

Programming Project 6 Exercises

1. **Rayleigh-Schrödinger perturbation theory.** Given a 0th order approximation $\hat{H}^{(0)}\Psi_K^{(0)} = E_K^{(0)}\Psi_K^{(0)}$ to the full Schrödinger equation $\hat{H}\Psi_K = E_K\Psi_K$, the exact wavefunctions and energies of well-behaved systems can be expanded in terms of their 0th order counterparts using Rayleigh-Schrödinger perturbation theory. The n^{th} order wavefunction and energy corrections, $\Psi_K^{(n)}$ and $E_K^{(n)}$, in the perturbation expansions, $\Psi_K = \Psi_K^{(0)} + \sum_{n=1}^{\infty} \Psi_K^{(n)}$ and $E_K = E_K^{(0)} + \sum_{n=1}^{\infty} E_K^{(n)}$, can be obtained from the RSPT equations

$$(\hat{H}^{(0)} - E_K^{(0)})\Psi_K^{(n)} = \sum_{p=0}^{n-1} E_K^{(n-p)}\Psi_K^{(p)} - \hat{W}\Psi_K^{(n-1)} \quad (1)$$

where $\hat{W} \equiv \hat{H} - \hat{H}^{(0)}$. Show that, assuming $\langle \Psi^{(0)} | \Psi^{(n)} \rangle = 0$ for $n \geq 1$ (intermediate normalization), the n^{th} order energy correction is given by

$$E_K^{(n)} = \langle \Psi_K^{(0)} | \hat{W} | \Psi_K^{(n-1)} \rangle. \quad (2)$$

2. The $\Psi^{(1)}$ RSPT equation (equation 1 with $n = 1$) is given by

$$(\hat{H}^{(0)} - E_K^{(0)})\Psi_K^{(1)} = (E_K^{(1)} - \hat{W})\Psi_K^{(0)}. \quad (3)$$

Using equation 3, show that the expansion coefficients of $\Psi_K^{(1)}$ in the basis of 0th order solutions $\{\Psi_L^{(0)}\}$

$$\Psi_K^{(1)} = \sum_{L \neq K} \Psi_L^{(0)} c_{LK}^{(1)}$$

are given by

$$c_{LK}^{(1)} = \frac{\langle \Psi_L^{(0)} | \hat{W} | \Psi_K^{(0)} \rangle}{E_L^{(0)} - E_K^{(0)}}. \quad (4)$$

3. Show that the RSPT energy up to second order is given by

$$E_K^{(0)} + E_K^{(1)} + E_K^{(2)} = \langle \Psi_K^{(0)} | \hat{H} | \Psi_K^{(0)} \rangle + \sum_{L \neq K} \frac{\langle \Psi_K^{(0)} | \hat{W} | \Psi_L^{(0)} \rangle \langle \Psi_L^{(0)} | \hat{W} | \Psi_K^{(0)} \rangle}{E_L^{(0)} - E_K^{(0)}}. \quad (5)$$

4. **Møller-Plesset perturbation theory.** When the exact electronic Hamiltonian

$$\hat{H}_e = \sum_{i=1}^n \hat{h}(i) + \frac{1}{2} \sum_{ij}^n \hat{g}(i, j)$$

is approximated by a sum of one-particle Fock operators $\hat{f}(i)$

$$\hat{H}_e^{(0)} = \sum_{i=1}^n \hat{f}(i) = \sum_{i=1}^n \hat{h}(i) + \sum_{i=1}^n \sum_{k=1}^n (\hat{J}_k(i) - \hat{K}_k(i))$$

the RSPT approach is called Møller-Plesset perturbation theory. Show that, given spin-orbitals satisfying

$$\hat{f}(1)\psi_p(1) = \epsilon_p\psi_p(1) \quad (\text{canonical Hartree-Fock equations}), \quad (6)$$

the determinants $\{\Phi, \Phi_i^a, \Phi_{ij}^{ab}, \Phi_{ijk}^{abc}, \dots\}$ formed from them provide 0th order solutions of the form

$$\hat{H}_e^{(0)}\Phi = \mathcal{E}\Phi \quad \hat{H}_e^{(0)}\Phi_i^a = \mathcal{E}_i^a\Phi_i^a \quad \hat{H}_e^{(0)}\Phi_{ij}^{ab} = \mathcal{E}_{ij}^{ab}\Phi_{ij}^{ab} \quad \hat{H}_e^{(0)}\Phi_{ijk}^{abc} = \mathcal{E}_{ijk}^{abc}\Phi_{ijk}^{abc} \quad \dots \quad (7)$$

where $\mathcal{E}_{ijk\dots}^{abc\dots}$ is the sum of the orbital energies for $\Phi_{ijk\dots}^{abc\dots}$.

5. Show that the Møller-Plesset energy is given to second order by

$$E^{(0)} + E^{(1)} + E^{(2)} = E_0 + \sum_i^a \frac{|\langle \Phi | \hat{W} | \Phi_i^a \rangle|^2}{\epsilon_i - \epsilon_a} + \sum_{\substack{a < b \\ i < j}} \frac{|\langle \Phi | \hat{W} | \Phi_{ij}^{ab} \rangle|^2}{\epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b} + \sum_{\substack{a < b < c \\ i < j < k}} \frac{|\langle \Phi | \hat{W} | \Phi_{ijk}^{abc} \rangle|^2}{\epsilon_i + \epsilon_j + \epsilon_k - \epsilon_a - \epsilon_b - \epsilon_c} + \dots$$

where $E_0 = \langle \Phi | \hat{H}_e | \Phi \rangle$ is the Hartree-Fock energy.¹

6. Use Slater's rules and Brillouin's theorem to show that the second-order Møller-Plesset (MP2) energy can be simplified to the following expression.

$$E^{(0)} + E^{(1)} + E^{(2)} = E_0 + \frac{1}{4} \sum_{ijab} \frac{|\langle ij || ab \rangle|^2}{\epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b} \quad (8)$$

¹Note that E_0 is not \mathcal{E} , the sum of Φ 's orbital energies