SQ23

a. The Slater determinant of 3 electrons is :

$$\psi(1,2,3) \propto \begin{vmatrix} \phi_a(1) & \phi_b(1) & \phi_c(1) \\ \phi_a(2) & \phi_b(2) & \phi_c(2) \\ \phi_a(3) & \phi_b(3) & \phi_c(3) \end{vmatrix}$$

To determine the normalization factor, we have to count the number of terms in the determinant.

How many terms are there ?

① Direct expansion :

$$\begin{vmatrix} \phi_a(1) & \phi_b(1) & \phi_c(1) \\ \phi_a(2) & \phi_b(2) & \phi_c(2) \\ \phi_a(3) & \phi_b(3) & \phi_c(3) \end{vmatrix} = \phi_a(1) \begin{vmatrix} \phi_b(2) & \phi_c(2) \\ \phi_b(3) & \phi_c(3) \end{vmatrix} - \phi_b(1) \begin{vmatrix} \phi_a(2) & \phi_c(2) \\ \phi_a(3) & \phi_c(3) \end{vmatrix}$$

$$+ \phi_c(1) \begin{vmatrix} \phi_a(2) & \phi_b(2) \\ \phi_a(3) & \phi_b(3) \end{vmatrix}$$

$$= \phi_a(1)\phi_b(2)\phi_c(3) - \phi_a(1)\phi_c(2)\phi_b(3)$$

$$- \phi_b(1)\phi_a(2)\phi_c(3) + \phi_b(1)\phi_c(2)\phi_a(3)$$

$$+ \phi_c(1)\phi_a(2)\phi_b(3) - \phi_c(1)\phi_b(2)\phi_a(3)$$

∴ Answer : 6 terms.

② By counting :

3 states (a, b, c) allocating to 3 electrons (1, 2, 3).

∴ The 1st electron has 3 choices,

the 2nd electron has 2 choices,

the remaining one has only one choice.

∴ Total $= 3 \times 2 \times 1 = 3! = 6$.

a. (cont.)

$\therefore$ The normalization factor is $\frac{1}{\sqrt{6}}$,

i.e. $\Psi(1,2,3) = \frac{1}{\sqrt{6}} \begin{vmatrix} \phi_a(1) & \phi_b(1) & \phi_c(1) \\ \phi_a(2) & \phi_b(2) & \phi_c(2) \\ \phi_a(3) & \phi_b(3) & \phi_c(3) \end{vmatrix}$

b. We illustrate it by interchanging 1 and 2.

① Direct expansion :

$$\Psi(2,1,3) = \frac{1}{\sqrt{6}} \Big(\phi_a(2)\phi_b(1)\phi_c(3) - \phi_a(2)\phi_c(1)\phi_b(3) - \phi_b(2)\phi_a(1)\phi_c(3) + \phi_b(1)\phi_c(2)\phi_a(3) + \phi_c(1)\phi_a(2)\phi_b(3) - \phi_c(1)\phi_b(2)\phi_a(3) \Big)$$

Comparing with the expansion of $\Psi(1,2,3)$ written in part a),

we got $\Psi(2,1,3) = -\Psi(1,2,3)$.

$\therefore$ $\Psi(1,2,3)$ is antisymmetric.

② By matrix algebra :

For every determinant, we can expand it with the Levi-Civita symbol:

$$\begin{vmatrix} \phi_a(1) & \phi_b(1) & \phi_c(1) \\ \phi_a(2) & \phi_b(2) & \phi_c(2) \\ \phi_a(3) & \phi_b(3) & \phi_c(3) \end{vmatrix} = \sum_{\substack{i=1,2,3 \\ j=1,2,3 \\ k=1,2,3}} \epsilon_{ijk} \phi_i(1)\phi_j(2)\phi_k(3),$$

When $\epsilon_{ijk} = \begin{cases} 1 & \text{if } (i,j,k) \text{ has even permutation} \\ -1 & \text{if } (i,j,k) \text{ has odd permutation} \\ 0 & \text{if } i=j \text{ or } i=k \text{ or } j=k \end{cases}$

b (cont.) With the definition of the Levi-Civita symbols,

we have $\epsilon_{ijk} = -\epsilon_{jik}$.

$$\therefore \psi(2,1,3) = \sum_{i,j,k} \phi_i(2)\,\phi_j(1)\,\phi_k(3)\,\epsilon_{ijk}$$

$$= -\sum_{i,j,k} \phi_i(2)\,\phi_j(1)\,\phi_k(3)\,\epsilon_{jik}$$

Rename i as j, j as i,

$$\psi(2,1,3) = -\sum_{j,i,k} \phi_j(2)\,\phi_i(1)\,\phi_k(3)\,\epsilon_{ijk}$$

$$= -\psi(1,2,3) \;//$$

$\therefore \psi(1,2,3)$ is antisymmetric.

c. If two particles occupy the same state, for example, both 1 and 2 have the state a, (ie, change b to a)

the slater determinant becomes:

$$\begin{vmatrix} \phi_a(1) & \phi_a(1) & \phi_c(1) \\ \phi_a(2) & \phi_a(2) & \phi_c(2) \\ \phi_a(3) & \phi_a(3) & \phi_c(3) \end{vmatrix},$$

which is obviously 0

$\therefore$ The wavefunction is vanished if we force 2 particles to be in the same state.

In other words, we cannot allow the particles (electrons) to occupy the same state,

This is exactly "Pauli Exclusion Principle".

d. Take the coordinates to be the spatial coordinates $\vec{r_1}, \vec{r_2}, \vec{r_3}$,

$\therefore$ The spatial wavefunction is expressed as the following slater determinant,

$$\Psi(\vec{r_1}, \vec{r_2}, \vec{r_3}) = \frac{1}{\sqrt{6}} \begin{vmatrix} \phi_a(\vec{r_1}) & \phi_b(\vec{r_1}) & \phi_c(\vec{r_1}) \\ \phi_a(\vec{r_2}) & \phi_b(\vec{r_2}) & \phi_c(\vec{r_2}) \\ \phi_a(\vec{r_3}) & \phi_b(\vec{r_3}) & \phi_c(\vec{r_3}) \end{vmatrix},$$

Then, if we require 2 fermions take on the same location,

e.g. $\vec{r_1} = \vec{r_2}$,

$$\Psi(\vec{r_1}, \vec{r_1}, \vec{r_3}) = \frac{1}{\sqrt{6}} \begin{vmatrix} \phi_a(\vec{r_1}) & \phi_b(\vec{r_1}) & \phi_c(\vec{r_1}) \\ \phi_a(\vec{r_1}) & \phi_b(\vec{r_1}) & \phi_c(\vec{r_1}) \\ \phi_a(\vec{r_3}) & \phi_b(\vec{r_3}) & \phi_c(\vec{r_3}) \end{vmatrix} = 0$$

- The wavefunction is vanished.

With Born's interpretation,

- $|\Psi(\vec{r_1}, \vec{r_2}, \vec{r_3})|^2 \, d^3r_1 \, d^3r_2 \, d^3r_3$ is the <u>probability density</u> of the 3 fermions located at $\vec{r_1}, \vec{r_2}, \vec{r_3}$ respectively.
- When $\vec{r_1} = \vec{r_2}$, this probability density vanishes.
- This indicates that we cannot have <u>more than one</u> fermions located at the same place.
  - In fact, if you plot the wavefunction of a system of 2 fermions, you can see that the fermions <u>avoid</u> each other, even that there is no physical interaction terms !

24. The transition amplitude induced by a perturbation H' from an intial state ψ_{initial} to a final state ψ_{final}

$$a_f(t) \propto \int \psi^*_{\text{final}}(\vec{r})\, \hat{H}'\, \psi_{\text{final}}(\vec{r})\, d^3r,$$

where we only focus on the spatial integral.

For the atom-light interaction,

$$\hat{H}' = -\vec{\mu}_{el} \cdot \vec{\varepsilon},$$

where $\vec{\mu}_{el}$ is the electric dipole moment and $\vec{\varepsilon}$ is the electric field. And for a hydrogen atom, $\vec{\mu}_{el} = -e\vec{r}$.

(a) We consider the transition in a hydrogen atom from the initial state ψ_{100} to the final state ψ_{200}.

$$a_2(t) \propto \int \psi^*_{200}(\vec{r})\, \vec{r}\, \psi_{100}(\vec{r})\, d^3r$$

$$= \underbrace{\int \psi^*_{200}(\vec{r})\, r\sin\theta\cos\phi\, \psi_{100}(\vec{r})\, d^3r}_{0}\, \hat{x} + \underbrace{\int \psi^*_{200}(\vec{r})\, r\sin\theta\sin\phi\, \psi_{100}(\vec{r})\, d^3r}_{0}\, \hat{y}$$

as the ϕ angular part $\int_0^{2\pi} \cos\phi\, d\phi = 0$

as the ϕ angular part $\int_0^{2\pi} \sin\phi\, d\phi = 0$

$$+ \underbrace{\int \psi^*_{200}(\vec{r})\, r\cos\theta\, \psi_{100}(\vec{r})\, d^3r}_{0}\, \hat{z}$$

$$\boxed{\begin{aligned} \psi_{100} &= \frac{1}{\sqrt{\pi}}\left(\frac{1}{a_0}\right)^{\frac{3}{2}} e^{-\frac{r}{a_0}} \\ \psi_{200} &= \frac{1}{4\sqrt{\pi}}\left(\frac{1}{a_0}\right)^{\frac{3}{2}} \left(2-\frac{r}{a_0}\right) e^{-\frac{r}{2a_0}} \end{aligned}}$$

as the θ angular part $\int_0^{\pi} \cos\theta\sin\theta\, d\theta = 0$.

$$= 0.$$

Hence the transition from ψ_{100} to ψ_{200} is impossible.

(b) (i) We then consider the transition from the initial state ψ_{100} to the final state ψ_{211}.

$$\boxed{\psi_{211} = \frac{1}{8}\sqrt{\frac{1}{\pi}}\left(\frac{1}{a_0}\right)^{\frac{3}{2}}\left(\frac{r}{a_0}\right) e^{-\frac{r}{2a_0}} \sin\theta\, e^{i\phi}}$$

$$a_2(t) \propto \int \psi^*_{211}(\vec{r})\, \vec{r}\, \psi_{100}(\vec{r})\, d^3r$$

$$= \int \psi^*_{211}(\vec{r})\, r\sin\theta\cos\phi\, \psi_{100}(\vec{r})\, d^3r\, \hat{x} + \int \psi^*_{211}(\vec{r})\, r\sin\theta\sin\phi\, d^3r\, \hat{y}$$

$$+ \int \psi^*_{211}(\vec{r})\, r\cos\theta\, \psi_{211}(\vec{r})\, d^3r$$

$$= I_x\,\hat{x} + I_y\,\hat{y} + I_z\,\hat{z}.$$

And $$I_x = \frac{1}{8\pi}\frac{1}{a_0^4} \underbrace{\int_0^\infty r^4 e^{-\frac{3r}{2a_0}}\, dr}_{4!\left(\frac{2}{3}a_0\right)^5} \underbrace{\int_0^\pi \sin^3\theta\, d\theta}_{\frac{4}{3}} \underbrace{\int_0^{2\pi} \cos\phi\, e^{-i\phi}\, d\phi}_{\pi}$$

(by the formula $\int_0^\infty x^n e^{-\beta x}\, dx = n!\, \beta^{-n-1}$)

$$= \frac{128}{243} a_0.$$

For I_y, only the ϕ part is different,

$$I_y = \frac{1}{8\pi}\frac{1}{a_0^4} \int_0^\infty r^4 e^{-\frac{2r}{3a_0}}\, dr \int_0^\pi \sin^3\theta\, d\theta \underbrace{\int_0^{2\pi} \sin\phi\, e^{-i\phi}\, d\phi}_{-i\pi}$$

$$= -i\,\frac{128}{243} a_0,$$

For I_z, its ϕ part $\int_0^{2\pi} e^{-i\phi}\, d\phi = 0 \Rightarrow I_z = 0$.

Hence the transition amplitude from ψ_{100} to ψ_{211} is proportional to

$$\overline{\vec{r}_{211,100}} = \frac{128}{243} a_0 (\hat{x} - i\hat{y}),$$

which is a complex vector.

(ii) If the electric field is linearly polarized at $\hat{z}$, i.e. $\vec{\varepsilon} = \varepsilon\hat{z}$,

$$a_2(t) \propto \int \psi^*_{211}(\vec{r})\, \hat{H}'\, \psi_{100}(\vec{r})\, d^3r$$

$$\propto \left(\overline{\vec{r}_{211,100}}\right) \cdot \vec{\varepsilon}$$

$$= \frac{128}{243} a_0 (\hat{x} - i\hat{y})(\varepsilon\hat{z})$$

$$= 0,$$

which implies that a linearly polarized light cannot stimulate an absorption from ψ_{100} to ψ_{211}.

(iii) If the electric field is circularly polarized, i.e. $\vec{\varepsilon} \propto (\hat{x} + i\hat{y})$,

$$a_2(t) \propto \left(\overline{\vec{r}_{211,100}}\right) \cdot \vec{\varepsilon}$$

$$\propto (\hat{x} - i\hat{y}) \cdot (\hat{x} + i\hat{y}) = 2,$$

which implies that a circularly polarized light can stimulate a transition between ψ_{100} and ψ_{211}.