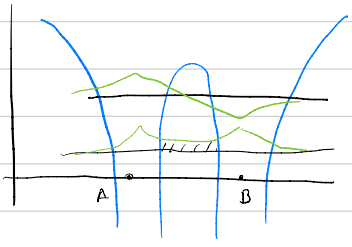
Lecture 13

Last Time: bonds and antibonds

ex:

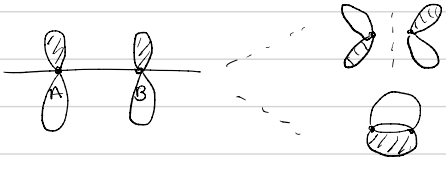


$1s_A - 1s_B$ σ^*

$1s_A + 1s_B$ σ

e^- is:
- in superposition state
- in forbidden region

ex:

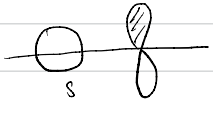


$\pi^* = p_A - p_B$

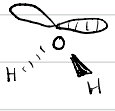
$\pi = p_A + p_B$

weaker than σ bond

ex:



nonbonding



Today: multielectron molecules (multiply!)

consider $2e^-$, satisfying $\mathcal{H}_1\Psi_1 = E_1\Psi_1$ and $\mathcal{H}_2\Psi_2 = E_2\Psi_2$. If the 2 electrons do not interact (repel) too much, what is the total energy and wave function $\Psi(x_1, x_2)$?

A: without interaction, $\mathcal{H}_1 + \mathcal{H}_2 = \mathcal{H}$

and $E = E_1 + E_2$

(energy conservation)

$\longrightarrow$

What about $\Psi(x_1, x_2)$?

$$\Psi(x_1, x_2) = \Psi_1(x_1)\,\Psi_2(x_2)$$

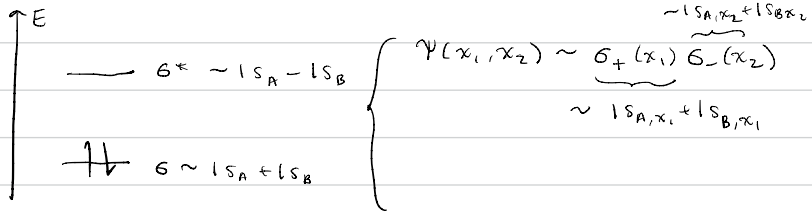
$$\begin{aligned} \mathcal{H}\Psi(x_1, x_2) &= (\mathcal{H}_1 + \mathcal{H}_2)\,\Psi_1(x_1)\,\Psi_2(x_2) \\ &= \Psi_2\,\mathcal{H}_1\Psi_1 + \Psi_1\,\mathcal{H}_2\Psi_2 \\ &= \Psi_2\,E_1\Psi_1 + \Psi_1\,E_2\Psi_2 \\ &= E_1\Psi_1\Psi_2 + E_2\Psi_1\Psi_2 \\ &= (E_1 + E_2)\,\Psi_1\Psi_2 \\ &= E\,\Psi(x_1, x_2) \end{aligned}$$

So, for 1 electron, can add up wavefunctions of same (similar) energy

For several electrons, must multiply together the above one electron wavefunctions, which can have different energies.

Product wavefunctions are called "Hartree Functions"

Ex: H_2



Ex: H_2^- (x_1, x_2, x_3) $\Psi \sim \sigma_+(x_1)\,\sigma_-(x_2)\,\sigma_+^*(x_3)$

Problem: Hartree wavefunction predicts that H_2 is unstable!

Solution:

$\Psi(1,2) = \Psi_1(1)\,\Psi_2(2)$ violates P4 (PEP)

If we switch e^- in the above wavefunction

$\Psi(1,2) = \Psi_1(1)\,\Psi_2(2) \longrightarrow \Psi(2,1) = \Psi_1(2)\,\Psi_2(1) \neq -\Psi(1,2)$ (in general)

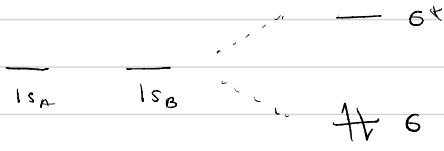
Fock: just switch and subtract

$$\Psi(1,2) \sim \Psi_1(1)\Psi_2(2) - \Psi_1(2)\Psi_2(1)$$

$$\Psi(2,1) \sim \Psi_1(2)\Psi_2(1) - \Psi_1(1)\Psi_2(2) = -\Psi(1,2)$$

"Hartree Fock"

ex: H_2 molecule



$\Psi_1(1) = \sigma_+(1) = 1s_A + 1s_B$ (spin = $+1/2$)

$\Psi_2(2) = \sigma_-(2) = 1s_A + 1s_B$ (spin = $-1/2$)

$$\Psi_{1,2}(1,2) = \sigma_+(1)\,\sigma_-(2) - \sigma_+(2)\,\sigma_-(1)$$

$$\sim \begin{vmatrix} \sigma_+(1) & \sigma_+(2) \\ \sigma_-(1) & \sigma_-(2) \end{vmatrix}$$

"determinantal wave functions"