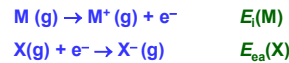


CHEMICAL BONDING

- Primary chemical bonding forces ($\Delta E > 100$ kJ/mol)
 - Ionic bonding (Kossel – 1916)
 - $\Delta x > 2$ occurrence: ionic solids
 - Covalent bonding (Lewis – 1916)
 - $\Delta x < 0.5$ occurrence: - molecules
- covalent network solids
 - Metallic bonding
 - $\Delta x \sim 0$ occurrence: metallic solids
- Secondary chemical bonding forces ($\Delta E < 100$ kJ/mol)
 - dispersion forces
 - dipole–dipole (induced dipole) interaction
 - hydrogen bonding

IONIC BONDS AND IONIC SOLIDS

An electron affinity never provides enough energy to compensate for an ionization energy.



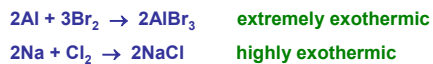
No matter what M and X are

$$E_i(M) > |E_{ea}(X)| \Rightarrow E_i(M) + E_{ea}(X) > 0 \text{ endothermic}$$

Ions cannot form in exothermic processes???

NO!!!!!!

IONIC BONDS AND IONIC SOLIDS



Electron affinities and ionization energies are gas-phase properties.

Ions are unlikely to form in gas phase at not very high temperatures!!!

Ionic compounds: solids (sometimes liquids) in a well-ordered crystal structure

Crystal lattice: held together by large forces

LATTICE ENERGY



the energy required to break up an ionic solid into individual gaseous ions

always high positive value

e.g. LiF 1036 kJ/mol, CaO 3401 kJ/mol

Depends on:

lattice geometry (distance and number of close neighbor ions)

charge of ions in the lattice

LATTICE ENERGY

Origin: interaction between charges,
Coulomb's law (for force)

$$F = k \frac{z_1 z_2}{d^2}$$

charges
Coulomb's constant distance

Like charges: repulsion

Unlike charges: attraction

$$E = k \frac{z_1 z_2}{d}$$

for energy

need to be summed for every possible pairs of ions in a lattice

Like charges: positive energy (high)

Unlike charges: negative energy (low)

LATTICE ENERGY (U)

The energy released during the formation of 1 mol ionic solid from 1 mol gaseous ions.

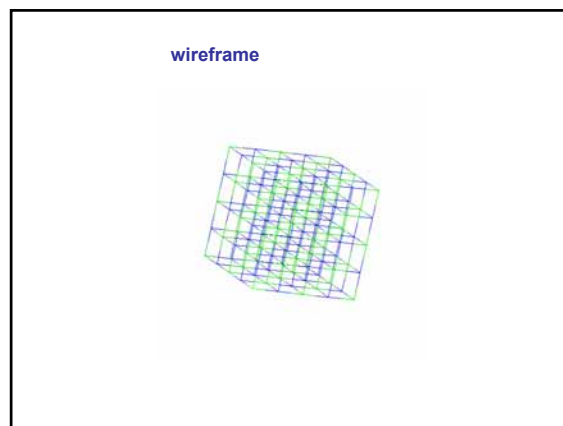
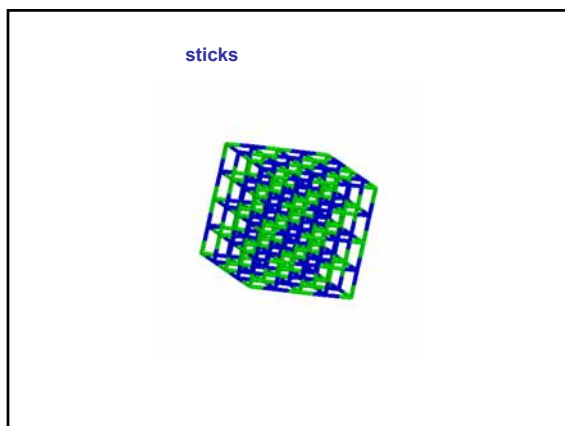
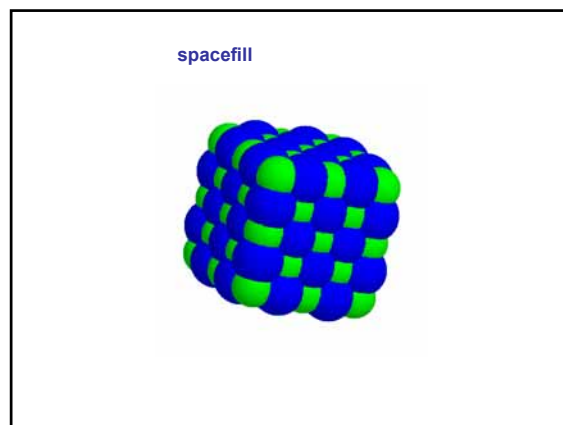
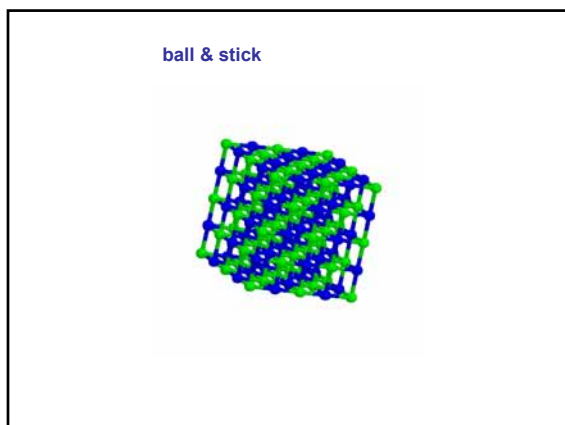
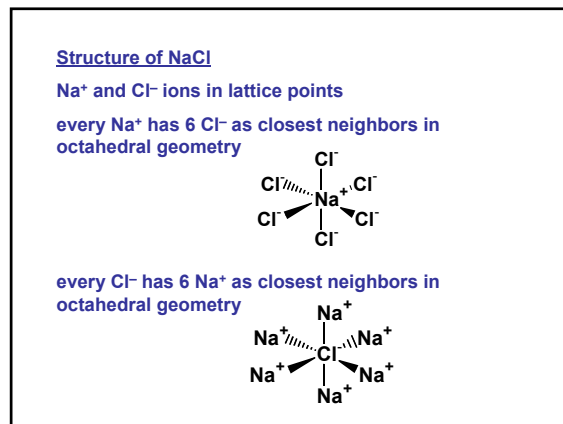
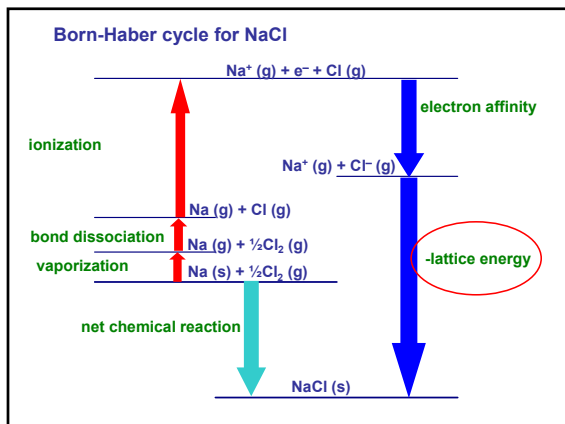
Calculation:
$$U = -Mk \frac{z_1 z_2}{d}$$

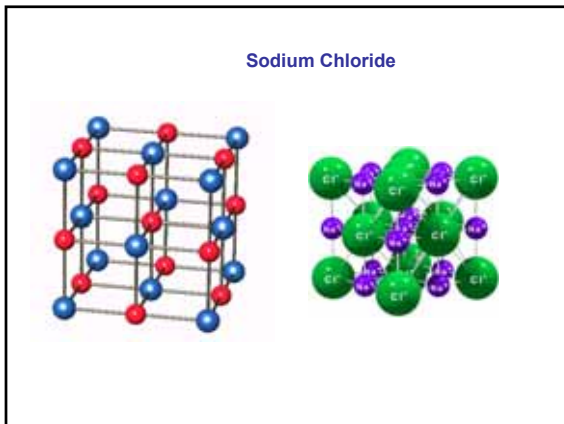
M: Madelung constant (depends on lattice type)
z_i: ionic charge d: distance between ions

$$M = \sum_i (\pm)_i \frac{d_0}{d}$$

for NaCl:
$$M = \sum_{i,j,k=-\infty}^{\infty} \frac{(-1)^{i+j+k}}{\sqrt{i^2 + j^2 + k^2}}$$

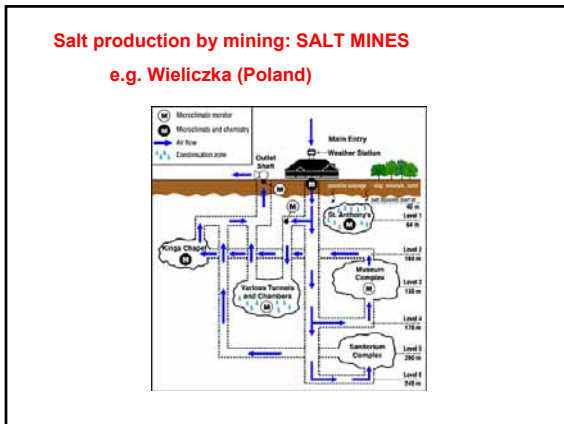
$$M = -6 + 12/\sqrt{2} - 8/\sqrt{3} + 6/2 - 24/\sqrt{5} + \dots = -1.74756$$





Common salt (NaCl)

known and used for millenia
 very important commercial material
 the human body needs ~ 5 g a day
 crystalline common salt: **HALITE**
 two sources:
 salt in seas and oceans (evaporation)
 salt in mines: left from ancient seas
Salt production by evaporation: SALT PAN
 e.g. Sečovlje (Slovenia)

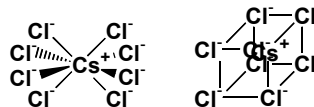




Structure of CsCl

Cs⁺ and Cl⁻ ions in lattice points

every Cs⁺ has 8 Cl⁻ as closest neighbors in cubic geometry



every Cl⁻ has 8 Cs⁺ as closest neighbors in cubic geometry

Lattice energies (kJ/mol)

	F ⁻	Cl ⁻	Br ⁻	I ⁻	O ²⁻
Li ⁺	1036	853	807	757	2925
Na ⁺	923	787	747	704	2695
K ⁺	821	715	682	649	2360
Be ²⁺	3505	3020	2914	2800	4443
Mg ²⁺	2957	2524	2440	2327	3791
Ca ²⁺	2630	2258	2176	2074	3401
Al ³⁺	5215	5492	5361	5218	15916

reminder $E = k \frac{Z_1 Z_2}{d}$

Octet rule

A simple rule (not law) useful for interpreting and predicting electronic structure of main group elements in compounds:

Main-group elements tend to undergo reactions that leave them with eight outer-shell electrons.

or

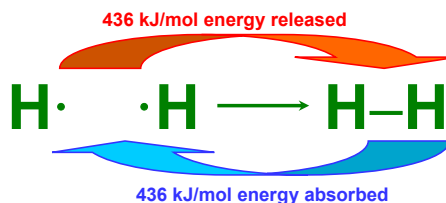
Main group elements react so that they attain a noble gas electron configuration with filled s and p sublevels in their valence electron shell.

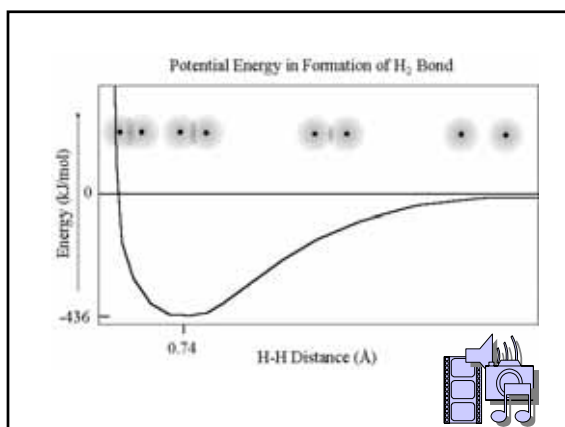
Octet rule

- Alkali metals tend to lose their ns^1 valence-shell electron, thereby adopting the electron configuration of the noble gas element in the previous row of the periodic table.
- Alkali earth metals tend to lose both of their ns^2 valence-shell electrons and adopt a noble gas configuration.
- Boron group elements tend to lose all three of their $ns^2 np^1$ electrons and adopt a noble gas configuration.
- Halogens tend to gain one electron, changing from $ns^2 np^5$ to $ns^2 np^6$, thereby adopting the configuration of the neighboring noble gas element in the same row.
- Noble gas elements are essentially inert; they rarely gain or lose electrons.
- More consequences in covalent bonding.....

COVALENT BONDS

bonds formed through sharing an electron pair



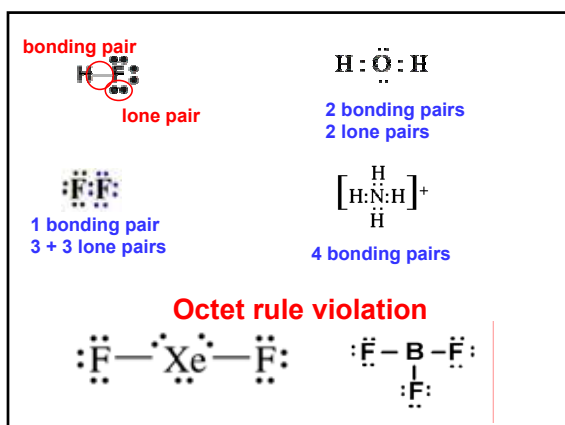
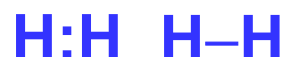


ELECTRON-DOT STRUCTURES

Lewis structures:

- ◆ represent every atom's valence electrons by dots
- ◆ the placement of the dots indicate how the valence electrons are distributed in the molecule
- ◆ non-valence electrons (core electrons) are never involved in bond-making
- ◆ **OCTET RULE:** an atom in a molecule is happy with eight electrons in the valence shell (exception: H ⇒ 2)

hydrogen molecule

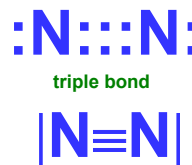


MULTIPLE BONDS

oxygen molecule



nitrogen molecule



SHAPES OF MOLECULES

Detailed experimental information mainly from diffraction methods

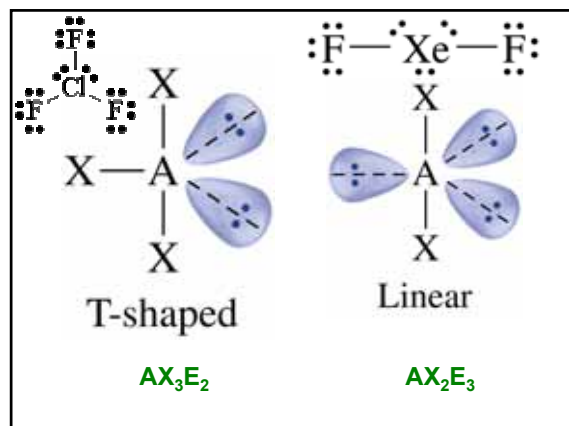
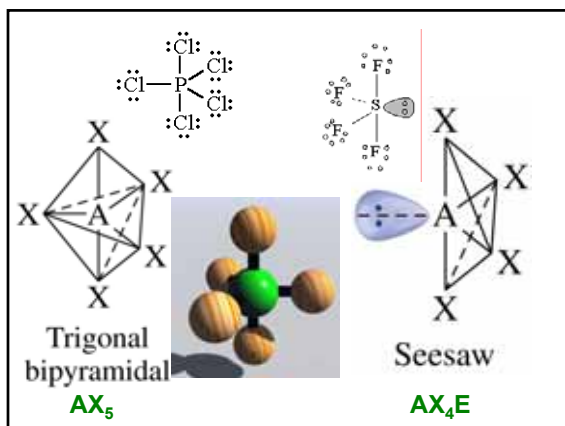
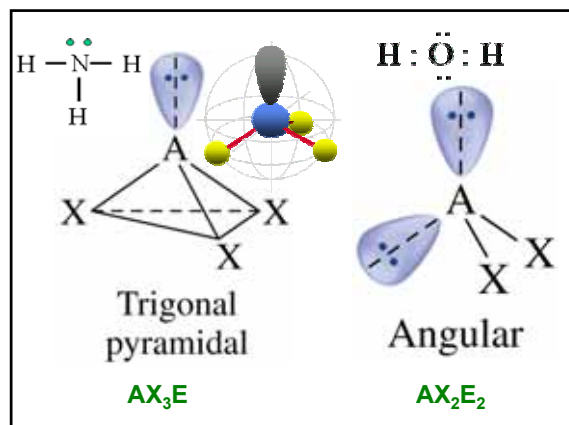
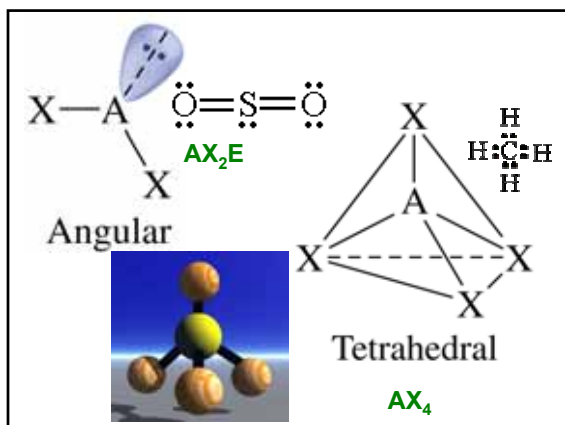
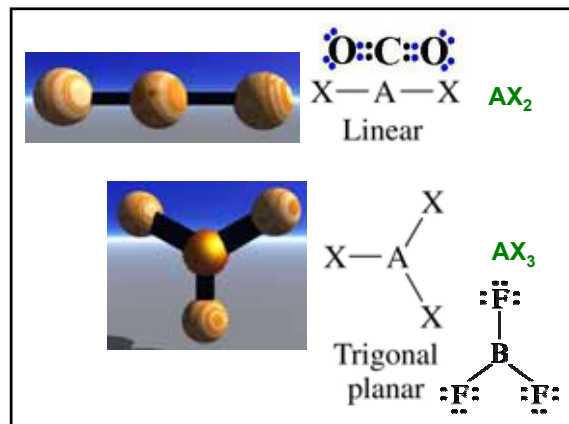
VSEPR: Valence Shell Electron Pair Repulsion theory

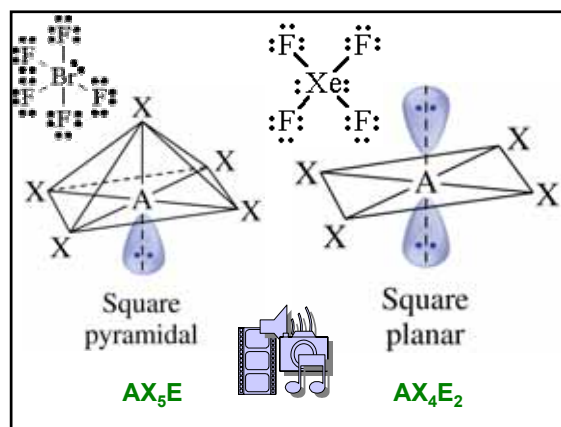
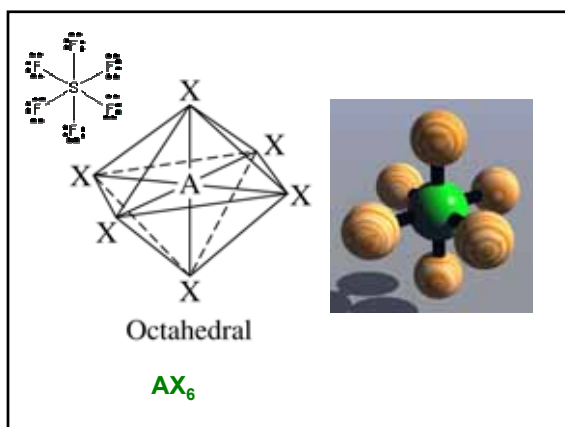
- ◆ write the electron-dot structure for the molecule
- ◆ count the number of electron charge clouds around the central atom (n)
- ◆ electron charge cloud = bonding electron pair or lone pair
- ◆ a multiple bond counts as one electron charge cloud

VSEPR

- ◆ electron charge clouds repel each other and assume positions that are the farthest away from each other
- ◆ two lone pairs repel each other more than two bonding pairs
- ◆ the shape of the arrangement of charge clouds is exclusively determined by their number
- ◆ the molecular geometry is determined by the arrangement of the charge clouds, the number of bonding electrons (X) and lone pairs (E)

n	X	E	symbol	molecular geometry	example
2	2	0	AX_2	linear	CO_2
3	3	0	AX_3	trigonal planar	BF_3
3	2	1	AX_2E	bent (angular)	SO_2
4	4	0	AX_4	tetrahedral	CH_4
4	3	1	AX_3E	trigonal pyramidal	NH_3
4	2	2	AX_2E_2	bent (angular)	H_2O
5	5	0	AX_5	trigonal bipyramidal	PCl_5
5	4	1	AX_4E	seesaw	SF_4
5	3	2	AX_3E_2	T-shaped	ClF_3
5	2	3	AX_2E_3	linear	XeF_2
6	6	0	AX_6	octahedral	SF_6
6	5	1	AX_5E	square pyramidal	BrF_5
6	4	2	AX_4E_2	square planar	XeF_4





OCTET RULE - GENERAL GUIDELINES FOR COVALENT BONDING

C, N, O, F: almost always octets in covalent molecules

C: 4 bonds **N:** 3 bonds **O:** 2 bonds **F:** 1 bond

H: always 1 bond

Cl, Br, I: octets except in molecules with higher electronegativity atoms (O, F)

B: usually 3 bonds (6 electrons), special structures, Lewis acids

Al, Ga, In, Tl: usually ionic compounds

STEPS OF WRITING LEWIS STRUCTURES

1. Find total number of valence electrons, add one for negative, subtract one for positive charges

$$\text{e.g. } SF_4 \quad 6 + 4 \times 7 = 34$$

2. Draw one line to represent each bond, remember general guidelines.



3. Calculate number of remaining electrons, assign them to terminal atoms to create octets.

$$34 - 8 = 26$$



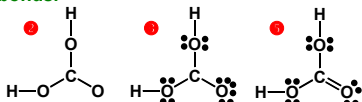
STEPS OF WRITING LEWIS STRUCTURES

4. If unassigned electrons remain, place them on the central atom.

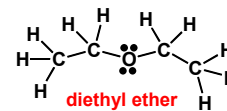
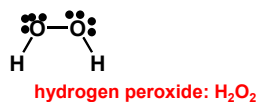
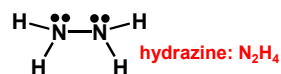
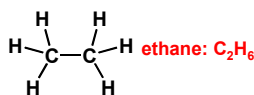


5. If no unassigned electrons remain for step 4, but the central atom still does not have an octet, use non-bonding electron pairs on terminal atoms to make double bonds.

H_2CO_3 ● ● ● ●
24 electrons



LEWIS STRUCTURES OF POLYATOMIC MOLECULES

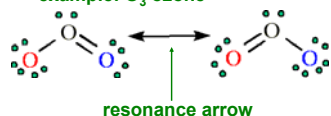


$C_4H_{10}O$ $C_2H_5OC_2H_5$
 $CH_3CH_2OCH_2CH_3$

RESONANCE

More than one possible Lewis structures

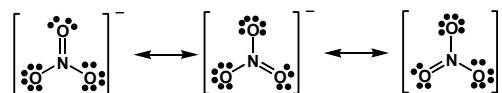
example: O₃ ozone



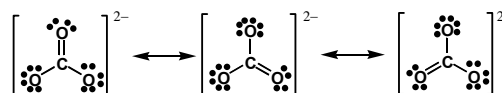
the two resonance hybrids differ only in the placement of valence electrons

the average of the two is the actual structure: the two oxygen-oxygen bonds are equivalent

EXAMPLES OF RESONANCE



NO₃⁻ nitrate ion



CO₃²⁻ carbonate ion

FORMAL CHARGES

Electron balance of an atom within the molecule

Never imply actual charges on atoms

Depend on the particular resonance hybrid chosen

$$\text{FORMAL CHARGE} = \left(\text{Number of valence electrons in free atom} \right) - \left(\text{Number of valence electrons in bonded atom} \right)$$

$$\text{FORMAL CHARGE} = \left(\text{Number of valence electrons in free atom} \right) - \frac{1}{2} \left(\text{Number of bonding electrons} \right) - \left(\text{Number of nonbonding electrons} \right)$$

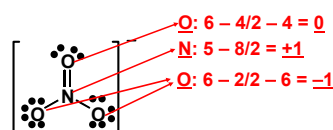
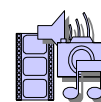
FORMAL CHARGES



ammonium ion

$$\text{N: } 5 - 8/2 = +1$$

$$\text{H: } 1 - 2/2 = 0$$



$$\text{O: } 6 - 4/2 - 4 = 0$$

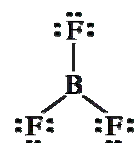
$$\text{C: } 4 - 8/2 = 0$$

$$\text{O: } 6 - 2/2 - 6 = -1$$

carbon dioxide

$$\text{C: } 4 - 8/2 = 0$$

$$\text{O: } 6 - 4/2 - 4 = 0$$



boron trifluoride

$$\text{B: } 3 - 6/2 = 0$$

$$\text{F: } 7 - 2/2 - 6 = 0$$

QUANTUM MECHANICAL DESCRIPTION OF COVALENT BONDS

VB: Valence bond method

some of the orbitals in the valence shells of atoms interact with orbitals in neighboring atoms to form bonds

MO: molecular orbital method

All electrons originally in separate atoms are on new molecular orbitals (σ or π , bonding, nonbonding, and antibonding)

Conclusions from the two different methods are often very similar.

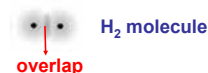
VALENCE BOND METHOD

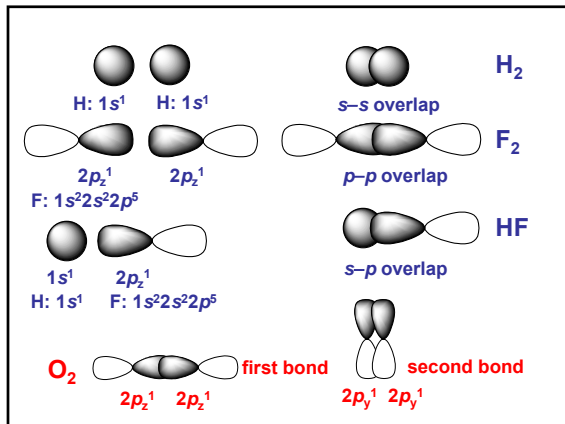
Quantum mechanical basis of Lewis dot structures

KEY IDEAS:

1. Covalent bonds are formed by overlap of singly occupied atomic orbitals.
2. Bonded atoms maintain their atomic orbitals, but overlapping orbitals are shared.
3. The greater the overlap, the stronger the bond.

Resonance is very important.





HYBRIDIZATION

Problem with VB theory: the directions of atomic orbitals do not match the experimentally confirmed shape of molecules e.g. CH₄, NH₃, H₂O

Hybridization: a tool to interpret the shapes of molecules in VB theory

known shape of molecule ⇒ hybridization of atoms

Mathematical basis

if wave functions Ψ_1 and Ψ_2 (two atomic orbitals) are solutions of the Schrödinger equation, then

$C_1\Psi_1 + C_2\Psi_2$ is also a solution

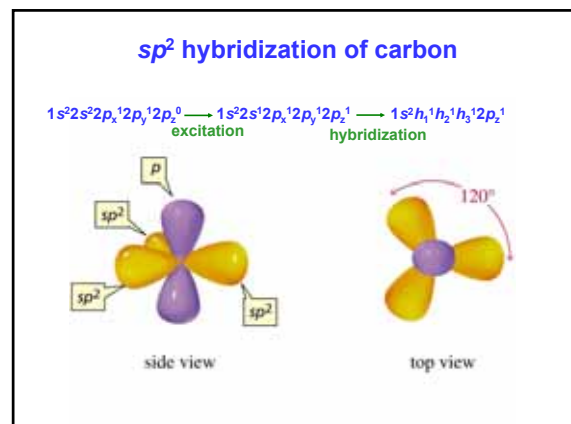
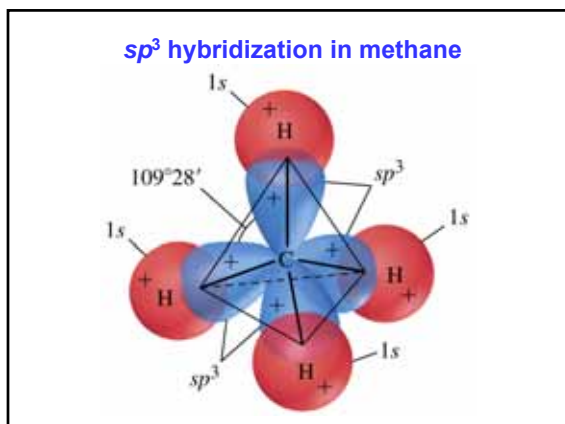
HYBRIDIZATION OF CARBON

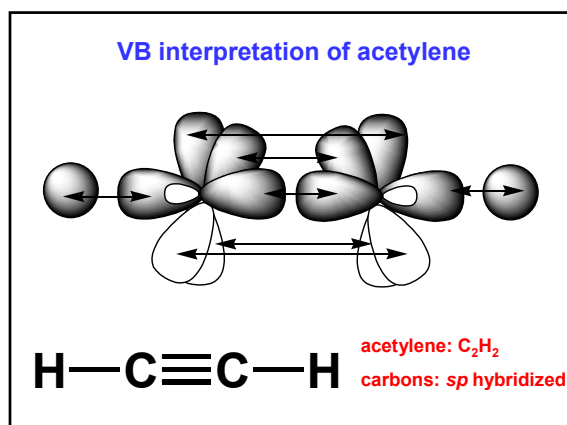
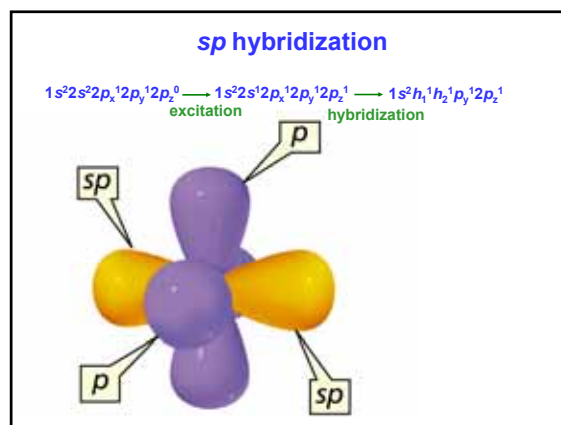
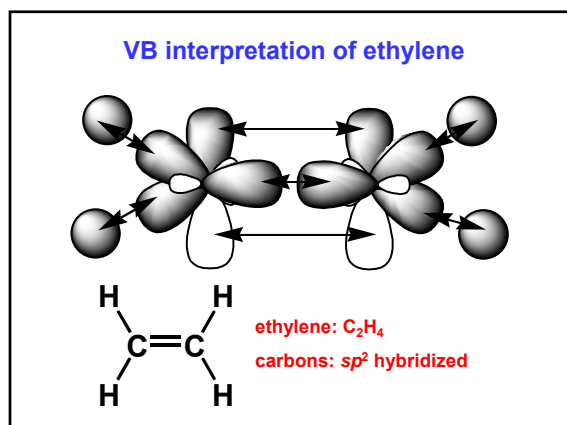
1s²2s²2p_x¹2p_y¹2p_z⁰ 1s²2s¹2p_x¹2p_y¹2p_z¹ 1s²h₁¹h₂¹h₃¹h₄¹

$\Psi(h_n) = c_{1n}\Psi(2s) + c_{2n}\Psi(2p_x) + c_{3n}\Psi(2p_y) + c_{4n}\Psi(2p_z)$

Hybrid orbitals (h₁, h₂, h₃, h₄):
equivalent orbitals in tetrahedral directions

Use of hybrid orbitals:
bond formation by overlapping with other atomic or hybrid orbitals in the usual VB way





HYBRIDIZATION OF OTHER ATOMS

sp^3 , sp^2 and sp hybridization: very common

sp^3 N in NH_3 , O in H_2O

sp^3d hybridization: five equivalent orbitals, trigonal bipyramidal spatial structure

e.g. P in PCl_5

sp^3d^2 hybridization: six equivalent orbitals, octahedral spatial structure

e.g. S in SF_6

MOLECULAR ORBITAL THEORY

Electrons in a molecule: belong to the whole molecule and not to individual atoms or pair of atoms

NO need for resonance structures!!

- All electrons in a molecule are on molecular orbitals (MOs)
- Molecular orbitals are formed by the combination of original atomic orbitals (LCAO method = linear combination of atomic orbitals)
- MOs lower in energy than combined atomic orbitals \Rightarrow BONDING ORBITALS
MOs higher in energy than combined atomic orbitals \Rightarrow ANTIBONDING ORBITALS

MOLECULAR ORBITAL THEORY

- Electrons fill the orbitals according to the *Aufbau* principles (same as for atoms)
- Bond order: the difference between the number of electron pairs in bonding and antibonding orbitals
- Symmetry considerations are important in selecting which atomic orbitals can be combined
- Frontier MOs are important
 - HOMO: highest occupied molecular orbital
 - LUMO: lowest unoccupied molecular orbital

