# Exercise 1: Derivatives of the exact wave function

In this exercise, we consider the first and second derivatives of the ground-state energy for exact wave functions. In particular, we demonstrate how the first- and second-order Rayleigh-Schr"odinger energy expressions are recovered in the FCI eigenvector representation. We assume that the electronic Hamiltonian $\hat{H}(x, y)$ depends on two external parameters $x$ and $y$ which both vanish for the unperturbed system and, for simplicity, that the wave function is real. We write the normalized FCI wave function as

$$|\Psi\rangle = \sum_{n=0}^{\infty} c_n |\Phi_n\rangle, \quad \mathbf{c}^{\mathrm{T}}\mathbf{c} = 1, \quad \langle \Phi_m \mid \Phi_n \rangle = \delta_{mn}$$

where the states $\Phi_n$ are normalized CI eigenstates of the unperturbed problem with eigenvalues $E_n$ and $c_n$ are the coefficients within the coefficient vector $\mathbf{c}$. We note that the unperturbed Hamiltonian matrix is already diagonal with elements

$$H_{mn}(0,0) = \langle \Phi_m \mid \hat{H}(0,0) \mid \Phi_n \rangle = \delta_{mn} E_n, \quad E_0 \leq E_1 \leq E_2 \leq \ldots$$

1. Show that the FCI Lagrangian is given by

   $$L(x, y, \mathbf{c}, \lambda) = \sum_{mn} c_m \langle \Phi_m \mid \hat{H}(x, y) \mid \Phi_n \rangle c_n - \lambda \left( \sum_n c_n^2 - 1 \right)$$

   where $\lambda$ is a Lagrange multiplier.

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

   $$\frac{\partial L}{\partial c_n} = 2\langle \Phi_n \mid \hat{H}(x, y) \mid \Psi \rangle - 2\lambda c_n = 0, \quad \frac{\partial L}{\partial \lambda} = \sum_n c_n^2 - 1 = 0.$$

   Argue that, for the optimized unperturbed electronic ground state, we have:

   $$c_0 = 1, \lambda = E_0, \text{ and } c_n = 0 \text{ for all } n > 0.$$

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

   $$\frac{\mathrm{d}E}{\mathrm{d}x} = \frac{\mathrm{d}L}{\mathrm{d}x} = \frac{\partial L}{\partial x},$$
   $$\frac{\mathrm{d}^2 E}{\mathrm{d}x\mathrm{d}y} = \frac{\mathrm{d}^2 L}{\mathrm{d}x\mathrm{d}y} = \frac{\partial^2 L}{\partial x \partial y} + \sum_n \frac{\partial^2 L}{\partial x \partial c_n} \frac{\partial c_n}{\partial y}$$

   Argue why here the second derivative with respect to the perturbations does not contain a contribution from the Lagrange multipliers. How can you get determining equations for the perturbed coefficients?

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

   $$\frac{\partial^2 L}{\partial x \partial c_n} = 2 \left\langle \Phi_n \middle| \frac{\partial \hat{H}}{\partial x} \middle| \Phi_0 \right\rangle,$$
   $$\frac{\partial^2 L}{\partial c_m \partial c_n} = 2 \left\langle \Phi_m \mid \hat{H} - E_0 \mid \Phi_n \right\rangle = 2(E_n - E_0)\delta_{mn},$$

   and show that the derivatives of the unperturbed ground-state energy become

   $$\frac{\mathrm{d}E}{\mathrm{d}x} = \left\langle \Phi_0 \middle| \frac{\partial \hat{H}}{\partial x} \middle| \Phi_0 \right\rangle,$$
   $$\frac{\mathrm{d}^2 E}{\mathrm{d}x\mathrm{d}y} = \left\langle \Phi_0 \middle| \frac{\partial^2 \hat{H}}{\partial x \partial y} \middle| \Phi_0 \right\rangle - 2 \sum_n \frac{\left\langle \Phi_0 \middle| \frac{\partial \hat{H}}{\partial x} \middle| \Phi_n \right\rangle \left\langle \Phi_n \middle| \frac{\partial \hat{H}}{\partial y} \middle| \Phi_0 \right\rangle}{E_n - E_0}.$$

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

# Exercise 2: London Orbitals and Magnetic Response

The following exercises concern the use of so-called *London orbitals*, which are basis functions with an extra, parametrized spatial dependence. London orbitals are often used in calculations involving an external magnetic field. Consider an atomic orbital $\psi_{lm}$ positioned at $\mathbf{O}$ which in the field-free case satisfies the Schrödinger equation

$$\hat{H}^{(0)}\psi_{lm} = E^{(0)}\psi_{lm}$$

In atomic units,

$$\hat{H}^{(0)} = -\frac{1}{2}\nabla^2 + V$$

for some effective, spherically symmetric potential $V$. The orbital is an eigenfunction of the $z$ component of the angular momentum about $\mathbf{O}$:

$$\begin{aligned} \hat{L}_z\psi_{lm} &= m\psi_{lm} \\ \hat{\mathbf{L}} &= (\hat{\mathbf{r}} - \hat{\mathbf{O}}) \times \hat{\mathbf{p}} \end{aligned}$$

We now apply a uniform external magnetic induction $\mathbf{B}$ along the $z$ axis. To construct the Hamiltonian, we need a vector potential. First choose it such that it disappears at the center $\mathbf{O}$:

$$\mathbf{A}_\mathbf{O}(\mathbf{r}) = \frac{\mathbf{B} \times (\mathbf{r} - \mathbf{O})}{2}$$

This potential gives the correct induction, as may be confirmed by calculating

$$\mathbf{B} = \nabla \times \mathbf{A}_\mathbf{O}(\mathbf{r})$$

With this potential, the Hamiltonian becomes

$$\hat{H}_\mathbf{O} = \frac{1}{2}\hat{\pi}_\mathbf{O}^2 + V$$

where the kinetic momentum is given by

$$\hat{\pi}_\mathbf{O} = -i\nabla + \mathbf{A}_\mathbf{O}(\mathbf{r})$$

and we have added the subscript $\mathbf{O}$ to the Hamiltonian to remind us that it is constructed from a vector potential vanishing at $\mathbf{O}$. You are now in a position to do the following exercises.

1. Show that to first order in B the Hamiltonian may be written

   $$\hat{H}_\mathbf{O} = \hat{H}^{(0)} + \frac{1}{2}BL_z + O(B^2)$$

   and that to the same order in B the Schrödinger equation is

   $$\hat{H}_\mathbf{O}\psi_{lm} = (E^{(0)} + \frac{1}{2}Bm)\psi_{lm} \quad \text{(gauge origin } \mathbf{O})$$

   Hence *with this choice of vector potential,* the unperturbed atomic orbital is correct to first order in the perturbation.

2. Now make a different choice of gauge origin:

   $$\mathbf{A}_\mathbf{G}(\mathbf{r}) = \frac{\mathbf{B} \times (\mathbf{r} - \mathbf{G})}{2}$$

   This is also a valid vector potential, since it describes the same induction as before:

   $$\nabla \times \mathbf{A}_\mathbf{G}(\mathbf{r}) = \nabla \times \mathbf{A}_\mathbf{O}(\mathbf{r})$$

   The Hamiltonian and kinetic momentum operators are now represented as

   $$\hat{H}_\mathbf{G} = \frac{1}{2}\hat{\pi}_\mathbf{G}^2 + V$$

$$\hat{\pi}_{\mathbf{G}} = -i\nabla + \mathbf{A}_{\mathbf{G}}(\mathbf{r})$$

Show that with this (equally valid) choice of gauge origin the unperturbed wave function $\psi_{lm}$ is no longer correct to first order in the perturbation.

We conclude that the atomic orbitals describes the perturbed wave function better for some gauge choices than for other. In general, magnetic properties calculated using LCAO orbitals are gauge dependent.

3. We now introduce a complex phase factor in the orbital as suggested by London:

$$\omega_{lm} = \exp(-i\mathbf{A}(\mathbf{O}) \cdot \mathbf{r})\psi_{lm}$$

where $\mathbf{A}(\mathbf{O})$ is the vector potential at the position of the atomic orbital. For example, with the vector potential $\mathbf{A}_{\mathbf{G}}(\mathbf{r})$ the London atomic orbital becomes

$$\omega_{lm} = \exp(\frac{i}{2}\mathbf{B} \times (\mathbf{G} - \mathbf{O}) \cdot \mathbf{r})\psi_{lm}$$

Show that the following relationship holds:

$$\hat{\pi}_{\mathbf{G}} \exp(-i\mathbf{A}_{\mathbf{G}}(\mathbf{O}) \cdot \mathbf{r}) = \exp(-i\mathbf{A}_{\mathbf{G}}(\mathbf{O}) \cdot \mathbf{r})\hat{\pi}_{\mathbf{O}}$$

and therefore

$$\hat{H}_{\mathbf{G}} \exp(-i\mathbf{A}_{\mathbf{G}}(\mathbf{O}) \cdot \mathbf{r}) = \exp(-i\mathbf{A}_{\mathbf{G}}(\mathbf{O}) \cdot \mathbf{r})\hat{H}_{\mathbf{O}}$$

Then show that, to first order,

$$\hat{H}_{\mathbf{G}}\omega_{lm} = (E^{(0)} + \frac{1}{2}Bm)\omega_{lm} \quad \text{(any gauge origin)}$$

4. We have seen that the London orbitals are well suited for the description of magnetic perturbations involving an external magnetic field. A further benefit is that the use of London orbitals makes LCAO calculations strictly gauge-origin independent. To prove this, it suffices to show that all integrals over London orbitals are independent of origin. Assume two atomic orbitals $\psi_\mu$ and $\psi_\nu$ are centered at $\mathbf{M}$ and $\mathbf{N}$ respectively, and form the London orbitals

$$\omega_\mu = \exp(-i\mathbf{A}_{\mathbf{G}}(\mathbf{M}) \cdot \mathbf{r})\psi_\mu$$

$$\omega_\nu = \exp(-i\mathbf{A}_{\mathbf{G}}(\mathbf{N}) \cdot \mathbf{r})\psi_\nu$$

Show that the kinetic energy integral

$$T_{\mu\nu} = \langle\omega_\mu|\frac{1}{2}\hat{\pi}^2_{\mathbf{G}}|\omega_\nu\rangle$$

may be written as

$$T_{\mu\nu} = \langle\psi_\mu| \exp(\frac{i}{2}\mathbf{B} \cdot (\mathbf{M} - \mathbf{N}) \times \mathbf{r})\frac{1}{2}\hat{\pi}^2_{\mathbf{N}}|\psi_\nu\rangle$$

which is manifestly independent of the gauge origin G.

5. The London orbitals depend on the choice of coordinate system since $\mathbf{r}$ appears in the phase factor. The same is true of integrals over London orbitals. Does our calculated results depend on the coordinate system?

# Exercise 3: Hellmann-Feynman theorem

1. Show for the exact wave function that the derivative of the energy $E$ with respect to a parameter $\alpha$ can be written as the expectation value of the derivate of the Hamiltonian with respect to this parameter (Hellman-Feynman theorem), i.e.,

$$\frac{\mathrm{d}E}{\mathrm{d}\alpha} = \left\langle \Psi \left| \frac{\partial \hat{H}}{\partial \alpha} \right| \Psi \right\rangle .$$

   Both the Hamiltonian $\hat{H}$ as well as the wave function $\Psi$ depend on the perturbation $\alpha$. The wave function $\Psi$ is normalized and eigenfunction of $\hat{H}$ with eigenvalue $E$.

2. Show that the Hellmann-Feynman theorem is also valid for the Hartree-Fock wave function $\Psi_{\mathrm{HF}}$.

   *hint:* Write the derivative of the wave function with respect to a infinitesimal perturbation $\alpha$ as

$$\frac{\partial \Psi}{\partial \alpha} = a\Psi + \Psi^{\perp}$$

   where $\Psi^{\perp}$ is the component perpendicular to $\Psi$ and $a$ is a scalar and use the fact that Hartree-Fock theory is variational.

3. Show that for the derivative of the Born-Oppenheimer potential it holds:

$$\frac{\mathrm{d}E_{\mathrm{tot}}(\mathbf{R})}{\mathrm{d}\mathbf{R}} = \frac{\partial V_{\mathrm{nn}}(\mathbf{R})}{\partial \mathbf{R}} + \left\langle \Psi_{\mathrm{el}}(\mathbf{r};\mathbf{R}) \left| \frac{\partial V_{\mathrm{ne}}(\mathbf{r},\mathbf{R})}{\partial \mathbf{R}} \right| \Psi_{\mathrm{el}}(\mathbf{r};\mathbf{R}) \right\rangle ,$$

   where $V_{\mathrm{nn}}$ and $V_{\mathrm{ne}}$ are the nuclear-nuclear and nuclear-electron potentials, respectively and $\Psi_{\mathrm{el}}$ is the electronic wave function. Which terms vanish due to the Hellmann-Feynman theorem?

4. Does the Hellmann-Feynman theorem hold when a finite basis set $\{\chi_\mu\}$ is employed to describe the molecular orbitals? Discuss the following cases:

   (a) The basis set $\{\chi_\mu\}$ is independent of the perturbation $\alpha$.

   (b) The basis set $\{\chi_\mu\}$ depends on the perturbation.

   Do you know examples for the respective cases?