


- Most simple version of a correlated system: z H atoms + $z e^-$.

$$\rightarrow H = h_1 + h_2 + V_{12}, \text{ where } h_i = h_z = -\nabla_i^2 \left(\frac{e^2}{4\pi \epsilon_0 r_i} \right) \frac{m}{2}$$

h_1 and h_2 are single particle terms and have the kinetic E_k + Coulomb attraction of each e^- by both nuclei.

$$V_{12} = \frac{1}{r_{12}} \quad \text{is the coulombic repulsion between } e^-$$

\rightarrow Simplest model: 1S orbital per e^- and spin per atom:

Nomenclature A, B (atoms, different lattice sites etc...)

$$|A\uparrow\rangle, |B\uparrow\rangle, |A\downarrow\rangle, |B\downarrow\rangle$$

1. Build The Basis of all possible Slater determinants:

$$\rightarrow SD \text{ Basis } |\phi_i\rangle, i=1 \dots \binom{4}{2} = 1 \dots \frac{4!}{2! 2!} = 1 \dots 6$$

We have 6 different Two-particle basis: (order does not matter,

$$|\phi_1\rangle = |A^\uparrow, A^\downarrow\rangle = \frac{1}{\sqrt{2}} \left\{ |A^\uparrow(1)\rangle |A^\downarrow(2)\rangle - |A^\downarrow(1)\rangle |A^\uparrow(2)\rangle \right.$$

↓

$$\begin{array}{l} \cancel{c^\uparrow \#1} \\ \cancel{c^\downarrow \#2} \end{array} \begin{pmatrix} A^\uparrow(1) & A^\downarrow(1) \\ A^\uparrow(2) & A^\downarrow(2) \end{pmatrix}$$

→ Repeat for all other SD

$$|\phi_2\rangle = |B^\uparrow, B^\downarrow\rangle = \frac{1}{\sqrt{2}} \left\{ |B^\uparrow(1)\rangle |B^\downarrow(2)\rangle - |B^\downarrow(1)\rangle |B^\uparrow(2)\rangle \right\}$$

$$|\phi_3\rangle = |A^\uparrow, B^\downarrow\rangle = \frac{1}{\sqrt{2}} \left\{ |A^\uparrow(1)\rangle |B^\downarrow(2)\rangle - |B^\downarrow(1)\rangle |A^\uparrow(2)\rangle \right\}$$

$$|\phi_4\rangle = |A^\downarrow, B^\uparrow\rangle = \frac{1}{\sqrt{2}} \left\{ |A^\downarrow(1)\rangle |B^\uparrow(2)\rangle - |B^\uparrow(1)\rangle |A^\downarrow(2)\rangle \right\}$$

$$|\phi_5\rangle = |A^\uparrow, B^\uparrow\rangle = \frac{1}{\sqrt{2}} \left\{ |A^\uparrow(1)\rangle |B^\uparrow(2)\rangle - |B^\uparrow(1)\rangle |A^\uparrow(2)\rangle \right\}$$

$$|\phi_6\rangle = |A^\downarrow, B^\downarrow\rangle = \frac{1}{\sqrt{2}} \left\{ |A^\downarrow(1)\rangle |B^\downarrow(2)\rangle - |B^\downarrow(1)\rangle |A^\downarrow(2)\rangle \right\}$$

2. Now let's build The Hamiltonian in this basis. Here is where The Hubbard Model comes in:

→ The single particle terms (kinetic energy + Coulomb attraction)

$$\left\{ \begin{array}{l} \langle A\sigma | \hat{h} | B\sigma' \rangle = \langle B\sigma | \hat{h} | A\sigma' \rangle = -t, \sigma' = \uparrow \downarrow \\ \langle A\sigma | h | A\sigma' \rangle = \langle B\sigma | h | B\sigma' \rangle = \epsilon \delta_{\sigma,\sigma'} \end{array} \right.$$

→ Note we can take $\epsilon = 0$, it's just a rigid energy shift.

→ Interaction Term : equal because of symmetry

$$\langle A^\dagger \uparrow \downarrow | V_{1z} | A^\dagger \uparrow \downarrow \rangle = \langle B^\dagger \uparrow \downarrow | V_{1z} | B^\dagger \uparrow \downarrow \rangle = U$$

All other 2 particle pairs are zero. Only onsite interactions (2 e^- of opposite spin in same site).

→ Single particle Term in The MB (SD) basis :

Note That $\langle A\sigma(i)|A\sigma'(i)\rangle = \langle B\sigma(i)|B\sigma'(i)\rangle = \delta_{\sigma\sigma'}$

$$\langle A\sigma(i)|B\sigma'(i)\rangle = \langle B\sigma(i)|A\sigma'(i)\rangle = 0$$

→ This is basically orthogonality of the orbitals
spin

We can go through all the combinations, as H is Hermitian (and real in this case) we only need a few terms :

$$\begin{aligned} \langle \phi_1 | h_1 + h_2 | \phi_1 \rangle &= \frac{1}{2} \left[\langle A^\dagger(i) | A^\dagger(z) | h_1 + h_2 | A^\dagger(i) | A^\dagger(z) \rangle \right. \\ &\quad \left. - \langle A^\dagger(i) | A^\dagger(z) | h_1 + h_2 | A^\dagger(z) | A^\dagger(i) \rangle \right] + \text{C.C.} \end{aligned}$$

$$\begin{aligned} &= \cancel{\neq} \cdot \frac{1}{2} \left[\cancel{\langle A^\dagger(i) | h_1 | A^\dagger(i) \rangle} \overset{\text{E}}{\cancel{\cdot}} \cancel{\langle A^\dagger(z) | A^\dagger(z) \rangle} + \right. \\ &\quad \cancel{\langle A^\dagger(z) | h_2 | A^\dagger(z) \rangle} \cancel{\langle A^\dagger(i) | A^\dagger(i) \rangle} - \\ &\quad \cancel{\langle A^\dagger(i) | h_1 | A^\dagger(i) \rangle} \cancel{\langle A^\dagger(z) | A^\dagger(z) \rangle} - \\ &\quad \cancel{\langle A^\dagger(z) | h_2 | A^\dagger(z) \rangle} \cancel{\langle A^\dagger(i) | A^\dagger(i) \rangle} = zE \\ &\quad \text{same for all } \langle \phi_i | h_1 + h_2 | \phi_i \rangle \end{aligned}$$

$$\rightarrow \langle \phi_i | h_1 + h_2 | \phi_j \rangle \text{ for } i \neq j$$

$$i=1, j=2 \Rightarrow 0$$

$$i=1, j=4 \Rightarrow 0$$

$$i=1, j=6 \Rightarrow 0$$

\rightarrow Because all 1 particle orbitals
are different (and the
overlap terms are all zero)

$$i=1, j=3$$

$$\langle \phi_1 | h_1 + h_2 | \phi_3 \rangle = \frac{1}{2} \left\{ \langle A^\uparrow(1) | h_1 | A^\uparrow(1) \rangle \langle A^\downarrow(2) | B^\downarrow(2) \rangle \right.$$

$$+ \langle A^\uparrow(1) | A^\uparrow(1) \rangle \langle A^\downarrow(2) | h_2 | B^\downarrow(2) \rangle \xrightarrow{-t}$$

$$- \langle A^\downarrow(1) | h_1 | A^\uparrow(1) \rangle \langle A^\uparrow(2) | B^\downarrow(2) \rangle \xrightarrow{0}$$

$$- \langle A^\downarrow(1) | A^\uparrow(1) \rangle \langle A^\uparrow(2) | h_2 | B^\downarrow(2) \rangle$$

$$- \langle A^\uparrow(1) | h_1 | B^\downarrow(1) \rangle \langle A^\downarrow(2) | A^\uparrow(2) \rangle$$

$$- \langle A^\uparrow(1) | B^\downarrow(1) \rangle \langle A^\downarrow(2) | h_2 | A^\uparrow(2) \rangle$$

$$+ \langle A^\downarrow(1) | h_1 | B^\downarrow(1) \rangle \langle A^\uparrow(2) | A^\uparrow(2) \rangle \xrightarrow{-t}$$

$$+ \langle A^\downarrow(1) | B^\downarrow(1) \rangle \langle A^\uparrow(2) | h_2 | A^\uparrow(2) \rangle$$

$$= -t$$

• Same for :

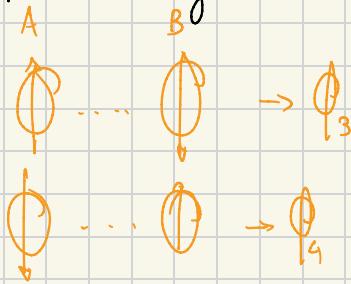
$$\langle \phi_1 | h_1 + h_2 | \phi_3 \rangle = -t$$

$$\langle \phi_2 | (h_1 + h_2) | \phi_3 \rangle = t$$

$$\langle \phi_2 | h_1 + h_2 | \phi_3 \rangle = -t$$

$$\langle \phi_1 | h_1 + h_2 | \phi_4 \rangle = t \quad (\text{do it! care with signs})$$

Another way :



inversion operator: around center, not
acting on spin.

$$i|A\rangle = |B\rangle$$

so $i|A^\dagger(1)\rangle = |B^\dagger(1)\rangle$ same for
spin down.

$$\text{so } i|\phi_3\rangle = \frac{1}{2} \{ |B^\dagger(1)|A^\dagger(z)\rangle - |B^\dagger(z)|A^\dagger(1)\rangle \}$$

$$= -|\phi_4\rangle$$

$$i|\phi_1\rangle = |\phi_2\rangle \text{ also}$$

$$i(h_1 + h_2) = h_1 + h_2 = (h_1 h_2)$$

$$\text{so } \langle \phi_1 | h_1 + h_2 | \phi_3 \rangle =$$

$$= \langle \phi_1 | (h_1 + h_2) i | \phi_3 \rangle = -\langle \phi_1 | h_1 + h_2 | \phi_4 \rangle = -t$$

QED

(also $i|\phi_1\rangle = |\phi_2\rangle$ and $i|\phi_2\rangle = |\phi_1\rangle$)

\rightarrow all other elements of $h_{1,1z}$ are zero

so The Full hamiltonian Matrix in The MB basis

is :

$$H = \begin{pmatrix} \phi_1 & \phi_2 & \phi_3 & \phi_4 & \phi_5 & \phi_6 \\ U+2\epsilon & 0 & -t & t & 0 & 0 \\ 0 & U+2\epsilon & -t & t & 0 & 0 \\ -t & -t & 2\epsilon & 0 & 0 & 0 \\ t & t & 0 & 2\epsilon & 0 & 0 \\ 0 & 0 & 0 & 0 & 2\epsilon & 0 \\ 0 & 0 & 0 & 0 & 0 & 2\epsilon \end{pmatrix} \begin{pmatrix} \phi_1 \\ \phi_2 \\ \phi_3 \\ \phi_4 \\ \phi_5 \\ \phi_6 \end{pmatrix}$$

$\rightarrow \phi_5$ & ϕ_6 are eigenstates of H , degenerate,

with energy $E_{5,6} = 2\epsilon \rightarrow$ let's analyze

why.

$$\hat{i} |\phi_5\rangle = -|\phi_5\rangle \quad i |\phi_6\rangle = -|\phi_6\rangle$$

\rightarrow (~~so~~ i and h_1 commute, so if ϕ_5 and ϕ_6 are eigenstates

of both, with symmetry "v" (ungerade), negative value of -1 of the inversion operator.

Under inversion states can be σ or σ_g (antisymmetric and symmetric)

Note: Symmetry group of a Homopolar diatomic molecule.

D_{2h} f. as rotations around molecule axis
f. Inversion center (σ or v , eigenvalue +1 -1)
f. Reflection plane

→ We can use \hat{C} to diagonalize the matrix:

$$i|\Phi_1\rangle = |\Phi_2\rangle \quad i|\Phi_2\rangle = |\Phi_1\rangle \quad (\hat{C}^2 = \mathbb{I})$$

$$i|\Phi_3\rangle = -|\Phi_4\rangle \quad i|\Phi_4\rangle = -|\Phi_3\rangle$$

we can build 2 g states:

$$|\Phi_{g_1}\rangle = \frac{1}{\sqrt{2}} (|\Phi_1\rangle + |\Phi_2\rangle)$$

$$|\Phi_{g_2}\rangle = \frac{1}{\sqrt{2}} (|\Phi_3\rangle - |\Phi_4\rangle)$$

and another two v states:

$$|\phi_{v_1}\rangle = \frac{1}{\sqrt{2}}(|\phi_1\rangle - |\phi_2\rangle)$$

$$|\phi_{v_2}\rangle = \frac{1}{\sqrt{2}}(|\phi_3\rangle + |\phi_4\rangle)$$

so we have the full set of common eigenvalues

So we can decompose the 6×6 H matrix in two blocks, a 2×2 g block and a 4×4 v block.

in the new basis:

$$\begin{aligned} \langle \phi_{g_1} | H | \phi_{g_1} \rangle &= \frac{1}{2} (\langle \phi_1 | H | \phi_1 \rangle + \langle \phi_2 | H | \phi_2 \rangle \\ &\quad + \langle \phi_1 | H | \phi_2 \rangle + \langle \phi_2 | H | \phi_1 \rangle) = 0 + 2\varepsilon \end{aligned}$$

$$\begin{aligned} \langle \phi_{g_2} | H | \phi_{g_2} \rangle &= \text{same but with } |\phi_3\rangle - |\phi_4\rangle \\ &= \frac{1}{2} (\langle \phi_3 | H | \phi_3 \rangle + \langle \phi_4 | H | \phi_4 \rangle - \end{aligned}$$

$$-\langle \phi_3 | H | \phi_4 \rangle - \langle \phi_4 | H | \phi_3 \rangle) = 2\varepsilon$$

$$\langle \phi_{g_1} | \phi_{g_2} \rangle = -zt = \langle \phi_{g_2} | \phi_{g_1} \rangle \leftarrow \text{Hermitian}$$

Now the 2×2 v block (without $| \phi_5 \rangle$ and $| \phi_6 \rangle$)

becomes : $H_v = \begin{pmatrix} v+z\epsilon & 0 \\ 0 & z\epsilon \end{pmatrix}$

\rightarrow So $| \phi_{v1} \rangle$ and $| \phi_{v2} \rangle$ are already eigenstates of H ($| \phi_z \rangle$ is degenerate with $| \phi_5 \rangle$ and $| \phi_6 \rangle$)

Now, in the $g_{1,0}$ basis :

$$H = \begin{pmatrix} \underbrace{\begin{pmatrix} v+z\epsilon & -zt \\ -zt & z\epsilon \end{pmatrix}}_{S=0} & \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} \\ \begin{pmatrix} 0 & 0 & v+z\epsilon & 0 & 0 & 0 \\ 0 & 0 & 0 & z\epsilon & 0 & 0 \\ 0 & 0 & 0 & 0 & z\epsilon & 0 \\ 0 & 0 & 0 & 0 & 0 & z\epsilon \end{pmatrix} & \begin{pmatrix} g_1 \\ g_2 \\ v_1 \\ v_2 \\ v_3 \\ v_4 \end{pmatrix} \end{pmatrix}$$

\hookrightarrow Now all that remains is diagonalizing this block.

→ Before diagonalizing The g block
it is useful To look at the spin of The states.

→ $S(L^2)$ and $M(L_z)$

$$M : \begin{cases} M = 0 \text{ for } |\Phi_{g_1}\rangle, |\Phi_{g_2}\rangle, |\Phi_{u_1}\rangle, |\Phi_{u_2}\rangle \\ M = 1 \text{ for } |\Phi_{u_3}\rangle = |\Phi_5\rangle \\ M = -1 \text{ for } |\Phi_{u_4}\rangle = |\Phi_6\rangle \end{cases}$$

* This explains why $|\Phi_5\rangle$ and $|\Phi_6\rangle$ were already eigenstates on Their own, They were already each one of its class (non degenerate in M).

• We can also look into S :

→ We have $S=1$ for $|\Phi_{u_2}\rangle, |\Phi_{u_3}\rangle, |\Phi_u\rangle$
They form The Triplet state.

→ The rest of The states have $S=0$

• So in terms of configurations we have :

$\rightarrow 2 \text{ g singlets } |\psi_{g_1}\rangle \& |\psi_{g_2}\rangle$

$\rightarrow 1 \text{ u singlet } |\psi_{u_1}\rangle \rightarrow \text{energy } V+z\epsilon$

~~$\rightarrow 1 \text{ u Triplet }$~~ $|\psi_{u_2}\rangle > |\psi_{u_3}\rangle > |\psi_{u_4}\rangle \text{ energy } z\epsilon$

(Note $|\psi_{u_1}\rangle$ is the only u singlet (hence an eigenstate))

\rightarrow Now we only need to diagonalize the g subspace

$$H_g = \begin{pmatrix} V+z\epsilon & -z\epsilon \\ -z\epsilon & z\epsilon \end{pmatrix} = z\epsilon \mathbb{I} + \begin{pmatrix} V & -z\epsilon \\ -z\epsilon & 0 \end{pmatrix}$$

$$\rightarrow \text{Scalar eq: } \begin{vmatrix} V-\epsilon & -z\epsilon \\ -z\epsilon & -\epsilon \end{vmatrix} = \epsilon^2 - VE + 4t^2 = 0$$

$$\Rightarrow E_{g\pm} = z\epsilon + \frac{V}{2} \pm \sqrt{\left(\frac{V}{2}\right)^2 + 4t^2}$$

• Ground state: $E_{g-} = z\epsilon + \frac{V}{2} - \sqrt{\left(\frac{V}{2}\right)^2 + 4t^2}$

→ Note that ϵ represents a global shift in H . This is why it appears in the diagonal. Basically ϵ is a single particle property. Adding ϵ in a single particle means adding $N\epsilon$ to $H(N)$. This is because the off-diagonal terms (here) are equal by symmetry.

→ We can plot the eigenstates as a function of t/v or v/t . But before that let's see the limits:

- Non interacting limit: $0 = 0$

$E_{gs} = 2\epsilon - t \Rightarrow$ Same as two non interacting e^- occupying the bonding state of the single particle H_2^+ problem (see phy 555, tight binding)

- $V \gg t \Rightarrow$ This is the atom limit, when the atoms are very far away:

$$|\Psi_- \rangle \sim |\Phi_{g2} \rangle = \frac{1}{\sqrt{2}} (|A^\uparrow, B^\uparrow \rangle - |A^\downarrow, B^\downarrow \rangle)$$

$E_{gs} \sim 2\epsilon$ (energy of the triplet). This corresponds

To having $1e^-$ on each atom, which is the exact solution (for the $1s$ basis orbitals) for two isolated atoms.

→ Hartree Fock Limit : (or HF solution)

→ Restricted HF

Note that the single particle solution of any \hat{h} in this basis is perfectly defined by symmetry.

RHF: For N even and with the highest occupied state being non degenerate RHF always gives a symmetry invariant singlet ($S=0$)

→ Any single particle Hamiltonian in this basis

has this form :

$$h = \begin{pmatrix} \epsilon' & -t' \\ -t' & \epsilon' \end{pmatrix} \quad \begin{array}{l} \text{Hermitic} \\ \text{symmetry} \end{array}$$

But we do not need to obtain it, because by symmetry the single particle gs is $|g\rangle = \frac{1}{\sqrt{2}}(|A\rangle + |B\rangle)$

so The RHF gs will be :

$$|\Psi_{GS}^{RHF}\rangle = |g\uparrow, g\downarrow\rangle = \frac{1}{2} (|A\uparrow, A\downarrow\rangle + |A\uparrow, B\downarrow\rangle + |B\uparrow, A\downarrow\rangle + |B\uparrow, B\downarrow\rangle)$$

$$= \frac{1}{\sqrt{2}} (|\Phi_{g_1}\rangle + |\Phi_{g_2}\rangle)$$

The energy : $E_{GS}^{RHF} = \langle \Psi_{GS}^{RHF} | \hat{H} | \Psi_{GS}^{RHF} \rangle =$

$$= \frac{1}{2} (\langle \Phi_{g_1} | \hat{H} | \Phi_{g_1} \rangle + \langle \Phi_{g_1} | \hat{H} | \Phi_{g_2} \rangle + \langle \Phi_{g_2} | \hat{H} | \Phi_{g_1} \rangle + \langle \Phi_{g_2} | \hat{H} | \Phi_{g_2} \rangle)$$

RHF

$$E_{GS}^{RHF} = 2\varepsilon + \frac{U}{2} - 2t$$

\rightarrow exact in $U=0$ limit
but as U grows it deviates
steadily failing to
reproduce the separate-atom
limit for $U \gg t$.

→ Let's analyze the particle correlations.

We can define the following correlation function:

$$C = \langle n_A^\uparrow n_A^\downarrow \rangle + \langle n_B^\uparrow n_B^\downarrow \rangle$$

n = # operator, which can be easily defined in second quantization.

All we need to know is:

$$\langle A^\uparrow, A^\downarrow | n_{A^\uparrow} n_{A^\downarrow} | A^\uparrow, A^\downarrow \rangle =$$

$$\langle B^\uparrow, B^\downarrow | n_{B^\uparrow} n_{B^\downarrow} | B^\uparrow, B^\downarrow \rangle = 1$$

And all other matrix elements of both are zero.

→ Measures probability of fluctuations with the two c^- on one atom.

Do!

For $|\Psi_{GS}^{HF}\rangle = |g^\uparrow, g^\downarrow\rangle$ we get $C = 1/2$, irrespective of V . It corresponds to the exact value for $V=0$.

How can we interpret this?

Because of the delocalization of both e^- (in the bonding single-particle state) the probability of finding both e^- in 1 atom = prob of one on each (50%). Since the single-particle state (HF) does not change with V it retains the same character when the atoms are pulled apart.

→ For the exact g_S (in the $\Omega=0$ limit we just saw $C=1/2$).

$$\text{for } V \gg T \quad |\Psi_{GS}\rangle \sim |\Phi_{g_2}\rangle = \frac{1}{\sqrt{2}} (|AP, B\downarrow\rangle - |AB, B^+\rangle)$$
$$C(V/T) \xrightarrow[V \gg T]{} 0$$

C diminishes smoothly from $1/2$ to 0 as V/T grows, indicating that quantum fluctuations finding both e^- on same side of the molecule

are suppressed by larger U/t .

Note That This is Totally suppressed in The RHF solution , showing That RHF has a big problem describing the breaking of a bond.

To Do as a HW :

→ If we want to obtain $C(U/t)$ for the exact solution we need the exact expression of the WF from the diagonalization of the singlet- g 2×2 block (we only obtained the energy).

$$\text{if you do it: } C = \frac{1}{2} \left\{ 1 - \frac{U}{\sqrt{U^2 + 16t^2}} \right\}$$