University of Strasbourg, Master in Chemoinformatics, Second year

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

January 2021

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

Neither documents nor calculators are allowed.

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1. Questions on the lecture material [8 points]

a) **[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?

b) **[2 pts]** What are the differences and similarities between Hartree–Fock and Kohn–Sham (KS) density-functional approaches?

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?

2. Galitskii–Migdal formula for total electronic energies [10 points]

In the following, the indices I, J, K, L, P, and Q refer to *spin-orbitals*. Let us define the *time-dependent* one-electron Green function matrix elements in second quantization as follows,

$$G_{PQ}(t) = \mathrm{i} \left\langle \Psi \middle| \hat{a}_Q^\dagger(t)\, \hat{a}_P \middle| \Psi \right\rangle , \tag{1}$$

where $t \geq 0$ denotes the time, i is the (*complex*) pure imaginary unit number [$\mathrm{i}^2 = -1$], and Ψ is an arbitrary many-body wave function. The time-dependent creation operator reads

$$\hat{a}_Q^\dagger(t) = e^{+\mathrm{i}\hat{H}t}\, \hat{a}_Q^\dagger\, e^{-\mathrm{i}\hat{H}t}, \qquad \text{where} \qquad e^{\pm\mathrm{i}\hat{H}t} \equiv \exp\Big\{\pm\mathrm{i}\hat{H}t\Big\} = \sum_{n=0}^{+\infty} \frac{\Big(\pm\mathrm{i}\hat{H}t\Big)^n}{n!}, \tag{2}$$

and $\hat{H} = \sum\limits_{IJ} h_{IJ}\, \hat{a}_I^\dagger \hat{a}_J + \dfrac{1}{2} \sum\limits_{IJKL} \langle IJ|KL\rangle\, \hat{a}_I^\dagger \hat{a}_J^\dagger \hat{a}_L \hat{a}_K$ is the electronic Hamiltonian.

a) **[0.5 pt]** Which energy contributions are described by the one-electron h_{IJ} and two-electron $\langle IJ|KL\rangle$ integrals, respectively?

b) **[1.5 pts]** How can we recover the one-electron reduced density matrix (1RDM) element $D_{IJ} = \left\langle \Psi \middle| \hat{a}_I^\dagger \, \hat{a}_J \middle| \Psi \right\rangle$ from the Green function? Can we evaluate the expectation value $\langle \Psi | \hat{H} | \Psi \rangle$ of the energy directly from the 1RDM?

c) **[1 pt]** Show that

$$\frac{\partial G_{PQ}(t)}{\partial t} = \mathrm{i} \left\langle \Psi \middle| \frac{\partial \hat{a}_Q^\dagger(t)}{\partial t} \, \hat{a}_P \middle| \Psi \right\rangle = - \left\langle \Psi \middle| e^{+\mathrm{i}\hat{H}t} \, \left[\hat{H}, \hat{a}_Q^\dagger \right] \, e^{-\mathrm{i}\hat{H}t} \, \hat{a}_P \middle| \Psi \right\rangle , \tag{3}$$

where $\left[\hat{A}, \hat{B} \right] \overset{notation}{=} \hat{A}\hat{B} - \hat{B}\hat{A}$ is the commutator of $\hat{A}$ and $\hat{B}$.

d) **[2 pts]** Verify that, for any operators $\hat{A}, \hat{B}, \hat{C}, \hat{D}$, and $\hat{E}$, we have $\hat{A} \left\{ \hat{B}, \hat{C} \right\} - \left\{ \hat{A}, \hat{C} \right\} \hat{B} = \left[\hat{A}\hat{B}, \hat{C} \right]$ and $\hat{A}\hat{B}\hat{C} \left\{ \hat{D}, \hat{E} \right\} - \hat{A}\hat{B} \left\{ \hat{C}, \hat{E} \right\} \hat{D} + \hat{A} \left\{ \hat{B}, \hat{E} \right\} \hat{C}\hat{D} - \left\{ \hat{A}, \hat{E} \right\} \hat{B}\hat{C}\hat{D} = \left[\hat{A}\hat{B}\hat{C}\hat{D}, \hat{E} \right]$, where $\left\{ \hat{A}, \hat{B} \right\} \overset{notation}{=} \hat{A}\hat{B} + \hat{B}\hat{A}$ is the *anticommutator* of $\hat{A}$ and $\hat{B}$. Deduce from the rules of second quantization the value of the anticommutators $\left\{ \hat{a}_J, \hat{a}_Q^\dagger \right\}$ and $\left\{ \hat{a}_I^\dagger, \hat{a}_Q^\dagger \right\}$.

e) **[2 pts]** By considering the two cases (i) $\hat{A} = \hat{a}_I^\dagger, \hat{B} = \hat{a}_J, \hat{C} = \hat{a}_Q^\dagger$ and (ii) $\hat{A} = \hat{a}_I^\dagger, \hat{B} = \hat{a}_J^\dagger, \hat{C} = \hat{a}_L, \hat{D} = \hat{a}_K, \hat{E} = \hat{a}_Q^\dagger$, show from question 2. d) that $\left[\hat{a}_I^\dagger \hat{a}_J, \hat{a}_Q^\dagger \right] = \delta_{JQ} \, \hat{a}_I^\dagger$ and $\left[\hat{a}_I^\dagger \hat{a}_J^\dagger \hat{a}_L \hat{a}_K, \hat{a}_Q^\dagger \right] = \delta_{KQ} \, \hat{a}_I^\dagger \hat{a}_J^\dagger \hat{a}_L - \delta_{LQ} \, \hat{a}_I^\dagger \hat{a}_J^\dagger \hat{a}_K$. We recall that $\langle JI|LQ\rangle = \langle IJ|QL\rangle$. After simplications, conclude *via* changes in the labels ($I \leftrightarrow J, K \rightarrow L$, for example) that $\left[\hat{H}, \hat{a}_Q^\dagger \right] = \sum_I h_{IQ} \, \hat{a}_I^\dagger + \sum_{IJL} \langle IJ|QL\rangle \, \hat{a}_I^\dagger \hat{a}_J^\dagger \hat{a}_L$.

f) **[1 pt]** Show from questions 2. c) and e) that

$$- \left. \frac{\partial G_{PP}(t)}{\partial t} \right|_{t=0} = \sum_I h_{IP} \left\langle \Psi \middle| \hat{a}_I^\dagger \hat{a}_P \middle| \Psi \right\rangle + \sum_{IJL} \langle IJ|PL\rangle \left\langle \Psi \middle| \hat{a}_I^\dagger \hat{a}_J^\dagger \hat{a}_L \hat{a}_P \middle| \Psi \right\rangle . \tag{4}$$

g) **[2 pts]** As readily seen from Eq. (4), the time derivative of the Green function trace at time $t = 0$ can be expressed as follows,

$$- \sum_J \left. \frac{\partial G_{JJ}(t)}{\partial t} \right|_{t=0} = \sum_{IJ} h_{IJ} \left\langle \Psi \middle| \hat{a}_I^\dagger \hat{a}_J \middle| \Psi \right\rangle + \sum_{IJKL} \langle IJ|KL\rangle \left\langle \Psi \middle| \hat{a}_I^\dagger \hat{a}_J^\dagger \hat{a}_L \hat{a}_K \middle| \Psi \right\rangle . \tag{5}$$

Deduce from Eq. (5) and question 2. b) the so-called Galitskii–Migdal formula:

$$\langle \Psi | \hat{H} | \Psi \rangle = -\frac{1}{2} \sum_J \left[\mathrm{i} \sum_I h_{IJ} G_{JI}(t) + \frac{\partial G_{JJ}(t)}{\partial t} \right]_{t=0} . \tag{6}$$

In the light of this formula and question 2. b), highlight the major difference between the one-electron Green function and the 1RDM when it comes to evaluate the total electronic energy.