Lecture 27

See review sheet

Localized orbitals: valence bond or hybrid basis functions

Last time: ground state of $H_2 \approx \psi_{MO} = \frac{1}{\sqrt{2}} |\sigma\rangle_1 |\sigma\rangle_2 \{\alpha_1\beta_2 - \alpha_2\beta_1\}$

($|\sigma\rangle_1$, $|\sigma\rangle_2$: bonding MOs)

$H_2 \longrightarrow H\cdot + \cdot H$

$H_2 \longrightarrow H^{+} + H^{-}$

$$\psi_{MO} = \frac{1}{\sqrt{2}}(|1s_A\rangle_1 + |1s_B\rangle_1)(|1s_A\rangle_2 + |1s_B\rangle_2) \cdot \text{spin}$$

$$= \frac{1}{\sqrt{2}}\{\underbrace{|1s_A\rangle_1|1s_A\rangle_2}_{H^{+}+H^{+}} + \underbrace{|1s_A\rangle_1|1s_B\rangle_2}_{H\cdot+H\cdot} + \underbrace{|1s_B\rangle_1|1s_A\rangle_2}_{H\cdot+H\cdot} + \underbrace{|1s_B\rangle_1|1s_B\rangle_2}_{H^{+}+H^{-}}\}$$

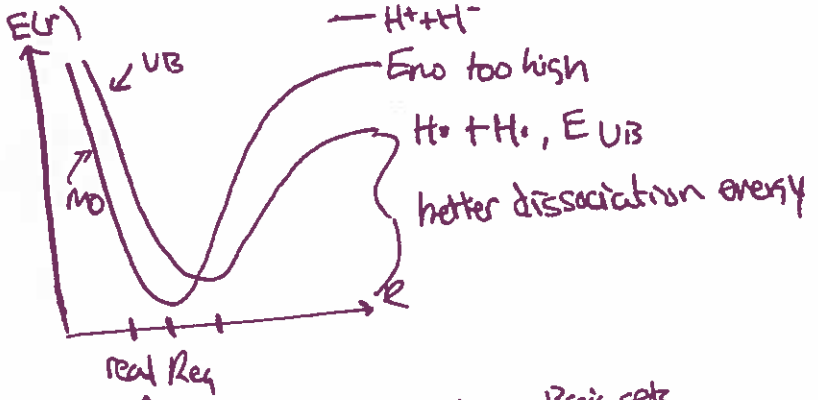
The delocalized MO does not dissociate correctly

Linus Pauling: keeps only the 'good' terms

$$\psi_{VB} = C\{|1s_A\rangle|1s_B\rangle + |1s_B\rangle|1s_A\rangle\}\{\alpha_1\beta_2 - \alpha_2\beta_1\}$$

↑ valence bond or hybrid basis function, always localized on each atom, not delocalized over the molecule

$\Rightarrow$ better dissociation, worse equilibrium geometry



↑ experiment, or very large basis sets

We can construct all kinds of "hybrid" basis functions localized on a single atom

ex 

ex $\psi_{CH} \approx |\Phi_1\rangle = \frac{1}{\sqrt{7}} \begin{vmatrix} |sp\rangle_1 \alpha_1 & |s_H\rangle_1\beta_1 \cdots \\ |sp\rangle_2\alpha_2 & |s_H\rangle_2\beta_2 \cdots \end{vmatrix} = \psi_{VB}$

Interesting fact about valence bonds basis functions

M = Me 

$\psi_{VB} = \{|D_A\rangle_1 |1S_B\rangle_2 + |1S_A\rangle_2 |1 B\rangle_1\} \cdot spin$

M > Me 

M >> Me H ⊙ H = H–H or H:H

$\lim_{M \to \infty} \psi_{VB}$ = Lewis dot structure