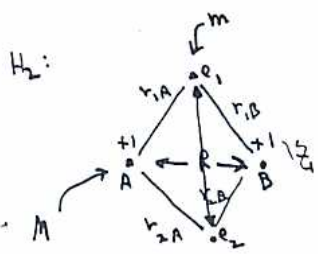


Chem. 1480  
April 16, 2007

Molecules



$$\hat{H} = -\frac{\hbar^2}{2M} (\nabla_A^2 + \nabla_B^2) - \frac{\hbar^2}{2m} (\nabla_1^2 + \nabla_2^2) + \frac{Ze^2}{4\pi\epsilon_0 R} + \frac{e^2}{4\pi\epsilon_0 r_{12}} - \frac{Ze^2}{4\pi\epsilon_0} \left( \frac{1}{r_{1A}} + \frac{1}{r_{1B}} + \frac{1}{r_{2A}} + \frac{1}{r_{2B}} \right)$$

Born-Oppenheimer: Clamp nuclei (for now);  $\nabla_A^2, \nabla_B^2 \rightarrow 0$ ,  $R \rightarrow$  "parameter"

thus, in AU's

$$[Z=1] \quad \hat{H} \rightarrow -\frac{1}{2} (\nabla_1^2 + \nabla_2^2) + \frac{1}{R} + \frac{1}{r_{12}} - \left( \frac{1}{r_{1A}} + \frac{1}{r_{1B}} + \frac{1}{r_{2A}} + \frac{1}{r_{2B}} \right); \quad \psi \rightarrow \psi(r_1, r_2; R)$$

Atomic units:

$\hbar = m_e = e = 4\pi\epsilon_0 = 1$ ; Then Bohr radius =  $4\pi\epsilon_0 \hbar^2 / m_e^2 = 1 =$  "1 Bohr" [ $a_0 \rightarrow 1$ ]  
 $2(13.6\text{eV}) = 27.21\text{eV} = 1 \text{ hartree} = \frac{m_e^4}{16\pi^2 \epsilon_0^2 \hbar^2} = 1 \text{ a.u.}$   
 then  $E_{\text{hydrogen}} = -\frac{1}{2} \text{ hartree}.$   
 $e^2 / 4\pi\epsilon_0 a_0$

(1 electron)  
MO's ["hydrogenic" orbitals]

Consider

$H_2^+$   $\hat{H} = -\frac{1}{2} \nabla^2 + \frac{1}{R} - \frac{1}{r_A} - \frac{1}{r_B}$

Let  $\psi = c_1 \psi_A + c_2 \psi_B \Rightarrow \begin{vmatrix} H_{AA} - E & H_{AB} - ES \\ H_{AB} - ES & H_{BB} - E \end{vmatrix} = 0$

$$S = \int \psi_A^* \psi_B \psi_C \leftarrow \text{as before}; \quad \hat{H} \psi_A = \left(-\frac{1}{2} - \frac{1}{R} + \frac{1}{R}\right)$$

$$S \quad H_{AA} = H_{BB} = -\frac{1}{2} + J'; \quad J' = \frac{1}{R} - \int \psi_A \frac{1}{r_B} \psi_A \, d\tau$$

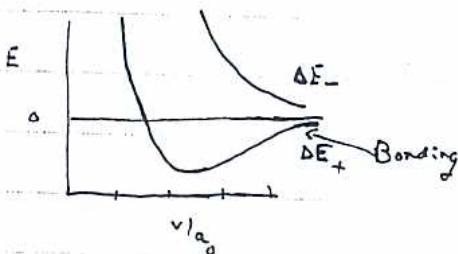
$$H_{AB} = H_{BA} = -S + K'; \quad K' = \int \psi_B \left[ \frac{1}{R} - \frac{1}{r_B} \right] \psi_A \, d\tau$$

evaluable

As for valence-band approach,  $(H_{AA} - E) = \pm (H_{AB} - ES) \Rightarrow E = -\frac{1}{2} + \frac{J' \pm K'}{1 \pm S}$

isolated  
H. + H+

$$E_{\pm} \rightarrow \begin{pmatrix} c_1 \\ c_2 \end{pmatrix} = \frac{1}{\sqrt{2(1 \pm S)}} \begin{pmatrix} 1 \\ \pm 1 \end{pmatrix}; \quad H. +$$



more details:

$$S = e^{-R} \left( 1 + R + \frac{R^2}{3} \right)$$

$$J' = e^{-2R} \left( 1 + \frac{1}{R} \right)$$

$$K' = \frac{S}{R} - e^{-R}(1 + R)$$

The energy  $\Delta E_+$  describes a stable molecular species whose dissociation energy is  $0.065 \text{ au} = 1.77 \text{ eV}$  and whose equilibrium bond length is  $2.49 \text{ au} = 0.132 \text{ nm}$ , compared to the experimental values of  $0.102 \text{ au} = 2.78 \text{ eV}$  and  $2.00 \text{ au} = 0.106 \text{ nm}$ , respectively. If we simply use  $1s$  orbitals with the exponent as a variational parameter, then we obtain a dissociation energy of  $0.083 \text{ au} = 2.25 \text{ eV}$  and a bond length of  $2.00 \text{ au} = 0.106 \text{ nm}$ .

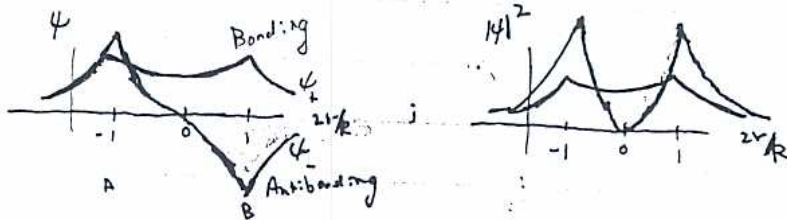
Notes: (i) improved robustness by variational minimization of  $\bar{E}$  in  $1s_A, 1s_B$

(ii) Get larger set of MO's [better approx, etc.] for larger basis of AO's.

E.g.

$$\psi_T = c_1 1s_A + c_2 2s_A + c_3 2p_z^A + c_4 1s_B + c_5 2s_B + c_6 2p_z^B \Rightarrow 6 \times 6 \text{ sec. det form; } 6 \text{ MO's}$$

Finally, w/ 1s:  
for  $H_2^+$



Hydrogen molecule,  $H_2$  for MO's:

$$\psi = \frac{1}{\sqrt{2}} [\psi_+(1)\psi_+(2) - \psi_-(1)\psi_-(2)] / \sqrt{2}$$

$$E_{gr} \equiv \int \psi \hat{H} \psi \, d\tau_1 \, d\tau_2, \quad \psi(\tau_1, \tau_2) = \frac{1}{2(1+S)} [1s_A(1) + 1s_B(1)][1s_A(2) + 1s_B(2)]$$

spin integrator out

$$\begin{aligned} E_{gr}(R) &\equiv \int \psi \hat{H} \psi \, d\tau_1 \, d\tau_2 = \frac{1}{2(1+S)} \int d\tau_1 \, d\tau_2 [1s_A(1) + 1s_B(1)][1s_A(2) + 1s_B(2)] \left\{ -\frac{1}{2} \nabla_1^2 - \frac{1}{2} \nabla_2^2 - \frac{1}{r_{1A}} - \frac{1}{r_{1B}} + \frac{1}{r_{12}} + \frac{1}{R} \right. \\ &\quad \left. - \frac{1}{r_{2A}} - \frac{1}{r_{2B}} \right\} [1s_A(1)1s_A(2) + 1s_A(1)1s_B(2) + 1s_B(1)1s_A(2) + 1s_B(1)1s_B(2)] \end{aligned}$$

$$\psi = \left[ -1 + \left( \frac{1}{r_{1A}} + \frac{1}{R} - \frac{1}{r_{1B}} - \frac{1}{r_{2A}} \right) \right] 1s_A(1)1s_A(2)$$

$$+ \left[ -1 + \left( \frac{1}{r_{1A}} + \frac{1}{R} - \frac{1}{r_{1B}} - \frac{1}{r_{2A}} \right) \right] 1s_A(1)1s_B(2)$$

$$+ \left[ -1 + \left( \frac{1}{r_{1A}} + \frac{1}{R} - \frac{1}{r_{1B}} - \frac{1}{r_{2A}} \right) \right] 1s_B(1)1s_A(2)$$

$$+ \left[ -1 + \left( \frac{1}{r_{1A}} + \frac{1}{R} - \frac{1}{r_{1B}} - \frac{1}{r_{2A}} \right) \right] 1s_B(1)1s_B(2)$$

Note: (i) Increase  $E_g$  by varying  $\frac{Z}{r}$ .

Covalent [VB]

Ionic

(ii) Character of MO  $H_2$  trial function  $\cong [1s_A(1)1s_B(2) + 1s_A(2)1s_B(1)] + [1s_A(1)1s_B(2) - 1s_A(2)1s_B(1)]$

$\underbrace{\hspace{10em}}_{\psi_{VB}}$ 
 $\underbrace{\hspace{10em}}_{\psi_{ionic}}$

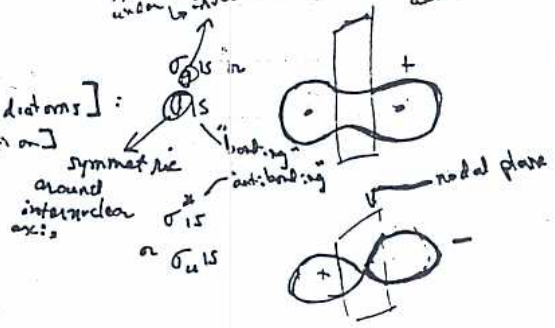
Through "soup up" VB:  $\psi_T = c_1 \psi_{VB} + c_2 \psi_{ionic}$   $\Rightarrow$  [Weitzbaum]  $c_2/c_1 = .16$  at  $R_{min}, Z=1$   
 1933  $= .26$  " ", optimized Z

Get identical result for "MO w CI", namely

$$\psi_T = \frac{1}{\sqrt{2}} \left( \psi_{+} + \psi_{-} \right)$$

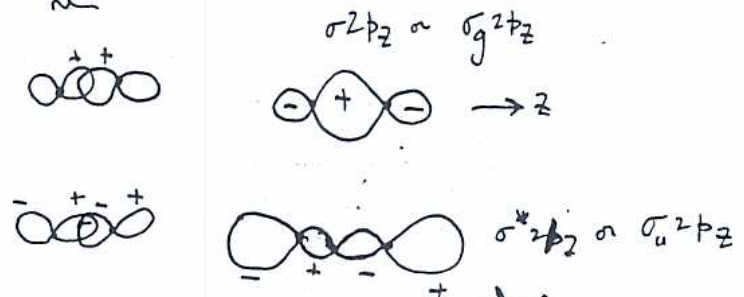
In practice, MO's [CI] easier to implement for polyatomics.

MO Aufbau [for Homonuclear diatoms]:  
 [LCAO - MO approximation]

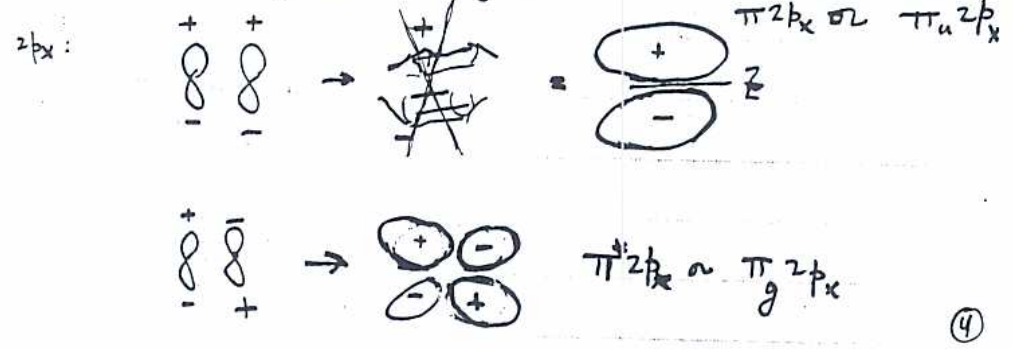


only AOs w similar energies mix strongly

Similarly for  $2p_z$ :

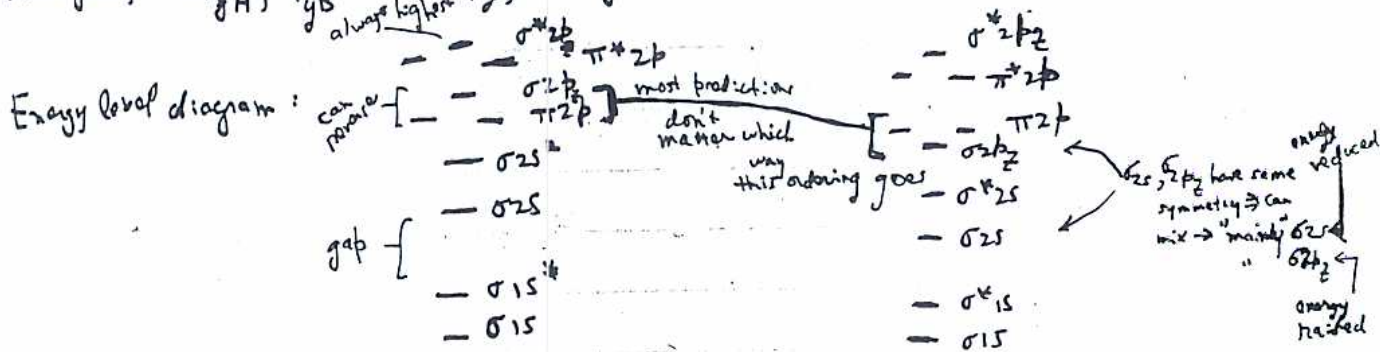


What abt.  $2p_x, 2p_y$ : not azimuthally symmetric; hence " $\pi$ "  $\leftarrow$  have nodal plane





Analogously  $2p_A, 2p_B \rightarrow \pi 2p, \pi^* 2p$



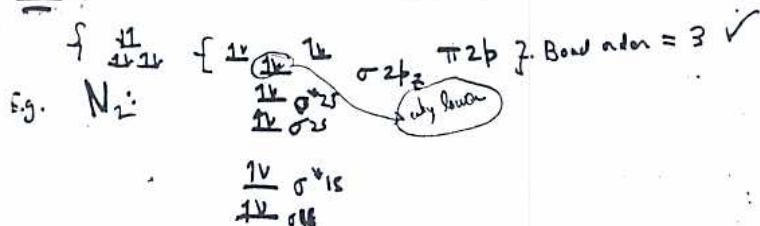
$H_2^+, H_2, He_2^+, He_2 \leftrightarrow$  "Bond Order"  $= \frac{[\#e^- \text{ in bonding orbitals}] - [\#e^- \text{ in anti bonding orbitals}]}{2} = \# \text{ of bonds}$

ground state config	BO	Exptl. Bond Energy
$(\sigma 1s)^1$	E.g. $H_2^+ = \frac{1}{2}$	255 kJ/mol
$(\sigma 1s)^2$	$H_2 = 1$	431
$(\sigma 1s)^2 (\sigma^* 1s)^1$	$He_2^+ = \frac{1}{2}$	251
$(\sigma 1s)^2 (\sigma^* 1s)^2$	$He_2 = 0$	not observed

← similar

more ...

Aufbau [Homonuclear Diatomic  $Li_2 - Ne_2$ ]

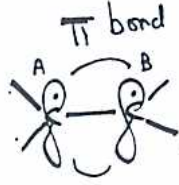


Similarly, find BO  $O_2 = 2, F_2 = 1, Ne_2 = 0$  ✓

↳ paramagnetism

also predicted via Hund's rule [all spins in different orbitals preferred]

# Hückel Theory [Pi bonding] of Ethylene



Assumptions: ① Assume  $\sigma$  core is not to  $\pi$  electrons bonding.  
 provides fixed, electrostatic potential:  $\alpha$  for isolated carbon

② [Usually]  $S_{ij} = 0 \quad i \neq j$   
 $1 \quad i = j$

Coulomb = energy of  $2p_z$  electron  
 Exchange =  $-75 \text{ kJ/m}$  [empirical]

So for ethylene,  $\psi_{\pi} = c_1 2p_{zA} + c_2 2p_{zB} \Rightarrow$

$$\begin{bmatrix} \alpha - E & \beta \\ \beta & \alpha - E \end{bmatrix} \begin{pmatrix} c_1 \\ c_2 \end{pmatrix} = 0$$

← double check  
 (i)  $\int \psi^2$  empirical  
 (ii)  $S_{12} = 0$

$\Rightarrow$

$$E_{\pi} = \alpha \pm \beta$$

$-\alpha - \beta \leftarrow$  anti-bonding

$\frac{1}{2} \alpha \leftarrow$  bonding

$\leftarrow \pi$  bond favored over non-bond by  $|\beta| \approx 150 \text{ kJ/m}$

check  $E = \alpha \pm \beta \rightarrow \begin{pmatrix} c_1 \\ c_2 \end{pmatrix} = \begin{pmatrix} 1 \\ \pm 1 \end{pmatrix} \frac{1}{\sqrt{2}}$

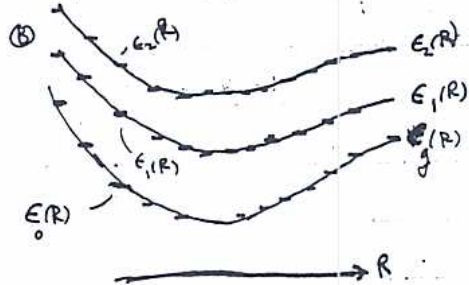
Note:

$$\pi\text{-bonding energy} = \pi\text{-bond formation energy} \equiv E_{\pi} - N\alpha$$

$\uparrow$   
 # pi electrons  
 (for ethylene,  $N=2$ )

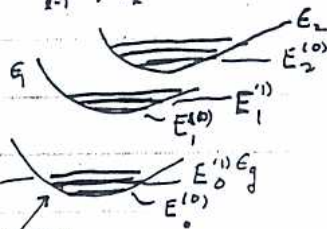
# The Born-Oppenheimer Approximation [essential for computing nuclear motion]

Born-Oppenheimer Approximation: (A) Clasp nuclei at  $R_0$ ; solve electronic structure problem



Nuclear motion on one of those surfaces:

$$\left( -\frac{\hbar^2}{2} \sum_{k=1}^N \frac{1}{M_k} \frac{d^2}{dR^2} + E_k(R) \right) \chi_k^{(0)}(R) = E_k^{(0)} \chi_k^{(0)}(R)$$



B.O. "Derivat. ansatz"  $\Psi(r, R) \approx \phi(r, R) \chi(R)$   
 (vibrations, rotations for each surface) (electronic)  
 Ansatz: system of nuclear degrees of freedom

SE:

$$\left[ -\frac{\hbar^2}{2m} \frac{d^2}{dr^2} - \frac{\hbar^2}{2M} \frac{d^2}{dR^2} + V(r, R) \right] \phi(r, R) \chi(R) = E \phi(r, R) \chi(R)$$

Note:  $\frac{d^2}{dR^2} [\phi \chi] = \phi'' \chi + 2 \phi' \chi' + \chi'' \phi$   
 neglect  $\frac{d\phi}{dR}$ ,  $\frac{d^2\phi}{dR^2}$  ← justified by  $(m/M)$  expansion.

[electronic + nuclear molecular energy levels]

then

$$\left[ -\frac{\hbar^2}{2m} \frac{d^2}{dr^2} \phi_k + V(r, R) \phi_k \right] \chi(R) - \frac{\hbar^2}{2M} \frac{d^2 \chi(R)}{dR^2} = E \phi_k \chi(R) \Rightarrow \frac{\hbar^2}{2M} \frac{d^2 \chi(R)}{dR^2} + E_k(R) \chi(R) = E \chi(R)$$

Focus on nuclear motion on one surface for diatomic,  $E_k(R_1, R_2) \rightarrow V(|R_1 - R_2|) \rightarrow V(R) =$

... in the next course!