Programming Project 6 Exercises

1. ***Rayleigh-Schrödinger perturbation theory.*** Given a 0^{th} 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 0^{th} 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

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

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

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

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

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

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

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

are given by

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

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

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

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

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

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

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

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

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

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

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 for a canonical Hartree-Fock reference determinant.

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

[1] Note that E_0 is <u>not</u> $\mathcal{E}$, the sum of Φ's orbital energies