Approximate Methods in Quantum Chemistry
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Lecture- 29
Self-Consistent Field Method

Hello students! Welcome to this lecture. So far, we have looked at two different approximate methods, variational principle and perturbation theory. In today's lecture, we will discuss yet another approximate method using which we would try to solve *N*-electron systems. The name of this method is the self-consistent field method.

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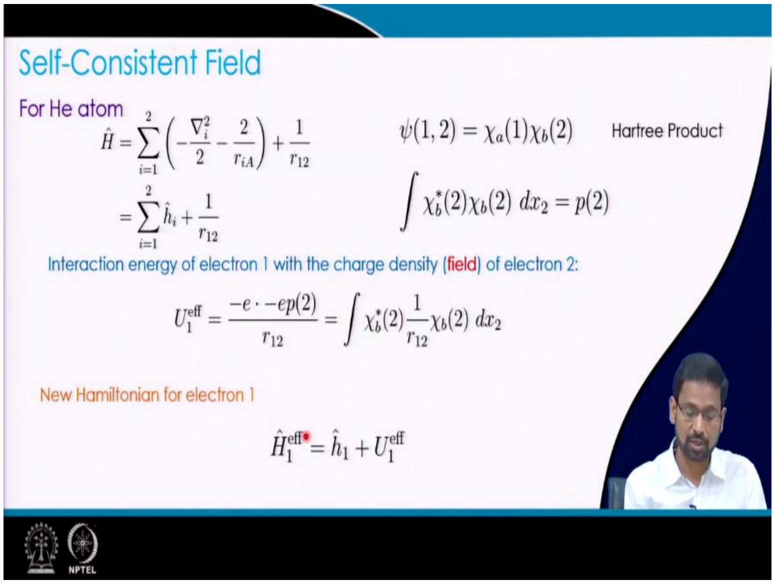

Self-Consistent Field

For He atom

$$\hat{H} = \sum_{i=1}^{2}\left(-\frac{\nabla_i^2}{2} - \frac{2}{r_{iA}}\right) + \frac{1}{r_{12}}$$
$$= \sum_{i=1}^{2}\hat{h}_i + \frac{1}{r_{12}}$$

$\psi(1,2) = \chi_a(1)\chi_b(2)$ Hartree Product

$$\int \chi_b^*(2)\chi_b(2)\,dx_2 = p(2)$$

Interaction energy of electron 1 with the charge density (field) of electron 2:

$$U_1^{\text{eff}} = \frac{-e\cdot -ep(2)}{r_{12}} = \int \chi_b^*(2)\frac{1}{r_{12}}\chi_b(2)\,dx_2$$

New Hamiltonian for electron 1

$$\hat{H}_1^{\text{eff}} = \hat{h}_1 + U_1^{\text{eff}}$$

Before we generalize it to larger systems, let us first keep our discussion restricted to a two-electronic system, the helium atom. The Hamiltonian of He atom has got two one-electron operators corresponding to each electron and one two-electron operator.

$$\hat{H} = \sum_{i=1}^{2}\left(-\frac{\nabla_i^2}{2} - \frac{2}{r_{iA}}\right) + \frac{1}{r_{12}}$$
$$= \sum_{i=1}^{2}\hat{h}_i + \frac{1}{r_{12}}$$

We have treated He atom with both variational and perturbation theory. In case of variational method, we made a guess trial function and tried to minimize the energy. In perturbation theory, we expressed the two-electron operator as the perturbation and obtained 1st order energy correction using the perturbation Hamiltonian and unperturbed wave functions. In the self-consistent field (SCF) method, we take a different approach to arrive at the final solution.

Let us consider the following Hartree product

$$\psi(1,2) = \chi_a(1)\chi_b(2)$$

where the $\chi_a(1)$ and $\chi_b(2)$ are two 1-electron spinorbitals. We can write down the probability density distribution related to electron in χ_b spinorbital as,

$$\int \chi_b^*(2)\chi_b(2)\ dx_2 = p(2)$$

If we multiply -*e* to the above expression, it would result in the electron charge density corresponding to electron 2. This electron charge density can interact with electron 1 through Coulomb interaction as following,

$$U_1^{\text{eff}} = \frac{-e \cdot -ep(2)}{r_{12}} = \int \chi_b^*(2)\frac{1}{r_{12}}\chi_b(2)\ dx_2$$

Where, r_{12} is the inter-electron distance. The above expression is in atomic units (e = 1 au). U_1^{eff} is effective electron-electron interaction experienced by electron 1 due to the charge density of electron 2. U_1^{eff} is a 1-electron operator with explicit dependence on electron 1, since the dependence on electron 2 is integrated out in the above expression. Now, the Hamiltonian corresponding to electron 1 can be written as, $\hat{H}_1^{\text{eff}} = \hat{h}_1 + U_1^{\text{eff}}$

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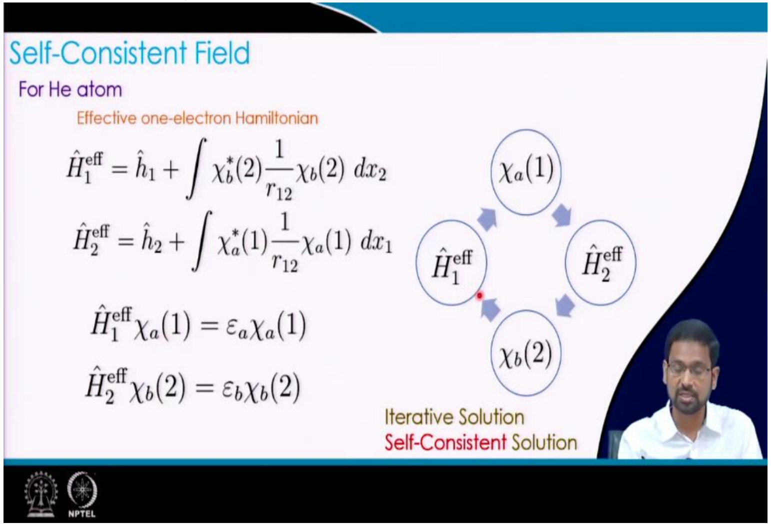

Self-Consistent Field

For He atom

Effective one-electron Hamiltonian

$$\hat{H}_1^{\text{eff}} = \hat{h}_1 + \int \chi_b^*(2)\frac{1}{r_{12}}\chi_b(2)\ dx_2$$

$$\hat{H}_2^{\text{eff}} = \hat{h}_2 + \int \chi_a^*(1)\frac{1}{r_{12}}\chi_a(1)\ dx_1$$

$$\hat{H}_1^{\text{eff}}\chi_a(1) = \varepsilon_a\chi_a(1)$$

$$\hat{H}_2^{\text{eff}}\chi_b(2) = \varepsilon_b\chi_b(2)$$

Iterative Solution

Self-Consistent Solution

Similar to the effective 1-electron Hamiltonian (H_1^{eff}) for electron number 1, we can also construct (H_2^{eff}) using the charge density of electron 1 and its interaction with electron 2, i.e.,

$$\hat{H}_2^{\text{eff}} = \hat{h}_2 + \int \chi_a^*(1) \frac{1}{r_{12}} \chi_a(1)\ dx_1$$

Since both H_1^{eff} and H_2^{eff} are 1-electron operators, in principle, we can solve the following equations,

$$\hat{H}_1^{\text{eff}} \chi_a(1) = \varepsilon_a \chi_a(1) \qquad \hat{H}_2^{\text{eff}} \chi_b(2) = \varepsilon_b \chi_b(2)$$

The above two equations appear as standard eigenvalue problem, but there is something very interesting hidden there. The solution of the 1st equation gives us $\chi_a(1)$ and ϵ_a. To solve the 1st equation, we need H_1^{eff} which depends on U_1^{eff} and which in turn depends $\chi_b(2)$. How do we get, $\chi_b(2)$? We get it from the solution of the 2nd equation. But to solve the 2nd equation, we need to know U_2^{eff} which requires us to know on $\chi_a(1)$.

This leaves us in a tricky situation where we need to know the solution ($\chi_a(1)$) before we can start solving the problem (H_1^{eff}). Such a problem can be solved by adopting an iterative method or in a self-consistent manner. In this approach, we first make a guess for $\chi_a(1)$ and $\chi_b(2)$; then construct H_1^{eff} and H_2^{eff} ; then solve the 1-electron operators to obtain $\chi_a(1)$ and $\chi_b(2)$. We then use these functions to construct effective Hamiltonian and repeat the entire process. The process is repeated until convergence, i.e., until the old set of $\chi_a(1)$ and $\chi_b(2)$ and new set of $\chi_a(1)$ and $\chi_b(2)$ are the same. This approach is called self-consistent field method.

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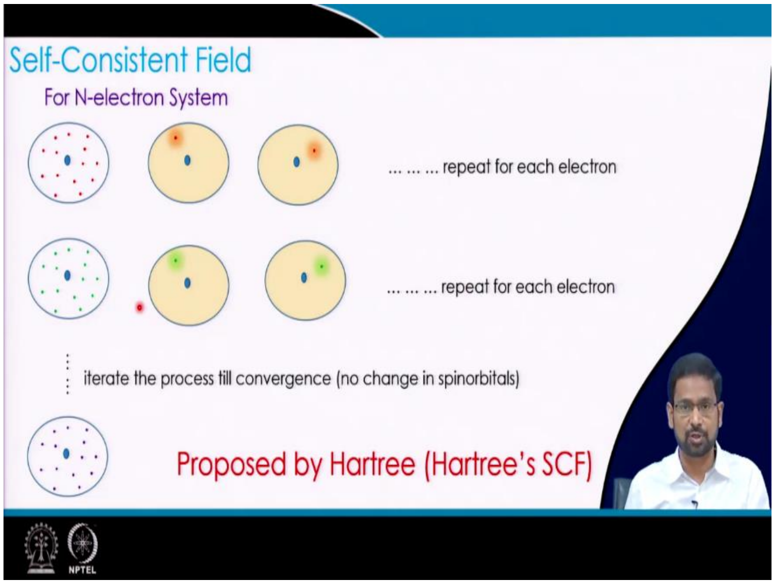

Self-Consistent Field

For N-electron System

… … … repeat for each electron

… … … repeat for each electron

iterate the process till convergence (no change in spinorbitals)

Proposed by Hartree (Hartree's SCF)

Now, we can generalize the process for *N*-electron system. In the schematic diagram above, the blue dots represent the central nucleus (or collection of nuclei in a molecule) and the red dots are electrons. We start with a guess for all spinorbitals $\{\chi_a(i)\}$. We consider electron 1 as a particle and the rest of the *N*-1 electrons as a field (shown by the yellow shade in the circle). Similarly, we treat electron 2, 3, ….*N*-1. In each case, we consider one electron as a particle and the rest as charge cloud. We solve each of these effective 1-electron operators and obtain a new set of spinorbitals $\{\chi'_a(i)\}$. We repeat the process with the spinorbitals $\{\chi'_a(i)\}$ and obtain a new set of spinorbitals $\{\chi''_a(i)\}$. This process is repeated until we observe no change in the spinorbitals of iteration *n* and *n*+1. In such a case, we consider the final spinorbitals as the converged set of spinorbitals.

Compared to variational principle and perturbation theory, the SCF method is quite different in its approach to obtain the wave function and energy of an *N*-electron system. This approach was first proposed by Hartree. Hence it is also known as Hartree's SCF method. Slater and Gaunt translated this concept to real system and formulated this approach in the language of variational principle. One limitation of Hartree's initial approach was to consider the Hartree product as the N-electron wave function.

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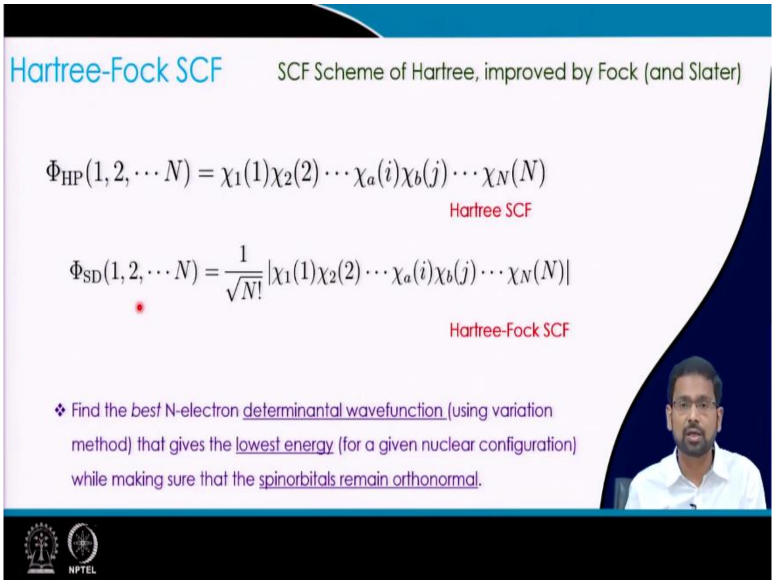

Hartree-Fock SCF

SCF Scheme of Hartree, improved by Fock (and Slater)

$$\Phi_{\mathrm{HP}}(1,2,\cdots N) = \chi_1(1)\chi_2(2)\cdots\chi_a(i)\chi_b(j)\cdots\chi_N(N)$$

Hartree SCF

$$\Phi_{\mathrm{SD}}(1,2,\cdots N) = \frac{1}{\sqrt{N!}}\left|\chi_1(1)\chi_2(2)\cdots\chi_a(i)\chi_b(j)\cdots\chi_N(N)\right|$$

Hartree-Fock SCF

- Find the *best* N-electron determinantal wavefunction (using variation method) that gives the lowest energy (for a given nuclear configuration) while making sure that the spinorbitals remain orthonormal.

Slater and Fock carried out Hartree's SCF method by using the Slater determinant instead of Hartree product as the N-electron wave function. This approach (where Slater determinant is used as the N-electron wave function) is called Hartree-Fock SCF. Next important step is to formulate the SCF approach as a variational method. Here the target of an SCF calculation is to find the best *N*-electron determinantal wavefunction (using variation method) that gives the lowest energy (for a given nuclear configuration) while making sure that the spinorbitals remain orthonormal. The nuclei are kept frozen since we are working within the Born-Oppenheimer approximation.

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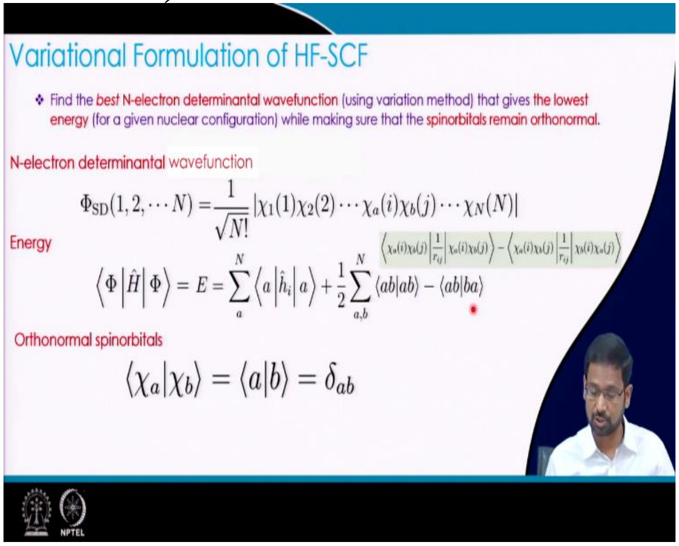

Variational Formulation of HF-SCF

- Find the *best* N-electron determinantal wavefunction (using variation method) that gives the lowest energy (for a given nuclear configuration) while making sure that the spinorbitals remain orthonormal.

N-electron determinantal wavefunction

$$\Phi_{\mathrm{SD}}(1,2,\cdots N) = \frac{1}{\sqrt{N!}}\left|\chi_1(1)\chi_2(2)\cdots\chi_a(i)\chi_b(j)\cdots\chi_N(N)\right|$$

Energy

$$\left\langle \chi_a(i)\chi_b(j)\left|\frac{1}{r_{ij}}\right|\chi_a(i)\chi_b(j)\right\rangle - \left\langle \chi_a(i)\chi_b(j)\left|\frac{1}{r_{ij}}\right|\chi_b(i)\chi_a(j)\right\rangle$$

$$\left\langle \Phi\left|\hat{H}\right|\Phi\right\rangle = E = \sum_{a}^{N}\left\langle a\left|\hat{h}_i\right|a\right\rangle + \frac{1}{2}\sum_{a,b}^{N}\langle ab|ab\rangle - \langle ab|ba\rangle$$

Orthonormal spinorbitals

$$\langle\chi_a|\chi_b\rangle = \langle a|b\rangle = \delta_{ab}$$

Now the task in hand is to obtain a variational formulation of the Hartree-Fock SCF, i.e., to find out the Slater determinant that minimizes the energy while retaining the orthonormality of the spinorbitals.

Let us consider the following N-electron Slater determinant in terms of the set of orthonormal spinorbitals $\{\chi_a\}$,

$$\Phi_{\mathrm{SD}}(1, 2, \cdots N) = \frac{1}{\sqrt{N!}} |\chi_1(1)\chi_2(2)\cdots\chi_a(i)\chi_b(j)\cdots\chi_N(N)|$$

Where $$\langle\chi_a|\chi_b\rangle = \langle a|b\rangle = \delta_{ab}$$

The energy expectation value corresponding to the above Slater determinant is given by,

$$\left\langle \Phi \left| \hat{H} \right| \Phi \right\rangle = E = \sum_{a}^{N} \left\langle a \left| \hat{h}_i \right| a \right\rangle + \frac{1}{2}\sum_{a,b}^{N} \langle ab|ab\rangle - \langle ab|ba\rangle$$

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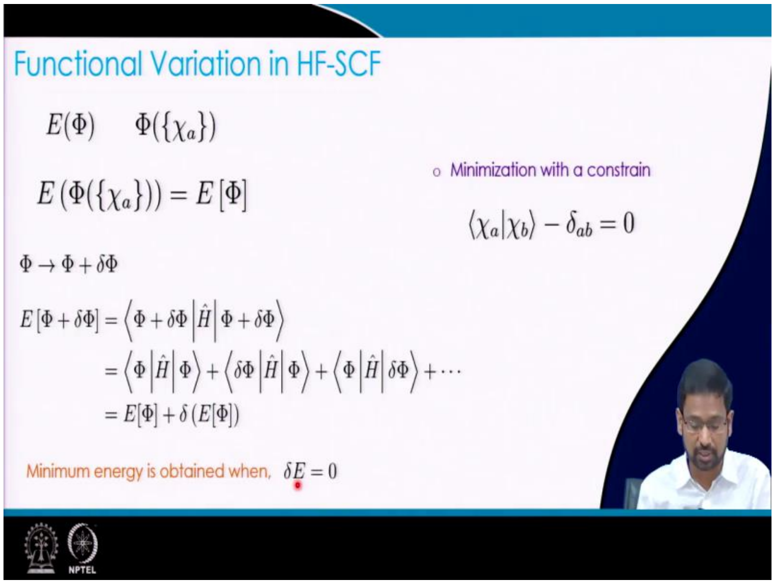

Functional Variation in HF-SCF

$E(\Phi) \quad \Phi(\{\chi_a\})$

$E\left(\Phi(\{\chi_a\})\right) = E\left[\Phi\right]$

- Minimization with a constrain

$\langle\chi_a|\chi_b\rangle - \delta_{ab} = 0$

$\Phi \to \Phi + \delta\Phi$

$$\begin{aligned} E\left[\Phi + \delta\Phi\right] &= \left\langle \Phi + \delta\Phi \left| \hat{H} \right| \Phi + \delta\Phi \right\rangle \\ &= \left\langle \Phi \left| \hat{H} \right| \Phi \right\rangle + \left\langle \delta\Phi \left| \hat{H} \right| \Phi \right\rangle + \left\langle \Phi \left| \hat{H} \right| \delta\Phi \right\rangle + \cdots \\ &= E[\Phi] + \delta\left(E[\Phi]\right) \end{aligned}$$

Minimum energy is obtained when, $\delta E = 0$

Next step is to minimize the energy. Here, the energy is a function of the Slater determinant $E(\Phi)$, and the Slater determinant is a function of the spinorbitals $\Phi(\chi_a)$. Hence, the energy is a function of a function of the spinorbitals, i.e., $\mathrm{E}(\Phi(\chi_a))$. In other words, the energy is a functional of the Slater determinant, denoted by $E[\Phi]$. To minimize energy with respect to the Slater determinant, we need to carry out the so-called functional variation.

For a small change in Φ, i.e., $\Phi \rightarrow \Phi + \delta\Phi$, the energy changes as following

$$\begin{aligned} E\left[\Phi+\delta\Phi\right] &= \left\langle \Phi+\delta\Phi \left| \hat{H} \right| \Phi+\delta\Phi \right\rangle \\ &= \left\langle \Phi \left| \hat{H} \right| \Phi \right\rangle + \left\langle \delta\Phi \left| \hat{H} \right| \Phi \right\rangle + \left\langle \Phi \left| \hat{H} \right| \delta\Phi \right\rangle + \cdots \\ &= E[\Phi] + \delta\left(E[\Phi]\right) \end{aligned}$$

The second term $\delta(E[\Phi])$ is known as the first variation (similar to first derivative). Since we aim to find that Φ which minimizes the energy, for the minimum energy Φ, the first variation must vanish, i.e., $\delta(E[\Phi]) = 0$.

Another important thing to keep in mind that we not only want to minimize the energy, but while doing so we must preserve the orthonormality of the spinorbitals. This minimization, therefore, is not an ordinary minimization, rather minimization with a constrain. In this case, the constrain is $\langle \chi_a | \chi_b \rangle - \delta_{ab} = 0$

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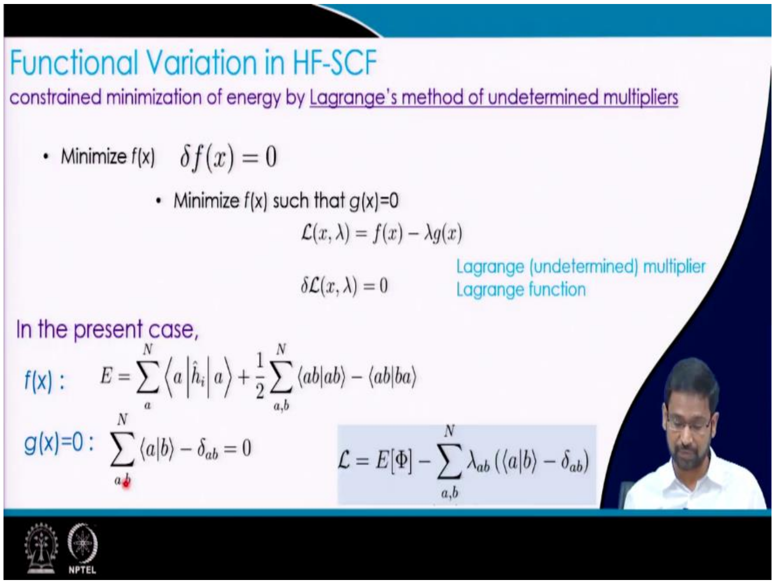

Functional Variation in HF-SCF

constrained minimization of energy by Lagrange's method of undetermined multipliers

- Minimize f(x) $\delta f(x) = 0$
  - Minimize f(x) such that g(x)=0

$$\mathcal{L}(x,\lambda) = f(x) - \lambda g(x)$$

$$\delta\mathcal{L}(x,\lambda) = 0$$

Lagrange (undetermined) multiplier
Lagrange function

In the present case,

f(x) : $E = \sum_{a}^{N} \left\langle a \left| \hat{h}_i \right| a \right\rangle + \frac{1}{2}\sum_{a,b}^{N} \langle ab|ab\rangle - \langle ab|ba\rangle$

g(x)=0 : $\sum_{a,b}^{N} \langle a|b\rangle - \delta_{ab} = 0$

$$\mathcal{L} = E[\Phi] - \sum_{a,b}^{N} \lambda_{ab}\left(\langle a|b\rangle - \delta_{ab}\right)$$

Now, we will discuss a technique for constrained minimization, using the poplular Lagrange's method of undetermined multipliers technique. If we want to carry out an ordinary minimization of a function $f(x)$, we will ensure $\delta f(x) = 0$. If we have an additional constrain ($g(x)$=0) while doing the minimization, we need to define a new function (Lagrange function) $\mathcal{L}(x,\lambda) = f(x) - \lambda g(x)$

and ensure $\delta\mathcal{L}(x,\lambda) = 0$

Here, λ is the undetermined multiplier.

In the HF-SCF case, the function to be minimized is the energy expectation value, i.e., $f(x) = E$, where

$$E = \sum_{a}^{N} \left\langle a \left| \hat{h}_i \right| a \right\rangle + \frac{1}{2} \sum_{a,b}^{N} \langle ab|ab\rangle - \langle ab|ba\rangle$$

The constrain ($g(x) = 0$) is

$$\sum_{a,b}^{N} \langle a|b\rangle - \delta_{ab} = 0$$

Hence, the Lagrange function is

$$\mathcal{L} = E[\Phi] - \sum_{a,b}^{N} \lambda_{ab} \left(\langle a|b\rangle - \delta_{ab} \right)$$

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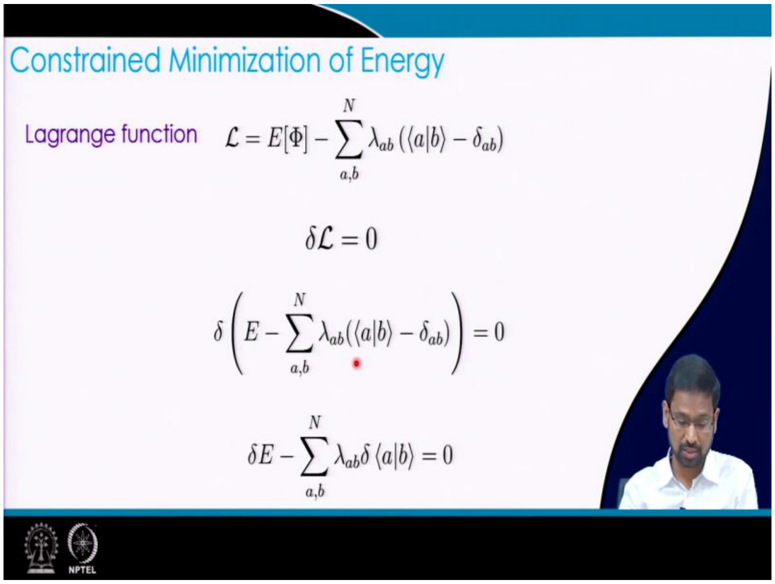

Constrained Minimization of Energy

Lagrange function $\mathcal{L} = E[\Phi] - \sum_{a,b}^{N} \lambda_{ab} \left(\langle a|b\rangle - \delta_{ab} \right)$

$$\delta\mathcal{L} = 0$$

$$\delta \left(E - \sum_{a,b}^{N} \lambda_{ab} (\langle a|b\rangle - \delta_{ab}) \right) = 0$$

$$\delta E - \sum_{a,b}^{N} \lambda_{ab} \delta \langle a|b\rangle = 0$$

For this constrained minimization problem, we need to have $\delta\mathcal{L} = 0$

In other words,

$$\delta\left(E - \sum_{a,b}^{N} \lambda_{ab}(\langle a|b\rangle - \delta_{ab})\right) = 0$$

Here, λ_{ab} is the undetermined multiplier. Since δ_{ab} is a constant (either 1 or 0), we have the following equation to solve,

$$\delta E - \sum_{a,b}^{N} \lambda_{ab}\delta\,\langle a|b\rangle = 0$$

The first term is the first variation of the energy and the second term is the first variation of the overlap integral.

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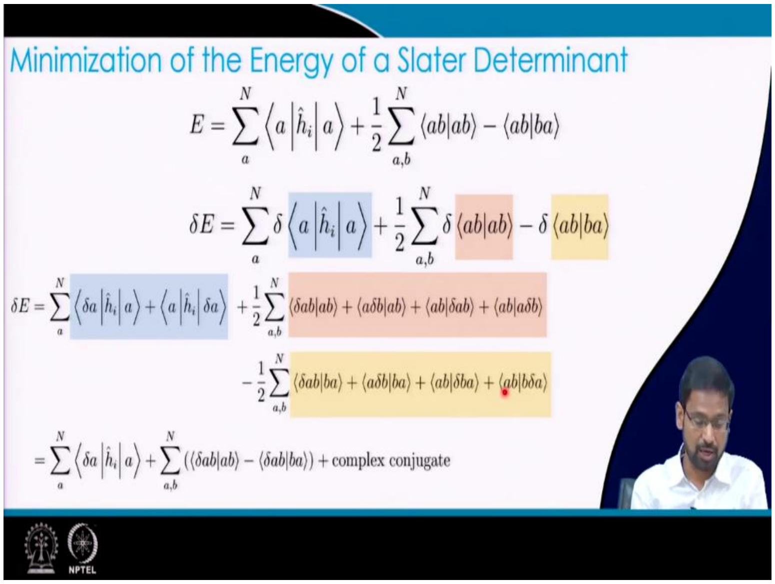

Minimization of the Energy of a Slater Determinant

$$E = \sum_{a}^{N}\left\langle a\left|\hat{h}_i\right|a\right\rangle + \frac{1}{2}\sum_{a,b}^{N}\langle ab|ab\rangle - \langle ab|ba\rangle$$

$$\delta E = \sum_{a}^{N}\delta\left\langle a\left|\hat{h}_i\right|a\right\rangle + \frac{1}{2}\sum_{a,b}^{N}\delta\,\langle ab|ab\rangle - \delta\,\langle ab|ba\rangle$$

$$\delta E = \sum_{a}^{N}\left\langle \delta a\left|\hat{h}_i\right|a\right\rangle + \left\langle a\left|\hat{h}_i\right|\delta a\right\rangle + \frac{1}{2}\sum_{a,b}^{N}\langle\delta ab|ab\rangle + \langle a\delta b|ab\rangle + \langle ab|\delta ab\rangle + \langle ab|a\delta b\rangle$$

$$-\frac{1}{2}\sum_{a,b}^{N}\langle\delta ab|ba\rangle + \langle a\delta b|ba\rangle + \langle ab|\delta ba\rangle + \langle ab|b\delta a\rangle$$

$$= \sum_{a}^{N}\left\langle \delta a\left|\hat{h}_i\right|a\right\rangle + \sum_{a,b}^{N}(\langle\delta ab|ab\rangle - \langle\delta ab|ba\rangle) + \text{complex conjugate}$$

Let us first consider the first variation of the energy, i.e.,

$$\delta E = \sum_{a}^{N}\delta\left\langle a\left|\hat{h}_i\right|a\right\rangle + \frac{1}{2}\sum_{a,b}^{N}\delta\,\langle ab|ab\rangle - \delta\,\langle ab|ba\rangle$$

if we expand all the terms we get,

$$\delta E = \sum_{a}^{N}\left\langle \delta a\left|\hat{h}_i\right|a\right\rangle + \left\langle a\left|\hat{h}_i\right|\delta a\right\rangle + \frac{1}{2}\sum_{a,b}^{N}\langle\delta ab|ab\rangle + \langle a\delta b|ab\rangle + \langle ab|\delta ab\rangle + \langle ab|a\delta b\rangle$$

$$-\frac{1}{2}\sum_{a,b}^{N}\langle\delta ab|ba\rangle + \langle a\delta b|ba\rangle + \langle ab|\delta ba\rangle + \langle ab|b\delta a\rangle$$

If you look carefully, you would find that the 1st two terms (in the 1-electron integrals) are complex conjugates of each other. Now, let us look at the 4 terms within the Coulomb integral. The 1st and 3rd as well as the 2nd and 4th terms (in the Coulomb integral) are complex conjugates of each other. The first two terms within the sum are equivalent and so are the last two terms. Multiplying these terms with ½ further simplifies the Coulomb integrals. Similar simplification can be done for the 4 exchange integral terms. At the end of this exercise, we obtain δE as

$$= \sum_{a}^{N} \left\langle \delta a \left| \hat{h}_i \right| a \right\rangle + \sum_{a,b}^{N} \left(\langle \delta ab | ab \rangle - \langle \delta ab | ba \rangle \right) + \text{complex conjugate}$$

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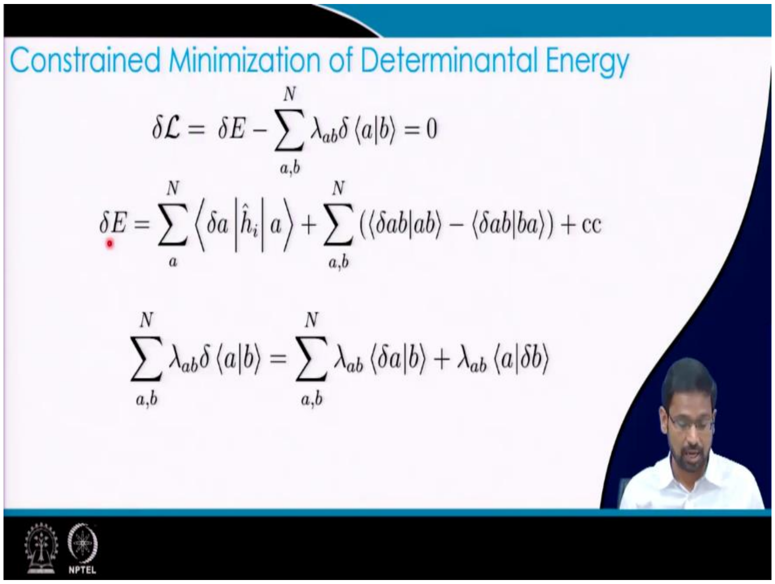

Constrained Minimization of Determinantal Energy

$$\delta\mathcal{L} = \delta E - \sum_{a,b}^{N} \lambda_{ab}\delta \langle a|b\rangle = 0$$

$$\delta E = \sum_{a}^{N} \left\langle \delta a \left| \hat{h}_i \right| a \right\rangle + \sum_{a,b}^{N} \left(\langle \delta ab | ab \rangle - \langle \delta ab | ba \rangle \right) + \mathrm{cc}$$

$$\sum_{a,b}^{N} \lambda_{ab}\delta \langle a|b\rangle = \sum_{a,b}^{N} \lambda_{ab} \langle \delta a|b\rangle + \lambda_{ab} \langle a|\delta b\rangle$$

For the constrained minimization, we need to solve the following equation

$$\delta\mathcal{L} = \delta E - \sum_{a,b}^{N} \lambda_{ab}\delta \langle a|b\rangle = 0$$

We have already obtained the first variation of energy (E) and now we can obtain the first variation of the constrain condition (orthonormality of the spinorbitals), i.e.,

$$\sum_{a,b}^{N} \lambda_{ab}\delta \langle a|b\rangle = \sum_{a,b}^{N} \lambda_{ab} \langle \delta a|b\rangle + \lambda_{ab} \langle a|\delta b\rangle$$

In this lecture, we have formulated the variational treatment of the HF-SCF approach. We will continue our discussion in the next lecture.

Thank you for your attention.