

# Exam in Advanced Quantum Chemistry – M2 course

January 2022, *Two-hour exam*

*Neither documents nor calculators are allowed.*

---

## 1. Questions on the lecture material [10 points]

- a) [2 pts] What is the key idea underlying the Hartree–Fock (HF) approximation? What is the definition of the correlation energy? Is FCI exact?
- b) [3 pts] Explain why the HF method can be formulated as an orbital rotation problem. How can the HF orbitals be optimized? How can we verify in a CI calculation that the determinants are constructed from HF orbitals? If we perform the FCI calculation with different molecular orbitals [the KS orbitals, for example] without changing the atomic orbital basis, do we obtain a different FCI energy?
- c) [3 pts] Define the concept of static correlation. What is the appropriate method for its description? How is the wavefunction parameterized within this method? Is it possible to describe excited states with this method? Does it provide accurate results?
- d) [2 pts] The local density approximation (LDA) fails in describing both bond dissociations and dispersion forces. What is the reason? Does it mean that KS-DFT can only be applied to some electronic systems but not all?

## 2. Exercise: Equation-of-Motion Coupled-Cluster theory [10+2 points]

In the so-called *Equation-of-Motion Coupled-Cluster* (EOM-CC) theory [it will become clear in the bonus question of the exercise where the name comes from], an excited-state wave function  $\Psi_k$  ( $k > 0$ ) is determined from the ground-state wave function  $\Psi_0$  as follows:

$$|\Psi_k\rangle \stackrel{k \geq 0}{=} \hat{\mathcal{R}} |\Psi_0\rangle, \quad (1)$$

where the excitation operator  $\hat{\mathcal{R}}$  (which is defined below) describes physical electronic excitations, *i.e.*, excitations that can be observed in spectroscopy experiment. The CC exponential ansatz is used for the ground-state wave function,

$$|\Psi_0\rangle = e^{\hat{T}} |\Phi_0\rangle, \quad (2)$$

where  $\Phi_0$  is the Hartree-Fock (HF) ground-state Slater determinant. Both  $\hat{T}$  and  $\hat{\mathcal{R}}$  operators can be written

in second quantization as follows:

$$\hat{T} = \sum_{I,A} t_I^A \hat{a}_A^\dagger \hat{a}_I + \sum_{I<J,A<B} t_{IJ}^{AB} \hat{a}_A^\dagger \hat{a}_B^\dagger \hat{a}_J \hat{a}_I + \sum_{I<J<K,A<B<C} t_{IJK}^{ABC} \hat{a}_A^\dagger \hat{a}_B^\dagger \hat{a}_C^\dagger \hat{a}_K \hat{a}_J \hat{a}_I + \dots \quad (3)$$

and

$$\hat{\mathcal{R}} = r_0 \hat{\mathbb{1}} + \sum_{I,A} r_I^A \hat{a}_A^\dagger \hat{a}_I + \sum_{I<J,A<B} r_{IJ}^{AB} \hat{a}_A^\dagger \hat{a}_B^\dagger \hat{a}_J \hat{a}_I + \sum_{I<J<K,A<B<C} r_{IJK}^{ABC} \hat{a}_A^\dagger \hat{a}_B^\dagger \hat{a}_C^\dagger \hat{a}_K \hat{a}_J \hat{a}_I + \dots, \quad (4)$$

respectively, where  $\hat{\mathbb{1}}$  is the identity operator, *i.e.*,  $\hat{\mathbb{1}}|\Psi\rangle = |\Psi\rangle$ . The indices  $I, J, K, \dots$  and  $A, B, C, \dots$  denote occupied and unoccupied spin-orbitals in  $\Phi_0$ , respectively.

- a) **[2 pts]** In principle, the alternative parameterization  $|\Psi_k\rangle = \hat{\mathcal{R}}|\Phi_0\rangle$ , which is *not* further discussed in the following, can be employed in place of the one in Eqs. (1) and (2), for computing excited states. What are the to-be-optimized parameters in this case? How is such a method usually referred to? What is the practical advantage of using as reference the CC wave function of Eq. (2) rather than the HF one  $\Phi_0$ ?
- b) **[1 pt]** Let  $\hat{H}$  and  $E_0$  denote the electronic Hamiltonian operator and the ground-state energy, respectively. Explain why, according to Eq. (2),  $e^{-\hat{T}}\hat{H}e^{\hat{T}}|\Phi_0\rangle = E_0|\Phi_0\rangle$ . How can the operator  $\hat{T}$  be determined from this observation? **Hint:** Evaluate  $\langle\mu|e^{-\hat{T}}\hat{H}e^{\hat{T}}|\Phi_0\rangle$ , where  $|\mu\rangle$  denotes an excited HF determinant.
- c) **[0.5 pt]** We focus in the rest of the exercise on the calculation of the excited-state energies  $\{E_k\}_{k>0}$ . Show that, according to Eqs. (1), (2), and the Schrödinger equation for the  $k$ th excited state, the excitation operator  $\hat{\mathcal{R}}$  is such that

$$e^{-\hat{T}}\hat{H}\hat{\mathcal{R}}e^{\hat{T}}|\Phi_0\rangle = E_k e^{-\hat{T}}\hat{\mathcal{R}}e^{\hat{T}}|\Phi_0\rangle. \quad (5)$$

- d) **[3 pts]** Explain why, according to Eqs. (3) and (4), the excitation operators  $\hat{T}$  and  $\hat{\mathcal{R}}$  commute. We recall that  $e^{\hat{T}} = \sum_{p=0}^{+\infty} \frac{\hat{T}^p}{p!} = \hat{\mathbb{1}} + \hat{T} + \frac{\hat{T}^2}{2} + \dots$ . Deduce that  $e^{\hat{T}}$  and  $\hat{\mathcal{R}}$  commute and, according to Eq. (5),

$$\hat{\mathcal{H}}\hat{\mathcal{R}}|\Phi_0\rangle = E_k \hat{\mathcal{R}}|\Phi_0\rangle, \quad (6)$$

where  $\hat{\mathcal{H}} = e^{-\hat{T}}\hat{H}e^{\hat{T}}$ . In the light of question 2. a), conclude that, in EOM-CC theory, the calculation of excited-state energies consists in applying the configuration interaction method to the modified (so-called *similarity transformed*) Hamiltonian  $\hat{\mathcal{H}}$ . What simplifications are made at the so-called EOM-CCSD level of approximation?

- e) **[1.5 pts]** Show that  $\hat{\mathcal{H}}^\dagger = e^{\hat{T}^\dagger}\hat{H}e^{-\hat{T}^\dagger}$ . Explain why  $\hat{T}$  differs from  $\hat{T}^\dagger$  and conclude that, unlike the true Hamiltonian  $\hat{H}$ , the similarity transformed Hamiltonian  $\hat{\mathcal{H}}$  is *not* hermitian. Explain why  $\hat{H}$ ,  $\hat{\mathcal{H}}$ , and  $\hat{\mathcal{H}}^\dagger$

share the same eigenvalues  $E_k$  by proving that

$$\hat{H} |\Psi_k\rangle = E_k |\Psi_k\rangle \Leftrightarrow \hat{\mathcal{H}} \left( e^{-\hat{T}} |\Psi_k\rangle \right) = E_k \times \left( e^{-\hat{T}} |\Psi_k\rangle \right) \Leftrightarrow \hat{\mathcal{H}}^\dagger \left( e^{\hat{T}^\dagger} |\Psi_k\rangle \right) = E_k \times \left( e^{\hat{T}^\dagger} |\Psi_k\rangle \right). \quad (7)$$

- f) [1 pt] As a consequence of question 2. e),  $\hat{\mathcal{H}}^\dagger$  has its own eigenvector (associated to the energy  $E_k$ ) that we denote  $\hat{\mathcal{L}}^\dagger |\Phi_0\rangle$ , where

$$\hat{\mathcal{L}}^\dagger = \ell_0 \hat{\mathbb{1}} + \sum_{I,A} \ell_I^A \hat{a}_A^\dagger \hat{a}_I + \sum_{I<J,A<B} \ell_{IJ}^{AB} \hat{a}_A^\dagger \hat{a}_B^\dagger \hat{a}_J \hat{a}_I + \sum_{I<J<K,A<B<C} \ell_{IJK}^{ABC} \hat{a}_A^\dagger \hat{a}_B^\dagger \hat{a}_C^\dagger \hat{a}_K \hat{a}_J \hat{a}_I + \dots \quad (8)$$

Deduce that [see also Eq. (6)], for any wave function  $\Psi$ , the following equalities are fulfilled:

$$\langle \hat{\mathcal{H}}^\dagger \hat{\mathcal{L}}^\dagger \Phi_0 | \Psi \rangle = \langle \hat{\mathcal{L}}^\dagger \Phi_0 | \hat{\mathcal{H}} | \Psi \rangle = E_k \langle \hat{\mathcal{L}}^\dagger \Phi_0 | \Psi \rangle, \quad (9)$$

$$\langle \Psi | \hat{\mathcal{H}} | \hat{\mathcal{R}} \Phi_0 \rangle = E_k \langle \Psi | \hat{\mathcal{R}} \Phi_0 \rangle. \quad (10)$$

Explain why  $\hat{\mathcal{L}}^\dagger \Phi_0$  and  $\hat{\mathcal{R}} \Phi_0$  are usually referred to as *left* and *right* eigenfunctions of  $\hat{\mathcal{H}}$ , respectively.

- g) [1 pt] Like the conventional normalization condition, the so-called *bi-orthonormalization* condition,  $\langle \hat{\mathcal{L}}^\dagger \Phi_0 | \hat{\mathcal{R}} \Phi_0 \rangle = 1$ , can always be imposed. Deduce from Eq. (9) that, in this case, the  $k$ th excited-state energy can be expressed as  $E_k = \langle \Phi_0 | \hat{\mathcal{L}} \hat{\mathcal{H}} \hat{\mathcal{R}} | \Phi_0 \rangle$ . Summarize the key steps in the EOM-CCSD method [see question 2. d)] and highlight the main differences with the conventional CISD method.

### BONUS QUESTION

- h) [2 pts] The purpose of this last question is to explain where the name “equation of motion” comes from. Show that, according to the excited-state wave function ansatz of Eq. (1) and the Schrödinger equation that is fulfilled by both  $\Psi_0$  and  $\Psi_k$  (with energies  $E_0$  et  $E_k$ , respectively), we have

$$[\hat{H}, \hat{\mathcal{R}}] |\Psi_0\rangle = (E_k - E_0) \hat{\mathcal{R}} |\Psi_0\rangle, \quad (11)$$

where  $[\hat{H}, \hat{\mathcal{R}}] = \hat{H} \hat{\mathcal{R}} - \hat{\mathcal{R}} \hat{H}$ . In the *time-dependent* formulation of quantum mechanics, the expectation value of  $\hat{\mathcal{R}}$  at a given time  $t$  can be determined from the time-dependent version of the operator,  $\hat{\mathcal{R}}(t) = e^{+i\hat{H}t} \hat{\mathcal{R}} e^{-i\hat{H}t}$ , where  $i$  is the complex pure imaginary unit number (*i.e.*,  $i^2 = -1$ ), and  $e^{\pm i\hat{H}t} \equiv \exp\{\pm i\hat{H}t\} = \sum_{n=0}^{+\infty} \frac{(\pm i\hat{H}t)^n}{n!}$ . Explain why  $\frac{d\hat{\mathcal{R}}(t)}{dt} = i e^{+i\hat{H}t} [\hat{H}, \hat{\mathcal{R}}] e^{-i\hat{H}t}$ . Deduce that Eq. (11) can be rewritten as follows,

$$-i \frac{d}{dt} \left( \hat{\mathcal{R}}(t) |\Psi_0\rangle \right) \Big|_{t=0} = (E_k - E_0) \hat{\mathcal{R}} |\Psi_0\rangle, \quad (12)$$

and conclude.