

13.4: The Exclusion Principle and the Periodic Table

Learning Objectives

By the end of this section, you will be able to:

- Explain the importance of Pauli's exclusion principle to an understanding of atomic structure and molecular bonding
- Explain the structure of the periodic table in terms of the total energy, orbital angular momentum, and spin of individual electrons in an atom
- Describe the electron configuration of atoms in the periodic table

So far, we have studied only hydrogen, the simplest chemical element. We have found that an electron in the hydrogen atom can be completely specified by five quantum numbers:

- n : principal quantum number
- l : angular momentum quantum number
- m : angular momentum projection quantum number
- s : spin quantum number
- m_s : spin projection quantum number

To construct the ground state of a neutral multi-electron atom, imagine starting with a nucleus of charge Ze (that is, a nucleus of atomic number Z) and then adding Z electrons one by one. Assume that each electron moves in a spherically symmetrical electric field produced by the nucleus and all other electrons of the atom. The assumption is valid because the electrons are distributed randomly around the nucleus and produce an average electric field (and potential) that is spherically symmetrical. The electric potential $U(\mathbf{r})$ for each electron does not follow the simple $-1/r$ form because of interactions between electrons, but it turns out that we can still label each individual electron state by quantum numbers, (n, l, m, s, m_s) . (The spin quantum number s is the same for all electrons, so it will not be used in this section.)

The structure and chemical properties of atoms are explained in part by **Pauli's exclusion principle**: No two electrons in an atom can have the same values for all four quantum numbers (n, l, m, m_s) . This principle is related to two properties of electrons: All electrons are identical ("when you've seen one electron, you've seen them all") and they have half-integral spin ($s = 1/2$). Sample sets of quantum numbers for the electrons in an atom are given in Table 13.4.1. Consistent with Pauli's exclusion principle, no two rows of the table have the exact same set of quantum numbers.

Table 13.4.1: Electron States of Atoms Because of Pauli's exclusion principle, no two electrons in an atom have the same set of four quantum numbers.

n	l	m	m_s	Subshell symbol	No. of electrons: subshell	No. of electrons: shell
1	0	0	$\frac{1}{2}$	1s	2	2
1	0	0	$-\frac{1}{2}$			
2	0	0	$\frac{1}{2}$	2s	2	
2	0	0	$-\frac{1}{2}$			
2	1	-1	$\frac{1}{2}$	2p	6	8
2	1	-1	$-\frac{1}{2}$			
2	1	0	$\frac{1}{2}$			
2	1	0	$-\frac{1}{2}$			
2	1	1	$\frac{1}{2}$			
2	1	1	$-\frac{1}{2}$			
3	0	0	$\frac{1}{2}$	3s	2	18

n	l	m	m_s	Subshell symbol	No. of electrons: subshell	No. of electrons: shell
3	0	0	$-\frac{1}{2}$	3p	6	
3	1	-1	$\frac{1}{2}$			
3	1	-1	$-\frac{1}{2}$			
3	1	0	$\frac{1}{2}$			
3	1	0	$-\frac{1}{2}$			
3	1	1	$\frac{1}{2}$			
3	1	1	$-\frac{1}{2}$			
3	2	-2	$\frac{1}{2}$	3d	10	
3	2	-2	$-\frac{1}{2}$			
3	2	-1	$\frac{1}{2}$			
3	2	-1	$-\frac{1}{2}$			
3	2	0	$\frac{1}{2}$			
3	2	0	$-\frac{1}{2}$			
3	2	1	$\frac{1}{2}$			
3	2	1	$-\frac{1}{2}$			
3	2	2	$\frac{1}{2}$			
3	2	2	$-\frac{1}{2}$			

Electrons with the same principal quantum number n are said to be in the same **shell**, and those that have the same value of l are said to occupy the same **subshell**. An electron in the $n = 1$ state of a hydrogen atom is denoted **1s**, where the first digit indicates the shell ($n = 1$) and the letter indicates the subshell (s, p, d, f, \dots correspond to $l = 0, 1, 2, 3, \dots$). Two electrons in the $n = 1$ state are denoted as $1s^2$, where the superscript indicates the number of electrons. An electron in the $n = 2$ state with $l = 1$ is denoted **2p**. The combination of two electrons in the $n = 2$ and $l = 0$ state, and three electrons in the $n = 2$ and $l = 1$ state is written as $2s^2 2p^3$, and so on. This representation of the electron state is called the **electron configuration** of the atom. The electron configurations for several atoms are given in Table 13.4.2. Electrons in the outer shell of an atom are called **valence electrons**. Chemical bonding between atoms in a molecule are explained by the transfer and sharing of valence electrons.

Table 13.4.2: Electron Configurations of Elements in an Atom. The symbol (\uparrow) indicates an unpaired electron in the outer shell, whereas the symbol ($\uparrow\downarrow$) indicates a pair of spin-up and -down electrons in an outer shell.

Element	Electron Configuration	Spin Alignment
H	$1s^1$	(\uparrow)
He	$1s^2$	($\uparrow\downarrow$)
Li	$1s^2 2s^1$	(\uparrow)
Be	$1s^2 2s^2$	($\uparrow\downarrow$)
B	$1s^2 2s^2 2p^1$	($\uparrow\downarrow$)(\uparrow)
C	$1s^2 2s^2 2p^2$	($\uparrow\downarrow$)(\uparrow)(\uparrow)
N	$1s^2 2s^2 2p^3$	($\uparrow\downarrow$)(\uparrow)(\uparrow)(\uparrow)
O	$1s^2 2s^2 2p^4$	($\uparrow\downarrow$)($\uparrow\downarrow$)(\uparrow)(\uparrow)

Element	Electron Configuration	Spin Alignment
F	$1s^2 2s^2 2p^5$	$(\uparrow\downarrow)(\uparrow\downarrow)(\uparrow)(\uparrow)$
Ne	$1s^2 2s^2 2p^6$	$(\uparrow\downarrow)(\uparrow\downarrow)(\uparrow\downarrow)(\uparrow\downarrow)$
Na	$1s^2 2s^2 2p^6 3s^1$	(\uparrow)
Mg	$1s^2 2s^2 2p^6 3s^2$	$(\uparrow\downarrow)$
Al	$1s^2 2s^2 2p^6 3s^1 3p^1$	$(\uparrow\downarrow)(\uparrow)$

The maximum number of electrons in a subshell depends on the value of the angular momentum quantum number, l . For a given value l , there are $2l + 1$ orbital angular momentum states. However, each of these states can be filled by two electrons (spin up and down, $\uparrow\downarrow$). Thus, the maximum number of electrons in a subshell is

$$N = 2(2l + 1) = 4l + 2.$$

In the $2s$ ($l = 0$) subshell, the maximum number of electrons is 2. In the $2p$ ($l = 1$) subshell, the maximum number of electrons is 6. Therefore, the total maximum number of electrons in the $n = 2$ shell (including both the $l = 0$ and 1 subshells) is $2 + 6$ or 8. In general, the maximum number of electrons in the n th shell is $2n^2$.

✓ Example 13.4.1: Subshells and Totals for $n = 3$

How many subshells are in the $n = 3$ shell? Identify each subshell and calculate the maximum number of electrons that will fill each. Show that the maximum number of electrons that fill an atom is $2n^2$.

Strategy

Subshells are determined by the value of l ; thus, we first determine which values of l are allowed, and then we apply the equation “maximum number of electrons that can be in a subshell = $2(2l + 1)$ ” to find the number of electrons in each subshell.

Solution

Because $n = 3$, we know that l can be 0, 1, or 2; thus, there are three possible subshells. In standard notation, they are labeled the $3s$, $3p$, and $3d$ subshells. We have already seen that two electrons can be in an s state, and six in a p state, but let us use the equation “maximum number of electrons that can be in a

subshell = $2(2l + 1)$ ” to calculate the maximum number in each:

$$3s \text{ has } l = 0; \text{ thus, } 2(2l + 1) = 2(0 + 1) = 2$$

$$3p \text{ has } l = 1; \text{ thus, } 2(2l + 1) = 2(2 + 1) = 6$$

$$3d \text{ has } l = 2; \text{ thus, } 2(2l + 1) = 2(4 + 1) = 10$$

$$\text{Total} = 18$$

(in the $n = 3$ shell).

The equation “maximum number of electrons that can be in a shell = $2n^2$ ” gives the maximum number in the $n = 3$ shell to be

$$\text{Maximum number of electrons} = 2n^2 = 2(3)^2 = 2(9) = 18.$$

Significance

The total number of electrons in the three possible subshells is thus the same as the formula $2n^2$. In standard (spectroscopic) notation, a filled $n = 3$ shell is denoted as $3s^2 3p^6 3d^{10}$. Shells do not fill in a simple manner. Before the $n = 3$ shell is completely filled, for example, we begin to find electrons in the $n = 4$ shell.

The structure of the **periodic table** (Figure 13.4.1) can be understood in terms of shells and subshells, and, ultimately, the total energy, orbital angular momentum, and spin of the electrons in the atom. A detailed discussion of the periodic table is left to a chemistry course—we sketch only its basic features here. In this discussion, we assume that the atoms are electrically neutral; that

is, they have the same number of electrons and protons. (Recall that the total number of protons in an atomic nucleus is called the atomic number, Z .)

First, the periodic table is arranged into columns and rows. The table is read left to right and top to bottom in the order of increasing atomic number (Z). Atoms that belong to the same column or **chemical group** share many of the same chemical properties. For example, the Li and Na atoms (in the first column) bond to other atoms in a similar way. The first row of the table corresponds to the $1s$ ($l = 0$) shell of an atom.

Consider the hypothetical procedure of adding electrons, one by one, to an atom. For hydrogen (H) (upper left), the $1s$ shell is filled with either a spin up or down electron (\uparrow or \downarrow). This lone electron is easily shared with other atoms, so hydrogen is chemically active. For helium (He) (upper right), the $1s$ shell is filled with both a spin up and a spin down ($\uparrow\downarrow$) electron. This “fills” the $1s$ shell, so a helium atom tends not to share electrons with other atoms. The helium atom is said to be chemically inactive, inert, or noble; likewise, helium gas is said to be an inert gas or noble gas.

Build an atom by adding and subtracting protons, neutrons, and electrons. How does the element, charge, and mass change? Visit [PhET Explorations: Build an Atom](#) to explore the answers to these questions.

Figure 13.4.1: The periodic table of elements, showing the structure of shells and subshells.

The second row corresponds to the $2s$ and $2p$ subshells. For lithium (Li) (upper left), the $1s$ shell is filled with a spin-up **and** spin-down electron ($\uparrow\downarrow$) and the $2s$ shell is filled with either a spin-up or -down electron (\uparrow or \downarrow). Its electron configuration is therefore $1s^2 2s^1$ or $[\text{He}]2s$, where $[\text{He}]$ indicates a helium core. Like hydrogen, the lone electron in the outermost shell is easily shared with other atoms. For beryllium (Be), the $2s$ shell is filled with a spin-up and -down electron ($\uparrow\downarrow$), and has the electron configuration $[\text{He}]2s^2$.

Next, we look at the right side of the table. For boron (B), the $1s$ and $2s$ shells are filled and the $2p$ ($l = 1$) shell contains either a spin up or down electron (\uparrow or \downarrow). From carbon (C) to neon (N), we fill the $2p$ shell. The maximum number of electrons in the $2p$

shells is $4l + 2 = 4(2) + 2 = 6$. For neon (Ne), the **1s** shell is filled with a spin-up and spin-down electron ($\uparrow\downarrow$), and the **2p** shell is filled with six electrons ($\uparrow\downarrow\uparrow\downarrow\uparrow\downarrow$). This “fills” the **1s**, **2s**, and **2p** subshells, so like helium, the neon atom tends not to share electrons with other atoms.

The process of electron filling repeats in the third row. However, beginning in the fourth row, the pattern is broken. The actual order of order of electron filling is given by

$$1s, 2s, 2p, 3s, 3p, 4s, \mathbf{3d}, 4p, 5s, \mathbf{4d}, 5p, 6s, \mathbf{4f}, \mathbf{5d}, 6p, 7s, \dots$$

Notice that the **3d**, **4d**, **4f**, and **5d** subshells (in bold) are filled out of order; this occurs because of interactions between electrons in the atom, which so far we have neglected. The **transition metals** are elements in the gap between the first two columns and the last six columns that contain electrons that fill the **d** ($l = 1$) subshell. As expected, these atoms are arranged in $4l + 2 = 4(2) + 2 = 10$ columns. The structure of the periodic table can be understood in terms of the quantization of the total energy (**n**), orbital angular momentum (**l**), and spin (**s**). The first two columns correspond to the **s** ($l = 0$) subshell, the next six columns correspond to the **p** ($l = 1$) subshell, and the gap between these columns corresponds to the **d** ($l = 2$) subshell.

The periodic table also gives information on molecular bonding. To see this, consider atoms in the left-most column (the so-called alkali metals including: Li, Na, and K). These atoms contain a single electron in the **2s** subshell, which is easily donated to other atoms. In contrast, atoms in the second-to-right column (the halogens: for example, Cl, F, and Br) are relatively stingy in sharing electrons. These atoms would much rather accept an electron, because they are just one electron shy of a filled shell (“of being noble”).

Therefore, if a Na atom is placed in close proximity to a Cl atom, the Na atom freely donates its **2s** electron and the Cl atom eagerly accepts it. In the process, the Na atom (originally a neutral charge) becomes positively charged and the Cl (originally a neutral charge) becomes negatively charged. Charged atoms are called ions. In this case, the ions are Na^+ and Cl^- , where the superscript indicates charge of the ion. The electric (Coulomb) attraction between these atoms forms a NaCl (salt) molecule. A chemical bond between two ions is called an **ionic bond**. There are many kinds of chemical bonds. For example, in an oxygen molecule O_2 electrons are equally shared between the atoms. The bonding of oxygen atoms is an example of a **covalent bond**.

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