Exercise 1: FCI Properties

We consider in this exercise the first and second derivatives of the FCI ground-state energy. In particular, we demonstrate how the first- and second-order Rayleigh–Schrödinger energy expressions are recovered in the FCI eigenvector repsresentation. We assume that the electronic Hamiltonian $H(x, y)$ depends on two external parameters x and y, which for the unperturbed system are both zero. We write the normalized FCI wave function in the form

$$|\mathbf{c}\rangle = \sum\nolimits_{n=0}^{\infty} c_n |n\rangle, \quad \mathbf{c}^{\mathrm{T}}\mathbf{c} = 1, \quad \langle m|n\rangle = \delta_{mn},$$

where the states $|n\rangle$ are normalized CI eigenstates of the unperturbed problem with eigenvalues E_n:

$$\langle m|H(0,0)|n\rangle = \delta_{mn} E_n, \quad E_0 \le E_1 \le E_2 \cdots .$$

1. Show that the FCI Lagrangian is given by

$$L(x, y, \mathbf{c}, \mu) = \sum_{mn} c_m \langle m|H(x, y)|n\rangle c_n - \mu \left(\sum\nolimits_n c_n^2 - 1\right),$$

   where μ is a Lagrange multiplier.

2. Show that the stationary conditions of the Lagrangian with respect to the CI coefficients and the multiplier are, for all $n \ge 0$, given by

$$\frac{\partial L}{\partial c_n} = 2\langle n|H(x, y)|\mathbf{c}\rangle - 2\mu c_n = 0, \quad \frac{\partial L}{\partial \mu} = \sum_n c_n^2 - 1 = 0.$$

   Argue that, for the optimized electronic ground state, we have $c_0 = 1$, $\mu = E_0$, and $c_n = 0$ for all $n > 0$.

3. Using the stationary conditions, demonstrate that that the first and second derivatives of the FCI energy of the unperturbed system are given by

$$\frac{\mathrm{d}E}{\mathrm{d}x} = \frac{\mathrm{d}L}{\mathrm{d}x} = \frac{\partial L}{\partial x},$$
$$\frac{\mathrm{d}^2 E}{\mathrm{d}x\mathrm{d}y} = \frac{\mathrm{d}^2 L}{\mathrm{d}x\mathrm{d}y} = \frac{\partial^2 L}{\partial x \partial y} - \sum_{mn} \frac{\partial^2 L}{\partial x \partial c_m} \left[\frac{\partial^2 L}{\partial c_m \partial c_n}\right]^{-1} \frac{\partial^2 L}{\partial c_n \partial y},$$

   where all derivatives have been evaluated at $(x, y) = (0, 0)$. In a slight abuse of notation, the $\left[\partial^2 L/\partial c_m \partial c_n\right]^{-1}$ are elements of the inverted electronic Hessian, whose elements are given by $\partial^2 L/\partial c_m \partial c_n$.

4. By evaluating the partial derivatives of L with respect to the CI coefficients, show that the

$$\begin{aligned}
\frac{\partial^2 L}{\partial x \partial c_n} &= 2\left\langle n \middle| \tfrac{\partial H}{\partial x} \middle| 0 \right\rangle, \\
\frac{\partial^2 L}{\partial c_m \partial c_n} &= 2\left\langle m \middle| H - E_0 \middle| n \right\rangle = 2(E_n - E_0)\delta_{mn},
\end{aligned}$$

and show that the derivatives of the FCI energy become

$$\begin{aligned}
\frac{\mathrm{d}E}{\mathrm{d}x} &= \left\langle 0 \middle| \tfrac{\partial H}{\partial x} \middle| 0 \right\rangle, \\
\frac{\mathrm{d}^2 E}{\mathrm{d}x\mathrm{d}y} &= \left\langle 0 \middle| \tfrac{\partial^2 H}{\partial x \partial y} \middle| 0 \right\rangle - 2\sum_n \frac{\left\langle 0 \middle| \tfrac{\partial H}{\partial x} \middle| n \right\rangle \left\langle n \middle| \tfrac{\partial H}{\partial y} \middle| 0 \right\rangle}{E_n - E_0}.
\end{aligned}$$

5. Compare these expressions with first- and second-order Rayleigh–Schrödinger energies.