Chapter 6

Electronic Structure of Atoms

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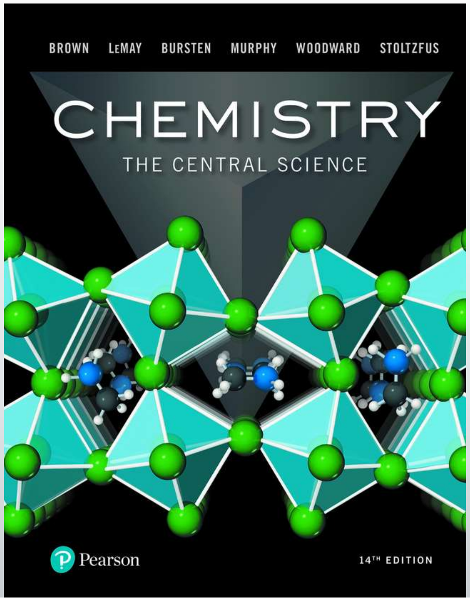


Orbitals and Quantum Numbers

- The solution to Schrödinger's equation for the hydrogen atom yields a set of wave functions called orbitals.
- The **quantum-mechanical model** uses three quantum numbers, n, l, and m_l.
- The principal quantum number, n, can have positive integral values **1, 2, 3, ...**
- As n increases, the orbital becomes larger, and the electron spends more time farther from the nucleus.
- An increase in n also means that the electron has a higher energy and is therefore less tightly bound to the nucleus.

6.5 Quantum Mechanics and Atomic Orbitals

- The angular momentum quantum number, l, can have integral values from $\mathbf{0}$ to $(\boldsymbol{n}-\mathbf{1})$ for each value of n.
- This quantum number define the shape of the orbital.

Value of l	0	1	2	3
Letter used	s	p	d	f

- The magnetic quantum number, m_l, can have integral values between $-\boldsymbol{l}$ and $+\boldsymbol{l}$, including **zero**.
- This quantum number describes the orientation of the orbital in space.

6.5 Quantum Mechanics and Atomic Orbitals

- At any given instant, the electron in a hydrogen atom is described by only one of these orbitals; therefore, we say that the electron **occupies** a certain orbital.
- The remaining orbitals are **unoccupied** for that particular state of the hydrogen atom.
- The collection of orbitals with the same value of n is called an electron shell.
- The set of orbitals that have the same n and l values is called a subshell.

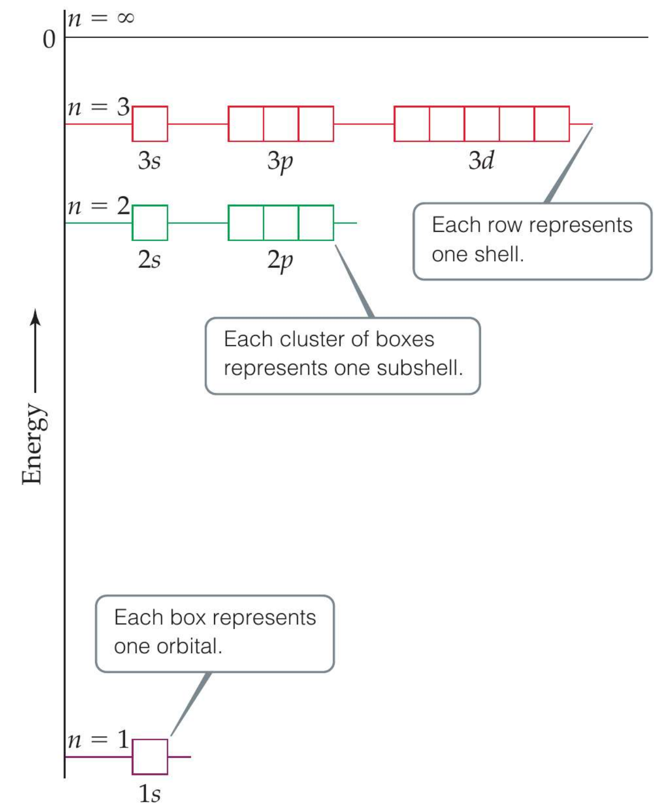
6.5 Quantum Mechanics and Atomic Orbitals

TABLE 6.2 Relationship among Values of n, l, and m_l through $n = 4$

n	Possible Values of l	Subshell Designation	Possible Values of m_l	Number of Orbitals in Subshell	Total Number of Orbitals in Shell
1	0	1s	0	1	1
2	0	2s	0	1	
	1	2p	1, 0, −1	3	4
3	0	3s	0	1	
	1	3p	1, 0, −1	3	
	2	3d	2, 1, 0, −1, −2	5	9
4	0	4s	0	1	
	1	4p	1, 0, −1	3	
	2	4d	2, 1, 0, −1, −2	5	
	3	4f	3, 2, 1, 0, −1, −2, −3	7	16

6.5 Quantum Mechanics and Atomic Orbitals

- The shell with principal quantum number n consists of exactly n subshells.
- Each subshell consists of a specific number of orbitals, and each orbital corresponds to a different allowed value of m_l.
- For a given value of l, there are $(2l + 1)$ allowed value of m_l.
- The total number of orbitals in a shell is n^2.



$n = 1$ shell has one orbital
$n = 2$ shell has two subshells composed of four orbitals
$n = 3$ shell has three subshells composed of nine orbitals

▲ **Figure 6.18** Energy levels in the hydrogen atom.

Sample Exercise 6.6

a. Predict the number of subshells in the fourth shell, that is, for $n = 4$.

- 4

b. Give the label for each of these subshells.

- 4*s*, 4*p*, 4*d*, and 4*f*

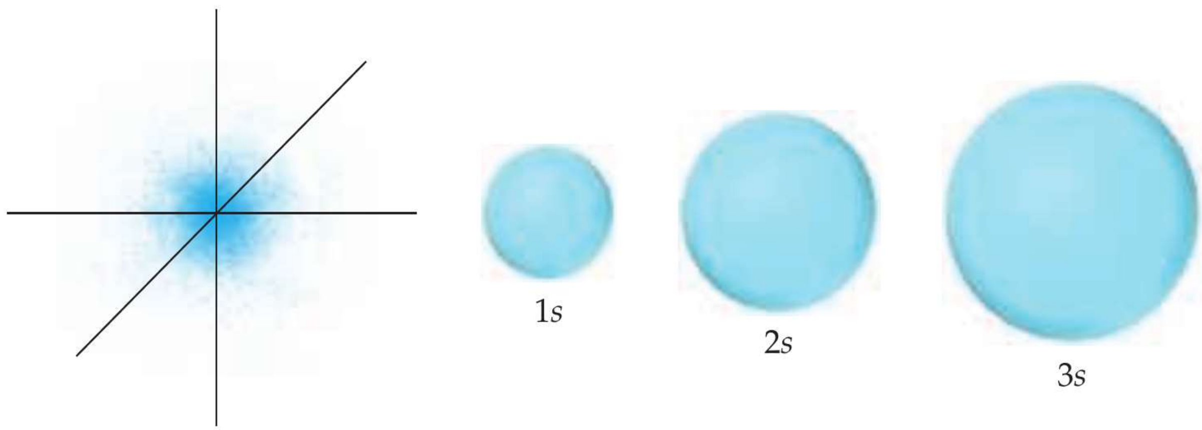
c. How many orbitals are in each of these subshells?

- For 4*s* → 1, for 4*p* → 3, for 4*d* → 5, and for 4*f* → 7.

6.6 Representations of Orbitals

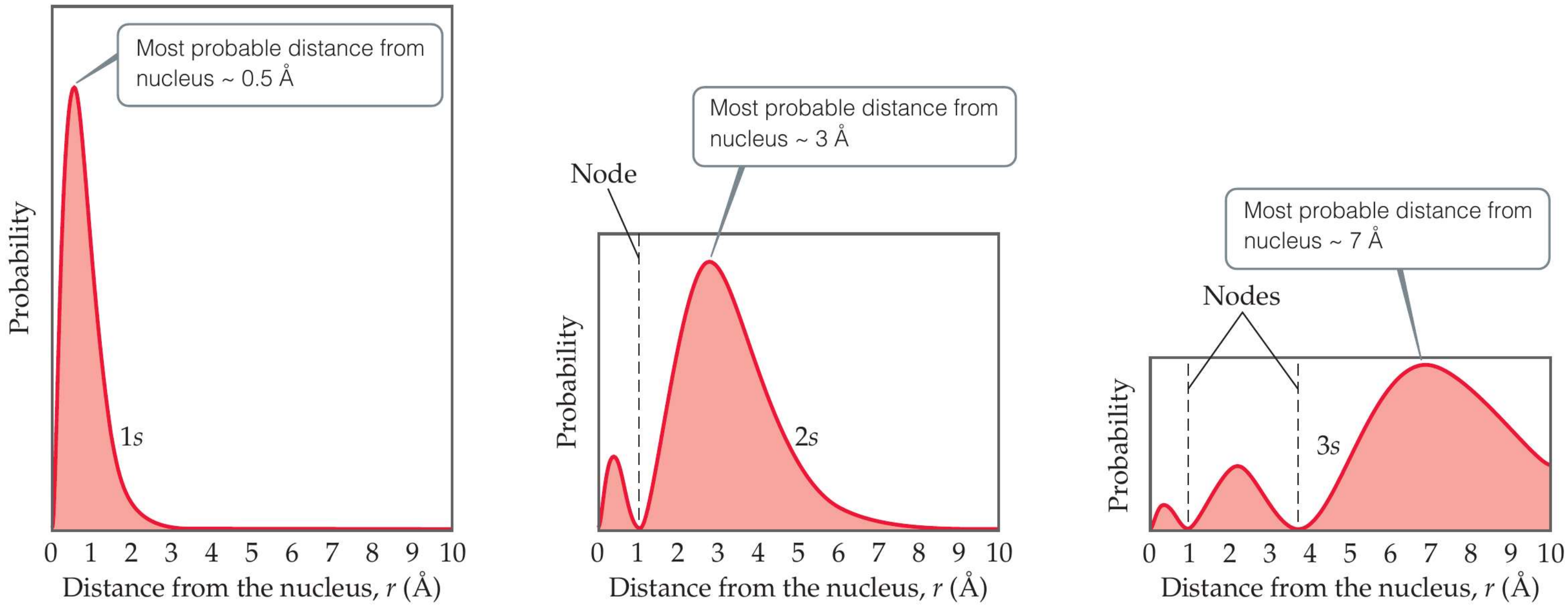
The *s* Orbitals

- The first thing we notice about the electron density for the *s* orbital is that it is spherically symmetric, in other words, the electron density at a given distance from the nucleus is the same regardless of the direction in which we proceed from the nucleus.



(a) An electron density model **(b)** Contour models

6.6 Representations of Orbitals

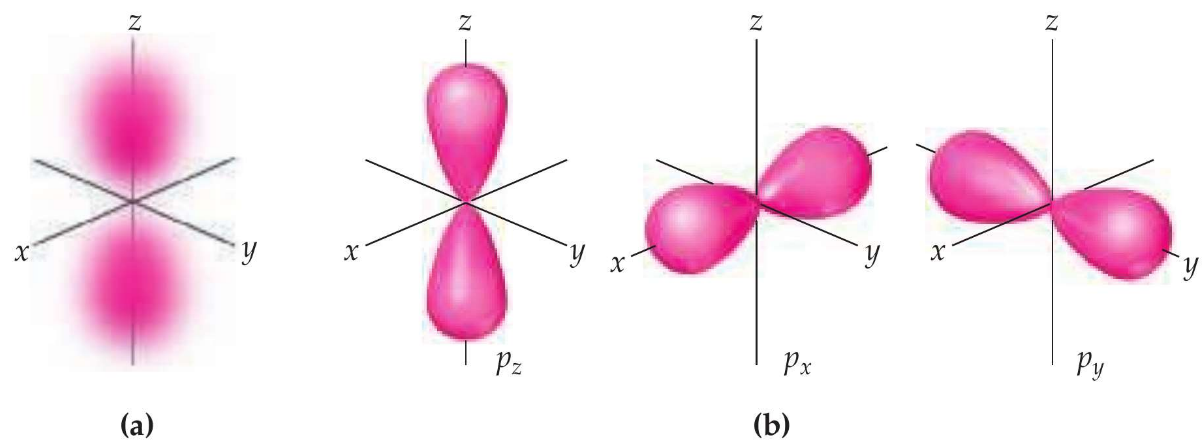


▲ **Figure 6.19 Radial probability functions for the 1*s*, 2*s*, and 3*s* orbitals of hydrogen.** These plots show the probability of finding the electron as a function of distance from the nucleus. As *n* increases, the most likely distance at which to find the electron (the highest peak) moves farther from the nucleus.

- Each resulting curve is the **radial probability** function for the orbital.

6.6 Representations of Orbitals

The *p* Orbitals

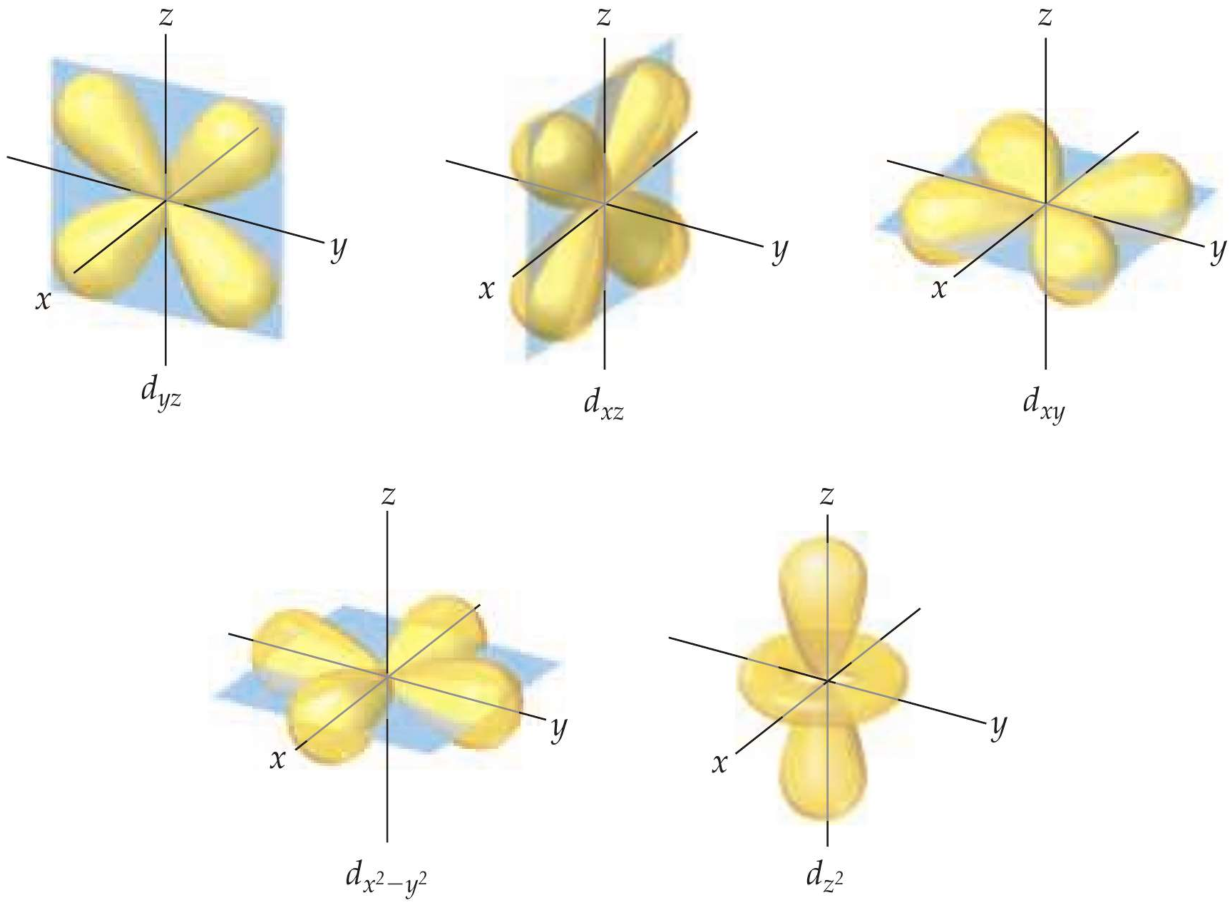


▲ **Figure 6.23 The *p* orbitals.** (**a**) Electron-density distribution of a 2*p* orbital. (**b**) Contour representations of the three *p* orbitals. The subscript on the orbital label indicates the axis along which the orbital lies.

- The dumbbell-shaped orbital has two lobes.
- *p* orbitals increase in size as we move from 2*p* to 3*p* to 4*p*, and so forth.

6.6 Representations of Orbitals

The *d* Orbitals

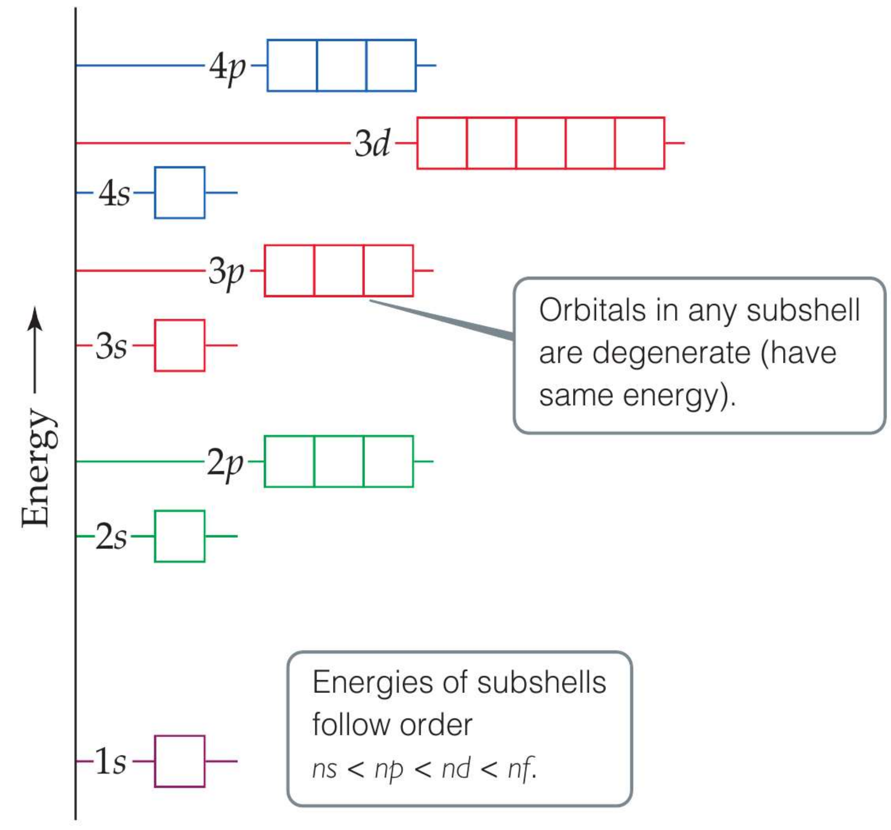


▲ Figure 6.24 Contour representations of the five *d* orbitals.

6.7 Many-Electron Atoms

Orbitals and Their Energies

- Although the shapes of the orbitals of a many-electron atom are the same as those for hydrogen, the presence of more than one electron greatly changes the energies of the orbitals.
- In a hydrogen atom, the 3*s*, 3*p*, and 3*d* subshells all have the same energy.
- Whereas in a many-electron atom, however, the energies of the various subshells in a given shell are different because of electron–electron repulsions.



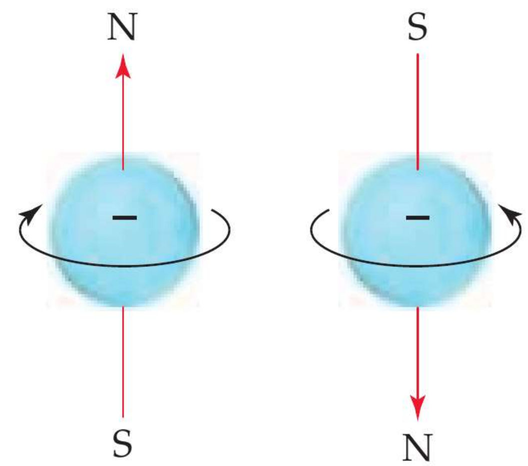
▲ **Figure 6.25** General energy ordering of orbitals for a many-electron atom.

6.7 Many-Electron Atoms

- In a many-electron atom, for a given value of n, the energy of an orbital increases with increasing value of l.
- For example, with $n = 3$, the orbitals increase in energy in the order $3s < 3p < 3d$.
- All orbitals of a given subshell (such as, d orbitals) have the same energy; therefore, the orbitals with the same energy are said to be degenerate.

Electron Spin and the Pauli Exclusion Principle

- Electrons have an intrinsic property, called electron spin, that causes each electron to behave as if it were a tiny sphere spinning on its own axis.
- A new quantum number, the spin magnetic quantum number, is denoted m_s.
- Two possible values are allowed for m_s, $+\frac{1}{2}$ or $-\frac{1}{2}$.



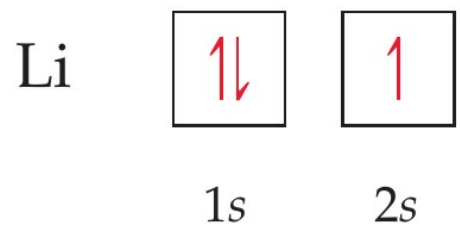
▲ **Figure 6.26 Electron spin.** The electron behaves as if it were spinning about an axis, thereby generating a magnetic field whose direction depends on the direction of spin. The two directions for the magnetic field correspond to the two possible values for the spin quantum number, m_s. The magnetic fields that emanate from materials, like iron, arise because there are more electrons with one spin direction than the other.

6.7 Many-Electron Atoms

- A spinning charge produces a magnetic field.
- The Pauli exclusion principle states that no two electrons in an atom can have the same set of four quantum numbers n, l, m_l, and m_s.
- For a given orbital, the values of n, l, and m_l are fixed.
- An orbital can hold a maximum of two electrons and they must have opposite spins.

6.8 Electron Configurations

- The way electrons are distributed among the various orbitals of an atom is called the electron configuration of the atom.
- The most stable electron configuration, the ground state, is that in which the electrons are in the lowest possible energy states.
- The orbitals are filled in order of increasing energy, with no more than two electrons per orbital.
- For example, consider the lithium atom: $1s^2 2s^1$.
- We can also show the arrangement of the electrons in a representation that is called an **orbital diagram**:

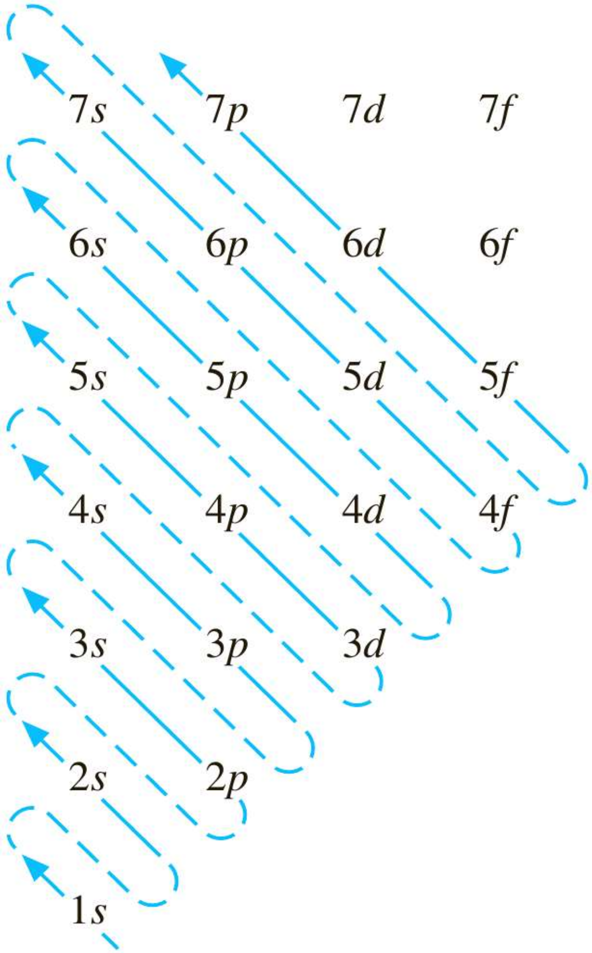


6.8 Electron Configurations

- In the orbital diagram representation, a half arrow pointing up (↿) represents an electron with a positive spin magnetic quantum number $\left(m_s = +\frac{1}{2}\right)$, and a half arrow pointing down (⇂) represents an electron with a negative spin magnetic quantum number $\left(m_s = -\frac{1}{2}\right)$.
- Chemists refer to the two possible spin states as "spin-up" and "spin-down" corresponding to the directions of the half arrows.
- Electrons having opposite spins are said to be **paired** when they are in the same orbital (↿⇂).
- An **unpaired** electron is one not accompanied by a partner of opposite spin.

Building-Up Principle (Aufbau Principle)

- A scheme used to reproduce the electron configurations of the ground states of atoms by successively filling subshells with electrons in a specific order (the building-up order).
- 1*s*, 2*s*, 2*p*, 3*s*, 3*p*, 4*s*, 3*d*, 4*p*, 5*s*, 4*d*, 5*p*, 6*s*, 4*f*, 5*d*, 6*p*, 7*s*, 5*f*.



6.8 Electron Configurations

Hund's Rule

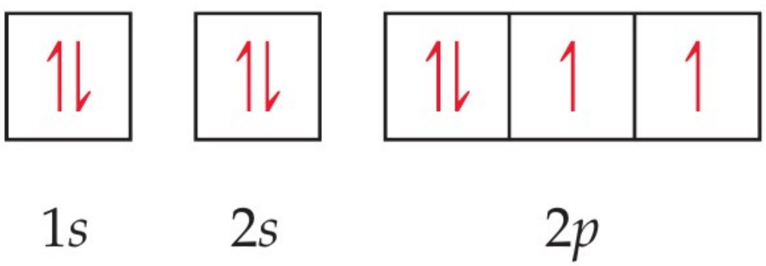
- Hund's rule states that when filling degenerate orbitals the lowest energy is attained when the number of electrons having the same spin is maximized.
- Electrons arranged in this way are said to have **parallel spins**.

TABLE 6.3 Electron Configurations of Several Lighter Elements

Element	Total Electrons	Orbital Diagram 1s	2s	2p			3s	Electron Configuration
Li	3	↑↓	↑					$1s^22s^1$
Be	4	↑↓	↑↓					$1s^22s^2$
B	5	↑↓	↑↓	↑				$1s^22s^22p^1$
C	6	↑↓	↑↓	↑	↑			$1s^22s^22p^2$
N	7	↑↓	↑↓	↑	↑	↑		$1s^22s^22p^3$
Ne	10	↑↓	↑↓	↑↓	↑↓	↑↓		$1s^22s^22p^6$
Na	11	↑↓	↑↓	↑↓	↑↓	↑↓	↑	$1s^22s^22p^63s^1$

Sample Exercise 6.7

Draw the orbital diagram for the electron configuration of Oxygen, atomic number 8. How many unpaired electrons does an Oxygen atom possess?



- The corresponding electron configuration is written $1s^22s^22p^4$.
- The atom has two unpaired electrons.

Condensed Electron Configurations

- In writing the condensed electron configuration of an element, the electron configuration of the nearest noble-gas element of lower atomic number is represented by its chemical symbol in brackets.
- **Example**: we can abbreviate the electron configuration of sodium as:

$$^{11}\text{Na}: 1s^2 2s^2 2p^6 3s^1 \equiv [\text{Ne}]3s^1$$

- We refer to the electrons represented by the bracketed symbol as the **noble-gas core** of the atom.
- These inner-shell electrons are referred to as the core electrons.

6.8 Electron Configurations

- The electrons given after the noble-gas core are called the outer-shell electrons.
- The outer-shell electrons include the electrons involved in chemical bonding, which are called the valence electrons.

Transition Metals

6.8 Electron Configurations

Atomic Number	Element	Partial Orbital Diagram (4s, 3d, and 4p Sublevels Only): 4s	3d	4p	Full Electron Configuration	Condensed Electron Configuration
19	K	↑			$[1s^2 2s^2 2p^6 3s^2 3p^6]\ 4s^1$	$[Ar]\ 4s^1$
20	Ca	↑↓			$[1s^2 2s^2 2p^6 3s^2 3p^6]\ 4s^2$	$[Ar]\ 4s^2$
21	Sc	↑↓	↑		$[1s^2 2s^2 2p^6 3s^2 3p^6]\ 4s^2 3d^1$	$[Ar]\ 4s^2 3d^1$
22	Ti	↑↓	↑ ↑		$[1s^2 2s^2 2p^6 3s^2 3p^6]\ 4s^2 3d^2$	$[Ar]\ 4s^2 3d^2$
23	V	↑↓	↑ ↑ ↑		$[1s^2 2s^2 2p^6 3s^2 3p^6]\ 4s^2 3d^3$	$[Ar]\ 4s^2 3d^3$
anomalous behavior 24	Cr	↑	↑ ↑ ↑ ↑ ↑		$[1s^2 2s^2 2p^6 3s^2 3p^6]\ 4s^1 3d^5$	$[Ar]\ 4s^1 3d^5$
25	Mn	↑↓	↑ ↑ ↑ ↑ ↑		$[1s^2 2s^2 2p^6 3s^2 3p^6]\ 4s^2 3d^5$	$[Ar]\ 4s^2 3d^5$
26	Fe	↑↓	↑↓ ↑ ↑ ↑ ↑		$[1s^2 2s^2 2p^6 3s^2 3p^6]\ 4s^2 3d^6$	$[Ar]\ 4s^2 3d^6$
27	Co	↑↓	↑↓ ↑↓ ↑ ↑ ↑		$[1s^2 2s^2 2p^6 3s^2 3p^6]\ 4s^2 3d^7$	$[Ar]\ 4s^2 3d^7$
28	Ni	↑↓	↑↓ ↑↓ ↑↓ ↑ ↑		$[1s^2 2s^2 2p^6 3s^2 3p^6]\ 4s^2 3d^8$	$[Ar]\ 4s^2 3d^8$
anomalous behavior 29	Cu	↑	↑↓ ↑↓ ↑↓ ↑↓ ↑↓		$[1s^2 2s^2 2p^6 3s^2 3p^6]\ 4s^1 3d^{10}$	$[Ar]\ 4s^1 3d^{10}$
30	Zn	↑↓	↑↓ ↑↓ ↑↓ ↑↓ ↑↓		$[1s^2 2s^2 2p^6 3s^2 3p^6]\ 4s^2 3d^{10}$	$[Ar]\ 4s^2 3d^{10}$

The Lanthanides and Actinides

- The 14 elements corresponding to the filling of the 4f orbitals are known as either the **lanthanide elements** or the **rare earth elements**.
- Because the energies of the 4*f* and 5*d* orbitals are very close to each other, the electron configurations of some of the lanthanides involve 5*d* electrons.

^{57}Lanthanum: $[Xe]6s^2 5d^1$

^{58}Cerium: $[Xe]6s^2 4f^1 5d^1$

^{59}Praseodymium: $[Xe]6s^2 4f^3$

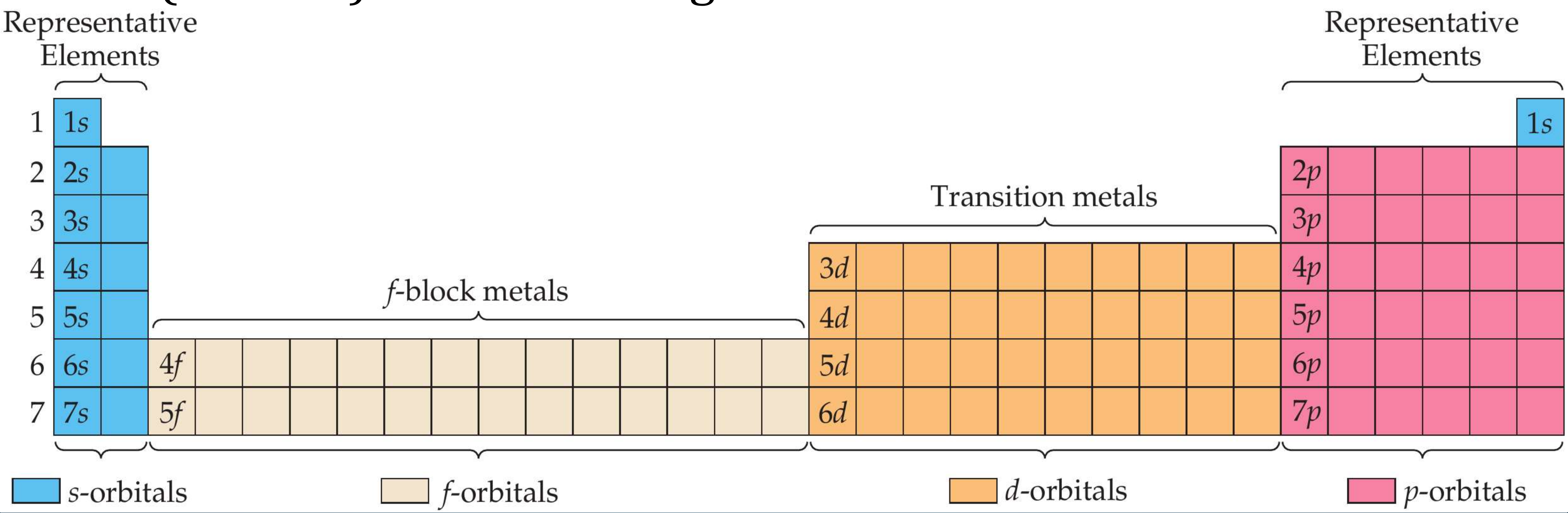
^{60}Neodymium: $[Xe]6s^2 4f^4$

6.8 Electron Configurations

- The final row of the periodic table begins by filling the 7*s* orbitals.
- The **actinide elements**, of which uranium (U, element 92) and plutonium (Pu, element 94) are the best known, are then built up by completing the 5*f* orbitals.

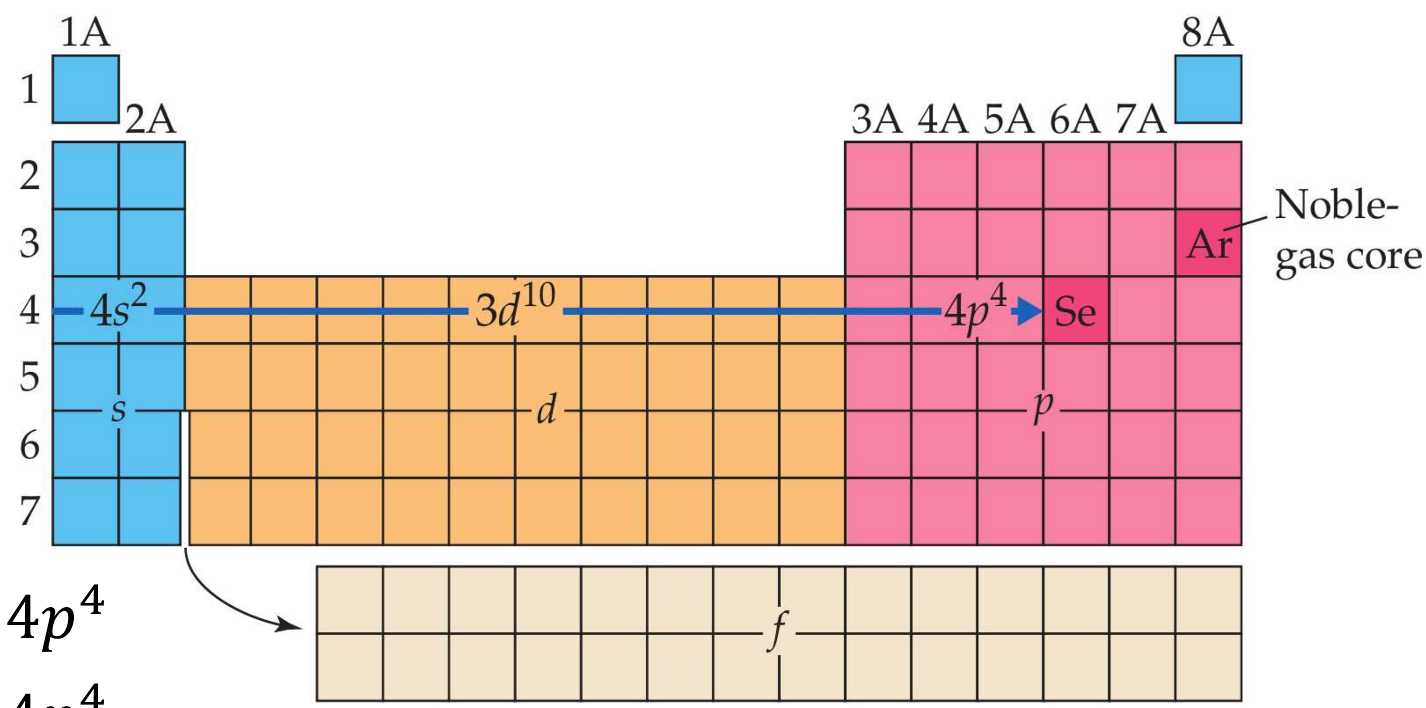
6.9 Electron Configurations and the Periodic Table

- The electron configurations of the elements correspond to their locations in the periodic table.
- Thus, elements in the same column of the table have related outer-shell (valence) electron configurations.



6.9 Electron Configurations and the Periodic Table

- You can write the electron configuration of an element based merely on its position in the periodic table.



^{34}Se: [Ar]$4s^2 3d^{10} 4p^4$

^{34}Se: [Ar]$3d^{10} 4s^2 4p^4$

Sample Exercise 6.8

What is the characteristic valence electron configuration of the group 7A elements, the halogens?

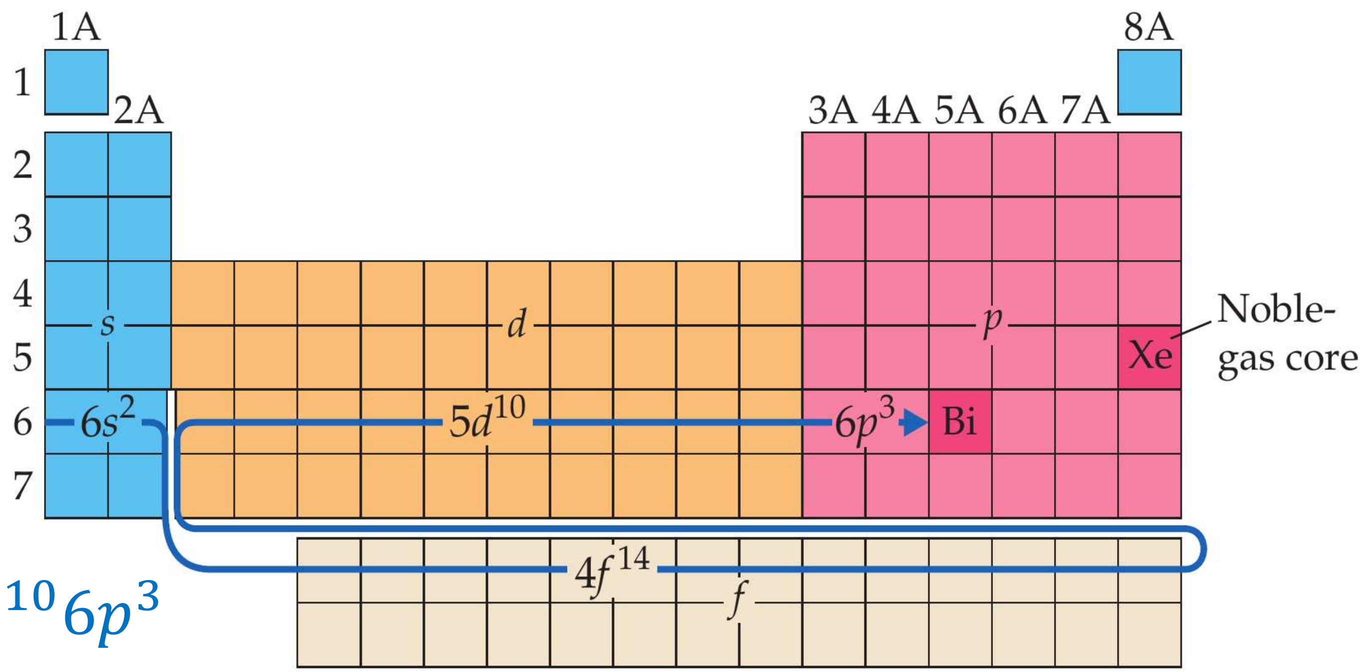
^{9}F: $[\mathrm{He}]2s^2 2p^5$

^{17}Cl: $[\mathrm{Ne}]3s^2 3p^5$

- The characteristic valence electron configuration of a halogen is ns^2np^5, where n ranges from 2 in the case of fluorine to 6 in the case of astatine.

Sample Exercise 6.9

a. Based on its position in the periodic table, write the condensed electron configuration for bismuth, element 83.

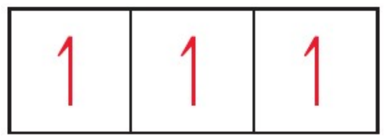


^{83}Bi: [Xe]$6s^2 4f^{14} 5d^{10} 6p^3$

^{83}Bi: [Xe]$4f^{14} 5d^{10} 6s^2 6p^3$

Sample Exercise 6.9

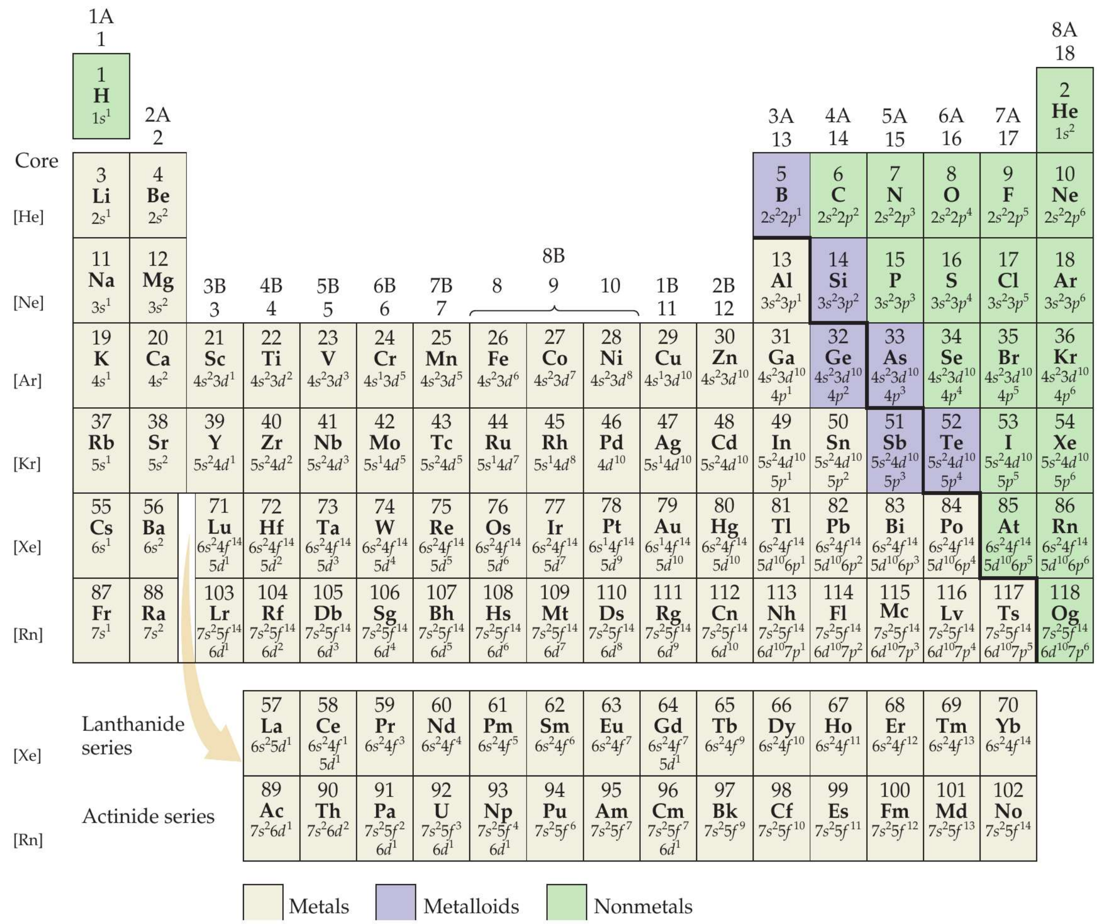
b. How many unpaired electrons does a bismuth atom have?



- There are three unpaired electrons in the bismuth atom.

6.9 Electron Configurations and the Periodic Table

- For representative elements, we do not consider the electrons in completely filled ***d*** or ***f*** subshells to be valence electrons, and for transition elements, we do not consider the electrons in a completely filled ***f*** subshell to be valence electrons.



▲ Figure 6.31 Outer-shell electron configurations of the elements.