

CHM 673

Lecture 12: Perturbation theory

Suggested reading:

Chapter 6.1, 6.5 from S&O

Chapter 4.8 from Jensen

Rayleigh-Schrodinger perturbation theory

Perturbation theory: to find solutions (Ψ_i and ε_i) of Hamiltonian H if solutions of similar Hamiltonian H_0 are known

$$\hat{H}|\Psi_i\rangle = (\hat{H}_0 + \lambda\hat{V})|\Psi_i\rangle = \varepsilon_i|\Psi_i\rangle$$

$$\hat{H}_0|\Phi_i^{(0)}\rangle = E_i^{(0)}|\Phi_i^{(0)}\rangle \quad E^0 \text{ and } \Phi^0 \text{ are known}$$

$$\hat{H} = \hat{H}_0 + \lambda\hat{V}$$

$$\varepsilon_i = E_i^{(0)} + \lambda E_i^{(1)} + \lambda^2 E_i^{(2)} + \dots$$

$$|\Psi_i\rangle = |\Phi_i^{(0)}\rangle + \lambda|\Phi_i^{(1)}\rangle + \lambda^2|\Phi_i^{(2)}\rangle + \dots$$

$$|\Phi_i^{(0)}\rangle = |i\rangle \quad \text{just to simplify notations}$$

The goal is to express n th-order wavefunction and energies in terms of the zeroth-order energies and matrix elements of the perturbation V between the unperturbed wavefunctions: $\langle i|\hat{V}|j\rangle$

Rayleigh-Schrodinger perturbation theory

H_0 eigenstates are normalized: $\langle i|i \rangle = 1$

Choose intermediate normalization: $\langle i|\Psi_i \rangle = 1$ 

$$\langle i|\Psi_i \rangle = \langle i|i \rangle + \lambda \langle i|\Phi_i^{(1)} \rangle + \lambda^2 \langle i|\Phi_i^{(2)} \rangle + \dots = 1$$

Since it holds for any lambda \rightarrow $\langle i|\langle\Phi_i^{(n)} \rangle = 0$

Substitute energy and wavefunction expansions into SE:

$$(\hat{H}_0 + \lambda \hat{V})(|i\rangle + \lambda \langle i|\Phi_i^{(1)} \rangle + \lambda^2 \langle i|\Phi_i^{(2)} \rangle + \dots) = \\ (E_i^{(0)} + \lambda E_i^{(1)} + \lambda^2 E_i^{(2)} + \dots)(|i\rangle + \lambda \langle i|\Phi_i^{(1)} \rangle + \lambda^2 \langle i|\Phi_i^{(2)} \rangle + \dots)$$

Rayleigh-Schrodinger perturbation theory

$$(\hat{H}_0 + \lambda \hat{V})(|i\rangle + \lambda \langle i|\Phi_i^{(1)}\rangle + \lambda^2 \langle i|\Phi_i^{(2)}\rangle + \dots) = \\ (E_i^{(0)} + \lambda E_i^{(1)} + \lambda^2 E_i^{(2)} + \dots)(|i\rangle + \lambda \langle i|\Phi_i^{(1)}\rangle + \lambda^2 \langle i|\Phi_i^{(2)}\rangle + \dots)$$

Equating coefficients for λ^n :

$$\lambda^0: \quad \hat{H}_0|i\rangle = E_i^{(0)}|i\rangle$$

$$\lambda^1: \quad \hat{H}_0|\Phi_i^{(1)}\rangle + \hat{V}|i\rangle = E_i^{(0)}|\Phi_i^{(1)}\rangle + E_i^{(1)}|i\rangle$$

$$\lambda^2: \quad \hat{H}_0|\Phi_i^{(2)}\rangle + \hat{V}|\Phi_i^{(1)}\rangle = E_i^{(0)}|\Phi_i^{(2)}\rangle + E_i^{(1)}|\Phi_i^{(1)}\rangle + E_i^{(2)}|i\rangle$$

$$\lambda^3: \quad \hat{H}_0|\Phi_i^{(3)}\rangle + \hat{V}|\Phi_i^{(2)}\rangle = E_i^{(0)}|\Phi_i^{(3)}\rangle + E_i^{(1)}|\Phi_i^{(2)}\rangle + E_i^{(2)}|\Phi_i^{(1)}\rangle + E_i^{(3)}|i\rangle$$

Multiply these equations by $\langle i|$ and use orthogonality $\langle i|\langle\Phi_i^{(n)}\rangle = 0$

Rayleigh-Schrodinger perturbation theory

Multiply these equations by $\langle i |$ and use orthogonality $\langle i | \langle \Phi_i^{(n)} \rangle = 0$

$$\hat{H}_0 |i\rangle = E_i^{(0)} |i\rangle \quad \xrightarrow{\hspace{10em}} \quad E_i^{(0)} = \langle i | \hat{H}_0 |i\rangle$$

$$\hat{H}_0 |\Phi_i^{(1)}\rangle + \hat{V} |i\rangle = E_i^{(0)} |\Phi_i^{(1)}\rangle + E_i^{(1)} |i\rangle \quad \xrightarrow{\hspace{10em}} \quad E_i^{(1)} = \langle i | \hat{V} |i\rangle$$

The first order correction to the energy is the expectation value of the perturbation, in the unperturbed state

$$\hat{H}_0 |\Phi_i^{(2)}\rangle + \hat{V} |\Phi_i^{(1)}\rangle = E_i^{(0)} |\Phi_i^{(2)}\rangle + E_i^{(1)} |\Phi_i^{(1)}\rangle + E_i^{(2)} |i\rangle \quad \xrightarrow{\hspace{10em}} \quad E_i^{(2)} = \langle i | \hat{V} |\Phi_i^{(1)}\rangle$$

$$\hat{H}_0 |\Phi_i^{(3)}\rangle + \hat{V} |\Phi_i^{(2)}\rangle = E_i^{(0)} |\Phi_i^{(3)}\rangle + E_i^{(1)} |\Phi_i^{(2)}\rangle + E_i^{(2)} |\Phi_i^{(1)}\rangle + E_i^{(3)} |i\rangle \quad \xrightarrow{\hspace{10em}} \quad E_i^{(3)} = \langle i | \hat{V} |\Phi_i^{(2)}\rangle$$

Need to obtain $|\langle \Phi_i^{(n)} \rangle|$ from previous equations

Rayleigh-Schrodinger perturbation theory

Can expand $|\Phi_i^{(1)}\rangle$ in eigenfunctions of H_0 : $|\Phi_i^{(1)}\rangle = \sum_{n \neq i} c_n^{(i)} |n\rangle$

Use Fourier trick and orthonormality of states $|n\rangle$: $\langle n | \Phi_i^{(1)} \rangle = c_n^{(i)}$

From intermediate normalization $c_i^{(i)} = 0$

Then $|\Phi_i^{(1)}\rangle = \sum_{n \neq i} |n\rangle \langle n | \Phi_i^{(1)} \rangle$

Rayleigh-Schrodinger perturbation theory

Rewrite equation for λ^1 : $\hat{H}_0|\Phi_i^{(1)}\rangle + \hat{V}|i\rangle = E_i^{(0)}|\Phi_i^{(1)}\rangle + E_i^{(1)}|i\rangle$ as

$$(E_i^{(0)} - \hat{H}_0)|\Phi_i^{(1)}\rangle = (\hat{V} - E_i^{(1)})|i\rangle$$

Multiply by $\langle n |$ and get $\langle n | (E_i^{(0)} - \hat{H}_0) |\Phi_i^{(1)}\rangle = \langle n | (\hat{V} - E_i^{(1)}) |i\rangle$

$$(E_i^{(0)} - E_n^{(0)}) \boxed{\langle n | \Phi_i^{(1)}\rangle} = \langle n | \hat{V} | i \rangle$$

Use $|\Phi_i^{(1)}\rangle = \sum_{n \neq i} |n\rangle \langle n | \Phi_i^{(1)}\rangle$ to obtain the second-order energy:

$$E_i^{(2)} = \langle i | \hat{V} | \Phi_i^{(1)}\rangle = \sum_{n \neq i} \langle i | \hat{V} | n \rangle \boxed{\langle n | \Phi_i^{(1)}\rangle} = \sum_{n \neq i} \frac{\langle i | \hat{V} | n \rangle \langle n | \hat{V} | i \rangle}{E_i^{(0)} - E_n^{(0)}} = \sum_{n \neq i} \frac{|\langle i | \hat{V} | n \rangle|^2}{E_i^{(0)} - E_n^{(0)}}$$

3rd order energy: $E_i^{(3)} = \langle i | \hat{V} | \Phi_i^{(2)}\rangle = \sum_{n \neq i, m \neq i} \frac{\langle i | \hat{V} | n \rangle \langle n | \hat{V} | m \rangle \langle m | \hat{V} | i \rangle}{(E_i^{(0)} - E_n^{(0)})(E_i^{(0)} - E_m^{(0)})} - E_i^{(1)} \sum_{n \neq i} \frac{|\langle i | \hat{V} | n \rangle|^2}{(E_i^{(0)} - E_n^{(0)})^2}$

Moller-Plesset many-body perturbation theory

Moller-Plesset many-body perturbation theory: MP, MBPT

number will define order, e.g. MP2, MP4

Back to the electronic structure theory

Goal: to compute electron correlation energy through perturbation

Key: partitioning of the electronic Hamiltonian $\hat{H} = \hat{H}_0 + \lambda \hat{V}$

Let's define \hat{H}_0 as a sum of Fock operators. Then

$$\hat{H}_0 = \sum_i \hat{f}(i) = \sum_i \left[\hat{h}(i) + \sum_j \left(\hat{J}_j(i) - \hat{K}_j(i) \right) \right]$$

$$\hat{H} = \sum_i \hat{h}(i) + \sum_{i < j} \frac{1}{r_{ij}}$$

$$\hat{V} = \hat{H} - \hat{H}_0 = \sum_{i < j} \frac{1}{r_{ij}} - \sum_{ij} \left(\hat{J}_j(i) - \hat{K}_j(i) \right)$$

Moller-Plesset many-body perturbation theory

0th order:

$$\hat{H}_0 |\Phi_0\rangle = E_0^{(0)} |\Phi_0\rangle \quad \text{ground state SD}$$

$$E_0^{(0)} = \sum_i \varepsilon_i \quad \text{sum of orbital energies}$$

0th order energy is NOT the Hartree-Fock energy!

Moller-Plesset many-body perturbation theory

1st order:

$$\begin{aligned} E_0^{(1)} &= \langle \Phi_0 | \hat{V} | \Phi_0 \rangle = \langle \Phi_0 | \sum_{i < j} \frac{1}{r_{ij}} | \Phi_0 \rangle - \langle \Phi_0 | \sum_{ij} (\hat{J}_j(i) - \hat{K}_j(i)) | \Phi_0 \rangle \\ &\quad \downarrow \text{recall derivation of Hartree-Fock energy} \\ &= \frac{1}{2} \langle \Phi_0 | \sum_{ij} (\hat{J}_j(i) - \hat{K}_j(i)) | \Phi_0 \rangle - \langle \Phi_0 | \sum_{ij} (\hat{J}_j(i) - \hat{K}_j(i)) | \Phi_0 \rangle \\ &= -\frac{1}{2} \langle \Phi_0 | \sum_{ij} (\hat{J}_j(i) - \hat{K}_j(i)) | \Phi_0 \rangle = -\frac{1}{2} \sum_{ij} (J_{ij} - K_{ij}) \\ &= -\frac{1}{2} \sum_{ij} (\langle ij | ij \rangle - \langle ij | ji \rangle) = -\frac{1}{2} \sum_{ij} \langle ij || ij \rangle \end{aligned}$$

$$E_0^{(0)} + E_0^{(1)} = \sum_i \varepsilon_i - \frac{1}{2} \sum_{ij} (\langle ij | ij \rangle - \langle ij | ji \rangle) = E_{HF}$$

Hartree-Fock energy is a sum of 0th and 1st order energies

Moller-Plesset many-body perturbation theory

2nd order:

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

$|0\rangle = |\Phi_0\rangle$ ground state SD

$|n\rangle = ?$ should be some excited states

Single excitations: $\langle \Phi_0 | \hat{V} | \Phi_i^a \rangle = \langle \Phi_0 | \hat{H} - \hat{H}_0 | \Phi_i^a \rangle = \langle \Phi_0 | \hat{H} | \Phi_i^a \rangle - \langle \Phi_0 | \sum_j \hat{f}(j) | \Phi_i^a \rangle$

Brillioun's theorem

$$\langle \Phi_0 | \hat{V} | \Phi_i^a \rangle = 0$$

$$\sum_j \varepsilon_j \langle \Phi_0 | \Phi_i^a \rangle$$

Triple excitations: $\langle \Phi_0 | \hat{V} | \Phi_{ijk}^{abc} \rangle = \langle \Phi_0 | \hat{H} - \hat{H}_0 | \Phi_{ijk}^{abc} \rangle = 0$

SDs differing by more than two orbitals → zero Hamiltonian matrix elements

Moller-Plesset many-body perturbation theory

2nd order:

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

Double excitations:

only two-electron integrals are non-zero

$$E_0^{(2)} = \sum_{i < j}^{\text{occ}} \sum_{a < b}^{\text{vir}} \frac{|\langle \Phi_0 | \hat{V} | \Phi_{ij}^{ab} \rangle|^2}{E_0^{(0)} - E_{ij}^{ab}} = \sum_{i < j}^{\text{occ}} \sum_{a < b}^{\text{vir}} \frac{|\langle ij | | ab \rangle|^2}{\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b} = \frac{1}{4} \sum_{ij}^{\text{occ}} \sum_{ab}^{\text{vir}} \frac{|\langle ij | | ab \rangle|^2}{\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b}$$

avoid double-counting
of excited states

Koopmans' theorem

Similarly to CI methods, electron correlation in perturbation theory is determined by double excitations

Moller-Plesset perturbation theory: summary

$$E_0^{(2)} = \frac{1}{4} \sum_{ij}^{\text{occ}} \sum_{ab}^{\text{vir}} \frac{|\langle ij || ab \rangle|^2}{\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b}$$

- Electron correlation is recovered in the 2nd order and is determined by double excitations
- Perturbation theory methods:
 - MP2 (2nd order) – scaling N⁵, covers ~80-90% of dynamical correlation
 - MP3 (3rd order) – scaling N⁶, covers ~90-95% of dynamical correlation
 - MP4 (4th order) – scaling N⁷, covers ~95-98% of dynamical correlation
- PT methods are size-consistent

All PT methods break when $\varepsilon_i - \varepsilon_a \rightarrow 0$ i.e., small HOMO-LUMO gaps:

- electronic degeneracies
- large non-dynamical correlation
- bond-breaking, radicals, diradicals

These are also the cases when HF breaks. **Do not use PT if HF is in trouble!!!**