#### Localized chemical bonds

# bonds are the net interaction of electrons with nuclei (Traylor and Traylor)

## energy determined by position in space relative to nuclei and electrons

## electrons occupy molecular orbitals, MO

## MO = linear combination of atomic orbitals

# MO properties based on atomic orbital properties

## if AO’s have high energy then MO’s have high energy

## energy related to distance from nuclei and number of nodes (i.e. where  = 0)

## Compare the wave functions for 1s, 2p, and 2s orbitals in Figure 1-5.bmp

### Two components radial (r) and angular (**)

###

K =constant, r = distance from nucleus, a0 = atomic radius, = angle with Z axis

### All orbitals have a node at r = ∞, p obital has a node at r = 0

### 2p orbital also has angular dependence, = 0 at 90 and 270o

### 2s orbital has a node at 2 - Zr/ao i. e.  changes sign

### 3s has two nodes, as does 3p, what about 3d?

### # of finite nodes = quantum level - 1

## nodes are apparent on macroscopic level: guitar string and waves (Figure 1-3.bmp)

## angular properties are shown in figure 1-10.bmp

## figure 1-9.bmp shows nodal properties

## Signficance of sign of  ? No physical significance, determines the overlap of orbitals consider s and p, or p and d overlap

##  Electron density is related to (r): figure 1-6.bmp

### total density at distance r from nucleus is 4r2(r): figure 1-6.bmp

###  note that density goes up near nucleus but the volume (4r2dr) goes down

##  The size of the orbital changes as the effective nuclear charge decreases: see 2s and 2 p orbitals, Figure 1-16.bmp

# atomic orbitals added and substracted to make molecular orbitals

## natural concept: electrons occupy space similar as in atoms, orbitals perturbed by other nuclei

##  MO for two atoms and two orbitals  Figure 2-2.bmp

## Plot the mathematical expression: Figure 2-3.bmp

### Note two components of  are identical but offset by half the bond length!

##  Number of orbitals does not change #AO’s = # MO’s

## Form bonding and and antibonding MO’s ,

##   and \*, formed from overlap of orbitals with no node along bond axis

##   and \* formed from overlap of orbitals with one node along bond axis

##  overlap is maximized versus charge repulsion

##  Only valence orbitals have significant overlap: Figure 2-4.bmp

## p-p and d-p overlap, Figure 2-8.bmp

## orbitals only effectively overlap with correct symmetry along bond axis

# Hybridization

## mathematically similar to bond formation

##  superposition of orbitals on one nucleus, Figure 3-7.bmp

##  advantage of hybridization? directional: Figure 3-9.bmp

## Plot of overlap integral = S =

### Note s-s () and p-p () orbitals has a unit overlap at r = 0

###  s-p overlap is zero (not shown) at r = 0

###  p-p () has small overlap and goes to zero at r = 0

###  Note that sp, sp2, and sp3 have large overlap at bonding distances (~1 Å)

### sp, sp2, and sp3 “point” in one direction unlike s or p.

## How do you determine hybridization?

### conservation of obitals: count  bonds, one p used for each  bond

###  remaining p and s orbitals are hybridized.

## sp3 hydridization implies 4 identical orbitals methane

###  PES: photoelectron spectroscopy

### Consider PES for boron atom: it should have 3 bands, 1s2, 2s2, 2p (2 valence bands)

### CH in methane, apparently has 4 identical  bonds

### methane should have one valence band for 4  bonds and one band for the carbon 1s2

### PES of methane indicates there are not 4 bonds using 4 equivalent sp3

### PES gives two valence bands, 14 (6e in t2 level, 3C 2p and 4H 1s) and 23 ev (2e in a1 level, carbon 2s and 4H 1s)

a1 t2

### Differences not detectable by other techniques

Physical/Chemical Properties

# electronegativity - tendency to attract electron density, determines reactivity of molecule

# dipole - created in molecule by differences in electronegativities and/or electron delocalization (azulene), center of negative and positive charges at different positions, dipole increases with distance between centers and magnitude of charges

# inductive effects - atoms or functional groups polarize adjacent groups (attraction or repulsion of charge) through bonds (polarized bonds create electron deficiency or electron excess

# field effects - polarization through space (example of one independent of the other? diammonium norbornane?)

#  bond lengths - constant unless atoms change, orbitals change, substituents change (show examples)

# bond angles - varies with hybridization, functional groups (electronegativity and steric bulk), lone pairs

# p orbital better donor than s (why?), electronegative group bonds with orbitals of greatest p character, remaining orbitals have more s character (*i. e.*, CH3Cl)

Bond Strengths show examples

# stronger with better overlap and low energy atomic orbitals, CC versus CO

# strong bonds with electronegative atoms, H (good overlap without repulsion)

<http://www.cem.msu.edu/~reusch/OrgPage/bndenrgy.htm#dissbe>

<http://www.sartep.com/chem/chartsandtools/bondenergy.cfm>

# shorter onds are stronger, more s character, bonds are weaker with steric repulsion or conjugation, stability of fragments

# bond dissociation energy - specific to molecule and site like norbornane v heptane

# average bond energy - average from several compounds

# bond energies can be used to calculate heats of reaction = difference of bonds formed and broken: methane and chlorine, HCl (102 kcal/mol) ClCl (57)

# affect how fast bonds are broken and equilibria

Delocalized chemical bonds (electrons)

# evidence of resonance energy

## definition: extra energy associated with alternate Lewis structures

## Often resonance energy is overestimated

### calculated enthalpy of formation from bond energies based on non-resonant compounds

### does not take into account stabilization due to hybridization changes

### benzene versus cyclohexatriene

### cyclohexene H(hydrogenation) = -28.6 kcal/mol, benzene = -49.8 kcal/mol ≠ 3x(-28.6) = -85.6. sp3- sp2 C-C bond not a good model for cyclohexatriene sp2-sp2single bond

## equivalent bond lengths in benzene definitive evidence of resonance

##  butadiene is planar, barrier is not steric effect



# HMO: Huckel Molecular Orbitals

##  orbitals are formed from adjacent p orbitals of conjugated polyenes and related compounds

## Signs/nodes pattern same as guitar string

## Number of nodes increase as energy increases

##  Alternating  plane and C2 symmetry (signs and coefficients: latter changes with diffent nuclei)

## Relative energies can be calculate from simple formula

### ,  for j = 1 to n (all carbon)

### E is the energy of a molecular orbital with one electron

### n is number of carbon atoms in chain

### j indicates specific molecular orbital

###  is Coulomb integral, energy of p orbital (negative)

###  is resonance integral (negative) bonding energy of 1e in ethane orbital

### n = 2 for ethene, 2cos/3 = 1 for j= 1, therefore  is bonding energy in ethane

### enegies of orbitals are symmetrical above and below 

### odd polyenes have extra orbital where E =  when j/n+1 = ½

### middle orbital always has same energy as p orbital

## HMO obtained by mixing atomic orbitals:

### Coefficients determine how much of each atomic orbital

### Coefficients are normalized and total contribution =

### exact calculation coefficients of MO, in text

## examine MO's for ethene, allyl, butadiene, pentadiene

### node occurs when sign of adjacent orbitals change

### First HMO has no node

### Each subsequent HMO has additional node

### Atomic orbitals with same sign have bonding interaction

### orbitals with opposite sign have antibonding interaction

### consider empty, radical, lone pair conjugation in allylic system

### butadiene  electrons are lower and higher in energy then ethene's

### compare reactivities and energies of methyl anion, ethene and allyl anion, (similarly for cation, ethene and allyl cation)



# perturbation theory

## allyl anion v enamine v carboxylate

## cross conjugation – ketone versus ester pKa competing conjugation inhibited

# favored resonance forms

## compare Lewis structures energetically

## electrons move but atoms do not

## maximize number bonding electrons (ketone versus amide)

## atoms contributing orbitals to delocalized bonds are coplanar

## forms with charge separation and fewer bonds are higher energy

## no distorted bond angles or length (norbornanone, amide at bridge)

## negative charge is on most electronegative atoms, etc. (nitrosomethane)

# p-d bonding and ylids

##

##  bonds with S and P with neutral formal charge have dipolar resonance form

## p-dbonds are ussually to O and C

## for C, known as ylide, signifcant charge on C makes it good nucleophile

# Hyperconjugation

## no-bond resonance form

## a better picture:  +  MO, 3-center two-electron bond

,, 

# Tautomers

# structural isomers in rapid equilibrium, usually proton shifts

# keto-enol, most enols are unfavorable, can be important intermediates, favored by stabilization of OH or C=C



# nitroso-oxime, CH3-N=O →CH2=NOH

# nitro-aci, CH3-NO2 → CH2=NO2H

# imine-enamine, CH3CH=NH → CH2=CHNH2

# Non-covalent bonding

# hydrogen bonds: three-center 4 electron bonds

## AH-B, three center MO, compare with two center

## A and B = O, N or F

## most are between 3-6 kcal/mol

##  lifetime on order of picoseconds

## linear, repulsion of A- and B-

## detection of H bonding: AH stretch, lower frequency with hydrogen bonding

## CH hydrogen bonding, for ethyne, hydrogen cyanide, chloroform (related halocarbons)

## SH forms weak hydrogen bonds, S and P can be lone-pair donor

## F-> Cl-> Br-> I-, carbanions and isonitriles can be lone pair donors

## very weak hydrogen bonds with  electrons and cyclopropane

# electron donor-acceptor complexes

## coordination complexes,  donation and  backbonding, get for benzene, http://instruct.uwo.ca/chemistry/373f/Nifty%20Stuff/aromaticity%201.htm

## olefin-Ag+, C6H6Cr(CO)3



# charge transfer complexes: ionic bonds

## electron transfer between highly oxidized (aromatics/olefins with electron withdrawing groups) and reduced (amines and olefins with amine and hydroxyl groups) compounds

 

# cryptands and related compounds

##  poly hetero cyclic and polycyclic compounds form complexes with ions, size selective, usually ion-dipole interaction