

Møller–Plesset Perturbation Theory

Post-HF Methods

- Hartree-Fock often provides a reasonable approximation to energy and electron density in a system
- However, HF is not exact, in particular due to not calculating electron correlation
- Post-HF methods calculate electron correlation using HF energy and wavefunctions as a starting point
- Examples include MP2, CCSD, and CI

Post-HF methods (cont.)

- $E_{Exact} = E_{HF} + E_{corr}$
- Because HF is variational, E_{corr} should always be negative

Perturbation Theory

- Assume total Hamiltonian is equal to:
 - $H = H_o + \lambda V$
 - H_o : Unperturbed Hamiltonian
 - V : Perturbation (generally small)
 - λ : Ordering parameter (primarily for bookkeeping)
- Where:
 - $E_i = E_i^{(0)} + \lambda E_i^{(1)} + \lambda^2 E_i^{(2)} + \dots$
 - $\psi_i = \psi_i^{(0)} + \lambda \psi_i^{(1)} + \lambda^2 \psi_i^{(2)} + \dots$

Perturbation Theory (cont.)

- For
 - $H|\Psi_i\rangle = E_i|\Psi_i\rangle$
- Substituting expressions from previous slide:
 - $(H_o + \lambda V)|\Psi_i^{(0)} + \lambda\Psi_i^{(1)} + \lambda^2\Psi_i^{(2)} + \dots\rangle =$
 $(E_i^{(0)} + \lambda E_i^{(1)} + \lambda^2 E_i^{(2)} + \dots)|\Psi_i^{(0)} + \lambda\Psi_i^{(1)} + \lambda^2\Psi_i^{(2)} + \dots\rangle$
- Expanding and equating terms with equal order of λ :
 - $H_o|\Psi_i^{(0)}\rangle = E^{(0)}|\Psi_i^{(0)}\rangle \quad \lambda^0$
 - $H_o|\Psi_i^{(1)}\rangle + V|\Psi_i^{(0)}\rangle = E^{(0)}|\Psi_i^{(1)}\rangle + E^{(1)}|\Psi_i^{(0)}\rangle \quad \lambda^1$
 - $H_o|\Psi_i^{(2)}\rangle + V|\Psi_i^{(1)}\rangle = E^{(0)}|\Psi_i^{(2)}\rangle + E^{(1)}|\Psi_i^{(1)}\rangle + E^{(2)}|\Psi_i^{(0)}\rangle \quad \lambda^2$
 - ...

Perturbation Theory (cont.)

- Multiplying by $\langle \Psi_i^{(0)} |$ gives the following expressions for energy:

- $E_i^{(0)} = \langle \Psi_i^{(0)} | H_0 | \Psi_i^{(0)} \rangle$

- $E_i^{(1)} = \langle \Psi_i^{(0)} | V | \Psi_i^{(0)} \rangle$

- $E_i^{(2)} = \langle \Psi_i^{(0)} | V | \Psi_i^{(1)} \rangle$

- If we take $|\Psi_i^{(1)}\rangle$ to be a linear combination of zeroth order wavefunctions $|\Psi_n^{(0)}\rangle$ ($n \neq i$), $E_i^{(2)}$ can be rewritten:

- $$E_i^{(2)} = \sum_{n \neq i} \frac{|\langle \Psi_i^{(0)} | V | \Psi_n^{(0)} \rangle|^2}{E_i^{(0)} - E_n^{(0)}}$$

Møller–Plesset Perturbation Theory

- In MP2, we use the following Hamiltonian:
 - $H = H_o + V$
- H_o is the Hartree-Fock Hamiltonian:
 - $H_o = \sum_i H^{core}(i) + v^{HF}(i)$
 - H^{core} : 1 electron integrals
 - v^{HF} : Effective electron potential
- V is our perturbation:
 - $V = \sum_{i<j} r_{ij}^{-1} - \sum_i v^{HF}(i)$
 - r_{ij}^{-1} : 2 electron integrals

Zeroth and First Order MP2 Energies

- Zeroth order energy of ground state:
 - $E_0^{(0)} = \langle \psi_0^{(0)} | H_o | \psi_0^{(0)} \rangle = \sum_a \varepsilon_a$
 - ε_a : Energy of occupied orbital a
- First order energy of ground state:
 - $E_0^{(1)} = \langle \psi_0^{(0)} | V | \psi_0^{(0)} \rangle = \langle \psi_0^{(0)} | \sum_{i < j} r_{ij}^{-1} | \psi_0^{(0)} \rangle - \langle \psi_0^{(0)} | \sum_i v^{HF}(i) | \psi_0^{(0)} \rangle = -\frac{1}{2} \sum_{ab} (\langle ab | ab \rangle - \langle ab | ba \rangle)$
- Sum of zeroth and first order energies gives the HF ground state energy

Second Order MP2 Energy

- Second order energy of ground state:

$$\bullet E_0^{(2)} = \sum_{0 \neq n} \frac{\langle 0|V|n\rangle\langle n|V|0\rangle}{E_0^{(0)} - E_n^{(0)}}$$

- Due to Brillouin's Theorem, $\langle \Psi_0 | r_{ij}^{-1} | \Psi_n \rangle$ equals zero except when Ψ_n is a doubly excited state. Therefore:

$$\bullet E_0^{(2)} = \sum_{a < b, r < s} \frac{|\langle \Psi_0 | \sum_{i < j} r_{ij}^{-1} | \Psi_{ab}^{rs} \rangle|^2}{E_0^{(0)} - E_n^{(0)}} = \sum_{a < b, r < s} \frac{|\langle ab|rs\rangle - \langle ab|sr\rangle|^2}{\varepsilon_a + \varepsilon_b - \varepsilon_r - \varepsilon_s}$$

MP2 Algorithm

- 1) Perform SCF calculation to obtain MO energies and coefficients
- 2) Convert 2-electron integrals from AO basis to MO basis
- 3) Use 2-electron integrals to compute MP2 energy over all occupied and unoccupied orbitals

Using MP2

- MP2 is widely available in almost all quantum chemistry programs
- MP2 scales at N^5 with system size, making it generally not practical for very large systems
- MP2 requires a reasonably good starting point. If HF does not give good results, neither will MP2 (this can sometimes be addressed by using a starting wavefunction other than HF)
- Will almost always give better results than pure HF, but is generally less accurate (although faster) than other post-HF methods like CCSD(T)

Frozen Core Approximation

- In most molecules, occupied orbitals can be divided in to core and valence orbitals
 - Core orbitals are low energy, and generally localized on one atom
 - Valence orbitals are higher in energy, often involved in bonding, and generally more chemically relevant
- The frozen core approximation skips calculating the correlation energy for electrons in core orbitals in post-HF methods
- To prevent errors, frozen core approximation should always be used unless the basis set explicitly includes functions for freezing the core. **Most standard basis sets do not!**
- **Frozen core is not the default for many QC programs! Always check the manual!**

Higher Order Terms

- While we've only considered perturbation theory through second order, higher order terms are sometimes used (MP3, MP4, etc.)
- Computational time increases dramatically with higher order perturbations
- Note that very high order perturbations do not necessarily converge, oscillation or divergence are possible