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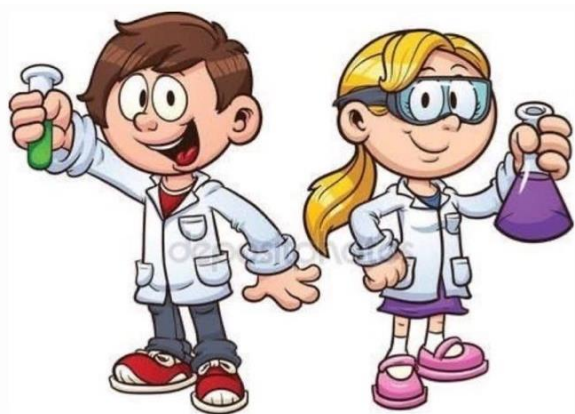
*General Chemistry*

*Course Support*

## *Chapter N° 4*

# *Electronic Structure of Atoms*

*(Update : 23/10/2023)*



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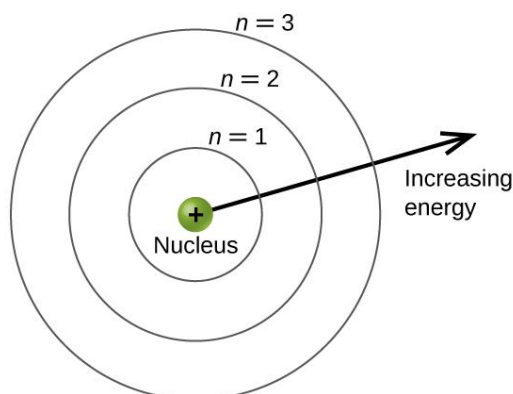
## IV. Electronic Structure of Atoms

### IV.1 Understanding Quantum Theory of Electrons in Atoms

The goal of this section is to understand the electron orbitals (location of electrons in atoms), their different energies, and other properties. The use of quantum theory provides the best understanding to these topics. This knowledge is a precursor to chemical bonding.

As was described previously, electrons in atoms can exist only on discrete energy levels but not between them. It is said that the energy of an electron in an atom is quantized, that is, it can be equal only to certain specific values and can jump from one energy level to another but not transition smoothly or stay between these levels.

The energy levels are labeled with an  $n$  value, where  $n = 1, 2, 3, \dots$ . Generally speaking, the energy of an electron in an atom is greater for greater values of  $n$ . This number,  $n$ , is referred to as the principal quantum number. The **principal quantum number** defines the location of the energy level. It is essentially the same concept as the  $n$  in the Bohr atom description. Another name for the principal quantum number is the shell number. The **shells** of an atom can be thought of concentric circles radiating out from the nucleus. The electrons that belong to a specific shell are most likely to be found within the corresponding circular area. The further we proceed from the nucleus, the higher the shell number, and so the higher the energy level **Figure 4.1**. The positively charged protons in the nucleus stabilize the electronic orbitals by electrostatic attraction between the positive charges of the protons and the negative charges of the electrons. So, the further away the electron is from the nucleus, the greater the energy it has.



**Figure 4.1** Different shells are numbered by principal quantum numbers.

This quantum mechanical model for where electrons reside in an atom can be used to look at electronic transitions, the events when an electron moves from one energy level to another. If the transition is to a higher energy level, energy is absorbed, and the energy change has a positive value. To obtain the amount of energy necessary for the transition to a higher energy level, a photon is absorbed by the atom. A transition to a lower energy level involves a release of energy, and the energy change is negative. This process is accompanied by emission of a photon by the atom. The following equation summarizes these relationships and is based on the hydrogen atom:

$$\begin{aligned}\Delta E &= E_{\text{final}} - E_{\text{initial}} \\ &= -2.18 \times 10^{-18} \left( \frac{1}{n_f^2} - \frac{1}{n_i^2} \right) \text{ J}\end{aligned}$$

The values  $n_f$  and  $n_i$  are the final and initial energy states of the electron. Example 4.1 in the previous section of the chapter demonstrates calculations of such energy changes.

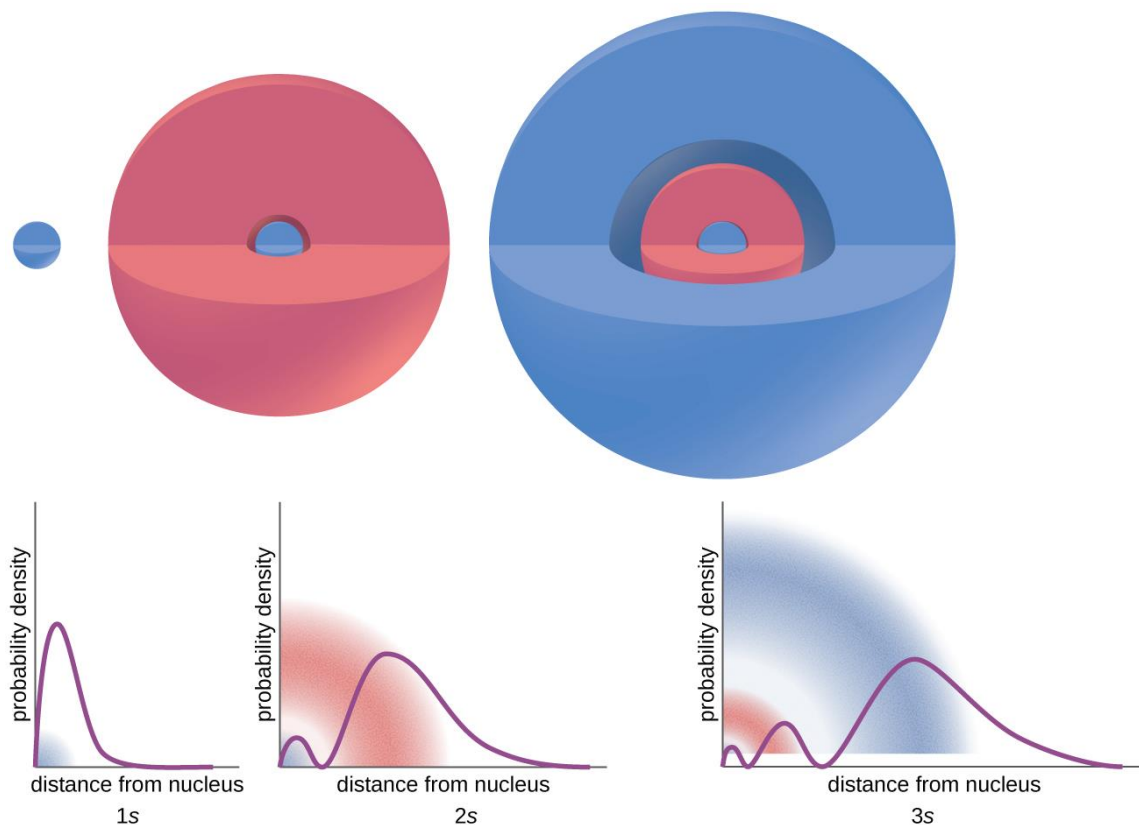
The principal quantum number is one of three quantum numbers used to characterize an orbital. An **atomic orbital** is a general region in an atom within which an electron is most probable to reside. The quantum mechanical model specifies the probability of finding an electron in the three-dimensional space around the nucleus and is based on solutions of the Schrödinger equation. In addition, the principal quantum number defines the energy of an electron in a hydrogen or hydrogen-like atom or an ion (an atom or an ion with only one electron) and the general region in which discrete energy levels of electrons in a multi-electron atoms and ions are located.

Another quantum number is  $l$ , the **secondary (angular momentum) quantum number**. It is an integer that may take the values,  $l = 0, 1, 2, \dots, n - 1$ . This means that an orbital with  $n = 1$  can have only one value of  $l$ ,  $l = 0$ , whereas  $n = 2$  permits  $l = 0$  and  $l = 1$ , and so on. Whereas the principal quantum number,  $n$ , defines the general size and energy of the orbital, the secondary quantum number  $l$  specifies the shape of the orbital. Orbitals with the same value of  $l$  define a **subshell**.

Orbitals with  $l = 0$  are called **s orbitals** and they make up the  $s$  subshells. The value  $l = 1$  corresponds to the  $p$  orbitals. For a given  $n$ , **p orbitals** constitute a  $p$  subshell (e.g.,  $3p$  if  $n =$

3). The orbitals with  $l = 2$  are called the ***d*** orbitals, followed by the *f*-, *g*-, and *h*-orbitals for  $l = 3, 4,$  and  $5$ .

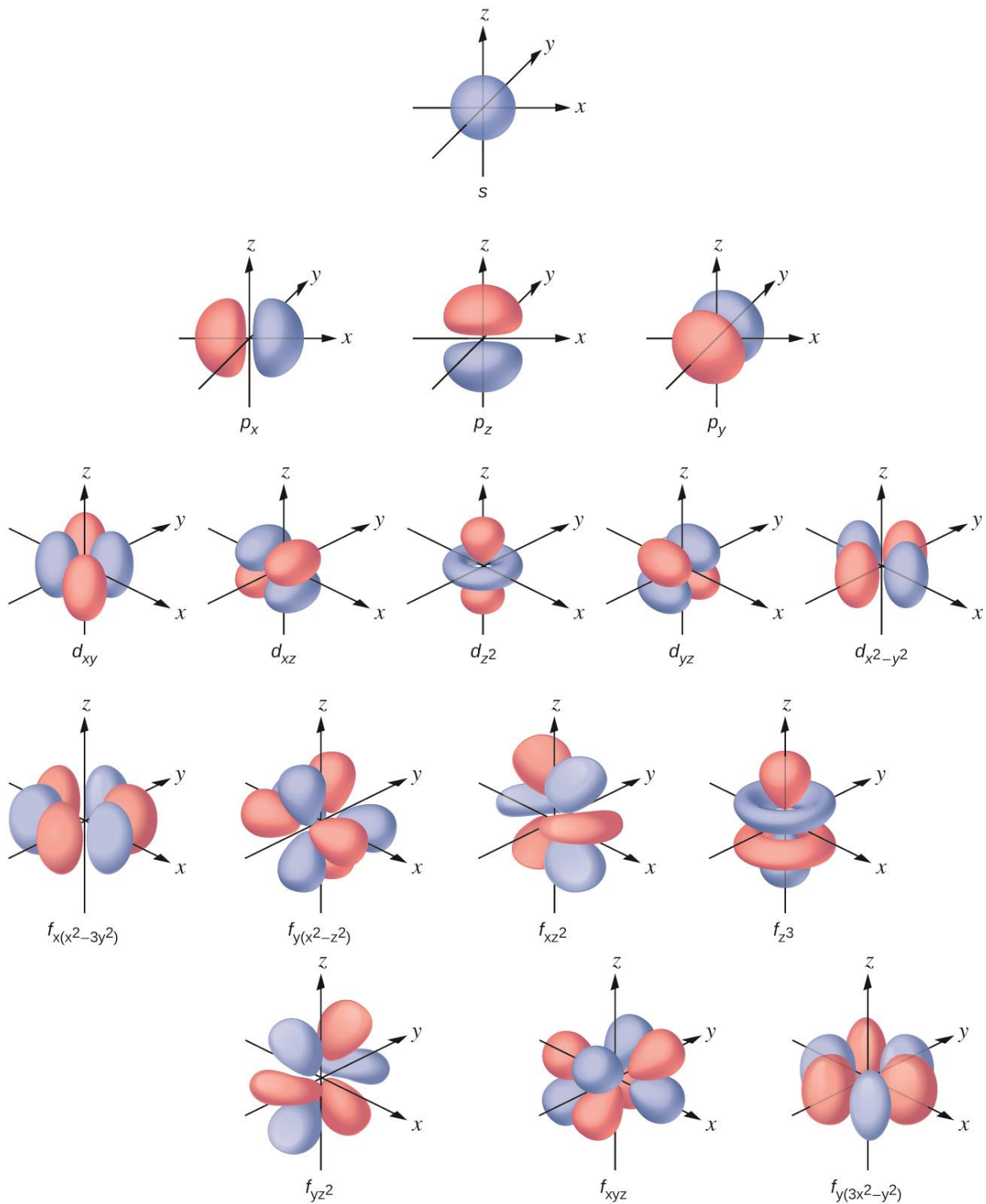
There are certain distances from the nucleus at which the probability density of finding an electron located at a particular orbital is zero. In other words, the value of the wavefunction  $\psi$  is zero at this distance for this orbital. Such a value of radius  $r$  is called a radial node. The number of radial nodes in an orbital is  $n - l - 1$ .



**Figure 4.2** The graphs show the probability (y axis) of finding an electron for the 1s, 2s, 3s orbitals as a function of distance from the nucleus.

Consider the examples in **Figure 4.2**. The orbitals depicted are of the *s* type, thus  $l = 0$  for all of them. It can be seen from the graphs of the probability densities that there are  $1 - 0 - 1 = 0$  places where the density is zero (nodes) for 1s ( $n = 1$ ),  $2 - 0 - 1 = 1$  node for 2s, and  $3 - 0 - 1 = 2$  nodes for the 3s orbitals.

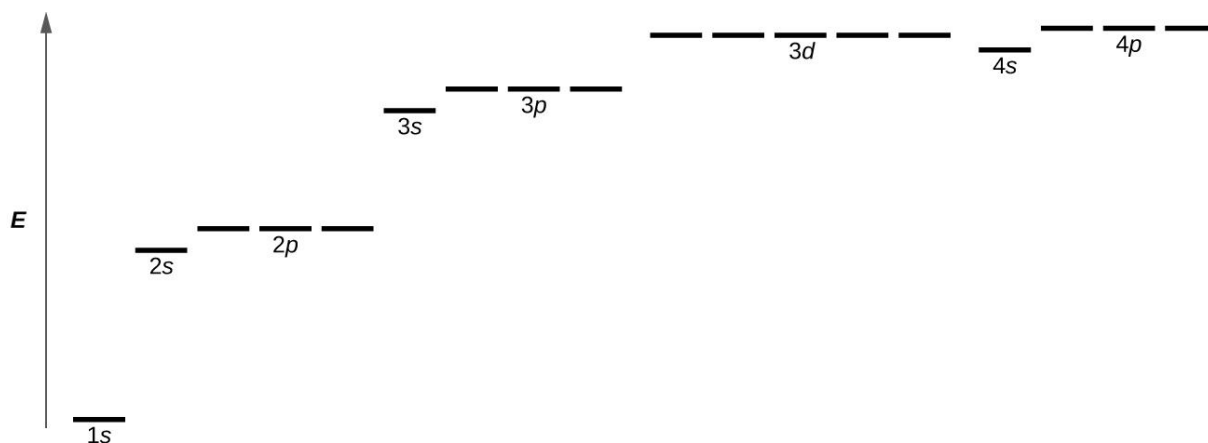
The *s* subshell electron density distribution is spherical and the *p* subshell has a dumbbell shape. The *d* and *f* orbitals are more complex. These shapes represent the three-dimensional regions within which the electron is likely to be found.



**Figure 4.3** Shapes of  $s$ ,  $p$ ,  $d$ , and  $f$  orbitals.

The **magnetic quantum number**,  $m$ , specifies the relative spatial orientation of a particular orbital. Generally speaking,  $m_l$  can be equal to  $-l, -(l - 1), \dots, 0, \dots, (l - 1), l$ . The total number of possible orbitals with the same value of  $l$  (that is, in the same subshell) is  $2l + 1$ . Thus, there is one  $s$ -orbital in an  $s$  subshell ( $l = 0$ ), there are three  $p$ -orbitals in a  $p$  subshell

( $l = 1$ ), five  $d$ -orbitals in a  $d$  subshell ( $l = 2$ ), seven  $f$ -orbitals in an  $f$  subshell ( $l = 3$ ), and so forth. The principal quantum number defines the general value of the electronic energy. The angular momentum quantum number determines the shape of the orbital. And the magnetic quantum number specifies orientation of the orbital in space, as can be seen in **Figure 4.3**.



**Figure 4.4** The chart shows the energies of electron orbitals in a multi-electron atom.

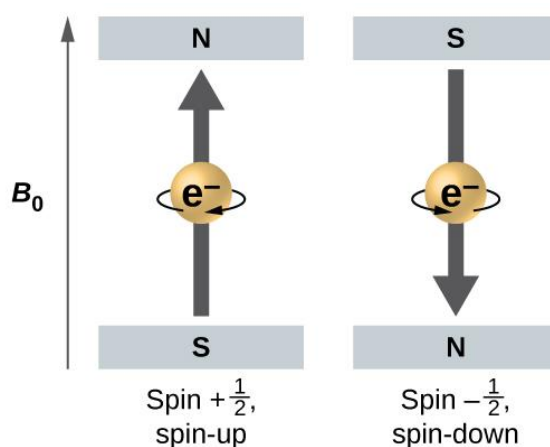
**Figure 4.4** illustrates the energy levels for various orbitals. The number before the orbital name (such as  $2s$ ,  $3p$ , and so forth) stands for the principal quantum number,  $n$ . The letter in the orbital name defines the subshell with a specific angular momentum quantum number  $l = 0$  for  $s$  orbitals,  $1$  for  $p$  orbitals,  $2$  for  $d$  orbitals. Finally, there are more than one possible orbitals for  $l \geq 1$ , each corresponding to a specific value of  $m_l$ . In the case of a hydrogen atom or a one-electron ion (such as  $\text{He}^+$ ,  $\text{Li}^{2+}$ , and so on), energies of all the orbitals with the same  $n$  are the same. This is called a degeneracy, and the energy levels for the same principal quantum number,  $n$ , are called **degenerate orbitals**. However, in atoms with more than one electron, this degeneracy is eliminated by the electron–electron interactions, and orbitals that belong to different subshells have different energies, as shown on **Figure 4.4**. Orbitals within the same subshell are still degenerate and have the same energy.

While the three quantum numbers discussed in the previous paragraphs work well for describing electron orbitals, some experiments showed that they were not sufficient to explain all observed results. It was demonstrated in the 1920s that when hydrogen-line spectra are examined at extremely high resolution, some lines are actually not single peaks but, rather, pairs of closely spaced lines. This is the so-called fine structure of the spectrum, and it implies that there are additional small differences in energies of electrons even when they are located in the same orbital. These observations led Samuel Goudsmit and George Uhlenbeck to

propose that electrons have a fourth quantum number. They called this the **spin quantum number**, or  $S$

The other three quantum numbers,  $n$ ,  $l$ , and  $m_l$ , are properties of specific atomic orbitals that also define in what part of the space an electron is most likely to be located. Orbitals are a result of solving the Schrödinger equation for electrons in atoms. The electron spin is a different kind of property. It is a completely quantum phenomenon with no analogues in the classical realm. In addition, it cannot be derived from solving the Schrödinger equation and is not related to the normal spatial coordinates (such as the Cartesian  $x$ ,  $y$ , and  $z$ ). Electron spin describes an intrinsic electron "rotation" or "spinning." Each electron acts as a tiny magnet or a tiny rotating object with an angular momentum, or as a loop with an electric current, even though this rotation or current cannot be observed in terms of spatial coordinates.

The magnitude of the overall electron spin can only have one value, and an electron can only "spin" in one of two quantized states. One is termed the  $\alpha$  state, with the  $z$  component of the spin being in the positive direction of the  $z$  axis. This corresponds to the spin quantum number  $S=1/2$ . The other is called the  $\beta$  state, with the  $z$  component of the spin being negative and  $S=-1/2$ . Any electron, regardless of the atomic orbital it is located in, can only have one of those two values of the spin quantum number. The energies of electrons having  $S=-1/2$  and  $S=1/2$  are different if an external magnetic field is applied.



**Figure 4.5** Electrons with spin values  $\pm 1/2$  in an external magnetic field.

**Figure 4.5** illustrates this phenomenon. An electron acts like a tiny magnet. Its moment is directed up (in the positive direction of the  $z$  axis) for the  $1/2$  spin quantum number and down (in the negative  $z$  direction) for the spin quantum number of  $-1/2$ . A magnet has a lower



energy if its magnetic moment is aligned with the external magnetic field (the left electron on **Figure 4.5** and a higher energy for the magnetic moment being opposite to the applied field. This is why an electron with  $S=1/2$  has a slightly lower energy in an external field in the positive  $z$  direction, and an electron with  $S=-1/2$  has a slightly higher energy in the same field. This is true even for an electron occupying the same orbital in an atom. A spectral line corresponding to a transition for electrons from the same orbital but with different spin quantum numbers has two possible values of energy; thus, the line in the spectrum will show a fine structure splitting.

### *IV.2 The Pauli Exclusion Principle*

An electron in an atom is completely described by four quantum numbers:  $n$ ,  $l$ ,  $m_l$ , and  $m_s$ . The first three quantum numbers define the orbital and the fourth quantum number describes the intrinsic electron property called spin. An Austrian physicist Wolfgang Pauli formulated a general principle that gives the last piece of information that we need to understand the general behavior of electrons in atoms. The **Pauli exclusion principle** can be formulated as follows: No two electrons in the same atom can have exactly the same set of all the four quantum numbers. What this means is that two electrons can share the same orbital (the same set of the quantum numbers  $n$ ,  $l$ , and  $m_l$ ) only if their spin quantum numbers  $S$  have different values. Since the spin quantum number can only have two values ( $\pm 1/2$ ), no more than two electrons can occupy the same orbital (and if two electrons are located in the same orbital, they must have opposite spins). Therefore, any atomic orbital can be populated by only zero, one, or two electrons.

The properties and meaning of the quantum numbers of electrons in atoms are briefly summarized in **Table 3.1**.

<b>Quantum Numbers, Their Properties, and Significance</b>			
<b>Name</b>	<b>Symbol</b>	<b>Allowed values</b>	<b>Physical meaning</b>
Principal quantum number	$n$	1, 2, 3, 4, ....	Shell, the general region for the value of energy for an electron on the orbital

Quantum Numbers, Their Properties, and Significance			
Name	Symbol	Allowed values	Physical meaning
Angular momentum or azimuthal quantum number	$l$	$0 \leq l \leq n - 1$	Subshell, the shape of the orbital
Magnetic quantum number	$m$	$-l \leq m_l \leq l$	Orientation of the orbital
Spin quantum number	$s$	$1/2, -1/2$	Direction of the intrinsic quantum "spinning" of the electron

**Table 3.1**

### EXAMPLE 1

#### *Working with Shells and Subshells*

Indicate the number of subshells, the number of orbitals in each subshell, and the values of  $l$  and  $m_l$  for the orbitals in the  $n = 4$  shell of an atom.

#### *Solution*

For  $n = 4$ ,  $l$  can have values of 0, 1, 2, and 3. Thus, s, p, d, and f subshells are found in the  $n = 4$  shell of an atom. For  $l = 0$  (the s subshell),  $m_l$  can only be 0. Thus, there is only one 4s orbital. For  $l = 1$  (p-type orbitals),  $m$  can have values of  $-1, 0, +1$ , so we find three 4p orbitals. For  $l = 2$  (d-type orbitals),  $m_l$  can have values of  $-2, -1, 0, +1, +2$ , so we have five 4d orbitals. When  $l = 3$  (f-type orbitals),  $m$  can have values of  $-3, -2, -1, 0, +1, +2, +3$ , and we can have seven 4f orbitals. Thus, we find a total of 16 orbitals in the  $n = 4$  shell of an atom.

#### *Check Your Learning*

Identify the subshell in which electrons with the following quantum numbers are found:

(a)  $n = 3, l = 1$ ; (b)  $n = 5, l = 3$ ; (c)  $n = 2, l = 0$ .

#### **ANSWER:**

(a) 3p (b) 5f (c) 2s

## EXAMPLE 2

### *Maximum Number of Electrons*

Calculate the maximum number of electrons that can occupy a shell with (a)  $n = 2$ , (b)  $n = 5$ , and (c)  $n$  as a variable. Note you are only looking at the orbitals with the specified  $n$  value, not those at lower energies.

### *Solution*

(a) When  $n = 2$ , there are four orbitals (a single  $2s$  orbital, and three orbitals labeled  $2p$ ). These four orbitals can contain eight electrons.

(b) When  $n = 5$ , there are five subshells of orbitals that we need to sum:

1 orbital labeled  $5s$

3 orbitals labeled  $5p$

5 orbitals labeled  $5d$

7 orbitals labeled  $5f$

+ 9 orbitals labeled  $5g$

-----

25 orbitals total

Again, each orbital holds two electrons, so 50 electrons can fit in this shell.

(c) The number of orbitals in any shell  $n$  will equal  $n^2$ . There can be up to two electrons in each orbital, so the maximum number of electrons will be  $2n^2$ .

### *Check Your Learning*

If a shell contains a maximum of 32 electrons, what is the principal quantum number,  $n$ ?

**ANSWER:**

$n = 4$

## EXAMPLE 3

### *Working with Quantum Numbers*

Complete the following table for atomic orbitals:

Orbital	$n$	$l$	$m_l$ degeneracy	Radial nodes (no.)
$4f$				
	4	1		
	7		7	3
$5d$				

**Solution**

The table can be completed using the following rules:

The orbital designation is  $nl$ , where  $l = 0, 1, 2, 3, 4, 5, \dots$  is mapped to the letter sequence  $s, p, d, f, g, h, \dots$ ,

The  $m_l$  degeneracy is the number of orbitals within an  $l$  subshell, and so is  $2l + 1$  (there is one  $s$  orbital, three  $p$  orbitals, five  $d$  orbitals, seven  $f$  orbitals, and so forth).

The number of radial nodes is equal to  $n - l - 1$ .

Orbital	$n$	$l$	$M$ degeneracy	Radial nodes (no.)
$4f$	4	3	7	0
$4p$	4	1	3	2
$7f$	7	3	7	3
$5d$	5	2	5	2

**Check Your Learning**

How many orbitals have  $l = 2$  and  $n = 3$ ?

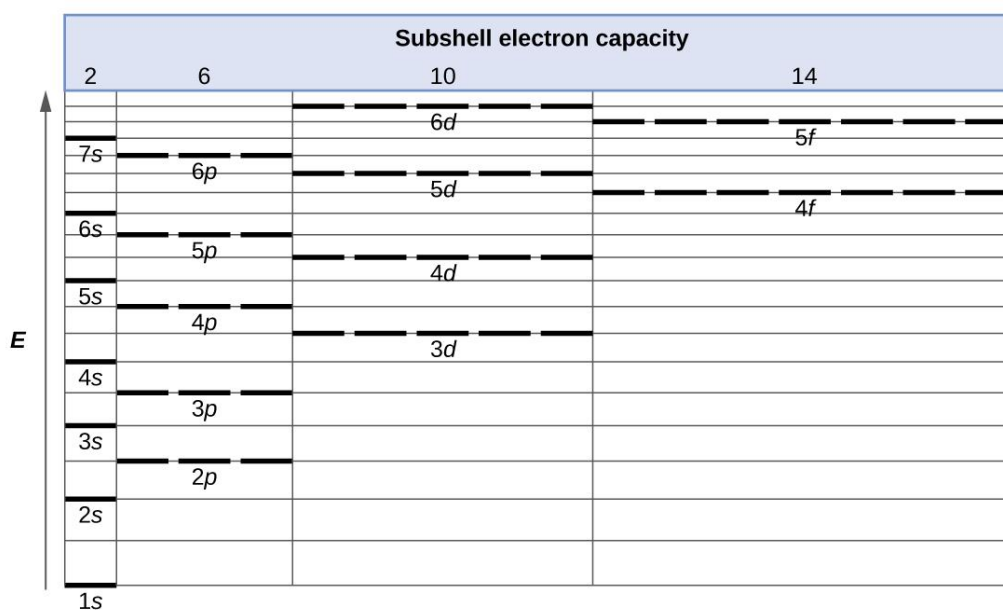
**ANSWER:**

The five degenerate  $3d$  orbitals

### IV.3 Orbital Energies and Atomic Structure

The energy of atomic orbitals increases as the principal quantum number,  $n$ , increases. In any atom with two or more electrons, the repulsion between the electrons makes energies of subshells with different values of  $l$  differ so that the energy of the orbitals increases within a shell in the order  $s < p < d < f$ . **Figure 4.6** depicts how these two trends in increasing energy

relate. The  $1s$  orbital at the bottom of the diagram is the orbital with electrons of lowest energy. The energy increases as we move up to the  $2s$  and then  $2p$ ,  $3s$ , and  $3p$  orbitals, showing that the increasing  $n$  value has more influence on energy than the increasing  $l$  value for small atoms. However, this pattern does not hold for larger atoms. The  $3d$  orbital is higher in energy than the  $4s$  orbital. Such overlaps continue to occur frequently as we move up the chart.



**Figure 4.6** Generalized energy-level diagram for atomic orbitals in an atom with two or more electrons (not to scale).

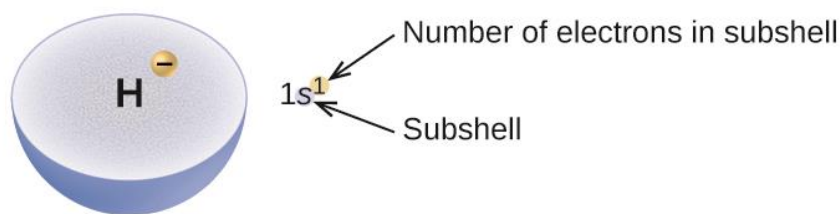
Electrons in successive atoms on the periodic table tend to fill low-energy orbitals first. Thus, many students find it confusing that, for example, the  $5p$  orbitals fill immediately after the  $4d$ , and immediately before the  $6s$ . The filling order is based on observed experimental results, and has been confirmed by theoretical calculations. As the principal quantum number,  $n$ , increases, the size of the orbital increases and the electrons spend more time farther from the nucleus. Thus, the attraction to the nucleus is weaker and the energy associated with the orbital is higher (less stabilized). But this is not the only effect we have to take into account. Within each shell, as the value of  $l$  increases, the electrons are less penetrating (meaning there is less electron density found close to the nucleus), in the order  $s > p > d > f$ . Electrons that are closer to the nucleus slightly repel electrons that are farther out, offsetting the more dominant electron–nucleus attractions slightly (recall that all electrons have  $-1$  charges, but nuclei have  $+Z$  charges). This phenomenon is called shielding and will be discussed in more detail in the next section. Electrons in orbitals that experience more shielding are less stabilized and thus higher in energy. For small orbitals ( $1s$  through  $3p$ ), the increase in energy due to  $n$  is more

significant than the increase due to  $l$ ; however, for larger orbitals the two trends are comparable and cannot be simply predicted. We will discuss methods for remembering the observed order.

The arrangement of electrons in the orbitals of an atom is called the **electron configuration** of the atom. We describe an electron configuration with a symbol that contains three pieces of information **Figure 4.7**:

1. The number of the principal quantum shell,  $n$ ,
2. The letter that designates the orbital type (the subshell,  $l$ ), and
3. A superscript number that designates the number of electrons in that particular subshell.

For example, the notation  $2p^4$  (read "two-p-four") indicates four electrons in a  $p$  subshell ( $l = 1$ ) with a principal quantum number ( $n$ ) of 2. The notation  $3d^8$  (read "three-d-eight") indicates eight electrons in the  $d$  subshell (i.e.,  $l = 2$ ) of the principal shell for which  $n = 3$ .

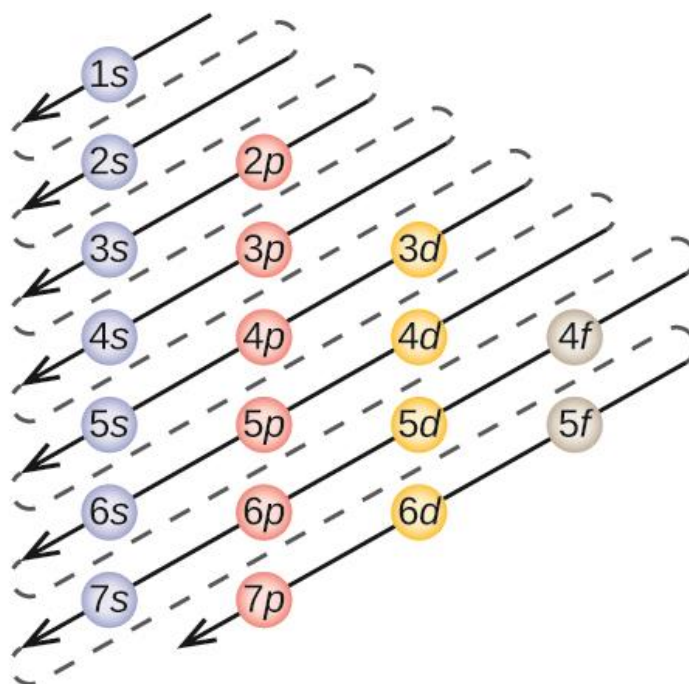


**Figure 4.7** The diagram of an electron configuration specifies the subshell ( $n$  and  $l$  value, with letter symbol) and superscript number of electrons.

#### *IV.4 The Aufbau Principle*

To determine the electron configuration for any particular atom, we can “build” the structures in the order of atomic numbers. Beginning with hydrogen, and continuing across the periods of the periodic table, we add one proton at a time to the nucleus and one electron to the proper subshell until we have described the electron configurations of all the elements. This procedure is called the **Aufbau principle**, from the German word *Aufbau* (“to build up”). Each added electron occupies the subshell of lowest energy available (in the order shown in **Figure 4.6**), subject to the limitations imposed by the allowed quantum numbers according to the Pauli exclusion principle. Electrons enter higher-energy subshells only after lower-energy subshells have been filled to capacity. **Figure 4.8** illustrates the traditional way to remember the filling order for atomic orbitals. Since the arrangement of the periodic table is based on the electron configurations, **Figure 4.9** provides an alternative method for determining the electron configuration. The filling order simply begins at hydrogen and includes each subshell

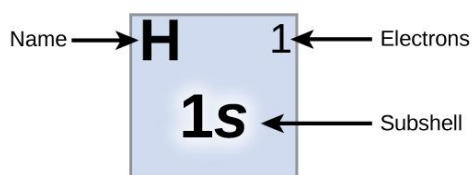
as you proceed in increasing  $Z$  order. For example, after filling the  $3p$  block up to Ar, we see the orbital will be  $4s$  (K, Ca), followed by the  $3d$  orbitals.



**Figure 4.8** This diagram depicts the energy order for atomic orbitals and is useful for deriving ground-state electron configurations.

**Electron Configuration Table**

Period	Group																	18
	1											13	14	15	16	17	18	
1	H 1s																He 1s	
2	Li 2s	2											B 2p	C	N	O	F	Ne
3	Na 3s	2	3	4	5	6	7	8	9	10	11	12	Al 3p	Si	P	S	Cl	Ar
4	K 4s	2	3	4	5	6	7	8	9	10	11	12	Ga 4p	Ge	As	Se	Br	Kr
5	Rb 5s	2	3	4	5	6	7	8	9	10	11	12	In 5p	Sn	Sb	Te	I	Xe
6	Cs 6s	2	3	4	5	6	7	8	9	10	11	12	Tl 6p	Pb	Bi	Po	At	Rn
7	Fr 7s	2	3	4	5	6	7	8	9	10	11	12	Nh	Fl	Mc	Lv	Ts	Og

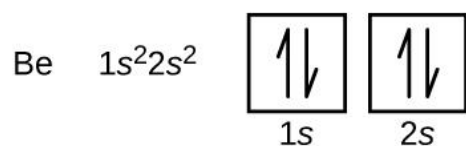


**Figure 4.9** This partial periodic table shows electron configurations for the valence subshells of atoms. By “building up” from hydrogen, this table can be used to determine the electron

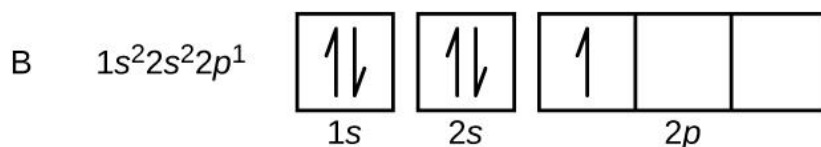




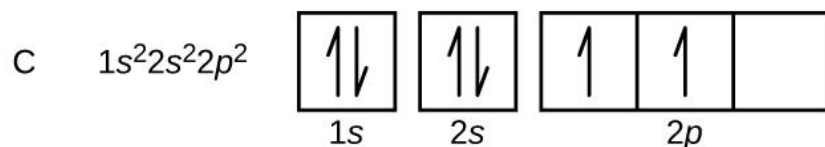
An atom of the alkaline earth metal beryllium, with an atomic number of 4, contains four protons in the nucleus and four electrons surrounding the nucleus. The fourth electron fills the remaining space in the  $2s$  orbital.



An atom of boron (atomic number 5) contains five electrons. The  $n = 1$  shell is filled with two electrons and three electrons will occupy the  $n = 2$  shell. Because any  $s$  subshell can contain only two electrons, the fifth electron must occupy the next energy level, which will be a  $2p$  orbital. There are three degenerate  $2p$  orbitals ( $m_l = -1, 0, +1$ ) and the electron can occupy any one of these  $p$  orbitals. When drawing orbital diagrams, we include empty boxes to depict any empty orbitals in the same subshell that we are filling.

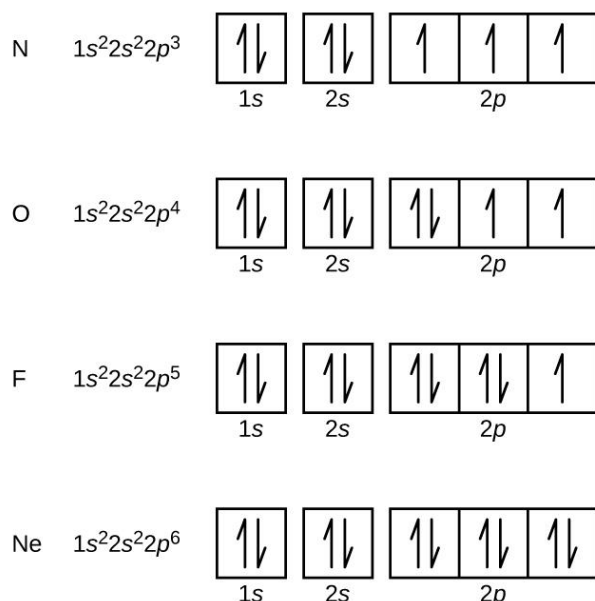


Carbon (atomic number 6) has six electrons. Four of them fill the  $1s$  and  $2s$  orbitals. The remaining two electrons occupy the  $2p$  subshell. We now have a choice of filling one of the  $2p$  orbitals and pairing the electrons or of leaving the electrons unpaired in two different, but degenerate,  $p$  orbitals. The orbitals are filled as described by **Hund's rule**: the lowest-energy configuration for an atom with electrons within a set of degenerate orbitals is that having the maximum number of unpaired electrons. Thus, the two electrons in the carbon  $2p$  orbitals have identical  $n$ ,  $l$ , and  $m_s$  quantum numbers and differ in their  $m_l$  quantum number (in accord with the Pauli exclusion principle). The electron configuration and orbital diagram for carbon are:



Nitrogen (atomic number 7) fills the  $1s$  and  $2s$  subshells and has one electron in each of the three  $2p$  orbitals, in accordance with Hund's rule. These three electrons have unpaired spins. Oxygen (atomic number 8) has a pair of electrons in any one of the  $2p$  orbitals (the electrons have opposite spins) and a single electron in each of the other two. Fluorine (atomic number 9) has only one  $2p$  orbital containing an unpaired electron. All of the electrons in the noble

gas neon (atomic number 10) are paired, and all of the orbitals in the  $n = 1$  and the  $n = 2$  shells are filled. The electron configurations and orbital diagrams of these four elements are:



The alkali metal sodium (atomic number 11) has one more electron than the neon atom. This electron must go into the lowest-energy subshell available, the  $3s$  orbital, giving a  $1s^2 2s^2 2p^6 3s^1$  configuration. The electrons occupying the outermost shell orbital(s) (highest value of  $n$ ) are called **valence electrons**, and those occupying the inner shell orbitals are called **core electrons** **Figure 4.9**. Since the core electron shells correspond to noble gas electron configurations, we can abbreviate electron configurations by writing the noble gas that matches the core electron configuration, along with the valence electrons in a condensed format. For our sodium example, the symbol [Ne] represents core electrons, ( $1s^2 2s^2 2p^6$ ) and our abbreviated or condensed configuration is [Ne] $3s^1$ .



**Figure 4.9** A core-abbreviated electron configuration (right) replaces the core electrons with the noble gas symbol whose configuration matches the core electron configuration of the other element.

Similarly, the abbreviated configuration of lithium can be represented as [He] $2s^1$ , where [He] represents the configuration of the helium atom, which is identical to that of the filled inner shell of lithium. Writing the configurations in this way emphasizes the similarity of the configurations of lithium and sodium. Both atoms, which are in the alkali metal family, have only one electron in a valence  $s$  subshell outside a filled set of inner shells.

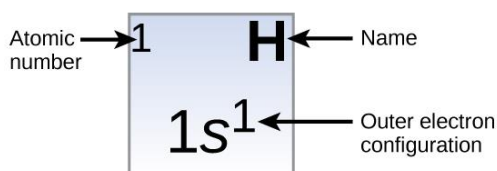
Li:  $[\text{He}]2s^1$  Na:  $[\text{Ne}]3s^1$

The alkaline earth metal magnesium (atomic number 12), with its 12 electrons in a  $[\text{Ne}]3s^2$  configuration, is analogous to its family member beryllium,  $[\text{He}]2s^2$ . Both atoms have a filled  $s$  subshell outside their filled inner shells. Aluminum (atomic number 13), with 13 electrons and the electron configuration  $[\text{Ne}]3s^23p^1$ , is analogous to its family member boron,  $[\text{He}]2s^22p^1$ .

The electron configurations of silicon (14 electrons), phosphorus (15 electrons), sulfur (16 electrons), chlorine (17 electrons), and argon (18 electrons) are analogous in the electron configurations of their outer shells to their corresponding family members carbon, nitrogen, oxygen, fluorine, and neon, respectively, except that the principal quantum number of the outer shell of the heavier elements has increased by one to  $n = 3$ . **Figure 4.10** shows the lowest energy, or ground-state, electron configuration for these elements as well as that for atoms of each of the known elements.

**Electron Configuration Table**

Period	Group																																																																																																											
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**Figure 4.10** This version of the periodic table shows the outer-shell electron configuration of each element. Note that down each group, the configuration is often similar.

When we come to the next element in the periodic table, the alkali metal potassium (atomic number 19), we might expect that we would begin to add electrons to the  $3d$  subshell.

However, all available chemical and physical evidence indicates that potassium is like lithium and sodium, and that the next electron is not added to the  $3d$  level but is, instead, added to the  $4s$  level **Figure 4.10**. As discussed previously, the  $3d$  orbital with no radial nodes is higher in energy because it is less penetrating and more shielded from the nucleus than the  $4s$ , which has three radial nodes. Thus, potassium has an electron configuration of  $[\text{Ar}]4s^1$ . Hence, potassium corresponds to Li and Na in its valence shell configuration. The next electron is added to complete the  $4s$  subshell and calcium has an electron configuration of  $[\text{Ar}]4s^2$ . This gives calcium an outer-shell electron configuration corresponding to that of beryllium and magnesium.

Beginning with the transition metal scandium (atomic number 21), additional electrons are added successively to the  $3d$  subshell. This subshell is filled to its capacity with 10 electrons (remember that for  $l = 2$  [ $d$  orbitals], there are  $2l + 1 = 5$  values of  $m_l$ , meaning that there are five  $d$  orbitals that have a combined capacity of 10 electrons). The  $4p$  subshell fills next. Note that for three series of elements, scandium (Sc) through copper (Cu), yttrium (Y) through silver (Ag), and lutetium (Lu) through gold (Au), a total of 10  $d$  electrons are successively added to the  $(n - 1)$  shell next to the  $n$  shell to bring that  $(n - 1)$  shell from 8 to 18 electrons. For two series, lanthanum (La) through lutetium (Lu) and actinium (Ac) through lawrencium (Lr), 14  $f$  electrons ( $l = 3$ ,  $2l + 1 = 7$   $m_l$  values; thus, seven orbitals with a combined capacity of 14 electrons) are successively added to the  $(n - 2)$  shell to bring that shell from 18 electrons to a total of 32 electrons.

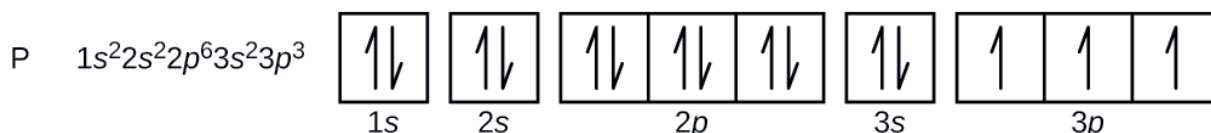
#### EXAMPLE 4

##### *Quantum Numbers and Electron Configurations*

What is the electron configuration and orbital diagram for a phosphorus atom? What are the four quantum numbers for the last electron added?

##### *Solution*

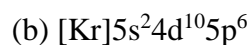
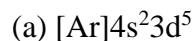
The atomic number of phosphorus is 15. Thus, a phosphorus atom contains 15 electrons. The order of filling of the energy levels is  $1s, 2s, 2p, 3s, 3p, 4s, \dots$ . The 15 electrons of the phosphorus atom will fill up to the  $3p$  orbital, which will contain three electrons:



The last electron added is a  $3p$  electron. Therefore,  $n = 3$  and, for a  $p$ -type orbital,  $l = 1$ . The  $m_l$  value could be  $-1, 0,$  or  $+1$ . The three  $p$  orbitals are degenerate, so any of these  $m_l$  values is correct. For unpaired electrons, convention assigns the value of  $+1/2$  for the spin quantum number; thus,  $S = +1/2$ .

### ***Check Your Learning***

Identify the atoms from the electron configurations given:



**ANSWER:**

(a) Mn (b) Xe

The periodic table can be a powerful tool in predicting the electron configuration of an element. However, we do find exceptions to the order of filling of orbitals that are shown in **Figure 4.8** or **Figure 4.9**. For instance, the electron configurations (shown in **Figure 4.10**) of the transition metals chromium (Cr; atomic number 24) and copper (Cu; atomic number 29), among others, are not those we would expect. In general, such exceptions involve subshells with very similar energy, and small effects can lead to changes in the order of filling.

In the case of Cr and Cu, we find that half-filled and completely filled subshells apparently represent conditions of preferred stability. This stability is such that an electron shifts from the 4s into the 3d orbital to gain the extra stability of a half-filled 3d subshell (in Cr) or a filled 3d subshell (in Cu). Other exceptions also occur. For example, niobium (Nb, atomic number 41) is predicted to have the electron configuration  $[\text{Kr}]5s^24d^3$ . Experimentally, we observe that its ground-state electron configuration is actually  $[\text{Kr}]5s^14d^4$ . We can rationalize this observation by saying that the electron–electron repulsions experienced by pairing the electrons in the 5s orbital are larger than the gap in energy between the 5s and 4d orbitals. There is no simple method to predict the exceptions for atoms where the magnitude of the repulsions between electrons is greater than the small differences in energy between subshells.

### ***IV.5 Electron Configurations and the Periodic Table***

As described earlier, the periodic table arranges atoms based on increasing atomic number so that elements with the same chemical properties recur periodically. When their electron configurations are added to the table **Figure 4.10**, we also see a periodic recurrence of similar electron configurations in the outer shells of these elements. Because they are in the outer shells of an atom, valence electrons play the most important role in chemical reactions. The outer electrons have the highest energy of the electrons in an atom and are more easily lost or shared than the core electrons. Valence electrons are also the determining factor in some physical properties of the elements.

Elements in any one group (or column) have the same number of valence electrons; the alkali metals lithium and sodium each have only one valence electron, the alkaline earth metals beryllium and magnesium each have two, and the halogens fluorine and chlorine each have seven valence electrons. The similarity in chemical properties among elements of the same group occurs because they have the same number of valence electrons. It is the loss, gain, or sharing of valence electrons that defines how elements react.

It is important to remember that the periodic table was developed on the basis of the chemical behavior of the elements, well before any idea of their atomic structure was available. Now we can understand why the periodic table has the arrangement it has—the arrangement puts elements whose atoms have the same number of valence electrons in the same group. This arrangement is emphasized in **Figure 4.10**, which shows in periodic-table form the electron configuration of the last subshell to be filled by the Aufbau principle. The colored sections of **Figure 4.10** show the three categories of elements classified by the orbitals being filled: main group, transition, and inner transition elements. These classifications determine which orbitals are counted in the **valence shell**, or highest energy level orbitals of an atom.

1. **Main group elements** (sometimes called **representative elements**) are those in which the last electron added enters an *s* or a *p* orbital in the outermost shell, shown in blue and red in **Figure 4.10**. This category includes all the nonmetallic elements, as well as many metals and the metalloids. The valence electrons for main group elements are those with the highest *n* level. For example, gallium (Ga, atomic number 31) has the electron configuration  $[\text{Ar}]4s^23d^{10}4p^1$ , which contains three valence electrons (underlined). The completely filled *d* orbitals count as core, not valence, electrons.
2. **Transition elements or transition metals**. These are metallic elements in which the last electron added enters a *d* orbital. The valence electrons (those added after the last noble gas configuration) in these elements include the *ns* and  $(n - 1) d$  electrons. The official IUPAC definition of transition elements specifies those with partially filled *d* orbitals. Thus, the elements with completely filled orbitals (Zn, Cd, Hg, as well as Cu, Ag, and Au in **Figure 4.10**) are not technically transition elements. However, the term is frequently used to refer to the entire *d* block (colored yellow in **Figure 4.10**), and we will adopt this usage in this textbook.
3. **Inner transition elements** are metallic elements in which the last electron added occupies an *f* orbital. They are shown in green in **Figure 4.10**. The valence shells of the inner transition elements consist of the  $(n - 2) f$ , the  $(n - 1) d$ , and the *ns* subshells. There are two inner transition series:

- a. The lanthanide series: lanthanum (La) through lutetium (Lu)
- b. The actinide series: actinium (Ac) through lawrencium (Lr)

Lanthanum and actinium, because of their similarities to the other members of the series, are included and used to name the series, even though they are transition metals with no  $f$  electrons.

### *IV.6 Electron Configurations of Ions*

Ions are formed when atoms gain or lose electrons. A cation (positively charged ion) forms when one or more electrons are removed from a parent atom. For main group elements, the electrons that were added last are the first electrons removed. For transition metals and inner transition metals, however, electrons in the  $s$  orbital are easier to remove than the  $d$  or  $f$  electrons, and so the highest  $ns$  electrons are lost, and then the  $(n - 1) d$  or  $(n - 2) f$  electrons are removed. An anion (negatively charged ion) forms when one or more electrons are added to a parent atom. The added electrons fill in the order predicted by the Aufbau principle.

#### **EXAMPLE 5**

##### *Predicting Electron Configurations of Ions*

What is the electron configuration of:

- (a)  $\text{Na}^+$
- (b)  $\text{P}^{3-}$
- (c)  $\text{Al}^{2+}$
- (d)  $\text{Fe}^{2+}$
- (e)  $\text{Sm}^{3+}$

##### ***Solution***

First, write out the electron configuration for each parent atom. We have chosen to show the full, unabbreviated configurations to provide more practice for students who want it, but listing the core-abbreviated electron configurations is also acceptable.

Next, determine whether an electron is gained or lost. Remember electrons are negatively charged, so ions with a positive charge have lost an electron. For main group elements, the last orbital gains or loses the electron. For transition metals, the last  $s$  orbital loses an electron before the  $d$  orbitals.

(a) Na:  $1s^2 2s^2 2p^6 3s^1$ . Sodium cation loses one electron, so  $\text{Na}^+$ :  $1s^2 2s^2 2p^6 3s^1 = \text{Na}^+$ :  $1s^2 2s^2 2p^6$ .

(b) P:  $1s^2 2s^2 2p^6 3s^2 3p^3$ . Phosphorus trianion gains three electrons, so  $\text{P}^{3-}$ :  $1s^2 2s^2 2p^6 3s^2 3p^6$ .

(c) Al:  $1s^2 2s^2 2p^6 3s^2 3p^1$ . Aluminum dication loses two electrons  $\text{Al}^{2+}$ :  $1s^2 2s^2 2p^6 3s^2 3p^1 = \text{Al}^{2+}$ :  $1s^2 2s^2 2p^6 3s^1$ .

(d) Fe:  $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^6$ . Iron (II) loses two electrons and, since it is a transition metal, they are removed from the 4s orbital  $\text{Fe}^{2+}$ :  $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^6 = 1s^2 2s^2 2p^6 3s^2 3p^6 3d^6$ .

(e). Sm:  $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^6 6s^2 4f^6$ . Samarium trication loses three electrons. The first two will be lost from the 6s orbital, and the final one is removed from the 4f orbital.  $\text{Sm}^{3+}$ :  $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^6 6s^2 4f^6 = 1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^6 4f^5$ .

### ***Check Your Learning***

Which ion with a  $+2$  charge has the electron configuration  $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 4d^5$ ?

Which ion with a  $+3$  charge has this configuration?

**ANSWER:**

$\text{Tc}^{2+}$ ,  $\text{Ru}^{3+}$