac{2e^2}{4\pi\varepsilon_o r_2}\right)\Psi_2(r_2) = E_2\Psi_2(r_2) \qquad 25.3.6$$

In the Schrödinger equation, note that ∇_1^2 only operates on the coordinates of electron 1 and ∇_2^2 only operates on the coordinates of electron 2:

$$\nabla_1^2\,\Psi_1(r_1)\,\Psi_2(r_2) = \Psi_2(r_2)\,\nabla_1^2\,\Psi_1(r_1)$$
$$\nabla_2^2\,\Psi_1(r_1)\,\Psi_2(r_2) = \Psi_1(r_1)\,\nabla_2^2\,\Psi_2(r_2) \qquad 25.3.7$$

Accordingly, substituting Eq. 25.3.4 for the wave function into Eq. 25.3.3 gives:

$$\Psi_2(r_2)\left(-\frac{\hbar^2}{2m}\nabla_1^2 - \frac{2e^2}{4\pi\varepsilon_o r_1}\right)\Psi_1(r_1) + \Psi_1(r_1)\left(-\frac{\hbar^2}{2m}\nabla_2^2 - \frac{2e^2}{4\pi\varepsilon_o r_2}\right)\Psi_2(r_2) = E\,\Psi_1(r_1)\Psi_2(r_2) \qquad 25.3.8$$

Since Ψ_1 and Ψ_2 are eigenfunctions of the one-electron Hamiltonians, substituting Eqs. 25.3.5 and 25.3.6 into the last equation gives the sum of two terms:

$$\Psi_2(r_2)\,E_1\,\Psi_1(r_1) + \Psi_1(r_1)\,E_2\,\Psi_2(r_2) = E\,\Psi_1(r_1)\,\Psi_2(r_2) \qquad 25.3.9$$

All the derivatives have been completed, only multiplicative functions remain, so we can divide through by the common factors to give:

$$E = E_1 + E_2 \qquad 25.3.10$$

This equation is an important point. In the independent electron approximation, the wave functions for the multi-electron atoms are the products of one-electron wave functions and the energies of the one-electron wave functions add to give the total atom energy.

In the independent electron approximation: one-electron orbitals multiply and energies add.

The electronic probability distribution is given by the square of the overall atomic wave function:

$$\Psi^2(r_1,r_2) = \Psi_1^2\,(r_1)\,\Psi_2^2\,(r_2) \qquad 25.3.11$$

The exact solutions to the one-electron Hamiltonians, Eqs. 25.3.5 and 25.3.6, are the hydrogen-like one-electron orbitals:

$$\Psi_1(r_1) = \frac{1}{\sqrt{\pi}}\left(\frac{Z}{a_o}\right)^{3/2} e^{-Zr_1/a_o} \qquad \Psi_2(r_2) = \frac{1}{\sqrt{\pi}}\left(\frac{Z}{a_o}\right)^{3/2} e^{-Zr_2/a_o} \qquad 25.3.12$$

with Z = 2 for helium. The one-electron energies add, using Eq. 25.1.23:

$$E_{He} = -\ 13.6\ eV \left(\frac{Z^2}{n_1^2} + \frac{Z^2}{n_2^2}\right) = -13.6\ eV \left(\frac{2^2}{1^2} + \frac{2^2}{1^2}\right) = -108.8\ eV \qquad (Z = 2) \qquad 25.3.13$$

We can now compare to experiment. The **ionization energy** or **ionization potential** is the energy necessary to remove an electron from an atom or ion. The reference energy zero is for $n \rightarrow \infty$. The completely separated nucleus and all electrons corresponds to zero energy. Using this energy reference, the experimental electronic energy of an atom is determined by the negative sum of the sequential ionization energies:

$He \rightarrow He^+ + e^-$ $\quad I_1 = 24.58$ eV
$He^+ \rightarrow He^{2+} + e^-$ $\quad I_2 = 54.42$ eV
$He^{2+} + 2\ e^- \rightarrow He$ $\quad E_{He,exp} = -\ (I_1 + I_2) = -79.00$ eV 25.3.14

Ionization energies of neutral atoms are positive, $I_1 > 0$, because energy is required to remove an electron from an atom. Compared to the zero reference, the electronic energy of the atom is negative, giving the negative sign in Eq. 25.3.14. The agreement between the predicted electronic energy using the independent electron approximation, -108.8 eV, and the experimental value, -79.00 eV, is disappointing. We must conclude that electron-electron repulsion is a significant factor in atomic energies, and cannot be neglected. However, the independent electron approximation is a good reference point for more exact theories. In particular, most theories adopt the form of Eq. 25.3.4. The wave function for a multi-electron atom is approximated as the product of one-electron orbitals, which is called the **orbital approximation**. Using the orbital approximation, we now need to find methods that include the effects of electron-electron repulsion.

Perturbation Method: A perturbation is a small change that is imposed upon a system. The perturbation method is useful when the Hamiltonian can be split into two parts, a part that can be solved exactly and a part that is a small perturbation. Let $\hat{\mathcal{H}}^{(o)}$ be the unperturbed Hamiltonian and $\hat{\mathcal{H}}'$ the perturbation. The strength of the perturbation is scaled by the constant λ to allow the effect of the perturbation to be investigated from no perturbation for λ = 0 to the full effect of the perturbation for λ = 1:

$$\hat{\mathcal{H}} = \hat{\mathcal{H}}^{(o)} + \lambda\ \hat{\mathcal{H}}' \qquad 25.3.15$$

The λ constant is called the **perturbation parameter**, which can be thought of as the volume control on a radio playing music that your roommate dislikes: λ ranges from no perturbation to full-bore aggravation. The wave functions, $\Psi_i^{(o)}$, are the solutions to the unperturbed Hamiltonian for the state of interest, i:

$$\hat{\mathcal{H}}^{(o)}\ \Psi_i^{(o)} = E_i^{(o)}\ \Psi_i^{(o)} \qquad 25.3.16$$

The perturbation approach is useful if the change in energy caused by the perturbation is small compared to the unperturbed energy. The perturbation method is generally useful. For the particular case of the helium atom, we consider the electron-electron repulsion term as a perturbation to the orbitals obtained by the independent electron approximation, Figure 25.3.2.

The energy of the system is expanded in a power series in λ:

$$E_i \cong E_i^{(0)} + \lambda E_i^{(1)} + \lambda^2 E_i^{(2)} + \ldots \qquad 25.3.17$$

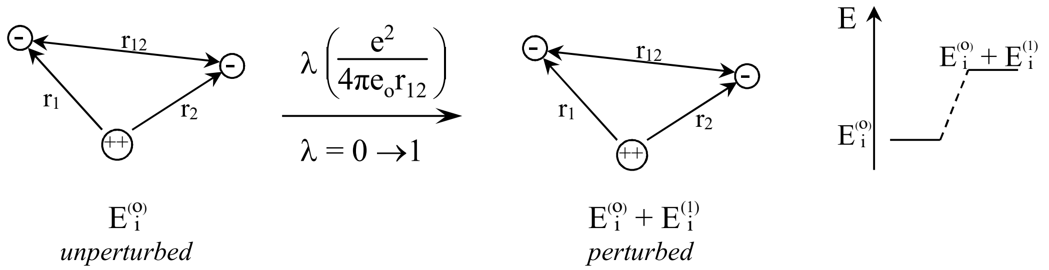


Figure 25.3.2: The electron-electron repulsion can be treated as a perturbation on the independent electron approximation.

For small values of λ, the expansion can be truncated at the first correction term, $E_i^{(1)}$. The result is called **first-order perturbation theory**. The first-order correction to the energy is given by the expectation value of the perturbation Hamiltonian:

$$E_i^{(1)} = <\mathcal{H}'> = \int \Psi_i^{(0)*}\, \hat{\mathcal{H}}'\, \Psi_i^{(0)}\, d\tau \qquad 25.3.18$$

This integral is evaluated using the unperturbed wave functions, Eq. 25.3.16. Formally, λ is the basis for the power series expansion. In practical applications, we set $\lambda = 1$ to find the full perturbation correction. Higher order corrections can also be determined. Perturbation corrections up to fourth order are not uncommon in electronic structure calculations that include the effects of electron-electron correlation.

The unperturbed energy for the He atom is given by Eq. 25.3.13 using $Z = 2$ for the nuclear charge, giving $E_{gs}^{(0)} = -108.8$ eV. The first order perturbation result, assuming the full perturbation with $\lambda = 1$, adds the expectation value of the electron-electron repulsion. The expectation value for the electron-electron repulsion for the ground state of the helium atom is evaluated in Addendum 25.7 giving the total electronic energy of the ground state of He as:

$$E_{gs} \cong E_1 + E_2 + \left\langle \frac{e^2}{4\pi\varepsilon_o r_{12}} \right\rangle = -74.0 \text{ eV} \qquad 25.3.19$$

Compared to the experimental value of -79.0 eV, the perturbation method gives a considerable improvement over the independent electron approximation. However, an error of 5 eV is too large to be useful for applications in chemical bonding.

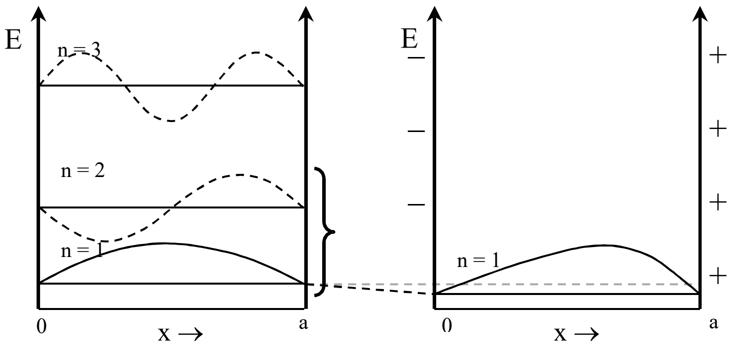
The wave function can also be corrected for the perturbation. The first-order correction to the wave function is:

$$\Psi_i^{(1)} \cong \Psi_i^{(0)} + \lambda \sum_{k \neq i} \frac{\mathcal{H}'_{ki}}{E_i^{(0)} - E_k^{(0)}} \Psi_k^{(0)} \qquad 25.3.20$$

The integral $\mathcal{H}'_{ki}$ is taken between the state of interest, i, and all other states k with the perturbation Hamiltonian:

$$\mathcal{H}'_{ki} = \int \Psi_i^{(0)*}\, \hat{\mathcal{H}}'\, \Psi_k^{(0)}\, d\tau \qquad 25.3.21$$

The corrected wave function, $\Psi_i^{(1)}$, is a combination of all the wave functions for the system for which the $\mathcal{H}'_{ki}$ integrals don't vanish. The denominator in the sum scales each term by the difference in energy between the state of interest and the various other states. The wave functions that are closest in energy to i are most important. For a diagrammatic example, consider the ground state of an electron in a box that is placed in an external electric field, Figure 25.3.3. The electron density is skewed towards the positive electrode. This change in the wave function shape is obtained by mixing in small amounts of the n = 2 wave function to the ground state. The n = 3 wave function does not contribute, because it is symmetrical with respect to the center of the box and does not skew the electron density.



unperturbed *perturbed*

Figure 25.3.3: The first order correction mixes excited state character into the unperturbed wave function. For a particle in a box in an external electric field, mixing small amounts of the n = 2 wave function into the ground state skews the electron distribution in response to the perturbation. Low energy excited states contribute more to the correction than high energy excited states.

The first-order correction for the ground state of the helium atom provides a big improvement, compared to the independent electron approximation. However, for the ground state of the helium atom and for atomic and molecular orbital treatments in general, the variation method is often preferable. The variation method is not restricted to small perturbations.

Variation Method: If you guess a solution to the Schrödinger equation, how do you determine how good a guess you have made? For example, the Schrödinger equation for the ground state of the helium atom can't be solved exactly, Eq. 25.3.2. However, we can guess that products of one-electron hydrogen like orbitals are reasonable approximate solutions. We know that the independent electron approximation, where the wave functions use the full nuclear charge of $Z = 2$, is quantitatively poor. However, might we be able to obtain a better approximate solution if the full nuclear charge of the nucleus is replaced by an effective nuclear charge, Z_{eff}? With this approximation the electron-electron repulsion is modeled as a shielding interaction, where the electrons shield each other from the full nuclear attraction. Shielding corresponds to $Z_{eff} < Z$.

First, consider the general case with an exact Hamiltonian $\hat{\mathcal{H}}$, for which we have a series of approximate wave functions, ϕ_1, ϕ_2, and ϕ_3. These guesses are called **trial wave functions**. How do we determine the best trial wave function? If we had the exact wave functions, they would be eigenfunctions of the exact Hamiltonian:

$$\hat{\mathcal{H}}\Psi_i = E_i\,\Psi_i \qquad \text{(exact)} \qquad 25.3.22$$

The approximate wave functions are <u>not</u> eigenfunctions of the Hamiltonian. Expectation values must be used to determine the energies that correspond to the trial wave functions. The expectation value of the Hamiltonian gives the average total energy. To set the stage, consider determining the expectation values of the energy using the exact wave functions from Eqs. 23.7.11 (Postulate III) and 25.3.22:

$$<E> = \frac{\int \Psi_i^*\,\hat{\mathcal{H}}\Psi_i\,d\tau}{\int \Psi_i^*\,\Psi_i\,d\tau} = \frac{\int \Psi_i^*\,E_i\,\Psi_i\,d\tau}{\int \Psi_i^*\,\Psi_i\,d\tau} = E_i \qquad \text{(exact)} \qquad 25.3.23$$

The expectation value reduces to the exact energy, since the exact wave functions are eigenfunctions of the Hamiltonian:

$$E_i = \frac{\int \Psi_i^*\,\hat{\mathcal{H}}\Psi_i\,d\tau}{\int \Psi_i^*\,\Psi_i\,d\tau} \qquad \text{(exact)} \qquad 25.3.24$$

If instead, a trial wave function is used in the expectation integrals, the **trial energy** E^ϕ results:

$$E^\phi = \frac{\int \phi^*\hat{\mathcal{H}}\phi\,d\tau}{\int \phi^*\phi\,d\tau} \qquad 25.3.25$$

The exact Hamiltonian is used in the integral. Calculated in this way, the trial energy is guaranteed to be greater than or equal to the exact energy by the **Variation Theorem**:

$$E^\phi \geq E_i \qquad 25.3.26$$

The trial wave function that gives the lowest energy is best, Figure 25.3.4.

Reflect for a moment on the situation if the Variation Theorem did not hold. If an improved trial wave function gave a lower energy than the previous guess, then nothing could be concluded. The new trial energy might be significantly lower than the exact energy and a correspondingly poorer approximation than the previous guess.

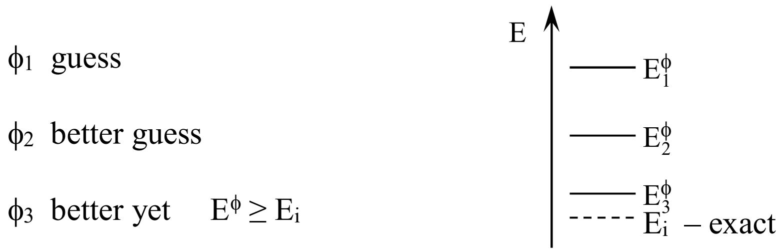


Figure 25.3.4: The trial wave function that gives the lowest energy, as calculated from the expectation integral of the exact Hamiltonian, is best.

For the specific case of the ground state of the helium atom in the orbital approximation, the product of the one-electron hydrogen like orbitals with effective nuclear charge Z_{eff} is given as:

$$\phi_{gs} = \phi_{1s}(r_1)\ \phi_{1s}(r_2) = \frac{1}{\pi}\left(\frac{Z_{eff}}{a_o}\right)^3 e^{-Z_{eff}\, r_1/a_o}\ e^{-Z_{eff}\, r_2/a_o} \qquad 25.3.27$$

Z_{eff} is an example of a **variation parameter**. The trial energy is evaluated in Addendum 25.7 giving for the ground state of the He atom:

$$E^{\phi} = \frac{\int \phi_{gs}^{*}\ \hat{\mathscr{H}}\ \phi_{gs}\ d\tau}{\int \phi_{gs}^{*}\ \phi_{gs}\ d\tau} = \frac{e^2}{4\pi\varepsilon_o\, a_o}\left(Z_{eff}^2 - \frac{27}{8}\, Z_{eff}\right) \qquad 25.3.28$$

The best value for the variation parameter gives the minimum energy. Taking the derivative of the trial energy with respect to Z_{eff} and setting the result equal to zero gives:

$$\frac{dE^{\phi}}{dZ_{eff}} = 0 = \frac{e^2}{4\pi\varepsilon_o\, a_o}\,(2\, Z_{eff} - {}^{27}/_{8}) \qquad 25.3.29$$

$$Z_{eff} = {}^{27}/_{16} = 1.6875 \qquad 25.3.30$$

The effective nuclear charge is less than the full nuclear charge. The two electrons in the 1s-orbital of the helium atom shield each other from the full nuclear charge. This approximation is often called the **effective charge model** of electron-electron repulsion. Substituting Z_{eff} back into Eq. 25.3.13 or Eq. 25.3.28 gives the approximate ground state energy of the helium atom as:

$$E_{gs} = -\ 13.6\ eV(Z_{eff}^2/n_1^2 + Z_{eff}^2/n_2^2) = -77.5\ eV \qquad 25.7.31$$

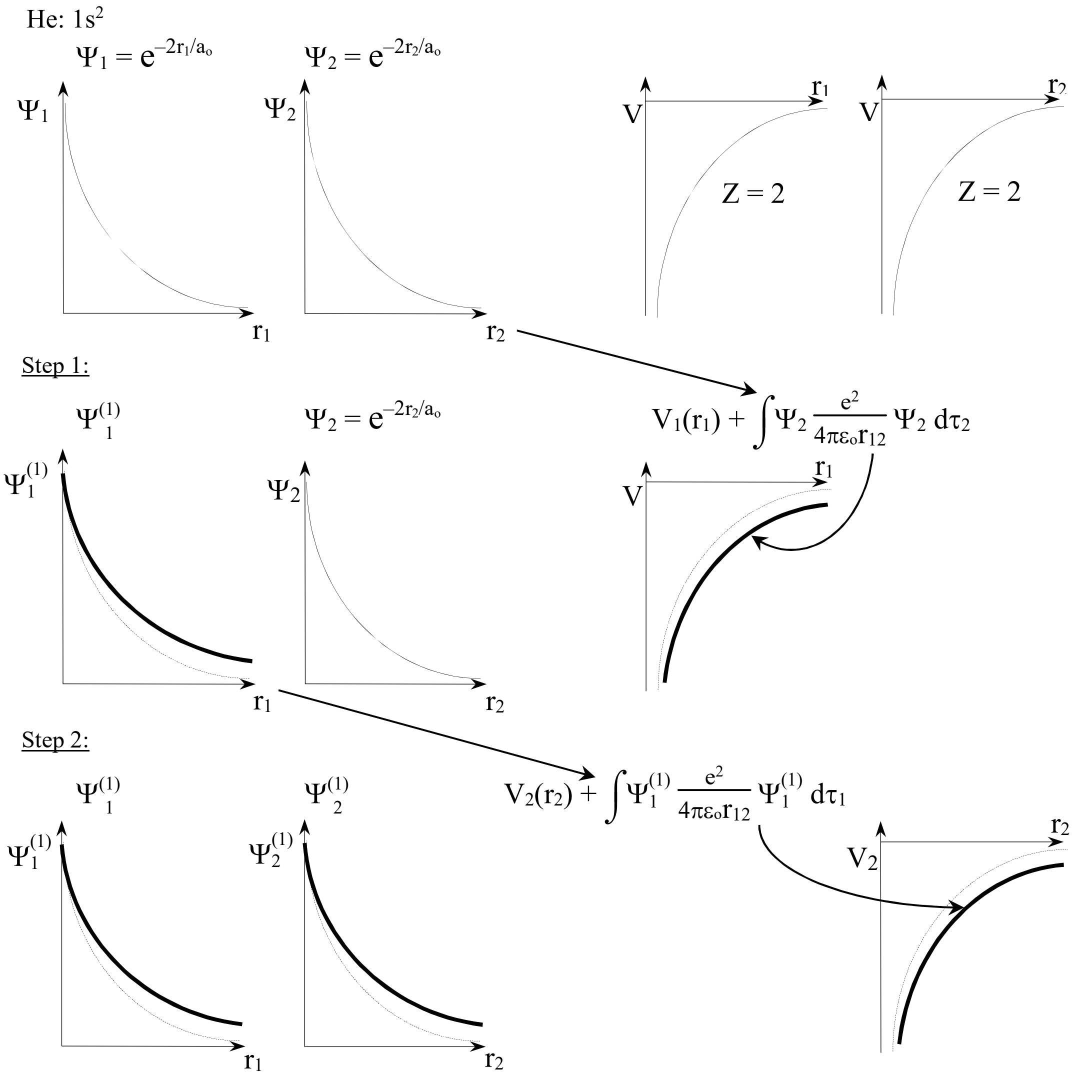
The experimental energy is -79.0 eV, so the variation approximation gives a greatly improved energy as compared to the independent electron approximation or the perturbation approach. Unfortunately, an error of 1.5 eV is still too large to be useful for applications in chemical bonding. A more accurate approximation method is required. Self-consistent field theory is the best approximation technique in common use for electronic structure calculations. The self-consistent field approach is based on the Variation Theorem. If the Variation Theorem applies to an approximation technique, that technique is said to be **variational**.

25.4 Self-Consistent Field Theory

Shielding of the Nuclear Charge and Electron-Electron Repulsion: In the **self-consistent field** approach, the Schrödinger equation is solved iteratively for the one-electron effective potential energy and wave function for each electron. An initial guess is made for the wave function of each electron. For the helium atom, this guess is made within the orbital approximation with the full nuclear charge, Z = 2. An effective potential energy function for electron 1 is then determined by averaging the electron-electron repulsion of the two electrons over the wave function for electron 2 for a series of r_1 values, Figure 25.4.1 Step 1:

$$V_{eff}(r_1) = V_1(r_1) + \int \Psi_2\ \frac{e^2}{4\pi\varepsilon_o r_{12}}\ \Psi_2\ d\tau_2 \qquad 25.4.1$$

where $V_1(r_1)$ is the Coulomb attraction of electron 1 for the nucleus. The effective potential is then integrated to give an improved wave function for electron 1, $\Psi_1^{(1)}$.



Repeat until converged: insignificant changes on subsequent iterations.

Figure 25.4.1: Self-consistent field calculations are iterative. The expectation value of the electron-electron repulsion is averaged over the coordinates of the opposite electron.

The improved wave function of electron 1 is then used to calculate the average electron-electron repulsion for electron 2 at a series of r_2 values, Figure 25.4.1 Step 2:

$$V_{eff}(r_2) = V_2(r_2) + \int \Psi_1^{(1)} \frac{e^2}{4\pi\varepsilon_o r_{12}} \Psi_1^{(1)} \, d\tau_1 \qquad 25.4.2$$

where $V_2(r_2)$ is the Coulomb attraction of electron 2 for the nucleus. The effective potential for electron 2 is then integrated to give an improved wave function for electron 2, $\Psi_2^{(1)}$. At this point, the wave functions for the two electrons are not comparable. The potential for electron 2 is based on a better approximation for the effective potential than for electron 1. Steps 1 and 2 are then repeated with the new wave functions to improve the solution for both electrons, giving an iterative process. The steps are repeated until the energy of the orbitals change by an insignificant amount from one iteration to the next. The overall process is variational; we are guaranteed that a minimum energy result gives the best approximation to the final approximate wave functions. The iterative approach guarantees that the two electrons are treated equivalently.

The self-consistent field, or SCF, approach can be realized in several ways. In Douglas Hartree's original method, the resulting atomic orbitals are numerical tables of the wave function amplitude as a function of r_1. This numerical integration, while most accurate, is computationally demanding. The resulting wave functions are not as easily interpreted as are closed-form functions, such as $\Psi_1 = N\ e^{-Zr_1/a_o}$. A more common and less demanding approach is to use closed-form orbitals based on variational coefficients that are optimized through the SCF procedure to give the minimum energy. For example, hydrogen-like orbitals can be used with an effective nuclear charge, Z_{eff}. The Hartree-SCF method neglects several important contributions to the overall electronic energy of the atom: the exchange energy, correlation energy, and spin-orbit coupling. We will address each of these deficiencies later in this chapter and the next. However, the Hartree method gives several important results.

Electron-Electron Repulsion Breaks the Orbital Degeneracy: Careful Hartree-SCF calculations show that the degeneracy of the orbitals with the same principle quantum number is broken for multi-electron atoms, Figure 25.4.2. For a given n, the orbital ordering is s < p < d < f. This effect can be explained using the effective charge model.

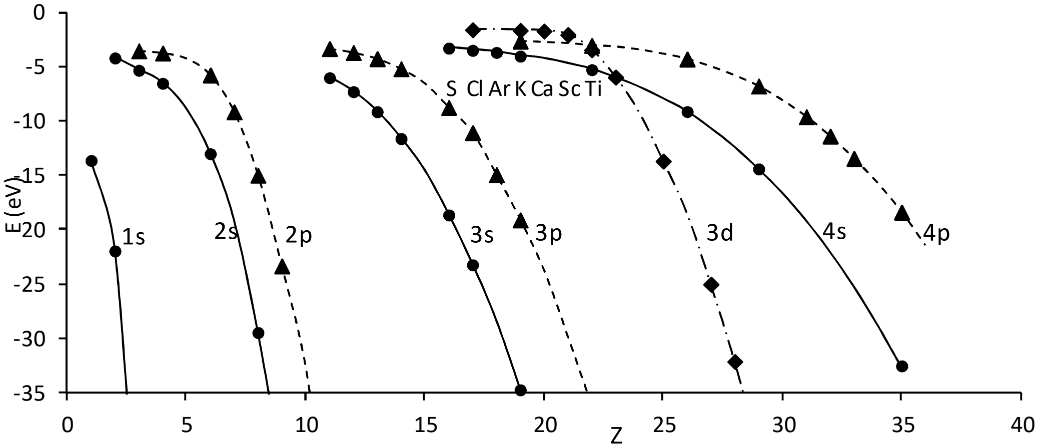


Figure 25.4.2: Atomic orbital energies from self-consistent field calculations.[2] Plotting symbols: s-orbitals •——, p-orbitals ▲- - - , 3d-orbtial ♦–·–.

Consider the 2s and 2p-orbitals, Figure 25.4.3a. The radial node for the s-orbital increases the electron density close to the nucleus for the 2s-orbital as compared to the 2p. This effect is called **orbital penetration**. The electrons in a 2s-orbital penetrate closer to the nucleus and feel a greater effective nuclear charge. The 1s-electrons are not as efficient in shielding the 2s-electrons from the full nuclear charge as compared to the 2p-electrons. The same effect is seen for third period elements with 3s, 3p, and 3d valence orbitals, Figure 25.4.3b. The inner core electrons are the 1s, 2s, and 2p for the third period. These inner core electrons are effective shielders for the valence electrons. The result is that low ℓ orbitals penetrate closer to the nucleus and feel a greater effective nuclear charge than high ℓ orbitals, in the order $Z_{eff,3s} > Z_{eff,3p} > Z_{eff,3d}$. The orbital energies are correspondingly 2s < 2p, 3s < 3p < 3d, and 4s < 4p < 4d < 4f.

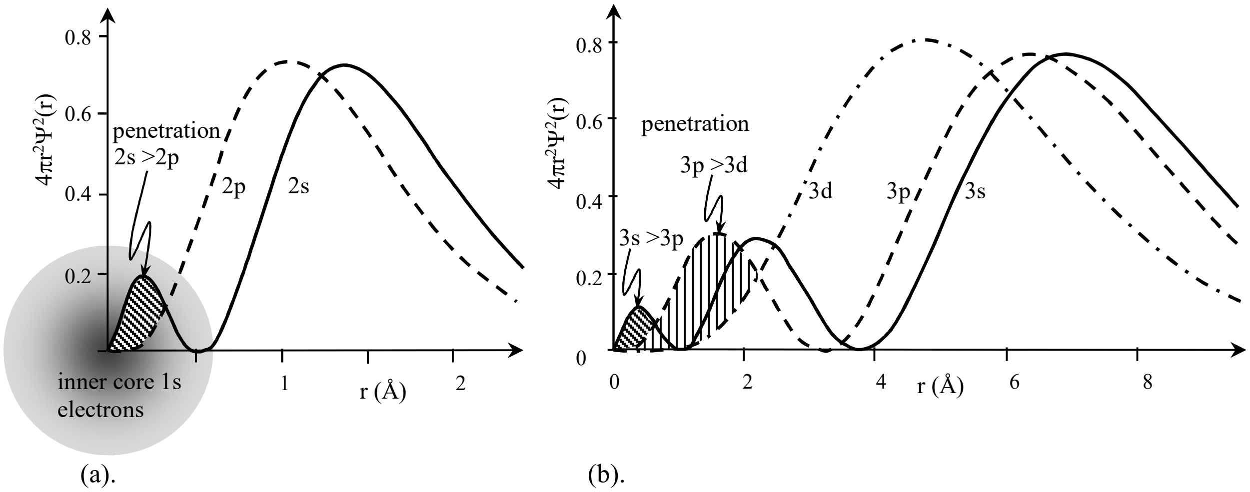


Figure 25.4.3: Low ℓ orbitals penetrate closer to the nucleus and feel a greater effective nuclear charge than high ℓ orbitals. (a). The 1s-electrons shield the 2s and 2p electrons from the full nuclear charge. (b). The 1s, 2s, and 2p-electrons shield the 3s, 3p, and 3d electrons from the full nuclear charge. Because of decreasing penetration, Z_{eff} (3s) > Z_{eff}(3p) > Z_{eff}(3d).

Reference to Figure 25.4.2 also shows that the inner core orbitals decrease in energy faster than outer valence orbitals with increasing Z. The inner core orbitals are closer to the nucleus and are less efficiently shielded than valence electrons, which are furthest on average from the nucleus. The Z_{eff} of the inner core electrons more closely parallels the full nuclear charge, Z, than the outer valence electrons. For the valence electrons, the completed shells of core electrons are efficient shielders, thus decreasing the effective nuclear charge of the valence electrons. We are now ready to predict the electronic configuration of the elements.

Pauli Exclusion Principle and Electron Spin: Careful analysis of atomic spectra led Wolfgang Pauli in 1925 to propose that no two electrons can have the same set of quantum numbers. The result is that the maximum number of electrons in a given orbital is two, one spin up and one spin down, with quantum numbers $m_s = +½$ and $-½$. As a consequence of the Pauli Exclusion Principle and the orbital energy ordering, the configurations of the alkali and alkaline earth elements have valence s-configurations, while B and Al have a single p-electron:

Li: $1s^22s^1$	Be: $1s^22s^2$	B : $1s^2\,2s^22p^1$
Na: $1s^22s^22p^63s^1$	Mg: $1s^22s^22p^63s^2$	Al: $1s^22s^22p^63s^23p^1$

For the fourth period, the 4s orbital is lower in energy than the 3d orbital at the beginning of the period, Figure 25.4.4. Figure 25.4.2 shows 4s below 3d for K, Ca, Sc, and Ti. As a result, the configurations for K and Ca have filled 4s orbitals, but not 3d. After filling the 4s orbitals, subsequent electrons fill the 3d sub-shell. The same ordering is seen in subsequent periods:

K : [Ar] $4s^1$	Ca: [Ar] $4s^2$	Sc: [Ar] $4s^23d^1$	Ti: [Ar] $4s^23d^2$
Rb: [Kr] $5s^1$	Sr: [Kr] $5s^2$	Y : [Kr] $4d^15s^2$	Zr: [Ar] $4d^25s^2$

To simplify configurations, a filled core is indicated by the corresponding noble gas configuration, e.g. [Ar] ≡ $1s^22s^22p^63s^23p^6$ and [Kr] ≡ $1s^22s^22p^63s^23p^63d^{10}4s^24p^6$. For the fourth period starting with V, the orbital energies return to principle quantum number order. These energy effects are the result of electron-electron repulsion.

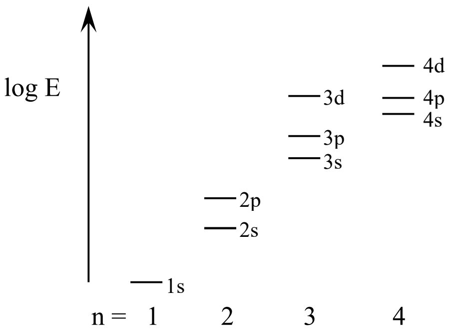
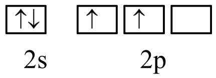


Figure 25.4.4: Relative orbital energies for K (Z = 19) and Ca (Z = 20). The log energy axis allows the core and valence orbital energies to be plotted on the same convenient scale.

Hund's First Rule Applies to Degenerate Sub-Shells: From empirical observation of atomic spectra, Friedrich Hund in 1927 proposed the rule: for a degenerate set of orbitals, the electron-electron repulsion is minimized when the electrons occupy different orbitals and have the same spin quantum number. Orbitals in the same subshell have distinctly different spatial distribution, as required by orthogonality. Placing electrons in different orbitals in the same subshell increases the average distance between the electrons, which in turn minimizes electron-electron repulsion. In addition, electrons with the same spin "avoid" each other. The probability of finding two electrons with parallel spins at the same spot is zero, which is required by wave function symmetry as discussed below. This quantum mechanical avoidance increases the average distance between electrons with parallel spins, which in turn minimizes electron-electron repulsion. For example, the configuration of carbon has two unpaired electrons:

C : $1s^2 2s^2 2p^2$



The Aufbau Principle Predicts the Configuration of the Elements: The ground state configurations of the atoms are predicted using the **Aufbau Principle**. Aufbau is German for "building up." The general rules that we have discussed are summarized as:

A. Electrons fill the orbitals of lowest energy.
B. Pauli Exclusion Principle: no two electrons can have the same set of quantum numbers.
C. Hund's First Rule: For a degenerate set of orbitals, the electron-electron repulsion is minimized when the electrons occupy different orbitals and have the same spin quantum number.

To determine the orbital energies we make the following observations on the effective nuclear charge, which are based on insights from SCF calculations and Hund's First Rule.

As Z increases:
(1). Inner orbitals decrease in energy faster than outer orbitals.

(2). Each successive shell is shielded to a greater extent by previous shells. For increasing principle quantum number, Z_{eff} does not increase as quickly as Z.

(3). Given the same principle quantum number, orbitals with low ℓ penetrate closer to the nucleus and feel a greater Z_{eff} than orbitals with high ℓ.

(4). Electrons in the same subshell have the same average radius and therefore don't shield each other well. Z_{eff} for electrons with the same n and ℓ increase with Z.

(5). Half filled or totally filled subshells have a special stability. (See Be, N, Cr and Cu)

(6). Half filled or totally filled subshells are efficient shielders. (See B and O)

The experimental ground state configurations show several exceptions to the Aufbau predictions, Figure 25.4.5. For example, exceptions occur for Cr and Mo, which are predicted by Aufbau rules to give d^4s^2 configurations. Exceptions also occur for Cu, Ag, and Au, which are predicted by Aufbau rules to give d^9s^2:

Aufbau Prediction			Experimental		
Cr: $[Ar]3d^4 4s^2$	$\boxed{\uparrow}\boxed{\uparrow}\boxed{\uparrow}\boxed{\uparrow}\boxed{}$	$\boxed{\uparrow\downarrow}$	Cr: $[Ar]3d^5 4s^1$	$\boxed{\uparrow}\boxed{\uparrow}\boxed{\uparrow}\boxed{\uparrow}\boxed{\uparrow}$	$\boxed{\uparrow}$
	3d	4s		3d	4s
Cu: $[Ar]3d^9 4s^2$	$\boxed{\uparrow\downarrow}\boxed{\uparrow\downarrow}\boxed{\uparrow\downarrow}\boxed{\uparrow\downarrow}\boxed{\uparrow}$	$\boxed{\uparrow\downarrow}$	Cu: $[Ar]3d^{10} 4s^1$	$\boxed{\uparrow\downarrow}\boxed{\uparrow\downarrow}\boxed{\uparrow\downarrow}\boxed{\uparrow\downarrow}\boxed{\uparrow\downarrow}$	$\boxed{\uparrow}$
	3d	4s		3d	4s

H $1s^1$							He $1s^2$
Li $2s^1$	Be $2s^2$	B $2s^2 2p^1$	C $2s^2 2p^2$	N $2s^2 2p^3$	O $2s^2 2p^4$	F $2s^2 2p^5$	Ne $2s^2 2p^6$
Na $3s^1$	Mg $3s^2$	Al $3s^2 3p^1$	Si $3s^2 3p^2$	P $3s^2 3p^3$	S $3s^2 3p^4$	Cl $3s^2 3p^5$	Ar $3s^2 3p^6$
K $4s^1$	Ca $4s^2$	Ga $3d^{10} 4s^2 4p^1$	Ge $3d^{10} 4s^2 4p^2$	As $3d^{10} 4s^2 4p^3$	Se $3d^{10} 4s^2 4p^4$	Br $3d^{10} 4s^2 4p^5$	Kr $3d^{10} 4s^2 4p^6$
Rb $5s^1$	Sr $5s^2$	In $4d^{10} 5s^2 5p^1$	Sn $4d^{10} 5s^2 5p^2$	Sb $4d^{10} 5s^2 5p^3$	Te $4d^{10} 5s^2 5p^4$	I $4d^{10} 5s^2 5p^5$	Xe $4d^{10} 5s^2 5p^6$
Cs $6s^1$	Ba $6s^2$	Tl $4f^{14} 5d^{10} 6s^2 6p^1$	Pb $4f^{14} 5d^{10} 6s^2 6p^2$	Bi $4f^{14} 5d^{10} 6s^2 6p^3$	Po $4f^{14} 5d^{10} 6s^2 6p^4$	At $4f^{14} 5d^{10} 6s^2 6p^5$	Rn $4f^{14} 5d^{10} 6s^2 6p^6$

Sc $3d^1 4s^2$	Ti $3d^2 4s^2$	V $3d^3 4s^2$	Cr $3d^5 4s^1$	Mn $3d^5 4s^2$	Fe $3d^6 4s^2$	Co $3d^7 4s^2$	Ni $3d^8 4s^2$	Cu $3d^{10} 4s^1$	Zn $3d^{10} 4s^2$
Y $4d^1 5s^2$	Zr $4d^2 5s^2$	Nb $4d^4 5s^1$	Mo $4d^5 5s^1$	Tc $4d^5 5s^2$	Ru $4d^7 5s^1$	Rh $4d^8 5s^1$	Pd $4d^{10}$	Ag $4d^{10} 5s^1$	Cd $4d^{10} 5s^2$
Lu $4f^{14} 5d^1 6s^2$	Hf $4f^{14} 5d^2 6s^2$	Ta $4f^{14} 5d^3 6s^2$	W $4f^{14} 5d^4 6s^2$	Re $4f^{14} 5d^5 6s^2$	Os $4f^{14} 5d^6 6s^2$	Ir $4f^{14} 5d^7 6s^2$	Pt $4f^{14} 5d^9 6s^1$	Au $4f^{14} 5d^{10} 6s^1$	Hg $4f^{14} 5d^{10} 6s^2$

La $5d^1 6s^2$	Ce $4f^2 6s^2$	Pr $4f^3 6s^2$	Nd $4f^4 6s^2$	Pm $4f^5 6s^2$	Sm $4f^6 6s^2$	Eu $4f^7 6s^2$	Gd $4f^8 6s^2$	Tb $4f^9 6s^2$	Dy $4f^{10} 6s^2$	Ho $4f^{11} 6s^2$	Er $4f^{12} 6s^2$	Tm $4f^{13} 6s^2$	Yb $4f^{14} 6s^2$
Ac $6d^1 7s^2$	Th $5f^2 7s^2$	Pa $5f^2 6d^1 7s^2$	U $5f^3 6d^1 7s^2$	Np $5f^4 6d^1 7s^2$	Pu $5f^6 7s^2$	Am $5f^7 7s^2$	Cm $5f^7 6d^1 7s^2$	Bk $5f^9 7s^2$	Cf $5f^{10} 7s^2$	Es $5f^{11} 7s^2$	Fm $5f^{12} 7s^2$	Md $5f^{13} 7s^2$	No $5f^{14} 7s^2$

Figure 25.4.5: Experimental ground state configuration of the elements, based on atomic absorption and emission spectroscopy.

The enhanced stability of half-filled and completely-filled sublevels can be optimized in several ways. The reason for the exceptions to the Aufbau rules is the similarlity of the valence atomic orbital energies and the contribution of electron-electron repulsion. The Aufbau rules are based on the approximation that the energy of the atom is the sum of one-electron energies. However, electron-electron repulsions exist among all the electrons and cannot rigorously be separated into one-electron terms. The Aufbau rules only provide a prediction for the most stable electronic state. The ground states of Cr and Mo minimize electron-electron repulsion with half-filled d- and s-subshells and the ground states of Cu, Ag, and Au minimize electron-electron repulsion with a completed d-subshell and half-filled s-orbital. In any event, it is easy to predict where exceptions to the Aufbau predictions are likely to occur, one element before half-way and one element before the d- or f-subshell is complete.

The first-ionization energies of the atoms provide an important experimental comparision to verify the configuration and ground state energies of the atoms, Figure 25.4.6. The first-ionization energies are a sensitive measure of the effective nuclear charge felt by the valence electrons. To a rough approximation, the first ionization energy of an atom is given by: $I_1 \approx 13.6\ \text{eV}\ (Z_{eff}^2/n^2)$ for the highest energy electron. High ionization energies correspond to high Z_{eff}; the electron is difficult to remove because of the strong attraction for the nucleus.

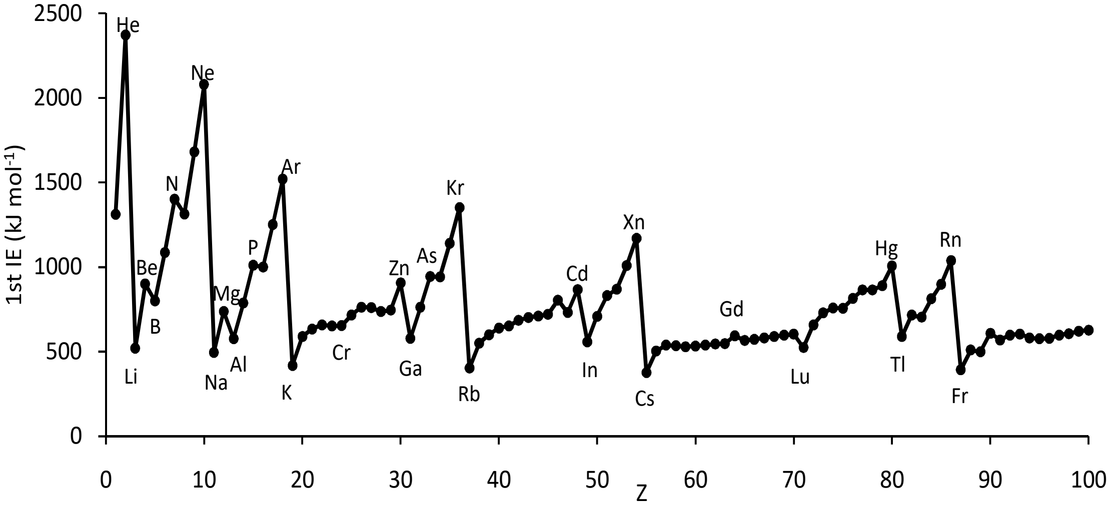


Figure 25.4.6: First-ionization energies for the elements.

Effective nuclear charge rule 2 is exemplified by the drop in ionization energy at the end of each period: for example, He to Li and Ne to Na. Rule 3 is exemplified by the drop in ionization energy after an s-subshell is complete: for example, from Be to B and Mg to Al. Rule 4 is exemplified by the general increase of ionization energy across each period: for example, the general increase from Li to Ne and Na to Ar. Place a straight-edge on the data points for Li and Ne and again for Na and Ar. Rule 5 is exemplified by the larger ionization energy for Be, N, Mg, and P compared to the linear trend across the period:

Be : $1s^2 2s^2$	N : $1s^2 2s^2 2p^3$	[↑↓] 2s	[↑][↑][↑] 2p
Mg: [Ne] $3s^2$	P : [Ne] $3s^2 3p^3$	[↑↓] 3s	[↑][↑][↑] 3p

By Hund's First Rule, the half-filled subshells for N and P minimize electron-electron repulsion. The decrease in ionization energy from N to O and from P to S results, in part, from the disruption of the enhanced stability of a half-filled subshell. The relatively large ionization energy for Zn, Cd, and Hg are the result of the special stability of a completed d-subshell. Again, consider the linear trend from Li to Ne and Na to Ar. Rule 6 is exemplified by the smaller ionization energy for B, Al, and Ga, relative to the linear trend across the period. Ionization of these elements is made easier by the efficient shielding of a completed s- or d-core. Rule 6 is also exemplified by the small ionization energy for O, S, and Se. Ionization of these elements is made easier by the efficient shielding of a half-filled p-subshell. Even though Figure 25.4.6 looks chaotic at first glance, the kinks in the trends are readily understandable on the basis of considerations of electron-electron repulsion as modeled by the effective nuclear charge model.

The Energy Levels for an Ion Are Different from the Neutral Atom: The monoatomic ions have distinctly different chemical reactivity than the parent elements. The interaction between the neutral elements is primarily covalent while the interaction between ions is primarily ionic. This difference in chemical reactivity is the result of the distinctly different orbital energy levels for the ions as compared to the neutral elements. Because cations have fewer electrons than the parent neutral element, electron-electron repulsions are less important. As a consequence, the orbital energies for the cations are always in principle quantum number order. The valence d-orbital is lower in energy than the valence s-orbital, giving the electron configurations of the transition metal cations with maximally filled d-orbitals:

Ti^{2+}: [Ar]$3d^2$ $\underbrace{\boxed{\uparrow}\boxed{\uparrow}\boxed{}\boxed{}\boxed{}}_{3d}$ Cr^{3+}: [Ar]$3d^3$ $\underbrace{\boxed{\uparrow}\boxed{\uparrow}\boxed{\uparrow}\boxed{}\boxed{}}_{3d}$

Cu^{2+}: [Ar]$3d^9$ $\underbrace{\boxed{\uparrow\downarrow}\boxed{\uparrow\downarrow}\boxed{\uparrow\downarrow}\boxed{\uparrow\downarrow}\boxed{\uparrow}}_{3d}$ Zn^{2+}: [Ar]$3d^{10}$ $\underbrace{\boxed{\uparrow\downarrow}\boxed{\uparrow\downarrow}\boxed{\uparrow\downarrow}\boxed{\uparrow\downarrow}\boxed{\uparrow\downarrow}}_{3d}$

The Exchange Interaction is the Result of Electron Indistinguishability: The SCF procedure is very powerful. However, basic Hartree-SCF theory is in poor quantitative agreement with experimental ionization energies. The deficiencies of Hartree theory can be accounted for, in part, by taking electron spin into account. The ground state configuration of helium can be listed in two equivalent ways:

$$\text{He: } 1s^2 \qquad \text{or equivalently} \qquad \text{He: } 1s\boxed{\uparrow\downarrow} \tag{25.4.3}$$

The full ground state wave function is a product of the spatial part of the wave function and the spin part:

$$\Psi_{He}(1,2) = \Psi_{1s}(1)\ \Psi_{1s}(2)\ \text{*spin part} \tag{25.4.4}$$

The spatial part describes the orbital motion about the nucleus. Using the orbital approximation, the spatial part is a product of one-electron wave function in coordinates r, θ, and ϕ for each electron. Using the ground state configuration, both electrons in the helium atom are in 1s-orbitals, one spin up and one spin down:

$$\Psi_{He}(1,2) = \Psi_{1s}(1)\ \Psi_{1s}(2)\ [\alpha(1)\ \beta(2)] \tag{25.4.5}$$

However, the electrons are **indistinguishable**. The identity of the electrons cannot be distinguished by experiment. Therefore, the last wave function is indistinguishable from the case with the opposite spin states:

$$\Psi_{He}(1,2) = \Psi_{1s}(1)\ \Psi_{1s}(2)\ [\beta(1)\ \alpha(2)] \qquad 25.4.6$$

The spin properties of electrons may be determined formally using a symmetry operation called the **exchange of spin labels**. The symmetry operation changes the label of electron 1 to 2 and the label of electron 2 to 1, Figure 25.4.7.

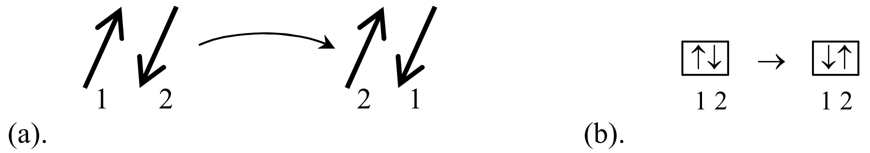


Figure 25.4.7 (a). Exchange of spin labels. (b). Electron 1 is listed first in box diagrams.

An overriding principle of quantum mechanics is to ensure that quantum mechanical solutions to problems can be verified by experiment. We should not state anything that cannot be determined in the laboratory. Consequently, we must take linear combinations of Eqs. 25.4.5 and 25.4.6 with equal weight:

$$\Psi_s = {}^{1}/_{\sqrt{2}}\ \Psi_{1s}(1)\ \Psi_{1s}(2)\ [\alpha(1)\ \beta(2) + \beta(1)\ \alpha(2)] \qquad 25.4.7$$

$$\Psi_a = {}^{1}/_{\sqrt{2}}\ \Psi_{1s}(1)\ \Psi_{1s}(2)\ [\alpha(1)\ \beta(2) - \beta(1)\ \alpha(2)] \qquad 25.4.8$$

We must take linear combinations with equal weight because both spin assignments are equally likely and we cannot tell the difference between the two. The factor of $1/\sqrt{2}$ is required to maintain normalization. The probability of occurrence is determined by the <u>square</u> of the wave function. There are two possible linear combinations, because upon exchange of spin labels both probabilities remain the same: $\Psi_s^2 \to \Psi_s^2$ and $\Psi_a^2 \to \Psi_a^2$. However, the wave functions themselves have opposite behavior under exchange of spin labels. For the Ψ_s possibility, exchange of spin labels leaves the wave function unchanged:

$${}^{1}/_{\sqrt{2}}\ \Psi_{1s}(1)\ \Psi_{1s}(2)\ [\alpha(1)\ \beta(2) + \beta(1)\ \alpha(2)] \ \to\ {}^{1}/_{\sqrt{2}}\ \Psi_{1s}(2)\ \Psi_{1s}(1)\ [\alpha(2)\ \beta(1) + \beta(2)\ \alpha(1)]$$

or $\Psi_s \to \Psi_s$ 25.4.9

However, for the Ψ_a possibility, exchange of spin labels changes the sign of the wave function:

$${}^{1}/_{\sqrt{2}}\ \Psi_{1s}(1)\ \Psi_{1s}(2)\ [\alpha(1)\ \beta(2) - \beta(1)\ \alpha(2)] \ \to\ {}^{1}/_{\sqrt{2}}\ \Psi_{1s}(1)\ \Psi_{1s}(2)\ [\alpha(2)\ \beta(1) - \beta(2)\ \alpha(1)] \qquad 25.4.10$$

The last wave function with the exchanged labels rearranges to give:

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

or $\Psi_a \to -\ \Psi_a$ 25.4.11

If a symmetry operation leaves a wave function unchanged, the wave function is said to be **symmetric**. If a symmetry operation changes the sign of a wave function, the wave function is said to be **antisymmetric**. The linear combination with addition is symmetric, Eq. 25.4.9, and the linear combination with subtraction is antisymmetric, Eq. 25.4.11, hence the subscripts Ψ_s and Ψ_a, respectively. The spatial part of the wave function is symmetric in both cases, because the electrons are in identical orbitals. In this case, the overall symmetry is determined by the spin part, because the electrons have opposite spin states:

$$\Psi_s = {}^{1}\!/\!\sqrt{2}\ \underbrace{\Psi_{1s}(1)\,\Psi_{1s}(2)}_{\substack{\textit{spatial part}\\ \textit{symmetric}}} \underset{*}{\ } \underbrace{[\alpha(1)\,\beta(2) + \beta(1)\,\alpha(2)]}_{\substack{\textit{spin part}\\ \textit{symmetric}}} \qquad 25.4.12$$

$$\Psi_a = {}^{1}\!/\!\sqrt{2}\ \underbrace{\Psi_{1s}(1)\,\Psi_{1s}(2)}_{\textit{symmetric}}\ \underbrace{[\alpha(1)\,\beta(2) - \beta(1)\,\alpha(2)]}_{\textit{antisymmetric}} \qquad 25.4.13$$

Which combination is the correct wave function? The Pauli Exclusion Principle results in an underlying fundamental symmetry restriction on the overall electronic wave function.

> Pauli Exclusion Principle: The wave function is overall antisymmetric with respect to exchange of any two electron spin labels.

As a result, only Ψ_a is a valid wave function for the ground state of the helium atom. The antisymmetric wave function, Eq. 25.4.13, can be diagrammed equivalently as:

$$\Psi_a = {}^{1}\!/\!\sqrt{2}\ \left(1s\boxed{\uparrow\downarrow} - 1s\boxed{\downarrow\uparrow}\right) \qquad 25.4.14$$

How does this fundamental statement of the Pauli Exclusion Principle relate to the more familiar statement that "no two electrons can have the same set of quantum numbers?"

Consider a ground state helium atom with both electrons spin up: $\Psi_{1s}(1)\ \Psi_{1s}(2)\ [\alpha(1)\ \alpha(2)]$. Now both electrons have quantum numbers $n,\ell,m_\ell,m_s = 1,0,0,½$. However, exchange of spin labels gives an identical result to the original wave function, so the proposed wave function is symmetric. However, the result must be antisymmetric to produce a valid solution. The proposed wave function cannot be valid. As a consequence, no two electrons can have the same set of quantum numbers. Each orbital can then hold at most two electrons, one spin up and one spin down, $m_s = +½$ and $m_s = -½$.

Using the antisymmetric wave function, Eq. 25.4.14, in self-consistent field calculations for the ground state of the helium atom results in much better agreement with experiment. The difference in energy with and without the use of the restriction based on electron indistinguishability is the **exchange energy**. Correspondingly, the wave functions for other multi-electron atoms must be constructed to guarantee antisymmetry. To guarantee antisymmetry, the overall wave function is expressed as a **Slater determinant**. For the ground state of the helium atom, the Slater determinant is given by:

$$\Psi_a = {}^{1}\!/\!\sqrt{2}\ \begin{vmatrix} \Psi_{1s}(1)\alpha(1) & \Psi_{1s}(1)\beta(1) \\ \Psi_{1s}(2)\alpha(2) & \Psi_{1s}(2)\beta(2) \end{vmatrix} \qquad \begin{array}{l}\text{rows: different electrons}\\ \text{columns: different wave functions}\end{array} \qquad 25.4.15$$

The rows correspond to the different electrons; row one is for electron 1, row two is for electron 2. The product of a spatial and spin wave function is called a **spin-orbital**. The columns of a Slater determinant correspond to all possible single electron spin-orbitals. Multiplying out the determinant gives Eq. 25.4.13, as required. A general property of determinants is that the sign of the determinant changes upon exchange of any two rows or any two columns. The exchange of rows corresponds to the exchange of spin labels, thus guaranteeing antisymmetry. The underlying fundamental idea is that we can know the orbitals that are occupied in an atom, but we cannot determine which electron occupies which orbital. In essence, all of the electrons spend time in each possible orbital. No one electron "belongs" to a given orbital. Using Slater determinants as the wave functions for Hartree self-consistent-field calculations is called the **Hartree-Fock self-consistent-field method**, **HF-SCF**, or just **HF** for short. Some additional examples will be instructive at this point.

The Configuration $1s^1 2s^1$ *gives a Singlet and Triplet State*: The lowest energy excited state of the helium atom has the configuration $1s^1 2s^1$. However, the box diagram can be drawn in two possible ways:

He Excited State: $1s^1 2s^1$ $\quad 1s\boxed{\uparrow}\ 2s\boxed{\downarrow} \quad$ or $\quad 1s\boxed{\uparrow}\ 2s\boxed{\uparrow}$ 25.4.16

Neither box diagram is valid. We need to take into account electron indistinguishabilty. The spatial part of the excited state wave function is the product of a 1s and 2s orbital: $\Psi^{ex}{}_{He}(1,2) = \Psi_{1s}(1)\,\Psi_{2s}(2)$. However, we cannot know which electron is in which orbital. To maintain indistinguishabilty we must take equal-weight linear combinations for the spatial part of the wave function, since the electrons are in different spatial orbitals:

$$\Psi^{ex}{}_{He}(1,2) = {}^{1}/_{\sqrt{2}}\,(\Psi_{1s}(1)\,\Psi_{2s}(2) \pm \Psi_{1s}(2)\,\Psi_{2s}(1)) \qquad 25.4.17$$

The spatial part of the wave function can then be either symmetric (+) or antisymmetric (–). Because the electrons are in different spatial orbitals, the electron spins can now be parallel. The four possible primitive spin wave functions are αα, αβ, βα, and ββ. However, the combinations αβ and βα distinguish between the two electrons, which we cannot do. We must also take equal-weight linear combinations of αβ and βα. The spin parts of the wave functions are then:

$$\begin{array}{ccc} \alpha(1)\alpha(2) & & \\ \alpha(1)\,\beta(2) + \beta(1)\,\alpha(2) & \text{and} & \alpha(1)\,\beta(2) - \beta(1)\,\alpha(2) \\ \beta(1)\beta(2) & & \\ \textit{symmetric} & & \textit{antisymmetric} \end{array} \qquad 25.4.18$$

The three spin wave functions on the left are all symmetric. The linear combination α(1) β(2) – β(1) α(2) is antisymmetric. We can now piece together the overall wave function, while maintaining antisymmetry. The symmetric spatial part must be paired with the antisymmetric spin part to give overall antisymmetry:

$${}^{1}\Psi^{ex} = \underset{\substack{\textit{spatial part}\\ \textit{symmetric}}}{{}^{1}/_{\sqrt{2}}\,(\Psi_{1s}(1)\,\Psi_{2s}(2) + \Psi_{1s}(2)\,\Psi_{2s}(1))} \; * \; \underset{\substack{\textit{spin part}\\ \textit{antisymmetric}}}{[\alpha(1)\,\beta(2) - \beta(1)\,\alpha(2)]} \qquad \text{(singlet)} \qquad 25.4.19$$

This state is called a singlet state because there is only one possible combination of spatial and spin parts. The antisymmetric spatial part must be paired with symmetric spin parts, which in this case occur in three ways:

$$ {}^3\Psi^{ex} = {}^1\!/\!\sqrt{2}\ \underset{\substack{\textit{spatial part}\\ \textit{antisymmetric}}}{(\Psi_{1s}(1)\,\Psi_{2s}(2) - \Psi_{1s}(2)\,\Psi_{2s}(1))} \overset{}{\underset{*}{}} \underset{\substack{\textit{spin part}\\ \textit{symmetric}}}{\begin{bmatrix} \alpha(1)\alpha(2) \\ \alpha(1)\beta(2) + \beta(1)\alpha(2) \\ \beta(1)\beta(2) \end{bmatrix}} \qquad \text{(triplet)} \qquad 25.4.20 $$

This state is called a triplet state because there are three possible spin wave functions that result in overall antisymmetry. In the absence of an external field (and spin orbit coupling), the three spin states are degenerate. Note that the multiplication rules are identical to the multiplication of factors of 1 and –1, since the symmetry is determined by the wave function sign:

$$ \begin{array}{ccc} (1)(1) = 1 & (1)(-1) = -1 & (-1)(-1) = 1 \\ \text{s s} = \text{s} & \text{s a} = \text{a} & \text{a a} = \text{s} \end{array} \qquad 25.4.21 $$

The spin multiplicity, in this case singlet or triplet, has an important impact on the spectroscopy and chemical reactivity of the excited state.

Recall the reasoning that we used to predict the effects of electron-electron repulsion using Hund's First Rule. The triplet state is lower in energy than the singlet state, because the electrons "avoid" each other since they have parallel spins. This quantum mechanical restriction is seen most strikingly by setting the position of the two electrons in the helium triplet state to the same value. The spatial term $\Psi_{1s}(1)\,\Psi_{2s}(2) - \Psi_{1s}(2)\,\Psi_{2s}(1)$ is zero when the electrons are at the same position. The resulting increase in average electron-electron distance decreases electron-electron repulsion, lowering the energy of the triplet state relative to the singlet state. The Jablonski diagram for the two lowest excited states of the helium atom is shown in Figure 25.4.8. The ground state of helium is a singlet, Eq. 25.4.13. Triplet excited states usually have longer lifetimes than the corresponding excited singlet states, which can enhance photochemical reactivity.

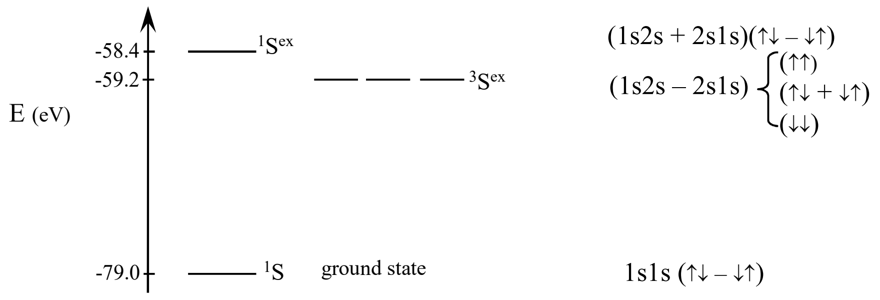


Figure 25.4.8: Several electronic energy levels of helium. There are many higher energy excited states. The first triplet state is 0.8 eV lower than the first excited singlet state.

Multiple Slater Determinants are Required for S > 0: Doublet states are another common spin multiplicity, which result from odd electron species. The ground state of the hydrogen atom is a doublet since the electron can be either up or down:

$$ {}^2\Psi_H = 1s(1)\begin{bmatrix} \alpha(1) \\ \beta(1) \end{bmatrix} \qquad 25.4.22 $$

Odd electron organic free radicals are almost always doublets for the same reason. Species with multiplicity higher than one must be represented by multiple Slater determinants. For example, the doublet ground state of the lithium atom requires two Slater determinants, one for the outer electron spin up and one for the outer electron spin down:

$$\text{Li:}1s^2\,2s^1\text{: } 1s\boxed{\uparrow\downarrow}\ 2s\boxed{\uparrow\ }$$

$$\Psi_a = {}^1/\sqrt{3!}\begin{vmatrix} 1s(1)\alpha(1) & 1s(1)\beta(1) & 2s(1)\alpha(1) \\ 1s(2)\alpha(2) & 1s(2)\beta(2) & 2s(2)\alpha(2) \\ 1s(3)\alpha(3) & 1s(3)\beta(3) & 2s(3)\alpha(3) \end{vmatrix} \qquad 25.4.23$$

$$\text{Li:}1s^2\,2s^1\text{: } 1s\boxed{\uparrow\downarrow}\ 2s\boxed{\downarrow\ }$$

$$\Psi_a = {}^1/\sqrt{3!}\begin{vmatrix} 1s(1)\alpha(1) & 1s(1)\beta(1) & 2s(1)\beta(1) \\ 1s(2)\alpha(2) & 1s(2)\beta(2) & 2s(2)\beta(2) \\ 1s(3)\alpha(3) & 1s(3)\beta(3) & 2s(3)\beta(3) \end{vmatrix} \qquad 25.4.31$$

In any event, the lithium ground state is a good example of Slater determinants. In general, the normalization of the Slater determinant for N electrons is $1/\sqrt{N!}$. Slater determinants are the foundation of the Hartree-Fock method. However, the functional form of the hydrogen orbitals is not well suited to practical electronic structure methods.

25.5 Representations of Atomic Orbitals

Slater Type Orbitals, STOs, have no Radial Nodes: The functional forms of the hydrogen orbitals, even with an effective nuclear charge, are not the solutions to the Schrödinger equation for multi-electron atoms. The hydrogen-like orbitals can be a suitable starting point for multi-electron atoms, but the functional form of the radial parts are difficult to use in the integrals necessary for evaluating electron-electron repulsion. The computational efficiency of the functional form is most critical when calculating molecular orbitals. Slater proposed simple atomic wave functions that have appropriate large r behavior. The behavior of the wave functions at large distances from the nucleus is important, because bond formation involves overlap of atomic orbitals at large r. A **Slater Type Orbital**, **STO**, is derived from the corresponding hydrogen-like orbital using an effective nuclear charge, Eqs. 25.2.1 and 25.2.8, but the radial polynomial is replaced by just the leading term in r:

$$\Psi_{n\ell m_\ell}(r) = N\, Y_{\ell,m_\ell}\, r^{(n_{eff}-1)}\, e^{-Z_{eff}\, r/n_{eff}\, a_o} \qquad 25.5.1$$

The resulting orbitals have the same large r dependence, but lack radial nodes. For principle quantum shells with n > 3, the principal quantum number is replaced by an effective principal quantum number, n_{eff}:

n	1	2	3	4	5	6
n_{eff}	1	2	3	3.7	4.0	4.2

25.5.2

The effective nuclear charge is optimized using the SCF approach, Table 25.5.1. The effective nuclear charge can be approximated as the difference between the full nuclear charge and a shielding constant, S: $Z_{eff} = Z - S$. The shielding constant accounts for the average electron-electron repulsion for the electrons.

Table 25.5.1: Slater Orbital Parameters[3], Z_{eff}.

	${}_{1}$H							${}_{2}$He
1s	1.0000							1.6875

	${}_{3}$Li	${}_{4}$Be	${}_{5}$B	${}_{6}$C	${}_{7}$N	${}_{8}$O	${}_{9}$F	${}_{10}$Ne
1s	2.6906	3.6843	4.6795	5.6727	6.6651	7.6579	8.6501	9.6421
2s	1.2792	1.9120	2.5762	3.2166	3.8474	4.4916	5.1276	5.7584
2p			2.4214	3.1358	3.8340	4.4532	5.1000	5.7584

	${}_{11}$Na	${}_{12}$Mg	${}_{13}$Al	${}_{14}$Si	${}_{15}$P	${}_{16}$S	${}_{17}$Cl	${}_{18}$Ar
1s	10.6259	11.6089	12.5910	13.5745	14.5578	15.5409	16.5239	17.5075
2s	6.5714	7.3920	8.2136	9.0200	9.8250	10.6288	11.4304	12.2304
2p	6.8018	7.8258	8.9634	9.9450	10.9612	11.9770	12.9932	14.0082
3s	2.5074	3.3075	4.1172	4.9032	5.6418	6.3669	7.0683	7.7568
3p			4.0656	4.2852	4.8864	5.4819	6.1161	6.7641

Slater's Rules are used to give approximations to the effective nuclear charge of the valence electrons. The shielding efficiency of electrons in the valence shell is 35% of the nuclear charge. The shielding efficiency of electrons in the next lowest energy shell is 85%, since those electrons are in contracted orbitals at much lower energy than the valence shell. For third and higher period elements, the shielding efficiency of the inner core levels is 100%:

1st period (first element in period $Z = 1$): $Z_{eff} = Z - 0.35\,(Z - 1)$ 25.5.3

2nd period (2 next shell core electrons, $Z > 3$):

$$Z_{eff} = Z - \underbrace{0.85\,(2)}_{\textit{next core shell}} - \underbrace{0.35\,(Z - 3)}_{\textit{valence shell}} \qquad 25.5.4$$

3rd period (2 inner core electrons, 8 next shell core electrons, $Z > 11$):

$$Z_{eff} = Z - \underbrace{1.00\,(2)}_{\substack{\textit{inner core}\\ \textit{100\% efficient}}} - \underbrace{0.85\,(8)}_{\substack{\textit{next core shell}\\ \textit{85\% efficient}}} - \underbrace{0.35\,(Z - 11)}_{\substack{\textit{valence shell}\\ \textit{35\% efficient}}} \qquad 25.5.5$$

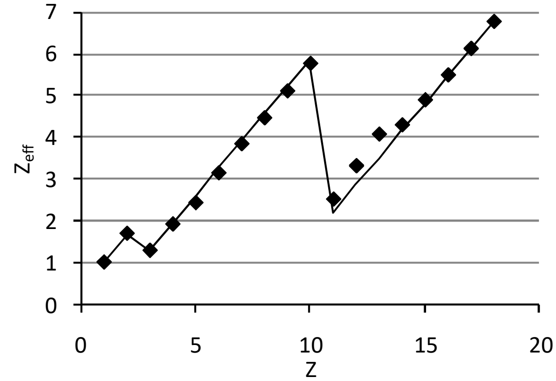


Figure 25.5.1: The Z_{eff} approximated using Slater's rules versus the SCF-optimized values from Table 25.5.1, for the highest energy sub-shell.

The effective nuclear charges approximated using Slater's Rules agree well with the SCF-optimized values, Figure 25.5.1. The shielding efficiencies in Salter's Rules give a useful insight into the ability of electrons in different shells to shield each other from the full nuclear charge. Slater-type orbitals are widely used in *semi-empirical* molecular orbital calculations, including CNDO, MNDO, AM1, and PM3 methods. However, STOs are poor approximations to the radial electron density in atoms. Gaussian-type orbitals provide greater flexibility in approximating the radial electron distribution in multi-electron atoms and ions.

Gaussian Orbitals are Easier to Integrate: Closed form expressions for the values of integrals involving r^n are available for wave functions with Gaussian forms. Gaussian orbitals are linear combinations of **Gaussian Primitives** of the form:

$$g_s(\alpha,r) = \left(\frac{2\alpha}{\pi}\right)^{3/4} e^{-\alpha r^2} \qquad g_x(\alpha,r) = \left(\frac{128\alpha^5}{\pi^3}\right)^{1/4} x\ e^{-\alpha r^2} \qquad 25.5.6$$

where $g_s(\alpha,r)$ is the Gaussian primitive for s-type orbitals and $g_x(\alpha,r)$ is the Gaussian primitive for p_x orbitals. Replacing the x factor in Eq. 25.5.6 with y or z gives the Gaussian primitives for p_y and p_z orbitals. The **Gaussian exponent**, α, plays the role of the effective nuclear charge. The set of atomic orbitals used in an atomic or molecular orbital calculation is called a **basis set**. The atomic orbitals are given by linear combinations of Gaussian primitives:

$$\phi_\mu = \sum_{i=1}^{n} d_{\mu i}\, g_i(\alpha,r) \qquad \mu = s, x, y, z \qquad 25.5.7$$

where the $d_{\mu i}$ are linear coefficients specific to the basis set and μ designates the type of orbital. The bell-curve shape of a single Gaussian primitive is not a good approximation to the radial electron distribution in an atom. However, the linear combination of several primitives provides considerable flexibility in the ability of the Gaussian atomic orbital to approximate accurate Hartree-Fock self-consistent field atomic orbitals. The larger the number of Gaussian primitives in the sum, the larger the number of adjustable coefficients, $d_{\mu i}$. More adjustable coefficients give better agreement with the accurate electron density. A sum of three Gaussian primitives is often used as a substitute for Slater-type orbitals, giving the **STO-3G basis set**. Accurate calculations require more Gaussian primitives than three. The core orbitals are treated separately from the valence orbitals, since the large r dependence of the valence orbitals is critical for applications in bonding.

In the 3-21G basis set, the core orbitals are taken as a sum of three Gaussian primitives and the valence orbitals are split into an inner and outer part. The inner part of the valence shell is taken as the sum of two Gaussian primitives and the outer part is given by a single Gaussian primitive, Figure 25.5.2. The orbital coefficients, $d_{\mu i}$, are determined to best fit accurate atomic electron densities and are held constant in electronic structure calculations. The 3-21G basis sets for lithium and carbon are given in Table 24.5.2.

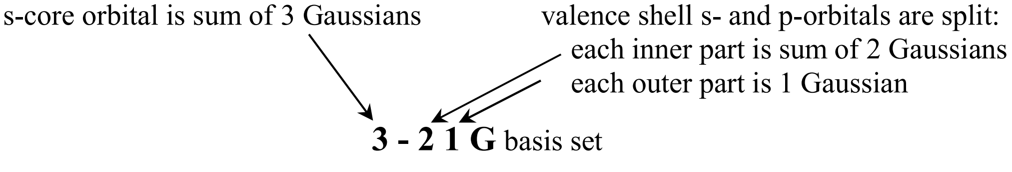


Figure 25.5.2: A Gaussian basis set with a split valence shell.

Table 25.5.2: Lithium and Carbon 3-21G Basis Sets.

Li			C		
α_i	d_{si}	d_{xi}	α_i	d_{si}	d_{xi}
1s core			1s core		
36.8382	0.0696686		172.256	0.0617669	
5.48172	0.381346		25.9109	0.358794	
1.11327	0.681702		5.53335	0.700713	
2s and 2p inner			2s and 2p inner		
0.540205	-0.263127	0.161546	3.66498	-0.395897	0.23646
0.102255	1.14339	0.915663	0.770545	1.21584	0.860619
2s and 2p outer			2s and 2p outer		
0.0285645	1.00000	1.00000	0.195857	1.00000	1.00000

Using the coefficients in Table 25.5.2, the explicit 1s-wave function for lithium is:

$$\Psi_{1s} = 0.0697\ g_s(36.8,r) \qquad + 0.381\ g_s(5.48,r) \qquad + 0.682\ g_s(1.11,r)$$

$$\Psi_{1s} = 0.0697 \left(\frac{2(36.8)}{\pi}\right)^{3/4} e^{-36.8r^2} + 0.381 \left(\frac{2(5.48)}{\pi}\right)^{3/4} e^{-5.48r^2} + 0.682 \left(\frac{2(1.11)}{\pi}\right)^{3/4} e^{-1.11r^2} \tag{25.5.8}$$

The explicit 2s- and $2p_x$-wave functions are given as:

$$\Psi_{2s}(\text{inner}) = -0.263\ g_s(0.540,r) + 1.14\ g_s(0.102,r) \qquad \Psi_{2s}(\text{outer}) = 1.00\ g_s(0.0286,r)$$

$$\Psi_{2px}(\text{inner}) = 0.162\ g_x(0.540,r) + 0.916\ g_x(0.102,r) \qquad \Psi_{2px}(\text{outer}) = 1.00\ g_x(0.0286,r) \tag{25.5.9}$$

The outer part has a smaller Gaussian exponent than the inner part, giving a larger spatial extent for the outer part of the orbital. The outer part is more diffuse. The split valence shell allows the inner and outer part of the valence orbitals to be optimized as part of an SCF procedure. In this way, the electron density of the atom adjusts to the environment of the atom:

$$\Psi_{2s} = \underset{\uparrow}{a}\Psi_{2s}(\text{inner}) + \underset{\uparrow}{b}\Psi_{2s}(\text{outer}) \tag{25.5.10}$$

optimize variationally

For example, the $2p_x$-coefficients for the carbon atom as an isolated atom and for the carbon atom in methane show how the electron density adjusts to bonding interactions:

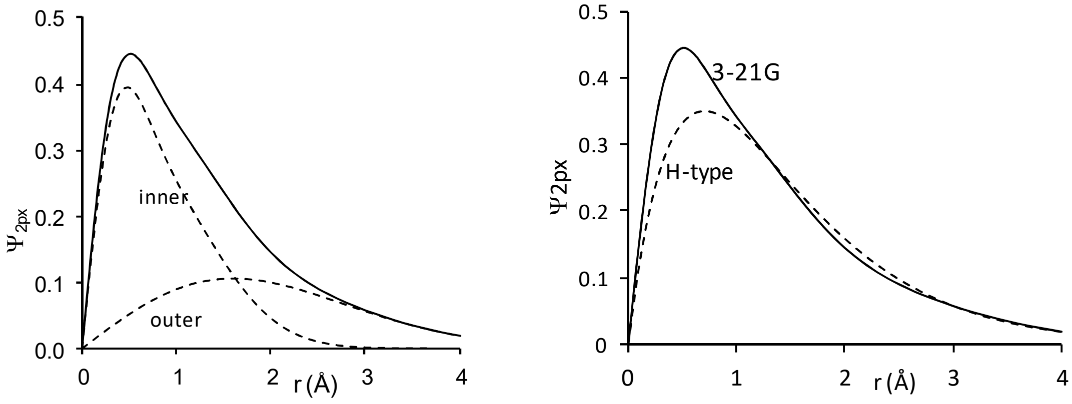
$$\text{C isolated atom:} \qquad \Psi_{2px} = 0.688\ \Psi_{2px}(\text{inner}) + 0.725\ \Psi_{2px}(\text{outer})$$

$$\text{C in CH}_4\text{:} \qquad \Psi_{2px} = 0.770\ \Psi_{2px}(\text{inner}) + 0.638\ \Psi_{2px}(\text{outer}) \tag{25.5.11}$$

The experimental electronic energy of lithium is the negative sum of the successive ionization energies:

$$E(\text{exp.}) = -(I_1 + I_2 + I_3) = -202.42\text{eV} \qquad E(\text{Li,3-21G}) = -200.78\text{ eV} \tag{25.5.12}$$

Using the 3-21G basis set, the calculated energy of the ground state of lithium is almost 2 eV higher than the experimental energy.



(a). (b).

Figure 25.5.3: (a). The 3-21G basis set has a split valence shell with an inner and outer part. (b). The 3-21G $2p_x$-orbital compared to the hydrogen-type orbital with $Z_{eff} = 1.5$.

A more accurate ground state energy is obtained with a larger basis set. The 6-311G basis set is commonly used for careful calculations, Figure 25.5.4 and Table 24.5.3. The valence shell is split into an inner, middle, and outer part to give more flexibility in adjusting the electron density to the environment of the atom.

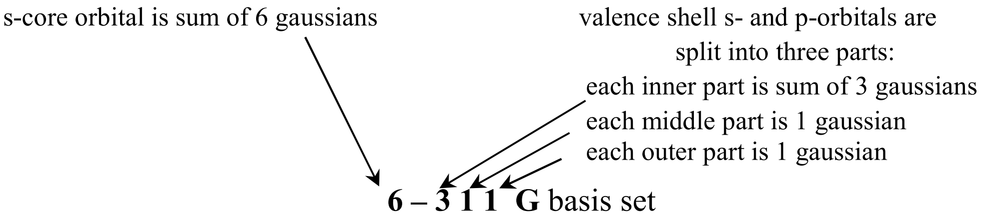


Figure 25.5.4: A 6-311G Gaussian basis set uses a triply split valence shell.

Table 24.5.3: Lithium 6-311G Basis Set.

α_i	d_{si}	d_{xi}
1s core		
900.46	0.00228704	
134.433	0.017635	
30.4365	0.0873434	
8.62639	0.280977	
2.48332	0.658741	
0.303179	0.118712	
2s and 2p inner		
4.8689	0.0933293	0.0327661
0.856924	0.943045	0.159792
0.243227	-0.00279827	0.885667
2s and 2p middle		
0.063507	1.00000	1.00000
2s and 2p outer		
0.0243683	1.00000	1.00000

The calculated ground state energy of the lithium atom is much improved with this more complete basis set: E(Li,6-311G) = –202.15eV. We will discuss even more complete basis sets in the next chapter. In practice, a series of calculations with increasing basis set size is completed and the electronic energy is extrapolated to the limit for very large basis sets. This limit is called the **Hartree-Fock limit**. The 6-311G basis set is close to the Hartree-Fock limit and is useful as a complement to experimental studies of the electronic absorption and emission spectra of atoms and molecules.

25.6 Atomic Spectra

Angular momentum plays an important role in chemical reactivity and electronic spectroscopy. The spin and orbital angular momentum of all the electrons in an atom combine vectorially to give an overall angular momentum. The angular momentum of the ground state and excited states determine the intensity of the possible spectroscopic transitions. We begin by considering the total spin angular momentum and orbital angular momentum separately. We've covered singlet, doublet, and triplet spin states, but how do you determine higher multiplicities?

Spin Angular Momentum Adds Vectorially: In multi-electron atoms the intrinsic spin angular momentum of the electrons adds vectorially to give the total spin angular momentum vector:

$$\vec{S} = \Sigma\, \vec{S}_i \qquad 25.6.1$$

where $\vec{S}$ is the total spin angular momentum and the $\vec{S}_i$ are the intrinsic angular momentum vectors for each of the electrons in the atom. The magnitude of the total spin angular momentum is determined by the **total spin quantum number**, S, in analogy with Eq. 24.5.34:

$$|S| = \sqrt{S(S+1)}\,\hbar \qquad 25.6.2$$

The projection of the total spin angular momentum on the z-axis is quantized with quantum number M_S and degeneracy g_S:

$$S_z = M_S\,\hbar \qquad M_S = -S,\ldots, 0,\ldots +S \quad \text{and degeneracy } g_S = 2S + 1 \qquad 25.6.3$$

M_S is the sum of the individual electron m_s quantum numbers, $m_{s,i}$:

$$M_S = \Sigma\, m_{s,i} \qquad 25.6.4$$

Since M_S varies from –S to +S, the total spin quantum number is given by the maximum of M_S:

$$S = M_{S,max} \qquad 25.6.5$$

The spin multiplicity is given by the degeneracy, g_S. A vector diagram will help to summarize these relationships, Figure 25.6.1. The vectorial addition of the individual spin angular momenta is complicated. Luckily, Eq. 25.6.4 shows that the z-axis projections of the individual electrons add to give the z-axis projection of the total angular momentum. The maximum value of M_S then allows us to infer the value of S. As a short cut, we only need to draw the box diagram for one configuration, the configuration with the electron spins aligned to give the largest M_S.

For example, for an atom with all spin paired electrons $\Sigma\, m_{s,i} = 0$, since half the electrons are spin up and half are spin down. A singlet state results for all spin paired electrons. For one unpaired electron, $S = (\Sigma\, m_{s,i})_{max} = ½$, giving $g_S = (2S + 1) = 2$, or a doublet state. The inner filled cores of atoms have half up and half down electrons, so the total angular momentum of a filled core is always zero. Effectively, only the valence electrons contribute to the overall angular momentum.

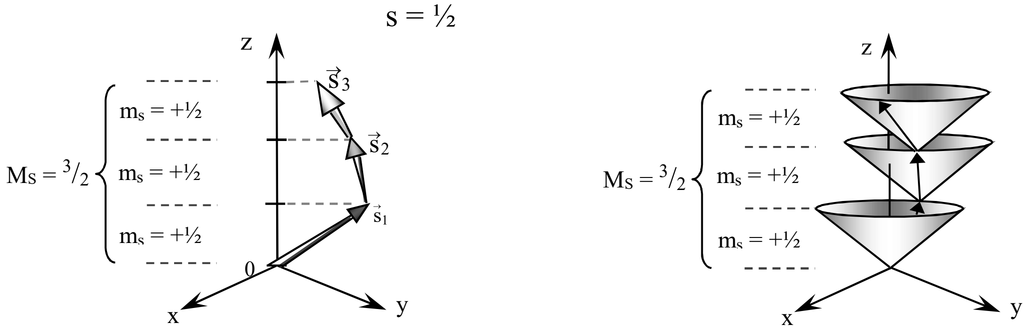


Figure 25.6.1: Vector addition for (↑↑↑). The individual angular momentum vectors are equal length and lie on the surfaces of cones. However, the cones have a definite z-axis projection. The z-axis projections of the individual electrons add algebraically to give the z-axis projection of the total angular momentum. The maximum value of M_S then gives S.

For example, ground state H, Li, Na, K, Cs, Rb all have doublet spin multiplicity, since there is one unpaired electron in the outer-most shell, with a completely filled inner core. For two parallel electrons, the sum of the m_s values for (↑↑) is 1, for (↑↓ + ↓↑) the sum is 0, and for (↓↓) the sum is -1. Since we take the maximum value, the total spin quantum number is $S = (\Sigma\, m_{s,i})_{max} = 1$, with a degeneracy of $g_S = (2S + 1) = 3$, giving a triplet state, Figure 25.6.2. As a short cut, we can represent the triplet state with the configuration with maximum M_S, (↑↑), keeping in mind that electron indistinguishability requires the remaining two degenerate configurations. A listing of common multiplicities is given in Table 25.6.1.

$$\left.\begin{array}{ll} 1s\,\boxed{\uparrow}\;\;2s\,\boxed{\uparrow} & M_S = +1 \\ 1s\,\boxed{\uparrow}\;\;2s\,\boxed{\downarrow} + 1s\,\boxed{\downarrow}\,2s\,\boxed{\uparrow} & M_S = 0 \\ 1s\,\boxed{\downarrow}\;\;2s\,\boxed{\downarrow} & M_S = -1 \end{array}\right\} \begin{array}{l} S = M_{S,max} = 1 \\ \qquad g_S = 2S + 1 = 3 \end{array}$$

Figure 25.6.2: The first excited state of helium represented as (↑↑) is a triplet state.

Electronic structure calculations of open-shell species are important for studies of energetic intermediates in mechanistic organic chemistry and for studies of transition metal complexes. The first step in doing an electronic structure calculation is to specify the spin multiplicity. Checking the final results to see if the desired multiplicity is maintained is an important step in validating the results of molecular orbital calculations. Electronic structure programs list the expectation value of the square of the spin angular momentum, rather than the multiplicity. The output files often label the expectation value alternately as:

$$<\hat{S}^2> = <S^2> = <S*S> = S(S+1)\hbar^2 \tag{25.6.6}$$

The values of the square of the spin angular momentum are listed in Table 25.6.1 in units of $\hbar^2$, as is listed in common electronic structure program output files. Deviation from the expected <S*S> values in molecular orbital calculations shows that some excited state character (of higher multiplicity) is being mixed into the desired state. This error is called **spin contamination**. More complete atomic basis sets or better-optimized geometries often correct this problem.[4]

Table 25.6.1: Common Multiplicities for Atoms, Ions, and Molecules: $g_S = (2S + 1)$.

Spin State	Example*	S	Multiplicity	$\langle S*S\rangle/\hbar^2$
↑↓ spin paired	Most molecules	0	1	0
↑	H, Li, B, F, Na, Cu(II) organic radicals	½	2	0.75
↑↑	C, O, Si, S, Ni(II), O_2, excited triplet states	1	3	2.0
↑↑↑	N, P, As, V, V(II), Cr(III), Co, Co(II)	1½	4	3.75
↑↑↑↑	Cr, Cr(II), Mn(III), Fe, Fe(II), Co(III), B_2	2	5	6.0
↑↑↑↑↑	Mn, Mn(II), Fe(III)	2½	6	8.75

* Atomic examples are for ground states.

Orbital Angular Momenta Add Vectorially: In multi-electron atoms the orbital angular momentum of the electrons adds vectorially to give the total orbital angular momentum vector, in an analogous fashion to the spin angular momentum:

$$\vec{L} = \Sigma\, \vec{L}_i \qquad 25.6.7$$

where $\vec{L}$ is the total orbital angular momentum and the $\vec{L}_i$ are the orbital angular momentum vectors for each of the electrons in the atom. The magnitude of the total orbital angular momentum is determined by the **total orbital angular momentum quantum number**, L, in analogy with Eq. 24.5.34 and Eqs. 25.6.2-25.6.5:

$$|L| = \sqrt{L(L+1)}\,\hbar \qquad 25.6.8$$

The projection of the total orbital angular momentum on the z-axis is quantized with quantum number M_L and degeneracy g_L:

$$L_z = M_L\,\hbar \qquad M_L = -L,\ldots, 0,\ldots +L \quad \text{and degeneracy } g_L = 2L + 1 \qquad 25.6.9$$

M_L is the sum of the individual electron magnetic quantum numbers, $m_{\ell,i}$:

$$M_L = \Sigma\, m_{\ell,i} \qquad 25.6.10$$

Since M_L varies from $-L$ to $+L$, the total orbital quantum number is given by the maximum of M_L:

$$L = M_{L,max} \qquad 25.6.11$$

Once again, we don't need to know the full angular momentum vector, knowing the L quantum number is sufficient. The L quantum number is inferred from the maximum of the sum of the m_ℓ projections of the individual electrons.

Term Symbols are Nicknames for Energy States: The L value for an electronic state is symbolized by a capital letter, which is called the **term**:

L	0	1	2	3	4	5
Term	S	P	D	F	G	H

25.6.12

The spin multiplicity is added as a superscript before the term to give a quick summary of the angular momentum relationships for a given atomic electronic state. Atoms with all closed shells give L = 0 and a corresponding ^1S term. Examples include the ground states of the inert gases (He, Ar, Xe) and the alkaline earths (Be, Mg, Ca, Sr). Atoms with only one unpaired electron in an s-orbital also give L = 0 with a ^2S term (H, Li, Na, K, Cu, Ag). Closed shells don't contribute to the angular momentum; for ground state atoms and monatomic ions we only need consider the valence electrons. The combined term and multiplicity is called a **term symbol**. Term symbols are nicknames for energy states.

A handy shortcut for determining the possible L values for a given configuration is given by a **Clebsch-Gordan series**. For two electrons with orbital angular momentum quantum numbers ℓ_1 and ℓ_2 the range of possible total L values is the series:

$$L = \ell_1 + \ell_2, \ell_1 + \ell_2 - 1, \ldots, |\ell_1 - \ell_2| \qquad 25.6.12$$

For example, consider a carbon atom, which has the ground state configuration $2p^2$. The individual orbital quantum numbers are $\ell_1 = 1$ and $\ell_2 = 1$. There are multiple box diagrams that can represent the possible spin configurations, two possibilities are shown:

$$\text{C: } 2p^2 \qquad \boxed{\uparrow}\boxed{\uparrow}\boxed{} \quad \text{or} \quad \boxed{\uparrow\downarrow}\boxed{}\boxed{} \qquad 25.6.13$$

The Clebsch-Gordan series gives the possible L values as:

$$2p^2\text{:} \quad 1 + 1, \ldots, |1 - 1| = 2, 1, 0 \qquad 25.6.14$$

The possible terms corresponding to a p^2 configuration are S, P, and D. How do these terms arise? The p sub-shell is triply degenerate with $m_\ell = 0, \pm 1$. All possible ways of filling the p-orbitals with two electrons are diagramed below with the corresponding M_L values.

p^2: $M_L = \Sigma m_\ell$		$M_L = \Sigma m_\ell$	
+1 0 -1			
$\boxed{\uparrow\downarrow}\boxed{}\boxed{}$	2	+1 0 -1	
$\boxed{\uparrow}\boxed{\downarrow}\boxed{}$	1	$\boxed{\uparrow}\boxed{\uparrow}\boxed{}$	1
$\boxed{\uparrow}\boxed{}\boxed{\downarrow}$	0	$\boxed{\uparrow}\boxed{}\boxed{\uparrow}$	0
$\boxed{}\boxed{\uparrow\downarrow}\boxed{}$	0	$\boxed{}\boxed{\uparrow}\boxed{\uparrow}$	-1
$\boxed{}\boxed{\uparrow}\boxed{\downarrow}$	-1	^3P	
$\boxed{}\boxed{}\boxed{\uparrow\downarrow}$	-2		
$^1D + {}^1S$			

25.6.15

We consider the singlet and triplet terms separately. The singlet (↑↓) explicit configurations are listed on the left and the triplet (↑↑) on the right. The overall list of singlet configuration M_L values is: 2, 1, 0, 0, -1, -2. The maximum is $M_L = 2$, giving the L for the first term as $L = 2$, or a ^1D term. The ^1D term has a degeneracy of 5: $g_L = 2L + 1 = 5$. The sublevels that correspond to the ^1D term are then:

$$\text{Singlets: } L = |M_L|_{max} = 2 \text{ for a } {}^1D \text{ with } M_L = 2, 1, 0, -1, -2 \qquad 25.6.16$$

Removing these M_L values from the singlet list leaves one remaining configuration with $M_L = 0$, which gives a ^1S term. We don't need to worry about which specific configurations are involved. But we do need to keep track of all the repeat M_L values. Turning to the triplet configurations, the maximum M_L is $M_L = 1$, which gives a ^3P term. The ^3P term has a degeneracy of 3: $g_L = 2L + 1 = 3$. The sublevels that correspond to the ^3P term are then:

$$\text{Triplets: } L = |M_L|_{max} = 1 \text{ for a } {}^3P \text{ with } M_L = 1, 0, -1 \qquad 25.6.17$$

These configurations exhaust the list of triplet configurations. In summary then, the p^2 configuration gives three terms $^1D + {}^1S + {}^3P$. Experimentally the ^3P term corresponds to the carbon atom ground state, while the ^1D and ^1S states are higher energy excited states. Each of these states has a different pattern of chemical reactivity.

One note of caution is required. The diagrams in Eq. 25.6.15 don't take into account electron indistinguishability. Many of the detailed configurations are incomplete. Schematically for example, to satisfy indistinguishablity:

$$\boxed{}\boxed{\uparrow\downarrow}\boxed{} \sim {}^1\!/\!\sqrt{2}\left(\boxed{}\ \boxed{\uparrow\downarrow}\ \boxed{} - \boxed{}\ \boxed{\downarrow\uparrow}\ \boxed{}\right) \qquad 25.6.18$$

In addition, each detailed configuration is represented in calculations by a Slater determinant so that all electrons take their turns in p_x, p_y, and p_z. Finally, all degenerate configurations mix as linear combinations (e.g. all the $M_L = 0$ configurations with the same spin multiplicity). However, for purposes of determining term symbols, the "short hand" configurations in Eq. 25.6.15 work well. Term symbols for some common configurations are given in Table 25.6.2.

Table 25.6.2: Term Symbols for Selected Configurations.[5]

s^1	^2S	s^2, p^6, d^{10}	^1S		
s^1p^1	$^{1,3}P$	s^1d^1	$^{1,3}D$	p^1d^1	$^{1,3}P,D,F$
p^1, p^5	^2P	p^2, p^4	$^1S,D;\ {}^3P$	p^3	$^2P,D;\ {}^4S$
d^1, d^9	^2D				
d^2, d^8	$^1S,D,G;\ {}^3P,F$				
d^3, d^7	$^2P,D,D,F,G,H;\ {}^4P,F$				
d^4, d^6	$^1S,S,D,D,F,G,G,I;\ {}^3P,P,D,F,F,G,H;\ {}^5D$				
d^5	$^2S,P,D,D,D,F,F,G,G,H,I;\ {}^4P,D,F,G;\ {}^6S$				

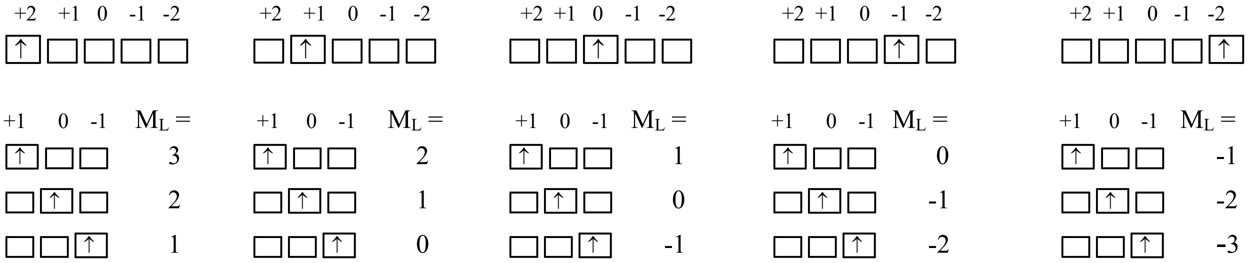
Note: $^{1,3}P,D,F$ indicates six possible terms: ^1P, ^1D, ^1F, ^3P, ^3D, ^3F

Example 25.6.1: *Total Orbital and Spin Angular Momentum*
Determine the terms for the atomic configuration, $d^1\ p^1$.

Answer: The orbital angular momentum quantum numbers for the individual electrons are $\ell_1 = 2$ and $\ell_2 = 1$. The Clebsch-Gordon series gives the terms as:

$$L = 2+1,\ldots,|2-1| = 3, 2, 1 \text{ or F, D, P}$$

We can explain why these terms arise by constructing the explicit configurations. The explicit configurations for $d^1\ p^1$ are diagrammed below, assuming triplet spin multiplicity. The d-orbital configuration at the top of each column is paired with each of the p-orbital configurations in the same column to give (5)(3) = 15 explicit configurations:



The overall list of M_L values is: 3, 2, 2, 1, 1, 1, 0, 0, 0, -1, -1, -1, -2, -2, -3.
The maximum M_L is L = 3 giving an F term with degeneracy of 7:

$$L = |M_L|_{max} = 3 \text{ for an } {}^3F \text{ term with } M_L = 3, 2, 1, 0, -1, -2, -3$$

Removing these M_L values from the list leaves 2, 1, 1, 0, 0, -1, -1, -2.
The maximum remaining M_L is $M_L = 2$ giving a ^3D term with a degeneracy of 5:

$$L = |M_L|_{max} = 2 \text{ for a } {}^3D \text{ term with } M_L = 2, 1, 0, -1, -2$$

Removing these last five M_L values from the list leaves: 1, 0, -1. The maximum remaining M_L is $M_L = 1$ giving a ^3P term with a degeneracy of 3:

$$L = |M_L|_{max} = 1 \text{ for a } {}^3P \text{ term with } M_L = 1, 0, -1$$

These final M_L values exhaust the list. The two electrons can also be placed in the same explicit configurations, but with paired electron spins (↑↓), which give a parallel set of singlet configurations: ^1F, ^1D, ^1P. A total of six terms arise from a d^1p^1 atomic configuration. Once again, we note that in the complete representation of the final states, degenerate individual configurations combine in the final terms and electron indistinguishability is maintained in the final spin-orbitals, through the use of Slater determinants. The exhaustive construction of the explicit configurations is, well, exhausting. We created the exhaustive list to show how the F, D, and P terms arise, but in general using the Clebsch-Gordon series is sufficient and much easier.

The total spin quantum number, S, and the total orbital angular momentum quantum number, L, are separately good descriptions of an electronic state only if the spin and orbital angular momenta don't interact. However, as we progress through the periodic table the spin and orbital angular momentum increasingly interact, or **couple** with each other. For the 5th and 6th period elements these interactions are strong and have a significant effect on chemical reactivity as well as the atomic spectroscopy.

Spin and Orbital Angular Momenta Couple: The spin and orbital angular momenta combine to give the total angular momentum of the electronic state, $\vec{J}$. The angular momentum vectors add vectorially:

$$\vec{J} = \vec{L} + \vec{S} \qquad 25.6.19$$

The total angular momentum behaves like any angular momentum, analogous to Eqs. 25.6.2-25.6.11:

$$\vec{J} = \Sigma\, \vec{j}_i \qquad 25.6.20$$

where $\vec{J}$ is the total angular momentum and the $\vec{j}_i$ are the total angular momentum vectors for each of the electrons in the atom. The magnitude of the total angular momentum is determined by the **total angular momentum quantum number**, J, in analogy with Eq. 24.5.34 and Eqs. 25.6.2-25.6.5:

$$|J| = \sqrt{J(J+1)}\,\hbar \qquad 25.6.21$$

The projection of the total angular momentum on the z-axis is quantized with quantum number M_J and degeneracy g_J:

$$J_z = M_J\,\hbar \qquad M_J = -J,\ldots, 0, \ldots, J \text{ with degeneracy } g_J = 2J + 1 \qquad 25.6.22$$

M_J is the sum of the individual electron total quantum numbers, $m_{j,i}$:

$$M_J = \Sigma\, m_{j,i} \qquad 25.6.23$$

Since M_J varies from –J to +J, the total quantum number is given by the maximum of M_J:

$$J = M_{J,max} \qquad 25.6.24$$

The coupling can be determined using Eq. 25.6.19 or Eq. 25.6.20. For light atoms using $\vec{J} = \vec{L} + \vec{S}$ is easier and is called the **L-S coupling** or **Russell-Saunders coupling** scheme. The allowed values of J in the Russell-Saunders coupling scheme are given by the Clebsch-Gordan series:

$$J = L + S, L + S - 1, \ldots, |L - S| \qquad 25.6.25$$

Once again, we don't need to know the full angular momentum vector, knowing the J quantum number is sufficient. A vector diagram will help to summarize these relationships. Consider a single unpaired electron in a p-orbital. For a p^1 configuration, L = 1 and S = ½. The Clebsch-Gordon series gives two terms:

$$J = 1 + \tfrac{1}{2}, |1 - \tfrac{1}{2}| = \tfrac{3}{2}, \tfrac{1}{2} \qquad 25.6.26$$

We can understand the Clebsch-Gordon results by enumerating all possible combinations of M_L and M_S, Figure 25.6.2. The full list is $M_J = -{}^3/_2, -{}^1/_2, -{}^1/_2, {}^1/_2, {}^1/_2, +{}^3/_2$. The $J = M_{J,max} = {}^3/_2$ term includes $M_J = -{}^3/_2, -{}^1/_2, {}^1/_2, +{}^3/_2$. The remaining configurations give a $J = M_{J,max} = {}^1/_2$ term, which includes $M_J = -{}^1/_2, {}^1/_2$. As noted before, we rarely need to enumerate all the possible M_L and M_S combinations. We did so in this case to help visualize the results of the Clebsch-Gordon series.

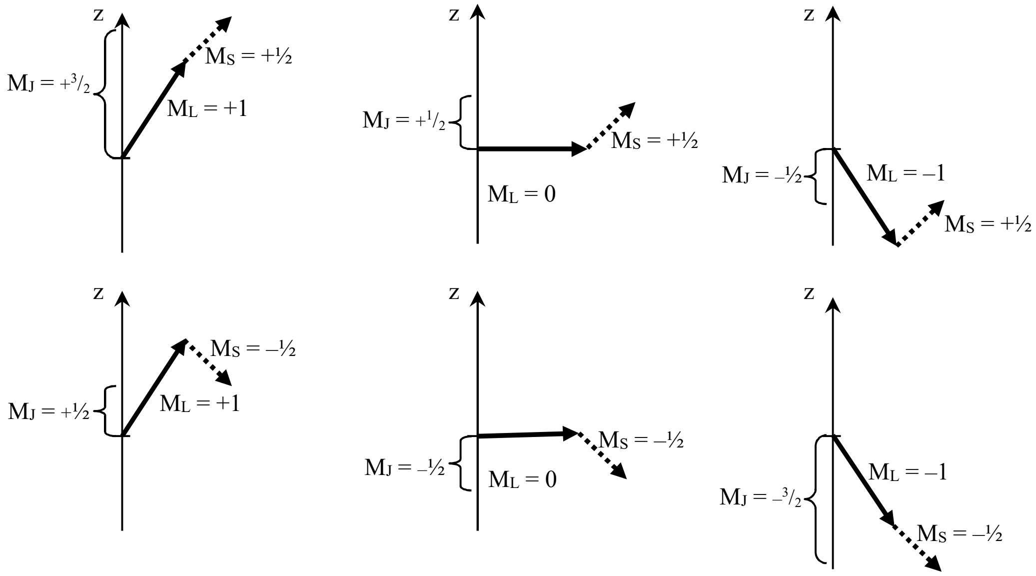
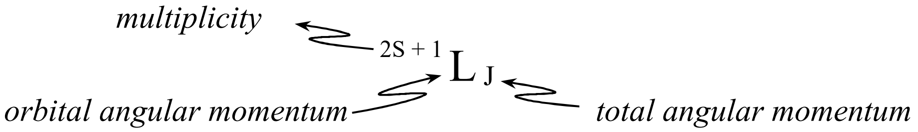


Figure 25.6.2: A p^1 configuration has $L = 1$ and $S = ½$ giving $J = {}^1/_2, {}^3/_2$ for two terms: ${}^2P_{½}$ and ${}^2P_{3/2}$.

The total angular momentum quantum number is included in the term symbol as a subscript:



$$ {}^{2S+1}L_J \qquad 25.6.27 $$

The J quantum number must be specified to provide a unique "nickname" for each possible electronic state. A good example of the effects of the coupling of angular momenta is the sodium atom emission spectrum. The prominent yellow emission line for sodium is a closely spaced doublet, because the p^1 excited state configuration gives two states, one with $J = {}^3/_2$ and one with $J = ½$: terms ${}^2P_{3/2}$ and ${}^2P_{½}$. The ground state configurations of the elements are shown in Figure 25.6.3. Several generalizations aid the assignment of term symbols for simple cases:

a). $S = 0$ and $L = 0$ for filled subshells. Only partially filled subshells contribute to S and L.
b). For a closed-shell atom the term is ${}^1S_o$.
c). For a single electron beyond a closed shell core, $S = s$, $L = \ell$, and $J = \ell + ½, \ell - ½$.
d). For m electrons in a single partially filled subshell that holds n electrons, an ℓ^m configuration and an ℓ^{n-m} configuration give the same terms. For example, p^2 and p^4configurations give the same terms and d^3 and d^7 configurations give the same terms.

We have given examples with only two electrons outside a closed shell. The total angular momenta for multiple electrons are determined in stages; first, two electrons are coupled, then the results are coupled with the next electron, and those results are coupled with the next electron, etc. Accordingly, at each stage the number of possible states increases rapidly. The experimental ramification of the large number of electronic states is that atomic spectra contain a large number of transitions, even for the lightest atoms.

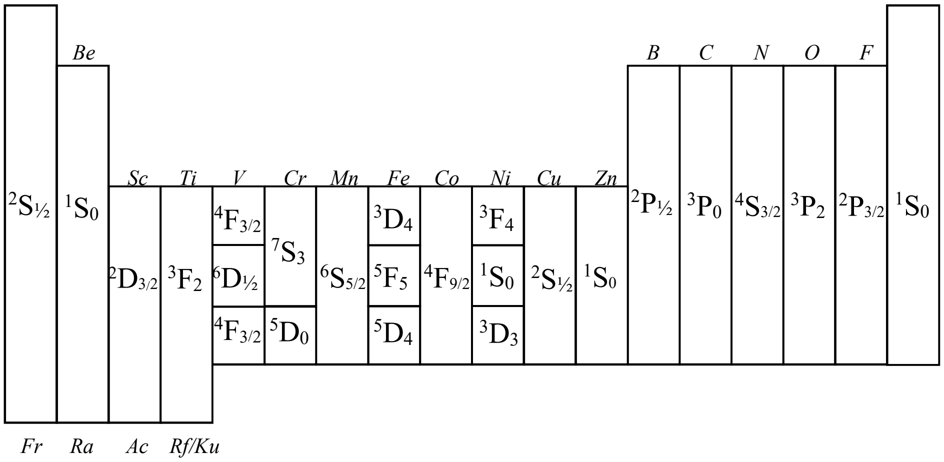


Figure 25.6.3: Ground state configurations of the elements.[6]

Example 25.6.2: *Total Angular Momentum*
Find the terms and total angular momentum states that result from the p^2 configuration of the carbon atom.

Answer: For the configuration C : p^2, the two electrons individually have orbital quantum numbers $\ell_1 = 1$ and $\ell_2 = 1$. The Clebsch-Gordon series gives the possible terms as L = 2, 1, 0 or D, P, and S terms, Eqs. 25.6.14 and 25.6.15. The two electrons individually have spin quantum numbers $s_1 = ½$ and $s_2 = ½$. The Clebsch-Gordon series results in total spin states S = 1, 0, giving triplet and singlet states. Taking each L state in turn gives the total angular momentum determined by the Clebsch-Gordon series as:

Term	Quantum Numbers	J = L + S, L + S – 1, …, |L – S|	Final terms
^1D	L = 2, S = 0	J = 2+0, 2–0 = 2	$^1D_2$
^3P	L = 1, S = 1	J = 1+1, 1+1–1, 1–1 = 2, 1, 0	$^3P_2$, $^3P_1$, $^3P_0$
^1S	L = 0, S = 0	J = 0	^1S_o

The L and S quantum numbers are not valid for heavy atoms with strong interactions between the orbital and spin angular momenta. For heavy atoms, Z > 40, the total angular momentum is calculated using the **j-j coupling scheme**, which is based on Eq. 25.6.20 (see Further Reading).

The strength of the coupling of the orbital and spin angular momentum is minimal for light elements and a significant fraction of the electronic energy for heavy elements. The interaction is called **spin-orbit coupling**. Consider a single electron in a p^1 configuration. Classically, a current flowing through a loop of wire creates a magnetic field. As the electron rotates around the nucleus a magnetic field is also generated. The intrinsic angular momentum of the electron in combination with the charge on the electron also generates a magnetic field, Figure 25.6.4.

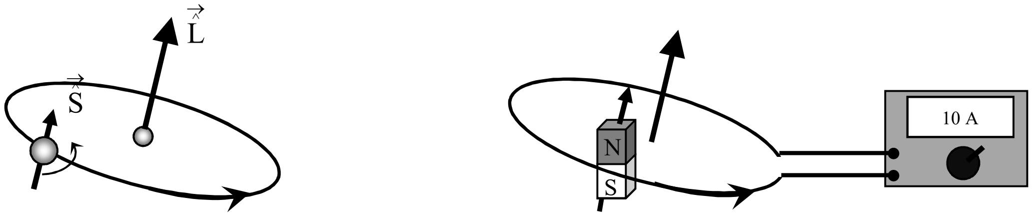


Figure 25.6.4: The magnetic field generated by the orbital motion of the electron and the intrinsic magnetic moment of the electron interact like a bar magnet in the magnetic field created by electrical current in a loop of wire.

The magnetic fields caused by the orbital motion and the intrinsic magnetic moment of the electron interact; the energy of the state is lower if the magnetic moments are in opposite directions and higher if the magnetic moments are parallel. For light elements, spin-orbit coupling may be treated as a perturbation. The Hamiltonian is broken into two terms, $\hat{\mathcal{H}}_o + \hat{\mathcal{H}}'_{so}$, where $\hat{\mathcal{H}}_o$ corresponds to no interaction and the perturbation, $\hat{\mathcal{H}}'_{so}$, is the **spin-orbit interaction**:

$$\hat{\mathcal{H}}'_{so} = \xi\, \vec{L}\cdot\vec{S} \qquad 25.6.28$$

The constant ξ is the spin-orbit coupling constant. $\vec{L}\cdot\vec{S}$ is related to the total angular momentum, $\vec{J} = \vec{L} + \vec{S}$. Taking the square of $\vec{J}$ gives:

$$\hat{J}^2 = \vec{J}\cdot\vec{J} = (\vec{L} + \vec{S})\cdot(\vec{L} + \vec{S}) = \vec{L}\cdot\vec{L} + \vec{S}\cdot\vec{S} + 2\vec{L}\cdot\vec{S} = \hat{L}^2 + \hat{S}^2 + 2\,\vec{L}\cdot\vec{S} \qquad 25.6.29$$

Solving this last equation for $\vec{L}\cdot\vec{S}$ gives:

$$\vec{L}\cdot\vec{S} = \tfrac{1}{2}\left(\hat{J}^2 - \hat{L}^2 - \hat{S}^2 \right) \qquad 25.6.30$$

If the perturbation is small, L and S remain separately good quantum numbers. To a good level of approximation, the total angular momentum wave function is the product of orbital and spin angular momentum eigenfunctions: $\Psi_{J,m_J} = \Psi_{L,m_L}\, \Psi_{S,m_S}$. Using Eqs. 25.6.30, 25.6.2, 25.6.8, and 25.6.21, the interaction operator then has the eigenvalue:

$$|\, \vec{L}\cdot\vec{S} \,| = \tfrac{1}{2}\, \hbar^2\, [J(J+1) - L(L+1) - S(S+1)] \qquad 25.6.31$$

Substitution of this last equation into Eq. 25.6.28 and finding the expectation value gives the spin-orbit interaction energy as:

$$E_{so} = \tfrac{1}{2}\, \mathcal{A}hc\, [J(J+1) - L(L+1) - S(S+1)] \qquad 25.6.32$$

where $\mathcal{A}$ is the spin-orbit interaction constant, expressed in wave numbers with $\mathcal{A}hc = \xi\hbar^2$. The spin-orbit interaction constant increases with the charge of the nucleus. The successive effects of electron-electron repulsion and spin-orbit coupling on the energy of the states for a p^2 configuration are shown in Figure 25.6.5. An external magnetic field further splits the levels.

Example 25.6.3: *Spin Orbit Coupling*
Find the spin-orbit splitting of the $^2P_{3/2}$ and $^2P_{1/2}$ terms for the sodium atom.

Answer: For the p^1 configuration of the alkali metals, the energy of the ${}^2P_{3/2}$ and ${}^2P_{1/2}$ terms are split by, respectively:

$$E_{so}\,(J = {}^3\!/_2) = {}^1\!/_2\, \mathcal{A}hc\, [{}^3\!/_2({}^3\!/_2 + 1) - 1(1+1) - {}^1\!/_2({}^1\!/_2+1)] = {}^1\!/_2\, \mathcal{A}hc\, [{}^{15}\!/_4 - {}^8\!/_4 - {}^3\!/_4] = {}^1\!/_2\, \mathcal{A}hc$$

$$E_{so}\,(J = {}^1\!/_2) = {}^1\!/_2\, \mathcal{A}hc\, [{}^1\!/_2({}^1\!/_2 + 1) - 1(1+1) - {}^1\!/_2({}^1\!/_2+1)] = {}^1\!/_2\, \mathcal{A}hc\, [{}^3\!/_4 - {}^8\!/_4 - {}^3\!/_4] = -1\, \mathcal{A}hc$$

giving $\Delta E_{so} = {}^3\!/_2\, \mathcal{A}hc$. This splitting is small, 17 cm^{-1}, since the Z for sodium is small.

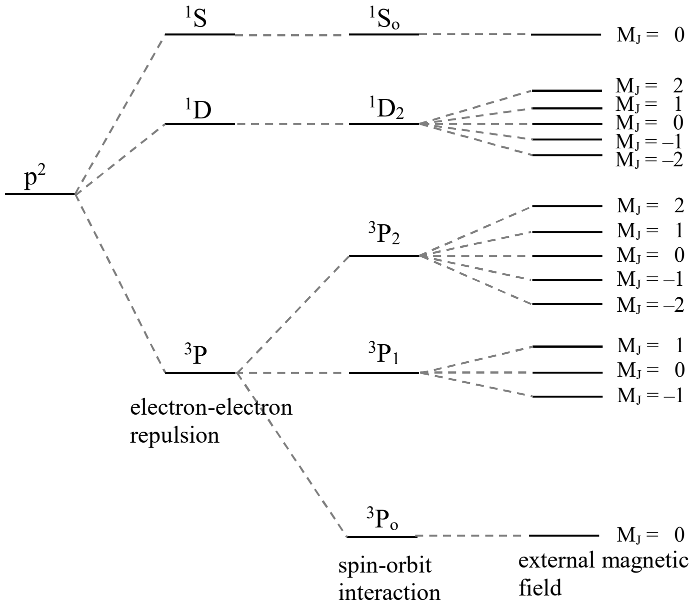


Figure 25.6.5: A p^2 configuration is split into ${}^3P$, ${}^1D$, and ${}^1S$ terms by electron-electron repulsion. The degeneracy of the resulting terms is split by spin-orbit coupling. The degeneracy of the total angular momentum J-states is split by an external magnetic field.

The energy order for the terms arising from a given ground state configuration is predicted by Hund's rules:

1). The terms with maximum S have lowest energy. (Rephrased from Sec. 25.4)
2). For a given value of S, the term with maximum L has lowest energy.
3). For a given S and L, if the open subshell is less than half-full then minimum J has lowest energy. If the open subshell is more than half-full then maximum J has lowest energy.

For an example, consider the carbon p^2 configuration, Figure 25.6.5. Using rule 2, ${}^1D_2$ is lower in energy than ${}^1S_o$. Both states have the same spin multiplicity, but the ${}^1D_2$ has higher L. Using rule 3, the energy order for the ${}^3P$ terms is ${}^3P_o < {}^3P_1 < {}^3P_2$, because the p subshell is less than half-full. Hund worked out these summary rules from analysis of atomic spectra. However, the predictions have now been verified through careful electronic structure calculations. The energy order for excited state terms usually follow Hund's rules, but exceptions occur.

Selection Rules Govern the Intensities of Transitions: Two conditions are necessary for the absorption or emission of light. The frequency of the light must match the transition energy,

$\Delta E = h\nu$, and the absorption or emission transition must give rise to a changing dipole moment. For absorption, the electric field of light interacts with the oscillating electric dipole moment that results from the transition. For example, a transition from an s-orbital to an s-orbital causes no skewing of the electron density, so no change in dipole results. A transition from an s-orbital to a p-orbital skews the electron distribution and is therefore called a **dipole allowed transition**. The intensity of an absorption or emission transition from the initial state Ψ_i to the final state Ψ_j is proportional to the **transition dipole moment**, μ_{tr}:

$$\mu_{tr} = \langle \hat{\mu} \rangle = \int \Psi_j^* \, (-e\,\hat{r})\, \Psi_i \, d\tau \qquad 25.6.33$$

The dipole moment operator is given by $\hat{\mu} = -\,e\,\hat{r}$, where e is the charge on the electron and $\hat{r}$ is the position operator for all the electrons in the atom or molecule. Atoms, of course, have no permanent dipole moment, but they can have a changing dipole moment upon interaction with light. The requirement for a non-vanishing transition dipole moment is called the **gross selection rule**. In addition, all interactions must conserve angular momentum. The photon has an angular momentum quantum number of s = 1, Sec. 24.5. The change in orbital angular momentum for the atom must then be ±1 upon the absorption or emission of light. The conservation of angular momentum is called the **specific selection rule**. We will discuss selection rules more completely in the electronic spectroscopy chapter. For now, we note that the selections rules for atomic absorption and emission are:

1. $\Delta S = 0$ for example singlet to triplet transitions are not allowed
2. $\Delta L = \pm 1$ for example $S \not\leftrightarrow S$ is not allowed, but $S \leftrightarrow P$ or $P \leftrightarrow D$ is allowed
3. $\Delta J = 0, \pm 1$ except $J = 0 \not\leftrightarrow J = 0$ for example ${}^2P_{1/2} \not\leftrightarrow {}^2D_{5/2}$ is not allowed 25.6.34

In addition, one n or ℓ must change for one electron (Laporte selection rule). In other words, transitions between states with the same configuration are not allowed. For example, the carbon p^2 configuration gives rise to ${}^3P$, ${}^1D$, and ${}^1S$ terms. Transitions among these states from the p^2 configuration are not allowed. The selection rule for spin multiplicity is often violated, especially for systems with strong spin-orbit coupling. Phosphorescence violates $\Delta S = 0$. Correspondingly, phosphorescence lifetimes are usually significantly longer than fluorescence lifetimes.

The ground state of Na is ${}^2S_{1/2}$. The bright yellow sodium doublet is the result of the emission transitions ${}^2P_{3/2} \rightarrow {}^2S_{1/2}$ and ${}^2P_{1/2} \rightarrow {}^2S_{1/2}$, for which $\Delta S = 0$, $\Delta L = -1$, and $\Delta J = 1$ or 0. The selection rules for atomic spectroscopy are examples of the importance of term symbols and the effect of angular momenta on the properties of atoms. The interaction of atoms with magnetic fields are another application where angular momentum states play a critical role.

25.7 Magnetic Interactions[7,8]

The behavior of systems in magnetic fields is becoming increasingly important, for example for magnetic resonance imaging contrast reagents and for use in manipulating nano-systems. Determination of the magnetic moment of transition metal complexes is an important characterization technique in inorganic chemistry. We consider first the classical expressions for the interaction of a magnetic moment with an external magnetic field. We then assume that the interaction energy is less than the spin-orbit coupling, so that Russell-Saunders coupling is valid.

Motion of a charged particle in a loop creates a magnetic field, Figure 25.6.4. Classically, the orbital magnetic moment of an electron generated by orbital angular momentum $\vec{L}$ is given by:

$$\vec{\mu}_L = -\frac{e}{2m_e}\vec{L} \qquad 25.7.1$$

The magnitude of the orbital magnetic moment is:

$$\mu_L = -\frac{e}{2m_e}\hbar\sqrt{L(L+1)} \qquad 25.7.2$$

The sign is negative because of the negative charge of the electron. The intrinsic spin magnetic moment generated by the total spin angular momentum $\vec{S}$ is given by:

$$\vec{\mu}_S = -2\,\frac{e}{2m_e}\vec{S} \qquad 25.7.3$$

The magnitude of the spin magnetic moment is:

$$\mu_S = -2\,\frac{e}{2m_e}\hbar\sqrt{S(S+1)} \qquad 25.7.4$$

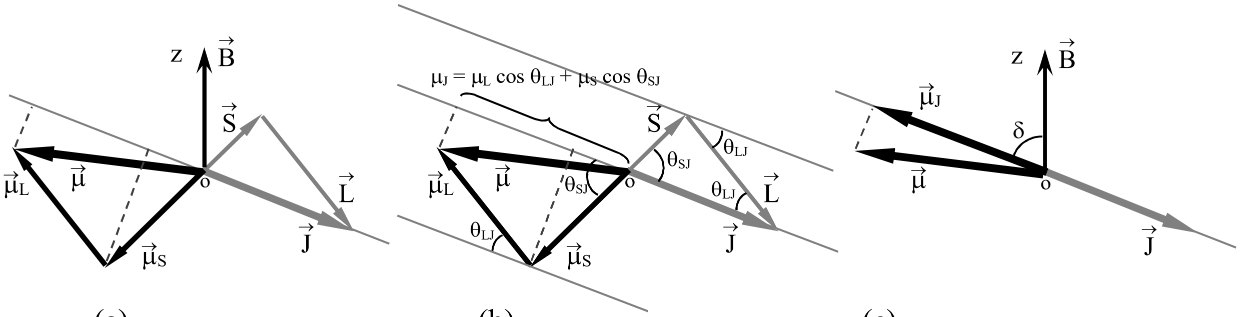
The factor of 2 is from the relativistic treatment of the electron. Careful studies of free electrons show the constant to be 2.0023, but 2 will be close enough for our purposes. The consequence is that the intrinsic electron spin creates twice the magnetic moment of the equivalent orbital angular momentum. The orbital and spin magnetic moment add vectorially to give the total magnetic moment of the atom:

$$\vec{\mu} = \vec{\mu}_L + \vec{\mu}_S = -\frac{e}{2m_e}(\vec{L} + 2\vec{S}) \qquad 25.7.5$$

Substituting the total angular momentum, $\vec{J} = \vec{L} + \vec{S}$, into the last expression gives:

$$\vec{\mu} = -\frac{e}{2m_e}(\vec{J} + \vec{S}) \qquad 25.7.6$$

The extra factor of two in the spin magnetic moment requires that the total magnetic moment and the total angular momentum are not collinear, Figure 25.7.1. The external magnetic field determines the direction of quantization, which is assigned as the z-axis. The orientation of $\vec{L}$ and $\vec{S}$ are quantized along the z-axis. The negative charge of the electron directs the magnetic moments in the opposite direction to the angular momenta, Figure 25.7.1a.



(a). (b). (c).

Figure 25.7.1: (a). The orbital and spin angular momenta add vectorially. The orbital and spin magnetic moments also add vectorially. (b). The Law of Cosines determines the angles relative to the total angular momentum. The effective magnetic moment, $\vec{\mu}_J$, is collinear with $\vec{J}$. (c). The interaction with the external magnetic field is: $\Delta E = -\vec{\mu}_J \cdot \vec{B} = -\mu_J B \cos\delta$.

The effective magnetic moment, μ_J, is the projection of the total magnetic moment along the direction of the total angular momentum, Figure 25.7.1b:

$$\mu_J = \mu_L \cos\theta_{LJ} + \mu_S \cos\theta_{SJ} \qquad 25.7.7$$

The angle θ_{LJ} is between the total orbital angular momentum, $\vec{L}$, and the total angular momentum, $\vec{J}$. The angle θ_{SJ} is between the spin angular momentum, $\vec{S}$, and the total angular momentum, $\vec{J}$. The angles are determined using the Law of Cosines, Figure 25.8.1b. For the θ_{SJ} angle the sides have length |S| and |J| with side opposite the angle $\vec{L}$:

$$L(L+1)\,\hbar^2 = S(S+1)\,\hbar^2 + J(J+1)\,\hbar^2 - 2\sqrt{S(S+1)}\sqrt{J(J+1)}\,\hbar^2 \cos\theta_{SJ} \qquad 25.7.8$$

In Figure 25.7.1b, the three grey diagonal lines are parallel to $\vec{J}$, which defines θ_{LJ}. For the θ_{LJ} angle the sides have length |L| and |J| with side opposite $\vec{S}$:

$$S(S+1)\,\hbar^2 = L(L+1)\,\hbar^2 + J(J+1)\,\hbar^2 - 2\sqrt{L(L+1)}\sqrt{J(J+1)}\,\hbar^2 \cos\theta_{LJ} \qquad 25.7.9$$

Substituting Eqs. 25.7.2, 25.7.4, 25.7.8, and 25.7.9 into Eq. 25.7.7 gives the magnitude of the projection of the magnetic moment on $\vec{J}$ as:[8,9]

$$\mu_J = -\frac{e}{2m_e}\hbar\,[J(J+1)]^{1/2}\left[1 + \frac{J(J+1) + S(S+1) - L(L+1)}{2J(J+1)}\right] \qquad 25.7.10$$

The last factor is called the **Landé *g*-factor** or the **gyromagnetic ratio**, *g*:

$$\mu_J = -g\frac{e}{2m_e}\hbar\sqrt{J(J+1)} \qquad 25.7.11$$

The **Bohr magneton** is the quantum unit for magnetic field strength and is defined as:

$$\mu_B = \frac{e}{2m_e}\hbar \qquad 25.7.12$$

The interaction energy of the atom with the external magnetic field is:

$$\Delta E = -\vec{\mu}_J \cdot \vec{B} = -\mu_J B \cos\delta \qquad 25.7.13$$

where B is the strength of the magnetic field and δ is the angle between the magnetic moment of the atom and the external field direction, Figure 25.7.1c. The effective magnetic moment, $\vec{\mu}_J$, is collinear with the total angular momentum. The z-projection of the total angular momentum is $J_z = M_J\hbar$. The magnitude of the total angular momentum is $|J| = \hbar\sqrt{J(J+1)}$. The angle between the total angular momentum vector and the z-axis is then:

$$\cos\delta = \frac{J_z}{|J|} = \frac{M_J\hbar}{[J(J+1)]^{1/2}\hbar} = \frac{M_J}{[J(J+1)]^{1/2}} \qquad 25.7.14$$

Substituting Eqs. 25.7.11, 25.7.12, and 25.7.14 into Eq. 25.7.13 gives the interaction energy as:

$$\Delta E = g\,\mu_B\,B\,M_J \qquad 25.7.15$$

The magnetic interaction is called the **Zeeman splitting**, which is proportional to the external magnetic field strength. Each M_J state gives a different energy, Figure 25.6.5. The splitting of the degenerate levels for a given J-state into 2J + 1 levels allows the J quantum numbers for a transition to be determined experimentally. Zeeman splitting is also used in background subtraction techniques in atomic absorption spectroscopy in elemental analysis.

25.8 Summary – Looking Ahead

The electronic structure of the hydrogen atom played a central role in the historical development of quantum mechanics. However, hydrogen-like orbitals are exact only for one-electron atoms and ions. Hydrogen-like orbitals may be used as approximations for multi-electron atoms, however current electronic structure methods often use sums of Gaussian primitives to estimate the radial electron distribution in multi-electron systems. The angular portion of atomic orbitals is exactly described by spherical harmonics. In the orbital approximation, products of one-electron atomic orbitals are used as approximations for the wave functions of multi-electron systems. The effective charge model is a descriptive method for understanding the effects of electron-electron repulsion. Electron-electron repulsion breaks the degeneracy of orbitals in the same principle quantum shell. Hund's Rules are statements about the minimization of electron-electron repulsion through the configuration of the electronic state with maximum spin multiplicity.

Perturbation and variation theory are generally useful approximation methods. The application to the electronic structure of atoms is just one specific example. Both methods play important roles in molecular structure calculations. Self-consistent field theory is variational. Hartree-Fock theory takes electron indistinguishability into account through the use of orbitals constructed as Slater determinants. The exchange energy is the difference in energy between the calculation of the energy of an atom, ion, or molecule with and without Slater determinants. The exchange energy is an important component in accurate electronic structure methods. Spin-orbit coupling is another important contribution to the electronic energy of atoms, especially heavy atoms. In spin-orbit coupling, the spin and orbital angular momentum of the atom interact. Taking proper account of electron indistinguishability leads to the Pauli Exclusion Principle.

The Pauli Exclusion Principle is one of several important fundamental principles in nature determined by symmetry. Were it not for the restriction, all the electrons in an atom might be found in the 1s-orbital, and then chemistry would occur only in very energetic circumstances. Detailed balance, the Gibbs Phase Rule, the Pauli Exclusion Principle, and the fluctuation dissipation theorem (Sec. 29.5) have wide-ranging ramifications for chemical interactions. While simple in statement, these principles describe the underlying foundations of chemistry. These central generalizations describe the interrelationships between different aspects of chemical reactivity and delineate the boundaries for possible chemical processes. We are now ready to develop the theory of the chemical bond.

25.8 Addendum: Electron-Electron Repulsion in Helium[9]

Perturbation Theory: The Expectation Value of the Electron-Electron Repulsion in Helium: The expectation value of the electron-electron repulsion is given by Eq. 25.3.18:

$$E^{(1)}_{gs} = \int \Psi^*_{1s}(r_1)\, \Psi^*_{1s}(r_2)\, \frac{e^2}{4\pi\varepsilon_o r_{12}}\, \Psi_{1s}(r_1)\, \Psi_{1s}(r_2)\, d\tau_1 d\tau_2 \qquad (25.3.18)$$

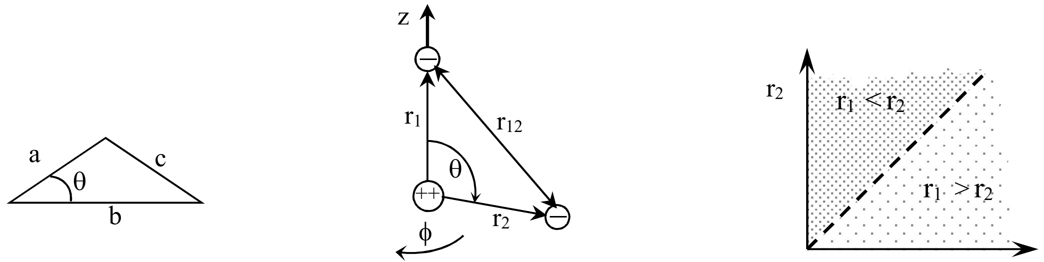
$$E^{(1)}_{gs} = \int_0^\infty\!\int_0^\pi\!\int_0^{2\pi}\!\int_0^\infty\!\int_0^\pi\!\int_0^{2\pi} \Psi^*_{1s}(r_1)\, \Psi^*_{1s}(r_2)\, \frac{e^2}{4\pi\varepsilon_o r_{12}}\, \Psi_{1s}(r_1)\, \Psi_{1s}(r_2)\, r_1^2 dr_1 \sin\theta_1\, d\theta_1\, d\phi_1\, r_2^2 dr_2 \sin\theta_2 d\theta_2\, d\phi_2 \qquad 25.8.1$$

The helium atom is spherical, so the integration over the θ_1 and ϕ_1 angles for electron 1 gives 4π. Again, given the helium atom is spherical, the orientation of the coordinate axis is arbitrary. For convenience, we position electron 1 along the z-axis. The position of electron 2 is then given by the θ angle between the z-axis and the vector pointing to electron 2 and the ϕ angle about the z-axis, Figure 25.8.1b. Substitution of single-electron 1s hydrogen-like atomic orbitals for the two electrons then gives:

$$E_{gs}^{(1)} = \frac{1}{\pi^2}\left(\frac{Z}{a_o}\right)^6 4\pi \int_0^\infty\int_0^\infty\int_0^\pi\int_0^{2\pi} e^{-2Zr_1/a_o}\, e^{-2Zr_2/a_o} \frac{e^2}{4\pi\varepsilon_o r_{12}}\, r_1^2\, r_2^2 \sin\theta\, dr_1 dr_2\, d\theta\, d\phi \qquad 25.8.2$$

The distance between the two electrons is given by the Law of Cosines, Figure 25.8.1b:

$$r_{12} = (r_1^2 + r_2^2 - 2\, r_1 r_2 \cos\theta)^{1/2} \qquad 25.8.3$$



$c^2 = a^2 + b^2 - 2ab\cos\theta$ (a).

$r_{12} = (r_1^2 + r_2^2 - 2\, r_1 r_2 \cos\theta)^{1/2}$ (b).

(c).

Figure 25.8.1: (a).The Law of Cosines. (b). The electron-electron distance from the Law of Cosines. (c). Integration domains for the electron-electron repulsion integral.

Using Eqs. 25.8.2 and 25.8.3, the expectation value for the ground state electron-electron repulsion is:

$$E_{gs}^{(1)} = \frac{1}{\pi^2}\left(\frac{Z}{a_o}\right)^6 \frac{e^2}{4\pi\varepsilon_o} 4\pi \int_0^\infty\int_0^\infty\int_0^\pi\int_0^{2\pi} e^{-2Zr_1/a_o}\, e^{-2Zr_2/a_o} \frac{1}{(r_1^2 + r_2^2 - 2\, r_1 r_2 \cos\theta)^{1/2}}\, r_1^2\, r_2^2 \sin\theta\, dr_1 dr_2\, d\theta\, d\phi \qquad 25.8.4$$

The integrand is independent of ϕ giving the remaining ϕ integral as 2π.The radial integrals are taken over all values of the distances of both electrons from the nucleus. Unfortunately, these integrals do not separate into a product of one-dimensional terms. The integrals must be broken into two domains, one for $r_1 > r_2$ and one for $r_1 < r_2$, Figure 25.8.1c, using:

$$\int_0^\pi \frac{1}{(r_1^2 + r_2^2 - 2\, r_1 r_2 \cos\theta)^{1/2}} \sin\theta\, d\theta = \frac{2}{r_1} \text{ for } r_1 > r_2 \qquad \text{or} \quad = \frac{2}{r_2} \text{ for } r_1 < r_2 \qquad 25.8.5$$

Substituting these integrals into Eq. 25.8.4 gives two terms, the first term for $r_1 > r_2$ and the second term for $r_1 < r_2$:

$$E_{gs}^{(1)} = 8\left(\frac{Z}{a_o}\right)^6 \frac{e^2}{4\pi\varepsilon_o} \left[\int_0^\infty\int_0^{r_1} e^{-2Zr_1/a_o}\, e^{-2Zr_2/a_o} \frac{2}{r_1} r_1^2\, r_2^2\, dr_1\, dr_2 + \int_0^\infty\int_{r_1}^\infty e^{-2Zr_1/a_o}\, e^{-2Zr_2/a_o} \frac{2}{r_2} r_1^2\, r_2^2\, dr_1 dr_2\right]$$

$$= 16\left(\frac{Z}{a_o}\right)^6 \frac{e^2}{4\pi\varepsilon_o}\left[\int_0^\infty\int_0^{r_1} e^{-2Zr_1/a_o}\, e^{-2Zr_2/a_o}\, r_1\, r_2^2\, dr_1\, dr_2 + \int_0^\infty \int_{r_1}^\infty e^{-2Zr_1/a_o}\, e^{-2Zr_2/a_o}\, r_1^2\, r_2\, dr_1 dr_2\right] \qquad 25.8.6$$

The integrals over r_2 are taken first, since they depend on r_1:

$$E_{gs}^{(1)} = 16\left(\frac{Z}{a_o}\right)^6 \frac{e^2}{4\pi\varepsilon_o}\left[\int_0^\infty e^{-2Zr_1/a_o}\, r_1 \left(\int_0^{r_1} e^{-2Zr_2/a_o}\, r_2^2\, dr_2\right) dr_1 + \int_0^\infty e^{-2Zr_1/a_o}\, r_1^2 \left(\int_{r_1}^\infty e^{-2Zr_2/a_o}\, r_2\, dr_2\right) dr_1\right] \qquad 25.8.7$$

The r_2 integrals are derived from tabulated integrals:

$$\int_{r_1}^\infty e^{-2Zr_2/a_o}\, r_2\, dr_2 = \frac{1}{2}\left(\frac{a_o}{Z}\right) r_1\, e^{-2Zr_1/a_o} + \frac{1}{2^2}\left(\frac{a_o}{Z}\right)^2 e^{-2Zr_1/a_o} \qquad 25.8.8$$

$$\int_0^{r_1} e^{-2Zr_2/a_o}\, r_2^2\, dr_2 = -\frac{1}{2}\left(\frac{a_o}{Z}\right) r_1^2\, e^{-2Zr_1/a_o} - \frac{1}{2}\left(\frac{a_o}{Z}\right)^2 r_1\, e^{-2Zr_1/a_o} - \frac{1}{2^2}\left(\frac{a_o}{Z}\right)^3 e^{-2Zr_1/a_o} + \frac{1}{2^2}\left(\frac{a_o}{Z}\right)^3 \qquad 25.8.9$$

Substitution of the last equation into the first integral in Eq. 25.8.7 gives:

$$\begin{aligned}\int_0^\infty e^{-2Zr_1/a_o}\, r_1 \left(\int_0^{r_1} e^{-2Zr_2/a_o}\, r_2^2\, dr_2\right) dr_1 &= -\frac{1}{2}\left(\frac{a_o}{Z}\right)\int_0^\infty r_1^3\, e^{-4Zr_1/a_o}\, dr_1 - \frac{1}{2}\left(\frac{a_o}{Z}\right)^2\int_0^\infty r_1^2\, e^{-4Zr_1/a_o}\, dr_1 \\ &\quad - \frac{1}{2^2}\left(\frac{a_o}{Z}\right)^3\int_0^\infty r_1\, e^{-4Zr_1/a_o}\, dr_1 + \frac{1}{2^2}\left(\frac{a_o}{Z}\right)^3\int_0^\infty r_1\, e^{-2Zr_1/a_o}\, dr_1 \qquad 25.8.10\end{aligned}$$

$$= -\frac{6}{2^9}\left(\frac{a_o}{Z}\right)^5 - \frac{1}{2^6}\left(\frac{a_o}{Z}\right)^5 - \frac{1}{2^6}\left(\frac{a_o}{Z}\right)^5 + \frac{1}{2^4}\left(\frac{a_o}{Z}\right)^5 \qquad 25.8.11$$

Substitution of Eq. 25.8.8 into the second integral in Eq. 25.8.7 gives:

$$\begin{aligned}\int_0^\infty e^{-2Zr_1/a_o}\, r_1^2 \left(\int_{r_1}^\infty e^{-2Zr_2/a_o}\, r_2\, dr_2\right) dr_1 &= \frac{1}{2}\left(\frac{a_o}{Z}\right)\int_0^\infty r_1^3\, e^{-4Zr_1/a_o}\, dr_1 + \frac{1}{2^2}\left(\frac{a_o}{Z}\right)^2\int_0^\infty r_1^2\, e^{-4Zr_1/a_o}\, dr_1 \\ &= \frac{6}{2^9}\left(\frac{a_o}{Z}\right)^5 + \frac{1}{2^7}\left(\frac{a_o}{Z}\right)^5 \qquad 25.8.12\end{aligned}$$

Substituting Eqs. 25.8.11 and 25.8.12 into Eq. 25.8.6 gives:

$$E_{gs}^{(1)} = 16\left(\frac{Z}{a_o}\right)^6 \frac{e^2}{4\pi\varepsilon_o}\frac{5}{2^7}\left(\frac{a_o}{4Z}\right)^5 = \frac{5Z}{8}\left(\frac{e^2}{4\pi\varepsilon_o\, a_o}\right) \qquad 25.8.13$$

The first-order perturbation theory correction is the expectation value of the electron-electron repulsion:

$$\begin{aligned}E_{gs}^{(1)} &= \left\langle\frac{e^2}{4\pi e_o r_{12}}\right\rangle = \frac{5Z}{8}\left(\frac{e^2}{4\pi\varepsilon_o\, a_o}\right) = \frac{5Z}{8}\left(\frac{m_e\, e^4}{16\pi^2\varepsilon_o^2\, \hbar^2}\right) \\ &= \frac{5Z}{8}\,(27.212\text{ eV}) = 34.01\text{ eV} \qquad 25.8.14\end{aligned}$$

The algebraic details for Eqs. 25.8.3-25.8.14 are worked out in Problems 38-42. This integral also gives an important contribution in the variation treatment of the helium atom.

Variation Theory: The Expectation Value of the Exact Helium Atom Hamiltonian: The trial energy for the variation treatment of the ground state of the helium atom is given by Eq. 25.3.25 evaluated with the trial wave function, Eq. 25.3.27. The one-electron wave functions, $\phi_{1s}(r_1)$ and

$\phi_{1s}(r_2)$, are normalized eigenfunctions of one-electron Hamiltonians with charge Z_{eff} and one-electron energies E_1 and E_2:

$$\left(\frac{-\hbar^2}{2m}\nabla_1^2 - \frac{Z_{eff}\,e^2}{4\pi\varepsilon_o r_1}\right)\phi_{1s}(r_1) = E_1\,\phi_{1s}(r_1) \qquad \left(\frac{-\hbar^2}{2m}\nabla_2^2 - \frac{Z_{eff}\,e^2}{4\pi\varepsilon_o r_2}\right)\phi_{1s}(r_2) = E_2\,\phi_{1s}(r_2)$$

$$E_1 = -½\left(\frac{e^2}{4\pi\varepsilon_o\, a_o}\right)Z_{eff}^2 = -13.6\text{ eV } Z_{eff}^2 \qquad E_2 = -½\left(\frac{e^2}{4\pi\varepsilon_o\, a_o}\right)Z_{eff}^2 = -13.6\text{ eV } Z_{eff}^2 \tag{25.8.15}$$

The one-electron orbitals are normalized giving:

$$\int \phi_{1s}^*(r_1)\,\phi_{1s}(r_1)\,d\tau_1 = 1 \qquad \int \phi_{1s}^*(r_2)\,\phi_{1s}(r_2)\,d\tau_2 = 1 \tag{25.8.16}$$

The exact Hamiltonian uses the full nuclear charge Z. We can relate the Coulomb portion of the exact Hamiltonian to the effective charge using $Z = Z_{eff} + (Z - Z_{eff})$:

$$\left(\frac{-\hbar^2}{2m}\nabla_1^2 - \frac{Ze^2}{4\pi\varepsilon_o r_1}\right)\phi_{1s}(r_1) = \left(\frac{-\hbar^2}{2m}\nabla_1^2 - \frac{Z_{eff}\,e^2}{4\pi\varepsilon_o r_1}\right)\phi_{1s}(r_1) - \frac{(Z - Z_{eff})\,e^2}{4\pi\varepsilon_o r_1}\,\phi_{1s}(r_1)$$

$$\left(\frac{-\hbar^2}{2m}\nabla_2^2 - \frac{Ze^2}{4\pi\varepsilon_o r_2}\right)\phi_{1s}(r_2) = \left(\frac{-\hbar^2}{2m}\nabla_2^2 - \frac{Z_{eff}\,e^2}{4\pi\varepsilon_o r_2}\right)\phi_{1s}(r_2) - \frac{(Z - Z_{eff})\,e^2}{4\pi\varepsilon_o r_2}\,\phi_{1s}(r_2) \tag{25.8.17}$$

Both electrons are in the same 1s-orbital so these two previous equations give the same energies. The electrons are identical, except for spin. To calculate the expectation value of the exact Hamiltonian, $\int \phi_{1s}^*(r_1)\,\phi_{1s}^*(r_2)\,\hat{\mathscr{H}}\,\phi_{1s}(r_1)\,\phi_{1s}(r_2)\,d\tau$, we find $\hat{\mathscr{H}}\,\phi_{1s}(r_1)\,\phi_{1s}(r_2)$ using the last two equations and Eqs. 25.8.15:

$$\hat{\mathscr{H}}\,\phi_{gs} = \phi_{1s}(r_2)\left(\frac{-\hbar^2}{2m}\nabla_1^2 - \frac{Ze^2}{4\pi\varepsilon_o r_1}\right)\phi_{1s}(r_1) + \phi_{1s}(r_1)\left(\frac{-\hbar^2}{2m}\nabla_2^2 - \frac{Ze^2}{4\pi\varepsilon_o r_2}\right)\phi_{1s}(r_2) + \frac{e^2}{4\pi\varepsilon_o r_{12}}\,\phi_{1s}(r_1)\phi_{1s}(r_2)$$

$$= -\left(\frac{e^2}{4\pi\varepsilon_o\, a_o}\right)Z_{eff}^2\,\phi_{1s}(r_1)\,\phi_{1s}(r_2) - 2\,\frac{(Z - Z_{eff})\,e^2}{4\pi\varepsilon_o r_1}\,\phi_{1s}(r_1)\,\phi_{1s}(r_2) + \frac{e^2}{4\pi\varepsilon_o r_{12}}\,\phi_{1s}(r_1)\phi_{1s}(r_2) \tag{25.8.18}$$

The variational energy for our guessed wave function is then:

$$E^\phi = \int \phi_{1s}^*(r_1)\,\phi_{1s}^*(r_2)\,\hat{\mathscr{H}}\,\phi_{1s}(r_1)\,\phi_{1s}(r_2)\,d\tau = -\left(\frac{e^2}{4\pi\varepsilon_o\, a_o}\right)Z_{eff}^2 - 2\left\langle \frac{(Z - Z_{eff})\,e^2}{4\pi\varepsilon_o r_1}\right\rangle + \left\langle \frac{e^2}{4\pi\varepsilon_o r_{12}}\right\rangle \tag{25.8.19}$$

The first expectation value is the difference in the Coulomb attraction of an electron with a nucleus of charge Z and a nucleus of charge Z_{eff}:

$$-\left\langle \frac{(Z - Z_{eff})\,e^2}{4\pi\varepsilon_o r_1}\right\rangle = -\,(Z - Z_{eff})\int \phi_{1s}^*(r_1)\,\phi_{1s}^*(r_2)\,\frac{e^2}{4\pi\varepsilon_o\, r_1}\,\phi_{1s}(r_1)\,\phi_{1s}(r_2)\,d\tau_1 d\tau_2 \tag{25.8.20}$$

$$= -\,(Z - Z_{eff})\underbrace{\int \phi_{1s}^*(r_2)\,\phi_{1s}(r_2)\,d\tau_2}_{normalization}\ \underbrace{\int \phi_{1s}^*(r_1)\,\frac{e^2}{4\pi\varepsilon_o\, r_1}\,\phi_{1s}(r_1)\,d\tau_1}_{\langle V\rangle} \tag{25.8.21}$$

The first integral is the normalization for electron 2. The second integral is the expectation value of the potential energy for a one-electron atom with nuclear charge Z_{eff}, $\langle V\rangle$, see Problem 25.6.

$$-\left\langle \frac{(Z - Z_{eff})\,e^2}{4\pi\varepsilon_o r_1}\right\rangle = -\,(Z - Z_{eff})\left(\frac{Z_{eff}\,e^2}{4\pi\varepsilon_o\, a_o}\right) \tag{25.8.22}$$

We evaluated the expectation value of the electron-electron repulsion for our perturbation treatment of the helium atom. We only need to substitute Z_{eff} for Z:

$$\left\langle \frac{e^2}{4\pi\varepsilon_o r_{12}} \right\rangle = \int \phi_{1s}^*(r_1)\, \phi_{1s}^*(r_2)\, \frac{e^2}{4\pi\varepsilon_o r_{12}}\, \phi_{1s}(r_1)\, \phi_{1s}(r_2)\, d\tau_1 d\tau_2 = \frac{5Z_{eff}}{8}\left(\frac{e^2}{4\pi\varepsilon_o\, a_o}\right) \tag{25.8.23}$$

Setting Z = 2 gives the final result as referenced in Eq. 25.3.28:

$$E^{\phi} = \left(\frac{e^2}{4\pi\varepsilon_o\, a_o}\right)\left(- Z_{eff}^2 - 2\, ZZ_{eff} + 2\, Z_{eff}^2 + \frac{5Z_{eff}}{8} \right) \tag{25.8.24}$$

$$E^{\phi} = \frac{e^2}{4\pi\varepsilon_o\, a_o}\left(Z_{eff}^2 - \frac{27}{8}\, Z_{eff}\right) = 27.211\ \text{eV}\left(Z_{eff}^2 - \frac{27}{8}\, Z_{eff}\right) \tag{25.8.25}$$

Chapter Summary

1. The potential energy for the hydrogen atom and one-electron ions is given by the Coulomb attraction of the electron for the nucleus with charge Z:

$$-\frac{\hbar^2}{2m}\nabla^2\,\Psi + \hat{V}\Psi = E\,\Psi \qquad \text{with } \hat{V}(r) = \frac{-Z\,e^2}{4\pi\varepsilon_o r}$$

2. The Schrödinger equation for the hydrogen atom is best expressed in spherical polar coordinates with the curvature:

$$\nabla^2 = \frac{1}{r}\left(\frac{\partial^2}{\partial r^2}\right) r + \left(\frac{1}{r^2}\right)\Lambda^2 \qquad\qquad \hat{L}^2 = -\hbar^2\Lambda^2$$

3. The hydrogen atom Schrödinger equation is separable in r, θ, and ϕ: $\Psi = R(r)\,\Theta(\theta)\,\Phi(\phi)$. R(r) is the radial wave function. $\Phi(\phi)$ gives the angular momentum of the electron in the x-y plane, $L_z = \hbar\, m_\ell$. The product of the angular wave functions are the spherical harmonics, $\Theta(\theta)\Phi(\phi) = Y_{\ell,m_\ell}$.

4. The atomic units of energy and length are the **Hartree**, H, and Bohr radius, a_o, respectively:

$$1\ \text{H} \equiv 27.211384\ \text{eV} = 219{,}474.6\ \text{cm}^{-1} = 2625.4996\ \text{kJ mol}^{-1} \qquad a_o = \frac{4\pi\varepsilon_o\,\hbar^2}{me^2} = 0.52918\ \text{Å}$$

5. The wave function for the ground state of the hydrogen atom is $R(r) = A\,e^{-\alpha r}$, with energy:

$$E_{gs} = -\frac{\hbar^2\alpha^2}{2m} \qquad \text{and} \quad \alpha = \frac{Z\,e^2\,m}{4\pi\varepsilon_o\,\hbar^2} = \frac{Z}{a_o} \qquad \Psi_{1s}(r) = \Psi_{100}(r) = R(r) = \frac{1}{\sqrt{\pi}}\left(\frac{Z}{a_o}\right)^{3/2} e^{-Zr/a_o}$$

6. The energy of the atomic orbitals of the hydrogen atom and one-electron ions is a function only of the principle quantum number, n:

$$E_n = -\left(\frac{m\,e^4}{32\pi^2\varepsilon_o{}^2\hbar^2}\right)\frac{Z^2}{n^2} = -\frac{\hbar^2}{2ma_o{}^2}\,\frac{Z^2}{n^2}$$

$$E_n = -13.606\ \text{eV}\,\frac{Z^2}{n^2} = -109{,}678\ \text{cm}^{-1}\,\frac{Z^2}{n^2} = -1312.7\ \text{kJ mol}^{-1}\,\frac{Z^2}{n^2} = -\frac{H}{2}\,\frac{Z^2}{n^2}$$

7. The most probable radius for the ground state of the hydrogen atom and one electron ions is $r_{mp} = a_o/Z$ and the average radius is given by the expectation value $<r> = {}^3/_2\ a_o/Z$:

8. The volume of the annular ring of thickness dr at distance r from the nucleus is $4\pi r^2$ dr. The probability of finding the electron at radius r, irrespective of θ and ϕ, is the radial probability distribution function: $P(r)\,dr = \Psi^2\, 4\pi r^2\, dr$.
9. The 90% contour surface for the normalized hydrogen 1s-orbital is at radius $r_{90\%} = 2.66\ a_o/Z$:

$$\int_0^{r_{90\%}} \int_0^{\pi} \int_0^{2\pi} \Psi^2\, r^2 \sin\theta\, dr\, d\theta\, d\phi = 0.90$$

10. Excited state atomic wave functions are the product of a polynomial and the asymptotic form given by the ground state wave function. The 2s- and 3s-orbitals are:

$$\Psi_{2s} = \frac{1}{4\sqrt{2\pi}}\left(\frac{Z}{a_o}\right)^{3/2}\left(2 - \frac{Zr}{a_o}\right) e^{-Zr/2a_o} \qquad \Psi_{3s} = \frac{1}{18\sqrt{3\pi}}\left(\frac{Z}{a_o}\right)^{3/2}\left(6 - \frac{4Zr}{a_o} + \frac{4Z^2r^2}{9a_o^2}\right) e^{-Zr/3a_o}$$

11. The polynomials generating the atomic orbitals with angular momentum are the spherical harmonics. The restrictions are: $n = 0,\ldots,\infty$; $\ell = 0,\ldots, n-1$; and $m_\ell = -\ell,\ldots, 0,\ldots, +\ell$
12. The nodes for the atomic orbitals are given by:
    total nodes = $n - 1$
    total angular nodes = ℓ
    angular nodes that include the z-axis = m_ℓ
    radial nodes = total nodes – angular nodes = $n - 1 - \ell$
13. The 2p-orbitals with pure angular momentum quantum numbers are:

$$\Psi_{2pz} = \frac{1}{4\sqrt{2\pi}}\left(\frac{Z}{a_o}\right)^{3/2} e^{-Zr/2ao}\,\frac{Zr}{a_o}\cos\theta \qquad m_\ell = 0 \qquad L_z = 0$$

$$\Psi_{211} = \frac{1}{4\sqrt{2\pi}}\left(\frac{Z}{a_o}\right)^{3/2} e^{-Zr/2ao}\,\frac{Zr}{a_o}\sin\theta\, e^{i\phi} \qquad m_\ell = +1 \qquad L_z = +1$$

$$\Psi_{21\text{-}1} = \frac{1}{4\sqrt{2\pi}}\left(\frac{Z}{a_o}\right)^{3/2} e^{-Zr/2ao}\,\frac{Zr}{a_o}\sin\theta\, e^{-i\phi} \qquad m_\ell = -1 \qquad L_z = -1$$

14. The oriented $2p_x$ and $2p_y$ orbitals are linear combinations of the $m_\ell = \pm l$ pure angular momentum orbitals. The oriented orbitals are poised for bonding interactions in molecules:

$$\Psi_{2px} = \frac{\Psi_{211} + \Psi_{21\text{-}1}}{2} = \frac{1}{4\sqrt{2\pi}}\left(\frac{Z}{a_o}\right)^{3/2} e^{-Zr/2ao}\,\frac{Zr}{a_o}\sin\theta\cos\phi = \frac{1}{4\sqrt{2\pi}}\left(\frac{Z}{a_o}\right)^{3/2} e^{-Zr/2ao}\,\frac{Z}{a_o}\,x$$

$$\Psi_{2py} = \frac{\Psi_{211} - \Psi_{21\text{-}1}}{2i} = \frac{1}{4\sqrt{2\pi}}\left(\frac{Z}{a_o}\right)^{3/2} e^{-Zr/2ao}\,\frac{Zr}{a_o}\sin\theta\sin\phi = \frac{1}{4\sqrt{2\pi}}\left(\frac{Z}{a_o}\right)^{3/2} e^{-Zr/2ao}\,\frac{Z}{a_o}\,y$$

15. The angular portion of the oriented d-orbitals are products of the Cartesian coordinates:
    $d_{xz} \Rightarrow xz = r^2 \sin\theta\cos\phi\cos\theta$
    $d_{yz} \Rightarrow yz = r^2 \sin\theta\sin\phi\cos\theta$
    $d_{xy} \Rightarrow xy = r^2 \sin\theta\cos\phi\sin\theta\sin\phi = r^2 \sin\theta^2 \cos\phi\sin\phi$
    $d_{x2\text{-}y2} \Rightarrow x^2 - y^2 = r^2(\sin^2\theta\cos^2\phi - \sin^2\theta\sin^2\phi)$
    $d_{z2} = d_{3z2\text{-}r2} \Rightarrow r^2(3\cos^2\theta - 1)$
16. The orbital angular momentum of an electron in an atom has magnitude: $|L| = \hbar\sqrt{\ell(\ell + 1)}$.
17. The z-axis projection of the intrinsic angular momentum of the electron is $s_z = \hbar m_s$, with $m_s = \pm\frac{1}{2}$. In the absence of an external magnetic field, the states are degenerate.

18. The potential energy for the helium atom, Z = 2, includes the attraction of electron 1 for the nucleus, the attraction of electron 2 for the nucleus, and the electron-electron repulsion:
$$\hat{V}(r) = \frac{1}{4\pi\varepsilon_o}\left(-\frac{2e^2}{r_1} - \frac{2e^2}{r_2} + \frac{e^2}{r_{12}}\right)$$
19. In the independent electron approximation, the electron-electron repulsion term is dropped giving the atomic wave function as the product of one-electron atomic orbitals: $\Psi(r_1,r_2) = \Psi_1(r_1)\ \Psi_2(r_2)$. Assuming that the orbital for a multi-electron atom or molecule is the product of one-electron orbitals is called the orbital approximation.
20. In the independent electron approximation: one-electron orbitals multiply and energies add. For the helium ground state, Z = 2:
$$E_{He} = E_1 + E_2 = -\ 13.6\ \text{eV}\left(\frac{Z^2}{n_1^2} + \frac{Z^2}{n_2^2}\right) = -108.8\ \text{eV}$$
21. The ionization energy is the energy necessary to remove an electron, $M \rightarrow M^+ + e^-$. The separated nucleus and electrons is the zero energy. The electronic energy of an atom is the negative sum of the sequential ionization energies: $E_{He,exp} = -\ (I_1 + I_2) = -79.00$ eV.
22. The Perturbation Method: the Hamiltonian is split into a part that can be solved exactly, $\hat{\mathcal{H}}^{(o)}$, and a small perturbation $\hat{\mathcal{H}}'$. The strength of the perturbation is scaled by the perturbation parameter, $\lambda = 0 \rightarrow 1$, with the full Hamiltonian, $\hat{\mathcal{H}} = \hat{\mathcal{H}}^{(o)} + \lambda\ \hat{\mathcal{H}}'$. The energy of the system is expanded in a power series in λ: $E_i \cong E_i^{(o)} + \lambda E_i^{(1)} + \lambda^2\ E_i^{(2)} + \ldots$
23. The first-order correction to the energy is the expectation value of the perturbation:
$$E_i^{(1)} = \langle \mathcal{H}' \rangle = \int \Psi_i^{(o)*}\ \hat{\mathcal{H}}'\ \Psi_i^{(o)}\ d\tau$$
The $\Psi_i^{(o)}$ are the eigenfunctions of the unperturbed Hamiltonian: $\hat{\mathcal{H}}^{(o)}\ \Psi_i^{(o)} = E_i^{(o)}\ \Psi_i^{(o)}$.
24. The first-order correction to the wave function is:
$$\Psi_i^{(1)} \cong \Psi_i^{(o)} + \lambda \sum_{k\neq i} \frac{\mathcal{H}'_{ki}}{E_i^{(o)} - E_k^{(o)}}\ \Psi_k^{(o)}$$
The integral $\mathcal{H}'_{ki}$ is taken between the state of interest, i, and all other states k with the perturbation Hamiltonian, $\mathcal{H}'_{ki} = \int \Psi_i^{(o)*}\ \hat{\mathcal{H}}'\ \Psi_k^{(o)}\ d\tau$.
25. The Variation Method: the trial energy, E^ϕ, is guaranteed to be greater than or equal to the exact energy, E_i, by the Variation Theorem:
$$E^\phi = \frac{\int \phi^* \hat{\mathcal{H}} \phi\ d\tau}{\int \phi^* \phi\ d\tau} \geq E_i$$
the trial wave function that gives the lowest energy is best.
26. The Effective Charge Model: the ground state of the helium atom is approximated as the product of one-electron 1s-orbitals with effective nuclear charge Z_{eff}:
$$\phi_{gs} = \phi_{1s}(r_1)\ \phi_{1s}(r_2) = \frac{1}{\pi}\left(\frac{Z_{eff}}{a_o}\right)^3 e^{-Z_{eff}\, r_1/a_o}\ e^{-Z_{eff}\, r_2/a_o}$$
Z_{eff} is a variation parameter. The trial energy for the ground state of the He atom:
$$E^\phi = \frac{\int \phi_{gs}^*\ \hat{\mathcal{H}}\, \phi_{gs}\ d\tau}{\int \phi_{gs}^*\ \phi_{gs}\ d\tau} = \frac{e^2}{4\pi\varepsilon_o\, a_o}\left(Z_{eff}^2 - \frac{27}{8}\ Z_{eff}\right) \quad \text{minimizes} \quad \frac{dE^\phi}{dZ_{eff}} = 0 \quad \text{to give } Z_{eff} = 1.6875$$
27. In the effective charge model, electron-electron repulsion is modeled as a shielding interaction, where the electrons shield each other from the full nuclear attraction, $Z_{eff} < Z$.

28. The Self-Consistent Field method: the Schrödinger equation is solved iteratively for the one-electron effective potential energy and wave function for each electron. The SCF-method is variational. For the helium atom, the effective potential for electron 1 includes the attraction for the nucleus, $V_1(r_1)$, and the average e^-–e^- repulsion with electron 2:

$$V_{eff}(r_1) = V_1(r_1) + \int \Psi_2 \frac{e^2}{4\pi\varepsilon_o r_{12}} \Psi_2 \, d\tau_2$$

29. Electron-electron repulsion breaks the orbital degeneracy, s < p < d < f. Radial nodes for the s- and p-orbitals increase the electron density close to the nucleus. Low ℓ orbitals penetrate closer to the nucleus and feel a greater effective nuclear charge than high ℓ orbitals.
30. The Pauli Exclusion Principle: no two electrons can have the same set of quantum numbers. The maximum number of electrons in a given orbital is two, with $m_s = +½$ and $–½$.
31. Hund's First Rule: for a degenerate set of orbitals, electron-electron repulsion is minimized when the electrons occupy different orbitals and have the same spin quantum number. Quantum mechanical avoidance increases the average distance between electrons with parallel spins, which decreases electron-electron repulsion.
32. The Aufbau Principle predicts the configuration of the elements: electrons fill the orbitals of lowest energy, subject to the Pauli Exclusion Principle and Hund's First Rule.
33. Electrons in the same subshell have the same average radius and don't shield each other well. Half filled or totally filled subshells have a special stability and are efficient shielders.
34. For the early transition metals, the valence shell s-orbital is lower in energy than the previous shell d-orbital. The Aufbau prediction is that the 4s fills before 3d and the 5s fills before 4d, in the respective periods.
35. The orbital energies for the monatomic cations are in principle quantum number order. Cations have fewer electrons than the parent neutral element, decreasing electron-electron repulsion and giving a different atomic orbital ordering for the early transition metals.
36. The Pauli Exclusion Principle: The wave function is overall antisymmetric with respect to exchange of any two electron spin labels. The spin-orbitals are the product of an orbital part and a spin part, which must be overall antisymmetric with respect to spin labels.
37. To guarantee antisymmetry, the spin-orbital is expressed as a Slater determinant. For the ground state of the helium atom, the Slater determinant is:

$$\Psi_a = \frac{1}{\sqrt{2}} \begin{vmatrix} \Psi_{1s}(1)\alpha(1) & \Psi_{1s}(1)\beta(1) \\ \Psi_{1s}(2)\alpha(2) & \Psi_{1s}(2)\beta(2) \end{vmatrix} \qquad \begin{array}{l} \text{rows: different electrons} \\ \text{columns: different wave functions} \end{array}$$

38. The ground state of helium is a singlet: ${}^1\Psi_{gs} = \frac{1}{\sqrt{2}} \Psi_{1s}(1)\, \Psi_{1s}(2)\, [\alpha(1)\, \beta(2) - \beta(1)\, \alpha(2)]$.
39. The lowest energy excited states of helium have the configuration $1s^1 2s^1$. The singlet excited state is: ${}^1\Psi^{ex} = \frac{1}{\sqrt{2}} (\Psi_{1s}(1)\, \Psi_{2s}(2) + \Psi_{1s}(2)\, \Psi_{2s}(1))\, [\alpha(1)\, \beta(2) - \beta(1)\, \alpha(2)]$. The triplet excited state is lower in energy, because of decreased e^-–e^- repulsion:

$${}^3\Psi^{ex} = \frac{1}{\sqrt{2}} (\Psi_{1s}(1)\, \Psi_{2s}(2) - \Psi_{1s}(2)\, \Psi_{2s}(1)) \begin{bmatrix} \alpha(1)\alpha(2) \\ \alpha(1)\beta(2) + \beta(1)\alpha(2) \\ \beta(1)\beta(2) \end{bmatrix}$$

40. A separate Slater determinant is required to represent each spin-orbital in a degenerate level (i.e. for S > 1).

41. The difference in energy with and without the use of the restriction based on electron indistinguishability is the exchange energy. The Hartee-Fock, HF, method is a self-consistent field calculation with the spin-orbitals as Slater determinants.
42. Slater type orbitals, STOs, have the same large r dependence as the corresponding hydrogen-like orbital, but lack radial nodes. The radial polynomial in the hydrogen-like orbital is replaced by just the leading term in r: $\Psi_{n\ell m_\ell}(r) = N\, Y_{\ell,m_\ell}\, r^{(n_{eff}-1)}\, e^{-Z_{eff}\, r/n_{eff}\, a_o}$.
43. Z_{eff} is approximated as the difference between the full nuclear charge and a shielding constant, S: $Z_{eff} = Z - S$. The shielding constant accounts for the average electron-electron repulsion for the electrons.
44. Slater's Rules: To approximate the Z_{eff} of the valence electrons, the shielding efficiency of electrons in the valence shell is 35%. The shielding efficiency of electrons in the next lower energy shell is 85%. For third and higher period elements, the shielding efficiency of electrons in the inner core levels is 100%.
45. Gaussian orbitals are a convenient functional form when evaluating electron-electron repulsion integrals. Gaussian primitives of the form:

$$g_s(\alpha,r) = \left(\frac{2\alpha}{\pi}\right)^{3/4} e^{-\alpha r^2} \qquad g_x(\alpha,r) = \left(\frac{128\alpha^5}{\pi^3}\right)^{1/4} x\, e^{-\alpha r^2}$$

are combined in linear combination to approximate the electron distribution in multi-electron atoms: $\phi_\mu = \Sigma\, d_{\mu i}\, g_i(\alpha,r)$ with the orbital type μ = s, x, y, z and fixed constants $d_{\mu i}$. The Gaussian exponent, α, plays the role of the effective nuclear charge.
46. A split valence shell allows the contribution of the inner and outer part of the valence orbitals to adjust to the bonding environment: $\Psi_{2s} = a\Psi_{2s}(\text{inner}) + b\Psi_{2s}(\text{outer})$. The constants a and b are optimized in an SCF calculation.
47. The total intrinsic spin angular momentum, $\vec{S}$, the total orbital angular momentum, $\vec{L}$, and the total angular momentum, $\vec{J}$, are the vector sums of each electron.

Angular Momentum	Intrinsic Spin	Orbital	Total
individual electron	$\vec{s}_i$	$\vec{L}_i$	$\vec{j}_i$
total	$\vec{S} = \Sigma\, \vec{s}_i$	$\vec{L} = \Sigma\, \vec{L}_i$	$\vec{J} = \Sigma\, \vec{j}_i$
magnitude	$\lvert S\rvert = \sqrt{S(S+1)}\, \hbar$	$\lvert L\rvert = \sqrt{L(L+1)}\, \hbar$	$\lvert J\rvert = \sqrt{J(J+1)}\, \hbar$
z-axis projection	$S_z = M_S\, \hbar$	$L_z = M_L\, \hbar$	$J_z = M_J\, \hbar$
magnetic quantum number	$M_S = \Sigma\, m_{s,i}$	$M_L = \Sigma\, m_{\ell,i}$	$M_J = \Sigma\, m_{j,i}$
M_S range	$M_S = -S, \ldots, 0, \ldots +S$	$M_L = -L, \ldots, 0, \ldots +L$	$M_J = -J, \ldots, 0, \ldots, +J$
degeneracy	$g_S = 2S + 1$	$g_L = 2L + 1$	$g_J = 2J + 1$

48. The possible L values for a given configuration is given by a Clebsch-Gordan series. For two electrons with orbital angular momentum quantum numbers ℓ_1 and ℓ_2 the range of possible total L values is the series: $L = \ell_1 + \ell_2, \ell_1 + \ell_2 - 1, \ldots, \lvert \ell_1 - \ell_2 \rvert$
49. The L value for an electronic state is symbolized by a term symbol, the term is determined from the following table. The spin multiplicity, g_s, is added as a superscript before the term. The total angular momentum quantum number, J, is included as a subscript.

L	0	1	2	3	4	5
Term	S	P	D	F	G	H

50. The total angular momentum is the vector sum of the spin and orbital angular momenta, $\vec{J} = \vec{L} + \vec{S}$. In the L-S coupling or Russell-Saunders coupling scheme, the possible total angular momentum quantum numbers are given by the Clebsch-Gordan series:

$$J = L + S,\ L + S - 1,\ \ldots,\ |L - S|$$

51. Spin-orbit coupling is the interaction of the total spin and total orbital angular momentum. For light elements the spin-orbit coupling is treated as a perturbation: $\hat{\mathscr{H}}'_{so} = \xi\, \hat{\vec{L}}\cdot\hat{\vec{S}}$.

52. The spin-orbit coupling is: $E_{so} = \frac{1}{2}\mathscr{A}hc\,[J(J+1) - L(L+1) - S(S+1)]$, where $\mathscr{A}$ is the spin-orbit interaction constant, expressed in wave numbers with $\mathscr{A}hc = \xi\hbar^2$.

53. The dipole moment operator is $\hat{\vec{\mu}} = -\,e\,\hat{\vec{r}}$, where $\hat{\vec{r}}$ specifies the position of all the electrons. The intensity of an absorption or emission transition from the initial state Ψ_i to the final state Ψ_j is proportional to the transition dipole moment, $\mu_{tr} = \langle\hat{\vec{\mu}}\rangle = \int \Psi_j^*\,(-e\,\hat{\vec{r}})\,\Psi_i\,d\tau$.

54. The selections rules for atomic absorption and emission are: $\Delta S = 0$, $\Delta L = \pm 1$, $\Delta J = 0, \pm 1$, except $J = 0 \not\leftrightarrow J = 0$. The Laporte selection rule requires that one n or ℓ must change.

55. The interaction energy of an atom with an external magnetic field is the Zeeman splitting: $\Delta E = g\,\mu_B\,B\,M_J$, with B the magnetic field strength, μ_B the Bohr magneton, and *g* the Landé *g*-factor or gyromagnetic ratio:

$$\mu_B = \frac{e}{2m_e}\hbar \qquad\qquad g = \left[1 + \frac{J(J+1) + S(S+1) - L(L+1)}{2J(J+1)}\right]$$

56. Zeeman splitting of the degenerate levels of a given J-state gives 2J + 1 energy levels.

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Atomic Structure Problems

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.

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.

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

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

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

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

(b) From your answer in (a), show that $<E_k> = -\,E_1$, where E_1 is the total energy of the ground state of the hydrogen atom.

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

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

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

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

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

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

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

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

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

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

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

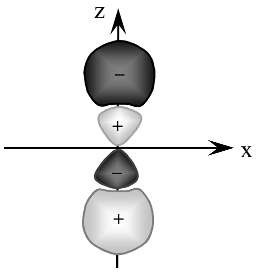
(c). Show the radius that gives the 90% contour surface is given by:

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

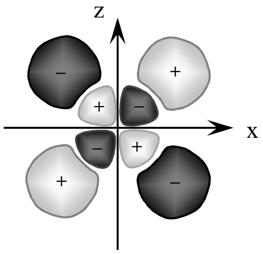
(d). Let $\rho = Zr_c/a_o$. Show that the last equation reduces to: $(-2\rho^2 - 2\rho - 1)\, e^{-2\rho} + 1 = 0.90$. Solve this equation for ρ numerically, to three significant figures, to find the 90% contour radius.

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

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



(a).



(b).

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

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

$\cos^2 x + \sin^2 x = 1$ and correspondingly $(\cos^2 x + \sin^2 x)^2 = 1$
$\cos^2 x - \sin^2 x = 2\cos^2 x - 1$

13. Normalize the angular portion of the orbital: $d_{yz} = N \sin\theta \cos\theta \sin\phi$. Note that:

$$\int_0^{\pi} \sin^3 x \cos^2 x \, dx = {}^4/_{15}$$

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.

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.

16. Hooke's Law is only an approximation of the true vibrational potential energy of a molecule. There are many other possible forms for the potential energy function of a chemical bond. Use perturbation theory to calculate the small change in energy for the harmonic oscillator ground state that is perturbed by the addition of a term = $b\,x^4$ to the potential energy function:

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

[Hint: Remember that the wave function is $\Psi(x) = \left(\frac{\alpha^2}{\pi}\right)^{1/4} e^{-\frac{1}{2}\alpha^2 x^2}$ where $\alpha^2 = \left(\frac{m\omega_o}{\hbar}\right)$. Just leave α^2 as a parameter until the last step and then substitute in at the last for α^2 to find that the change in energy is $\frac{3b}{4}\left(\frac{\hbar}{m\omega_o}\right)^2$]

17. Using the Aufbau Principle predict the ground state electron configuration for: (a). Si, (b). Ti, (c). Ti^{2+}, (d). Cr, (e). Cr^{2+}, and (f). Ag. Show both the condensed configuration (e.g. [Ne] $3s^2$) and the orbital diagram (e.g. 3s: $\boxed{\uparrow\downarrow}$). For which species is the Aufbau prediction expected to differ from the experimental configuration?

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 is in each of these orbitals, the space part of the triplet and singlet wave functions is:

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

respectively. Suppose that electron 1 is in a small element of length dx at x = 0.250 a and electron 2 is in a small element of length dx at x = 0.255 a. The quantity a is the length of the box. Show that Ψ_A has a very small value under these conditions while Ψ_S is large. What happens to Ψ_A if both electrons are at x = 0.250 a? This problem shows how an anti-symmetric spatial wave function keeps the electrons apart, that is "quantum mechanical avoidance."[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.

19. Two possible wave functions for the ground state of the helium atom are:

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

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

Show that the squares of both wave functions transform to give back the original wave function upon exchange of spin labels: $\Psi_s^2 \rightarrow \Psi_s^2$ and $\Psi_a^2 \rightarrow \Psi_a^2$.

20. Give the spatial and spin parts for the singlet excited state of helium atom that has the configuration, He: $1s^1\ 2p^1$.

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

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

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

24. Determine the expectation value for the total spin angular momentum squared, that is $<S^2>$ for a triplet state.

25. Give the expectation value for the total spin angular momentum squared, that is $<S^2>$ for a quartet state. For example:

$$\begin{array}{cc} \boxed{\uparrow\downarrow} & \boxed{\uparrow}\boxed{\uparrow}\boxed{\uparrow}\boxed{}\boxed{} \\ 4s & 3d \end{array}$$

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

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

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

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

Assume that the interaction is weak enough to be treated as a perturbation, which allows ℓ and s to remain separately good quantum numbers. Accordingly, to a good level of approximation, the total angular momentum wave function is the product of orbital and spin angular momentum eigenfunctions: $\Psi_{j,m_j} = \Psi_{\ell,m_\ell}\,\Psi_{s,m_s}$.

27. Find the spin-orbit splitting of the ${}^2D_{5/2}$ and ${}^2D_{3/2}$ terms for the yttrium ground state.

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:

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

(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:

↑	↑			

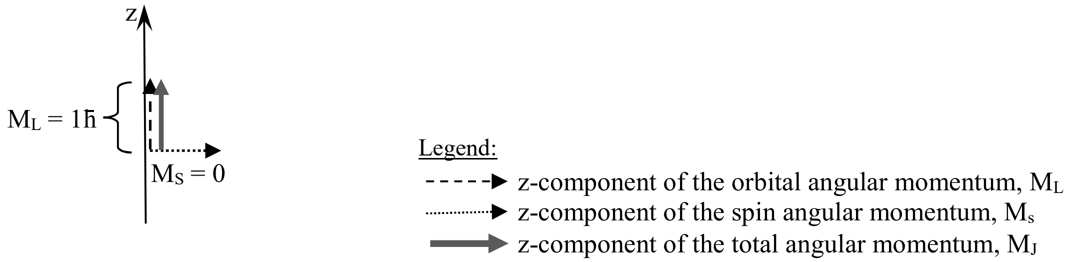
(g). Verify that the Clebsch-Gordon series applied to the total orbital angular momentum gives the same results.

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.

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.

31. The previous problem uses the Clebsch-Gordon series to find the possible values for the total angular momentum for a ^3P term. This problem takes a graphical approach to reach the same conclusion. (a). Draw all the angular momentum diagrams to show the possible total angular momentum M_J states for a ^3P term. (b). Find M_J for each explicit configuration. (c). Determine the possible values for J. Consider only the projections on the z-axis. One example, for $M_L = 1$ and $M_S = 0$ giving $M_J = 1$, is:

$M_J = 1$:



32. (a). Use the Clebsch-Gordon series and the Russell-Saunders coupling scheme to find the possible total angular momentum J states for a ^3D term. (b). Determine the complete set of explicit M_J states for a ^3D term. Determine the possible total angular momentum J states from the complete set of M_J values. Compare your results with part (a). For example, two explicit M_J states are tabulated below:

M_L	M_S	M_J
2	1	3
2	0	2

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.

34. A p^2 configuration gives ^1S, ^1D, ^3P terms. Give the terms for a p^4 configuration.

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.

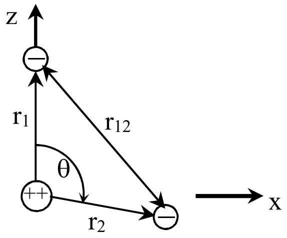
36. A d^3 configuration gives ^2P, ^2D, ^2D, ^2F, ^2G,^2H, ^4P, ^4F terms. Give the terms for a d^7 configuration. Give the lowest energy term for ground state d^3 and d^7 configurations.

37. Write a spreadsheet to plot the 3-21G Gaussian orbital for a $2p_x$ orbital on carbon, along the x-axis.

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

(a). The distance between the two electrons is the magnitude of the vector difference: $r_{12} = |\vec{r}_1 - \vec{r}_2|$, where $\vec{r}_1$ is the vector pointing to electron 1 and $\vec{r}_2$ is the vector pointing to electron 2. The length of $\vec{r}_1$ is r_1 and of $\vec{r}_2$ is r_2. The angle between the two vectors is θ. The distance between the two electrons does not dependent on how the coordinate system is oriented, only the difference is important. We orient the coordinate system with $\vec{r}_1$ pointing along the z-axis and $\vec{r}_2$ parallel to the x-axis. The x, y, and z coordinates are then conveniently expressed in terms of r, θ, and ϕ. Show that the coordinates of the two electrons are given as:

$$\vec{r}_1 = (0, 0, r_1)$$
$$\vec{r}_2 = (r_2 \sin\theta, 0, r_2 \cos\theta)$$



(b). From the position vectors in part (a), find $r_{12} = |\vec{r}_1 - \vec{r}_2|$. Remember that $\sin^2\theta + \cos^2\theta = 1$.

39. Using the substitution $q = \cos\theta$, show that (Eq. 25.7.5):

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

40. Evaluate the following integrals, verifying Eqs. 25.7.8 and 25.7.9:

$$\int_{r_1}^{\infty} e^{-2Zr_2/a_o}\, r_2\, dr_2 \qquad \text{and} \qquad \int_0^{r_1} e^{-2Zr_2/a_o}\, r_2^2\, dr_2$$

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.

42. Using Eqs. 25.7.7, 25.7.11, and 25.7.12, verify Eq. 25.7.14.

Literature Cited:

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