COMPUTATIONAL CHEMISTRY SEMESTER II M.SC CHEMISTRY M.G UNIVERSITY, KOTTAYAM

POST HARTREE – FOCK METHODS

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POINTS TO CONSIDER

- **ELECTRONIC CORRELATIONS**

- **MØLLER-PLESSET PERTURBATION THEORY**

- **CONFIGURATION INTERACTION (CI)**

- **COUPLED CLUSTERS**

- **SEMI EMPIRICAL METHODS**

APPROXIMATION METHODS

1) Variation Method (Hartrees Method, HF Method, CI etc)

2) Perturbation Method (MP Perturbation Theory)

DRAWBACKS OF HF METHOD

- It is based on the SCF theory and therefore considers average interactions of the electrons only

- It does not consider instantaneous interaction of electrons

- The calculated energy is always higher than true energy (Hartree Fock Limit)

- This is because correlation energy is not included

POST HARTREE – FOCK METHODS

- Post-Hartree–Fock methods are the set of methods developed to improve on the Hartree–Fock method.

- They add electron correlation which is a more accurate way of including the repulsions between electrons than in the Hartree–Fock method where repulsions are only averaged.

ELECTRONIC CORRELATIONS

- *It refers to the electronic interactions in a system*

- *Correlation energy* is defined as the difference between the exact energy and the HF energy

- The correlation energy is always negative

- There are two components to the correlation energy:

- *Dynamic correlation* is the energy associated with the electrons as they try to avoid one another.

- This is important in bond breaking processes.

- *Static correlation* arises from deficiencies in the single determinant wavefunction and is important in systems with stretched bonds and low-lying excited states.

- Since in certain cases an electronic state can be well described only by a linear combination of more than one degenerate Slater determinants.

- Computing the correlation energy is the single most important problem in quantum chemistry

MOLLER PLESSET PERTURBATION THEORY

- Based on perturbational theory

- In Møller-Plesset Perturbation Theory the Hamiltonian is divided into two parts

- $\widehat{H} = \widehat{H_0} + \lambda V$

- The perturbation λV, is assumed to be small

- The wave function and energy are then expanded as a power series in λ

- $\Psi_\lambda = \Psi_0 + \lambda \Psi_1 + \lambda^2 \Psi_2 + \ldots\ldots + \lambda^n \Psi_n$

- $E_\lambda = E_0 + \lambda E_1 + \lambda^2 E_2 + \ldots\ldots + \lambda^n E_n$

- Ψ_0 is the HF wave function

- E_0 is the HF energy

- MPn is obtained by truncating (cutting) the expansion at order λ^n

- The MP1 energy is the same as the HF energy

- The MP2 calculations typically recovers 80-90% of the correlation energy

- Second order Møller-Plesset perturbation theory (MP2) is one of the simplest and most useful levels of theory beyond the Hartree-Fock approximation.

- Second (MP2) third (MP3) and fourth (MP4) order Møller–Plesset calculations are standard levels used in calculating small systems and are implemented in many computational chemistry codes.

- Higher level MP calculations, generally only MP5, are possible in some codes.

- However, they are rarely used because of their cost.

CONFIGURATION INTERACTION

- Configuration interaction (CI) methods are one of the conceptually simplest methods for solving the many-body Hamiltonian.

- The basis for CI methods is the simple observation that an *exact* many-body wavefunction, may be written as a linear combination of Slater determinants (D_k)

 ie $\Psi = \sum_{k=0}^{\alpha} c_k\, D_k$

Where C_k is the variational coefficient

In these methods one includes excited state occupancies in these additional determinants (not included in HF method)

- Configuration simply describes the linear combination of Slater determinants used for the wave function.

- In terms of a specification of orbital occupation (for instance, $(1s)2(2s)2(2p)1...$), interaction means the mixing (interaction) of different electronic configurations (states).

- Due to the long CPU time and large memory required for CI calculations, the method is limited to relatively small systems.

- The scientific problem in adapting the CI method into a practical one is to obtain the best wavefunction, and hence lowest CI energy, with the shortest expansion length.

- Typical approach would be to truncate the expansion after only double or quadruple excitations from the reference determinant

- As the size of system increases, the proportion of the electronic correlation energy contained within a fixed reference space (such as all single and double excitations) decreases.

- The lack of size-extensivity results in a non-cancellation of errors when systems of different sizes are compared, resulting in difficulties when interaction or bonding energies are required.

- A method is size-consistent if it yields M times the energy of a single monomer when applied to M non-interacting monomers.

- • HF and Full-CI theories are size consistent, but truncated (shortened) CI approaches are not.

# TRUNCATED CI METHODS & THE TYPES OF EXCITATIONS

- CIS adds only single excitations

- CID adds only double excitations

- CISD adds single and double excitations

- CISDT adds single, double and triple excitations

COUPLED CLUSTER

- CC assumes that electrons interact in pairs

- CC uses a more complicated, exponential excitation operator (CI used linear operator)

- Therefore CC results in a product of excitations

- $\Psi^{CI} = (1 + C_1 + C_2 + C_3 + \cdots \ldots) \Psi^{HF}$

- $\Psi^{CC} = exp(T_1 + T_2 + T_3 + \cdots \ldots) \Psi^{HF}$

- Where C and T are excitation operators respectively

- CCSD is preferred in nearly all cases because of size-consistency.

- CISD only accounts correlation energy for up to double excitations and not at all for higher excitations. (CCSD accounts for correlation up to double excitations and then approximates higher excitations as combinations of the single and double excitations it has already calculated).

- This gives much more accurate numbers for pretty much all systems and provides for size-consistency.

	HF	MP2	MP3	CISD	CCSD	FULL CI
Minimal	Low Accuracy	....	....	....	....	Unbalanced
Split valance	....					
Polarised	....					
Diffuse	....					
Polarise + Diffuse . . . Infinite	.... Unbalanced					Exact!
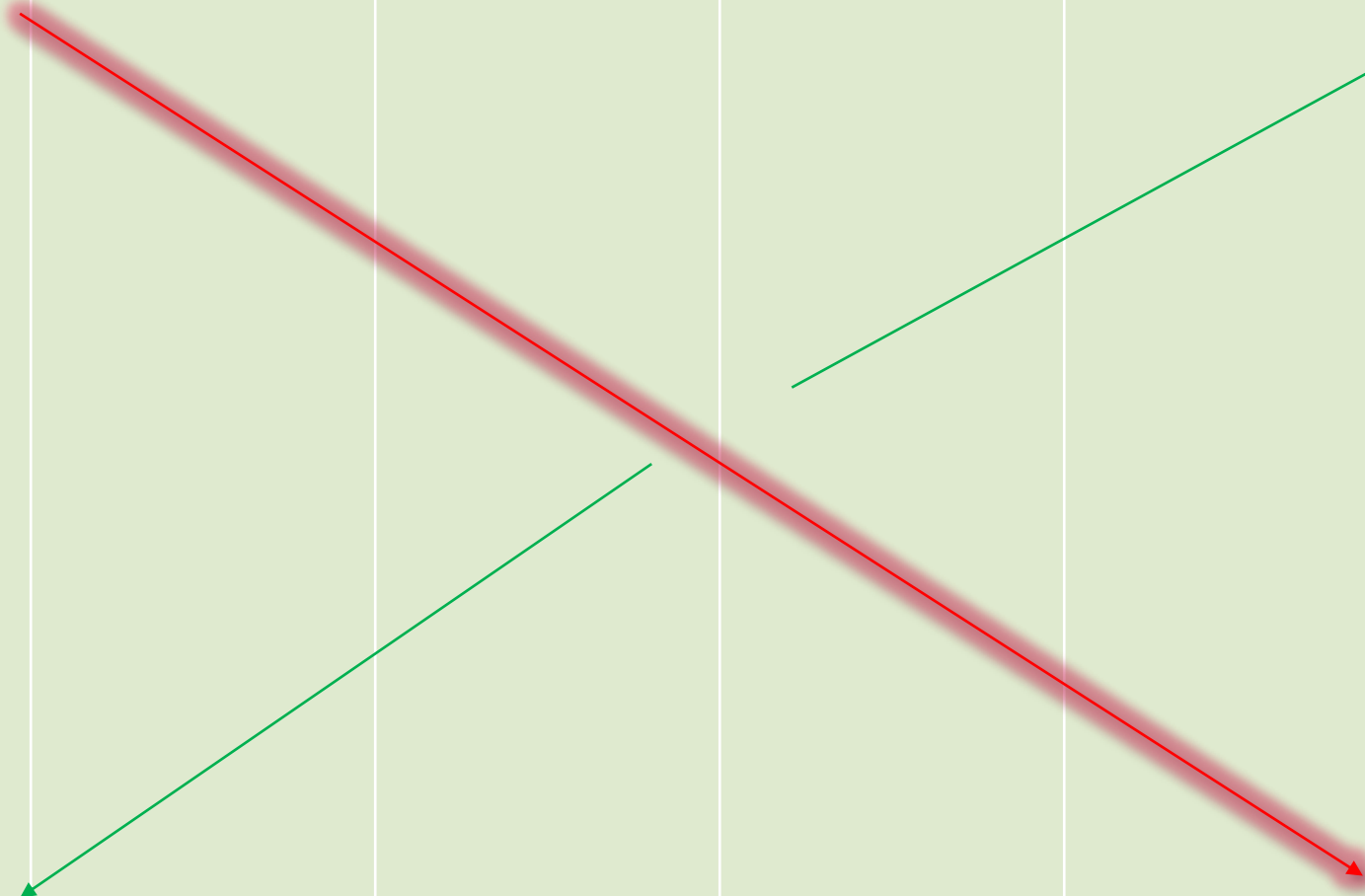
SEMIEMPIRICAL METHODS

- Approximate version of Hartree-Fock method

- Some two-electron and sometimes one electron integrals are neglected to speed up the computation

- Empirical parameters are inserted to compensate the neglected integrals

- Only valence electrons considered: core is treated by adding special core functions

- Only a minimum basis is used

- All 3 & 4 centre 2- electron integrals are neglected

- For integrals that are used, some are computed exactly, and others are computed using parameters from experiment

- They perform well for systems where experimental data available

- Not reliable for relatively unknown systems

- Dependable than some force field methods because it is based on QM