Perturbation theory in QM

\[ H = H_0 + \alpha H' \]

\[ H_0 \phi_i = E_i^0 \phi_i, \quad i = 0, 1, 2, \ldots, \infty \]

\( \alpha \) varied to move system from unperturbed \((\alpha = 0)\) to fully perturbed \((\alpha = 1)\).

Assume time-independent perturbation and a non-degenerate reference wavefunction.

Derivation for lowest energy state \((i = 0)\):

\[ H \psi_0 = E_0 \psi_0 \]

The perturbed Schrödinger equation.

For \( \alpha = 0 \):

\[ H = H_0 \]

\[ \psi_0 = \phi_0 \]

\[ E_0 = E^0 \]

Increasing \( \alpha \) should increase new energy and wavefunction continuously, which can be written as Taylor expansions:
\[ E(\lambda) = \lambda^0 E^{(0)} + \lambda^1 E^{(1)} + \lambda^2 E^{(2)} + \cdots \]

\[ \Psi(\lambda) = \lambda^0 \Psi^{(0)} + \lambda^1 \Psi^{(1)} + \lambda^2 \Psi^{(2)} + \cdots \]

\[ \lambda = 0 : \quad \Psi^{(0)} = \Phi \quad \{ \text{unperturbed or zero-order} \} \]

\[ E^{(0)} = E^o \]

\[ \Psi^{(1)}, \Psi^{(2)}, \ldots \quad \{ \text{first-, second-, \ldots order corrections} \} \]

Convenient to set overlap of perturbed with unperturbed wave function equal to 1.→ all correction terms are orthogonal to reference \( \Phi \):

\[ \langle \Psi | \Phi \rangle = 1 \]

\[ \langle \Psi^{(0)} + \lambda^1 \Psi^{(1)} + \lambda^2 \Psi^{(2)} + \cdots | \Phi \rangle = 1 \]

\[ \langle \Psi^{(0)} | \Phi \rangle + \lambda^1 \langle \Psi^{(1)} | \Phi \rangle + \lambda^2 \langle \Psi^{(2)} | \Phi \rangle + \cdots = 1 \]

implying

\[ \langle \Psi^{(i+0)} | \Phi \rangle = 0 \]
Rewrite Schrödinger equation:

\[(H_0 + H') (\psi^{(0)} + \psi^{(1)} + \psi^{(2)} + \ldots) =
(\tilde{\psi}^{(0)} + \tilde{\psi}^{(1)} + \tilde{\psi}^{(2)} + \ldots)(\psi^{(0)} + \psi^{(1)} + \psi^{(2)} + \ldots)\]

which holds for any \(\tilde{\psi}\), allowing to collect terms with the same power of \(\tilde{\psi}\):

\[H_0 \psi^{(0)} = E^{(0)} \psi^{(0)} \quad (\text{two unknowns})\]

\[H_0 \psi^{(1)} + H' \psi^{(0)} = E^{(0)} \psi^{(1)} + E^{(1)} \psi^{(0)}\]

\[H_0 \psi^{(2)} + H' \psi^{(1)} = E^{(0)} \psi^{(2)} + E^{(1)} \psi^{(1)} + E^{(2)} \psi^{(0)}\]

\[\vdots\]

\[H_0 \psi^{(n)} + H' \psi^{(n-1)} = \sum_{j=0}^{n} E^{(j)} \psi^{(n-j)}\]

Rayleigh–Schrödinger perturbation

Solutions of unperturbed Schrödinger equations form a complete set of orthogonal functions. The unknown 1st order correction can be expanded in these \(\{\psi_i\}_{i=0}^{\infty}\). (Rayleigh–Schrödinger perturbation theory)
1st order:
\[ \text{1st terms: } \left( H_0 - E^{(0)} \right) \psi^{(1)} + (H' - E^{(1)}) \phi_0 = 0 \]
with \[ \psi^{(1)} = \sum_{i=0}^{\infty} c_i \phi_i \]

\[ \Rightarrow \ldots \Rightarrow E^{(1)} = \langle \phi_0 | H' | \phi_0 \rangle \]

\( \Rightarrow \) average of perturbation operator over unperturbed wave function.

Take 1st equation, multiply from the left by the function corresponding to a given \( g_j \langle \phi_j | \) and integrate:
\[ g_j = \frac{\langle \phi_j | H' | \phi_0 \rangle}{E_0 - E_j} \]

2nd order:
2nd terms and intermediate normalization
\[ (c_0 = d_0 = 0) : \quad \psi^{(2)} = \sum_i d_i \phi_i \]

with \[ E^{(2)} = \sum_i c_i \left( \phi_1 | H' | \phi_i \right) = \sum_i \frac{\langle \phi_0 | H' | \phi_i \rangle \langle \phi_i | H' | \phi_0 \rangle}{E_0 - E_i} \]
Higher-order corrections are complex, but all corrections can be expressed in terms of matrix elements of the perturbation Hamiltonian over the unperturbed wavefunctions and energies.

\textbf{Møller–Plesset perturbation theory (MPn)}

Unperturbed Hamiltonian the sum of single-particle Fock operators and perturbation is the difference between full Hamiltonian and Hartree–Fock Hamiltonian.

Fock operator: \( \hat{F}_{ij} = \hat{t}_{ij} + \sum_{j}^{N} (\hat{J}_{ij} - \hat{K}_{ij}) \)

\( \hat{t}_{ij} \) exchange \( \hat{J}_{ij} \) Coulomb

It can be shown that:

\( \hat{\mathcal{C}}_{ij}^\text{HF} = \hat{J}_{ij} - \hat{K}_{ij} \)

\( \hat{F}_{ij} \phi_i(x_i) = \varepsilon_i \phi_i^*(x_i) \)
N-electron operator and reference Hamiltonian:

\[ H_0 = \sum_{i=1}^{N} \hat{H}_i + \sum_{i=1}^{N} \sum_{j=1}^{N} \left( \hat{k}_{ij} - \hat{c}_{ij} \right) \]

\[ = \sum_{i=1}^{N} \hat{H}_i + \sum_{i=1}^{N} \hat{V}_{HF} \]

and

\[ H' = H - H_0 = \sum_{i=1}^{N} \hat{V}_{ij} - \sum_{i=1}^{N} \hat{V}_{HF} \]

For a given Slater determinant, many-electron wavefunction \( \Phi_0 \), expressed in the HF orbital basis \( \{ \phi_i \} \)

\[ \langle \Phi_0 | \sum_{i=1}^{N} \hat{V}_{ij} | \Phi_0 \rangle = \frac{1}{2} \langle \Phi_0 | \sum_{i=1}^{N} \hat{V}_{HF} | \Phi_0 \rangle = \langle \Phi_0 | \Phi_0 \rangle \]

0-order wavefunction is the HF and

0-order energy a sum of

\[ E^{(0)} = \sum_{i=1}^{N} \langle \phi_i | \hat{E}_i | \phi_i \rangle = \sum_{i=1}^{N} \varepsilon_i^{HF} \]
1st order energy correction:

\[ E^{(1)} = \langle \phi_0 | \hat{H}' | \phi_0 \rangle = \]

\[ = \langle \phi_0 | \sum_{i<j} \hat{V}_{ij} | \phi_0 \rangle - \langle \phi_0 | \sum_{j=1}^{N} \hat{V}_{ij}^{HF} | \phi_0 \rangle \]

\[ = \langle \text{Vee} \rangle - 2\langle \text{Vee} \rangle = -\langle \text{Vee} \rangle \]

(perturbation operator over 0-order wavefunction)

\[ E^{(MP_0)} : n\text{-order correction} \]

\[ MP_0 : \quad E(\text{MP}_0) = \sum_{a} \varepsilon_{a}^{\text{HF}} \]

\[ MP_1 : \quad E(\text{MP}_0) + E(\text{MP}_1) = E(\text{HF}) \]

1st order correction is exactly the HF energy

2nd order is the 1st contribution to correlation energy. The correction is a sum over doubly excited determinants (single excited ones do not contribute to energy: Brillouin theorem).

Generate by promoting two electrons from occupied orbitals \(a, b\) to virtual orbitals \(r, s\).
\[ E^{(2)} = \sum_{a<b} \sum_{r<s} \frac{\langle \Phi_0 | H' | \Phi_{ab} \rangle \langle \Phi_{ab} | H' | \Phi_0 \rangle}{E_0 - E_{ab}} \]

explicit formula for MP2:

\[ E_{\text{MP2}} = \sum_{a<b} \sum_{r<s} \frac{\langle \phi_{a}\Phi_{b} | \partial_r \Phi_s \rangle - \langle \phi_{a}\Phi_{b} | \partial_s \Phi_r \rangle^2}{(\varepsilon_a + \varepsilon_b - \varepsilon_r - \varepsilon_s)} \]

Once two-electron integrals over molecular orbitals are available, the 2nd order energy correction can be calculated as a sum of M4 integrals: calculation of energy increases as \( N^4 \) with system size.

MP2 typically includes 80-90% of correlation.

MP2 energy for 100-150 basis functions at a calculation cost similar to \( E^\text{HF} \).
Post Hartree-Fock methods

Scaling:
- Hartree-Fock $O(N^3-N^4)$, error $\approx 15$ kcal/mol
  (compare to $O(N-N^3)$ scaling of DFT and an error of $\approx 4$ kcal/mol)
- Möller-Plesset (MPn)
  MP2 $O(N^5)$, error $\approx 5$ kcal/mol
  MP4 $O(N^6)$
  (perturbation method; adds correlation effects)
- Configuration Interaction (CI, CISD, QCISD ...)
  CISD $O(N^6)$
  CISD+Q $O(N^{10})$

Cl,inear combination of Slater determinants +
mixing of different electronic states: increase phase-
space of possible many-electron wavefunction.
N-electron basis functions as "excitations" from
Hartree-Fock "reference" determinant; CID limited
to double excitations only, CISD to single and
double excitations, etc.)
- Coupled cluster (CC, CCSD, CCSD(T))
  $O(N^7)$
  (based on HF and constructs multi-electron wavefunction
  using the exponential cluster operator: $|\psi> = e^T|\phi_0>$
  with $|\phi_0>$ the reference; $T$ cluster operator)