Perturbation Theory

In order to apply Rayleigh Schrödinger Perturbation Theory (RSPT) to the Schroödinger equation for electron correlation on top of some reference energy E_0, define the correlated Hamiltonian $\hat{H}_c = \hat{H}_c^{(0)} + \hat{H}_c^{(1)}$, where

$$\hat{H}_c^{(0)} = \hat{H}^{(0)} - \langle \Phi_0 | \hat{H}^{(0)} | \Phi_0 \rangle \qquad \hat{H}_c^{(1)} = \hat{H}^{(1)} - \langle \Phi_0 | \hat{H}^{(1)} | \Phi_0 \rangle \qquad \hat{H}_c^{(0)} |\Phi_P\rangle = \left(E_P^{(0)} - E_0^{(0)} \right) |\Phi_P\rangle$$

Define a basis set $\Phi_0 \ \cup \ \{\Phi_P\}$, where $|\Phi_0\rangle$ is the reference state and $\{\Phi_P\}$ is some complete, unique set of excitations from the reference.

$$|\Psi\rangle = |\Phi_0\rangle + \sum_P c_P |\Phi_P\rangle$$

It is conventional to assume that this basis is orthonormal, i.e., that

$$\langle \Phi_0 | \Phi_P \rangle = 0 \ \forall \ P$$

I. Energy expression

Left-project with the reference state $|\Phi_0\rangle$ onto the Schrödinger equation:

$$\langle \Phi_0 | \hat{H}_c |\Psi\rangle = \langle \Phi_0 | E_c |\Psi\rangle$$
$$\langle \Phi_0 | \hat{H}_c |\Phi_0\rangle + \langle \Phi_0 | \hat{H}_c |\Psi\rangle = E_c \langle \Phi_0 | \Phi_0 \rangle + E_c \sum_P \cancel{\langle \Phi_0 | \Phi_P \rangle}$$

Equate terms of order 0.

$$\begin{aligned} E_c^{(0)} &= \langle \Phi_0 | \hat{H}_c^{(0)} |\Phi_0\rangle \\ &= \langle \Phi_0 | \hat{H}^{(0)} | \Phi_0 \rangle - \langle \Phi_0 | \hat{H}^{(0)} | \Phi_0 \rangle \langle \Phi_0 | \Phi_0 \rangle \\ &= 0 \end{aligned}$$

Equate terms of order 1.

$$\begin{aligned} E_c^{(1)} &= \sum_P c_P^{(1)} \langle \Phi_0 | \hat{H}_c^{(0)} |\Phi_P\rangle + \langle \Phi_0 | \hat{H}_c^{(1)} | \Phi_0 \rangle \\ &= \sum_P c_P^{(1)} \left(\langle \Phi_0 | \hat{H}^{(0)} | \Phi_P \rangle - \langle \Phi_0 | \hat{H}^{(0)} | \Phi_0 \rangle \langle \Phi_0 | \Phi_P \rangle \right) + \langle \Phi_0 | \hat{H}^{(1)} | \Phi_0 \rangle - \langle \Phi_0 | \hat{H}^{(1)} | \Phi_0 \rangle \langle \Phi_0 | \Phi_0 \rangle \\ &= 0 \end{aligned}$$

Equate terms of order 2.

$$E_c^{(2)} = \sum_P \langle \Phi_0 | \hat{H}_c^{(1)} | \Phi_P \rangle c_P^{(1)} = \sum_P \langle \Phi_P | \hat{H}_c^{(1)} | \Phi_0 \rangle c_P^{(1)}$$

In order to evaluate the second-order energy, solve the first-order amplitude equations for coefficients $\{c_P^{(1)}\}$.

II. Amplitude Equations

To solve for the first-order expansion coefficient of the state Φ_Q, project onto the Schrödinger equation with $\langle \Phi_Q |$.

$$\begin{aligned}
\langle \Phi_Q | \, \hat{H}_c^{(0)} + \hat{H}_c^{(1)} \, | \Phi_0 + \sum_P c_P \Phi_P \rangle &= E_c \sum_P c_P \, \langle \Phi_Q | \Phi_P \rangle \\
&= \left(E_c^{(2)} + ... \right) \sum_P c_P \delta_{PQ} \\
&= c_Q \left(E_c^{(2)} + ... \right)
\end{aligned}$$

Equate terms of order 1.

$$\begin{aligned}
\langle \Phi_Q | \, \hat{H}_c^{(1)} \, | \Phi_0 \rangle + \sum_P c_P^{(1)} \, \langle \Phi_Q | \, \hat{H}_c^{(0)} \, | \Phi_P \rangle &= 0 \\
\langle \Phi_Q | \, \hat{H}_c^{(1)} \, | \Phi_0 \rangle + \sum_P c_P^{(1)} \left(E_P^{(0)} - E_0^{(0)} \right) d_{QP} &= 0 \\
\langle \Phi_Q | \, \hat{H}_c^{(1)} \, | \Phi_0 \rangle + c_Q^{(1)} \left(E_Q^{(0)} - E_0^{(0)} \right) &= 0
\end{aligned}$$

Rearrange to solve for the first-order coefficients:

$$c_Q^{(1)} = \frac{\langle \Phi_Q | \hat{H}_c^{(1)} | \Phi_0 \rangle}{E_0^{(0)} - E_Q^{(0)}} \tag{1}$$

Combine (1) and (2) to yield the general second-order energy expression.

$$E_c^{(2)} = \sum_P \frac{| \, \langle \Phi_P | \hat{H}_c^{(1)} | \Phi_0 \rangle \, |^2}{E_0^{(0)} - E_P^{(0)}} \tag{2}$$

This expression can be applied to any reference state Φ_0 and a basis set of excitations $\{\Phi_P\}$, as long as the Hamiltonian $\hat{H}_c$ is expressed in that same basis, to obtain the perturbative second-order correction to the energy.

III. Traditional MP2 Equations

$$|\Phi_0\rangle = |\Phi\rangle \qquad \hat{H}_c = \hat{H}_c^{(0)} + \hat{H}_c^{(1)} = f_p^q \, \tilde{a}_q^p + \tfrac{1}{4} \bar{g}_{pq}^{rs} \, \tilde{a}_{rs}^{pq} \qquad \{|\Phi_P\rangle\} = \{\tilde{a}_{ij}^{ab} \, |\Phi\rangle\}$$

$$\begin{aligned}
\langle \Phi | \, \tilde{a}_{ab}^{ij} \hat{H}_c^{(1)} \, | \Phi \rangle &= \tfrac{1}{4} \bar{g}_{pq}^{rs} \, \langle \Phi | \, \tilde{a}_{ab}^{ij} \tilde{a}_{rs}^{pq} \, | \Phi \rangle \\
&= \tfrac{1}{4} \bar{g}_{pq}^{rs} \, \hat{P}_{(rs)}^{(pq)} \vdots \tilde{a}_{a^{\bullet} b^{\bullet\bullet}}^{i^{\circ} j^{\circ\circ}} \tilde{a}_{r^{\circ} s^{\circ\circ}}^{p^{\bullet} q^{\bullet}} \vdots \\
&= \bar{g}_{pq}^{rs} \, \tilde{a}_{r^{\circ} s^{\circ\circ} a^{\bullet} b^{\bullet\bullet}}^{i^{\circ} j^{\circ\circ} p^{\bullet} q^{\bullet}} \\
&= \bar{g}_{pq}^{rs} \, \gamma_i^r \gamma_s^j \eta_a^p \eta_b^q \\
&= \bar{g}_{ab}^{ij}
\end{aligned}$$

$$E_c^{(2)} = \sum_{\substack{i>j \\ a>b}} \frac{| \, \langle \Phi | \, \tilde{a}_{ab}^{ij} \hat{H}_c \, | \Phi \rangle \, |^2}{\epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b}$$

$$\boxed{E_c^{(2)} = \tfrac{1}{4} \sum_{ijab} \frac{|\bar{g}_{ab}^{ij}|^2}{\epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b}} \tag{3}$$

Canonically Transformed MP2 (CT-MP2) Equations

$$|\Phi_0\rangle = |\widetilde{\text{vac}}\rangle \qquad\qquad \{|\Phi_P\rangle\} = \{\tilde{a}_p^\dagger \tilde{a}_q^\dagger \tilde{a}_r^\dagger \tilde{a}_s^\dagger \, |\widetilde{\text{vac}}\rangle\}$$

$$\hat{H}_c = \sum_{pq} \left(\tilde{t}_p^q \tilde{a}_p^\dagger \tilde{a}_q + \tilde{g}_p^q \tilde{a}_p^\dagger \tilde{a}_q^\dagger\right) + \tfrac{1}{4} \sum_{pqrs} \left(\tilde{v}_{pqrs}\, \tilde{a}_p^\dagger \tilde{a}_q^\dagger \tilde{a}_r \tilde{a}_s + \tilde{x}_{pqrs}\, \tilde{a}_p^\dagger \tilde{a}_q^\dagger \tilde{a}_r^\dagger \tilde{a}_s + \tilde{w}_{pqrs}\, \tilde{a}_p^\dagger \tilde{a}_q^\dagger \tilde{a}_r^\dagger \tilde{a}_s^\dagger + h.c.\right)$$

$$\begin{aligned}
\langle pqrs|\, \hat{H}_c \, |\widetilde{\text{vac}}\rangle &= \tfrac{1}{4} \sum_{p'q'r's'} \tilde{w}_{p'q'r's'} \, \langle\widetilde{\text{vac}}|\, \tilde{a}_s \tilde{a}_r \tilde{a}_q \tilde{a}_p \tilde{a}_{p'}^\dagger \tilde{a}_{q'}^\dagger \tilde{a}_{r'}^\dagger \tilde{a}_{s'}^\dagger \, |\widetilde{\text{vac}}\rangle \\
&= \tfrac{1}{4} \sum_{p'q'r's'} \tilde{w}_{p'q'r's'} \, \langle\widetilde{\text{vac}}|\, \Big[:\!\tilde{a}_s \tilde{a}_r \tilde{a}_q \tilde{a}_p \tilde{a}_{p'}^\dagger \tilde{a}_{q'}^\dagger \tilde{a}_{r'}^\dagger \tilde{a}_{s'}^\dagger\!: + (:\!\tilde{a}_s \tilde{a}_r \tilde{a}_q \tilde{a}_p \tilde{a}_{p'}^\dagger \tilde{a}_{q'}^\dagger \tilde{a}_{r'}^\dagger \tilde{a}_{s'}^\dagger\!:)_{F.C.} \Big] \, |\widetilde{\text{vac}}\rangle \\
&= \tfrac{1}{4} \sum_{p'q'r's'} \tilde{w}_{p'q'r's'} (:\!\tilde{a}_s \tilde{a}_r \tilde{a}_q \tilde{a}_p \tilde{a}_{p'}^\dagger \tilde{a}_{q'}^\dagger \tilde{a}_{r'}^\dagger \tilde{a}_{s'}^\dagger\!:)_{F.C.} \\
&= \tfrac{1}{4} \sum_{p'q'r's'} \tilde{w}_{p'q'r's'} \, \hat{P}_{(p/q/r/s)} \, \tilde{a}_s \tilde{a}_r \tilde{a}_q \tilde{a}_p \tilde{a}_{p'}^\dagger \tilde{a}_{q'}^\dagger \tilde{a}_{r'}^\dagger \tilde{a}_{s'}^\dagger \\
&= \tfrac{1}{4} \sum_{p'q'r's'} \tilde{w}_{p'q'r's'} \, \hat{P}_{(p/q/r/s)} \, \left(\delta_{pp'} \delta_{qq'} \delta_{rr'} \delta_{ss'}\right) \\
&= \tfrac{1}{4} \hat{P}_{(p/q/r/s)} \left[\sum_{p'q'r's'} \tilde{w}_{p'q'r's'} \, \delta_{pp'} \delta_{qq'} \delta_{rr'} \delta_{ss'} \right] \\
&= \tfrac{1}{4} \hat{P}_{(p/q/r/s)} \, (\tilde{w}_{pqrs})
\end{aligned}$$

$$\implies \; c_{pqrs}^{(1)} = \frac{\langle pqrs|\, \hat{H}_c \, |\widetilde{\text{vac}}\rangle}{\epsilon_p + \epsilon_q + \epsilon_r + \epsilon_s} = \frac{\tfrac{1}{4} \hat{P}_{(p/q/r/s)} \, (\tilde{w}_{pqrs})}{\epsilon_p + \epsilon_q + \epsilon_r + \epsilon_s}$$

$$\implies \quad E_c^{(2)} = \frac{1}{4!} \sum_{pqrs} \frac{|\, \langle pqrs|\, \hat{H}_c \, |\widetilde{\text{vac}}\rangle \,|^2}{-(\epsilon_p + \epsilon_q + \epsilon_r + \epsilon_s)}$$

$$\begin{aligned}
E_c^{(2)} &= \frac{1}{4!} \sum_{pqrs} \frac{\left[\tfrac{1}{4} \hat{P}_{(p/q/r/s)} \, (\tilde{w}_{pqrs})\right]^2}{-(\epsilon_p + \epsilon_q + \epsilon_r + \epsilon_s)} \\
&= -\frac{1}{4!} \sum_{pqrs} \frac{\left[\tfrac{1}{4} \cdot 4 \left(\tilde{w}_{pqrs} + \tilde{w}_{prsq} + \tilde{w}_{psqr} + \tilde{w}_{qrps} + \tilde{w}_{qsrp} + \tilde{w}_{rspq}\right)\right]^2}{\epsilon_p + \epsilon_q + \epsilon_r + \epsilon_s} \\
&= -\frac{1}{4!} \sum_{pqrs} \frac{\left(6 \tilde{w}_{pqrs}^2 + \ldots\right)}{\epsilon_p + \epsilon_q + \epsilon_r + \epsilon_s} \\
&= \boxed{-\frac{1}{4} \sum_{pqrs} \frac{\tilde{w}_{pqrs}^2}{\epsilon_p + \epsilon_q + \epsilon_r + \epsilon_s}} + \ldots
\end{aligned}$$