

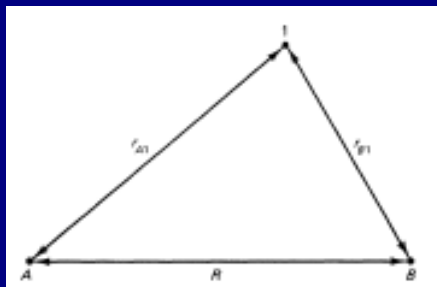
Bonding in H_2^+ : MO Theory

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H_2^+ is the simplest molecular species



The Hamiltonian is

$$\hat{\mathcal{H}} = \frac{\hat{p}^2}{2m} - \frac{e^2}{r_A} - \frac{e^2}{r_b} + \frac{e^2}{R}$$

Two equally likely dissociation pathways for H_2^+

- ① $\text{H}_2^+ \rightarrow \text{H}_A + \text{H}_B^+$
- ② $\text{H}_2^+ \rightarrow \text{H}_B + \text{H}_A^+$

When $R = \infty$, ψ has significant amplitude only “near A” and “near B”

- ① Electron “near A” $\implies \psi = c_A 1s_A$
- ② Electron “near B” $\implies \psi = c_B 1s_B$

Guess that $\psi = c_A 1s_A + c_B 1s_B$ everywhere in space

Matter wave ψ constructed by superposition of H AO

Physically measurable quantities unaffected on interchanging particle labels

- $|\psi|^2$ is unaffected by particle interchange

$$\begin{aligned} |\psi(A, B)|^2 &= |\psi(B, A)|^2 \\ \implies |c_A|^2 &= |c_B|^2 = |c|^2 \end{aligned}$$

- For real values, $c_A = c_B$ and $c_A = -c_B$ or

$$\psi = c(1s_A \pm 1s_B)$$

Normalization provides a recipe to find c .

$$\int |\psi|^2 d\tau = c^2 \int |1s_A \pm 1s_B|^2 d\tau$$
$$1 = c^2 \left(\int |1s_A|^2 d\tau \pm \int 1s_A^* 1s_B d\tau \pm \int 1s_A 1s_B^* d\tau + \int |1s_B|^2 d\tau \right)$$

When $R \rightarrow \infty$,

$$\int 1s_A^* 1s_B d\tau = \int 1s_A 1s_B^* d\tau = 0.$$

Would you know why?

$$1 = c^2(1 + 0 + 0 + 1)$$

At infinite internuclear distance $E(\text{H}_2^+) = E_H(1s)$

$$\begin{aligned} E(\infty) &= \int_{\text{all space}} \psi^* \hat{\mathcal{H}} \psi d\tau \\ &= \int_{\text{near A}} \frac{1s(A)^*}{\sqrt{2}} \hat{\mathcal{H}}_A \frac{1s(A)}{\sqrt{2}} d\tau \\ &+ \int_{\text{near B}} \frac{1s(B)^*}{\sqrt{2}} \hat{\mathcal{H}}_B \frac{1s(B)}{\sqrt{2}} d\tau \\ &= \frac{1}{2} E_H(1s) + \frac{1}{2} E_H(1s) = E_H(1s) \end{aligned}$$

Define this as the zero of energy

At finite R , ψ is approximately a sum of atomic orbitals

$$\psi_+ = c_0 (1s(A) + 1s(B))$$

$$\psi_- = c_1 (1s(A) - 1s(B))$$

Linear Combination of Atomic Orbitals (LCAO)

- ① Maximum simplicity with reasonable accuracy
- ② Natural and intuitive appeal
- ③ Simplifies calculations - atomic orbitals already determined to high accuracy
- ④ Wavefunctions around atoms in molecules like those around free atoms

Bond formation a small perturbation to atomic structure

$$\int |\psi_+|^2 d\tau = 1 = c_0^2 \left(\int |1s(A)|^2 + \int |1s(B)|^2 d\tau + \int 1s(A)^* 1s(B) d\tau + \int 1s(A) 1s(B)^* d\tau \right)$$

The overlap integral of the orbitals $1s(A)$ and $1s(B)$

$$S = \int 1s(A)^* 1s(B) d\tau, \text{ is}$$

- zero when A and B are infinitely far apart, and
- has a large contribution from regions where $1s(A)$ and $1s(B)$ are both appreciable

Because

$$\int |\psi_+|^2 d\tau = c_0^2 (1 + 1 + S + S)$$

$$\psi_+ = \frac{1s(A) + 1s(B)}{\sqrt{2(1+S)}}$$

More electron density between the nuclei in ψ_+

The electron density in the ψ_+ MO is

$$|\psi_+|^2 = \frac{|1s(A)|^2 + |1s(B)|^2 + 2(1s(A)1s(B))}{2(1 + S)}$$

S reduces the electron density everywhere.

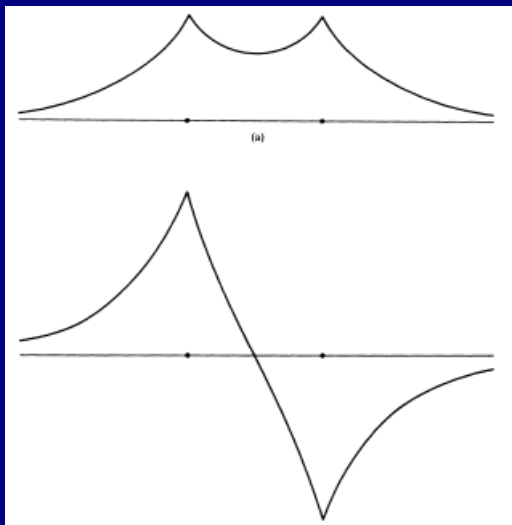
Between the nuclei $2(1s(A)1s(B))$ is dominant and

$$\implies |\psi_+|^2 > |1s(A)|^2 + |1s(B)|^2$$

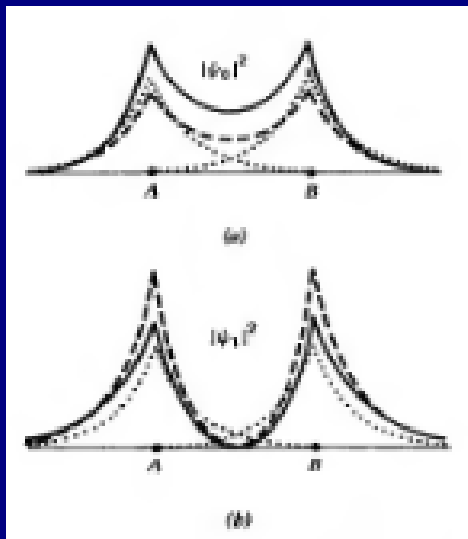
Constructive interference of the two atomic orbitals between the nuclei in ψ_+ .

ψ_+ describes a bonding state

There are 0 and 1 nodes in the two lowest MO's



Electron density in the two lowest MO's



The approximate energy of ψ_+ is given by $\int \psi_+^* \mathcal{H} \psi_+ d\tau$

$$E_+(R) = \frac{\int 1s(A)\mathcal{H}1s(A)d\tau + \int 1s(A)\mathcal{H}1s(B)d\tau + \int 1s(B)\mathcal{H}1s(A)d\tau + \int 1s(B)\mathcal{H}1s(B)d\tau}{2(1+S)}$$

Define an integral

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

$$E_+(R) = \frac{H_{AA} + H_{AB} + H_{BA} + H_{BB}}{2(1+S)}$$

$$E_+(R) = \frac{H_{AA} + H_{AB}}{(1+S)}$$

The atomic integral H_{AA} has a Coulomb term

$$\begin{aligned} H_{AA} &= \int 1s(A)^* \left(\frac{\hat{p}^2}{2m} - \frac{e^2}{r_A} \right) 1s(A) d\tau + \frac{e^2}{R} \int 1s(A) 1s(A) d\tau \\ &\quad - \int 1s(A)^* 1s(A) \frac{e^2}{r_B} d\tau \\ &= E_H(1s) + \frac{e^2}{R} + J \end{aligned}$$

where

$$J = - \int \frac{e^2}{r_B} 1s(A)^* 1s(A) d\tau$$

is the Coulombic interaction between the orbital around one atom and the other nucleus.

The resonance integral H_{AB} has an exchange term

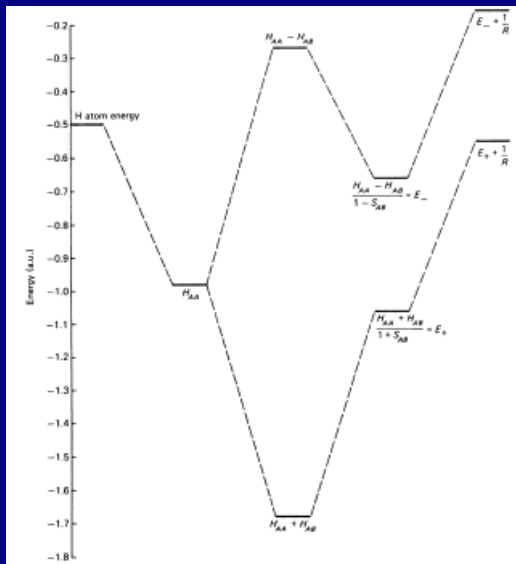
$$\begin{aligned} H_{AB} &= \int 1s(A)^* \left(\frac{\hat{p}^2}{2m} - \frac{e^2}{r_B} \right) 1s(B) d\tau + \frac{e^2}{R} \int 1s(A) 1s(B) d\tau \\ &\quad - \int 1s(A)^* 1s(B) \frac{e^2}{r_A} d\tau \\ &= S \left(E_H(1s) + \frac{e^2}{R} \right) + K \end{aligned}$$

where

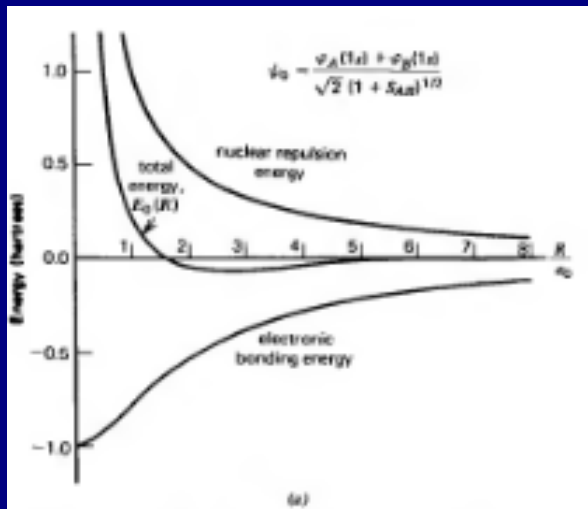
$$K = - \int \frac{e^2}{r_A} 1s(A)^* 1s(B) d\tau$$

has no classical interpretation.

In the GS the electron has a net bonding effect



Bonding energy comes from the exchange integral



The LCAO method can be generalized

If $\psi = c_1 f_1 + c_2 f_2$ then $E = \int \psi \mathcal{H} \psi d\tau$ is

$$E(c_1, c_2) = \frac{c_1^2 H_{11} + 2c_1 c_2 H_{12} + c_2^2 H_{22}}{c_1^2 S_{11} + 2c_1 c_2 S_{12} + c_2^2 S_{22}}$$

At the minimum of the energy

$$\frac{\partial E}{\partial c_1} = \frac{\partial E}{\partial c_2} = 0$$

$$c_1(H_{11} - ES_{11}) + c_2(H_{12} - ES_{12}) = 0$$

$$c_1(H_{21} - ES_{21}) + c_2(H_{22} - ES_{22}) = 0$$