What have we learnt so far :

Variational principle :

- Energy is a functional of ψ. Making this functional stationary gives the Schrödinger equation i.e. true ~~solution~~ wavefunction of a system.
- If functional is made stationary with restricted variation of ψ (say one parameter) then approximate wavefunction will be obtained

The former is related to

Full variation of ψ $\quad \dfrac{\delta[\langle\psi|H|\psi\rangle - E\langle\psi|\psi\rangle]}{\delta\psi} = 0$

The latter to

Restricted variation of ψ. $\quad \dfrac{\partial}{\partial(\text{parameter})}\{\langle\psi|H|\psi\rangle - E\langle\psi|\psi\rangle\} = 0$

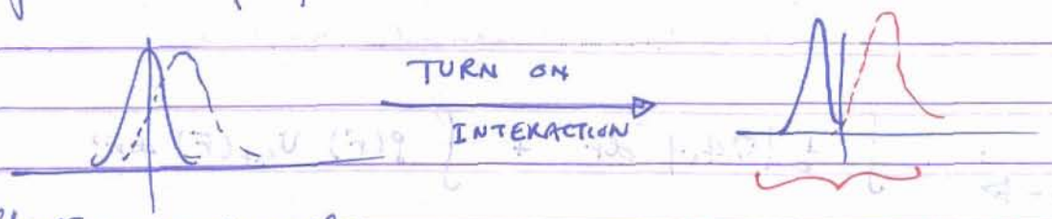
EXERCISE : Whatever has been proved for single particle Hamiltonian above is also true for a many-particle interacting Hamiltonian. Prove it.

A system of many-electrons :

$$H = \sum_i -\frac{1}{2}\nabla_i^2 + \sum_i v_{ext}(\vec{r}_i) + \frac{1}{2}\sum_{i}{}' \sum_{j} \frac{1}{r_{ij}}$$

Suppose the Vee term $\frac{1}{r_{ij}}$ were not there, electron will come as close to each other as possible

(+) possible wavef^n for two electron without interaction



Electrons can come close to each other

Electrons get far away

Introduction of (e-e) interaction modifies the wavefunction qualitatively, in particular 'ψ' becomes a function of (r_{ij}) as so that

$\psi \to 0$ as $r_{ij} \to 0$

$$\psi(r_1, r_2) \simeq \phi(\vec{r}_1)\,\phi(\vec{r}_2)\left(1 - e^{-r_{ij}/a}\right)$$

Unfortunately, the Schrödinger equation cannot be solved exactly so we do not know how the wavefunction gets modified. This is where we are forced to make approximations for the wavefunction. This is where extensive use of VARIATIONAL PRINCIPLE is made in many-electron theory.

We now discuss three theories which have been developed. These are all approximate theories but provide a benchmark.

(1) **Hartree-Theory** : Approximation for the wavefunction is that we assume particles to be moving independently. i.e.

$$\psi(\vec{r}_1, \vec{r}_2 \ldots \vec{r}_N) = \underbrace{\phi_{\alpha_1}(r_1)}_{\text{occupied orbitals}}\,\underbrace{\phi_{\alpha_2}(r_2)}_{\text{occupied orbitals}} \ldots \underbrace{\phi_{\alpha_N}(\vec{r}_N)}_{\text{occupied orbitals}}$$

Let us call the electron in 'α_1' orbital 1, in α_2^{th} 2nd and α_N the n^{th} electron.

Expectation value of the Hamiltonian

$$H = \sum_i -\frac{1}{2}\nabla_i^2 + \sum_i v_{ext}(\vec{r}_i) + \frac{1}{2}\sum_{ij}\frac{1}{r_{ij}}$$

Sum over electrons

$$\langle H \rangle = \sum_i \langle \phi_{\alpha_i} | -\frac{1}{2}\nabla^2 | \phi_{\alpha_i} \rangle + \sum_i \langle \phi_{\alpha_i} | v_{ext}(\vec{r}) | \phi_{\alpha_i} \rangle + \frac{1}{2}\sum_{ij}{}' \left\langle \phi_{\alpha_i}(\vec{r}) \phi_{\alpha_j}(\vec{r}') \left| \frac{1}{|\vec{r}-\vec{r}'|} \right| \phi_{\alpha_i}(\vec{r}) \phi_{\alpha_j}(\vec{r}') \right\rangle$$

Sum over occupied orbitals

$$= \int \frac{1}{2}|\nabla \phi_i|^2 d\vec{r} + \int \rho(\vec{r}) v_{ext}(\vec{r}) d\vec{r} + \frac{1}{2}\iint \frac{\rho(\vec{r})\rho(\vec{r}')}{|\vec{r}-\vec{r}'|} - \frac{1}{2}\sum_i \iint \frac{|\phi_i(\vec{r})|^2 |\phi_i(\vec{r}')|^2}{|\vec{r}-\vec{r}'|} d\vec{r} d\vec{r}'$$

Kinetic energy

External energy

$\rho(\vec{r}) = \sum_i |\phi_i(\vec{r})|^2$ is the density of electrons

Coulomb energy with self interaction

Self-interaction energy

The best possible orbitals are determined by the variational principle i.e. by making $\langle H \rangle$ stationary. To make sure that every orbital is normalized i.e.

$$\int |\phi_i(\vec{r})|^2 d\vec{r} = 1$$

we use the method of Lagrange multipliers and instead make

$$\langle H \rangle - \sum_i \varepsilon_i |\phi_i|^2 \quad \text{Stationary}$$

This gives

$$-\frac{1}{2}\nabla^2\phi_i + v_{ext}\phi_i + \left(\int \frac{\rho(\vec{r}')}{|\vec{r}-\vec{r}'|} d\vec{r}'\right)\phi_i - \sum_j \left(\left(\int \frac{|\phi_j(\vec{r}')|^2}{|\vec{r}-\vec{r}'|} d\vec{r}'\right)\phi_j = \varepsilon_i \phi_i\right)$$

This is known as Hartree equations.

Interpretation: Electrons in this approximation are moving in an effective potential

$$\left\{ V_{ext}(\vec{r}) + \int \frac{\rho(\vec{r}') - |\phi_i(\vec{r}')|^2}{|\vec{r}-\vec{r}'|} d\vec{r}' \right\}$$

The potential is determined from the orbitals themselves

Hartree equation itself is a non-linear ~~eqn~~ equation where the solution depends on the solution itself

How to solve Hartree equation? Idea of self-consistency

Suppose we assume that a set of orbitals $\{\phi_{\alpha i}\}$ are the solutions of the Hartree equation. This implies that these orbitals satisfy the differential equation

$$-\frac{1}{2}\nabla^2\phi_i + V_{ext}\phi_i + \left(\int \frac{\rho(\vec{r}') - |\phi_i(\vec{r}')|^2}{|\vec{r}-\vec{r}'|} d\vec{r}' \right) \phi_i = \epsilon_i \phi_i$$

where $\rho(\vec{r}') = \sum_j |\phi_j(\vec{r}')|^2$

How to find these. This is where the idea of self-consistency comes in

Step 1: ~~Assume~~ Take a set of orbitals $\{\phi_{\alpha i}^{(0)}\}$

Step 2: Construct the potential $\int \frac{\rho^{(0)}(\vec{r}') - |\phi_i^{(0)}(\vec{r}')|^2}{|\vec{r}-\vec{r}'|} d\vec{r}'$ for each orbital

Step 3: Check if $\{\phi_{\alpha i}^{(0)}(\vec{r})\}$ satisfy the Hartree equation

If they do satisfy the

Step 4: Solve the Hartree equation with effective potential ⊛

$$V_{ext}(\vec{r}) + \int \frac{\rho^{0}(\vec{r}') - |\phi_i^{(0)}(\vec{r}')|^2}{|\vec{r}-\vec{r}'|} d\vec{r}'.$$

And get a new set of orbitals $\{\phi_{\alpha i}^{(1)}\}$

GO TO STEP 2

⊛ Since the potential depends on $\{\phi_{\alpha i}\}$ non linearly we may end up in a situation where we flip-flop between two ~~sets~~ sets of solutions

$$\{\phi_{\alpha i}^{(n)}\} \text{ and } \{\phi_{\alpha i}^{(n+1)}\}$$

Therefore new potential is constructed by mixing only a fraction of the new potential

$$\text{Thus } V_{eff}^{(n+1)}(\vec{r}) = \alpha V_{eff}^{(n)}(\vec{r}) + (1-\alpha)\left[V_{ext}(\vec{r}) + \int \frac{\rho^{n}(\vec{r}') - |\phi_i^{(n)}(\vec{r}')|^2}{|\vec{r}-\vec{r}'|} d\vec{r}'\right]$$

This makes the solution converge if a solution exists.

This procedure is called the self-consistent field (SCF) procedure. The solutions obtained are the self-consistent solutions.

TOTAL ENERGY AFTER OBTAINING THE SOLUTION

Once we have obtained the wavefunction the energy is calculated as the expectation value

$$\langle H \rangle = \sum_i \int \frac{1}{2}|\nabla\phi_i|^2 + \int V(\vec{r})\rho(\vec{r})d\vec{r}$$

$$+ \frac{1}{2}\iint \frac{\rho(\vec{r})\rho(\vec{r}')}{|\vec{r}-\vec{r}'|} d\vec{r}\,d\vec{r}' - \frac{1}{2}\sum_i \iint \frac{|\phi_i(\vec{r})|^2 |\phi_i(\vec{r}')|^2}{|\vec{r}-\vec{r}'|} d\vec{r}\,d\vec{r}'$$

Energy is NOT equal to

$$\sum \epsilon_{n'}$$

Since $\psi(r_1 r_2 \cdots r_N) = \prod_n \phi_{n_1}(r_1)\, \phi_{n_2}(r_2) \cdots$

is NOT an eigenfunction of the Hamiltonian. Therefore it is not a solution of the Schrödinger equation but only an approximation to it.

PROPERTIES OF THE TRUE SOLUTION:

Since the Hamiltonian is symmetric under the exchange of any coordinates the solns of the Schrodinger equation are such that if

$\psi(\vec{r}_1 \vec{r}_2)$ is a solution then $\psi(\vec{r}_2, \vec{r}_1)$ is also a solution. Further since particles are indistinguishable, we cannot ask the question: where is electron 1 and where is electron 2. Rather we ask what is the probability of finding one electron at $\vec{r}_1$ & other at $\vec{r}_2$. This is given by

$$|\psi(\vec{r}_1', \vec{r}_1)|^2 = |\psi(\vec{r}_2, \vec{r}_1)|^2$$

$$\Rightarrow \quad \psi(\vec{r}_2', \vec{r}_1') = e^{i\theta} \psi(\vec{r}_1', \vec{r}_2')$$

Change $\vec{r}_1'$ & $\vec{r}_2$ once more (they are arbitrary) to get

$$\psi(\vec{r}_1 \vec{r}_2) = e^{2i\theta} \psi(\vec{r}_1 \vec{r}_2)$$

$$\Rightarrow \quad e^{2i\theta} = 1 \quad \text{or} \quad e^{i\theta} = \pm 1.$$

Thus Hartree wavefunction is can be further improved by incorporating the symmetry property of the wavefunction. This is done in Hartree Fock theory.

Hartree-Fock Theory:

Question: How do we construct symmetric or antisymmetric function out of Hartree-product

Example of two electrons:

$$\psi = \phi_{\alpha 1}(\vec{r}_1)\,\phi_{\alpha 2}(\vec{r}_2) \qquad |\psi|^2 = |\phi_{\alpha_1}(\vec{r}_1)|^2 |\phi_{\alpha_2}(\vec{r}_2)|^2$$

~~Symmetric product~~ This gives probability of finding electron with label 1 $|\phi_{\alpha_1}(\vec{r}_1)|^2$ and that with label 2 as $|\phi_{\alpha_2}(\vec{r}_2)|^2$. They are DISTINGUISHABLE

Besides $|\phi_{\alpha_1}(\vec{r}_1)\phi_{\alpha_2}(\vec{r}_2)|^2 \neq |\phi_{\alpha 1}(\vec{r}_1)|^2 |\phi_{\alpha_2}(\vec{r}_2)|^2$

When we symmetrize the product we take

$$\psi(\vec{r}_1, \vec{r}_2) = \phi_{\alpha_1}(\vec{r}_1)\,\phi_{\alpha_2}(\vec{r}_2) \pm \phi_{\alpha_1}(\vec{r}_2)\,\phi_{\alpha_2}(\vec{r}_1)$$

$$|\psi(\vec{r}_1\vec{r}_2)|^2 = |\phi_{\alpha 1}(\vec{r}_1)|^2 |\phi_{\alpha_2}(\vec{r}_2)|^2 + |\phi_{\alpha_1}(\vec{r}_2)|^2 |\phi_{\alpha_2}(\vec{r}_1)|^2 \pm 2\,\phi^*_{\alpha_1}(r_1)\phi_{\alpha_1}(\vec{r}_2)\,\phi^*_{\alpha_2}(\vec{r}_2)\phi_{\alpha_2}(\vec{r}_1)$$

Better way of thinking here is that electron in orbital $(\alpha 1)$ is labeled 1 and that in $(\alpha 2)$ is labeled 2. And we can track these electrons. Question we ask: what is the probability of finding electron in $(\alpha 1)$ at $\vec{r}$ and that in $(\alpha 2)$ orbital at $\vec{r}'$. The answer is $|\phi_{\alpha 1}(\vec{r})|^2 |\phi_{\alpha_2}(\vec{r}')|^2$

In this case we cannot ~~label~~ label any electron i.e. electron in $(\alpha 1)$ can't be labeled 1 or 2. Both are there with equal probability. So it is only this question that we can ask: what is the probability of finding an electron at $\vec{r}$ and another at $\vec{r}'$. The answer is

$$|\phi_{\alpha_1}(\vec{r})|^2 |\phi_{\alpha_2}(\vec{r}')|^2 + |\phi_{\alpha_1}(\vec{r}')|^2 |\phi_{\alpha 2}(\vec{r})|^2$$

In the second case we can't really ask the question we asked earlier: What is the probability of finding electron in orbital (α_1) at $\vec{r}_1$. In the previous case we called that electron 1 so we could say the probability of finding electron 1 at $\vec{r}_1$ is

$|\phi_{\alpha_1}(\vec{r}_1)|^2$ and multiply that with finding probability of finding electron 2 (in orbital α_2) at $\vec{r}_2$ i.e

$|\phi_{\alpha_1}(\vec{r}_1)|^2 |\phi_{\alpha_2}(\vec{r}_2)|^2$

In the symmetric case one could write the probability by symmetrizing probability itself and write

$$\frac{|\phi_{\alpha_1}(\vec{r}_1)|^2 |\phi_{\alpha_2}(\vec{r}_2)|^2 + |\phi_{\alpha_1}(\vec{r}_2)|^2 |\phi_{\alpha_2}(\vec{r}_1)|^2}{2}$$

Could a trial wavefunction be

$$\sqrt{\frac{|\phi_{\alpha_1}(r_1)|^2 |\phi_{\alpha_2}(r_2)|^2 + \vec{r}_1 \leftrightarrow \vec{r}_2}{2}}$$

Notice that in the second case electron designated 1 and identified by $\vec{r}_1$ is in ϕ_{α_1} and ϕ_{α_2}, both orbitals and so is electron 2. ~~Both the electrons~~

In this sense the electrons are indistinguishable in that we can't really say which one is in which orbital. They are all equivalent.

Best way to think is that indistinguishability is expressed mathematically by symmetrizing with respect to coordinate labels of electrons. In orbital picture this brings each electron to all the orbitals and (with) all their distinguishability

A possible wavefunction for excited state singlet:

$$\frac{1}{2}\left[\phi_1^2(\vec{r}_1)\,|\phi_2(\vec{r}_2)|^2 + |\phi_1(\vec{r}_2)|^2\,\phi_1^2(\vec{r}_1)\right]$$

(FUTURE)

To construct symmetric or antisymmetric product take all possible permutations and add them for symmetric product and put alternate positive and negative signs for alternate permutations. This is easily done by writing the product as a determinant

$$\frac{1}{\sqrt{N!}}\begin{vmatrix} \phi_1(\vec{r}_1) & \phi_1(\vec{r}_2) & \phi_1(\vec{r}_3) \cdots \\ \phi_2(\vec{r}_1) & \phi_2(\vec{r}_2) \cdots \\ \vdots \\ \phi_N(\vec{r}_1) & \phi_N(\vec{r}_2) \cdots \end{vmatrix}$$

In effect in each orbital there is a bit of all electrons so can't really distinguish them.

Keep all signs + for symmetric functions

At the same time, electrons also have spin ~~orbit~~. So the corresponding spin wavefunction is also to be brought in. In Hartree-Fock theory this is done by taking spin-orbitals

$$\chi(x) = \phi_\alpha(\vec{r})\,\alpha(s_z)$$

$$x = (\vec{r}, s_z)$$

Make an antisymmetric wavefn

$$\frac{1}{\sqrt{N!}}\begin{vmatrix} \chi_1(x_1) & \chi_1(x_2) & \chi_1 \cdots \chi_1(x_N) \\ \chi_2(x_1) & \chi_2(x_2) \cdots \chi_2(x_N) \\ \vdots \\ \chi_N(x_1) & \chi_N(x_2) \cdots \chi_N(x_N) \end{vmatrix}$$

Expectation value of the Hamiltonian

$$\langle \Psi_{HF} | H | \Psi_{HF} \rangle = \sum_{\sigma} \sum_{i} \frac{|\nabla \phi_{\alpha i \sigma}(\vec{r})|^2}{2}$$

$$+ \int \rho(\vec{r})\, U(\vec{r})\, d\vec{r}$$

$$+ \frac{1}{2} \iint \frac{\rho(\vec{r})\, \rho(\vec{r}')}{|\vec{r}-\vec{r}'|} d\vec{r} d\vec{r}'$$

$$- \frac{1}{2} \sum_{\sigma} \sum_{ij} \iint \frac{\phi^{*}_{\alpha i \sigma}(\vec{r})\, \phi^{*}_{\alpha j \sigma}(\vec{r}')\, \phi_{\alpha i \sigma}(\vec{r}')\, \phi_{\alpha j \sigma}(\vec{r})}{|\vec{r}-\vec{r}'|} d\vec{r} d\vec{r}'$$

In this expression, all terms are familiar except the last one. In Hartree theory the last term was

$$- \frac{1}{2} \sum_{i} \iint \frac{|\phi_{\alpha i}(\vec{r})|^2\, |\phi_{\alpha i}(\vec{r}')|^2}{|\vec{r}-\vec{r}'|} d\vec{r} d\vec{r}'$$

but now it is more complicated. Besides the self-interaction energy, there is interaction between different orbitals. This is known as exchange energy. Let us discuss this a bit.

Exchange energy:

$$E_x = -\frac{1}{2} \sum_{\sigma} \sum_{ij} \iint \frac{\phi^{*}_{\alpha i \sigma}(\vec{r})\, \phi^{*}_{\alpha j \sigma}(\vec{r}')\, \phi_{\alpha i \sigma}(\vec{r}')\, \phi_{\alpha j \sigma}(\vec{r})}{|\vec{r}-\vec{r}'|} d\vec{r} d\vec{r}'$$

$$= -\frac{1}{2} \sum_{\sigma} \iint \frac{|\gamma_{\sigma}(\vec{r}, \vec{r}')|^2}{|\vec{r}-\vec{r}'|} d\vec{r}\, d\vec{r}'$$

$$\gamma_{\sigma}(\vec{r}, \vec{r}') = \sum_{i} \phi^{*}_{\alpha i \sigma}(\vec{r})\, \phi_{\alpha i \sigma}(\vec{r}')$$

Thus

(1) Exchange energy is negative. It leads to lowering of energy.

(2) Exchange energy arises from interaction between electrons of the same spin

(3) Interpretation of exchange energy:

Let us ask what is the probability of finding one electron at $\vec{r}$ and another one at $\vec{r}'$

$$\rho_2(\vec{r},\vec{r}') = \frac{1}{N(N-1)} \sum_{ij}{}' \delta(\vec{r}-\vec{r}_i)\,\delta(\vec{r}'-\vec{r}_j)$$

Expectation value of $\rho_2(\vec{r},\vec{r}')$ with respect to determinantal wavefunction

$$= \frac{1}{N(N-1)} \left[\rho(\vec{r})\rho(\vec{r}') - \sum_{\sigma}\sum_{ij} \phi^*_{\alpha_i\sigma}(\vec{r})\,\phi^*_{\alpha_j\sigma}(\vec{r}')\,\phi_{\alpha_i\sigma}(\vec{r}')\,\phi_{\alpha_j\sigma}(\vec{r}) \right]$$

$$= \frac{\rho(\vec{r})}{N} \cdot \frac{1}{(N-1)} \left[\rho(\vec{r}') - \frac{1}{\rho(\vec{r})} \sum_{\sigma}\sum_{ij} |\gamma_\sigma(\vec{r},\vec{r}')|^2 \right]$$

Classically this probability would have been

$$\frac{\rho(\vec{r})}{N} \cdot \frac{1}{(N-1)} \left[\rho(\vec{r}') - \frac{\rho(\vec{r}')}{N} \right]$$

$\frac{\rho(\vec{r})}{N}$: Probability of finding one electron at $\vec{r}$ (total # of ele. = N)

$\rho(\vec{r}') - \frac{\rho(\vec{r}')}{N}$: Probability of finding one electron at $\vec{r}'$ (total # of electrons = N−1).

In classical case the probability gets lowered all over the space by $\left(\frac{\rho(\vec{r}')}{N}\right)$ but in quantum case it is more

Complicated