Tuesday, April 9, 2013

## Bosons Permutation Symmetry

Identical Bosons are particles whose wavefunction is symmetric under exchange of any two particles.

2 particles: $\psi(\vec{r}_1, \vec{r}_2) = +\psi(\vec{r}_2, \vec{r}_1) = \frac{1}{\sqrt{2}}\left(\psi_a(\vec{r}_1)\psi_b(\vec{r}_2) + \psi_b(\vec{r}_1)\psi_a(\vec{r}_2)\right)$

$P\psi(\vec{r}_1, \vec{r}_2) = +\psi(\vec{r}_2, \vec{r}_1)$

N particles: $\psi(\vec{r}_1, \vec{r}_2, \ldots, \vec{r}_i, \ldots, \vec{r}_j, \ldots, \vec{r}_N)$

$= +\psi(\vec{r}_1, \vec{r}_2, \ldots, \vec{r}_j, \ldots, \vec{r}_i, \ldots, \vec{r}_N)$

special case: if only one state is available, the $\psi(\vec{r}_1, \ldots, \vec{r}_N) = \psi_a(\vec{r}_1)\ldots\psi_a(\vec{r}_N)$ (i.e. BEC)

Identical Fermions are particles whose wavefunction is anti-symmetric under exchange of any two particles.

2 particles: $\psi(\vec{r}_1, \vec{r}_2) = -\psi(\vec{r}_2, \vec{r}_1) = \frac{1}{\sqrt{2}}\left(\psi_a(\vec{r}_1)\psi_b(\vec{r}_2) - \psi_b(\vec{r}_1)\psi_a(\vec{r}_2)\right)$

$P\psi(\vec{r}_1, \vec{r}_2) = -\psi(\vec{r}_2, \vec{r}_1)$

N particles: $\psi(\vec{r}_1, \vec{r}_2, \ldots, \vec{r}_i, \ldots, \vec{r}_j, \ldots, \vec{r}_N)$

$= -\psi(\vec{r}_1, \vec{r}_2, \ldots, \vec{r}_j, \ldots, \vec{r}_i, \ldots \vec{r}_N)$

Note:
- You cannot construct an anti-symmetric wavefunction with only a single state
- Each identical fermion must be in a different state, otherwise anti symmetry is not possible.
  - ↳ Pauli exclusion principle
    - ↳ responsible for chemical differences between elements

## Spin-statistics theorem (proof requires relativistic QFT)

All half-integer spin particles are fermions
($e^-$, $p^+$, $u$, $^{40}K$, $^3H$, $^6Li$, etc...) (i.e. obey Fermi-Dirac statistics)

All integer spin particles are bosons
($\gamma$, $^{87}Rb$, $^1H$, $^3H$, $Z^0$, $W^\pm$, Higgs, etc...) (i.e. obey Bose-Einstein statistics)

⚠ Quantum statistics of multiparticle systems strongly affects their behavior.

### Example: excited states of He

$$H = \frac{\vec{p}_1^{\,2}}{2m_e} - \frac{2e^2}{r_1} + \frac{\vec{p}_2^{\,2}}{2m_e} - \frac{2e^2}{r_2} + \frac{e^2}{|\vec{r}_{12} - \vec{r}_2|} + \text{cst}\ \vec{S}_1 \cdot \vec{S}_2$$

neglect

$S_{TOT} = \vec{S}_1 + \vec{S}_2$ is a good quantum number $[H, S_{TOT}] = 0$

Ground state: $\psi(\vec{r}_1, \vec{r}_2) = \psi_{1s}(\vec{r}_1)\,\psi_{1s}(\vec{r}_2)\left(|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle\right)$ (singlet)

(neglects $e^-$-$e^-$ repulsion term)

symmetric — anti-symmetric

$$\psi(\vec{r}_2, \vec{r}_1) = \psi_{1s}(\vec{r}_2)\,\psi_{1s}(\vec{r}_1)\left(|\downarrow\uparrow\rangle - |\uparrow\downarrow\rangle\right)$$

$$= \psi(\vec{r}_1, \vec{r}_2)$$

Excited state (1 $e^-$ excited, 1 $e^-$ in ground state)
we have two choices:

Para-Helium state:
$$\psi_{para}(\vec{r}_1, \vec{r}_2) = \frac{1}{\sqrt{2}}\left[\psi_{1s}(\vec{r}_1)\,\psi_{2s}(\vec{r}_2) + \psi_{2s}(\vec{r}_1)\,\psi_{1s}(\vec{r}_2)\right]\left[|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle\right]\frac{1}{\sqrt{2}}$$

symmetric spatial part — singlet, anti-symmetric spin part

Ortho-Helium state:
$$\psi_{ortho}(\vec{r}_1, \vec{r}_2) = \frac{1}{\sqrt{2}}\left[\psi_{1s}(\vec{r}_1)\,\psi_{2s}(\vec{r}_2) - \psi_{2s}(\vec{r}_1)\,\psi_{1s}(\vec{r}_2)\right]\begin{cases} |\uparrow\uparrow\rangle \\ \frac{1}{\sqrt{2}}\left(|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle\right) \\ |\downarrow\downarrow\rangle \end{cases}$$

anti-symmetric spatial part — triplet, symmetric spin part

$E_{para} > E_{ortho}$

We can now treat the $e^- - e^-$ repulsion term perturbatively. The 1st order correction to the energy is given by

$$\langle \psi_{\substack{para \\ ortho}} | \frac{e^2}{|\vec{r}_1 - \vec{r}_2|} | \psi_{\substack{para \\ ortho}} \rangle$$

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

$$= \underbrace{\left(\frac{1}{2}+\frac{1}{2}\right)\int d^3r_1\, d^3r_2\, |\psi_{1s}(\vec{r}_1)|^2 |\psi_{2s}(\vec{r}_2)|^2 \frac{e^2}{|\vec{r}_1 - \vec{r}_2|}}_{I} \underbrace{\pm \left(\frac{1}{2}+\frac{1}{2}\right)\int d^3r_1\, d^3r_2\, \psi_{1s}^*(\vec{r}_1)\,\psi_{2s}^*(\vec{r}_2) \frac{e^2}{|\vec{r}_1 - \vec{r}_2|} \psi_{2s}(\vec{r}_1)\,\psi_{1s}(\vec{r}_2)}_{J}$$

(+ : para, − : ortho)

Energy levels of He


(due to spatial anti-symmetry $e^-$'s avoid each other more ⇒ repulsion energy is smaller)

1s 1s — spin-singlet para helium

⇒ $e^-$ spin plays a role even if there is no explicit ~~spin-spin~~ spin-based interaction

## Structure of Larger Atoms:

### Hartree's Self consistent field

the multi-electron wavefunction has the form

$$\psi = u_1(\vec{r}_1)\,u_2(\vec{r}_2) \cdots u_n(\vec{r}_n) \quad \text{with} \int |u_i|^2 d^3r_i = 1$$

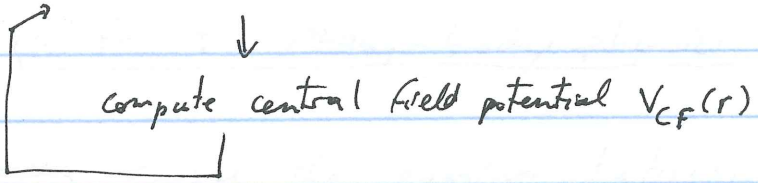
Consider the expectation value for the total energy of the atom

$$\langle H\rangle = \langle\psi|H|\psi\rangle = \int \psi^* \left[ -\sum_{i=1}^{n} \frac{\hbar^2}{2m_e}\nabla_{r_i}^2 - \sum_i \frac{Ze^2}{r_i} + \sum_{i>j} \frac{e^2}{|\vec{r}_i - \vec{r}_j|} \right] \psi \, d^3r_1 d^3r_2 \cdots d^3r_n$$

(replace with a central field approximation $V_{CF}(r)$)

Now use the variational method: vary $u_1, u_2, \ldots, u_n$ independently such that $\delta\langle H\rangle = 0$

algorithm: vary $u_1, \ldots, u_n$ such that $\delta\langle H\rangle = 0$




algorithm converges on self-consistent set $u_1, \ldots, u_n$ and $V_{CF}(r)$.

Hartree–Fock: use an anti-symmetric $\psi$ based on the Slater determinant:

$$\psi = \frac{1}{\sqrt{N!}} \begin{vmatrix} \psi_a(\vec{r}_1) & \psi_a(\vec{r}_2) & \cdots & \psi_a(\vec{r}_n) \\ \psi_b(\vec{r}_1) & \psi_b(\vec{r}_2) & \cdots & \psi_b(\vec{r}_n) \\ \vdots & \vdots & & \vdots \\ \psi_z(\vec{r}_1) & \psi_z(\vec{r}_2) & \cdots & \psi_z(\vec{r}_n) \end{vmatrix}$$

$a, b, \ldots, z$ = possible sets of quantum numbers

e.g. $1s\uparrow$, $2s\downarrow$

$1s\,\chi_{singlet}$, $2s\,\chi_{triplet}$

**Problem:** As we increase the number of identical particles the multi-particle wavefunctions get very large

**3 bosons / fermions in 3 states:** $\psi_a(\vec{r}_1)$, $\psi_b(\vec{r}_2)$, $\psi_c(\vec{r}_3)$

particle #1 #2 #3

$$|\psi\rangle_{total} = \frac{1}{\sqrt{6}}\left\{|\psi_a\,\psi_b\,\psi_c\rangle \pm |\psi_b\,\psi_a\,\psi_c\rangle + |\psi_b\,\psi_c\,\psi_a\rangle \pm |\psi_c\,\psi_b\,\psi_a\rangle + |\psi_c\,\psi_a\,\psi_b\rangle \pm |\psi_a\,\psi_c\,\psi_b\rangle\right\}$$

$\Rightarrow$ complicated, cumbersome

## 2nd Quantization for many-body physics

**Idea:** ~~Transfer~~ Embed the quantum statistics of the particles in the operators, while keeping track of particle numbers with the wavefunction.

**Origin:** 2nd quantization was originally developed for QFT in which the wavefunctions become operators (i.e. 2nd level of quantization)

Consider a single particle Hamiltonian $H$ with eigenstates $|\psi_j\rangle$:

$$H|\psi_j\rangle = E_j|\psi_j\rangle$$

We define the multiparticle occupation number state as (all particles are identical)

$$|\psi\rangle = |n_1, n_2, \ldots, n_j, \ldots, n_N\rangle$$

$n_1$ particles in state $|\psi_1\rangle$ ; $n_j$ particles in state $|\psi_j\rangle$

**Fock space**: the "occupation number" states, or Fock states, by definition are orthonormal and span a space called **Fock space**.

**note**: $|0, 0, \ldots, n_j=1, \ldots, 0\rangle \equiv |4_j\rangle$

**Vacuum state**: the state $|0\rangle = |0, 0, \ldots, 0\rangle \neq 0$ is referred to as the vacuum state.

stopped here

In analogy with the creation and annihilation operators for excitations of the harmonic oscillator, we define the operators $a_j^+$ and $a_j$:

$$a_j^+ |0\rangle = |0, 0, \ldots, n_j=1, \ldots 0\rangle = |4_j\rangle$$

$$a_j |0, 0, \ldots, n_j=1, \ldots 0\rangle = |0\rangle$$

and $a_j |0\rangle = 0$

note $a_i |0, \ldots, n_j=1, \ldots 0\rangle = 0$ if $i \neq j$

the quantum statistics of the particles are embedded in the "commutation" relations for $a_j$ and $a_j^+$:

**Bosons**: (commutators)

$$[a_i^+, a_j^+] = 0$$

$$[a_i, a_j] = 0$$

$$[a_i, a_j^+] = \delta_{ij}$$

**Fermions**: (anti-commutators)

$$\{a_i^+, a_j^+\} = 0$$

$$\{a_i, a_j\} = 0$$

$$\{a_i, a_j^+\} = \delta_{ij}$$