Approximate Methods in Quantum Chemistry
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Lecture 37: Electron Correlation and Post HF Methods

Hello students! Welcome to this lecture. In last several lectures we discussed Hartree-Fock SCF method and basis sets that allow us to obtain wave function and energy for many-electron atoms or molecules. One way to improve the accuracy of the calculations is to take better and larger basis sets that allow a more accurate representation of the wave function. While a larger basis can improve accuracy, but only to a certain extent. The limiting factor here is the accuracy of the underlying method. Hartree-Fock SCF method does not include explicit electron correlation. In this lecture we will discuss some methods with that can go beyond the Hartree-Fock method. These methods are collectively calle the post Hartree-Fock methods and obtain the electron correlation that is missing in the Hartree-Fock method.

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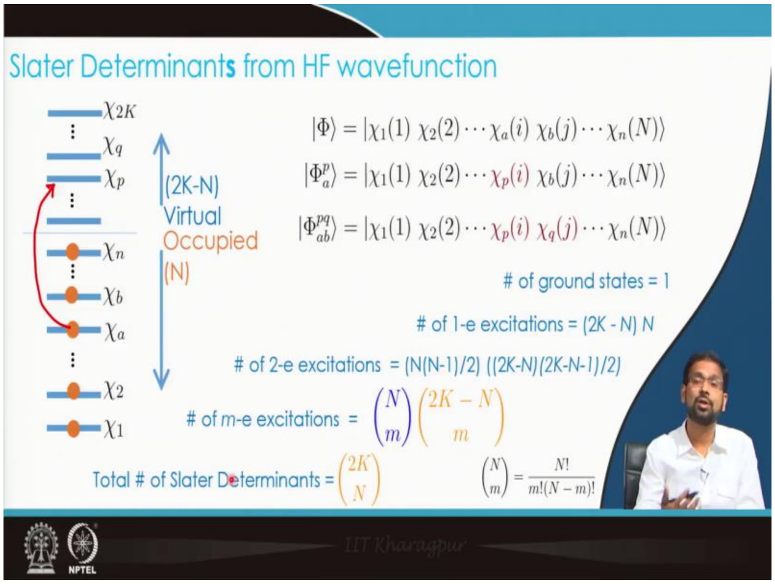

Slater Determinants from HF wavefunction

$$|\Phi\rangle = |\chi_1(1)\,\chi_2(2)\cdots\chi_a(i)\,\chi_b(j)\cdots\chi_n(N)\rangle$$

$$|\Phi_a^p\rangle = |\chi_1(1)\,\chi_2(2)\cdots\chi_p(i)\,\chi_b(j)\cdots\chi_n(N)\rangle$$

$$|\Phi_{ab}^{pq}\rangle = |\chi_1(1)\,\chi_2(2)\cdots\chi_p(i)\,\chi_q(j)\cdots\chi_n(N)\rangle$$

# of ground states = 1

# of 1-e excitations = (2K - N) N

# of 2-e excitations = (N(N-1)/2) ((2K-N)(2K-N-1)/2)

of *m*-e excitations = $\binom{N}{m}\binom{2K-N}{m}$

Total # of Slater Determinants = $\binom{2K}{N}$

$$\binom{N}{m} = \frac{N!}{m!(N-m)!}$$

For an *N*-electron system if we carry out Hartree-Fock calculation using *K* basis functions, at the end of HF-SCF calculations, we will obtain 2*K* number of spinorbitals. The HF wave function is obtained by constructing a Slater determinant where electrons are occupied in the lowest *N* spinorbitals. This leaves us with 2*K*-*N* empty (virtual) spinorbitals.

The ground state HF wave function is given by the Slater determinant,

$$|\Phi\rangle = |\chi_1(1)\ \chi_2(2)\cdots\chi_a(i)\ \chi_b(j)\cdots\chi_n(N)\rangle$$

We can generate another electronic configuration within which one electron from spinorbital *a* is promoted to a virtual spinorbital *p*. The one-electron excited Slater determinant corresponding to this configuration is,

$$|\Phi_a^p\rangle = |\chi_1(1)\ \chi_2(2)\cdots\chi_p(i)\ \chi_b(j)\cdots\chi_n(N)\rangle$$

We can generate *N*(2*K*-*N*) number such 1-electron excited Slater derterminants. Similarly, we can generate (N(N-1)/2) * ((2*K*-*N*)(2*K*-*N*-1)/2) number of 2-electron excited Slater determinants, such as,

$$|\Phi_{ab}^{pq}\rangle = |\chi_1(1)\ \chi_2(2)\cdots\chi_p(i)\ \chi_q(j)\cdots\chi_n(N)\rangle$$

We can generalize and state that the number of *m*-electron excited Slater determinants is

$$\binom{N}{m}\binom{2K-N}{m}$$

This simply says that we can choose *m* electrons out of *N* occupied spin orbitals in

$$\binom{N}{m} = \frac{N!}{m!(N-m)!}$$

ways and we can occupy these *m* electrons in the 2*K*-*N* virtual orbitals in $\binom{2K-N}{m}$ ways.

The total number of Slater determinants that can be generated from the 2*K* spinorbitals is $\binom{2K}{N}$.

We realized that we can generate a large number of excited Slater determinants from the HF spinorbitals. The HF ground state wave function is the lowest energy configuration. Next we discuss how to use the excited Slater determinants to include the electron correlation missing in HF treatment.

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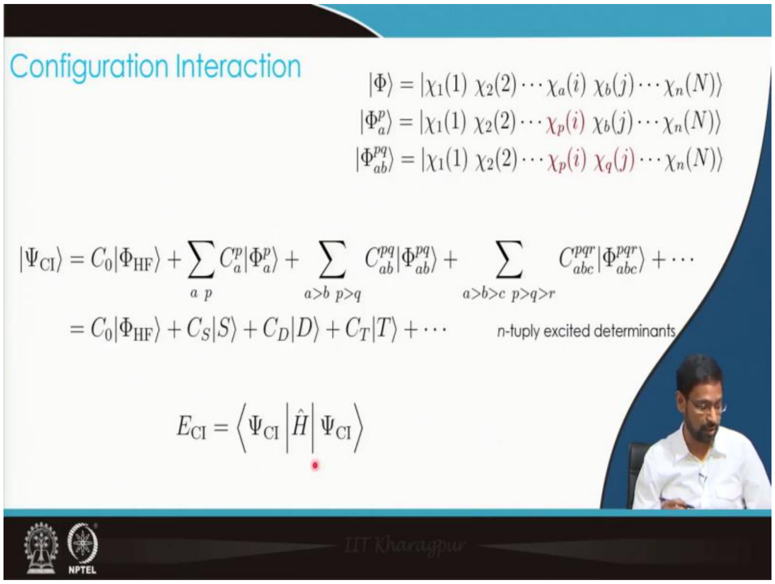

Configuration Interaction

$$|\Phi\rangle = |\chi_1(1)\,\chi_2(2)\cdots\chi_a(i)\,\chi_b(j)\cdots\chi_n(N)\rangle$$

$$|\Phi_a^p\rangle = |\chi_1(1)\,\chi_2(2)\cdots\chi_p(i)\,\chi_b(j)\cdots\chi_n(N)\rangle$$

$$|\Phi_{ab}^{pq}\rangle = |\chi_1(1)\,\chi_2(2)\cdots\chi_p(i)\,\chi_q(j)\cdots\chi_n(N)\rangle$$

$$|\Psi_{\mathrm{CI}}\rangle = C_0|\Phi_{\mathrm{HF}}\rangle + \sum_{a\ p} C_a^p|\Phi_a^p\rangle + \sum_{a>b\ p>q} C_{ab}^{pq}|\Phi_{ab}^{pq}\rangle + \sum_{a>b>c\ p>q>r} C_{abc}^{pqr}|\Phi_{abc}^{pqr}\rangle + \cdots$$

$$= C_0|\Phi_{\mathrm{HF}}\rangle + C_S|S\rangle + C_D|D\rangle + C_T|T\rangle + \cdots$$

n-tuply excited determinants

$$E_{\mathrm{CI}} = \left\langle \Psi_{\mathrm{CI}} \middle| \hat{H} \middle| \Psi_{\mathrm{CI}} \right\rangle$$

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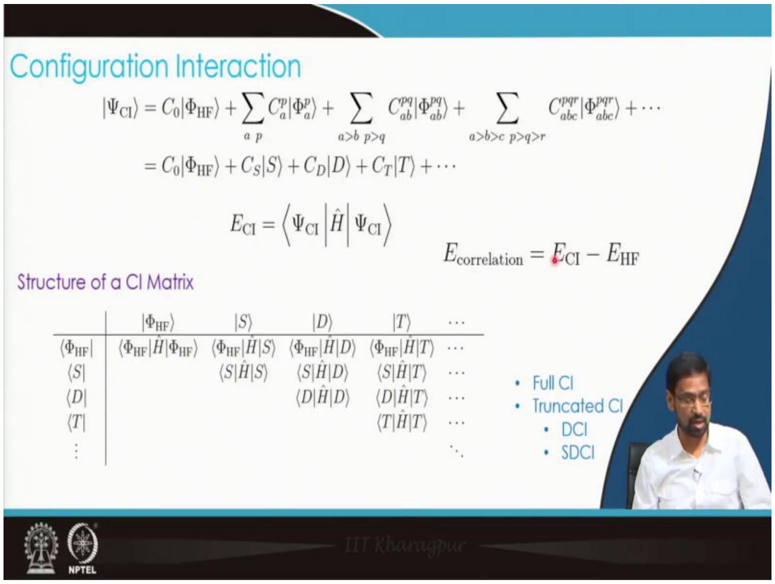

Configuration Interaction

$$|\Psi_{\mathrm{CI}}\rangle = C_0|\Phi_{\mathrm{HF}}\rangle + \sum_{a\ p} C_a^p|\Phi_a^p\rangle + \sum_{a>b\ p>q} C_{ab}^{pq}|\Phi_{ab}^{pq}\rangle + \sum_{a>b>c\ p>q>r} C_{abc}^{pqr}|\Phi_{abc}^{pqr}\rangle + \cdots$$

$$= C_0|\Phi_{\mathrm{HF}}\rangle + C_S|S\rangle + C_D|D\rangle + C_T|T\rangle + \cdots$$

$$E_{\mathrm{CI}} = \left\langle \Psi_{\mathrm{CI}} \middle| \hat{H} \middle| \Psi_{\mathrm{CI}} \right\rangle$$

$$E_{\mathrm{correlation}} = E_{\mathrm{CI}} - E_{\mathrm{HF}}$$

Structure of a CI Matrix

$$\begin{array}{c|ccccc}
 & |\Phi_{\mathrm{HF}}\rangle & |S\rangle & |D\rangle & |T\rangle & \cdots \\
\hline
\langle\Phi_{\mathrm{HF}}| & \langle\Phi_{\mathrm{HF}}|\hat{H}|\Phi_{\mathrm{HF}}\rangle & \langle\Phi_{\mathrm{HF}}|\hat{H}|S\rangle & \langle\Phi_{\mathrm{HF}}|\hat{H}|D\rangle & \langle\Phi_{\mathrm{HF}}|\hat{H}|T\rangle & \cdots \\
\langle S| & & \langle S|\hat{H}|S\rangle & \langle S|\hat{H}|D\rangle & \langle S|\hat{H}|T\rangle & \cdots \\
\langle D| & & & \langle D|\hat{H}|D\rangle & \langle D|\hat{H}|T\rangle & \cdots \\
\langle T| & & & & \langle T|\hat{H}|T\rangle & \cdots \\
\vdots & & & & & \ddots
\end{array}$$

- Full CI
- Truncated CI
  - DCI
  - SDCI

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One such idea is the configuration interaction (CI), where the *N*-electron wave function is expressed as a linear combination of all possible Slater determinants from a Hartree-Fock calculation, i.e.,

$$|\Psi_{\mathrm{CI}}\rangle = C_0|\Phi_{\mathrm{HF}}\rangle + \sum_{a\ p} C_a^p|\Phi_a^p\rangle + \sum_{a>b\ p>q} C_{ab}^{pq}|\Phi_{ab}^{pq}\rangle + \sum_{a>b>c\ p>q>r} C_{abc}^{pqr}|\Phi_{abc}^{pqr}\rangle + \cdots$$

$$= C_0|\Phi_{\mathrm{HF}}\rangle + C_S|S\rangle + C_D|D\rangle + C_T|T\rangle + \cdots$$

Here, Φ_{HF} is the HF Slater determinant and |*S*>, |*D*>, |*T*> represent all singly-, doubly-, or triply-excited Slater determinants, respectively. The CI correlation energy is obtained by the energy expectation value when the state is defined by the CI wave function, i.e.,

$$E_{\mathrm{CI}} = \left\langle \Psi_{\mathrm{CI}} \middle| \hat{H} \middle| \Psi_{\mathrm{CI}} \right\rangle$$

Where the correlation energy is obtained as E_{CI} - E_{HF}.

Using the above definition of the CI wave functions, the energy expectation value can be expressed as the following CI matrix,

$$\begin{array}{c|ccccc}
 & |\Phi_{\mathrm{HF}}\rangle & |S\rangle & |D\rangle & |T\rangle & \cdots \\
\hline
\langle\Phi_{\mathrm{HF}}| & \langle\Phi_{\mathrm{HF}}|\hat{H}|\Phi_{\mathrm{HF}}\rangle & \langle\Phi_{\mathrm{HF}}|\hat{H}|S\rangle & \langle\Phi_{\mathrm{HF}}|\hat{H}|D\rangle & \langle\Phi_{\mathrm{HF}}|\hat{H}|T\rangle & \cdots \\
\langle S| & & \langle S|\hat{H}|S\rangle & \langle S|\hat{H}|D\rangle & \langle S|\hat{H}|T\rangle & \cdots \\
\langle D| & & & \langle D|\hat{H}|D\rangle & \langle D|\hat{H}|T\rangle & \cdots \\
\langle T| & & & & \langle T|\hat{H}|T\rangle & \cdots \\
\vdots & & & & & \ddots
\end{array}$$

The dimension of the CI matrix will depend on the number of electrons and spinorbitals present in the HF calculations. When all excited Slater determinants are absent, the CI matrix reduces to one term (the first term) which is nothing but the HF energy. The mixing of all configurations counts for electron correlation. We can further use some rules (such as, Brillouin theorem, Condon-Slater rules, symmetry, etc.) to show that some of the matrix elements are zero. Still, for a realistic system, this CI matrix becomes very large. To overcome this, we often carry out truncated CI calculations, such as, CI-singles (CIS, where only singly excited Slater determinants are included in the CI wave function), CI-single-and-doubles (CI-SD, where both singly and doubly excited Slater determinants are included in the CI wave function).

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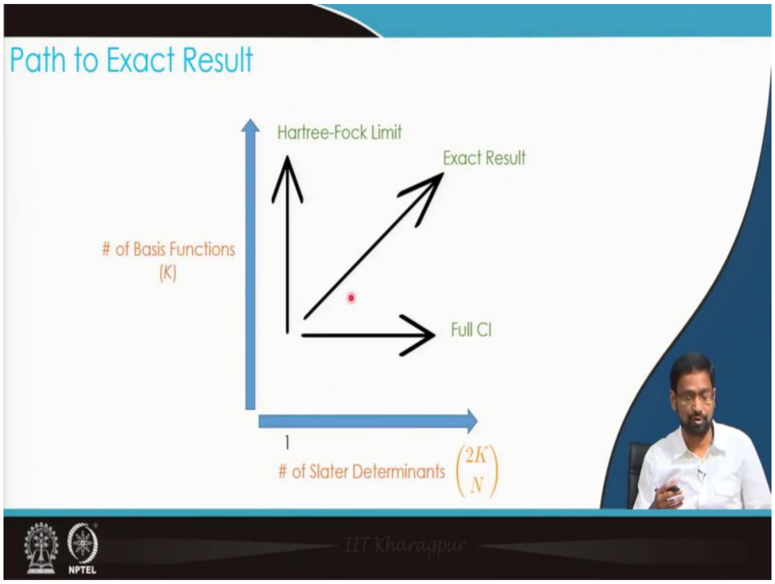

Path to Exact Result

The above diagram shows two possible ways to improve our calculations. When we take a single determinant (within HF calculation), even if we use the best basis set, we can only reach the HF limit. To improve further, we need to increase the number of Slater determinants in the wave function. But we can include all the Slater determinants in our calculation, when our basis set is small (Full CI limit). However, to obtain exact result, we must improve in both dimensions: increasing number of determinants and increasing number of basis functions. That would lead us to the exact results.

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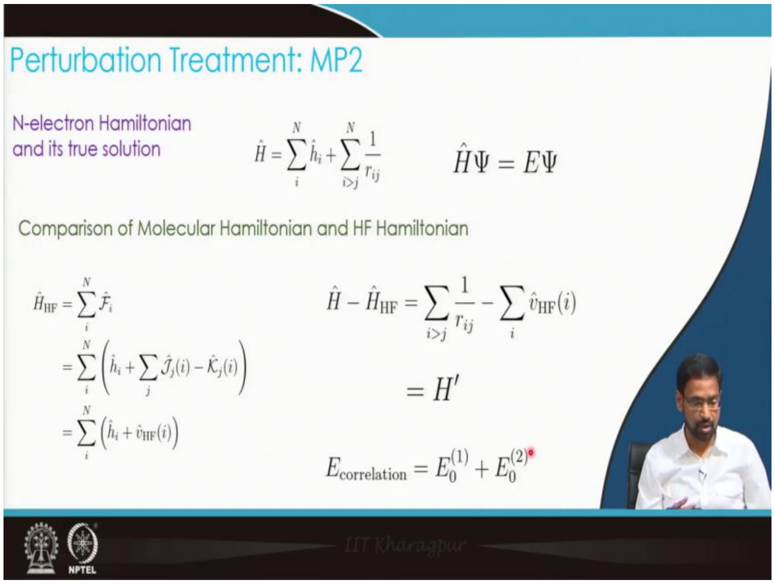

Perturbation Treatment: MP2

N-electron Hamiltonian and its true solution

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

Comparison of Molecular Hamiltonian and HF Hamiltonian

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

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

$$E_{\mathrm{correlation}} = E_0^{(1)} + E_0^{(2)}$$

There exists yet another class of methods to include the missing electron correlation in the HF theory. This method uses perturbation theory to extract this correlation.

The exact solution of the Hamiltonian is given by, $\hat{H}\Psi = E\Psi$

where, the molecular Hamiltonian has the form

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

Unlike the molecular Hamiltonian, the HF Hamiltonian is sum of (effective)-1-electron Fock operators, i.e.,

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

Since we have solved the HF Hamilotonan exactly, we can treat H - H_{HF} as the perturbation.

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

Now since we have defined the perturbation Hamiltonian, we can evalauate the 1st order, 2nd order energy corrections and 1st order wave function correction by using the relations we derived earlier in the course. For such calculations, we require the unperturbed wave functions, which, in this case, is the HF wave function. This approach goes by this name Møller-Plesset Perturbation Theory of Second Order (MP2), because the lowest order energy correction appears only in the second order.

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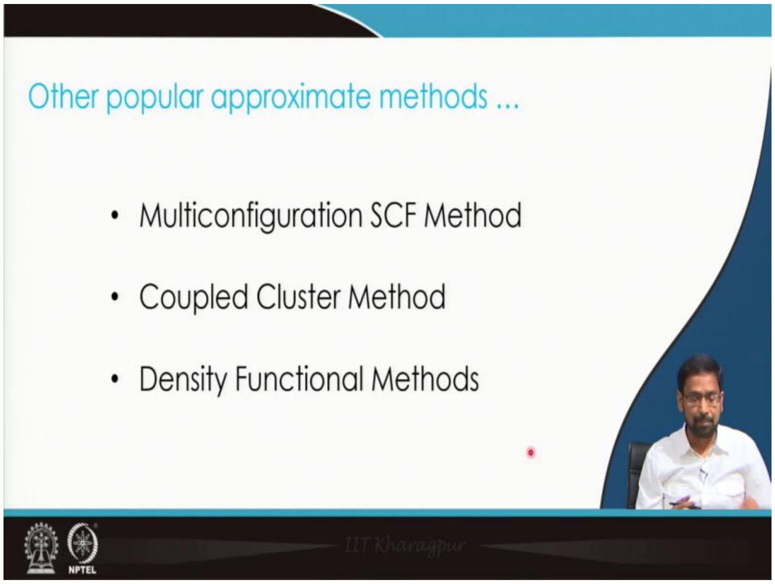

Other popular approximate methods ...

- Multiconfiguration SCF Method
- Coupled Cluster Method
- Density Functional Methods

Apart from the methods like the configuration interaction and MP2, there are a few other post HF methods that have been popularly used for electronic structure calculations. Some of the most prominent ones are the Multi-configuration SCF (MCSCF), the Coupled Cluster methods. These methods start from the HF wave functions and include correlation in different ways. Apart from these wave-functional methods, there is another method that uses electron density as the most fundamental quantity and derives all other properties from the density. This approach, called the Density Functional Theory (DFT), has become the most popular quantum chemical method for large molecular systems. More elaborate discussion on these methods is beyond the scope of the present course. However, it must be pointed out that within HF scheme, we have discussed most essential features of quantum chemical calculations. With a proper understanding of HF-SCF method, it will be rather straightforward to understand the advanced quantum chemical methods.

Thank you for your attention.