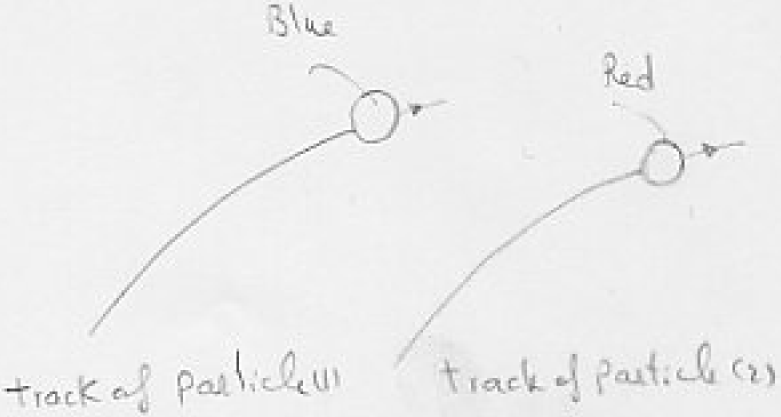
Chapter 6

Identical Particles:

6.1 Permutation symmetry:

In classical Phys.:



i- It is possible to keep track of individual particles even though the may look alike.

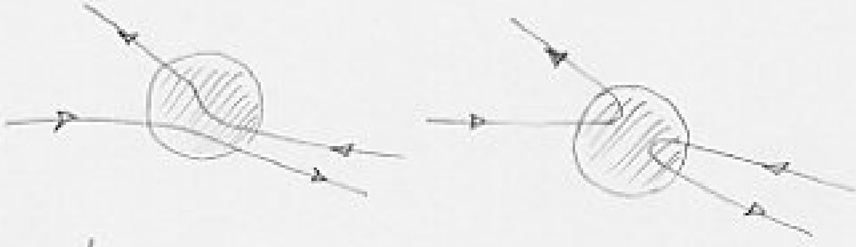
ii- We may color them.

iii- Any experiment to determine their positions does not disturb the system.

In quantum Phys.;

The identical particles are truly indistinguishable.

i- We can not follow the trajectory, because any measurement of the position will disturb the system ii – Two situations (a) and (b) cannot be distinguished – not even in principle.



(a) (b)

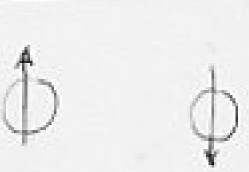
What is required for two particles to be identical is that each of them should be described by the same complete commuting set of observables, besides being identical in the physical attributes that are not described as eigenvalues of these observables.

Ex– For electrons

$\hat{P}_z$ and $\hat{S}_z$ constitute a complete commuting set of observables. (or $\hat{X}$ and $\hat{S}_z$).

Ex– Spin up-electron and spin-down electron are still identical, because the values of spin-component merely designate different dynamical states of an electron

(we can not make further identification of the electrons, i.e. we can not say which one up or which one is down)



Ex. - The electrons are identical because one electron cannot be distinguished from another electron by means of any of its inherent physical attributes such as mass, electric charge, spin, etc. .

Particles that are different from the view point of their physical attributes, could be considered identical;

→ If we could ascribe the differences $\xrightarrow{\text{to}}$ the different eigenvalues of one or more observables that commute with H of the system.

Ex - Proton and Neutron, → Isospin deg. of freedom

$$T = \frac{1}{2} \rightarrow \begin{cases} T_z = \frac{1}{2} & p \\ T_z = -\frac{1}{2} & n \end{cases}$$

But this is not true in the presence of Electromag. ints..

Consider two-particles ; the state ket for the two particles;

$|\psi_1\rangle = |\alpha\rangle|\beta\rangle \qquad \text{or} \quad |\psi_2\rangle = |\beta\rangle|\alpha\rangle$

For $\alpha \neq \beta \quad \langle\psi_1|\psi_2\rangle = 0$

Suppose we make a measurement on the two-particle system.

We may obtain α for one particle and β for the other.

However, we don't know a priori whether the state ket

is ; $|\alpha\rangle|\beta\rangle$ or $|\beta\rangle|\alpha\rangle$ or in general $c_1|\alpha\rangle|\beta\rangle + c_2|\beta\rangle|\alpha\rangle$

All $c_1|\alpha\rangle|\beta\rangle + c_2|\beta\rangle|\alpha\rangle \xrightarrow{\text{lead}}$ to an identical set of eigenvalues

when the measurement is performed.

This is known as exchange degeneracy.

Ex.-
$(O_1+O_2)[c_1|\alpha\rangle|\beta\rangle + c_2|\beta\rangle|\alpha\rangle]$
$= (\alpha+\beta)[\qquad '' \qquad]$
$\forall c_1, \forall c_2$!

$\longrightarrow$ Exchange degeneracy presents a difficulty;

because unlike the single particle case, a specification of the eigenvalue of a complete set of observables doesn't completely determine the state ket i.e.

In single particle case; $|\alpha\rangle$

" two " " $|\alpha\rangle|\beta\rangle$ or $|\beta\rangle|\alpha\rangle$

We define the permutation op.;

$$P_{12}\,|\alpha\rangle|\beta\rangle = |\beta\rangle|\alpha\rangle$$

$$P_{21} = P_{12} \quad , \quad P_{12}^2 = 1$$

For a observable A;

$$A_1|a'\rangle|a''\rangle = a'\,|a'\rangle|a''\rangle \qquad (1)$$

$$A_2|a'\rangle|a''\rangle = a''|a'\rangle|a''\rangle \qquad (2)$$

$$(1) \rightarrow \quad P_{12}\,A_1\,P_{12}^{-1}\,P_{12}\,|a'\rangle|a''\rangle = a'\,P_{12}\,|a'\rangle|a''\rangle$$

$$\rightarrow P_{12}\,A_1\,P_{12}^{-1}\,|a''\rangle|a'\rangle = a'\,|a''\rangle|a'\rangle$$

$$(1)(2) \longrightarrow \quad P_{12}\,A_1\,P_{12}^{-1} = A_2$$

Consider the H of a system of 2-identical particles

It has a symmetric form;

$$H = \frac{P_1^2}{2m} + \frac{P_2^2}{2m} + V_{pair}(|\vec{x}_1 - \vec{x}_2|) + V_{ext}(\vec{x}_1) + V_{ext}(\vec{x}_2)$$

Clearly; $P_{12} H P_{12}^{-1} = H \quad \rightarrow [P_{12}, H] = 0$

$\rightarrow P_{12}$: a const. of motion

Also since $P_{12}^2 = 1 \longrightarrow$ its eigenvalues $= \pm 1$

$\longrightarrow$ two-particle state ket remains symmetric or antisymmetric at all Time.

Eigenkets of P_{12} ;

$$|\alpha \beta\rangle_+ \equiv \frac{1}{\sqrt{2}} \left(|\alpha\rangle |\beta\rangle + |\beta\rangle |\alpha\rangle \right)$$

$$|\alpha \beta\rangle_- \equiv \frac{1}{\sqrt{2}} \left(|\alpha\rangle |\beta\rangle - |\beta\rangle |\alpha\rangle \right)$$

We define

$S_{12} \equiv \frac{1}{2} (1 + P_{12})$ symmetrizer

$A_{12} \equiv \frac{1}{2} (1 - P_{12})$ Anti- "

$$\begin{Bmatrix} S_{12} \\ A_{12} \end{Bmatrix} \left[c_1|\alpha\rangle|\beta\rangle + c_2|\beta\rangle|\alpha\rangle \right]$$

$$= \frac{1}{2}\left(c_1|\alpha\rangle|\beta\rangle + c_2|\beta\rangle|\alpha\rangle\right) \pm \frac{1}{2}\left(c_1|\alpha\rangle|\beta\rangle + c_2|\beta\rangle|\alpha\rangle\right)$$

$$= \frac{c_1 \pm c_2}{2}\left(|\alpha\rangle|\beta\rangle \pm |\beta\rangle|\alpha\rangle\right)$$ necessarily sym. or anti-sym.

In general:
$$P_{ij}\left(|k'\rangle|k''\rangle \ldots |k^i\rangle|k^{i+1}\rangle \ldots |k^j\rangle \ldots\right)$$
$$= |k'\rangle|k''\rangle \ldots |k^j\rangle|k^{i+1}\rangle \ldots |k^i\rangle \ldots$$

clearly $P_{ij}^2 = 1$ $\longrightarrow$ eigenvalues $= \pm 1$

$$[P_{ij}, P_{kl}] \neq 0 \quad \text{in general}$$

Ex. – 3-identical particles

There are $3! = 6$ possible kets of form;

$$|\alpha\rangle|\beta\rangle|\gamma\rangle$$

where $\alpha \neq \beta \neq \gamma$

$\longrightarrow$ 6-fold exchange degeneracy

There are only one totally symmetrical and one totally antisymmetrical states formed by a linear combinations of these 6-forms.

$$|\alpha\beta\gamma\rangle_{\pm} \equiv \frac{1}{\sqrt{6}}\Big\{ |\alpha\rangle|\beta\rangle|\gamma\rangle \pm |\beta\rangle|\alpha\rangle|\gamma\rangle$$
$$+ |\beta\rangle|\gamma\rangle|\alpha\rangle \pm |\gamma\rangle|\beta\rangle|\alpha\rangle$$
$$+ |\gamma\rangle|\alpha\rangle|\beta\rangle \pm |\alpha\rangle|\gamma\rangle|\beta\rangle \Big\} \quad (1)$$
$$\alpha \neq \beta \neq \gamma$$

$$P_{ij}\,|\alpha,\beta,\gamma\rangle_{\pm} = \pm|\alpha,\beta,\gamma\rangle_{\pm} \qquad i \neq j \quad i,j = 1,2,3$$

Since there are 6-independent state kets $\xrightarrow{\text{therefore}}$

there are 6-2 independent kets that are neither totally symmetric nor totally antisymmetric

Define
$$P_{123}\left(|\alpha\rangle|\beta\rangle|\gamma\rangle\right) = |\beta\rangle|\gamma\rangle|\alpha\rangle$$

$$P_{123} = P_{12}\,P_{13}$$

because, $P_{12}P_{13}\left(|\alpha\rangle|\beta\rangle|\gamma\rangle\right) = P_{12}\left(|\gamma\rangle|\beta\rangle|\alpha\rangle\right) = |\beta\rangle|\gamma\rangle|\alpha\rangle$

In (1) we assumed $\alpha \neq \beta \neq \gamma$, if for example $\alpha = \beta$;

$$|\alpha,\alpha,\gamma\rangle_{+} = \frac{1}{\sqrt{3}}\left(|\alpha\rangle|\alpha\rangle|\gamma\rangle + |\alpha\rangle|\gamma\rangle|\alpha\rangle + |\gamma\rangle|\alpha\rangle|\alpha\rangle\right)$$

$$|\alpha,\alpha,\gamma\rangle_{-} = 0$$

where $\frac{1}{\sqrt{3}} = \sqrt{\frac{2!}{3!}}$ normalization factor

More generally;

$$\sqrt{\frac{N_1!\,N_2!\cdots N_n!}{N!}}$$ normalization factor

N: total number of particles

N_i: the number of times $|K^i\rangle$ occurs.

6.2 Symmetrization Postulate;

What does the nature say about a state to be sym. or antisym.?

Systems of N-identical particles are $\left\{\begin{array}{l}\text{either sym.}\\ \text{or anti-''}\end{array}\right.$

under the interchange of any pair.

$P_{ij}\,|\text{N-identical Bosons}\rangle = +\,|\text{N-identical Bosons}\rangle$

$P_{ij}\,|\text{'' - '' Fermions}\rangle = -\,|\text{'' '' Fermions}\rangle$

Bosons obey Bose-Einstein (B-E) statistics (sym.)

Fermions '' Fermi-Dirac (F-D) '' (anti-sym.)

It is emprical fact that a mixed symmetry does not occur.

Connection between $\left\{\begin{array}{l}\text{the spin of a particle} \\ \text{and the statistics obeyed by it}\end{array}\right.$;

Half-integer spin particles are Fermions

Integer " " " Bosons

Ex.- ^3He : Fermion like e^- or p

^4He : Boson " π^+ or π^0

spin-statistics connection is an exact law of nature.

In nonrelativistic quantum mechanics, this principle must be accepted as an empirical postulate.

In relativistic quantum theory it can be proved.

Dramatic differences:

i- For Fermions we have only one possibility;

$$\frac{1}{\sqrt{2}}\left(|\alpha\rangle|\beta\rangle - |\beta\rangle|\alpha\rangle\right)$$

It is impossible for both particles to occupy the same state (Pauli exclusion principle).

ii- For Bosons; there are 3-possible states;

$$|\alpha\rangle|\alpha\rangle \quad , \quad |\beta\rangle|\beta\rangle, \quad \frac{1}{\sqrt{2}}\left(|\alpha\rangle|\beta\rangle + |\beta\rangle|\alpha\rangle\right)$$

iii- For classical particles satisfying Maxwell-Boltzman (M-B) statistics, there is <u>no</u> restriction on <u>symmetry</u>, there are 4-indep. states;

$$|\alpha\rangle|\beta\rangle \quad , \quad |\beta\rangle|\alpha\rangle \quad , \quad |\alpha\rangle|\alpha\rangle, \quad |\beta\rangle|\beta\rangle$$

In the (i) case it is impossile for two particles to be in the <u>same state</u>.

In the (ii) case in $\frac{2}{3}$ of the allowed kets, the particles occupy the <u>same states</u>.

In the (iii) case " $\frac{2}{4}$ " " " " " " "
the <u>same states</u>.

⟶ Fermions are the <u>least</u> sociable.

Bosons " " <u>most</u> " (even more than classical particles)

6.3 Two-Electron System

$$\Psi = \sum_{m_{s1}} \sum_{m_{s2}} c(m_{s1}, m_{s2}) < \bar{x}_1, m_{s1}; \bar{x}_2, m_{s2} | \alpha)$$

$$P_{12} \Psi = -\Psi$$

If $[S^2, H] = 0$

the eigenfunc. of H is expected to be an eigenfunc. of S^2,

If $\Psi = \varphi(x_1, x_2)\chi$

then
$$\chi(m_{1s}, m_{2s}) = \begin{cases} \left.\begin{array}{l} \chi_+\chi_+ \\ \frac{1}{\sqrt{2}}(\chi_+\chi_- + \chi_-\chi_+) \end{array}\right\} \text{triplet (sym.)} \\ \chi_-\chi_- \\ \frac{1}{\sqrt{2}}(\chi_+\chi_- - \chi_-\chi_+) \quad \text{singlet (anti-sym.)} \end{cases}$$

<u>Triplet</u> states are all <u>sym.</u> ; this is reasonable, because

$$\begin{cases} [S_-, P_{12}] = 0 \qquad (S_- = S_{1-} + S_{2-}) \\ \text{and } P_{12}(\chi_+\chi_+) = +\chi_+\chi_+ \end{cases}$$

$\rightarrow$ S_- does <u>not</u> change the symmetry when acting on $\chi_+\chi_+$ and so, =

We note

$$\langle \bar{x}_1, m_{s1}; \bar{x}_2, m_{s2} | P_{12} | \alpha \rangle = \langle \bar{x}_2, m_{s2}; \bar{x}_1, m_{s1} | \alpha \rangle$$

Fermi-Dirac statistics requires;

$$\langle \bar{x}_1, m_{1s}; \bar{x}_2, m_{2s} | \alpha \rangle = - \langle \bar{x}_2, m_{s2}; \bar{x}_1, m_{s1} | \alpha \rangle \quad (1)$$

Where $P_{12} = P_{12}^{space} \, P_{12}^{spin}$

Now, Since, $S_1 \cdot S_2 = \frac{1}{2} \left(S^2 - S_1^2 - S_2^2 \right)$

$$S_1 \cdot S_2 | \text{triplet} \rangle = \frac{1}{2} \left[s(s+1) - s_1(s_1+1) - s_2(s_2+1) \right] \hbar^2 | \text{triplet} \rangle$$

$$= \frac{1}{2} \left(1(1+1) - \frac{1}{2}\left(\frac{1}{2}+1\right) - \frac{1}{2}\left(\frac{1}{2}+1\right) \right) \hbar^2 \, | \text{triplet} \rangle = \frac{\hbar^2}{4} | \text{triplet} \rangle$$

$$S_1 \cdot S_2 | \text{singlet} \rangle = \frac{1}{2} \left(0(0+1) - \frac{1}{2}\left(\frac{1}{2}+1\right) - \frac{1}{2}\left(\frac{1}{2}+1\right) \right) | \text{singlet} \rangle$$

$$= -\frac{3}{4} \hbar^2 | \quad " \quad \rangle$$

$$\rightarrow P_{12}^{spin} = \frac{1}{2} \left(1 + \frac{4}{\hbar^2} S_1 \cdot S_2 \right)$$

$$\left\{ \begin{array}{l} \Psi = \varphi(\bar{x}_1, \bar{x}_2) \chi \\ \text{and } | \alpha \rangle \rightarrow P_{12} | \alpha \rangle \end{array} \right. \longrightarrow \left\{ \begin{array}{l} \varphi(x_1, x_2) \rightarrow \varphi(x_2, x_1) \\ \chi(m_{1s}, m_{2s}) \rightarrow \chi(m_{2s}, m_{1s}) \end{array} \right. \quad (2)$$

$$(1)(2) \rightarrow \left\{ \begin{array}{l} \text{if } \varphi \text{ is sym.} \longrightarrow \chi \text{ must be antisym} \\ \text{" } \varphi \text{ " anti-sym.} \longrightarrow \chi \text{ " " sym.} \end{array} \right.$$

$$\Psi = \varphi(\text{sym})\,\chi_{\text{sing.}}$$

or $$\Psi = \varphi(\text{antisym})\,\chi_{\text{trip.}}$$

$$|\varphi(x_1, x_2)|^2 \, d^3x_1 \, d^3x_2$$

the probability of finding electron 1 in a volume element d^3x_1 centered around x_1 and electron 2 in a volume d^3x_2

What is the meaning of this ?

Let us ignore the mutual int. between the two electrons

(for example $V_{pair}(|x_1 - x_2|)\, S_1 \cdot S_2$)

If there is no spin dependence $\longrightarrow$ the wave equ. for Ψ

$$\left[-\frac{\hbar^2}{2m}\nabla_1^2 - \frac{\hbar^2}{2m}\nabla_2^2 + V_{ext}(x_1) + V_{ext}(x_2)\right]\Psi = E\Psi$$

is now separable.

$$[S^2, H] = 0 \longrightarrow \Psi \sim W_A(x_1)\, W_B(x_2)\, \chi$$

Note: In spin-dep. case the non-vanishing matrix elements may occur between two different spin states like;

$$\langle S=0 |\, H_{\text{spin-dep.}} \,| S=1 \rangle \neq 0$$

$$\langle S=0 | \quad '' \quad | S=0 \rangle = 0$$

$\longrightarrow$ spin part of Ψ must be $\begin{cases} \text{a triplet} \\ \text{or singlet} \end{cases}$ (pure)

i.e. $P_{12}\, \chi = \pm\, \chi_{\substack{\text{trip.} \\ \text{sing.}}}$

Also, $\varphi_{\pm}(x_1, x_2) = \frac{1}{\sqrt{2}} \left[\omega_A(x_1)\, \omega_B(x_2) \pm \omega_A(x_2)\, \omega_B(x_1) \right]$

$$\Psi = \varphi_+ \chi_{\text{sing.}} \quad \text{or} \quad \Psi = \varphi_- \chi_{\text{trip.}} \quad (\text{pure with no spin-dep. in } H)$$

Thus, the probability of observing electron $\underline{1}$ in d^3x_1 around x_1 and electron $\underline{2}$ in d^3x_2 around x_2 is given by:

$$\frac{1}{2} \Big\{ |\omega_A(x_1)|^2 |\omega_B(x_2)|^2 + |\omega_A(x_2)|^2 |\omega_B(x_1)|^2 \pm$$
$$\pm\, 2\, \underbrace{\mathrm{Re}\left(\omega_A(x_1)\, \omega_B(x_2)\, \omega_A^*(x_2)\, \omega_B^*(x_1) \right)}_{\text{exchange density}} \Big\}\, d^3x_1\, d^3x_2$$

Now, when

i - The electrons are in the spin-triplet state $\chi_{\text{trip.}} \longrightarrow \varphi = \varphi_-$

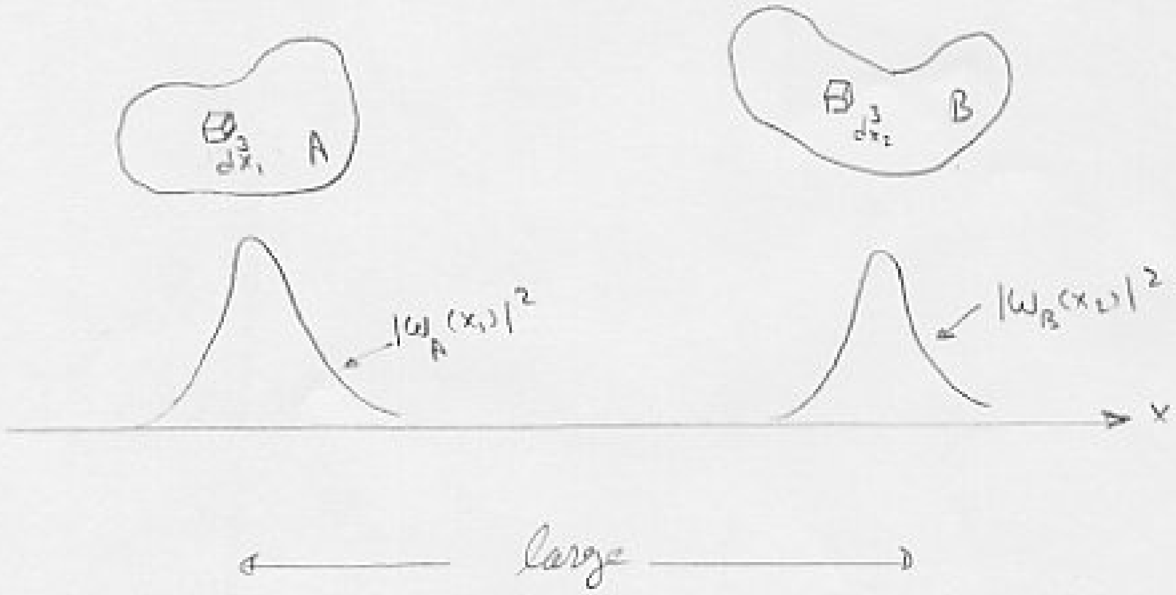
$$\longrightarrow \left| \varphi_-(x_1, x_2) \right|^2 d^3x_1\, d^3x_2 \Big|_{x_1 = x_2} = 0$$

ii- The electrons are in the spin-singlet state $\chi_{\text{sing.}} \rightarrow T = \Phi_+$

$$\rightarrow \left|\Phi_+(x_1,x_2)\right|^2_{x_1=x_2} d^3_{x_1} d^3_{x_2} = \text{large} \quad \text{(due to exchange density)}$$

Clearly, the question of identity is important only when the exchange density is nonnegligible.

Ex.



$$|\Phi(x_1,x_2)|^2 d^3_{x_1} d^3_{x_2} \simeq |\omega_A(x_1)|^2 |\omega_B(x_2)|^2 \quad \text{(the only important term)}$$

This is nothing more than the joint probability density expected for classical particles.

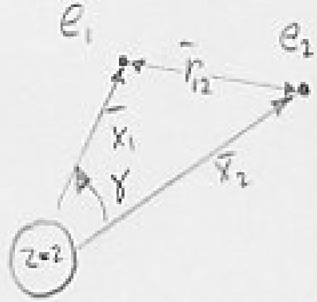
Recall that, classical particles are necessarily well localized and the question of identity does not arise.

→ The exchange density term is important when regions A and B overlap.

→ There is no need for antisymmetrization if the identical particles are far apart.

6.4 The Helium Atom

$$H = \frac{P_1^2}{2m} + \frac{P_2^2}{2m} - \frac{Ze^2}{r_1} - \frac{Ze^2}{r_2} + \frac{e^2}{r_{12}}$$



$r_1 \equiv |x_1|$, $r_2 \equiv |x_2|$, $r_{12} \equiv |x_1 - x_2|$

$$H = H_1 + H_2 + V$$

$$H_i = \frac{P_i^2}{2m} - \frac{Ze^2}{r_i} \qquad V = \frac{e^2}{r_{12}} \qquad , Z = 2$$

H_i: Hamiltonian for Hydrogen-like atom

Despite $\frac{Ze^2}{r_1} \sim \frac{Ze^2}{r_2} \sim V$, we ignore V and treat it as a perturbation (this is done only for simplicity).

If we ignore the question of identity;

$$\longrightarrow \psi(r_1, r_2) = \psi_{n_1 l_1 m_1}(r_1)\, \psi_{n_2 l_2 m_2}(r_2)$$

$$[H_1 + H_2]\, \psi(\bar{r}_1, \bar{r}_2) = E\, \psi(\bar{r}_1, \bar{r}_2)$$

$$E = E_{n_1} + E_{n_2} \qquad , \quad E_n = -\frac{mc^2}{2}\left(\frac{Z}{\alpha}\right)^2 \frac{1}{n^2}$$

i - $E = 2E_1 = -2\left(\frac{mc^2}{2}\right)(2\alpha)^2 = -2(54.4) = -108.8 \text{ ev}$ $\qquad n_1 = 1, n_2 = 1 \quad (Z=2)$ ground state

Note that $E = 2Z^2 E_H = 8 E_H = 8 \times 13.6$

ii - The first excited state $\begin{cases} n_1 = 1, n_2 = 2 \\ \text{or} \\ n_1 = 2, n_2 = 1 \end{cases}$

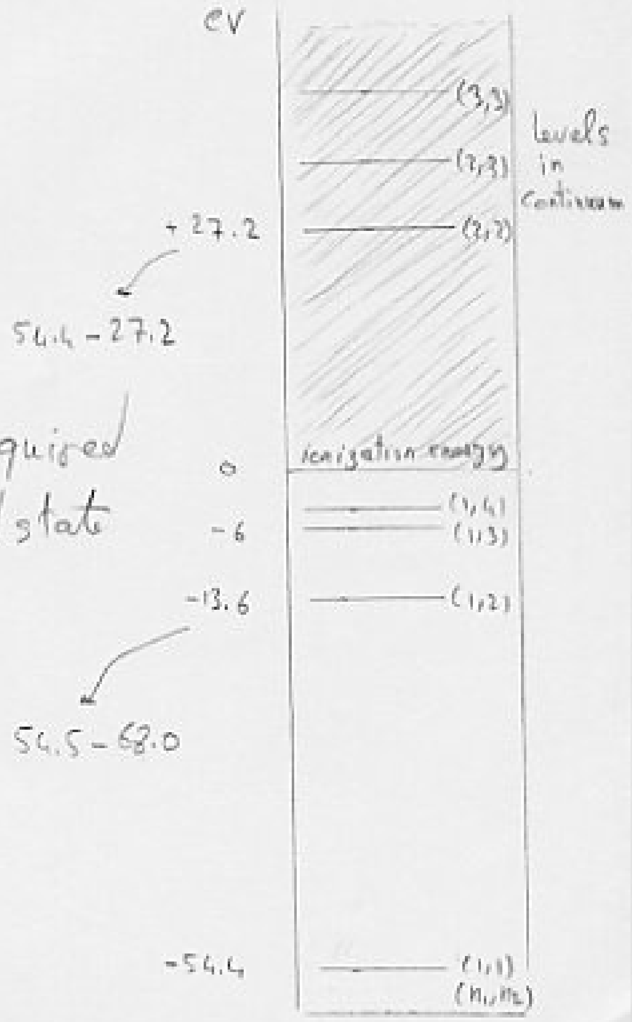
$$E = E_1 + E_2 = -54.4 - 13.6 = -68.0$$

iii - $n_1 = 2, n_2 = 2$ Case

$$E = 2E_2 = -2(13.6) = -27.2 \text{ ev}$$

The ionization energy (the energy required to remove one electron from the ground state to infinity) is;

$$E_{\text{ioniz}} = E_\infty - E_1 = 54.4 \text{ ev}$$



The ground state of two electrons as two identical Fermions

neglecting V,

$$\psi_0(r_1, r_2) = \psi_{100}(x_1)\, \psi_{100}(x_2)\, \chi_{sing.} \quad \begin{cases} n_1 = 1 & l_1 = 0 \\ n_2 = 1 & l_2 = 0 \end{cases}$$

If one electron is in the ground state and the other in the excited state; (for $V = 0$)

$$\left.\begin{aligned} \psi^s &= \frac{1}{\sqrt{2}} \left[\psi_{100}(x_1)\, \psi_{n\ell m}(x_2) + \psi_{n\ell m}(x_1)\, \psi_{100}(x_2) \right] \chi_{sing.} \\ \psi^t &= \frac{1}{\sqrt{2}} \left[\quad '' \quad - \quad '' \quad \right] \chi_{trip} \end{aligned}\right\} \text{with } V = 0 \text{ degenerate}$$

Now we treat V as a perturbation to the <u>first order</u>;

For the <u>ground</u> state;

$$\Delta E = \langle n | V | n \rangle = \langle \psi_0 | V | \psi_0 \rangle_{(1s)^2}$$

$$= \iint dr_1^3\, dr_2^3\, \psi_0^*(r_1, r_2)\, \frac{e^2}{r_{12}}\, \psi_0(r_1, r_2)$$

Since V is spin-indep.

$$\Delta E = \iint d r_1^3\, d r_2^3\ |\psi_{100}(r_1)|^2 \frac{e^2}{|r_1 - r_2|} |\psi_{100}(r_2)|^2$$

Since $e|\psi_{100}(r_1)|^2$ is charge density due electron 1,

$$\rightarrow \quad U(r_2) = -\int d r_1^3\ \frac{e|\psi_{100}(r_1)|^2}{|r_1 - r_2|}$$

the pot. at r_2 due to the charge dist of electron 1.

$$\Delta E = -\int d r_2^3\ e|\psi_{100}(r_2)|^2\ U(r_2)$$

This is the electrostatic energy of int. of electron 2 with the pot. of electron 1.

Since $\psi_{100}(r) = \frac{2}{\sqrt{4\pi}}\left(\frac{Z}{a_0}\right)^{3/2} e^{-\frac{Z}{a_0} r}$

$$\Delta E = \left(\frac{1}{\pi}\left(\frac{Z}{a_0}\right)^3\right)^2 e^2 \int_0^\infty r_1^2\, dr_1\, e^{-\frac{2Z}{a_0} r_1} \int_0^\infty r_2^2\, dr_2\, e^{-\frac{2Z}{a_0} r_2}$$

$$\int d\Omega_1 \int d\Omega_2 \frac{1}{|r_1 - r_2|}$$

$$\frac{1}{|r_1 - r_2|} = \frac{1}{\sqrt{r_1^2 + r_2^2 - 2 r_1 r_2 \cos\gamma}}$$

a) We choose $r_1 \parallel \hat{z} \longrightarrow \gamma = \theta$

$$\int d\Omega_2 \frac{1}{|r_1 - r_2|} = \int_0^{2\pi} d\varphi \int_{-1}^{1} d(\cos\theta)\ \frac{1}{\sqrt{r_1^2 + r_2^2 - 2 r_1 r_2 \cos\theta}}$$

$$\int d\Omega_2 \frac{1}{|r_1-r_2|} = -2\pi \frac{1}{r_1 r_2}\left[(r_1^2+r_2^2-2r_1r_2\cos\theta)^{\frac{1}{2}}\right]_{-1}^{+1}$$

$$= \frac{2\pi}{r_1 r_2}\left(r_1+r_2-|r_1-r_2|\right)$$

and $\int d\Omega_1 = 4\pi$

$$\Delta E = \left(\frac{Z}{a_0}\right)^6 \int_0^\infty r_1\, dr_1\, e^{-\frac{2Z}{a_0}r_1} \int_0^\infty r_2\, dr_2\, e^{-\frac{2Z}{a_0}r_2} \left(r_1+r_2-|r_1-r_2|\right)$$

b) $$\frac{1}{\sqrt{r_1^2+r_2^2-2r_1r_2\cos\gamma}} = \sum_{\ell=0}^{\infty} \frac{r_<^\ell}{r_>^{\ell+1}} P_\ell(\cos\gamma)$$

$$P_\ell(\cos\gamma) = \frac{4\pi}{2\ell+1}\sum_{m=-\ell}^{\ell} Y_\ell^{m*}(\theta_1,\varphi_1)\, Y_\ell^m(\theta_2,\varphi_2)$$

$$\frac{1}{2}\int_{-1}^{1} d(\cos\theta)\, P_\ell(\cos\theta)\, P_{\ell'}(\cos\theta) = \frac{\delta_{\ell\ell'}}{2\ell+1}$$

$$\rightarrow \frac{1}{2}\int_{-1}^{1} d(\cos\theta)\, P_\ell(\cos\theta) = \delta_{\ell 0}$$

$$\int d\Omega\, Y_\ell^{m*}(\theta,\varphi)\, Y_{\ell'}^{m'}(\theta,\varphi) = \delta_{\ell\ell'}\delta_{mm'}$$

$$\rightarrow \int d\Omega\, Y_\ell^m(\theta,\varphi) = \frac{1}{\sqrt{4\pi}}(4\pi)\,\delta_{\ell 0}\delta_{m0}$$

In any case;

$$\Delta E = 8e^2\left(\frac{Z}{a_0}\right)^6 \int_0^\infty r_1\, dr_1\, e^{-\frac{2Z}{a_0}r_1}\left\{2\int_0^{r_1} \underline{r_2^2}\, dr_2\, e^{-\frac{2Z}{a_0}r_2} + 2r_1\int_{r_1}^\infty \underline{r_2}\, dr_2\, e^{-\frac{2Z}{a_0}r_2}\right\}$$

$$\Delta E = \frac{5}{8}\frac{Ze^2}{a_0} = \frac{+5}{4} Z\left(\frac{1}{2}mc^2\alpha^2\right) \qquad (1)$$ (+ : repulsive force)

$Z=2 \rightarrow \Delta E = 34\ eV$

$$E = E_0 + \Delta E_{(1s)^2} \simeq -108.8+34 = 74.8\ eV$$

$$E_{exp} = 78.975\ eV$$

A sizable discrepancy is seen.

The discrepancy is due to screening effect.

i.e. One electron tends to decrease the net charge seen by the other electron

If we assume roughly one electron is 50% of the time between the other and the nucleus

$\rightarrow$ the $\begin{cases} 50\% \text{ of the time the outer electron sees } (Z-1) \text{ charge and} \\ \text{〃 〃 〃 〃 〃 } Z \text{ 〃} \end{cases}$

Then, in $E+\Delta E = -\frac{1}{2}mc^2\alpha^2\left(2Z^2 - \frac{5}{4}Z\right)$

we have to make a change of $Z \longrightarrow Z-\frac{1}{2}$

This does improve agreement, but it is not sufficient, because the choice of 50% probability is not sufficient.

Now we try the variational method;

We propose to use Z as the variational parameter.

$$Z \longrightarrow Z_{eff}$$

The Physical reason;

The effective Z, seen by one of the electron is smaller than 2 because the charge of nucleus $Ze = 2e$ is screened by the negatively charged cloud of the other electron.

$$\Psi_0(r_1, r_2) = \Psi_{100}(r_1, Z')\,\Psi_{100}(r_2, Z') = \left(\frac{Z'^3}{\pi a_0^3}\right) e^{-\frac{Z'}{a_0} r_1}\, e^{-\frac{Z'}{a_0} r_2}$$

$$\langle H \rangle = \int d^3r_1 \int d^3r_2\, \Psi^*_{100}(r_1, Z')\,\Psi^*_{100}(r_2, Z') \left[\frac{P_1^2}{2m} + \frac{P_2^2}{2m} - \frac{Ze^2}{r_1} - \frac{Ze^2}{r_2} + \frac{e^2}{|r_1 - r_2|}\right] \Psi_{100}(r_1, Z')\,\Psi_{100}(r_2, Z')$$

Now

$$\int d^3r_1 \int d^3r_2\, \Psi^*_{100}(r_1, Z')\,\Psi^*_{100}(r_2, Z') \left(\frac{P_1^2}{2m} - \frac{Ze^2}{r_1}\right) \Psi_{100}(r_1, Z')\,\Psi_{100}(r_2, Z')$$

$$= \int d^3r_1\, \Psi^*_{100}(r_1, Z') \left[\left(\frac{P_1^2}{2m} - \frac{Z'e^2}{r_1}\right) + \frac{(Z'-Z)e^2}{r_1}\right] \Psi_{100}(r_1, Z')$$

$$= E_0 + (Z'-Z)e^2 \int d^3r_1\, |\Psi_{100}(r_1, Z')|^2 \frac{1}{r_1}$$

$$= E_0 + (Z'-Z)e^2 \frac{Z'}{a_0} = E_0 + Z'(Z'-Z)mc^2\alpha^2$$

where $\left(\frac{p^2}{2m} - \frac{Z'e^2}{r} \right) \psi_{100}(r, Z') = E_0 \psi_{100}(r, Z')$

$$E_0 = -\frac{1}{2} mc^2 (Z'\alpha)^2$$

An identical factor comes from the Hamiltonian for the second electron, and for the contribution of electron-electron repulsion we have to make a change of $Z \to Z'$ in Equ. 1 P320,

$$\langle \psi_0 | H | \psi_0 \rangle = -\frac{1}{2} mc^2 \alpha^2 \left(2Z'^2 + 4Z'(Z - Z') - \frac{5}{4} Z' \right)$$

$$= -\frac{1}{2} mc^2 \alpha^2 \left(4ZZ' - 2Z'^2 - \frac{5}{4} Z' \right)$$

$$\frac{\partial \langle H \rangle}{\partial Z'} = 0 \longrightarrow Z' = Z - \frac{5}{16} = 1.6875$$

$$E \leqslant -\frac{1}{2} mc^2 \alpha^2 \left[2 \left(Z - \frac{5}{6} \right)^2 \right] = -77.38 \text{ ev} \quad (Z = 2)$$

A better and complicated trial wave func. than $\psi_0(r_1, r_2) = \psi_{100}(r_1) \psi_{100}(r_2)$ gives better result.

Next we consider the excited states;

we consider $\underline{(1s)(nl)}$ configuration;

$$E = E_{100} + E_{nlm} + \Delta E$$

We also consider ψ^s and ψ^t (with $m=0$)

Because $[V, L_z] = 0 \longrightarrow$ the perturbation energy is

indep. of m.

$$\Delta E^{(s,t)} = \frac{1}{2} e^2 \int d r_1^3 \int d r_2^3 \left[\psi_{100}(r_1)\, \psi_{nlm}(r_2) \underset{\searrow t}{\overset{\nearrow s}{\pm}} \psi_{nlm}(r_1)\, \psi_{100}(r_2) \right]^*$$

$$\cdot \frac{1}{|r_1 - r_2|} \left[\psi_{100}(r_1)\, \psi_{nlm}(r_2) \pm \psi_{nlm}(r_1)\, \psi_{100}(r_2) \right]$$

$$= e^2 \int d r_1^3 \int d r_2^3 \, |\psi_{100}(r_1)|^2 \, |\psi_{nlm}(r_2)|^2 \frac{1}{|r_1 - r_2|}$$

$$\pm\ e^2 \int d r_1^3 \int d r_2^3 \, \psi_{100}^*(r_1)\, \psi_{nlm}^*(r_2) \frac{1}{|r_1 - r_2|} \psi_{nlm}(r_1)\, \psi_{100}(r_2) \qquad (m=0)$$

where we have used the symmetry of V under $r_1 \longleftrightarrow r_2$

$$\Delta E^{(s,t)} = I \pm J$$

I: The electrostatic int. between two electron clouds.

This is a generalization of the term, we found for the ground state energy shift.

J: This term has no classical interpretation. Its origin lies in the Pauli principle, and its sign depends on whether the state has spin 0 or 1.

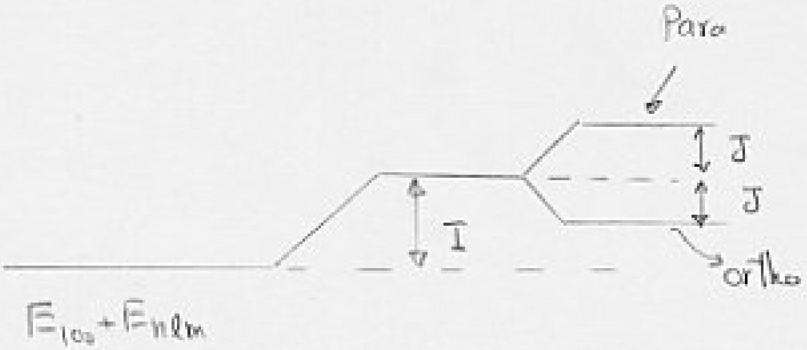
Because of this exchange contribution the singlet and triplet states are no longer degenerate.

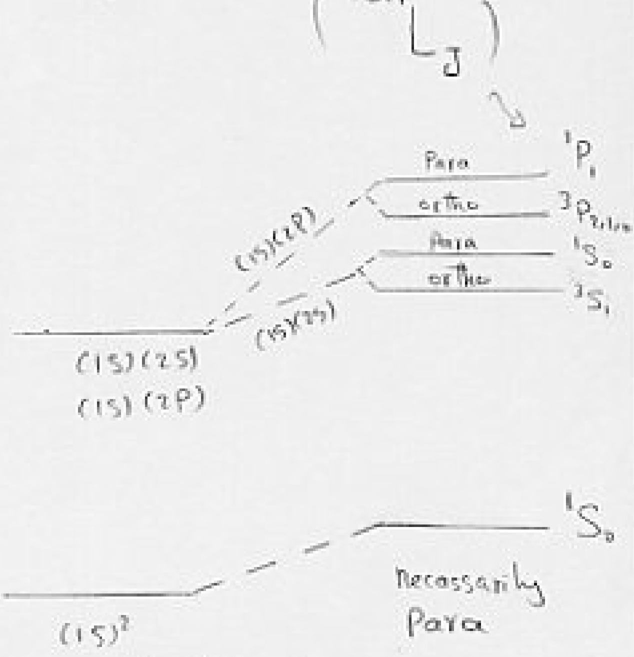
$$\Delta E^{t}_{n\ell} = I_{n\ell} - J_{n\ell}$$

$$\Delta E^{s}_{n\ell} = I_{n\ell} + J_{n\ell}$$

It can be shown $I_{n\ell} > 0$ and $J_{n\ell} > 0$

$$\Delta E^{s}_{n\ell} > \Delta E^{t}_{n\ell}$$





(Helium)

The physical interpretation.

i- In the singlet case; space wave func. = sym.

→ the electrons have a tendency to come close to each other.

→ the effect of electrostatic repulsion is more serious.

→ a higher energy results. (Parahelium)

ii - In the triplet case; space wave func = antisym.

→ the electrons tend to avoid each other

→ $\left\{ \begin{array}{l} \text{reduction in screening effect} \\ \quad \text{"} \qquad \text{" repulsion} \end{array} \right.$

→ a lower energy results. (orthohelium)

It is very important to recall that the original H is spin-independent,

However, the energy is spin-dependent!

This arises from Fermi-Dirac statistics.

Now

$$S^2 = S_1^2 + S_2^2 + 2 S_1 \cdot S_2$$

Acting on χ_{sing} ad χ_{trip}

$$\rightarrow \; s(s+1)\hbar^2 = \frac{3}{4}\hbar^2 + \frac{3}{4}\hbar^2 + 2 S_1 \cdot S_2$$

$$\frac{2 S_1 \cdot S_2}{\hbar^2} = s(s+1) - \frac{3}{2} = \begin{cases} \frac{1}{2} & \text{triplet} \\ -\frac{3}{2} & \text{singlet} \end{cases}$$

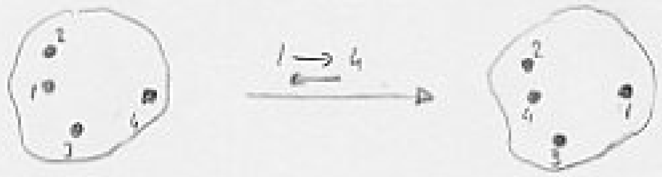
$$S_i = \frac{\hbar}{2} \sigma_i$$

$$\Rightarrow \; \Delta E_{nl} = I_{nl} - \frac{1}{2}(1 + \sigma_1 \cdot \sigma_2) J_{nl}$$

Identical Particles

Permutation Symmetry:

Two Physical situations that differ <u>only</u> by the <u>interchange</u> of indentical particles are indistinguishable.



One of the consequences of this fact;

Any physical Hamiltonian must be invariant under permutation of identical particles.

$$H(i, j, k, l \ldots n) = H(i, l, k, j, \ldots n) = \ldots$$

Consider first a system of <u>two</u> identical particles;

$|\alpha\rangle|\beta\rangle \equiv |\alpha\rangle \otimes |\beta\rangle$ basis vectors for the state space in terms of single particle basis vectors

α: eigenvalue of the first particle

β: " " " second "

An arbitrary vector;

$$|\psi\rangle = \sum_{\alpha,\beta} C_{\alpha\beta} \, |\alpha\rangle|\beta\rangle$$

A state func. in the two-particle configuration space;

$$\psi(\bar{x}_1,\bar{x}_2) = (\langle\bar{x}_1| \otimes \langle\bar{x}_2|)|\psi\rangle = \sum_{\alpha,\beta} \langle\bar{x}_1|\alpha\rangle\langle\bar{x}_2|\beta\rangle$$

We define a permutation op.; $\quad P_{12}|\alpha\rangle|\beta\rangle = |\beta\rangle|\alpha\rangle$

$$P_{12} = P_{12}^{-1} \quad , P_{12} = P_{12}^{+} \quad , P_{12} P_{12}^{-1} = I \quad , (P_{12})^2 = I$$

$$P_{12}\,\psi(\bar{x}_1,\bar{x}_2) = \psi(\bar{x}_2,\bar{x}_1)$$

Now, since $[P_{12}, H] = 0 \longrightarrow$ H and P_{12} have common eigenvalue

since $P_{12}^2 = I \longrightarrow$ its eigenvalues $\begin{cases} +1 \\ -1 \end{cases}$

$$\begin{cases} P_{12}\,\psi(\bar{x}_1,\bar{x}_2) = \psi(\bar{x}_1,\bar{x}_2) \\ P_{12}\,\psi(\bar{x}_1,x_2) = -\psi(\bar{x}_1,\bar{x}_2) \end{cases} \quad \text{or} \quad \longrightarrow \begin{cases} \psi(\bar{x}_2,\bar{x}_1) = \psi(\bar{x}_1,\bar{x}_2) \\ \psi(x_2,\bar{x}_1) = -\psi(\bar{x}_1,\bar{x}_2) \end{cases}$$

$\longrightarrow$ its eigenfuncs are either <u>sym.</u> or <u>anti-sym.</u>, under interchange of the two particles.

Hence;

For a system of two identical particles the eigenvectors of H can be chosen to have either symmetry or antisymmetry under permutation of the particles.

The situation is more complicated if there are more than 2-particles.

The general principles can be illustrated by considering a system of 3-identical particles.

The basis vectors are of the form $|\alpha\rangle|\beta\rangle|\gamma\rangle$;

There are 6-distinct permutations of 3-objects

$\longrightarrow$ we can define 6-different permutation ops..

I : identity op

P_{12}, P_{23}, P_{31} : pair interchange ops.

P_{123}, $(P_{123})^2$: cyclic permutations

$$P_{12}|\alpha\rangle|\beta\rangle|\gamma\rangle = |\beta\rangle|\alpha\rangle|\gamma\rangle$$

$$P_{23}|\alpha\rangle|\beta\rangle|\gamma\rangle = |\alpha\rangle|\gamma\rangle|\beta\rangle$$

$$P_{31}|\alpha\rangle|\beta\rangle|\gamma\rangle = |\gamma\rangle|\beta\rangle|\alpha\rangle$$

$$P_{123}|\alpha\rangle|\beta\rangle|\gamma\rangle = |\gamma\rangle|\alpha\rangle|\beta\rangle$$

$$(P_{123})^2|\alpha\rangle|\beta\rangle|\gamma\rangle = |\beta\rangle|\gamma\rangle|\alpha\rangle$$

These 6-permutation ops. <u>are not</u> mutually commutative.

$$[P, P'] \neq 0 \qquad (P, P' \text{ : permutation ops.})$$

$\longrightarrow$ There is <u>no</u> complete set of <u>common</u> eigenvectors for these ops.

$\longrightarrow$ And so it is <u>not</u> possible <u>for every</u> eigenvector of H to be sym. or antisym. under pair interchanges.

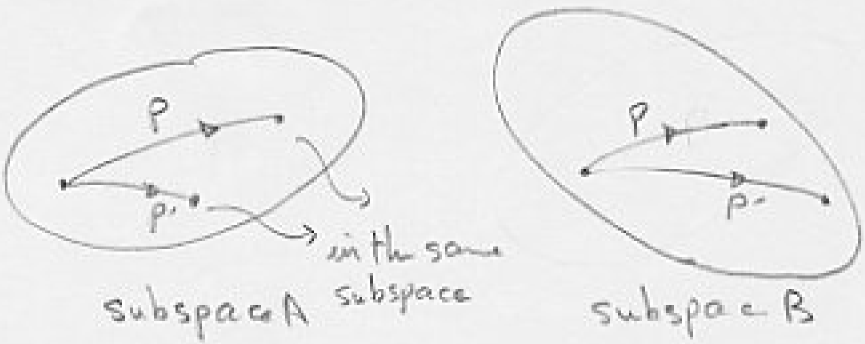
Remark:

Ex: $[J^2, \vec{J}] = 0$ but $[J_i, J_j] = i\epsilon_{ijk} J_k \neq 0$

$J^2|j,m\rangle = j(j+1)|j,m\rangle \qquad J_z|jm\rangle = m|jm\rangle$

but $J_x|jm\rangle \neq C|jm\rangle$

However, we can <u>divide</u> the vector space into <u>invariant subspaces</u>,



The basis vector $|\alpha\rangle|\beta\rangle|\gamma\rangle$ (with $\alpha \neq \beta \neq \gamma$) and its permutations span a 6-dim vector space.

This may be reduced into 4-invariant subspaces, spanned by the following vectors, all of which are orthogonal.

Symmetric:

$$\frac{1}{\sqrt{6}}\Big\{|\alpha\rangle|\beta\rangle|\gamma\rangle + |\beta\rangle|\alpha\rangle|\gamma\rangle + |\alpha\rangle|\gamma\rangle|\beta\rangle + |\gamma\rangle|\beta\rangle|\alpha\rangle + |\gamma\rangle|\alpha\rangle|\beta\rangle + |\beta\rangle|\gamma\rangle|\alpha\rangle\Big\}$$

Antisymmetric:

$$\frac{1}{\sqrt{6}}\Big\{|\alpha\rangle|\beta\rangle|\gamma\rangle - |\beta\rangle|\alpha\rangle|\gamma\rangle - |\alpha\rangle|\gamma\rangle|\beta\rangle - |\gamma\rangle|\beta\rangle|\alpha\rangle + |\gamma\rangle|\alpha\rangle|\beta\rangle + |\beta\rangle|\gamma\rangle|\alpha\rangle\Big\}$$

Partially symmetric:

$$\frac{1}{\sqrt{12}}\Big\{2|\alpha\rangle|\beta\rangle|\gamma\rangle + 2|\beta\rangle|\alpha\rangle|\gamma\rangle - |\alpha\rangle|\gamma\rangle|\beta\rangle - |\gamma\rangle|\beta\rangle|\alpha\rangle - |\gamma\rangle|\alpha\rangle|\beta\rangle - |\beta\rangle|\gamma\rangle|\alpha\rangle\Big\}$$

$$\frac{1}{2}\Big\{0 + 0 - |\alpha\rangle|\gamma\rangle|\beta\rangle + |\gamma\rangle|\beta\rangle|\alpha\rangle + |\gamma\rangle|\alpha\rangle|\beta\rangle - |\beta\rangle|\gamma\rangle|\alpha\rangle\Big\}$$

Partially symmetric:

$$\frac{1}{2}\Big\{0 + 0 - |\alpha\rangle|\gamma\rangle|\beta\rangle + |\gamma\rangle|\beta\rangle|\alpha\rangle - |\gamma\rangle|\alpha\rangle|\beta\rangle + |\beta\rangle|\gamma\rangle|\alpha\rangle\Big\}$$

$$\frac{1}{\sqrt{12}}\Big\{2|\alpha\rangle|\beta\rangle|\gamma\rangle - 2|\beta\rangle|\alpha\rangle|\gamma\rangle + |\alpha\rangle|\gamma\rangle|\beta\rangle + |\gamma\rangle|\beta\rangle|\alpha\rangle - |\gamma\rangle|\alpha\rangle|\beta\rangle - |\beta\rangle|\gamma\rangle|\alpha\rangle\Big\}$$

i- The symmetric subspace is invariant under all permutations.

ii- The antisymmetric " changes sign under P_{12}, P_{23}, and P_{31} and is unchanged by the other permutations.

iii- In general, the action of permutation ops. on the vectors in a partially symmetric subspace is to transform them into linear combinations of each other, however under P_{12} the first member in each subspace is even, and the second member is odd.

Since $[H, P_{12}] = [H, P_{23}] = \cdots [H, P_{123}^2] = 0$

it is possible, to form eigenvectors of H, so that each eigenvector ψ is constructed from basis vectors that belong to only one of these invariant subspaces.

Thus $\rightarrow$

The stationary states may be classified acc. to their symmetry-type under permutations.

Moreover; this symmetry type will be conserved by any permutation invariant int.

This is because;

Permutation symmetry of $(H\psi)$ = Permutation symmetry of (ψ)

(Since $HP = PH$ P: Permutation)

hence $\frac{\partial \psi}{\partial t} = (i\hbar)^{-1} H\psi$ must have the same symmetry as ψ.

$\longrightarrow$ The symmetry type does not change.

These conclusions can be generalized to any number of particles by means of group representation theory.

Remark:

In the subspace each vector under permutation changes to another vector which is a combination of the basis vectors in the same subspace.