

H₂: Independent electron treatment

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



this is a constant

Say we have atomic orbitals

ϕ_1, ϕ_2

Hydrogen 1s states:

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

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

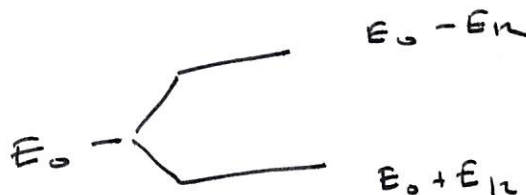
$$\psi_B(r) = \frac{1}{\sqrt{2(1+S)}} (\phi_1(r) + \phi_2(r))$$

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

← show on board

$$E_B = \frac{E_0 + E_{12}}{1 + S}$$

one orbital overlap



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

$$E_0 = \langle \phi_1 | \hat{H} | \phi_1 \rangle$$

$$E_{12} = \langle \phi_1 | \hat{H} | \phi_2 \rangle$$

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?

Test 2: 10/11/17



$$\frac{1}{1.5-1} = \frac{1}{0.5} = 2$$

distance from center

distance from center

distance from center

$$(1, 2) \rightarrow (1, 2) = \frac{1}{(1-1)^2 + (2-2)^2} = \frac{1}{0} = \infty$$

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distance from center



$$\frac{1}{1+1} = \frac{1}{2}$$

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$$\langle (1, 2), (1, 2) \rangle = 2$$

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distance from center

distance from center

distance from center

[Karlsruhe]

Walter H. 1904-81
Fritz L. 1900-54

[Breslow]

Heitler - London Theory

Zeitschrift für Phys. 44, 455 (1927)

two non-interacting hydrogen atoms.

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

$$+ \frac{e^2}{|r_1 - r_2|} + \frac{e^2}{|R_1 - R_2|} - \frac{e^2}{|r_1 - R_2|} - \frac{e^2}{|r_2 - R_1|}$$

e-e repulsion

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

1. independent electron model: neglect

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

$$\hat{H} = \frac{p_1^2}{2m} - \frac{e^2}{|r_1 - R_1|} - \frac{e^2}{|r_1 - R_2|}$$

$\hat{H}_1^+$
- molecule 1

$$+ \frac{p_2^2}{2m} - \frac{e^2}{|r_2 - R_1|} - \frac{e^2}{|r_2 - R_2|}$$

- molecule 2
another $\hat{H}_1^+$

$$+ \frac{1}{|R_1 - R_2|}$$



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

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

SAME AS HF These are molecular orbitals!!! (MO)

1. $\frac{1}{(s-1)^2} = \frac{A}{s-1} + \frac{B}{(s-1)^2}$
 2. $\frac{1}{(s-1)^2} = \frac{A}{s-1} + \frac{B}{(s-1)^2}$

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9. $\frac{1}{(s-1)^2} = \frac{A}{s-1} + \frac{B}{(s-1)^2}$

10. $\frac{1}{(s-1)^2} = \frac{A}{s-1} + \frac{B}{(s-1)^2}$

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

$$X_{\text{sym}} = \begin{cases} d d \\ \frac{1}{\sqrt{2}} (d\beta + \beta d) \\ \beta \beta \end{cases}$$

$$S=1$$

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

$$S = \langle \phi_1(r_1) \phi_2(r_2) | \phi_1(r_2) \phi_2(r_1) \rangle \leftarrow \text{"double" overlap.}$$

$$\psi_{(1,2)}^S = \frac{1}{2\sqrt{1+S}} (\phi_1(r_1) \phi_2(r_2) + \phi_2(r_1) \phi_1(r_2)) [d_1 \beta_2 - \beta_1 d_2]$$

let's drop it!!!

$$+ \frac{1}{2\sqrt{1+S}} [\phi_1(r_1) \phi_1(r_2) + \phi_2(r_1) \phi_2(r_2)] [d_1 \beta_2 - \beta_1 d_2]$$

ionic functions!

H-L kept this

has wrong long distance limit!!!

$$\psi_{(1,2)}^T = \frac{1}{\sqrt{2(1-S)}} [\phi_2(r_1) \phi_1(r_2) - \phi_1(r_1) \phi_2(r_2)] \chi_{\text{sym.}}$$

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! And this is the H-L approximation.
Guess the wavefunction and estimate the energy.

$$y = \frac{1}{2} [f(x) + g(x) - f(x) + g(x)] = \frac{1}{2} [2g(x)] = g(x)$$

$$f(x) = \frac{1}{2} [f(x) + g(x) - f(x) + g(x)] = g(x)$$

To find the value of $f(x)$ in terms of $g(x)$, we use the definition of $f(x)$ and $g(x)$.

$$f(x) = \frac{1}{2} [f(x) + g(x) - f(x) + g(x)] = g(x)$$

$$f(x) = \frac{1}{2} [f(x) + g(x) - f(x) + g(x)] = g(x)$$

Let $f(x)$ and $g(x)$ be functions defined on a set S . Then $f(x) = g(x)$ if and only if $f(x) = g(x)$ for all $x \in S$.

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If we calculate the energy: ^{← variational estimate.}

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

ged notes.

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

EXCHANGE:

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

$J < 0$ for H_2

$$J = -2.24 \text{ eV}$$

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.

$$\text{say } S=0 \Rightarrow E_S = 2E_0 + C + X$$

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

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

and there are two options here!

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

comment

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

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

Y-axis: $\log_{10}(\text{relative abundance})$

!!! $\log_{10}(\text{relative abundance})$

$$C = \frac{X+1}{n+1} = \frac{1}{n+1} \cdot \frac{(n+1)X}{n+1} = \frac{X}{n+1}$$

$$T = \frac{X+1}{n+1} = \frac{1}{n+1} \cdot \frac{(n+1)X}{n+1} = \frac{X}{n+1}$$

EXERCISE

$$X = 5, n = 10, T = 5, C = \frac{5}{10+1} = \frac{5}{11}$$

with $n=10$

10 to 11

There is a constant interval between the logarithms.

$$X = 5, n = 10, T = 5, C = \frac{5}{10+1} = \frac{5}{11}$$

in the plot, you will see a straight line with a slope of 1.

EXERCISE

$$H = \frac{1}{n} \sum_{i=1}^n \log_{10} \left(\frac{1}{p_i} \right)$$

EXERCISE

and there are 10 species

$$H = \frac{1}{10} \sum_{i=1}^{10} \log_{10} \left(\frac{1}{p_i} \right)$$

$$H = \frac{1}{10} \left(\log_{10} \left(\frac{1}{0.1} \right) + \log_{10} \left(\frac{1}{0.1} \right) + \dots + \log_{10} \left(\frac{1}{0.1} \right) \right)$$

$$H = \frac{1}{10} \left(1 + 1 + \dots + 1 \right) = \frac{1}{10} \cdot 10 = 1$$

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

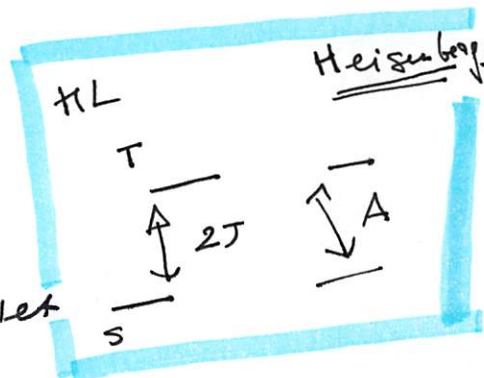
$$S^2 = S_1^2 + S_2^2 + 2 \hat{S}_1 \cdot \hat{S}_2$$

Spin operators for two electrons.

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

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

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



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

But I would like to focus on the Hubbard model.

② $H_{\text{eff}} = 2H_0 + H_{\text{Hub}}$. The coupling of 2 atoms is done by:

$$H_{\text{Hub}} = -t \sum_{\sigma=\uparrow\downarrow} (C_1^\dagger C_2 + C_2^\dagger C_1) + U (n_{1\uparrow} n_{1\downarrow} + n_{2\uparrow} n_{2\downarrow})$$

Hubbard Hamiltonian.

$$\{C_i^\dagger C_k\} = \delta_{ik}$$

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

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... ..

$$\begin{aligned} & \dots \\ & \dots \end{aligned}$$

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$$\dots = \dots$$

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$$\dots = \dots$$

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$$\dots = \dots$$

②

$$\dots = \dots$$

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②

He atom

$$H(r_1, r_2) = \underbrace{\frac{p_1^2}{2m} + \frac{p_2^2}{2m} - \frac{2e^2}{4\pi\epsilon_0|r_1|} - \frac{2e^2}{4\pi\epsilon_0|r_2|}}_{H_0} + \underbrace{\frac{e^2}{4\pi\epsilon_0|r_2-r_1|}}_{V_1}$$

for H_0 : $\psi_{gs}(ab) = \frac{1}{2} (\psi_{100}(r_1)\psi_{100}(r_2) + \psi_{100}(r_1)\psi_{100}(r_2)) \underbrace{[\alpha\beta - \beta\alpha]}_{\chi_{as}}$

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

$$E_1 = \langle \psi_p | H' | \psi_p \rangle = 5e^2 / (4\pi\epsilon_0 a_0)$$

excited states $\Rightarrow$ Heisenberg 1926

$$\psi_{gs}^S = \frac{1}{\sqrt{2}} [\psi_{100}(r_1)\psi_{n\ell m}(r_2) + \psi_{100}(r_2)\psi_{n\ell m}(r_1)] \chi_{as} (s_1 s_2)$$

$$\psi_{gs}^T = \frac{1}{\sqrt{2}} [\psi_{100}(r_1)\psi_{n\ell m}(r_2) - \psi_{100}(r_2)\psi_{n\ell m}(r_1)] \chi_{sm} (s_1 s_2)$$

$$\langle \psi^{S,T} | H_0 | \psi^{S,T} \rangle = E_{gs} = E_{100} + E_{n\ell m}$$

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

$$\boxed{\overset{\uparrow\downarrow}{E}_{ee}^S - \overset{\uparrow\uparrow}{E}_{ee}^T = 2J} \quad \text{— exchange !!!}$$

$$I = \iint |\psi_{100}(r_1)|^2 \frac{e^2}{r_{12}} |\psi_{n\ell m}(r_2)|^2 dr_1 dr_2 \quad \text{— Coulomb integral}$$

$$J = \iint \psi_{100}(r_1)\psi_{n\ell m}(r_2) \frac{e^2}{r_{12}} \psi_{100}^*(r_2)\psi_{n\ell m}^*(r_1) dr_1 dr_2$$

in He $J > 0$ in H_2 $J < 0$

He atom continued

$$\begin{array}{l} 1s2s \\ \hline \end{array} \begin{array}{l} \text{--- S } \underline{3.98 \text{ eV}} \\ \text{--- T } \underline{4.77 \text{ eV}} \end{array}$$

$$\begin{array}{l} 1s2p \\ \hline \end{array} \begin{array}{l} \text{--- S } \underline{3.37 \text{ eV}} \\ \text{--- T } \underline{3.62 \text{ eV}} \end{array}$$

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

$$1s1s \quad \underline{24.59 \text{ eV}}$$

1s2p	<u>2.37</u>	1s2p	<u>3.62</u>
1s2s	<u>3.98</u>	<u>4.77</u>	1s2s
1s1s	<u>24.59</u>		
	singlet	triplet	

— Heisenberg's theory.

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