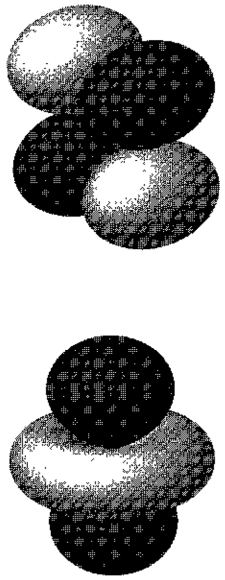

CHAPTER

2

Atomic Structure

The theories of atomic and molecular structure depend on quantum mechanics to describe atoms and molecules in mathematical terms. Although the details of quantum mechanics require considerable mathematical sophistication, it is possible to understand the principles involved with only a moderate amount of mathematics. This chapter presents the fundamentals needed to explain atomic and molecular structures in qualitative or semiquantitative terms.

2-1

HISTORICAL DEVELOPMENT OF ATOMIC THEORY

Although the Greek philosophers Democritus (460–370 BC) and Epicurus (341–270 BC) presented views of nature that included atoms, many hundreds of years passed before experimental studies could establish the quantitative relationships needed for a coherent atomic theory. In 1808, John Dalton published *A New System of Chemical Philosophy*,[1] in which he proposed that

> . . . the ultimate particles of all homogeneous bodies are perfectly alike in weight, figure, etc. In other words, every particle of water is like every other particle of water, every particle of hydrogen is like every other particle of hydrogen, etc.[2]

and that atoms combine in simple numerical ratios to form compounds. The terminology he used has since been modified, but he clearly presented the ideas of atoms and molecules, described many observations about heat (or caloric, as it was called), and made quantitative observations of the masses and volumes of substances combining to form new compounds. Because of confusion about elemental molecules such as H_2 and O_2, which he assumed to be monatomic H and O, he did not find the correct formula for water. Dalton said that

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[1] John Dalton, *A New System of Chemical Philosophy*, 1808; reprinted with an introduction by Alexander Joseph, Peter Owen Limited, London, 1965.

[2] *Ibid.*, p. 113.

> When two measures of hydrogen and one of oxygen gas are mixed, and fired by the electric spark, the whole is converted into steam, and if the pressure be great, this steam becomes water. It is most probable then that there is the same number of particles in two measures of hydrogen as in one of oxygen.[3]

In fact, he then changed his mind about the number of molecules in equal volumes of different gases:

> At the time I formed the theory of mixed gases, I had a confused idea, as many have, I suppose, at this time, that the particles of elastic fluids are all of the same size; that a given volume of oxygenous gas contains just as many particles as the same volume of hydrogenous; or if not, that we had no data from which the question could be solved. . . . I [later] became convinced . . . That every species of pure elastic fluid has its particles globular and all of a size; but that no two species agree in the size of their particles, the pressure and temperature being the same.[4]

Only a few years later, Avogadro used data from Gay-Lussac to argue that equal volumes of gas at equal temperatures and pressures contain the same number of molecules, but uncertainties about the nature of sulfur, phosphorus, arsenic, and mercury vapors delayed acceptance of this idea. Widespread confusion about atomic weights and molecular formulas contributed to the delay; in 1861, Kekulé gave 19 different possible formulas for acetic acid![5] In the 1850s, Cannizzaro revived the argument of Avogadro and argued that everyone should use the same set of atomic weights rather than the many different sets then being used. At a meeting in Karlsruhe in 1860, he distributed a pamphlet describing his views.[6] His proposal was eventually accepted, and a consistent set of atomic weights and formulas gradually evolved. In 1869, Mendeleev[7] and Meyer[8] independently proposed periodic tables nearly like those used today, and from that time the development of atomic theory progressed rapidly.

2-1-1 THE PERIODIC TABLE

The idea of arranging the elements into a periodic table had been considered by many chemists, but either the data to support the idea were insufficient or the classification schemes were incomplete. Mendeleev and Meyer organized the elements in order of atomic weight and then identified families of elements with similar properties. By arranging these families in rows or columns, and by considering similarities in chemical behavior as well as atomic weight, Mendeleev found vacancies in the table and was able to predict the properties of several elements (gallium, scandium, germanium, polonium) that had not yet been discovered. When his predictions proved accurate, the concept of a periodic table was quickly established (see Figure 1-10). The discovery of additional elements not known in Mendeleev's time and the synthesis of heavy elements have led to the more complete modern periodic table, shown inside the front cover of this text.

In the modern periodic table, a horizontal row of elements is called a **period**, and a vertical column is a **group** or **family**. The traditional designations of groups in the United States differ from those used in Europe. The International Union of Pure and Applied Chemistry (IUPAC) has recommended that the groups be numbered 1 through 18, a recommendation that has generated considerable controversy. In this text, we will

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[3] *Ibid.*, p. 133

[4] *Ibid.*, pp. 144–145.

[5] J.R. Partington, *A Short History of Chemistry*, 3rd ed., Macmillan, London, 1957; reprinted, 1960, Harper & Row, New York, p. 255.

[6] *Ibid.*, pp. 256–258.

[7] D. I. Mendeleev, *J. Russ. Phys. Chem. Soc.*, **1869**, *i*, 60.

[8] L. Meyer, *Justus Liebigs Ann. Chem.*, **1870**, *Suppl. vii*, 354.

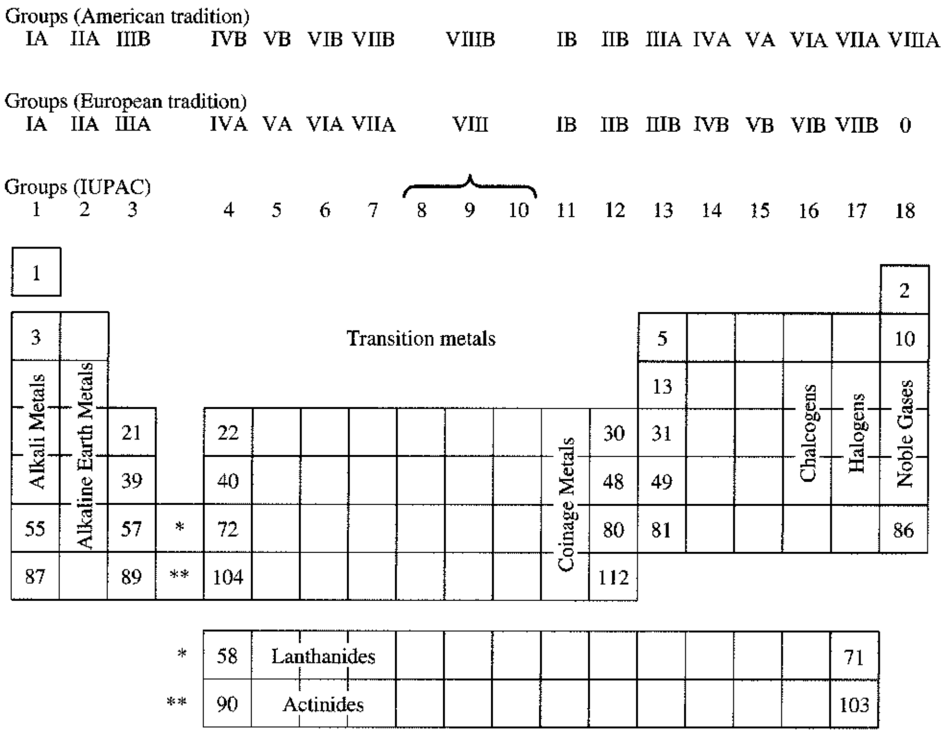

FIGURE 2-1 Names for Parts of the Periodic Table.

use the IUPAC group numbers, with the traditional American numbers in parentheses. Some sections of the periodic table have traditional names, as shown in Figure 2-1.

2-1-2 DISCOVERY OF SUBATOMIC PARTICLES AND THE BOHR ATOM

During the 50 years after the periodic tables of Mendeleev and Meyer were proposed, experimental advances came rapidly. Some of these discoveries are shown in Table 2-1.

Parallel discoveries in atomic spectra showed that each element emits light of specific energies when excited by an electric discharge or heat. In 1885, Balmer showed that the energies of visible light emitted by the hydrogen atom are given by the equation

$$E = R_H\left(\frac{1}{2^2} - \frac{1}{n_h^2}\right)$$

TABLE 2-1
Discoveries in Atomic Structure

1896	A. H. Becquerel	Discovered radioactivity of uranium
1897	J. J. Thomson	Showed that electrons have a negative charge, with charge/mass = 1.76×10^{11} C/kg
1909	R. A. Millikan	Measured the electronic charge (1.60×10^{-19} C); therefore, the mass of the electron is 9.11×10^{-31} kg, $\frac{1}{1836}$ of the mass of the H atom
1911	E. Rutherford	Established the nuclear model of the atom (very small, heavy nucleus surrounded by mostly empty space)
1913	H. G. J. Moseley	Determined nuclear charges by X-ray emission, establishing atomic numbers as more fundamental than atomic masses

where

n_h = integer, with $n_h > 2$

R_H = Rydberg constant for hydrogen $= 1.097 \times 10^7\ \text{m}^{-1} = 2.179 \times 10^{-18}\ \text{J}$

and the energy is related to the wavelength, frequency, and wave number of the light, as given by the equation

$$E = h\nu = \frac{hc}{\gamma} = hc\bar{\nu}$$

where[9]

h = Planck's constant $= 6.626 \times 10^{-34}\ \text{J s}$

ν = frequency of the light, in s^{-1}

c = speed of light $= 2.998 \times 10^8\ \text{m s}^{-1}$

λ = wavelength of the light, frequently in nm

$\bar{\nu}$ = wavenumber of the light, usually in cm^{-1}

The Balmer equation was later made more general, as spectral lines in the ultraviolet and infrared regions of the spectrum were discovered, by replacing 2^2 by n_l^2, with the condition that $n_l < n_h$. These quantities, n_i, are called **quantum numbers.** (These are the **principal quantum numbers**; other quantum numbers are discussed in Section 2-2-2.) The origin of this energy was unknown until Niels Bohr's quantum theory of the atom,[10] first published in 1913 and refined over the following 10 years. This theory assumed that negative electrons in atoms move in stable circular orbits around the positive nucleus with no absorption or emission of energy. However, electrons may absorb light of certain specific energies and be excited to orbits of higher energy; they may also emit light of specific energies and fall to orbits of lower energy. The energy of the light emitted or absorbed can be found, according to the Bohr model of the hydrogen atom, from the equation

$$E = R_H\left(\frac{1}{n_l^2} - \frac{1}{n_h^2}\right)$$

where

$$R = \frac{2\pi^2 \mu Z^2 e^4}{(4\pi\varepsilon_0)^2 h^2}$$

μ = reduced mass of the electron-nucleus combination

$$\frac{1}{\mu} = \frac{1}{m_e} + \frac{1}{m_{nucleus}}$$

m_e = mass of the electron

$m_{nucleus}$ = mass of the nucleus

Z = charge of the nucleus

e = electronic charge

h = Planck's constant

n_h = quantum number describing the higher energy state

n_l = quantum number describing the lower energy state

$4\pi\varepsilon_0$ = permittivity of a vacuum

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[9] More accurate values for the constants and energy conversion factors are given inside the back cover of this book.

[10] N. Bohr, *Philos. Mag.*, **1913**, *26*, 1.

This equation shows that the Rydberg constant depends on the mass of the nucleus as well as on the fundamental constants.

Examples of the transitions observed for the hydrogen atom and the energy levels responsible are shown in Figure 2-2. As the electrons drop from level n_h to n_l (h for higher level, l for lower level), energy is released in the form of electromagnetic radiation. Conversely, if radiation of the correct energy is absorbed by an atom, electrons are raised from level n_l to level n_h. The inverse-square dependence of energy on n_l results in energy levels that are far apart in energy at small n_l and become much closer in energy at larger n_l. In the upper limit, as n_l approaches infinity, the energy approaches a limit of zero. Individual electrons can have more energy, but above this point they are no longer part of the atom; an infinite quantum number means that the nucleus and the electron are separate entities.

EXERCISE 2-1

Find the energy of the transition from $n_h = 3$ to $n_l = 2$ for the hydrogen atom in both joules and cm^{-1} (a common unit in spectroscopy). This transition results in a red line in the visible emission spectrum of hydrogen. (Solutions to the exercises are given in Appendix A.)

When applied to hydrogen, Bohr's theory worked well; when atoms with more electrons were considered, the theory failed. Complications such as elliptical rather than circular orbits were introduced in an attempt to fit the data to Bohr's theory.[11] The developing experimental science of atomic spectroscopy provided extensive data for testing of the Bohr theory and its modifications and forced the theorists to work hard to explain the spectroscopists' observations. In spite of their efforts, the Bohr theory eventually proved unsatisfactory; the energy levels shown in Figure 2-2 are valid only for the hydrogen atom. An important characteristic of the electron, its wave nature, still needed to be considered.

According to the de Broglie equation,[12] proposed in the 1920s, all moving particles have wave properties described by the equation

$$\lambda = \frac{h}{mv}$$

where
λ = wavelength of the particle
h = Planck's constant
m = mass of the particle
v = velocity of the particle

Particles massive enough to be visible have very short wavelengths, too small to be measured. Electrons, on the other hand, have wave properties because of their very small mass.

Electrons moving in circles around the nucleus, as in Bohr's theory, can be thought of as forming standing waves that can be described by the de Broglie equation. However, we no longer believe that it is possible to describe the motion of an electron in an atom so precisely. This is a consequence of another fundamental principle of modern physics, **Heisenberg's uncertainty principle,**[13] which states that there is a relationship

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[11] G. Herzberg, *Atomic Spectra and Atomic Structure*, 2nd ed., Dover Publications, New York, 1994, p. 18.

[12] L. de Broglie, *Philos. Mag.* **1924**, *47*, 446; *Ann. Phys.*, **1925**, *3*, 22.

[13] W. Heisenberg, *Z. Phys.*, **1927**, *43*, 172.

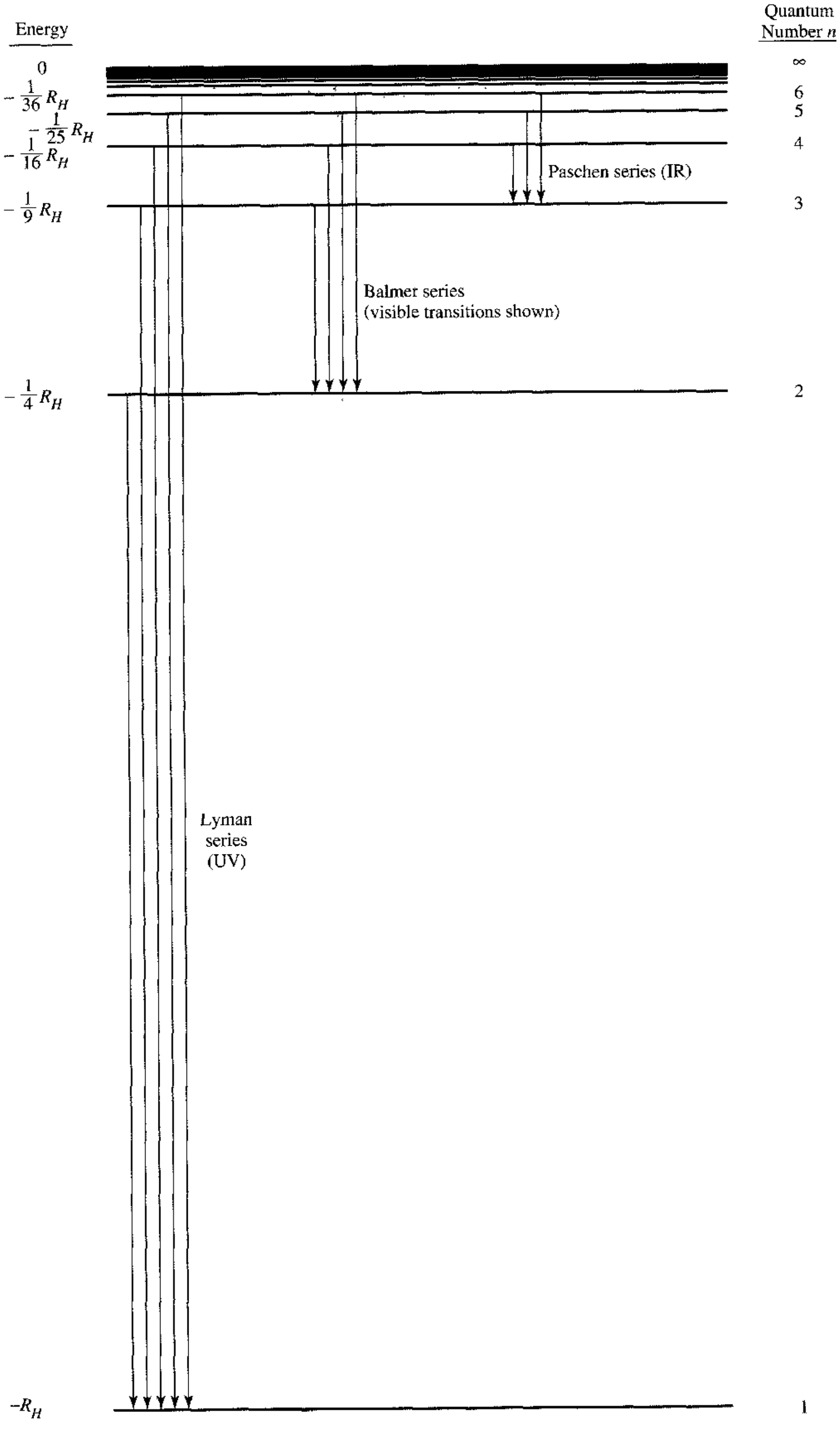

FIGURE 2-2 Hydrogen Atom Energy Levels.

between the inherent uncertainties in the location and momentum of an electron moving in the x direction:

$$\Delta x \, \Delta p_x \geq \frac{h}{4\pi}$$

where

Δx = uncertainty in the position of the electron
Δp_x = uncertainty in the momentum of the electron

The energy of spectral lines can be measured with great precision (as an example, the Rydberg constant is known to 11 significant figures), in turn allowing precise determination of the energy of electrons in atoms. This precision in energy also implies precision in momentum (Δp_x is small); therefore, according to Heisenberg, there is a large uncertainty in the location of the electron (Δx is large). These concepts mean that we cannot treat electrons as simple particles with their motion described precisely, but we must instead consider the wave properties of electrons, characterized by a degree of uncertainty in their location. In other words, instead of being able to describe precise **orbits** of electrons, as in the Bohr theory, we can only describe **orbitals**, regions that describe the probable location of electrons. The **probability** of finding the electron at a particular point in space (also called the **electron density**) can be calculated, at least in principle.

2-2 THE SCHRÖDINGER EQUATION

In 1926 and 1927, Schrödinger[14] and Heisenberg[13] published papers on wave mechanics (descriptions of the wave properties of electrons in atoms) that used very different mathematical techniques. In spite of the different approaches, it was soon shown that their theories were equivalent. Schrödinger's differential equations are more commonly used to introduce the theory, and we will follow that practice.

The Schrödinger equation describes the wave properties of an electron in terms of its position, mass, total energy, and potential energy. The equation is based on the **wave function**, Ψ, which describes an electron wave in space; in other words, it describes an atomic orbital. In its simplest notation, the equation is

$$H\Psi = E\Psi$$

where

H = the Hamiltonian operator
E = energy of the electron
Ψ = the wave function

The **Hamiltonian operator** (frequently just called the Hamiltonian) includes derivatives that **operate** on the wave function.[15] When the Hamiltonian is carried out, the result is a constant (the energy) times Ψ. The operation can be performed on any wave function describing an atomic orbital. Different orbitals have different Ψ functions and different values of E. This is another way of describing quantization in that each orbital, characterized by its own function Ψ, has a characteristic energy.

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[14] E. Schrödinger, *Ann. Phys.* (Leipzig), **1926**, *79*, 361, 489, 734; **1926**, *80*, 437; **1926**, *81*, 109; *Naturwissenshaften*, **1926**, *14*, 664; *Phys. Rev.*, **1926**. *28*, 1049.

[15] An operator is an instruction or set of instructions that states what to do with the function that follows it. It may be a simple instruction such as "multiply the following function by 6," or it may be much more complicated than the Hamiltonian. The Hamiltonian operator is sometimes written $\hat{H}$, with the ^ (hat) symbol designating an operator.

In the form used for calculating energy levels, the Hamiltonian operator is

$$H = \frac{-h^2}{8\pi^2 m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right) - \frac{Ze^2}{4\pi\varepsilon_0\sqrt{x^2 + y^2 + z^2}}$$

This part of the operator describes the *kinetic energy* of the electron

This part of the operator describes the *potential energy* of the electron, the result of electrostatic attraction between the electron and the nucleus. It is commonly designated as V.

where

h = Planck's constant

m = mass of the particle (electron)

e = charge of the electron

$\sqrt{x^2 + y^2 + z^2} = r$ = distance from the nucleus

Z = charge of the nucleus

$4\pi\varepsilon_0$ = permittivity of a vacuum

When this operator is applied to a wave function Ψ,

$$\left[\frac{-h^2}{8\pi^2 m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right) + V(x,y,z)\right]\Psi(x,y,z) = E\Psi(x,y,z)$$

where

$$V = \frac{-Ze^2}{4\pi\varepsilon_0 r} = \frac{-Ze^2}{4\pi\varepsilon_0\sqrt{x^2 + y^2 + z^2}}$$

The potential energy V is a result of electrostatic attraction between the electron and the nucleus. Attractive forces, like those between a positive nucleus and a negative electron, are defined by convention to have a negative potential energy. An electron near the nucleus (small r) is strongly attracted to the nucleus and has a large negative potential energy. Electrons farther from the nucleus have potential energies that are small and negative. For an electron at infinite distance from the nucleus ($r = \infty$), the attraction between the nucleus and the electron is zero, and the potential energy is zero.

Because every Ψ matches an atomic orbital, there is no limit to the number of solutions of the Schrödinger equation for an atom. Each Ψ describes the wave properties of a given electron in a particular orbital. The probability of finding an electron at a given point in space is proportional to Ψ^2. A number of conditions are required for a physically realistic solution for Ψ:

1. The wave function Ψ must be single-valued.	There cannot be two probabilities for an electron at any position in space.
2. The wave function Ψ and its first derivatives must be continuous.	The probability must be defined at all positions in space and cannot change abruptly from one point to the next.
3. The wave function Ψ must approach zero as r approaches infinity.	For large distances from the nucleus, the probability must grow smaller and smaller (the atom must be finite).

4. The integral

$$\int_{all\ space} \Psi_A \Psi_A^* \, d\tau = 1$$

The total probability of an electron being *somewhere* in space = 1. This is called **normalizing** the wave function.[16]

5. The integral

$$\int_{all\ space} \Psi_A \Psi_B \, d\tau = 0$$

All orbitals in an atom must be orthogonal to each other. In some cases, this means that the orbitals must be perpendicular, as with the p_x, p_y, and p_z orbitals.

2-2-1 THE PARTICLE IN A BOX

A simple example of the wave equation, the one-dimensional particle in a box, shows how these conditions are used. We will give an outline of the method; details are available elsewhere.[17] The "box" is shown in Figure 2-3. The potential energy $V(x)$ inside the box, between $x = 0$ and $x = a$, is defined to be zero. Outside the box, the potential energy is infinite. This means that the particle is completely trapped in the box and would require an infinite amount of energy to leave the box. However, there are no forces acting on it within the box.

The wave equation for locations within the box is

$$\frac{-h^2}{8\pi^2 m}\left(\frac{\partial^2 \Psi(x)}{\partial x^2}\right) = E\Psi(x), \quad \text{because } V(x) = 0$$

Sine and cosine functions have the properties that we associate with waves—a well-defined wavelength and amplitude—and we may therefore propose that the wave characteristics of our particle may be described by a combination of sine and cosine functions. A general solution to describe the possible waves in the box would then be

$$\Psi = A \sin rx + B \cos sx$$

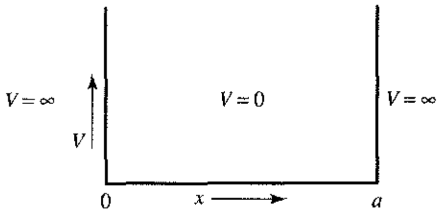

FIGURE 2-3 Potential Energy Well for the Particle in a Box.

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[16] Because the wave functions may have imaginary values (containing $\sqrt{-1}$), $\Psi\Psi^*$ is used to make the integral real. In many cases, the wave functions themselves are real, and this integral becomes

$$\int_{all\ space} \Psi_A^2 \, d\tau.$$

[17] G. M. Barrow, *Physical Chemistry*, 6th ed., McGraw-Hill, New York, 1996, pp. 65, 430, calls this the "particle on a line" problem. Many other physical chemistry texts also include solutions.

where A, B, r, and s are constants. Substitution into the wave equation allows solution for r and s (see Problem 4 at the end of the chapter):

$$r = s = \sqrt{2mE}\,\frac{2\pi}{h}$$

Because Ψ must be continuous and must equal zero at $x < 0$ and $x > a$ (because the particle is confined to the box), Ψ must go to zero at $x = 0$ and $x = a$. Because $\cos sx = 1$ for $x = 0$, Ψ can equal zero in the general solution above only if $B = 0$. This reduces the expression for Ψ to

$$\Psi = A \sin rx$$

At $x = a$, Ψ must also equal zero; therefore, $\sin ra = 0$, which is possible only if ra is an integral multiple of π:

$$ra = \pm n\pi \quad \text{or} \quad r = \frac{\pm n\pi}{a}$$

where n = any integer $\neq 0$.[18] Substituting the positive value (because both positive and negative values yield the same results) for r into the solution for r gives

$$r = \frac{n\pi}{a} = \sqrt{2mE}\,\frac{2\pi}{h}$$

This expression may be solved for E:

$$E = \frac{n^2h^2}{8ma^2}$$

These are the energy levels predicted by the particle in a box model for any particle in a one-dimensional box of length a. The energy levels are quantized according to **quantum numbers** $n = 1, 2, 3, \ldots$

Substituting $r = n\pi/a$ into the wave function gives

$$\Psi = A \sin\frac{n\pi x}{a}$$

and applying the normalizing requirement $\int \Psi\Psi^*\,d\tau = 1$ gives

$$A = \sqrt{\frac{2}{a}}$$

The total solution is then

$$\Psi = \sqrt{\frac{2}{a}}\sin\frac{n\pi x}{a}$$

---

[18] If $n = 0$, then $r = 0$ and $\Psi = 0$ at all points. The probability of finding the electron is $\int \Psi\Psi^*\,dx = 0$, and there is no electron at all.

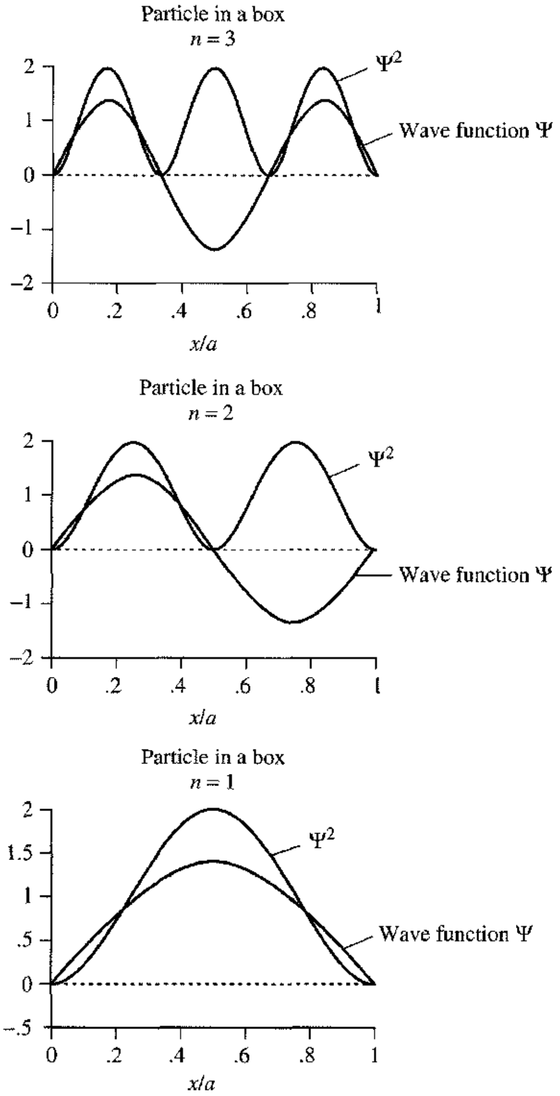


FIGURE 2-4 Wave Functions and Their Squares for the Particle in a Box with $n = 1, 2,$ and 3.

The resulting wave functions and their squares for the first three states (the ground state and first two excited states) are plotted in Figure 2-4.

The squared wave functions are the probability densities and show the difference between classical and quantum mechanical behavior. Classical mechanics predicts that the electron has equal probability of being at any point in the box. The wave nature of the electron gives it the extremes of high and low probability at different locations in the box.

2-2-2 QUANTUM NUMBERS AND ATOMIC WAVE FUNCTIONS

The particle in a box example shows how a wave function operates in one dimension. Mathematically, atomic orbitals are discrete solutions of the three-dimensional Schrödinger equations. The same methods used for the one-dimensional box can be expanded to three dimensions for atoms. These orbital equations include three quantum numbers, n, l, and m_l. A fourth quantum number, m_s, a result of relativistic corrections to the Schrödinger equation, completes the description by accounting for the magnetic moment of the electron. The quantum numbers are summarized in Tables 2-2, 2-3, and 2-4.

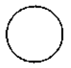
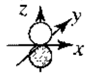
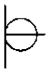
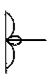
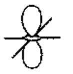
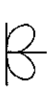
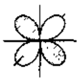
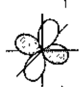
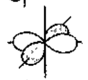
TABLE 2-2
Quantum Numbers and Their Properties

Symbol	*Name*	*Values*	*Role*
n	Principal	$1, 2, 3, \ldots$	Determines the major part of the energy
l	Angular momentum	$0, 1, 2, \ldots, n-1$	Describes angular dependence and contributes to the energy
m_l	Magnetic	$0, \pm 1, \pm 2, \ldots, \pm l$	Describes orientation in space (angular momentum in the z direction)
m_s	Spin	$\pm \frac{1}{2}$	Describes orientation of the electron spin (magnetic moment) in space

Orbitals with different l values are known by the following labels, derived from early terms for different families of spectroscopic lines:

l	0	1	2	3	4	5, . . .
Label	s	p	d	f	g	continuing alphabetically

TABLE 2-3
Hydrogen Atom Wave Functions: Angular Functions

		Angular factors			*Real wave functions*			
		Related to angular momentum		*Functions of* θ	*In Polar coordinates*	*In Cartesian coordinates*	*Shapes*	*Label*
l	m_l	Φ	Θ		$\Theta\Phi(\theta, \phi)$	$\Theta\Phi(x, y, z)$		
$0(s)$	0	$\frac{1}{\sqrt{2\pi}}$	$\frac{1}{\sqrt{2}}$		$\frac{1}{2\sqrt{\pi}}$	$\frac{1}{2\sqrt{\pi}}$		s
$1(p)$	0	$\frac{1}{\sqrt{2\pi}}$	$\frac{\sqrt{6}}{2}\cos\theta$		$\frac{1}{2}\sqrt{\frac{3}{\pi}}\cos\theta$	$\frac{1}{2}\sqrt{\frac{3}{\pi}}\frac{z}{r}$		p_z
	+1	$\frac{1}{\sqrt{2\pi}}e^{i\phi}$	$\frac{\sqrt{3}}{2}\sin\theta$		$\frac{1}{2}\sqrt{\frac{3}{\pi}}\sin\theta\cos\phi$	$\frac{1}{2}\sqrt{\frac{3}{\pi}}\frac{x}{r}$		p_x
	−1	$\frac{1}{\sqrt{2\pi}}e^{-i\phi}$	$\frac{\sqrt{3}}{2}\sin\theta$		$\frac{1}{2}\sqrt{\frac{3}{\pi}}\sin\theta\sin\phi$	$\frac{1}{2}\sqrt{\frac{3}{\pi}}\frac{y}{r}$		p_y
$2(d)$	0	$\frac{1}{\sqrt{2\pi}}$	$\frac{1}{2}\sqrt{\frac{5}{2}}(3\cos^2\theta - 1)$		$\frac{1}{4}\sqrt{\frac{5}{\pi}}(3\cos^2\theta - 1)$	$\frac{1}{4}\sqrt{\frac{5}{\pi}}\frac{(2z^2 - x^2 - y^2)}{r^2}$		d_{z^2}
	+1	$\frac{1}{\sqrt{2\pi}}e^{i\phi}$	$\frac{\sqrt{15}}{2}\cos\theta\sin\theta$		$\frac{1}{2}\sqrt{\frac{15}{\pi}}\cos\theta\sin\theta\cos\phi$	$\frac{1}{2}\sqrt{\frac{15}{\pi}}\frac{xz}{r^2}$		d_{xz}
	−1	$\frac{1}{\sqrt{2\pi}}e^{-i\phi}$	$\frac{\sqrt{15}}{2}\cos\theta\sin\theta$		$\frac{1}{2}\sqrt{\frac{15}{\pi}}\cos\theta\sin\theta\sin\phi$	$\frac{1}{2}\sqrt{\frac{15}{\pi}}\frac{yz}{r^2}$		d_{yz}
	+2	$\frac{1}{\sqrt{2\pi}}e^{2i\phi}$	$\frac{\sqrt{15}}{4}\sin^2\theta$		$\frac{1}{4}\sqrt{\frac{15}{\pi}}\sin^2\theta\cos 2\phi$	$\frac{1}{4}\sqrt{\frac{15}{\pi}}\frac{(x^2 - y^2)}{r^2}$		$d_{x^2\;y^2}$
	−2	$\frac{1}{\sqrt{2\pi}}e^{-2i\phi}$	$\frac{\sqrt{15}}{4}\sin^2\theta$		$\frac{1}{4}\sqrt{\frac{15}{\pi}}\sin^2\theta\sin 2\phi$	$\frac{1}{4}\sqrt{\frac{15}{\pi}}\frac{xy}{r^2}$		d_{xy}

SOURCE: Adapted from G. M. Barrow, *Physical Chemistry*, 5th ed., McGraw-Hill, New York, 1988, p. 450, with permission.

NOTE: The relations $(e^{i\phi} - e^{-i\phi})/(2i) = \sin\phi$ and $(e^{i\phi} + e^{-i\phi})/2 = \cos\phi$ can be used to convert the exponential imaginary functions to real trigonometric functions, combining the two orbitals with $m_l = \pm 1$ to give two orbitals with $\sin\phi$ and $\cos\phi$. In a similar fashion, the orbitals with $m_l = \pm 2$ result in real functions with $\cos^2\phi$ and $\sin^2\phi$. These functions have then been converted to Cartesian form by using the functions $x = r\sin\theta\cos\phi$, $y = r\sin\theta\sin\phi$, and $z = r\cos\theta$.

TABLE 2-4
Hydrogen Atom Wave Functions: Radial Functions

Radial Functions $R(r)$, with $\sigma = Zr/a_0$

Orbital	*n*	*l*	*R(r)*
1s	1	0	$R_{1s} = 2\left[\frac{Z}{a_0}\right]^{3/2} e^{-\sigma}$
2s	2	0	$R_{2s} = \left[\frac{Z}{2a_0}\right]^{3/2} (2 - \sigma)e^{-\sigma/2}$
2p		1	$R_{2p} = \frac{1}{\sqrt{3}}\left[\frac{Z}{2a_0}\right]^{3/2} \sigma e^{-\sigma/2}$
3s	3	0	$R_{3s} = \frac{2}{27}\left[\frac{Z}{3a_0}\right]^{3/2} (27 - 18\sigma + 2\sigma^2)e^{-\sigma/3}$
3p		1	$R_{3p} = \frac{1}{81\sqrt{3}}\left[\frac{2Z}{a_0}\right]^{3/2} (6 - \sigma)\sigma e^{-\sigma/3}$
3d		2	$R_{3d} = \frac{1}{81\sqrt{15}}\left[\frac{2Z}{a_0}\right]^{3/2} \sigma^2 e^{-\sigma/3}$

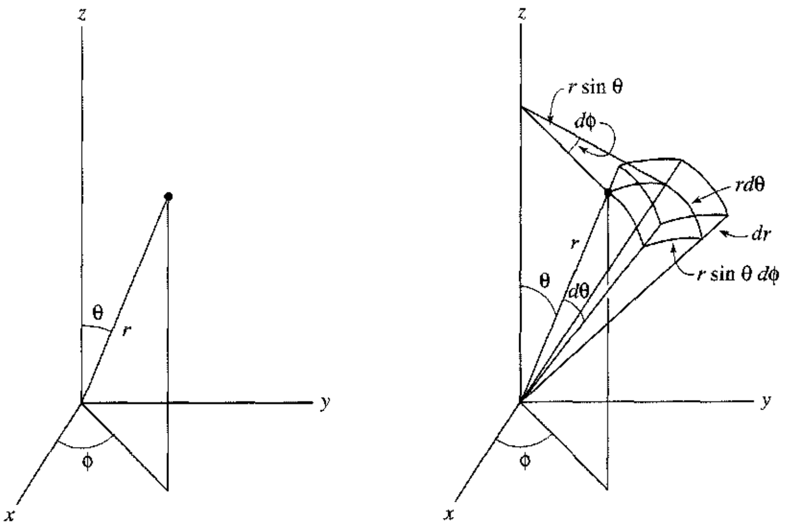
The fourth quantum number explains several experimental observations. Two of these observations are that lines in alkali metal emission spectra are doubled, and that a beam of alkali metal atoms splits into two parts if it passes through a magnetic field. Both of these can be explained by attributing a magnetic moment to the electron; it behaves like a tiny bar magnet. This is usually described as the spin of the electron because a spinning electrically charged particle also has a magnetic moment, but it should not be taken as an accurate description; it is a purely quantum mechanical property.

The quantum number n is primarily responsible for determining the overall energy of an atomic orbital; the other quantum numbers have smaller effects on the energy. The quantum number l determines the angular momentum of the orbital or shape of the orbital and has a smaller effect on the energy. The quantum number m_l determines the orientation of the angular momentum vector in a magnetic field, or the position of the orbital in space, as shown in Table 2-3. The quantum number m_s determines the orientation of the electron magnetic moment in a magnetic field, either in the direction of the field $\left(+\frac{1}{2}\right)$ or opposed to it $\left(-\frac{1}{2}\right)$. When no field is present, all m_l values (all three p orbitals or all five d orbitals) have the same energy and both m_s values have the same energy. Together, the quantum numbers n, l, and m_l define an atomic orbital; the quantum number m_s describes the electron spin within the orbital.

One feature that should be mentioned is the appearance of i $(= \sqrt{-1})$ in the p and d orbital wave equations in Table 2-3. Because it is much more convenient to work with real functions than complex functions, we usually take advantage of another property of the wave equation. For differential equations of this type, any linear combination of solutions (sums or differences of the functions, with each multiplied by any coefficient) to the equation is also a solution to the equation. The combinations usually chosen for the p orbitals are the sum and difference of the p orbitals having $m_l = +1$ and -1, normalized by multiplying by the constants $\frac{1}{\sqrt{2}}$ and $\frac{i}{\sqrt{2}}$, respectively:

$$\Psi_{2px} = \frac{1}{\sqrt{2}}(\Psi_{+1} + \Psi_{-1}) = \frac{1}{2}\sqrt{\frac{3}{\pi}}[R(r)] \sin\theta \cos\phi$$

$$\Psi_{2py} = \frac{i}{\sqrt{2}}(\Psi_{+1} - \Psi_{-1}) = \frac{1}{2}\sqrt{\frac{3}{\pi}}[R(r)] \sin\theta \sin\phi$$



Spherical Coordinates

Volume Element

FIGURE 2-5 Spherical Coordinates and Volume Element for a Spherical Shell in Spherical Coordinates.

The same procedure used on the *d* orbital functions for $m_l = \pm 1$ and ± 2 gives the functions in the column headed $\Theta\Phi(\theta, \phi)$ in Table 2-3, which are the familiar *d* orbitals. The d_{z^2} orbital ($m_l = 0$) actually uses the function $2z^2 - x^2 - y^2$, which we shorten to z^2 for convenience. These functions are now real functions, so $\Psi = \Psi^*$ and $\Psi\Psi^* = \Psi^2$.

A more detailed look at the Schrödinger equation shows the mathematical origin of atomic orbitals. In three dimensions, Ψ may be expressed in terms of Cartesian coordinates (x, y, z) or in terms of spherical coordinates (r, θ, ϕ). Spherical coordinates, as shown in Figure 2-5, are especially useful in that *r* represents the distance from the nucleus. The spherical coordinate θ is the angle from the *z* axis, varying from 0 to π, and ϕ is the angle from the *x* axis, varying from 0 to 2π. It is possible to convert between Cartesian and spherical coordinates using the following expressions:

$$x = r \sin\theta \cos\phi$$

$$y = r \sin\theta \sin\phi$$

$$z = r \cos\theta$$

In spherical coordinates, the three sides of the volume element are $r\,d\theta$, $r \sin\theta\, d\phi$, and dr. The product of the three sides is $r^2 \sin\theta\, d\theta\, d\phi\, dr$, equivalent to $dx\,dy\,dz$. The volume of the thin shell between r and $r + dr$ is $4\pi r^2\, dr$, which is the integral over ϕ from 0 to π, and over θ from 0 to 2π. This integral is useful in describing the electron density as a function of distance from the nucleus.

Ψ can be factored into a radial component and two angular components. The **radial function, *R***, describes electron density at different distances from the nucleus; the **angular functions**, **Θ** and **Φ**, describe the shape of the orbital and its orientation in space. The two angular factors are sometimes combined into one factor, called *Y*:

$$\Psi(r, \theta, \phi) = R(r)\Theta(\theta)\Phi(\phi) = R(r)Y(\theta, \phi)$$

R is a function only of *r*; *Y* is a function of θ and ϕ, and gives the distinctive shapes of *s, p, d,* and other orbitals. *R*, Θ, and Φ are shown separately in Tables 2-3 and 2-4.

The angular functions

The angular functions Θ and Φ determine how the probability changes from point to point at a given distance from the center of the atom; in other words, they give the shape of the orbitals and their orientation in space. The angular functions Θ and Φ are determined by the quantum numbers l and m_l. The shapes of *s*, *p*, and *d* orbitals are shown in Table 2-3 and Figure 2-6.

In the center of Table 2-3 are the shapes for the Θ portion; when the Φ portion is included, with values of $\phi = 0$ to 2π, the three-dimensional shapes in the far-right column are formed. In the diagrams of orbitals in Table 2-3, the orbital lobes are shaded where the wave function is negative. The probabilities are the same for locations with positive and negative signs for Ψ, but it is useful to distinguish regions of opposite signs for bonding purposes, as we will see in Chapter 5.

The radial functions

The radial factor $R(r)$ (Table 2-4) is determined by the quantum numbers n and l, the principal and angular momentum quantum numbers.

The **radial probability function** is $4\pi r^2 R^2$. This function describes the probability of finding the electron at a given distance from the nucleus, summed over all angles, with the $4\pi r^2$ factor the result of integrating over all angles. The radial wave functions and radial probability functions are plotted for the $n = 1, 2$, and 3 orbitals in Figure 2-7. Both $R(r)$ and $4\pi r^2 R^2$ are scaled with a_0, the Bohr radius, to give reasonable units on the axes of the graphs. The Bohr radius, $a_0 = 52.9$ pm, is a common unit in quantum mechanics. It is the value of r at the maximum of Ψ^2 for a hydrogen 1*s* orbital and is also the radius of a 1*s* orbital according to the Bohr model.

In all the radial probability plots, the electron density, or probability of finding the electron, falls off rapidly as the distance from the nucleus increases. It falls off most quickly for the 1*s* orbital; by $r = 5a_0$, the probability is approaching zero. By contrast, the 3*d* orbital has a maximum at $r = 9a_0$ and does not approach zero until approximately $r = 20a_0$. All the orbitals, including the *s* orbitals, have zero probability at the center of the nucleus, because $4\pi r^2 R^2 = 0$ at $r = 0$. The radial probability functions are a combination of $4\pi r^2$, which increases rapidly with r, and R^2, which may have maxima and minima, but generally decreases exponentially with r. The product of these two factors gives the characteristic probabilities seen in the plots. Because chemical reactions depend on the shape and extent of orbitals at large distances from the nucleus, the radial probability functions help show which orbitals are most likely to be involved in reactions.

Nodal surfaces

At large distances from the nucleus, the electron density, or probability of finding the electron, falls off rapidly. The 2*s* orbital also has a **nodal surface**, a surface with zero electron density, in this case a sphere with $r = 2a_0$ where the probability is zero. Nodes appear naturally as a result of the wave nature of the electron; they occur in the functions that result from solving the wave equation for Ψ. A node is a surface where the wave function is zero as it changes sign (as at $r = 2a_0$, in the 2*s* orbital); this requires that $\Psi = 0$, and the probability of finding the electron at that point is also zero.

If the probability of finding an electron is zero ($\Psi^2 = 0$), Ψ must also be equal to zero. Because

$$\Psi(r, \theta, \phi) = R(r)Y(\theta, \phi)$$

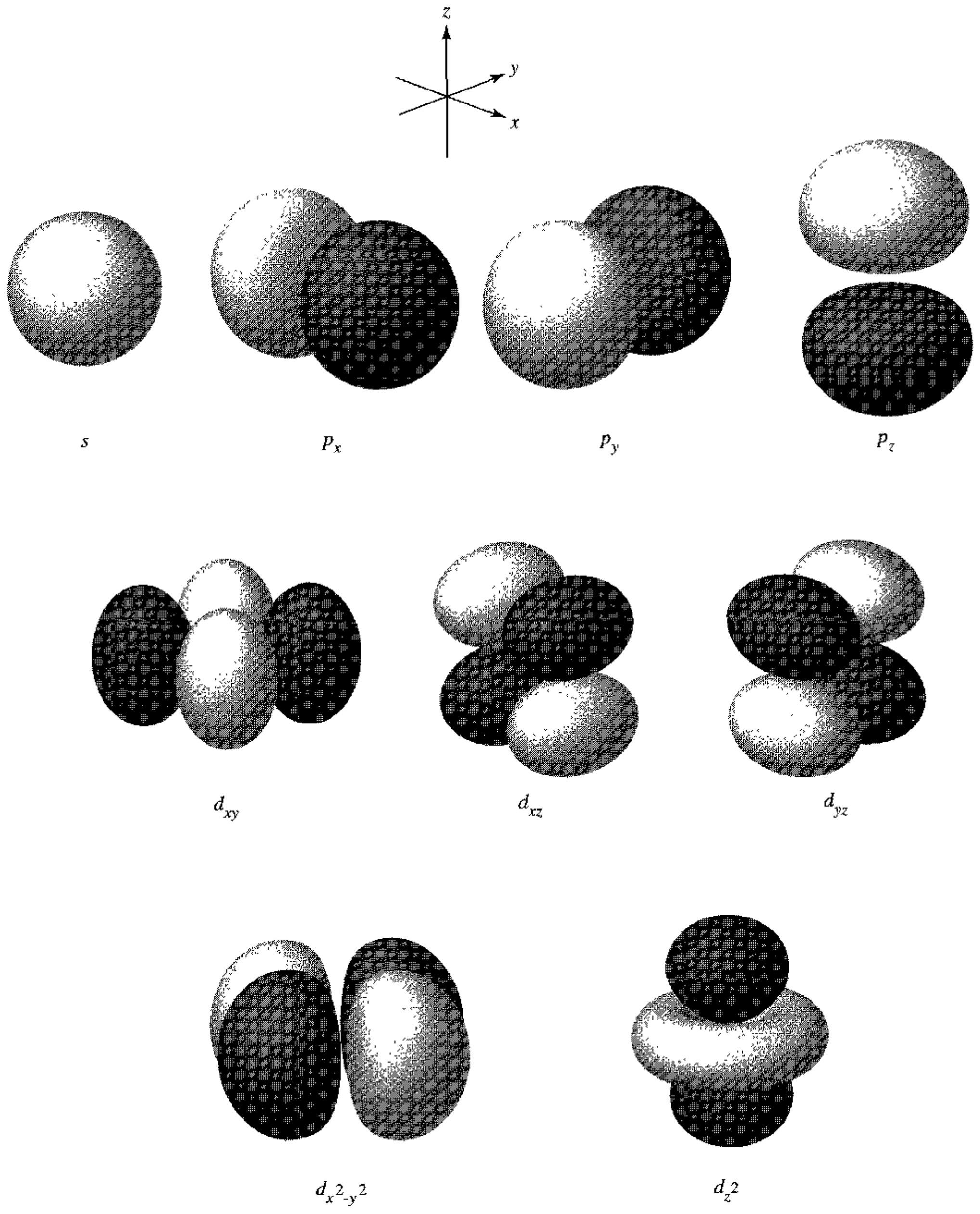


FIGURE 2-6 Selected Atomic Orbitals. (Adapted with permission from G. O. Spessard and G. L. Miessler, *Organometallic Chemistry*, Prentice Hall, Upper Saddle River, NJ, 1997, p. 11, Fig. 2-1.)

in order for $\Psi = 0$, either $R(r) = 0$ or $Y(\theta, \phi) = 0$. We can therefore determine nodal surfaces by determining under what conditions $R = 0$ or $Y = 0$.

Table 2-5 summarizes the nodes for several orbitals. Note that the total number of nodes in any orbital is $n - 1$ if the conical nodes of some d and f orbitals count as 2.[19]

Angular nodes result when $Y = 0$ and are planar or conical. Angular nodes can be determined in terms of θ and ϕ, but may be easier to visualize if Y is expressed in

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[19] Mathematically, the nodal surface for the d_{z^2} orbital is one surface, but in this instance it fits the pattern better if thought of as two nodes.

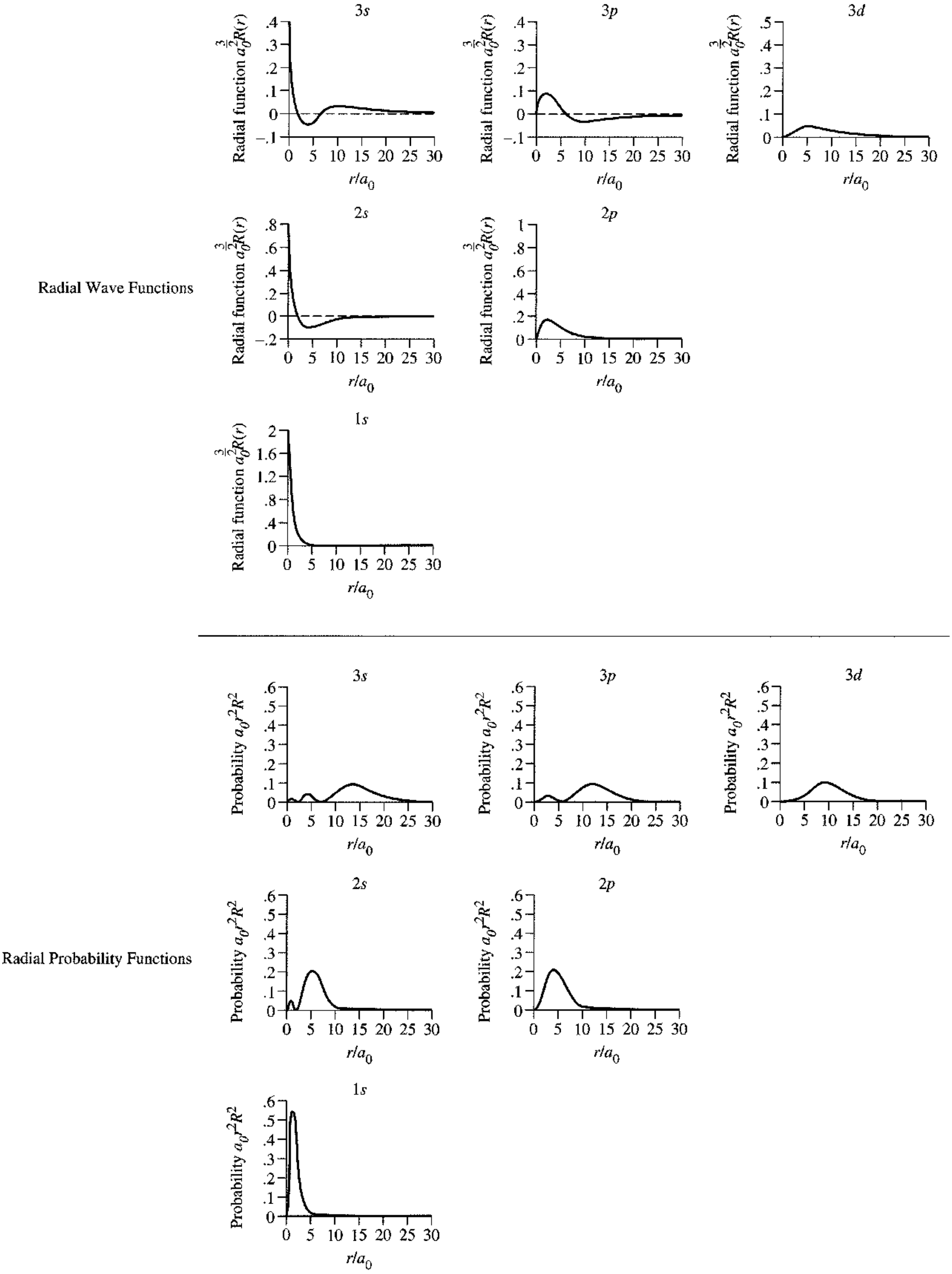
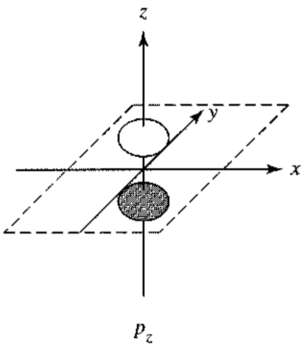


FIGURE 2-7 Radial Wave Functions and Radial Probability Functions.

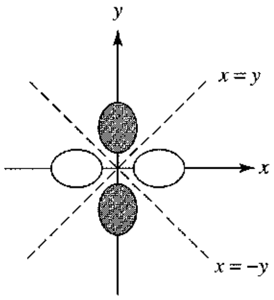
TABLE 2-5
Nodal Surfaces

Spherical nodes $[R(r) = 0]$					
Examples (number of spherical nodes)					
1*s*	0	2*p*	0	3*d*	0
2*s*	1	3*p*	1	4*d*	1
3*s*	2	4*p*	2	5*d*	2

Angular nodes $[Y(\theta, \phi) = 0]$	
Examples (number of angular nodes)	
s orbitals	0
p orbitals	1 plane for each orbital
d orbitals	2 planes for each orbital except d_{z^2} 1 conical surface for d_{z^2}



p_z



$d_{x^2-y^2}$

Cartesian (x, y, z) coordinates (see Table 2-3). In addition, the regions where the wave function is positive and where it is negative can be found. This information will be useful in working with molecular orbitals in later chapters. There are l angular nodes in any orbital, with the conical surface in the d_{z^2} and similar orbitals counted as two nodes.

Radial nodes, or **spherical nodes**, result when $R = 0$, and give the atom a layered appearance, shown in Figure 2-8 for the 3*s* and $3p_z$ orbitals. These nodes occur when the radial function changes sign; they are depicted in the radial function graphs by $R(r) = 0$ and in the radial probability graphs by $4\pi r^2R^2 = 0$. The 1*s*, 2*p*, and 3*d* orbitals (the lowest energy orbitals of each shape) have no radial nodes and the number of nodes increases as n increases. The number of radial nodes for a given orbital is always equal to $n - l - 1$.

Nodal surfaces can be puzzling. For example, a *p* orbital has a nodal plane through the nucleus. How can an electron be on both sides of a node at the same time without ever having been at the node (at which the probability is zero)? One explanation is that the probability does not go quite to zero.[20]

Another explanation is that such a question really has no meaning for an electron thought of as a wave. Recall the particle in a box example. Figure 2-4 shows nodes at $x/a = 0.5$ for $n = 2$ and at $x/a = 0.33$ and 0.67 for $n = 3$. The same diagrams could represent the amplitudes of the motion of vibrating strings at the fundamental frequency $(n = 1)$ and multiples of 2 and 3. A plucked violin string vibrates at a specific frequency, and nodes at which the amplitude of vibration is zero are a natural result. Zero amplitude does not mean that the string does not exist at these points, but simply that the magnitude of the vibration is zero. An electron wave exists at the node as well as on both sides of a nodal surface, just as a violin string exists at the nodes and on both sides of points having zero amplitude.

Still another explanation, in a lighter vein, was suggested by R. M. Fuoss to one of the authors (DAT) in a class on bonding. Paraphrased from St. Thomas Aquinas, "Angels are not material beings. Therefore, they can be first in one place and later in another, without ever having been in between." If the word "electrons" replaces the word "angels," a semitheological interpretation of nodes could result.

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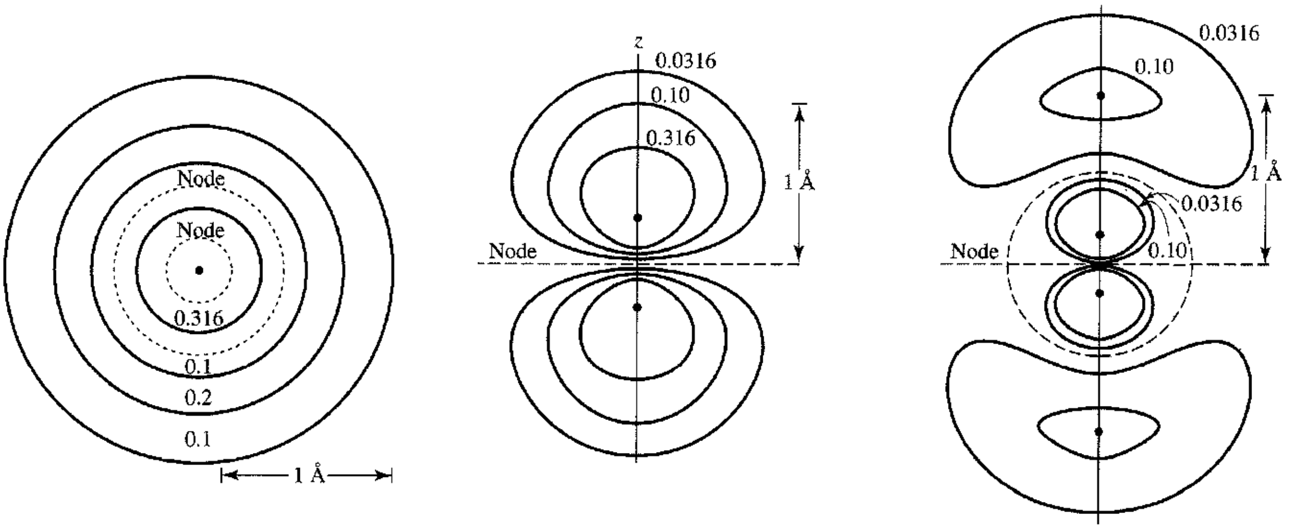
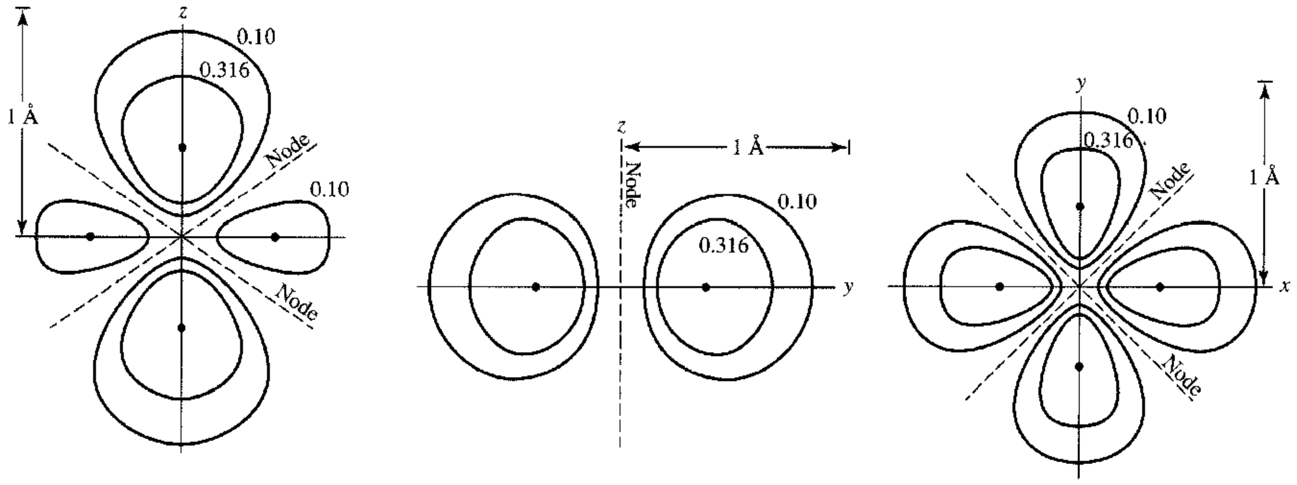
[20] A. Szabo, *J. Chem. Educ.*, **1969**, *46*, 678, uses relativistic arguments to explain that the electron probablity at a nodal surface has a very small, but finite, value.



(a) Cl:3s

(b) C:2p_z

(c) Cl:3p_z



(d) Ti^{3+}:3d_{z^2}

(e) Ti^{3+}:3$d_{x^2-y^2}$

(f) Ti^{3+}:3$d_{x^2-y^2}$

FIGURE 2-8 Constant Electron Density Surfaces for Selected Atomic Orbitals. (a)–(d) The cross-sectional plane is any plane containing the z axis. (e) The cross section is taken through the xz or yz plane. (f) The cross section is taken through the xy plane. (Figures (b)–(f) reproduced with permission from E. A. Orgyzlo and G. B. Porter, *J. Chem. Educ.*, **1963**, *40*, 258.)

EXAMPLES

p_z The angular factor Y is given in Table 2-3 in terms of Cartesian coordinates:

$$Y = \frac{1}{2}\sqrt{\frac{3}{\pi}}\,\frac{z}{r}$$

This orbital is designated p_z because z appears in the Y expression. For an angular node, Y must equal zero, which is true only if $z = 0$. Therefore, $z = 0$ (the xy plane) is an angular nodal surface for the p_z orbital as shown in Table 2-5 and Figure 2-8. The wave function is positive where $z > 0$ and negative where $z < 0$. In addition, a $2p_z$ orbital has no spherical nodes, a $3p_z$ orbital has one spherical node, and so on.

$d_{x^2-y^2}$

$$Y = \frac{1}{4}\sqrt{\frac{15}{\pi}}\frac{(x^2 - y^2)}{r^2}$$

Here, the expression $x^2 - y^2$ appears in the equation, so the designation is $d_{x^2-y^2}$. Because there are two solutions to the equation $Y = 0$ (or $x^2 - y^2 = 0$), $x = y$ and $x = -y$, the planes defined by these equations are the angular nodal surfaces. They are planes containing the z axis and making 45° angles with the x and y axes (see Table 2-5). The function is positive where $x > y$ and negative where $x < y$. In addition, a $3d_{x^2-y^2}$ orbital has no spherical nodes, a $4d_{x^2-y^2}$ has one spherical node, and so on.

EXERCISE 2-2

Describe the angular nodal surfaces for a d_{z^2} orbital, whose angular wave function is

$$Y = \frac{1}{4}\sqrt{\frac{5}{\pi}}\frac{(2z^2 - x^2 - y^2)}{r^2}$$

EXERCISE 2-3

Describe the angular nodal surfaces for a d_{xz} orbital, whose angular wave function is

$$Y = \frac{1}{2}\sqrt{\frac{15}{\pi}}\frac{xz}{r^2}$$

The result of the calculations is the set of atomic orbitals familiar to all chemists. Figure 2-7 shows diagrams of *s*, *p*, and *d* orbitals and Figure 2-8 shows lines of constant electron density in several orbitals. The different signs on the wave functions are shown by different shadings of the orbital lobes in Figure 2-7, and the outer surfaces shown enclose 90% of the total electron density of the orbitals. The orbitals we use are the common ones used by chemists; others that are also solutions of the Schrödinger equation can be chosen for special purposes.[21]

2-2-3 THE AUFBAU PRINCIPLE

Limitations on the values of the quantum numbers lead to the familiar **aufbau** (German, *Aufbau*, building up) **principle**, where the buildup of electrons in atoms results from continually increasing the quantum numbers. Any combination of the quantum numbers presented so far correctly describes electron behavior in a hydrogen atom, where there is only one electron. However, interactions between electrons in polyelectronic atoms require that the order of filling of orbitals be specified when more than one electron is in the same atom. In this process, we start with the lowest n, l, and m_l, values (1, 0, and 0, respectively) and either of the m_s values (we will arbitrarily use $-\frac{1}{2}$ first). Three rules will then give us the proper order for the remaining electrons as we increase the quantum numbers in the order m_l, m_s, l, and n.

1. Electrons are placed in orbitals to give the lowest total energy to the atom. This means that the lowest values of n and l are filled first. Because the orbitals within each set (p, d, etc.) have the same energy, the orders for values of m_l and m_s are indeterminate.

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[21] R. E. Powell, *J. Chem. Educ.*, **1968**, *45*, 45.

2. The **Pauli exclusion principle**[22] requires that each electron in an atom have a unique set of quantum numbers. At least one quantum number must be different from those of every other electron. This principle does not come from the Schrödinger equation, but from experimental determination of electronic structures.
3. **Hund's rule of maximum multiplicity**[23] requires that electrons be placed in orbitals so as to give the maximum total spin possible (or the maximum number of parallel spins). Two electrons in the same orbital have a higher energy than two electrons in different orbitals, caused by electrostatic repulsion (electrons in the same orbital repel each other more than electrons in separate orbitals). Therefore, this rule is a consequence of the lowest possible energy rule (Rule 1). When there are one to six electrons in p orbitals, the required arrangements are those given in Table 2-6. The **multiplicity** is the number of unpaired electrons plus 1, or $n + 1$. This is the number of possible energy levels that depend on the orientation of the net magnetic moment in a magnetic field. Any other arrangement of electrons results in fewer unpaired electrons. This is only one of Hund's rules; others are described in Chapter 11.

TABLE 2-6
Hund's Rule and Multiplicity

Number of Electrons	*Arrangement*	*Unpaired e^-*	*Multiplicity*
1	↑ ___ ___	1	2
2	↑ ↑ ___	2	3
3	↑ ↑ ↑	3	4
4	↑↓ ↑ ↑	2	3
5	↑↓ ↑↓ ↑	1	2
6	↑↓ ↑↓ ↑↓	0	1

This rule is a consequence of the energy required for pairing electrons in the same orbital. When two electrons occupy the same part of the space around an atom, they repel each other because of their mutual negative charges with a **Coulombic energy of repulsion,** Π_c, per pair of electrons. As a result, this repulsive force favors electrons in different orbitals (different regions of space) over electrons in the same orbitals.

In addition, there is an **exchange energy,** Π_e, which arises from purely quantum mechanical considerations. This energy depends on the number of possible exchanges between two electrons with the same energy and the same spin.

For example, the electron configuration of a carbon atom is $1s^22s^22p^2$. Three arrangements of the $2p$ electrons can be considered:

(1) ↑↓ ___ ___ (2) ↑ ↓ ___ (3) ↑ ↑ ___

The first arrangement involves Coulombic energy, Π_c, because it is the only one that pairs electrons in the same orbital. The energy of this arrangement is higher than that of the other two by Π_c as a result of electron-electron repulsion.

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[22] W. Pauli, *Z. Physik*, **1925**, *31*, 765.

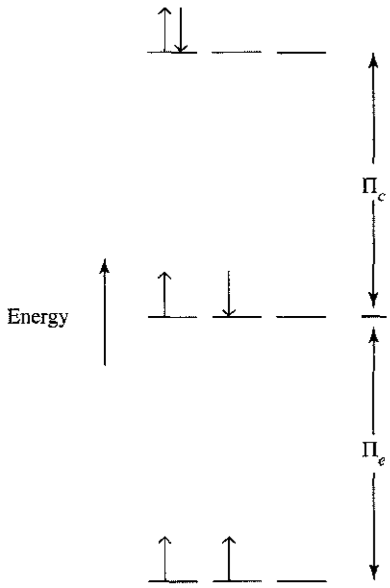
[23] F. Hund, *Z. Physik*, **1925**, *33*, 345.

In the first two cases there is only one possible way to arrange the electrons to give the same diagram, because there is only a single electron in each having + or − spin. However, in the third case there are two possible ways in which the electrons can be arranged:

↑1 ↑2 ___   ↑2 ↑1 ___   (one exchange of electron)

The exchange energy is Π_e per possible exchange of parallel electrons and is negative. The higher the number of possible exchanges, the lower the energy. Consequently, the third configuration is lower in energy than the second by Π_e.

The results may be summarized in an energy diagram:



These two pairing terms add to produce the total pairing energy, Π:

$$\Pi = \Pi_c + \Pi_e$$

The Coulombic energy, Π_c, is positive and is nearly constant for each pair of electrons. The exchange energy, Π_e, is negative and is also nearly constant for each possible exchange of electrons with the same spin. When the orbitals are **degenerate** (have the same energy), both Coulombic and pairing energies favor the unpaired configuration over the paired configuration. If there is a difference in energy between the levels involved, this difference, in combination with the total pairing energy, determines the final configuration. For atoms, this usually means that one set of orbitals is filled before another has any electrons. However, this breaks down in some of the transition elements, because the 4*s* and 3*d* (or the higher corresponding levels) are so close in energy that the pairing energy is nearly the same as the difference between levels. Section 2-2-4 explains what happens in these cases.

EXAMPLE

Oxygen With four p electrons, oxygen could have two unpaired electrons (↑↓ ↑ ↑), or it could have no unpaired electrons (↑↓ ↑↓ ___). Find the number of electrons that could be exchanged in each case and the Coulombic and exchange energies for the atom.

↑↓ ↑ ↑ has one pair, energy contribution Π_c.

↑↓ ↑ ↑ has one electron with ↓ spin and no possibility of exchange.

↑ ↑ ↑ has four possible arrangements, three exchange possibilities (1–2, 1–3, 2–3), energy contribution 3 Π_e:

↑1 ↑2 ↑3   ↑2 ↑1 ↑3   ↑3 ↑2 ↑1   ↑1 ↑3 ↑2

Overall, 3 $\Pi_e + \Pi_c$.

↑↓ ↑↓ ___ has one exchange possibility for each spin pair and two pairs.

Overall, 2 Π_e + 2 Π_c.

Because Π_c is positive and Π_e is negative, the energy of the first arrangement is lower than the second; ↑↓ ↑ ↑ has the lower energy.

EXERCISE 2-4

A nitrogen atom with three p electrons could have three unpaired electrons (↑ ↑ ↑), or it could have one unpaired electron (↑↓ ↑ ___). Find the number of electrons that could be exchanged in each case and the Coulombic and exchange energies for the atom. Which arrangement would be lower in energy?

Many schemes have been used to predict the order of filling of atomic orbitals. One, known as Klechkowsky's rule, states that the order of filling the orbitals proceeds from the lowest available value for the sum $n + l$. When two combinations have the same value, the one with the smaller value of n is filled first. Combined with the other rules, this gives the order of filling of most of the orbitals.

One of the simplest methods that fits most atoms uses the periodic table blocked out as in Figure 2-9. The electron configurations of hydrogen and helium are clearly $1s^1$

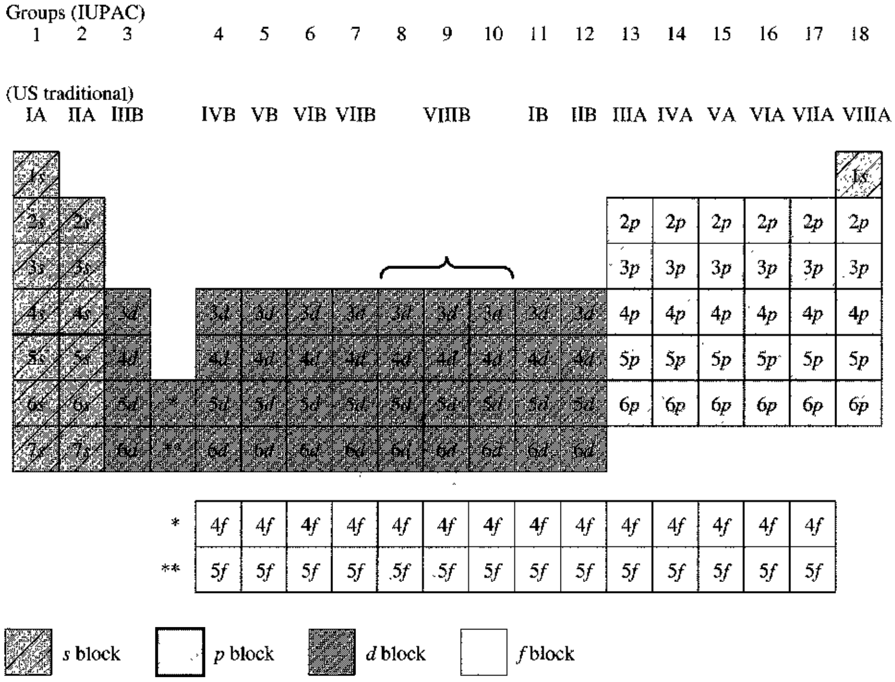


FIGURE 2-9 Atomic Orbital Filling in the Periodic Table.

and $1s^2$. After that, the elements in the first two columns on the left (Groups 1 and 2 or IA and IIA) are filling s orbitals, with $l = 0$; those in the six columns on the right (Groups 13 to 18 or IIIA to VIIIA) are filling p orbitals, with $l = 1$; and the ten in the middle (the transition elements, Groups 3 to 12 or IIIB to IIB) are filling d orbitals, with $l = 2$. The lanthanide and actinide series (numbers 58 to 71 and 90 to 103) are filling f orbitals, with $l = 3$. Either of these two methods is too simple, as shown in the following paragraphs, but they do fit most atoms and provide starting points for the others.

2-2-4 SHIELDING

In atoms with more than one electron, energies of specific levels are difficult to predict quantitatively, but one of the more common approaches is to use the idea of shielding. Each electron acts as a shield for electrons farther out from the nucleus, reducing the attraction between the nucleus and the distant electrons.

Although the quantum number n is most important in determining the energy, l must also be included in the calculation of the energy in atoms with more than one electron. As the atomic number increases, the electrons are drawn toward the nucleus and the orbital energies become more negative. Although the energies decrease with increasing Z, the changes are irregular because of shielding of outer electrons by inner electrons. The resulting order of orbital filling for the electrons is shown in Table 2-7.

As a result of shielding and other more subtle interactions between the electrons, the simple order of orbitals (in order of energy increasing with increasing n) holds only at very low atomic number Z and for the innermost electrons of any atom. For the outer orbitals, the increasing energy difference between levels with the same n but different l values forces the overlap of energy levels with $n = 3$ and $n = 4$, and $4s$ fills before $3d$. In a similar fashion, $5s$ fills before $4d$, $6s$ before $5d$, $4f$ before $5d$, and $5f$ before $6d$ (Figure 2-10).

Slater[24] formulated a set of simple rules that serve as a rough guide to this effect. He defined the effective nuclear charge Z^* as a measure of the nuclear attraction for an electron. Z^* can be calculated from $Z^* = Z - S$, where Z is the nuclear charge and S is the shielding constant. The rules for determining S for a specific electron are as follows:

1. The electronic structure of the atom is written in groupings as follows: $(1s)$ $(2s, 2p)$ $(3s, 3p)$ $(3d)$ $(4s, 4p)$ $(4d)$ $(4f)$ $(5s, 5p)$, etc.
2. Electrons in higher groups (to the right in the list above) do not shield those in lower groups.
3. For ns or np valence electrons:
    a. Electrons in the same ns, np group contribute 0.35, except the $1s$, where 0.30 works better.
    b. Electrons in the $n - 1$ group contribute 0.85.
    c. Electrons in the $n - 2$ or lower groups contribute 1.00.
4. For nd and nf valence electrons:
    a. Electrons in the same nd or nf group contribute 0.35.
    b. Electrons in groups to the left contribute 1.00.

The shielding constant S obtained from the sum of the contributions above is subtracted from the nuclear charge Z to obtain the effective nuclear charge Z^* affecting the selected electron. Some examples follow.

---

[24] J.C. Slater. *Phys. Rev.*, **1930**, *36*, 57.

TABLE 2-7
Electron Configurations of the Elements

Element	*Z*	*Configuration*
H	1	$1s^1$
He	2	$1s^2$
Li	3	[He]$2s^1$
Be	4	[He]$2s^2$
B	5	[He]$2s^2 2p^1$
C	6	[He]$2s^2 2p^2$
N	7	[He]$2s^2 2p^3$
O	8	[He]$2s^2 2p^4$
F	9	[He]$2s^2 2p^5$
Ne	10	[He]$2s^2 2p^6$
Na	11	[Ne]$3s^1$
Mg	12	[Ne]$3s^2$
Al	13	[Ne]$3s^2 3p^1$
Si	14	[Ne]$3s^2 3p^2$
P	15	[Ne]$3s^2 3p^3$
S	16	[Ne]$3s^2 3p^4$
Cl	17	[Ne]$3s^2 3p^5$
Ar	18	[Ne]$3s^2 3p^6$
K	19	[Ar]$4s^1$
Ca	20	[Ar]$4s^2$
Sc	21	[Ar]$4s^2 3d^1$
Ti	22	[Ar]$4s^2 3d^2$
V	23	[Ar]$4s^2 3d^3$
Cr	24	*[Ar]$4s^1 3d^5$
Mn	25	[Ar]$4s^2 3d^5$
Fe	26	[Ar]$4s^2 3d^6$
Co	27	[Ar]$4s^2 3d^7$
Ni	28	[Ar]$4s^2 3d^8$
Cu	29	*[Ar]$4s^1 3d^{10}$
Zn	30	[Ar]$4s^2 3d^{10}$
Ga	31	[Ar]$4s^2 3d^{10} 4p^1$
Ge	32	[Ar]$4s^2 3d^{10} 4p^2$
As	33	[Ar]$4s^2 3d^{10} 4p^3$
Se	34	[Ar]$4s^2 3d^{10} 4p^4$
Br	35	[Ar]$4s^2 3d^{10} 4p^5$
Kr	36	[Ar]$4s^2 3d^{10} 4p^6$
Rb	37	[Kr]$5s^1$
Sr	38	[Kr]$5s^2$
Y	39	[Kr]$5s^2 4d^1$
Zr	40	[Kr]$5s^2 4d^2$
Nb	41	*[Kr]$5s^1 4d^4$
Mo	42	*[Kr]$5s^1 4d^5$
Tc	43	[Kr]$5s^2 4d^5$
Ru	44	*[Kr]$5s^1 4d^7$
Rh	45	*[Kr]$5s^1 4d^8$
Pd	46	*[Kr]$4d^{10}$
Ag	47	*[Kr]$5s^1 4d^{10}$
Cd	48	[Kr]$5s^2 4d^{10}$
In	49	[Kr]$5s^2 4d^{10} 5p^1$
Sn	50	[Kr]$5s^2 4d^{10} 5p^2$
Sb	51	[Kr]$5s^2 4d^{10} 5p^3$
Te	52	[Kr]$5s^2 4d^{10} 5p^4$
I	53	[Kr]$5s^2 4d^{10} 5p^5$
Xe	54	[Kr]$5s^2 4d^{10} 5p^6$
Cs	55	[Xe]$6s^1$
Ba	56	[Xe]$6s^2$
La	57	*[Xe]$6s^2 5d^1$
Ce	58	*[Xe]$6s^2 4f^1\ 5d^1$
Pr	59	[Xe]$6s^2 4f^3$
Nd	60	[Xe]$6s^2 4f^4$
Pm	61	[Xe]$6s^2 4f^5$
Sm	62	[Xe]$6s^2 4f^6$
Eu	63	[Xe]$6s^2 4f^7$
Gd	64	*[Xe]$6s^2 4f^7\ 5d^1$
Tb	65	[Xe]$6s^2 4f^9$
Dy	66	[Xe]$6s^2 4f^{10}$
Ho	67	[Xe]$6s^2 4f^{11}$
Er	68	[Xe]$6s^2 4f^{12}$
Tm	69	[Xe]$6s^2 4f^{13}$
Yb	70	[Xe]$6s^2 4f^{14}$
Lu	71	[Xe]$6s^2 4f^{14} 5d^1$
Hf	72	[Xe]$6s^2 4f^{14} 5d^2$
Ta	73	[Xe]$6s^2 4f^{14} 5d^3$
W	74	[Xe]$6s^2 4f^{14} 5d^4$
Re	75	[Xe]$6s^2 4f^{14} 5d^5$
Os	76	[Xe]$6s^2 4f^{14} 5d^6$
Ir	77	[Xe]$6s^2 4f^{14} 5d^7$
Pt	78	*[Xe]$6s^1 4f^{14} 5d^9$
Au	79	*[Xe]$6s^1 4f^{14} 5d^{10}$
Hg	80	[Xe]$6s^2 4f^{14} 5d^{10}$
Tl	81	[Xe]$6s^2 4f^{14} 5d^{10} 6p^1$
Pb	82	[Xe]$6s^2 4f^{14} 5d^{10} 6p^2$
Bi	83	[Xe]$6s^2 4f^{14} 5d^{10} 6p^3$
Po	84	[Xe]$6s^2 4f^{14} 5d^{10} 6p^4$
At	85	[Xe]$6s^2 4f^{14} 5d^{10} 6p^5$
Rn	86	[Xe]$6s^2 4f^{14} 5d^{10} 6p^6$
Fr	87	[Rn]$7s^1$
Ra	88	[Rn]$7s^2$
Ac	89	*[Rn]$7s^2\ \ 6d^1$
Th	90	*[Rn]$7s^2\ \ 6d^2$
Pa	91	*[Rn]$7s^2 5f^2\ 6d^1$
U	92	*[Rn]$7s^2 5f^3\ 6d^1$
Np	93	*[Rn]$7s^2 5f^4\ 6d^1$
Pu	94	[Rn]$7s^2 5f^6$
Am	95	[Rn]$7s^2 5f^7$
Cm	96	*[Rn]$7s^2 5f^7\ 6d^1$
Bk	97	[Rn]$7s^2 5f^9$
Cf	98	*[Rn]$7s^2 5f^9\ 6d^1$
Es	99	[Rn]$7s^2 5f^{11}$
Fm	100	[Rn]$7s^2 5f^{12}$
Md	101	[Rn]$7s^2 5f^{13}$
No	102	[Rn]$7s^2 5f^{14}$
Lr	103	[Rn]$7s^2 5f^{14} 6d^1$ or [Rn]$7s^2 5f^{14} 7p^1$
Rf	104	[Rn]$7s^2 5f^{14} 6d^2$
Db	105	[Rn]$7s^2 5f^{14} 6d^3$
Sg	106	[Rn]$7s^2 5f^{14} 6d^4$
Bh	107	[Rn]$7s^2 5f^{14} 6d^5$
Hs	108	[Rn]$7s^2 5f^{14} 6d^6$
Mt	109	[Rn]$7s^2 5f^{14} 6d^7$
Uun	110	*[Rn]$7s^1 5f^{14} 6d^9$
Uuu	111	[Rn]$7s^1 5f^{14} 6d^{10}$
Uub	112	[Rn]$7s^2 5f^{14} 6d^{10}$

* Elements with configurations that do not follow the simple order of orbital filling.

NOTE: Actinide configurations are from J. J. Katz, G. T. Seaborg, and L. R. Morss, *The Chemistry of the Actinide Elements*, 2nd ed., Chapman and Hall, New York and London, 1986. Configurations for elements 100 to 112 are predicted, not experimental.

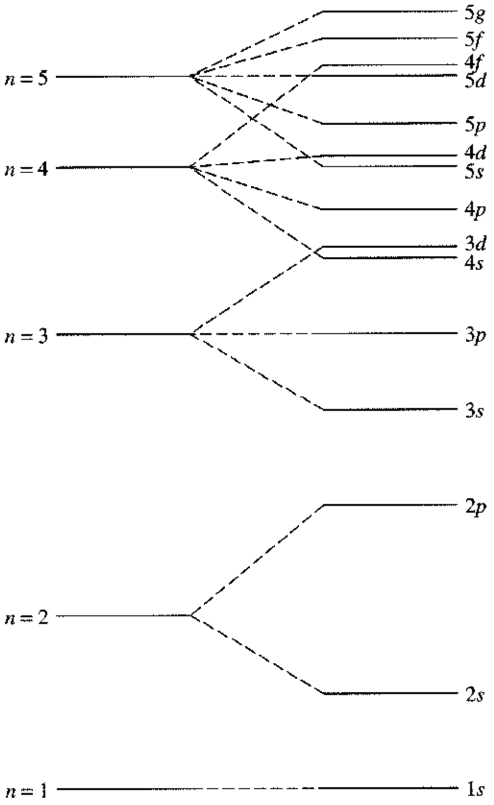


FIGURE 2-10 Energy Level Splitting and Overlap. The differences between the upper levels are exaggerated for easier visualization.

EXAMPLES

Oxygen The electron configuration is $(1s^2)\ (2s^2\ 2p^4)$.

For the outermost electron,

$$\begin{aligned} Z^* &= Z - S \\ &= 8 - \underset{(1s)}{[2 \times (0.85)]} - \underset{(2s,\,2p)}{[5 \times (0.35)]} = 4.55 \end{aligned}$$

The two $1s$ electrons each contribute 0.85, and the five $2s$ and $2p$ electrons (the last electron is not counted, as we are finding Z^* for it) each contribute 0.35, for a total shielding constant $S = 3.45$. The net effective nuclear charge is then $Z^* = 4.55$. Therefore, the last electron is held with about 57% of the force expected for a +8 nucleus and a −1 electron.

Nickel The electron configuration is $(1s^2)\ (2s^2\ 2p^6)\ (3s^2\ 3p^6)\ (3d^8)\ (4s^2)$.

For a $3d$ electron,

$$\begin{aligned} Z^* &= Z - S \\ &= 28 - \underset{(1s,\,2s,\,2p,\,3s,\,3p)}{[18 \times (1.00)]} - \underset{(3d)}{[7 \times (0.35)]} = 7.55 \end{aligned}$$

The 18 electrons in the $1s$, $2s$, $2p$, $3s$, and $3p$ levels contribute 1.00 each, the other 7 in $3d$ contribute 0.35, and the $4s$ contribute nothing. The total shielding constant is $S = 20.45$ and $Z^* = 7.55$ for the last $3d$ electron.

For the $4s$ electron,

$$\begin{aligned} Z^* &= Z - S \\ &= 28 - \underset{(1s,\,2s,\,2p)}{[10 \times (1.00)]} - \underset{(3s,\,3p,\,3d)}{[16 \times (0.85)]} - \underset{(4s)}{[1 \times (0.35)]} = 4.05 \end{aligned}$$

The ten $1s$, $2s$, and $2p$ electrons each contribute 1.00, the sixteen $3s$, $3p$, and $3d$ electrons each contribute 0.85, and the other $4s$ electron contributes 0.35, for a total $S = 23.95$ and $Z^* = 4.05$, considerably smaller than the value for the $3d$ electron above. The $4s$ electron is held less tightly than the $3d$ and should therefore be the first removed in ionization. This is consistent with experimental observations on nickel compounds. Ni^{2+}, the most common oxidation state of nickel, has an electron configuration of $[Ar]3d^8$ (rather than $[Ar]3d^6 4s^2$), corresponding to loss of the $4s$ electrons from nickel atoms. All the transition metals follow this same pattern of losing ns electrons more readily than $(n - 1)d$ electrons.

EXERCISE 2-5

Calculate the effective nuclear charge on a $5s$, a $5p$, and a $4d$ electron in a tin atom.

EXERCISE 2-6

Calculate the effective nuclear charge on a $7s$, a $5f$, and a $6d$ electron in a uranium atom.

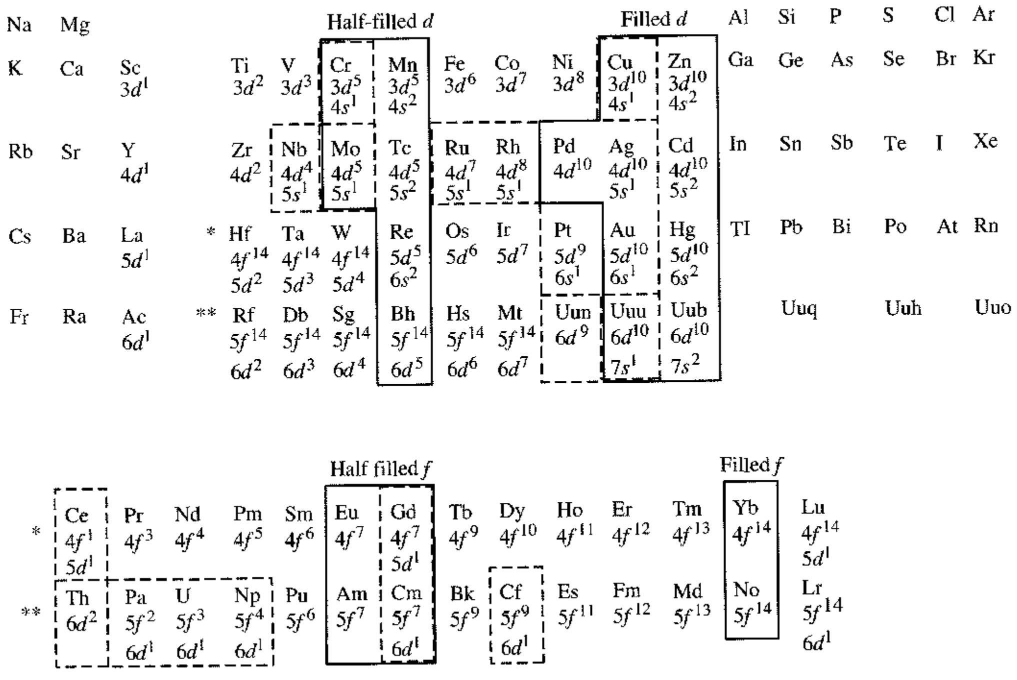
Justification for Slater's rules (aside from the fact that they work) comes from the electron probability curves for the orbitals. The s and p orbitals have higher probabilities near the nucleus than do d orbitals of the same n, as shown earlier in Figure 2-7. Therefore, the shielding of $3d$ electrons by $(3s, 3p)$ electrons is calculated as 100% effective (a contribution of 1.00). At the same time, shielding of $3s$ or $3p$ electrons by $(2s, 2p)$ electrons is only 85% effective (a contribution of 0.85), because the $3s$ and $3p$ orbitals have regions of significant probability close to the nucleus. Therefore, electrons in these orbitals are not completely shielded by $(2s, 2p)$ electrons.

A complication arises at Cr $(Z = 24)$ and Cu $(Z = 29)$ in the first transition series and in an increasing number of atoms under them in the second and third transition series. This effect places an extra electron in the $3d$ level and removes one electron from the $4s$ level. Cr, for example, has a configuration of $[Ar]4s^1 3d^5$ (rather than $[Ar]4s^2 3d^4$). Traditionally, this phenomenon has often been explained as a consequence of the "special stability of half-filled subshells." Half-filled and filled d and f subshells are, in fact, fairly common, as shown in Figure 2-11. A more accurate explanation considers both the effects of increasing nuclear charge on the energies of the $4s$ and $3d$ levels and the interactions (repulsions) between the electrons sharing the same orbital.[25] This approach requires totaling the energies of all the electrons with their interactions; results of the complete calculations match the experimental results.

Another explanation that is more pictorial and considers the electron-electron interactions was proposed by Rich.[26] He explained the structure of these atoms by specifically considering the difference in energy between the energy of one electron in an orbital and two electrons in the same orbital. Although the orbital itself is usually assumed to have only one energy, the electrostatic repulsion of the two electrons in one orbital adds the electron pairing energy described previously as part of Hund's rule. We can visualize two parallel energy levels, each with electrons of only one spin, separated by the electron pairing energy, as shown in Figure 2-12. As the nuclear charge increases, the electrons are more strongly attracted and the energy levels decrease in energy, becoming more stable, with the d orbitals changing more rapidly than the s orbitals because the d orbitals are not shielded as well from the nucleus. Electrons fill the

[25] L. G. Vanquickenborne, K. Pierloot, and D. Devoghel, *J. Chem. Educ.*, **1994**, *71*, 469.

[26] R. L. Rich, *Periodic Correlations*, W. A. Benjamin, Menlo Park, CA, 1965, pp. 9–11.



							Half-filled *d*					Filled *d*							
Na	Mg													Al	Si	P	S	Cl	Ar
K	Ca	Sc $3d^1$		Ti $3d^2$	V $3d^3$	Cr $3d^5$ $4s^1$	Mn $3d^5$ $4s^2$	Fe $3d^6$	Co $3d^7$	Ni $3d^8$	Cu $3d^{10}$ $4s^1$	Zn $3d^{10}$ $4s^2$		Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y $4d^1$		Zr $4d^2$	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 $4d^{10}$ $5s^2$		In	Sn	Sb	Te	I	Xe
Cs	Ba	La $5d^1$	*	Hf $4f^{14}$ $5d^2$	Ta $4f^{14}$ $5d^3$	W $4f^{14}$ $5d^4$	Re $5d^5$ $6s^2$	Os $5d^6$	Ir $5d^7$	Pt $5d^9$ $6s^1$	Au $5d^{10}$ $6s^1$	Hg $5d^{10}$ $6s^2$		Tl	Pb	Bi	Po	At	Rn
Fr	Ra	Ac $6d^1$	**	Rf $5f^{14}$ $6d^2$	Db $5f^{14}$ $6d^3$	Sg $5f^{14}$ $6d^4$	Bh $5f^{14}$ $6d^5$	Hs $5f^{14}$ $6d^6$	Mt $5f^{14}$ $6d^7$	Uun $6d^9$	Uuu $6d^{10}$ $7s^1$	Uub $6d^{10}$ $7s^2$			Uuq		Uuh		Uuo

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

FIGURE 2-11 Electron Configurations of Transition Metals, Including Lanthanides and Actinides. Solid lines surrounding elements designate filled (d^{10} or f^{14}) or half-filled (d^6 or f^7) subshells. Dashed lines surrounding elements designate irregularities in sequential orbital filling, which is also found within some of the solid lines.

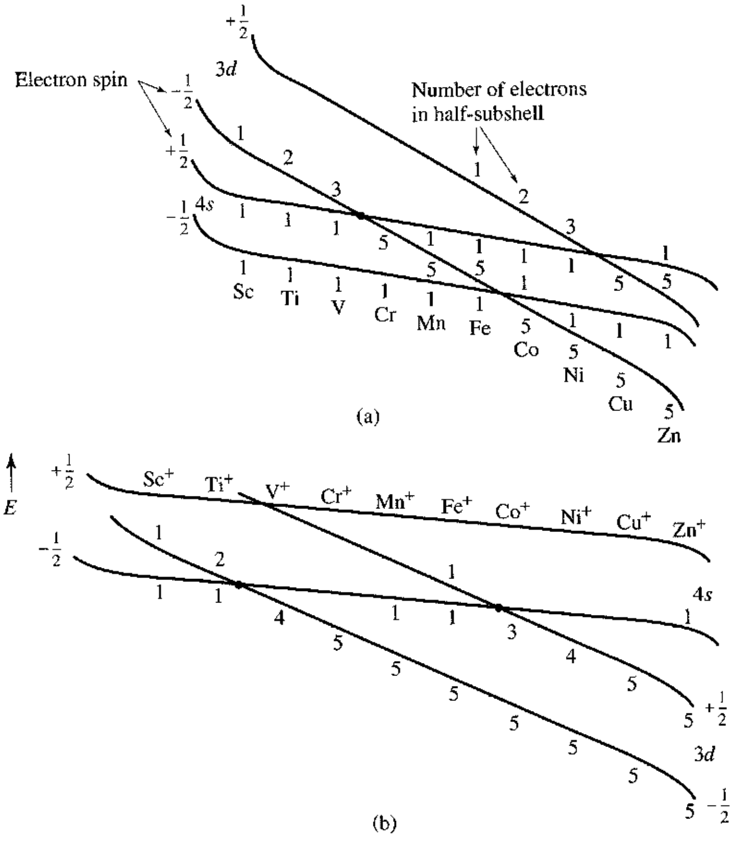


FIGURE 2-12 Schematic Energy Levels for Transition Elements. (a) Schematic interpretation of electron configurations for transition elements in terms of intraorbital repulsion and trends in subshell energies. (b) A similar diagram for ions, showing the shift in the crossover points on removal of an electron. The diagram shows that *s* electrons are removed before *d* electrons. The shift is even more pronounced for metal ions having 2+ or greater charges. As a consequence, transition metal ions with 2+ or greater charges have no *s* electrons, only *d* electrons in their outer levels. Similar diagrams, although more complex, can be drawn for the heavier transition elements and the lanthanides. (Reprinted with permission from R. L. Rich, *Periodic Correlations*, W. A. Benjamin, Menlo Park, CA, 1965, pp. 9–10.)

lowest available orbitals in order up to their capacity, with the results shown in Figure 2-12 and in Table 2-7, which gives electronic structures.

The schematic diagram in Figure 2-12(a) shows the order in which the levels fill, from bottom to top in energy. For example, Ti has two 4*s* electrons, one in each spin level, and two 3*d* electrons, both with the same spin. Fe has two 4*s* electrons, one in each spin level, five 3*d* electrons with spin $-\frac{1}{2}$ and one 3*d* electron with spin $+\frac{1}{2}$.

For vanadium, the first two electrons enter the 4*s*, $-\frac{1}{2}$ and 4*s*, $+\frac{1}{2}$ levels, the next three are all in the 3*d*, $-\frac{1}{2}$ level, and vanadium has the configuration $4s^2 3d^3$. The 3*d*, $-\frac{1}{2}$ line crosses the 4*s*, $+\frac{1}{2}$ line between V and Cr. When the six electrons of chromium are filled in from the lowest level, chromium has the configuration $4s^1 3d^5$. A similar crossing gives copper its $4s^1 3d^{10}$ structure. This explanation does not depend on the stability of half-filled shells or other additional factors; those explanations break down for zirconium ($5s^2 4d^2$), niobium ($5s^1 4d^4$), and others in the lower periods.

Formation of a positive ion by removal of an electron reduces the overall electron repulsion and lowers the energy of the *d* orbitals more than that of the *s* orbitals, as shown in Figure 2-12(b). As a result, the remaining electrons occupy the *d* orbitals and we can use the shorthand notion that the electrons with highest *n* (in this case, those in the *s* orbitals) are always removed first in the formation of ions from the transition elements. This effect is even stronger for 2+ ions. Transition metal ions have no *s* electrons, but only *d* electrons in their outer levels. The shorthand version of this phenomenon is the statement that the 4*s* electrons are the first ones removed when a first-row transition metal forms an ion.

A similar, but more complex, crossing of levels appears in the lanthanide and actinide series. The simple explanation would have them start filling *f* orbitals at lanthanum (57) and actinium (89), but these atoms have one *d* electron instead. Other elements in these series also show deviations from the "normal" sequence. Rich has shown how these may also be explained by similar diagrams, and the reader should refer to his book for further details.

2-3 PERIODIC PROPERTIES OF ATOMS

2-3-1 IONIZATION ENERGY

The ionization energy, also known as the ionization potential, is the energy required to remove an electron from a gaseous atom or ion:

$$A^{n+}(g) \longrightarrow A^{(n+1)+}(g) + e^- \qquad \text{ionization energy} = \Delta U$$

where $n = 0$ (first ionization energy), 1, 2, ... (second, third, ...).

As would be expected from the effects of shielding, the ionization energy varies with different nuclei and different numbers of electrons. Trends for the first ionization energies of the early elements in the periodic table are shown in Figure 2-13. The general trend across a period is an increase in ionization energy as the nuclear charge increases. A plot of Z^*/r, the potential energy for attraction between an electron and the shielded nucleus, is nearly a straight line, with approximately the same slope as the shorter segments (boron through nitrogen, for example) shown in Figure 2-13 (a different representation is shown later, in Figure 8-3). However, the experimental values show a break in the trend at boron and again at oxygen. Because the new electron in B is in a new *p* orbital that has most of its electron density farther away from the nucleus than the other electrons, its ionization energy is smaller than that of the $2s^2$ electrons of Be. At the fourth *p* electron, at oxygen, a similar drop in ionization energy occurs. Here, the new electron shares an orbital with one of the previous 2*p* electrons, and the fourth *p* electron has a higher energy than the trend would indicate because it must be paired with another in the same *p* orbital. The pairing energy, or repulsion between two electrons in the same region of space, reduces the ionization energy. Similar patterns appear in lower periods. The transition elements have smaller differences in ionization energies, usually with a lower value for

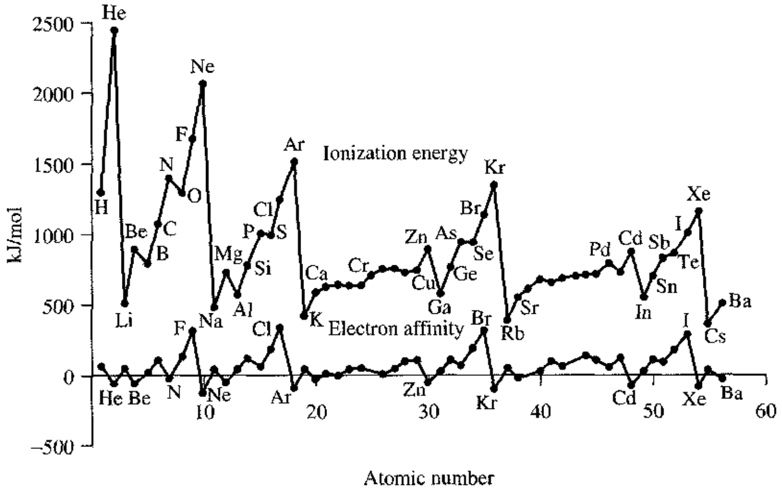


FIGURE 2-13 Ionization Energies and Electron Affinities. Ionization energy = ΔU for $M(g) \longrightarrow M^+(g) + e$ (Data from C.E. Moore, *Ionization Potentials and Ionization Limits*, National Standards Reference Data Series, U. S. National Bureau of Standards, Washington, DC, **1970**, NSRDS-NBS 34) Electron affinity = ΔU for $M^-(g) \longrightarrow M(g) + e^-$ (Data from H. Hotop and W. C. Lineberger, *J. Phys. Chem. Ref. Data*, **1985**, *14*, 731). Numerical values are in Appendices B-2 and B-3.

heavier atoms in the same family because of increased shielding by inner electrons and increased distance between the nucleus and the outer electrons.

Much larger decreases in ionization energy occur at the start of each new period, because the change to the next major quantum number requires that the new s electron have a much higher energy. The maxima at the noble gases decrease with increasing Z because the outer electrons are farther from the nucleus in the heavier elements. Overall, the trends are toward higher ionization energy from left to right in the periodic table (the major change) and lower ionization energy from top to bottom (a minor change). The differences described in the previous paragraph are superimposed on these more general changes.

2-3-2 ELECTRON AFFINITY

Electron affinity can be defined as the energy required to remove an electron from a negative ion:

$$A^-(g) \longrightarrow A(g) + e^- \quad \text{electron affinity} = \Delta U(\text{or } EA)$$

(Historically, the definition is $-\Delta U$ for the reverse reaction, adding an electron to the neutral atom. The definition we use avoids the sign change.) Because of the similarity of this reaction to the ionization for an atom, electron affinity is sometimes described as the zeroth ionization energy. This reaction is endothermic (positive ΔU), except for the noble gases and the alkaline earth elements. The pattern of electron affinities with changing Z shown in Figure 2-13 is similar to that of the ionization energies, but for one larger Z value (one more electron for each species) and with much smaller absolute numbers. For either of the reactions, removal of the first electron past a noble gas configuration is easy, so the noble gases have the lowest electron affinities. The electron affinities are all much smaller than the corresponding ionization energies because electron removal from a negative ion is easier than removal from a neutral atom.

2-3-3 COVALENT AND IONIC RADII

The sizes of atoms and ions are also related to the ionization energies and electron affinities. As the nuclear charge increases, the electrons are pulled in toward the center of the atom, and the size of any particular orbital decreases. On the other hand, as the nuclear charge increases, more electrons are added to the atom and their mutual repulsion keeps the outer orbitals large. The interaction of these two effects (increasing nuclear charge and increasing number of electrons) results in a gradual decrease in atomic size across each period. Table 2-8 gives nonpolar covalent radii, calculated for ideal molecules with

TABLE 2-8
Nonpolar Covalent Radii (pm)

1	*2*	*3*	*4*	*5*	*6*	*7*	*8*	*9*	*10*	*11*	*12*	*13*	*14*	*15*	*16*	*17*	*18*
H 32																	He 31
Li 123	Be 89											B 82	C 77	N 75	O 73	F 71	Ne 69
Na 154	Mg 136											Al 118	Si 111	P 106	S 102	Cl 99	Ar 98
K 203	Ca 174	Sc 144	Ti 132	V 122	Cr 118	Mn 117	Fe 117	Co 116	Ni 115	Cu 117	Zn 125	Ga 126	Ge 122	As 120	Se 117	Br 114	Kr 111
Rb 216	Sr 191	Y 162	Zr 145	Nb 134	Mo 130	Tc 127	Ru 125	Rh 125	Pd 128	Ag 134	Cd 148	In 144	Sn 140	Sb 140	Te 136	I 133	Xe 126
Cs 235	Ba 198	La 169	Hf 144	Ta 134	W 130	Re 128	Os 126	Ir 127	Pt 130	Au 134	Hg 149	Tl 148	Pb 147	Bi 146	Po (146)	Al (145)	Ra

Source: R. T. Sanderson, *Inorganic Chemistry*, Reinhold, New York, 1967, p. 74; and E. C. M. Chen, J. G. Dojahn, and W. E. Wentworth, *J. Phys. Chem. A*, 1997, *101*, 3088.

TABLE 2-9
Crystal Radii for Selected Ions

	Z	*Element*	*Radius (pm)*
Alkali metal ions	3	Li^+	90
	11	Na^+	116
	19	K^+	152
	37	Rb^+	166
	55	Cs^+	181
Alkaline earth ions	4	Be^{2+}	59
	12	Mg^{2+}	86
	20	Ca^{2+}	114
	38	Sr^{2+}	132
	56	Ba^{2+}	149
Other cations	13	Al^{3+}	68
	30	Zn^{2+}	88
Halide ions	9	F^-	119
	17	Cl^-	167
	35	Br^-	182
	53	I^-	206
Other anions	8	O^{2-}	126
	16	S^{2-}	170

SOURCE: R. D. Shannon, *Acta Crystallogr.* **1976**, *A32*, 751. A longer list is given in Appendix B-1. All the values are for 6-coordinate ions.

no polarity. There are other measures of atomic size, such as the van der Waals radius, in which collisions with other atoms are used to define the size. It is difficult to obtain consistent data for any such measure, because the polarity, chemical structure, and physical state of molecules change drastically from one compound to another. The numbers shown here are sufficient for a general comparison of one element with another.

There are similar problems in determining the size of ions. Because the stable ions of the different elements have different charges and different numbers of electrons, as well as different crystal structures for their compounds, it is difficult to find a suitable set of numbers for comparison. Earlier data were based on Pauling's approach, in which the ratio of the radii of isoelectronic ions was assumed to be equal to the ratio of their effective nuclear charges. More recent calculations are based on a number of considerations, including electron density maps from X-ray data that show larger cations and smaller anions than those previously found. Those in Table 2-9 and Appendix B were called "crystal radii" by Shannon,[27] and are generally different from the older values of "ionic radii" by +14 pm for cations and −14 pm for anions, as well as being revised because of more recent measurements. The radii in Table 2-9 and Appendix B-1 can be used for rough estimation of the packing of ions in crystals and other calculations, as long as the "fuzzy" nature of atoms and ions is kept in mind.

Factors that influence ionic size include the coordination number of the ion, the covalent character of the bonding, distortions of regular crystal geometries, and delocalization of electrons (metallic or semiconducting character, described in Chapter 7). The radius of the anion is also influenced by the size and charge of the cation (the anion exerts a smaller influence on the radius of the cation).[28] The table in Appendix B-1 shows the effect of coordination number.

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[27] R. D. Shannon, *Acta Crystallogr.*, **1976**, A32, 751.

[28] O. Johnson, *Inorg. Chem.*, **1973**, *12*, 780.

The values in Table 2-10 show that anions are generally larger than cations with similar numbers of electrons (F^- and Na^+ differ only in nuclear charge, but the radius of fluoride is 37% larger). The radius decreases as nuclear charge increases for ions with the same electronic structure, such as O^{2-}, F^-, Na^+, and Mg^{2+}, with a much larger change with nuclear charge for the cations. Within a family, the ionic radius increases as Z increases because of the larger number of electrons in the ions and, for the same element, the radius decreases with increasing charge on the cation. Examples of these trends are shown in Tables 2-10, 2-11, and 2-12.

TABLE 2-10
Crystal Radius and Nuclear Charge

Ion	*Protons*	*Electrons*	*Radius (pm)*
O^{2-}	8	10	126
F^-	9	10	119
Na^+	11	10	116
Mg^{2+}	12	10	86

TABLE 2-11
Crystal Radius and Total Number of Electrons

Ion	*Protons*	*Electrons*	*Radius (pm)*
O^{2-}	8	10	126
S^{2-}	16	18	170
Se^{2-}	34	36	184
Te^{2-}	52	54	207

TABLE 2-12
Crystal Radius and Ionic Charge

Ion	*Protons*	*Electrons*	*Radius (pm)*
Ti^{2+}	22	20	100
Ti^{3+}	22	19	81
Ti^{4+}	22	18	75

GENERAL REFERENCES

Additional information on the history of atomic theory can be found in J. R. Partington, *A Short History of Chemistry*, 3rd ed., Macmillan, London, 1957, reprinted by Harper & Row, New York, 1960, and in the *Journal of Chemical Education*. A more thorough treatment of the electronic structure of atoms is in M. Gerloch, *Orbitals, Terms, and States*, John Wiley & Sons, New York, 1986.

PROBLEMS

2-1 Determine the de Broglie wavelength of
- **a.** An electron moving at one-tenth the speed of light.
- **b.** A 400 g Frisbee moving at 10 km/h.

2-2 Using the equation $E = R_H\left(\frac{1}{2^2} - \frac{1}{n_h^2}\right)$, determine the energies and wavelengths of the four visible emission bands in the atomic spectrum of hydrogen arising from $n_h = 4, 5,$ and 6. (The red line in this spectrum was calculated in Exercise 2-1.)

2-3 The transition from the $n = 7$ to the $n = 2$ level of the hydrogen atom is accompanied by the emission of light slightly beyond the range of human perception, in the ultraviolet region of the spectrum. Determine the energy and wavelength of this light.

2-4 The details of several steps in the particle in a box model in this chapter have been omitted. Work out the details of the following steps:

a. Show that if $\Psi = A \sin rx + B \cos sx$ (A, B, r, and s are constants) is a solution to the wave equation for the one-dimensional box, then

$$r = s = \sqrt{2mE}\left(\frac{2\pi}{h}\right)$$

b. Show that if $\Psi = A \sin rx$, the boundary conditions ($\Psi = 0$ when $x = 0$ and $x = a$) require that $r = \pm\frac{n\pi}{a}$, where $n =$ any integer other than zero.

c. Show that if $r = \pm\frac{n\pi}{a}$, the energy levels of the particle are given by

$$E = \frac{n^2h^2}{8ma^2}$$

d. Show that substituting the above value of r into $\Psi = A \sin rx$ and applying the normalizing requirement gives $A = \sqrt{2/a}$.

2-5 For the $3p_z$ and $4d_{xz}$ hydrogen-like atomic orbitals, sketch the following:

a. The radial function R.

b. The radial probability function $a_0r^2R^2$.

c. Contour maps of electron density.

2-6 Repeat the exercise in Problem 5 for the $4s$ and $5d_{x^2-y^2}$ orbitals.

2-7 Repeat the exercise in Problem 5 for the $5s$ and $4d_{z^2}$ orbitals.

2-8 The $4f_{z(x^2-y^2)}$ orbital has the angular function $Y = (\text{constant})z(x^2 - y^2)$.

a. How many spherical nodes does this orbital have?

b. How many angular nodes does it have?

c. Describe the angular nodal surfaces.

d. Sketch the shape of the orbital.

2-9 Repeat the exercise in Problem 8 for the $5f_{xyz}$ orbital, which has $Y = (\text{constant})xyz$.

2-10 **a.** Find the possible values for the l and m_l quantum numbers for a $5d$ electron, a $4f$ electron, and a $7g$ electron.

b. Find the possible values for all four quantum numbers for a $3d$ electron.

2-11 Give explanations of the following phenomena:

a. The electron configuration of Cr is $[\text{Ar}]4s^13d^5$ rather than $[\text{Ar}]4s^23d^4$.

b. The electron configuration of Ti is $[\text{Ar}]4s^23d^2$, but that of Cr^{2+} is $[\text{Ar}]3d^4$.

2-12 Give electron configurations for the following:

a. V **b.** Br **c.** Ru^{3+} **d.** Hg^{2+} **e.** Sb

2-13 Which 2+ ion has five $3d$ electrons? Which one has two $3d$ electrons?

2-14 Determine the Coulombic and exchange energies for the following configurations and determine which configuration is favored (of lower energy):

a. $\underline{\ \uparrow\ }\ \underline{\ \uparrow\ }$ and $\underline{\uparrow\downarrow}\ \underline{\qquad}$

b. $\underline{\ \uparrow\ }\ \underline{\ \uparrow\ }\ \underline{\ \uparrow\ }$ and $\underline{\uparrow\downarrow}\ \underline{\ \uparrow\ }\ \underline{\qquad}$

2-15 Using Slater's rules, determine Z^* for

a. A $3p$ electron in P, S, Cl, and Ar. Is the calculated value of Z^* consistent with the relative sizes of these atoms?

b. A $2p$ electron in O^{2-}, F^-, Na^+, and Mg^{2+}. Is the calculated value of Z^* consistent with the relative sizes of these ions?

c. A 4*s* and a 3*d* electron of Cu. Which type of electron is more likely to be lost when copper forms a positive ion?
d. A 4*f* electron in Ce, Pr, and Nd. There is a decrease in size, commonly known as the **lanthanide contraction**, with increasing atomic number in the lanthanides. Are your values of Z^* consistent with this trend?

2-16 Select the better choice in each of the following, and explain your selection briefly.
a. Higher ionization energy: Ca or Ga
b. Higher ionization energy: Mg or Ca
c. Higher electron affinity: Si or P
d. More likely configuration for Mn^{2+}:$[Ar]4s^23d^3$ or $[Ar]3d^5$

2-17 Ionization energies should depend on the effective nuclear charge that holds the electrons in the atom. Calculate Z^* (Slater's rules) for N, P, and As. Do their ionization energies seem to match these effective nuclear charges? If not, what other factors influence the ionization energies?

2-18 The ionization energies for Cl^-, Cl, and Cl^+ are 349, 1251, and 2300 kJ/mol, respectively. Explain this trend.

2-19 Why are the ionization energies of the alkali metals in the order Li > Na > K > Rb?

2-20 The second ionization of carbon ($C^+ \longrightarrow C^{2+} + e^-$) and the first ionization of boron ($B \longrightarrow B^+ + e^+$) both fit the reaction $1s^22s^22p^1 = 1s^22s^2 + e^-$. Compare the two ionization energies (24.383 eV and 8.298 eV, respectively) and the effective nuclear charges, Z^*. Is this an adequate explanation of the difference in ionization energies? If not, suggest other factors.

2-21 In each of the following pairs, pick the element with the higher ionization energy and explain your choice.
a. Fe, Ru **b.** P, S **c.** K, Br **d.** C, N **e.** Cd, In

2-22 On the basis of electron configurations, explain why
a. Sulfur has a lower electron affinity than chlorine.
b. Iodine has a lower electron affinity than bromine.
c. Boron has a lower ionization energy than beryllium.
d. Sulfur has a lower ionization energy than phosphorus.
e. Chlorine has a lower ionization energy than fluorine.

2-23 **a.** The graph of ionization energy versus atomic number for the elements Na through Ar (Figure 2-13) shows maxima at Mg and P and minima at Al and S. Explain these maxima and minima.
b. The graph of electron affinity vs. atomic number for the elements Na through Ar (Figure 2-13) also shows maxima and minima, but shifted one element in comparison with the ionization energy graph. Why are the maxima and minima shifted in this way?

2-24 The second ionization energy of He is almost exactly four times the ionization energy of H, and the third ionization energy of Li is almost exactly nine times the ionization energy of H:

	IE (MJ mol^{-1})
$H(g) \longrightarrow H^+(g) + e^-$	1.3120
$He^+(g) \longrightarrow He^{2+}(g) + e^-$	5.2504
$Li^{2+}(g) \longrightarrow Li^{3+}(g) + e^-$	11.8149

Explain this trend on the basis of the Bohr equation for energy levels of single-electron systems.

2-25 The size of the transition metal atoms decreases slightly from left to right in the periodic table. What factors must be considered in explaining this decrease? In particular, why does the size decrease at all, and why is the decrease so gradual?

2-26 Predict the largest and smallest in each series:

a. Se^{2-} Br^{-} Rb^{+} Sr^{2+}

b. Y^{3+} Zr^{4+} Nb^{5+}

c. Co^{4+} Co^{3+} Co^{2+} Co

2-27 Prepare a diagram such as the one in Figure 2-12(a) for the fifth period in the periodic table, elements Zr through Pd. The configurations in Table 2-7 can be used to determine the crossover points of the lines. Can a diagram be drawn that is completely consistent with the configurations in the table?

2-28 There are a number of websites that display atomic orbitals. Use a search engine to find
a. A complete set of the *f* orbitals.
b. A complete set of the *g* orbitals.
Include the URL for the site with each of these, along with sketches or printouts of the orbitals. [One website that allows display of any orbital, complete with rotation and scaling, is http://www.orbital.com/.]