Focus 2 MOLECULES

Topic 2A: IONIC BONDING

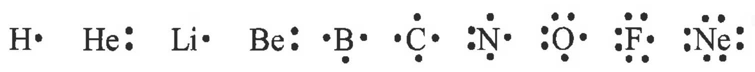
2A.1 The Ions That Elements Form

- **Cations**
  → Remove outermost electrons in the order np, ns, $(n-1)\mathrm{d}$
- **Metallic s-block elements and metallic p-block elements in Periods 2 and 3**
  → Form cations by losing electrons down to the noble-gas core
  Examples: Mg, $[\mathrm{Ne}]\,3s^2$ → magnesium(II), Mg^{2+}, [Ne];
  Al, $[\mathrm{Ne}]\,3s^2\,3p^1$ → aluminum(III), Al^{3+}, [Ne]
- **Metallic p-block elements in Periods 4 and higher**
  → Form cations with complete, typically unreactive d-subshells
  Example: Ga, $[\mathrm{Ar}]\,4s^2\,3d^{10}\,4p^1$ → gallium(III), Ga^{3+}, $[\mathrm{Ar}]\,3d^{10}$
- **Metallic d-block elements**
  → Lose s-electrons and often a variable number of d-electrons
  Examples: iron(II), Fe^{2+}, $[\mathrm{Ar}]\,3d^6$ and iron(III), Fe^{3+}, $[\mathrm{Ar}]\,3d^5$
- **Many metallic p-block elements**
  → May lose either their *p*-electrons or all their *s*- and *p*-electrons in the valence shell
  Example: Sn, $[\mathrm{Kr}]\,5s^2\,4d^{10}\,5p^2$ → tin(II), Sn^{2+}, $[\mathrm{Kr}]\,5s^2\,4d^{10}$ *or* tin(IV), Sn^{4+}, $[\mathrm{Kr}]\,4d^{10}$
- **Anions**
  → Add electrons until the next noble-gas configuration is reached.

Examples:	Carbide (methanide), C^{4-}, $[\mathrm{He}]\,2s^2 2p^6$ or [Ne]	{octet}
	Hydride, H^-, $1s^2$ or [He]	{duplet}

2A.2 Lewis Symbols (Atoms and Ions)

- **Valence electrons**
  → Depicted as dots; a pair of dots represents two paired electrons; single dots represent unpaired electrons
  → Lewis symbols for neutral atoms in the first two periods of the Periodic Table:



H· He: Li· Be: ·B· ·C· :N· :O· :F· :Ne:

Note: Ground-state structures for B and C are :B· and :C·. B and C have one and two unpaired electrons, respectively.

- **Variable valence**
  → Ability of an element to form two or more ions with different oxidation numbers

- → Displayed by many d-block and p-block elements

  Examples: Lead in lead(II) oxide, PbO, and in lead(IV) oxide, PbO_2

  Iron in iron(II) oxide, FeO, and in iron(III) oxide, Fe_2O_3

- → Lewis symbols for ions: use brackets where necessary to show charge is associated with an ion as a whole.

  Example: $Ca^{2+}, 2\,[:\!\ddot{\underset{\cdot\cdot}{Cl}}\!:]^-$

2A.3 The Energetics of Ionic Bond Formation

- **Ionic bond** → Electrostatic attraction (coulombic) of *oppositely* charged ions
- **Ionic model** → Energy for the *formation* of ionic bonds is supplied *mainly* by coulombic attraction of *oppositely* charged ions. This model gives a good description of bonding between the ions of metals (particularly *s*-block) and those of nonmetals.

- **Ionic solids and ionic crystals**
  - → Are assemblies of cations and anions arranged in regular arrays.
  - → The ionic bond is *nondirectional*; each ion is "bound" to *all* its neighbors.
  - → Typically have *high* melting and boiling points and are brittle, for example NaCl.
  - → Form electrolyte solutions if they dissolve in water.

- **Formulas of compounds composed of monatomic ions**
  - → Formulas are predicted by assuming that atoms forming cations lose all valence electrons and those forming anions gain electrons in the valence subshell(s) until each ion has an octet of electrons or a duplet in the case of H, He, and Be.
  - → For cations with variable valence, the oxidation number is used.

    Example: Iron(III) chloride, $FeCl_3$
  - → Relative numbers of cations and anions are chosen to achieve electrical neutrality, using the smallest possible integers as subscripts.

    Example: Iron(III) oxide, Fe_2O_3

2A.4 Interactions between Ions

- **In an ionic solid**
  - → All the cations repel each other, and all the anions repel each other.
  - → Each cation is attracted to all the anions to a greater or lesser extent.
  - → In this view, an ionic bond is a "global" characteristic of the entire crystal.

- **Coulomb potential energy between two ions, E_P**

$$\boxed{E_{P,12}=\frac{(z_1e)\times(z_2e)}{4\pi\varepsilon_0 r_{12}}=\frac{z_1z_2e^2}{4\pi\varepsilon_0 r_{12}}}$$

e is the fundamental charge; z_1 and z_2 are the charge numbers of the two ions; r_{12} is the distance between the centers of the ions; ε_0 is the vacuum permittivity.

- **Madelung constant (*A*) for a three-dimensional crystal lattice**

$$\boxed{E_P=-A\times\frac{|z_1z_2|N_Ae^2}{4\pi\varepsilon_0 d}}$$

A is a positive number; *d* is the distance between the centers of nearest neighbors in the crystal; N_A is the Avogadro constant (number of species per mol).

- → *A* depends on the *arrangement* of ions in the solid (Madelung constant).
- → E_P is always negative and *A* is positive.
- → Therefore, ionic crystals with **small ions** (short interionic distances), **large values of *A***, and **highly charged ions** tend to have large attractive energies.

- **Values of *A***
  - → 1.747 56 (NaCl structure) [d = 279.8 pm for NaCl (actual value near 0 K)]
  - → 1.762 67 (CsCl structure) [d = 348 pm for CsCl (sum of ionic radii)]
- **Lattice energy**
  - → Energy required to totally convert the solid-phase ions of the crystal into gas-phase ions infinitely far apart
- **Potential energy of an ionic solid (opposite sign = lattice energy)**
  - → Takes attractive and repulsive interionic interactions into account
  - → Is estimated by the **Born-Mayer** equation
- **Born-Mayer equation (Not Covered in Text)**

$$\boxed{E_{P,\min}=-\frac{N_A|z_Az_B|e^2}{4\pi\varepsilon_0 d}\left(1-\frac{d^*}{d}\right)A}$$

The constant d^* is commonly taken to be 34.5 pm. It results from the repulsive effects of overlapping electron charge clouds.

- **More accurate repulsive energy correction**

$E_P^* \propto e^{-d/d^*}$ where d^* is a constant (34.5 pm).

Topic 2B: COVALENT BONDING

2B.1 Lewis Structures

- **Covalent bond**
  - → Pairs of electrons *shared* between two atoms.
  - → Located between two neighboring atoms and *binds* them together.

    Examples: Nonmetallic elements such as H_2, N_2, O_2, F_2, Cl_2, Br_2, I_2, P_4, and S_8
- **Rules**
  - → Atoms attempt to complete duplets or octets by sharing pairs of valence electrons.
  - → Valence of an atom is the number of bonds it can form.
  - → A line (–) represents a shared pair of electrons.
  - → A lone pair of nonbonding electrons is represented by two dots (:).

    Example: H–H, (single bond) duplet on each atom (valence of hydrogen = 1) and :N≡N:, (triple bond and two lone pairs) octet on each atom (valence of nitrogen = 3)
- **Lone pairs of electrons**
  - → Electron pairs *not* involved in bonding.

    Example: The electrons indicated as dots in the Lewis structure of N_2 shown earlier.
- **Polyatomic species**
  - → Show which atoms are bonded (atom connectivity) and which contain lone pairs of electrons.
  - → Do not portray the *shape* of a molecule or ion.
- **Rules**
  - → Count total number of valence electrons in the species.
  - → Arrange atoms next to bonded neighbors.
  - → Use minimum number of electrons to make all single bonds.
  - → Count the number of nonbonding electrons required to satisfy octets.
  - → Compare to the actual number of electrons left.
  - → If lacking a sufficient number of electrons to satisfy octets, make *one extra bond* for each deficit pair of electrons.
  - → Sharing pairs of electrons with a neighbor completes the octet or duplet.
  - → Each shared pair of electrons counts as one *covalent bond* (line).

One shared pair	**single bond**	(–)	Bond order = 1
Two shared pairs	**double bond**	(=)	Bond order = 2 (multiple bond)
Three shared pairs	**triple bond**	(≡)	Bond order = 3 (multiple bond)

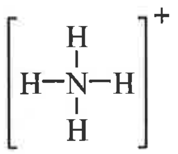
- **Bond order**
  - → Number of bonds that link a specific pair of atoms
- **Terminal atom**
  - → Bonded to only one other atom

- **Central atom**
  - → Bonded to at least two other atoms
- **Molecular ions**
  - → Contain *covalently* bonded atoms: NH_4^+, Hg_2^{2+}, SO_4^{2-}
- **Rules of thumb**
  - → Usually, the element with the lowest I_1 is a central atom, but *electronegativity* (introduced in **Topic 2D.1**) is a better indicator. For example, in HCN, carbon has the lowest I_1 and is the central atom. It is also less electronegative than nitrogen.
  - → Usually, there is a symmetrical arrangement about the central atom. For example, in SO_2, OSO is symmetrical, with S as the central atom and the two O atoms terminal.
  - → Oxoacids have H atoms bonded to O atoms; H_2SO_4 is actually $(HO)_2SO_2$, with two O atoms and two OH groups bonded to S.

    Examples: Ethyne (acetylene), C_2H_2 (10 valence electrons): H–C≡C–H

    Hydrogen cyanide, HCN (10 valence electrons): H–C≡N:

    Ammonium ion, NH_4^+ (8 valence electrons):



2B.2 Resonance

- **Multiple Lewis structures**
  - → Some molecules can be represented by different Lewis structures (*contributing structures*) in which the *locations* of the electrons, *but not the nuclei*, vary.
  - → Multiple Lewis structures used to represent a given species are called *resonance structures*.
- **Electron delocalization**
  - → Species requiring multiple Lewis structures often involve *electron delocalization* with some electron pairs distributed over *more* than two atoms.
- **Blending of structures**
  - → Double-headed arrows (⟷) are used to relate contributing Lewis structures, indicating that a blend of the contributing structures is a better representation of the bonding than any one structure alone.
- **Resonance hybrid**
  - → Blended structure of individual contributing Lewis structures

- **Resonance structures**

  → Several examples follow:

  Example: N_2O, nitrous oxide, has 2(5) + 6 = 16 valence electrons or eight pairs.

  $$:\ddot{N}=N=\ddot{O}: \longleftrightarrow :N\equiv N-\underset{\cdot\cdot}{\ddot{O}}:$$

  Blending of two structures, both of which follow the octet rule.

  Note: The central N atom is the least electronegative atom (**Topic 2D.1**).

  Note: A triple bond to an O atom is found only in species such as BO^-, CO, NO^+, and O_2^{2+}.

  Example: C_6H_6, benzene, has 6(4) + 6(1) = 30 valence electrons, or 15 pairs.

Kekulé structures

Resonance hybrid

Note: Carbon atoms lie at the vertices of the hexagon (the six C–H bonds radiating from each corner are not shown in the stick structures). The last structure depicts six valence electrons *delocalized* around the ring. The resonance hybrid between the two Kekulé structures suggests that all bonds between neighboring carbon atoms in benzene are equivalent, which, in contrast to an individual Kekulé structure, agrees with experiment.

2B.3 Formal Charge

- **Formal charge**

  → An atom's number of valence electrons (V) minus the number of electrons assigned to it in a Lewis structure

- **Electron assignment in a Lewis structure**

  → Atom possesses all of its lone pair electrons (L) and half of its bonding electrons (B) [B means shared bonding electrons]

  → Formal charge = $V - (L + \frac{1}{2}B)$

- **Contribution of individual Lewis structures to a resonance hybrid**

  → Structures with individual formal charges closest to **zero** usually have the lowest energy and are the major contributors.

  Example: N_2O: $\underset{-1}{:\ddot{N}}=\underset{+1}{N}=\underset{0}{\ddot{O}:} \longleftrightarrow \underset{0}{:N}\equiv\underset{+1}{N}-\underset{-1}{\underset{\cdot\cdot}{\ddot{O}}:} \longleftrightarrow \underset{-2}{:\underset{\cdot\cdot}{\ddot{N}}}-\underset{+1}{N}\equiv\underset{+1}{O:}$

  (high formal charges)

- **Plausibility of isomers**

  → The isomer with the lowest formal charges is *usually* preferred.

  Examples: N_2O: $\underset{-1}{:\ddot{N}}=\underset{+1}{N}=\underset{0}{\ddot{O}:}$ and $\underset{-1}{:\ddot{N}}=\underset{+2}{O}=\underset{-1}{\ddot{N}:}$

  (low formal charges) (high formal charges)

  HCN: $\underset{0}{H}-\underset{0}{C}\equiv\underset{0}{N:}$ and $\underset{0}{H}-\underset{+1}{N}\equiv\underset{-1}{C:}$

  Note: In each example, the first structure with lower formal charges is preferred.

Summary

- **Formal charge**

  → Indicates the extent to which atoms have gained or lost electrons in a Lewis structure (covalent bonding)

  → Exaggerates the *covalent* character of bonds by assuming that electrons are shared equally

  → Structures with the lowest formal charges usually have the lowest energy (major contributors to the resonance hybrid).

  → Isomers with lowest formal charges are usually favored.

- **Oxidation number**

  → Exaggerates the *ionic* character of bonds

  Example: Carbon disulfide, $:\ddot{S}=C=\ddot{S}:$ Here, C has an oxidation number of +4 [all the electrons in the double bonds are assigned to the more electronegative S atoms (**Topic 2D.1**] and a formal charge of zero (the electrons in the double bonds are shared equally between the C and S atoms).

Topic 2C: BEYOND THE OCTET RULE

2C.1 Radicals and Biradicals

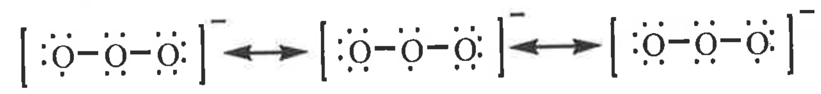
- **Radicals**

  → Species with an unpaired electron

  → All species with an odd number of electrons are radicals.

  → Are highly reactive, important for reactions in the upper atmosphere, cause rancidity in foods, degradation of plastics in sunlight, and perhaps contribute to human aging

Examples: CH_3 (methyl radical), OH (hydroxyl), OOH (hydrogenperoxyl), NO (nitric oxide), NO_2 (nitrogen dioxide), O_3^- (ozonide ion)



Note: Ozonide ion does not follow the octet rule.

- **Biradicals**

→ Species containing *two* unpaired electrons

Examples: O (oxygen atom) and CH_2 (methylene) [unpaired electrons on a single atom]
O_2 (oxygen molecule) and larger organic molecules [on different atoms]

- **Antioxidant**

→ Species that reacts rapidly with radicals before they have a chance to do damage

Examples: Vitamins A, C, and E; coenzyme Q; substances in coffee, orange juice, chocolate

2C.2 Expanded Valence Shells

- **Expanded valence shells**

→ More than eight electrons associated with an atom in a Lewis structure (expanded octet)
A *hypervalent compound* contains an atom with more atoms attached to it than is permitted by the octet rule. Empty *d*-orbitals are utilized to permit octet expansion.

→ Electrons may be present as bonding pairs or lone pairs.

→ Are characteristic of nonmetal atoms in *Period 3 or higher.*

→ *First- and second-period elements do not utilize expanded valence shells.*

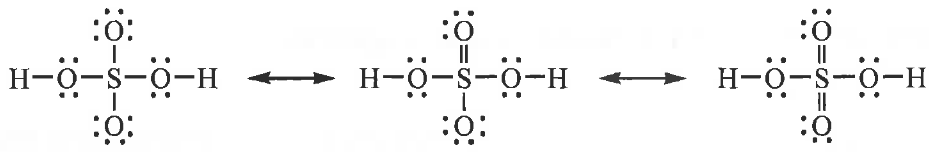
- **Variable covalence**

→ Ability to form different numbers of covalent bonds

→ Elements showing variable covalence include those in the table:

	Valence Shell Occupancy		
Elements	**8 electrons**	**10 electrons**	**12 electrons**
P	PCl_3 / PCl_4^+	PCl_5	PCl_6^-
S	SF_2	SF_4	SF_6
I	IF	IF_3	IF_5

Example: Major Lewis structures for sulfuric acid, H_2SO_4 (32 valence electrons)



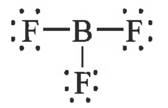
In the structure on the right, all atoms have zero formal charge and the S atom is surrounded by 12 electrons (expanded octet). *Because it has the lowest formal charges, this structure is expected to be the most favored one energetically and the one to make the greatest contribution to the resonance hybrid.* An additional Lewis structure has one double bond (not shown). Similar examples include SO_4^{2-}, SO_2, and S_3O (S is the central atom).

2C.3 Incomplete Octets

- **Incomplete octet**

→ Fewer than eight valence electrons on an atom in a Lewis structure

Example: BF_3,



The single-bonded structure with an incomplete octet makes the major contribution.

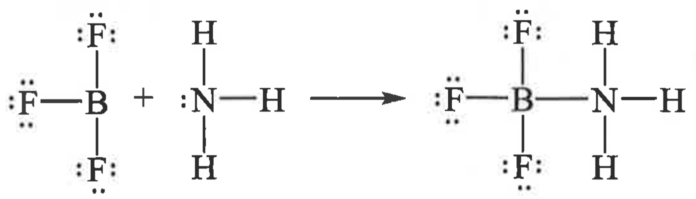
→ Other compounds with incomplete octets are BCl_3 and $AlCl_3$ both vapor at high temperature.

→ At room temperature, aluminum chloride exists as the dimer, Al_2Cl_6, which follows the octet rule (see **Margin Figure 17**, page 93, in the text).

- **Coordinate covalent bond**

→ One in which both electrons come from one atom

Example: Donation of a lone pair by one atom to form a bond that completes the otherwise incomplete octet of another atom. In the Lewis structure for the reaction of BF_3 with NH_3, both electrons in the B–N bond are derived from the N lone pair.



Topic 2D: THE PROPERTIES OF BONDS

2D.1 Correcting the Covalent Model: Electronegativity

- **Bonds**
  - → *All molecules* may be viewed as resonance hybrids of pure covalent and ionic structures.

    Example: H_2 The structures are $H{-}H \longleftrightarrow H^+[H:]^- \longleftrightarrow [:H]^- H^+$

    Here, the two ionic structures make equal contributions to the resonance hybrid, but the single covalent structure is of major importance.
- **Partial charges**
  - → When the bonded atoms are different, the ionic structures are not energetically equivalent.
  - → Unequal sharing of electrons results in a polar covalent bond.

    Example: HF The structures are

Note: The electron affinity of F is greater than that of H, resulting in a small negative charge on F and a corresponding small positive charge on H:

$$E_{ea}(F) > E_{ea}(H) \Rightarrow {}^{\delta+}H{-}F^{\delta-} \text{ (partial charges, } |\delta+| = |\delta-|)$$

$$E(H^+F^-) << E(H^-F^+) \Rightarrow H^-F^+ \text{ is a very } \textit{minor} \text{ contributor}$$

- **Electric dipole**
  - → A partial *positive* charge separated from an equal but *negative* partial charge
- **Electric dipole moment (μ)**
  - → Magnitude of an electric dipole: partial charge times distance between charges
  - → Units: debye (D)
  - → 4.80 D ≡ an electron (−) separated by 100 pm from a proton (+)
  - → $\boxed{\mu = (4.80\ \text{D}) \times \delta \times (\text{distance in pm}/100\ \text{pm})}$
- **Electronegativity (χ)**
  - → Electron-attracting power of an atom when it is bonded to another atom
  - → Mulliken scale: $\chi = \frac{1}{2}(I_1 + E_{ea})$
  - → Follows same periodic table trends as I_1 and E_{ea}
  - → *Increases from left to right and from bottom to top*
  - → Pauling numerical scale based on bond energies [$\chi(F) = 3.98$] is used in text (qualitatively similar to Mulliken's scale).
  - → See **Figure 2D.2** in the text for a tabulation of values for selected elements.

- **Rough rules of thumb for A-B bonds:**

$(\chi_A - \chi_B) \geq 2$	Bond is *essentially* ionic
$0.5 \leq (\chi_A - \chi_B) \leq 1.5$	Bond is *polar* covalent
$(\chi_A - \chi_B) \leq 0.5$	Bond is *essentially* covalent

- **Electric dipole moment (μ) conventions**
  - → In the original convention, the vector points towards the negative charge. Many chemists continue to use this convention.
  - → In the modern convention, the vector points towards the positive charge. Physicists employ this convention.

2D.2 Correcting the Ionic Model: Polarizability

- **Ionic bonds**
  - → All have *some* covalent character.

    A cation's positive charge attracts the electrons of an anion or atom in the direction of the cation (*distortion* of spherical electron cloud).
- **Highly *polarizable* atoms and ions**
  - → Readily undergo a *large* distortion of their electron cloud

    Examples of polarizable species: Large anions and atoms such as I^-, Br^-, Cl^-, I, Br, and Cl
- **Polarizing power**
  - → Property of ions (and atoms) that cause distortions of electron clouds
  - → Increases as size decreases and increases as charge of a cation increases

    Examples of species with significant polarizing power:

    The small and/or highly charged cations Li^+, Be^{2+}, Mg^{2+}, and Al^{3+}
- **Significant covalent bonding character**
  - → Bonds between highly polarizing cations and highly polarizable anions have significant covalent character.
  - → The Be^{2+} cation is highly polarizing and the Be–Cl bond has significant covalent character (even though there is an electronegativity difference of 1.59).
  - → In the series AgCl to AgI, the bonds become more covalent as the polarizability (also size) of the anion increases ($Cl^- < Br^- < I^-$).

2D.3 Bond Strengths

- **Dissociation energy (*D*)**
  - → Energy is required to separate bonded atoms in neutral molecules.
  - → Bond breaking is *homolytic*, which means that each atom retains half of the bonding electrons.
  - → Determines the *strength* of a chemical bond.
  - → The *greater* the dissociation energy, the *stronger* the bond.
  - → *D* is defined exactly for diatomic (two-atom) molecules.

→ For polyatomic (greater than two-atom) molecules, D also depends on the other bonds in the molecule. However, for many molecules, this dependence is slight.

- **Values of D (Table 2D.1)**
  - → Vary from about 139 kj·mol^{-1} (I–I single bond) to 1062 kj·mol^{-1} (C≡O triple bond)
- ***D* for several diatomic molecules**

$H{-}H(g) \rightarrow H(g) + H(g)$ $D = 424$ kJ·mol^{-1} (strong)
$H{-}F(g) \rightarrow H(g) + F(g)$ $D = 543$ kJ·mol^{-1} (strong)
$F{-}F(g) \rightarrow F(g) + F(g)$ $D = 146$ kJ·mol^{-1} (weak)
$I{-}I(g) \rightarrow I(g) + I(g)$ $D = 139$ kJ·mol^{-1} (weak)
$O{=}O(g) \rightarrow O(g) + O(g)$ $D = 484$ kJ·mol^{-1} (strong)
$N{\equiv}N(g) \rightarrow N(g) + N(g)$ $D = 932$ kJ·mol^{-1} (very strong)

- **Bond strength**
  - → For polyatomic molecules, bond strength is defined as the *average* dissociation energy for one type of bond found in different molecules.

    For example, the tabulated C–H single bond value is the *average* strength of such bonds in a selection of organic molecules, such as methane (CH_4), ethane (C_2H_6), and possibly ethene (C_2H_4).

    Note: Values of average dissociation energies in text **Table 2D.2** are actually those for the property of *bond enthalpy* (see **Topic 4E**), measured at 298.15 K. The bond *dissociation energies* of diatomic molecules given in **Table 2D.1** apply at 0 K (absolute zero).

- **Factors influencing bond strength**

→ Bond multiplicity	(C≡C > C=C > C–C)
→ Resonance	(C=C > C$\overset{\cdots}{-}$C (benzene) > C–C)
→ Lone pairs on neighboring atoms	(F–F < H–H)
→ Atomic radii	(HF > HCl > HBr > HI)

Note: The smaller the radius, the stronger the bond.

2D.4 Bond Lengths

- **Bond length**
  - → Internuclear distance, at the potential energy minimum, of two atoms linked by a covalent bond
  - → Helps determine the overall size and shape of a molecule
  - → Evaluated by using spectroscopic or x-ray diffraction (for solids) methods
  - → For bonds between the same elements, length is *inversely* proportional to strength.
- **Factors influencing bond length**

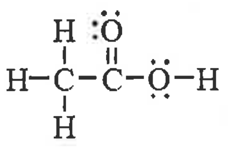
→ Bond multiplicity	(C≡C < C=C < C–C)
→ Resonance	(C=C < C$\overset{\cdots}{-}$C (benzene) < C–C)
→ Lone pairs on neighboring atoms	(F–F > H–H)
→ Atomic radii	(HF < HCl < HBr < HI)

Note: The smaller the radius, the shorter the bond.
Note: These trends are the *opposite* of the ones for bond strength.

- **Covalent radius**
  - → Contribution an atom makes to the length of a covalent bond
  - → *Half* the distance between the centers (nuclei) of neighboring atoms joined by a covalent bond (*for like atoms*)
  - → Covalent radii may be added to estimate bond lengths in molecules.
  - → Tabulated values are *averages* of radii in polyatomic molecules.
  - → *Decreases* from left to right in the periodic table
  - → *Increases* going down a group in the periodic table
  - → Decreases for a given atom with increasing multiple-bond character

Example: Use the covalent radii given in **Figure 2D.11** in the text to *estimate* the several bond lengths in the acetic acid molecule, CH_3COOH.

Lewis Structure:



Bond type	**Bond length estimate (pm)**	**Actual (pm)**
C–H	77 + 37 = 114	≈109
C–C	77 + 77 = 154	≈150
C–O	77 + 66 = 143	134
C=O	67 + 60 = 127	120
O–H	66 + 37 = 103	97

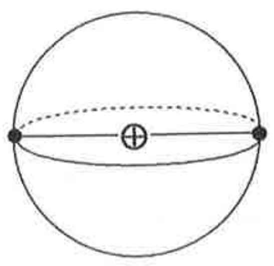
Topic 2E: THE VSEPR MODEL

2E.1 The Basic VSEPR (Valence-Shell Electron-Pair Repulsion) Model

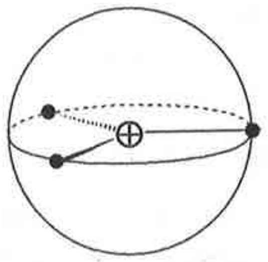
- **Valence electrons about central atom(s)**
  - → Control the shape of a molecule
- **Lewis structure**
  - → Shows distribution of *valence* electrons in bonding pairs (bonds) and as lone pairs or unpaired electrons
- **Bonds, lone pairs**
  - → Regions of high electron density that repel each other (Coulomb's law) by rotating about a central atom, thereby maximizing their separation
- **Bond angle(s)**
  - → Angle(s) between bonds joining atom centers

- **Multiple bonds**
  - → Treated as a *single* region of high electron concentration in VSEPR
- **Electron arrangement**
  - → Ideal locations of bond pairs and lone pairs about a central atom (angles between electron pairs define the geometry)

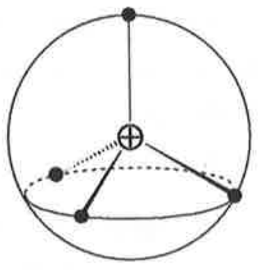
Typical Electron Arrangements in Molecules with *One* Central Atom



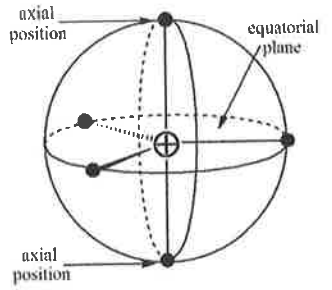
Linear (180°)



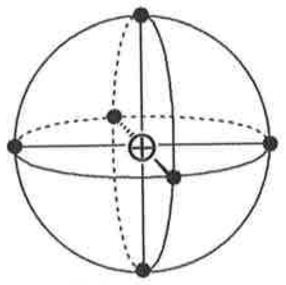
Trigonal planar (120°)



Tetrahedral (109.5°)



Trigonal bipyramidal (120° equatorial, 90° axial-equatorial)



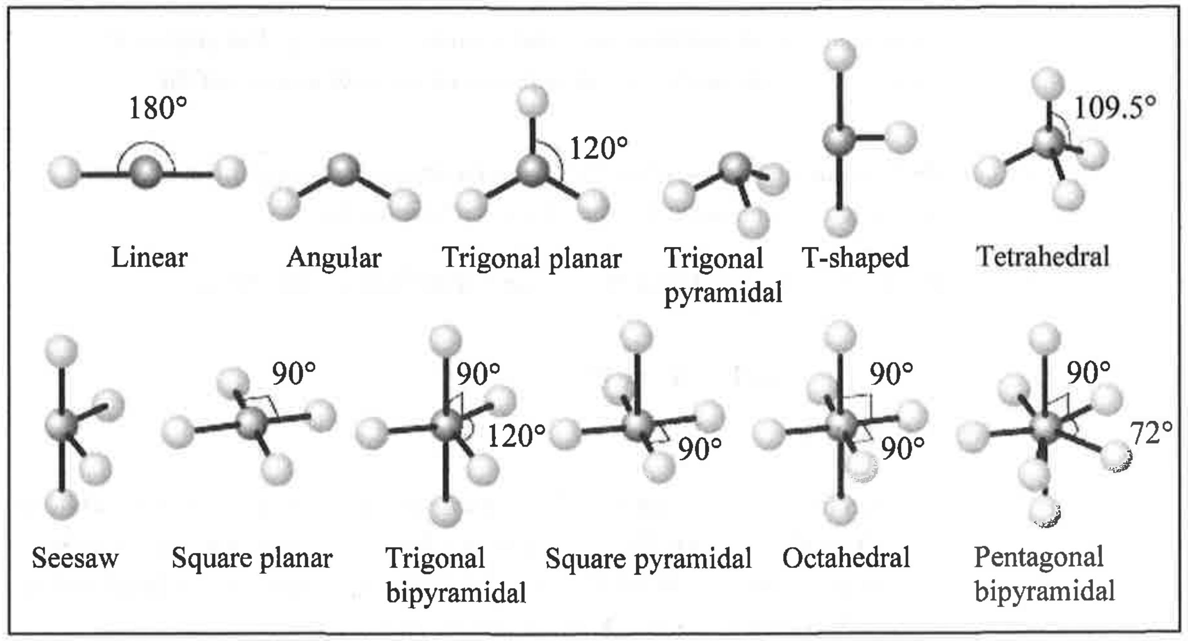
Octahedral (90° and 180°)

- **VSEPR formula, AX_nE_m** (See **Topic 2E.2** in the text)
  - → A = central atom
  - → X_n = *n* atoms (*same* or *different*) bonded to central atom
  - → E_m = *m* lone pairs on central atom
  - → Formula is useful for generalizing types of structures.

Note: Molecular shape is defined by the location of the *atoms alone.*
The bond angles are ∠ X–A–X.

Some Examples: Linear, BeF_2 (AX_2); trigonal planar, BF_3 (AX_3); tetrahedral, CH_4 (AX_4); trigonal bipyramidal, PCl_5 (AX_5); octahedral, SF_6 (AX_6)

Typical Shapes of Molecules with *One* Central Atom*



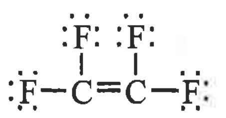
* These figures depict the locations of the atoms only, *not* lone pairs.

- **VSEPR (sometimes pronounced "vesper") method** (See **Toolbox 2E.1** in the text)
  - → Write the Lewis structure(s). If there are resonance structures, pick *any* one.
  - → Count the number of electron pairs (bonding and nonbonding) around the central atom(s). Treat a multiple bond as a *single* unit of high electron density.
  - → Identify the *electron arrangement*. Place electron pairs as far apart as possible.
  - → Locate the *atoms* and classify the *shape* of the molecule.
  - → Optimize *bond angles* for molecules with *lone pairs* on the central atom(s) with the concept in mind that repulsions are in this order:

    lone pair-lone pair > lone pair-bonding pair > bonding pair-bonding pair.

Example: Use the VSEPR model to predict the *shape* of tetrafluoroethene, C_2F_4.

Lewis structure:



There are three concentrations of electron density around each C atom, so the shape is *trigonal planar* about each C atom. C_2F_4 is an AX_3AX_3 species.

2E.2 Molecules with Lone Pairs on the Central Atom

- **VSEPR method for molecules with lone pairs ($m \neq 0$)**
  - → Lone-pair electrons have preferred positions in certain electron arrangements.

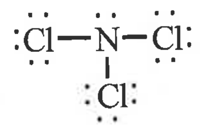
→ In the *trigonal bipyramidal* arrangement, lone pairs prefer the *equatorial* positions, in which electron repulsions are minimized.

→ In the *octahedral* arrangement, all positions are *equivalent by symmetry*. The preferred electron arrangement for *two lone pairs* is the occupation of *opposite* corners of the octahedron.

→ Lone pairs contribute to the electron arrangement about a central atom and influence the shape of molecules, which is determined by the location of the nuclei.

Example: Use the VSEPR model to predict the shape of trichloroamine, NCl_3.

Lewis structure:



The four electron pairs around N yield a *tetrahedral* electron arrangement, while the shape is *trigonal pyramidal* (like a badminton birdie). Because lone pair-bonding pair repulsion is greater than bonding pair-bonding pair repulsion, the bond angles [∠ Cl–N–Cl] will be less than the tetrahedral value, 109.5°.

2E.3 Polar Molecules

- **Polar molecule**
  → Molecule with a *nonzero* dipole moment
- **Polar bond**
  → Bond with a *nonzero* dipole moment
- **Molecular dipole moment**
  → *Vector sum* of bond dipole moments
- **Representation of dipole**
  → Single arrow with head pointed toward the *positive* end of the dipole, the H atom in the following example.

  Example: Lewis structure: $\mathrm{H}-\ddot{\underset{\cdot\cdot}{\mathrm{Cl}}}:$ and polar (dipole) representation: $\mathrm{H} \leftarrow\!\!\!+ \mathrm{Cl}$
- **Predicting molecular polarity**
  → Determine molecular *shape* using VSEPR theory.
  → Estimate electric dipole (bond) moments (text Section 2E.3) or use text **Figure 2E.7** to decide whether the molecular *symmetry* leads to a *cancellation* of bond moments (*nonpolar molecule*, no dipole moment) or not (*polar molecule*, nonzero dipole moment).

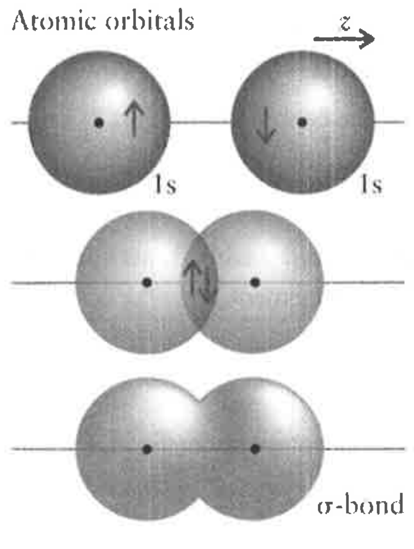
Example: Is XeF_2 a polar or nonpolar molecule?

Lewis structure: $:\ddot{\underset{\cdot\cdot}{\mathrm{F}}}-\ddot{\underset{\cdot\cdot}{\mathrm{Xe}}}-\ddot{\underset{\cdot\cdot}{\mathrm{F}}}:$ The *electron* arrangement is *trigonal bipyramidal*; the *shape* is *linear* (lone pairs prefer the equatorial positions). The bond angle is 180°, the bond dipoles cancel, and the molecule is *nonpolar*: $\mathrm{F} +\!\!\!\rightarrow \mathrm{Xe} \leftarrow\!\!\!+ \mathrm{F}$.

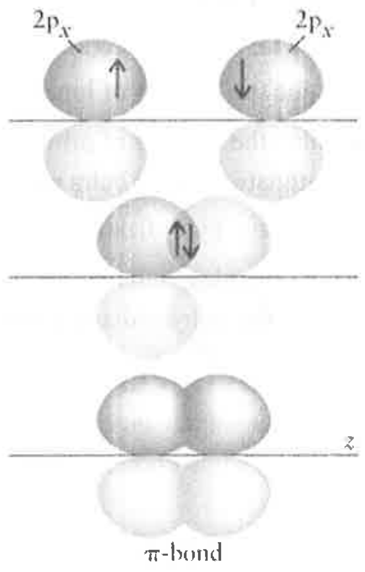
Topic 2F: VALENCE-BOND (VB) THEORY

2F.1 Sigma (σ) and Pi (π) Bonds

- **Two major types of *bonding* orbitals**
  → σ and π
- **σ-orbital**
  → Has no *nodal surface* containing the interatomic (bond) axis
  → Is cylindrical or "sausage" shaped
  → Formed by overlapping in several ways: two s-orbitals, an s-orbital and a p-orbital end to end, two p-orbitals end to end, a certain hybrid orbital and an s-orbital, a p-orbital end to end with a certain hybrid orbital, or two certain hybrid orbitals end to end
- **π-orbital**
  → *Nodal plane* containing the interatomic (bond) axis.
  → Two quasi-cylindrical shapes (lobes), one above and the other below the nodal plane.
  → Formed from side-by-side overlap of two *p*-orbitals.
- **Schematic of σ-orbital formation**
  → Two 1s-orbitals of H atoms combine to form a σ-orbital of H_2.



- **Schematic of π-orbital formation**
  → Two $2p_x$-orbitals overlap side by side.



- **Electron occupancy**
  - → σ- and π-orbitals can hold 0, 1, or 2 electrons, corresponding to no bond, a half-strength bond, or a full covalent bond, respectively.
  - → In any orbital, the spins of two electrons must be *paired* (opposite direction of arrows).
- **Types of bonds according to valence-bond theory**
  - → **Single bond** is a σ-bond. [H_2, for example]
  - → **Double bond** is a σ-bond plus one π-bond. [O_2, for example]
  - → **Triple bond** is a σ-bond plus two π-bonds. [N_2, for example]

2F.2 Electron Promotion and the Hybridization of Orbitals *and*

2F.3 Other Common Types of Hybridization

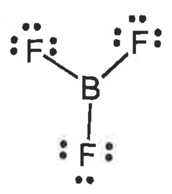
- **Hybrid orbitals**
  - → Produced by mixing (hybridizing) orbitals of a central atom
  - → A construct consistent with observed shapes and bonding in molecules

Hybridization Schemes

Electron arrangement around the central atom	Hybrid orbitals (number)	Angle(s) between σ-bonds	Example(s) [central atoms]
Linear	sp (two)	180°	$BeCl_2$, CO_2
Trigonal planar	sp^2 (three)	120°	BF_3, CH_3^+
Tetrahedral	sp^3 (four)	109.5°	CCl_4, NH_4^+
Trigonal bipyramidal	sp^3d (five)	120°, 90°, and 180°	PCl_5
Octahedral	sp^3d^2 (six)	90° and 180°	SF_6

- **Determination of hybridization schemes**
  - → Write the Lewis structure(s). If there are resonance structures, pick *any* one.
  - → Determine the number of lone pairs and σ-bonds on the central atom.
  - → Determine the number of orbitals required for hybridization on the central atom to accommodate the lone pairs and σ-bonds.
  - → Determine the hybridization scheme from the preceding table.
  - → Use VSEPR rules to determine the molecular *shape* and *bond angle(s)*. (π-bonds are formed from the overlap of unhybridized atomic p-orbitals in a side-by-side arrangement.)

Example: Describe the bonding in BF_3 using VB theory and hybridization. The shape is trigonal planar (VSEPR). The hybridization at B is sp^2 (see table). The three σ-bonds are formed from overlap of B(sp^2) orbitals with F(2p) orbitals (B(sp^2)–F(2p) bonds).

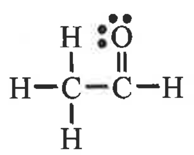


Note: Detailed studies indicate that both s- and p-orbitals take part in the bond formation of terminal atoms, such as F.

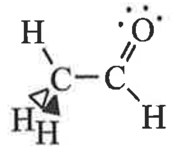
- **Central atoms**
  - → Each central atom can be represented using a hybridization scheme, as in the example that follows.

Example: Use VB theory to describe the bonding in and shape of acetaldehyde, a molecule with two central atoms.

Lewis Structure



3-D Representation



Bonds: C–C σ-bond from overlap of a methyl C sp^3 with an aldehyde C sp^2 hybrid orbital
C=O σ-bond from overlap of an aldehyde C sp^2 hybrid orbital with an O 2p orbital
C=O π-bond from side-by-side overlap of C 2p and O 2p atomic orbitals
C–H single bond (three) from overlap of an H 1*s* atomic orbital and a methyl C sp^3 hybrid orbital
C–H single bond from the overlap of a H 1s atomic orbital and an aldehyde C sp^2 hybrid orbital

Angles: Three ∠ H–C–H ~ 109.5°; three ∠ H–C–C ~ 109.5°; one ∠ C–C=O ~ 120°; one ∠ O=C–H ~ 120°; and one ∠ C–C–H ~ 120°

Molecular shape: Tetrahedral at methyl carbon atom, trigonal planar at aldehyde C atom

2F.4 Characteristics of Multiple Bonds

- **Alkanes (C_nH_{2n+2}, n = 1, 2, 3, ...)**
  - → Characteristics: tetrahedral geometry and sp^3 hybridization at C atoms; all C–C and C–H single (σ) bonds; rotation allowed about C–C single bonds

    Examples: Methane, CH_4; and propane, $CH_3CH_2CH_3$
- **Alkenes (C_nH_{2n}, n = 2, 3, 4, ...)**
  - → Characteristics: one C=C double bond (σ plus π); other C–C bonds and all C–H bonds single (σ); trigonal-planar geometry and sp^2 hybridization at double-bonded C atoms; tetrahedral geometry at other C (sp^3) atoms; rotation *not* allowed about double C=C bond; rotation allowed about C–C single bonds

    Examples: Ethene (ethylene), $H_2C{=}CH_2$; and propylene, $CH_3CH{=}CH_2$

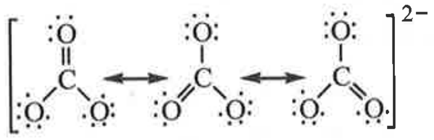
- **Alkynes (C_nH_{2n-2}, n= 2, 3, 4, ...)**
  - → Characteristics: one C≡C triple bond (σ plus two π); other C–C bonds and all C–H bonds (σ); linear geometry and sp hybridization at triple-bonded C atoms; tetrahedral geometry at other C (sp^3) atoms

    Examples: Ethyne (acetylene), HC≡CH; 2-butyne (dimethylacetylene), $H_3CC{\equiv}CCH_3$
- **Benzene (C_6H_6)**
  - → Characteristics: *Planar* molecule with hexagonal C framework; trigonal-planar geometry and sp^2 hybridization at C atoms; σ framework has C–C and C–H single bonds; 2p-orbitals (one from each C atom) that overlap side-by-side to form *three* π-bonds (*six* π-electrons) *delocalized over the entire six C atom ring*
  - → See Lewis resonance structures in **Topic 2B.2** of this study guide.
- **Double bonds**
  - → Consist of *one* σ- and *one* π-bond and are always *stronger* than a single σ-bond:

    C=C is *weaker* than two single C–C σ-bonds
    N=N is *stronger* than two single N–N σ-bonds
    O=O is *stronger* than two single O–O σ-bonds
  - → Formed readily by Period 2 elements (C, N, O)
  - → Rarely found in Period 3 and higher period elements
  - → Impart rigidity to molecules and influence molecular shape

Example: Describe the structure of the carbonate anion in terms of hybrid orbitals, bond angles, and σ- and π-bonds.

Lewis resonance structures:



Trigonal-planar geometry with sp^2 hybridization at C, 120° ∠ O–C–O angles, and C sp^3-O 2p single bonds. Remaining C 2p-orbital can overlap with O 2p-orbitals to form a π-bond in each of three ways corresponding to the resonance structures. Therefore, each carbon-oxygen bond can be viewed as one σ-bond and one-third of a π-bond.

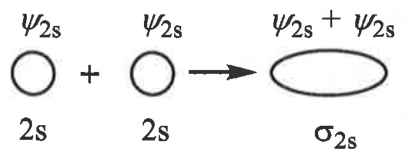
Topic 2G: MOLECULAR ORBITAL (MO) THEORY

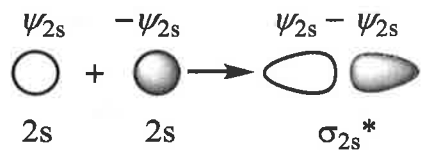
2G.1 Molecular Orbitals

- **Valence Bond (VB) deficiencies**
  - → Cannot explain *paramagnetism* of O_2 (see text Box 2G.2 for explanation of paramagnetism and *diamagnetism*)

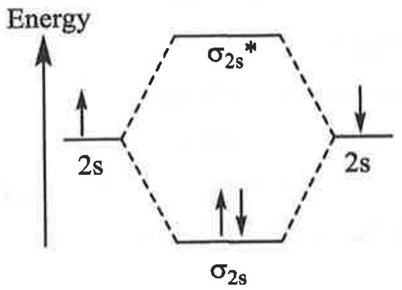
  - → Difficulty treating *electron-deficient* compounds such as diborane, B_2H_6
  - → No simple explanation for *spectroscopic properties* of compounds such as color
- **Molecular Orbital (MO) advantages**
  - → Addresses *all* of these shortcomings of VB theory
  - → Provides a *deeper* understanding of electron-pair bonds
  - → Accounts for the *structure and properties* of metals and semiconductors
  - → More facile for *computer calculations* than VB theory
- **MO theory**
  - → In MO theory, electrons occupy MOs that are *delocalized* over the *entire* molecule.
  - → In VB theory, bonding electrons are *localized* between the two atoms.
- **Molecular Orbitals (MO)**
  - → Formed by superposition (**linear combination**) of atomic orbitals (**LCAO-MO**)
  - → **Bonding orbital** (constructive interference):
    Increased amplitude or electron density between atoms
  - → **Antibonding orbital** (destructive interference):
    Decreased amplitude or electron density between atoms
- **Types of Molecular Orbitals**
  - → **Bonding MO:** energy *lower* than that of the constituent AOs
  - → **Nonbonding MO:** energy *equal* to that of the constituent AOs
  - → **Antibonding MO:** energy *greater* than that of the constituent AOs
- **Rules for combining AOs to obtain MOs**
  - → *N* atomic orbitals (AOs) yield *N* molecular orbitals (MOs)
  - → Conservation of orbitals
  - → Little overlap of inner shell AOs, and these MOs are usually *nonbonding.*
- **MO energy-level diagrams**
  - → Relative energies of original AOs and resulting MOs are shown schematically in energy-level diagrams.
  - → Arrows used to show electron spin and to indicate location of the electrons in the separated atoms and the molecule

Example: Formation of bonding and antibonding MOs by LCAO method and MO energy-level diagram for the formation of Li_2 from Li atoms.





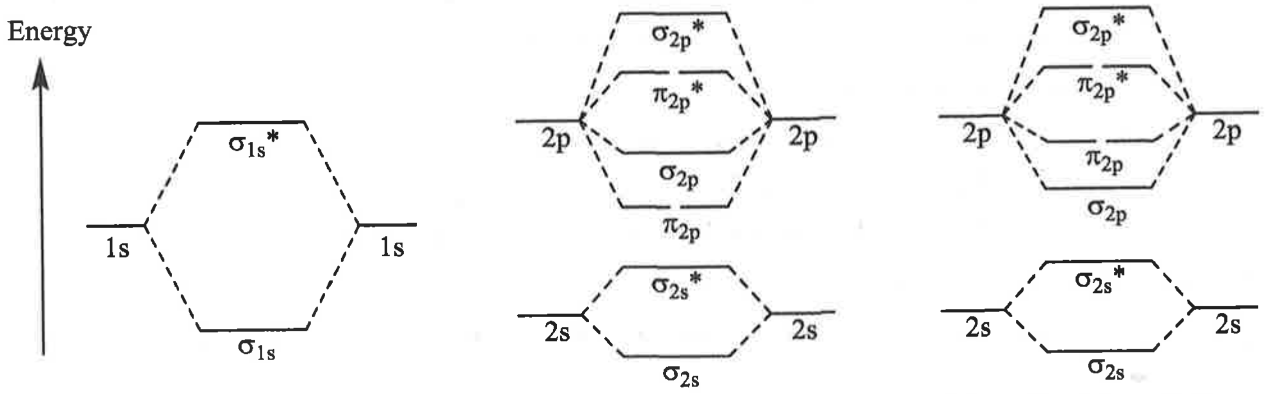
Energy-level diagram



2G.2 The Electron Configurations of Diatomic Molecules

- **Procedure for determining the electronic configuration of diatomic molecules**
  - → Construct all possible MOs from *valence-shell* AOs.
  - → Place *valence electrons* in the lowest energy, unoccupied MOs.
  - → Follow the **Pauli exclusion principle** and **Hund's rule** as for AOs: Electrons have *spins paired* in a fully occupied molecular orbital and enter unoccupied *degenerate* orbitals with *parallel spins.*
- ***Valence-shell MOs*** **for Period 1 and Period 2** ***homonuclear*** **diatomic molecules**

Correlation Diagrams



Schematic order of MO energy levels for H_2, He_2

Schematic order of MO energy levels for Li_2, Be_2, B_2, C_2, N_2

Schematic order of MO energy levels for O_2, F_2, Ne_2

- **Bond order (*b*)** → $\boxed{b = \frac{1}{2}(N_e - N_e^*)}$

N_e = total number of electrons in *bonding* MOs

N_e^* = total number of electrons in *antibonding* MOs

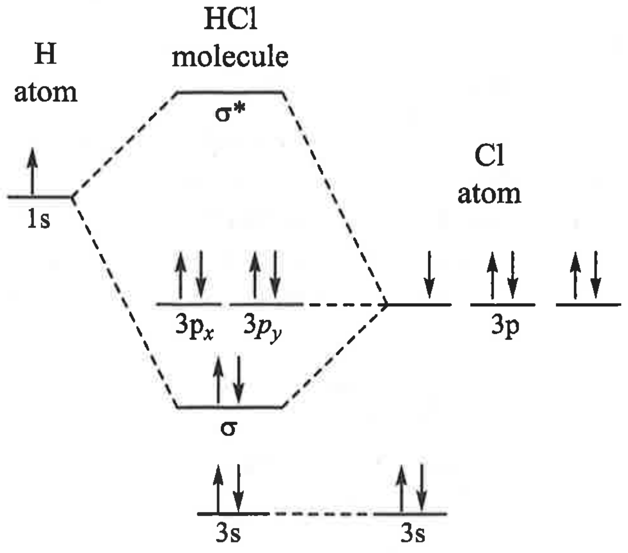
Examples: *b* in Li_2 = 1 (two valence electrons in bonding 2sσ MO). ***b*** in H_2^- = 1/2 (two electrons in 1*s*σ bonding MO, one electron in 1sσ*-antibonding MO).

O_2^+ has 11 valence electrons, which are placed in the 2sσ, 2sσ*, 2pσ, two *degenerate* 2pπ, and one of the *degenerate* 2pπ* MOs. The valence electron configuration is $(2s\sigma)^2 (2s\sigma^*)^2 (2p\sigma)^2 (2p\pi)^4 (2p\pi^*)^1$. There is one unpaired electron. $N_e = 8$ and $N_e^* = 3$. Bond order = (1/2) × (8 – 3) = 5/2.

2G.3 Bonding in Heteronuclear Diatomic Molecules

- **Bond properties**
  - → Polar in nature
  - → Atomic orbital from the *more* electronegative atom is *lower* in energy.
  - → *Bonding* orbital has a *greater* contribution from the *more* electronegative atom.
  - → *Antibonding* orbital has a *greater* contribution from the *less* electronegative atom.
- **Result of bond properties is modified, unsymmetrical correlation diagrams.**

Example:



Bonding in HCl using MO theory. The correlation diagram shows occupied valence orbitals for H and Cl atoms, resulting MOs from overlap of 1sH and $3p_z$ Cl orbitals, lone pair nonbonding orbitals $3p_x$ and $3p_y$ of Cl, and the nonbonding Cl 3s orbital. The electronic configuration is $(\text{Cl } 3s)^2\,\sigma^2\,(\text{Cl } 3p_x)^2\,(\text{Cl } 3p_y)^2$.

2G.4 Orbitals in Polyatomic Molecules

- **Bond properties**
  - → All atoms in the molecule are encompassed by the MOs.
  - → Electrons in MOs bond all the atoms in a molecule.
  - → Electrons are *delocalized* over all the atoms.
  - → Energies of the MOs are obtained by using spectroscopic techniques.

- **Effectively localized electrons**
  - → While MO theory requires MOs to be *delocalized* over all atoms, electrons sometimes are *effectively localized* on an atom or group of atoms.

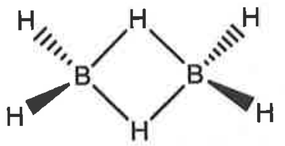
    Example: See the HCl example, shown previously, with nonbonding Cl $3p_x$ and Cl $3p_y$ orbitals effectively localized on Cl.

- **Combining VB and MO theories**
  - → VB and MO theory are sometimes jointly invoked to describe the bonding in complex molecules.

    Example: In benzene, localized sp^2 hybridization (hybrids of C 2s-, C $2p_x$-, and C $2p_y$-orbitals on each C) is used to describe the σ-bonding framework of the ring, while delocalized MOs (LCAOs of six C $2p_z$-orbitals) are used to describe the π-bonding.

- **Triumphs of MO theory**
  - → Accounts for paramagnetism of O_2
  - → Accounts for bonding in electron-deficient molecules

    Example: In diborane (B_2H_6, with 12 valence electrons), *six* electron pairs bond *eight* atoms using *six* MOs. VB theory with only localized covalent bonds requires *eight* electron pairs and fails to describe the bonding. A combination of MO and VB theories has been used to describe the bonding in B_2H_6 as four B–H single bonds (8 electrons) and two, two-electron, 3-center B–H–B delocalized bonds (4 electrons).



Diborane

  - → Provides a framework for interpreting visible and ultraviolet (UV) spectra

    Example: For benzene (schematic energy levels shown in the following figure), the UV spectrum is interpreted as the excitation of an electron from the *highest occupied molecular orbital* (**HOMO,** *bonding* π MO) to the *lowest unoccupied molecular orbital* (**LUMO,** *antibonding* π* MO). Excitation changes the bond order of the π-system from 3 to 2.