- Most simple version of a correlated system: 2 H atoms + 2 e^-.

$\longrightarrow H = h_1 + h_2 + V_{12}$, where $h_1 = h_2 = \sum_i -\nabla_i^2 \left(\frac{\hbar^2}{2m}\right) - \sum_\alpha \frac{1}{r_\alpha}$

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

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

$\longrightarrow$ Simplest model: 1 S 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:

→ SD Basis $|\phi_i\rangle$; $i = 1 \ldots \binom{4}{2} = 1 \ldots \frac{4!}{2!\,2!} = 1 \ldots 6$

We have 6 different Two-particle basis: (order does not matter, but consistency does).

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

$$\downarrow$$

$$\begin{array}{c c} e^- \#1 \longrightarrow & \begin{pmatrix} A\uparrow(1) & A\downarrow(1) \\ A\uparrow(2) & A\downarrow(2) \end{pmatrix} \\ e^- \#2 \longrightarrow & \end{array}$$

→ Repeat for all other SD

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

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

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

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

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

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)

$$\begin{cases} \langle A\sigma|\hat{h}|B\sigma\rangle = \langle B\sigma|\hat{h}|A\sigma\rangle = -t & \sigma = \uparrow,\downarrow \\ \langle A\sigma|\hat{h}|A\sigma\rangle = \langle B\sigma|\hat{h}|B\sigma\rangle = \varepsilon & \sigma = \uparrow,\downarrow \end{cases}$$

Note! spin is conserved in hopping!

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

(There was an error in first version!).

→ Interaction Term:

equal because of symmetry

$$\langle A\uparrow A\downarrow|V_{12}|A\uparrow A\downarrow\rangle = \langle B\uparrow B\downarrow|V_{12}|B\uparrow B\downarrow\rangle = U$$

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
$$\begin{cases} \langle A\sigma(i)|A\sigma'(i)\rangle = \langle B\sigma(i)|B\sigma'(i)\rangle = \delta_{\sigma\sigma'} \\ \langle A\sigma(i)|B\sigma'(i)\rangle = \langle B\sigma(i)|A\sigma'(i)\rangle = 0 \end{cases}$$

→ 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:

$$\langle\Phi_1|h_1+h_2|\Phi_1\rangle = \frac{1}{2}\Big[\langle A\uparrow(1)|A\downarrow(2)|h_1+h_2|A\uparrow(1)|A\downarrow(2)\rangle$$

$$-\langle A\uparrow(1)|A\downarrow(2)|h_1+h_2|A\uparrow(2)|A\downarrow(1)\rangle\Big] + \frac{1}{2}\,C.C.$$

$$= \cancel{2}\cdot\frac{1}{\cancel{2}}\Big[\cancelto{\varepsilon}{\langle A\uparrow(1)|h_1|A\uparrow(1)\rangle}\cdot\cancelto{1}{\langle A\downarrow(2)|A\downarrow(2)\rangle} +$$

$$\cancelto{\varepsilon}{\langle A\downarrow(2)|h_2|A\downarrow(2)\rangle}\cancelto{1}{\langle A\uparrow(1)|A\uparrow(1)\rangle} -$$

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

$$\langle A\downarrow(2)|h_2|A\uparrow(2)\rangle\cancelto{0}{\langle A\uparrow(1)|A\downarrow(1)\rangle} = 2\varepsilon$$

same for all $\langle\Phi_i|h_1+h_2|\Phi_i\rangle$

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

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

$i=1, j=4 \Rightarrow 0$ → Because all 1 particle orbitals are different (and the overlap terms are all zero)

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

$i=1, j=3$

$$\langle \phi_1 | h_1 + h_2 | \phi_3 \rangle = \frac{1}{2} \Big\{ \langle A\uparrow(1) | h_1 | A\uparrow(1) \rangle \cancelto{0}{\langle A\downarrow(2) | B\downarrow(2) \rangle}$$

$$+ \langle A\uparrow(1) | A\uparrow(1) \rangle \langle A\downarrow(2) | h_2 | B\downarrow(2) \rangle \rightarrow -t$$

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

$$- \cancelto{0}{\langle A\downarrow(1) | A\uparrow(1) \rangle} \langle A\uparrow(2) | h_2 | B\downarrow(2) \rangle$$

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

$$- \cancelto{0}{\langle A\uparrow(1) | B\downarrow(1) \rangle} \langle A\downarrow(2) | h_2 | A\uparrow(2) \rangle$$

$$+ \langle A\downarrow(1) | h_1 | B\downarrow(1) \rangle \langle A\uparrow(2) | A\uparrow(2) \rangle \rightarrow -t$$

$$+ \cancelto{0}{\langle A\downarrow(1) | B\downarrow(1) \rangle} \langle A\uparrow(2) | h_2 | A\uparrow(2) \rangle$$

$$= -t$$

- Same for :

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

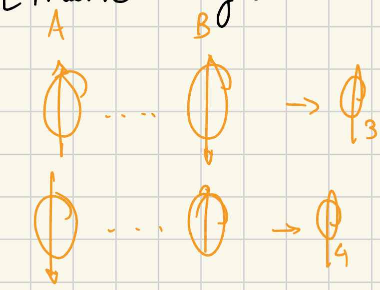
$$\langle \phi_2 | (h_1 + h_2) | \phi_3 \rangle = t$$

$$\langle \phi_2 | h_1 + h_2 | \phi_4 \rangle = -t$$

$$\langle \phi_1 | h_1 + h_2 | \phi_4 \rangle = t$$

(do iT! care with signs)

(Another way.



inversion operator: around center, not acting on spin.

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

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

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

$$= -|\phi_4\rangle$$

$i|\phi_1\rangle = |\phi_2\rangle$ also

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

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 $i|\phi_2\rangle = |\phi_1\rangle$)

→ all other elements of $h_1 + h_2$ are zero

so the full hamiltonian matrix in the MB basis is:

$$H = \begin{array}{cccccccc} & \phi_1 & \phi_2 & \phi_3 & \phi_4 & \phi_5 & \phi_6 & \\ \left(\begin{array}{c} \\ \\ \\ \\ \\ \\ \end{array}\right. & U+2\varepsilon & 0 & -t & t & 0 & 0 & \phi_1 \\ & 0 & U+2\varepsilon & -t & t & 0 & 0 & \phi_2 \\ & -t & -t & 2\varepsilon & 0 & 0 & 0 & \phi_3 \\ & t & t & 0 & 2\varepsilon & 0 & 0 & \phi_4 \\ & 0 & 0 & 0 & 0 & 2\varepsilon & 0 & \phi_5 \\ & 0 & 0 & 0 & 0 & 0 & 2\varepsilon & \phi_6 \end{array}$$

→ ϕ_5 & ϕ_6 are eigenstates of H, degenerate, with energy $E_{5,6} = 2\varepsilon$ ⇒ let's analyze why.

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

→ (~~so~~ i and H commute, so if ϕ_5 and ϕ_6 are eigenstates of both, with symmetry "u" (ungerade, negative value of -1 of the inversion operator. Under inversion states can be u or g (antisymmetric and symmetric)

<u>Note</u> : Symmetry group of a Homopolar diatomic molecule.

$D_{\infty h}$
- ∞ rotations around molecule axis
- Inversion center (g or u, eigenvalue +1 -1)
- Reflection plane

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

$$i|\phi_1\rangle = |\phi_2\rangle \quad i|\phi_2\rangle = |\phi_1\rangle \quad (\hat{i}^2 = \mathbb{1})$$

$$i|\phi_3\rangle = -|\phi_4\rangle \quad i|\phi_4\rangle = -|\phi_3\rangle$$

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 u states:

$$|\phi_{u1}\rangle = \frac{1}{\sqrt{2}}\left(|\phi_1\rangle - |\phi_2\rangle\right)$$

$$|\phi_{u2}\rangle = \frac{1}{\sqrt{2}}\left(|\phi_3\rangle + |\phi_4\rangle\right)$$

so we have the full set of common eigenvalues

So we can decompose the 6x6 H matrix in Two blocks, a 2x2 g block and a 4x4 u block.

in The new basis:

$$\langle\phi_{g1}|H|\phi_{g1}\rangle = \frac{1}{2}\left(\langle\phi_1|H|\phi_1\rangle + \langle\phi_2|H\phi_2\rangle + \langle\phi_1|H|\phi_2\rangle + \langle\phi_2|H|\phi_1\rangle\right) = U + 2\varepsilon$$

$$\langle\phi_{g2}|H|\phi_{g2}\rangle = \checkmark\ \text{same but with } |\phi_3\rangle - |\phi_4\rangle$$

$$= \frac{1}{2}\left(\langle\phi_3|H\phi_3\rangle + \langle\phi_4|H|\phi_4\rangle - \langle\phi_3|H|\phi_4\rangle - \langle\phi_4|H|\phi_3\rangle = 2\varepsilon\right.$$

$$\langle\phi_{g1}|\phi_{g2}\rangle = -2t = \langle\phi_{g2}|\phi_{g1}\rangle \leftarrow \text{Hermitian}$$

Now the 2x2 u block (without $|\phi_5\rangle$ and $|\phi_6\rangle$)

becomes :
$$H_u = \begin{pmatrix} U+2\varepsilon & 0 \\ 0 & 2\varepsilon \end{pmatrix}$$

→ So $|\phi_{u1}\rangle$ and $|\phi_{u2}\rangle$ are already eigenstates of H ($|\phi_2$ is degenerate with $|\phi_5\rangle$ and $|\phi_6\rangle$)

Now, in the g, u basis :

$$H = \left(\begin{array}{cccccc|c}
\multicolumn{2}{c}{\overbrace{\qquad\qquad\qquad}^{S=0}} & & \multicolumn{3}{c}{\overbrace{\qquad\qquad\qquad}^{S=1}} & \\
U+2\varepsilon & -2t & 0 & 0 & 0 & 0 & g_1 \\
-2t & 2\varepsilon & 0 & 0 & 0 & 0 & g_2 \\
0 & 0 & U+2\varepsilon & 0 & 0 & 0 & u_1 \\
0 & 0 & 0 & 2\varepsilon & 0 & 0 & u_2 \\
0 & 0 & 0 & 0 & 2\varepsilon & 0 & u_3 \\
0 & 0 & 0 & 0 & 0 & 2\varepsilon & u_4 \\
\multicolumn{3}{c}{\underbrace{\qquad\qquad\qquad\qquad}_{M=0}} & 0 & 1 & -1 & \\
\end{array}\right)$$

→ m_s

Now all it remains is diagonalizing this block.

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

$\longrightarrow S(L^2)$ and $M(L_z)$

$$M: \begin{cases} M=0 \text{ for } |\Phi_{g_1}\rangle, |\Phi_{g_2}\rangle, |\Phi_{u1}\rangle, |\Phi_{u2}\rangle \\ M=1 \text{ for } |\Phi_{u3}\rangle = |\Phi_5\rangle \\ M=-1 \text{ for } |\Phi_{u4}\rangle = |\Phi_6\rangle \end{cases}$$

* This explains why $|\phi\rangle_5$ 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:

$\rightarrow$ We have $S=1$ for $|\phi_{u2}\rangle |\phi_{u3}\rangle |\phi_{u4}\rangle$
They form The Triplet state.

$\longrightarrow$ The rest of the states have $S=0$

· So in terms of configurations we have :

→ 2 g singlets $|\phi_{g_1}\rangle$ & $|\phi_{g_2}\rangle$

→ 1 u singlet $|\phi_{u_1}\rangle$ → energy $U+2\varepsilon$

→ 1 u Triplet $|\phi_{u_2}\rangle\, |\phi_{u_3}\rangle\, |\phi_{u_4}\rangle$ energy 2ε

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

→ Now we only need to diagonalize the g subspace

$$H_g = \begin{pmatrix} U+2\varepsilon & -2t \\ -2t & 2\varepsilon \end{pmatrix} = 2\varepsilon\,\mathbb{1} + \begin{pmatrix} U & -2t \\ -2t & 0 \end{pmatrix}$$

→ Secular eq: $\begin{vmatrix} U-E & -2t \\ -2t & -E \end{vmatrix} = E^2 - UE + 4t^2 = 0$

$$\Rightarrow \boxed{E_{g_\pm} = 2\varepsilon + \frac{U}{2} \pm \sqrt{\left(\frac{U}{2}\right)^2 + 4t^2}}$$

• Ground state : $E_{g_-} = 2\varepsilon + \frac{U}{2} - \sqrt{\left(\frac{U}{2}\right)^2 + 4t^2}$

→ 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 ading $N \cdot \varepsilon$ to $H(N)$. This is because the onsite terms (here) are equal by symmetry.

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

- Non interacting limit: $U = 0$

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

- $U >> t$ ⇒ This is the atom limit, when the atoms are very far away: → see later: $|g_-\rangle \sim \frac{2t}{U}\phi_{g1} + \frac{U}{2t}\phi_{g2}$

$$|g_-\rangle \overset{U>>t}{\sim} |\phi_{g2}\rangle = \frac{1}{\sqrt{2}}\left(|A\uparrow, B\downarrow\rangle - |A\downarrow B\uparrow\rangle\right)$$

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

To having 1 e^- 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.

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

→ Any single particle Hamiltonian in this basis has this form:

$$h = \begin{pmatrix} \varepsilon' & -t' \\ -t' & \varepsilon' \end{pmatrix}$$

. Hermitic

. symmetry

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

lowest energy single particle MO

so the RHF gs will be :

$$|\Psi^{RHF}_{GS}\rangle = \underbrace{|g\uparrow, g\downarrow\rangle}_{\text{single slater determinant Built from } |g\rangle} \xrightarrow{\text{linear combination of single}} = \frac{1}{2}\left(|A\uparrow, A\downarrow\rangle + |A\uparrow, B\downarrow\rangle + |B\uparrow, A\downarrow\rangle + |B\uparrow, B\downarrow\rangle\right) \rightarrow$$

This can be shown, building the HF SD

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

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

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

$$\boxed{E^{RHF}_{GS} = 2\varepsilon + \frac{U}{2} - 2t}$$

→ exact in $U=0$ limit but as U grows it deviates steadily, failing to reproduce the separate-atom limit for $U >> t$.

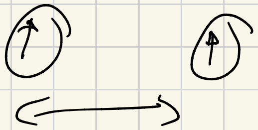
→ This solution makes sense in the $U \to 0$ limit.

for $U/t \to 0$ the HF wave function is the same as for "Free" (Non interacting e^-). This is the 2-site equivalent of a metal, where each e^- is equally shared between all sites.

but for $U/t \to \infty$ (Not shown, can be demostrated) the HF WF is one with one spin ↑ in 1 atom and spin ↓ in the other ⇒ i.e. 2 neutral atoms with opposite spin.

→ (The SD is independent of U)*

This configuration in HF is less than →



For atoms very far apart.

This is wrong!
Both should be allowed!

→ Note about The HF W.F Vs The GS WF

Exact

→ 1.- The GS WF is obtained by diagonalizing The 2x2 block made by $|\Phi_{g1}\rangle$ and $|\Phi_{g2}\rangle$

Remember: For The eigenvectors:

- $[H-E][\Psi]=0$ → solve for E_+ and E_-

we get: $$|\Psi_\pm\rangle = \frac{1}{\sqrt{1+\left(\frac{U-E_\pm}{2t}\right)}}\left(\Phi_{g1}+\frac{(U-E_\pm)}{2t}\Phi_{g2}\right)$$

→ This is a linear combination of Φ_{g1} and Φ_{g2} (They are both singlet states).

iT is a singleT $(S=0)$, with spacial "g" symmetry.

→ BuT - , a singlet state can never be written as a single Slater determinant, because iT is antisymmetric in spin, but not antisymmetric To

(S=0, singleT)

particle exchange in The spatial sector.

Note The HF WF is a single determinant in The molecular orbital basis, but can look like a LCSD in The atomic basis

→ Let's see The UHF solution:
(also called spin polarized)

$$|\phi_{GS}^{UHF}\rangle = |\underbrace{\phi_1 \uparrow, \phi_2 \downarrow}\rangle = \frac{1}{\sqrt{2}} \left\| \, |\phi_1 \uparrow\rangle \; |\phi_2 \downarrow\rangle \, \right\|$$

Now ϕ_1 and ϕ_2 are not forced
To have the same symmetry and $S=0$ (NoT singleT).

Now ϕ_1 and ϕ_2 can Take any shape, unconstrained by spin or (inversion) symmeTry.

$$|\phi_1\rangle = \cos\theta_1 |A\rangle + e^{i\xi_1} \sin\theta_1 |B\rangle$$

$$|\phi_2\rangle = \cos\theta_2 |A\rangle + e^{i\xi_2} \sin\theta_2 |B\rangle$$

→ MosT general way of writing the MO.

We need To minimize $E_{GS}^{UHF} = \langle \Psi_{GS}^{UHF} | H | \Psi_{GS}^{UHF} \rangle$ as a funcion of $\theta_1, \theta_2, \xi_1, \xi_2$. This can be done (long derivation see Falikov-Harris). The solution depends on U/t:

Can be Taken =0

→ $U/t \leq 2$ → same solution as UHF

$$|\phi_1\rangle = |\phi_2\rangle = |g\rangle \quad ; \quad E_{GS}^{UHF} = E_{GS}^{HF}$$

$$E(\theta_1, \theta_2) = 2\varepsilon - 2t\sin(\theta_1+\theta_2)\cos(\theta_1-\theta_2) + \frac{U}{2}\left[\cos^2(\theta_1+\theta_2) + \cos^2(\theta_1-\theta_2)\right]$$

- For $U/t > 2$ Then symmetry breaks down giving 2 degenerate minima (a very common situation for broken symmetries!, one can break it in either direction).

→ The resulting 2 particle states are given in Falicov-Harris 1969 ($|SDW1\rangle$ and $|SDW2\rangle$ in The paper)

We can characterize The solution with energy and spin polarization:

$$E_{GS}^{UHF} = 2\epsilon - \frac{2t^2}{U} \quad (U/t > 2)$$

$$\delta n_A \equiv \langle n_{A\uparrow} \rangle - \langle n_{A\downarrow} \rangle = \sqrt{1 - \frac{4t^2}{U^2}}$$

→ starts from zero with discontinuous derivative at $U/t = 0$ and grows asymptotically To 1 (Full polarization)

as $\delta n_B = -\delta n_A$, The excess of spin ↑ in one atom is compensated by excess ↓ on The other.

Note: both atoms continue To have 1 particle in average

$$\langle n_A \rangle = \langle n_{A\uparrow} \rangle + \langle n_{A\downarrow} \rangle = \langle n_B \rangle = 1$$

Total spin polarization $N_\uparrow - N_\downarrow = 0$

This is the antiferromagnetic solution

(The other minimum $|SDW2\rangle$ is the same but with $A\downarrow$ and $B\uparrow$

In the large U limit $U \gg t$

$$|\Psi_{GS}^{EXACT}\rangle = |{}^1\Phi_{g-}\rangle \longrightarrow |\Phi_{g2}\rangle = \frac{1}{\sqrt{2}}\left(|A\uparrow B\downarrow\rangle - |A\downarrow B\uparrow\rangle\right)$$

$$|\Psi_{GS}^{UHF}\rangle \longrightarrow |A\uparrow B\downarrow\rangle$$ (or for the other minimum $|A\downarrow B\uparrow\rangle$)

$\rightarrow \Psi_{GS}^{UHF}$ has broken both inversion and total spin symmetry.

- inversion: obvious neither g or u character
- spin: $|\Psi_{GS}^{UHF}\rangle = \frac{1}{\sqrt{2}}\Big(\underbrace{|\Phi_{g2}\rangle}_{\text{singlet}} + |\Phi_{u2}\rangle\Big) \rightarrow$ part of the triplet

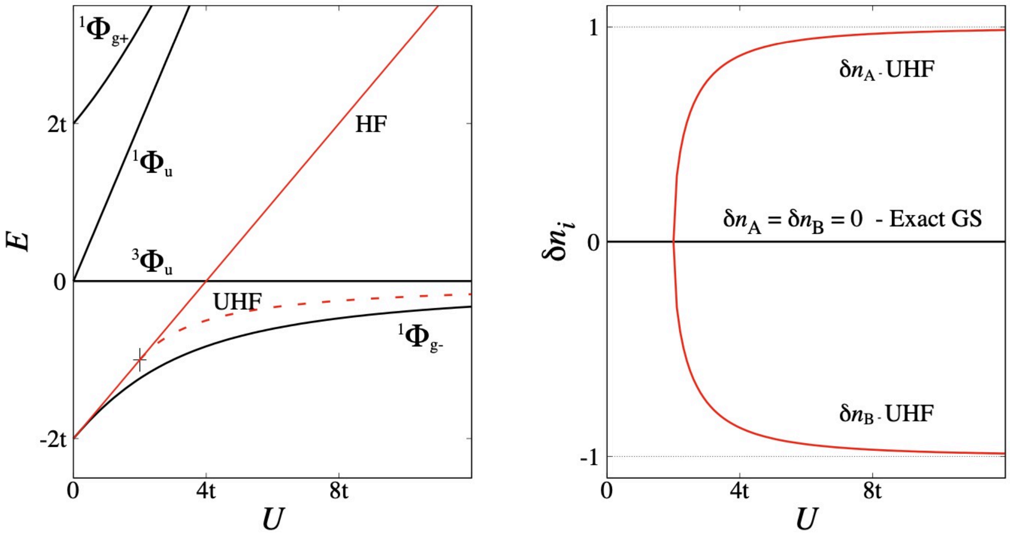
it is a singlet - triplet mix (in the large U limit)
This is what is called <u>spin contamination</u>

<u>Summary</u>:

- HF (mean field) in UHF (not spin polarized) gives a very wrong description of Bond breaking or the highly correlated regime ($U >> t$).

- Allowing for spin polarization recovers some qualitative behavior, but at the cost of introducing fictitious symmetry breaking, including magnetic moments that are unreal. It is the "poor man" way of describing correlations. But, the <u>real</u> solution is very different!

  "exact



$^1\Phi_{g+}$
2t
$^1\Phi_u$
HF
E
$^3\Phi_u$
0
UHF
$^1\Phi_{g-}$
-2t
0
4t
8t
U
1
δn_A - UHF
$\delta n_A = \delta n_B = 0$ - Exact GS
δn_i
0
δn_B - UHF
-1
0
4t
8t
U

→ 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 e^- on one atom.

Do!

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

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 U it retains the same character when the atoms are pulled appart.

→ For the exact gs (in the $U=0$ limit we just saw $C=1/2$).

for $U \gg t$ $|\Psi_{GS}\rangle \sim |\Phi_{g2}\rangle = \frac{1}{\sqrt{2}}\left(|A\uparrow, B\downarrow\rangle - |A\downarrow, B\uparrow\rangle\right)$

$$C(U/t) \xrightarrow{U \gg t} 0$$

C diminishes smoothly from 1/2 to 0 as U/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).

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

Hubbard Dimer in second quantization:

$$\hat{H} = \epsilon\left(n_{A\uparrow} + n_{A\downarrow} + n_{B\uparrow} + n_{B\downarrow}\right) - t\left(c^{\dagger}_{A\uparrow} c_{B\uparrow} + c^{\dagger}_{B\uparrow} c_{A\uparrow} + c^{\dagger}_{A\downarrow} c_{B\downarrow} + c^{\dagger}_{B\downarrow} c_{A\downarrow}\right) + U\left(n_{A\uparrow} n_{A\downarrow} + n_{B\uparrow} n_{B\downarrow}\right)$$

→ Basis: It is important to choose an order and stic to it! A before B, ↑ before ↓.

$$|\phi_1\rangle = |A\uparrow A\downarrow\rangle = c^{\dagger}_{A\uparrow} c^{\dagger}_{A\downarrow} |0\rangle = |1\,1\,0\,0\rangle$$

$$|\phi_2\rangle = |B\uparrow B\downarrow\rangle = c^{\dagger}_{B\uparrow} c^{\dagger}_{B\downarrow} |0\rangle = |0\,0\,1\,1\rangle$$

$$|\phi_3\rangle = |A\uparrow B\downarrow\rangle = c^{\dagger}_{A\uparrow} c^{\dagger}_{B\downarrow} |0\rangle = |1\,0\,0\,1\rangle$$

$$|\phi_4\rangle = |A\downarrow B\uparrow\rangle = c^{\dagger}_{A\downarrow} c^{\dagger}_{B\uparrow} |0\rangle = |0\,1\,1\,0\rangle$$

$$|\phi_5\rangle = |A\uparrow B\uparrow\rangle = c^{\dagger}_{A\uparrow} c^{\dagger}_{B\uparrow} |0\rangle = |1\,0\,1\,0\rangle$$

$$|\phi_6\rangle = |A\downarrow B\downarrow\rangle = c^{\dagger}_{A\downarrow} c^{\dagger}_{B\downarrow} |0\rangle = |0\,1\,0\,1\rangle$$

n is a diagonal operator so the ϵ term (onsite) gives a 2ϵ in the diagonal.

• For The Hoping Terms :

ex : $C_{A\uparrow}^{+} C_{B\uparrow} \longrightarrow$

Best is To use anticommutator rules and operator definition.

Let's see with $|\phi_1\rangle = |1\,1\,\overset{\overset{B\uparrow}{\downarrow}}{0}\,0\rangle$

it's obviously 0 (

So only Terms with 1 in "3" will not be zero : ϕ_2, ϕ_4

ϕ_5

$\to \phi_2$

let'see: $C_{A\uparrow}^{+} C_{B\uparrow} |\phi_2\rangle = C_A^{+} (-1)^0 |0\,0\,0\,1\rangle$

$= |1\,0\,0\,1\rangle$ (positive) $= |\phi_3\rangle$

So we get $\langle \phi_3 | H_t | \phi_2 \rangle = -t$ (Same as CC (Hermitian))

$\to \phi_4$

$C_{A\uparrow}^{+} C_{B\uparrow} |\phi_4\rangle = C_{A\uparrow} (-1)^1 |0\,1\,0\,0\rangle = -\underbrace{|1\,1\,0\,0\rangle}_{\phi_1}$

So we obtain $\langle \phi_1 | H_t | \phi_4 \rangle = +t$

$\to \phi_5$

$C_{A\uparrow}^{+} C_{B\uparrow} |\phi_5\rangle = C_{A\uparrow}^{+} (-1)^1 |1\,0\,0\,0\rangle = 0$

→ Once we do This we have :

$$\langle \phi_3 | H_t | \phi_1 \rangle = -t$$ (and Conjugates)

$$\langle \phi_4 | H_t | \phi_1 \rangle = +t$$

$$\langle \phi_3 | H_t | \phi_2 \rangle = -t$$

$$\langle \phi_4 | h_t | \phi_2 \rangle = +t$$

→ Finally Onsite repulsion :

$$H_U = U\left(n_{A\uparrow} n_{A\downarrow} + n_{B\uparrow} n_{B\downarrow}\right)$$

⇒ # operators are diagonal and commute with each other. Only non-zero for the doubly occ. states (ϕ_1 and ϕ_2)

$$\langle \phi_1 | H_t | \phi_1 \rangle = \langle \phi_2 | H_t | \phi_2 \rangle = U$$

→ and That is it!

$$H = \begin{pmatrix} U+2\epsilon & 0 & -t & t & 0 & 0 \\ 0 & U+2\epsilon & -t & t & 0 & 0 \\ -t & -t & 2\epsilon & 0 & 0 & 0 \\ t & t & 0 & 2\epsilon & 0 & 0 \\ 0 & 0 & 0 & 0 & 2\epsilon & 0 \\ 0 & 0 & 0 & 0 & 0 & 2\epsilon \end{pmatrix}$$

different changes in the order used for the basis definition would change sign but if done consistently they represent changes on the global sign of the MB basis states, which does not affect the eigen states or eigen values.