The two particle problem with spin!

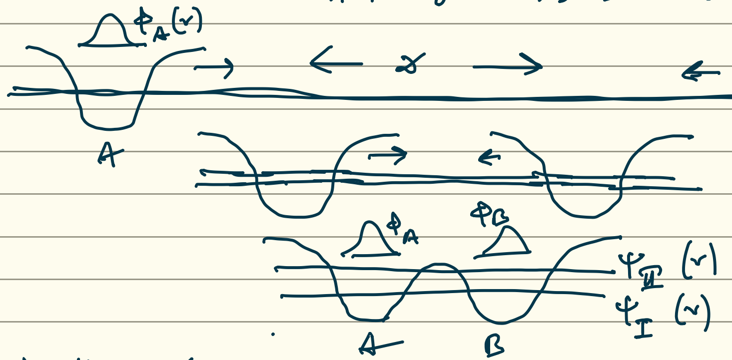
Consider two atoms (potential wells) having one electron each approaching each other.

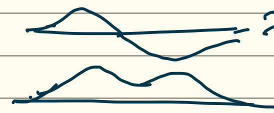
Recall, within the single particle picture where we don't consider the two electron explicitly.

Let $\phi_A(r) = \phi_0(r - r_A)$; $\phi_B(r) = \phi_0(r - r_B)$.

Each electron feels an average effect of the other electron..

In the simplest scenario we completely neglect interaction between them.





$\approx \frac{1}{\sqrt{2}}(\phi_A(r) - \phi_B(r))$

$\approx \frac{1}{\sqrt{2}}(\phi_A(r) + \phi_B(r))$

Within single particle picture:

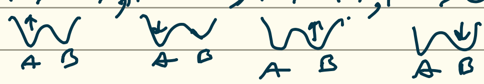
We just populate the lowest energy state by two electrons with opposite spin

$\Rightarrow$ Ground state is non-magnetic.

Then How do we get states with non zero net magnetic moment.?

We need to go beyond single particle picture to construct explicit many electron states.
To respect Pauli exclusion principle the state must be antisymmetric on the whole including the space and spin parts.

Available states for each of the two electron to occupy: $|A\rangle \otimes |\alpha\rangle$, $|A\rangle \otimes |\beta\rangle$, $|B\rangle \otimes |\alpha\rangle$, $|B\rangle \otimes |\beta\rangle$



When $S_z|\alpha\rangle = \frac{\hbar}{2}|\alpha\rangle$,
$S_z|\beta\rangle = -\frac{\hbar}{2}|\beta\rangle$

$$\left.\begin{array}{l} S^2|\alpha\rangle = \hbar^2 \frac{3}{4}|\alpha\rangle \\ S^2|\beta\rangle = \hbar^2 \frac{3}{4}|\beta\rangle \end{array}\right\} s = \frac{1}{2},$$

Recall
$S^2|s m_s\rangle = \hbar^2 s(s+1)|s m_s\rangle$, $|\vec{\mu}_s| = \mu_B\sqrt{s(s+1)}$
$S_z|s m_s\rangle = \hbar m_s|s m_s\rangle$ $\hookrightarrow$ mag dip. mom (measurable)

Recall, for 2 electron:

$$\left.\begin{array}{l} |\alpha(1)\rangle \otimes |\alpha(2)\rangle \\ |\beta(1)\rangle \otimes |\beta(2)\rangle \\ \frac{1}{\sqrt{2}}(|\alpha(1)\rangle \otimes |\beta(2)\rangle + |\beta(1)\rangle \otimes |\alpha(2)\rangle) \end{array}\right\}$$

Triplet
$= |tri\rangle \rightarrow$ symmetric

$\hat{S}_z|tri\rangle = \hbar|tri\rangle$; $S^2|tri\rangle = 2\hbar^2|tri\rangle \Rightarrow \underline{s=1}$

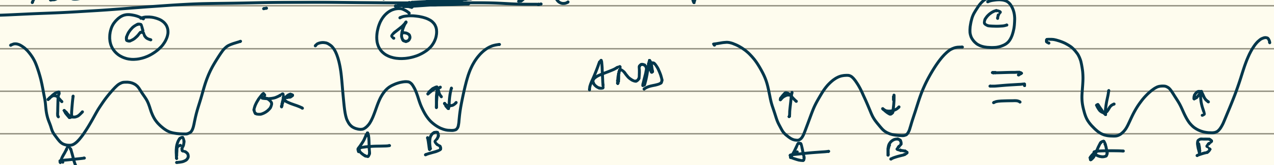
$\Rightarrow$ Two electron states with $\underline{s=1}$ will have antisymmetric space part.

$\frac{1}{\sqrt{2}}(|\alpha(1)\rangle \otimes |\beta(2)\rangle - |\beta(1)\rangle \otimes |\alpha(2)\rangle) = |Si\rangle$, Singlet.

$\hat{S}_z|Si\rangle = 0|Si\rangle$; $S^2|Si\rangle = 0|Si\rangle \Rightarrow \underline{s=0}$

$\downarrow$
Antisymmetric $\Rightarrow$ 2 electron states with $\underline{s=0}$ will have symmetric space part.

Possible scenarios with $s=0$; (net magnetic moment $|\vec{\mu}_s| = 0$)



$|\Psi_a\rangle = |A1\rangle|A2\rangle|Si\rangle$ ($\otimes$ implied)

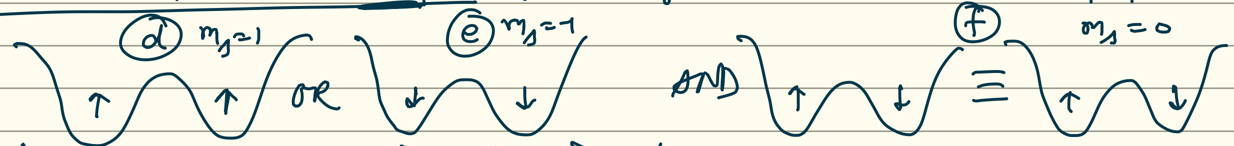
$|\Psi_b\rangle = |B1\rangle|B2\rangle|Si\rangle$

site $\hookrightarrow$ electron.

$|\Psi_c\rangle = \frac{1}{\sqrt{2}}(|A1\rangle|B2\rangle + |B1\rangle|A2\rangle)|Si\rangle$

$\downarrow$
Note that we can not have "$-$" sign here for $s=0$ for the spin part to be $|Si\rangle$ which is antisymmetric.

Possible scenarios with $S=1$ (net magnetic moment nonzero: $|\vec{\mu}_s| = \mu_B\sqrt{2}$)



$$|\psi_d\rangle = \frac{1}{\sqrt{2}}\left(|A1\rangle|B2\rangle - |B1\rangle|A2\rangle\right)|\alpha 1\rangle|\alpha 2\rangle$$

$$|\psi_e\rangle = \frac{1}{\sqrt{2}}\left(|A1\rangle|B2\rangle - |B1\rangle|A2\rangle\right)|\beta 1\rangle|\beta 2\rangle$$

$$|\psi_f\rangle = \frac{1}{2}\left(|A1\rangle|B2\rangle - |B1\rangle|A2\rangle\right)\otimes\left(|\alpha 1\rangle|\beta 2\rangle + |\beta 1\rangle|\alpha 2\rangle\right)$$

Let us see the energies of these states: $\hat{H} = \hat{T}_1 + \hat{T}_2 + \hat{V}_1 + \hat{V}_2 + \hat{V}_{ee}$

$$V_1(r_1) = V_A(r_1) + V_B(r_1)\ ;\ V_2(r_2) = V_A(r_2) + V_B(r_2)\ ;\ V_{ee} = \frac{1}{|r_1 - r_2|}$$

$$\hat{H}_A = T + V_A\ ;\ H_A|A\rangle = E_A|A\rangle,\ H_B|B\rangle = E_B|B\rangle$$

(a) $S=0$

$$E_a = \langle\psi_a|\hat{H}|\psi_a\rangle = \langle\psi_a|\hat{T}_1+\hat{V}_1|\psi_a\rangle + \langle\psi_a|\hat{T}_2+\hat{V}_2|\psi_a\rangle + \langle\psi_a|\hat{V}_{ee}|\psi_a\rangle$$

$$\langle\psi_a|T_1+V_1|\psi_a\rangle = \left(\langle S_i|\otimes\langle A2|\otimes\langle A1|\right)\left(T_1+V_1\right)\left(|A1\rangle\otimes|A2\rangle\otimes|S_i\rangle\right)$$

$$= \left(\langle S_i|\otimes\langle A2|\right)\langle A1|\left(T_1+V_A(r_1)\right)|A1\rangle\left(|A2\rangle\otimes|S_i\rangle\right)$$

$$= E_A\underbrace{\langle S_i|\ \langle A2|A2\rangle\ |S_i\rangle}_{1} + \left(\langle S_i|\otimes\langle A2|\right)\underbrace{\langle A_1|V_B(r_1)|A_1\rangle}_{\delta}\left(|A2\rangle\otimes|S_i\rangle\right)$$

$$= E_A + \delta\quad ;\quad \delta < 0 \because$$ $\to |\psi_A(r_1)|^2 \to +ve$, $-ve\ V_B(r_1)$

let $E_A = E_B = E_0$

Similarly $\langle\psi_a|T_2+V_2|\psi_a\rangle = E_A + \delta$

$$\langle\psi_a|V_{ee}|\psi_a\rangle = \left(\langle S_i|\otimes\langle A2|\int|r_2\rangle\langle r_2|dr_2\right)\otimes\langle A1|\int|r_1\rangle\langle r_1|dr_1\ \frac{1}{|r_1-r_2|}\left(|A1\rangle\otimes|A2\rangle\otimes|S_i\rangle\right)$$

$$= \iint_{r_1 r_2}\frac{|\psi_A(r_1)|^2|\psi_A(r_2)|^2}{|r_1-r_2|}d^3r_1 d^3r_2$$ $\to$ overlapping orbs. $\to$ ↗ +ve

$$= U_{AA}\ ,\ \text{let } U_{AA} = U_{AB} = U$$

$$\Rightarrow \boxed{E_a = 2E_0 - 2|\delta| + U}$$ similar for (b) $\Rightarrow$ (a) and (b) can not be Ground state due to high +ve U

(c) $S=0$

Net spin $=0 \Rightarrow$ spin singlet $\Rightarrow$ Antisym $\Rightarrow$ space part symmetric.

$$\Rightarrow |\psi_c\rangle = \frac{1}{\sqrt{2}}\left(|A1\rangle\otimes|B2\rangle + |B1\rangle\otimes|A2\rangle\right)\otimes|S_i\rangle.$$

$$E_c = \langle\psi_c|H|\psi_c\rangle = \frac{1}{2}\left(\langle B2|\langle A1| + \langle A2|\langle B1|\right)H\left(|A1\rangle|B2\rangle + |B1\rangle|A2\rangle\right)$$

$$= \frac{1}{2}\underbrace{\left(\langle B2|\langle A1|H|A1\rangle|B2\rangle + \langle A2|\langle B1|H|B1\rangle|A2\rangle\right)}_{\mathrm{I}} + \frac{1}{2}\underbrace{\left(\langle B2|\langle A1|H|B1\rangle|A2\rangle + \langle A2|\langle B1|H|A1\rangle|B2\rangle\right)}_{\mathrm{II}}$$

$$\mathrm{I}:\ \langle A2|\otimes\langle B1|\ H\ |B1\rangle\otimes|A2\rangle = 2E_0 - 2|\delta| + U_{AB}\ ;$$

$$U_{AB} = \iint_{r_1 r_2} d^3r_1 d^3r_2\frac{|\psi_A(r_1)|^2|\psi_B(r_2)|^2}{|r_1-r_2|}$$

$\text{II}: \langle A2| \otimes \langle B1| H |A1\rangle \otimes |B2\rangle$

$$= \langle A2| \otimes \langle B1| \int |r_1\rangle\langle r_1| \, H \, |A1\rangle \otimes |B2\rangle \, dr_1$$

$\int |r_2\rangle\langle r_2| \, dr$

$$= \langle A2| \int \psi_B^*(r_1)\,(T_1+T_2+V_1+V_2)\,\psi_A(r_1) \, |B2\rangle + \langle A2| \int \frac{\psi_B^*(r_1)\,\psi_A(r_1)}{|r_1-r_2|} \, |B2\rangle$$

$$= \underbrace{S_{AB}}_{\langle A2|B2\rangle} \; \underbrace{t_{AB}}_{\text{hopping}} + \int \frac{\psi_A^*(r_2)\,\psi_B^*(r_1)\,\psi_A(r_1)\,\psi_B(r_2)}{|r_1-r_2|} \, dr_1 \, dr_2$$

$$= S_{AB}\, t_{AB} + E_x$$

$$\therefore \; \boxed{E_c = \frac{1}{2}\left(4E_0 - 4|\delta| + 2U_{AB}\right) + \frac{1}{2}\left(2 S_{AB} t_{AB} + 2E_x\right) = 2E_0 - 2|\delta| + U_{AB} + S_{AB} t_{AB} + E_x}$$

$S_{AB}\, t_{AB} = 0$ if $\phi_A \phi_B$ orthogonal.

S = 1

(d) (e) (f)

$$|\psi_d\rangle = \frac{1}{\sqrt{2}}\left(|A1\rangle \otimes |B2\rangle - |B1\rangle \otimes |A2\rangle\right) |\text{tri}\rangle$$

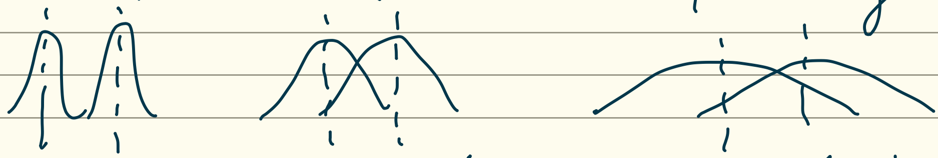
$\therefore$ by analogy to (c) (only change of sign)

$$E_d = E_e = E_f = 2E_0 - 2|\delta| + U_{AB} - S_{AB}\, t_{AB} - E_x$$

$\Rightarrow$ (c) / (d) / (e) / (f) could be possible Ground state depending on the sign of the E_x

$S = 0$ (c); $S = 1$ (d), (e), (f)

Note the E_x becomes optimally strong at particular level of localization and proximity of orbitals.



Weak due to poor overlap

Can be optimal.

Weak due to large $|r_1 - r_2|$

Overlap should be strong but the region of overlap should not be very large so that $\frac{1}{|r_1 - r_2|}$ does not become very low.