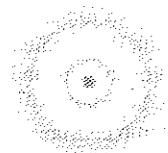$n = 1, \ell = m_\ell = 0$
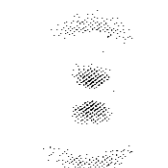
$n = 2, \ell = m_\ell = 0$

$n = 3, \ell = m_\ell = 0$

$n = 2, \ell = 1, m_\ell = 0$

$n = 3, \ell = 1, m_\ell = 0$

Figure 28.18 Electron cloud representations of the probability density $|\psi|^2$ for a few of the quantum states of the hydrogen atom. The sketches show the probability densities in a single plane. For an idea of what the electron clouds look like in three dimensions, imagine rotating each of the sketches about a vertical axis.

For a given n, the **orbital angular momentum quantum number** ℓ can be any integer from 0 to $n - 1$. In the ground state $(n = 1)$, $\ell = 0$ is the only possible value; the angular momentum in the ground state must be $L = 0$. For higher n, there are states both with nonzero and zero L. Note that L is called the *orbital* angular momentum because it is associated with the *motion* of the electron, but remember that the electron does not follow a well-defined orbit.

The orbital angular momentum quantum number ℓ determines only the magnitude L of the orbital angular momentum; what about the direction? The direction also turns out to be quantized. For a given n and ℓ, the component of $\vec{L}$ along some direction that we'll call the z-axis can have one of $2\ell + 1$ quantized values:

$$L_z = m_\ell \hbar, \quad m_\ell = -\ell, -\ell + 1, \ldots, -1, 0, +1, \ldots, \ell - 1, \ell \quad (28\text{-}13)$$

The **orbital magnetic quantum number** m_ℓ can be any integer from $-\ell$ to $+\ell$.

Figure 28.18 shows the probability density $|\psi|^2$ for several quantum states of the H atom. Notice that the states with zero orbital angular momentum $(\ell = 0)$ are spherically symmetrical, while $\ell \neq 0$ states are not.

In addition to the angular momentum associated with its motion, an electron has an intrinsic angular momentum $\vec{S}$ whose magnitude is $S = (\sqrt{3}/2)\hbar$. Originally, it was thought that the electron was spinning about an axis—we still call S the *spin angular momentum*—but it can't be. The electron is, as far as we know, a point particle; to generate this angular momentum by spinning, the electron would have to be large and would have to violate relativity. The spin angular momentum is an intrinsic property of the electron, like its charge or mass.

Electrons always have the same *magnitude* spin angular momentum, but the z-component of $\vec{S}$ has two possible values:

$$S_z = m_s \hbar, \quad m_s = \pm \tfrac{1}{2} \quad (28\text{-}14)$$

The two values of the **spin magnetic quantum number** m_s are often referred to as *spin up* and *spin down*. (The quantum numbers m_ℓ and m_s are called *magnetic* because the energy of a state depends on their values when the atom is in an external magnetic field.)

The state of the electron in a hydrogen atom is completely determined by the values of the four quantum numbers n, ℓ, m_ℓ, and m_s.

√ CHECKPOINT 28.6

List the quantum numbers for all possible electron states in the hydrogen atom with principal quantum number $n = 2$.

28.7   THE EXCLUSION PRINCIPLE; ELECTRON CONFIGURATIONS FOR ATOMS OTHER THAN HYDROGEN

According to the **Pauli exclusion principle**—named after the Austrian-Swiss physicist Wolfgang Pauli (1900–1958)—no two electrons in an atom can be in the same quantum state. The quantum state of an electron in any atom is specified by the same four quantum numbers used for hydrogen: n, ℓ, m_ℓ, and m_s (Table 28.1). However, the electron energy levels are not the same as those of hydrogen. In atoms with more than one electron, interactions between electrons must be taken into account. In addition, the nuclear charge varies from one element to another. Thus, the same set of four quantum numbers do not correspond to the same energy level from one species of atom to another.

Table 28.1   Quantum Numbers for Electron States in an Atom

Symbol	Quantum Number	Possible Values
n	principal	$1, 2, 3, \ldots$
ℓ	orbital angular momentum	$0, 1, 2, 3, \ldots, n - 1$
m_ℓ	orbital magnetic	$-\ell, -\ell + 1, \ldots, -1, 0, 1, \ldots, \ell - 1, \ell$
m_s	spin magnetic	$-\tfrac{1}{2}, +\tfrac{1}{2}$

Shells and Subshells   The set of electron states with the same value of n is called a **shell**. Each shell is composed of one or more **subshells**. A subshell is a unique combination of n and ℓ. Subshells are often represented by the numerical value of n followed by a lowercase letter representing the value of ℓ. The letters s, p, d, f, g, and h stand for $\ell = 0$, 1, 2, 3, 4, and 5, respectively (Table 28.2). For example, $3p$ is the subshell with $n = 3$ and $\ell = 1$. The letters s, p, and d came from the appearance of the associated spectral lines long before the advent of quantum theory. The dominant or *principal* spectral lines came from the $\ell = 1$ subshell; the spectral lines from the $\ell = 0$ subshell were especially sharp in appearance; and those from the $\ell = 2$ subshell looked more diffuse than the others.

Since the orbital angular momentum quantum number ℓ can be any integer from 0 to $n - 1$, with n possible values, there are n subshells in a given shell. Thus, there are three subshells in the $n = 3$ shell: $3s$, $3p$, and $3d$. A superscript following the subshell label indicates how many electrons are present in that subshell. This compact notation represents the configuration of electrons in an atom. For example, the ground state of the nitrogen atom is $1s^2 2s^2 2p^3$; it has two electrons in the $1s$ subshell, two in the $2s$ subshell, and three in the $2p$ subshell.

Application: electron orbitals, electronic configuration of atoms

Orbitals   Each subshell, in turn, consists of one or more **orbitals**, which are specified by n, ℓ, and m_ℓ. Since m_ℓ can be any integer from $-\ell$ to $+\ell$, there are $2\ell + 1$ orbitals in a subshell. Therefore, s subshells have only one orbital, p subshells have three orbitals, d subshells have five orbitals, and so forth. Each orbital can accommodate two electrons: one spin up $\left(m_s = +\tfrac{1}{2}\right)$ and one spin down $\left(m_s = -\tfrac{1}{2}\right)$. It can be shown (Problem 79) that

$$\text{the number of electron states in a subshell is } 4\ell + 2,$$
$$\text{and the number of states in a shell is } 2n^2 \quad (28\text{-}15)$$

Ground-State Configuration   The ground-state (lowest energy) electronic configuration of an atom is found by filling up electron states, starting with the lowest energy, until all the electrons have been placed. According to the exclusion principle, there can only be one electron in each state. Generally, the subshells in order of increasing energy are

$$1s, 2s, 2p, 3s, 3p, 4s, 3d, 4p, 5s, 4d, 5p, 6s, 4f, 5d, 6p, 7s \quad (28\text{-}16)$$

However, there are some exceptions. The energies of the subshells are not the same in different atoms; different nuclear charges and the interaction of the electrons make the energy levels differ from one atom to another. So, for example, the ground state of chromium (Cr, atomic number 24) is $1s^2 2s^2 2p^6 3s^2 3p^6 4s^1 3d^5$ instead of $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^4$. Similarly, the ground state of copper (Cu, atomic number 29) is $1s^2 2s^2 2p^6 3s^2 3p^6 4s^1 3d^{10}$ instead of $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^9$. There are only 8 elements among the first 56 that are exceptions to the subshell order in Eq. (28-16):

Cr, Cu, Nb, Mo, Ru, Rh, Pd, Ag

Table 28.2	Electron Subshells Summarized					
$\ell =$	0	1	2	3	4	5
Spectroscopic notation	s	p	d	f	g	h
Number of states in subshell	2	6	10	14	18	22

Many more exceptions are found in the electron configurations of elements with atomic numbers greater than 56.

Example 28.4

Electron Configuration of Arsenic

What is the ground-state electron configuration of arsenic (atomic number 33)?

Strategy Arsenic has atomic number 33, so there are 33 electrons in the neutral atom. Arsenic is not one of the above-mentioned exceptions for atomic numbers ≤ 56, so subshells are filled in the order listed in Eq. (28-16) until the total number of electrons reaches 33. A subshell can hold up to $4\ell + 2$ electrons. Each s $(\ell = 0)$ subshell holds a maximum of $4 \times 0 + 2 = 2$ electrons, each p $(\ell = 1)$ subshell holds $4 \times 1 + 2 = 6$, and each d $(\ell = 2)$ subshell holds $4 \times 2 + 2 = 10$.

Solution We fill up subshells and keep track of the total number of electrons: $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10}$ has $2 + 2 + 6 + 2 + 6 + 2 + 10 = 30$ electrons. Then the remaining 3 go into the subshell with the next highest energy—$4p$. The ground-state configuration of arsenic is therefore

$$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^3$$

Discussion To double-check an electron configuration for an element that is not one of the exceptions:

- Add up the total number of electrons.
- Check that the subshells go in the order of Eq. (28-16).
- Make sure that all subshells except the last are full (s^2, p^6, d^{10}).

If the configuration passes those three tests, it is correct.

Practice Problem 28.4   Electron Configuration of Phosphorus

What is the electron configuration of phosphorus (atomic number 15)?

Filling the Orbitals If a subshell is not full, how are the electrons distributed among that subshell's orbitals? Recall that a subshell contains $2\ell + 1$ orbitals and each orbital contains two electron states. As a rule, electrons do not double up in an orbital until each orbital has one electron in it. The two electrons in an orbital have the same spatial distribution—the same electron cloud. Thus, the two electrons in a single orbital are closer together, on average, than are two electrons in different orbitals. Due to the electrical repulsion, the energy is lower if the electrons are in different orbitals, since they are farther apart. For example, the three $4p$ electrons in arsenic (Example 28.4) are in different orbitals in the ground state: one has $m_\ell = 0$, one has $m_\ell = +1$, and one has $m_\ell = -1$.

Application: Understanding the Periodic Table

The elements in the periodic table (see inside back cover) are arranged in order of increasing atomic number Z. The nucleus of an element has charge $+Ze$ and the neutral atom has Z electrons. Furthermore, the elements are arranged in columns according to the configuration of their electrons (Table 28.3). Elements with similar electronic configurations tend to have similar chemical properties.

Although the energy level of a subshell differs from one atom to another, Fig. 28.19 gives a *general* idea of the energies of the various atomic subshells. Note the larger than

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Table 28.3		The Periodic Table Organizes the Elements According to Electronic Configuration							
1A	**2A**	**3B–8B, 1B, 2B**		**3A**	**4A**	**5A**	**6A**	**7A**	**8A**
Alkali Metals	Alkaline Earths	Transition Elements, Lanthanides, and Actinides						Halogens	Noble Gases
s^1	s^2	$d^n s^2$, $d^n s^1$, or $f^m d^n s^2$		$s^2 p^1$	$s^2 p^2$	$s^2 p^3$	$s^2 p^4$	$s^2 p^5$	$s^2 p^6$ (except He)

The periodic table of the elements is arranged in columns by electronic configuration. Elements with similar electronic configurations tend to have similar chemical properties. The table lists only the subshells beyond the configuration of the previously occurring noble gas.
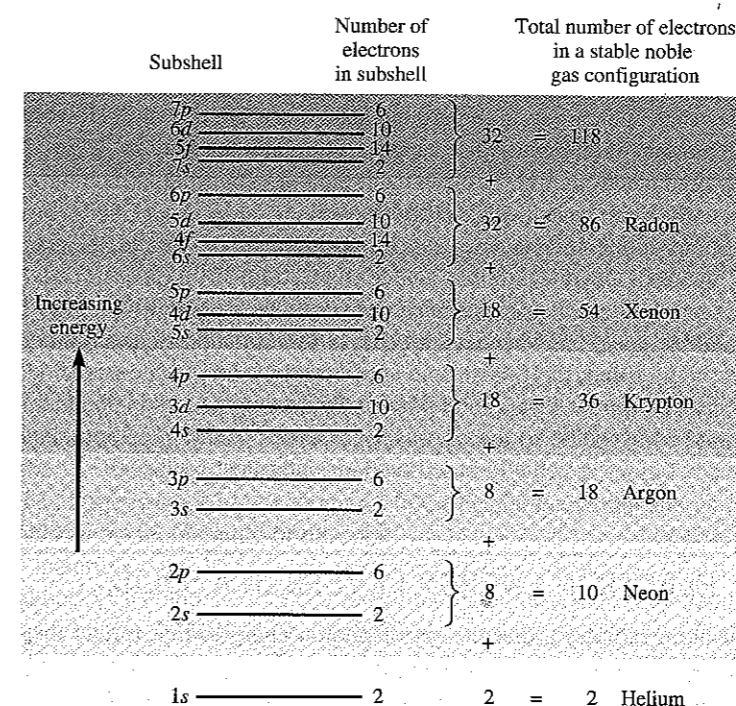

Figure 28.19 Energy level diagram for atomic subshells. The energies of the subshells differ from one atom to another, but this diagram gives a general idea of the relative spacing of the energies. The subshells are filled from the bottom (lowest energy) up.

usual spacing between each s-subshell and the subshell below it. The s-subshell is the lowest energy subshell in a given shell. When starting a new shell (with a higher value of n), the electrons are farther from the nucleus and more weakly bound. The most stable electronic configurations—those that are difficult to ionize and are chemically nonreactive—are those that have all the subshells below an s-subshell full. Elements with this stable configuration are called the *noble gases* (Group 8A). Helium has configuration $1s^2$—the only subshell below $2s$ is full. The rest of the noble gases have a full p-subshell as their highest energy subshell: neon (all subshells below $3s$ full), argon (full below $4s$), krypton (full below $5s$), xenon (full below $6s$), and radon (full below $7s$).

The energy required to excite a helium atom into its first excited state $(1s^1 2s^1)$ is quite large—about 20 eV—due to the large energy gap between the $1s$ and $2s$ subshells. The energy required to excite a lithium atom into its first excited state is much smaller (about 2 eV). Lithium and the other *alkali metals* (Group 1A) have one electron beyond a noble gas configuration. As a shorthand, we often write the spectroscopic notation only for the electrons in an atom that are beyond the configuration of a noble gas, since only those electrons participate in chemical reactions; thus, lithium's configuration is $[\mathrm{He}]2s^1$, sodium's is $[\mathrm{Ne}]3s^1$, and so on. The single electron in the s-subshell is quite weakly bound, so it can easily be removed from the atom, making the alkali metals highly reactive. They can easily give up their "extra" electron to achieve a noble gas configuration as an ion with charge $+e$ (alkali metals have valence +1).

Valence: the number of electrons that an atom will gain, lose, or share in chemical reactions

The alkali metals form ionic bonds with the highly reactive *halogens* (Group 7A), which are one electron shy of a noble gas configuration. For instance, chlorine (Cl, [Ne]$3s^2 3p^5$) needs to gain only one electron to have the electron configuration of the noble gas argon (Ar, [Ne]$3s^2 3p^6$). Thus, the halogens have valence -1. Sodium can give its weakly bound electron to chlorine, leaving both ions (Na$^+$ and Cl$^-$) in stable noble gas configurations. The electrostatic attraction between the two forms an ionic bond: NaCl.

The *alkaline earths* (Group 2A) all have a full *s*-subshell (s^2) beyond a noble gas configuration. They are not as reactive as the alkali metals, since the full *s*-subshell lends some stability, but they can give up both *s* electrons to achieve a noble gas configuration, so alkaline earths usually act with valence $+2$.

Toward the middle of the periodic table, the chemical properties of elements are more subtle. Covalent bonds tend to form when two or more elements have unpaired electrons in orbitals that they can share. Carbon is particularly interesting. Its ground state is $1s^2 2s^2 2p^2$. The two $2p$ electrons are in different orbitals; then there are two unpaired electrons and carbon in the ground state has a valence of 2. However, it takes only a small amount of energy to raise a carbon atom into the state $1s^2 2s^1 2p^3$. Now there are four unpaired electrons (the $2s$ orbital and the three $2p$ orbitals each have one electron). Thus, carbon can have a valence of 4 as well.

In the groups numbered 1A, 2A, . . . , 7A, the numeral before the "A" represents the number of electrons beyond a noble gas configuration. In the *transition elements*, a *d*-subshell is being filled; their electronic configurations are usually [noble gas]$d^n s^2$ but sometimes [noble gas]$d^n s^1$, where $0 \leq n \leq 10$. In the *lanthanides* and the *actinides*, an *f*-subshell is being filled; their electronic configurations are [noble gas] $f^m d^n s^2$, where $0 \leq m \leq 14$ and $0 \leq n \leq 10$. The *d*- and *f*-subshells participate less in chemical reactions than the *s*- and *p*-subshells, so the chemical properties of the transition elements, lanthanides, and actinides are chiefly based on their outermost *s*-subshell.
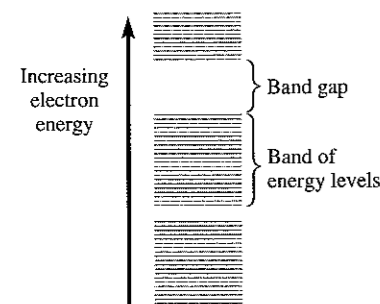
Figure 28.20 Electron energies in a solid form bands of closely spaced energy levels. Band gaps are ranges of energy in which there are no electron energy levels.

See ⊗ for more information on energy levels in solids.

28.8   ELECTRON ENERGY LEVELS IN A SOLID

An isolated atom radiates a discrete set of photon energies that reflect the quantized electron energy levels in the atom. Although a gas discharge tube contains a large number of gas atoms (or molecules), the pressure is low enough that the atoms are, on average, quite far apart. As long as the wave functions of electrons in different atoms do not overlap appreciably, each atom radiates photons of the same energies as would a single isolated atom.

On the other hand, solids radiate a continuous spectrum rather than a line spectrum. What has happened to the quantization of electron energies? The energy levels are still quantized, but they are so close together that in many circumstances we can think of them as continuous **bands** of energy levels. A **band gap** is a range of energies in which no electron energy levels exist (Fig. 28.20).

Constructing the electronic ground state of a solid is similar to constructing the ground state of an atom: the electron states are filled up in order of increasing energy starting from the lowest energy states, according to the exclusion principle. A solid at room temperature isn't in the ground state, but its electron configuration is not very different from the ground state; the extra thermal energy available promotes a small fraction of the electrons (still a large number, though) into higher energy levels, leaving some lower energy states vacant. The energy range of electron states that are thermally excited is small—of the order of $k_B T$, where k_B is the Boltzmann constant ($k_B = 1.38 \times 10^{-23}$ J/K $= 8.62 \times 10^{-5}$ eV/K).

Conductors, Semiconductors, and Insulators

The ground-state electron configuration (i.e., the configuration at absolute zero) of a solid determines its electrical conductivity. If the highest-energy electron state filled at
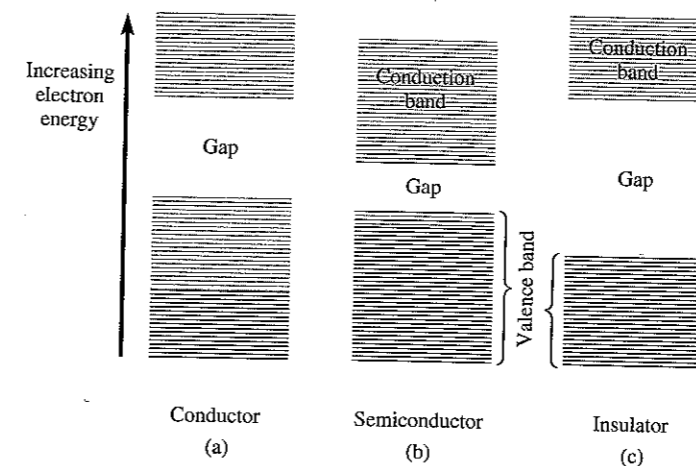
Figure 28.21 Electron energy bands in (a) a conductor, (b) a semiconductor, and (c) an insulator. Horizontal lines indicate electron energy levels; the darker lines are those levels that are occupied by electrons. In a semiconductor at room temperature (b), the valence band is mostly full but a relatively small number of electrons are thermally excited into the conduction band, leaving some vacancies near the top of the valence band.

$T = 0$ is in the middle of a band, so that this band is only partially filled, the solid is a conductor (Fig. 28.21). In order for current to flow, an electric field (perhaps due to a battery connected to the conductor) must be able to change the momentum and energy of the conduction electrons; this can only happen if there are vacant electron states nearby into which the conduction electrons can make transitions. Since the band is only partly full, there are plenty of available electron states at energies only slightly higher than the highest occupied.

On the other hand, if the ground-state configuration fills up the electron states right to the top of a band, then the solid is a semiconductor or an insulator. The difference between the two depends on how the size of the band gap E_g above the completely occupied band (the *valence band*) compares to the available thermal energy ($\approx k_B T$) and thus depends on the temperature of the solid.

Most materials considered semiconductors at room temperature have band gaps between about 0.1 eV and 2.2 eV. The technologically most important semiconductor, silicon, has a gap of 1.1 eV, which is about 40 times the available thermal energy at room temperature (≈ 0.025 eV). The number of electrons excited to higher energy states is much smaller than in a conductor, since there are no available energy levels nearby in the same band. The only electrons that can carry current are those promoted to the mostly empty band above the gap (the *conduction band*).

Because a relatively small number of electrons move into the conduction band, an equal number of vacant electron states exist near the top of the valence band. Electrons in nearby states can easily "fall" into these **holes**, filling one vacancy and creating another. The holes act like particles of charge $+e$ that, in response to an external electric field, move in a direction opposite that of the conduction electrons. The electric current in a semiconductor has two components: the electron current and the hole current.

28.9   LASERS

A laser produces an intense, parallel beam of coherent, monochromatic light. The word **laser** is an acronym for *light amplification by stimulated emission of radiation*.

Stimulated Emission

When a photon has energy $\Delta E = E' - E$, where E' is a vacant energy level in an atom and E is a lower energy level that is filled, the photon can be absorbed, kicking the electron up into the higher energy level (Fig. 28.22a). If the higher energy level is filled and the lower one is vacant, the electron can drop into the lower energy level by spontaneously emitting a photon of energy ΔE (Fig. 28.22b).