H_2: Independent electron treatment

$$\hat{H} = \frac{p^2}{2m} - \frac{e^2}{|r-R_1|} - \frac{e^2}{|r-R_2|} + \frac{e^2}{|R_1-R_2|}$$

H_2^+

this is a constant.

Say we have atomic orbitals ϕ_1, ϕ_2

Hydrogen 1S states:

$$\frac{1}{\sqrt{4\pi}} 2 e^{-r/a_0} \left(\frac{1}{a_0}\right)^{3/2}$$

$$S = \langle \phi_1 | \phi_2 \rangle$$

$$\psi_B(r) = \frac{1}{\sqrt{2(1+S)}} \left(\phi_1(r) + \phi_2(r)\right)$$

$$\psi_{AB}(r) = \frac{1}{\sqrt{2(1-S)}} \left(\phi_1(r) - \phi_2(r)\right)$$

← show on board.

$$\epsilon_B = \frac{E_0 + E_{12}}{1+S}$$ — one orbital overlap

$$\epsilon_{AB} = \frac{E_0 - E_{12}}{1-S}$$

$E_0 - E_{12}$

E_0 —

$E_0 + E_{12}$

$$E_0 = \langle \phi_1 | H | \phi_1 \rangle$$

$$E_{12} = \langle \phi_1 | H | \phi_2 \rangle$$ it is negative! (often called $-t$)

↓ connect to Hubbard.

You can now populate with 2 electrons. We take into account the Pauli principle:

$\uparrow\downarrow$ $2(E_0 + E_{12})$ is the ground state.

The wave function is $\psi_B(r_1)\alpha(\omega_1)\,\psi_B(r_2)\beta(\omega_2) = \Psi(r_1\omega_1; r_2\omega_2)$

You need to properly symmetrize! can you do it?

Heitler - London Theory

[Karlsruhe]
Walter H. 1904-81
Fritz L. 1900-54
[Breslow]

Zeitschrift für Phys. 44, 455 (1927)

- two non-interacting hydrogen atoms.

$$\hat{H} = \underbrace{\frac{p_1^2}{2m} - \frac{e^2}{|r_1 - R_1|} + \frac{p_2^2}{2m} - \frac{e^2}{|r_2 - R_2|}}_{\hat{H}_0} + \frac{e^2}{|r_1 - r_2|} + \frac{e^2}{|R_1 - R_2|} - \frac{e^2}{|r_1 - R_2|} - \frac{e^2}{|r_2 - R_1|}$$

$\frac{e^2}{|r_1 - r_2|}$: e-e repulsion

$$\hat{H} = \hat{H}_0 + \hat{H}'$$

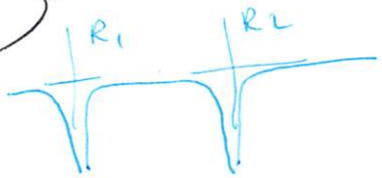
1. independent electron model: neglect $+\frac{e^2}{|r_1 - r_2|}$.

$$\hat{H} = \underbrace{\frac{p_1^2}{2m} - \frac{e^2}{|r_1 - R_1|} - \frac{e^2}{|r_1 - R_2|}}_{\hat{H}_1} + \underbrace{\frac{p_2^2}{2m} - \frac{e^2}{|r_2 - R_2|} - \frac{e^2}{|r_2 - R_1|}}_{\hat{H}_2} + \frac{1}{|R_1 - R_2|}$$

$\hat{H}_1$ - Molecule 1

$\hat{H}_2$ - molecule 2

molecule 2 another H_2^+



Then we can build a singlet and a triplet wave functions:

$$\psi^S = \frac{1}{\sqrt{2}} \left[\psi_B(r_1)\,\psi_B(r_2) + \psi_B(r_2)\,\psi_B(r_1) \right] \underbrace{\frac{1}{\sqrt{2}} \left[\alpha\beta - \beta\alpha \right]}_{S=0,\ \chi_{AS}}$$

SAME as MF. These are molecular orbitals!!! (MO)

$$\psi^T = \frac{1}{\sqrt{2}}\left[\psi_B(r_1)\psi_{AB}(r_2) - \psi_B(r_2)\psi_{AB}(r_1)\right]\chi_{sym}.$$

$$\chi_{sym} = \begin{cases} \alpha\alpha \\ \frac{1}{\sqrt{2}}(\alpha\beta+\beta\alpha) \\ \beta\beta \end{cases}$$

$S=1$

To get further insight in the situation, I can re-write this in terms of atomic orbitals:

$$S = \langle \phi_1(r_1)\phi_2(r_2) \mid \phi_1(r_2)\phi_2(r_1) \rangle$$ ← "double" overlap.

$$\psi^S_{(1,2)} = \frac{1}{2\sqrt{1+S}}\left(\phi_1(r_1)\phi_2(r_2) + \phi_2(r_1)\phi_1(r_2)\right)\left[\alpha_1\beta_2 - \beta_1\alpha_2\right]$$

let's drop it!!! ← H-L kept this

$$+ \frac{1}{2\sqrt{1+S}}\left[\phi_1(r_1)\phi_1(r_2) + \phi_2(r_1)\phi_2(r_2)\right]\left[\alpha_1\beta_2 - \beta_1\alpha_2\right]$$

ionic functions! ≈ has wrong long distance limit!!!

$$\psi^T_{(1,2)} = \frac{1}{\sqrt{2(1-S)}}\left[\phi_2(r_1)\phi_1(r_2) - \phi_1(r_1)\phi_2(r_2)\right]\chi_{sym}.$$

Note a problem! ψ^S will always have a 50/50 mixture of ionic term and two atoms!

Heitler and London suggested dropping the offending term!

Guess the wavefunction and estimate the energy.

And this is the H-L approximation.

variational estimate.

If we calculate the energy: ← not eigenvectors!!!

$$E^S = \frac{\langle \psi^S_{HL} | \hat{H} | \psi^S_{HL} \rangle}{\langle \psi^S_{HL} | \psi^S_{HL} \rangle} = 2E_0 + \frac{C+X}{1+S} = \frac{K+J}{1+S}$$

Good notes.

$$E^T = \frac{\langle \psi^T_{HL} | \hat{H} | \psi^T_{HL} \rangle}{\langle \psi^T_{HL} | \psi^T_{HL} \rangle} = 2E_0 + \frac{C-X}{1+S} = \frac{K-J}{1-S}$$

EXCHANGE:

$$E^S - E^T \equiv 2J = 2\frac{X - SC}{1-S^2} \quad ; \text{ if } S=0, \quad J=X$$

$J<0$ for H_2 ($J \approx -2.24$ eV)

Here C is the coulomb integral $\langle \phi_1(r_1)\phi_2(r_2) | \hat{H}' | \phi_1(r_1)\phi_2(r_2) \rangle$
And J/X is the exchange.

Say $S=0 \Rightarrow E_S = 2E_0 + C + X$

So Heisenberg / Hubbard came up with a model Hamiltonian that will have E_S as its eigenvalue!!!

$$H_{eff} = \underbrace{2H_0}_{\text{2 independent H atoms!}} + H_{coul} + H_{ex}$$

and there are two options here!

(I) Heisenberg Ham: $H_{ex} = A\, \hat{S}_1 \cdot \hat{S}_2$

comment

$$X = \langle \phi_1(r_1)\phi_2(r_2) | \hat{H}' | \phi_1(r_2)\phi_2(r_1) \rangle \sim \text{falls off fast!!!}$$

$$H' = e^2\left(-\frac{1}{|r_1 - R_2|} - \frac{1}{|r_2 - R_1|} + \frac{1}{|r_1 - r_2|} + \frac{1}{|R_1 - R_2|} \right)$$

$$\hat{S} \equiv \hat{S}_1 + \hat{S}_2$$

$$S^2 \equiv S_1^2 + S_2^2 + 2\, S_1 \cdot S_2$$

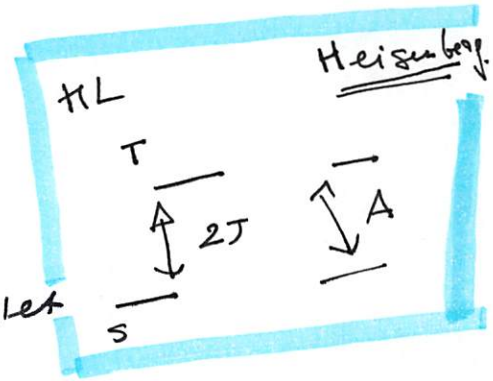
Spin operators for two electrons.

$$\langle S^2 \rangle = S(S+1)$$

$$\langle S_i^2 \rangle = \tfrac{1}{2}\left(\tfrac{1}{2}+1\right) = 3/4$$

$$\hat{S}_1 \cdot \hat{S}_2 = \begin{cases} 1/4 & \text{~~singlet~~ triplet} \quad S=1 \\ -3/4 & \text{singlet} \quad S=0 \end{cases}$$

Heisenberg



$A = -2J$ to make the difference $E^S - E^T = 2J$!

But I would like to focus on the Hubbard model.

(2) $H_{eff} = 2H_0 + H_{hub}$. The coupling of 2 atoms is done by:

$$H_{hub} = -t \sum_{\sigma=\uparrow\downarrow} \left(c_{1\sigma}^{\dagger} c_{2\sigma} + c_{2\sigma}^{\dagger} c_{1\sigma} \right) + U\left(n_{1\uparrow} n_{1\downarrow} + n_{2\uparrow} n_{2\downarrow} \right)$$

↳ Hubbard Hamiltonian.

$$\{ c_{\epsilon}^{\dagger} c_{k} \} = \delta_{\epsilon k}$$

This requires some background. I am using second quantization here. Do you all understand what this means?

the atom

$$H(r_1, r_2) = \underbrace{\frac{\hbar^2}{2m} + \frac{p_2^2}{2m} - \frac{2e^2}{4\pi\epsilon_0 |r_1|} - \frac{2e^2}{4\pi\epsilon_0 |r_2|}}_{H_0} + \underbrace{\frac{e^2}{4\pi\epsilon_0 |r_2 - r_1|}}_{H_1}$$

for $\hat{H}_0$: $\psi_{gs}(ab) = \frac{1}{2}\left(\psi_{100}(r_1)\psi_{100}(r_2) + \psi_{100}(r_1)\psi_{100}(r_2)\right)\underbrace{[\beta\beta - \beta\alpha]}_{\chi_{as}}$

$$E_0 = \langle \psi_{gs} | H_0 | \psi_{gs} \rangle = -\frac{4e^2}{8\pi\epsilon_0 a_0}$$

$$E_1 = \langle \psi_{gs} | H' | \psi_{gs} \rangle = 5e^2 / (4(8\pi\epsilon_0 a_0))$$

excited states $\Rightarrow$ Heisenberg 1926

$$\psi_{es}^{S} = \frac{1}{\sqrt{2}}\left[\psi_{100}(r_1)\psi_{nem}(r_2) + \psi_{100}(r_2)\psi_{nem}(r_1)\right]\chi_{as}(s_1 s_2)$$

$$\psi_{es}^{T} = \frac{1}{\sqrt{2}}\left[\psi_{100}(r_1)\psi_{nem}(r_2) - \psi_{100}(r_2)\psi_{nem}(r_1)\right]\chi_{sm}(s_1 s_2)$$

$$\langle \psi^{S,T} | \hat{H}_0 | \psi^{S,T} \rangle = E_{es} = E_{100} + E_{nem}$$

$$E_{ee}^{S} = I + J \qquad E_{ee}^{T} = I - J = \langle \psi^{T} | H_1 | \psi^{T} \rangle$$

$$\boxed{E_{ee}^{S} - E_{ee}^{T} = 2J}$$ — exchange!!!

$$I = \iint |\psi_{100}(r_1)|^2 \frac{e^2}{r_{12}} |\psi_{nem}(r_2)|\, dr_1\, dr_2$$ — Coulomb integral

$$J = \iint \psi_{100}(r_1)\psi_{nem}(r_2)\frac{e^2}{r_{12}}\psi_{100}^{*}(r_2)\psi_{nem}^{*}(r_1)$$

in the $J > 0$ in H_2 $J < 0$.

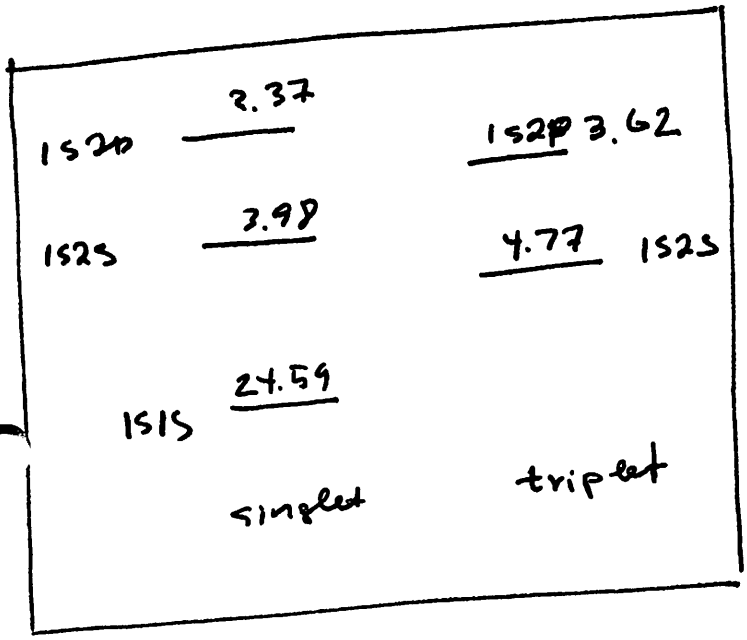
the atom continued

1s 2s — S 3.99 eV
1s 2s — T 4.77 eV

1s 2p — S 3.37 eV
1s 2p — T 3.62 eV

if $J > 0$ $\quad E^S = 2J + E^T$

1s 1s 24.59 eV



Heisenberg's theory.

$\Delta L = \pm 1$ $\quad \Delta S = 0$ dipole selection rules.