

THE STRUCTURE OF ATOMS – A BASIC QM TREATMENT

❑ LEARNING OBJECTIVES

- The electronic structure of hydrogenic atoms: *Quantum Mechanical Model*
- To introduce the basic quantum mechanical principles of hydrogenic atomic structures, different types of quantum numbers, electron distributions, etc.

❑ THE ELECTRONIC STRUCTURE OF HYDROGENIC ATOMS: *Quantum Mechanical Model*

Quantum Mechanics

- The main postulate of quantum mechanics establishes that the ***state of a quantum mechanical system*** is specified by a function called the **wavefunction** (ψ).
- The wavefunction is a ***function of*** the coordinates of the particle (the ***position***) and ***time***.
- The function: $|\psi(r)|^2 dV = \psi^*(r)\psi(r)dV$ is the ***probability*** that the particle lies in the volume element dV located at r .

Quantum Mechanics

- ❑ Three additional postulates:
- ❑ Each **observable in classical mechanics** has an associated **operator in quantum mechanics**.
 - ✓ Examples of observables are *position, momentum, kinetic energy, total energy, angular momentum, etc.*
- ❑ An **operator is defined to be a mathematical symbol** that applied to a function gives a new function.
 - We have $\hat{A} f(x) = \phi(x)$, \hat{A} is an operator.
- ❑ Exceptionally *the function $f(x)$ may be such that $\phi(x)$ is proportional to $f(x)$* ; then we have $\hat{A} f(x) = \phi(x) = a f(x)$ where **a is some constant of proportionality**.
 - In this case **$f(x)$** is called an **eigenfunction** of \hat{A} and **a** is the corresponding **eigenvalue**. ('eigen' in German means 'own' or 'inherent'.)
- ❑ **The outcomes of any measurement of the observable associated with the operator \hat{A} are the eigenvalues a** that satisfy the eigenvalue equation $\hat{A} f(x) = a f(x)$.
 - The **average value** of the *observable* corresponding to \hat{A} is given by $\iiint_{-\infty}^{\infty} \psi^* \hat{A} \psi dV$ where dV is the differential of volume in the coordinates used to express ψ .

□ \hat{x} and $\hat{p} = -i\hbar\nabla$

they are called “fundamental operators”.

...Many operators are constructed from \hat{x} and \hat{p} ; for example, the Hamiltonian for a single particle:

$$H = \frac{\hat{p}^2}{2m} + \hat{V}(\hat{x}) \quad \text{where } \frac{\hat{p}^2}{2m} \text{ is the K.E. operator and } \hat{V} \text{ is the P.E. operator.}$$

Example: Consider the function $f(x,t) = e^{i(kx-\omega t)}$.

This represents a wave travelling in x direction.

Operate on $f(x)$ with the momentum operator:

$$\hat{p} f(x) = -i\hbar \frac{d}{dx} [f(x)] = (-i\hbar)(ik)e^{i(kx-\omega t)} = \hbar k f(x)$$

and since by the de Broglie relation $\hbar k$ is the momentum p of the particle, we have $\hat{p} f(x) = pf(x)$

Quantum mechanical operators for some physical observables.			
Observable	symbol in classical physics	Operator in QM	Operation
Position	\mathbf{r}	$\hat{\mathbf{r}}$	multiply by \mathbf{r}
Momentum	p_x	\hat{p}_x	$-i\hbar \frac{\partial}{\partial x}$
	p_y	\hat{p}_y	$-i\hbar \frac{\partial}{\partial y}$
	p_z	\hat{p}_z	$-i\hbar \frac{\partial}{\partial z}$
Kinetic Energy	T	\hat{T}	$-\frac{\hbar^2}{2m} \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right)$
Potential Energy	$V(\mathbf{r})$	$\hat{V}(\mathbf{r})$	multiply by $\hat{V}(\mathbf{r})$
Total Energy	E	\hat{H}	$\hat{T} + \hat{V}$
Angular Momentum	l_x	\hat{l}_x	$-i\hbar \left(y \frac{\partial}{\partial z} - z \frac{\partial}{\partial y} \right)$
	l_y	\hat{l}_y	$-i\hbar \left(z \frac{\partial}{\partial x} - x \frac{\partial}{\partial z} \right)$
	l_z	\hat{l}_z	$-i\hbar \left(x \frac{\partial}{\partial y} - y \frac{\partial}{\partial x} \right)$

Table 11.3.1: Quantum mechanical operators for some physical observables.

❑ THE ELECTRONIC STRUCTURE OF HYDROGENIC ATOMS: *Quantum Mechanical Model*

- Hydrogen has one electron and atomic number $Z = 1$. A ***hydrogenic atom*** is an atom or an ion of arbitrary atomic number Z but having a single electron.
- The Schrödinger equation for ***hydrogenic atom*** is similar to the particle in one dimensional box, except in three dimensions.
- ❑ The **Schrödinger equation** is commonly written as
 - $H \psi = E \psi$, where H is called the ***hamiltonian*** for the system.
 - The Schrödinger equation is used to **calculate both the wavefunction ψ and the corresponding energy E .**

➤ *Quantum Mechanical Model* for a particle of mass m moving in *one dimension* (along x-axis) in a region where the potential energy is $V(x)$ the equation is given by the **Schrödinger equation which** takes the simple form:

➤
$$-\frac{\hbar^2}{2m} \frac{d^2\psi(x)}{dx^2} + V(x)\psi(x) = E\psi(x)$$

where

- \hbar is the reduced Planck Constant where $\hbar = h/2\pi$
 - m is the mass of the particle
 - $\psi(x)$ is the stationary time-independent wavefunction
 - $V(x)$ is the potential energy as a function of position
 - E is the energy, a real number
- The term $d^2\psi(x)/dx^2$ can be thought of as a measure of how sharply the wavefunction $\psi(x)$ is curved.

➤ The hydrogen atom, consisting of an electron and a proton, is a two-particle system, and the internal motion of two particles around their center of mass is equivalent to the motion of a single particle with a reduced mass. This reduced particle is located at r , where r is the vector specifying the position of the electron relative to the position of the proton. The length of r is the distance between the proton and the electron, and the direction of r and the direction of r is given by the orientation of the vector pointing from the proton to the electron. Since the proton is much more massive than the electron, we will assume throughout this chapter that the reduced mass equals the electron mass and the proton is located at the center of mass.

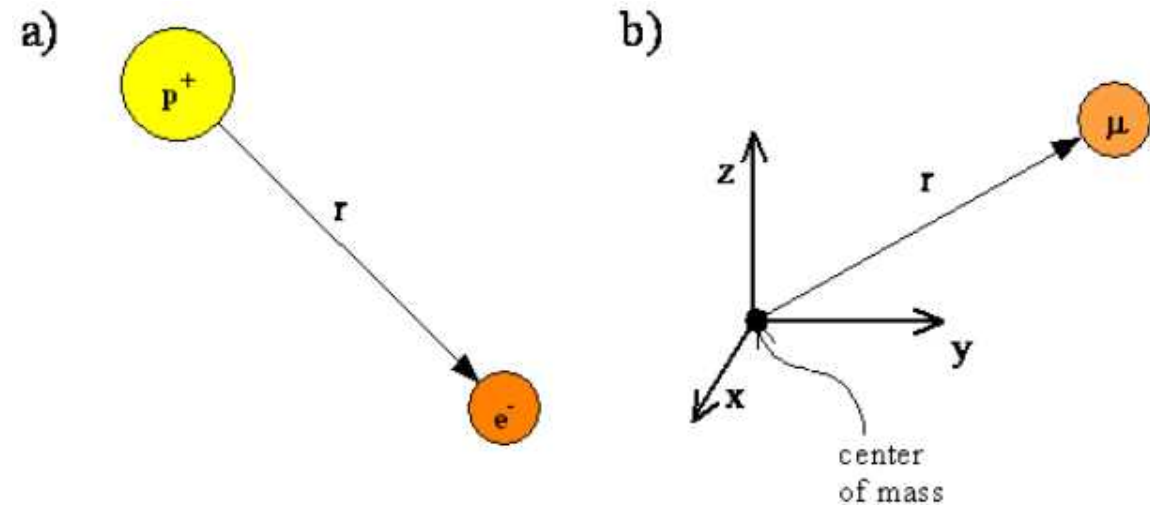
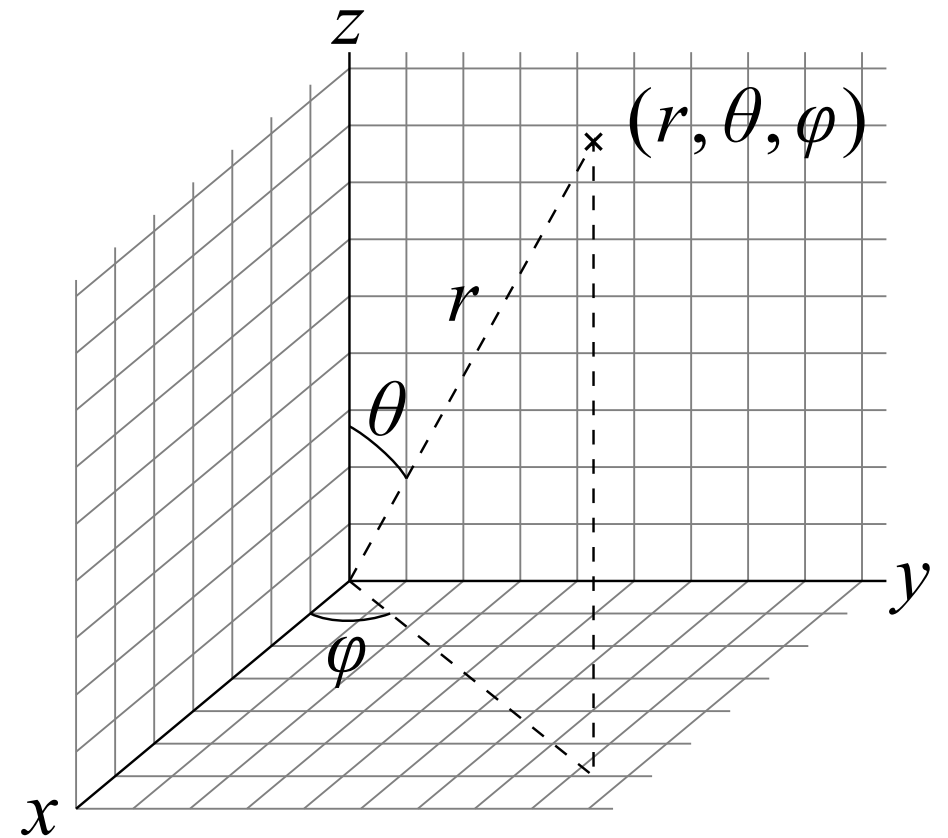
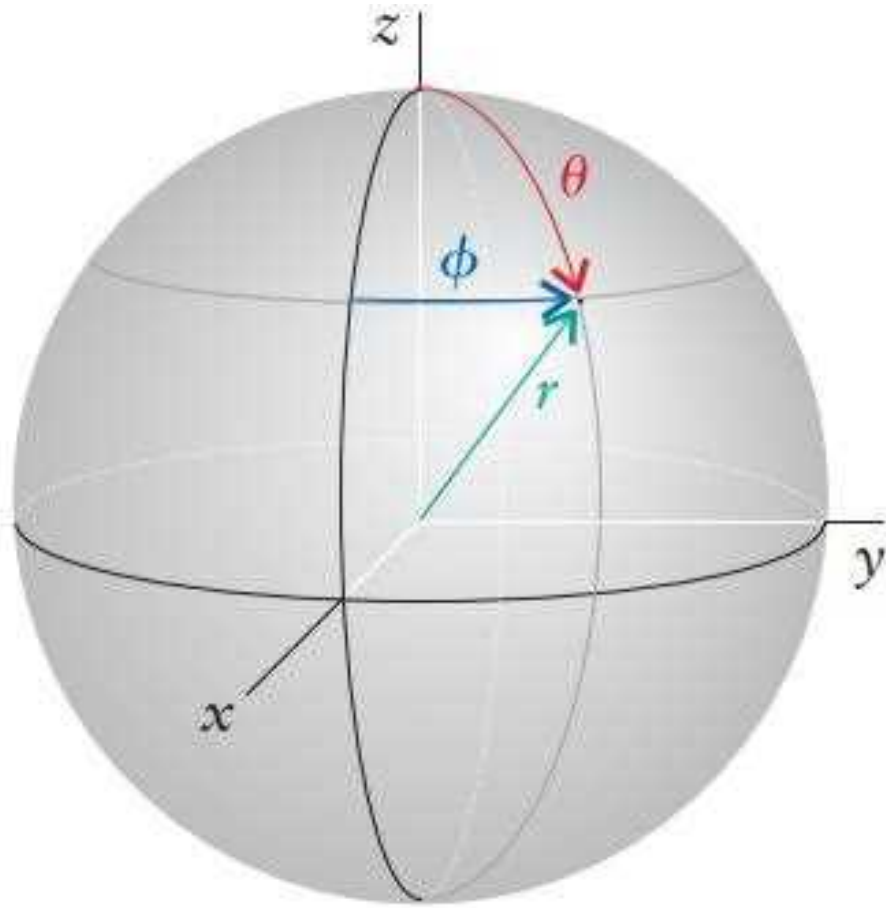


Figure 4.10.1: a) The proton (p^+) and electron (e^-) of the hydrogen atom.

b) Equivalent reduced particle with reduced mass μ at distance r from center of mass.

It is convenient to switch from Cartesian coordinates x, y, z to spherical (polar) coordinates in terms of a radius r , as well as angles ϕ , which is measured from the positive x axis in the xy plane and may be between 0 and 2π , and θ , which is measured from the positive z axis towards the xy plane and may be between 0 and π .



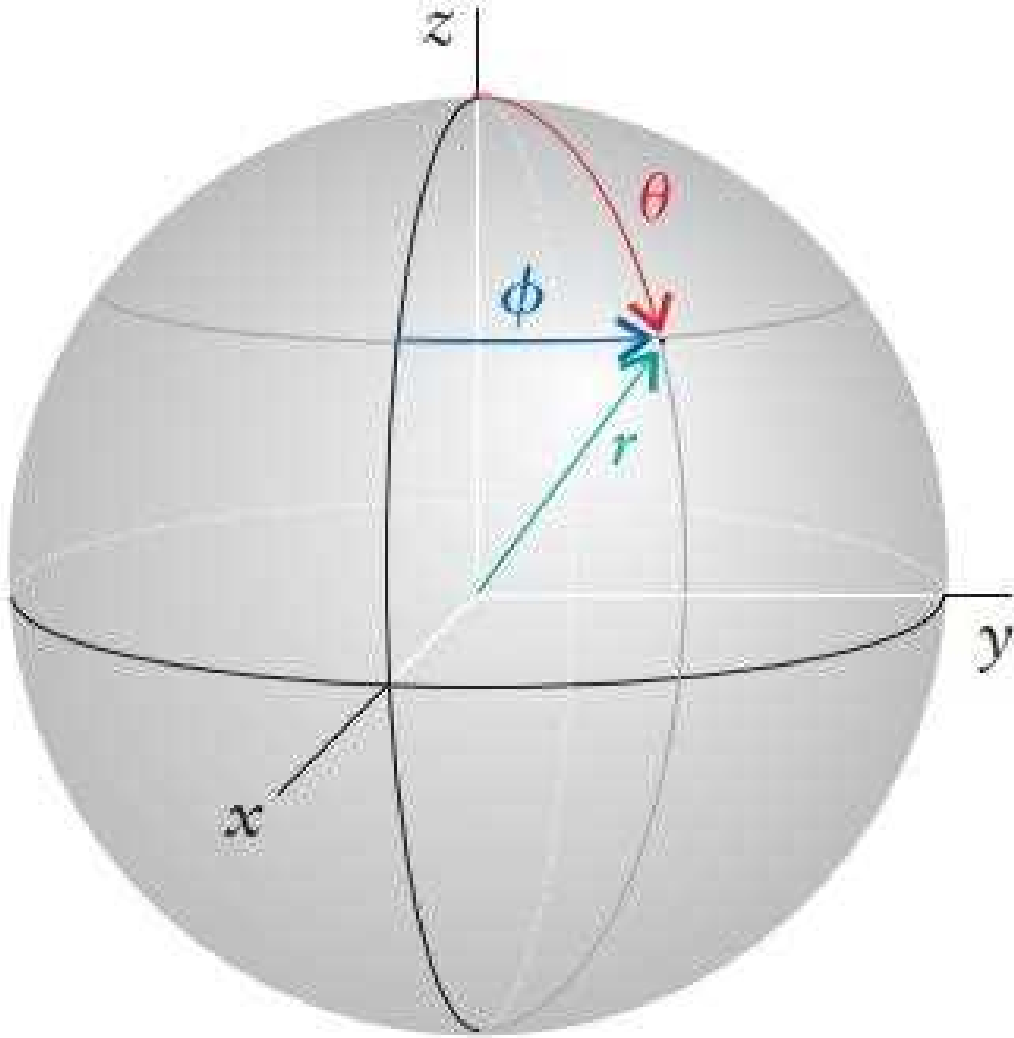


FIGURE 1.29 The spherical polar coordinates: r is the radius, which gives the distance from the center, θ is the *colatitude*, which gives the angle from the z -axis, and ϕ , the “longitude,” is the azimuth, which gives the angle from the x -axis.

Conventionally, θ is the angle from the z axis and ϕ is the angle from the x axis.

- Spherical coordinates are defined in Figure 5.1: r is the distance of the electron at P from the nucleus at O , and the angles θ and ϕ are similar to those used to locate points on the surface of the globe; θ is related to the latitude, and ϕ is related to the longitude.

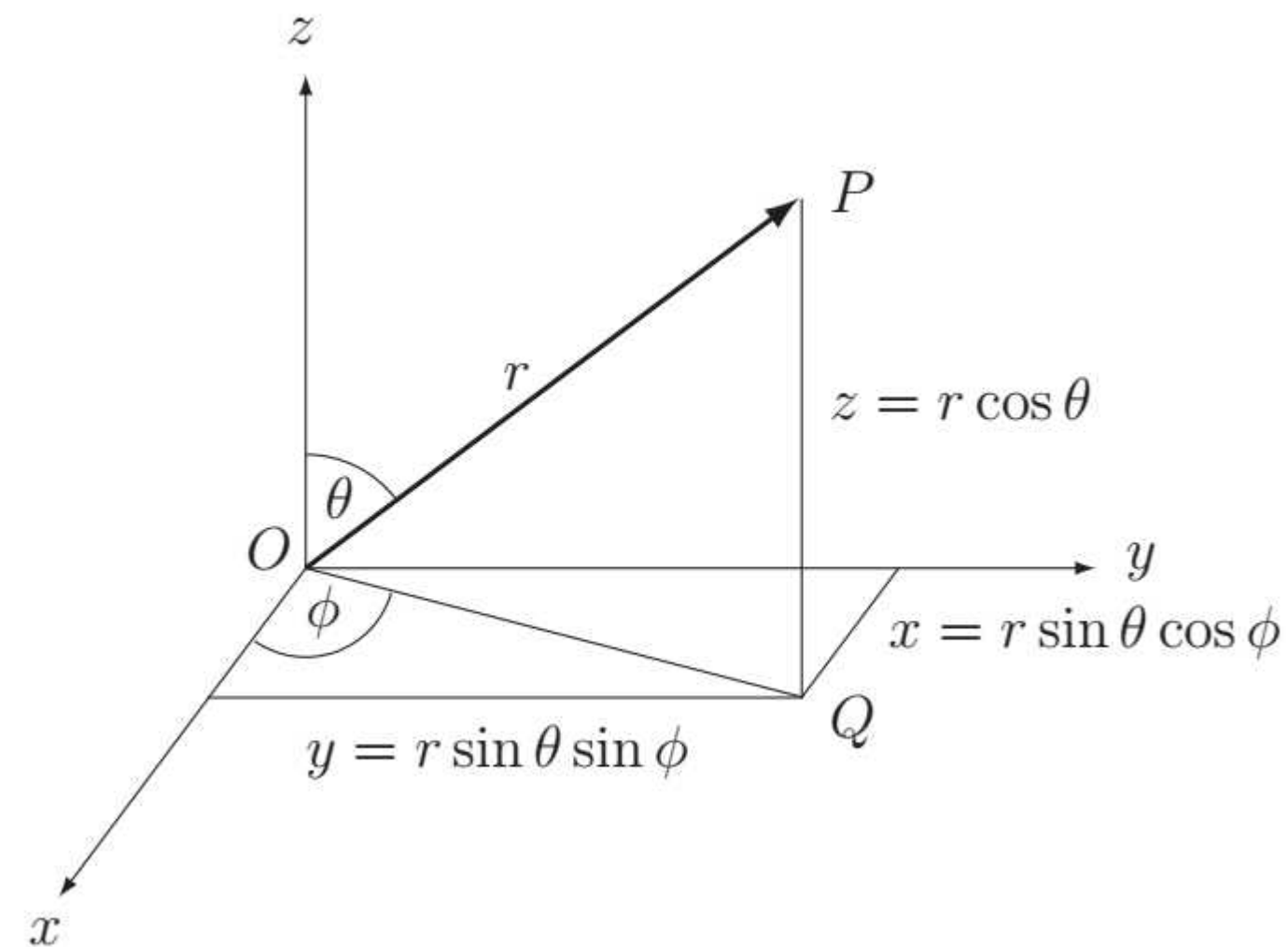


Figure 5.1 The relationship between spherical coordinates (r, θ, ϕ) and Cartesian coordinates (x, y, z) . Here, θ is the angle with respect to the Cartesian z -axis, which ranges from 0 to π , and ϕ is the azimuthal angle (the angle between the x -axis and the projection onto the x - y plane of the arrow from the origin to P), which ranges from 0 to 2π . Here, r is the distance of the electron from the nucleus at the origin, and ranges from 0 to ∞ .

- The time-independed Schrödinger equation (in spherical coordinates) for an electron around a positively charged nucleus is then

$$-\frac{\hbar^2}{2\mu}\nabla^2\psi + V\psi = -\frac{\hbar^2}{2\mu}\left(\frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r} + \frac{1}{r^2}\Lambda^2\right)\psi + V\psi = E\psi$$

- where

$$\Lambda^2 = \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2} + \frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta}$$

- The hydrogen atom Hamiltonian also contains a potential energy term, V , to describe the attraction between the proton and the electron. This term is the Coulomb potential energy, $V = -e^2/4\pi\epsilon_0 r$ where r is the distance between the electron and the proton.
- The ***Coulomb potential energy*** depends inversely on the distance between the electron and the nucleus and ***does not depend on any angles***. Such a potential is called a ***central potential***.

- Because the potential energy is *centrosymmetric* (independent of angle), the equation for the wavefunction is expected to be separable into radial and angular components.
- Since the angular momentum operator does not involve the radial variable, r , we can separate variables in the above Equation by using a product wavefunction. We know that the eigenfunctions of the angular momentum operator are the Spherical Harmonic functions, $Y(\theta, \phi)$, so a good choice for a product function is *the **product of a function that depends only on r and another function that depends only on the angles θ and ϕ :***
- $$\psi(r, \theta, \phi) = R(r) Y(\theta, \phi) \quad (4.10.4)$$
- The Spherical Harmonic $Y(\theta, \phi)$ functions provide information about where the electron is around the proton, and the radial function $R(r)$ describes how far the electron is away from the proton.

- The function $Y(\theta, \phi)$ is called the ***angular wavefunction***; it tells us how the wavefunction varies as the angles θ and ϕ change.
- The function $R(r)$ is called the ***radial wavefunction***; it tells us how the wavefunction varies as we move away from the nucleus in any direction.
- Thus, the above equation can be *separated into a radial part and an angular part*, such that the wave function ψ can be taken as the product of a radial function R and an angular function Y , as shown in Equation (4.3).

- The method of separation of variables yields the slightly more manageable form of the Schrödinger equation for the hydrogen atom:

$$-\frac{\hbar^2}{2\mu} \left(Y \frac{d^2 R}{dr^2} + \frac{2Y}{r} \frac{dR}{dr} + \frac{R}{r^2} \Lambda^2 Y \right) + VRY = ERY$$

- where the partial derivatives with respect to r have been replaced by complete derivatives because R depends only on r . Multiply through by r^2/R and obtain

$$-\frac{\hbar^2}{2\mu R} \left(r^2 \frac{d^2 R}{dr^2} + 2r \frac{dR}{dr} \right) + Vr^2 - \frac{\hbar^2}{2\mu Y} \Lambda^2 Y = Er^2$$

- The functions Y satisfy the equation: $\Lambda^2 Y = -l(l+1)Y$

- so eqn becomes

$$-\frac{\hbar^2}{2\mu R} \left(r^2 \frac{d^2 R}{dr^2} + 2r \frac{dR}{dr} \right) + Vr^2 + \overbrace{\frac{\hbar^2 l(l+1)}{2\mu Y} Y}^{\text{Independent of } \theta, \phi \text{ because the } Y\text{s cancel}} = Er^2$$

- Continuing the argument, rewrite above eqn by dividing both sides by r^2 and multiplying by R . The result is

$$-\frac{\hbar^2}{2\mu}\left(\frac{d^2R}{dr^2} + \frac{2}{r}\frac{dR}{dr}\right) + VR + \frac{\hbar^2 l(l+1)}{2\mu r^2}R = ER$$

- Because for a hydrogenic atom $V = -Ze^2/4\pi\epsilon_0 r$, write

➤ and the equation becomes
$$-\frac{\hbar^2}{2\mu}\left(\frac{d^2R}{dr^2} + \frac{2}{r}\frac{dR}{dr}\right) + V_{\text{eff}}R = ER$$

- This expression, the radial wave equation, has the form of a Schrödinger equation.

- It describes the motion of a particle of mass μ in the region $0 \leq r < \infty$ where the potential energy is V_{eff} . Solving this equation gives the ***radial wavefunctions*** R .

- The equation does separate, and the two contributions to the wavefunction are solutions of two equations:

$$\Lambda^2 Y = -l(l+1)Y$$

$$-\frac{\hbar^2}{2\mu} \left(\frac{d^2 R}{dr^2} + \frac{2}{r} \frac{dR}{dr} \right) + V_{\text{eff}} R = ER \quad \text{where} \quad V_{\text{eff}}(r) = -\frac{Ze^2}{4\pi\epsilon_0 r} + \frac{l(l+1)\hbar^2}{2\mu r^2}$$

- The **first** Equation is the same as the *Schrödinger equation for a particle free to move at a constant radius around a central point*. The **allowed** solutions (Angular wavefunctions) are the **spherical harmonics**, and are **specified by the quantum numbers l and m_l** .
- The **second** Equation is called *the radial wave equation*. The radial wave equation describes the motion of a particle of mass μ in a one-dimensional region $0 \leq r < \infty$ where the potential energy is $V_{\text{eff}}(r)$.

❑ The Spherical Harmonics solutions

- From Quantum mechanics, we can show that L^2 commutes with the Cartesian components of L , e.g., $[L^2, L_x] = 0$; $[L^2, L_y] = 0$; and $[L^2, L_z] = 0$.
- This suggests that both the magnitude of the angular momentum and (any) one of its components can be simultaneously determined, since there is always a set of eigenfunctions that is common to L^2 and any of the three Cartesian components. Remember, however, that none of the individual components commute with each other. Therefore, if one component is determined the other two are completely undetermined.
- Therefore, if there is an eigenfunction Y that is common to L^2 and L_z ,
- $L^2 Y = aY$, and $L_z Y = bY$.

➤ If Y is an eigenfunction of L_z then, $L_z Y = bY$.

$$-i\hbar \frac{\partial Y}{\partial \phi} = bY \quad \Rightarrow \quad \frac{\partial \ln Y}{\partial \phi} = \frac{1}{Y} \frac{\partial Y}{\partial \phi} = -\frac{b}{i\hbar}.$$

$$Y = A \exp\left(\frac{ib\phi}{\hbar}\right)$$

➤ Since $Y(\phi + 2\pi) = Y(\phi)$, we must have

$$e^{i\frac{2\pi b}{\hbar}} = 1, \quad \Rightarrow \quad 2\pi \frac{b}{\hbar} = 2\pi m, \quad \text{with} \quad m = 0, \pm 1, \pm 2, \dots$$

➤ Therefore, $b = m\hbar$, where m is an integer.

➤ Schrödinger equation also quantizes L^2 , the square magnitude of the angular momentum, like L_z , the projection of the angular momentum along the z-axis. Quantization of the square of the angular momentum as well as its projection along the z-axis requires **two additional quantum numbers**.

- The allowed values of the square of the angular momentum L and its z -projection are given by:

$$\text{Allowed values of } L^2 = \ell(\ell + 1) \frac{h^2}{4\pi^2} \quad \ell = 0, 1, \dots, n - 1$$

$$\text{Allowed values of } L_z = m \frac{h}{2\pi} \quad m = -\ell, -\ell + 1, \dots, 0, \dots, \ell - 1, \ell$$

- For $n = 1$ (the ground state), the only allowed values for the angular momentum quantum numbers are ($\ell = 0, m = 0$). For $n = 2$, there are $n^2 = 4$ allowed sets of quantum numbers:

$$(\ell = 0, m = 0), (\ell = 1, m = 1), (\ell = 1, m = 0), (\ell = 1, m = -1)$$

- Finding eigenfunctions that are common to L_z and L^2 , leads to associated Legendre equations.
- The solutions of the *associated Legendre equations* are the associated *Legendre polynomials*, $A(l, m) = P_l^{|m|}(\cos\theta)$
- The *associated Legendre equation's* solutions exist only for $a = \hbar^2 l(l + 1)$, and $b = -l\hbar, (-l + 1)\hbar, \dots, l\hbar$ (i.e., the quantum number l is an integer greater or equal to zero, with $|m| \leq l$).
- The eigenstates that are common to L^2 and L_z are called *spherical harmonics* and are defined as follows, $Y_l^m(\theta, \phi) = P_l^{|m|}(\cos\theta)e^{im\phi}$
- So, a particular solution can be written as: $\Psi_{n,l,m_l}(r, \theta, \phi) = R_{n,l}(r)Y_{l,m_l}(\theta, \phi)$
- where $n = 1, 2, 3, \dots; l = 0, 1, \dots, n-1; m_l = -l, \dots, -2, -1, 0, +1, +2, \dots, l$
- The radial wave function is only dependent on n and l , while the angular wavefunction is only dependent on l and m_l .

❑ Three Quantum Numbers

- Thus, Schrödinger Equation for hydrogenic atom can be solved by separation of variables in spherical polar coordinates.
- This three-dimensional problem provides *three numbers* in the *solutions that* are known as *three different quantum numbers* (QNs): n , l , and m_l (or m).
- The *boundary conditions restrict their values*.
- The principal quantum number $n = 1, 2, \dots$ is a positive integer (NOT zero), the angular momentum quantum number l is restricted to $0, 1, \dots, n - 1$, and the magnetic quantum number m is restricted to $-l, -l + 1, \dots, l - 1, l$. More concisely, $n > l \geq |m|$.
- These quantum numbers arise naturally in the course of mathematics *because of the requirement that acceptable solutions are well-behaved functions*. This is in contrast to the older theory where the quantum numbers had to be added, apparently arbitrarily, to the classical description.

- The three quantum numbers can only assume certain values.
- **1. PRINCIPAL QUANTUM NUMBER (n)** - Represents the **main energy level, or *shell*, occupied by an electron**. It is always a positive integer, that is $n = 1, 2, 3 \dots$
- **2. SECONDARY QUANTUM NUMBER (l ; Azimuthal (Orbital Angular Momentum) Q.N.)** - Represents the energy sublevel, or **type of orbital**, occupied by the electron. The value of l depends on the value of n such that $l = 0, 1, \dots, n-1$. This number is sometimes also called *azimuthal*, or *subsidiary*.
- **3. MAGNETIC QUANTUM NUMBER (m_l)** - Represents the number of possible orientations in 3-D space for each type of orbital. Since the type of orbital is determined by l , the value of m_l ranges between $-l$ and $+l$ such that $m_l = -l, \dots, 0, \dots, +l$.

 $m_l = 0, \pm 1, \pm 2, \dots, \pm l \dots\dots\dots$

- The third quantum number required to specify an orbital is m_l , the magnetic quantum number, which distinguishes the individual orbitals within a subshell.
- This quantum number can take the values $m_l = l, (l - 1), \dots, 0, \dots, -l$.
- For example, when $l = 1$ (p-orbital), $m_l = 1, 0, -1$; so, there are three p-orbitals in a given shell.
- Alternatively, we can say that a subshell with $l = 1$ consists of three orbitals.
- The magnetic quantum number tells us the *orientation of the orbital motion of the electron*.
- Specifically, it tells us that the orbital angular momentum around an arbitrary axis is equal to $m_l h/2\pi$, *the rest of the orbital motion* (to make up the full amount of $\{l(l + 1)\}^{1/2}$) being around other axes.

- As its name suggests, l tells us the orbital angular momentum of the electron, a measure of the rate at which (in classical terms) the electron “circulates” round the nucleus:
- Orbital angular momentum = $\{l(l + 1)\}^{1/2} h/2\pi$
- An electron in an s-orbital (an “s-electron”), for which $l = 0$, has zero orbital angular momentum.
- ✓ That means that we should imagine it not as circulating around the nucleus but simply as distributed evenly around it.
- An electron in a p-orbital ($l = 1$) has nonzero orbital angular momentum (of magnitude??); so, it can be thought of as circulating around the nucleus.
- An electron in a d-orbital ($l = 2$) has a higher orbital angular momentum, one in an f-orbital ($l = 3$) has an even higher angular momentum, and so on.

- The orbitals of a shell with principal quantum number n therefore fall into **n subshells**, groups of orbitals that have the same value of l .
- Value of l 0 1 2 3.....
- Orbital type s p d f.....
- The labels come from the fact that spectroscopic lines were once classified as sharp, principal, diffuse, and fundamental. *next label*...?

- *Owing to the separation of variables, however, each solution will consist of two parts: **a radial wavefunction $R(r)$** and **an angular wavefunction $Y(\theta, \phi)$** .*
- *The **solutions to the angular part** are referred to as the **spherical harmonics**, a fairly common type of function in a wide variety of physical problems.*
- *So a particular orbital solution can be written as:*
- $\Psi_{n,l,m_l}(r, \theta, \phi) = R_{n,l}(r) Y_{l,m_l}(\theta, \phi)$
- *Where $n = 1, 2, 3, \dots$*
 - $l = 0, 1, \dots, n-1$
 - $m_l = -l, \dots, -2, -1, 0, +1, +2, \dots, l$
- *The radial wave function is only dependent on n and l , while the angular wavefunction is only dependent on l and m_l .*

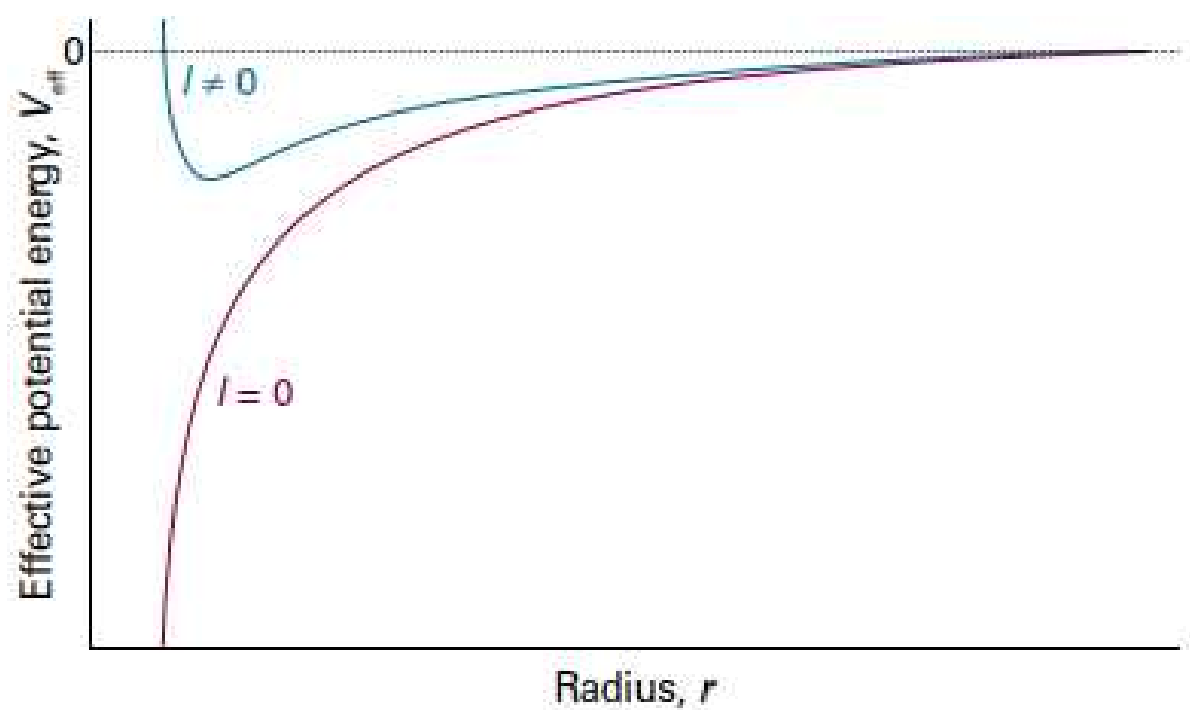
□ The radial solutions

- *Some features* of the shapes of the *radial wavefunctions* can be anticipated by examining the form of $V_{\text{eff}}(r)$.

$$V_{\text{eff}}(r) = -\frac{Ze^2}{4\pi\epsilon_0 r} + \frac{l(l+1)\hbar^2}{2\mu r^2}$$

- The *first term* in the eqn. is the *Coulomb potential energy* of the electron in the field of the nucleus.
- The *second term* stems from what in classical physics would be called the *centrifugal force* arising from the angular momentum of the electron around the nucleus.
- **When $l = 0$** , the electron has **no angular momentum**, and the effective potential energy is *purely Coulombic*, and the *force exerted on the electron is attractive at all radii* (Fig. 8A.2).

- When $l \neq 0$, the centrifugal term gives a *positive contribution* to the effective potential energy, corresponding to *a repulsive force at all radii*.
- When *the electron is close to the nucleus ($r \approx 0$)*, the *positive contribution to the potential energy (which is proportional to $1/r^2$) dominates the Coulombic contribution (which is proportional to $1/r$)*, and the *net result* is an *effective repulsion of the electron from the nucleus*.
- The **two effective potential energies**, the one for $l = 0$ and the one for $l \neq 0$, are therefore qualitatively *very different close to the nucleus*.
- However, *they are similar at large distances* because the centrifugal contribution tends to zero more rapidly (as $1/r^2$) than the Coulombic contribution (as $1/r$).
- Therefore, the solutions with $l = 0$ and $l \neq 0$ are expected to be quite different near the nucleus but similar far away from it.



$$V_{\text{eff}}(r) = -\frac{Ze^2}{4\pi\epsilon_0 r} + \frac{l(l+1)\hbar^2}{2\mu r^2}$$

Figure 8A.2 The effective potential energy of an electron in the hydrogen atom.

- ✓ When the electron has **zero orbital angular momentum** ($l = 0$), the effective potential energy is the **Coulombic potential energy**.
- ✓ When the electron has **non-zero orbital angular momentum** ($l \neq 0$), the **centrifugal effect gives rise to a positive contribution which is very large close to the nucleus**.
- ✓ The $l = 0$ and $l \neq 0$ wavefunctions are therefore **very different near the nucleus**.

- The *detailed solution* of the radial equation for the full range of radii shows how the form r^l close to the nucleus blends into the *exponentially decaying form at great distances*.
- It turns out that the two regions are bridged by a *polynomial* in r and that

$$R(r) = r^l L(r) e^{-r}$$

$$R(r) = \overbrace{r^l}^{\text{Dominant close to the nucleus}} \times \overbrace{(\text{polynomial in } r)}^{\text{Bridges the two ends of the function}} \times \overbrace{(\text{decaying exponential in } r)}^{\text{Dominant far from the nucleus}}$$

➤ The radial wavefunction therefore has the form:

$$R(r) = r^l L(r) e^{-r}$$

✓ with various constants and where $L(r)$ is the bridging polynomial.

➤ **Close to the nucleus** ($r \approx 0$) the *polynomial is a constant* and $e^{-r} \approx 1$, so $R(r) \propto r^l$; *far from the nucleus* the *dominant term in the polynomial is proportional to r^{n-l-1}* , where ***n is an integer***, so regardless of the value of l , all the wavefunctions of a given value of n are proportional to $r^{n-l} e^{-r}$ and *decay exponentially to zero in the same way (exponential functions e^{-x} always dominate simple powers, x^n)*.

➤ The detailed solution also shows that, for *the wavefunction to be acceptable, the value of n that appears in the polynomial can take only positive integral values, and specifically $n = 1, 2, \dots$*

➤ ***This number*** also determines the ***allowed energies*** through the expression as shown later.

- **Two features** of the radial wavefunction are important (physical interpretation):
- **Close to the nucleus the radial wavefunction is proportional to r^l** , and *the higher the orbital angular momentum, the less likely it is that the electron will be found there* (Fig. 8A.3).
 - *Far from the nucleus all radial wavefunctions approach zero exponentially.*

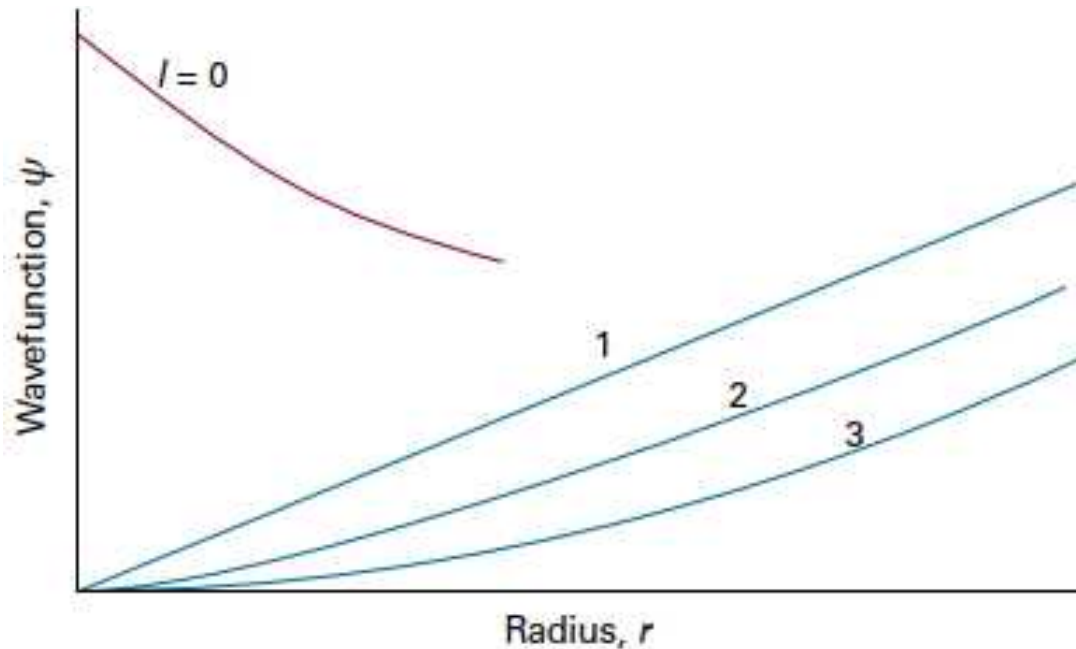


Figure 8A.3 **Close to the nucleus**, orbitals with $l = 1$ are proportional to r , orbitals with $l = 2$ are proportional to r^2 , and orbitals with $l = 3$ are proportional to r^3 . *Electrons are progressively excluded from the neighbourhood of the nucleus as l increases.* An orbital with $l = 0$ has a finite, non-zero value at the nucleus.

❑ Atomic Orbitals and their energies

- We need to find the *wavefunctions*. *Knowing the form of the wavefunctions allows us to go beyond the information provided by spectroscopy* and determine not only the *allowed energies* of the electron in a hydrogen atom but also *how the electron is distributed around* the nucleus.
- The *one-electron wave functions* are called (**atomic**) **orbitals** and form an orthonormal set.
- They can be written as the product of a radial function and an angular function as: $\psi_{n,\ell,m}(r, \theta, \phi) = R_{n,\ell}(r) \mathcal{Y}_{\ell,m}(\theta, \phi)$.
- *The wavefunctions of electrons in atoms are called **atomic orbitals**.*
- The name was chosen to suggest something less definite than an “orbit” of an electron around a nucleus and to take into account the wave nature of the electron.

- The single electron hydrogen atom wavefunctions, $\psi(r,\theta,\phi)$, are called ***atomic orbitals***.
- An *atomic orbital* is a function that describes one electron in an atom.
- The wavefunction with $n = 1$, $l = 0$ is called the 1s orbital, and an electron that is described by this function is said to be “in” the 1s orbital, i.e. have a 1s orbital state.
- The constraints on n , l , and m_l that are imposed during the solution of the hydrogen atom Schrödinger equation explain why there is a single 1s orbital, why there are three 2p orbitals, five 3d orbitals, etc.
- The quantum numbers provide information about the spatial distribution of an electron.
- We will see when we consider multi-electron atoms, these constraints explain the features of the Periodic Table. In other words, the Periodic Table is a manifestation of the Schrödinger model and the physical constraints imposed to obtain the solutions to the Schrödinger equation for the hydrogen atom.

- The mathematical expressions for atomic orbitals—which are obtained as solutions of the Schrödinger equation—are more complicated than the sine functions for the particle in a box, but their essential features are straightforward.
- Moreover, we must never lose sight of *their interpretation*, that the ***square of a wavefunction tells us the probability density*** of an electron at each point.
- To visualize this probability density, imagine a cloud centered on the nucleus. The density of the cloud at each point represents the probability of finding an electron there.
- Denser regions of the cloud therefore represent locations where the electron is more likely to be found.

- We need to know, as we describe in more detail immediately below, that *each wavefunction is labeled by **three quantum numbers**: n is related to the **size and energy** of the orbital, l is related to its **shape**, and m_l is related to its **orientation in space**.*
- We have already encountered n , the *principal quantum number*, which specifies the energy of the orbital in a one-electron atom.
- *In a one-electron atom*, all atomic orbitals with the same value of the principal quantum number n have the same energy and are said to belong to the same shell of the atom.
- The name “**shell**” reflects the fact that as n increases, the region of greatest probability density is like a nearly hollow shell of increasing radius.
- The higher the number of the shell, the further away from the nucleus are the electrons in that shell.

❑ The Energies and Principal Quantum Number (n)

- An electron in an atom is like a particle in a box, in the sense that it is confined within the atom by the pull of the nucleus.
- We can therefore expect the electron's wavefunctions to obey certain boundary conditions, like the constraints we encountered when fitting a wave between the walls of a container.
- As we saw for a particle in a box, these ***constraints result in the quantization of energy and the existence of discrete energy levels.***
- Even at this early stage, we can expect the electron to be confined to certain energies, just as the spectroscopic observations require.

- To ***find the wavefunctions and energy levels*** of an electron in a hydrogen atom, we must solve the appropriate Schrödinger equation.
- The potential energy of an electron of charge $-e$ at a distance r from a nucleus of charge $+e$ (the “Coulomb” potential energy) is

$$V(r) = \frac{(-e)(+e)}{4\pi\epsilon_0 r} = -\frac{e^2}{4\pi\epsilon_0 r}$$

- Solving the Schrödinger equation for a particle with this potential energy, Schrödinger found (1927) that the allowed energy levels for an electron in a hydrogen atom are:

$$E_n = -\frac{h\mathcal{R}}{n^2} \quad \mathcal{R} = \frac{m_e e^4}{8h^3 \epsilon_0^2} \quad n = 1, 2, \dots$$

- These energy levels have exactly the form suggested spectroscopically, but now we also have an expression for **R** in terms of more fundamental constants.
- When the fundamental constants are inserted into the expression for **R** , the value obtained is 3.29×10^{15} Hz, the same as the experimental value of the **Rydberg constant**.
- This agreement is a triumph for Schrödinger's theory and for quantum mechanics.
- The integer n , called the principal quantum number, indexes the individual energy levels. These are identical to the energy levels predicted by the Bohr theory.
- *Quantization arises because of the physical boundary conditions imposed on the solutions to the Schrödinger equation rather than from making arbitrary assumptions about the angular momentum.*

- A very similar expression applies to other one-electron ions, such as He^+ and even C^{5+} , with atomic number Z (They differ only in the charge $+Ze$ on the nucleus, and therefore in the magnitude of the attractive force experienced by the electron.):

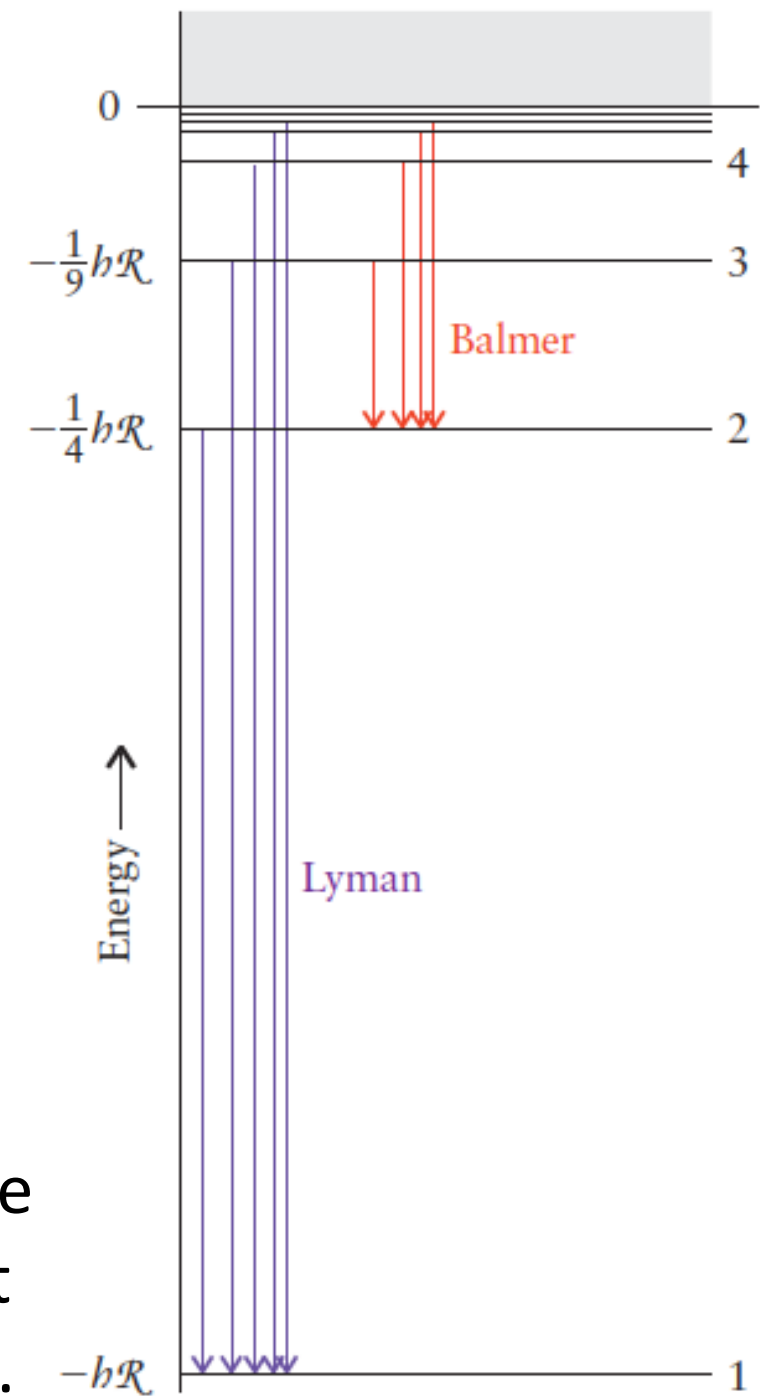
$$E_n = -\frac{Z^2 h \mathcal{R}}{n^2} \quad n = 1, 2, \dots$$

- What does this equation tell us?
- Because Z appears in the numerator, we see that ***the greater the value of the nuclear charge the more tightly the electron is bound to a nucleus.***
- That n appears in the denominator shows that as n increases, the energy becomes less negative.
- All the ***energies are negative***, meaning that the electron has a lower energy in the atom than when it is far from the nucleus.

- ✓ They refer to the **bound states** of the atom, in which the energy of the atom is lower than that of the infinitely separated, stationary electron and nucleus (which corresponds to the zero of energy).
- ✓ There are also solutions of the Schrödinger equation with *positive energies*. These solutions correspond to **unbound states** of the electron, the states to which an electron is raised when it is ejected from the atom by a high-energy collision or photon.
- ✓ The energies of the ***unbound electron are not quantized*** and form the continuum states of the atom.

- Figure 1.28 shows the energy levels calculated.
- We see that they come closer together as n increases.
- Each level is labeled by the integer n , which is called the ***principal quantum number***, from $n = 1$ for the first (lowest, most negative) level, $n = 2$ for the second, continuing to infinity.
- The lowest energy possible for an electron in a hydrogen atom, $-hR$, is obtained when $n = 1$.
- ✓ This ***lowest energy state*** is called the ***ground state*** of the atom.

FIGURE 1.28 The permitted energy levels of a hydrogen atom as calculated above. The levels are labeled with the quantum number n , which ranges from 1 (for the lowest state) to infinity (for the separated proton and electron).



- A hydrogen atom is normally found in its ground state, with its electron in the level with $n = 1$.
- *When the bound electron is excited by absorbing a photon, its energy climbs up the ladder of levels as n increases.*
- *It reaches the top of the ladder, corresponding to $E = 0$ and freedom, when n reaches infinity. At that point, the electron has left the atom. This process is called **ionization**.*
- The difference in energy between the ground state and the ionized state is the energy required to remove an electron from the neutral atom in its ground state. The “**ionization energy**” itself, is the minimum energy needed to achieve ionization, with the electron removed from the orbital with $n = 1$ to a final state in which it has zero energy: *in this final state it is free of the nucleus and has zero kinetic energy.*
- ***The energy levels of a hydrogen atom are defined by the principal quantum number, $n = 1, 2, \dots$, and form a converging series, as shown in Fig. 1.28.***

- The *energy of a one-electron atom* depends *only* on the *principal quantum number n* , because the potential energy depends only on the radial distance.
- The *angular momentum quantum number l* , may take on any integral value from 0 to $n - 1$, and the angular momentum projection quantum number *m_l* may take on any integral value from $-l$ to l . The quantum number m_l is referred to as the *magnetic quantum number* because its value helps *determine how the energy of the atom would shift* when placed in an *external magnetic field*.

TABLE 1.2 Hydrogenlike Wavefunctions* (Atomic Orbitals), $\psi = RY$

(a) Radial wavefunctions			(b) Angular wavefunctions			
n	l	$R_{nl}(r)$	l	$^a m_l^{*†}$	$Y_{l,m_l}(\theta, \phi)$	
1	0	$2\left(\frac{Z}{a_0}\right)^{3/2} e^{-Zr/a_0}$	0	0	$\left(\frac{1}{4\pi}\right)^{1/2}$	
2	0	$\frac{1}{2\sqrt{2}}\left(\frac{Z}{a_0}\right)^{3/2} \left(2 - \frac{Zr}{a_0}\right) e^{-Zr/2a_0}$	1	x	$\left(\frac{3}{4\pi}\right)^{1/2} \sin\theta \cos\phi$	
	1	$\frac{1}{2\sqrt{6}}\left(\frac{Z}{a_0}\right)^{3/2} \left(\frac{Zr}{a_0}\right) e^{-Zr/2a_0}$		y	$\left(\frac{3}{4\pi}\right)^{1/2} \sin\theta \sin\phi$	
3	0	$\frac{2}{9\sqrt{3}}\left(\frac{Z}{a_0}\right)^{3/2} \left(3 - \frac{2Zr}{a_0} + \frac{2Z^2 r^2}{9a_0^2}\right) e^{-Zr/3a_0}$	2	z	$\left(\frac{3}{4\pi}\right)^{1/2} \cos\theta$	
	1	$\frac{2}{9\sqrt{6}}\left(\frac{Z}{a_0}\right)^{3/2} \left(2 - \frac{Zr}{3a_0}\right) e^{-Zr/3a_0}$		xy	$\left(\frac{15}{16\pi}\right)^{1/2} \sin^2\theta \sin 2\phi$	
	2	$\frac{4}{81\sqrt{30}}\left(\frac{Z}{a_0}\right)^{3/2} \left(\frac{Zr}{a_0}\right)^2 e^{-Zr/3a_0}$		yz	$\left(\frac{15}{4\pi}\right)^{1/2} \cos\theta \sin\theta \sin\phi$	
				zx	$\left(\frac{15}{4\pi}\right)^{1/2} \cos\theta \sin\theta \cos\phi$	
				$x^2 - y^2$	$\left(\frac{15}{16\pi}\right)^{1/2} \sin^2\theta \cos 2\phi$	
			z^2	$\left(\frac{5}{16\pi}\right)^{1/2} (3 \cos^2\theta - 1)$		

*Note: In each case, $a_0 = 4\pi\epsilon_0^2/m_e e^2$, or close to 52.9 pm; for hydrogen itself, $Z = 1$.

†In all cases except $m_l = 0$, the orbitals are sums and differences of orbitals with specific values of m_l .

❖ What do these equations tell us?

- Earlier, only the general form of the radial wavefunctions has been given. It is now time to show how they depend on various fundamental constants and the atomic number of the atom.
- For example, the *wavefunction corresponding to the ground state of the hydrogen atom* ($n = 1$) is

$$\psi(r, \theta, \phi) = \frac{\overbrace{2e^{-r/a_0}}^{R(r)}}{a_0^{3/2}} \times \frac{\overbrace{1}^{Y(\theta, \phi)}}{2\pi^{1/2}} = \frac{e^{-r/a_0}}{(\pi a_0^3)^{1/2}} \quad a_0 = \frac{4\pi\epsilon_0\hbar^2}{m_e e^2}$$

- The quantity a_0 is called the **Bohr radius**; when the values of the fundamental constants are inserted, we find $a_0 = 52.9$ pm.

- What does this equation tell us?
- The ***radial wavefunction $R(r)$ decays exponentially toward zero as r increases, which means that the probability density is highest close to the nucleus ($e^0 = 1$).***
- The Bohr radius tells us how sharply the wavefunction falls away with distance: when $r = a_0$, ψ has fallen to $1/e$ (37%) of its value at the nucleus.

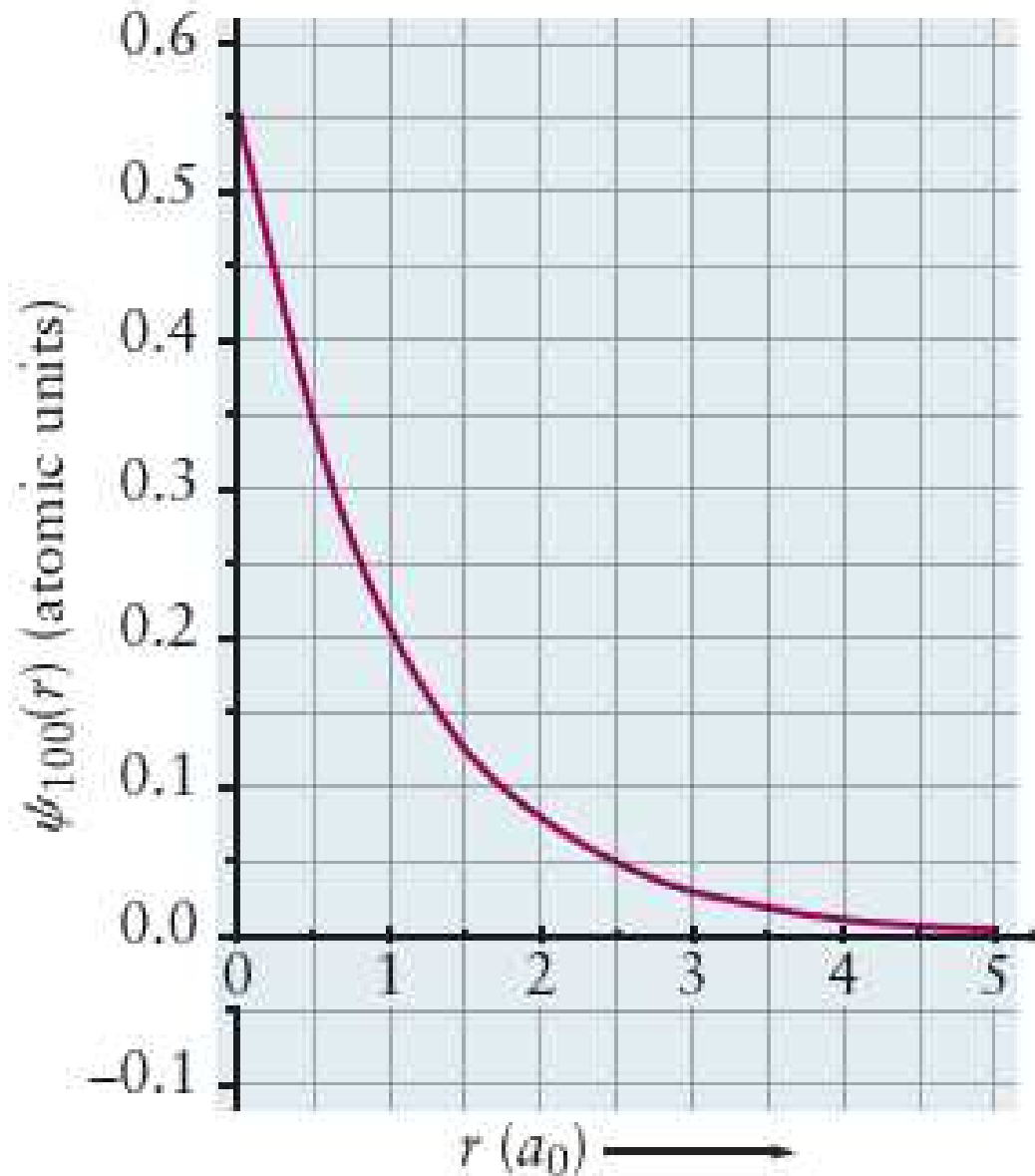


Figure 5.5 Plot of the hydrogen 1s orbital against distance from the nucleus.

The distance is measured in units of the Bohr radius a_0 .

❖ What does this equation tell us?

- *The radial wave functions all show an exponential decay as the radius increases.*
- Notice, though, that the *exponential function is multiplied by the factor r* , so is zero at the nucleus (at $r = 0$) as well as far away from it.
- *The exponential decay is slower with increasing n because the denominator in the exponential term contains a factor of na_0 .*
- *Thus, the average radius (or size) of an orbital also increases with n .*
- We discuss the angular dependence shortly. For this wavefunction, the **angular wavefunction Y is a constant, independent of the angles**, which means that **the wavefunction is the same in all directions**.

- For $n > 1$, the radial functions all have at least one radial node.
- ✓ For the 2s orbital, for instance, which has the quantum numbers $n=2$, $l=0$, $m_l=0$, the radial node occurs when $r = 2a_0/Z$ because this makes the second term in the parentheses zero ($a_0 = 52.9$ pm, the Bohr radius).
- A **general rule** is that **there are $(n - l - 1)$ radial nodes** and **l angular nodes**. Thus, a 2s orbital has **one radial node** (**no angular node**), while a 2p orbital has **no (zero) radial nodes** but **one angular node**.
- ✓ For $n = 2$ and $l = 1$, there are 0 (zero) radial node and 1 angular node.

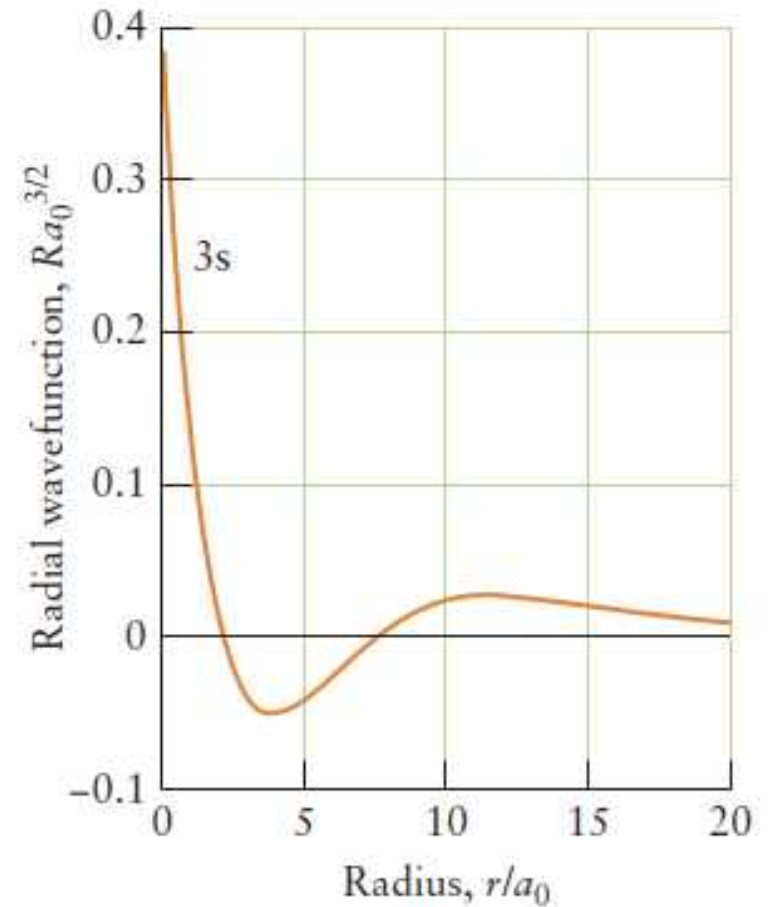
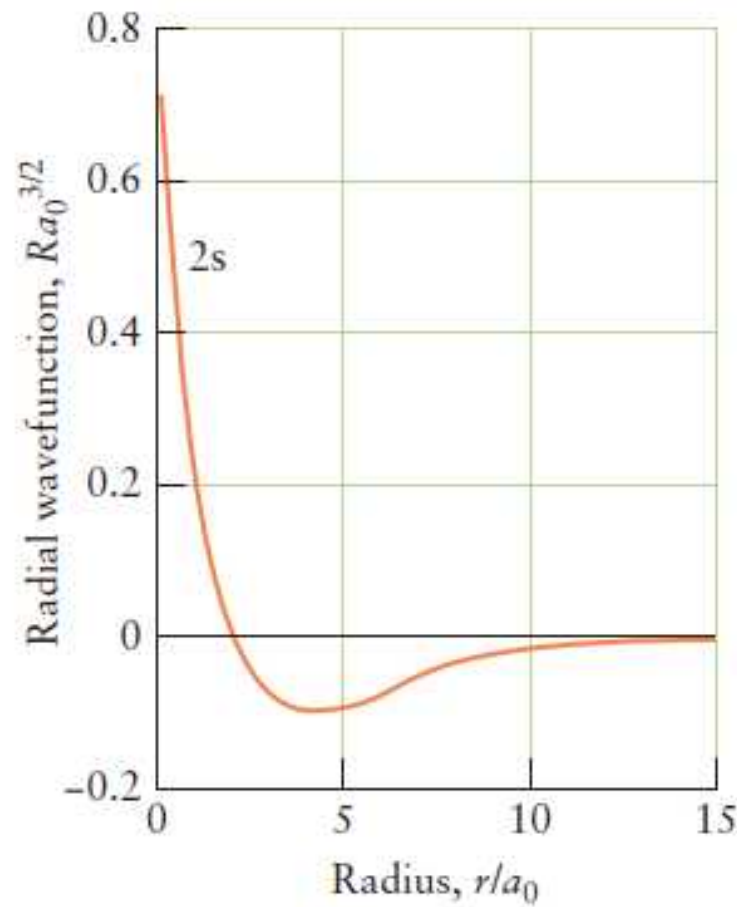
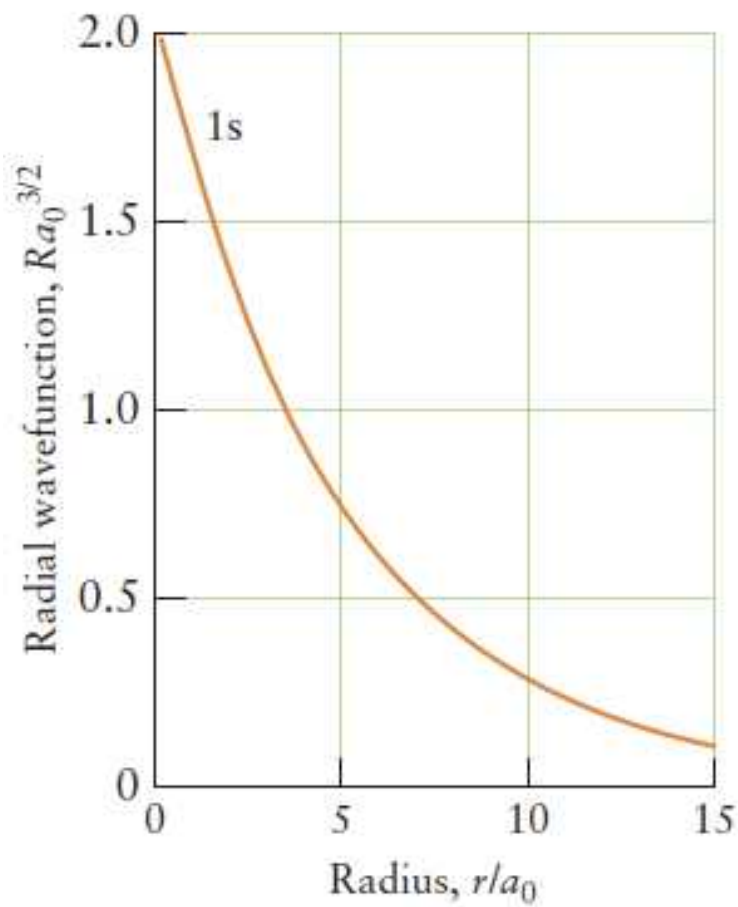


FIGURE 1.34 The radial wavefunctions of the first three s-orbitals of a hydrogen atom. Note that the number of radial nodes increases (as $n - 1$), as does the average distance of the electron from the nucleus. Because the probability density is given by 2 , all s-orbitals correspond to a nonzero probability density at the nucleus.

- The presence of the radial nodes is clearly indicated on the diagram.
- A second noteworthy feature is that the ***probability*** of the ***electron being close to the nucleus*** for a given value of n ***decreases*** in the order $s > p > d > f$.
- In other words, ***the s orbital “penetrates” the nucleus better than a p orbital having the same principal quantum number.***
- This fact is of ***utmost importance in the forthcoming section of shielding and influences a large number of an element’s chemical properties.***

- When the Schrödinger equation is solved in detail, it turns out that *three quantum numbers are needed to label each wavefunction* (because the atom is three-dimensional).
- The three quantum numbers are designated n , l , and m_l . However, it turns out that, for a hydrogen atom, wavefunctions with the ***same value of n all have the same energy (degenerate states: n^2)*** regardless of the values of the other two quantum numbers. (*A set of equal energy levels is termed **degenerate**.*)
- $1s < 2s = 2p < 3s = 3p = 3d < 4s = 4p = 4d = 4f < 5s = 5p = 5d = 5f < \dots$

❑ Electron density and orbital size

- A more useful quantity than the *radial wave function* is the ***radial distribution function***, also called the ***radial probability function***.
- We use techniques to generate graphical representations of $(\psi_{nlm})^2$, where $|\psi_{nlm}|^2 dV$ is the probability of finding the electron in a small volume element dV .
- The ***radial distribution function is the probability that the electron will exist in a thin volume element dV at a distance r from the nucleus.***
- One way of visualizing this is to think of the volume element as a thin spherical shell, similar to one of the layers in an onion skin, existing at a distance r away from the nucleus.
- The volume element dV shown in Figure 4.2 represents a fraction of this “onion skin.”

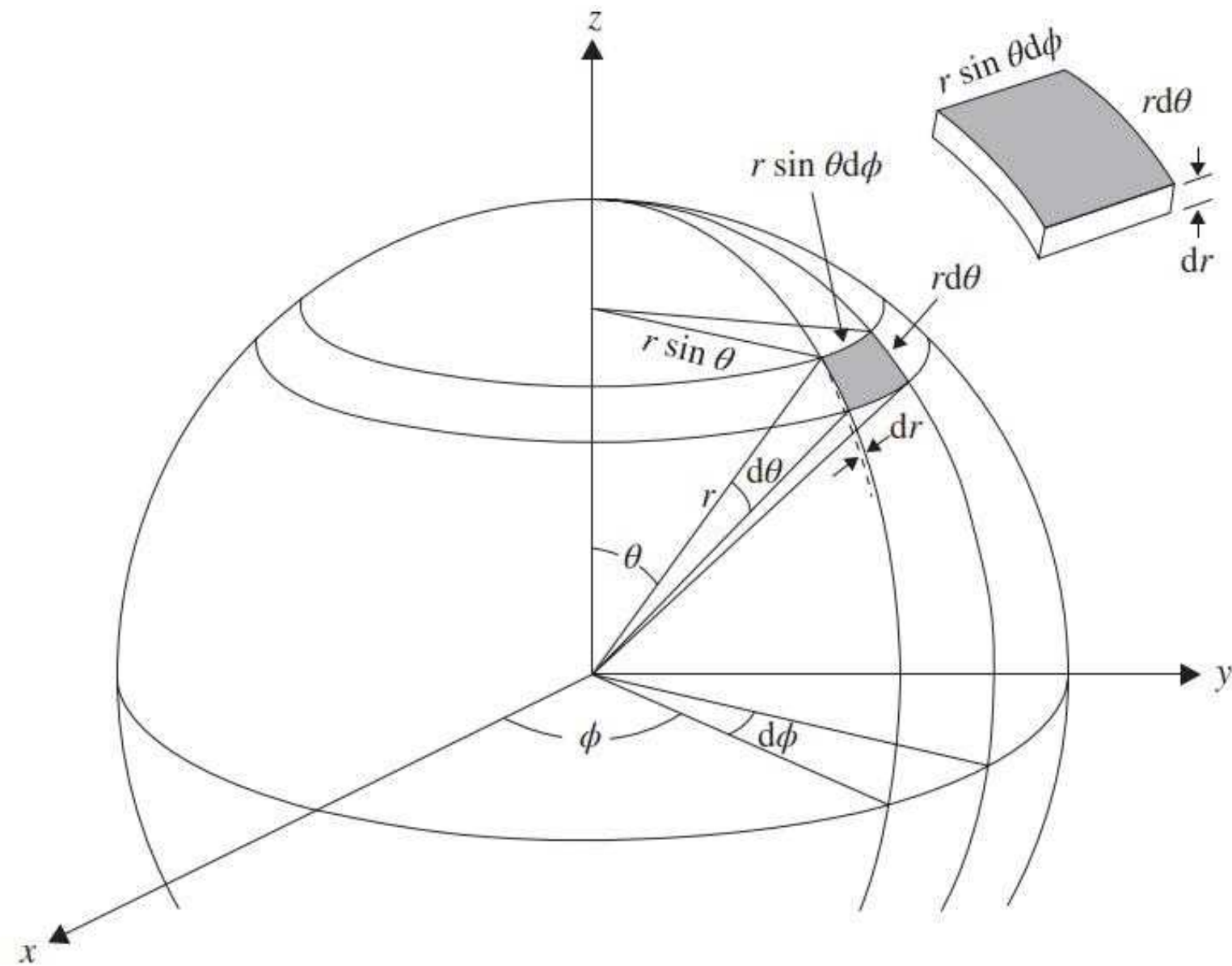


FIGURE 4.2.

Definition of the volume element $d\tau$ in polar coordinates:

$$d\tau = dV = r^2 \sin\theta \, dr \, d\theta \, d\phi.$$

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- Because the probability of finding an electron in a given region of space goes as the square of the wavefunction (the Born interpretation), the radial distribution function is equal to $R(r)^2 dV$.
- The volume of a sphere is $V = (4/3)\pi r^3$, and therefore $dV/dr = 4\pi r^2$.
- After substitution, the ***radial distribution function*** is defined as ***$4\pi r^2 R(r)^2 dr$*** .
- Plots of the radial distribution function for the first several types of orbitals in the hydrogen atom are shown in Figure 4.3.

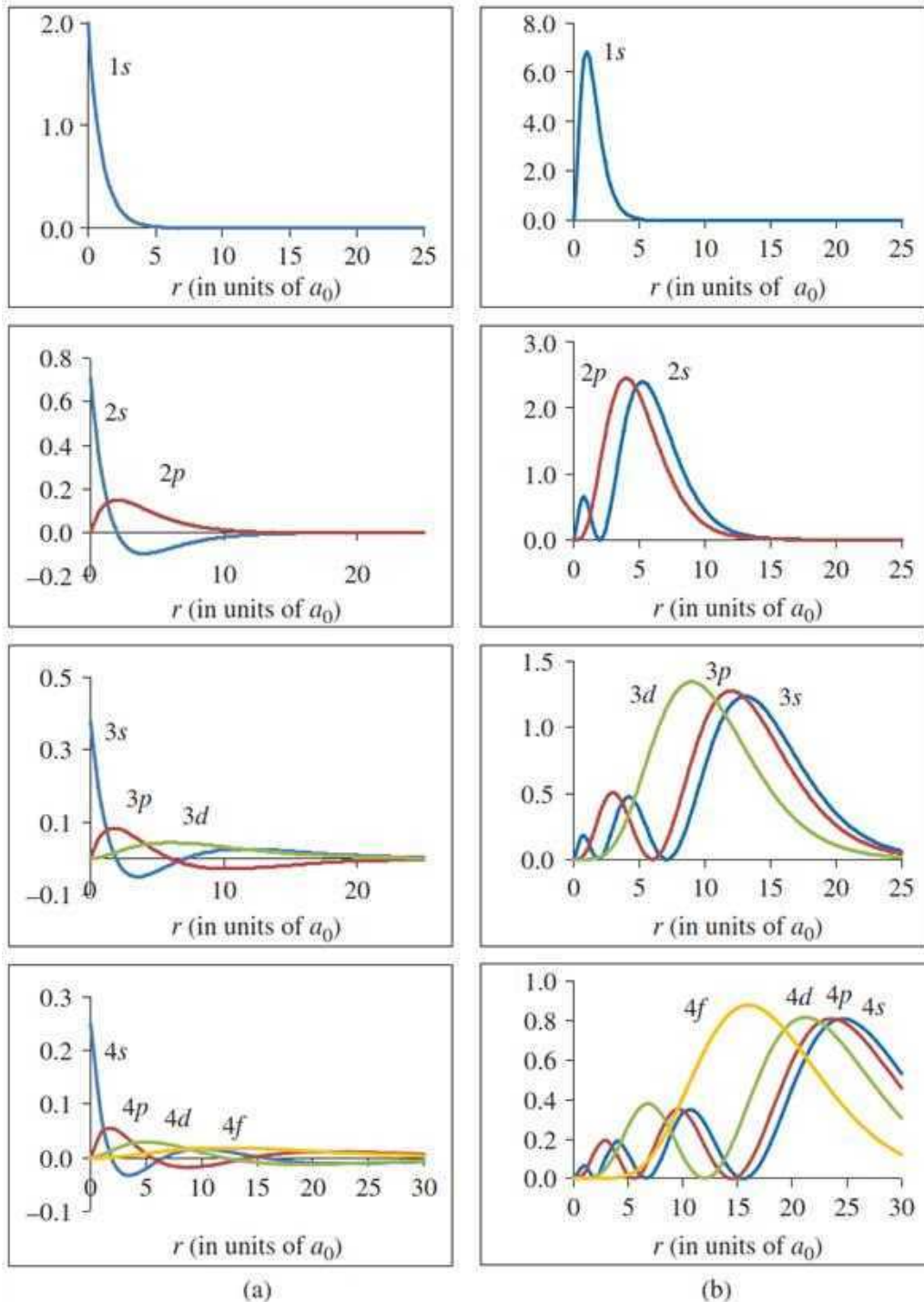


FIGURE 4.3

The radial function $R(r)$ (a) and the ***radial distribution function*** (b) for several types of orbitals in the hydrogen atom. The y-scale varies from one orbital to the next.

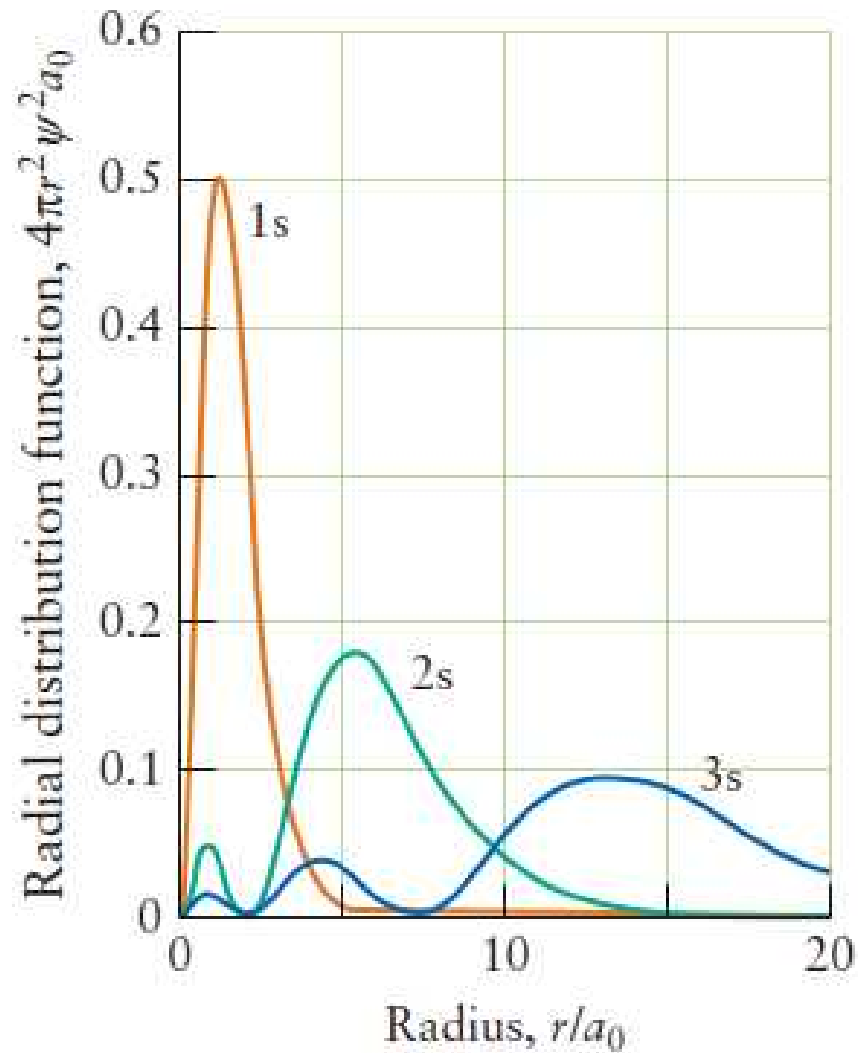
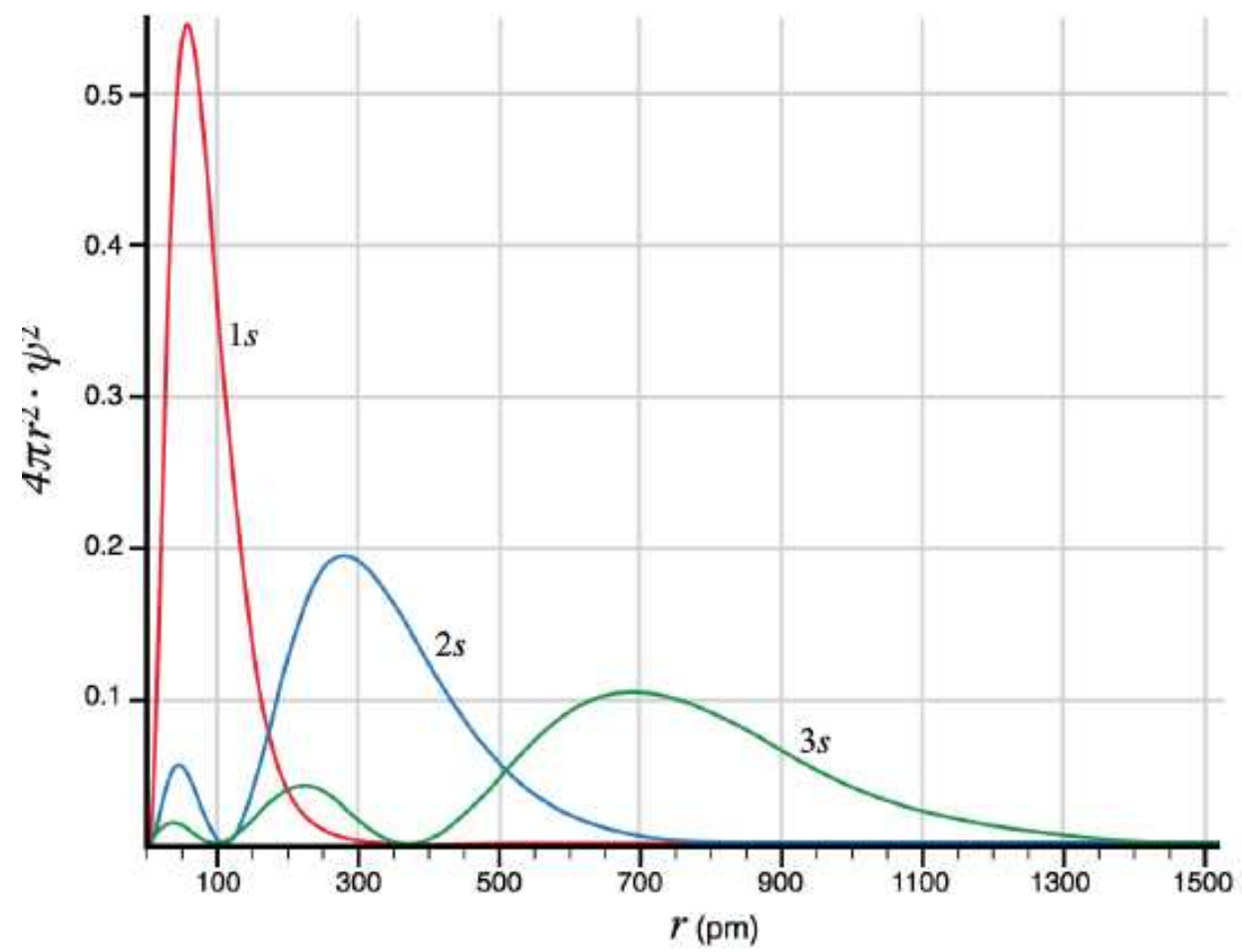


FIGURE 1.32 The radial distribution function tells us the probability density for finding an electron at a given radius summed over all directions. The graph shows the radial distribution function for the 1s-, 2s-, and 3s-orbitals in hydrogen. Note how the most probable radius (corresponding to the greatest maximum) increases as n increases.



Bohr Radius:

❖ **Example 4-2.** Show that the most probable radius for an electron in the 1s orbital of hydrogen is equal to the **Bohr radius, a_0** .

➤ **Solution:**

- ✓ The ***most probable radius can be obtained from the highest peak in the radial distribution function***, because this function is a measure of the probability of finding an electron in a volume element at a certain distance from the nucleus.
- ✓ Because the radial distribution function for a 1s orbital has a single peak, the radius at which this peak occurs can be calculated by taking the first derivative of the function with respect to r and setting it equal to zero.
- ✓ For a 1s orbital, $R(r)$ and the first derivative of the radial probability function are

$$R(r) = 2 \left(\frac{Z}{a_0} \right)^{3/2} e^{-\frac{Zr}{a_0}}$$

$$\begin{aligned}\frac{d(4\pi r^2 R^2)}{dr} &= \frac{d}{dr} \left[16\pi^2 \left(\frac{Z}{a_0} \right)^3 r^2 e^{-\frac{2Zr}{a_0}} \right] \\ &= 16\pi^2 \left(\frac{Z}{a_0} \right)^3 \left[2r e^{-\frac{2Zr}{a_0}} - \frac{2Z}{a_0} r^2 e^{-\frac{2Zr}{a_0}} \right] = 0\end{aligned}$$

which implies that

$$\left[2r - \frac{2Z}{a_0} r^2 \right] = 0$$

Hence, $r = a_0/Z$. Because $Z = 1$ for H, $r = a_0 = \mathbf{52.9 \text{ pm}}$, the same result as in the Bohr model of the atom.

Radial Node:

Example 4-3. At what distance from the nucleus does the radial node in a 2s orbital occur?

Solution. The radial wave function for a 2s orbital is given here:

$$\left(\frac{Z}{2a_0}\right)^{3/2} \left(2 - \frac{Zr}{a_0}\right) e^{-\frac{Zr}{2a_0}}$$

Setting the middle term equal to zero, we find that $2 = \frac{Zr}{a_0}$ and hence $r = \frac{2a_0}{Z}$
= 106 pm.

❑ Sizes and Shapes of Orbitals

- The sizes and shapes of the hydrogen atom orbitals are important in chemistry because they provide the foundations for the quantum description of chemical bonding and the molecular shapes to which it leads.
- Sizes and shapes of the orbitals are revealed by graphical analysis of the wave functions.

❑ The Angular Wave Functions

- The *solutions to the angular part of the hydrogen atom* are known as the ***spherical harmonics***.
- The angular wavefunctions $Y(\theta, \phi)$ depend on two variables and are therefore governed by the quantum numbers l and m_l .
- It is ***these quantum numbers that dictate the shape of the atomic orbitals***.
- Thus, for example, all of the s orbitals are spherical regardless of their principal quantum number and they each have the same angular dependence on θ and ϕ .
- Because $l = 0$ for s orbitals, m_l can only be zero; therefore, only one type of s orbital exists for any given value of n .

❖ ***s* Orbitals**

- Let's begin with the *s* orbital, corresponding to ψ_{nlm} with $l = 0$, (therefore, $m_l = 0$ as well).
- For all *s* orbitals, the angular part *Y* is a constant. Because ψ does not depend on either θ or φ , all *s* orbitals are ***spherically symmetric*** about the nucleus.
- This means that the value of the wave function for an *s* orbital (and therefore also the probability of finding the electron near some point in space) depends only on its distance, *r*, from the nucleus and not on its direction in space.
- There are several ways to visualize the *ns* orbitals with $n = 1, 2, 3, \dots$, and the probability density they describe.

- Figure 5.7 displays the relationships between the radial dependence of ψ and ψ^2 and the electron density representation for the 1s, 2s, and 3s orbitals.
- These schematic images display key features of these functions, but the radial dependence shown is not quantitative. The 2s and 3s orbitals have nodes, values of r at which the value of the wave function is 0, with lobes of positive phase and negative phase separated by the nodes. See Figure 5.7b.
- Figure 5.7c shows that ψ^2 passes through a local maximum value after r crosses each node, and then continues to fall off after the final node as r approaches very large values.
- From this behavior we generate the electron density representations in Figure 5.7a, in which the intensity of shading indicates the magnitude of the electron density in each region. The shading will be greatest at the local maximum values in ψ^2 and must fade to white at the nodes.

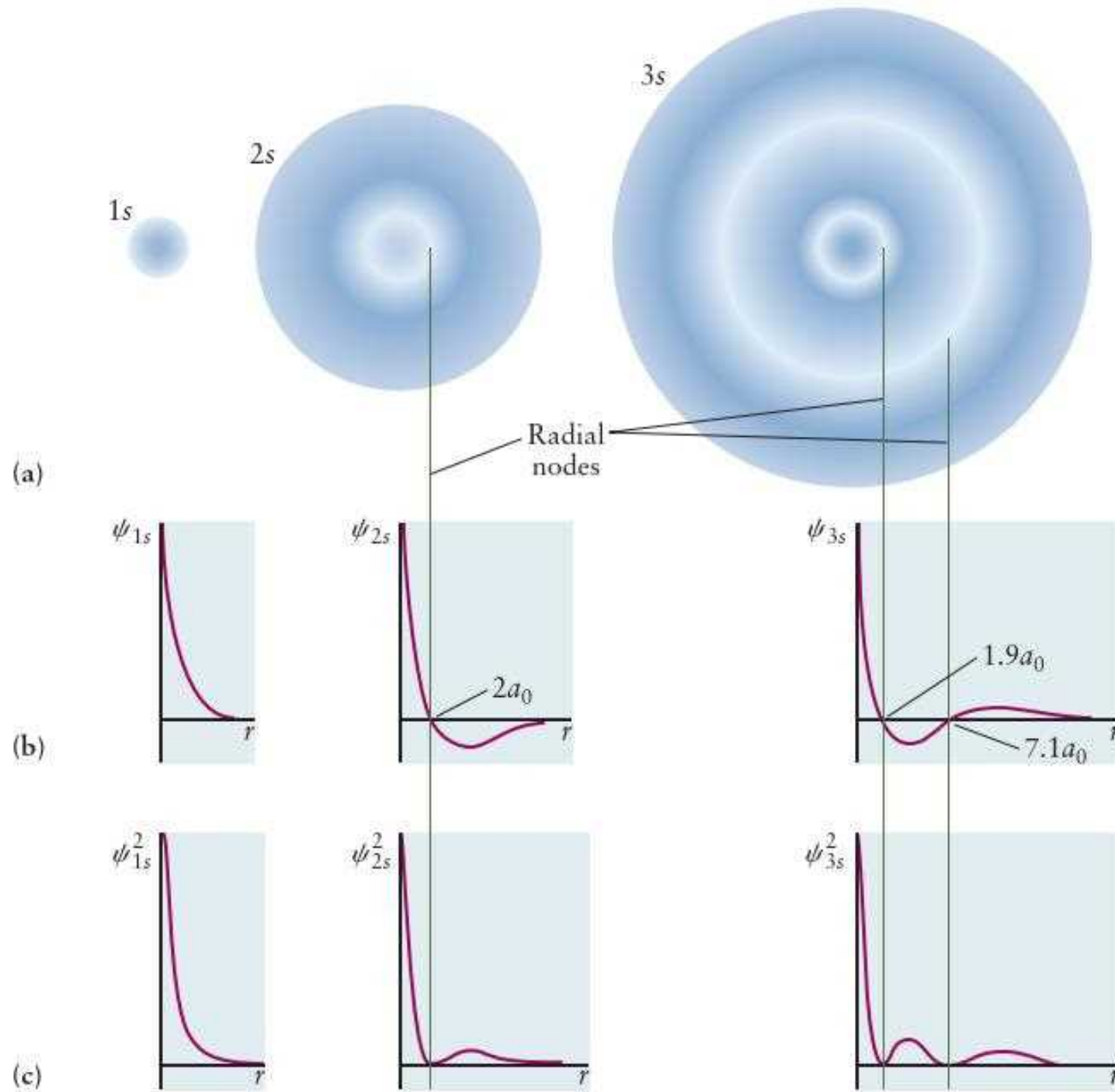


Figure 5.7 Qualitative representations of hydrogen s orbitals.

(a) An electron probability density representation of a hydrogen atom in its 1s, 2s, and 3s states. The spheres are cut off at a radius that encloses 90% of the probability density.

(b) The radial wave functions plotted against distance from the nucleus, r .

(c) Dependence of the probability density on the distance from the nucleus, given by the square of the wave function (prior to integrating over a thin spherical shell a distance r from the nucleus).

- A measure of the size of an orbital is the most probable distance of the electron from the nucleus in that orbital. The most probable location of the electron is progressively farther from the nucleus in ns orbitals for larger n .
- Nonetheless, ***there is a finite probability density for finding the electron at the nucleus*** in both 2s and 3s orbitals.
- ✓ This happens because electrons in s orbitals have no angular momentum ($l = 0$), and thus can approach the nucleus along the radial direction.
- The ability of electrons in s orbitals to “penetrate” close to the nucleus has important consequences in the structure of many-electron atoms and molecules (see later).

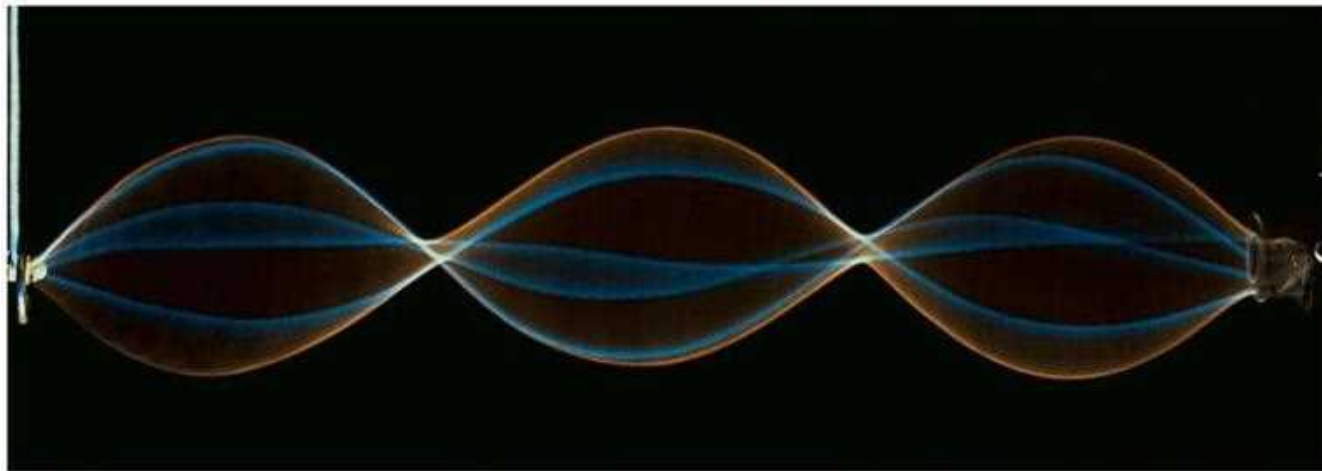
- Finally, note that an ns orbital has $n - 1$ radial nodes; a radial node is a spherical surface about the nucleus on which ψ and ψ^2 are 0.
- These spherical surfaces are the analogues of the nodal planes in the wave functions for a particle in a cubic box.
- The more the nodes in an orbital, the higher the energy of the corresponding quantum state of the atom. Just as for the particle in a box, the energies of orbitals increase as the number of nodes increases.
- Finally, we want to describe the ***size of the orbital***. What is meant by the size of an orbital? Strictly speaking, the wave function of an electron in an atom stretches out to infinity, so an atom has no clear boundary.
- ✓ We define the size of an atom as the extent of a “balloon skin” inside which 90% of the probability density of the electron is contained.

- Calculations show that spheres containing 90% of the probability density for an electron in the 1s, 2s, and 3s orbitals of the hydrogen atom have radii equal to 1.41 Å, 4.83 Å, and 10.29 Å, respectively.
- These results show that the size of an orbital increases with increasing quantum number n .
- A 3s orbital is larger than a 2s orbital, which, in turn, is larger than a 1s orbital.
- ✓ This is the quantum analog of the increase in radius of the Bohr orbits with increasing n .

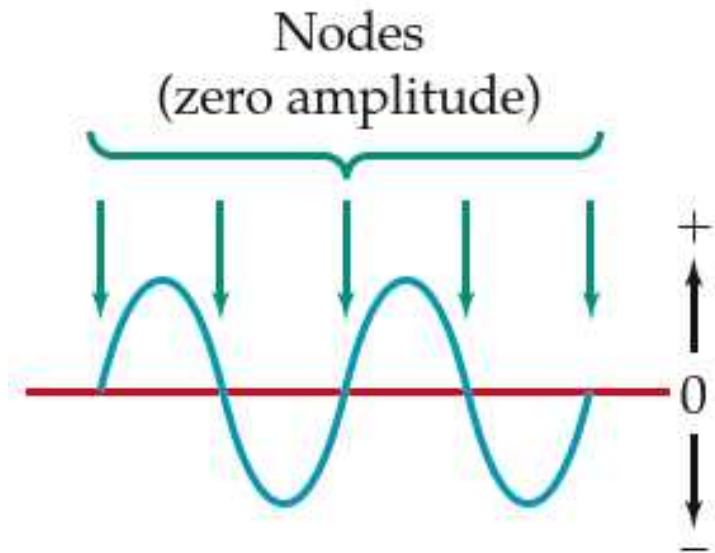
- Although all s orbitals are spherical, there are significant differences among the s orbitals in different shells.
- First, the size of the s orbital increases in successively higher shells, implying that an electron in an outer-shell s orbital is farther from the nucleus on average than an electron in an inner-shell s orbital and is therefore higher in energy.
- Second, the electron distribution in an outer-shell s orbital has more than one region of high probability. For example, *a $2s$ orbital is essentially a sphere within a sphere and has two regions of high probability, separated by **a surface of zero electron probability** called a **node**.*
- Similarly, a $3s$ orbital has three regions of high probability and two spherical nodes.

- The concept of ***an orbital node—a surface of zero electron probability separating regions of nonzero probability***—is difficult to grasp because it raises the question: How does an electron get from one region of the orbital to another if it can't be at the node?
- The question is misleading, though, because it assumes particle-like behavior for the electron rather than *the wavelike behavior that forms the basis of the quantum mechanical model*.
- In fact, nodes are an intrinsic property of all waves, from moving waves of water in the ocean to the stationary, or standing, wave generated by vibrating a rope or guitar string (Figure 2.11).

- A node simply corresponds to the zero-amplitude part of the wave. On either side of the node is a nonzero wave amplitude.
- Note that a wave has two phases—peaks above the zero line and troughs below—corresponding to different algebraic signs, + and -. Similarly, the different regions of 2s and 3s orbitals have different phases, + and -, as indicated in Figures.



When a rope is fixed at one end and vibrated rapidly at the other, a standing wave is generated.



The wave has two phases with different algebraic signs, + and -, separated by zero-amplitude regions, called *nodes*.

❖ **p Orbitals**

- Orbitals with angular quantum numbers different from 0 are not spherically symmetric.
- Interesting *angular effects arise from the quantization of angular momentum*.
- The angular wave function $Y_{lm}(\theta, \varphi)$ has separate lobes with positive and negative phase, with a node between them.
- There are $(2l + 1)$ projections of these angular momentum values along the z-axis.
- The three angular wave functions with $l = 1$, for which the allowed m values are -1, 0, and +1, lead to three orbitals (each called a p orbital) with the same shapes but different orientations in space.

➤ If we consider the wave functions with $n = 2$, the possible wave functions with $n = 2$ are:

➤ $2s$ $2p_0$ $2p_1$ $2p_{-1}$
 ➤ Ψ_{200} Ψ_{210} Ψ_{211} Ψ_{21-1}

$$\psi_{2s} = \frac{1}{\sqrt{\pi}} \left(\frac{z}{2a} \right)^{3/2} \left(1 - \frac{zr}{2a} \right) e^{-zr/2a}, \quad \psi_{2p_{-1}} = \frac{1}{8\sqrt{\pi}} \left(\frac{z}{a} \right)^{5/2} r e^{-zr/2a} \sin\theta e^{-i\phi},$$

$$\psi_{2p_0} = \frac{1}{\sqrt{\pi}} \left(\frac{z}{2a} \right)^{5/2} r e^{-zr/2a} \cos\theta, \quad \psi_{2p_1} = \frac{1}{8\sqrt{\pi}} \left(\frac{z}{a} \right)^{5/2} r e^{-zr/2a} \sin\theta e^{i\phi}.$$

➤ When $m_l = 0$, the angular wavefunction is real, and the shape of the orbital consists of two lobes that lie along the z coordinate axis. Because its lobes lie along the z -axis, the p_0 orbital is also known as the p_z orbital.

➤ The angular wave functions $Y_{11}(\theta, \phi)$ for $l = 1, m = 1$ and $Y_{1,-1}(\theta, \phi)$ for $l = 1, m = -1$ do not have a simple geometrical interpretation.

- Notice that in general the Spherical Harmonics are complex functions. Often, we are *interested in the directionality of the wave function*. Therefore, we construct linear combinations of Spherical Harmonics to represent orbitals.
- Any linear combination of degenerate eigenfunctions of energy E is also an eigenfunction of the Hamiltonian with the same eigenvalue E . Certain linear combinations of hydrogen-like wavefunctions generate real eigenfunctions. Therefore, their sum and their difference, which are also allowed solutions of the Schrödinger equation for the hydrogen atom, do have simple interpretations.
- For example, when $l = 1$,

$$\frac{1}{\sqrt{2}} (\psi_{n11} + \psi_{n1-1}) = R_{n1}(r) \sin\theta \cos\phi \equiv \psi_{P_{2x}},$$

$$\frac{1}{\sqrt{2}i} (\psi_{n11} - \psi_{n1-1}) = R_{n1}(r) \sin\theta \sin\phi \equiv \psi_{P_{2y}},$$

$$\psi_{210} \equiv \psi_{2P_z},$$
- are real and mutually orthogonal eigenfunctions.

- This process is also known as the *hybridization of atomic orbitals*. According to quantum theory, the hybrid orbitals must also be orthogonal to one another. These particular linear combinations ensure that all three p orbitals will have the same shape with their lobes pointing along the three orthogonal Cartesian axes.
- Function ψ_{2P_z} *is zero in the xy plane, positive above such plane, and negative below it.*
- Functions ψ_{2P_x} *and* ψ_{2P_y} *are zero at the zy and xz planes, respectively.*
- $\psi_{2P_{-1}}$ and ψ_{2P_1} are eigenfunctions of L^2 with eigenvalue $2\hbar^2$. However, since $\psi_{2P_{-1}}$ and ψ_{2P_1} are eigenfunctions of L_z with different eigenvalues (e.g., with eigenvalues \hbar and $-\hbar$, respectively), linear combinations ψ_{2P_x} , and ψ_{2P_y} , are eigenfunctions of L^2 but not eigenfunctions of L_z .
- The angular wave function $Y_{10}(\theta, \varphi)$ with the combination $l = 1, m = 0$ is called the angular portion of the p_0 orbital.

- When $m_l = 0$, the angular wavefunction is real, and the shape of the orbital consists of two lobes that lie along the z coordinate axis. Because its lobes lie along the z -axis, the p_0 orbital is also known as the p_z orbital.
- The wave function Y_{p_z} for the p_z orbital is proportional to $\cos \theta$. From the relation between spherical and Cartesian coordinates, you can see that $\cos \theta \propto z$; thus, the maximum probability density for this orbital (Figure 5.9b) is along the z -axis (where $\theta = 0$ or π).
- There is a node in the x - y plane (where $\theta = \pi/2$, so $\cos \theta = 0$) (Fig. 5.9a). This nodal plane is called an **angular node**; *the wave function changes sign across it*.
- The p_z orbital therefore points along the z -axis, with its positive phase (red in Fig. 5.9a) on the side of the x - y plane where the z -axis is positive and negative phase (blue in Fig. 5.9a) on the side where the z -axis is negative.

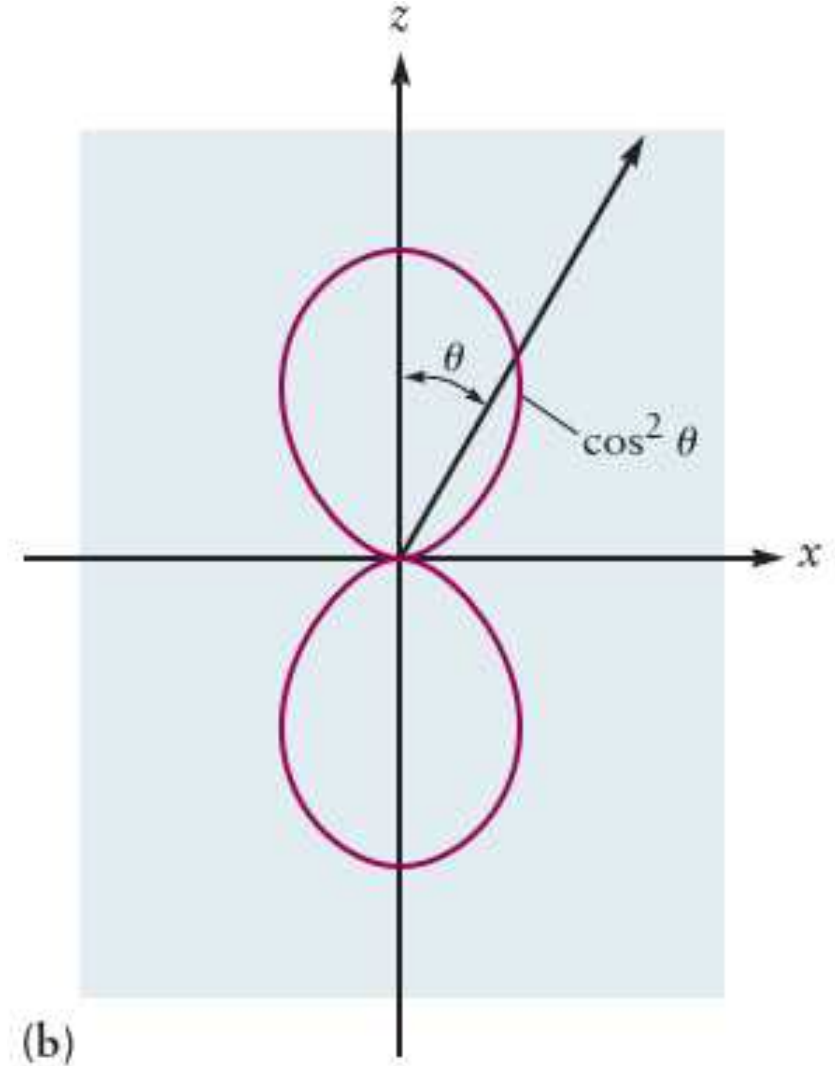
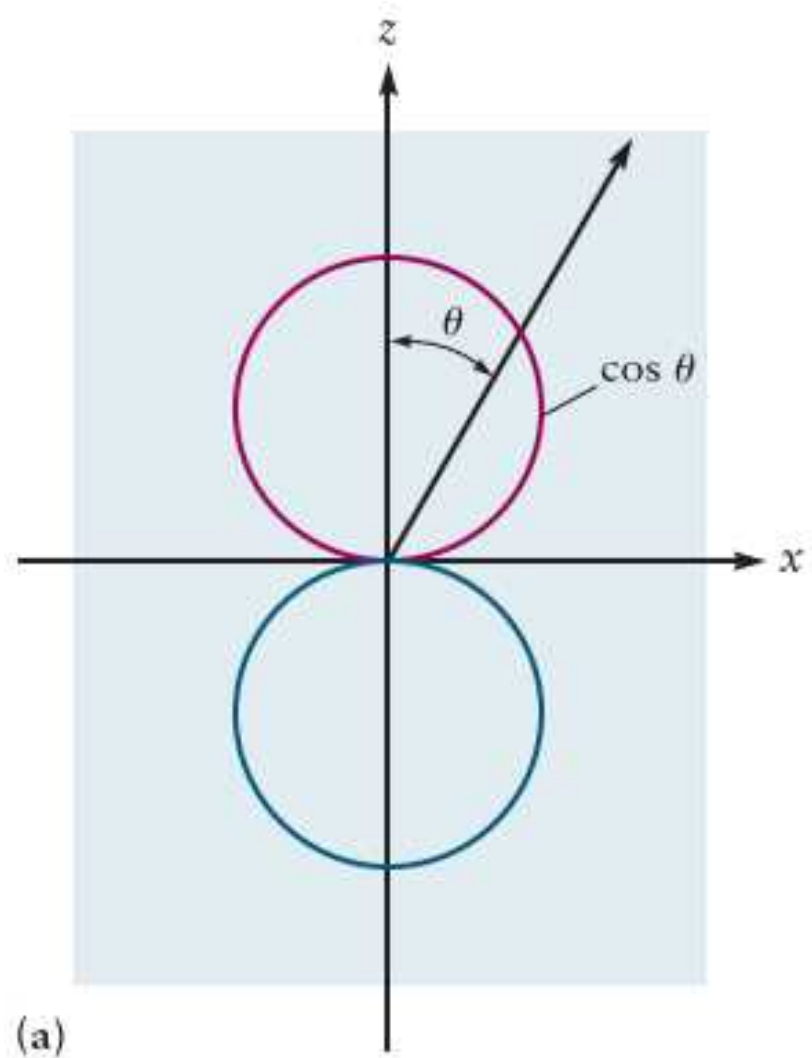


Figure 5.9 Two aspects of hydrogen p orbitals. (a) The angular wave function for the p_z orbital. The p_x and p_y orbitals are the same, but are oriented along the x - and y -axis, respectively. (b) The square of the angular wave function for the p_z orbital. Results for the p_x and p_y orbitals are the same, but are oriented along the x - and y -axis, respectively.

- As a rule, every orbital will exhibit l angular nodal surfaces, which can be either planar or conical in shape.
- Thus, all three of the p orbitals will have a single angular nodal plane. Likewise, each d orbital will have two angular nodal surfaces and each f orbital will have three.

$$2P_x = \frac{1}{\sqrt{2}} [Y_1^1 + Y_1^{-1}] = \sqrt{\frac{3}{4\pi}} \sin(\theta) \cos(\phi) ,$$

$$2P_y = \frac{1}{\sqrt{2}} \left[\frac{Y_1^1 - Y_1^{-1}}{i} \right] = \sqrt{\frac{3}{4\pi}} \sin(\theta) \sin(\phi) .$$

- A comparison of these expressions with Figure shows that Yp_x lies along the x -axis and Yp_y lies along the y -axis, but otherwise have the same shape as Yp_z . They have nodes at the y - z and x - z planes, respectively.

- The shapes of these orbitals are shown in Figure 4.4, where the orbital boundary indicates a 90% or greater probability of finding the electron in the enclosed region of space.

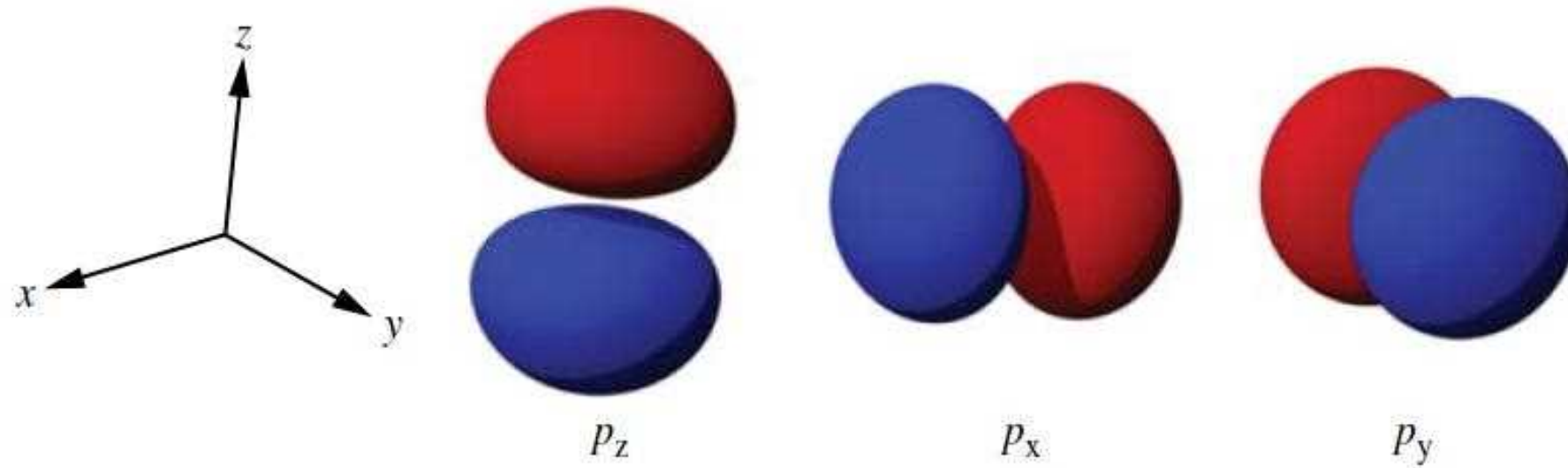
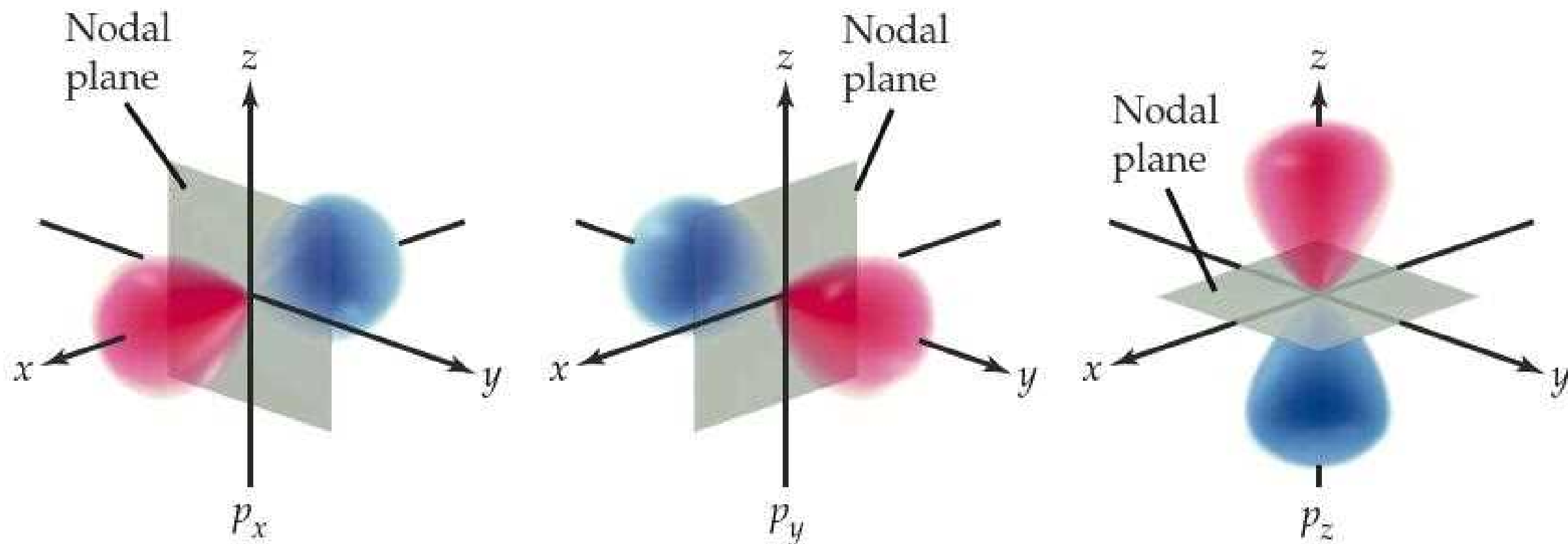


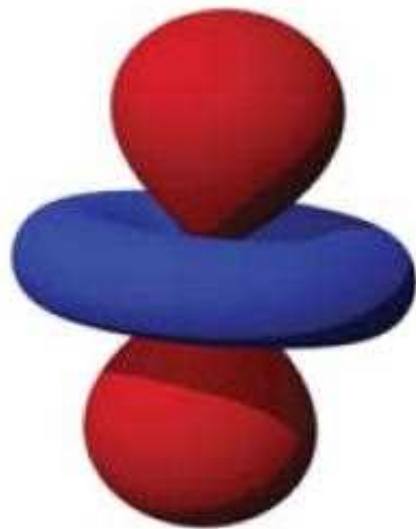
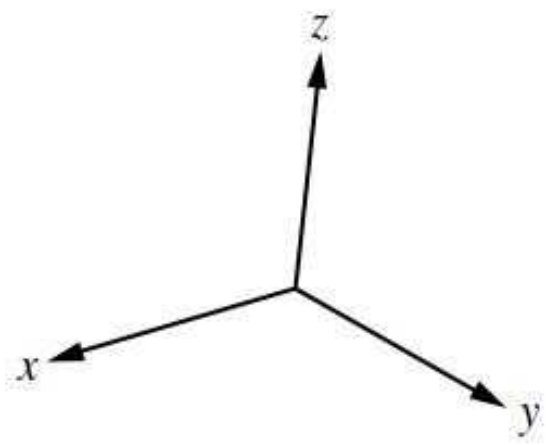
FIGURE 4.4. Shapes of the three p orbitals.

Each p orbital has two lobes of high electron probability separated by a nodal plane passing through the nucleus.



The **different colors** of the lobes represent different algebraic signs, analogous to the different phases of a wave.

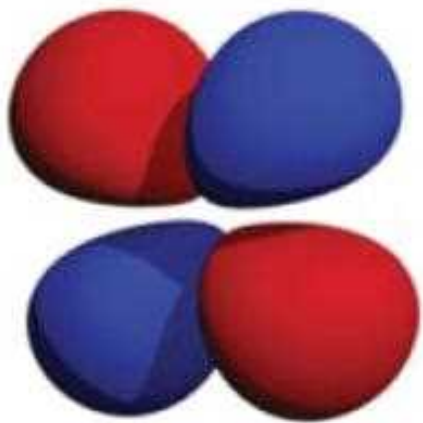
- The five different kinds of **d orbitals** are shown in Figure 4.6.
- When $m_l = 0$, the d_z^2 orbital results.
- This orbital has two lobes of the same sign pointing along the z-axis, with a donut-shaped lobe of the opposite sign in the xy plane.
- Notice that there are two conical nodes, each beginning at the origin and pointing in a different direction along the z-axis.
- When $|m_l| = 1$, the product Y^*Y yields a probability function containing two donuts centered on the z-axis, where one lies above the xy plane and the other lies beneath it.



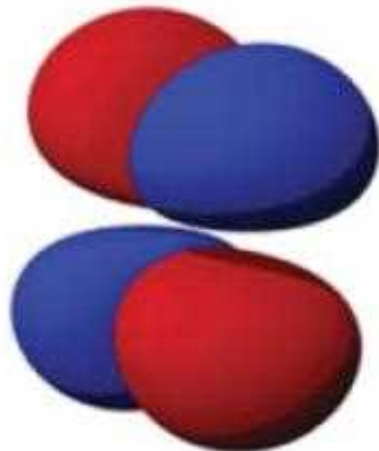
d_z^2



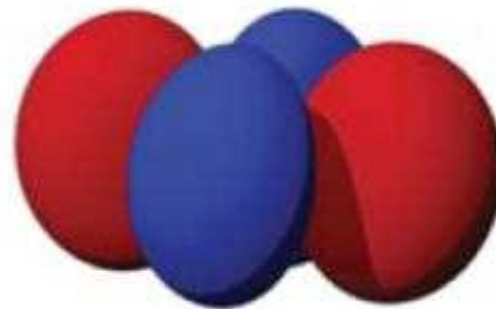
$d_{x^2-y^2}$



d_{xz}



d_{yz}



d_{xy}

FIGURE 4.6. Shapes of the five d orbitals.

- When $|m_l| = 2$, the product Y^*Y looks similar to a single hollow donut lying in the xy plane, as shown in Figure 4.7.
- Taking the positive and negative linear combinations of $Y(2,1)$ with $Y(2,-1)$ yields the d_{xz} and the d_{yz} orbitals shown in Figure 4.6. Both of these orbitals contain four lobes (as in a four-leaf clover) of alternating sign of the wave function and lying in the xz and yz planes, respectively. Each of the four lobes lies between the coordinate axes.
- Likewise, linear combinations of the $Y(2,2)$ and $Y(2,-2)$ wave functions yield the d_{xy} and $d_{x^2-y^2}$ orbitals shown in Figure 4.6. Both orbitals lie in the xy plane and have the same alternating four-leaf clover shape. However, the d_{xy} orbital has its lobes pointing between the coordinate axes, while the $d_{x^2-y^2}$ orbital's lobes lie squarely on the coordinate axes.
- The names and shapes of the five d-orbitals are especially important in the field of coordination chemistry.

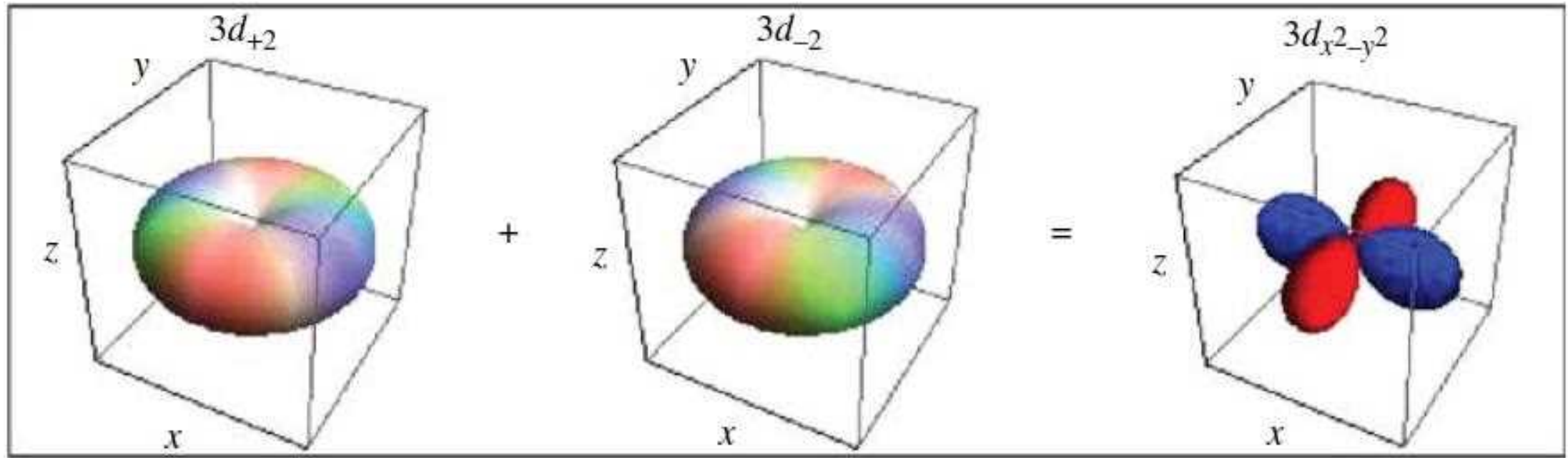


FIGURE 4.7. Illustration of how a linear combination of the $3d_{+2}$ and $3d_{-2}$ orbitals can be used to construct the more familiar $3d_{x^2-y^2}$ orbital. [Images by Lisa M. Goss. Used by permission.]

- The shapes of the seven f orbitals are shown in Figure 4.8.
- When $m_l = 0$, the f_z^3 orbital results, which has lobes of opposite sign along the z -axis and two donuts encircling that axis that also have opposite signs.
- For $|m_l| = 1$, the positive and negative linear combinations $Y(3,1) \pm Y(3,-1)$ yield the f_{xz}^2 and f_{yz}^2 orbitals, which have six lobes each lying in the xz and yz planes, respectively.
- For $|m_l| = 2$, the two hybrids are the f_{xyz} and $f_{z(x^2-y^2)}$ orbitals.
- Both of these orbitals have eight lobes forming a cubic shape, with the former lying between the x - and y -axes and the latter lying on the coordinate axes.
- Lastly, for $|m_l| = 3$, the hybrid orbitals are the $f_x(x^2-3y^2)$ and $f_y(3x^2-y^2)$ orbitals, which have six lobes each lying in the xy plane.
- The shapes of the seven f -orbitals are typically unimportant in chemical bonding and do not need to be memorized.

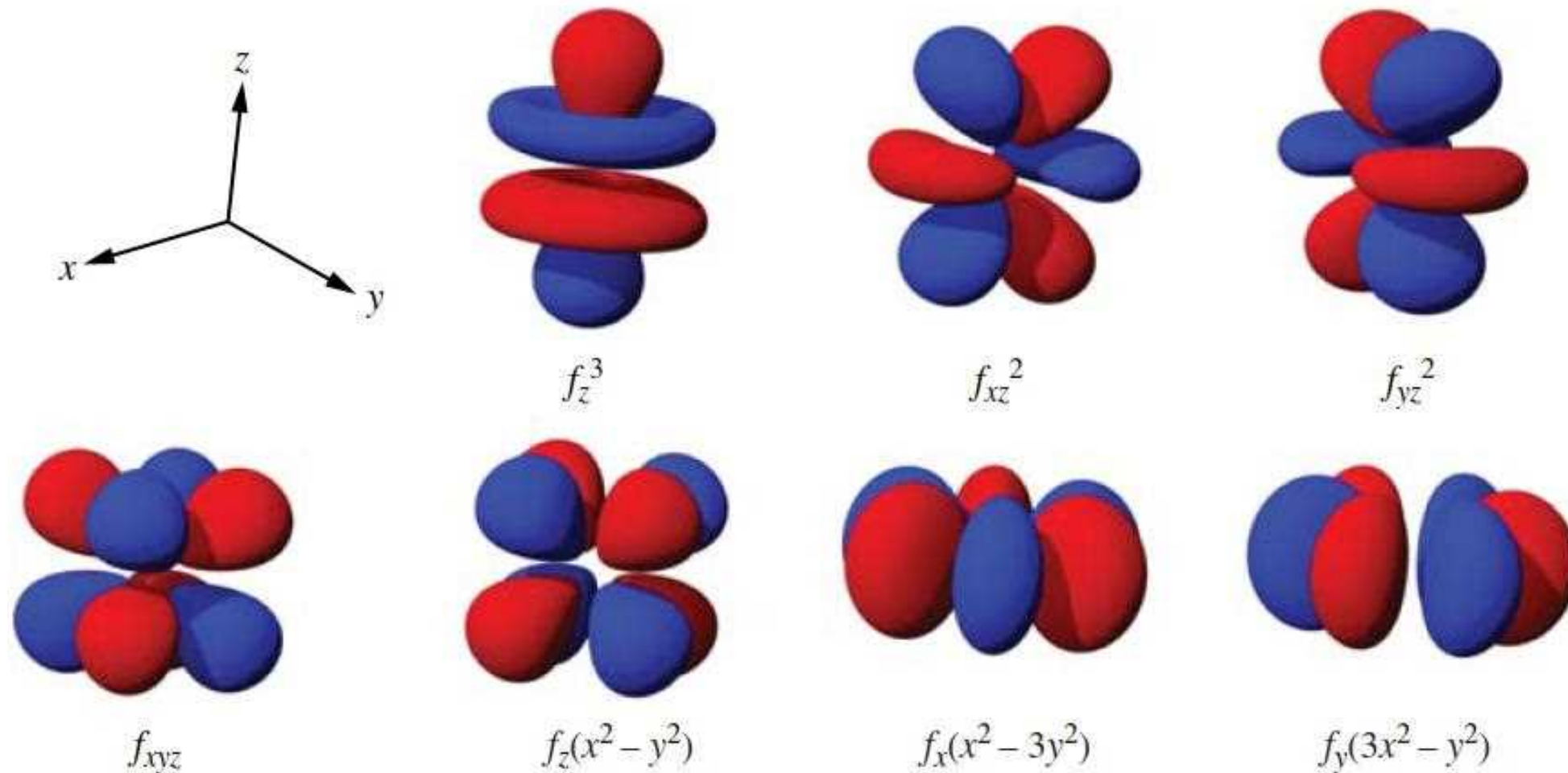


FIGURE 4.8. Shapes of the seven f orbitals, with $|m_l|$ increasing from left to right in the diagram.

□ We summarize the *important features of orbital shapes and sizes* as follows:

- 1. For a given value of l , an increase in n leads to an increase in the average distance of the electron from the nucleus, and therefore in the size of the orbital.
- 2. The radial function $R_{n,l}$ has **$(n - l - 1)$ radial nodes** and the angular part $Y_{l,m}$ has **l angular nodes**, giving a *total* of $(n - 1)$ nodes.
- An angular node appears as a nodal plane in plots of p orbitals. The value of the radial or angular part of the wave function changes sign as you cross a radial or angular node respectively. For a one-electron atom or ion, the energy depends only on the number of nodes – that is, on n but not on l , or m . **The energy increases as the number of nodes increases.**
- 3. The radial functions $R_{n,l}$ grow in size with n because the exponential factor, $e^{-r/n}$, decays more slowly as n increases. Since the radial functions $R_{n,l}$ have a r^l factor, they vanish at the nucleus ($r = 0$) unless $l = 0$.

It follows that only s -type radial functions ($l = 0$) have a non-zero value at the nucleus. As r approaches 0, $\psi(r, \theta, \varphi)$ vanishes for all orbitals except s orbitals; thus, only an electron in an s orbital can “*penetrate to the nucleus*,” that is, have a finite probability density right at the nucleus.

- The s and p orbital shapes are important in understanding the chemistry of all the elements. The d orbital shapes are important in transition metal and organometallic chemistry. Lanthanide and actinide chemists need the shapes of f orbitals.

❑ Several features common to all of the atomic orbitals are as follows:

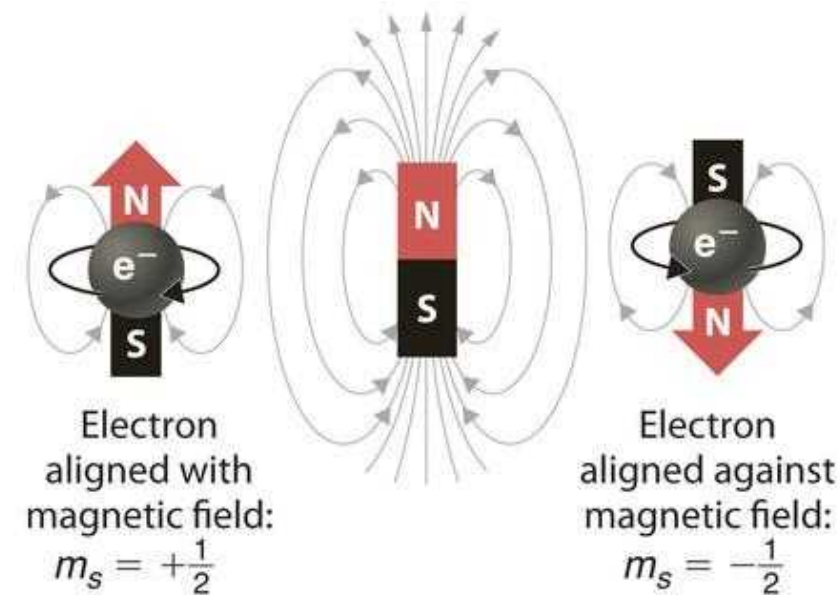
- • For any given value of l , the summation of the electron density probabilities for the complete set of orbitals will be a sphere. This is known as Unsöld's theorem. Thus, for example, the sum of the electron density for the $2p_x$, $2p_y$, and $2p_z$ orbitals is a sphere, as is the case for the lone $2s$ orbital.
- • The absolute value of m_l is the number of angular nodes that present themselves when the orbital is viewed from either direction along the z -axis.
- ✓ Thus, a p_z orbital ($m_l = 0$), when viewed from the “top” of the z -axis, will present with a positive lobe. The negative lobe that lies beneath this will not be observed from this vantage point.
- However, the p_x and p_y orbitals ($|m_l| = 1$) will each present one angular nodal plane when viewed along the z -axis.

- • The *symmetry of the atomic orbitals* with respect to *inversion* alternates in a regular pattern. The inversion operation means that if one takes any point (x, y, z) back through the origin an equal distance to point $(-x, -y, -z)$, the probability density will be identical in magnitude and sign. All *s* and *d* orbitals are symmetric (or *gerade*) with respect to inversion. All *p* and *f* orbitals are antisymmetric (or *ungerade*) with respect to inversion (they have the opposite sign). More generally, whenever l is odd, the atomic orbitals will be *gerade* and whenever l is even, they will be *ungerade*.
- • Both the number of nodal planes through the nucleus and the overall geometric complexity of the orbitals increase with the l quantum number of the subshell: An *s* orbital has one lobe and no nodal plane through the nucleus, a *p* orbital has two lobes and one nodal plane, and a *d* orbital has four lobes and two nodal planes. The seven *f* orbitals are more complex still, having eight lobes of maximum electron probability separated by three nodal planes through the nucleus.

❑ Electron Spin: The Fourth Quantum Number

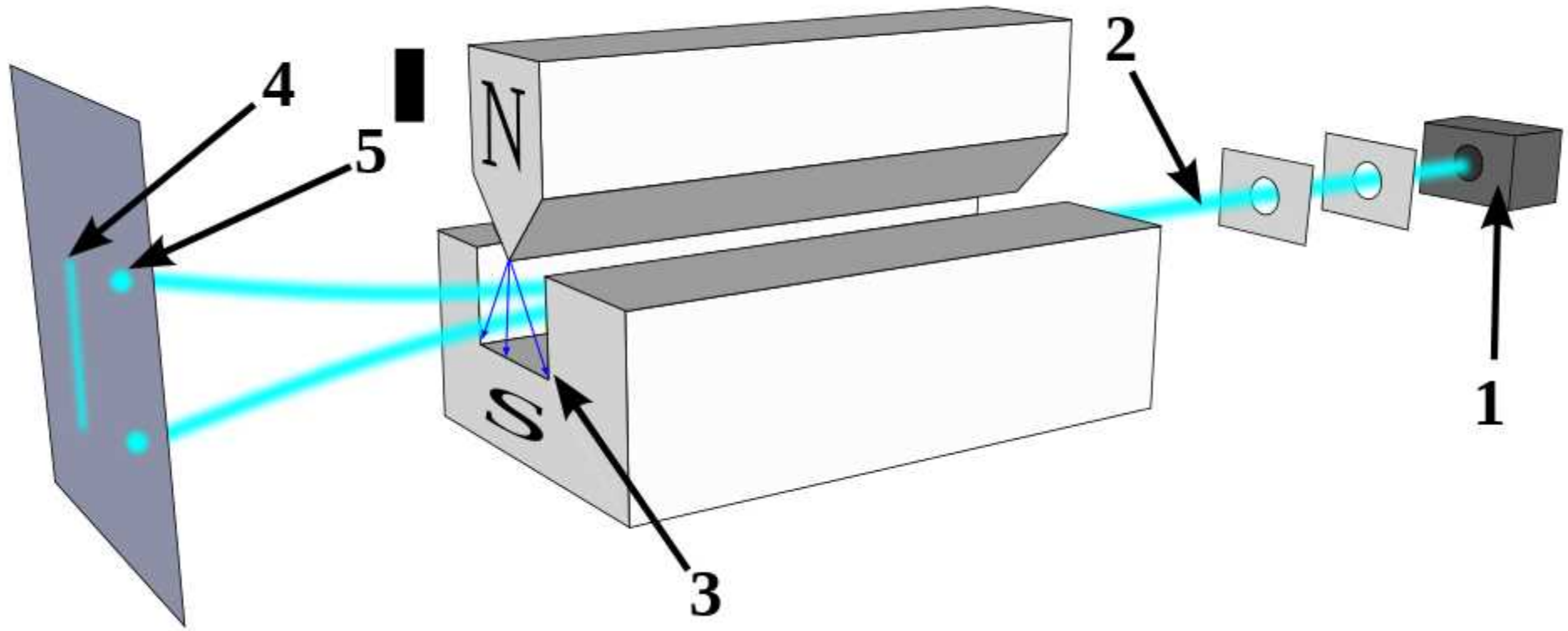
- When scientists analyzed the emission and absorption spectra of the elements more closely, they saw that for elements having more than one electron, nearly all the lines in the spectra were actually pairs of very closely spaced lines. Because each line represents an energy level available to electrons in the atom, there are twice as many energy levels available as would be predicted solely based on the quantum numbers n , l , and m_l .
- Scientists also discovered that applying a magnetic field caused the lines in the pairs to split farther apart.
- Following Pauli's proposal of a new quantum number to explain atomic spectra, Ralph Kronig, George Uhlenbeck, and Samuel Goudsmit introduced an intrinsic angular momentum called spin for elementary particles like electrons. A simple picture of electron spin is to think of it as arising from the spinning of the electron about its own axis. They proposed that the spectral splittings were caused by an electron spinning about its axis.

- Spin has to be grafted onto non-relativistic quantum mechanics but arises naturally in relativistic quantum mechanics.
- When an electrically charged object spins, it produces a magnetic moment parallel to the axis of rotation, making it behave like a magnet. Although the electron cannot be viewed solely as a particle, spinning or otherwise, it is indisputable that it does have a magnetic moment. ***This magnetic moment is called electron spin.*** In an external magnetic field, the electron has two possible orientations (Figure 6.7.2).
- These are described by a fourth quantum number (m_s), which for any electron can have only two possible values, designated $+\frac{1}{2}$ (up) and $-\frac{1}{2}$ (down) to indicate that the two orientations are opposites; the subscript s is for spin.
- An electron behaves like a magnet that has one of two possible orientations, aligned either with the magnetic field or against it.



❑ ELECTRON SPIN AND THE PAULI PRINCIPLE

- The concept of *electron spin* was first postulated by Goudsmit and Uhlenbeck in 1925 in order to explain the fine structure (or splitting) of the line spectra of several of the alkali metals.
- The *Stern–Gerlach experiment*, depicted in Figure 4.13, provided the first experimental confirmation for the quantization of electron spin.
- In their 1922 experiment, Otto Stern and Walther Gerlach showed that a beam of silver atoms could be split into two beams by passing it through an inhomogeneous magnetic field.
- In addition to electrons, many nuclei also exhibit spin, forming the basis of nuclear magnetic resonance (NMR) and electron spin resonance (ESR) analytical techniques.



Ground-state Hydrogen atoms travel through an inhomogeneous magnetic field and are deflected up or down depending on their spin (which is based on the electron spin). (1) the hydrogen atom source, (2) collimated atomic beam, (3) inhomogeneous magnetic field, (4) the observed bifurcation of the beam (5) the predicted spread for a classical atom with no intrinsic electron spin.

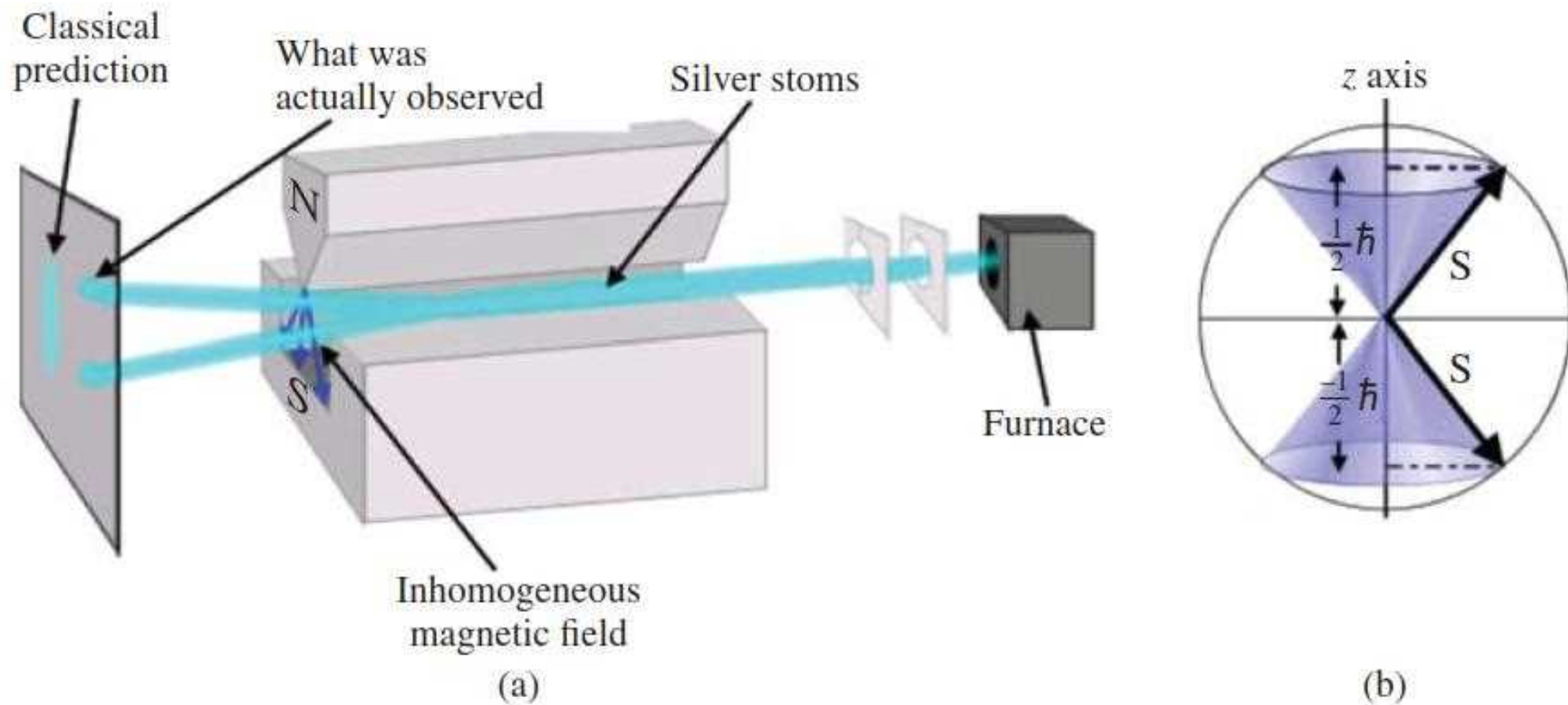


FIGURE 4.13. (a,b) Schematic diagram of the Stern–Gerlach experiment, showing how a beam of Ag atoms can be split by an inhomogeneous magnetic field into two different trajectories as a result of the different spin states they possess.

- You may recall from classical physics that a small bar magnet will rotate to orient itself in the presence of an external magnetic field.
- If the magnetic field changes strength along a particular direction, then a force will be exerted on the bar magnet that will cause it to move in the direction of the changing field, and not just rotate to a new direction.
- If the *magnetic dipole moments of the silver atoms were **randomly** oriented* in space (as predicted by classical physics), then the *beam would be **smeared** out* at the detector to reflect *all possible orientations of the magnetic moment*.
- That the ***original beam is split into only two well-defined beams*** in this experiment ***demonstrates*** the unexpected fact that ***the orientation of the magnetic moment of the electron is quantized***.
- We can use a magnetic field to inquire into the nature of the spin angular momentum as well.

- The beam of hydrogen atoms was split into just **two components** in the atomic beam experiment. This means that the component of the electron's spin magnetic moment (and spin angular momentum) along a given axis may have only one of two possible values; **the component may be aligned with the field and hence be attracted, or it may be opposed to the field and be repelled.**
- The electron's spin magnetic moment has been detected in many different kinds of experiments and the results are remarkable in that only two components of constant magnitude are ever observed. The electron is always either repelled by the field or attracted to it. This implies that the magnitude of the spin angular momentum for a single electron may have *only one possible value*.

□ Spin Angular Momentum

- Since the number of possible values for the component of a given amount of angular momentum of any type in quantum mechanics is $(2l + 1)$, in analogy with the rotational angular momentum, the square of the spin angular momentum is $\langle S^2 \rangle = s(s + 1)\hbar^2$.
- Thus, an electron has $2s + 1 = 2$ degenerate spin states, where $s = 1/2$ for electrons.
- Like L_z , the z component of the spin angular momentum $\langle S_z \rangle$ is restricted to the values $m_s\hbar$ with $m_s = -s, -s + 1, \dots, s - 1, s$.
- Therefore, an electron has $2s + 1 = 2$ degenerate spin states, namely $m_s = 1/2$ and $m_s = -1/2$, sometimes denoted m and k , respectively. These two spin states are described by the spin functions α and β , respectively. These functions depend on a notional spin variable σ and form an orthonormal pair: $\int \alpha^2 d\sigma = 1, \int \beta^2 d\sigma = 1$, and $\int \alpha\beta d\sigma = 0$.

- Consideration of electron spin leads to each of the hydrogen atom orbitals $\psi_{n,l,m}$ being turned into two degenerate spin orbitals $\psi_{n,l,m}\alpha$ and $\psi_{n,l,m}\beta$. Then, the *degeneracy of the hydrogen atom energy levels* doubles to $2n^2$. An orbital times a spin function is called a **spin orbital**.
- The main difference between the angular momenta S , and L , is that S can have half-integer quantum numbers. Remember that the quantization rules established by the commutation relations did not rule out the possibility of half-integer values. However, such possibility was ruled out by the periodicity requirement, $Y(\theta + 2\pi) = Y(\theta)$, associated with the eigenfunctions of L_z and L^2 . Since the spin eigenfunctions (i.e., the spinors) do not depend on spatial coordinates, they do not have to satisfy any periodicity condition and therefore their eigenvalues can be half-integer.
- $s = 1/2$ for protons and neutrons also. Photons have $s = 1$.
- Particles with half-integer spin s are called **fermions** after Enrico Fermi, whereas those with integer spin are called **bosons** after Satyendra Bose.

- It should be stressed that the ***splitting*** of the beam of hydrogen atoms into only two components is again evidence of ***quantization***. If the atomic magnets (the hydrogen atoms) behaved according to classical mechanics, then the effect of the magnetic field would be simply to broaden the beam. The orientations of the atomic magnets would be random when they first entered the field of the magnet and classically the individual atomic magnets could be aligned at any and all angles with respect to the field, giving all possible components of the spin magnetic moment along the direction of the field. The inhomogeneous field would then exert a force proportional to the magnitude of the component, and the beam would broaden but not split.
- A given ***electron may exhibit only one of two possible components***; it may be aligned with the field or against it. Hence ***only one quantum number is required*** to describe *completely the spin properties of a single electron*.

➤ Since the spin magnetic moment is an intrinsic property of the electron, even a beam of free electrons should be split into two components in a magnetic field. However, the charge possessed by the free electron also interacts with the magnetic field and the much smaller magnetic-magnetic interaction is masked by the usual deflection of a charge species in a magnetic field. By employing a neutral atom, the complications of the electronic charge may be avoided. The original experiment was performed on a beam of silver atoms by Stern and Gerlach in 1921. (We shall see shortly that the electrons in a silver atom do not possess any orbital angular momentum.)

- The result of this experiment is explained by introducing a **fourth quantum number**, m_s , which can take on two values, conventionally chosen to be $+1/2$ and $-1/2$. For historical reasons, the fourth quantum number is referred to as the ***spin quantum number***. When $m_s = +1/2$, the electron spin is said to be “up,” and when $m_s = -1/2$, the spin is “down.”
- Schrödinger’s theory did not account for spin, but it emerged naturally when the British physicist Paul Dirac found a way (in 1928) to combine Einstein’s theory of relativity with Schrödinger’s approach.
- A *fourth quantum number*, called the ***spin quantum number***, is required when the relativistic effects of electronic motion are taken into consideration.
- In 1928, Paul Dirac developed a relativistic theory of quantum mechanics from which the concept of spin arose naturally.
- The inclusion of a *fourth variable (time)* required the *presence of a fourth quantum number*.

- According to Dirac's derivation, an electron possesses both orbital (L) and spin (S) angular momentum.
- The total angular momentum (J) is a linear combination of the two, as shown in Equation (4.13).

$$\hat{J} = \hat{L} + \hat{S} = -i\hbar \frac{\partial}{\partial \phi} \pm \frac{\hbar}{2} \quad (4.13)$$

- The spin angular momentum vector S can take values of $\pm m_s \hbar/2$, where m_s can take values of **+1/2** (α) or $-1/2$ (β), depending on whether it aligns **against** or **with** the external magnetic field, respectively.

- The usual classical picture of electron spin, where the electron can be considered as a top spinning on its axis either in the clockwise or the counterclockwise direction, is only useful as a conceptual tool. In actuality, *spin is strictly a quantum mechanical phenomenon* and it has no classical analogy.
- The spin quantum number arises from relativistic effects that are not included in the Schrödinger equation.
- For most practical purposes in chemistry, it is sufficient simply to solve the ordinary Schrödinger equation, and then associate with each electron a spin quantum number $m_s = +1/2$ or $-1/2$ which *does not affect the spatial probability distribution of the electron*.
- Including the **spin doubles the number of allowed quantum states with principal quantum number n , from n^2 to $2 n^2$** .
- This fact will assume considerable importance when considering the many-electron atoms in the next section.

➤ A total of *four quantum numbers* is required to specify completely the state of an electron when it is bound to an atom. The **quantum numbers n , l and m** determine its energy, **orbital angular momentum and its component of orbital angular momentum**. The ***fourth quantum number, the spin quantum number, summarizes all that can be known about the spin angular momentum of the electron***. This final quantum number may have only one of two possible values corresponding to the magnetic moment component being (a) aligned with the field or (b) opposed to it.

Subshell name	Name source	Value of ' <i>l</i> '	Value of ' <i>m</i> ' (0 to $\pm l$)	Number of orbital ($2l+1$)	Electrons holding capacity $2(2l+1)$
s	Sharp	0	0	1	2
p	Principal	1	-1, 0, +1	3	6
d	Diffuse	2	-2, -1, 0, +1, +2	5	10
f	Fundamental	3	-3, -2, -1, 0, +1, +2, +3	7	14

❑ Effects of nuclear charge

- The basic shapes of orbitals are unchanged by changes in the nuclear charge, although their extensions into space depend inversely on the value of Z .
- Fig. 2.13 shows the radial density curve for the 1s orbital of *helium-like* species with different values of the nuclear charge.

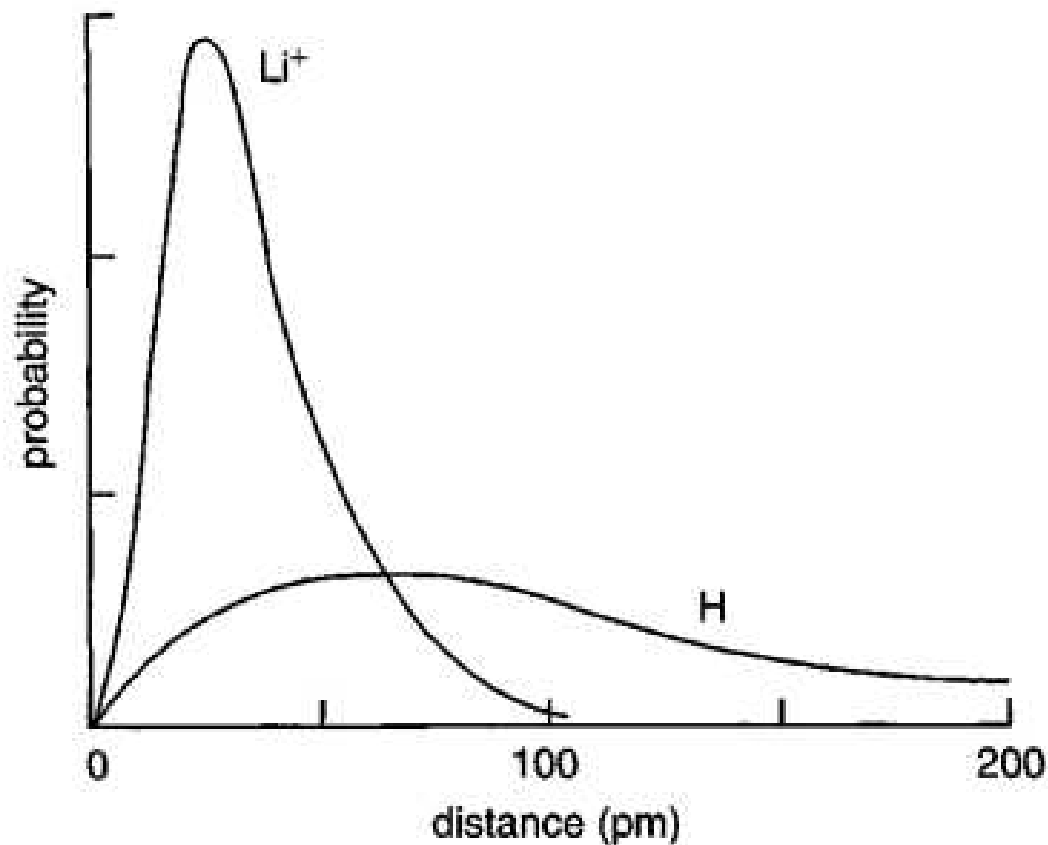


FIG. 2.13 Radial density curves for ions containing two electrons and with different nuclear charges.

This plot for isoelectronic ions illustrates the ***effect of increasing the nuclear charge*** from $Z = 1$ to $Z = 3$ on the spatial distribution of the electron probability density.

- The radius of the electron cloud around an atom is the resultant of this contraction of the charge cloud with increasing Z , and the fact that orbitals further and further out from the nucleus are being occupied as the atomic number rises.
- There is a general increase in atomic size as Z increases, but this change occurs in a very irregular manner (compare the plot of atomic radius against atomic number).
- The greatest jumps in radius come when the outermost electron starts to fill the s level of a new quantum shell and there are less sharp increases when any new level starts to be occupied and when spin-pairing occurs at p^4 and d^6 configurations.

❑ POLYELECTRONIC ATOMS: MANY-ELECTRON ATOMS

- A neutral atom other than a hydrogen atom has more than one electron and is known as a many-electron atom.
- In the next sections, we build on what we have learned about the hydrogen atom to see how the presence of more than one electron affects the energies of atomic orbitals.
- The resulting electronic structures are the key to the periodic properties of the elements and the abilities of atoms to form chemical bonds. This material therefore underlies almost every aspect of chemistry.

❖ MANY-ELECTRON ATOMS: Orbital Energies

- The *electrons in a many-electron atom occupy orbitals like those of hydrogen.*
- However, ***the energies of these orbitals are not the same*** as those for a hydrogen atom.
- The *nucleus of a many-electron atom is more highly charged* than the hydrogen nucleus, and *the greater charge attracts electrons more strongly and hence lowers their energy.*
- However, ***the electrons also repel one another***; this *repulsion opposes the nuclear attraction and raises the energies of the orbitals.*

- In a helium atom, for instance, with two electrons, the charge of the nucleus is $2e$ and the total potential energy is given by three terms:

$$V = \underbrace{-\frac{2e^2}{4\pi\epsilon_0 r_1}}_{\text{Attraction of electron 1 to the nucleus}} \underbrace{-\frac{2e^2}{4\pi\epsilon_0 r_2}}_{\text{Attraction of electron 2 to the nucleus}} + \underbrace{\frac{e^2}{4\pi\epsilon_0 r_{12}}}_{\text{Repulsion between the two electrons}}$$

- where r_1 is the distance of electron 1 from the nucleus, r_2 is the distance of electron 2 from the nucleus, and r_{12} is the distance between the two electrons.
- The two terms with negative signs (indicating that the potential energy falls as r_1 or r_2 decreases when either electron gets closer to the nucleus) represent the attractions between the nucleus and the two electrons. The term with a positive sign (indicating an increase in energy as r_{12} decreases) represents the repulsion between the two electrons.

- The Schrödinger equation based on this potential energy is impossibly difficult to solve exactly, but highly accurate numerical solutions can be obtained by using computers.
- The hydrogen atom, with one electron, has **no electron–electron repulsions** and all the orbitals of a given shell are ***degenerate***. For instance, the 2s-orbital and all three 2p-orbitals have the same energy.
- When dealing with many-electron atoms, we have to ***consider spin and electron-electron interaction***.
- By introducing the electron-electron interaction the hydron-like energy levels split reducing the degeneracy.
- In many-electron atoms, the results of spectroscopic experiments and calculations show that electron–electron repulsions cause the energy of a 2p-orbital to be higher than that of a 2s-orbital.

- Similarly, in the $n = 3$ shell, the three 3p-orbitals lie higher than the 3s-orbital, and the five 3d-orbitals lie higher still.
- ***How can we explain these energy differences?***
- As well as being attracted to the nucleus, each electron in a many-electron atom is repelled by the other electrons present.
- As a result, it is less tightly bound to the nucleus than it would be if those other electrons were absent.
- We say that each electron is ***shielded*** from the full attraction of the nucleus by the other electrons in the atom.
- The shielding effectively reduces the pull of the nucleus on an electron. The ***effective nuclear charge***, Z_{eff} , experienced by the electron is always less than the actual nuclear charge, Ze , because the electron–electron repulsions work against the pull of the nucleus.

- A very *approximate* form of the energy of an electron in a many-electron atom is a version of hydrogen energy expression in which the true atomic number is replaced by the effective atomic number:

$$E_n = -\frac{Z_{\text{eff}}^2 h\mathcal{R}}{n^2}$$

$$V_n^{\text{eff}}(r) \approx -\frac{Z_{\text{eff}}(n)e^2}{r}$$

- Note that the other electrons do not “block” the influence of the nucleus; they simply provide additional repulsive coulombic interactions that partly counteract the pull of the nucleus.
- For example, the pull of the nucleus on an electron in the helium atom is less than its charge of +2e would exert but greater than the net charge of +e that we would expect if each electron balanced one positive charge exactly.

- An s-electron of any shell can be found very close to the nucleus (remember that ψ^2 for an s-orbital is nonzero at the nucleus), and so we say that it can penetrate through the inner shells.
- A p-electron penetrates much less because its orbital angular momentum prevents it from approaching close to the nucleus.
- We have seen that its wavefunction vanishes at the nucleus, and so there is zero probability density for finding a p-electron there.
- Because a p-electron penetrates less than an s-electron through the inner shells of the atom, it is more effectively shielded from the nucleus and hence experiences a smaller effective nuclear charge than an s-electron does.
- In other words, an s-electron is bound more tightly than a p-electron and has a slightly lower (more negative) energy.

- A *d*-electron is bound less tightly than a *p*-electron of the same shell because its orbital angular momentum is higher and it is therefore even less able to approach the nucleus closely.
- ✓ That is, *d*-electrons are higher in energy than *p*-electrons of the same shell, which are in turn higher in energy than *s*-electrons of that shell.
- ***In a many-electron atom, because of the effects of penetration and shielding, the order of energies of orbitals in a given shell is $s < p < d < f$.***
- ***The effects of penetration and shielding can be large.*** A 4*s*-electron generally has much lower energy than that of a 4*p*- or 4*d*-electron; *it may even have lower energy than that of a 3*d*-electron of the same atom.*
- The precise ordering of orbitals depends on the number of electrons in the atom, as we shall see in the next section.

- Still each level is $(2l + 1)$ **degenerate** and each level can accommodate two electrons. But these electrons have to satisfy Pauli exclusion principle which stipulates that *no two electrons can have the same quantum numbers n , l , m_l , and m_s .*
- ✓ For example, we consider 22 electrons. These electrons are accommodated as:
- ✓ $(1s)^2 (2s)^2 (2p)^6 (3s)^2 (3p)^6 (3d)^4$.
- ✓ But the four d-electrons have several possibilities since the level is 5-fold degenerate.
- For **multiple electrons** we usually *consider the total atoms spin, orbital angular momentum and total angular momentum*

$$\vec{L} = \sum_{i=1}^n \vec{L}_i$$

$$\vec{S} = \sum_{i=1}^n \vec{S}_i$$

$$\vec{J} = \vec{L} + \vec{S},$$

with

$$|J| = \{|\vec{L} + \vec{S}|, |\vec{L} + \vec{S}| - 1, \dots, |\vec{L}| - |\vec{S}|\}$$

With this definitions the atomic notation

$$^{2S+1}L_J$$

is used. In order to accommodate these electrons, we follow **Hund's rules**.

Hund's rules:

- 1) - The state with the largest value of total S is the most stable.
- 2) - If total S is the same, the largest total L is the most stable.
- 3) - If S and L are the same,
 - (a) *subshell less than half full* with the *smallest J* is the most stable.
 - (b) On the other hand, *subshell half or more than half full* with *largest J* is the most stable.

❖ **The Pauli Exclusion Principle**

- The consequences of the spin quantum number, when applied to the problem of the electronic structure of atoms, are not immediately obvious.
- The small magnitude of the electron's magnetic moment does not directly affect the energy of the electron to any significant degree.
- To see just how the spin of the electron does influence the problem, let us reconsider our atomic orbital model in light of this new degree of freedom for the electron. In particular, let us reconsider those instances in which our model failed to account for the observations.

- If a beam of helium atoms is passed through a magnetic field, no splitting and no deflection are observed. The helium atom, unlike the hydrogen atom is not magnetic.
- We could account for the absence of a magnetic moment for helium if we assumed that of the two electrons in the helium 1s orbital, one had its magnetic moment component up (\uparrow) and the other down (\downarrow).
- ✓ The two components would then cancel and there would be no resultant magnetic effect.
- Our complete description of the electronic configuration of the helium atom would be $1s^2(\uparrow\downarrow)$, i.e., both electrons have $n = 1$, $l = 0$, $m = 0$ and one has a spin (\uparrow) and the other a spin (\downarrow).
- You may wonder why the states of helium corresponding to the configurations $1s^2(\uparrow\uparrow)$ or $1s^2(\downarrow\downarrow)$ are not observed.
- These states should exhibit twice the magnetism possessed by a hydrogen atom. They are, however not found to occur.

- What about the excited states of the helium atom?
- An **excited state** results when one electron is raised in energy to an orbital with a higher n value. The electrons are thus in different orbitals.
- The spin assignments for an excited configuration can be made in more than one way and are such as to predict the occurrence of both magnetic and non-magnetic helium.
- For example, the configuration $1s^1 2s^1$ could be $1s^1(\uparrow) 2s^1(\downarrow)$ and be **nonmagnetic** or it could equally well be $1s^1(\downarrow) 2s^1(\downarrow)$ or $1s^1(\uparrow) 2s^1(\uparrow)$ and be **magnetic**.
- **Both** the magnetic and non-magnetic forms are indeed found to occur for helium in an excited state.
- There are in fact two kinds of excited helium atoms, those which are **non-magnetic** and those which are **magnetic**.

- Care must be exercised in the use of the abbreviated notation $1s^1(\uparrow)2s^1(\downarrow)$ to indicate the configuration and spin of a many-electron atom.
- ✓ In the present example, all we mean to imply is that the total component of the spin is zero. We do not imply that the electron in the 1s orbital necessarily has a spin "up" and that in the 2s orbital a spin "down."
- ✓ The situation could equally well be described by the notation $1s^1(\downarrow)2s^1(\uparrow)$.
- There is no experimental method by which we can distinguish between electrons in an atom, or, for that matter, determine any property of an individual electron in a many-electron system.
- Only the total magnetic moment, or total angular momentum, may be determined experimentally.

- If the two forms of helium possess different energies even though they have the same orbital configuration (we shall see why this should be so later) then we have an explanation for the previously noted discrepancy that helium exhibits twice the number of line spectra as does hydrogen.
- For every set of lines in the spectrum which arises from the transition of the electron from the configurations $1s^1(\uparrow)np^1(\downarrow)$ to the configuration $1s^1(\uparrow)2s^1(\downarrow)$ for example, there will be another set of lines due to transitions from $1s^1(\uparrow)np^1(\downarrow)$ to $1s^1(\uparrow)2s^1(\downarrow)$.
- The study of the magnetic properties of the ground and excited states of helium is sufficient to point out a general principle.
- For the ground state of helium, in which both electrons are in the same atomic orbital, ***only the non-magnetic form exists***.
- This would imply that when two electrons are in the same atomic orbital their spins must be paired, that is, one up (\uparrow) and one down (\downarrow).

- This is ***an experimental fact*** because helium is never found to be magnetic when it is in its electronic ground state.
- When the electrons are in different orbitals, then it is again an experimental fact that their spins may now be either paired ($\uparrow\downarrow$) or unpaired, e.g., ($\uparrow\uparrow$ or $\downarrow\downarrow$).
- Thus, **when two electrons are in the same orbital (i.e., they possess the same n , l and m values) their spins must be paired.**
- When they are in different orbitals (one or more of their n , l and m values are different) then their spins may be paired or unpaired.
- We could *generalize these observations* by stating that "***no two electrons in the same atom may have all four quantum numbers the same.***"
- Stated in this way we see immediately that *any given orbital may **hold no more than two electrons.***

- Since two electrons in the same orbital have the same values of n , l and m , they can differ only through their spin quantum number.
- However, the spin quantum number may have only one of two possible values, and these possibilities are given by (n, l, m, \uparrow) or (n, l, m, \downarrow) .
- We have indeed found *the principle* we were seeking, one which limits the occupation of an atomic orbital. This principle is known as the ***Pauli exclusion principle***.
- One form of it, suitable for use within the framework of the orbital approximation, is the statement given in quotation marks above.
- *The Pauli principle cannot be derived from, nor is it predicted by, quantum mechanics.*
- It is a law of nature that must be taken into account along with quantum mechanics if the properties of matter are to be correctly described.

- The concept of atomic orbitals, as derived from quantum mechanics, together with the Pauli exclusion principle which limits the occupation of a given orbital, provides an understanding of the electronic structure of many-electron atoms.
- We shall demonstrate this by "predicting" the existence of the periodic table.
- *Calculations* show that for the *atoms* from scandium to zinc the energies of the *3d orbitals are always lower than the energy of the 4s orbital*, in spite of the greater penetration of a 4s electron.
- However, *spectroscopic results* show that *Sc has the configuration [Ar]3d¹4s²*, not [Ar]3d³ or [Ar]3d²4s¹. It is due to the nature of electron–electron repulsions in 3d and 4s orbitals. Because the *average distance* of a 3d electron from the nucleus *is less* than that of a 4s electron, *two 3d electrons are so close together that they repel each other more strongly* than two 4s electrons do and 3d² and 3d³ configurations are *disfavoured*.

- As a result, Sc has the configuration $[\text{Ar}]3d^14s^2$ rather than the two alternatives, for *then the strong electron–electron repulsions in the 3d orbitals are minimized*. The total energy of the atom is lower despite the cost of allowing electrons to populate the high energy 4s orbital.
- The *electron configurations for scandium to zinc are of the form $[\text{Ar}]3d^n4s^2$* , where $n = 1$ for scandium and $n = 10$ for zinc.
- Two **notable exceptions**, which are observed experimentally, are Cr, with electron configuration $[\text{Ar}]3d^54s^1$, and **Cu**, with electron configuration $[\text{Ar}]3d^{10}4s^1$.
- *Half-filled and fully-filled subshells have got extra stability*. Therefore, one of the $4s^2$ electrons jumps to the $3d^4$ or $3d^9$ giving rise to $3d^54s^1$ and $3d^{10}4s^1$ configurations.

❑ The Electronic Basis of the Periodic Table

- The hydrogen-like orbitals for a many-electron atom are listed in order of increasing energy in Fig. 4-2.
- This energy level diagram differs from the corresponding diagram for the hydrogen atom, a one-electron system.
- In the many-electron atom all orbitals with the same value of the principal quantum number n do not have the same energy as they do in the case of hydrogen.

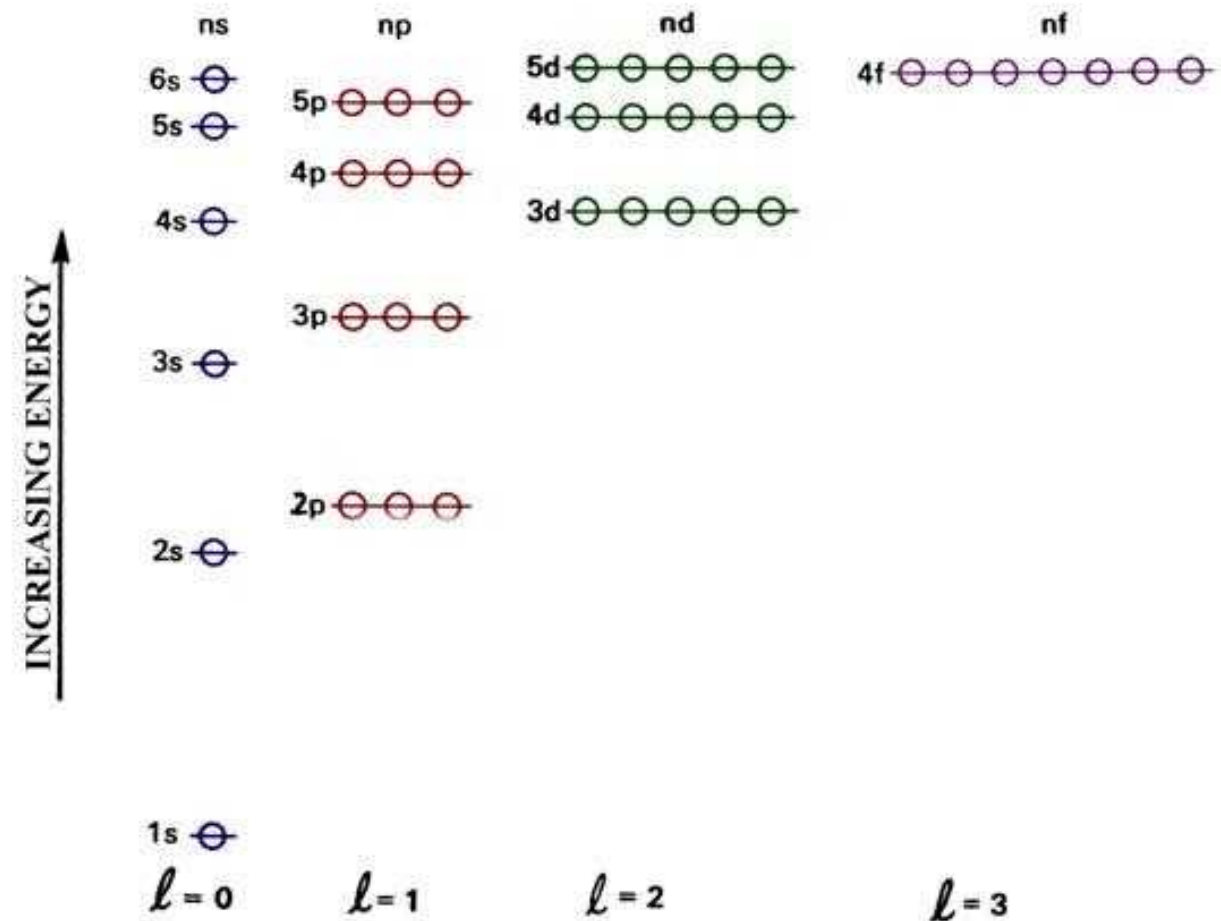


Fig. 4.2. An orbital energy level diagram for a many-electron atom.

- For the many-electron atoms, the energy of an orbital depends on both n and l , the energy increasing as l increases even when n is constant.
- For example, from Fig. 4-2 it is evident that the $3d$ orbital possesses a higher energy than does the $3p$ orbital which in turn has a higher energy than does the $3s$ orbital.
- The reason for this difference between the one- and the many-electron case will be discussed below.
- The energy of the orbital is still independent of the magnetic quantum number m .
- Thus when $l = 1$, there are three p orbitals which are still degenerate (all possess the same energy) and this is indicated by the three open circles which are superimposed on each of the p levels.
- The open circles thus represent the number of available orbitals or the degeneracy of each orbital energy level.

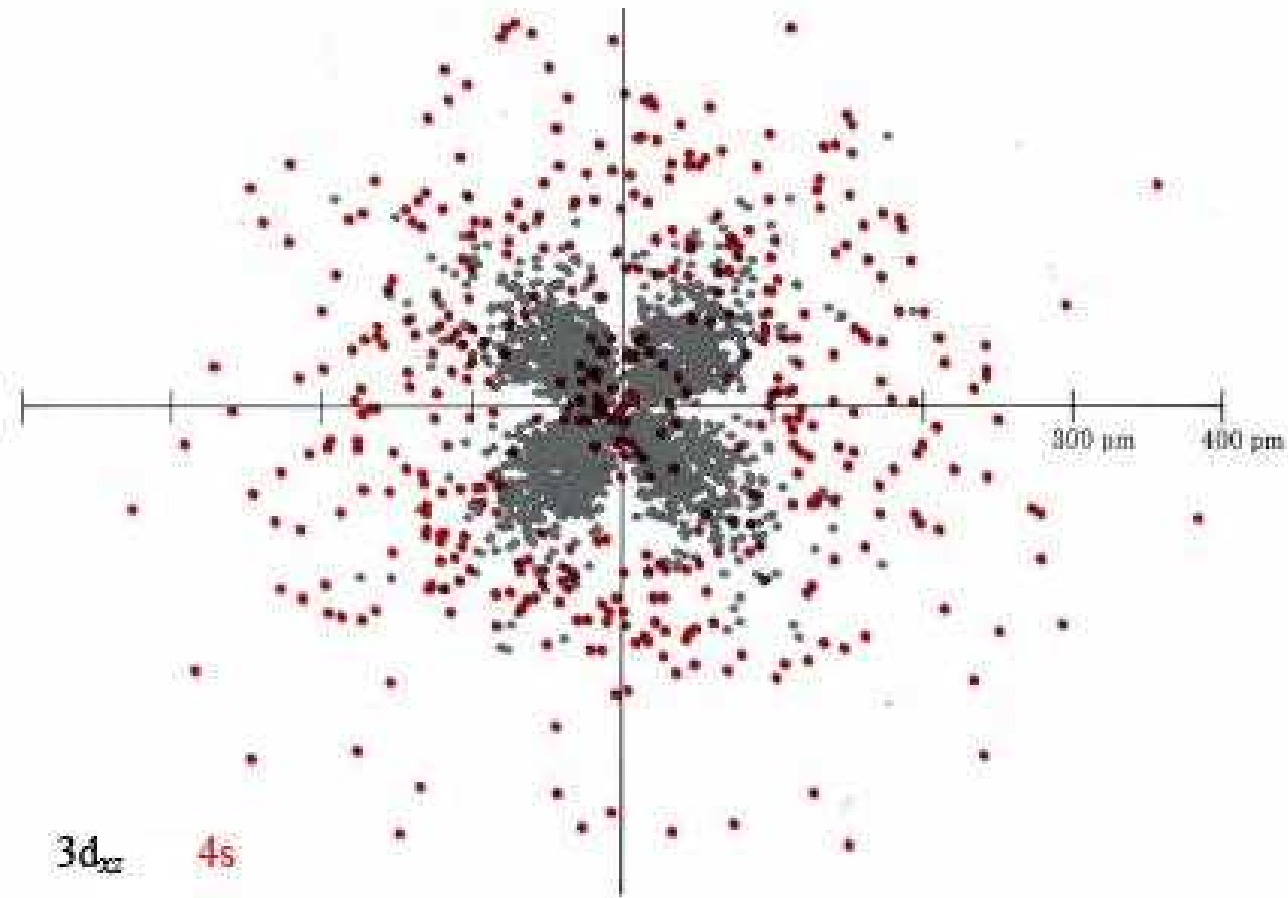


Figure 5.17.1 compares the probability distributions of a 4s and a 3d electron in a V atom. Although the 4s electron cloud lies farther from the nucleus on average than does the 3d cloud, a small portion of the 4s electron density is found very close to the nucleus where it is hardly shielded from the total nuclear charge of +23. It is the very strong attractive force of this small fraction of the total 4s electron density that lowers the energy of the 4s electron below that of the 3d.

Figure 5.17.1 Comparison of 3d (gray) and 4s (red) electron clouds for a vanadium atom.

- ❖ The fact that ***the 4s electron cloud is more extensive than the 3d has an important influence on the chemistry of the transition elements.***
- When an atom such as V (Figure 5.17.1) interacts with another atom, it is the 4s electrons extending farthest from the nucleus which first contact the other atom. Thus, the 4s electrons are often more significant than the 3d in determining valence and the formulas of compounds. The 3d electrons are “buried” under the surfaces of the atoms of the transition metals.
- Adding one more 3d electron has considerably less effect on their chemical properties than adding one more 3s or 3p electron did in the case of the representative elements. Hence there is a slow but steady transition in properties from one transition element to another.
- Notice, for example, that except for Sc, all of the transition metals form chlorides, MCl_2 , where the metal has a valence of 2; examples are $TiCl_2$, VCl_2 , $CrCl_2$, and so on. The valence of 2 corresponds with the two 4s valence electrons.

- Each of the transition metals also exhibits other valences where one or more of the $3d$ electrons are also involved. For example, in some compounds (vanadium) has a valence of 2 (VO , VCl_2) in others it has a valence of 3 (V_2O_3 , VCl_3), in still others it has a valence of 4 (VO_2 , VCl_4), and in at least one case (V_2O_5) it has a valence of 5.
- The chemistry of the transition metals is more complicated and a wider variety of formulas for transition-metal compounds is possible because of this variable valence.
- In some cases, electrons in the d subshells act as valence electrons, while in other cases they do not.
- Although the $3d$ electron clouds do not extend farther from the nucleus than $3s$ and $3p$ (and hence do not constitute another shell as the $4s$ electrons do), they are thoroughly shielded from the nuclear charge and thus often act as valence electrons. This Jekyll and Hyde behavior (having a two-sided personality: good and evil) of $3d$ electrons makes life more complicated (and often far more interesting) for chemists who study the transition elements.

- With the aid of this energy level scheme and the Pauli principle we may proceed to build up the electronic structures of all the atoms.
- We do this by assigning electrons one at a time to the vacant orbital which possesses the lowest energy. An orbital is "filled" when it contains two electrons with their spins paired.
- **Hydrogen.** The nuclear charge is 1 and the single electron is placed in the 1s orbital. The electronic configuration is $1s^1$.
- **Helium.** The nuclear charge is increased by one unit to 2 and the extra electron is again placed in the 1s orbital, with its spin opposed to that of the electron already present. The electronic configuration is $1s^2$.
- **Lithium.** The nuclear charge is 3 and the third electron, because of the Pauli principle, must be placed in the 2s orbital as the 1s orbital is doubly occupied. The electronic configuration of lithium is therefore $1s^2 2s^1$.

- We can now answer the question as to why the 2s orbital is more stable than the 2p orbital, i.e., why Li is described as $1s^2 2s^1$ and not as $1s^2 2p^1$.
- The two inner electrons of lithium (those in the 1s orbital) partially shield the nuclear charge from the outer electron.
- Recall that as n increases, the average distance between the electron and the nucleus increases.
- Thus most of the electron density of the electron with $n = 2$ will lie outside of the charge density of the two inner electrons which have $n = 1$.
- When the outer electron is at large distances from the nucleus and thus essentially outside of the inner shell of electron density it will experience a force from only one of the three positive charges on the lithium nucleus. However, as the outer electron does have a small but finite probability of being close to the nucleus, it will penetrate to some extent the tightly bound electron density of the two 1s electrons. In doing so it will "see" much more of the total nuclear charge and be more tightly bound.

- *The closer the outer electron can get to the nucleus, that is, the more it can penetrate the density distribution of the inner shell electrons, the more tightly bound it will be.*
- An electron in an s orbital has a finite probability of being found right at the nucleus. An electron in a p orbital on the other hand has a node in its density distribution at the nucleus.
- Thus an s electron penetrates the inner shell density more effectively than does a p electron and is consequently more tightly bound to the atom.
- ***In a hydrogen atom, there are no inner electrons and both a $2s$ and $2p$ electron always experience the full nuclear charge and have the same energy.***
- The crux of this penetration effect on the energy is that the inner shell electron density does possess a finite extension in space.
- Thus an outer electron can penetrate inner shell density and the screening effect is reduced.

- If the inner shell density was contracted right onto the nucleus, then no matter how close the outer electron came to the lithium nucleus, it would always experience only a charge of +1. *This dependence of the orbital energies on their l value is aptly called the **penetration effect**.*
- The electron density of a d electron is concentrated even further away from the nucleus than is that of a p electron. Consequently, the orbital energy of a d electron is even less stable than that of a p electron.
- ***In some atoms the penetration of the inner shell density by a d electron is so slight that its energy is raised even over that of the s electron with the next highest n value.***
- ✓ For example, a $3d$ electron possesses a higher energy than does a $4s$ electron in the atoms Sc to Zn ***with the exceptions of Cr and Cu.***
- The penetration effect in these elements overrides the principal quantum number for d electrons in determining their relative energies.

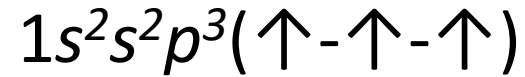
- Notice that the configuration $1s^2 2s^1$ for lithium overcomes the difficulties of our earlier attempts to describe the electronic structure of this atom.
- The Pauli principle, of which we were ignorant in our previous attempt, forces the third electron to occupy the $2s$ orbital and forces in turn the beginning of a new quantum shell, that is, a new value of n . Thus lithium, like hydrogen, possesses one outer electron in an s orbital.
- Since it is only the outer electron density which in general is involved in a chemical change, lithium and hydrogen should have some chemical properties in common, as indeed they do.
- Hydrogen is the beginning of the first period ($n = 1$) and lithium marks the beginning of the second period ($n = 2$).

☐ **Carbon.** $Z = 6$.

- The placing of the sixth electron of carbon requires some comment. It will obviously go into a $2p$ orbital. But in which of the three should it be placed?
- Should it be placed in the $2p$ orbital which already possesses one electron, or should it be placed in one of the vacant $2p$ orbitals?
- If it is placed in the occupied $2p$ orbital its spin must be paired with that of the electron already present and the result would be a nonmagnetic carbon atom.
- If, however, it is placed in one of the vacant $2p$ orbitals it may be assigned a spin parallel to the first electron.
- The question is decided on the grounds of which situation gives the lowest energy.
- As a result of the Pauli principle, two electrons with parallel spins (both up or both down) have only a very small probability of being close to one another. In fact the wave function which describes the two-electron case for parallel spins vanishes when both electrons approach one another. When the wave function vanishes, the corresponding probability distribution goes to zero.

- On the average, then, electrons with parallel spins tend to keep out of each other's way.
- Two electrons with paired spins, whether in the same or different orbitals are not prevented by the Pauli principle from being close to one another. The wave function for this situation is finite even when they are on top of one another!
- Obviously, two electrons with parallel spins will have a smaller value for the electrostatic energy of repulsion between them than will two electrons with paired spins.
- This is a general result which holds almost without exception in the orbital approximation. It is known as one of Hund's rules as he was the first to state it.
- Thus the most stable electronic configuration of the carbon atom is $1s^2 2s^2 2p^2(\uparrow\uparrow)$ where we have emphasized the fact that the two $2p$ electrons have parallel spins and hence must be in different $2p$ orbitals.

❑ **Nitrogen.** $Z = 7$. Because of Hund's rule the electronic configuration is



i.e., one electron in each of the $2p$ orbitals.

The configuration with the largest possible component of the spin magnetic moment will be the most stable.

❑ **Neon.** $Z = 10$. The tenth electron will occupy the last remaining vacancy in the second quantum shell (the set of orbitals with $n = 2$). $1s^22s^22p^6$

Thus neon represents the end of the second period and all the electrons have paired spins.

- When all the orbitals in a given shell are doubly occupied, the resulting configuration is called a "***closed shell***."
- Helium and neon are similar in that they both possess closed shell configurations. Because neither of these elements possesses a vacancy in its outer shell of orbitals both are endowed with similar chemical properties.

- When the orbitals belonging to a given l value contain either one electron each (are half-filled) or are completely filled, the ***resulting density distribution is spherical in shape***. Thus, the electron density distributions of nitrogen and neon, for example, will be spherical.
- Reference to Fig. 4-2 indicates that the next element, sodium, will have its outer electron placed in the 3s orbital and it will be the first element in the third period. Since its outer electronic structure is similar to that of the preceding elements, lithium and hydrogen, it is placed beneath them in the periodic table.
- ✓ It is obvious that in passing from sodium to argon, all of the preceding outer electronic configurations found in the second period ($n = 2$) will be duplicated by the elements of the third period by filling the 3s and 3p orbitals.
- ✓ For example, the electronic structure of phosphorus ($Z = 15$) will be $1s^2 2s^2 2p^6 3s^2 3p^3 (\uparrow - \uparrow - \uparrow)$ and thus resemble nitrogen.
- ✓ **Argon.** $Z = 18$. Argon will have filled 3s and 3p orbitals and will represent the end of a period. Argon, like helium and neon, possesses a closed shell structure and is placed beneath these two elements in the periodic table.

Electronic Configurations of Cations and Anions

- The way we designate electronic configurations for cations and anions is essentially similar to that for neutral atoms in their ground state. That is, we follow the three important rules: Aufbau Principle, Pauli-exclusion Principle, and Hund's Rule.
- The ***electronic configuration of cations*** is assigned by removing electrons first in the outermost p orbital, followed by the s orbital and finally the d orbitals (if any more electrons need to be removed).
- For instance, the ground state electronic configuration of calcium ($Z=20$) is $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2$. The calcium ion (Ca^{2+}), however, has two electrons less. Hence, the electron configuration for Ca^{2+} is $1s^2 2s^2 2p^6 3s^2 3p^6$. Since we need to take away two electrons, we first remove electrons from the outermost shell ($n=4$). In this case, all the 4p subshells are empty; hence, we start by removing from the s orbital, which is the 4s orbital. The electron configuration for Ca^{2+} is the same as that for Argon, which has 18 electrons. Hence, we can say that both are isoelectronic.

- The ***electronic configuration of anions*** is assigned by adding electrons according to Aufbau Principle.
- We add electrons to fill the outermost orbital that is occupied, and then add more electrons to the next higher orbital.
- The neutral atom chlorine ($Z=17$), for instance has 17 electrons. Therefore, its ground state electronic configuration can be written as $1s^2 2s^2 2p^6 3s^2 3p^5$.
- The chloride ion (Cl^-), on the other hand, has an additional electron for a total of 18 electrons. Following Aufbau Principle, the electron occupies the partially filled 3p subshell first, making the 3p orbital completely filled.
- The electronic configuration for Cl^- can, therefore, be designated as $1s^2 2s^2 2p^6 3s^2 3p^6$.
- Again, the electron configuration for the chloride ion is the same as that for Ca^{2+} and Argon. Hence, they are all isoelectronic to each other.

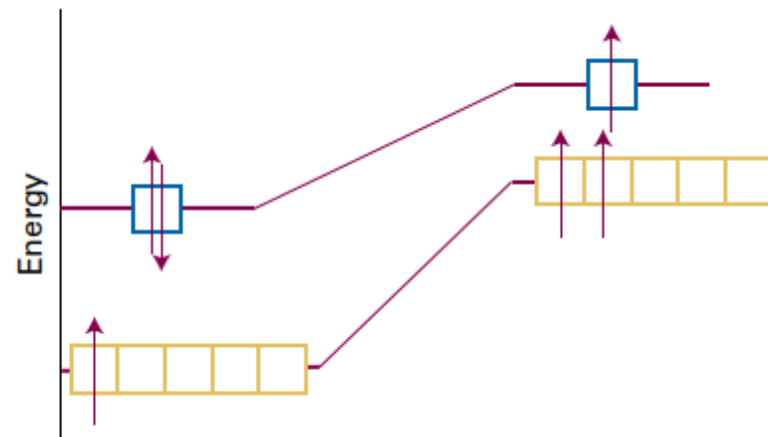
❑ The Transition Elements

- The beginning of the fourth period will be marked by the single and double occupation of the 4s orbital to give potassium and calcium respectively.
- However, reference to the orbital energy level diagram indicates that the 3d orbital is more stable than the 4p orbital.
- Since there are five d orbitals they may hold a total of ten electrons.
- Thus the ten elements beginning with scandium ($Z = 21$) will possess electronic structures which differ from any preceding them as they are the first elements to fill the d orbitals.
- A typical electronic configuration of one of these elements is that of manganese: $[\text{Ar}]4s^23d^5$. The symbol [Ar] is an abbreviated way of indicating that the inner shells of electrons on manganese possess the same orbital configuration as those of argon. In addition, the symbol $3d^5$ indicates that there are five electrons in the 3d orbitals, no distinction being made between the five different d orbitals. This series of elements in which the 3d orbitals are filled is called the ***first transition series***.

- The element zinc with a configuration $[\text{Ar}]4s^23d^{10}$ marks the end of this series.
- The six elements from gallium to krypton mark the filling of the $4p$ orbitals and the closing, with krypton, of the fourth quantum shell and the fourth period of the table.
- While the ***3d orbitals are less stable than the 4s orbitals in the neutral atom*** (with the ***exceptions of Cr and Cu***) and are filled only after the $4s$ orbitals are filled, ***the relative stability of the 4s and 3d orbitals is reversed in the ionic forms*** of the transition metals.
- ✓ For example, the configuration of the ion which results when the manganese atom loses two electrons is $\text{Mn}^{+2} [\text{Ar}]3d^5$ and not $[\text{Ar}]4s^23d^3$. This is a general result.
- ✓ The d orbitals of quantum number n are filled only after the s orbital of quantum number $(n + 1)$ is filled *in the neutral atom*, but the ***nd orbital is more stable than the $(n + 1)s$ orbital in the corresponding ion.***

Calculations show that for the atoms from scandium to zinc the energies of the 3d orbitals are always lower than the energy of the 4s orbital, in spite of the greater penetration of a 4s electron. However, spectroscopic results show that Sc has the configuration $[\text{Ar}]3d^14s^2$, not $[\text{Ar}]3d^3$ or $[\text{Ar}]3d^24s^1$. To understand this observation, consider the nature of electron–electron repulsions in 3d and 4s orbitals. Because the average distance of a 3d electron from the nucleus is less than that of a 4s electron, two 3d electrons are so close together that they repel each other more strongly than two 4s electrons do and $3d^2$ and $3d^3$ configurations are disfavoured. As a result, Sc has the configuration $[\text{Ar}]3d^14s^2$ rather than the two alternatives, for then the strong electron–electron repulsions in the 3d orbitals are minimized. The total energy of the atom is lower despite the cost of allowing electrons to populate the high energy 4s orbital (Fig. 8B.7).

Figure 8B.7 Strong electron–electron repulsions in the 3d orbitals are minimized in the ground state of Sc if the atom has the configuration $[\text{Ar}]3d^14s^2$ (shown on the left) instead of $[\text{Ar}]3d^24s^1$ (shown on the right). The total energy of the atom is lower when it has the $[\text{Ar}]3d^14s^2$ configuration despite the cost of populating the high energy 4s orbital.



The effect just described is generally true for scandium to zinc, so Their electron configurations are of the form $[\text{Ar}]3d^n4s^2$, where $n = 1$ for scandium and $n = 10$ for zinc. Two notable exceptions, which are observed experimentally, are Cr, with electron configuration $[\text{Ar}]3d^54s^1$, and Cu, with electron configuration $[\text{Ar}]3d^{10}4s^1$. Because the configuration of vanadium is $[\text{Ar}]3d^34s^2$, the V^{2+} cation has the configuration $[\text{Ar}]3d^3$. It is reasonable to remove the more energetic 4s electrons in order to form the cation, but it is not obvious why the $[\text{Ar}]3d^3$ configuration is preferred in V^{2+} over the $[\text{Ar}]3d^14s^2$ configuration, which is found in the isoelectronic Sc atom. Calculations show that the energy difference between $[\text{Ar}]3d^3$ and $[\text{Ar}]3d^14s^2$ depends on Z_{eff} . As Z_{eff} increases, transfer of a 4s electron to a 3d orbital becomes more favourable because the electron–electron repulsions are compensated by attractive interactions between the nucleus and the electrons in the spatially compact 3d orbital. Indeed, calculations reveal that, for a sufficiently large Z_{eff} , $[\text{Ar}]3d^3$ is lower in energy than $[\text{Ar}]3d^14s^2$. This conclusion explains why V^{2+} has a $[\text{Ar}]3d^3$ configuration and also **accounts for the observed $[\text{Ar}]4s^03d^n$ configurations of the M^{2+} cations of Sc through Zn.**

The ground state electron configuration of palladium is:

${}_{46}\text{Pd}:1s^2,2s^2,2p^6,3s^2,3p^6,4s^2,3d^{10},4p^6,5s^0,4d^{10}$.

The short electron configuration of palladium is $[\text{Kr}] 4d^{10}$.

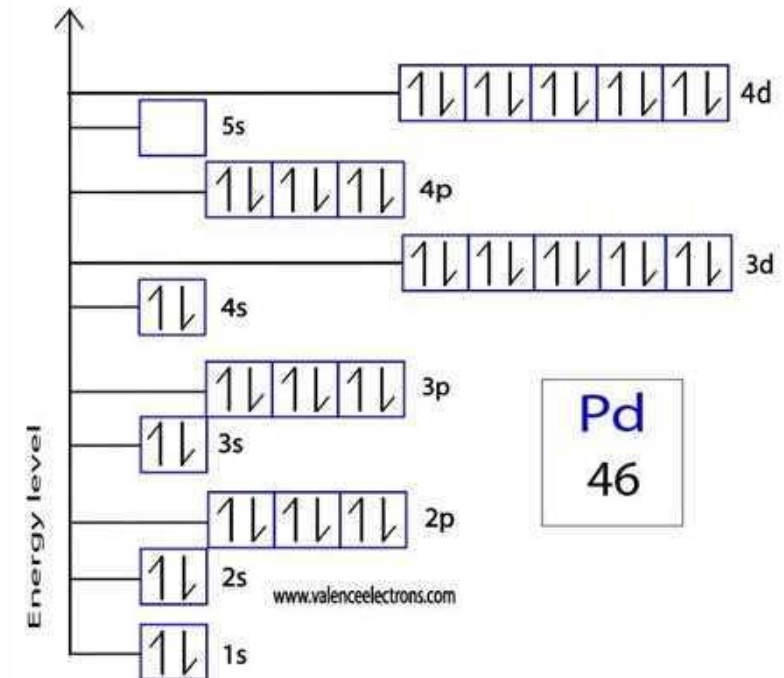
This electron configuration shows that the d-orbital has a total of ten electrons.

Therefore, the ***valence electrons of palladium are ten***. Electrons that by the Madelung rule would be expected to occupy the $5s$ instead fill the $4d$ orbitals, as it is more energetically favorable to have a completely filled $4d^{10}$ shell instead of the $5s^2 4d^8$ configuration.

This $5s^0$ configuration, unique in period 5, makes palladium the heaviest element having only one incomplete electron shell, with all shells above it empty.

1. Full d orbitals are more stable than partially filled ones.

2. At higher energy levels, they have very close energies and then electrons can jump from one orbital to another easily.



The elements that form bonds by donating electrons are called cation. Palladium atom donates two electrons in the 4d orbital to convert a palladium ion(Pd^{2+}).



The electron configuration of palladium ion(Pd^{2+}) is $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^8$.

This electron configuration shows that the palladium ion (Pd^{2+}) has four shells and the last shell has sixteen electrons. Palladium atom exhibits +2, +3, +4 oxidation state. The oxidation state of the element changes depending on the bond formation.

- The fifth period begins with the filling of the $5s$ orbital, followed by the filling of the $4d$ orbitals, which generates the second transition series of elements. The period closes with the filling of the $5p$ orbitals and ends with xenon.

❑ The lanthanide and actinide elements

- The sixth period is started by the filling of the $6s$ orbital. The next element, lanthanum, has the electronic configuration $[\text{Xe}]6s^25d^1$. However, the next fourteen elements represent the beginning of another new series as the filling of the $4f$ orbitals is now energetically favoured over a continued increase in the population of the $5d$ orbitals.
- Note that the very small penetration effect possessed by the $4f$ orbitals ($n = 4$) delays their appearance until the sixth quantum shell has been partially filled. There are fourteen elements in this series, called the ***lanthanide series***, since there are seven $4f$ orbitals ($l = 3$ and $2 \times 3 + 1 = 7$).

- The third transition series follows the lanthanide elements as the occupation of the $5d$ orbitals is completed. This in turn is followed by the filling of the $6p$ orbitals.
- The final period begins with the filling of the $7s$ orbital and continues with the filling of the $5f$ orbitals. This second series of elements with electrons in f orbitals is called the ***actinide series***.
- The concept of atomic orbitals in conjunction with the Pauli principle has indeed predicted a ***periodicity in the electronic structures of the elements***.
- The form of this periodicity duplicates exactly that found in the periodic table of the elements in which the periodicity is founded on the observed chemical and physical properties of the elements.
- Our next task will be to determine whether or not our proposed electronic structures will properly predict and explain the observed variations in the chemical and physical properties of the elements.

Figure 5.21 The filling of shells and the structure of the periodic table. Only the “anomalous” electron configurations are shown.

Figure 5.21 The filling of shells and the structure of the periodic table. Only the “anomalous” electron configurations are shown.

1s																		1s					
H																		He					
2s–filling																		2p–filling					
Li	Be																	B	C	N	O	F	Ne
3s–filling																		3p–filling					
Na	Mg																	Al	Si	P	S	Cl	Ar
4s–filling		3d–filling										4p–filling											
K	Ca	Sc	Ti	V	Cr $3d^5 4s^1$	Mn	Fe	Co	Ni	Cu $3d^{10} 4s^1$	Zn	Ga	Ge	As	Se	Br	Kr						
5s–filling		4d–filling										5p–filling											
Rb	Sr	Y	Zr	Nb $4d^4 5s^1$	Mo $4d^5 5s^1$	Tc	Ru $4d^7 5s^1$	Rh $4d^8 5s^1$	Pd $4d^{10}$	Ag $4d^{10} 5s^1$	Cd	In	Sn	Sb	Te	I	Xe						
6s–filling		5d–filling										6p–filling											
Cs	Ba	Lu	Hf	Ta	W	Re	Os	Ir	Pt $5d^9 6s^1$	Au $5d^{10} 6s^1$	Hg	Tl	Pb	Bi	Po	At	Rn						
7s–filling		6d–filling																					
Fr	Ra	Lr	Rf	Ha	Sg	Ns	Hs	Mt	Ds	Rg	Cn												

4f-filling													
La $5d^1 6s^2$	Ce $4f^1 5d^1 6s^2$	Pr	Nd	Pm	Sm	Eu	Gd $4f^7 5d^1 6s^2$	Tb	Dy	Ho	Er	Tm	Yb

5f-filling													
Ac $6d^1 7s^2$	Th $6d^2 7s^2$	Pa $5f^3 6d^1 7s^2$	U $5f^3 6d^1 7s^2$	Np $5f^4 6d^1 7s^2$	Pu	Am	Cm $5f^7 6d^1 7s^2$	Bk	Cf	Es	Fm	Md	No