Spin Review, addition of Spin

Recall

Hydrogen $\rightarrow \psi_{n\ell m} = R_n^\ell Y_{\ell m}$

$n = 1, 2, 3, \ldots$

$\ell \in n-1$ $\qquad$ $\ell \rightarrow$ angular $\rightarrow$ orbital Momentum

$m_\ell \in [-\ell, \ell] \rightarrow 2\ell+1$ m_ℓ's

need to add Spin

For one electron $\quad S = \frac{1}{2} \quad m_s = \pm\frac{1}{2} \quad \uparrow\downarrow$

$\chi \rightarrow$ Spin component, choose S_z

$|S\, m_s\rangle \rightarrow |\tfrac{1}{2}, \tfrac{1}{2}\rangle, \; |\tfrac{1}{2}, -\tfrac{1}{2}\rangle$

$|S|$

$S^2 |S\, m_s\rangle = \hbar^2 S(S+1) |S\, m_s\rangle$

$S_z |S\, m_s\rangle = \hbar m_s |S\, m\rangle$

Now $\quad \psi_{n\ell m_\ell m_s} = \chi R_n^\ell Y_{\ell m} \qquad \chi = a\chi_+ + b\chi_-$

$\chi_+ = \begin{pmatrix} 1 \\ 0 \end{pmatrix} = |\tfrac{1}{2}, \tfrac{1}{2}\rangle \qquad \chi_- = \begin{pmatrix} 0 \\ 1 \end{pmatrix} |\tfrac{1}{2}, -\tfrac{1}{2}\rangle$

$S^2 = \frac{3}{4}\hbar^2 \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}, \quad S_z = \frac{\hbar}{2} \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$

How to determine S, m_s for 2 particle systems?

electron and proton?

$\uparrow\uparrow, \uparrow\downarrow, \downarrow\uparrow, \downarrow\downarrow$

Product

Let $S = S^1 + S^2 \rightarrow$ Spin for 2 $\rightarrow \chi_1 \chi_2$

$|S| = 1 \quad \frac{1}{2}+\frac{1}{2} \quad m_s$?

$S_z = S_z^1 + S_z^2$ only acts on 1 or 2

$$S_z \chi_1 \chi_2 = (S_z^1 + S_z^2)\chi_1 \chi_2 = S_z^1 \chi_1 \chi_2 + \chi_1 S_z^2 \chi_2$$

$$= \hbar m_1 \chi_1 \chi_2 + \chi_1 \hbar m_2 \chi_2 = \hbar(m_1 + m_2)\chi_1 \chi_2$$

$\uparrow\uparrow \; m_s = 1 \quad \uparrow\downarrow \; m_s = 0 \quad \downarrow\uparrow \; m_s = 0 \quad \downarrow\downarrow \; m_s = -1$

?

2 with zero

$|11\rangle = \uparrow\uparrow, \quad |1\,{-1}\rangle = \downarrow\downarrow, \quad \downarrow\uparrow \to |10\rangle, \quad \uparrow\downarrow \to |10\rangle$

$S=1 \qquad S=1$

Now $\quad S_- |s\, m_s\rangle = \hbar\sqrt{s(s+1) - m_s(m_s - 1)}\; |s\; m_s - 1\rangle$

$$S_- |\tfrac{1}{2}\tfrac{1}{2}\rangle = \hbar\sqrt{\tfrac{3}{4} - \tfrac{1}{2}(-\tfrac{1}{2})}\;\; |\tfrac{1}{2}\,{-\tfrac{1}{2}}\rangle$$

$$= \hbar\sqrt{\tfrac{3}{4} + \tfrac{1}{4}}\;\; |\tfrac{1}{2}\,{-\tfrac{1}{2}}\rangle$$

$$= \hbar\, |\tfrac{1}{2}\,{-\tfrac{1}{2}}\rangle$$

$$S_- \to S_-^1 + S_-^2 \qquad S_- |\uparrow\uparrow\rangle = S_- \chi_1 \chi_2 = S_- \underset{\uparrow}{|\tfrac{1}{2}\tfrac{1}{2}\rangle}\underset{\uparrow}{|\tfrac{1}{2}\tfrac{1}{2}\rangle}$$

$$= S_-^1 \overset{\uparrow}{|\tfrac{1}{2}\tfrac{1}{2}\rangle}\overset{\uparrow}{|\tfrac{1}{2}\tfrac{1}{2}\rangle} + \overset{\uparrow}{|\tfrac{1}{2}\tfrac{1}{2}\rangle} S_-^2 \overset{\uparrow}{|\tfrac{1}{2}\tfrac{1}{2}\rangle}$$

$$= \underset{\hbar\,\downarrow\uparrow}{\hbar\, |\tfrac{1}{2}\,{-\tfrac{1}{2}}\rangle |\tfrac{1}{2}\tfrac{1}{2}\rangle} + \underset{\uparrow\,\hbar\,\downarrow}{|\tfrac{1}{2}\tfrac{1}{2}\rangle\, \hbar\, |\tfrac{1}{2}, -\tfrac{1}{2}\rangle}$$

$$= \hbar(\downarrow\uparrow + \uparrow\downarrow)$$

Normalized State $\quad |10\rangle = \dfrac{1}{\sqrt{2}}(\uparrow\downarrow + \downarrow\uparrow) \quad S=1$

$S_- |10\rangle \longrightarrow |00\rangle = \dfrac{1}{\sqrt{2}}(\uparrow\downarrow - \downarrow\uparrow)$

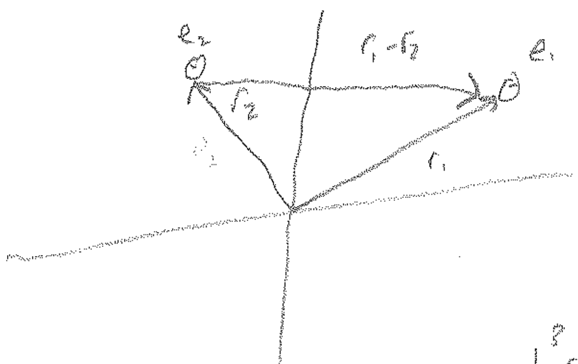
Chapter 5

For 1 $\Psi(r, t)$

For 2 $\Psi(r_1, r_2, t)$

Where $i\hbar \frac{\partial \Psi}{\partial t} = \hat{H}\Psi$ $\quad \hat{H} = -\frac{\hbar^2}{2m}(\nabla_1^2 + \nabla_2^2) + V(r_1, r_2, t)$

∇_1^2 acts only on r_1
∇_2^2 " " r_2



$P(r_1) \in d^3 r_1$, $P(r_2) \in d^3 r_2 = |\Psi(r_1, r_2, t)|^2 d^3 r_1 d^3 r_2$

$\int |\Psi(r_1, r_2, t)|^2 d^3 r_1 d^3 r_2 = 1$

For $V(r_1, r_2)$ only $\Psi(r_1, r_2, t) = \psi(r_1, r_2) e^{-iEt/\hbar}$

and TISE $= -\frac{\hbar^2}{2m}(\nabla_1^2 \psi + \nabla_2^2 \psi) + V\psi = E\psi$

Bosons and Fermions

Assume 1 is in state $\psi_a(r)$
2 is in state $\psi_b(r)$

Then $\psi(r_1, r_2) = \psi_a(r_1)\psi_b(r_2)$

Can we tell ψ_1 from ψ_2?

if classical yes, Paint a label on them

In QM one electron is indistinguishable from another

No way to differentiate

Be Non-classical, give either chance to be in either state

$$\psi_{\pm}(r_1, r_2) = A\left[\psi_a(r_1)\psi_b(r_2) \pm \psi_b(r_1)\psi_a(r_2)\right]$$

if a particle has an integer spin it is a boson, + sign

" " a halfinteger spin it is a fermion, - sign

So if $\psi_a = \psi_b$ → think, same n, l, m_l, m_s for a, b

Then $\psi_-(r_1, r_2) = A\left[\psi_a(r_1)\psi_a(r_2) - \psi_a(r_1)\psi_a(r_2)\right] = 0$

PEP Fermions may not occupy same state.

Exchange Operator $r_1 \longleftrightarrow r_2$

$\hat{P}\psi(r_1, r_2) = \psi(r_2, r_1)$

$\hat{P}^2 = 1$ So $\hat{P}$ has eigenvalues ± 1

Implies $[P, H]\psi = [PH - HP]\psi = PE\psi - HP\psi = 0$

or Simultaneous Solutions to both $H\psi$, $P\psi$

So $\psi(r_1, r_2) = \pm\, \psi(r_2, r_1)$

Symmetrization Requirement

Ex 1 Particle ISW

$$\psi_n(x) = \sqrt{\frac{2}{a}}\, \sin\left(\frac{n\pi x}{a}\right) \quad E_n = n^2 K \quad K = \frac{\pi^2 \hbar^2}{2ma^2}$$

2 Particle distinguishable

$$\psi_{n_1 n_2}(x_1, x_2) = \psi_{n_1}(x_1)\, \psi_{n_2}(x_2) \quad E_{n_1 n_2} = (n_1^2 + n_2^2) K$$

$$\psi_{11} = \frac{2}{a} \sin\left(\frac{\pi x_1}{a}\right) \sin\left(\frac{\pi x_2}{a}\right) \quad E_{11} = 2K$$

1st excited State

$$\frac{2}{a} \sin\left(\frac{\pi x_{12}}{a}\right) \sin\left(\frac{\pi x_{21}}{a}\right) \quad \text{2 eqs} \quad E_{12} = 5K,\ E_{21} = 5K$$

For bosons → ground State unchanged

1st excited State

$$\frac{\sqrt{2}}{a}\left[\sin\left(\frac{\pi x_1}{a}\right)\sin\left(\frac{2\pi x_2}{a}\right) + \sin\left(\frac{2\pi x_1}{a}\right)\sin\left(\frac{\pi x_2}{a}\right)\right] \quad E = 5K$$

For Fermions → may not have Same States

ground State is the above with $E = 5K$

No 2K State

What functional difference does Boson vs Fermion make?

1 Distinguishable $\psi(x_1, x_2) = \psi_a(x_1)\psi_b(x_2)$

Indistinguishable

2 Boson $\psi_+(x_1, x_2) = \frac{1}{\sqrt{2}}\left[\psi_a(x_1)\psi_b(x_2) + \psi_b(x_1)\psi_a(x_2)\right]$

3 Fermion $\psi_-(x_1, x_2) = \frac{1}{\sqrt{2}}\left[\psi_a(x_1)\psi_b(x_2) - \psi_b(x_1)\psi_a(x_2)\right]$

What is $\langle(x_1 - x_2)\rangle^2 \rightarrow$ Separation distance

$$\langle x_1^2\rangle + \langle x_2^2\rangle - 2\langle x_1 x_2\rangle$$

$$\langle x_1^2\rangle = \underbrace{\int x_1^2 |\psi_a(x_1)|^2 dx_1}_{\langle x_1^2\rangle_a} \underbrace{\int |\psi_b(x_2)|^2 dx_2}_{1} = \langle x_1^2\rangle_a$$

$$\langle x_2^2\rangle = \underbrace{\int |\psi_a(x_1)|^2 dx_1}_{1} \underbrace{\int x_2^2 |\psi_b(x_2)|^2 dx_2}_{\langle x^2\rangle_b} = \langle x^2\rangle_b$$

$$\langle x_1 x_2\rangle = \int x_1 |\psi_a(x_1)|^2 dx_1 \int x_2 |\psi_b(x_2)|^2 dx_2 = \langle x\rangle_a \langle x\rangle_b$$

$$\langle(x_1 - x_2)\rangle_d^2 = \langle x^2\rangle_a + \langle x^2\rangle_b - 2\langle x\rangle_a\langle x\rangle_b$$

Similarly

$$\langle (x_1 - x_2)^2 \rangle_\pm = \langle x^2 \rangle_a + \langle x^2 \rangle_b - 2\langle x \rangle_a \langle x \rangle_b \mp 2 |\langle x \rangle_{ab}|^2$$

both in same $p_{\pm}$

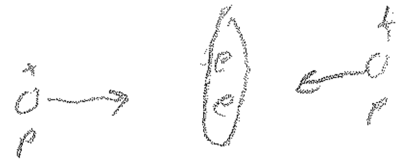
$$\langle (\Delta x)^2 \rangle_\pm = \langle (\Delta x)^2_d \rangle \mp 2 |\langle x \rangle_{ab}|^2$$

bosons → closer

Fermions → Farther

$$\langle x \rangle_{ab} = \int x \psi_a^*(x) \psi_b(x)\, dx$$

$= 0$ unless overlap



Symmetric

bonding

covalent bond

anti bonding

by themselves, Fermions can't bond

?

SPIN → whole function

$|1\,1\rangle = \uparrow\uparrow$

$|1\,0\rangle = \frac{1}{\sqrt{2}}(\uparrow\downarrow + \downarrow\uparrow)$ Symmetric States of χ, triplet $S=1$

$|1\,{-1}\rangle = \downarrow\downarrow$

$|0\,0\rangle\ \frac{1}{\sqrt{2}}(\uparrow\downarrow - \downarrow\uparrow)$ $S=0$, singlet, anti-Symmetric

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For Fermions $\psi(r)\chi(s)$ has to be antiSymmetric

So Symmetric $\psi(r)$, anti-Symmetric $\chi(s)$

must be $|00\rangle$ State

Atoms

$$\hat{H} = \sum_{j=1}^{Z} \left(-\frac{\hbar^2}{2m} - \frac{1}{4\pi\epsilon_0} \frac{Ze^2}{r_j} \right) + \frac{1}{2}\left(\frac{1}{4\pi\epsilon_0}\right) \sum_{j \neq k}^{Z} \frac{e^2}{|r_j - r_k|}$$

?

need $\psi(r_1, r_2, \ldots, r_Z)\,\chi(s_1, s_2, \ldots, s_Z)$ anti-symmetric

Not solvable if $Z > 1$

$$\hat{H}_{\text{for } He} = -\frac{\hbar^2}{2m}\nabla_1^2 - \frac{1}{4\pi\epsilon_0}\frac{2e^2}{r_1} - \frac{\hbar^2}{2m}\nabla_2^2 - \frac{2e^2}{r_2} + \frac{1}{4\pi\epsilon_0}\frac{e^2}{|r_1 - r_2|}$$

ignoring the last term

$$\psi(r_1, r_2) = \psi_{n\ell m}(r_1)\,\psi_{n'\ell' m'}(r_2)$$

$a_0\ He = \frac{a_0}{2}\ H$, $E = 4(E_n + E_{n'})$ $E_n = \frac{-13.6}{n^2}\,eV$

$$\psi_0(r_1, r_2) = \psi_{100}(r_1)\,\psi_{100}(r^2) = \frac{8}{\pi a^3} e^{-2(r_1 + r_2)/a}$$

$E_0 = -109\,eV$, ψ_0 symmetric so $\chi_0 \rightarrow$ anti

real $E_0 = -78.975\,eV$

Atoms

To first order, electrons occupy orbitals with distinct

n, ℓ, m_ℓ, m_s states

Each value of n has n^2 n, ℓ, m states with two spin states

So each level can accomodate $2n^2$ electrons

$n=1$ 2 $\qquad \ell=0$ s

$n=2$ 8 $\qquad \ell=1$ p

$n=3$ 18 $\qquad \ell=2$ d $\qquad g, h, i, k \ldots$

$n=4$ 32 $\qquad \ell=3$ f

$\vdots$

Levels fill up with $n+\ell$ giving priority to lower n

$4p: 5 \qquad 3D = 5$

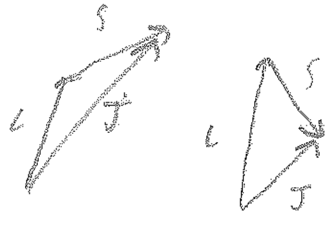
first

Labeled with ${}^{2S+1}L_j$ where $j \in [|L-S|, |L+S|]$

$\vec{L} \in [|\ell_1 - \ell_2|, |\ell_1 + \ell_2|]$

Single electron atom

$\vec{J} = \vec{L} + \vec{S}$



Need to review L, S, J