Approximate Methods in Quantum Chemistry
Professor Sabyashachi Mishra
Department of Chemistry
Indian Institute of Technology, Kharagpur
Lecture-31
Hartree-Fock Energy

Hello students! Welcome to this lecture. In the last lecture we discussed about the Hartree-Fock equations. In this lecture we will learn more about the Hartree-Fock energy.

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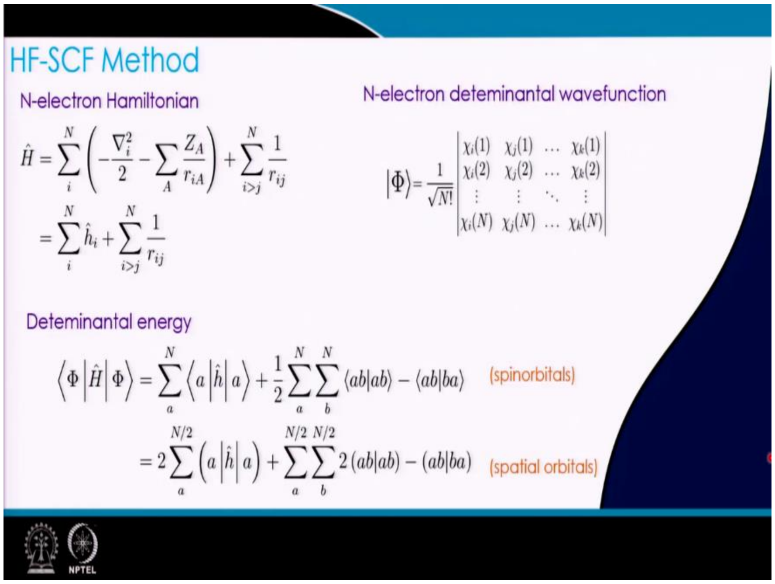

HF-SCF Method

N-electron Hamiltonian

$$\hat{H} = \sum_{i}^{N}\left(-\frac{\nabla_i^2}{2} - \sum_{A}\frac{Z_A}{r_{iA}}\right) + \sum_{i>j}^{N}\frac{1}{r_{ij}}$$

$$= \sum_{i}^{N}\hat{h}_i + \sum_{i>j}^{N}\frac{1}{r_{ij}}$$

N-electron deteminantal wavefunction

$$|\Phi\rangle = \frac{1}{\sqrt{N!}}\begin{vmatrix} \chi_i(1) & \chi_j(1) & \cdots & \chi_k(1) \\ \chi_i(2) & \chi_j(2) & \cdots & \chi_k(2) \\ \vdots & \vdots & \ddots & \vdots \\ \chi_i(N) & \chi_j(N) & \cdots & \chi_k(N) \end{vmatrix}$$

Deteminantal energy

$$\left\langle \Phi \left| \hat{H} \right| \Phi \right\rangle = \sum_{a}^{N}\left\langle a \left| \hat{h} \right| a \right\rangle + \frac{1}{2}\sum_{a}^{N}\sum_{b}^{N}\langle ab|ab\rangle - \langle ab|ba\rangle \quad \text{(spinorbitals)}$$

$$= 2\sum_{a}^{N/2}\left(a \left| \hat{h} \right| a \right) + \sum_{a}^{N/2}\sum_{b}^{N/2} 2\,(ab|ab) - (ab|ba) \quad \text{(spatial orbitals)}$$

For an N-electron system the Hamiltonian is composed of some 1-electron and 2-electron operators. The wave function of the N-electron system can be expressed as a Slater determinant defined in terms of N-orthonormal spinorbitals. The energy expectation value when the wave function is given by a Slater determinant is given by

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

$$= 2\sum_{a}^{N/2}\left(a \left| \hat{h} \right| a \right) + \sum_{a}^{N/2}\sum_{b}^{N/2} 2\,(ab|ab) - (ab|ba)$$

The first line is for spinorbitals (note the angular brackets) and the second line is for (spatial) orbitals after spin integration (note the round brackets). The first term corresponds to the core energy of an electron. The second term has two components: the Coulomb term and the exchange term.

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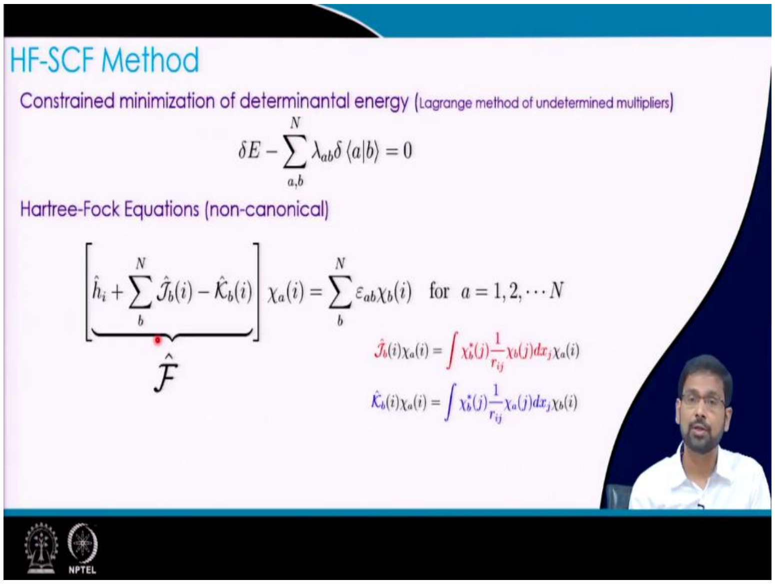

HF-SCF Method

Constrained minimization of determinantal energy (Lagrange method of undetermined multipliers)

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

Hartree-Fock Equations (non-canonical)

$$\underbrace{\left[\hat{h}_i + \sum_{b}^{N} \hat{\mathcal{J}}_b(i) - \hat{\mathcal{K}}_b(i)\right]}_{\hat{\mathcal{F}}} \chi_a(i) = \sum_{b}^{N} \varepsilon_{ab}\chi_b(i) \quad \text{for} \quad a = 1, 2, \cdots N$$

$$\hat{\mathcal{J}}_b(i)\chi_a(i) = \int \chi_b^*(j)\frac{1}{r_{ij}}\chi_b(j)dx_j\chi_a(i)$$

$$\hat{\mathcal{K}}_b(i)\chi_a(i) = \int \chi_b^*(j)\frac{1}{r_{ij}}\chi_a(j)dx_j\chi_b(i)$$

In the variational formulation of Hartree-Fock SCF procedure, we wanted to find the best N-electron Slater determinant that minimized the energy while keeping the spin orbital orthonormal. By solving this constrained minimization problem (via Lagrange method of undetermined multipliers), we needed to solve the following equation

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

After obtaining the first variation of the energy and the same of the internal product of spinorbitals, we arrived at the (non-canonical) HF equation:

$$\underbrace{\left[\hat{h}_i + \sum_{b}^{N} \hat{\mathcal{J}}_b(i) - \hat{\mathcal{K}}_b(i)\right]}_{\hat{\mathcal{F}}} \chi_a(i) = \sum_{b}^{N} \varepsilon_{ab}\chi_b(i) \quad \text{for} \quad a = 1, 2, \cdots N$$

$$\hat{\mathcal{J}}_b(i)\chi_a(i) = \int \chi_b^*(j)\frac{1}{r_{ij}}\chi_b(j)dx_j\chi_a(i)$$

$$\hat{\mathcal{K}}_b(i)\chi_a(i) = \int \chi_b^*(j)\frac{1}{r_{ij}}\chi_a(j)dx_j\chi_b(i)$$

The above equation defines the Fock operator ($\hat{\mathcal{F}}$) which is the sum of the 1-electron Hamiltonian, and the Coulomb operator ($\hat{\mathcal{J}}$) and exchange operator ($\widehat{\mathcal{K}}$).

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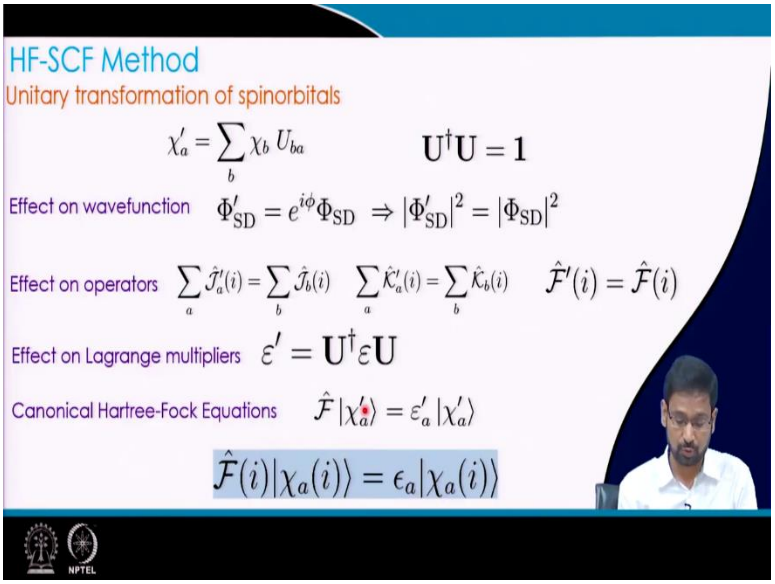

HF-SCF Method

Unitary transformation of spinorbitals

$$\chi'_a = \sum_b \chi_b U_{ba} \qquad \mathbf{U}^\dagger\mathbf{U} = 1$$

Effect on wavefunction $\Phi'_{\mathrm{SD}} = e^{i\phi}\Phi_{\mathrm{SD}} \Rightarrow |\Phi'_{\mathrm{SD}}|^2 = |\Phi_{\mathrm{SD}}|^2$

Effect on operators $\sum_a \hat{\mathcal{J}}'_a(i) = \sum_b \hat{\mathcal{J}}_b(i) \quad \sum_a \hat{\mathcal{K}}'_a(i) = \sum_b \hat{\mathcal{K}}_b(i) \quad \hat{\mathcal{F}}'(i) = \hat{\mathcal{F}}(i)$

Effect on Lagrange multipliers $\varepsilon' = \mathbf{U}^\dagger \varepsilon \mathbf{U}$

Canonical Hartree-Fock Equations $\hat{\mathcal{F}}\,|\chi'_a\rangle = \varepsilon'_a\,|\chi'_a\rangle$

$$\hat{\mathcal{F}}(i)|\chi_a(i)\rangle = \epsilon_a|\chi_a(i)\rangle$$

The noncanonical HF equation was converted to its canonical form by a unitary transformation of the HF spinorbitals. We showed that this unitary transformation retains the orthogonality of the spinorbitals, the Slater determinant *N*-electron wave-function changes by a phase factor, the expectation values do not change, the sum of the Coulomb operators and exchange operators, and thus the Fock operator, are invariant. Finally, we discussed that we can obtain the unitary matrix as the matrix that diagonalizes the Lagrange multipliers. This led us to the canonical HF equation.

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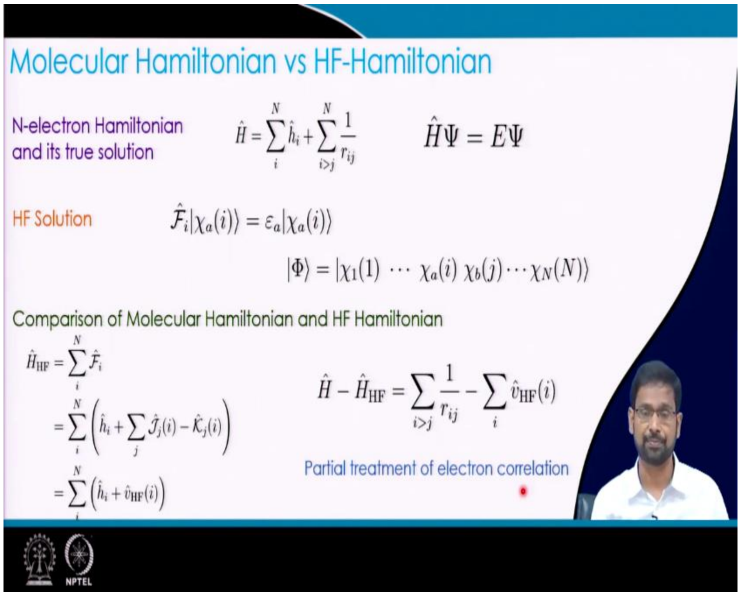

Molecular Hamiltonian vs HF-Hamiltonian

N-electron Hamiltonian and its true solution $\hat{H} = \sum_i^N \hat{h}_i + \sum_{i>j}^N \frac{1}{r_{ij}} \qquad \hat{H}\Psi = E\Psi$

HF Solution $\hat{\mathcal{F}}_i|\chi_a(i)\rangle = \varepsilon_a|\chi_a(i)\rangle$

$$|\Phi\rangle = |\chi_1(1) \cdots \chi_a(i)\,\chi_b(j) \cdots \chi_N(N)\rangle$$

Comparison of Molecular Hamiltonian and HF Hamiltonian

$$\hat{H}_{\mathrm{HF}} = \sum_i^N \hat{\mathcal{F}}_i = \sum_i^N \left(\hat{h}_i + \sum_j \hat{\mathcal{J}}_j(i) - \hat{\mathcal{K}}_j(i)\right) = \sum_i^N \left(\hat{h}_i + \hat{v}_{\mathrm{HF}}(i)\right)$$

$$\hat{H} - \hat{H}_{\mathrm{HF}} = \sum_{i>j} \frac{1}{r_{ij}} - \sum_i \hat{v}_{\mathrm{HF}}(i)$$

Partial treatment of electron correlation

We started from the N-electron Hamiltonian $\hat{H} = \sum_{i}^{N} \hat{h}_i + \sum_{i>j}^{N} \frac{1}{r_{ij}}$

and sought its solution $\hat{H}\Psi = E\Psi$

However, what we have actually solved using the HF-SCF method is not the full Hamiltonian. Rather, by solving the HF equations we obtain a set of spinorbitals,

$$\hat{\mathcal{F}}_i|\chi_a(i)\rangle = \varepsilon_a|\chi_a(i)\rangle$$

which are used to generate the N-electron Slater determinantal wave function

$$|\Phi\rangle = |\chi_1(1) \ \cdots \ \chi_a(i) \ \chi_b(j) \cdots \chi_N(N)\rangle$$

Since the Fock operator is an effective 1-electron operator, in a HF calculation the HF Hamiltonian can be expressed as,

$$\begin{aligned}\hat{H}_{\mathrm{HF}} &= \sum_{i}^{N} \hat{\mathcal{F}}_i \\ &= \sum_{i}^{N} \left(\hat{h}_i + \sum_{j} \hat{\mathcal{J}}_j(i) - \hat{\mathcal{K}}_j(i) \right) \\ &= \sum_{i}^{N} \left(\hat{h}_i + \hat{v}_{\mathrm{HF}}(i) \right)\end{aligned}$$

Compared to the real molecular Hamiltonian, the HF Hamiltonian lacks explicit electron-electron correlation

$$\hat{H} - \hat{H}_{\mathrm{HF}} = \sum_{i>j} \frac{1}{r_{ij}} - \sum_{i} \hat{v}_{\mathrm{HF}}(i)$$

Note here that HF method is not an entirely uncorrelated method, rather it considers a partial treatment of electron correlation. However, conventionally the HF method is known as an uncorrelated method and the corrections in all post HF methods are known as the corrections due to electron correlation.

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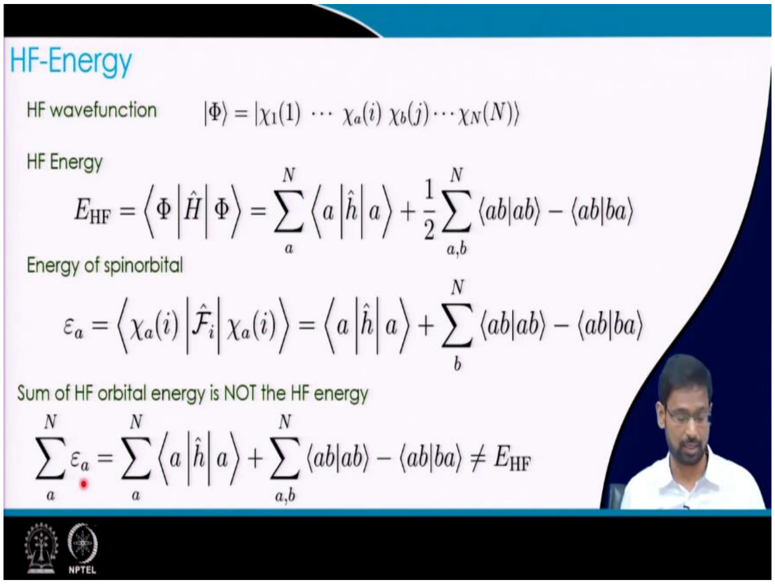

HF-Energy

HF wavefunction $|\Phi\rangle = |\chi_1(1)\,\cdots\,\chi_a(i)\,\chi_b(j)\cdots\chi_N(N)\rangle$

HF Energy

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

Energy of spinorbital

$$\varepsilon_a = \left\langle \chi_a(i) \middle| \hat{\mathcal{F}}_i \middle| \chi_a(i) \right\rangle = \left\langle a \middle| \hat{h} \middle| a \right\rangle + \sum_{b}^{N} \langle ab|ab\rangle - \langle ab|ba\rangle$$

Sum of HF orbital energy is NOT the HF energy

$$\sum_{a}^{N} \varepsilon_a = \sum_{a}^{N} \left\langle a \middle| \hat{h} \middle| a \right\rangle + \sum_{a,b}^{N} \langle ab|ab\rangle - \langle ab|ba\rangle \neq E_{\text{HF}}$$

The Hartree-Fock energy is defined as the energy expectation value when the state of the system is defined by the Slater determinant composed of the HF spinorbitals. For a Slater determinant (Φ) defined in terms of the HF spinorbitals $\{\chi_a\}=\{a\}$, the HF energy is given by,

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

Please note, we also have another set of energies, (ϵ_a) that are defined as the eigenvalue of the Fock operator, i.e.,

$$\varepsilon_a = \left\langle \chi_a(i) \middle| \hat{\mathcal{F}}_i \middle| \chi_a(i) \right\rangle = \left\langle a \middle| \hat{h} \middle| a \right\rangle + \sum_{b}^{N} \langle ab|ab\rangle - \langle ab|ba\rangle$$

This energy is popularly known as the orbital energy. Please note that sum of all the orbital energies is NOT the HF energy, i.e.,

$$\sum_{a}^{N} \varepsilon_a = \sum_{a}^{N} \left\langle a \middle| \hat{h} \middle| a \right\rangle + \sum_{a,b}^{N} \langle ab|ab\rangle - \langle ab|ba\rangle \neq E_{\text{HF}}$$

The HF energy is the energy expectation value corresponding to the HF wave function. The orbital energy, on the other hand, is the eigenvalue of the Fock operator.

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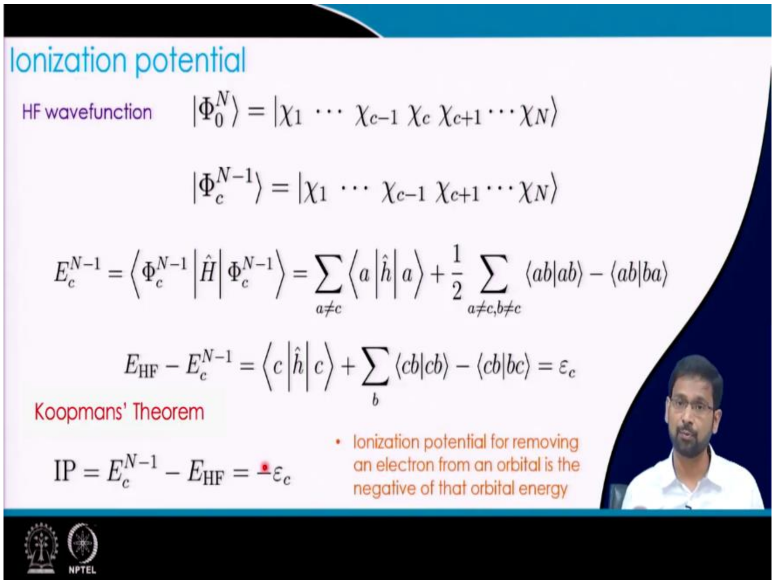

Ionization potential

HF wavefunction $|\Phi_0^N\rangle = |\chi_1 \;\cdots\; \chi_{c-1}\;\chi_c\;\chi_{c+1}\cdots\chi_N\rangle$

$$|\Phi_c^{N-1}\rangle = |\chi_1 \;\cdots\; \chi_{c-1}\;\chi_{c+1}\cdots\chi_N\rangle$$

$$E_c^{N-1} = \left\langle \Phi_c^{N-1} \middle| \hat{H} \middle| \Phi_c^{N-1} \right\rangle = \sum_{a\neq c} \left\langle a \middle| \hat{h} \middle| a \right\rangle + \frac{1}{2}\sum_{a\neq c, b\neq c} \langle ab|ab\rangle - \langle ab|ba\rangle$$

$$E_{\mathrm{HF}} - E_c^{N-1} = \left\langle c \middle| \hat{h} \middle| c \right\rangle + \sum_b \langle cb|cb\rangle - \langle cb|bc\rangle = \varepsilon_c$$

Koopmans' Theorem

$$\mathrm{IP} = E_c^{N-1} - E_{\mathrm{HF}} = -\varepsilon_c$$

- Ionization potential for removing an electron from an orbital is the negative of that orbital energy

Now let us if there is any physical interpretation of the orbital energy. Consider an *N*-electron HF wave function as

$$|\Phi_0^N\rangle = |\chi_1 \;\cdots\; \chi_{c-1}\;\chi_c\;\chi_{c+1}\cdots\chi_N\rangle$$

Suppose, we ionize the electron from the spinorbital *c*. The resulting *N*-1 electron system can be expressed by the following wave function

$$|\Phi_c^{N-1}\rangle = |\chi_1 \;\cdots\; \chi_{c-1}\;\chi_{c+1}\cdots\chi_N\rangle$$

Now, let us evaluate the energy expectation value of this cationic system as

$$E_c^{N-1} = \left\langle \Phi_c^{N-1} \middle| \hat{H} \middle| \Phi_c^{N-1} \right\rangle = \sum_{a\neq c} \left\langle a \middle| \hat{h} \middle| a \right\rangle + \frac{1}{2}\sum_{a\neq c, b\neq c} \langle ab|ab\rangle - \langle ab|ba\rangle$$

Compared to the HF energy, the energy of the above cationic system can be obtained as following

$$E_{\mathrm{HF}} - E_c^{N-1} = \left\langle c \middle| \hat{h} \middle| c \right\rangle + \sum_b \langle cb|cb\rangle - \langle cb|bc\rangle = \varepsilon_c$$

But we know that the energy in the left-hand side is essentially the negative of the ionization $\mathrm{IP} = E_c^{N-1} - E_{\mathrm{HF}} = -\varepsilon_c$ potential, i.e., The above result is known as the Koopmans theorem which states that the ionization potential for removing an electron from an orbital is the negative of that orbital energy, thus giving a physical interpretation of the orbital energy.

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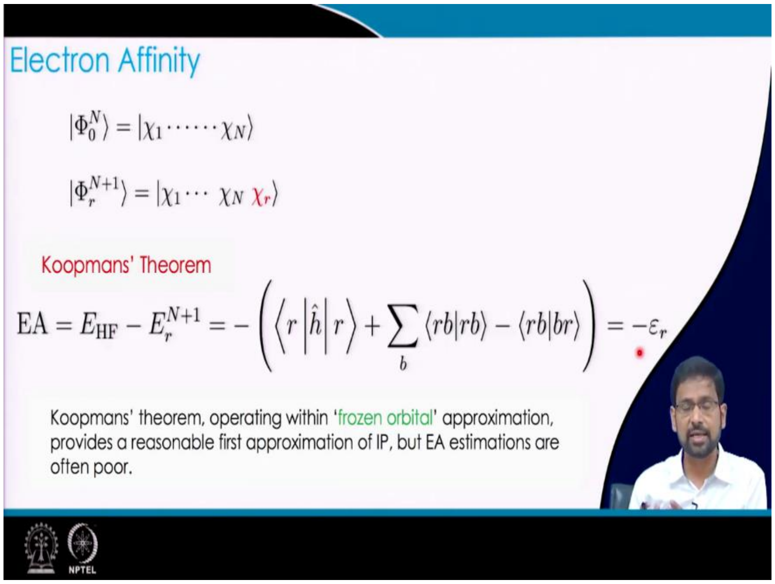

Electron Affinity

$$|\Phi_0^N\rangle = |\chi_1 \cdots\cdots \chi_N\rangle$$

$$|\Phi_r^{N+1}\rangle = |\chi_1 \cdots\ \chi_N\ \chi_r\rangle$$

Koopmans' Theorem

$$\mathrm{EA} = E_{\mathrm{HF}} - E_r^{N+1} = -\left(\left\langle r\left|\hat{h}\right|r\right\rangle + \sum_b \langle rb|rb\rangle - \langle rb|br\rangle\right) = -\varepsilon_r$$

Koopmans' theorem, operating within 'frozen orbital' approximation, provides a reasonable first approximation of IP, but EA estimations are often poor.

Now, we can do a similar exercise for the electron affinity. Consider that we have added an electron in orbital *r* of an *N*-electronic system. The wave functions of the corresponding *N* and *N*+1 electron system is given by,

$$|\Phi_0^N\rangle = |\chi_1 \cdots\cdots \chi_N\rangle$$

$$|\Phi_r^{N+1}\rangle = |\chi_1 \cdots\ \chi_N\ \chi_r\rangle$$

We can obtain the energy expectation value of the *N*+1 electron system and compare it with the HF energy to obtain,

$$\mathrm{EA} = E_{\mathrm{HF}} - E_r^{N+1} = -\left(\left\langle r\left|\hat{h}\right|r\right\rangle + \sum_b \langle rb|rb\rangle - \langle rb|br\rangle\right) = -\varepsilon_r$$

We have arrived at the 2nd Koopmans theorem that states the electron affinity of a system is the negative of the energy of that orbital where the extra electron is accommodated.

While Koopmans theorem is quite useful in estimating the IP and EA of a molecule, one key limitation of the approach is that it is assumed that the orbitals of the *N*-electron system can be used for *N*+1 and *N*-1 electron systems. While it is a good approximation for the IP, the EA is often poorly estimated from Koopmans theorem. For accurate treatment of IP and EA orbital relaxation is necessary. Nonetheless, Koopmans theorem provides an easy and effective tool for a reasonable estimation of the IP and EA with a reasonable computational cost.

Thank you for your attention.