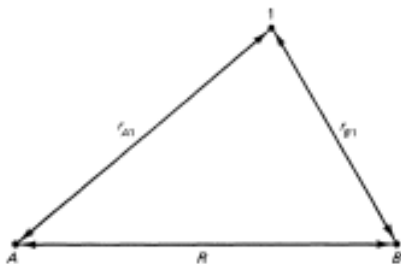# Bonding in H_2^+: MO Theory

Narayanan Kurur

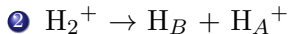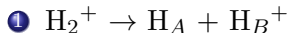Department of Chemistry
IIT Delhi

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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. $H_2^+ \rightarrow H_A + H_B^+$
2. $H_2^+ \rightarrow H_B + H_A^+$

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

$$|\psi(A, B)|^2 = |\psi(B, A)|^2$$
$$\implies |c_A|^2 = |c_B|^2 = |c|^2$$

- 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 $R \to \infty$,

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

Would you know why?

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

At infinite internuclear distance $E(H_2^+) = E_H(1s)$

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

Define this as the zero of energy

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

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

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

Normalization constant depends on the overlap integral

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

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

$$|\psi_+|^2 = \frac{|1s(A)|^2 + |1s(B)|^2 + 2(1s(A)1s(B))}{2(1+S)}$$
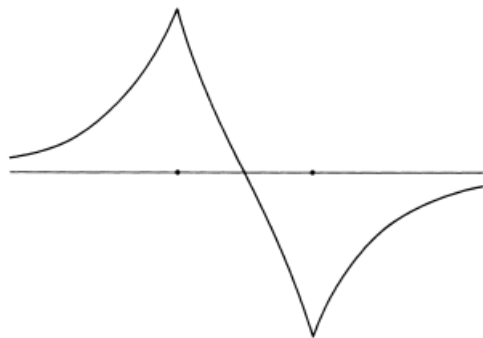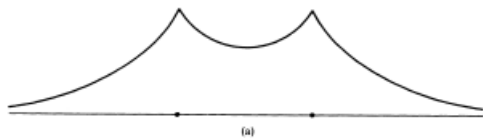
S reduces the electron density everywhere.

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_+.
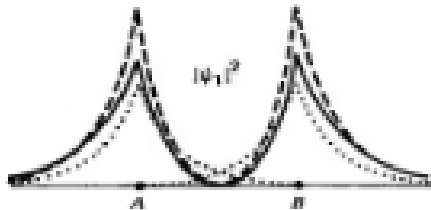
ψ_+ describes a bonding state

(a)

$|\psi_0|^2$

(a)

$|\psi_1|^2$

(b)

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

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

$$H_{AA} = \int 1s(A)^* \left(\frac{\hat{p}^2}{2m} - \frac{e^2}{r_A} \right) 1s(A)d\tau + \frac{e^2}{R} \int 1s(A)1s(A)d\tau$$

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

$$= E_H(1s) + \frac{e^2}{R} + J$$

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.
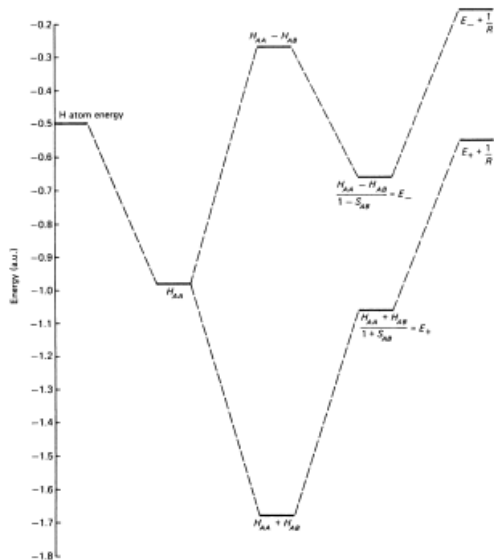
$$H_{AB} = \int 1s(A)^* \left(\frac{\hat{p}^2}{2m} - \frac{e^2}{r_B} \right) 1s(B)d\tau + \frac{e^2}{R} \int 1s(A)1s(B)d\tau$$

$$- \int 1s(A)^* 1s(B) \frac{e^2}{r_A} d\tau$$
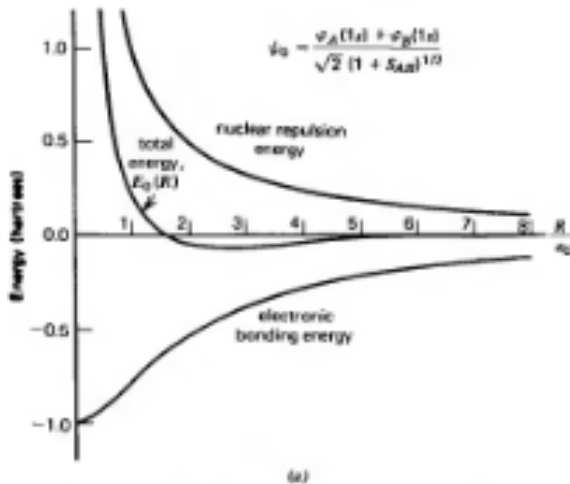
$$= S \left(E_H(1s) + \frac{e^2}{R} \right) + K$$

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

$$\psi_0 = \frac{\varphi_A(1s) + \varphi_B(1s)}{\sqrt{2}\,(1 + S_{AB})^{1/2}}$$

nuclear repulsion energy

total energy, $E_0(R)$

electronic bonding energy

(a)

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

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

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

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