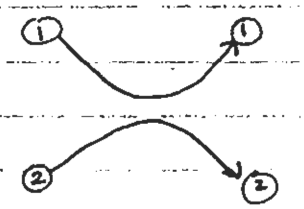
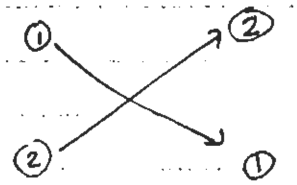
7.5 Identical particles (2 particles)

Classically, electrons can be distinguished ("labelled")



is distinguishable from



Not so in QM. – both processes contribute.

2-particle Hilbert space

$$\mathcal{H}_{12} = \mathcal{H}_1 \otimes \mathcal{H}_2 = \mathcal{H} \otimes \mathcal{H} \quad \text{for identical particles.}$$

1-particle basis $\{|n\rangle\}$

2-particle basis $\{|n,m\rangle = |n\rangle \otimes |m\rangle\}$ (sometimes $|n\rangle|m\rangle$)

Cannot experimentally distinguish $|n,m\rangle$ from $|m,n\rangle$ for identical particles. (exchange degeneracy)

Recall quantization of EM field:

2-photon states

$$a^{\dagger}_{k,\alpha}\, a^{\dagger}_{k',\alpha'} |0\rangle = a^{\dagger}_{k',\alpha'}\, a^{\dagger}_{k,\alpha} |0\rangle$$

same state in multi-particle Fock space.

[degeneracy is artifact of 1st-quantized formalism]

Permutation operator

$$P_{12}\,|n,m\rangle = |m,n\rangle$$

exchanges particles.

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

P_{12} generates a $\mathbb{Z}_2$ symmetry group, $P_{12} = \mathcal{D}(a)$, $a^2 = 1$.

Irreps of $\mathbb{Z}_2$: $P_{12} = \pm 1$, on 1D eigenspaces.

eigenstates: $|n,m\rangle_{S,A} = \frac{1}{\sqrt{2}}\left(|n,m\rangle \pm |m,n\rangle\right)$, $n \neq m$

for $n=m$, $P_{12}|n,n\rangle = +|n,n\rangle$, so no A state.

For identical particles, H symmetric under $1 \longleftrightarrow 2$

e.g. $$H = \frac{p_1^2}{2m} + \frac{p_2^2}{2m} + V_{ext}(x_1) + V_{ext}(x_2) + V(|x_1 - x_2|)$$

$$\underline{P_{12} H P_{12} = H}$$

Two kinds of particles appear in nature:

<u>Bosons</u>: $P_{12} = +1$ (Bose-Einstein statistics)
ex. photons.

<u>Fermions</u>: $P_{12} = -1$ (Fermi statistics)
ex. electrons (leptons), quarks

[note: in 2nd quant formalism, $a^\dagger$'s <u>anticommute</u>]

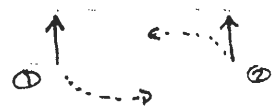
Spin – statistics theorem (provable in relativistic QFT) assuming axioms of locality, etc.

- Integer spin particles are bosons [presumably can choose any statistics for e in NRQM (?)]
- ½-integer spin particles are fermions.

Theorem holds for elementary particles & composites.

→ e^- fermion
→ H atom boson.

Ex. consider 2 electrons in state $S = 1$, $m = 1$

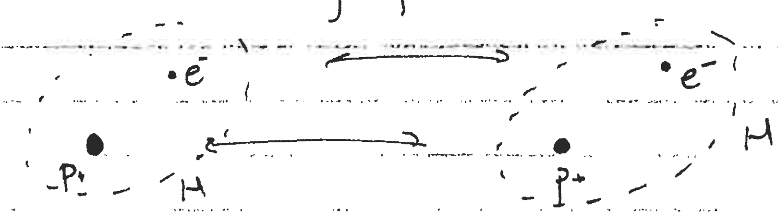


composite state rotates by 180° as $e^{im\pi} = -1$.

Rotation exchanges e^-'s, gives -1 by Fermi statistics.

Assuming thm. for elementary particles ⇒ result for composites

e.g.



$$P_{12}^{(H)} = P_{12}^{(e)} P_{12}^{(p)} = (-1)(-1) = +1$$

(−1 for each ½-spin particle)

Pauli exclusion principle

2 fermions cannot be in the same state

since $P_{12} \, |n,n\rangle = + \, |n,n\rangle$

But bosons can — leads to dramatically different physics.

fermions in solids — electronics ═ ⁝ bands, etc.
Bose-einstein condensate $|0,0,0,0,\ldots\rangle$
Astrophysics — Fermi gases, etc.. (neutron stars..)

Many particles

Generalize to N identical particles.
Statistics fixes one of N! states — antisymm. or symmetric

e.g. for 3 bosons / fermions

$$|n,m,p\rangle_{\substack{S\\A}} = \frac{1}{\sqrt{6}}\Big[\,|n,m,p\rangle \pm |n,p,m\rangle + |m,p,n\rangle \pm |m,n,p\rangle + |p,n,m\rangle \pm |p,m,n\rangle\,\Big]$$

has eigenvalue ± 1 for P_{12}, P_{23}, P_{13}.

More on $N > 2$ later.

2-electron systems

$\mathcal{H} = (\mathcal{H}_1 \otimes \mathcal{H}_2)_A$ restricts to -1 eigenspace of P_{12}

Can write states as

$$\psi = \sum \phi_{m,m'}(x,x') \, |m, m'\rangle \qquad m, m' \in \{-1/2, +1/2\}$$

$$\mathcal{H}_1 \otimes \mathcal{H}_2 = \mathcal{H}_1^{(x)} \otimes \mathcal{H}_2^{(x)} \otimes \mathcal{H}_1^{(s)} \otimes \mathcal{H}_2^{(s)}$$

Basis for $\mathcal{H}_1^{(s)} \otimes \mathcal{H}_2^{(s)}$ $\qquad (S = S_1 + S_2)$

$$\left.\begin{aligned} \chi_{11} &= |++\rangle \\ \chi_{10} &= \tfrac{1}{\sqrt{2}}\left(|+-\rangle + |-+\rangle\right) \\ \chi_{1-1} &= |--\rangle \end{aligned}\right\} P_{12}^{(s)} = +1 \qquad S^2 = 1$$

triplet (symmetric)

$$\chi_{00} = \tfrac{1}{\sqrt{2}}\left(|+-\rangle - |-+\rangle\right) \Big\} \; P_{12}^{(s)} = -1 \qquad S^2 = 0$$

singlet (antisymmetric)

For 2 particles, can choose basis for $\mathcal{H}$

$$\psi_A^{(x)} \, \psi_S^{(spin)} \quad , \quad \psi_S^{(x)} \, \psi_A^{(spin)}$$

- not possible for $N > 2$ particles; more complicated.

For triplet states

$$\psi = \sum_{m = \pm 1, 0} \phi_m(x,x') \, \chi_{1m}$$

$$\phi_m(x,x') = -\phi_m(x',x)$$

For singlets

$$\psi = \phi(x,x') \, \chi_{00}$$

$$\phi(x,x') = +\phi(x',x)$$

Triplets: spin symmetric, pos. antisymmetric
— particles avoid each other

Singlets: spin antisymm., pos. symmetric.
— particles can have same position.

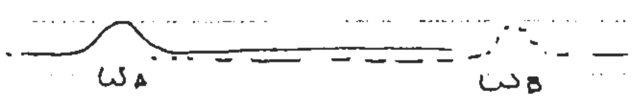
If no interaction,

$$\phi = \frac{1}{\sqrt{2}}\left(\omega_A(x_1)\,\omega_B(x_2) \pm \omega_A(x_2)\,\omega_B(x_1) \right) \quad \begin{matrix}\text{sing.}\\ \text{trip.}\end{matrix}$$

$$|\phi|^2 = \frac{1}{2}\Big[|\omega_A(x_1)|^2 |\omega_B(x_2)|^2 + |\omega_A(x_2)|^2 |\omega_B(x_1)|^2 \pm 2\,\mathrm{Re}\big(\underbrace{\omega_A(x_1)\,\omega_B(x_2)\,\omega_A^*(x_2)\,\omega_B^*(x_1)}_{\text{exchange density}} \big) \Big]$$

when $x_1 = x_2$, $|\phi|^2 \to 0$ for triplets.
$\to$ doubles for singlets
(enhances prob. @ same position)

Note that for widely separated particles



exchange density $\to 0$,
Fermi statistics are irrelevant

2-electron atoms H^-, He, Li^+, ...

$$H = \underbrace{\frac{p_1^2}{2m} + \frac{p_2^2}{2m} - \frac{Ze^2}{r_1} - \frac{Ze^2}{r_2}}_{H_0} + \underbrace{\frac{e^2}{r_{12}}}_{V}$$

In absence of interaction, have states

$2E_0^{(0)}\left\{ |1s,\ 1s\rangle_s = |(100)(100)\rangle_s \ \chi_{00} \right.$

$E_0^{(0)}+E_1^{(0)}\left\{\begin{array}{l} |1s,\ 2s\rangle_s = |(1,00)(200)\rangle_s \ \chi_{00} \\ |1s,\ 2s;\ m\rangle_A = |(100)(200)\rangle_A \ \chi_{1m} \\ |1s,\ 2p;\ \mu\rangle_s = |(100)(21\mu)\rangle_s \ \chi_{00} \\ |1s,\ 2p;\ \mu, m\rangle_A = |(100)(21\mu)\rangle_A \ \chi_{1m} \end{array}\right.$

more coulomb repulsion

Spatially symmetric states (singlet) have more energy from Coulomb repulsion, since electrons tend to come together.

Can use pert. theory to estimate energies.

Helium

Ground state w/o interaction:

$$E_0 = 2\left(-\frac{Z^2 e^2}{2a_0}\right) \sim -109\,\text{eV} \qquad (8 \cdot (-13.6\,\text{eV}))$$

adding $\left\langle \frac{e^2}{r_{12}} \right\rangle_{(1s,1s)} \Rightarrow -74.8\ \text{eV} \quad \left[\left(-Z^2+\frac{5}{8}Z\right)\left(\frac{e^2}{a_0}\right)\right]$

Experimental value: -78.8 eV.

Using variational method can get to 10^{-6} accuracy, given enough params.
[~~...~~ see book for example] [HW: do pert, var. cal for 1D analog]

Excited states of helium

$$\phi_{\substack{S\\A}}(x_1, x_2) = \frac{1}{\sqrt{2}}\left(\psi_1(x_1)\psi_2(x_2) \pm \psi_1(x_2)\psi_2(x_1)\right)$$

$$\left\langle \frac{e^2}{r} \right\rangle_{\substack{S\\A}} = e^2 \int d^3x_1\, d^3x_2 \Big[\psi_1(x_1)\psi_2(x_2)\frac{1}{r_{12}}\psi_1^*(x_1)\psi_2^*(x_2)$$
$$\pm \psi_1(x_1)\psi_2(x_2)\frac{1}{r_{12}}\psi_2^*(x_1)\psi_1^*(x_2)\Big]$$

$$= \underset{\text{(direct)}}{V_D} \pm \underset{\text{(exchange)}}{V_E}$$

Note that:

a) $V_D \geq 0$ clearly

b) $$\int \frac{|\psi_1(x_1)\psi_2(x_2) \pm \psi_1(x_2)\psi_2(x_1)|^2}{r_{12}} = 2V_D \pm 2V_E > 0$$

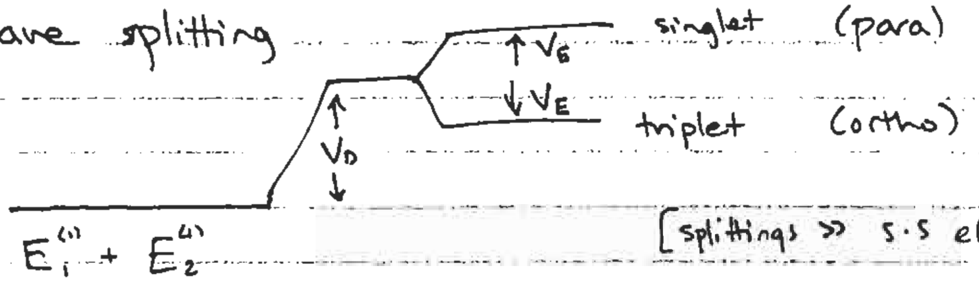
$$\Rightarrow V_D > |V_E|$$

c) Fourier xform: $$\frac{1}{r_{12}} = \int d^3k \, \frac{e^{i\vec{k}\cdot(\vec{x}_1 - \vec{x}_2)}}{k^2}$$

$$V_E = \int \frac{d^3k}{k^2} \underbrace{\left(\int d^3x_1\, e^{i\vec{k}\cdot\vec{x}_1}\psi_1(x_1)\psi_2^*(x_1)\right)}_{f(k)} \underbrace{\left(\int d^3x_2\, e^{-i\vec{k}\cdot\vec{x}_2}\psi_2(x_2)\psi_1^*(x_2)\right)}_{f^*(k)}$$

$$\geq 0$$

so have splitting



[splittings >> s·s effects]

Although Hamiltonian is spin-independent, can describe as spin-dependent interaction

$$\langle V \rangle_{\substack{S \\ A}} = V_D - \tfrac{1}{2}\left(1 + \vec{\sigma}_1 \cdot \vec{\sigma}_2\right) V_E$$

[$\vec{\sigma}_1 \cdot \vec{\sigma}_2 = 2(S^2 - S_1^2 - S_2^2) = 2S^2 - 3$

	S^2	$-\frac{1}{2}(1+\vec{\sigma}_1\cdot\vec{\sigma}_2)$	
triplet :	2	-1	✓]
singlet :	0	$+1$	

spin singlets : parahelium
spin triplets : orthohelium

Can analyze other 2-electron atoms

e.g. bound state of H^-

- subtle; pert thy. $\Rightarrow -0.4726 \frac{e^2}{a_0} > (-0.5 + 0)\left(\frac{e^2}{a_0}\right)$

but var. calc $\Rightarrow -0.528 \frac{e^2}{a_0}$.

Central field approximation

No analytic solutions known for atomic systems with $N \geq 2$ electrons.

Can go beyond pert. theory using Central field approximation

Assume effective potential for each e^- comes from nucleus + charge distribution of other e^-'s.

Simplest version:

Hartree self-consistent field approximation

For an N-electron system,

assume potential for electron i arises from

a) nuclear potential $-Ze^2/r$

b) charge distribution of other electrons $\sum_{k \neq i} -e|\phi_k|^2$

Take wavefunction to be product form

$$\psi(x_1, \dots, x_N) = \phi_1(x_1)\,\phi_2(x_2) \cdots \phi_N(x_N)$$

Hartree equations:

$$H_i \phi_i = -\frac{1}{2}\nabla_i^2 \phi_i - \frac{Ze^2}{r_i}\phi_i + \sum_{k \neq i}\left(\int dx_k \frac{|\phi_k(x_k)|^2 e^2}{r_{ki}}\right)\phi_i$$

$$= \varepsilon_i \phi_i$$

[meaning of ε_i?]
Assume $\int \phi_i^*(x_i)\,\phi_i(x_i)\,dx_i = 1$

$$\langle \psi | H_i | \psi \rangle = \varepsilon_i$$

and

count each pair once

$$\langle \psi | H | \psi \rangle = \langle \psi | \sum_i \left(-\tfrac{1}{2}\nabla_i^2 - \frac{Ze^2}{r_i} \right) + \sum_{i<j} \frac{e^2}{r_{ij}} | \psi \rangle$$

$$= \sum \varepsilon_i - \sum_{i<j} \langle \frac{e^2}{r_{ij}} \rangle$$

So $\langle H \rangle_{\text{Hartree}}$ follows once solve Hartree eqns.

Ex. ground state of helium

$$\psi(\vec{x}_1, \vec{x}_2) = \phi(\vec{x}_1)\,\phi(\vec{x}_2)$$ (assume symmetric state)

Hartree eqn

$$-\tfrac{1}{2}\nabla^2\phi(\vec{x}) - \frac{Ze^2}{|x|}\phi(\vec{x}) + \int d^3\vec{y}\, \frac{e^2}{|\vec{x}-\vec{y}|}\, \phi(\vec{y})^2\, \phi(\vec{x}) = \varepsilon\, \phi(\vec{x})$$

Tricky integro-differential equation.

Can solve recursively:

Start with trial function $\phi_0(\vec{x})$.
Use to compute $V(\vec{x}) = \int d^3\vec{y}\, \frac{e^2}{|\vec{x}-\vec{y}|}\, \phi(\vec{y})^2$
Plug into Schrödinger – solve for $\phi_1(\vec{x})$ . . .

$$\langle H \rangle = 2\varepsilon - \langle \frac{e^2}{|\vec{x}_1 - \vec{x}_2|} \rangle .$$

Can solve 1D analogue exactly [MW]