

Quantum Many Body Theory

NIUS Midterm Report

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Abstract

This is a review of basic Quantum Mechanics and the variational methods used in Quantum many-body theory.

The Schrodinger equation for a single particle of mass m is given by

$$\frac{-\hbar^2}{2m} \nabla^2 \psi + V(\mathbf{r}, t) \psi = i\hbar \frac{\partial \psi}{\partial t}$$

(time dependent form). For cases that are of interest to us, $V(\mathbf{r}, t) = V(\mathbf{r})$ (i.e independent of time), and in those cases we are interested in solving the time independent equation for the eigenstates of the hamiltonian, i.e solving the eigenvalue equation

$$\frac{-\hbar^2}{2m} \nabla^2 \psi + V(\mathbf{r}) \psi = E \psi$$

At a point in time, a permissible state can be represented as a linear combination of orthonormal energy eigenstates of the Hamiltonian which is Hermitian. In that case, the time evolution of the state is given by the equation $|\psi(t)\rangle = e^{-\frac{it}{\hbar} \hat{H}} |\psi(0)\rangle$.

Let an operator \hat{O} of an observable (hence it is hermitian), commute with an operator, for some other observable, say, \hat{O}' , i.e, $[\hat{O}, \hat{O}'] = 0$, then, one can construct an orthonormal basis, each element of which is simultaneously an eigenstate of \hat{O} and \hat{O}' .

The Hydrogen Atom

The Hamiltonian for hydrogen is of the form

$$\frac{-\hbar^2}{2m} \nabla^2 - \frac{1}{4\pi\epsilon r} = \hat{H}$$

which in the spherical polar coordinates presents itself as

$$-\frac{\hbar^2}{2m} \left(\frac{\partial}{r^2 \partial r} (r^2 \frac{\partial}{\partial r}) + \frac{1}{r^2 \sin\theta} \frac{\partial}{\partial \theta} (\sin\theta \frac{\partial}{\partial \theta}) + \frac{1}{r^2 \sin^2\theta} \frac{\partial^2}{\partial \phi^2} \right) - \frac{e^2}{4\pi\epsilon r} = \hat{H}$$

Now the operator for z-component of angular momentum, $\hat{L}_z = -i\hbar \frac{\partial}{\partial \phi}$ and that for the total angular momentum, $\hat{L}^2 = -\hbar^2 \left[\frac{1}{\sin\theta} \frac{\partial}{\partial \theta} (\sin\theta \frac{\partial}{\partial \theta}) + \frac{1}{\sin^2\theta} \frac{\partial^2}{\partial \phi^2} \right]$ can be shown to obey the commutation relations - $[\hat{L}_z, \hat{L}^2] = 0$ and $[\hat{L}^2, \hat{H}] = 0$. Now, the eigenfunctions of \hat{L}_z are of the form $\Phi(\phi) = ce^{im\phi}$ where m is

an integer (so that $\Phi(\phi + 2\pi) = \Phi(\phi)$) and c is independent of ϕ . Clearly, the common eigenfunctions of \hat{L}_z and \hat{L}^2 are of the form $A(\theta, \phi) = k\Theta(\theta).e^{im\phi}$, k being independent of θ and ϕ . Now, putting this in the eigenvalue equation of \hat{L}^2 , we obtain,

$$-\hbar^2 \left[\frac{1}{\sin\theta} (\partial_\theta(\sin\theta \partial_\theta \Theta)) + \frac{-m^2}{\sin^2\theta} \Theta \right] = \lambda \Theta$$

which reduces to the associated Legendre equation on the substitution $z = \cos\theta$, and has desirable solutions of the form $\Theta(\theta) = N'_{l,m} P_l^m(\cos\theta)$, where $l = 0, 1, 2, 3, \dots$ and $-l \leq m \leq l$, $\lambda = \hbar^2 l(l+1)$. Now, we can write for the angular part,

$$A_{l,m}(\theta, \phi) = N_{l,m} P_l^m(\cos\theta) e^{im\phi}$$

Since the \hat{L}^2 operator does not have an explicit r dependence, the common eigenfunctions of \hat{L}^2 and \hat{H} have the form - $\psi(r, \theta, \phi) = R(r)A(\theta, \phi)$. Substituting it into the eigenvalue equation of the hamiltonian, we get the radial part, and hence the final solution turns out to be,

$$\psi(r, \theta, \phi) = \sqrt{\left(\frac{2}{na_0}\right)^3 \frac{(n-l-1)!}{2n(n+l)!}} e^{-r/2} r^l L_{n-l-1}^{2l+1}(r) Y(\theta, \phi)$$

Thus we obtain the eigenfunctions of the hamiltonian.

The Many Electron problem

The wave function for system of several particles is given by :

$$\psi = \psi(x_1, x_2, x_3, \dots, x_n)$$

where x_i represents the generalised coordinate (i.e, position and spin) for the i th particle, the total number of particles being n . If the system is made up of n identical fermions, the wave function must follow the following property,

$$P_{ij}\psi(x_1, x_2, \dots, x_i, \dots, x_j, \dots, x_n) = \psi(x_1, x_2, \dots, x_j, \dots, x_i, \dots, x_n) = -\psi(x_1, x_2, \dots, x_i, \dots, x_j, \dots, x_n)$$

which follows from Pauli's Spin Statistics Theorem.

we state the general statement of our problem: there are m nuclei and n electrons. We fix the position of the nuclei initially and then only the electronic part of the Hamiltonian is what matters.

$$\hat{H} = -\hbar^2/2m \sum_{i=1}^n \nabla_i^2 - \sum_{a,i} \frac{Z_a e^2}{|\mathbf{R}_a - \mathbf{r}_i|} + \frac{e^2}{2} \sum_{i \neq j} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}$$

where index i relates to electrons and index 'a' relates to nuclei. We have omitted:

- 1) Nuclear kinetic energy, nuclear-nuclear repulsion (Born Oppenheimer approximation)
- 2) Magnetic interactions (relativistic corrections)

In a more compact notation , we may write ,

$$\hat{H} = \hat{H}(x_1, x_2, x_3, \dots, x_n) = \sum_{i=1}^n H(i) + \frac{1}{2} \sum_{i \neq j} V(i, j)$$

where, $H(i)$: first two terms on the RHS of the original equation and $V(i, j)$: last term on RHS of the original equation. We note, $V(i, j) = V(j, i)$.

Let's consider a many body problem that has been solved exactly.

Rubber Band Helium:

Two particles of mass m each, are attached to a heavy nucleus by springs each of which has a force constant of $m\omega^2$ and they also interact among themselves by a similar Hooke's law spring, its spring constant being $\lambda \frac{m}{2} \omega^2$. The Hamiltonian of such a system is of the form

$$\hat{H} = -\frac{\hbar^2}{2m}(\nabla_1^2 + \nabla_2^2) + \frac{1}{2}m\omega^2(r_1^2 + r_2^2) + \frac{\lambda}{4}m\omega^2|\mathbf{r}_1 - \mathbf{r}_2|^2$$

We go to a new coordinate system given by

$$\mathbf{u} = \frac{1}{\sqrt{2}}(\mathbf{r}_1 + \mathbf{r}_2); \mathbf{v} = \frac{1}{\sqrt{2}}(\mathbf{r}_1 - \mathbf{r}_2)$$

We look at the new form of Hamiltonian that we get under this variable change. Now, we have,

$$\psi(\mathbf{r}_1, \mathbf{r}_2) = \phi(\mathbf{u}, \mathbf{v})$$

i.e,

$$\psi(x_1, y_1, z_1, x_2, y_2, z_2) = \phi(u_x, u_y, u_z, v_x, v_y, v_z)$$

where, c

$$u_p = \frac{1}{\sqrt{2}}(p_1 + p_2); v_p = \frac{1}{\sqrt{2}}(p_1 - p_2)$$

We clearly observe,

$$\frac{\partial \phi}{\partial x_1} = \frac{\partial \phi}{\partial u_x} \frac{\partial u_x}{\partial x_1} + \frac{\partial \phi}{\partial v_x} \frac{\partial v_x}{\partial x_1} = \frac{1}{\sqrt{2}} \left(\frac{\partial \phi}{\partial u_x} + \frac{\partial \phi}{\partial v_x} \right)$$

and,

$$\frac{\partial \phi}{\partial x_2} = \frac{\partial \phi}{\partial u_x} \frac{\partial u_x}{\partial x_2} + \frac{\partial \phi}{\partial v_x} \frac{\partial v_x}{\partial x_2} = \frac{1}{\sqrt{2}} \left(\frac{\partial \phi}{\partial u_x} - \frac{\partial \phi}{\partial v_x} \right)$$

carrying out the same process for a second time, we get,

$$\frac{\partial^2 \phi}{\partial x_1^2} = \frac{1}{2} \left(\frac{\partial^2 \phi}{\partial u_x^2} + 2 \frac{\partial^2 \phi}{\partial u_x \partial v_x} + \frac{\partial^2 \phi}{\partial v_x^2} \right)$$

and,

$$\frac{\partial^2 \phi}{\partial x_2^2} = \frac{1}{2} \left(\frac{\partial^2 \phi}{\partial u_x^2} - 2 \frac{\partial^2 \phi}{\partial u_x \partial v_x} + \frac{\partial^2 \phi}{\partial v_x^2} \right)$$

Thus,

$$\frac{\partial^2 \phi}{\partial x_1^2} + \frac{\partial^2 \phi}{\partial x_2^2} = \frac{\partial^2 \phi}{\partial u_x^2} + \frac{\partial^2 \phi}{\partial v_x^2}$$

Similarly, computing the other terms, we get,

$$\nabla_1^2 \phi + \nabla_2^2 \phi = \nabla_u^2 \phi + \nabla_v^2 \phi$$

Also, it can be easily exhibited that

$$r_1^2 + r_2^2 = u^2 + v^2$$

Thus, under the given transformation, the hamiltonion is of the form,

$$\hat{H} = \left[\frac{-\hbar^2}{2m} \nabla_u^2 + \frac{1}{2} m \omega^2 u^2 \right] + \left[\frac{-\hbar^2}{2m} \nabla_v^2 + \frac{1}{2} (1 + \lambda) m \omega^2 v^2 \right] = \hat{H}_u + \hat{H}_v$$

where \hat{H}_u and \hat{H}_v are nothing but three dimensional harmonic oscillator Hamiltonia in u and v respectively. Clearly the eigenfunctions would be the product of the eigenfunctions of the individual Hamiltonia and eigenvalue, the sum of individual eigenvalues. Thus, the ground state energy is the sum of ground state energies of the two Hamiltonia.

$$E_g = \frac{3\hbar\omega}{2} (1 + \sqrt{1 + \lambda})$$

The Thomas-Fermi model of the atom

In atoms consisting of a large number of electrons, the motion of the electrons can be approximated as that of a free electron gas in a central potential.

From Quantum Mechanics, we know that the Fermi radius of a free electron gas is given by $k_F = (3\pi^2 n(r))^{1/3}$, where $n(r)$ is the number density of electrons as a function of radial separation from the origin.

As the Fermi radius is interpreted as a boundary separating occupied and unoccupied states in k -space, the maximum kinetic energy a single electron in the gas is

$$(K.E)_{max} = \frac{\hbar^2 k_F^2}{2\mu} = \frac{\hbar^2}{2\mu} (3\pi^2 n(r))^{2/3} \quad (1)$$

where μ is the reduced mass of the electron-nucleus pair.

We now present some arguments to develop the form of the central potential. Total energy of an electron in the gas

$$E = \frac{p^2}{2\mu} - q\phi(r) \quad (2)$$

where $\phi(r)$ is the central potential, and $-q$ the charge of the electron.

For the electron to be bound, we need $E < 0$. We choose

$$q\phi(r) = (K.E)_{max} \quad (3)$$

so as to satisfy the criterion (Note that this is only an approximation).

$$q\phi(r) = \frac{\hbar^2}{2\mu} (3\pi^2 n(r))^{2/3} \Rightarrow n(r) = \frac{(2\mu q\phi(r))^{3/2}}{3\pi^2 \hbar^3} \quad (4)$$

Classically, we also require the potential $\phi(r)$ to satisfy Poisson's equation.

$$\nabla^2 \phi = -\frac{\rho(r)}{\epsilon_0} \quad (5)$$

Here $\rho(r) = -qn(r)$, and $\nabla^2 \phi = \frac{1}{r^2} \frac{d}{dr} (r^2 \frac{d\phi}{dr})$ as ϕ is purely radial in nature.

$$\Rightarrow \frac{1}{r^2} \frac{d}{dr} \left(r^2 \frac{d\phi}{dr} \right) = \frac{q(2\mu q)^{3/2}}{3\pi^2 \hbar^3 \epsilon_0} \phi^{3/2} \quad (6)$$

In invoking the degenerate free electron gas system in Quantum mechanics, the model neglects inter-electronic repulsion. However we can deal with the electronic contribution to the classical potential $\phi(r)$ in an average way.

We thus suggest a change of variables in equation (6), along with boundary conditions, to obtain forms of ϕ we physically expect.

Observe that as $r \rightarrow 0$, the potential will essentially be due to the nucleus, behaving as $\frac{Zq}{4\pi\epsilon_0 r}$. This suggests that we introduce a change of variables as

$$\phi(r) = \frac{Zq}{4\pi\epsilon_0 r} \chi(r) \quad (7)$$

with the boundary condition $\chi(0) = 1$.

Equation (6) becomes

$$\frac{d^2 \chi}{dr^2} = \frac{4Z^{1/2}}{3\pi \hbar^3} \left(\frac{2\mu q^2}{4\pi\epsilon_0} \right)^{3/2} \frac{1}{r^{1/2}} \chi^{3/2} \quad (8)$$

To simplify this equation, we introduce the change of variables $r = \gamma x$, where x is dimensionless, defining the constant γ later.

Under this change, equation (8) becomes

$$\frac{d^2\chi(x)}{dx^2} = \left[\gamma^{\frac{3}{2}} \frac{4Z^{\frac{1}{2}}}{3\pi\hbar^3} \left(\frac{2\mu q^2}{4\pi\epsilon_0} \right)^{\frac{3}{2}} \right] \frac{\chi(x)^{\frac{3}{2}}}{x^{\frac{1}{2}}} \quad (9)$$

We now choose γ such that the quantity inside brackets is 1. Thus

$$\gamma = \frac{1}{2} \left(\frac{3\pi}{4} \right)^{\frac{2}{3}} \frac{1}{Z^{\frac{1}{3}}} \frac{4\pi\epsilon_0\hbar^2}{\mu q^2} \simeq \frac{0.8853a_0}{Z^{\frac{1}{3}}} \quad (10)$$

where

$$a_0 = \frac{4\pi\epsilon_0\hbar^2}{\mu q^2} \simeq 0.53 A^o$$

is the Bohr radius. Equation (9) thus takes the form

$$\frac{d^2\chi}{dx^2} = \frac{\chi^{\frac{3}{2}}}{x^{\frac{1}{2}}} \quad (11)$$

with $\chi(0) = 1$. This is known as the dimensionless Thomas-Fermi equation, abbreviated the TF equation. As the TF equation is of second order, we need another boundary condition to solve it uniquely. For numerical analysis, it is convenient to use $\chi'(0)$ as the other boundary condition, varying it as a parameter to obtain a class of solutions. Observe that for an isolated atom, $\chi(\infty) = 0$ as we know that $\phi(\infty) = 0$.

Once we know $\chi(r)$, from equation (4),

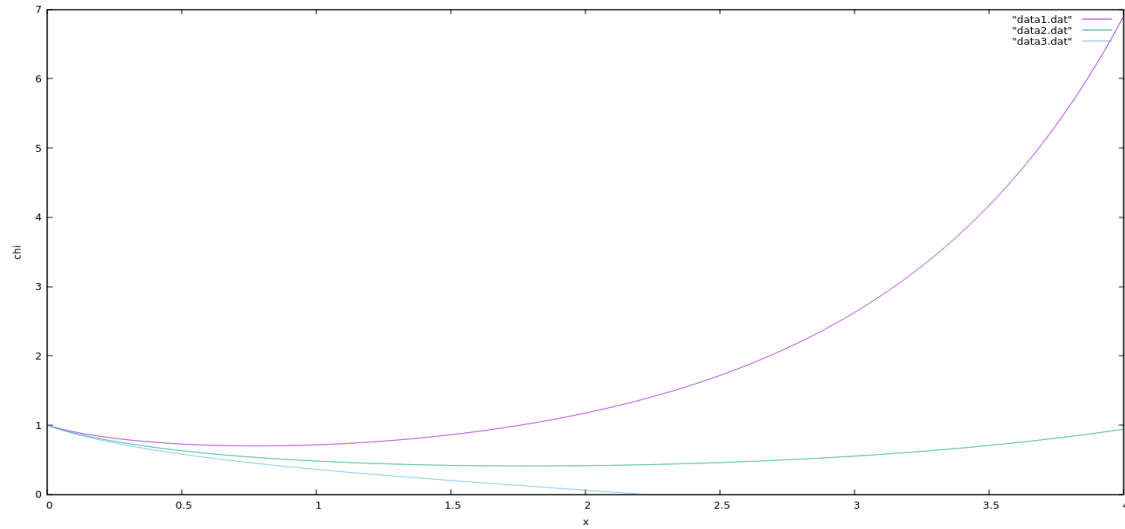
$$n(r) = \frac{(2\mu q\phi(r))^{\frac{3}{2}}}{3\pi^2\hbar^3} = \frac{1}{3\pi^2\hbar^3} \left(\frac{2\mu Z q^2}{4\pi\epsilon_0 r} \chi(r) \right)^{\frac{3}{2}} = \frac{1}{3\pi^2} \left(\frac{2Z}{a_0} \frac{\chi(r)}{r} \right)^{\frac{3}{2}} \quad (12)$$

Notice that since $\chi(0) = 1$, $n(r)$ blows up at $r = 0$. This is a basic error in the TF model, that it predicts an infinite electron density at the nucleus. It has been shown that the TF model for the atom is accurate only in the domain

$$\frac{a_0}{Z} < r < a_0$$

For $r < \frac{a_0}{Z}$, the quasi classical approximation underlying the TF model breaks down. For $r > a_0$, the de-Broglie wavelength of the electron becomes large, and the assumption that $\phi(r)$ doesn't vary significantly over a wavelength becomes weak. The Thomas Fermi model thus deals with the atom, with approximations, in a quasi classical way, invoking both the free electron gas system from Quantum Mechanics, and Poisson's equation from Classical Electrodynamics.

We attempted to solve equation (11) numerically for certain values of $\chi'(0)$, using Euler's method to implement an algorithm in Python, obtaining sets of datapoints, and plotted it using GNUplot.



The lowermost curve(light blue) corresponds to $\chi'(0) = -1.6$, the middle curve(green) to $\chi'(0) = -1.5$ and the topmost curve(violet) to $\chi'(0) = -1.4$. This suggests that the isolated atom case($\chi(\infty) = 0$) occurs for $\chi'(0)$ lying somewhere between 1.5 and 1.6.

The Variational Principle

Suppose we have a system in an arbitrary quantum state

$$|\psi\rangle = \sum_i c_i |\phi_i\rangle \quad i = 1, 2, 3 \dots$$

where $|\phi_i\rangle$ are the energy eigenstates, satisfying $H|\phi_i\rangle = \lambda_i|\phi_i\rangle$, and $\langle\phi_i|\phi_j\rangle = \delta_{ij}$ following from the hermiticity of the hamiltonian operator.

Subject to normalization, $\langle\psi|\psi\rangle = \sum_i |c_i|^2 = 1$.

Ground state energy $E_{gs} = \lambda_1 < \lambda_2 < \lambda_3 \dots$

The expectation value of energy for the state $|\psi\rangle$ is determined as-

$$\langle\psi|H|\psi\rangle = \sum_i \lambda_i |c_i|^2$$

Since $\lambda_1 < \lambda_2 < \lambda_3 \dots$

$$\sum_i \lambda_i |c_i|^2 \geq \sum_i \lambda_1 |c_i|^2 = \lambda_1 = E_{gs}$$

Thus,

$$\langle\psi|H|\psi\rangle \geq E_{gs}$$

for any normalized $|\psi\rangle$ we guess as the ground state wavefunction.

This is a fundamental result for systems that are not exactly solvable, as it essentially tells us that if we minimize $\langle\psi|H|\psi\rangle$ with respect to parameters we define within our guess function $|\psi\rangle$, we will come closer to the exact experimentally observed ground state energy, and hence the form of the ground state wavefunction. We will now illustrate this technique applying it on the He atom, one of the simplest many body system- consisting of 2 electrons and a nucleus of charge $+2e$.

Variational principle on the Helium Atom

The exact hamiltonian for the helium atom is-

$$H = -\frac{\hbar^2}{2m}(\nabla_1^2 + \nabla_2^2) - \frac{e^2}{4\pi\epsilon_0}\left(\frac{2}{r_1} + \frac{2}{r_2}\right) + \frac{e^2}{4\pi\epsilon_0|\mathbf{r}_1 - \mathbf{r}_2|}$$

Here, \mathbf{r}_1 and \mathbf{r}_2 are the position vectors of electrons labelled 1 and 2, with the nucleus chosen as origin. The nucleus being much more massive than an electron, can be assumed to be fixed(Born-Oppenheimer approximation)

The hamiltonian can be re-written as-

$$H = -\frac{\hbar^2}{2m}(\nabla_1^2 + \nabla_2^2) - \frac{e^2}{4\pi\epsilon_0}\left(\frac{Z}{r_1} + \frac{Z}{r_2}\right) + \frac{e^2}{4\pi\epsilon_0}\left(\frac{Z-2}{r_1} + \frac{Z-2}{r_2} + \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|}\right)$$

The first two terms now represent a separated hamiltonian for 2 Hydrogen like atoms(with nuclear charge Z) defined independently in the coordinate systems of \mathbf{r}_1 and \mathbf{r}_2 respectively. We may thus take a guess for the ground state wavefunction ψ as a product of the ground state wavefunctions(in this case- 1s orbitals) of two H like atoms. That is, trial ground state wavefunction-

$$\psi(r_1, r_2) = \frac{Z^3}{\pi a_0^3} e^{-\frac{Z(r_1+r_2)}{a_0}}$$

where a_0 is the Bohr radius (0.529 \AA). Observe that Z here is a parameter with respect to which we would like to minimize expected energy.

Expected ground state energy -

$$\langle \psi | H | \psi \rangle = 2 \times Z^2 E_1 + 2 \times \frac{(Z-2)e^2}{4\pi\epsilon_0} \left\langle \frac{1}{r} \right\rangle + \langle V_{ee} \rangle$$

Here $V_{ee} = \frac{e^2}{4\pi\epsilon_0 |\mathbf{r}_1 - \mathbf{r}_2|}$, and $E_1 = -\frac{e^2}{8\pi\epsilon_0 a_0} = -13.6 \text{ eV}$ which is the ground state energy of the H atom.

(Recall: For a H like atom, $E_n^Z = \frac{Z^2 E_1}{n^2}$)

It can be shown that

$$\left\langle \frac{1}{r} \right\rangle = \frac{Z}{a_0}$$

and

$$\langle V_{ee} \rangle = -\frac{5Z}{4} E_1$$

Thus

$$\langle H \rangle = \left(2Z^2 - 4Z(Z-2) - \frac{5Z}{4} \right) E_1 = \left(-2Z^2 + \frac{27Z}{4} \right) E_1$$

$$\frac{d\langle H \rangle}{dZ} = 0 \Rightarrow Z = \frac{27}{16} = 1.6875$$

For this value of Z ,

$$\langle H \rangle = -77.45625 \text{ eV}$$

The experimentally observed ground state energy of Helium is -79 eV . We are within 2% of the correct answer. This suggests that our trial ground state wavefunction for $Z=1.6875$ is a fairly accurate guess for the exact ground state wavefunction of the He atom. More complicated forms of the trial function have been shown to give more accurate results. However heuristically, we have seen that a product of single electron wavefunctions can perform reasonably well upon optimization.

The Hartree Approximation

Consider the exact hamiltonian of a many electron many nuclei system-

$$H = -\frac{\hbar^2}{2m} \sum_i \nabla_i^2 - \sum_{i,k} \frac{Z_k e^2}{4\pi\epsilon_0 |\mathbf{x}_k - \mathbf{x}_i|} + \frac{1}{2} \sum_{i,j(i \neq j)} \frac{e^2}{4\pi\epsilon_0 |\mathbf{x}_i - \mathbf{x}_j|}$$

Electrons are indexed by i & j and nuclei by k . Nuclear kinetic energy and inter-nuclear repulsion are ignored (Born-Oppenheimer approximation). The first two terms of this hamiltonian can be combined, and we'll have a hamiltonian of the form-

$$H = \sum_i h(i) + \frac{1}{2} \sum_{i,j(i \neq j)} V(i,j) \quad (1)$$

$h(i)$ is the combination of electron kinetic energy and electron-nuclear potentials for the electron indexed by i , and $V(i,j)$ is electron-electron repulsion potential between electrons i and j . [Note: $V(i,j) = V(j,i)$, hence the half factor]. Hartree attempted to separate this hamiltonian into N single electron hamiltonians. Let

$$\psi(x_1, x_2 \dots x_N) = u_1(x_1)u_2(x_2) \dots u_N(x_N) \quad (2)$$

which is a simple product of N single electron wavefunctions. Each u_i is defined by its coordinate x_i , and is normalized. However the set $\{u_i\}$ is not necessarily orthogonal.

$$\langle \psi | H | \psi \rangle = \sum_i \langle u_i | h(i) | u_i \rangle + \frac{1}{2} \sum_{i,j(i \neq j)} \langle u_i u_j | V(i,j) | u_i u_j \rangle \quad (3)$$

We want to minimize $\langle \psi | H | \psi \rangle$ under the constraint of normalization of each u_i . Applying the technique of Lagrange multipliers from the Calculus of variations,

$$\delta(\langle \psi | H | \psi \rangle - \sum_i \lambda_i (\langle u_i | u_i \rangle - 1)) = 0 \quad (4)$$

where each λ_i is a lagrange multiplier. We obtain N equations from this variation. For $k = 1, 2 \dots N$ -

$$2 \left(\langle \delta_k u_k | h(k) | u_k \rangle + \frac{1}{2} \sum_{j(\neq k)} \langle \delta_k u_k u_j | V(k,j) | u_k u_j \rangle - \lambda_k \langle \delta_k u_k | u_k \rangle \right) = 0 \quad (5)$$

Here we choose the derivative operator as $\delta_k = i \frac{d}{dx_k}$ so as to keep it Hermitian, and the factor of 2 stems from this. (Had we chosen $\delta_k = \frac{d}{dx_k}$, which is anti-hermitian, the variation would be identically 0). So while applying chain rule on equation (4), observe that

$$\begin{aligned} \langle \delta_k u_k | h(k) | u_k \rangle &= \langle u_k | \delta_k (h(k) u_k) \rangle \\ \langle \delta_k u_k u_j | V(k,j) | u_k u_j \rangle &= \langle u_k u_j | \delta_k (V(k,j) u_k u_j) \rangle \end{aligned}$$

and

$$\langle \delta_k u_k | u_k \rangle = \langle u_k | \delta_k u_k \rangle$$

Writing equation (5) in its integral form,

$$\int \delta_k u_k^* h(k) u_k dx_k + \frac{1}{2} \int \delta_k u_k^* \left(\sum_{j(\neq k)} \int u_j^* V(k,j) u_j dx_j \right) u_k dx_k - \lambda_k \int \delta_k u_k^* u_k dx_k = 0$$

$$\Rightarrow \int \delta_k u_k^* \left(h(k) + \frac{1}{2} \sum_{j(\neq k)} \langle u_j | V(k, j) | u_j \rangle - \lambda_k \right) u_k dx_k = 0$$

As $\delta_k u_k^* \neq 0$ in general,

$$\left(h(k) + \frac{1}{2} \sum_{j(\neq k)} \langle u_j | V(k, j) | u_j \rangle - \lambda_k \right) u_k = 0$$

Hence

$$\left(h(k) + \frac{1}{2} \sum_{j(\neq k)} \langle u_j | V(k, j) | u_j \rangle \right) u_k = \lambda_k u_k \quad (6)$$

Equation (6) thus gives us N single electron *Schrödinger* equations.

$$h'_k u_k = \lambda_k u_k \quad (7)$$

$$h'_k = h(k) + \frac{1}{2} \sum_{j(\neq k)} \langle u_j | V(k, j) | u_j \rangle \quad (8)$$

For a fixed k , multiplying both sides of equation (7) by all u_i ($i \neq k$),

$$\left(h(k) + \frac{1}{2} \sum_{j(\neq k)} \langle u_j | V(k, j) | u_j \rangle \right) \prod_i u_i = \lambda_k \prod_i u_i$$

Summing over k ,

$$\left(\sum_k h(k) + \frac{1}{2} \sum_{j,k(j \neq k)} \langle u_j | V(k, j) | u_j \rangle \right) \prod_i u_i = \left(\sum_k \lambda_k \right) \prod_i u_i \quad (9)$$

We thus have an effective N electron Hartree hamiltonian

$$H' = \sum_k h(k) + \frac{1}{2} \sum_{j,k(j \neq k)} \langle u_j | V(k, j) | u_j \rangle \quad (10)$$

satisfying

$$H' \prod_i u_i = \left(\sum_k \lambda_k \right) \prod_i u_i \quad (11)$$

As seen from the form of H' , equation (11) has to be solved self-consistently. We initially supply a normalized function set u_i to construct H' , find its separable eigenfunctions to reconstruct H' and repeat the process until self-consistency is achieved; that is, the eigenvalues for a certain set of product functions $\{\psi_i = u_{i1}(x_1)u_{i2}(x_2) \dots u_{iN}(x_N)\}$ doesn't change significantly over iteration.

SLATER'S DETERMINANT

According to Pauli Exclusion Principle the wave function representing a system of 2 electrons (fermions), is antisymmetric w.r.t. transposition (permutation) operator. $\hat{P}\psi = -\psi$
 From Hartree product we have ψ_{HP} for a 'n' electron system in the form:

$$\psi_{HP} = \psi_1\psi_2\dots\psi_n \quad (1)$$

Let ψ_a and ψ_b be two normalised wave function associated with either of two electrons. To satisfy Pauli Spin Statistics theorem ψ_{HP} needs to be of the form:

$$\psi_{HP} = \psi_a(\mathbf{x}_1)\psi_b(\mathbf{x}_2) - \psi_b(\mathbf{x}_1)\psi_a(\mathbf{x}_2) \quad (2)$$

where \mathbf{x} denotes both \vec{r} which is spatial variable, and also α which is spin variable.
 This can be represented also in a determinant form called Slater Determinant as

$$\psi_{SD} = \frac{1}{\sqrt{2}} \begin{vmatrix} \psi_a(\mathbf{x}_1) & \psi_b(\mathbf{x}_1) \\ \psi_a(\mathbf{x}_2) & \psi_b(\mathbf{x}_2) \end{vmatrix} \quad (3)$$

We can generalize this for system of N electrons.

$$\psi_{SD} = \frac{1}{\sqrt{N!}} \begin{vmatrix} \psi_1(\mathbf{x}_1) & \psi_2(\mathbf{x}_1) & \dots & \psi_n(\mathbf{x}_1) \\ \psi_1(\mathbf{x}_2) & \psi_2(\mathbf{x}_2) & \dots & \psi_n(\mathbf{x}_2) \\ \dots & \dots & \dots & \dots \\ \psi_1(\mathbf{x}_n) & \psi_2(\mathbf{x}_n) & \dots & \psi_n(\mathbf{x}_n) \end{vmatrix}$$

HARTREE FOCK APPROXIMATION

Assumptions

- All ψ_i s are orthonormal
- All of them are normalized.
- In short

$$\int \psi_i^*(x_i)\psi_j(x_j) dx_i dx_j = \delta_{ij} \quad (4)$$

Consider N electron system. Hamiltonian of the system can be written as

$$\hat{H} = \sum_i H_i + \frac{1}{2} \sum_{i \neq j} V(i, j)$$

where $H_i = \frac{-\hbar^2}{2m} \nabla_i^2$ and $V(i, j) = V(j, i)$

Consider 2 electron system again, then we can use method of Lagrange's multiplier with the constraint of normalisation on ψ_{SD} . Variation of expectation value of hamiltonian is zero constrained to normalization.

$$\delta[\langle \psi_{SD} | H | \psi_{SD} \rangle - \sum_{ij} \lambda_{ij} \langle \psi_i | \psi_j \rangle] = 0$$

$$\langle \psi_{SD} | H | \psi_{SD} \rangle = \sum_i \langle \psi_{SD} | H_i | \psi_{SD} \rangle + \frac{1}{2} \sum_{i \neq j} \langle \psi | V(i, j) | \psi \rangle \quad (5)$$

So for a two electron case the equation is:

$$\langle \psi_{SD} | H | \psi_{SD} \rangle = \langle \psi_{SD} | H_1 + H_2 | \psi_{SD} \rangle + \frac{1}{2} \langle \psi | V(1, 2) + V(2, 1) | \psi \rangle \quad (6)$$

Now consider the First term:

$$\begin{aligned} \langle \psi_{SD} | H_1 + H_2 | \psi_{SD} \rangle = & \frac{1}{2} \int \int [\psi_1^*(\mathbf{x}_1) \psi_2^*(\mathbf{x}_2) - \psi_2^*(\mathbf{x}_1) \psi_1^*(\mathbf{x}_2)] (\mathbf{H}_1 + \mathbf{H}_2) \\ & [\psi_1(\mathbf{x}_1) \psi_2(\mathbf{x}_2) - \psi_2(\mathbf{x}_1) \psi_1(\mathbf{x}_2)] \mathbf{d}\mathbf{x}_1 \mathbf{d}\mathbf{x}_2 \end{aligned} \quad (7)$$

Note that H_1 operates only on wavefunction of the form $\psi_i(\mathbf{x}_1)$ and H_2 only on $\psi_i(\mathbf{x}_2)$. As a result we have four integrals as follows:

(Also note that the $\frac{1}{\sqrt{(2)}}$ factor of each wave function is squared due to product of 2 ψ s and taken out common as $\frac{1}{2}$)

$$\begin{aligned} \langle \psi_{SD} | H_1 + H_2 | \psi_{SD} \rangle = & \frac{1}{2} \int \int [\psi_1^*(\mathbf{x}_1) \psi_2^*(\mathbf{x}_2) - \psi_2^*(\mathbf{x}_1) \psi_1^*(\mathbf{x}_2)] \mathbf{H}_1(\psi_1(\mathbf{x}_1)) \psi_2(\mathbf{x}_2) \mathbf{d}\mathbf{x}_1 \mathbf{d}\mathbf{x}_2 - \\ & \frac{1}{2} \int \int [\psi_1^*(\mathbf{x}_1) \psi_2^*(\mathbf{x}_2) - \psi_2^*(\mathbf{x}_1) \psi_1^*(\mathbf{x}_2)] \mathbf{H}_1(\psi_2(\mathbf{x}_1)) \psi_1(\mathbf{x}_2) \mathbf{d}\mathbf{x}_1 \mathbf{d}\mathbf{x}_2 + \\ & \frac{1}{2} \int \int [\psi_1^*(\mathbf{x}_1) \psi_2^*(\mathbf{x}_2) - \psi_2^*(\mathbf{x}_1) \psi_1^*(\mathbf{x}_2)] \mathbf{H}_2(\psi_2(\mathbf{x}_2)) \psi_1(\mathbf{x}_1) \mathbf{d}\mathbf{x}_1 \mathbf{d}\mathbf{x}_2 - \\ & \frac{1}{2} \int \int [\psi_1^*(\mathbf{x}_1) \psi_2^*(\mathbf{x}_2) - \psi_2^*(\mathbf{x}_1) \psi_1^*(\mathbf{x}_2)] \mathbf{H}_2(\psi_1(\mathbf{x}_2)) \psi_2(\mathbf{x}_1) \mathbf{d}\mathbf{x}_1 \mathbf{d}\mathbf{x}_2 \end{aligned} \quad (8)$$

In equation 7 we apply result from equation 4; finally we get:

$$\begin{aligned}
\langle \psi_{SD} | H_1 + H_2 | \psi_{SD} \rangle = & \frac{1}{2} \int \psi_1^*(\mathbf{x}_1) \mathbf{H}_1(\psi_1(\mathbf{x}_1)) d\mathbf{x}_1 + \\
& \frac{1}{2} \int \psi_2^*(\mathbf{x}_1) \mathbf{H}_1(\psi_2(\mathbf{x}_1)) d\mathbf{x}_1 + \\
& \frac{1}{2} \int \psi_2^*(\mathbf{x}_2) \mathbf{H}_2(\psi_2(\mathbf{x}_2)) d\mathbf{x}_2 + \\
& \frac{1}{2} \int \psi_1^*(\mathbf{x}_2) \mathbf{H}_2(\psi_1(\mathbf{x}_2)) d\mathbf{x}_2
\end{aligned}
\tag{9}$$

Now since under integration the two variables x_1 and x_2 are interchangeable, we have:

$$\begin{aligned}
\langle \psi_{SD} | H_1 + H_2 | \psi_{SD} \rangle = & \int \psi_1^*(\mathbf{x}_1) \mathbf{H}_1(\psi_1(\mathbf{x}_1)) d\mathbf{x}_1 + \\
& \int \psi_2^*(\mathbf{x}_2) \mathbf{H}_2(\psi_2(\mathbf{x}_2)) d\mathbf{x}_2 +
\end{aligned}
\tag{10}$$

$$\begin{aligned}
\langle \psi_{SD} | H_1 + H_2 | \psi_{SD} \rangle = & \langle \psi_1(\mathbf{x}_1) | \mathbf{H}_1 | \psi_1(\mathbf{x}_1) \rangle + \\
& \langle \psi_2(\mathbf{x}_2) | \mathbf{H}_2 | \psi_2(\mathbf{x}_2) \rangle +
\end{aligned}
\tag{11}$$

We can now generalise this result to N electron system:

$$\begin{aligned}
\Sigma_i \langle \psi_{SD} | \mathbf{H}_i | \psi_{SD} \rangle = & \Sigma_i \langle \psi_i(\mathbf{x}_i) | \mathbf{H}_i | \psi_i(\mathbf{x}_i) \rangle = \\
\Sigma_i \int \psi_i^*(\mathbf{x}_i) \mathbf{H}_i(\psi_i(\mathbf{x}_i)) d\mathbf{x}_i
\end{aligned}
\tag{12}$$

Now lets consider the potential (second) term in eq.6 :

$$\begin{aligned}
\frac{1}{2} \langle \psi | V(1, 2) + V(2, 1) | \psi \rangle = & \frac{1}{2} \left\{ \frac{1}{2} \int \int [\psi_1^*(\mathbf{x}_1) \psi_2^*(\mathbf{x}_2) - \psi_2^*(\mathbf{x}_1) \psi_1^*(\mathbf{x}_2)] (\mathbf{V}(\mathbf{1}, \mathbf{2}) + \mathbf{V}(\mathbf{2}, \mathbf{1})) \right. \\
& \left. [\psi_1(\mathbf{x}_1) \psi_2(\mathbf{x}_2) - \psi_2(\mathbf{x}_1) \psi_1(\mathbf{x}_2)] d\mathbf{x}_1 d\mathbf{x}_2 \right\}
\end{aligned}
\tag{13}$$

But we know that V is dependent on $|\mathbf{r}_2 - \mathbf{r}_1|$, so $V(1,2) = V(2,1)$. Hence eq.13 now becomes:

$$\begin{aligned}
\frac{1}{2} \langle \psi | V(1, 2) + V(2, 1) | \psi \rangle = & \frac{1}{2} \left\{ \int \int [\psi_1^*(\mathbf{x}_1) \psi_2^*(\mathbf{x}_2) - \psi_2^*(\mathbf{x}_1) \psi_1^*(\mathbf{x}_2)] (\mathbf{V}(\mathbf{1}, \mathbf{2})) \right. \\
& \left. [\psi_1(\mathbf{x}_1) \psi_2(\mathbf{x}_2) - \psi_2(\mathbf{x}_1) \psi_1(\mathbf{x}_2)] d\mathbf{x}_1 d\mathbf{x}_2 \right\}
\end{aligned}
\tag{14}$$

$$\begin{aligned}
\frac{1}{2} \langle \psi | V(1, 2) + V(2, 1) | \psi \rangle = & \frac{1}{2} \left\{ \int \int [\psi_1^*(\mathbf{x}_1) \psi_2^*(\mathbf{x}_2)] \mathbf{V}(\mathbf{1}, \mathbf{2}) [\psi_1(\mathbf{x}_1) \psi_2(\mathbf{x}_2)] \mathbf{d}\mathbf{x}_1 \mathbf{d}\mathbf{x}_2 \quad + \right. \\
& \int \int [\psi_2^*(\mathbf{x}_1) \psi_1^*(\mathbf{x}_2)] \mathbf{V}(\mathbf{1}, \mathbf{2}) [\psi_2(\mathbf{x}_1) \psi_1(\mathbf{x}_2)] \mathbf{d}\mathbf{x}_1 \mathbf{d}\mathbf{x}_2 \quad - \\
& \int \int [\psi_1^*(\mathbf{x}_1) \psi_2^*(\mathbf{x}_2)] \mathbf{V}(\mathbf{1}, \mathbf{2}) [\psi_2(\mathbf{x}_1) \psi_1(\mathbf{x}_2)] \mathbf{d}\mathbf{x}_1 \mathbf{d}\mathbf{x}_2 \quad - \\
& \left. \int \int [\psi_2^*(\mathbf{x}_1) \psi_1^*(\mathbf{x}_2)] \mathbf{V}(\mathbf{1}, \mathbf{2}) [\psi_1(\mathbf{x}_1) \psi_2(\mathbf{x}_2)] \mathbf{d}\mathbf{x}_1 \mathbf{d}\mathbf{x}_2 \right\} \quad (15)
\end{aligned}$$

Therefore,

$$\begin{aligned}
\frac{1}{2} \langle \psi | V(1, 2) + V(2, 1) | \psi \rangle = & \frac{1}{2} \left\{ \int \int [\psi_1^*(\mathbf{x}_1) \psi_2^*(\mathbf{x}_2)] \mathbf{V}(\mathbf{1}, \mathbf{2}) [\psi_1(\mathbf{x}_1) \psi_2(\mathbf{x}_2)] \mathbf{d}\mathbf{x}_1 \mathbf{d}\mathbf{x}_2 - \right. \\
& \left. \int \int [\psi_2^*(\mathbf{x}_2) \psi_1^*(\mathbf{x}_1)] \mathbf{V}(\mathbf{1}, \mathbf{2}) [\psi_2(\mathbf{x}_1) \psi_1(\mathbf{x}_2)] \mathbf{d}\mathbf{x}_1 \mathbf{d}\mathbf{x}_2 \right\} \quad (16)
\end{aligned}$$

This result can be generalised as

$$\begin{aligned}
\frac{1}{2} \sum_{i \neq j} \langle \psi | V(i, j) | \psi \rangle = & \frac{1}{2} \sum_{i \neq j} \frac{2}{N!} \left\{ \int \int [\psi_i^*(\mathbf{x}_i) \psi_j^*(\mathbf{x}_j)] \mathbf{V}(\mathbf{i}, \mathbf{j}) [\psi_i(\mathbf{x}_i) \psi_j(\mathbf{x}_j)] \mathbf{d}\mathbf{x}_i \mathbf{d}\mathbf{x}_j - \right. \\
& \left. \int \int [\psi_i^*(\mathbf{x}_i) \psi_j^*(\mathbf{x}_j)] \mathbf{V}(\mathbf{i}, \mathbf{j}) [\psi_j(\mathbf{x}_i) \psi_i(\mathbf{x}_j)] \mathbf{d}\mathbf{x}_i \mathbf{d}\mathbf{x}_j \right\} \quad (17)
\end{aligned}$$

Therefore,

$$\begin{aligned}
\frac{1}{2} \sum_{i \neq j} \langle \psi | V(i, j) | \psi \rangle = & \frac{1}{N!} \sum_{i \neq j} \left\{ \int \int [\psi_i^*(\mathbf{x}_i) \psi_j^*(\mathbf{x}_j)] \mathbf{V}(\mathbf{i}, \mathbf{j}) [\psi_i(\mathbf{x}_i) \psi_j(\mathbf{x}_j)] \mathbf{d}\mathbf{x}_i \mathbf{d}\mathbf{x}_j - \right. \\
& \left. \int \int [\psi_i^*(\mathbf{x}_i) \psi_j^*(\mathbf{x}_j)] \mathbf{V}(\mathbf{i}, \mathbf{j}) [\psi_j(\mathbf{x}_i) \psi_i(\mathbf{x}_j)] \mathbf{d}\mathbf{x}_i \mathbf{d}\mathbf{x}_j \right\} \quad (18)
\end{aligned}$$

So now we plug in the integrals from equations 12 and 18 back into equation 5 and then apply the variational principle as stated before:

$$\begin{aligned}
\langle \psi_{SD} | H | \psi_{SD} \rangle = & \sum_i \int \psi_i^*(\mathbf{x}_i) \mathbf{H}_i(\psi_i(\mathbf{x}_i)) \mathbf{d}\mathbf{x}_i \quad + \\
& \frac{1}{N!} \sum_{i \neq j} \left\{ \int \int [\psi_i^*(\mathbf{x}_i) \psi_j^*(\mathbf{x}_j)] \mathbf{V}(\mathbf{i}, \mathbf{j}) [\psi_i(\mathbf{x}_i) \psi_j(\mathbf{x}_j)] \mathbf{d}\mathbf{x}_i \mathbf{d}\mathbf{x}_j - \right. \\
& \left. \int \int [\psi_i^*(\mathbf{x}_i) \psi_j^*(\mathbf{x}_j)] \mathbf{V}(\mathbf{i}, \mathbf{j}) [\psi_j(\mathbf{x}_i) \psi_i(\mathbf{x}_j)] \mathbf{d}\mathbf{x}_i \mathbf{d}\mathbf{x}_j \right\} \quad (19)
\end{aligned}$$

Also,

$$\delta[\langle \psi_{SD} | H | \psi_{SD} \rangle - \sum_{ij} \lambda_{ij} \langle \psi_i | \psi_j \rangle] = 0$$

$$\begin{aligned}
& \delta_k \Sigma_i \int \psi_i^*(\mathbf{x}_i) \mathbf{H}_i(\psi_i(\mathbf{x}_i)) \mathbf{d}\mathbf{x}_i + \delta_k \left[\frac{1}{N!} \Sigma_{i \neq j} \right. \\
& \left. \left[\int \int [\psi_i^*(\mathbf{x}_i) \psi_j^*(\mathbf{x}_j)] \mathbf{V}(\mathbf{i}, \mathbf{j}) [\psi_i(\mathbf{x}_i) \psi_j(\mathbf{x}_j)] \mathbf{d}\mathbf{x}_i \mathbf{d}\mathbf{x}_j \right. \right. \\
& \left. \left. \int \int [\psi_i^*(\mathbf{x}_i) \psi_j^*(\mathbf{x}_j)] \mathbf{V}(\mathbf{i}, \mathbf{j}) [\psi_j(\mathbf{x}_i) \psi_i(\mathbf{x}_j)] \mathbf{d}\mathbf{x}_i \mathbf{d}\mathbf{x}_j \right] \right] - \\
& \delta_k \Sigma_{ij} \lambda_{ij} \langle \psi_i | \psi_j \rangle = \mathbf{0}
\end{aligned}$$

(20)

1. Note the meaning of the $\Sigma_{i \neq j}$ sign: it says sum over i and sum over j but $i \neq j$. Whereas $\Sigma_{i(\neq j)}$ would mean only sum over i and $i \neq j$ and also don't sum over j.
2. Note that $\delta_k \langle \psi_i | H | \psi_i \rangle = \langle \psi_i | H | \delta_k \psi_i \rangle + \langle \delta_k^* \psi_i | H | \psi_i \rangle = 2 \langle \psi_i | H | \delta_k \psi_i \rangle$ because H is hermitian operator.

$$\begin{aligned}
& \int \delta_k \psi_k^*(\mathbf{x}_k) \mathbf{H}_k(\psi_k(\mathbf{x}_k)) \mathbf{d}\mathbf{x}_k + \left[\frac{1}{N!} \Sigma_{\mathbf{k}(\neq \mathbf{j})} \right. \\
& \mathbf{2} \left[\int \int \delta_k \psi_k^*(\mathbf{x}_k) \psi_j^*(\mathbf{x}_j) \mathbf{V}(\mathbf{k}, \mathbf{j}) \psi_k(\mathbf{x}_k) \psi_j(\mathbf{x}_j) \mathbf{d}\mathbf{x}_k \mathbf{d}\mathbf{x}_j \right. \\
& \left. \left. \int \int \delta_k \psi_k^*(\mathbf{x}_k) \psi_j^*(\mathbf{x}_j) \mathbf{V}(\mathbf{k}, \mathbf{j}) \psi_j(\mathbf{x}_k) \psi_k(\mathbf{x}_j) \mathbf{d}\mathbf{x}_k \mathbf{d}\mathbf{x}_j \right] \right] - \\
& \delta_k \Sigma_{\mathbf{j}} \lambda_{\mathbf{k}\mathbf{j}} \langle \psi_{\mathbf{k}} | \psi_{\mathbf{j}} \rangle = \mathbf{0}
\end{aligned}$$

(21)

Now we demand that $\lambda_{kj} = 0$ iff $k \neq j$. Also that $\lambda_{kj} = \epsilon_j$ iff $k = j$ (Since the λ s are arbitrary) Hence eq 21 becomes :

$$\begin{aligned}
& 2 \int \delta_k \psi_k^*(\mathbf{x}_k) \mathbf{H}_k(\psi_k(\mathbf{x}_k)) \mathbf{d}\mathbf{x}_k + \left[\frac{1}{N!} \Sigma_{\mathbf{j}(\neq \mathbf{k})} \right. \\
& \mathbf{2} \left[\int \int \delta_k \psi_k^*(\mathbf{x}_k) \psi_j^*(\mathbf{x}_j) \mathbf{V}(\mathbf{k}, \mathbf{j}) \psi_k(\mathbf{x}_k) \psi_j(\mathbf{x}_j) \mathbf{d}\mathbf{x}_k \mathbf{d}\mathbf{x}_j \right. \\
& \left. \left. - \int \int \delta_k \psi_k^*(\mathbf{x}_k) \psi_j^*(\mathbf{x}_j) \mathbf{V}(\mathbf{k}, \mathbf{j}) \psi_j(\mathbf{x}_k) \psi_k(\mathbf{x}_j) \mathbf{d}\mathbf{x}_k \mathbf{d}\mathbf{x}_j \right] \right] \\
& = \delta_k \epsilon_j \langle \psi_{\mathbf{k}} | \psi_{\mathbf{j}} \rangle \\
& = \mathbf{2} \epsilon_j \int \delta_k \psi_k^* \psi_j \mathbf{d}\mathbf{x}_k
\end{aligned}$$

Since we can take $\delta_k \psi_k^*$ where δ_k is arbitrary hence the rest of the integrand must be zero:

$$\begin{aligned}
& H_k(\psi_k(\mathbf{x}_k)) + \frac{1}{N!} \Sigma_{\mathbf{j}(\neq \mathbf{k})} \int \psi_j^*(\mathbf{x}_j) \mathbf{V}(\mathbf{k}, \mathbf{j}) \psi_k(\mathbf{x}_k) \psi_j(\mathbf{x}_j) \mathbf{d}\mathbf{x}_j - \\
& \frac{1}{N!} \Sigma_{\mathbf{j}(\neq \mathbf{k})} \int \psi_j^*(\mathbf{x}_j) \mathbf{V}(\mathbf{k}, \mathbf{j}) \psi_j(\mathbf{x}_k) \psi_k(\mathbf{x}_j) \mathbf{d}\mathbf{x}_j \\
& = \epsilon_j \psi_k(\mathbf{x}_k)
\end{aligned} \tag{22}$$

The first term is called the DIRECT integral and the second one is called EXCHANGE integral. Note how the x_i and x_j are exchanged in the ψ s of the second term.

EXCHANGE INTEGRAL AND ITS INTERPRETATION

PROPERTIES OF THE EXCHANGE OPERATOR

DEFINITION We define the EXCHANGE operator only when it operates on a function ψ , as:

$$(23) \quad H_{ex}\psi_k(\mathbf{x}_k) = - \sum_{\mathbf{j}} \int \psi_{\mathbf{j}}^*(\mathbf{x}_{\mathbf{j}}) \mathbf{V}(\mathbf{k}, \mathbf{j}) \psi_{\mathbf{j}}(\mathbf{x}_{\mathbf{k}})\psi_{\mathbf{k}}(\mathbf{x}_{\mathbf{j}})d\mathbf{x}_{\mathbf{j}}$$

HERMITICITY It can be shown that, $\langle l|H_{ex}|m \rangle^* = \langle m|H_{ex}|l \rangle$

PROOF:

$$\begin{aligned} & \left[- \sum_{\mathbf{j}} \int u_l(\mathbf{x}_{\mathbf{j}}) \int \psi_{\mathbf{j}}^*(\mathbf{x}_{\mathbf{j}}) \mathbf{V}(\mathbf{k}, \mathbf{j}) \psi_{\mathbf{j}}(\mathbf{x}_{\mathbf{k}})\psi_{\mathbf{k}}(\mathbf{x}_{\mathbf{j}})d\mathbf{x}_{\mathbf{j}} d\mathbf{x}_{\mathbf{k}} \right]^* \\ &= - \sum_{\mathbf{j}} \int u_l(\mathbf{x}_{\mathbf{j}}) \int \psi_{\mathbf{j}}^*(\mathbf{x}_{\mathbf{j}}) \mathbf{V}(\mathbf{k}, \mathbf{j}) \psi_{\mathbf{j}}(\mathbf{x}_{\mathbf{k}})u_m(\mathbf{x}_{\mathbf{j}})d\mathbf{x}_{\mathbf{j}}d\mathbf{x} \end{aligned}$$

Consequence: In equation 22 now we can see that all operators are hermitian , as a result ϵ_j on r.h.s. of the eqn should be real.

Comparing Hartree and Hartree Fock Approximations

THE FERMI HOLE

The wave function ψ has both spatial and spin functions : $\psi = u(\mathbf{r})\alpha(\mathbf{w})$

So once again we not the exchange term as given in equation 23

The integral right now denotes integration over both spin and spatial coordinates. We can rewrite this as

$$H_{ex}\psi_k(x_k) = - \sum_{j(\hat{i})} \int \psi_j^*(\mathbf{x}_{\mathbf{j}}) \mathbf{V}(\mathbf{k}, \mathbf{j}) \psi_{\mathbf{j}}(\mathbf{x}_{\mathbf{k}})\psi_{\mathbf{k}}(\mathbf{x}_{\mathbf{j}})d\mathbf{x}_{\mathbf{j}}$$

Note $j(\hat{i})$ represents summation over only those j whose spin is parallel to i . Lets assume coulombic interactions, then $V(i, j) = \frac{e^2}{r_{ij}}$

We write the Exchange Integral as $H_{ex}\psi_k(x_k) = - \sum_{j(\hat{i})} \int \frac{e^2}{r_{ij}} \left[\frac{\psi_k(x_k)}{\psi_k(x_k)} \psi_j^*(\mathbf{x}_{\mathbf{j}}) \psi_{\mathbf{j}}(\mathbf{x}_{\mathbf{k}})\psi_{\mathbf{k}}(\mathbf{x}_{\mathbf{j}}) \right] d\mathbf{x}_{\mathbf{j}}$

So,

$$H_{ex}\psi_k(x_k) = - \sum_{j(\hat{i})} \int \frac{e^2}{r_{ij}} \psi_k(x_k) \left[\frac{\psi_j^*(\mathbf{x}_{\mathbf{j}}) \psi_{\mathbf{j}}(\mathbf{x}_{\mathbf{k}})\psi_{\mathbf{k}}(\mathbf{x}_{\mathbf{j}})}{\psi_k(x_k)} \right] d\mathbf{x}_{\mathbf{j}}$$

Hence we define $\rho(j, k)$ such that

$$\rho(j, k) = e \sum_{j(\hat{i})} \left[\frac{\psi_j^*(\mathbf{x}_{\mathbf{j}}) \psi_{\mathbf{j}}(\mathbf{x}_{\mathbf{k}})\psi_{\mathbf{k}}(\mathbf{x}_{\mathbf{j}})}{\psi_k(x_k)} \right]$$

and

$$H_{ex}\psi_k(x_k) = \int \frac{-e}{r_{ij}} \psi_k(\mathbf{x}_{\mathbf{k}})\rho(\mathbf{j}, \mathbf{k}) d\mathbf{x}_{\mathbf{j}}$$

]

This form of the exchange integral may be interpreted as interaction of the electron at $\mathbf{x}(\mathbf{k})$ with the average potential field created by all the electrons.

Physically the direct term implies the interaction of the electron at $\mathbf{x}(\mathbf{k})$ with the average field. But this also includes 'Self Interaction terms' .

If you note , the exchange term is nothing but opposite in sign and same in magnitude to sum of charge density of parallel spin electrons. Hence... The exchange term accounts for (i)removal of this self interacting term in the direct integral. (ii)It also cancels out interaction of parallel spin in neighbourhood of $\mathbf{x}(\mathbf{k})$.

We interpret this cancellation of parallel spins as some kind of screening effect and say that there exists an "Exchange charge hole" or the "Fermi Hole" around electron with given spin at point $\mathbf{x}(\mathbf{k})$.

Density Functional Theory:

Consider a system of n electrons under the influence of external potentials v_{ext} , which give nondegenerate ground states ψ_o and corresponding densities ρ_o . Then, consider the following sets,

$$V = \{v_{ext} | v'_{ext} \neq v_{ext} + \text{constant}\}$$

set of all external potentials that do not differ by constant ,

$$G = \{\psi_o | \psi'_o \neq e^{i\phi} \psi_o, \phi : \text{global phase}\}$$

i.e, set of all nondegenerate groundstates corresponding to each $v_{ext} \in V$ that do not differ by a global phase,

$$D = \{\rho_o | \rho_o = \int \psi_o^* \psi_o dV, \forall \psi_o \in G\}$$

the set of densities corresponding to each element of G . Then, by construction, the maps we have defined from V to G and from G to D are surjective. The question is whether they are injective, i.e, if two v_{ext} s that do not differ by a constant can have the same ψ_o (ground state wave function) and if two ground state wave functions that do not differ by a global phase belonging to G can have the same density.

Theorem (Hohenberg-Kohn): The map that associates each v_{ext} in V to the corresponding $\psi_o \in G$ is injective, i.e, two unequal v_{ext} s in V cannot give the same $\psi_o \in G$. Again, the map that associates a groundstate wavefunction in G to its corresponding density in D is injective, i.e, two unequal elements of G cannot have the same density.

Taking both maps together, one has a one-to-one correspondence between the external potential v_{ext} in the Hamiltonian, the (non-degenerate) ground state ψ_0 resulting from solution of the Schrodinger equation and the associated ground state density ρ_0 . Taking both maps together, one has a one-to-one correspondence between the external potential v_{ext} in the Hamiltonian, the (non-degenerate) ground state ψ_0 resulting from solution of Schrödinger equation and the associated ground state density ρ_0 . Thus v_{ext} , ψ_0 and ρ_0 determine each other uniquely. In mathematical terms: the ground state is a unique functional of the ground state density, denoted as $\Psi[\rho]$. Upon insertion of one element $\rho_0 \in D$, this functional yields the ground state ψ_0 associated with this particular ρ_0 , $\psi_0 = \Psi[\rho_0]$. Note that no explicit information on v_{ext} is required to construct ψ_0 from ρ_0 . Ψ has the same functional form for all kinds of many-particle systems with the same interaction. The same functional Ψ applies to atoms, molecules and solids. The particular geometry of the systems under consideration is mediated by the structure of the density. $\Psi[\rho]$ is therefore called universal.

The existence of the functional $\Psi[\rho]$ leads to the statement that any ground state observable is a density functional, $O[\rho] = \langle \Psi[\rho] | \hat{O} | \Psi[\rho] \rangle$. This is true, in particular, for the ground state energy, which turns out to be the most important density functional, $E[\rho] = \langle \Psi[\rho] | \hat{H}_{self} + \hat{v}_{ext} | \Psi[\rho] \rangle = H_{self}[\rho] + v_{ext}[\rho]$, where, $H_{self}[\rho]$ is the universal part of the total energy functional. There exists a minimum principle for $E[\rho_0]$. If ρ_0 is the ground state density corresponding to v_{ext} , one has for all densities $\rho'_0(\mathbf{r}) \neq \rho_0(\mathbf{r})$, $E[\rho'_0] > E[\rho_0]$. This is a direct consequence of the unique relation between ρ_0 and ψ_0 and the Ritz variational principle.

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