

The H₂ molecule

2 electrons, must take e-e interaction into account

Separation of S.E. not possible any more

⇒ approximate, numerical methods

take Pauli Principle into account! (He atom)

b Heitler-London-approximation

$$\psi = \underbrace{\chi^+(1)\chi^+(2)}_{\text{symmetric spin wf.}} \left[\underbrace{\phi_A(\vec{r}_1)\phi_B(\vec{r}_2)}_{\substack{e^- \#1 \text{ close to proton A} \\ \text{and } e^- \#2 \text{ - " - B}}} - \underbrace{\phi_A(\vec{r}_2)\phi_B(\vec{r}_1)}_{\text{vice versa}} \right] \cdot \underbrace{N}_{\text{normalization}}$$

antisymm. pos. wf. → "ungerade"

or

$$\psi = \left[\phi_A(\vec{r}_1)\phi_B(\vec{r}_2) + \phi_A(\vec{r}_2)\phi_B(\vec{r}_1) \right] \times \underbrace{\left[\chi^+(1)\chi^-(2) - \chi^+(2)\chi^-(1) \right]}_{\text{antisymm. spin wf.}} \cdot N$$

symmetric → "gerade"

or ansatz

a

$$\psi = \psi_s(\vec{r}_1)\psi_s(\vec{r}_2) \cdot \left[\chi^+(1)\chi^-(2) - \chi^+(2)\chi^-(1) \right] \cdot N$$

↑
...
ant-spin wf. |

↑
 Symm. H_2^+ w.r.t.
 for $1e^-$ each

anti-spin-urf.
 Symm

$$= \frac{1}{2 + 2S_{AB}} \left[\chi^{(+)} \dots - \dots \right]$$

$$\cdot \left\{ \left[\phi_A(\vec{r}_1) + \phi_B(\vec{r}_2) \right] \cdot \left[\phi_A(\vec{r}_2) + \phi_B(\vec{r}_1) \right] \right\}$$

$$= \frac{1}{2 + 2S_{AB}} \left[\chi \dots \right] \times$$

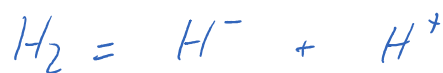
$$\times \left\{ \phi_A(\vec{r}_1) \phi_A(\vec{r}_2) + \phi_B(\vec{r}_1) \phi_B(\vec{r}_2) + \right.$$

$$\left. + \phi_A(\vec{r}_1) \phi_B(\vec{r}_2) + \phi_A(\vec{r}_2) \phi_B(\vec{r}_1) \right\}$$

Comparison: Heitler-London does not have the

states $\phi_A(\vec{r}_1) \phi_A(\vec{r}_2)$ and
 $\phi_B(\vec{r}_1) \phi_B(\vec{r}_2)$

$\hat{=}$ both e^- at the same nucleus

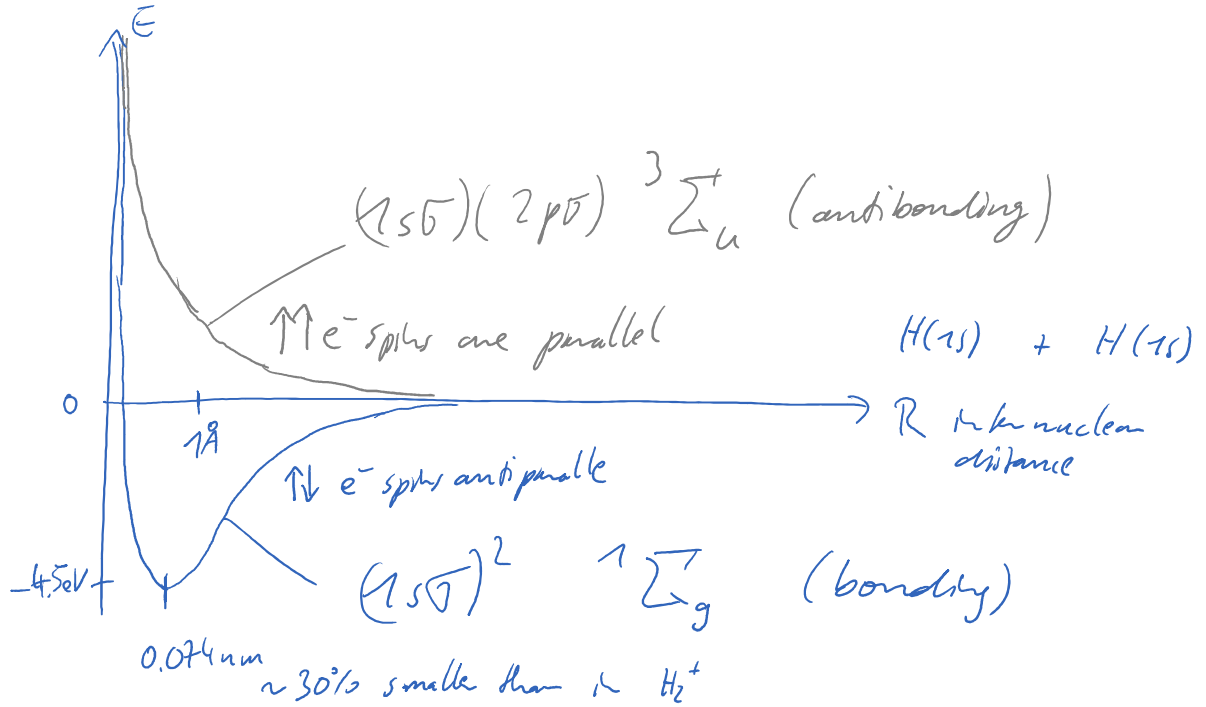


This ionic state is much less probable than

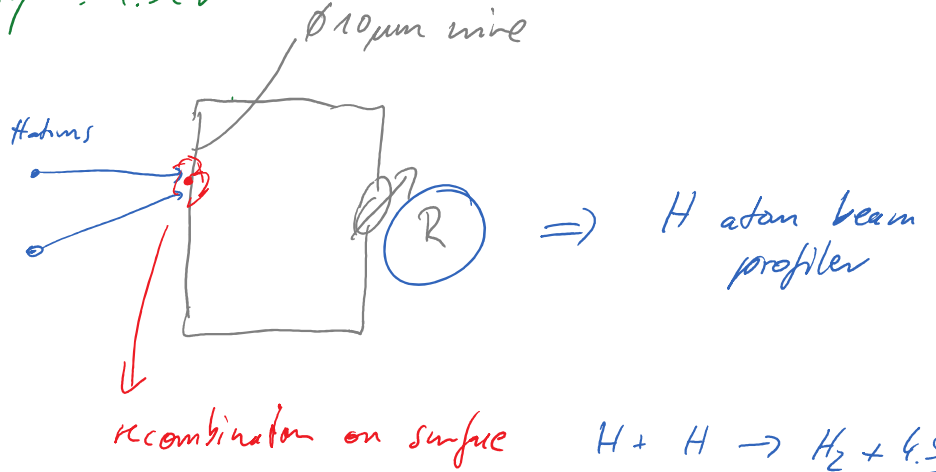
$\phi_A(\vec{r}_1) \phi_B(\vec{r}_2)$ and

$$\phi_A(\vec{r}_2) \phi_B(\vec{r}_1)$$

ignore ionic states, find equilibrium distance,
introduce ionic states as per perturbation



H_2 binding energy : 4.5eV



ΔT
↓
 ΔR