Let's take a step back!
What would a Chemist do?

This allows me to avoid the second quantization.

H_2 minimal basis. Molecular orbitals!

$$\psi_1 = \frac{1}{\sqrt{2(1+S)}}(\phi_1 + \phi_2)$$

$$\psi_2 = \frac{1}{\sqrt{2(1-S)}}(\phi_1 - \phi_2)$$

} LCAO is a sensible choice of a single-particle basis.

α, β : spin functions $(\downarrow), (\uparrow)$.

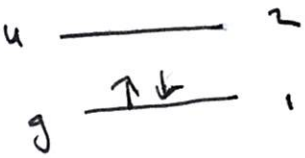
Spin orbitals

$$\chi_1(x) = \psi_1(r)\,\alpha(\omega) \qquad \chi_2(x) = \psi_1(r)\,\beta(\omega)$$

$$\chi_3(x) = \psi_2(r)\,\alpha(\omega) \qquad \chi_4(x) = \psi_2(r)\,\beta(\omega)$$

4 orbitals, 2 electrons (how many ways to fill? Six!)

HF ground state : $|\Psi_0\rangle = |\chi_1 \chi_2\rangle$ ①



$|1\bar{1}\rangle$ notation

Singly excited determinants:

② $|2\bar{1}\rangle$ 

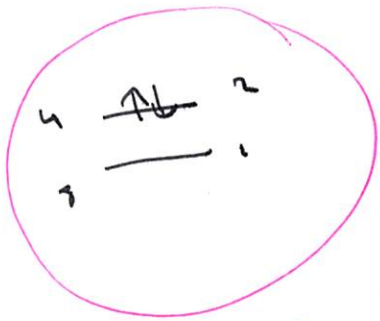
③ $|\bar{2}\bar{1}\rangle$ 

④ $|12\rangle$ 

⑤ $|1\bar{2}\rangle$ 

doubly excited determinant :

⑥ $|2\bar{2}\rangle$



the only even!!! [besides the ground state]

The Hilbert space is $N = 6$!

The exact ground state should be g-state!

$$|\Psi_0\rangle = c_0 |\Phi_0\rangle + c_{2\bar{2}} |2\bar{2}\rangle \qquad \left(|2\bar{2}\rangle = |\chi_3 \chi_4\rangle\right)$$

Φ_0: u·u ≡ even

$2\bar{2}$: g·g ≡ even

The CI matrix is 2×2:

$$H = \begin{vmatrix} \langle\Psi_0|\hat{H}|\Psi_0\rangle & \langle\Psi_0|\hat{H}|2\bar{2}\rangle \\ \langle 2\bar{2}|\hat{H}|\Psi_0\rangle & \langle 2\bar{2}|\hat{H}|2\bar{2}\rangle \end{vmatrix}$$

The "full CI"!

need matrix elements of $\hat{H}$ on two determinantal functions! This is what we called $2\hat{H}_0$

$$\hat{H} = \hat{h}(1) + \hat{h}(2) + \frac{1}{(r_1 - r_2)}$$

notation for the integrals.

$$\langle ij|kl\rangle = \iint dx_1 dx_2 \, \chi_i^*(x_1)\chi_j(x_2)\, \hat{r}_{12}^{-1}\, \chi_k(x_1)\chi_l(x_2)$$

HF ground state!

$$H(CI) = \begin{vmatrix} \langle 1|h|1\rangle + \langle 2|h|2\rangle + \langle 12|12\rangle - \langle 12|21\rangle & \langle 12|34\rangle - \langle 12|43\rangle \\ \langle 34|12\rangle - \langle 34|21\rangle & \langle 3|h|3\rangle + \langle 4|h|4\rangle + \langle 34|34\rangle - \langle 34|43\rangle \end{vmatrix}$$

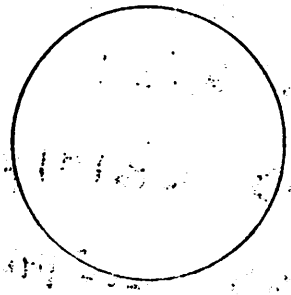
This is what a chemist calls the Full CI matrix!

The lowest eigen value should be compared with the HF result:

$$E_{HF} = \langle\Psi_0|\hat{H}|\Psi_0\rangle = \langle 1|h|1\rangle + \langle 2|h|2\rangle + \langle 12|12\rangle - \langle 12|21\rangle$$

exchange integral

Coulomb integral



If you integrate out spin, the full CI matrix comes out as:

J_{11} K_{12} refer to 2 / 1

$$H = \begin{pmatrix} 2(1|h|1) + (11|11) & (12|12) \\ (21|21) & 2(2|h|2) + (22|22) \end{pmatrix}$$

How do I go from spin orbitals to spatial orbitals?

space spin

$$\langle 1|h|1\rangle = \int_{1} \int_{\omega_1} \psi_1^*(r_1)\,\alpha^*(\omega_1)\, h(r_1)\, \psi_1(r_1)\,\alpha(\omega_1) \equiv$$

$$\equiv (\psi_1|h|\psi_1).$$

$\langle \alpha|\alpha\rangle = 1$

$\langle \alpha|\beta\rangle = 0$

need the eigen-values, so I J_{11} compute $\det|\underline{\underline{H}} - \lambda \underline{\underline{I}}| = 0$

$$\boxed{E_{HF} = 2(1|h|1) + (11|11)}$$

on the other hand: (the secular equation)

$$(2(1|h|1) + J_{11} - \lambda)(2(2|h|2) + J_{22} - \lambda) - |K_{12}|^2 = 0$$

$$4(1|h|1)(2|h|2) + 2(2|h|1)J_{22} - \lambda\, 2(1|h|1) + 2J_{11}(2|h|2)$$

$$+ J_{11}J_{22} - \lambda J_{11} - \lambda\,(2(2|h|2) + J_{22}) + \lambda^2 - |K_{12}|^2 = 0$$

$$\lambda^2 - \lambda\Big(2(1|h|1) + J_{11} + J_{22} + 2(2|h|2)\Big) +$$

$$+ \; 4(1|h|1)(2|h|2) + 2(1|h|1)J_{22} + 2(2|h|2)J_{11} -$$

$$+ J_{11}J_{22} - |K_{12}|^2 = 0 \qquad \text{CI secular equation.}$$

$$\lambda_{\pm} = \frac{2(1|h|1) + J_{11} + 2(2|h|2) + J_{22}}{2} \pm \ldots$$

correlation energy is everything beyond exchange:

$$\lambda - E_{HF} \equiv E_{correlation.}$$

← mixing in a double excited state lowered the HF energy.

Question:

Now, can I find a better wavefunction than

$\psi(1)\alpha(\omega_1)$?

Yes I can, I need to solve the Hartree-Fock equations. Let's formulate the HF problem for H_2 with a minimal basis.

Hubbard continued.

Last time, we started with

$$\hat{H}_{Hub} = -t \sum_{\sigma=\uparrow,\downarrow} \left(c^{+}_{1\sigma} c_{2\sigma} + c^{+}_{2\sigma} c_{1\sigma} \right) + U \left(n_{1\uparrow} n_{1\downarrow} + n_{2\uparrow} n_{2\downarrow} \right).$$

Then we built a Hilbert space of 6 two-electron wave functions:

$|1010\rangle = c^{+}_{1\uparrow} c^{+}_{2\uparrow} |0\rangle$ $\quad S = 1$ $\quad \uparrow\uparrow$

$|1001\rangle = c^{+}_{1\downarrow} c^{+}_{2\downarrow} |0\rangle$ $\quad S = -1$ $\quad \downarrow\downarrow$

etc. Note that it is different from what we have done before:

$|12\rangle = \uparrow\downarrow$ $\qquad \chi_1 = \psi_1(r)\alpha(\omega)$ $\quad \chi_2 = \psi_2(r)\alpha(\omega)$

These refer to molecular orbitals!!! (chemists like them)

I am now working with atomic orbitals!!!

EXAMPLE:

$$\underbrace{\langle x_1 x_2|}_{\langle x_1| \otimes \langle x_2|} \underbrace{c^{+}_{1\uparrow} c^{+}_{2\downarrow} |0\rangle}_{\text{2-e Hilbert space}} = \frac{1}{\sqrt{2}} \left\{ \varphi_1(r_1)\alpha(\omega_1)\,\varphi_2(r_2)\beta(\omega_2) - \varphi_1(r_2)\alpha(\omega_2)\varphi_2(r_1)\beta(\omega_1) \right\}$$

This state is $\uparrow\downarrow$

Remember:
A wavefunction is the inner product of your ket and a bra based on the appropriate set of position operators.

Take kinetic energy:

$$-t\left(c_{1\uparrow}^{+}c_{2\uparrow} + c_{1\downarrow}^{+}c_{2\downarrow} + c_{2\uparrow}^{+}c_{1\uparrow} + c_{2\downarrow}^{+}c_{1\downarrow}\right)$$

and use it on $c_{1\uparrow}^{+}c_{2\downarrow}^{+}|0\rangle$: $\boxed{\uparrow\ \downarrow}$

$$c_{1\uparrow}^{+}c_{2\uparrow}\,c_{1\uparrow}^{+}c_{2\downarrow}^{+}|0\rangle = -c_{1\uparrow}^{+}c_{1\uparrow}^{+}c_{2\uparrow}c_{2\downarrow}^{+}|0\rangle =$$

$$= c_{1\uparrow}^{+}c_{1\downarrow}^{+}c_{2\downarrow}^{+}\underbrace{c_{2\uparrow}|0\rangle}_{\emptyset} = 0$$

$$c_{1\downarrow}^{+}c_{2\downarrow}\,c_{1\uparrow}^{+}c_{2\downarrow}^{+}|0\rangle = c_{1\uparrow}^{+}c_{1\downarrow}^{+}|0\rangle \qquad \boxed{\uparrow\downarrow\ \ -}$$

$$c_{2\uparrow}^{+}c_{1\uparrow}\,c_{1\uparrow}^{+}c_{2\downarrow}^{+}|0\rangle = c_{2\uparrow}^{+}\left(1 - c_{1\uparrow}^{+}c_{1\uparrow}\right)c_{2\downarrow}^{+}|0\rangle =$$

$$= c_{2\uparrow}^{+}c_{2\downarrow}^{+}|0\rangle \Rightarrow \qquad \boxed{-\ \ \uparrow\downarrow}$$

$$c_{2\downarrow}^{+}c_{1\uparrow}\,c_{1\uparrow}^{+}c_{2\downarrow}^{+}|0\rangle = 0$$

This says that we can have NON-ZERO contributions

$$\boxed{\begin{aligned}\langle 0011|KE|1001\rangle &= -t\\ \langle 1100|KE|1100\rangle &= -t\end{aligned}}$$

clearer way instead of page 6!!

Let me spell it out:

$$\hat{H} = -t\left(c^+_{1\uparrow}c_{2\uparrow} + c^+_{2\uparrow}c_{1\uparrow} + c^+_{1\downarrow}c_{2\downarrow} + c^+_{2\downarrow}c_{1\downarrow}\right)$$

$$+ U\,\hat{n}_{1\uparrow}\hat{n}_{1\downarrow} + U\,\hat{n}_{2\uparrow}\hat{n}_{2\downarrow} + \underbrace{2\text{ H's}}_{\text{two independent Hydrogen atoms.}}$$

I have 2 sites, and two spin states. So I have 4 spin orbitals. 6 possible ways to distribute 2 electrons over

$$\frac{4!}{2!\,(4-2)!} = \frac{4\cdot 3\cdot 2\cdot 1}{2\cdot 1\,(2\cdot 1)} = 6.$$

It is convenient to classify them by spin:

$|1010\rangle$ $\quad S_z = 1$

$|0101\rangle$ $\quad S_z = -1$

$|0110\rangle$, $|1001\rangle$ and $|1100\rangle$, $|0011\rangle$ all have $S_z = 0$

	$\lvert 1010\rangle$	$\lvert 0101\rangle$	$\lvert 0110\rangle$	$\lvert 1001\rangle$	$\lvert 1100\rangle$	$\lvert 0011\rangle$
$\lvert 1010\rangle$	$2E_0$	0	0	0	0	0
$\lvert 0101\rangle$	0	$2E_0$				
$\lvert 0110\rangle$			$2E_0$	0	$+t$	$+t$
$\lvert 1001\rangle$			0	$2E_0$	$-t$	$+t$
$\lvert 1100\rangle$			$+t$	$-t$	$2E_0+U$	0
$\lvert 0011\rangle$			$+t$	$-t$	0	$2E_0+U$

Let's take 4x4 and add the first two columns.

This creates a $S_z=0$ component of the triplet!

$|1001\rangle + |0110\rangle$

So we will have three states with Energy $2E_0$:

$|1010\rangle$
$|0101\rangle$
$[|1001\rangle + |0110\rangle]$

} $2E_0$ This is a triplet

The ground state is a singlet

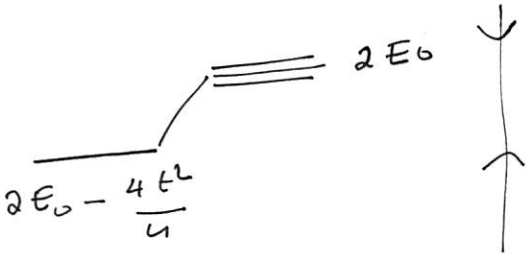
$$|GS\rangle = -|1001\rangle + |0110\rangle + \frac{-U+\sqrt{U^2+16t^2}}{4t}\left(|1100\rangle + |0011\rangle\right)$$

$$E_{gs} = 2E_0 + \frac{U}{2} - \frac{1}{2}\sqrt{U^2+16t^2}$$

And you get two high energy states (so the total is 6!).

CASE 1 $U >> t$

$$E_0 \approx 2E_0 + \frac{U}{2} - \frac{U}{2}\sqrt{1+\left(\frac{4t}{U}\right)^2} \approx 2E_0 - \frac{4t^2}{U}$$



(this is what is called t–J model).

$$|GS\rangle = -|1001\rangle + |0110\rangle + \frac{2t}{U}\left(|1100\rangle + |0011\rangle\right)$$

Case 2 $t \gg U$

$$E_0 = 2E_0 + \frac{U}{2} - 2t \qquad 2J = \frac{U}{2} - 2t$$

Here the energy is lowered mainly by hopping!
If $U \to 0$ the single independent electron picture is restored.

we also can to the "Hartree-Fock" on H_{Hub}:

Mean field: $\hat{n} = \hat{n} - \bar{n} + \bar{n}$

number — operator

$$H^{MF}_{Hub} = -t \sum_{\substack{i,j \\ \sigma=\uparrow,\downarrow}} c^{\dagger}_{i\sigma} c_{j\sigma} + U \sum_{i} \left(\bar{n}_{i\uparrow} \hat{n}_{i\downarrow} + \hat{n}_{i\uparrow} \bar{n}_{i\downarrow} - \bar{n}_{i\uparrow} \bar{n}_{i\downarrow} \right)$$

↑ single particle problem!

$$(n_\uparrow - \bar{n}_\uparrow)(n_\downarrow - \bar{n}_\downarrow) \approx 0$$

Let's look at $i = 1, 2$:

$$U \bar{n}_{1\uparrow} \hat{n}_{1\downarrow} + U \hat{n}_{1\uparrow} \bar{n}_{1\downarrow} + U \bar{n}_{2\uparrow} \hat{n}_{2\downarrow} + U \hat{n}_{2\uparrow} \bar{n}_{2\downarrow} -$$

one particle object

$$- U \bar{n}_{1\uparrow} \bar{n}_{1\downarrow} - U \bar{n}_{2\uparrow} \bar{n}_{2\downarrow} .$$

$|1100\rangle$
$|1010\rangle$
$|1001\rangle$
$|0110\rangle$
$|0101\rangle$
$|0011\rangle$

$= c^{\dagger}_{1\uparrow} |0\rangle$

A linear combination of those to diagonalize $\hat{H}^{mf}$.

$H^{mf}(\bar{n}_{1\uparrow}, \bar{n}_{1\downarrow}, \ldots)$ parametric.

$$d_j = \sum_i^{\dagger} u_i^j c_i$$

$E(\bar{n}_{1\uparrow}, \bar{n}_{2\uparrow}, \bar{n}_{1\downarrow}, \bar{n}_{2\downarrow})$

For two electrons H_2

$d_1^{\dagger}|0\rangle$
$d_2^{\dagger}|0\rangle$

$d_1^{\dagger} d_2^{\dagger}|0\rangle$ ← mean field.

$|GS\rangle$ $\quad \langle GS| n_{1\uparrow} |GS\rangle$ ← $c^{\dagger}_{1\uparrow} c_{1\uparrow}$ ← one of the (spin) pairs

} 4 of them.

and see if $\bar{n}$ is the same ⇒ SCF another.

$\rightarrow E^{MF}(\{\bar{n}_{SCF}\})$

$n^{new} = (1-\alpha)\, n^{old} + \alpha\, n^{computed}$