2nd Quantization : The Many Body Problem

** Usual Quantum Mechanics (wave mechanics) is "first quantized".

$\mathcal{H}\Psi = \mathcal{E}\Psi$ for stationary states

$$\mathcal{H} = -\sum_{i=1}^{N} \nabla_i^2 + \sum_{i=1}^{N} v_{ext}(\underset{\sim}{r}_i) + e^2 \sum_{i<j}^{N} \frac{1}{|r_i - r_j|} \qquad \left(\frac{\hbar^2}{2m} = 1\right)$$

for N electrons in an external potential v_{ext}

Can write (introducing notation)

$$\mathcal{H} = \sum_{i=1}^{N} h_i^0 + \frac{1}{2} \sum_{i \neq j}^{N} \frac{e^2}{|r_i - r_j|}$$

$$= \sum_{i=1}^{N} \left(-\nabla_i^2 + v_{ext}(r_i) \right) + \frac{1}{2} \sum_{i \neq j}^{N} v(r_i - r_j) \,.$$

Supplementary condition:

the particles are identical and have spin ½ ⇒ electrons.

In this case $\Psi \equiv \Psi(\underset{\sim}{r}_1 s_1, \underset{\sim}{r}_2 s_2, \underset{\sim}{r}_3 s_3, \ldots\ldots, \underset{\sim}{r}_N s_N)$ (s_i denotes spin)

must be antisymmetric under exchange of the labels of any two electrons:

$\boxed{\text{FERMIONS}}$ e.g. $\Psi(r_1 s_1, \ldots r_N s_N \ldots, r_5 s_5) = -\Psi(r_1 s_1, \cdots r_5 s_5 \ldots r_N s_N)$.

Notice: the many body Hamiltonian $\mathcal{H}$ is invariant under exchange of the labels of any two electrons (identicality).

FACT: the many body problem is hard!
One reason: the wavefn Ψ must be kept antisymmetric.

A SIMPLE PROBLEM: no interparticle interaction ≡ "1 body problem"

$$\mathcal{H} = \sum_{i=1}^{N} \overset{\circ}{h}_i \quad , \quad \overset{\circ}{h}_i = \overset{\circ}{h}(r_i) \; .$$

due to separability of the Hamiltonian

A product wavefunction is a solution. Enumerate the eigenstates of $\overset{\circ}{h}$:

$$\overset{\circ}{h}(r)\,\phi_n(r) = \varepsilon_n \phi_n(r) \;,\quad n = 0, 1, 2, \ldots\ldots\ldots \infty$$

A product wavefn has the form (forget spin for now)

$$\begin{aligned}\Psi(r_1, r_2, \cdots, r_N) &= \phi_{n_1}(r_1)\,\phi_{n_2}(r_2)\cdots\phi_{n_N}(r_N) \\ &= \prod_{m=1}^{N} \phi_{n_m}(r_m)\end{aligned}$$

where $\{n_m\}$ is some (any) set of integer labels of states ϕ_i.

But — this wavefn is not antisymmetric. Solution: construct a Slater determinant out of the states $\{\phi_{n_m}\}$.

This is done by the form

$$D(r_1, r_2, \ldots r_N) = \mathcal{N} \begin{array}{|cccc|l} \phi_{n_1}(r_1) & \phi_{n_2}(r_1) & \cdots\cdots & \phi_{n_N}(r_1) & \leftarrow r_1 \\ \phi_{n_1}(r_2) & \phi_{n_2}(r_2) & \cdots\cdots & \phi_{n_N}(r_2) & \leftarrow r_2 \\ \vdots & \vdots & & \vdots & \vdots \\ \phi_{n_1}(r_N) & \phi_{n_2}(r_N) & & \phi_{n_N}(r_N) & \\ \multicolumn{1}{c}{\uparrow} & \multicolumn{1}{c}{\uparrow} & & & \\ \multicolumn{1}{c}{n_1} & \multicolumn{1}{c}{n_2} & \multicolumn{1}{c}{\cdots\cdots} & & \end{array}$$

normalization constant

The Slater determinant can be abbreviated

$$D = \left| \phi_{n_1}(r_1) \; \phi_{n_2}(r_2) \; \cdots \; \phi_{n_N}(r_N) \right|$$

and is specified by the set of occupied one-electron states $\{n_i\}$.
Labels $\{r_i\}$ are redundant.

FACT: D vanishes if any two coordinates are the same, because two rows of the determinant are identical. ⇒ 2 electrons of the same spin cannot be at the same point.

FACT: D vanishes if any two single particle orbitals are the same, because two columns are identical. ⇒ An orbital can be occupied at most <u>once</u> (for each spin).

These two facts are fundamental properties of <u>fermion systems</u>.

* "Occupation factors" in a Slater determinant are only 0 or 1. *

An aside, for later: including spin in the problem — in the non-interacting case, you just group the "up" spins and "down" spins and form two separate determinants:

$$\Psi = D^{\uparrow}(r_1, r_2, r_3, \ldots r_J)\, D^{\downarrow}(r_{J+1}, r_{J+2}, \ldots, r_N)$$

= product of two separate problems.

More general forms of (approximate) wavefunctions:
(when there are interactions)

- sums of determinants ⇝ "configuration interaction" (CI).

- symmetric function × determinant ⇝ "Jastrow" (or "Jastrow-Slater") type wavefunction

- spin-coupled wavefunctions:
  - * orbital part symmetric × spin part antisymmetric
  - * (vice versa)

  ⇝ "singlet," "triplet" pairing; more complex

- combinations of these.

Optimizing wavefunctions: interacting systems

How are the "one electron" orbitals determined, anyway? Usually – vary them in order to minimize the energy.

Given $\Psi = \Psi[\{\phi_i\}]$, require

VARIATIONAL METHOD.

$$\frac{\delta \mathcal{E}[\{\phi_i\}]}{\delta \phi_j^*} \equiv \frac{\delta}{\delta \phi_j^*}\left\{ \frac{\langle \Psi | \mathcal{H} | \Psi \rangle}{\langle \Psi | \Psi \rangle} \right\} = 0.$$

Strictly, this makes the energy stationary, not necessarily minimum.

Hartree-Fock Approximation is the most common of this type of approach. The result is a set of one-electron equations

SINGLE DETERMINANT WAVEFN

$$\hat{h}^{HF}\phi_i^{HF} = \varepsilon_i^{HF}\phi_i^{HF}, \quad \text{where } \hat{h}^{HF} = \hat{h}^{HF}\left[\{\phi_i^{HF}\}\right]$$

is a one-electron, Hamiltonian-like operator, which has a potential that depends on $\{\phi_i^{HF}\}$. It must be obtained self-consistently, blah-blah-.....

With the orbitals $\{\phi_i^{HF}\}$ thus determined, $\mathcal{E}\left[\{\phi_i^{HF}\}\right]$ gives the Hartree-Fock energy, which is the minimum energy for a single determinant approximation to the ground state many body wavefunction.

Never mind Hartree-Fock theory (for now), except that it is one common way of determining useful single particle orbitals $\phi_i = \phi_i^{HF}$.

There are many other ways to determine a useful set of such orbitals. A very common one is Density Functional Theory. Without going into the theory – it leads to the "Kohn-Sham equation"

$$\hat{h}^{KS}\phi_i^{KS} = \left(-\nabla^2 + v^{KS}\right)\phi_i^{KS} = \varepsilon_i^{KS}\phi_i^{KS}.$$

Unlike Hartree-Fock, v^{KS} is a local potential

$$v^{KS} = v^{KS}(\underset{\sim}{r})$$

whereas the Hartree-Fock potential is a somewhat nasty, non-local potential

$$v^{HF} = v^{HF}(\underset{\sim}{r},\underset{\sim}{r}') .$$

But that's all for another time. Each method gives a useful set of orbitals (actually, usually they are very similar; only the resulting energies are rather different).

Both HFA and DFT lead to an "effective mean field like theory:" electrons in a set of single particle orbitals all seeing the same

"mean field" ≡ average potential

Both HFA and DFT give a mean field representation v^{MF} of the electron-electron interaction, so the many body Hamiltonian can be written

$$\mathcal{H} = \underbrace{-\sum_{i=1}^{N}\nabla_i^2 + \sum_{i=1}^{N} v_{ext}(r_i) + \sum_{i=1}^{N} v^{MF}(r_i)} + \left[\frac{1}{2}\sum_{i\neq j}^{N}{}' \frac{e^2}{|r_i-r_j|} - \sum_{i=1}^{N} v^{MF}(r_i)\right]$$

$$= \sum_{i=1}^{N} h^{MF}(r_i) + \Delta V$$

If the choice of v^{MF} is good (i.e. useful), then the effect of ΔV is much smaller than the effect of the el-el interaction itself (which is huge).

So, let's drop the "MF" label & write generically

$$\mathcal{H} = \sum_{i=1}^{N} h(r_i) + \Delta V, \quad \text{with}$$

$$h\phi_i = \varepsilon_i \phi_i \text{ giving a "single particle basis"}$$

which is different from the h^0 of page 1 (which would be a very bad choice).

[Aside: the choice $h(r_i) = -\nabla_i^2$, whose eigenfunctions are just $e^{\pm i\underline{k}\cdot\underline{r}}$, would lead to a <u>plane wave</u> basis.]

Neglecting ΔV, leading to a non-interacting <u>fermion</u> problem, the ground state would be the Slater Determinant constructed from the lowest N single particle states. One notation for this is

$$D_{gs} = \left| \phi_1(1) \quad \phi_2(2) \;\ldots\; \phi_N(N) \right| \;\dot{=}\; \mathcal{D}et\{\phi_1, \phi_2, \ldots \phi_N\}$$

However, much of even this simplified notation is redundant. The ϕ's just denote the basis fns, which are known anyway. And note that $1, 2, \cdots N$ in both argument and subscript occur in order and don't supply any information.

In fact, this is simply the unique reference state, the single particle ground state, which doesn't need any notation at all.

It is useful to consider a "vacuum state" $|0\rangle$ which satifies:

① $\langle 0|0\rangle = 1$

② $|0\rangle$ is orthogonal to any other state

Now, we define a state that has an electron in orbital ϕ_j by out of the set $\{\phi_m\}$ of states

$$a_j^+|0\rangle ,$$

"a_j^+ creates an electron in state ϕ_j": $a_j^+|0\rangle \longleftrightarrow \phi_j$.

Putting 2 electrons in states j and k is done by, first j, then k;

$$|jk\rangle = a_k^+ a_j^+ |0\rangle \quad \Longleftrightarrow \quad \frac{1}{\sqrt{2}} \begin{vmatrix} \phi_k(1) & \phi_j(1) \\ \phi_k(2) & \underset{\overset{\uparrow}{j}}{\phi_{\textcircled{k}}(2)} \end{vmatrix}$$

which corresponds to the determinant.

↑ normalized !

~~We denote~~ ~~$\frac{1}{\sqrt{2}}|$~~

If we interchange the positions of ϕ_k and ϕ_j in the determinant changes phase (sign), which means

$$a_j^+ a_k^+ |0\rangle = -a_k^+ a_j^+ |0\rangle$$

which is consistent with anticommutation relation

$$\{a_j^+, a_k^+\} = a_j^+ a_k^+ + a_k^+ a_j^+ = 0 \text{ if } j \neq k.$$

Also $\quad a_j a_k + a_k a_j = 0$ if $j \neq k$.

Separately $\quad a_j a_j = 0 = a_j^+ a_j^+$ (determinant vanishes).

so $\{a_j, a_k\} = 0$ always.

$a_j|\cdots 1_j\cdots\rangle = |\cdots 0_j\cdots\rangle$ where $\cdots$ indicates anything can be there – it is irrelevant. However, if there is no particle in the state to annihilate (remove), then

$$a_j|\cdots 0_j\cdots\rangle = 0.$$

Likewise

$$a_j^+|\cdots 1_j\cdots\rangle = 0$$ because of no double occupancy.

What is the effect of $a_j^+ a_j$? It is the "number operator", i.e. if orbital j is occupied, it gives 1; if not, it gives 0. (Work it out.)

$$\hat{n}_j \equiv a_j^+ a_j$$

$$\langle\cdots 1_j\cdots|\hat{n}_j|\cdots 1_j\cdots\rangle = 1$$
$$\langle\cdots 0_j\cdots|\hat{n}_j|\cdots 0_j\cdots\rangle = 0$$

(All other occupancies of these state are fixed.)

Stronger statement: $\hat{n}_j|\cdots n_j\cdots\rangle = n_j|\cdots n_j\cdots\rangle$ ← eigenvalue

In the $\{\phi_j\}$ representation, n_j has eigenvalues 0 or 1. ↕ if a pure state

Longuet-Higgins notation: $a_j \longrightarrow \phi_j$
$a_j^+ \longrightarrow \phi_j^+$

Convenient if you want to transform $\{\phi_j\} \longrightarrow \{\psi_j\}$, for example.

A general state in this representation can be denoted

$|n_1 n_2 n_3 \cdots n_M\rangle$ where M is as large as necessary to include all of the $n_j = 1$ (occupancies).

In general, $\{a_i, a_j^\dagger\} = \delta_{ij}$, $\{a_i, a_j\} = 0 = \{a_i^\dagger, a_j^\dagger\}$

Then $a_i a_i^\dagger + a_i^\dagger a_i = 1 \Rightarrow a_i a_i^\dagger = 1 - a_i^\dagger a_i = 1 - \hat{n}_i$

so

$a_i a_i^\dagger$ is the "opposite" of the fermion number operator.