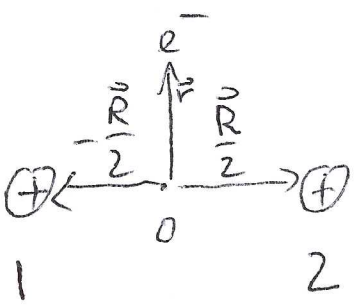
$e^- - e^-$ interaction prevents us from solving H_2 analytically.

→ find approximation methods

Linear combinations of Atomic Orbitals (LCAO)

H_2^+



$$\psi\left(\vec{r}+\frac{\vec{R}}{2}\right) = a(\vec{r})$$

$$\psi\left(\vec{r}-\frac{\vec{R}}{2}\right) = b(\vec{r})$$

$$\psi_{MO} = c_a\, a(\vec{r}) + c_b\, b(\vec{r})$$

should be normalized:

$$\int |\psi_{MO}|^2 dr = c_a^2 \underbrace{\int |a(\vec{r})|^2 d\vec{r}}_{1} + c_b^2 \underbrace{\int |b(\vec{r})|^2 d\vec{r}}_{1} + 2 c_a c_b \underbrace{\int a(\vec{r})\, b(\vec{r})\, d\vec{r}}_{\text{overlap integral } S_{ab}} \overset{!}{=} 1$$

$$\Rightarrow c_a^2 + c_b^2 + 2 c_a c_b S_{ab} = 1$$

and for H_2^+: $|c_a|^2 = |c_b|^2$

$$c^2 + c^2 + 2c^2 S_{ab} = 1$$

$$\sim \quad c = \frac{1}{\sqrt{2 \pm 2 S_{ab}}}$$

$$\psi_+ = \frac{1}{\sqrt{2+2S}} \left(\vec{a}(\vec{r}) + \vec{b}(\vec{r}) \right)$$

symmetric

g = gerade (even)

$$\psi_- = \frac{1}{\sqrt{2-2S}} \left(\vec{a}(\vec{r}) - \vec{b}(\vec{r}) \right)$$

antisymmetric

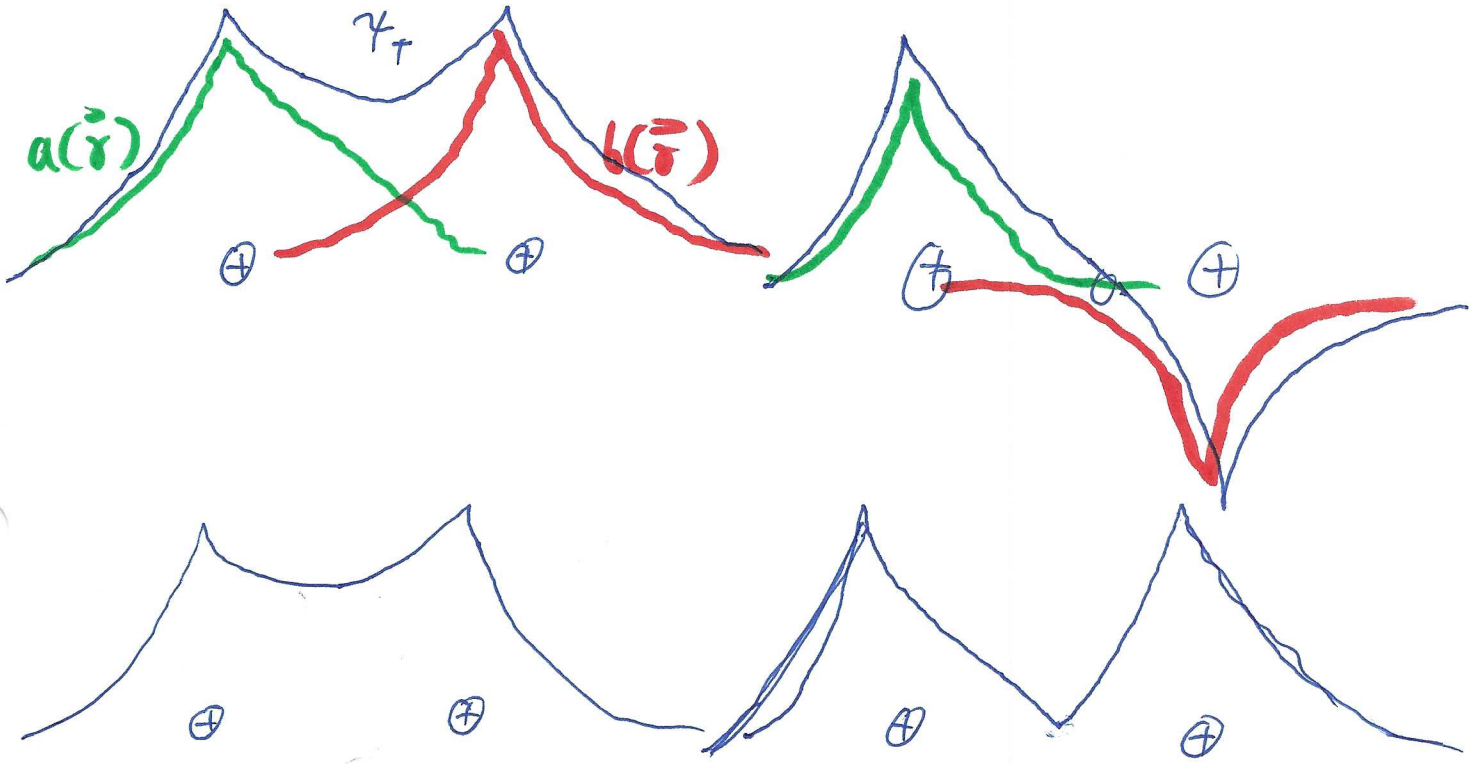
u = ungerade (odd)

$$\psi_+ = \frac{1}{\sqrt{2+2S}}\left(a(\vec{r}) + b(\vec{r})\right)$$

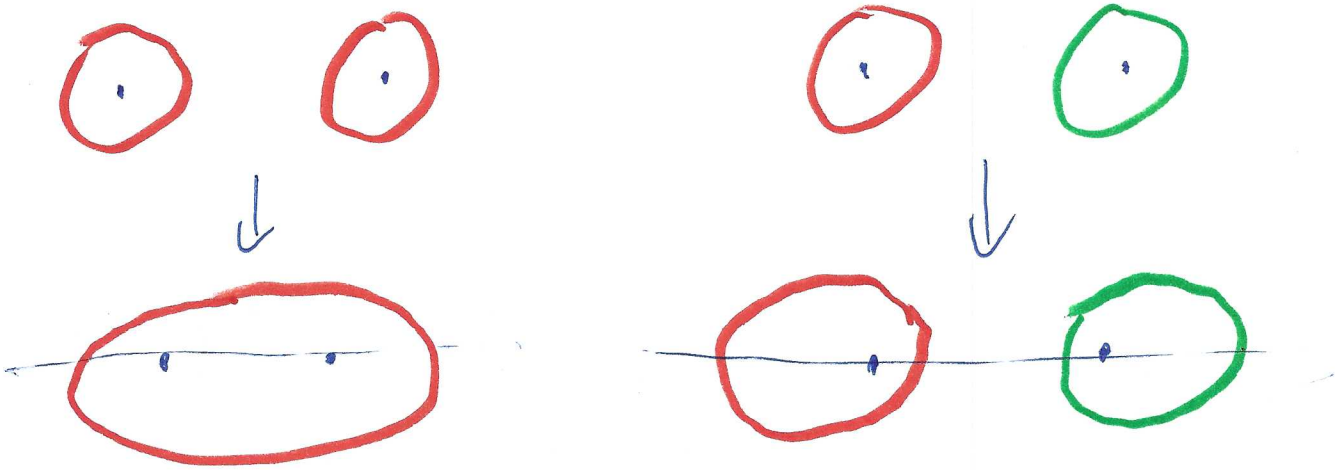
symmetric
g = gerade (even)

$$\psi_- = \frac{1}{\sqrt{2-2S}}\left(a(\vec{r}) - b(\vec{r})\right)$$

antisymmetric
u = ungerade (even)



alternative visualization



ψ_+ : increased probability in between nuclei

→ e^- attracted by both nuclei

→ lower in energy than atomic orbital

ψ_- : decreased probability in between nuclei

→ weaker binding

→ higher energy than atomic orbitals

molecular orbital diagrams :