

Exam in Advanced Quantum Chemistry – Part 2 (18 points)

January 2020

Examination time: 2h (for Parts 1 and 2)

Neither documents nor calculators are allowed.

1. Questions on the lecture material (8 points)

- a) [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?
- b) [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?
- c) [2 pts] Are the excited-state energies functional of the ground-state density? Is it straightforward to calculate excited-state energies in DFT? Is there a variational principle for excited states?

2. Seniority-zero many-body wavefunctions (10 points)

An N -electron many-body wavefunction $\tilde{\Psi}$ is said to have no seniority (hence its name “seniority-zero wavefunction”) if it can be written as a linear combination of Slater determinants \mathcal{D} in which *orbitals are either doubly occupied or not occupied at all*:

$$|\tilde{\Psi}\rangle = \sum_{\mathcal{D}} C_{\mathcal{D}} |\mathcal{D}\rangle, \quad (1)$$

where

$$|\mathcal{D}\rangle = \left| (p_1)^2 (p_2)^2 \dots \left(p_{\frac{N}{2}} \right)^2 \right\rangle \equiv \prod_{i=1}^{\frac{N}{2}} \hat{a}_{p_i, \alpha}^\dagger \hat{a}_{p_i, \beta}^\dagger |\text{vac}\rangle. \quad (2)$$

- a) [1 pt] Can we use the ansatz of Eqs. (1) and (2) for describing electron correlation? Justify your answer by referring, for example, to the MP2 wavefunction.
- b) [1 pt] Show, by considering the simple example of the stretched H_2 molecule, that seniority-zero wavefunctions are well adapted to the description of strong correlation effects.

- c) [1.5 pts] In the following, we consider a single set of molecular orbitals $\{\varphi_p\}_p$ from which all the seniority-zero Slater determinants \mathcal{D} are constructed. Let us first assume that these orbitals are Hartree–Fock orbitals. A configuration interaction (CI) calculation based on the wavefunction ansatz of Eq. (1) is referred to as *doubly occupied* CI (DOCI). Explain briefly how the coefficients $C_{\mathcal{D}}$ and the ground-state energy would be determined within the DOCI method. Is DOCI equivalent to full CI (FCI)?
- d) [1 pt] In the spirit of the *multiconfigurational self-consistent field* (MCSCF) method, one may opt for a reoptimization of the orbitals within a DOCI calculation. Explain how this could be achieved by means of an orbital rotation operator.
- e) [2 pts] Let us consider the (so-called *one-electron reduced*) density matrix elements:

$$D_{pq}^{\tilde{\Psi}} = \sum_{\sigma=\alpha,\beta} \langle \tilde{\Psi} | \hat{a}_{p,\sigma}^\dagger \hat{a}_{q,\sigma} | \tilde{\Psi} \rangle. \quad (3)$$

Prove that, according to Eq. (1), the density matrix is diagonal and the diagonal elements read

$$n_p^{\tilde{\Psi}} = D_{pp}^{\tilde{\Psi}} = 2 \sum_{\mathcal{D} \ni p} C_{\mathcal{D}}^2, \quad (4)$$

where “ $\mathcal{D} \ni p$ ” means that the sum runs over the seniority-zero Slater determinants \mathcal{D} in which the orbital φ_p is (doubly) occupied. What is the physical meaning of $n_p^{\tilde{\Psi}}$?

- f) [1 pt] Let us write the electronic Hamiltonian as $\hat{H} = \sum_{pq,\sigma=\alpha,\beta} h_{pq} \hat{a}_{p,\sigma}^\dagger \hat{a}_{q,\sigma} + \hat{W}_{ee}$ where \hat{W}_{ee} is the two-electron repulsion operator. What are the energy contributions described by the one-electron integrals h_{pq} ? Show that $\langle \tilde{\Psi} | \hat{H} | \tilde{\Psi} \rangle = \sum_p v_p n_p^{\tilde{\Psi}} + \langle \tilde{\Psi} | \hat{W}_{ee} | \tilde{\Psi} \rangle$, where $v_p = h_{pp}$.
- g) [2.5 pts] Let \mathcal{E}_0 be the seniority-zero ground-state energy:

$$\mathcal{E}_0 = \min_{\tilde{\Psi}} \langle \tilde{\Psi} | \hat{H} | \tilde{\Psi} \rangle = \langle \tilde{\Psi}_0 | \hat{H} | \tilde{\Psi}_0 \rangle = \sum_p v_p n_p^{\tilde{\Psi}_0} + \langle \tilde{\Psi}_0 | \hat{W}_{ee} | \tilde{\Psi}_0 \rangle, \quad (5)$$

where the minimization is restricted to *normalized* seniority-zero wavefunctions $\tilde{\Psi}$ [we assume that the orbitals are fixed]. By changing the diagonal elements of the one-electron integrals, i.e. $v_p \rightarrow h'_{pp} = v'_p$, we obtain a new ground-state seniority-zero wavefunction $\tilde{\Psi}'_0$, new occupations $n_p^{\tilde{\Psi}'_0}$, and therefore a new seniority-zero ground-state energy \mathcal{E}'_0 . We assume that ground states are *not degenerate* and that they have exactly the same orbital occupations, i.e. $n_p^{\tilde{\Psi}'_0} = n_p^{\tilde{\Psi}_0} = n_p^0$. Prove that, under these assumptions, $\mathcal{E}_0 < \mathcal{E}'_0 + \sum_p (v_p - v'_p) n_p^0$ and $\mathcal{E}'_0 < \mathcal{E}_0 - \sum_p (v_p - v'_p) n_p^0$. Conclude. Why can this result be seen as a kind of Hohenberg–Kohn theorem for seniority-zero wavefunctions?