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# Exam in Advanced Quantum Chemistry – M2 course

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## 1. Essay about the diversity of quantum chemical methods [10 points]

Why are there so many methods available in quantum chemistry softwares? This is the question you are expected to answer in your essay. Of course, it raises several subquestions that should guide you: *Are they in-principle exact? Which approximation do they rely on? What kind of physical effects do they treat (well or not?) or do they miss? What is the computational advantage of one method over the other?* You are encouraged to illustrate your prose with well-explained and enlightening equations.

## 2. Exercise: Electron correlation energy from transition one-electron density matrices

[12 points]

Let  $\hat{H} = \sum_{PQ} h_{PQ} \hat{a}_P^\dagger \hat{a}_Q + \frac{1}{2} \sum_{PQRS} \langle PQ|RS \rangle \hat{a}_P^\dagger \hat{a}_Q^\dagger \hat{a}_S \hat{a}_R$  be the electronic Hamiltonian (we work within the Born–Oppenheimer approximation) written in second quantization.

- a) [1 pt] What do the indices  $P, Q, R$  and  $S$  refer to? Which name is usually given to  $h_{PQ}$  and  $\langle PQ|RS \rangle$ , respectively? Give their physical meaning.
- b) [1 pt] Let  $\Psi_0$  denote the exact normalized  $N$ -electron ground-state wavefunction of  $\hat{H}$  with energy  $E_0$ . Explain why  $E_0 = \langle \Psi_0 | \hat{H} | \Psi_0 \rangle$  and deduce that 
$$E_0 = \sum_{PQ} h_{PQ} D_{PQ}^{\Psi_0} + \frac{1}{2} \sum_{PQRS} \langle PQ|RS \rangle D_{PQRS}^{\Psi_0}$$
 where the one- and two-electron density matrices are defined as follows for *any normalized  $N$ -electron wavefunction  $\Psi$* :  $D_{PQ}^{\Psi} = \langle \Psi | \hat{a}_P^\dagger \hat{a}_Q | \Psi \rangle$  and  $D_{PQRS}^{\Psi} = \langle \Psi | \hat{a}_P^\dagger \hat{a}_Q^\dagger \hat{a}_S \hat{a}_R | \Psi \rangle$ .
- c) [1 pt] Show that  $D_{PQRS}^{\Psi} = \Gamma_{PQRS}^{\Psi} - \delta_{QR} D_{PS}^{\Psi}$ , where  $\Gamma_{PQRS}^{\Psi} = \langle \Psi | \hat{a}_P^\dagger \hat{a}_R \hat{a}_Q^\dagger \hat{a}_S | \Psi \rangle$  will be referred to as the *reordered two-electron density matrix* in the following. **Hint:** Use the anti-commutation rules of second quantization.
- d) [1 pt] Show that the one-electron density matrix is completely known from the reordered two-electron one. **Hint:** Explain physically why  $\left( \sum_R \hat{a}_R^\dagger \hat{a}_R \right) | \Psi \rangle = N | \Psi \rangle$  and deduce that  $\sum_R \Gamma_{PQRR}^{\Psi} = N D_{PQ}^{\Psi}$ . Conclude.
- e) [1 pt] Conclude from questions 2. b), c), and d) that the ground-state energy is an explicit functional of the ground-state reordered two-electron density matrix.

In the rest of the problem we focus on the calculation of  $\Gamma_{PQRS}^{\Psi_0}$ .

f) [1 pt] Explain why  $|\hat{a}_R^\dagger \hat{a}_P \Psi_0\rangle$  and  $|\hat{a}_Q^\dagger \hat{a}_S \Psi_0\rangle$  are  $N$ -electron quantum states.

g) [1 pt] Let  $\{\Psi_i\}_{i=0,1,2,\dots}$  be the complete orthonormal basis of  $N$ -electron ground and excited states of  $\hat{H}$  with energies  $\{E_i\}_{i=0,1,2,\dots}$ . Show that  $\langle \hat{a}_R^\dagger \hat{a}_P \Psi_0 | \hat{\mathbf{1}}_N | \hat{a}_Q^\dagger \hat{a}_S \Psi_0 \rangle = \Gamma_{PQRS}^{\Psi_0} = D_{PR}^{\Psi_0} D_{QS}^{\Psi_0} + \sum_{i \geq 1} D_{PR}^{0 \rightarrow i} D_{SQ}^{0 \rightarrow i}$ , where, for any  $N$ -electron wavefunction  $\Psi$ ,  $\hat{\mathbf{1}}_N |\Psi\rangle = |\Psi\rangle$ , and the so-called *transition* one-electron density matrix elements are defined for any spin-orbitals  $U$  and  $V$  as  $D_{UV}^{0 \rightarrow i} = \langle \Psi_0 | \hat{a}_U^\dagger \hat{a}_V | \Psi_i \rangle$ . **Hint:** Use real algebra and the resolution of the identity formula  $\hat{\mathbf{1}}_N = |\Psi_0\rangle \langle \Psi_0| + \sum_{i \geq 1} |\Psi_i\rangle \langle \Psi_i|$ .

h) [2 pts] From now on we work within the Hartree-Fock (HF) approximation, *i.e.*,  $\{\Psi_i\}_{i \geq 0} \stackrel{\text{HF}}{\approx} \{\Phi_i\}_{i \geq 0}$ , where  $\Phi_0$  is the reference ground-state HF determinant and  $\{\Phi_i\}_{i \geq 1}$  are the excited-state HF determinants. Explain why  $D_{PR}^{\Phi_0}$  equals zero if either  $P$  or  $R$  is not occupied in  $\Phi_0$ . We denote in the following  $I, J, \dots$  and  $A, B, \dots$  occupied and virtual spin-orbitals, respectively. Show that  $D_{IJ}^{\Phi_0} = \delta_{IJ}$ . Explain why, for a given excited-state HF determinant  $\Phi_i$  ( $i \geq 1$ ), the transition density matrix element  $\langle \Phi_0 | \hat{a}_U^\dagger \hat{a}_V | \Phi_i \rangle$  differs from zero only if  $U = I$  is occupied and  $V = A$  is a virtual spin-orbital, and, therefore, that it is nonzero only if  $|\Phi_i\rangle = \hat{a}_A^\dagger \hat{a}_I |\Phi_0\rangle$ . How would you refer to the corresponding electronic excitation process?

i) [1.5 pts] Deduce from the previous question that

$$\sum_{PQ} h_{PQ} D_{PQ}^{\Psi_0} \stackrel{\text{HF}}{\approx} \sum_I h_{II}, \quad (1a)$$

$$\frac{1}{2} \sum_{PQRS} \langle PQ|RS\rangle D_{PR}^{\Psi_0} D_{QS}^{\Psi_0} \stackrel{\text{HF}}{\approx} \frac{1}{2} \sum_{IJ} \langle IJ|IJ\rangle, \quad (1b)$$

$$-\frac{1}{2} \sum_{PQRS} \langle PQ|RS\rangle \delta_{QR} D_{PS}^{\Psi_0} \stackrel{\text{HF}}{\approx} -\frac{1}{2} \sum_{IQ} \langle IQ|QI\rangle, \quad (1c)$$

$$\frac{1}{2} \sum_{PQRS} \langle PQ|RS\rangle \sum_{i \geq 1} D_{PR}^{0 \rightarrow i} D_{SQ}^{0 \rightarrow i} \stackrel{\text{HF}}{\approx} \frac{1}{2} \sum_{IA} \langle IA|AI\rangle. \quad (1d)$$

Conclude from questions 2. b), c) and g) that we recover the expected HF energy expression

$$E_{\text{HF}} = \sum_I h_{II} + \frac{1}{2} \sum_{IJ} \left( \langle IJ|IJ\rangle - \langle IJ|JI\rangle \right).$$

j) [1.5 pts] Revisit the description of electron correlation from the perspective of the present exercise.