Physics 492
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Lecture 14: Indistinguishable Particles

Electrons (or other quantum particles e.g. protons, photons) are in principle indistinguishable. The multi-particle state must not contain more information than exists in principle.

Profound consequence of exchange symmetry.

Two particle state is a linear combination of basis states

$$|a,b\rangle \equiv |a\rangle_1 \otimes |b\rangle_2 \qquad 1,2 \text{ label particle}$$
$$|b,a\rangle \equiv |b\rangle_1 \otimes |a\rangle_2 \qquad a,b \text{ label state}$$

for example $|a\rangle = |\psi_a\rangle \otimes |\tfrac{1}{2}, m_a\rangle$
$|b\rangle = |\psi_b\rangle \otimes |\tfrac{1}{2}, m_b\rangle$

$\psi_a(\vec{r}_1) = \langle r_1|\psi_a\rangle$

$|a,b\rangle$, $|b,a\rangle$ distinguish the electrons. We must form linear combinations.

Define particle exchange operator:

$$\hat{P}_{12}|a,b\rangle = |b,a\rangle$$
$$\hat{P}_{12}|b,a\rangle = |a,b\rangle$$

$(\hat{P}_{12})^2 = \hat{1}$ identity.

Partical Echange Symmetry

operator $\hat{P}_{12}|a,b\rangle \equiv |b,a\rangle$

$$\hat{P}_{12}^2|a,b\rangle = |a,b\rangle$$

$\hat{P}_{12}^2 = \hat{I} \Rightarrow \hat{P}_{12} = P_{12}^{\dagger} = P_{12}^{-1}$

Want eigenstates of $\hat{P}_{12}$ operator -
linear combination $|\psi_n\rangle = \frac{1}{\sqrt{2}}\{|a,b\rangle + \eta|b,a\rangle\}$

require $\langle\psi_n|\hat{P}_{12}^2|\psi_n\rangle = \langle\psi_n|\psi_n\rangle$

$$\hat{P}_{12}|\psi_n\rangle = e^{i\alpha}|\psi_n\rangle = \frac{1}{\sqrt{2}}\{|b,a\rangle + \eta|a,b\rangle\}$$

$$= \frac{1}{\sqrt{2}}\eta\{|a,b\rangle + \eta^{-1}|b,a\rangle\}$$

$\eta = e^{i\alpha}$ $\quad \eta = \eta^{-1}$ so $\eta^2 = 1$

$$\eta = \pm 1$$

We have two possibilities symmetric, antisymmetric under particle exchange -

$$|\psi_{\pm}\rangle = \frac{1}{\sqrt{2}}\{|a,b\rangle \pm |b,a\rangle\}$$

$$\hat{P}_{12}|\psi_{\pm}\rangle = \pm|\psi_{12}\rangle$$

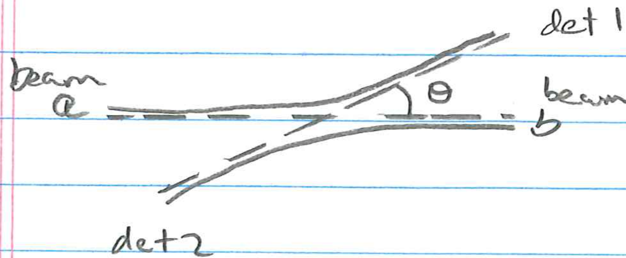
antisymmetric combination obeys Pauli Exclusion,

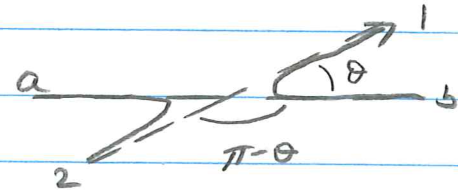
$$\frac{1}{\sqrt{2}}\{|a,a\rangle - |a,a\rangle\} = 0$$

Spin-Statistics theorem of QFT:

$|\psi_+\rangle$ integral spin; $|\psi_-\rangle$ $\frac{1}{2}$ integral spin

Scattering (Feynman Vol. III)





direct $A(\theta)$ exchang $A(\pi-\theta)$

identical polarized Fermions (w/o spin flip)

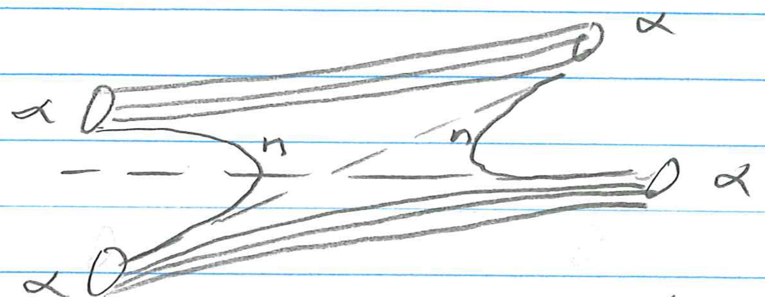
$$A^F_{TOT} = A(\theta) - A(\pi-\theta)$$

identical Bosons

$$A^B_{TOT} = A(\theta) + A(\pi-\theta)$$

α-scattering α(pnpn) is Spin 1 Boson at low energy, direct & exchange add

at high energy, neutron exchange (Fermion) gets minus sign relative to non-exchange



neutron exchange

Exchange force

$|\psi\rangle = |\text{space}\rangle \otimes |\text{spin}\rangle$

$$|\psi_+\rangle = \begin{cases} |\text{space}\rangle_S \; |\text{spin}\rangle_S & S \equiv \text{symmetric} \\ |\text{space}\rangle_A \; |\text{spin}\rangle_A & A \equiv \text{antisymmetric} \end{cases}$$

boson

$$|\psi_-\rangle = \begin{cases} |\text{space}\rangle_S \; |\text{spin}\rangle_A \\ |\text{space}\rangle_A \; |\text{spin}\rangle_S \end{cases}$$

fermion

Consider space part of wave function
(for simplicity, 1D) (from Griffiths)

I. distinguishable particles (e, p)

$$\psi_{ep} = \psi_e(x_1)\,\psi_p(x_2)$$

$$\langle x_1\rangle = \int dx_1\, x_1 |\psi_e|^2 \int dx_2 |\psi_p|^2 = \langle x\rangle_e$$

$$\langle x_2\rangle = \langle x\rangle_p$$

$$\langle x_1 x_2\rangle = \langle x\rangle_e \langle x\rangle_p$$

$$\langle (\hat{x}_1 - \hat{x}_2)^2 \rangle = \langle x^2\rangle_e + \langle x^2\rangle_p - 2\langle x\rangle_e \langle x_p\rangle$$

II, indistinguishable — Consider only spatial part for simplicity

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

a, b spatial state labels

$\eta = \pm 1$

$$\langle \hat{x}_1^2 \rangle = \int dx_1\, dx_2\, x_1^2 |\psi_\eta|^2$$

$$= \frac{1}{2}\int dx_1\, x_1^2 \int dx_2 \Big\{ |\psi_a(1)|^2 |\psi_b(2)|^2 + |\psi_b(1)|^2 |\psi_a(2)|^2$$

$$+ \eta\, \psi_a^*(1)\, \psi_b^*(2)\, \psi_a(2)\, \psi_b(1)$$

$$+ \eta\, \psi_a^*(2)\, \psi_b^*(1)\, \psi_a(1)\, \psi_b(2)$$

orthogonal

$$= \frac{1}{2}\left[\langle x^2\rangle_a + \langle x^2\rangle_b\right] = \langle \hat{x}_2^2 \rangle$$

However, for $\langle \hat{x}_1 \hat{x}_2 \rangle$

$$\langle \hat{x}_1 \hat{x}_2 \rangle_\eta = \frac{1}{2}\Big[2\langle x\rangle_a \langle x\rangle_b + 2\eta\, \underbrace{\langle a|\hat{x}|b\rangle\langle b|\hat{x}|a\rangle}_{|\langle a|\hat{x}|b\rangle|^2} \Big]$$

So

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

$$- 2\eta\, |\langle a|\hat{x}|b\rangle|^2$$

$\rightarrow$ exchange "force"

Exchange force term $\eta = \pm 1$ acts as attractive (repulsive) "force".

Physical example: laser (bosons)
degeneracy pressure (fermions)

Covalent bond - electrons are $\uparrow\downarrow$ so spatial part is symmetric, binding

Technical point - symmetric inner product

symmetrized basis:

$$|r_\eta\rangle = \frac{1}{\sqrt{2}}\left(|\vec{r}_1,\vec{r}_2\rangle + \eta\,|\vec{r}_2,\vec{r}_1\rangle\right)$$

$$\hat{I} = \frac{1}{2}\int d^3r_1 \int d^3r_2 \; |r_\eta\rangle\langle r_\eta|$$

$\frac{1}{2}$ to avoid double counting

$$|\Psi_\eta\rangle = \frac{1}{2}\int d^3r_1 \int d^3r_2 \left(\frac{1}{\sqrt{2}}\right)^2 \left(|\vec{r}_1\vec{r}_2\rangle + \eta\,|\vec{r}_2\vec{r}_1\rangle\right)$$

$$\times\left(\langle\vec{r}_1\vec{r}_2| + \eta\,\langle\vec{r}_2\vec{r}_1|\right)|\Psi_\eta\rangle$$

where $|\Psi_\eta\rangle = \frac{1}{\sqrt{2}}\left(|a,b\rangle + \eta|b,a\rangle\right)$

Expansion of $|\Psi_\eta\rangle$ gives 4 identical terms

but $|\Psi_\eta\rangle = \int d^3r_1 \int d^3r_2 \; |\vec{r}_1\vec{r}_2\rangle\langle\vec{r}_1\vec{r}_2|\Psi_\eta\rangle =$

$\int d^3\vec{r}_1 d^3\vec{r}_2 \; |\vec{r}_\eta\rangle\langle\vec{r}_\eta|\Psi_\eta\rangle$

where $\langle\vec{r}_1\vec{r}_2|\Psi_\eta\rangle = \frac{1}{\sqrt{2}}\left(\Psi_a(\vec{r}_1)\Psi_b(\vec{r}_2) + \eta\,\Psi_b(\vec{r}_1)\Psi_a(\vec{r}_2)\right)$

Proof.
Explicitly, 4 terms are

$$\left.\begin{aligned}&\frac{1}{4}\int d^3r_1\int d^3r_2\ |r_1 r_2\rangle\langle r_1 r_2|\Psi_n\rangle\\ &+\frac{1}{4}\int d^3r_1\int d^3r_2\ |r_2 r_1\rangle\langle r_2 r_1|\Psi_n\rangle\end{aligned}\right]\ \vec{r}_1, \vec{r}_2 \text{ dummy variables}$$

$$\left.\begin{aligned}&+\frac{\eta}{4}\int d^3r_1\int d^3r_2\ |r_1 r_2\rangle\langle r_2 r_1|\Psi_n\rangle\\ &+\frac{\eta}{4}\int d^3r_1\, d^3r_2\ |r_2 r_1\rangle\langle r_1 r_2|\Psi_n\rangle\end{aligned}\right]\ \text{dummy variables again}$$

$$\hat{P}_{12}|\vec{r}_2, \vec{r}_1\rangle = |\vec{r}_1, \vec{r}_2\rangle$$

$$\hat{P}_{12}|\Psi_n\rangle = \eta|\Psi_n\rangle$$

so $\langle \vec{r}_2\vec{r}_1|\Psi_n\rangle = \langle \vec{r}_2\vec{r}_1|\hat{P}_{12}^2|\Psi_n\rangle = \eta\langle \vec{r}_1\vec{r}_2|\Psi_n\rangle$

giving $\eta^2 = 1$ for each of the η terms.

therefore, all 4 terms are the same.

Giving

$$|\Psi_n\rangle = \int d^3r_1\, d^3r_2\ |r_1 r_2\rangle\langle r_1 r_2|\Psi_n\rangle$$

$$\langle r_1 r_2|\Psi_n\rangle = \frac{1}{\sqrt{2}}\left(\Psi_a(\vec{r}_1)\Psi_b(\vec{r}_2) + \eta\,\Psi_a(\vec{r}_2)\Psi_b(\vec{r}_1)\right)$$

as you would naively expect

Helium Ground State

Ignoring e^--e^- Coulomb interaction, the lowest state is

$$|1S^0\rangle = |1,0,0\rangle_1 \, |1,0,0\rangle_2 \, \chi_A(0,0)$$

where $\chi_A = \frac{1}{\sqrt{2}}\left(\uparrow_1 \downarrow_2 - \uparrow_2 \downarrow_1\right)$ spin-0, antisymmetric spinor state

Spatial part is symmetric.

Treat e^--e^- Coulomb as perturbation

$$\hat{H}' = \frac{e^2}{|\vec{r}_1 - \vec{r}_2|}$$

$$E^{(1)} = \langle 1S^0 | \hat{H}' | 1S^0 \rangle$$

$$|1S^0\rangle = \int d^3r_1 \, d^3r_2 \, |\vec{r}_1 \vec{r}_2\rangle \, \psi_{1s}(\vec{r}_1) \, \psi_{1s}(\vec{r}_2) \, \chi_A$$

formally

$$\langle \vec{r}_1{}', \vec{r}_2{}' | \hat{H}' | \vec{r}_1, \vec{r}_2 \rangle = \frac{e^2}{|\vec{r}_1 - \vec{r}_2|} \delta^3(\vec{r}_1 - \vec{r}_1{}') \, \delta^3(\vec{r}_2 - \vec{r}_2{}')$$

$$\chi_A^\dagger \chi_A = 1$$

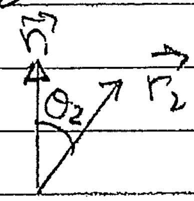
$$E^{(1)} = \int d^3r_1 \, d^3r_2 \, |\psi_{1s}(\vec{r}_1)|^2 \frac{e^2}{|\vec{r}_1 - \vec{r}_2|} |\psi_{1s}(\vec{r}_2)|^2$$

charge density $e\,|\psi_{1s}(\vec r)|^2 = \rho(\vec r)$

$$E^{(1)} = \int d^3r_1\, d^3r_2 \, \frac{\rho(r_1)\,\rho(r_2)}{|\vec r_1 - \vec r_2|}$$

$$= \int_0^\infty r_1^2\, dr_1 \int_0^\infty r_2^2\, dr_2\, \rho(r_1)\rho(r_2) \int d\Omega_1 \int d\Omega_2 \, \frac{1}{|\vec r_1 - \vec r_2|}$$

to evaluate, choose $\vec r_1 = r_1 \hat z$



$$|\vec r_1 - \vec r_2|^2 = r_1^2 + r_2^2 - 2 r_1 r_2 \cos\theta_2 \qquad c_2 \equiv \cos\theta_2$$

$$\int d\Omega_1 \int d\Omega_2 \, \frac{1}{|\vec r_1 - \vec r_2|} = \int d\Omega_1 \int_0^{2\pi} d\phi_2 \int_{-1}^{1} dc_2 \left(r_1^2 + r_2^2 - 2 r_1 r_2 c_2\right)^{-1/2}$$

$$= \int d\Omega_1\, (2\pi) \left(\frac{-1}{r_1 r_2}\right) \left(r_1^2 + r_2^2 - 2 r_1 r_2 c_2\right)^{1/2} \Big|_{-1}^{+1}$$

$$= \int d\Omega_1\, (2\pi) \left(-\frac{1}{r_1 r_2}\right) \left[\sqrt{(r_1 - r_2)^2} - \sqrt{(r_1 + r_2)^2}\right]$$

$$= 8\pi^2 \left\{ \frac{r_1 + r_2 - |r_1 - r_2|}{r_1 r_2} \right\}$$

note - factor 2 is missing in eq 12.30
fixed, 2nd edition

$$\left.\begin{array}{ll} = 16\pi^2/r_1 & r_1 > r_2 \\ 16\pi^2/r_2 & r_1 < r_2 \end{array}\right\} \equiv 16\pi^2 f(r_1, r_2)$$

Charge densities

$$\rho(r) = -e\,|\psi_{1s}(r)|^2 = -e\left[\frac{1}{\pi}\left(\frac{Z}{a_0}\right)^3\right]e^{-2Zr/a_0}$$

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

$$\times\, 16\pi^2 f(r_1, r_2)$$

$$= e^2\, 16\left(\frac{Z}{a_0}\right)^6 \int_0^\infty r_1^2 dr_1\, e^{-2Zr_1/a_0}$$

$$\times \left\{\frac{1}{r_1}\int_0^{r_1} dr_2\, r_2^2 e^{-2Zr_2/a_0} + \int_{r_1}^\infty r_2 dr_2\, e^{-2Zr_2/a_0}\right\}$$

$$= e^2\, 16\left(\frac{Z}{a_0}\right)^6\left(\frac{a_0}{2Z}\right)^5 \int_0^\infty x^2 dx\, e^{-x}$$

$$\times\left\{\frac{1}{x}\int_0^x y^2 dy\, e^{-y} + \int_x^\infty y\, dy\, e^{-y}\right\}$$

$$\{\} = -\frac{1}{x}(y^2+2y+2)e^{-y}\Big|_0^x - (y+1)e^{-y}\Big|_x^\infty$$

$$= -\frac{1}{x}(x^2+2x+2)e^{-x} + \frac{2}{x} + (x+1)e^{-x}$$

$$= \frac{2}{x} - e^{-x}\left(1+\frac{2}{x}\right)$$

$$E^{(1)} = e^2\,\frac{1}{2}\left(\frac{Z}{a_0}\right)\left[-\int_0^\infty x^2 dx\, e^{-2x} - 2\int_0^\infty x\,dx\, e^{-2x} + 2\int_0^\infty x\,dx\,e^{-x}\right]$$

$$[\;] = -\frac{1}{8}2! - \frac{2}{4} + 2 = 5/4$$

$$E^{(1)} = e^2 \left(\frac{1}{2}\right)\left(\frac{Z}{a_0}\right)\frac{5}{4} = \frac{5}{8} Z \frac{e^2}{a_0} = \underline{\frac{5}{8} Z\, mc^2 \alpha^2}$$

with $Z = 2$

$$E^{(1)} = \frac{5}{4} mc^2 \alpha^2 = 34.0 \text{ eV}$$

$$E_1^{(0)} = \underset{\substack{\uparrow \\ \text{2 electrons}}}{2}\left(-\frac{1}{2} mc^2 (2\alpha)^2\right) = 8\left(-\frac{1}{2} mc^2 \alpha^2\right) = -108.8 \text{ eV}$$

check $\left|\frac{E^{(1)}}{E_1^{(0)}}\right| = \frac{5/2}{8} = \frac{5}{16}$ not a very small correction

Nevertheless,

$$E_1^{\text{perturb.}} = E_1^{(0)} + E_1^{(1)} = -74.8 \text{ eV}$$

$$E_1^{exp} = -79.0 \text{ eV}$$

pretty good. We can do better using a different method – the <u>variational method</u>

He Ground state by variational method

True Ground state is minimum energy. Vary wave function to get lower energy.

Improved result based on partial shielding of nucleus by other electron: Vary Z.

note: I use Z as variable parameter and 2 for He charge (book uses $\tilde{Z}, Z$).

$$\psi_Z = \frac{1}{\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{3/2} e^{-Zr/a_0}$$

Choose $\hat{H}_0$ to be the problem we know how to solve and $\hat{H}_1$ to contain the remainder.

$$\hat{H} = -\frac{\hbar^2}{2m}\left(\nabla_1^2+\nabla_2^2\right) - \frac{2e^2}{r_1} - \frac{2e^2}{r_2} + \frac{e^2}{|\vec{r}_1-\vec{r}_2|}$$

$$\hat{H}_0 = -\frac{\hbar^2}{2m}\left(\nabla_1^2+\nabla_2^2\right) - \frac{Ze^2}{r_1} - \frac{Ze^2}{r_2}$$

$$\hat{H}_1 = \frac{(Z-2)e^2}{r_1} + \frac{(Z-2)e^2}{r_2} + \frac{e^2}{|\vec{r}_1-\vec{r}_2|}$$

$$\langle \hat{H}_0 \rangle = 2Z^2\left(-\tfrac{1}{2}mc^2\alpha^2\right)$$

$$\langle \hat{H}_1 \rangle = 2(Z-2)e^2\left\langle \frac{1}{r}\right\rangle + \frac{5}{4}Z\left(\tfrac{1}{2}mc^2\alpha^2\right)$$

$$e^2\left\langle \frac{1}{r}\right\rangle = \frac{Ze^2}{a_0} = Z\frac{mc}{\hbar}(\alpha\hbar c) = 2Z\left(\tfrac{1}{2}mc^2\alpha^2\right)$$

giving

$$E(Z) = \langle \hat{H}\rangle = \tfrac{1}{2}mc^2\alpha^2\left(-2Z^2+4(Z-2)Z+\tfrac{5}{4}Z\right)$$

$$= \tfrac{1}{2}mc^2\alpha^2\left(2Z^2-8Z+\tfrac{5}{4}Z\right)$$

$$\left.\frac{dE}{dZ}\right|_{Z_{min}} = 0 = \tfrac{1}{2}mc^2\alpha^2\left(4Z_{min}-\tfrac{27}{4}\right)$$

$$Z_{min} = \frac{27}{16} = 1.66$$

As we argued physically, effective Z should be $2 < Z_{min} < 1$,

$$E(Z_{min}) = -\frac{1}{2}\left(\frac{3}{2}\right)^6\left(\frac{1}{2}mc^2\alpha^2\right) = -77.5\ \text{eV}.$$

Close to experimental value of -79.0 eV