Perturbation Theory MP2 and ….

Perturbation Theory

$$\hat{H} = \hat{H}^0 + \hat{H}'$$

$$\hat{H}^0 = \text{zeroth order Hamiltonian}$$

$$\hat{H}' = \text{perturbation Hamiltonian}$$

$$\hat{H}^0 \psi_n^{(0)} = E_n^{(0)} \psi_n^{(0)}$$

We know the solution for the zeroth order Hamiltonian

Obtain the full solution

$$\hat{H} \psi_n = E_n \psi_n$$

Expanding the exact solutions

$$\hat{H} = \hat{H}^0 + \lambda \hat{H}'$$

Expand solution in terms of λ then make it equal to 1 at the end

$$E_n = E_n^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + \dots.$$

$$\psi_n = \psi_n^{(0)} + \lambda \psi_n^{(1)} + \lambda^2 \psi_n^{(2)} + \dots.$$

$E_n^{(1)}$ $\psi_n^{(1)}$ First order correction to energy and wavefuntion of n^{th} state

$E_n^{(2)}$ $\psi_n^{(2)}$ Second order correction to energy and wavefuntion of n^{th} state

Perturbation Theory 1

$$\hat{H} = \hat{H}^0 + \lambda \hat{H}'$$

$$H|n\rangle = E_n|n\rangle$$

What we want

$$H^0|n^0\rangle = E_n^{(0)}|n^0\rangle$$

What we know

$$\psi_n = \psi_n^{(0)} + \lambda\psi_n^{(1)} + \lambda^2\psi_n^{(2)} + \ldots. \quad\Rightarrow\quad |n\rangle = |n^0\rangle + \lambda|n^1\rangle + \lambda^2|n^2\rangle + \lambda^3|n^3\rangle\ldots$$

$$E_n = E_n^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + \lambda^3 E_n^{(3)} + ..$$

$$\langle n|n\rangle = \left(\langle n^0| + \lambda\langle n^1| + \lambda^2\langle n^2| + \lambda^3\langle n^3|\ldots\right)\left(|n^0\rangle + \lambda|n^1\rangle + \lambda^2|n^2\rangle + \lambda^3|n^3\rangle\ldots\right)$$

$$= \langle n^0|n^0\rangle + \lambda\left(\langle n^1|n^0\rangle + \langle n^0|n^1\rangle\right) + \lambda^2\left(\langle n^2|n^0\rangle + \langle n^0|n^2\rangle + 2\langle n^1|n^1\rangle\right) = 1$$

$$\langle n^0|n^0\rangle = 1$$

$$\lambda\left(\langle n^1|n^0\rangle + \langle n^0|n^1\rangle\right) = 0$$

$$\lambda^2\left(\langle n^2|n^0\rangle + \langle n^0|n^2\rangle + 2\langle n^1|n^1\rangle\right) = 0$$

Conditions that have to be satisfied

Perturbation Theory 2

$$\hat{H}|n\rangle = \hat{H}^0 + \lambda\hat{H}'\left(|n^0\rangle + \lambda|n^1\rangle + \lambda^2|n^2\rangle + \lambda^3|n^3\rangle ...\right)$$

$$= \left(E_n^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + \lambda^3 E_n^{(3)} + ..\right)\left(|n^0\rangle + \lambda|n^1\rangle + \lambda^2|n^2\rangle + \lambda^3|n^3\rangle ...\right)$$

Collect equal orders of λ

$$\hat{H}^0\left(|n^0\rangle\right) = \left(E_n^{(0)}\right)\left(|n^0\rangle\right)$$

$$\lambda\left(\hat{H}'|n^0\rangle + \hat{H}^0|n^1\rangle\right) = \lambda\left(E_n^{(1)}|n^0\rangle + E_n^{(0)}|n^1\rangle\right)$$

$$\lambda^2\left(\hat{H}'|n^1\rangle + \hat{H}^0|n^2\rangle\right) = \lambda^2\left(E_n^{(2)}|n^0\rangle + E_n^{(1)}|n^1\rangle + E_n^{(0)}|n^2\rangle\right)$$

Mutiply from the left with $\langle n^0|$

First Order Perturbation Theory 1

Multiply from the left with $\langle n^0 |$

$$\hat{H}'|n^0\rangle + \hat{H}^0|n^1\rangle = E_n^{(1)}|n^0\rangle + E_n^{(0)}|n^1\rangle$$

$$\langle n^0|\hat{H}'|n^0\rangle + \langle n^0|\hat{H}^0|n^1\rangle = \langle n^0|n^0\rangle E_n^{(1)} + \langle n^0|n^1\rangle E_n^{(0)}$$

$$\langle n^0|\hat{H}'|n^0\rangle + \underline{E_n^{(0)}\langle n^0|n^1\rangle} = E_n^{(1)} + \underline{\langle n^0|n^1\rangle E_n^{(0)}}$$

The same thing

$$E_n^{(1)} = \langle n^0|\hat{H}'|n^0\rangle$$

Let’s get first order wavefuntion

$$\hat{H}'|n^0\rangle + \hat{H}^0|n^1\rangle = E_n^{(1)}|n^0\rangle + E_n^{(0)}|n^1\rangle$$

$$\hat{H}^0|n^1\rangle - E_n^{(0)}|n^1\rangle = E_n^{(1)}|n^0\rangle - \hat{H}'|n^0\rangle$$

$$\left(\hat{H}^0 - E_n^{(0)}\right)|n^1\rangle = \left(E_n^{(1)} - \hat{H}'\right)|n^0\rangle$$

Expand the first order perturbed wavefunction with zeroth order wavefunction

$$|n^1\rangle = \sum_j C_{nj}|j^0\rangle$$

First Order Perturbation Theory 2

$$\sum_j C_{nj}\left(\hat{H}^0 - E_n^{(0)}\right)\left| j^0 \right\rangle = \left(E_n^1 - \hat{H}'\right)\left| n^0 \right\rangle$$

Multiply both sides by $\left\langle k^0 \right|$ Then integrate

$$\sum_j C_{nj}\left\langle k^0 \right|\left(\hat{H}^0 - E_n^0\right)\left| j^0 \right\rangle = \left\langle k^0 \right|\left(E_n^1 - \hat{H}'\right)\left| n^0 \right\rangle$$

$$\sum_j C_{nj}\left\langle k^0 \right|\left(\hat{H}^0 - E_n^0\right)\left| j^0 \right\rangle = E_n^1\left\langle k^0 \| n^0 \right\rangle - \left\langle k^0 \right|\left(\hat{H}'\right)\left| n^0 \right\rangle$$

if $k = n$ $\quad \sum_j C_{nj}\left(E_n^{(0)} - E_n^{(0)}\right)\left\langle n^0 \| j^0 \right\rangle = E_n^{(1)}\left\langle n^0 \| n^0 \right\rangle - \left\langle n^0 \right|\left(\hat{H}'\right)\left| n^0 \right\rangle$

$$0 = E_n^{(1)} - \left\langle n^0 \right|\left(\hat{H}'\right)\left| n^0 \right\rangle$$

Same thing as page before

First Order Perturbation Theory 3

$$\sum_j C_{nj}\left(\hat{H}^0 - E_n^{(0)}\right)\left| j^0 \right\rangle = \left(E_n^{(1)} - \hat{H}'\right)\left| n^0 \right\rangle$$

Multiply both sides by $\left\langle k^0 \right|$

$$\sum_j C_{nj}\left\langle k^0 \left| \left(\hat{H}^0 - E_n^0\right) \right| j^0 \right\rangle = E_n^1 \left\langle k^0 \| n^0 \right\rangle - \left\langle k^0 \left| \left(\hat{H}'\right) \right| n^0 \right\rangle$$

$$\text{if } k \neq n \quad \sum_j C_{nj}\left(E_k^0 - E_n^0\right)\left\langle k^0 \| j^0 \right\rangle = E_n^1 \left\langle k^0 \| n^0 \right\rangle - \left\langle k^0 \left| \left(\hat{H}'\right) \right| n^0 \right\rangle$$

$$C_{nk}\left(E_k^{(0)} - E_n^{(0)}\right) = -\left\langle k^0 \left| \left(\hat{H}'\right) \right| n^0 \right\rangle$$

$$C_{nk} = \frac{\left\langle k^0 \left| \left(\hat{H}'\right) \right| n^0 \right\rangle}{\left(E_n^{(0)} - E_k^{(0)}\right)} \qquad \left| n^1 \right\rangle = \sum_{k \neq n} C_{nk}\left| k^0 \right\rangle$$

Second Order Perturbation 1

$$\left(\hat{H}'\left|n^1\right\rangle + \hat{H}^0\left|n^2\right\rangle\right) = \left(E_n^{(2)}\left|n^0\right\rangle + E_n^{(1)}\left|n^1\right\rangle + E_n^{(0)}\left|n^2\right\rangle\right)$$

Mutiply from the left with $\left\langle n^0\right|$

$$\left\langle n^0\left|\hat{H}'\right|n^1\right\rangle + \left\langle n^0\left|\hat{H}^0\right|n^2\right\rangle = E_n^{(2)}\left\langle n^0 \| n^0\right\rangle + E_n^{(1)}\left\langle n^0 \| n^1\right\rangle + E_n^{(0)}\left\langle n^0 \| n^2\right\rangle$$

$$\left\langle n^0\left|\hat{H}'\right|n^1\right\rangle + \underline{E_n^{(0)}\left\langle n^0 \| n^2\right\rangle} = E_n^{(2)} + \underline{E_n^{(0)}\left\langle n^0 \| n^2\right\rangle}$$

Same thing

$$E_n^{(2)} = \left\langle n^0\left|\hat{H}'\right|n^1\right\rangle$$

$$\left|n^1\right\rangle = \sum_{k\neq n} C_{nk}\left|k^0\right\rangle \qquad C_{nk} = \frac{\left\langle k^0\left|\left(\hat{H}'\right)\right|n^0\right\rangle}{\left(E_n^{(0)} - E_k^{(0)}\right)}$$

$$E_n^{(2)} = \left\langle n^0\left|\hat{H}'\right|n^1\right\rangle = \sum_{k\neq n} C_{nk}\left\langle n^0\left|\hat{H}'\right|k^0\right\rangle = \sum_{k\neq n} \frac{\left\langle k^0\left|\hat{H}'\right|n^0\right\rangle}{\left(E_n^{(0)} - E_k^{(0)}\right)}\left\langle n^0\left|\hat{H}'\right|k^0\right\rangle$$

Perturbation Theory Summary

$$E_n^{(1)} = \left\langle n^0 \middle| \hat{H}' \middle| n^0 \right\rangle$$

First order perturbation to energy is expectation value of the perturbation

$$\left| n^1 \right\rangle = \sum_{k \neq n} \frac{\left\langle k^0 \middle| \left(\hat{H}' \right) \middle| n^0 \right\rangle}{\left(E_n^{(0)} - E_k^{(0)} \right)} \left| k^0 \right\rangle$$

First order perturbation to wave function usually mixes the states that are close in energy

$$E_n^{(2)} = \sum_{k \neq n} \frac{\left| \left\langle k^0 \middle| \hat{H}' \middle| n^0 \right\rangle \right|^2}{\left(E_n^{(0)} - E_k^{(0)} \right)}$$

Second order perturbation to energy is obtained from the first order perturbed wave function

For electron Hartree Fock is 0th order answer

$$\left[h(\mathbf{r}_1)+\sum_{j=1}^{n}\left(J_j(\mathbf{x}_1)-K_j(\mathbf{x}_1)\right)\right]\psi_i(\mathbf{x}_1)=\varepsilon_i\psi_i(\mathbf{x}_1) \qquad i=1,2,\ldots n$$

$$f(1)\psi_i(\mathbf{x}_1)=\varepsilon_i\psi_i(\mathbf{x}_1) \qquad i=1,2,\ldots n$$

$$\varepsilon_i : \text{orbital energy} \qquad \varepsilon_i=\langle\psi_i|f|\psi_i\rangle=h_{ii}+\sum_{j=1}^{n}\left(J_{ij}-K_{ij}\right)$$

Wave function is a slater determinant of the spin orbitals

$$|\psi_1\psi_2\ldots\psi_n\rangle=\frac{1}{\sqrt{n!}}\begin{vmatrix}\psi_i(\mathbf{x}_1) & \psi_j(\mathbf{x}_1) & \ldots\ldots\ldots\ldots & \psi_n(\mathbf{x}_1)\\ \psi_i(\mathbf{x}_2) & \psi_j(\mathbf{x}_2) & \ldots\ldots\ldots\ldots & \psi_n(\mathbf{x}_2)\\ \ldots\ldots & \ldots\ldots & \ldots\ldots\ldots\ldots & \ldots\ldots\\ \psi_i(\mathbf{x}_n) & \psi_j(\mathbf{x}_n) & \ldots\ldots\ldots\ldots & \psi_n(\mathbf{x}_n)\end{vmatrix}$$

What is 1st 2nd perturbation energy?

$$\langle D_0|F+H'|D_0\rangle = \langle D_0|F|D_0\rangle + \langle D_0|H'|D_0\rangle = \sum_i^n \varepsilon_i + \langle D_0|H'|D_0\rangle$$

Zeroth order portion is
$$\sum_{i=1}^{n}\varepsilon_i = \sum_{i=1}^{n} h_{ii} + \sum_{i=1}^{n}\sum_{j=1}^{n}\left(J_{ij}-K_{ij}\right)$$

$$\langle D_0|F+H'|D_0\rangle = \sum_i^n h_{ii} + \frac{1}{2}\sum_{i=1}^{n}\sum_{j=1}^{n}(J_{ij}-K_{ij})$$

1st order correction to the energy is
$$\langle D_0|H'|D_0\rangle = \frac{-1}{2}\sum_{i=1}^{n}\sum_{j=1}^{n}(J_{ij}-K_{ij})$$

Second Order Correction to the ground state is?

$$\sum_{K}^{excited\ states} \frac{\left|\langle D_K|\hat{H}|D_0\rangle\right|^2}{E_0^{HF} - E_K^{HF}}$$

Since only two electron excitation from the ground state Hartree Fock solution have values

$$\sum_{K}^{2e\ excite} \frac{\left|\langle D_K|\hat{H}|D_0\rangle\right|^2}{E_0^{HF} - E_K^{HF}} = \sum_{i}\sum_{j>i}\sum_{a}\sum_{b>a} \frac{|\langle ij|ab\rangle - \langle ij|ba\rangle|^2}{\epsilon_a + \epsilon_b - \epsilon_i - \epsilon_j}$$

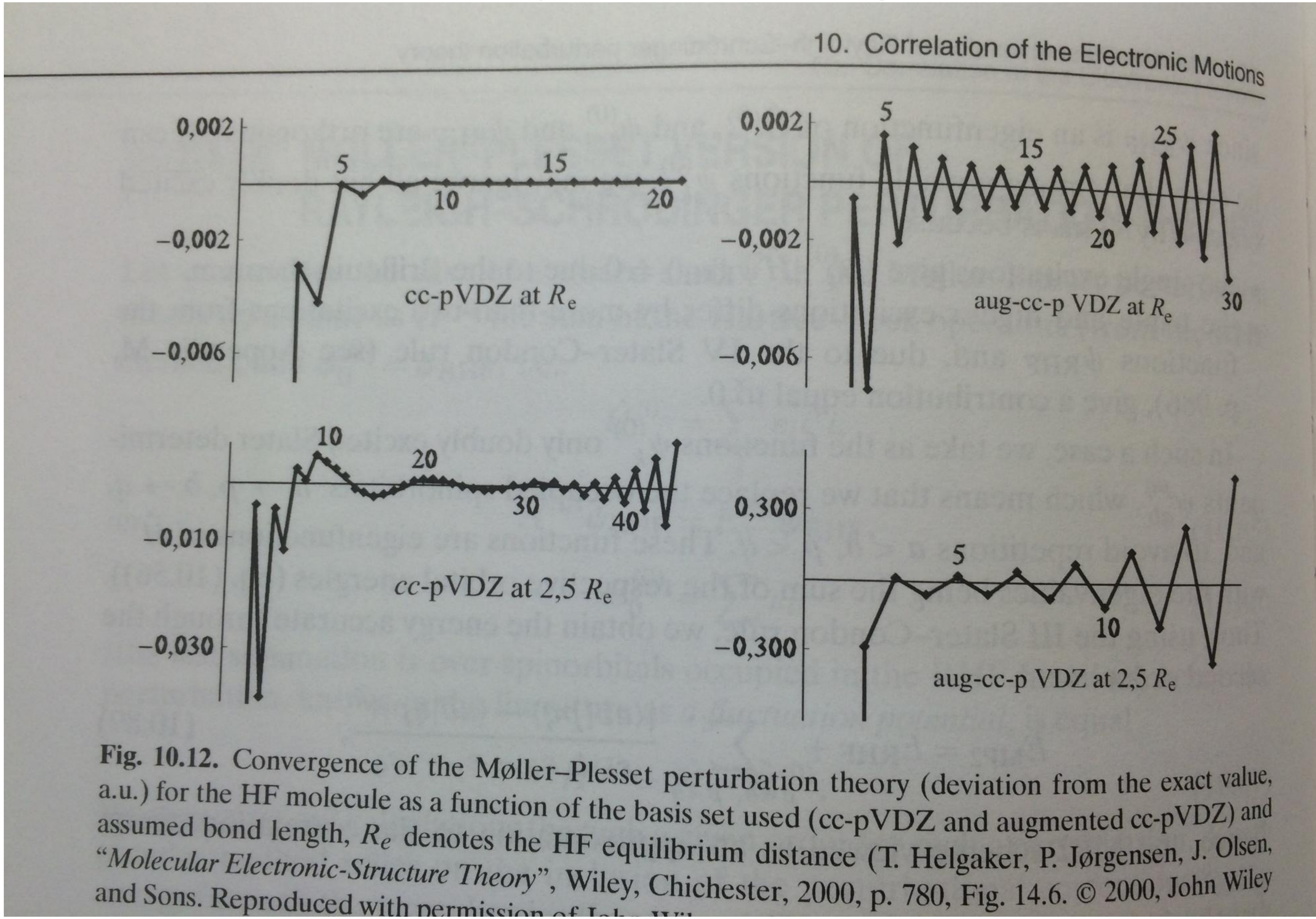
Just need the orbital energies and the exchange and coulomb integral of orbitals

Perturbation Convergence

STO-3G

Method	HCN	CN^-	CN
MP2	-91.82033	-91.07143	-91.11411
MP3	-91.82242	-91.06862	-91.12203
MP4	-91.82846	-91.07603	-91.13538
MP5	-91.83129	-91.07539	-91.14221
MP6	-91.83233	-91.07694	-91.14855
MP7	-91.83264	-91.07678	-91.15276
MP8	-91.83289	-91.07699	-91.15666
Full CI	-91.83317	-91.07706	-91.17006
$\Delta E < 0.001$ at	MP6	MP6	MP19
Full CI – MP4 (kcal-mol^{-1})	-2.96	-0.65	-21.76

Perturbation theory Convergence CRAZY



MP2 calculations

- Can be calculated by small extra effort of Hartree Fock
- Can include van Der Waals interactions that are becoming important due to protein folding or Metal surface interactions
- Only works when two electron excitation from Hartree Fock are the most important contribution

- PROBABLY BETTER TO STOP AT MP2 AND NOT WORTH GOING MORE HIGHER TO MP3 MP4…
- If you stop, STOP AT EVEN ORDERS