

1 Theory

1.1 Hartree-Fock, Coupled Cluster, and Møller Plesset Methods

1.1.1 Hartree-Fock

The Hartree-Fock (HF) or self-consistent field (SCF) method is a fundamental approach to solving electronic structure problems. The wave-function of our system, $|\Psi\rangle$, is represented by the determinant of a square matrix of one-electron orbital functions. For a two electron system, the wavefunction takes the form

$$|\Psi\rangle = \frac{1}{\sqrt{2}} \begin{vmatrix} \phi_1(x_1) & \phi_1(x_2) \\ \phi_1(x_1) & \phi_2(x_2) \end{vmatrix}$$

This notation can be simplified, and the wavefunction is written in shorthand using the ket symbol,

$$|\Psi\rangle = |\phi_i\rangle |\phi_j\rangle \dots |\phi_n\rangle$$

$$|\Psi\rangle = |\phi_i\phi_j\dots\phi_n\rangle$$

Or, even more simply, as

$$|\Psi\rangle = |i\rangle |j\rangle \dots |n\rangle$$

$$|\Psi\rangle = |ij\dots n\rangle$$

The $|i\rangle, |j\rangle \dots$ then correspond to occupied orbitals in the system. We will also introduce a notation corresponding to virtual orbitals; $|a\rangle, |b\rangle \dots$

The HF ground state energy is given by

$$\begin{aligned} E_{HF} &= \langle |\Psi\rangle | H | \Psi\rangle \\ &= \sum_i \langle i|h|i\rangle + \frac{1}{2} \sum_{i,j} \langle ij||ij\rangle \end{aligned}$$

Hartree-Fock is a fair starting point for systems which can be accurately described by a single determinant. Unfortunately, the results leave much to be desired. HF excludes energy contributions from electron correlation [?]. While these contributions are small in magnitude

compared to the overall energy of the system, their absolute values are still quite large, and it is essential to include them when calculating energy differences, such as in thermochemical calculations.

1.1.2 MP

Møller-Plesset perturbation theory (MP) is a method in which a starting Hartree-Fock calculation is perturbatively corrected to include electron correlation energies. The Schroedinger equation used in MP methods is

$$\hat{H}\Psi = (\hat{H}^0 + \lambda\hat{V})\Psi = E\Psi \quad \lambda \in \mathbb{R}$$

Where \hat{V} is the correction to the unperturbed Hamiltonian, \hat{H}^0 , and λ is an arbitrary parameter which controls the level of perturbation. The n-th order terms are determined by expanding Ψ and E in terms of powers of λ .

$$(\hat{H}^0 + \hat{V}) \sum_i^n \lambda^i \Psi^{(i)} = \sum_j^n \lambda^j E^{(j)} \sum_k^n \lambda^k \Psi^{(k)}$$

The zeroth order (uncorrected) energy is the energy of the unperturbed system, as expected. The first order correction to the energy ($E^{(1)}$) is given by

$$\begin{aligned} \hat{H}^0 |\Psi^{(1)}\rangle + \hat{V} |\Psi^{(0)}\rangle &= E^{(0)} |\Psi^{(1)}\rangle + E^{(1)} |\Psi^{(0)}\rangle \\ \langle \Psi^{(0)} | \hat{H}^0 | \Psi^{(1)} \rangle + \langle \Psi^{(0)} | \hat{V} | \Psi^{(0)} \rangle &= \langle \Psi^{(0)} | E^{(0)} | \Psi^{(1)} \rangle + \langle \Psi^{(0)} | E^{(1)} | \Psi^{(0)} \rangle \\ \langle \Psi^{(0)} | \hat{V} | \Psi^{(0)} \rangle &= E^{(1)} \langle \Psi^{(0)} | \Psi^{(0)} \rangle \\ E^{(1)} &= \langle \Psi^{(0)} | \hat{V} | \Psi^{(0)} \rangle \end{aligned}$$

Which is the expectation value of the correction. The most widely used version of MP theory is MP2, which truncates after the n=2 terms. The MP2 correction to the Hartree-Fock state is given by

$$E^{(2)} = \sum_{i,j}^{N_{vert}} \sum_{a,b}^{N_{occ}} \frac{|\langle ab || ij \rangle|^2}{\varepsilon_a + \varepsilon_b - \varepsilon_i - \varepsilon_j}$$

Since MP2 is just a Hartree-Fock calculation with a perturbative correction, it is cheap and gives better results than HF. More complex methods may make use of MP theory

to calculate contributions from higher-ordered excitations. An example of this is CCSD(T) which uses perturbation theory to calculate the contributions from triple excitations.

1.1.3 Coupled Cluster

Coupled cluster (CC) methods are a set of widely used methods which provide accurate energies and geometries. They are useful in determining a wide variety of difficult to predict properties such as NMR shifts and excited state properties. Our wave-function takes the form $\Psi = e^{\hat{T}} |\Phi\rangle$ where $|\Phi\rangle$ is the regular Hartree-Fock wavefunction. \hat{T} is the total excitation operator for the system,

$$\begin{aligned}\hat{T} &= \hat{T}_1 + \hat{T}_2 + \hat{T}_3 \dots \\ \hat{T}_1 &= \sum t_i^a \{a^+ i\} \\ \hat{T}_2 &= \frac{1}{(2!)^2} \sum t_{ij}^{ab} \{a^+ i b^+ j\} \\ \hat{T}_n &= \frac{1}{(n!)^2} \sum t_{ij\dots q}^{ab\dots p} \{a^+ i b^+ j \dots p^+ q\}\end{aligned}$$

The a^+ and i refer to the creation and annihilation operators, written in normal order, and the t refer to t-amplitudes, which are parameters that must be determined.

To evaluate Ψ , we use the Taylor expansion for e^x

$$\begin{aligned}e^{\hat{T}} &= \sum_{n=0}^{\infty} \frac{\hat{T}^n}{n!} \\ e^{\hat{T}} &= (1 + \hat{T} + \frac{\hat{T}^2}{2!} \dots) \\ e^{\hat{T}} &= (1 + \hat{T}_1 + \hat{T}_2 + \frac{\hat{T}_1^2}{2} + \hat{T}_1 \hat{T}_2 + \dots)\end{aligned}$$

The Schroedinger equation is written

$$\begin{aligned}H e^{\hat{T}} |\Phi\rangle &= e^{\hat{T}} |\Phi\rangle E \\ e^{-\hat{T}} H e^{\hat{T}} |\Phi\rangle &= e^{-\hat{T}} e^{\hat{T}} |\Phi\rangle E \\ \bar{\mathbf{H}} |\Phi\rangle &= |\Phi\rangle E\end{aligned}$$

We now obtain the coupled cluster equations, which are used to solve for T amplitudes

$$\begin{aligned}
\langle \Phi | e^{-\hat{T}} H e^{\hat{T}} | \Phi \rangle &= E \langle \Phi | \Phi \rangle = E \\
\langle \Phi_i^a | e^{-\hat{T}} H e^{\hat{T}} | \Phi \rangle &= E \langle \Phi_i^a | \Phi \rangle = 0 \\
\langle \Phi_{ij}^{ab} | e^{-\hat{T}} H e^{\hat{T}} | \Phi \rangle &= E \langle \Phi_{ij}^{ab} | \Phi \rangle = 0 \\
&\vdots
\end{aligned}$$

Once the CC equations are solved, the ground state energy is readily available.

If excited state properties are desired, it is possible to diagonalize $\bar{\mathbf{H}}$ over the states of interest (e.g. singles and doubles). This extension is called equation of motion coupled cluster (EOM-CC) and is an extremely useful tool in calculating excited state properties. Full CC includes contributions from all possible electronic configurations and it can be shown that the CC methods converge to the full configuration-interaction (CI) solution. The most common implementations of CC methods are CC singles and doubles (CCSD) and CC singles, doubles, triples (CCSDT), which, as the names imply, truncate with the \hat{T}_2 and \hat{T}_3 excitation operators, respectively. MP2, CCSD, CCSD(T) and CCSDT scale as N^4 , N^6 , N^7 , and N^8 , respectively, while Hartree-Fock scales as N^4 [?]