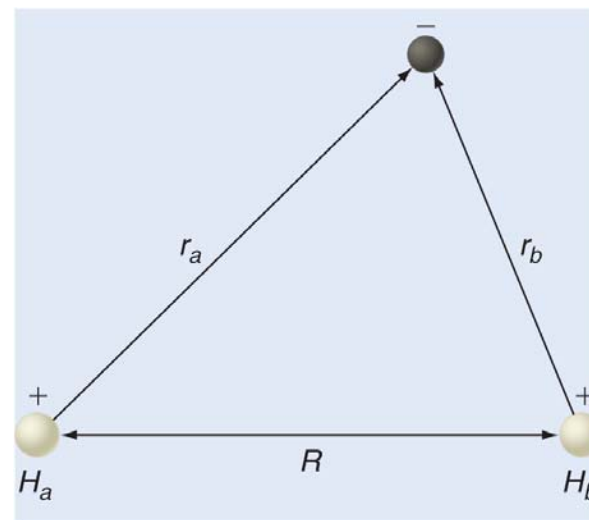


Chemical Bonding – Chapter 12

$$H_2^+$$

$$H^{e1} = \underbrace{-\frac{1}{2} \nabla^2 - \frac{1}{r_a} - \frac{1}{r_b} + \frac{1}{R}}_{\text{in atomic units}}$$



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We have assumed the Born-Oppenheimer approximation is valid

fix R → solve E(R)

R = R₁, R₂, R₃, ... → potential energy curve/surface

trial function $\psi = c_a 1s_a + c_b 1s_b$

by symmetry $|c_a| = |c_b| \Rightarrow c_a = \pm c_b$

$$\psi_+ = \psi_g = c_g (1s_a + 1s_b)$$

$$\psi_- = \psi_u = c_u (1s_a - 1s_b)$$

g: + under inversion

u: - under inversion

$$\psi(x, y, z) \rightarrow$$

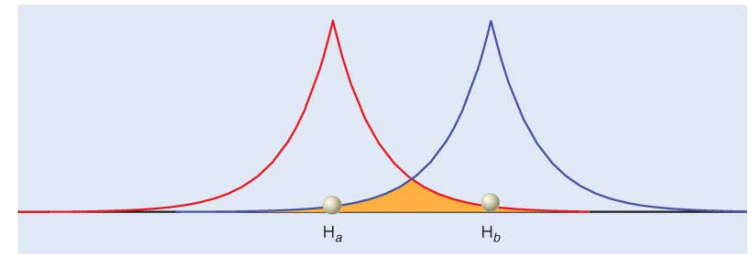
$$\pm \psi(-x, -y, -z)$$

$$c_g = \frac{1}{\sqrt{2 + 2S_{ab}}}$$

$$c_u = \frac{1}{\sqrt{2 - 2S_{ab}}}$$

$$S_{ab} = \int 1s_a 1s_b d\tau$$

overlap
falls off exponentially
as $R \rightarrow \infty$



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$$E_g = \frac{H_{aa} + H_{ab}}{1 + S_{ab}}$$

$$E_u = \frac{H_{aa} - H_{ab}}{1 - S_{ab}}$$

$$H_{ij} = \int \phi_i H \phi_j d\tau$$

$$H_{aa} = E_{1s} + \frac{1}{R} - J, \quad J = \int 1s_A \frac{1}{r_b} 1s_A d\tau \quad \text{Coulomb integral}$$

$$H_{ab} = S_{ab} \left[E_{1s} + \frac{1}{R} \right] - K, \quad K = \int 1s_b \frac{1}{r_b} 1s_a d\tau$$

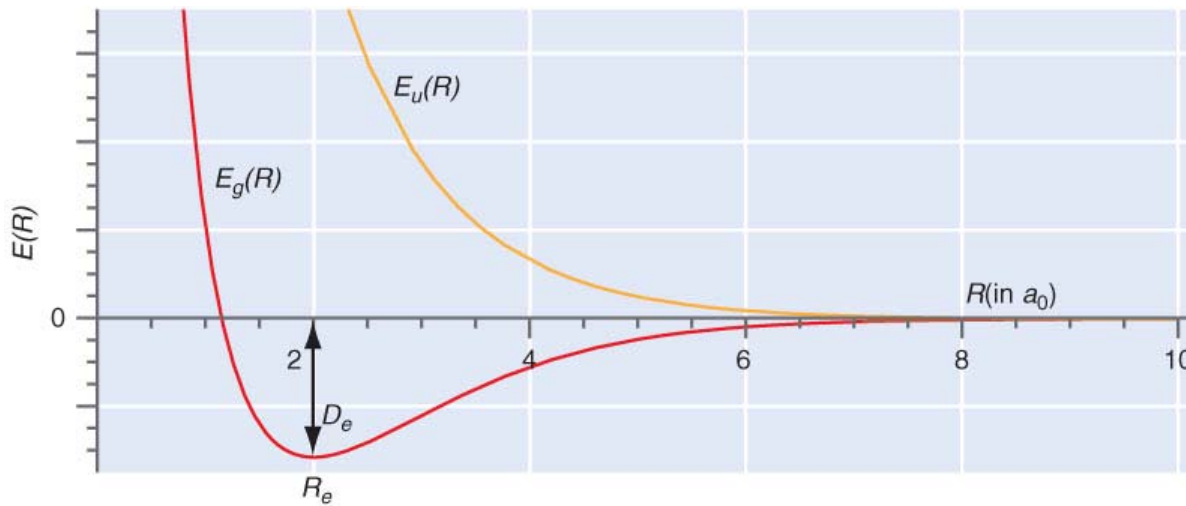
resonance or
exchange integral

$$E_g = \frac{H_{aa} + H_{ab}}{1 + S_{ab}}$$

$$= \frac{\left(E_{1s} + \frac{1}{R} - J \right) + S_{ab} \left(E_{1s} + \frac{1}{R} \right) - K}{1 + S_{ab}}$$

$$= \frac{\left(E_{1s} + \frac{1}{R} \right) (1 + S_{ab})}{1 + S_{ab}} + \frac{-J - K}{1 + S_{ab}} = E_{1s} + \frac{1}{R} - \frac{J + K}{1 + S_{ab}} \leftarrow \text{gives chemical bonding}$$

$$E_u = \frac{H_{aa} - H_{ab}}{1 - S_{ab}} = E_{1s} + \frac{1}{R} + \frac{J + K}{1 - S_{ab}}$$



$$\phi_{1s} = \frac{1}{\sqrt{\pi}} \left(\frac{\xi}{a_0} \right) e^{-\xi r/a_0}$$

find optimal ξ at each R

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at $R_e = 2a_0$, $\xi(\psi_g) = 1.24$ ← electron density contracts compared to an isolated H atom
 $\xi(\psi_u) = 0.90$

D_e from these calculations = 2.36 eV
 D_e exact = 2.70 eV

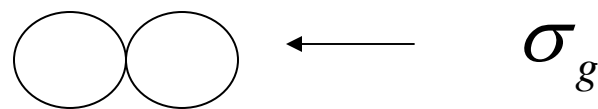
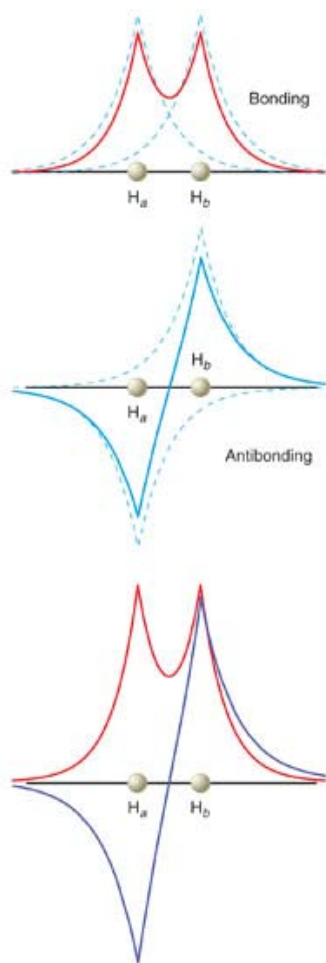
Why does our result differ from the exact value?

More complete description

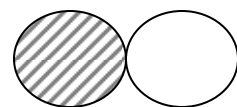
$$\psi_g = c_1(1s_A + 1s_B) + c_2(2s_A + 2s_B) + c_3 \underbrace{(2p_{zA} - 2p_{zB}) + \dots}_{\text{polarization}}$$

polarization

polarization allows for non-spherical densities around each atom with a large enough expansion \rightarrow converge to expt. D_e, R_e

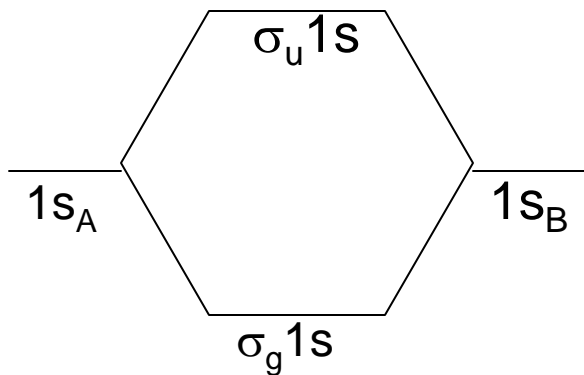


$$\langle \sigma_g 1s \equiv 1\sigma_g \rangle$$

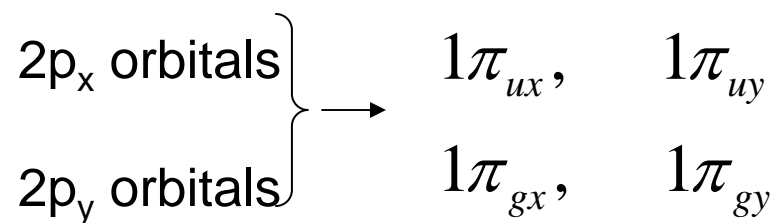
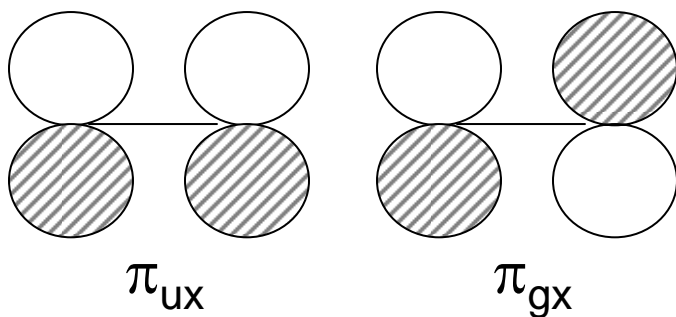
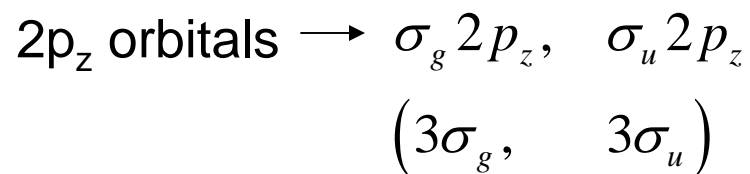
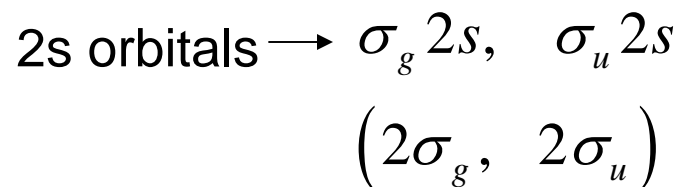


$$\langle \sigma_u 1s \equiv 1\sigma_u \rangle$$

$\sigma \Rightarrow$ cylindrically symmetrical



Similarly can combine



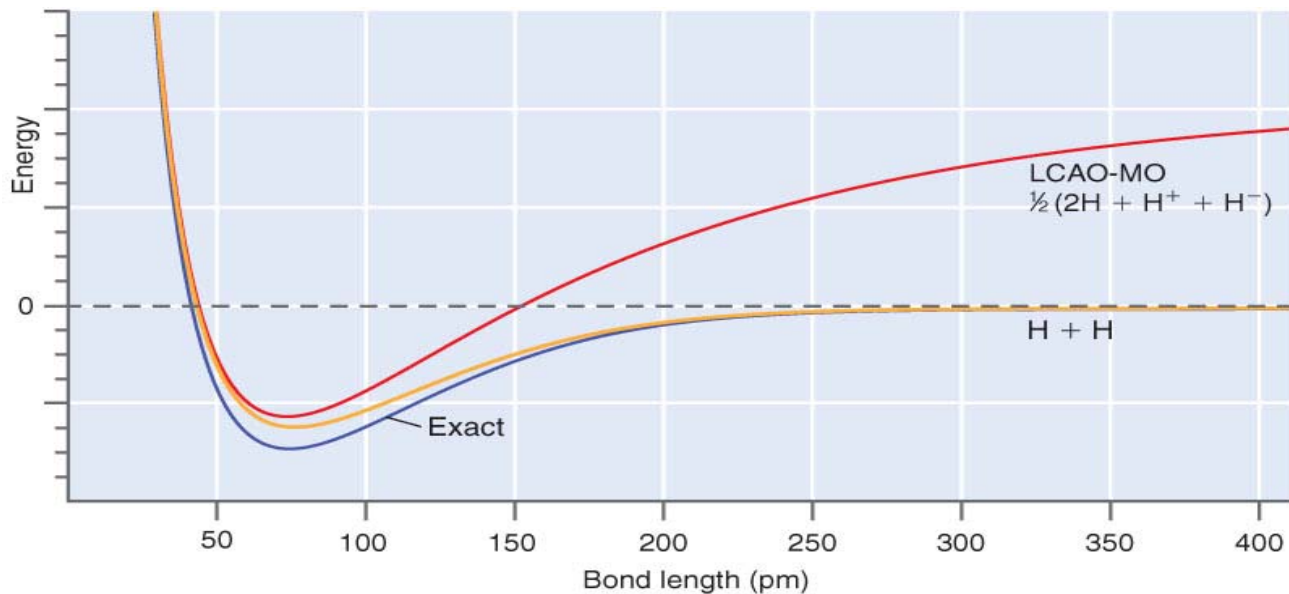
H_2 : the simplest many-electron molecule

valence-bond (VB) $\psi = (1s_a 1s_b + 1s_b 1s_a)(\alpha\beta - \beta\alpha)$

molecular orbital (MO) $\psi = \sigma_g \sigma_g (\alpha\beta - \beta\alpha)$

$$\sigma_g(1)\sigma_g(2) = (1s_a + 1s_b)(1s_a + 1s_b) =$$

$$\underbrace{(1s_a^2 + 1s_b^2)}_{\text{ionic}} + \underbrace{(1s_a 1s_b + 1s_b 1s_a)}_{\text{covalent}}$$



MO unrealistic in its dissociation ($R \rightarrow \infty$) limit

VB dissociates correctly, but does not include any ionic character for $R \approx R_e$

$$E^{VB} = 2E_{1s} + \frac{J + K}{1 + S_{ab}^2}$$

$$J = - \left\langle 1s_a 1s_b \left| \left(\frac{1}{r_{a2}} + \frac{1}{r_{b1}} - \frac{1}{r_{12}} \right) \right| 1s_a 1s_b \right\rangle$$

$$K = - \left\langle 1s_a 1s_b \left| \left(\frac{1}{r_{a2}} + \frac{1}{r_{b1}} - \frac{1}{r_{12}} \right) \right| 1s_b 1s_a \right\rangle$$

How to improve on the MO result

$$\begin{aligned} \psi &= c_1 1\sigma_g^2 + c_2 1\sigma_u^2 \rightarrow c_1 (a+b)^2 + c_2 (a-b)^2 \\ &= c_1 [a^2 + b^2 + (ab + ba)] + c_2 [a^2 + b^2 - (ab + ba)] \end{aligned}$$

$$R \rightarrow \infty$$

$$c_1 = -c_2$$