1. ATOMIC STRUCTURE FUNDAMENTALS

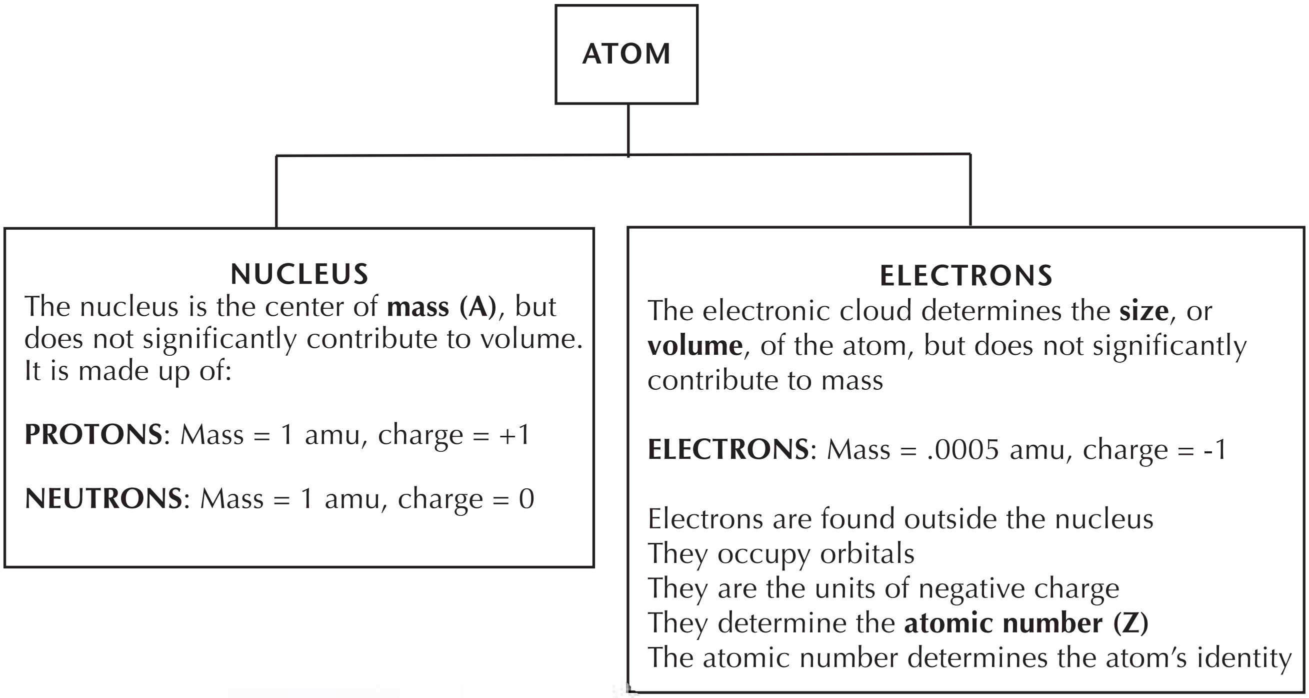
LEARNING OBJECTIVES

To review the basics concepts of atomic structure that have direct relevance to the fundamental concepts of organic chemistry. This material is essential to the understanding of organic molecular structure and, later on, reaction mechanisms.

BASIC CONCEPTS

Most of this material is a review of general chemistry. You might find it helpful to keep a general chemistry textbook available for reference purposes throughout the organic chemistry course.

The following diagram summarizes the basic facts of the structure of the atom.



ATOM

NUCLEUS
The nucleus is the center of **mass (A)**, but does not significantly contribute to volume. It is made up of:

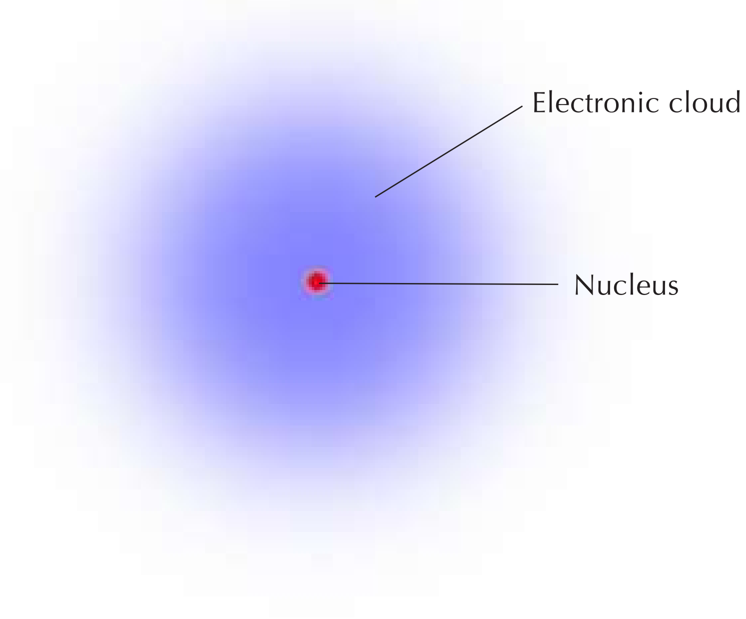
PROTONS: Mass = 1 amu, charge = +1

NEUTRONS: Mass = 1 amu, charge = 0

ELECTRONS
The electronic cloud determines the **size**, or **volume**, of the atom, but does not significantly contribute to mass

ELECTRONS: Mass = .0005 amu, charge = -1

Electrons are found outside the nucleus
They occupy orbitals
They are the units of negative charge
They determine the **atomic number (Z)**
The atomic number determines the atom’s identity



A simplified view of the hydrogen atom, which consists of only one electron outside the nucleus. The nucleus contains only one proton and no neutrons. All other elements contain neutrons in their nuclei.

Elements in the periodic table are indicated by SYMBOLS. To the left of the symbol we find the **atomic mass (A)** at the upper corner, and the **atomic number (Z)** at the lower corner.

$$^{A}_{Z}\text{Symbol}$$

Examples: $^{1}_{1}\text{H}$ $^{12}_{6}\text{C}$ $^{23}_{11}\text{Na}$

Electron trade constitutes the currency of chemical reactions. The number of electrons in a neutral atom (that is, the atomic number) gives the element its unique identity. **No two different elements can have the same atomic number**. The periodic table is arranged by order of increasing atomic number, which is always an integer.

In contrast to the atomic number, **different forms of the same element can have different masses**. They are called **isotopes**. The following are representations for some of the isotopes of hydrogen and carbon.

$^{1}_{1}\text{H}$	$^{2}_{1}\text{H}$	$^{12}_{6}\text{C}$	$^{13}_{6}\text{C}$
regular hydrogen	deuterium	regular carbon, or C-12	carbon-13, or C-13

The atomic mass reported in the periodic table for any given element is actually a **weighted average** of the masses of its isotopes as found in nature. Thus the mass of carbon is reported as 12.01115 rather than 12.00000 because it contains the relative contributions of both isotopes. The natural abundance of carbon-12 is nearly 100%, whereas that of carbon-13 is only about 1%. The reported mass is slightly greater than 12.00000 because of the small contribution of carbon-13. Therefore the mass number, as found in periodic tables, does not have to be an integer like the atomic number.

THE FOUR QUANTUM NUMBERS

The quantum numbers are parameters that describe the distribution of electrons in the atom, and therefore its fundamental nature. They are:

1. PRINCIPAL QUANTUM NUMBER (n) - Represents the **main energy level, or *shell*, occupied by an electron**. It is always a positive integer, that is $n = 1, 2, 3 \ldots$

2. SECONDARY QUANTUM NUMBER (l) - Represents the energy sublevel, or **type of orbital**, occupied by the electron. The value of l depends on the value of n such that $l = 0, 1, \ldots n-1$. This number is sometimes also called *azimuthal*, or *subsidiary*.

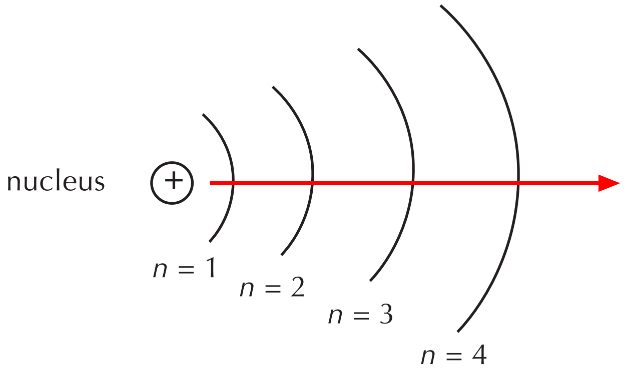
3. MAGNETIC QUANTUM NUMBER (m_l) - Represents the number of possible orientations in 3-D space for each type of orbital. Since the type of orbital is determined by l, the value of m_l ranges between $-l$ and $+l$ such that $m_l = -l, \ldots 0, \ldots +l$.

4. SPIN QUANTUM NUMBER (m_s) - Represents the **two possible orientations** that an electron can have in the presence of a magnetic field, or in relation to another electron occupying the same orbital. Only two electrons can occupy the same orbital, and they must have opposite spins. When this happens, **the electrons are said to be paired**. The allowed values for the spin quantum number m_s are +1/2 and -1/2.

According to Heisenberg's **uncertainty principle**, it is impossible to know the electron's velocity and its position simultaneously. The exact position of the electron at any given time cannot be known. Therefore, it is impossible to obtain a photographic picture of the atom like we could of a busy street. Electrons are more like fast-moving mosquitoes in a swarm that cannot be photographed without appearing blurred. The uncertainty about their position persists even in the photograph. An alternative picture of the swarm can be obtained by describing the area where the mosquitoes tend to be concentrated and the factors that determine their preference for certain locations, and that's the best we can do.

The quantum numbers provide us with a picture of the electronic arrangement in the atom relative to the nucleus. This arrangement is not given in terms of exact positions, like the photograph of a street, but rather in terms of **probability distributions** and **potential energy levels**, much like the mosquito swarm. The potential energy levels are described by the main quantum number n and by the secondary quantum number l. The probability distributions are given by the secondary quantum number l and by the magnetic quantum number m_l.

The now outdated solar system model of the atom allows us to visualize the meaning of the potential energy levels. The main energy levels, also called shells, are given by the main quantum number n.



The potential energy increases as the distance from the nucleus increases

THE RELATIONSHIP BETWEEN POTENTIAL ENERGY AND STABILITY IS INVERSE

As the potential energy of a system increases, the system's stability is more easily disrupted. As an example consider the objects on the earth. Objects that are positioned at ground level have lower potential energy than objects placed at high altitudes. The object that's placed at high altitude, be it a plane or a rock at the top of a mountain, has a higher "potential" to fall (lower stability) than the object that's placed at ground level. Systems tend towards lower levels of potential energy, thus the tendency of the plane or the rock to fall. Conversely, an object placed in a hole on the ground does not have a tendency to "climb out" because its potential energy is even lower than the object placed at ground level. Systems do not naturally tend towards states of higher potential energy. Another way of saying the same thing is to say that systems tend towards states of higher stability.

In the case of the electrons in the atom, those at lower levels of potential energy (lower shells, or lower n) are more stable and less easily disrupted than those at higher levels of potential energy. Chemical reactions are fundamentally electron transfers between atoms. In a chemical reaction, it is the electrons in the **outermost shell** that react, that is to say, get transferred from one atom to another. That's because they are the most easily disrupted, or the most available for reactions. The outermost shell is the marketplace where all electron trade takes place. Accordingly, it has a special name. It is called the **valence shell**.

Now, the solar system model of the atom is outmoded because it does not accurately depict the electronic distribution in the atom. Electrons do not revolve around the nucleus following elliptical, planar paths. They reside in 3-D regions of space of various shapes called **orbitals**.

An orbital is a region in 3-D space where there is a high probability of finding the electron.

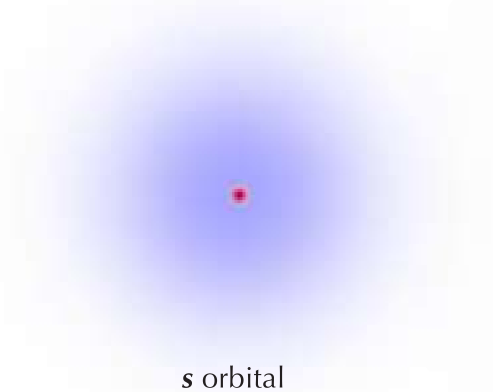
An orbital is, so to speak, a house where the electron resides. Only two electrons can occupy an orbital, and they must do so with opposite spin quantum numbers m_s. In other words, they must be paired.

The type and shape of orbital is given by the secondary quantum number l. As we know, this number has values that depend on n such that $l = 0, 1, \ldots n-1$. Furthermore, orbitals are not referred to by their numerical l values, but rather by small case letters associated with those values. Thus, when $l = 0$ we talk about ***s*** orbitals. When $l = 1$ we talk about ***p*** orbitals. When $l = 2$ we talk about ***d*** orbitals, and so on. In organic chemistry, we are mostly concerned with the elements of the second row and therefore will seldom refer to l values greater than 1. We'll be talking mostly about ***s*** and ***p*** orbitals, and occasionally about ***d*** orbitals in reference to third row elements.

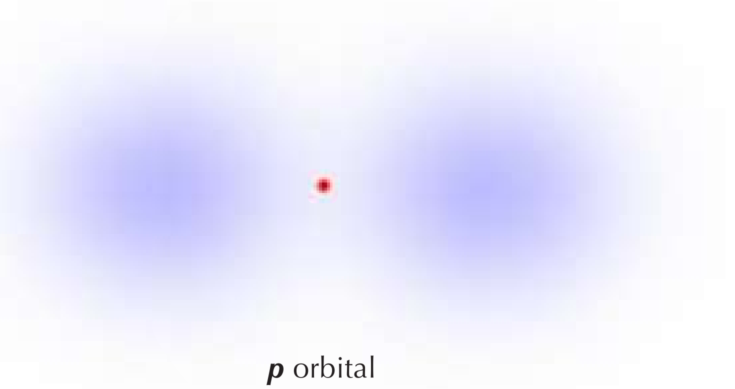
Since the value of l depends on the value of n, only certain types of orbitals are possible for each n, as follows (only the highest energy level is shown for each row of elements):

FIRST ROW ELEMENTS:	$n = 1$	$l = 0$	only ***s*** orbitals are possible, denoted as **1*s* orbitals**.
SECOND ROW ELEMENTS:	$n = 2$	$l = 0$	***s*** orbitals are possible, denoted as **2*s* orbitals**,
		$l = 1$	and ***p*** orbitals are possible, denoted as **2*p* orbitals**.
THIRD ROW ELEMENTS:	$n = 3$	$l = 0$	***s*** orbitals are possible, denoted as **3*s* orbitals**,
		$l = 1$	***p*** orbitals are possible, denoted as **3*p* orbitals**,
		$l = 2$	and ***d*** orbitals are possible, denoted as **3*d* orbitals**.

The shapes associated with ***s*** and ***p*** orbitals are shown below. For ***d*** orbitals refer to your general chemistry textbook. The red dot represents the nucleus

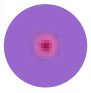


s orbital

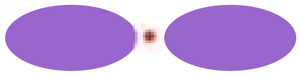


p orbital

Spherical, or



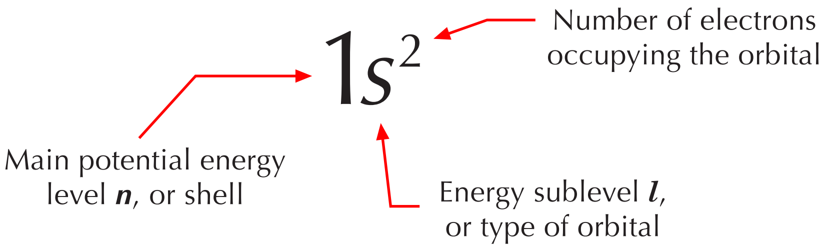
Dumbbell, or



Finally, the orientations of each orbital in 3-D space are given by the magnetic quantum number m_l. This number depends on the value of l such that $m_l = -l, \ldots 0, \ldots +l$. Thus, when $l = 0$, $m_l = 0$. There is only one value, or only one possible orientation in 3-D space for *s*-orbitals. That stands to reason, since they are spherical. In the case of *p*-orbitals $l = 1$, so $m_l = -1$, 0, and +1. Therefore, there are three possible orientations in 3-D space for *p*-orbitals, namely along the *x*, *y*, and *z* axes of the Cartesian coordinate system. More specifically, those orbitals are designated as p_x, p_y, and p_z respectively.

ELECTRONIC CONFIGURATIONS

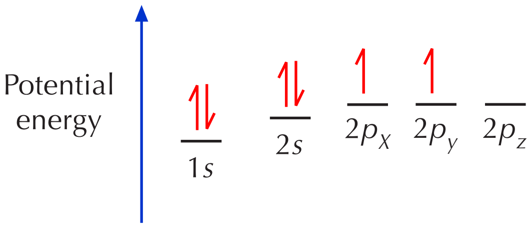
To indicate the electronic configuration of the atom, that is to say, where the electrons reside, we use the following notation.



Given a periodic table, **all we need to know to write the electronic configuration for a given atom is the atomic number *Z***, which tells us the number of electrons in the neutral atom. We start by writing the first potential energy level (*n*=1), then the possible types of orbitals in this level (*s*, *p*, etc.), and then the number of electrons occupying that orbital, which is always either 1or 2. It will always be 2 unless *Z* is an odd number and we're down to the last electron in the valence shell. In this course we will seldom be concerned with elements beyond the second row, so we'll keep it simple. The electronic configurations for the nonmetals of the second row are shown below.

BORON	B	Z=5	$1s^2$, $2s^2$, $2p_X{}^1$	Total of 5 electrons, 3 in the valence shell
CARBON	C	Z=6	$1s^2$, $2s^2$, $2p_X{}^1$, $2p_Y{}^1$	Total of 6 electrons, 4 in the valence shell
NITROGEN	N	Z=7	$1s^2$, $2s^2$, $2p_X{}^1$, $2p_Y{}^1$, $2p_Z{}^1$	Total of 7 electrons, 5 in the valence shell
OXYGEN	O	Z=8	$1s^2$, $2s^2$, $2p_X{}^2$, $2p_Y{}^1$, $2p_Z{}^1$	Total of 8 electrons, 6 in the valence shell
FLUORINE	F	Z=9	$1s^2$, $2s^2$, $2p_X{}^2$, $2p_Y{}^2$, $2p_Z{}^1$	Total of 9 electrons, 7 in the valence shell
NEON	Ne	Z=10	$1s^2$, $2s^2$, $2p_X{}^2$, $2p_Y{}^2$, $2p_Z{}^2$	Total of 10 electrons, 8 in the valence shell

We can also write electronic configurations where electrons are shown as half-arrows and potential energy levels are shown as horizontal dashes positioned at different heights to indicate those levels. The following diagram shows the electronic configuration for carbon.



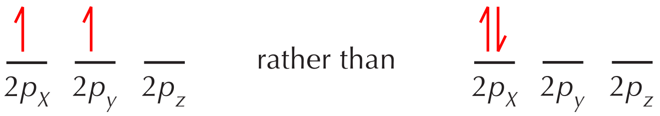
The half-arrows shown together in opposite directions indicate that the electrons are paired. Single arrows indicate unpaired electrons. Notice that an empty orbital does not mean that such orbital does not exist. It only means there are no electrons in it. Given the right circumstances, it could hold electrons. This is in opposition to an orbital whose existence is not possible. For example *d* orbitals are not possible for second row elements and therefore are nonexistent in those elements.

Orbitals which are of exactly the same energy, such as the $2p_X$, $2p_Y$, and $2p_Z$ orbitals, are said to be **degenerate**.

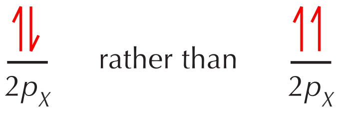
In writing electronic configurations, we follow the **Aufbau principle**, **Hund's rule**, and the **Pauli exclusion principle**.

The **Aufbau principle** (German for *building up*) makes reference to the process of building an atom from the ground up. That is to say, the manner in which electrons are placed in the atom one by one. We start by placing the first electron at the lowest potential energy level, which is the 1*s* orbital, and then following with the rest of the electrons always placing them at the lowest available level of potential energy. In other words, ***electrons always go into orbitals with the lowest possible energy***.

Hund's rule says that ***when electrons go into degenerate orbitals, they occupy them singly before pairing begins***. That's the reason why in the carbon atom shown in the previous page, the electrons in the $2p_X$ and $2p_Y$ orbitals are placed one in each orbital, unpaired, rather than two in one orbital and paired.



Finally, the **Pauli exclusion principle** states that only electrons with opposite spins can occupy the same orbital. In other words, ***if two electrons must go into the same orbital, they must be paired***. In the example shown above we have



CHEMICAL BONDING

As stated earlier, all chemistry except for nuclear reactions involve electron transfers from one atom to another. More specifically, this electron trade takes place at the valence shells of the atoms. In general chemistry, we learn about two major types of chemical bonds, namely i**onic** and **covalent**.

Ionic bonding is more likely to take place between elements of highly different electronegativities, especially between metals and nonmetals. We can use Lewis formulas to indicate the manner of the electron transfer in a highly simplified fashion. The dots around the atomic symbol represent the electrons in the valence shell of each element. In the classic example of the reaction between sodium and chlorine, the only electron in the valence shell of sodium is **completely transferred** to the valence shell of chlorine. Sodium then forms a positive ion and chlorine a negative ion. **The electrostatic attraction between oppositely charged ions forms the basis of the ionic bond and is the force that keeps the atoms together**.

Covalent bonding is more likely to take place between elements of similar electronegativities, especially between nonmetals. In the reaction between two hydrogen atoms, for instance, the electron transfer is never complete. Instead, **the two atoms share the electrons**, which in this case spend equal amounts of time around both nuclei. There is no formation of full positive or negative charges and therefore there is no electrostatic attraction. The force that keeps the atoms together is the **fulfillment of the octet rule**, which will be discussed shortly.