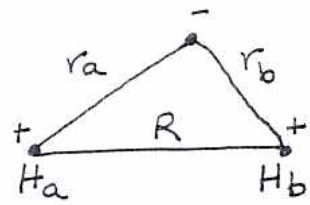
Chemical Bonding – Chpt. 12



H_2^+

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

we have assumed the Born-oppenheimer approx is valid.

fix $R \rightarrow$ solve $E(R)$

$R = R_1, R_2, R_3, \ldots \rightarrow$ potential energy curve

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

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

$$\left.\begin{aligned} c_g &= \frac{1}{\sqrt{2 + 2S_{ab}}} \\ c_u &= \frac{1}{\sqrt{2 - 2S_{ab}}} \end{aligned}\right\}$$

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

overlap

falls off exponentially as $R \rightarrow \infty$

$$\left.\begin{aligned} E_g &= \frac{H_{aa} + H_{ab}}{1 + S_{ab}} \\ E_u &= \frac{H_{aa} - H_{ab}}{1 - S_{ab}} \end{aligned}\right\}$$

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

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

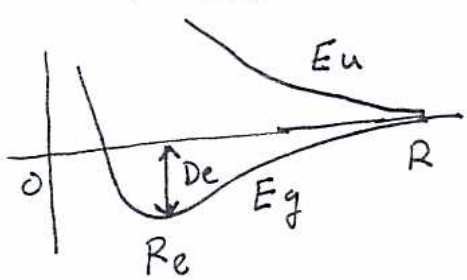
$$H_{ab} = S_{ab}\left[E_{1s} + \frac{1}{R}\right] - K \,, \quad \underbrace{K = \int 1s_b \frac{1}{r_b} 1s_a \, d\tau}_{\text{resonance or exchange integral}}$$

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

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

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

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



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

find optimal ξ at each R.

$R_e = 2\,a_0$, $\xi(\psi_g) = 1.24$ ← electron density contracts

$\xi(\psi_u) = 0.90$

D_e from these calculations $= 2.36$ eV

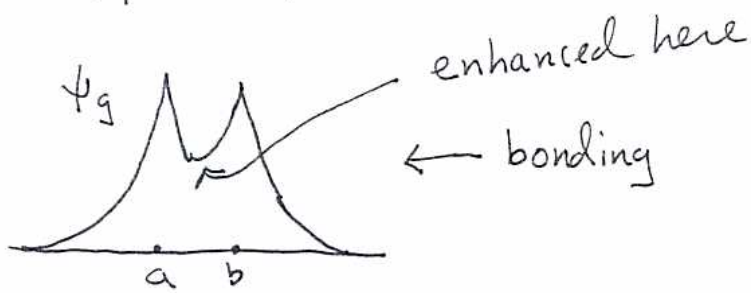
D_e exact $= 2.70$ eV

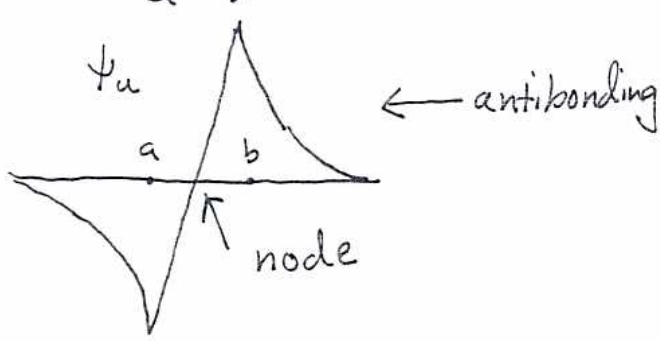
why does our result differ from the exact value?

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

polarization allows for nonspherical densities around each atom

with a large enough expansion → converge to expt D_e, R_e.





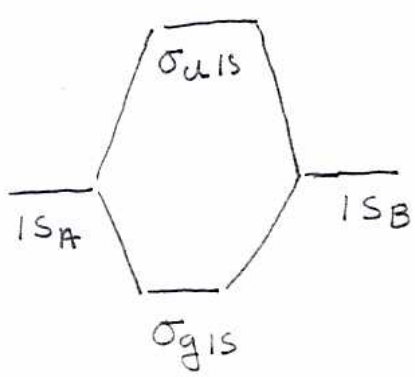

← σ_g

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


← σ_u

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

$\sigma \Rightarrow$ cylindrically symmetrical



Similarly can combine

2s orbitals → $\sigma_g 2s$, $\sigma_u 2s$ ($2\sigma_g$, $2\sigma_u$)

$2p_z$ orbitals → $\sigma_g 2p_z$, $\sigma_u 2p_z$ ($3\sigma_g$, $3\sigma_u$)


π_{ux} π_{gx}

$\left\{ \begin{array}{l} 2p_x \text{ orbitals} \\ 2p_y \text{ orbitals} \end{array} \right\} \rightarrow \begin{array}{l} 1\pi_{ux},\ 1\pi_{uy} \\ 1\pi_{gx},\ 1\pi_{gy} \end{array}$