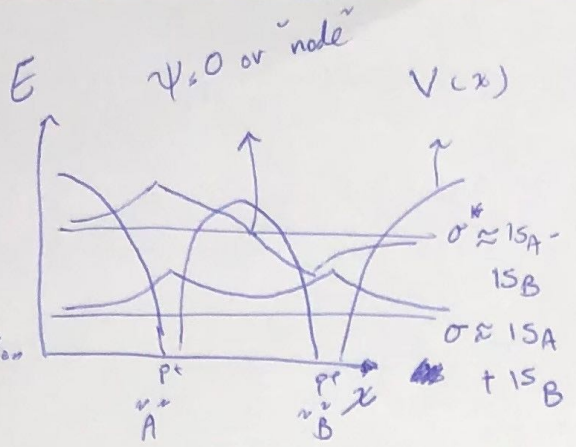
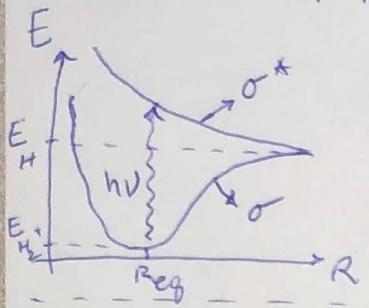
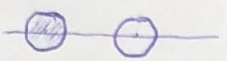
L13 : review

Bonding:

- tunneling
- quantum superposition

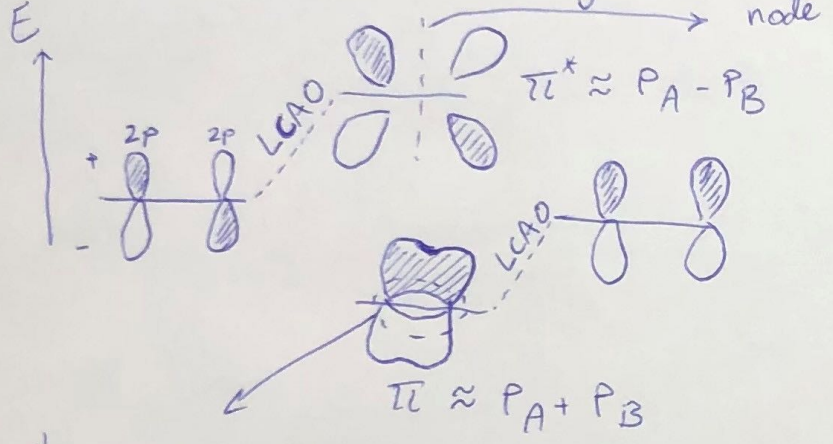




σ*: 

σ: 

Another example: π bonding

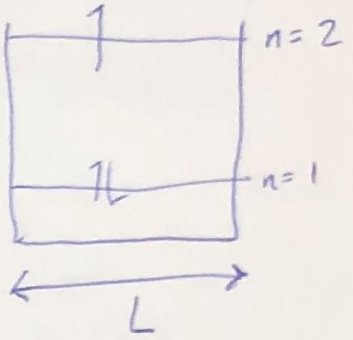


the absence of electron density along the axis of the bond makes π bond slightly weaker than σ bond.

* note the presence of an extra node in π*

Multi-e molecule:

- particle in box



thought experiment: let's say we have 2 electrons,

$\hat{H}_1 \psi_1 = E_1 \psi_1$ ($\hat{H}_1$ ↙ é #1)

$\hat{H}_2 \psi_2 = E_2 \psi_2$

} if these electrons are far enough apart, there are no "cross terms". what will the total energy E and the total wavefunction be?

$\Rightarrow E = E_1 + E_2$; $\hat{H} = \hat{H}_1 + \hat{H}_2 \Rightarrow \hat{H}\psi = E\psi$

$(\hat{H}_1 + \hat{H}_2)\psi = (E_1 + E_2)\psi$

let's say, $\psi = \psi_1 + \psi_2 \overset{?}{\Rightarrow} \hat{H}\psi = E\psi$

$\hat{H}\psi = (\hat{H}_1 + \hat{H}_2)\psi_1\psi_2 = (E_1\psi_1)\psi_2 + \psi_1(E_2\psi_2)$

$= (E_1 + E_2)\psi_1\psi_2 = E\psi$ ☑

* note that for a single particle wavefunc, e.g. H_2^+, the LCAO gives correct sdutions to the Schrödinger equation, whereas for multi-particle cases such as the example above the multiplication product is a solution and not $\psi_1 + \psi_2$.

⇒ multi-electron wavefunctions are products over single e^- wavefunctions. These functions are called "Hartree" functions.

* It is noteworthy that $\psi = \psi_1 \psi_2$ violates postulate #4:

$$\psi = \psi_1(x_1)\,\psi_2(x_2)$$

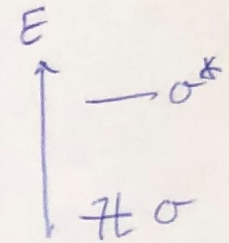
$$\psi' = \psi_1(x_2)\,\psi_2(x_1)$$

$$\psi \neq \psi'$$

⇒ ψ needs to be slightly modified

Fock to the rescue:

$$\psi(x_1, x_2) = -\psi(x_2, x_1)$$



ex: $\psi_1 = \sigma_{1+}$ (e^- #1, spin up) $\quad \psi_2 = \sigma_{2-}$ (e^- #2, spin down)

$$\psi_{\text{Hartree}} = \sigma_{1+}\,\sigma_{2-}$$

$$\psi_{\text{Hartree-Fock}} = \frac{1}{\sqrt{2}}\left(\sigma_{1+}\sigma_{2-} - \sigma_{2+}\sigma_{1-}\right)$$

↓ normalization coefficient

$$\text{normalization}: \int |\psi_{HF}|^2 \, dx_1 dx_2 = 1$$

let's see if $\psi_{\text{Hartree-Fock}}$ meets Postulate #4

Switching e^- #1 and e^- #2:

$$\frac{1}{\sqrt{2}}\left(\sigma_{2+}\sigma_{1-} - \sigma_{1+}\sigma_{2-}\right) = -\frac{1}{\sqrt{2}}\left(\sigma_{1+}\sigma_{2-} - \sigma_{2+}\sigma_{1-}\right)$$

ψ_{HF} can be expressed by the determinant of a 2×2 matrix:

$$\psi_{HF} = \frac{1}{\sqrt{2}} \begin{vmatrix} \sigma_{1+} & \sigma_{2+} \\ \sigma_{1-} & \sigma_{2-} \end{vmatrix} = \psi_{\text{determinantal}}$$

It turns out ψ_{HF} is a very good approx solution. But what did we neglect?

When we have many electrons, there is an extra type of term in the Hamiltonian,

e^- #1 and e^- #2, $\dfrac{+e^2}{4\pi\varepsilon_0 r_{12}}$