

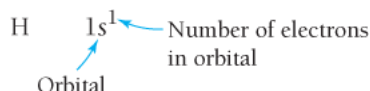
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3.3: Electron Configurations: How Electrons Occupy Orbitals

Key Concept Video Electron Configurations

As we saw in [Chapter 2](#), electrons in atoms exist within orbitals. An **electron configuration** for an atom shows the particular orbitals that electrons occupy for that atom. For example, consider the **ground state**—or lowest energy state—electron configuration for a hydrogen atom:



The electron configuration indicates that hydrogen's one electron is in the 1s orbital. Electrons generally occupy the lowest energy orbitals available. Since the 1s orbital is the lowest energy orbital in hydrogen (see [Section 2.5](#)), hydrogen's electron occupies that orbital. If we could write electron configurations for all the elements, we could see how the arrangements of the electrons within their atoms correlate with the element's chemical properties. However, the Schrödinger equation solutions (the atomic orbitals and their energies) described in [Chapter 2](#) are for the hydrogen atom only. What do the atomic orbitals of *other atoms* look like? What are their relative energies?

The Schrödinger equation for multi-electron atoms includes terms to account for the interactions of the electrons with one another that make it too complicated to solve exactly. However, approximate solutions indicate that the orbitals in multi-electron atoms are hydrogen-like—they are similar to the *s*, *p*, *d*, and *f* orbitals we examined in [Chapter 2](#). In order to see how the electrons in multi-electron atoms occupy these hydrogen-like orbitals, we must examine two additional concepts: *the effects of electron spin*, a fundamental property of all electrons that affects the number of electrons allowed in any one orbital; and *sublevel energy splitting*, which determines the order of orbital filling within a level.

Electron Spin and the Pauli Exclusion Principle

We can represent the electron configuration of hydrogen ($1s^1$) in a slightly different way with an **orbital diagram**, which is similar to an electron configuration but symbolizes the electron as an arrow and the orbital as a box. The orbital diagram for a hydrogen atom is:



In an orbital diagram, the direction of the arrow (pointing up or pointing down) represents the orientation of the *electron's spin*. Recall from [Section 2.5](#) that the orientation of the electron's spin is quantized, with only two possibilities: spin up ($m_s = +\frac{1}{2}$) and spin down ($m_s = -\frac{1}{2}$). In an orbital

diagram, we represent $m_s = +\frac{1}{2}$ with a half-arrow pointing up (\uparrow) and $m_s = -\frac{1}{2}$ with a half-arrow pointing down (\downarrow). In a collection of hydrogen atoms, the electrons in about half of the atoms are spin up and the electrons in the other half are spin down. Since no additional electrons are present within the hydrogen atom, we conventionally represent the hydrogen atom electron configuration with its one electron as spin up.

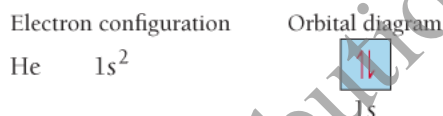
Helium is the first element on the periodic table that contains two electrons. Its two electrons occupy the 1s orbital.



How do the spins of the two electrons in helium align relative to each other? The answer to this question is addressed by the **Pauli exclusion principle**, formulated by Wolfgang Pauli (1900–1958) in 1925:

Pauli exclusion principle: No two electrons in an atom can have the same four quantum numbers.

Because the two electrons occupying the same orbital have three identical quantum numbers (n , l , and m_l), they each must have a different spin quantum number. Since there are only two possible spin quantum numbers ($+\frac{1}{2}$ and $-\frac{1}{2}$), the Pauli exclusion principle implies that *each orbital can have a maximum of only two electrons, with opposing spins*. By applying the exclusion principle, we can write an electron configuration and orbital diagram for helium:



The following table shows the four quantum numbers for each of the two electrons in helium.

n	l	m_l	m_s
1	0	0	$+\frac{1}{2}$
1	0	0	$-\frac{1}{2}$

The two electrons have three quantum numbers in common (because they are in the same orbital), but each electron has a different spin quantum number (as indicated by the opposing half-arrows in the orbital diagram).

Sublevel Energy Splitting in Multi-electron Atoms

A major difference in the (approximate) solutions to the Schrödinger equation for multi-electron atoms compared to the solutions for the hydrogen atom is the energy ordering of the orbitals. In the hydrogen atom, the energy of an orbital depends only on n , the principal quantum number. For example, the 3s, 3p, and 3d orbitals (which are empty for hydrogen in its lowest energy state) all have the same energy—we say they are **degenerate**. The orbitals within a principal level of a *multi-electron atom*, in contrast, are not degenerate—their energy depends on the value of l . We say that the energies of the sublevels are *split*. In general, the lower the value of l within a principal level, the lower the energy (E) of the corresponding orbital. Thus, for a given value of n :

$$E(s \text{ orbital}) < E(p \text{ orbital}) < E(d \text{ orbital}) < E(f \text{ orbital})$$

To understand why the sublevels split in this way, we must examine three key concepts associated with the energy of an electron in the vicinity of a nucleus: (1) Coulomb's law, which describes the interactions between charged particles; (2) shielding, which describes how one electron can shield another electron from the full charge of the nucleus; and (3) penetration, which describes how one atomic orbital can overlap spatially with another, thus penetrating into a region that is close to the nucleus (and therefore is less shielded from nuclear charge). We then examine how these concepts, together with the spatial distributions of electron probability for each orbital, result in the energy ordering presented above.

Coulomb's Law

The attractions and repulsions between charged particles, first introduced in [Section 1.6](#), are described by **Coulomb's law**, which states that the potential energy (E) of two charged particles depends on their charges (q_1 and q_2) and on their separation (r):

[3.1]

$$E = \frac{1}{4\pi\epsilon_0} \frac{q_1 q_2}{r}$$

In this equation, ϵ_0 is a constant ($\epsilon_0 = 8.85 \times 10^{-12} \text{ C}^2/\text{J} \cdot \text{m}$). The potential energy is positive for the interaction of charges with the same sign (plus \times plus, or minus \times minus) and negative for charges of the opposite sign (plus \times minus, or minus \times plus). The *magnitude* of the potential energy depends inversely on the separation between the charged particles.

We can draw three important conclusions from Coulomb's law:

- The potential energy (E) associated with the interaction of like charges is positive but decreases as the particles get *farther apart* (as r increases). Since systems tend toward lower potential energy (see [Section 1.6](#)), like charges that are close together have high potential energy and tend to move away from each other (toward lower potential energy). Like charges therefore repel one another (in much the same way that like poles of two magnets repel each other).
- The potential energy (E) associated with the interaction of unlike charges is negative and becomes more negative as the particles get closer together. Since systems tend toward lower potential energy, the interaction of unlike charges draws them closer together (toward lower potential energy). Unlike charges therefore attract one another (like the opposite poles of a magnet).
- The *magnitude* of the interaction between charged particles increases as the charges of the particles increase. Consequently, an electron with a charge of $1-$ is more strongly attracted to a nucleus with a charge of $2+$ than it is to a nucleus with a charge of $1+$.

Conceptual Connection 3.2 Coulomb's Law

Shielding

For multi-electron atoms, any single electron experiences both the positive charge of the nucleus (which is attractive) and the negative charges of the other electrons (which are repulsive). We can think of the repulsion of one electron by other electrons as *screening* or **shielding** that electron from the full effects of the nuclear charge.

For example, consider a lithium ion (Li^+). Because the lithium ion contains two electrons, its electron configuration is identical to that of helium:

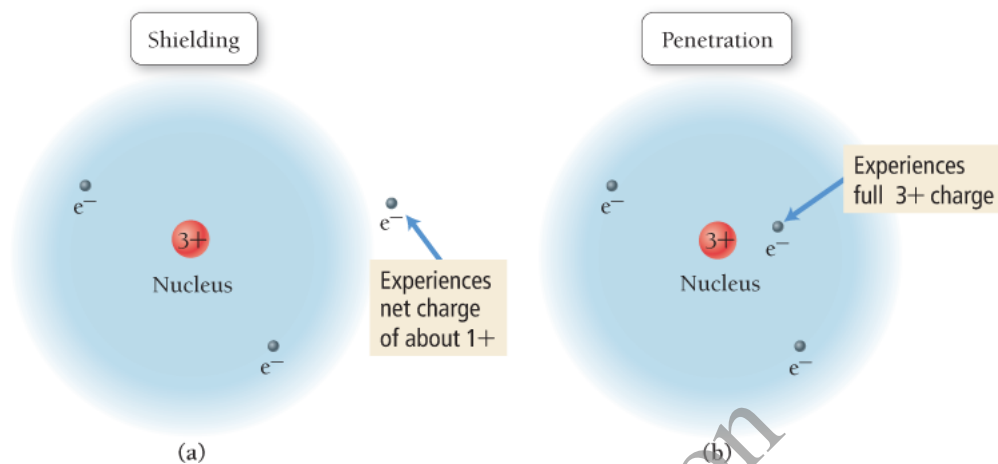


Now imagine bringing a third electron toward the lithium ion. When the third electron is far from the

now imagine bringing a third electron toward the helium ion. When the third electron is far from the nucleus, it experiences the 3+ charge of the nucleus through the *screen* or *shield* of the 2- charge of the two 1s electrons, as shown in [Figure 3.5a](#). We can think of the third electron as experiencing an **effective nuclear charge** (Z_{eff}) of approximately 1+ (3+ from the nucleus and 2- from the electrons, for a net charge of 1+). The inner electrons in effect *shield* the outer electron from the full nuclear charge.

Figure 3.5 Shielding and Penetration

(a) An electron far from the nucleus is partly shielded by the electrons in the 1s orbital, reducing the effective net nuclear charge that it experiences. (b) An electron that penetrates the electron cloud of the 1s orbital experiences more of the nuclear charge.



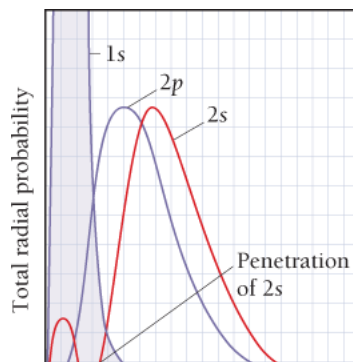
Penetration

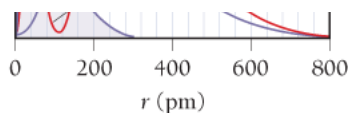
Now imagine that this third electron comes closer to the nucleus. As the electron *penetrates* the electron cloud of the 1s electrons, it begins to experience the 3+ charge of the nucleus more fully because the third electron is less shielded by the intervening electrons. If the electron could somehow get closer to the nucleus than the 1s electrons, it would experience the full 3+ charge, as shown in [Figure 3.5b](#). In other words, as the outer electron undergoes **penetration** into the region occupied by the inner electrons, it experiences a greater nuclear charge and therefore (according to Coulomb's law) a lower energy.

Electron Spatial Distributions and Sublevel Splitting

We have now examined all of the concepts we need to understand the energy splitting of the sublevels within a principal level. The splitting is a result of the spatial distributions of electrons within a sublevel. Recall from [Section 2.6](#) that the radial distribution function for an atomic orbital shows the total probability of finding the electron within a thin spherical shell at a distance r from the nucleus. [Figure 3.6](#) shows the radial distribution functions of the 2s and 2p orbitals superimposed on one another (the radial distribution function of the 1s orbital is also shown).

Figure 3.6 Radial Distribution Functions for the 1s, 2s, and 2p Orbitals





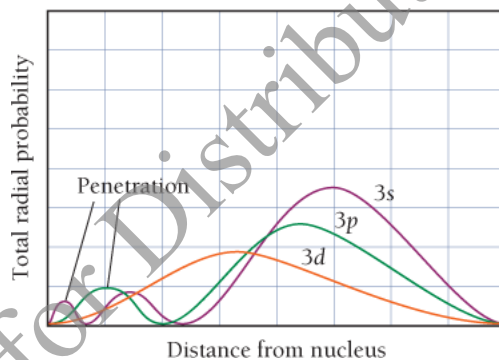
Notice that, in general, an electron in a $2p$ orbital has a greater probability of being found closer to the nucleus than an electron in a $2s$ orbital. We might initially expect, therefore, that the $2p$ orbital would be lower in energy. However, exactly the opposite is true—the $2s$ orbital is actually lower in energy *but only when the $1s$ orbital is occupied*. (When the $1s$ orbital is empty, the $2s$ and $2p$ orbitals are degenerate.) Why?

The reason is the bump near $r = 0$ the nucleus for the $2s$ orbital. This bump represents a significant probability of the electron being found very close to the nucleus. Even more importantly, this area of the probability penetrates into the $1s$ orbital—it gets into the region where shielding by the $1s$ electrons is less effective. In contrast, most of the probability in the radial distribution function of the $2p$ orbital lies *outside* the radial distribution function of the $1s$ orbital. Consequently, almost all of the $2p$ orbital is shielded from nuclear charge by the $1s$ orbital. The $2s$ orbital—because it experiences more of the nuclear charge due to its greater *penetration*—is lower in energy than the $2p$ orbital.

The situation is similar when we compare the $3s$, $3p$, and $3d$ orbitals. The s orbitals penetrate more fully than the p orbitals, which in turn penetrate more fully than the d orbitals, as shown in [Figure 3.7](#).

Figure 3.7 Radial Distribution Functions for the $3s$, $3p$, and $3d$ Orbitals

The $3s$ electrons penetrate most deeply into the inner orbitals, are least shielded, and experience the greatest effective nuclear charge. The $3d$ electrons penetrate least. This accounts for the energy ordering of the sublevels: $s < p < d$.

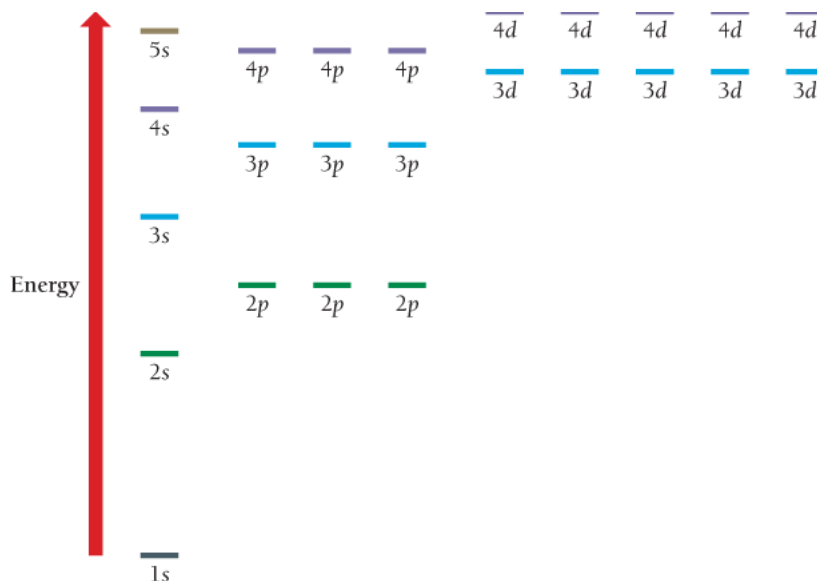


[Figure 3.8](#) shows the energy ordering of a number of orbitals in multi-electron atoms. Notice these features of [Figure 3.8](#):

- Because of penetration, the sublevels of each principal level are *not* degenerate for multi-electron atoms.
- In the fourth and fifth principal levels, the effects of penetration become so important that the $4s$ orbital is lower in energy than the $3d$ orbitals and the $5s$ orbital is lower in energy than the $4d$ orbitals.
- The energy separations between one set of orbitals and the next become smaller for $4s$ orbitals and beyond, and the relative energy ordering of these orbitals can actually vary among elements. These variations result in irregularities in the electron configurations of the transition metals and their ions (as we shall see in [Section 3.4](#)).

Figure 3.8 General Energy Ordering of Orbitals for Multi-electron Atoms

General Energy Ordering of Orbitals for Multi-electron Atoms



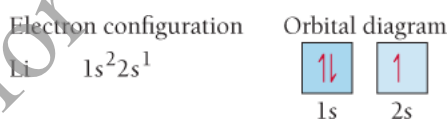
Conceptual Connection 3.3 Penetration and Shielding

Electron Configurations for Multi-electron Atoms

Now that we know the energy ordering of orbitals in multi-electron atoms, we can determine ground state electron configurations for the rest of the elements. Because electrons occupy the lowest energy orbitals available when the atom is in its ground state, and only two electrons (with opposing spins) are allowed in each orbital, we can systematically build up the electron configurations for the elements. This pattern of orbital filling is known as the **aufbau principle** (the German word *aufbau* means “build up”).

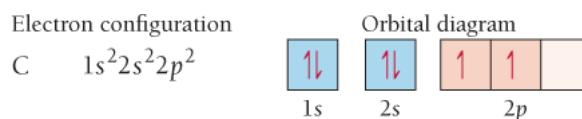
Unless otherwise specified, we use the term *electron configuration* to mean the ground state (or lowest energy) configuration.

For lithium, with three electrons, the electron configuration and orbital diagram are:



Remember that the number of electrons in a neutral atom is equal to its atomic number.

For carbon, which has six electrons, the electron configuration and orbital diagram are:



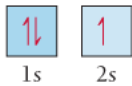
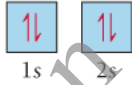


Notice that the $2p$ electrons occupy the p orbitals (of equal energy) singly, rather than pairing in one orbital. This way of filling orbitals follows **Hund's rule**, which states that *when filling degenerate orbitals, electrons fill them singly first, with parallel spins*. Hund's rule is a result of an atom's tendency to find the lowest energy state possible. When two electrons occupy separate orbitals of equal energy, the repulsive interaction between them is lower than when they occupy the same orbital because the electrons are spread out over a larger region of space. By convention, we denote these parallel spins with half arrows pointing up.

Electrons with parallel spins have correlated motion that minimizes their mutual repulsion.

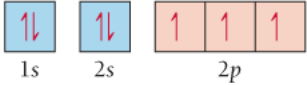



Summarizing Orbital Filling

- Electrons occupy orbitals so as to minimize the energy of the atom; therefore, lower-energy orbitals fill before higher-energy orbitals. Orbitals fill in the following order: $1s$ $2s$ $3s$ $3p$ $4s$ $3d$ $4p$ $5s$ $4d$ $5p$ $6s$.
- Orbitals can hold no more than two electrons each. When two electrons occupy the same orbital, their spins are opposite. This is another way of expressing the Pauli exclusion principle (no two electrons in one atom can have the same four quantum numbers).
- When orbitals of identical energy are available, electrons first occupy these orbitals singly with parallel spins rather than in pairs (Hund's rule). Once the orbitals of equal energy are half-full, the electrons start to pair.

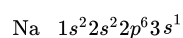
Consider the electron configurations and orbital diagrams for the elements with atomic numbers 3–10:

Symbol	Number of electrons	Electron configuration	Orbital diagram
Li	3	$1s^2 2s^1$	
Be	4	$1s^2 2s^2$	
B	5	$1s^2 2s^2 2p^1$	
C	6	$1s^2 2s^2 2p^2$	

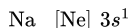
Notice that, as a result of Hund's rule, the p orbitals fill with single electrons before the electrons pair:

N	7	$1s^2 2s^2 2p^3$	
O	8	$1s^2 2s^2 2p^4$	
F	9	$1s^2 2s^2 2p^5$	
Ne	10	$1s^2 2s^2 2p^6$	

The electron configuration of neon represents the complete filling of the $n = 2$ principal level. When writing electron configurations for elements beyond neon, or beyond any other noble gas, we abbreviate the electron configuration of the previous noble gas—sometimes called the *inner electron configuration*—by the symbol for the noble gas in square brackets. For example, the electron configuration of sodium is:



We write this configuration more compactly by using [Ne] to represent the inner electrons:



[Ne] represents $1s^2 2s^2 2p^6$, the electron configuration for neon.

To write an electron configuration for an element, we first find its atomic number from the periodic table—this number equals the number of electrons. Then we use the order of filling to distribute the electrons in the appropriate orbitals. Remember that each orbital can hold a maximum of two electrons.

Consequently,

- The s sublevel has only one orbital and can therefore hold only two electrons.
- The p sublevel has three orbitals and can hold six electrons.
- The d sublevel has five orbitals and can hold ten electrons.
- The f sublevel has seven orbitals and can hold 14 electrons.

Example 3.1 Electron Configurations

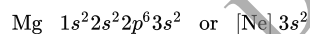
Write the electron configuration for each element.

- Mg
- P
- Br
- Al

SOLUTION

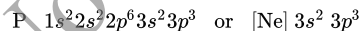
- Mg

Magnesium has 12 electrons. Distribute two electrons into the $1s$ orbital, two into the $2s$ orbital, six into the $2p$ orbitals, and two into the $3s$ orbital.



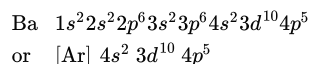
- P

Phosphorus has 15 electrons. Distribute two electrons into the $1s$ orbital, two into the $2s$ orbital, six into the $2p$ orbitals, two into the $3s$ orbital, and three into the $3p$ orbitals.



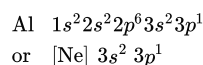
- Br

Bromine has 35 electrons. Distribute two electrons into the $1s$ orbital, two into the $2s$ orbital, six into the $2p$ orbitals, two into the $3s$ orbital, six into the $3p$ orbitals, two into the $4s$ orbital, ten into the $3d$ orbitals, and five into the $4p$ orbitals.



- Al

Aluminum has 13 electrons. Distribute two electrons into the $1s$ orbital, two into the $2s$ orbital, six into the $2p$ orbitals, two into the $3s$ orbital, and one into the $3p$ orbital.



FOR PRACTICE 3.1 Write the electron configuration for each element.

- a. Cl
- b. Si
- c. Sr
- d. O

Example 3.2 Writing Orbital Diagrams

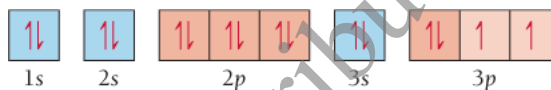
Write the orbital diagram for sulfur and determine its number of unpaired electrons.

SOLUTION

Sulfur's atomic number is 16, so it has 16 electrons and the electron configuration $1s^2 2s^2 2p^6 3s^2 3p^4$. Draw a box for each orbital, putting the lowest energy orbital (1s) on the far left and proceeding to orbitals of higher energy to the right.



Distribute the 16 electrons into the boxes representing the orbitals, allowing a maximum of two electrons per orbital and obeying Hund's rule. You can see from the diagram that sulfur has two unpaired electrons.



Two unpaired electrons

FOR PRACTICE 3.2 Write the orbital diagram for Ar and determine its number of unpaired electrons.

Conceptual Connection 3.4 Electron Configurations and Quantum Numbers

Interactive

Not for Distribution

Not for Distribution

Not for Distribution