

# 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)
    - $\lambda$ : 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  $\lambda$ :
  - $H_o|\Psi_i^{(0)}\rangle = E^{(0)}|\Psi_i^{(0)}\rangle$   $\lambda^0$
  - $H_o|\Psi_i^{(1)}\rangle + V|\Psi_i^{(0)}\rangle = E^{(0)}|\Psi_i^{(1)}\rangle + E^{(1)}|\Psi_i^{(0)}\rangle$   $\lambda^1$
  - $H_o|\Psi_i^{(2)}\rangle + V|\Psi_i^{(1)}\rangle = E^{(0)}|\Psi_i^{(2)}\rangle + E^{(1)}|\Psi_i^{(1)}\rangle + E^{(2)}|\Psi_i^{(0)}\rangle$   $\lambda^2$
  - ...

# 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:
  - $E_0^{(0)} = \langle \psi_0^{(0)} | H_o | \psi_0^{(0)} \rangle = \sum_a \varepsilon_a$
  - $\varepsilon_a$ : 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:

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

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

- $E_0^{(2)} = \sum_{a < b, r < s} \frac{|\langle \Psi_0 | \sum_{i < j} r_{ij}^{-1} | \Psi_{ab}^{rs} \rangle|^2}{E_0^{(0)} - E_n^{(0)}} = \sum_{a < b, r < s} \frac{|\langle ab|rs\rangle - \langle ab|sr\rangle|^2}{\epsilon_a + \epsilon_b - \epsilon_r - \epsilon_s}$

# 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)

# 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