CHEMICAL BONDING in Organic Compounds

Valence electrons play a fundamental role in chemical bonding. In the electron configuration of an atom, the outermost shell is called the valence shell, and the ***electrons in the valence shell (outermost shell)*** are known as **valence electrons**. Take the carbon atom for example: the electron configuration of carbon is $1s^2 2s^2 2p^2$. The outermost shell is the 2nd principal shell, so there are 4 valence electrons in carbon. Valence electrons are the electrons that are the furthest away from the nucleus, and thus they experience the least attraction from the nucleus and are the most reactive. They play the most important role in chemical bonding.

Ionic Bonds and Covalent Bonds

There are two major types of chemical bonds: **ionic bonds** and **covalent bonds**. An ionic bond is an interaction that results from the electrostatic attraction (force) between ions of opposite charges. Ionic bonds apply to ionic compounds, such as sodium chloride (NaCl).

In simple ionic compounds, the metal element loses valence electron(s) to form the cation and the non-metal element gains electron(s) to form the anion. With the proper number of electron(s) lost or gained, both the cation and the anion achieve a full outer shell that contains eight electrons, as in the following examples of Na^+, Ca^2, Cl^- and O^{2-}. According to Lewis's Theory, ***an atom is most stable if its outer shell is filled or contains eight electrons***. This is also called the **octet rule**.

Na (atom) → $Na^+ + e^-$
Cl (atom) + $e^- \rightarrow Cl^-$

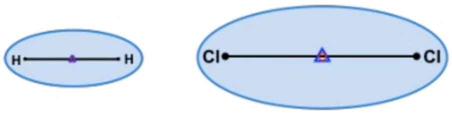
Ca (atom) → $Ca^{2+} + 2e^-$
O (atom) + $2e^- \rightarrow O^{2-}$

A covalent bond is a bond formed through the sharing of electron pairs between the two bonding atoms. The shared electron pairs are mutually attracted by the nuclei of both atoms. By sharing the electron pairs, both atoms also gain a filled outer shell, or an **octet**.

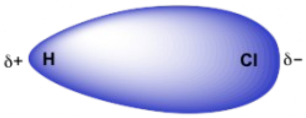
Almost all the bonds involved in organic compounds are covalent bonds.

Covalent bonds can be non-polar or polar.

For covalent bonds formed between two identical atoms, the electron pairs are shared equally between the two nuclei. Electron density is distributed evenly through the bond, making it a non-polar bond. Examples include all homonuclear molecules, such as H-H, Cl-Cl, O=O, N≡N.

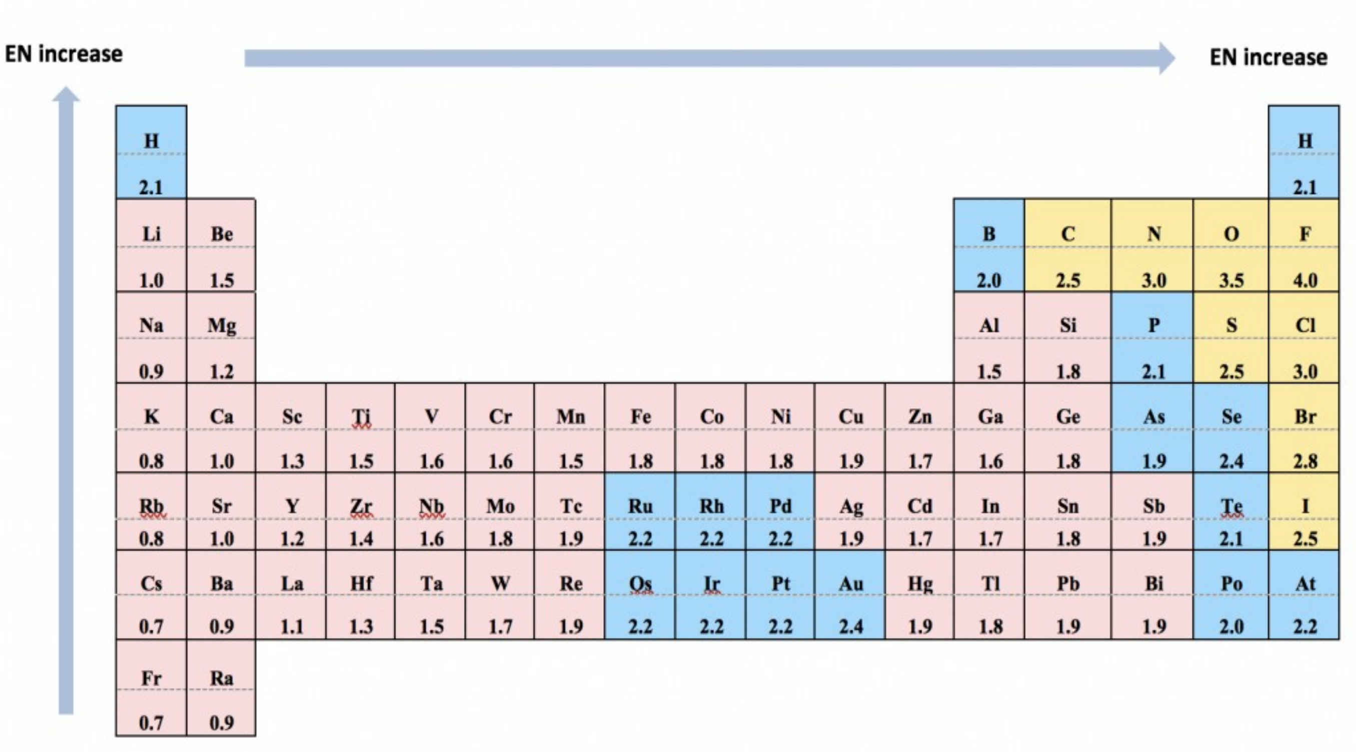


nonpolar covalent bond



polar covalent bond

For heteronuclear bonds (the bond formed between two different atoms), the electron pairs are not shared evenly and the bond is polar. The electron pairs are *more* attracted to the atom that has the stronger ability to pull the electron pairs towards itself. This ability is measured with **electronegativity** (EN). The relative values of EN are listed using the scale devised by Linus Pauling, as summarized in the **Table below:**

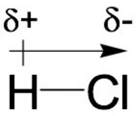


H 2.1																H 2.1
Li 1.0	Be 1.5											B 2.0	C 2.5	N 3.0	O 3.5	F 4.0
Na 0.9	Mg 1.2											Al 1.5	Si 1.8	P 2.1	S 2.5	Cl 3.0
K 0.8	Ca 1.0	Sc 1.3	Ti 1.5	V 1.6	Cr 1.6	Mn 1.5	Fe 1.8	Co 1.8	Ni 1.8	Cu 1.9	Zn 1.7	Ga 1.6	Ge 1.8	As 1.9	Se 2.4	Br 2.8
Rb 0.8	Sr 1.0	Y 1.2	Zr 1.4	Nb 1.6	Mo 1.8	Tc 1.9	Ru 2.2	Rh 2.2	Pd 2.2	Ag 1.9	Cd 1.7	In 1.7	Sn 1.8	Sb 1.9	Te 2.1	I 2.5
Cs 0.7	Ba 0.9	La 1.1	Hf 1.3	Ta 1.5	W 1.7	Re 1.9	Os 2.2	Ir 2.2	Pt 2.2	Au 2.4	Hg 1.9	Tl 1.8	Pb 1.9	Bi 1.9	Po 2.0	At 2.2
Fr 0.7	Ra 0.9															

Notes about electronegativity values for Organic Chemistry purposes:

- It is much more important to know the trend of EN than to memorize the values. The trend is that EN values decrease along the group from top to bottom and increase along the period from left to right (the trend mainly works for Main Group elements, not transition metal elements).
- It is very useful (although not mandatory) to know the EN values of a few select elements: F (4.0, highest), O (3.5), N (3.0), C (2.5) and H (2.1).
- The EN of C (2.5) and H (2.1) is close, which makes the C-H bond (the bond involved in all organic compounds) technically non-polar.

With the introduction to the concept of EN, bond polarity can be represented with the EN difference between the two bonding atoms, which is known as ΔEN. For non-polar bonds, ΔEN equals to zero, and for polar bonds, ΔEN is not zero. The greater the ΔEN, the more polar the bond is.



- **Bonding pair:** The pair of valence electrons involved in a covalent bond. One covalent bond means one pair of bonding electrons, that is, 2 electrons. Single bonds and multiple bonds (double or triple bonds) may be involved.
- **Lone pair**: The pairs of valence electrons **not** involved in a covalent bond. Lone pair electrons can also be called ***non-bonding electron pairs***.

Special note: Non-bonding electrons can also be unpaired (single) electrons. A species with one or more unpaired (single) electrons is called a radical (free radical).

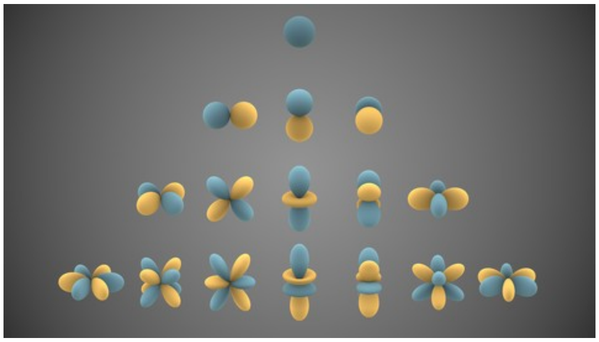
We have discussed how covalent bonds are formed through the sharing of a pair of electrons; here we will apply the **valence bond theory** to explain in more detail how the sharing happens. The **valence bond theory** describes the covalent bond formed from the overlap of two half-filled atomic orbitals on different atoms.

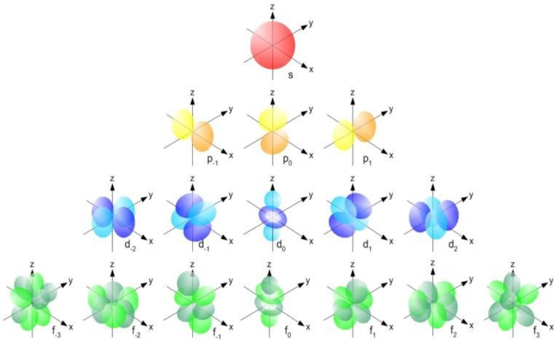
Let’s start with the simple molecule H_2. The atomic electron configuration of a hydrogen atom is $1s^1$, meaning is one electron (which is also the valence electron) in the sphere-shaped 1s there orbital.

An atomic orbital is the probability of finding an electron (belonging to an atom) in a specific region around the nucleus of the atom. It is also a mathematical term in atomic theory and quantum mechanics that describes the position and wavelike behaviour of an electron in an atom. A maximum of two electrons, each with its own spin quantum number m_s, will occupy each of those orbitals. Atomic orbital’ can also be used to refer to the physical space or physical region around an atom’s nucleus in which the probability of a specific electron being present is maximum, thus can be termed as an ***electron cloud***.. The presence of an electron in such a region is predicted by the mathematical form of the atomic orbital.

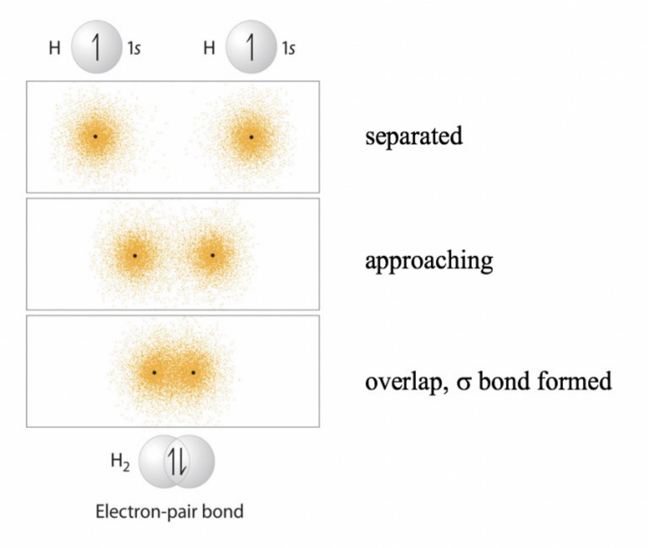
Each orbital in an atom is characterized by a set of values of three quantum numbers n, ℓ, and m_ℓl which respectively correspond to electron's energy, its orbital angular momentum, and its orbital angular momentum projected along a chosen axis (magnetic quantum number).

The shapes of atomic orbitals in one-electron atom are related to 3-dimensional spherical harmonics- which are special mathematical functions defined on the surface of a sphere



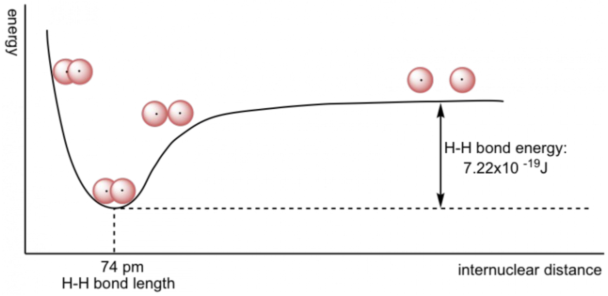


When two hydrogen atoms are approaching each other, the two 1s orbitals overlap, allowing the two electrons (each H donates 1 electron) to pair up for the bonding with the overlapping orbitals. The shared pair of electrons are under the attraction of both hydrogen nuclei simultaneously, resulting in them acting as a “glue” that holds the two nuclei together.



Formation of H-H σ bond

The overall energy changes of the system *versus* the distance between the two hydrogen nuclei can be summarized in the energy diagram below.

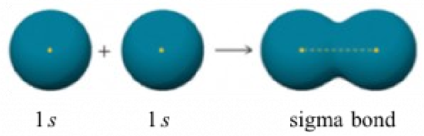


When the two atoms are separate, there is no overlap and no interaction. As they get closer, orbitals start to overlap, and there is attraction between the nucleus of one atom and the electron of the other atom, so the total energy of the system lowers. The energy lowers to its minimum level when the two atoms approach the optimal distance. The optimal distance is also defined as the **bond length**. H_2 molecules have a bond length of 74 pm often referred to as 0.74 Å,

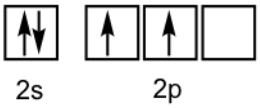
(1Å=10^{-10}m). The energy difference between the most stable state (lowest energy state with optimum distance) and the state in which the two atoms are completely separated is called the **bond (dissociation) energy**. The bond energy is 7.22×10^{-19} J for one H-H bond or 435 kJ/mol.

When the two atoms get closer than the optimal distance, the repulsion between the two nuclei becomes predominant, and the energy of the system becomes even higher.

Another important character of the covalent bond in H_2 is that the two 1s orbitals overlap in a way that is referred to as head-to-head. The bond formed by head-to-head overlap is called **σ (sigma) bond**. σ bonds are cylindrically symmetrical, meaning if a cross-sectional plane is taken of the bond at any point, it will form a circle.



However, when the valence bond theory is applied to organic molecules, for instance CH_4, it does **not** work. The valence electron configuration of a carbon atom is $2s^2 2p^2$ as shown in the orbital diagram.



Based on the valence bond theory, with two half-filled orbitals available, the carbon atom should be able to form two bonds. However, carbon always has four bonds in any stable organic compound. To explain the bonding of carbon and other atoms that cannot fit into the simple valence bond theory, a new theory called orbital **hybridization** will be introduced as a supplement to the valence bond theory.