

Chemical bonding

CHEMICAL BONDS

- Atoms or ions are held together in molecules or compounds by **chemical bonds**.
- The type and number of electrons in the outer electronic shells of atoms or ions are instrumental in how atoms react with each other to form stable chemical bonds.
- Over the last 150 years scientists developed several theories to explain why and how elements combine with each other.

Bonding Theories

- Lewis bond Theory
- Valence Bond Theory
- Molecular Orbital Theory



Gilbert Newton Lewis

Lewis Bonding Theory

- Atoms *ONLY* come together to produce a more stable electron configuration.
- Atoms bond together by either transferring or sharing electrons.
- Many of atoms like to have 8 electrons in their outer shell.
 - Octet rule.
 - There are some exceptions to this rule—the key to remember is to try to get an electron configuration like a noble gas. Li and Be try to achieve the He electron arrangement.

The Octet Rule

Chemical compounds tend to form so that each atom, by gaining, losing, or sharing electrons, has **eight** electrons in its highest occupied energy level.

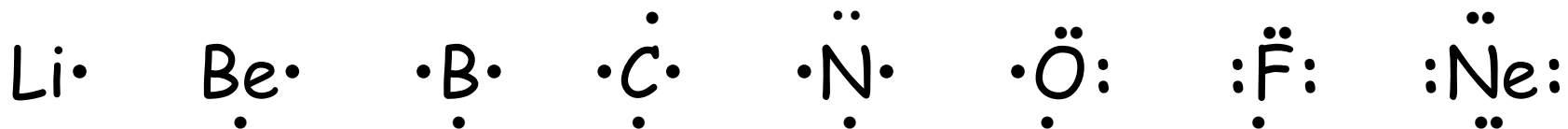
The same number of electrons as in the nearest noble gas

The first exception to this is hydrogen, which follows the duet rule.

The second exception is helium which does not form bonds because it is already "full" with its two electrons

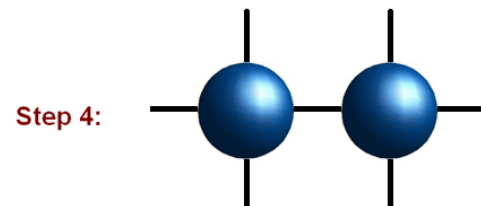
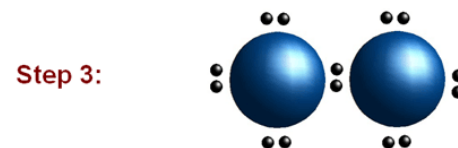
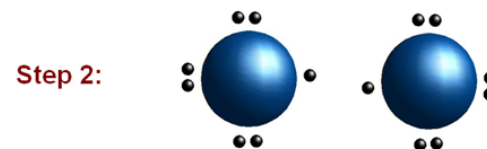
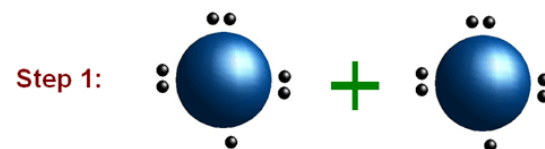
Lewis Symbols of Atoms

- Uses symbol of element to represent nucleus and inner electrons.
- Uses dots around the symbol to represent valence electrons.
 - Puts one electron on each side first, then pair.
- Remember that elements in the same group have the same number of valence electrons; therefore, their Lewis dot symbols will look alike.



Rules for Lewis structures of molecules

1. Write out valence electrons for each atom
2. Connect lone electrons because lone electrons are destabilizing
 1. Become two shared electrons
 1. Called a "bond"
3. Check to see if octet rule is satisfied
 1. Recall electron configuration resembling noble gas
 1. In other words, there must be 8 electrons (bonded or non-bonded) around atom
 1. Non-bonded electron-pair
 1. Called "lone pair"



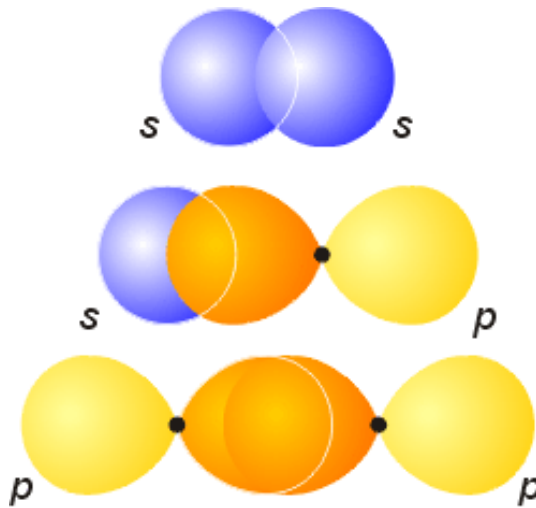
Valence Bonding Theory

- Valence bond theory (VBT) is a localized quantum mechanical approach to describe the bonding in molecules.
- VBT provides a mathematical justification for the Lewis interpretation of electron pairs making bonds between atoms.
- VBT asserts that electron pairs occupy *directed* orbitals localized on a particular atom.
- The directionality of the orbitals is determined by the geometry around the atom which is obtained from the predictions of Valence Shell Electron Pair Repulsion (VSEPR) theory.

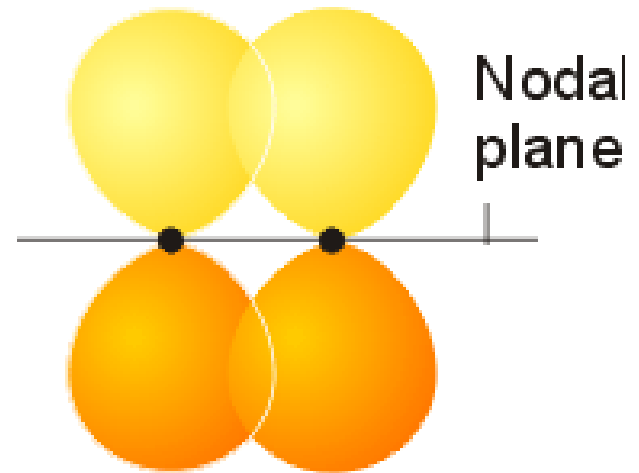
In VBT, a bond will be formed if there is overlap of appropriate orbitals on two atoms and these orbitals are populated by a maximum of two electrons.

Valence bond theory considers the interactions between separate atoms as they are brought together to form molecules.

overall description of the covalently bonded H_2 molecule; Ψ_{covalent} is a linear combination of wave functions ψ_1 and ψ_2 .



σ bonds: symmetric about the inter-nuclear axis



π bonds: have a node on the inter-nuclear axis and the sign of the lobes changes across the axis.

Single bond: σ bond

Double bond: σ bond + π bond

Triple bond: σ bond + 2 π bond

In a ***diamagnetic species***, all electrons are spin-paired; a diamagnetic substance is repelled by a magnetic field.

A ***paramagnetic species*** contains one or more unpaired electrons; a paramagnetic substance is attracted by a magnetic field.

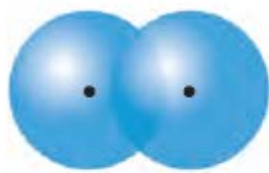
The Lewis approach and VBT predict that O_2 is diamagnetic - this is wrong!

Molecular Orbital Theory

In molecular orbital (MO) theory, we begin by placing the nuclei of a given molecule in their equilibrium positions and then calculate the molecular orbitals

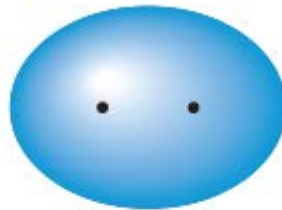
such interactions are:

- allowed if the symmetries of the atomic orbitals are compatible with one another.
- efficient if the region of overlap between the two atomic orbitals is significant.
- efficient if the atomic orbitals are relatively close in energy.

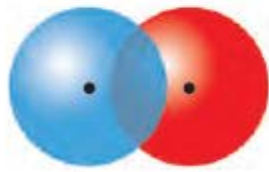


$\psi_{\text{MO bonding}}$

is equivalent to

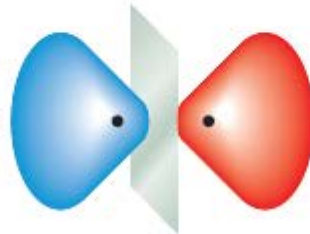


(a)

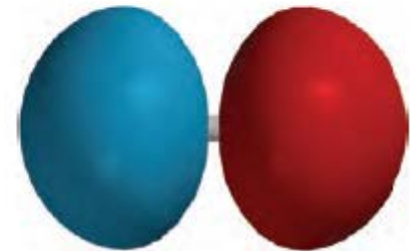


$\psi_{\text{MO antibonding}}$

is equivalent to



Nodal
plane



Schematic representations of (a) the bonding and (b) the antibonding molecular orbitals in the H_2 molecule

Forms of Chemical Bonds

- There are 2 extreme forms of connecting or bonding atoms:
- **Ionic**—complete transfer of electrons from one atom to another
- **Covalent**—electrons shared between atoms

Most bonds are somewhere in between.

IONIC BOND

**bond formed between
two ions by the
transfer of electrons**

Formation of Ions from Metals

- Ionic compounds result when metals react with nonmetals
- Metals *lose* electrons to match the *number of valence electrons* of their nearest noble gas
- *Positive ions* form when the number of electrons are *less* than the number of protons

Group 1 metals \longrightarrow ion 1^+

Group 2 metals \longrightarrow ion 2^+

Group 13 metals \longrightarrow ion 3^+

Formation of Sodium Ion

Sodium atom



2-8-1

$$\begin{array}{r} 11 \text{ p}^+ \\ \underline{11 \text{ e}^-} \\ 0 \end{array}$$

Sodium ion



2-8 (= Ne)

$$\begin{array}{r} 11 \text{ p}^+ \\ \underline{10 \text{ e}^-} \\ 1^+ \end{array}$$

Formation of Magnesium Ion

Magnesium atom

Magnesium ion



2-8-2

2-8 (=Ne)

$$\begin{array}{r} 12 \text{ p}^{+} \\ 12 \text{ e}^{-} \\ \hline 0 \end{array}$$

$$\begin{array}{r} 12 \text{ p}^{+} \\ 10 \text{ e}^{-} \\ \hline 2^{+} \end{array}$$

Some Typical Ions with Positive Charges (Cations)

Group 1



Group 2

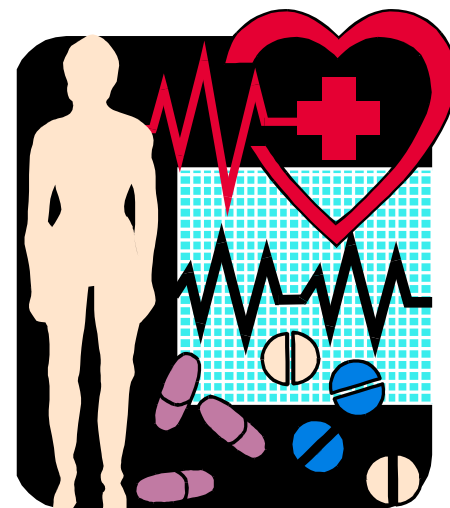


Group 13



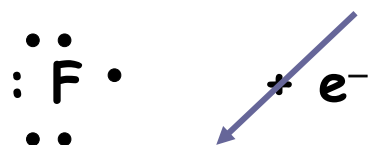
Ions from Nonmetal Ions

- In ionic compounds, nonmetals in 15, 16, and 17 gain electrons from metals
- Nonmetal add electrons to achieve the octet arrangement
- Nonmetal ionic charge:
3-, 2-, or 1-



Fluoride Ion

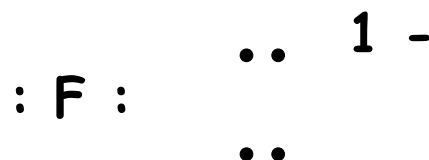
unpaired electron



2-7

$$\begin{array}{r} 9 p^+ \\ \hline 9 e^- \\ 0 \end{array}$$

octet



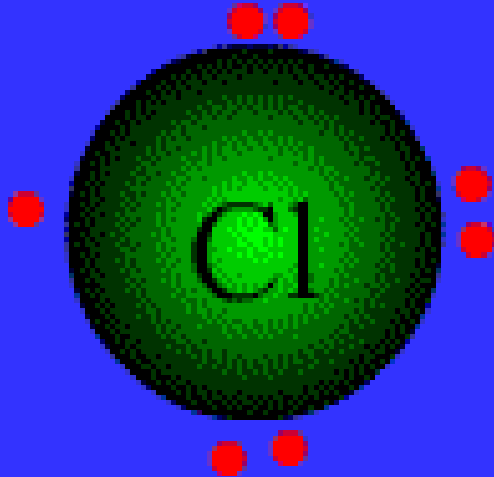
2-8 (= Ne)

$$\begin{array}{r} 9 p^+ \\ \hline 10 e^- \\ 1^- \end{array}$$

ionic charge

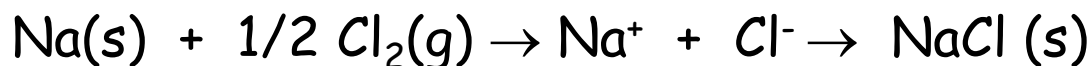
Ionic Bond

- Between atoms of metals and nonmetals with very different electronegativity
- Bond formed by transfer of electrons
- Produce charged ions all states. Conductors and have high melting point.
- Examples; NaCl, CaCl₂, K₂O



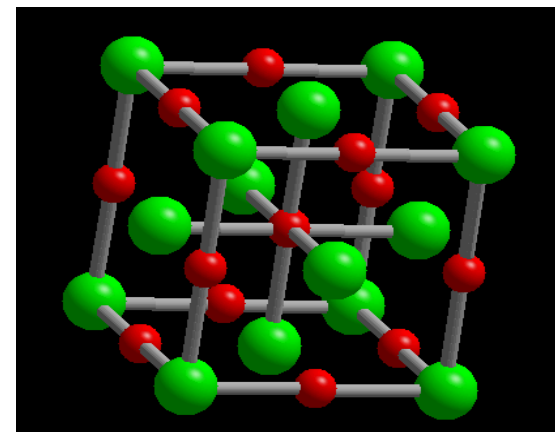
Ionic compounds

essentially complete electron transfer from an element of low IE (metal) to an element of high electron affinity (EA) (nonmetal)



- primarily between **metals** (Grps 1A, 2A and transition metals) and **nonmetals** (esp O and halogens)

- **NON-DIRECTIONAL** bonding
via Coulomb (charge) interaction



Ionic Bond characteristics

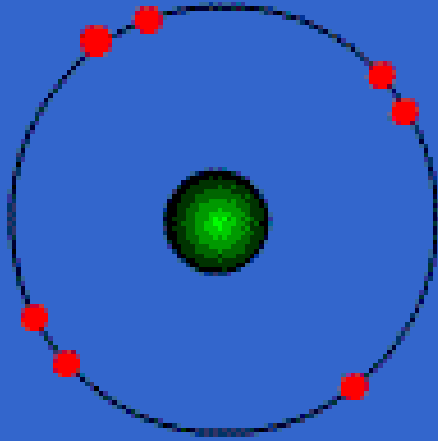
- Three dimensional ionic structure called a giant ionic crystal lattice structure.
- Ionic compounds are soluble in water as the ions form favourable interactions with water molecules which release sufficient energy to break away from the lattice.
- In a solid state they do not conduct electricity. However, in a liquid state or when dissolved in water, they will conduct electricity well because the ions are free to move and can carry charge.
- Ionic bonds are generally a lot weaker than covalent bonds.
- Ionic compounds have high melting/boiling point due to the strong electrostatic forces of attraction, which require a large amount of heat energy to overcome.

COVALENT BOND

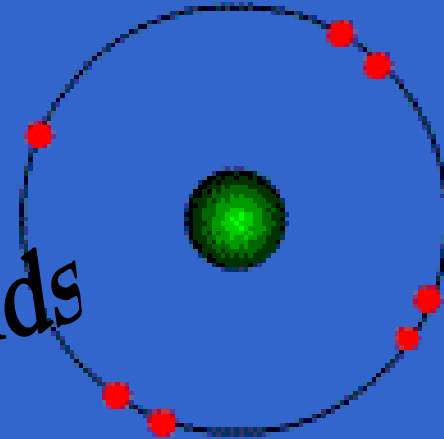
bond formed by
the *sharing* of
electrons

Covalent Bond

- Between nonmetallic elements of similar electronegativity.
- Formed by sharing electron pairs
- Stable non-ionizing particles, they are not conductors at any state
- Examples; O_2 , CO_2 , C_2H_6 , H_2O , SiC



Covalent Bonds



**Bonds in all the
polyatomic ions
and diatomics
are all covalent
bonds**

NONPOLAR COVALENT BONDS

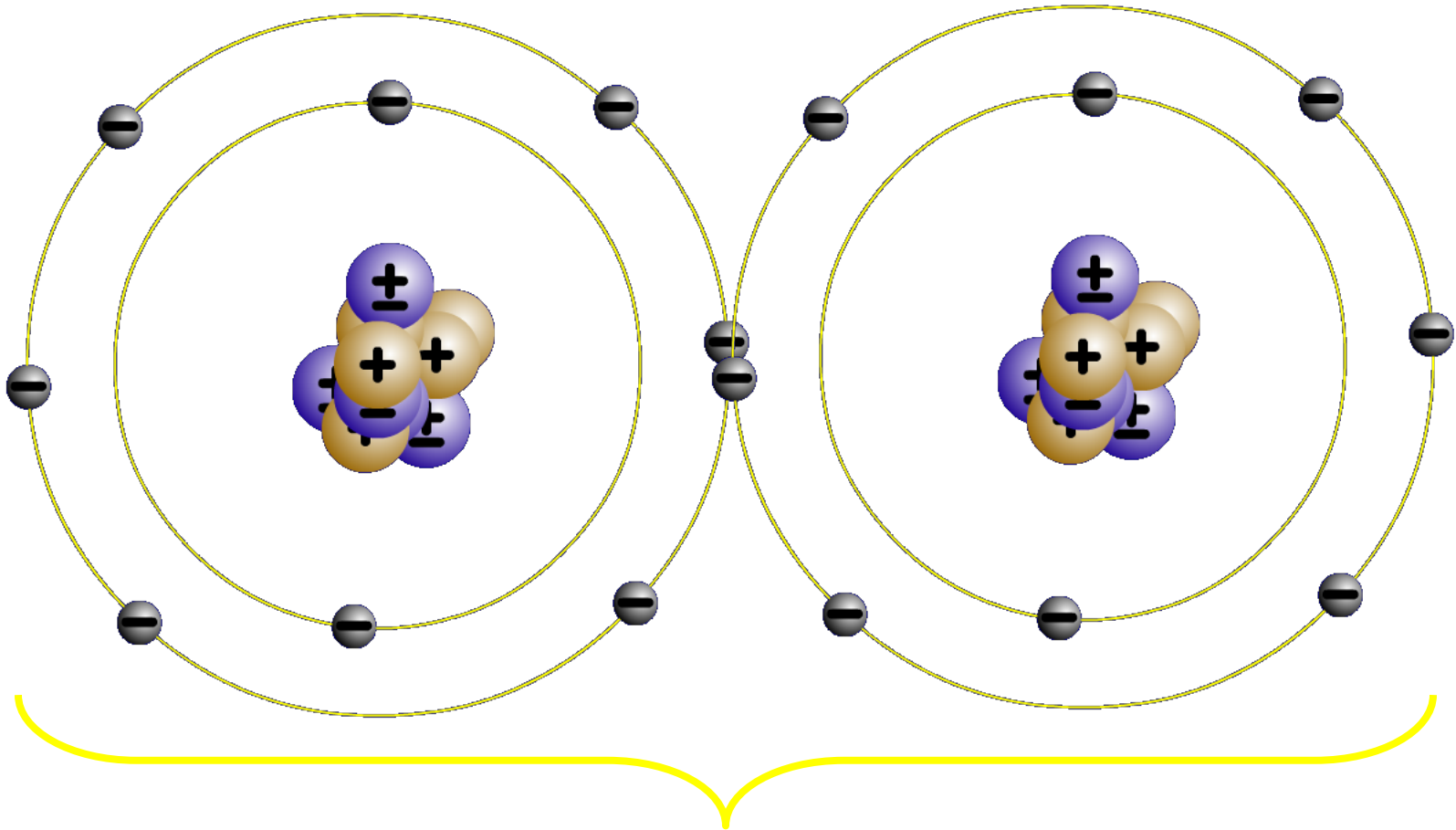
when electrons are shared *equally*



Covalent bonds- Two atoms share one or more pairs of outer-shell electrons.

Oxygen Atom

Oxygen Atom

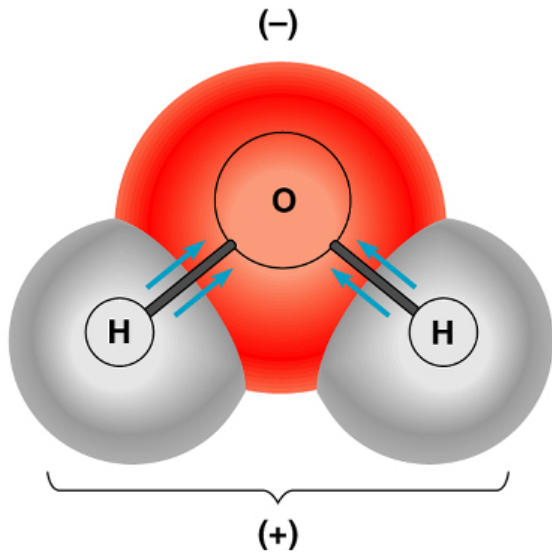


Oxygen Molecule (O₂)

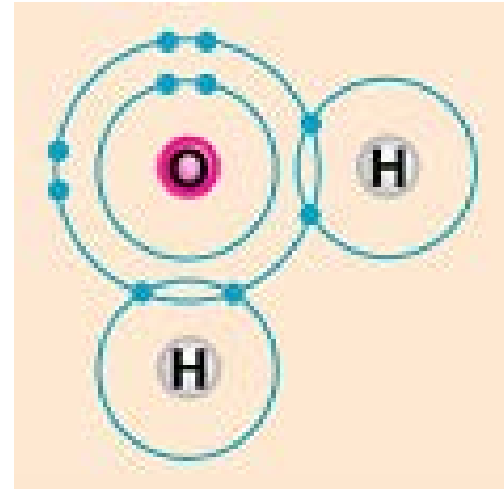
POLAR COVALENT BONDS

when electrons are shared but shared
unequally





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- water is a *polar molecule* because oxygen is more electronegative than hydrogen, and therefore electrons are pulled closer to oxygen.

Electronegativity

Electronegativity: The relative ability of an atom in a molecule to attract shared electrons to itself.

Example: Fluorine has the highest electronegativity.

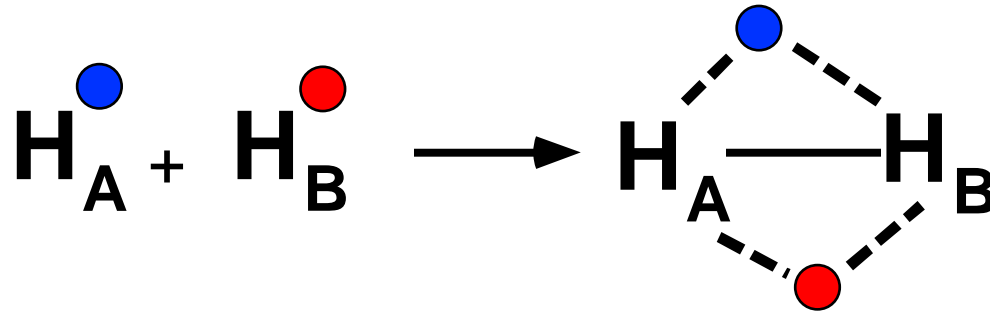
- **Similar** electronegativities between elements give non-polar covalent bonds (0.0-0.4)
- **Different** electronegativities between elements give polar covalent bonds (0.5-1.9)
- If the difference between the electronegativities of two elements is about 2.0 or greater, the bond is ionic

Dipole moment

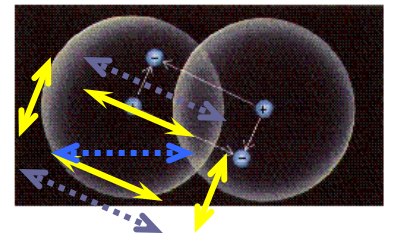
- Dipole Moment
 - A molecule that has a center of positive charge and a center of negative charge
 - Will line up on electric field
- In Debye units
 - $1 \text{ D} = 3.34 \times 10^{-30} \text{ C} \cdot \text{m}$

Covalent Bonding

The bond arises from the mutual attraction of 2 nuclei for the same electrons.

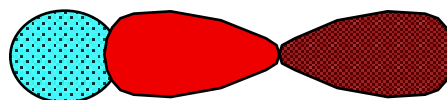
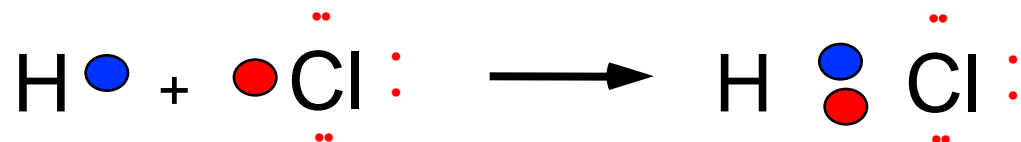


A covalent bond is a balance of **attractive** and **repulsive** forces.



Bond Formation

A bond can result from a "head-to-head" overlap of atomic orbitals on neighboring atoms.

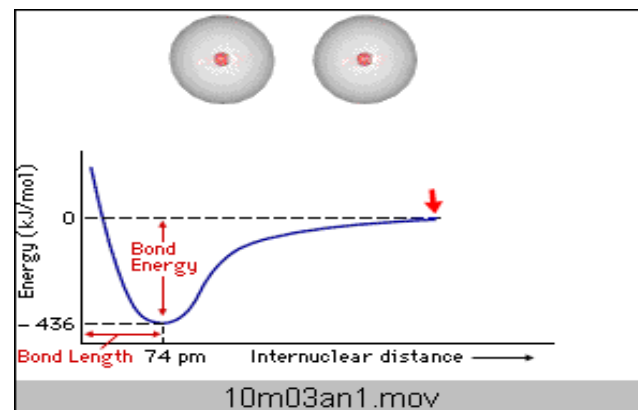
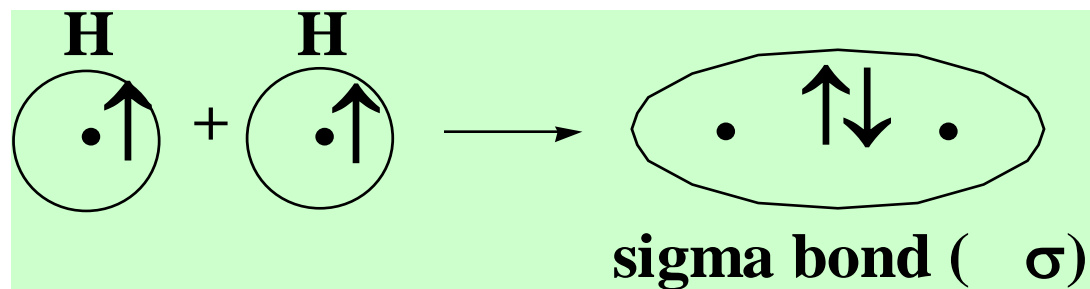


Overlap of H (1s) and Cl (2p)

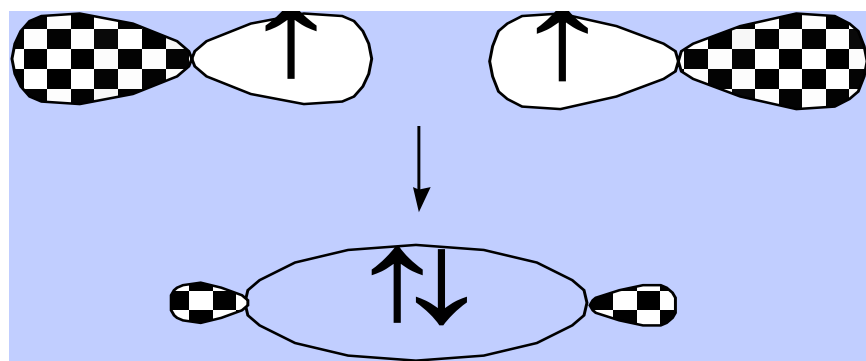
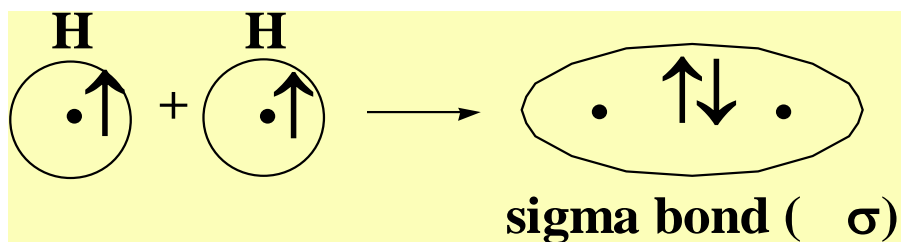
This type of overlap places bonding electrons in a **MOLECULAR ORBITAL** along the line between the two atoms and forms a **SIGMA BOND (s)**.

Sigma Bond Formation by Orbital Overlap

Two s Atomic Orbitals (A.O.s) overlap to form an $s \sigma$ (sigma) Molecular Orbital (M.O.)

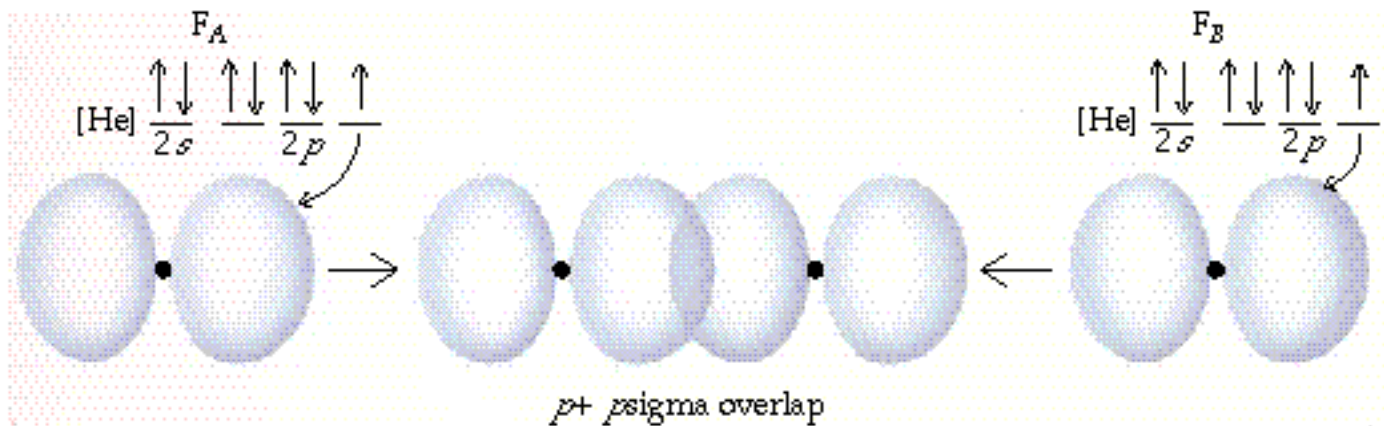


Sigma Bond Formation by Orbital Overlap



Similarly, two p A.O.s can overlap end-on to form a $p\sigma$ M.O.

e.g.
 F_2



Multiple Covalent Bonds

- sigma (s) bonds: results from the end-to-end overlap of simple or hybridized atomic orbitals along the straight line joining the nuclei of the bonded atoms.
- pi (p) bonds: results from the side-to-side overlap of p orbitals, producing a high electron charge density above and below the line joining the bonded atoms.

Covalent Bond characteristics

- Bond length: defined as the average distance between the nuclei of two bonded atoms in a molecule.
- Bond angle: may be defined as the internal angle between the orbitals containing electron pairs in the valence shell of the central atom in a covalent molecule.
- Bond strength or bond energy - the energy, which is invariably required to break a chemical bond.
- Polarity in Covalent Bonds - A covalent bond formed between two identical or similar atoms is said to be a non-polar covalent bond but if formed between two dissimilar atoms, it is said to be a polar covalent bond.

Hybridization

- Extends the Lewis concept of electron pair bonds by introducing the notion of **orbital overlap** and **hybridization**.
- Hybridization is necessary to account for **molecular geometry** predicted by valence shell electron-pair repulsion (VSEPR) theory.
- Hybrid atomic orbitals are constructed by making **linear combinations** (sums and differences) between hydrogen-like orbitals in the valence shell of each atom.

What is hybridization

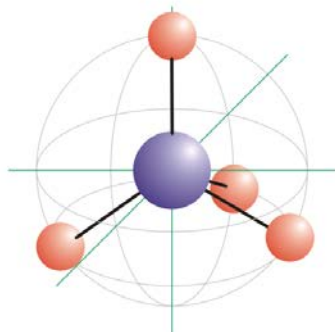
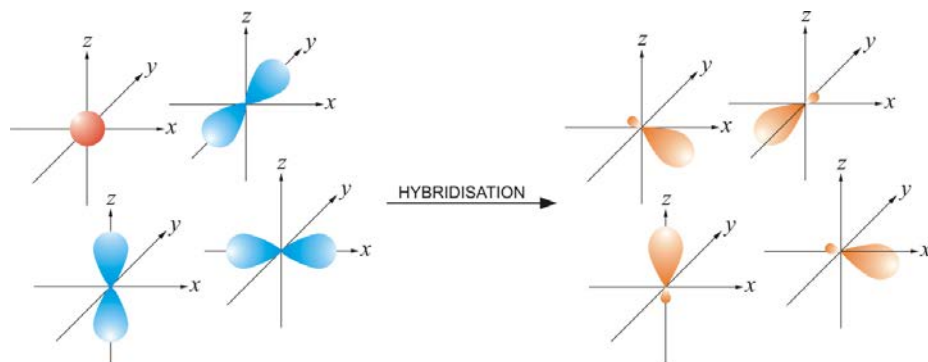
In chemistry, **orbital hybridisation** (or **hybridization**) is the concept of mixing atomic orbitals into new *hybrid orbitals* (with different energies, shapes, etc., than the component atomic orbitals) suitable for the pairing of electrons to form chemical bonds in valence bond theory. Hybrid orbitals are very useful in the explanation of molecular geometry and atomic bonding properties.

The new orbital can hold the same total number of electrons as the old ones. The properties and energy of the new, hybridized orbital are an 'average' of the original unhybridized orbitals.

Types of hybridization

sp³ hybridization:

sp³ hybridization can explain the tetrahedral structure of molecules.

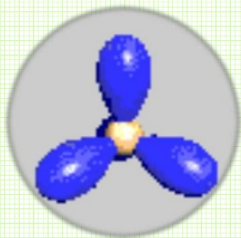


In it, the 2s orbitals and all three of the 2p orbitals hybridize to form four sp orbitals, each consisting of 75% p character and 25% s character.

The frontal lobes align themselves in the manner shown.

In this structure, electron repulsion is minimized.

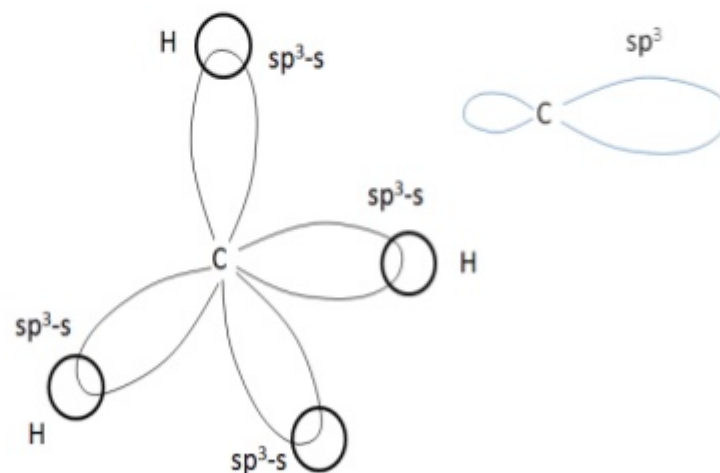
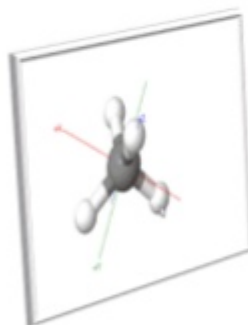
sp^3 Hybridization



A.K.Gupta, PGT Chemistry, KVS
ZIET BBSR

Bonding in Methane (CH_4)

Bonding in Methane : Carbon uses sp^3 hybridized orbital to form 4 covalent bond with hydrogen in methane.



A.K.Gupta, PGT Chemistry, KVS
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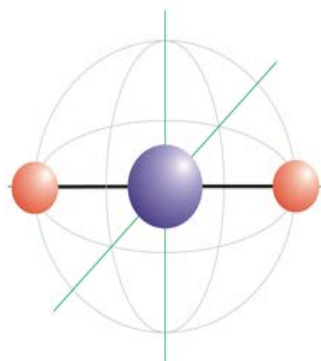
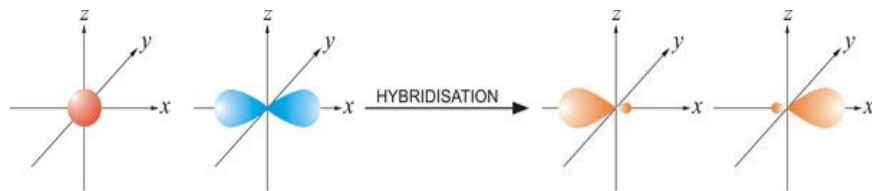
Summary

- sp^3 hybridization occurs when a C has 4 attached groups
- sp^3 hybrid orbital has 25% s and 75% p character
- the 4 sp^3 hybrids point towards the corners of a tetrahedron at 109.28° to each other
- each sp^3 hybrid orbital is involved in σ bond formation.

Types of hybridization

sp² hybridization:

sp² hybridization can explain the trigonal planar structure of molecules.

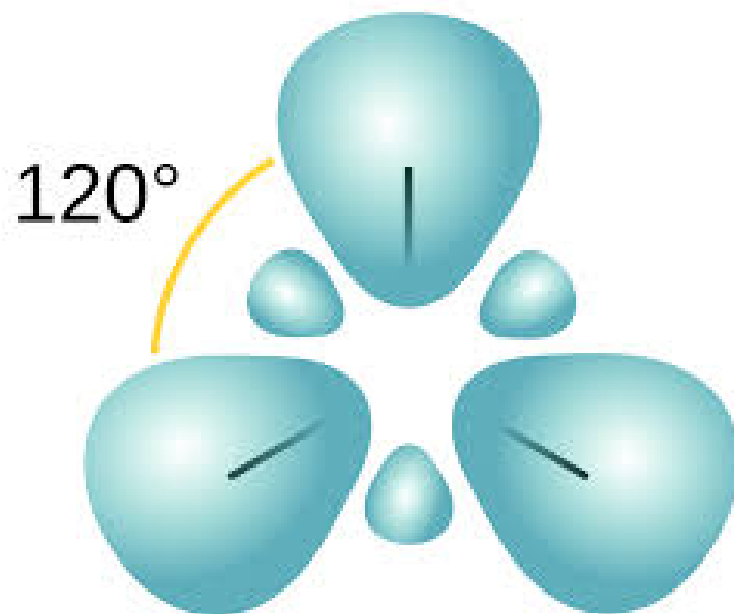
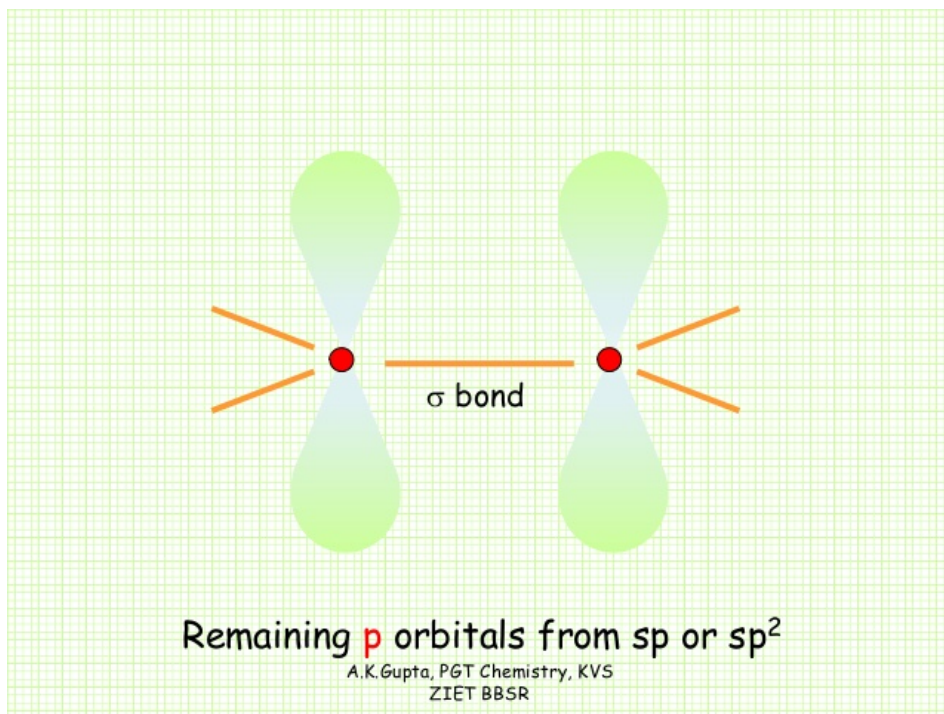


In it, the 2s orbitals and two of the 2p orbitals hybridize to form three sp orbitals, each consisting of 67% p and 33% s character.

The frontal lobes align themselves in the trigonal planar structure, pointing to the corners of a triangle in order to minimize electron repulsion and to improve overlap. The remaining p orbital remains unchanged and is perpendicular to the plane of the three sp² orbitals.

sp² hybridization:

Hybridization of an s orbital with two p orbitals (p_x and p_y) results in three sp² hybrid orbitals that are oriented at 120° angle to each other. sp² hybridization results in trigonal geometry.

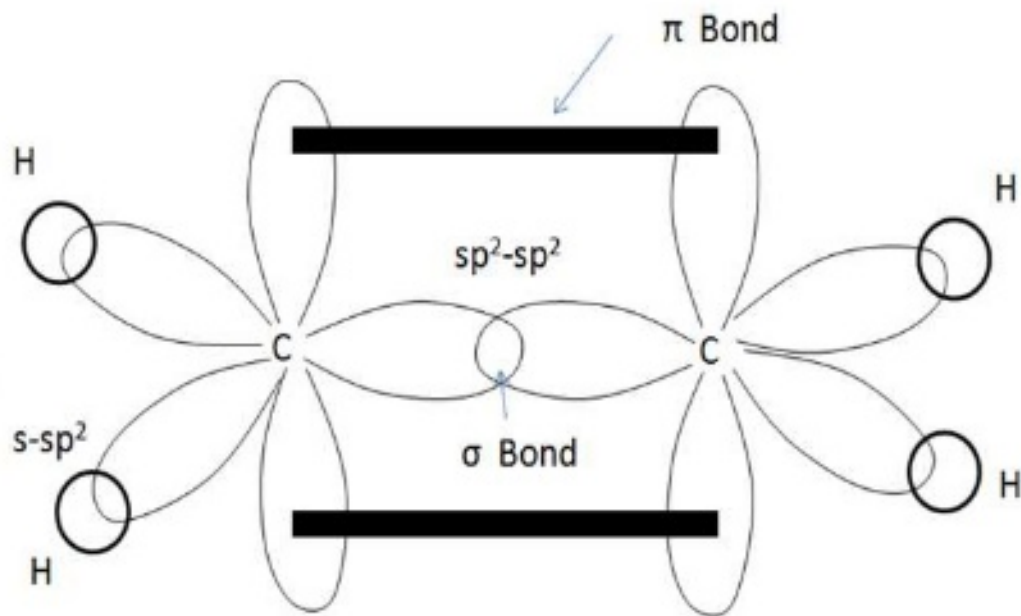
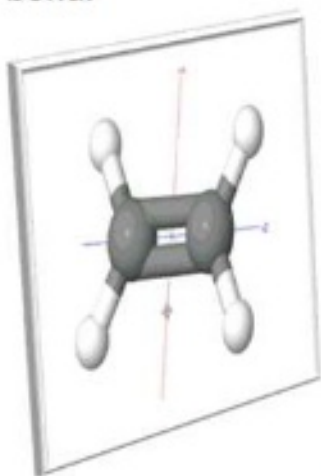


Summary

- sp^2 hybridization occurs when a C has 3 attached groups
- sp^2 hybrid orbital has 33% s and 67% p character
- the 3 sp^2 hybrids point towards the corners of a triangle at 120° to each other
- each sp^2 hybrid orbital is involved in a σ bond formation and the remaining p orbital forms the π bond
- a double bond as a $\sigma + \pi$ bond

Bonding in Ethene ($\text{H}_2\text{C}=\text{CH}_2$)

Each carbon uses sp^2 hybridized orbital to form 2 sigma bonds with hydrogen and 1 sigma bond with other carbon. Pure p-orbital of C forms Pi bond.

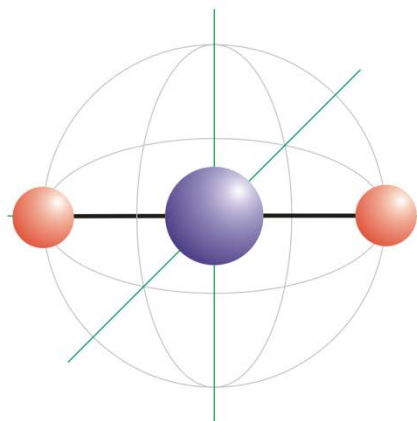
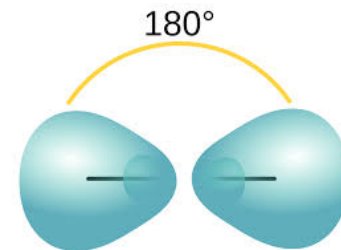
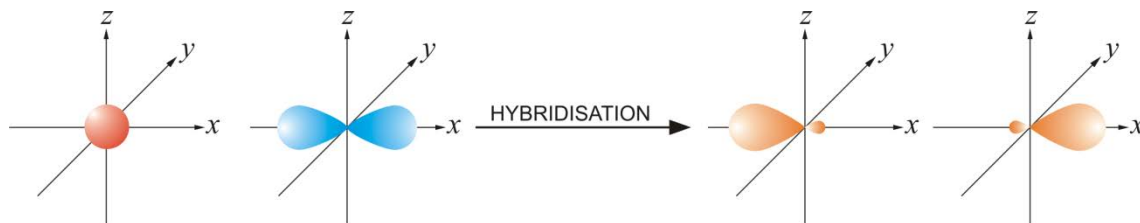


Types of hybridization

sp hybridization:

sp hybridization can explain the linear structure of molecules.

In it, the 2s orbital and one of the 2p orbitals hybridize to form two sp orbitals, each consisting of 50% s and 50% p character. The front lobes face away from each other and form a straight line leaving a 180° angle between the two orbitals. This formation minimizes electron repulsion.





Because only one p orbital was used, two unaltered 2p orbitals are left, that the atom can use. These p orbitals are at right angles to one another and to the line formed by the two sp orbitals.

Summary

- sp hybridization occurs when a C has 2 attached groups
- sp hybrid orbital has 50% s and 50% p character
- the 2 sp hybrids are oriented at an angle of 180° to each other
- each sp hybrid orbital is involved in a σ bond formation and the remaining two p orbitals form two π bonds
- a triple bond = one σ + two π bonds

Bond formation from hybridization

- Single bond
- sigma bond  end-to-end
- Double bond
- sigma bond + pi bond  side-to-side
- Triple bond
- sigma bond + pi bond + pi bond

How are the two pi bonds in the triple bond oriented?