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Identical particles :-

For distinguishable particles :-

$1, 2, \ldots, N$ particles

$|\psi_{i_1}\rangle_1 \otimes |\psi_{i_2}\rangle_2 \otimes \cdots |\psi_{in}\rangle_{(N)}$.

We use tensor product.

Say two identical electrons.

$|+\rangle, \quad |-\rangle.$

$$\underbrace{|+\rangle_{①} \otimes |-\rangle_{②} \quad , \quad |-\rangle_{①} \otimes |+\rangle_{②}}_{\text{which one ?}}$$

* if they were equivalent.

$$|\psi(\alpha,\beta)\rangle = \alpha|+\rangle|-\rangle + \beta|-\rangle|+\rangle$$

$$|\alpha|^2 + |\beta|^2 = 1.$$

$$|\psi_0\rangle = |+,x\rangle \otimes |+,x\rangle$$

$$= \frac{1}{2}\left(|+\rangle + |-\rangle\right) \otimes \left(|+\rangle + |-\rangle\right)$$

$$= \frac{1}{2}\left(|+\rangle|+\rangle + |+\rangle|-\rangle + |-\rangle|+\rangle + |-\rangle|-\rangle\right)$$

$$|\langle\psi_0|\psi(\alpha,\beta)\rangle|^2 = \frac{1}{4}(\alpha+\beta)^2$$

Permutation operators :-

Two particle hilbert space $V \otimes V$.

$$|u_i\rangle_{(1)} \otimes |u_j\rangle_{(2)}$$

$$\hat{P}_{21} \in \mathcal{L}(V \otimes V)$$

$$P_{21}\left(|u_i\rangle_1 |u_j\rangle_2\right) = |u_j\rangle_1 |u_i\rangle_2$$

$P_{21}^2 = \mathbb{1} \Rightarrow P_{21}$ is unitary & Hermitian.

$$\langle P_{21}|u_i\rangle|u_j\rangle, |u_k\rangle|u_l\rangle\rangle = \delta_{jk}\delta_{il}$$

$$\langle|u_i\rangle|u_j\rangle, P_{21}|u_k\rangle, |u_l\rangle\rangle = \delta_{li}\delta_{kj}$$

$\Rightarrow V = (\text{null}(P)) \oplus (R(P))$

Define :-

$$\hat{S} = \frac{1}{2}(\mathbb{1} + \hat{P}_{21})$$

$$\hat{A} = \frac{1}{2}(\mathbb{1} - \hat{P}_{21})$$

then
$S^2 = S, \quad A^2 = A, \quad A + S = \mathbb{1}$ and $[A, S] = 0$

and $\hat{P}_{21} S |\psi\rangle = S|\psi\rangle$ --- sym

$\hat{P}_{21} A |\psi\rangle = -A|\psi\rangle$ ... ant-sym

* if $\hat{B}(n)$ is operator acting on n^{th} state.

$B(1) \; |u_1\rangle|u_2\rangle = B|u_1\rangle \otimes \mathbb{1} \; |u_2\rangle$

$B(2) \; |u_1\rangle|u_2\rangle = |u_1\rangle \otimes B_2|u_2\rangle$.

and $P_{21} B(1) P_{21}^{+} = B(2)$

so therefore for any general operator $\Theta(1,2)$.

$P_{21} \Theta(1,2) P_{21}^{+} = \Theta(2,1)$.

and Θ is sym $\leftrightarrow [P_{21}, \Theta(1,2)] = 0$

* N particles :-

4 :-

$P_{3142} |a\rangle|b\rangle|c\rangle|d\rangle$

$= |c\rangle|a\rangle|d\rangle|b\rangle$

and $P_{2413} P_{3142} = \mathbb{1}$

$N = 3 \Rightarrow P_{123} = \mathbb{1}, \; \overbrace{P_{312}, P_{231}}^{\text{even}} \; \Big| \; \underbrace{P_{132}, P_{321}, P_{213}}_{\text{odd}}$.

* All are ~~Hermitian~~, Unitary.
* All permutations are even or odd.

Complete (Symmetrizer + Anti-sym)

Sym state $|\psi_S\rangle \Rightarrow P_\alpha |\psi_S\rangle = |\psi_S\rangle$

Anti-sym state $|\psi_A\rangle \Rightarrow P_\alpha |\psi_A\rangle = \varepsilon_\alpha |\psi_A\rangle$

$$\varepsilon_\alpha = \begin{cases} 1 & P_\alpha \text{ is even} \\ -1 & P_\alpha \text{ is odd} \end{cases}$$

if $|\psi_S\rangle$ is ~~sy~~ simultaneous eigenvector of P_α which do not commute.

Space of syms $\rightarrow$ $\text{Sym}(\underbrace{V \otimes V \otimes \cdots V}_{N}) \subset \underbrace{V \otimes V \otimes \cdots V}_{N}$

Space of antsyms $\rightarrow$ $\text{Ant Sym}(V^{\otimes N}) \subset V^{\otimes N}$ strict.

and Sym $\oplus$ Antisym $\subsetneq V^{\otimes N}$ for $N > 2$.

strict

So syms and antisyms do not make up the whole space.

Symmetrization postulate :-

In a system with 'N' identical particles in $V^{\otimes N}$ are ~~tott~~ in Sym or Antisym and not anywhere else.

Sym $\rightarrow$ Bosons

Ant-sym $\Rightarrow$ Fermions.

2-particle spin-$1/2$

Singlet :- $\frac{1}{\sqrt{2}}\left(|+-\rangle, -|-+\rangle\right)$

Triplet :-

$\frac{1}{\sqrt{2}}\left(|+-\rangle + |-+\rangle\right)$, $|++\rangle$, $|--\rangle$.

* For two electrons in same state.

$|1s, 1s\rangle = |1,0,0\rangle|1,0,0\rangle|\text{Singlet}\rangle$.

* Excited.

$|1s, 2, l, m\rangle = \frac{1}{\sqrt{2}}\left(|1,0,0\rangle|2,l,m\rangle - |2,l,m\rangle|1,0,0\rangle\right)|++\rangle$

& $\frac{1}{\sqrt{2}}\left(|1,0,0\rangle|2,l,m\rangle - |2,l,m\rangle|1,0,0\rangle\right)|--\rangle$.

& $\frac{1}{\sqrt{2}}\left(|1,0,0,+\rangle|2,l,m,-\rangle - |2,l,m,-\rangle|1,0,0,+\rangle\right)$

& $\frac{1}{\sqrt{2}}\left(|1,0,0,-\rangle|2,l,m,+\rangle - |2,l,m,+\rangle|1,0,0,-\rangle\right)$

Identical particles:-

We specify 2-particle states by

$|a,b\rangle = |a\rangle_1 \otimes |b\rangle_2$

Exchange operator:- $\hat{P}_{12}(|a,b\rangle) = |b,a\rangle$.

Exchanged state can differ from a physical state by atmost an overall phase as both are same.

$P_{12}|\psi\rangle = e^{i\delta}|\psi\rangle = \lambda|\psi\rangle$

and $P_{12}^2 = 1$

$\Rightarrow \lambda^2 = 1 \Rightarrow \lambda = \pm 1$.

$\therefore P_{12}|a,a\rangle = |a,a\rangle. \quad \lambda = 1.$

$$\text{or } [\hat{P}_{12}] = \begin{pmatrix} \langle a,b|P_{12}|a,b\rangle & \langle a,b|P_{12}|b,a\rangle \cdots \\ \langle b,a|P_{12}|a,b\rangle & \langle b,a|P_{12}|b,a\rangle \end{pmatrix}$$

$$= \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \Rightarrow \lambda = \pm 1$$

eigenstates are.

Sym $\quad |\psi_s\rangle = \frac{1}{\sqrt{2}}\left(|a,b\rangle + |b,a\rangle\right)$

Anti-Sym $\quad |\psi_A\rangle = \frac{1}{\sqrt{2}}\left(|a,b\rangle - |b,a\rangle\right)$

identical particles can only exist in one of these states ~~as~~ and not in super-position.

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Particles with integral spin,
$S = 0, 1, 2, ---$ i.e. bosons
only exist in $|\psi_S\rangle$ states.
they obey Bose-Einstein statistics

Example:-
Photons, gluons, $W^{\pm}$, Z_0, graviton &
composite like pions & He^4

Particles with half-integral spin
$S = \frac{1}{2}, \frac{3}{2}, \frac{5}{2}, ---$ i.e. fermions
only exist in $|\psi_A\rangle$ states.
and obey Fermi-Dirac statistics

Example:-
electrons, muons, neutrinos, quarks --
He^3, protons, nuetrons.

Spin-Statistics theorem.

∴ if 2- identical particles are in same states, they are symmetric.
∴ 2- spin-$\frac{1}{2}$ particles cannot occupy the same state.
Pauli- Exclusion Principle.

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Helium atom :-

$$\hat{H} = \frac{p_1^2}{2m} + \frac{p_2^2}{2m} - \frac{Ze^2}{|\hat{r}_1|} - \frac{Ze^2}{|\hat{r}_2|} + \frac{e^2}{|\hat{r}_1 - \hat{r}_2|}$$

Break it in $(Z = 2)$

$$H_0 = \frac{p_1^2}{2m} + \frac{p_2^2}{2m} - \frac{Ze^2}{|r_1|} - \frac{Ze^2}{|r_2|}$$

$$H_1 = \frac{e^2}{|\hat{r}_1 - \hat{r}_2|}$$

for H_0 can be seperated to 2-Hamiltonians

so eigenstates.

$$|n_1, l_1, m_1\rangle_1 \otimes |n_2, l_2, m_2\rangle_2$$

Ground state :-

$$|1,0,0\rangle_1 \otimes |1,0,0\rangle_2$$

The spin state is anti-symmetric,

$$S = \frac{1}{\sqrt{2}}\left(|+z\rangle_1 |-z\rangle_2 - |-z\rangle_1 |+z\rangle_2\right).$$

$$\Rightarrow |1s, 1s\rangle = |1,0,0\rangle_1 |1,0,0\rangle_2 \frac{1}{\sqrt{2}} S.$$

$$|0,0\rangle = \frac{1}{\sqrt{2}}\left(|+z\rangle_1 |-z\rangle_2 - |-z\rangle_1 |+z\rangle_2\right)$$

$$(\hat{S}_1 + \hat{S}_2)|0,0\rangle = 0, \quad (\hat{S}_{1z} + \hat{S}_{2z})|0,0\rangle = 0.$$

total spin is '0'.

$$E^0_{1s,1s} = -2(Z^2)\, 13.6 = -108.8 \text{ eV}.$$

$$E^1_{1s,1s} = \cancel{\langle 1,0,0|}\ \langle 1s, 1s| \frac{e^2}{|\hat{r}_1 - \hat{r}_2|} |1s, 1s\rangle.$$

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$$|\psi_s\rangle = \frac{1}{2}\int d^3r_1\, d^3r_2 \left(\frac{1}{\sqrt{2}}|r_1,r_2\rangle + \frac{1}{\sqrt{2}}|r_2,r_1\rangle\right) \times \left(\frac{1}{\sqrt{2}}\langle r_1,r_2|\psi_s\rangle + \frac{1}{\sqrt{2}}\langle r_2,r_1|\psi_s\rangle\right)$$

$$\Rightarrow |\psi_s\rangle = \frac{4}{2}\int d^3r_1\, d^3r_2\, |r_1;r_2\rangle\langle r_1;r_2|\psi_s\rangle$$

$$E^1_{1s,1s} = \iint d^3r_1\, d^3r_2\, |\langle r_1|1,0,0\rangle|^2 |\langle r_2|1,0,0\rangle|^2 \times \frac{e^2}{|\hat{r}_1-\hat{r}_2|}$$

$|\langle r_1|1,0,0\rangle|^2 = \frac{\rho(r_1)}{e}$ ... charge density.

$$E^1_{1s,1s} = \iint d^3r_1\, d^3r_2\, \frac{\rho(r_1)\rho(r_2)}{|r_1-r_2|}$$

$$= \frac{1}{\pi^2}\frac{Z^6}{a_0^6} e^2 \int_0^\infty r_1^2 dr_1\, e^{-2Zr_1/a_0} \int_0^\infty r_2^2 dr_2\, e^{-2Zr_2/a_0} \times \int d\Omega_1 \int d\Omega_2 \frac{1}{|r_2-r_1|}$$

$$\int d\Omega_2 \frac{1}{|r_2-r_1|} = \frac{\pi}{r_1 r_2}(r_1+r_2-|r_1-r_2|)$$

$$\Rightarrow E^1_{1s,1s} = \frac{Z^6}{a_0^6} 4e^2 \int_0^\infty dr_1\, r_1\, e^{-2Zr_1/a_0} \times \left(2\int_0^{r_1} dr_2\, r_2^2\, e^{-2Zr_2/a_0} + 2r_1\int_{r_1}^\infty dr_2\, r_2\, e^{-2Zr_2/a_0}\right)$$

$$= \frac{5}{8} Z mc^2\alpha^2 = 34 \text{ eV}.$$

$$\Rightarrow E_{1s,1s} \approx -108.8 + 34 = -74.8\text{ eV}$$

Experimental value $= -79$ eV.

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Excited States :-

* $\frac{1}{\sqrt{2}}\left(|1,0,0,+z\rangle_1 |2,l,m,+z\rangle_2 - |2,l,m,+z\rangle_1 |1,0,0,+z\rangle_2\right)$

$= \frac{1}{\sqrt{2}}\left(|1,0,0\rangle_1 |2,l,m\rangle_2 - |2,l,m\rangle_1 |1,0,0\rangle_2\right) |+z\rangle_1 |+z\rangle_2$

* $\frac{1}{\sqrt{2}}\left(|1,0,0,-z\rangle_1 |2,l,m,-z\rangle_2 - |2,l,m,-z\rangle_1 |1,0,0,-z\rangle_2\right)$

$= \frac{1}{\sqrt{2}}\left(|1,0,0\rangle_1 |2,l,m\rangle_2 - |2,l,m\rangle_1 |1,0,0\rangle_2\right) |-z\rangle_1 |-z\rangle_2$

* $\frac{1}{\sqrt{2}}\left(|1,0,0,+z\rangle_1 |2,l,m,-z\rangle_2 - |2,l,m,-z\rangle_1 |1,0,0,+z\rangle_2\right)$

* $\frac{1}{\sqrt{2}}\left(|1,0,0,-z\rangle_1 |2,l,m,+z\rangle_2 - |2,l,m,+z\rangle_1 |1,0,0,-z\rangle_2\right)$

$E^0_{1s,2s/2p} = -13.6\left(1+\frac{1}{4}\right)(4) = -68 \text{ eV}.$

all these states are degenerate.

New exchange operator :-

$P_{12} = P_{12}^{space} P_{12}^{spin}$

$[H_1, P_{12}^s] = [H_1, P_{12}^{spin}] = 0$

So H_1 can be diagonal in P_{12} basis.

$E^1_{1s,2s/2p} = \frac{1}{2}\left({}_1\langle 1 0 0|_2\langle 2,l,m| \pm {}_1\langle 2,l,m|_2\langle 1,0,0|\right) \frac{e^2}{|r_2 - r_1|} \left(|1,0,0\rangle_1 |2,l,m\rangle_2 \pm |2lm\rangle_1 |1,0 0\rangle_2\right)$

$\Rightarrow \iint d^3r_1\, d^3r_2\, |\langle 1,0,0|r_1\rangle|^2 |\langle 2,l,m|r_2\rangle|^2 \frac{e^2}{|r_1 - r_2|}$

$\pm \iint d^3r_1\, d^3r_2\, \langle 1,0,0|r_1\rangle\langle 2,l,m|r_2\rangle \frac{e^2}{r_2 - r_1} \langle r_1|2,l,m\rangle\langle r_2|1,0,0\rangle$

$$E'_{2s,2s} = 11.4 \pm 1.2 \ eV$$
$$E'_{1s,2p} = 13.2 \pm 0.9 \ eV$$

Elementary Variational method :-

$$\langle E \rangle = \langle \psi | \hat{H} | \psi \rangle.$$
$$|\psi\rangle = \sum c_n |E_n\rangle$$
$$\Rightarrow \langle E \rangle = \sum |c_n|^2 E_n \geq \sum |c_n|^2 E_0 = E_0$$

assuming E_0 is ground and - - -.

$$\Rightarrow E_0 \leq \langle \psi | H | \psi \rangle = \langle E \rangle.$$

Now we use variational methods to find the ground state of Helium.

* we shall take a $|\psi(\alpha_1, \alpha_2, \alpha_3 \ldots)\rangle$ and tune the parameters to minimise $\langle E \rangle$

let $|\psi\rangle = |1,0,0[\tilde{Z}]\rangle_1 |1,0,0[\tilde{Z}]\rangle_2$

$\tilde{Z}$ can be thought of as the effective charge

$$\langle r | 1,0,0[\tilde{Z}]\rangle = \frac{1}{\sqrt{\pi}} \left(\frac{\tilde{Z}}{a_0}\right)^{3/2} e^{-\tilde{Z}r/a_0}$$

H is of the usual form

then,

$$H = \left[\frac{p_1^2}{2m} - \frac{\tilde{Z}e^2}{|r_1|} + \frac{p_2^2}{2m} - \frac{\tilde{Z}e^2}{|r_2|}\right] + \frac{(\tilde{Z}-Z)e^2}{|r_1|} + \frac{(\tilde{Z}-Z)e^2}{|r_2|} + \frac{e^2}{|r_2 - r_1|}$$

$$\Rightarrow \langle E \rangle = \frac{1}{2} mc^2\alpha^2 \left(-2\tilde{Z}^2 + 4\tilde{Z}(\tilde{Z}-Z) + \frac{5}{4}\tilde{Z}\right)$$

$$\frac{\partial \langle E \rangle}{\partial \tilde{Z}} = 0 \Rightarrow \tilde{Z} = Z - \frac{5}{16}$$

$E_0 \leq -77.4 \text{ eV}$

if trial state is orthonormal to ground then ~~then~~ one can estimate E_1,

$$E_1 \leq \langle E \rangle$$

by choosing a trial state for original ground trial by

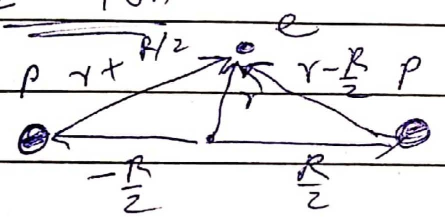
$$|\phi\rangle \to \frac{|\phi\rangle - |\psi\rangle\langle\psi|\phi\rangle}{\sqrt{1 - |\langle\psi|\phi\rangle|^2}}$$

Covalent Bonding :-

$$\langle r|1\rangle = \frac{1}{\sqrt{\pi a_0^3}} e^{-\frac{|r - \frac{R}{2}|}{a_0}}$$

H_2^+ ion

$$\langle r|2\rangle = \frac{1}{\sqrt{\pi a_0^3}} e^{-\frac{|r + \frac{R}{2}|}{a_0}}$$



$$\hat{H} = \frac{p^2}{2m} - \frac{e^2}{|r - \frac{R}{2}|} - \frac{e^2}{|r + \frac{R}{2}|} + \frac{e^2}{R}.$$

$$H_{11} = E_1 - \int d^3r \, \frac{e^2}{|r + \frac{R}{2}|} |\langle r|1\rangle|^2 + \frac{e^2}{R}.$$

$$H_{22} = E_1 - \int d^3r \, \frac{e^2}{|r - \frac{R}{2}|} |\langle r|2\rangle|^2 + \frac{e^2}{R} = H_{11}$$

$$H_{12} = H_{21} = \left(E_1 + \frac{e^2}{R}\right)\langle 1|2\rangle - \int d^3r \, \langle 1|r\rangle \frac{e^2}{|r - \frac{R}{2}|} \langle r|2\rangle$$

$H_{11} = H_{22}$, $H_{12} = H_{21}$.

$$|\pm\rangle = \frac{1}{\sqrt{2 \pm 2\langle 1|2\rangle}} \left(|1\rangle \pm |2\rangle\right)$$

$$\Rightarrow E_\pm = \frac{1}{1 \pm \langle 1|2\rangle} \left(H_{11} \pm H_{12}\right)$$

(+) is bonding
(−) is anti-bonding