The orbital part of 2 electron system

In our previous discussion, we argued that the triplet $(s=1)$ and singlet state $(s=0)$ have different energies (E_t and E_s). The energy of the 2-electron system depends on the space part of the total wave function. Let us show this quantitatively. To simplify our problem, we will assume a hydrogen like atom with two-electrons. We will show that electron-electron interaction naturally leads to exchange interaction.

The two-electron Hamiltonian is

$$H = h_o(\vec{r}_1) + h_o(\vec{r}_2) + \frac{e^2}{|\vec{r}_1 - \vec{r}_2|}$$

when $\vec{r}_1$ and $\vec{r}_2$ are the positions of the two electron and $h_o(r)$ is the single-electron hamiltonian for a hydrogen-like atom. The interaction term (Coulomb repulsion) $e^2/|r_1 - r_2|$ is the <u>only</u> new interaction term

We assume that the one-electron wave functions has been solved with orthogonal eigenstates $\phi_a, \phi_b \cdots$ with eigenenergies $\epsilon_a, \epsilon_b, \cdots$

~~ie $h_o(\vec{r}$~~

ie $h_o(r)\phi_a = \epsilon_a \phi_a$; $h_o(r)\phi_b = \epsilon_b \phi_b$ and $\int \phi_a^*(r)\phi_b(r)\,dr = 0$

Ignoring the Coulomb repulsion term, the energy of the two electron system is $\epsilon = \epsilon_a + \epsilon_b$

and the wave fun $\rightarrow \phi_a \phi_b$

Of course with e-e interaction term the energies are going to change. And...

1) The spin part of the wave function also should be considered

2) The total wave function must be antisymmetric
=> accomplished by a slater determinant construction

Previously, we constructed 4 spin states with two electrons $|\uparrow\uparrow\rangle$, $|\downarrow\downarrow\rangle$, $|\downarrow\uparrow\rangle$ and $|\uparrow\downarrow\rangle$
2 with parallel spins and 2 with antiparallel spins. We will combine these states with orbital part to make the entire wave function (basis)
~~If we only~~ obey pauli-exclusion.

Let us denote $\alpha \rightarrow$ spin $|\uparrow\rangle$ and $\beta \rightarrow$ down spin $|\downarrow\rangle$

So, $\alpha(s_1) = |\uparrow\rangle_1$ $\quad \beta(s_1) = |\downarrow\rangle_1$

$\alpha(s_2) = |\uparrow\rangle_2$ $\quad \beta(s_2) = |\downarrow\rangle_2$

So the basis state with spins up is $|\uparrow\rangle_1 |\uparrow\rangle_2$

$$\Psi_1 = \frac{1}{\sqrt{2}} \begin{vmatrix} \phi_a(\bar{r}_1)\alpha(s_1) & \phi_a(r_2)\alpha(s_2) \\ \phi_b(\bar{r}_1)\alpha(s_1) & \phi_b(r_2)\alpha(s_2) \end{vmatrix}$$

$$= \frac{1}{\sqrt{2}} \left\{ \alpha(s_1)\alpha(s_2) \right\} \left[\phi_a(\bar{r}_1)\phi_b(\bar{r}_2) - \phi_a(\bar{r}_2)\phi_b(\bar{r}_1) \right]$$

Check that $\Psi_1(r_1, r_2) = -\Psi_1(r_2, r_1)$ upon exchange of two electrons.

or

$\cancel{\Psi_1(r_1, r_2)}$

Similarly, for down spins $|\downarrow\rangle_1 |\downarrow\rangle_2$

$$\psi_4 = \frac{1}{\sqrt{2}} \beta(s_1)\beta(s_2)\left[\phi_a(\bar{r}_1)\phi_b(\bar{r}_2) - \phi_a(\bar{r}_2)\phi_b(\bar{r}_1)\right]$$

In both cases, the spin and space part factorizes
But in the ~~mixed~~ antiparallel spin cases it does not factorize

$$\psi_2 = \frac{1}{\sqrt{2}} \begin{vmatrix} \phi_a(\bar{r}_1)\beta(s_1) & \phi_a(\bar{r}_2)\beta(s_2) \\ \phi_b(\bar{r}_1)\alpha(s_1) & \phi_b(\bar{r}_2)\alpha(s_2) \end{vmatrix} \quad |\downarrow\rangle_1 |\uparrow\rangle_2$$

$$= \frac{1}{\sqrt{2}} \left[\phi_a(\bar{r}_1)\phi_b(\bar{r}_2)\beta(s_1)\alpha(s_2) - \phi_a(\bar{r}_2)\phi_b(\bar{r}_1)\alpha(s_1)\beta(s_2)\right]$$

Check $\psi_2(r_2, r_1, s_2, s_1) = \frac{1}{\sqrt{2}}\left[\phi_a(\bar{r}_2)\phi_b(\bar{r}_1)\beta(s_2)\alpha(s_1) - \phi_a(\bar{r}_1)\phi_b(r_2)\alpha(s_2)\beta(s_1)\right]$

$$= -\psi_2(r_1, r_2, s_1, s_2)$$

Similarly, for $|\uparrow\rangle_1 |\downarrow\rangle_2$

$$\psi_3 = \frac{1}{\sqrt{2}}\left[\phi_a(\bar{r}_1)\phi_b(\bar{r}_2)\alpha(s_1)\beta(s_2) - \phi_b(r_1)\phi_a(r_2)\beta(s_1)\alpha(s_2)\right]$$

Note in the basis of $\psi_1, \psi_2, \psi_3, \psi_4$, H is not diagonal i.e $\psi_1, \psi_2, \psi_3, \psi_4$ are not eigenstates of H. Let us evaluate the matrix elements of $\frac{e^2}{|r_1 - r_2|}$ in the basis.

$$\langle\psi_1| \frac{e^2}{r_1 - r_2} |\psi_1\rangle = \frac{1}{2}\alpha^*(s_1)\alpha^*(s_2)\alpha(s_1)\alpha(s_2) \int d\bar{r}_1 \int d\bar{r}_2$$
$$\times \left[\phi_a^*(\bar{r}_1)\phi_b^*(r_2) - \phi_a^*(\bar{r}_2)\phi_b^*(\bar{r}_1)\right] \frac{e^2}{|r_1 - r_2|} \times$$
$$\left[\phi_a(\bar{r}_1)\phi_b(\bar{r}_2) - \phi_a(\bar{r}_2)\phi_b(\bar{r}_1)\right]$$

Also, note that the eigenfunction of the $|10\rangle$ state

$$= \frac{1}{\sqrt{2}}\left(|\Psi_2\rangle + |\Psi_3\rangle\right) = \frac{1}{\sqrt{2}}\left[\phi_a(r_1)\phi_b(r_2) - \phi_a(r_2)\phi_b(r_1)\right] \times \left[\alpha(s_1)\beta(s_2) + \beta(s_1)\alpha(s_2)\right]$$

This wavefunction is sym in spin part and anti sym in space ~~spat~~ part.

Similarly the $|00\rangle$ state $= \frac{1}{\sqrt{2}}\left(|\Psi_2\rangle - |\Psi_3\rangle\right)$

$$= \frac{1}{2}\left[\phi_a(r_1)\phi_b(r_2) + \phi_a(r_2)\phi_b(r_1)\right]\left[\alpha(s_1)\beta(s_2) - \beta(s_1)\alpha(s_2)\right]$$

The wavefunction is antisym in spin part and sym in space part.

$\alpha^*(s_1)\,\alpha(s_2)$ is normalized ...

So, $\langle \psi_1 | \frac{e^2}{|r_2 - r_1|} | \psi_1 \rangle = \frac{1}{2} e^2 \int dr_1 \int dr_2 \left[\phi_a^*(\bar{r}_1)\,\phi_a(r_1)\,\phi_b^*(\bar{r}_2)\,\phi_b(\bar{r}_2) \right.$

$\left. + \cdots 3 \text{ other terms} \right]$

$$= \frac{e^2}{2} \iint dr_1\, dr_2 \left[\frac{|\phi_a(r_1)|^2 |\phi_b(r_2)|^2}{|r_1 - r_2|} + \frac{|\phi_a(r_2)|^2 |\phi_b(r_1)|^2}{|r_1 - r_2|} \right]$$

Equal value

$$- \frac{e^2}{2} \iint dr_1 dr_2 \left[\phi_a^*(r_1)\,\phi_a(r_2)\,\phi_b^*(r_2)\,\phi_b(r_1) + \phi_a^*(r_2)\,\phi_a(r_1)\,\phi_b^*(r_1)\,\phi_b(r_2) \right]$$

Equal

Note that changing $r_1 \leftrightarrow r_2$ double terms are equal when integrated

$$\Rightarrow \boxed{\langle \psi_1 | \frac{e^2}{|r_1 - r_2|} | \psi_1 \rangle = C_{ab} - J_{ab}}$$

$$C_{ab} = e^2 \iint dr_1\, dr_2 \frac{|\phi_a(r_1)|^2 |\phi_b(r_2)|^2}{|r_1 - r_2|}$$

$$J_{ab} = e^2 \iint dr_1\, dr_2 \frac{\phi_a^*(r_1)\,\phi_b(r_1)\,\phi_b^*(r_2)\,\phi_a(r_2)}{|r_1 - r_2|}$$

C_{ab} is positive, J_{ab} is also positive (to be proved)

Similarly $\langle \psi_4 | \frac{e^2}{|r_1 - r_2|} | \psi_4 \rangle = C_{ab} - J_{ab}$

$\langle \psi_2 | \frac{e^2}{r_1 - r_2} | \psi_2 \rangle = C_{ab}$ No J_{ab} term as spin functions are orthogonal

$$= \frac{e^2}{2} \int dr_1 dr_2 \left[\frac{|\phi_a(r_1)|^2 |\phi_b(r_2)|^2}{|r_1 - r_2|} |\alpha(s_2)|^2 |\beta(s_1)|^2 + \text{other term } (r_2 \leftrightarrow r_1) \right] \Rightarrow C_{ab}$$

$$-\frac{e^2}{2}\int dr_1\,dr_2\,\frac{\phi_a^*(r_1)\,\phi_b^*(r_2)\,\phi_a(r_2)\,\phi_b(r_1)\,\beta^*(s_1)\,\alpha^*(s_2)\,\alpha(s_1)\,\beta(s_2)}{|r_2-r_1|}$$

+ other term $(r_2 \leftrightarrow r_1)$

$\beta(s_1)$ is orthogonal to $\beta(s_2)$

and $\alpha(s_2)$ is orthogonal $\alpha(s_1)$

$$\langle \beta(s_2) | \beta(s_1) \rangle = 0$$

Similarly $\langle \psi_3 | \frac{e^2}{|r_1 - r_2|} | \psi_3 \rangle = C_{ab}$

There is an off-diagonal term between ~~ϕ~~ ψ_3 and ψ_2

$$\langle \psi_2 | \frac{e^2}{|r_1-r_2|} | \psi_3 \rangle = \langle \psi_3 | \frac{e^2}{|r_1-r_2|} | \psi_2 \rangle = -J_{ab}$$

~~So the matrix element of the 2~~

So, the Hamiltonian of the interacting 2-electron system is

$$H = \epsilon_a + \epsilon_b \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix} + \begin{pmatrix} C_{ab} - J_{ab} & 0 & 0 & 0 \\ 0 & C_{ab} & -J_{ab} & 0 \\ 0 & -J_{ab} & C_{ab} & 0 \\ 0 & 0 & 0 & C_{ab} - J_{ab} \end{pmatrix}$$

The eigenvalues of the 2nd matrix ($e^2/|r_1 - r_2|$ term)

are $C_{ab} - J_{ab} \rightarrow |\psi_1\rangle$ and $|\psi_4\rangle$ and $|\psi_2\rangle + |\psi_3\rangle$

$C_{ab} + J_{ab} \rightarrow |\psi_2\rangle - |\psi_3\rangle$

So three states have total energies

$\epsilon_a + \epsilon_b + C_{ab} - J_{ab} = E_t \rightarrow$ Triplet states

and one state has.

$\epsilon_a + \epsilon_b + C_{ab} + J_{ab} = E_s \longrightarrow$ singlet state

The eigenfunctions of the interacting two-electron Hamiltonian are $|\psi_1\rangle$, $|\psi_4\rangle$, $\frac{|\psi_2\rangle + |\psi_3\rangle}{\sqrt{2}}$, $\frac{|\psi_2\rangle - |\psi_3\rangle}{\sqrt{2}}$

$$\Downarrow \quad \Downarrow \quad \Downarrow \quad \Downarrow$$

$|S, S_z\rangle = |1,1\rangle$ $|1,-1\rangle$ $|1,0\rangle$ $|0,0\rangle$

Using ideas discussed previously we can show that

$H = \text{constant} - 2 J_{ab}\, S_1 \cdot S_2$

Note that exchange interaction is merely a manifestation of coulomb repulsion and pauli exclusion and <u>NOT</u> a new form of interaction.