

IX. Molecular Structure and Chemical Bonding

G. N. Lewis' *Octet Rule*

In stable compounds each atom is isoelectronic with a **Noble gas** atom.

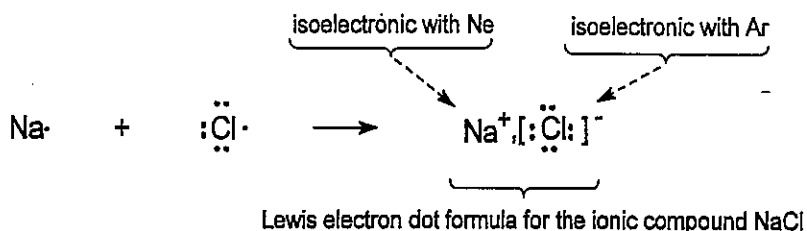
Isoelectronic means the same number of electrons.

Lewis Symbols are the chemical symbol for the element plus dots that represent the **valence electrons**.

Example:



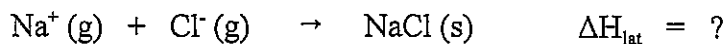
A) Ionic Bond



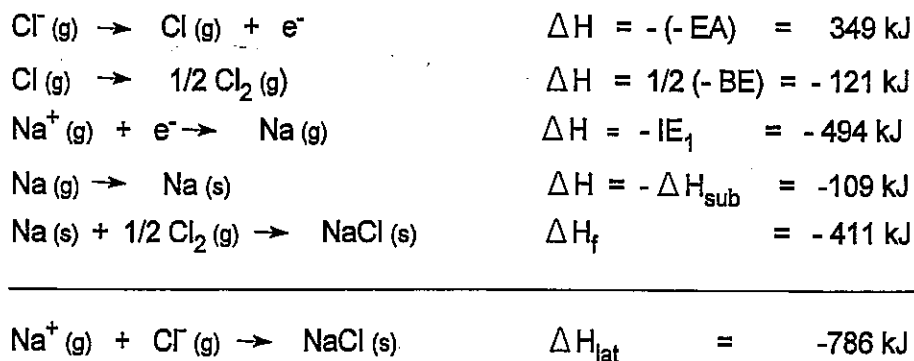
The transfer of electrons from one atom to another results in an *ionic bond*.

Electron transfer that results in an ionic bond is more likely to occur when an atom with a low ionization energy reacts with an atom that has a large electron affinity.

How much energy is released when the gaseous ions Na^+ and Cl^- form the ionic solid NaCl?

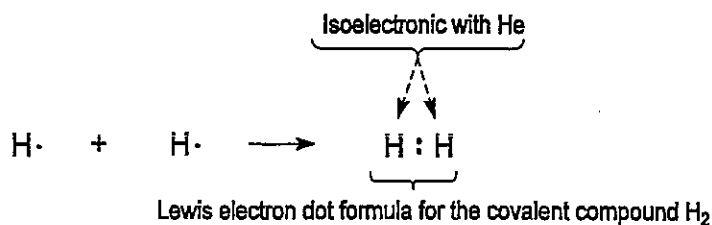


where ΔH_{lat} is called the *lattice energy*.



where EA is the electron affinity for Cl (g), BE is the bond energy for the Cl-Cl bond, IE_1 is the first ionization for Na (g), and ΔH_{sub} is the enthalpy of sublimation.

B) Covalent Bond



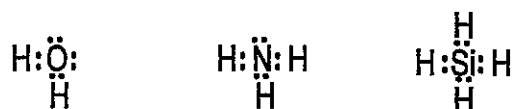
The sharing of an electron pair results in a *covalent bond*.

The *covalency* of an atom is the number of covalent bonds formed by the atom.

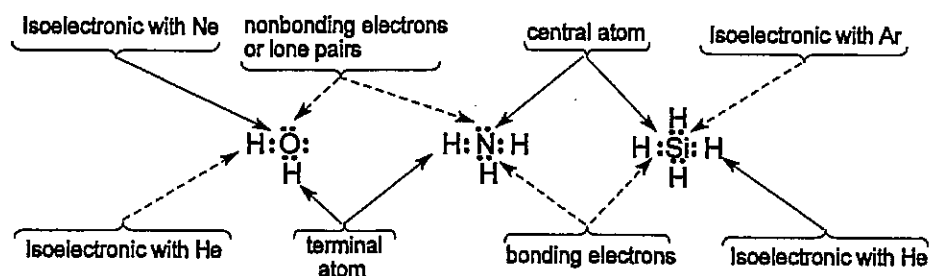
| Element | Common Covalency |
|--------------|------------------|
| H | 1 |
| F, Cl, Br, I | 1 |
| O, S, Se | 2 |
| N, P, As | 3 |
| C, Si, Ge | 4 |

The underlined elements may have other covalencies.

Example: Illustrations of Lewis Electron Dot Formula and Common Covalency



Note: Each atom in the formulas satisfies the octet rule. Shared electron pairs (bonding electrons) are considered to belong to both atoms and are counted in the determination of the number of valence electrons around each atom sharing the pair of electrons.



Note: The sum of the bonding and nonbonding electrons in a Lewis electron dot formula is equal to the sum of the valence electrons for each atom in the formula.

Example: H₂O

$$\frac{[\text{Total number of bonding electrons} + \text{Total number of nonbonding electrons}]}{[\text{Total number of valence electrons}]} =$$

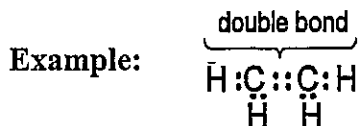
$$[4_{\text{bonding electrons}} + 4_{\text{nonbonding electrons}}] = [6_{\text{O}} + 2(1_{\text{H}})] = 8$$

A *central atom* is any atom bonded to two or more other atoms. A *terminal atom* is any atom bonded to one and only one other atom.

C) Multiple Bonds

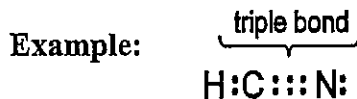
Multiple bonds result from the sharing of more than one pair of electrons by two atoms.

The sharing of two pairs of electrons results in a *double bond*.



Note: Each atom satisfies the octet rule and is consistent with the common covalency of the element.

The sharing of three pairs of electrons results in a *triple bond*.



Generally, only elements in the second period and sulfur form multiple bonds and maintain an octet of electrons.

Procedure #1: Method for the Determination of Lewis Electron Dot Formula for Covalent Compounds

When the central atom is in the second period or sulfur and obeys the octet rule,

- Determine the number of bonding electrons,

$$\text{Number of bonding electrons} =$$

$$\sum_i^{\text{all atoms}} (\text{octet of electrons})_i - \sum_i^{\text{all atoms}} (\text{valence electrons})_i$$

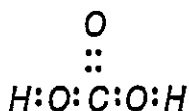
- Distribute the bonding electrons among the various bonded atoms using common covalency as a guide,

- And place the remaining valence electrons [$\sum_i^{\text{all atoms}} (\text{valence electrons})_i - \text{number of bonding electrons}$] around the atoms so that each satisfies the octet rule.

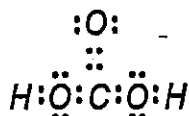
Example: Write the Lewis electron dot formula for carbonic acid, $\text{OC}(\text{OH})_2$.

In these notes the formula $\text{OC}(\text{OH})_2$ indicates that the atoms are arranged in the following sequence $\overset{\text{O}}{\text{HOCO}}\text{H}$.

$$\begin{aligned} \text{Number of bonding electrons} &= \\ \sum_i^{\text{all atoms}} (\text{octet of electrons})_i - \sum_i^{\text{all atoms}} (\text{valence electrons})_i &= \\ [8_{\text{C}} + 3(8_{\text{O}}) + 2(2_{\text{H}})] - [4_{\text{C}} + 3(6_{\text{O}}) + 2(1_{\text{H}})] &= \\ 36 \text{ electrons} - 24 \text{ electrons} &= 12 \text{ bonding electrons} \end{aligned}$$

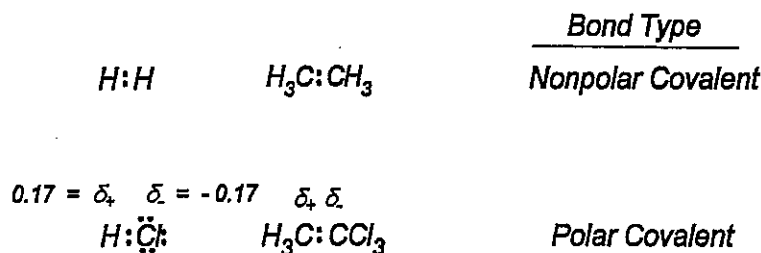


- Number of remaining electrons = total number of valence electrons - number of bonding electrons = $24 - 12 = 12$ electrons



D) Polar Covalent Bonds, Electronegativity, and Oxidation Numbers

1) Polar Covalent Bonds



The fractional charge, δ , is the charge that results from the unequal sharing of electrons. In heteronuclear bonds one of the bonding atoms attracts the bonding pair of electrons more strongly than the other bonding atom. The numeric value of δ is the fraction of the charge ($4.80 \cdot 10^{-10}$ esu) on an electron.

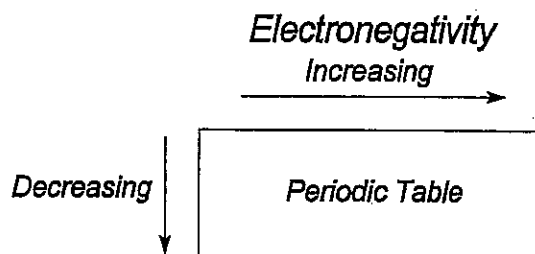
The unequal sharing of an electron pair results in a *polar covalent bond*.

| <i>Bond Type</i> | | | | |
|-----------------------------------|-----------------|--|----------------|-----------------------|
| <i>Increasing Bond Polarity</i> → | | | | |
| <i>Type</i> | <i>Nonpolar</i> | <i>Polar Covalent</i> | | <i>Ionic</i> |
| <i>Example</i> | $H:H$ | $\begin{array}{c} H \\ \\ H:C:H \\ \\ H \end{array}$ | $H:\ddot{O}:H$ | $Na^+ [:\ddot{O}:]^-$ |
| δ | 0 | 0.07 | 0.17 | 1.00 |
| $\Delta\chi = \chi_B - \chi_A$ | 0 | 0.30 | 0.74 | 2.21 |

2) Electronegativity

Electronegativity, χ , is a measure of the relative tendency of a bonded atom to attract electrons.

The electronegativity of an atom is not experimentally measured but calculated from bond energies, ionization energies, and electron affinities.



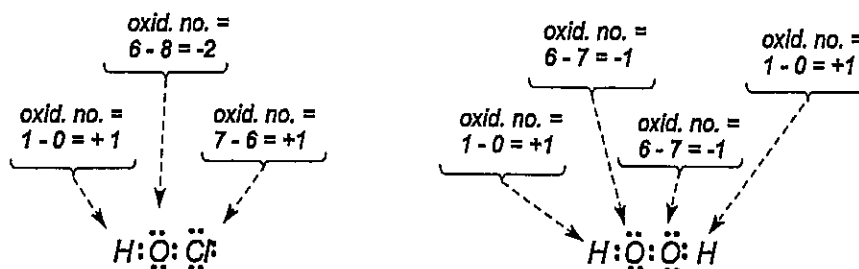
A Rough Approximation of Bond Type for AB Based on $\Delta\chi$

| $\Delta\chi = \chi_B - \chi_A$ | <i>Bond Type</i> |
|--------------------------------|-------------------|
| ≥ 1.7 | Ionic |
| < 1.7 | Polar Covalent |
| 0 | Nonpolar Covalent |

3) Oxidation Number

The oxidation number (oxid. no.) of an atom is the number of valence electrons on the neutral atom **minus** the number of valence electrons **assigned** to the atom in the compound *on the basis that the bonding electrons belong to the more electronegative atom.*

Example:

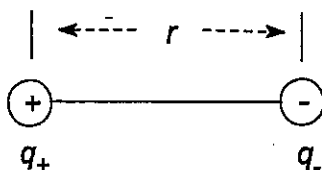


Bonding electrons are equally divided between atoms of the same element.

E) Dipole Moments and Polarity

1) Bond Dipole

An electric *dipole* is a positive charge, q_+ , and a negative charge, q_- , of equal magnitude that are separated by a distance, r .



The *dipole moment*, μ , is

$$\mu = qr$$

where q is the magnitude of the charge in esu (electrostatic units) and r is the distance between the positive and negative charges in centimeters.

A polar covalent bond is a dipole and has a dipole moment.

Example: Calculate the dipole moment, μ_{HCl} , for HCl. The magnitude of the fractional charge, δ , is 0.17 and the bond distance, r_{HCl} , is 1.27 Å.

$$q = \delta(4.80 \cdot 10^{-10} \text{ esu}) = (0.17)(4.80 \cdot 10^{-10} \text{ esu}) = 8.16 \cdot 10^{-11} \text{ esu}$$

$$\mu_{\text{HCl}} = qr = (8.16 \cdot 10^{-11} \text{ esu})(1.27 \text{ \AA})(1 \cdot 10^{-8} \frac{\text{cm}}{\text{\AA}}) = 1.03 \cdot 10^{-18} \text{ esu-cm}$$

$$1D = 1 \text{ Debye} = 1 \cdot 10^{-18} \text{ esu-cm}$$

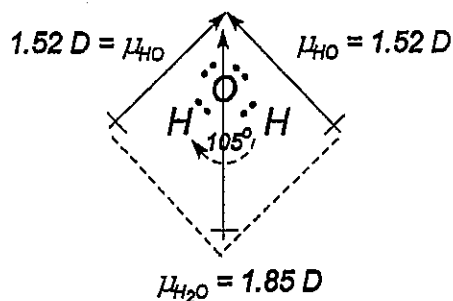
$$\mu_{\text{HCl}} = (1.03 \cdot 10^{-18} \text{ esu-cm}) \left(\frac{1D}{10^{-18} \text{ esu-cm}} \right) = 1.03 D$$

The magnitude and direction of the dipole moment is represented by the vector, \longleftrightarrow .

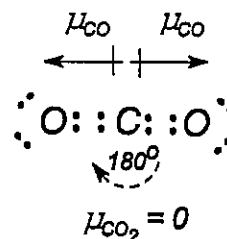
2) Molecular Dipole

The dipole moment for a molecule is the resultant dipole moment obtained from the vector sum of the individual bond dipole moments. Molecules that have a dipole moment are said to be *polar*. Molecules with $\mu = 0$ are said to be *nonpolar*.

Example:




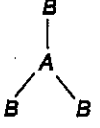
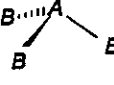
H₂O is a polar molecule.

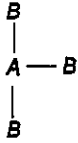
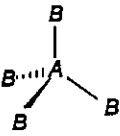
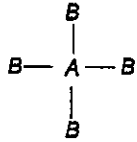

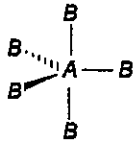
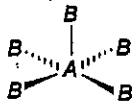
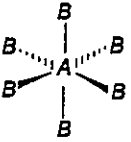


CO₂ is a nonpolar molecule.

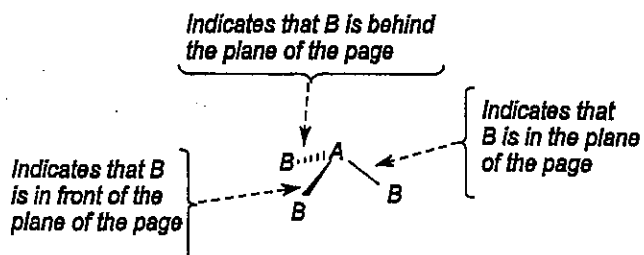
Note: The **polarity** of a molecule depends on the **bond dipole moments** and **molecular geometry**.

Molecular Geometries and Polarities

| Formula | Molecular Geometry | Polarity ^a | Example (Exception) |
|-----------------|--|-----------------------|---------------------------------------|
| AB | linear $A-B$ | polar | HCl |
| AB ₂ | linear $B-A-B$ | nonpolar | CO ₂ (HCN) |
| AB ₂ | bent  | polar | H ₂ O |
| AB ₃ | trigonal planar  | nonpolar | BF ₃ (BBrCl ₂) |
| AB ₃ | trigonal pyramidal  | polar | NH ₃ |

| | | | | |
|--------|-----------------------|--|----------|-----------------------|
| AB_3 | T-shaped |  | polar | ClF_3 |
| AB_4 | tetrahedral |  | nonpolar | CH_4 (CCl_4) |
| AB_4 | square planar |  | nonpolar | XeF_4 |
| AB_4 | distorted tetrahedral |  | polar | SF_4 |
| AB_5 | trigonal bipyramidal |  | nonpolar | PF_5 (F_3PCl_2) |
| AB_5 | square pyramidal |  | polar | BrF_5 |
| AB_6 | octahedral |  | nonpolar | SF_6 |

^a Valid when the bonds are covalent, $\chi_B \neq \chi_A$, and all AB bonds in the nonpolar cases are identical in all respects, i.e. the same bond energies and bond lengths.

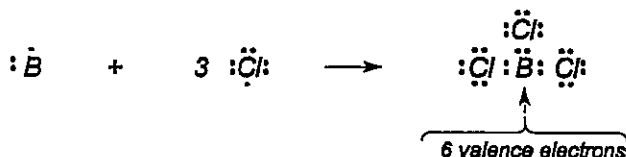


F) Exceptions to the Octet Rule

1) Less than an Octet of Electrons

Atoms that have less than four valence electrons and form covalent bonds may not satisfy the octet rule.

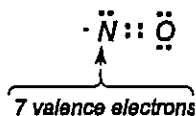
Example: BCl_3



2) Free Radicals

Free radicals are compounds with one or more unpaired electrons.

Example: NO



3) More than an Octet of Electrons

Example: PF_5

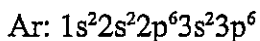
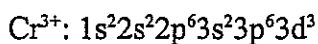


The phosphorus atom in PF_5 has ten valence electrons.

Atoms in the second period never exceed on octet of electrons.

4) Ions of the Transition and Post-Transition Metals

Example: Cr^{3+} is not isoelectronic with Ar.

5) **Procedure #2:** Method for the Determination of Lewis Electron Dot Formula for Covalent Compounds

When the central atom is in the third, fourth, etc. period, determine the total number of valence electrons and distribute them as follows.

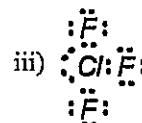
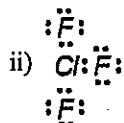
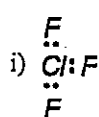
i) *Place two electrons between each bonding pair of atoms.*

ii) Place sufficient electrons around each *terminal atom* so that the terminal atoms satisfy the octet rule.

iii) Assign the remaining valence electrons to the *central atom*.

Example: ClF_3

$$\text{Total number of valence electrons} = 7_{\text{Cl}} + 3(7_{\text{F}}) = 28 \text{ valence electrons}$$



Twenty four of the twenty eight valence electrons are displayed in ii. Four valence electrons remain and these electrons are assigned to the central atom in iii.

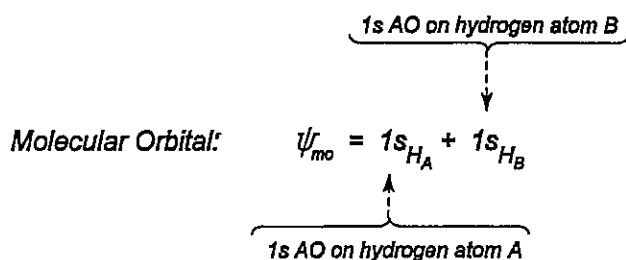
G) Molecular Orbital Theory

The energy of an electron, described by ψ_{mo} , in a molecule is calculated by substituting ψ_{mo} into the Schrödinger wave equation.

The wavefunction, ψ_{mo} , is called a *molecular orbital* and is the linear combination of atomic orbitals.

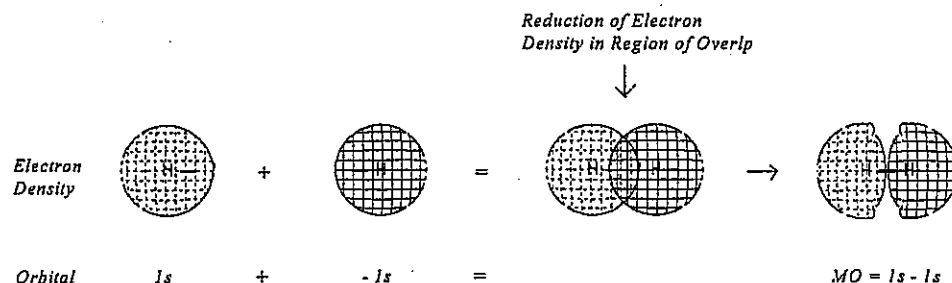
1) Bonding Molecular Orbital

Consider the hydrogen molecule $H_A : H_B$



$$\text{Electron Density: } (\psi_{\text{mo}})^2 = (1s_{H_A})^2 + 2(1s_{H_A})(1s_{H_B}) + (1s_{H_B})^2$$

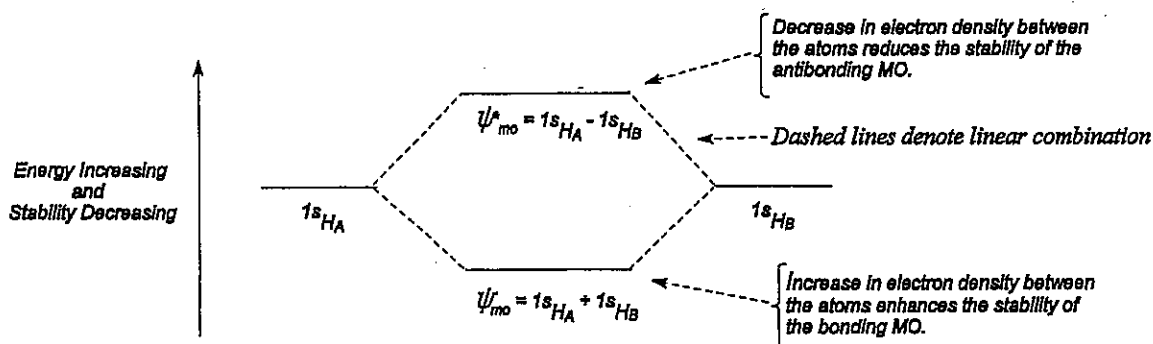
Boundary surfaces of the electron density clouds for the antibonding MO, ψ_{mo}^* , and the linearly combining 1s AOs.



The change from solid cross-hatching to dashed cross-hatching on the boundary surfaces indicates an algebraic sign change in the wave function, ψ .

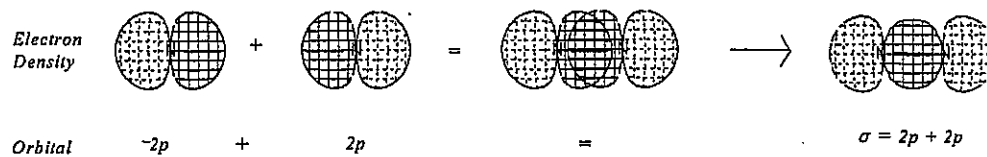
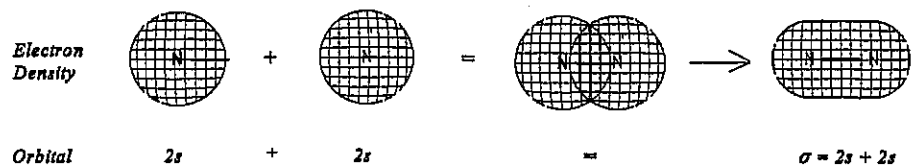
Conservation of Orbitals: The number of MOs equals the number of linearly combining orbitals.

Relative Orbital Energy Level Diagram for H_2
Illustrates the relative energies of the MOs and linearly combining AOs.



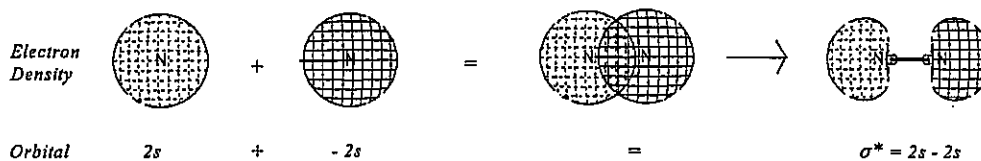
3) Types of MOs: Sigma and Pi

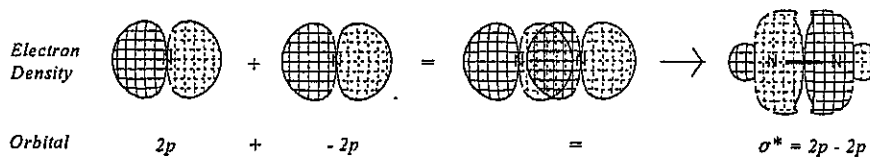
a) Sigma (σ) Bonding MOs



The *head-to-head* overlap of AOs that results in an electron density increase between the bonding atoms is called a sigma (σ) bonding MO.

b) Sigma Star (σ^*) Antibonding MOs

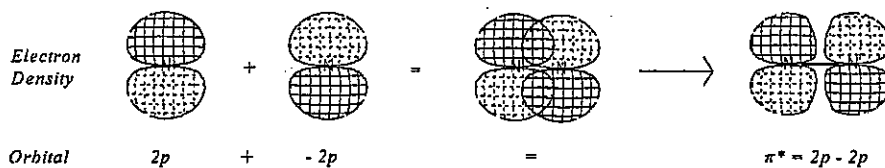
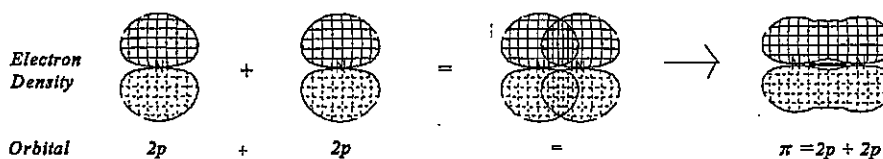




The *head-to-head* overlap of AOs that results in an electron density decrease between the bonding atoms is called a sigma star (σ^*) antibonding MO.

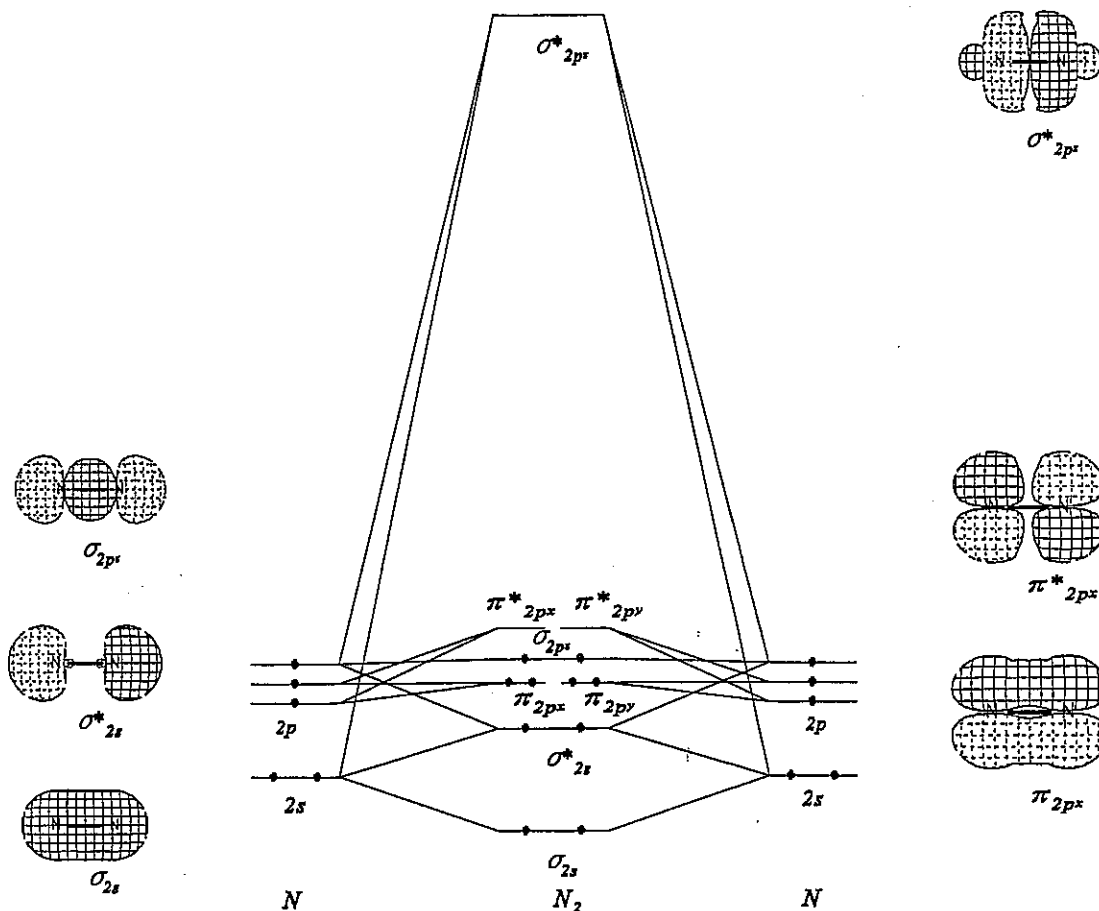
c) Pi (π) MOs

The *side-to-side* overlap of p type AOs results in a π MO.



H) Energy Level Diagram for Homonuclear Diatomic Molecules

Orbital Energy Level Diagram for N₂ and Boundary Surfaces of the Electron Density Clouds for the MOs



To determine the ground state electron configuration of a diatomic molecule, determine the total number of valence electrons and distribute the electrons as follows.

- Fill the most stable MO according to the Pauli principle.
- Fill the next most stable MO according to the Pauli principle.
- Continue in this fashion until all of the electrons have been distributed. Note: Hund's Rule applies.

In order for bonding to occur between the atoms, the *bond order* must be greater than zero.

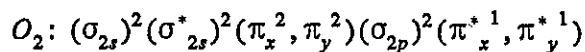
$$\text{Bond Order} = BO = \frac{(\text{Number of bonding electrons}) - (\text{Number of antibonding electrons})}{2}$$

I) Application of Molecular Orbital Theory to Diatomic Molecules

1) Homonuclear

Example: Write the electron configuration for O_2 .

Total number of valence electrons = $2(6_o) = 12$



$$BO = \frac{(\text{Number of bonding electrons}) - (\text{Number of antibonding electrons})}{2}$$

$$BO = \frac{(8) - (4)}{2} = 2 = \text{number of covalent bonds}$$

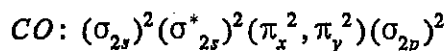
O_2 is paramagnetic. *Paramagnetism* is associated with substances that have unpaired electrons and are attracted to a magnetic field.

2) Heteronuclear

The orbital energy level diagram for heteronuclear diatomic molecules of second period elements is similar to the diagram for homonuclear diatomic molecules

Example: Write the electron configuration for CO.

Total number of valence electrons = $4_c + 6_o = 10$



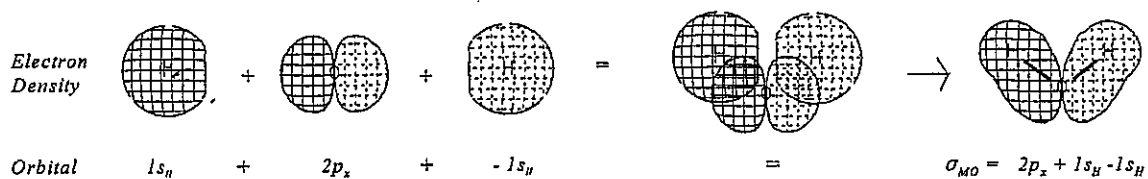
$$BO = \frac{(8) - (2)}{2} = 3 = \text{number of covalent bonds}$$

CO is diamagnetic. *Diamagnetism* is associated with substances that have no unpaired electrons. These substances are repelled by a magnetic field.

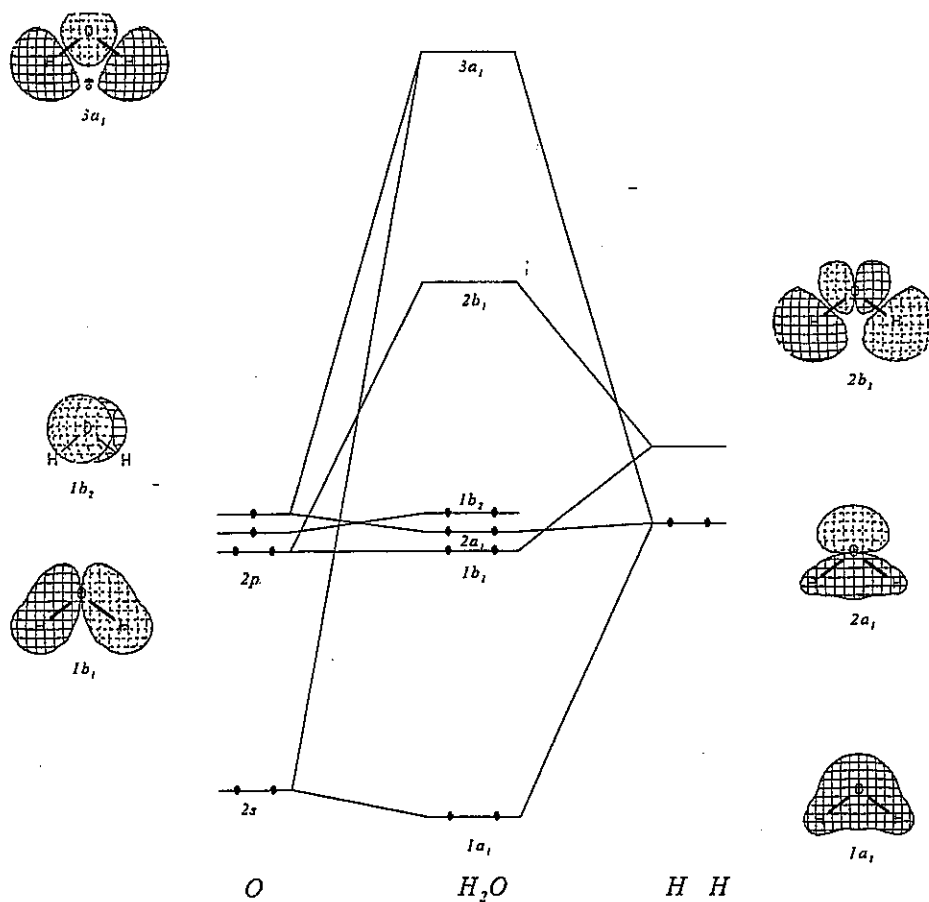
J) Application of Molecular Orbital Theory to Polyatomic Molecules

In Molecular Orbital theory the bonding in polyatomic molecules is described in terms of delocalized MOs. *Delocalized molecular orbitals* result from the linear combination of three or more AOs. The electron density clouds for delocalized MOs cover the entire molecule.

Example: H₂O



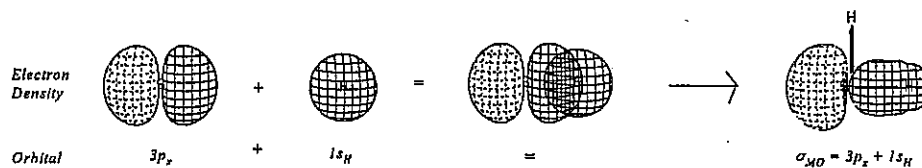
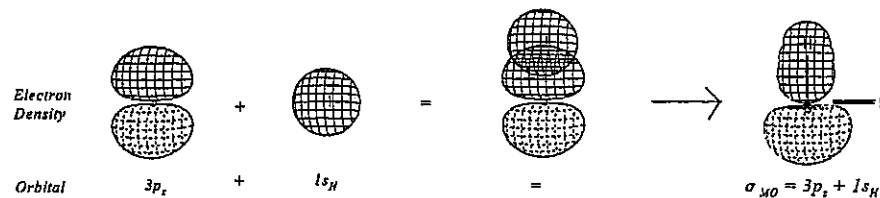
Orbital Energy Level Diagram for H₂O and Boundary Surfaces of the Electron Density Clouds for the Delocalized MOs



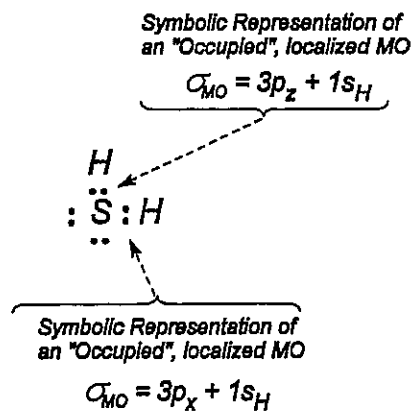
J) Valence Bond Theory and Hybridization

In Valence Bond theory the bonding in polyatomic molecules is described in terms of localized MOs. A *localized molecular orbital* is the linear combination of two and only two orbitals. The electron density cloud for a localized MO covers just two atoms in the molecule.

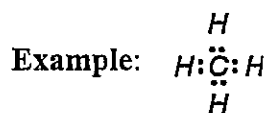
Example: SH₂



The bonding electrons are localized in a Lewis electron dot formula.



1) sp³ Hybridization

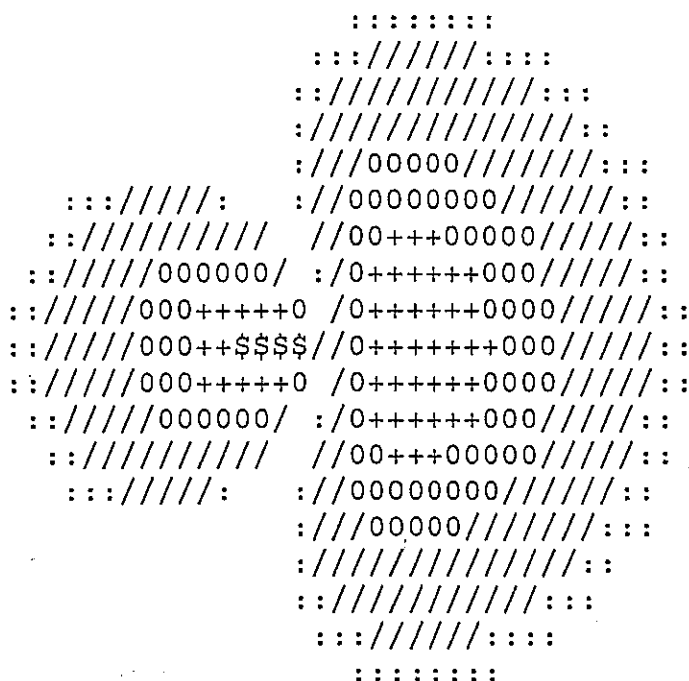


- All four C-H bonds are identical, i.e. bond energy = 415.5 kJ and bond length =

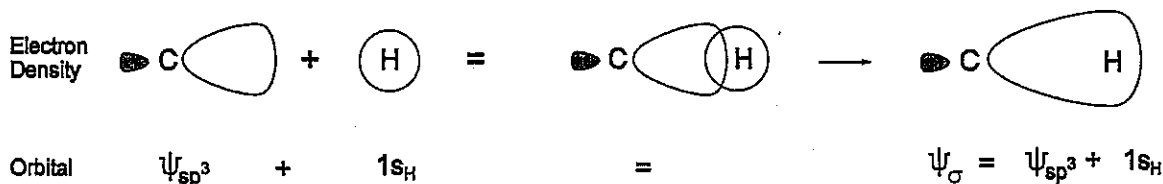
$$\begin{aligned}\psi_{sp^3}^{(1)} &= 0.5(2s + 2p_x + 2p_y + 2p_z) & \psi_{sp^3}^{(2)} &= 0.5(2s + 2p_x - 2p_y - 2p_z) \\ \psi_{sp^3}^{(3)} &= 0.5(2s - 2p_x + 2p_y - 2p_z) & \psi_{sp^3}^{(4)} &= 0.5(2s - 2p_x - 2p_y + 2p_z)\end{aligned}$$

The sp^3 nomenclature means that the sp^3 hybrid orbitals are formed from the linear combination of one s AO and three p AOs.

Contour plot for the ψ_{sp^3} hybrid orbital on C atom in CH_4



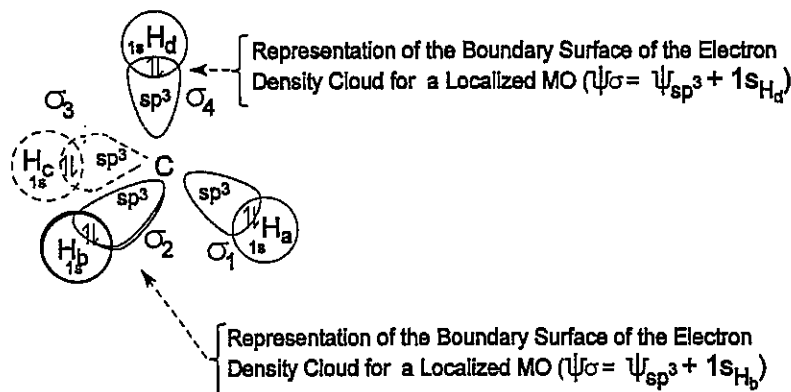
Outline of the boundary surfaces of the electron density clouds for a localized MO and the linearly combining orbitals



The molecule assumes a geometry in which the bond angles are maximized in order to minimize the repulsion between centers of high electron density. A tetrahedral geometry gives the largest bond angles for CH_4 .

An *orbital representation* is an outline of the boundary surfaces of the electron density clouds for bonding MOs. The electron density clouds for the MOs are represented by the overlap of the electron density clouds for the linearly combining orbitals

Orbital representation for CH₄

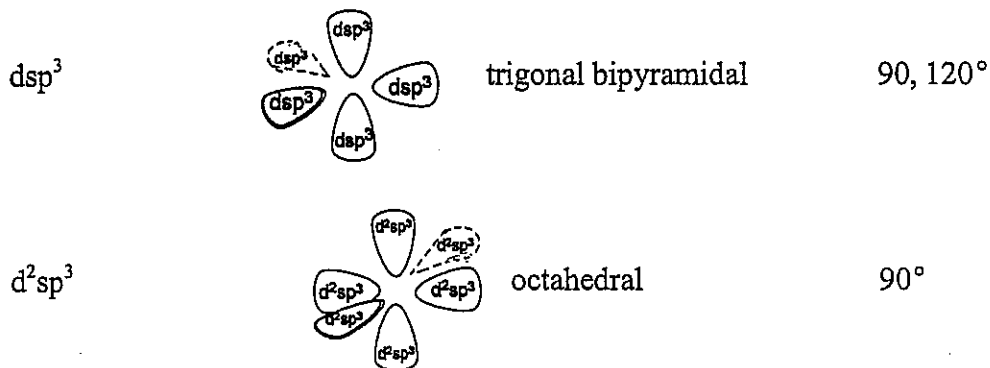


Note: The smaller lobes of the electron density clouds for the hybrid orbitals have been omitted for clarity.

2) Types of Hybridization

Types and Characteristics of Hybrid Orbitals

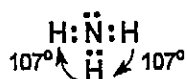
| Type | Geometric Arrangement of the Hybrid Orbitals | Angle between Hybrid Orbitals |
|------------------|--|-------------------------------|
| sp | linear | 180° |
| sp ² | trigonal planar | 120° |
| sp ³ | tetrahedral | 109° |
| dsp ² | square planar | 90° |



Note: The hybrid orbital label indicates the AOs that are linearly combined, e.g. d^2sp^3 means that two d AOs, one s AO, and three p AOs are linearly combined to form six new d^2sp^3 hybrid orbitals.

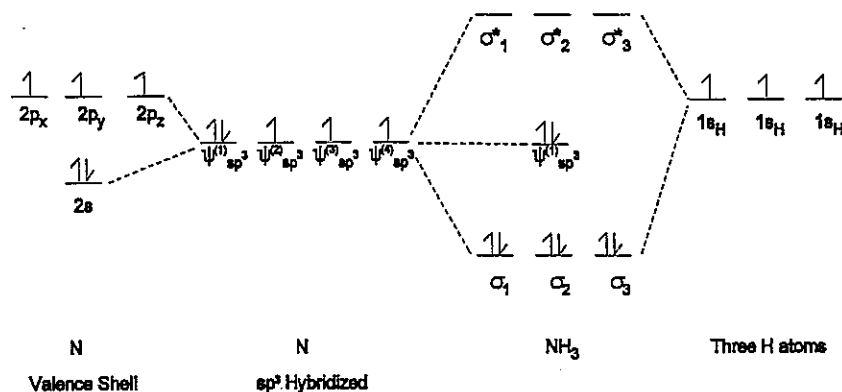
3) Application

Example: Draw an orbital representation of the bonding MOs for NH_3 . All H-N-H angle are 107° .

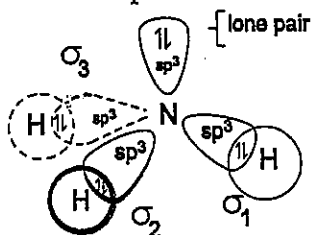


Since the H-N-H angles are 107° , we need hybrid orbitals on the nitrogen atom that are at angles of 107° in order to construct localized bonding MOs between the nitrogen and hydrogen atoms. We will use sp^3 hybridization. The angle of 109° is near in magnitude to the angle of 107° .

Relative Orbital Energy Level Diagram for NH_3



Orbital Representation

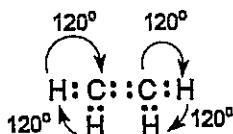


What is the molecular geometry of NH_3 ?

K) Multiple Bonded Molecules

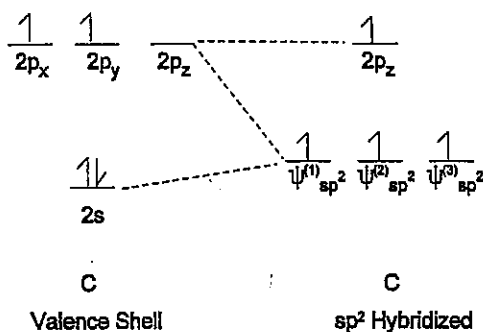
No more than one bonding MO between *two atoms* can be a sigma (σ) bonding MO and all additional bonding MOs must be pi (π) bonding MOs.

Example: Draw an orbital representation of the bonding in ethylene, H_2CCH_2 . All H-C-C and H-C-H angles are 120° .

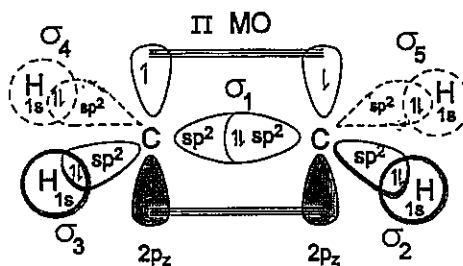


Three hybrid orbitals that are directed from a carbon atom toward the neighboring hydrogen and carbon atoms are needed to construct the localized sigma MOs. What hybridization has three hybrid orbitals with angles of 120° ?

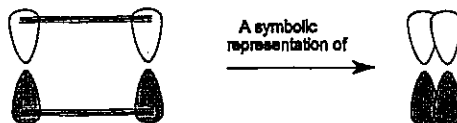
Relative Orbital Energy Level Diagram for Carbon



Orbital Representation



where



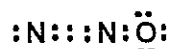
The second localized MO between the two carbon atoms is a π MO that results from the side-to-side overlap of the $2p_z$ AOs on the carbons.

L) Resonance and Delocalized π Molecular Orbitals

1) Resonance

Write the Lewis electron dot formula for NNO.

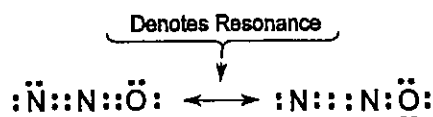
$$\text{number of bonding electrons} = [2(8_N) + 8_O] - [2(5_N) + 6_O] = 8$$



Both Lewis electron dot formulas are consistent with the octet rule. Which formula then correctly describes the bonding in NNO? To answer this question, we will compare the experimental bond lengths with the average bond lengths for $\text{N}\equiv\text{N}$, $\text{N}=\text{N}$, $\text{N}=\text{O}$, and $\text{N}-\text{O}$.

| | | |
|---|--|--|
| | $:\ddot{\text{N}}::\text{N}::\ddot{\text{O}}:$ | $:\text{N}:::\text{N}::\ddot{\text{O}}:$ |
| Experimental | 1.126 1.186 | 1.126 1.186 Å |
| Average Bond Length for a Specific Bond Order | 1.25 1.21 | 1.10 1.40 Å |

Neither formula accurately describes the bonding in NNO. In situations such as NNO two or more Lewis electron dot formulas are required to express a true picture of the bonding. These formulas are called *resonance structures*. The concept that two or more formulas are needed to describe the bonding in a molecule is called *resonance*.



Interpretation: The N-N bond order in NNO is not three or two but something in between those values. The N-O bond order is not one or two but a value somewhere in between one and two.

Rules for Writing Resonance Structures

- i) The relative positions of all the atoms must be the same for each resonance structure.

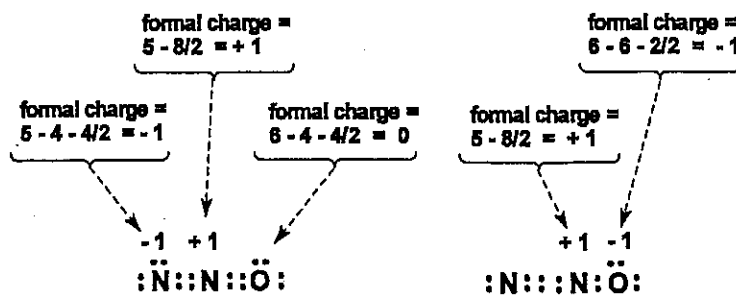
Example: $:\ddot{\text{N}}::\text{O}::\ddot{\text{N}}:$ is not a valid resonance structure for NNO.

- ii) The number of paired and unpaired electrons must be the same in each resonance structure.

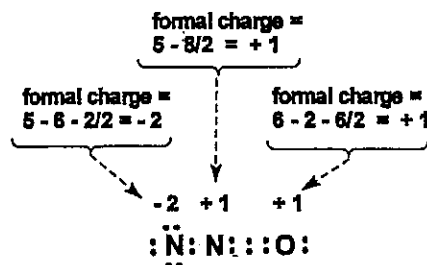
- iii) The *formal charges* on neighboring atoms should not have the same signs, formal charges of opposite signs should not be greatly separated, nonzero formal charges should be minimized, and a positive formal charge should not reside on the most electronegative atom nor should a negative formal charge reside on the most electropositive atom.

$$\text{formal charge on an atom} = \left(\text{number of valence electrons on the isolated atom} \right) - \left(\text{number of nonbonding electrons on the atom} \right) - \left(\frac{\text{number of bonding electrons on the atom}}{2} \right)$$

Example:

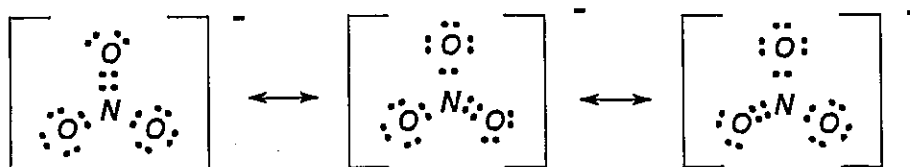


Why is $:\ddot{\text{N}}:\text{N}::\ddot{\text{O}}:$ not a valid resonance structure for NNO?



Example: Draw the resonance structures for the nitrate ion, NO_3^- . All three N-O bond lengths are 1.22\AA .

$$\text{number of bonding electrons} = [8_{\text{N}} + 3(8_{\text{O}})] - [5_{\text{N}} + 3(6_{\text{O}}) + 1] = 8 \text{ bonding electrons}$$



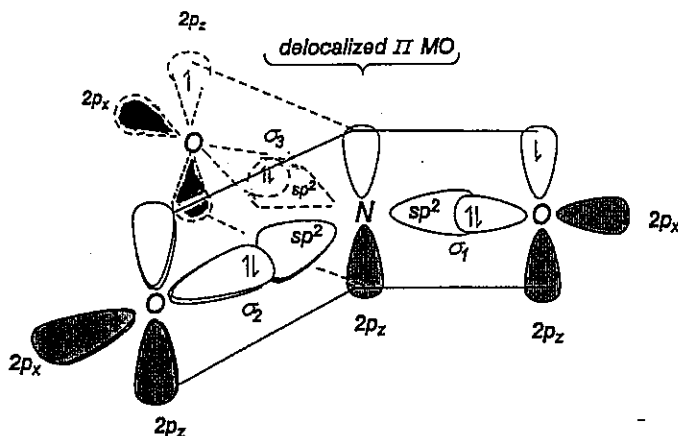
2) Delocalized π Molecular Orbitals

Molecules that are described by resonance structures and have multiple bonds will have at least one delocalized π MO.

Example: Draw an orbital representation of the bonding in the nitrate ion, NO_3^- . All O-N-O bond angles are 120° .

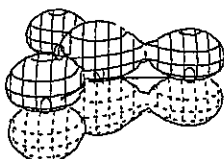
The N atom will be sp^2 hybridized.

Orbital Representation

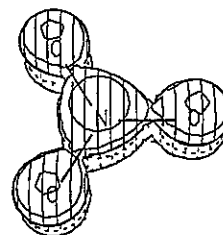


Side and Top View of the Boundary Surface of the Electron Density Cloud for the Delocalized π MO on the Nitrate Ion

Side View



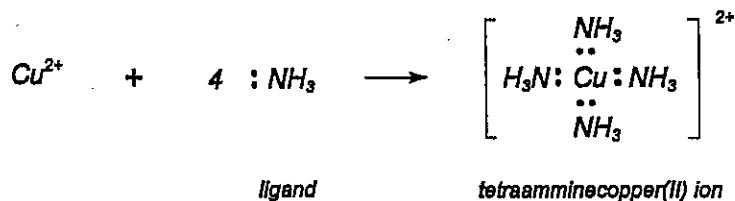
Top View



M) Coordination Compounds

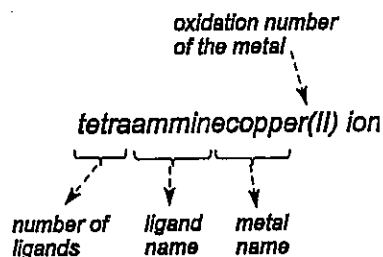
A coordination compound or complex ion is a compound or ion that contains several electron pair donor species, called *ligands*, bonded to a central transition metal atom or ion. Both electrons in the bond between the ligand and the metal are donated by the ligand. This bond is called a *coordinate covalent bond*.

Example: $\text{Cu}(\text{NH}_3)_4^{2+}$



The number of ligands bonded to the metal is called the *coordination number* of the metal. Coordination numbers from 1 to 9 are known, but 4 and 6 are the most common.

Nomenclature:



N) Determination of Molecular Structure

- Procedure: Drago, R. S. *J. Chem. Educ.* 1973, 50, 244.

- 1) Draw the Lewis electron dot formula and determine the sigma and pi bonds. Note: **The pi electrons do not count as "groups" or lone pairs in the following scheme.**

A "group" is a single atom or a substituent (a collection of atoms) attached to the **central atom**. A lone pair of electrons may count as a "group" in certain cases.

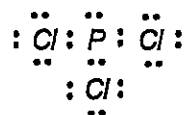
- 2) When there are *no* lone pairs of electrons on the **central atom**, the type of hybridization is determined by the number of "groups." *Each "group" needs one hybrid orbital on the central atom with which to connect.* The molecular geometry is the same as the geometric arrangement of the hybrid orbitals.
- 3) When there are lone pairs of electrons on the **central atom** and
 - i) There are *eight or less* electrons around the **central atom**, then the lone pair of electrons counts as a "group" if the **central atom** belongs to the second period or if the **central atom** belongs to the third, fourth, etc. period and the "groups" attached to the **central atom** are oxygen or halogen.

If the **central atom** belongs to the third, fourth, etc. period and the "groups" attached to the **central atom** are *less electronegative* than bromine (*generally all elements other than a halogen or oxygen*), then there is *no hybridization* on the **central atom**. The p AOs on the **central atom** are used as the "connectors."

- ii) There are *ten electrons* around the **central atom**, then the lone pairs count as "groups" and the hybridization on the **central atom** is dsp^3 . Note: *The most electronegative "groups" occupy the axial (apical) sites in the trigonal bipyramid.*

- iii) There are *twelve electrons* around the **central atom**, then the lone pairs count as “groups” and the hybridization on the **central atom** is d^2sp^3 .

Example: Draw an orbital representation of the bonding in PCl_3 . Clearly indicate which orbitals are overlapping, what hybridization takes place (if any), which molecular orbitals are sigma or pi MOs, and which orbitals are “occupied” by lone pairs (if any). Predict the bond angles, molecular geometry, and polarity of the molecule.



(See Flow Diagram in the *Study Guide for Chemistry 115*)

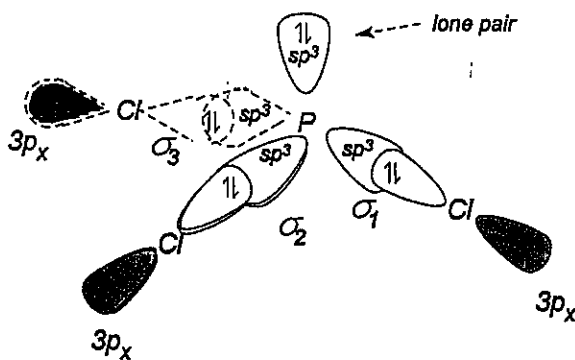
Lone pairs on the central atom? *Yes* Number of electrons around central atom? *8*

Is the central atom in the second period or bonded to oxygen or a halogen? *Yes*

The number of “groups” on the central atom = number of hybrid orbitals needed = ? *4*

Hybridization that provides 4 hybrid orbitals is ? sp^3

Orbital Representation



(Build a molecular model of PCl_3)

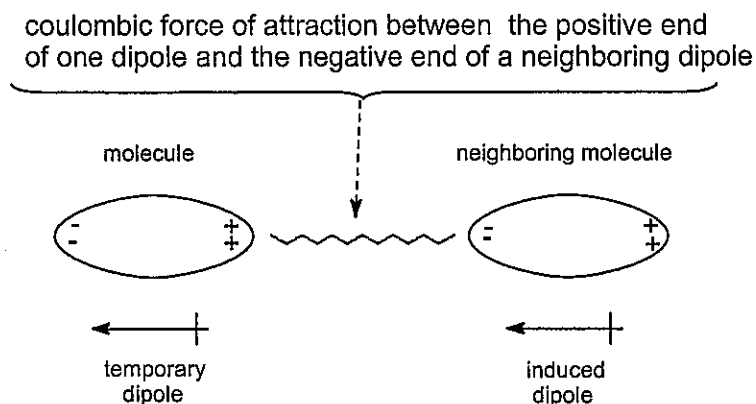
Cl-P-Cl bond angle = 109° , the molecular geometry is trigonal pyramid, and PCl_3 is a polar molecule.

O) Intermolecular Forces of Attraction

The forces of attraction between molecules are called *van der Waals forces*. The magnitude of these forces are reflected in the melting and boiling points.

1) London Force

The London Force is the coulombic force of attraction between molecules with temporary, fluctuating



The energy associated with the London force is

$$E = - \frac{2\bar{\mu}\alpha}{r^6}$$

where $\bar{\mu}$ is the average instantaneous dipole moment, r is the distance between the neighboring molecules, and α , called the polarizability, is a measure of the ease with which a dipole can be induced in a molecule.

The London force increases with an increase in the “size” (number of atoms and/or electrons) of the molecule and there is a corresponding increase in the melting and boiling points.

| Example: | <u>Compound</u> | <u>Boiling Point (°C)</u> |
|-----------------|-----------------|---------------------------|
| | Cl ₂ | - 34.6 |
| | Br ₂ | 58.8 |

2) Keeson Force

The Keeson force is the coulombic force of attraction between molecules with permanent dipoles.

The energy associated with the Keeson force is

$$E = - \frac{2\mu_1\mu_2}{r^3}$$

where μ_1 and μ_2 are the dipole moments for molecules 1 and 2 and r is the distance between molecules 1 and 2.

