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# Exam in Advanced Quantum Chemistry – M2 course

January 2023, Two-hour exam

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## 1. Questions on the lecture material [8 points]

- a) [3 pts] What are the main differences between the first and second quantization formalisms? How is the Pauli principle formulated in second quantization?
- b) [3 pts] What is the Born–Oppenheimer approximation? Are the nuclei treated in classical mechanics within such an approximation? How are vibrational energies and electronic energies related?
- c) [2 pts] What are the differences and similarities between the Hartree–Fock and Kohn–Sham density-functional approaches?

## 2. Exercise: Static analog of the self-energy in density-matrix functional theory [10 points]

Let  $|\Psi_0\rangle$  denote the exact ground state of the electronic quantum chemical Hamiltonian  $\hat{H}$  that reads in second quantization  $\hat{H} = \sum_{KL} h_{KL} \hat{a}_K^\dagger \hat{a}_L + \frac{1}{2} \sum_{KLMN} \langle KL|MN\rangle \hat{a}_K^\dagger \hat{a}_L^\dagger \hat{a}_N \hat{a}_M$ . We use real algebra in the following and assume that the orthonormal spin-orbitals  $\{|\varphi_K\rangle \equiv \hat{a}_K^\dagger |\text{vac}\rangle\}$  are the so-called *natural spin-orbitals*, which means that they diagonalize the one-electron reduced density matrix (1RDM):  $\langle \Psi_0 | \hat{a}_K^\dagger \hat{a}_L | \Psi_0 \rangle = n_K \delta_{KL}$ , where  $n_K$  is the occupation number of the spin-orbital  $\varphi_K$  and  $\delta_{KL}$  is the usual Kronecker delta symbol.

**Note that the key equations of the exercise are boxed.**

- a) [2 pts] Give the mathematical expression of the one-  $h_{KL}$  and two-electron  $\langle KL|MN\rangle$  integrals. What energy contributions do they respectively describe?
- b) [0.5 pts] Deduce from the Schrödinger equation the so-called *anti-Hermitian contracted Schrödinger equation* (ACSE),  $\langle \Psi_0 | [\hat{a}_I^\dagger \hat{a}_J, \hat{H}] | \Psi_0 \rangle = 0$ , which holds for *any* spin-orbitals  $I$  and  $J$ , and where  $[\hat{A}, \hat{B}] = \hat{A}\hat{B} - \hat{B}\hat{A}$  denotes the commutator of the quantum operators  $\hat{A}$  and  $\hat{B}$  [Hint: Explain why  $\langle \Psi_0 | \hat{H} \hat{a}_I^\dagger \hat{a}_J | \Psi_0 \rangle = E_0 \langle \Psi_0 | \hat{a}_I^\dagger \hat{a}_J | \Psi_0 \rangle$ , where  $E_0$  is the exact ground-state energy].
- c) [0.5 pts] Verify that, for any quantum operators  $\hat{A}$ ,  $\hat{B}$ , and  $\hat{C}$ ,  $[\hat{A}, \hat{B} + \hat{C}] = [\hat{A}, \hat{B}] + [\hat{A}, \hat{C}]$  and  $[\hat{A}, \xi \hat{B}] = \xi [\hat{A}, \hat{B}]$ , where  $\xi$  is a (real here) number.
- d) [0.5 pts] It can be shown from the anticommutation rules of second quantization that  $[\hat{a}_I^\dagger \hat{a}_J, \hat{a}_K^\dagger \hat{a}_L] = \delta_{JK} \hat{a}_I^\dagger \hat{a}_L - \delta_{IL} \hat{a}_K^\dagger \hat{a}_J$  and  $[\hat{a}_I^\dagger \hat{a}_J, \hat{a}_K^\dagger \hat{a}_L^\dagger \hat{a}_N \hat{a}_M] = \delta_{JK} \hat{a}_I^\dagger \hat{a}_L^\dagger \hat{a}_N \hat{a}_M + \delta_{JL} \hat{a}_K^\dagger \hat{a}_I^\dagger \hat{a}_N \hat{a}_M - \delta_{IN} \hat{a}_K^\dagger \hat{a}_L^\dagger \hat{a}_J \hat{a}_M - \delta_{IM} \hat{a}_K^\dagger \hat{a}_L^\dagger \hat{a}_N \hat{a}_J$ . Deduce from the introduction of the exercise, the previous question, and the second-quantized Hamiltonian expression that the boxed ACSE of question 2. b) can be rewritten as follows,

$h_{JI}(n_I - n_J) + \frac{1}{2} \left[ \sum_{LMN} \langle JL|MN \rangle D_{MN}^{IL} + \sum_{KMN} \langle KJ|MN \rangle D_{MN}^{KI} - \sum_{KLM} \langle KL|MI \rangle D_{MJ}^{KL} - \sum_{KLN} \langle KL|IN \rangle D_{JN}^{KL} \right] = 0$ , where  $D_{MN}^{KL} = \langle \Psi_0 | \hat{a}_K^\dagger \hat{a}_L^\dagger \hat{a}_N \hat{a}_M | \Psi_0 \rangle$  are the two-electron reduced density matrix (2RDM) elements.

e) [0.5 pts] It can be shown that  $\sum_{KMN} \langle KJ|MN \rangle D_{MN}^{KI} = \sum_{LMN} \langle JL|MN \rangle D_{MN}^{IL}$  and  $\sum_{KLM} \langle KL|MI \rangle D_{MJ}^{KL} = \sum_{KLN} \langle KL|IN \rangle D_{JN}^{KL} = \sum_{LMN} \langle IL|MN \rangle D_{MN}^{JL}$ . Conclude from the previous question that the ACSE can finally be written in a compact form as follows,  $\boxed{h_{JI}(n_I - n_J) + \Sigma_{JI} n_I - \Sigma_{IJ} n_J = 0}$ ,

where  $\boxed{\Sigma_{IJ} = \frac{1}{n_J} \sum_{LMN} \langle IL|MN \rangle D_{MN}^{JL}}$ .

f) [1 pt] In the following we refer to  $\Sigma \equiv \{\Sigma_{IJ}\}$  as the *static self-energy* matrix, by analogy with Green's function theory. Is  $\Sigma$  *a priori* Hermitian, *i.e.*, is  $\Sigma_{IJ}$  equal to  $\Sigma_{JI}$ ? Show that, if  $\Sigma$  were Hermitian, then solving the ACSE would consist in diagonalizing  $\mathbf{h} + \Sigma$ , where  $\mathbf{h} \equiv \{h_{IJ}\}$  [Hint: Consider spin-orbitals  $I$  and  $J$  that have different occupations, for simplicity].

g) [2 pts] At the Hartree–Fock (HF) level of theory, the following approximations are made:

$D_{MN}^{JL} \stackrel{\text{HF}}{\approx} \langle \Phi_0 | \hat{a}_J^\dagger \hat{a}_L^\dagger \hat{a}_N \hat{a}_M | \Phi_0 \rangle$  and  $n_J \delta_{JM} \stackrel{\text{HF}}{\approx} \langle \Phi_0 | \hat{a}_J^\dagger \hat{a}_M | \Phi_0 \rangle$ , where  $\Phi_0$  is the HF determinant. What values can the occupations  $n_J$  take in this case?

Explain why  $\langle \Phi_0 | \hat{a}_J^\dagger \hat{a}_L^\dagger \hat{a}_N \hat{a}_M | \Phi_0 \rangle = \langle \Phi_0 | \hat{a}_J^\dagger \hat{a}_L^\dagger \hat{a}_N \hat{a}_M | \Phi_0 \rangle \times n_L$  [Hint: Consider the two cases where  $L$  is either occupied or unoccupied in  $\Phi_0$ ]. Deduce that  $D_{MN}^{JL} \stackrel{\text{HF}}{\approx} (\delta_{LN} \delta_{JM} - \delta_{LM} \delta_{JN}) n_J n_L$  and conclude that, at the HF level of approximation, the self-energy can be determined from Coulomb and exchange integrals as follows,  $\Sigma \approx \Sigma^{\text{HF}} \equiv \{\Sigma_{IJ}^{\text{HF}}\}$ , where  $\Sigma_{IJ}^{\text{HF}} = \sum_{L \text{ occupied in } \Phi_0} (\langle IL|JL \rangle - \langle IL|LJ \rangle)$ .

h) [1 pt] How is  $\mathbf{f} = \mathbf{h} + \Sigma^{\text{HF}}$  usually referred to? Is  $\Sigma^{\text{HF}}$  Hermitian [we recall that  $\langle KL|MN \rangle = \langle ML|KN \rangle = \langle NM|LK \rangle$ ]? Deduce from 2. f) that the ACSE reduces to the HF equations when  $\Sigma \approx \Sigma^{\text{HF}}$ .

i) [0.5 pts] Inspired by the so-called “power” density matrix functionals, where powers of the occupation numbers are used to variationally go beyond the HF level of calculation, we consider the following approximation to the 2RDM elements:  $D_{MN}^{JL} \stackrel{\text{power}}{\approx} \delta_{LN} \delta_{JM} n_J n_L - \delta_{LM} \delta_{JN} (n_J)^\alpha (n_L)^\alpha$ , where the exponent  $\alpha$  can be tuned in the range  $\frac{1}{2} \leq \alpha \leq 1$ . Explain from 2. g) why, by choosing a value of  $\alpha$  that is *strictly* lower than 1, we do deviate from the HF approximation and thus introduce electron correlation.

j) [1.5 pts] Show from the exact boxed expression in 2. e) that, at the “power” level of approximation, the self-energy can be split into Hartree (H) and exchange-correlation (xc) contributions as follows,  $\Sigma_{IJ} \stackrel{\text{power}}{\approx} \Sigma_{IJ}^{\text{H}} + \Sigma_{IJ}^{\text{xc},\alpha}$ , where  $\Sigma_{IJ}^{\text{H}} = \sum_L \langle IL|JL \rangle n_L$  and  $\Sigma_{IJ}^{\text{xc},\alpha} = -(n_J)^{\alpha-1} \sum_L \langle IL|LJ \rangle (n_L)^\alpha$ . Deduce from the previous question that electron correlation can *a priori* break the Hermiticity of the static self-energy. What conclusion can we draw from question 2. f)?