University of Strasbourg, second year Master's level

# **Exam in advanced Quantum Chemistry – Part 1** (18 points)

January 2019

*Two-hour exam* **(for Parts 1** ***and*** **2)**

***Neither documents nor calculators are allowed.***

***The grading scale might be changed.***

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## 1. Questions on the lecture material (8 points)

a) [**1 pt**] Give the main difference between variational and non-variational quantum chemical methods.

b) [**2 pts**] What are the main differences between the first and second quantization formalisms ? How is the Pauli principle formulated in second quantization ?

c) [**2 pts**] What are the various strategies used in wavefunction theory for modeling dynamical electron correlation ? What are the advantages and drawbacks of theses strategies ?

d) [**1 pt**] What is the motivation for using a Coupled-Cluster (CC) ansatz for the wavefunction ?

e) [**2 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 ?

## 2. Optimization of Kohn–Sham orbitals through orbital rotations (10 points)

We will discuss in this problem the optimization of Kohn–Sham (KS) orbitals in practical density-functional theory calculations. ***Real algebra will be used***. Within the *local density approximation* (LDA), the ground-state energy is obtained variationally as follows,

$$E_0^{\mathrm{LDA}} = \min_{\Phi} \left\{ \langle \Phi|\hat{h}|\Phi\rangle + E_{\mathrm{Hxc}}^{\mathrm{LDA}}[n_\Phi] \right\} = \langle \Phi_0|\hat{h}|\Phi_0\rangle + E_{\mathrm{Hxc}}^{\mathrm{LDA}}[n_{\Phi_0}], \tag{1}$$

where $\Phi$ is a trial Slater determinant, $n_\Phi$ its density, and $\hat{h} \equiv \left(-\frac{\nabla_{\mathbf{r}}^2}{2} + v_{\mathrm{ne}}(\mathbf{r})\times\right)$ is the one-electron kinetic and nuclear potential operator that reads $\hat{h} \equiv \sum\limits_{pq} \left\langle \phi_p \middle| \hat{h} \middle| \phi_q \right\rangle \hat{E}_{pq}$ in second quantization with $\hat{E}_{pq} = \sum_\sigma \hat{a}_{p\sigma}^\dagger \hat{a}_{q\sigma}$. At the LDA level of approximation the Hartree-exchange-correlation (Hxc) functional can be written as

$$E_{\mathrm{Hxc}}^{\mathrm{LDA}}[n] = \frac{1}{2}\int_{\mathbb{R}^3}\int_{\mathbb{R}^3} d\mathbf{r}d\mathbf{r}'\ \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} + \int_{\mathbb{R}^3} d\mathbf{r}\ \ e_{\mathrm{xc}}(\nu)\big|_{\nu=n(\mathbf{r})}, \tag{2}$$

where $e_{\text{xc}}(\nu)$ is a *function* of the value $\nu$ that has the density $n$ at a given position $\mathbf{r}$.

a) **[0.5 pt]** Explain with a simple argument why LDA is (in principle) an approximation.

b) **[1.5 pts]** Explain (with words) why $|\Phi\rangle$ can be parameterized as $|\Phi\rangle \equiv |\Phi(\boldsymbol{\kappa})\rangle = e^{-\hat{\kappa}}|\Phi_0\rangle$ where $\boldsymbol{\kappa} \equiv \{\kappa_{lm}\}_{l>m}$ and $\hat{\kappa} = \sum\limits_{l>m} \kappa_{lm}\left(\hat{E}_{lm} - \hat{E}_{ml}\right)$. Show that the energy expression in Eq. (1) can be rewritten as

$$E_0^{\text{LDA}} = \min_{\boldsymbol{\kappa}}\left\{E^{\text{LDA}}(\boldsymbol{\kappa})\right\}, \quad \text{where} \quad \boxed{E^{\text{LDA}}(\boldsymbol{\kappa}) = \sum_{pq}\left\langle\phi_p\middle|\hat{h}\middle|\phi_q\right\rangle D_{pq}(\boldsymbol{\kappa}) + E_{\text{Hxc}}^{\text{LDA}}\left[n(\boldsymbol{\kappa})\right]}, \tag{3}$$

$$D_{pq}(\boldsymbol{\kappa}) = \left\langle\Phi_0\middle|e^{\hat{\kappa}}\hat{E}_{pq}e^{-\hat{\kappa}}\middle|\Phi_0\right\rangle, \quad \text{and} \quad n(\boldsymbol{\kappa}) = n_{\Phi(\boldsymbol{\kappa})}.$$

c) **[0.5 pt]** For which value of $\boldsymbol{\kappa}$ do we reach the minimum in Eq. (3)? **Hint:** see Eq. (1).

d) **[2 pts]** Let $n(\boldsymbol{\kappa}, \mathbf{r})$ be the value of the density $n(\boldsymbol{\kappa})$ at position $\mathbf{r}$. Prove that, according to Eq. (2),

$$\left.\frac{\partial E_{\text{Hxc}}^{\text{LDA}}\left[n(\boldsymbol{\kappa})\right]}{\partial \kappa_{lm}}\right|_{\boldsymbol{\kappa}=0} = \int_{\mathbb{R}^3} d\mathbf{r}\; v_{\text{Hxc}}^{\text{LDA}}\left[n_{\Phi_0}\right](\mathbf{r})\left.\frac{\partial n(\boldsymbol{\kappa}, \mathbf{r})}{\partial \kappa_{lm}}\right|_{\boldsymbol{\kappa}=0}, \tag{4}$$

where $v_{\text{Hxc}}^{\text{LDA}}[n](\mathbf{r}) = \left.\dfrac{\partial e_{\text{xc}}(\nu)}{\partial \nu}\right|_{\nu=n(\mathbf{r})} + \displaystyle\int_{\mathbb{R}^3} d\mathbf{r}'\,\frac{n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}$.

e) **[1 pt]** It can be shown that $n(\boldsymbol{\kappa}, \mathbf{r}) = \sum\limits_{pq} \phi_p(\mathbf{r})\phi_q(\mathbf{r})D_{pq}(\boldsymbol{\kappa})$. Deduce from Eqs. (3) and (4) that

$$\left.\frac{\partial E^{\text{LDA}}(\boldsymbol{\kappa})}{\partial \kappa_{lm}}\right|_{\boldsymbol{\kappa}=0} = \sum_{pq}\left\langle\phi_p\middle|\hat{f}^{\text{KS}}\middle|\phi_q\right\rangle\left.\frac{\partial D_{pq}(\boldsymbol{\kappa})}{\partial \kappa_{lm}}\right|_{\boldsymbol{\kappa}=0}, \quad \text{where} \quad \hat{f}^{\text{KS}} \equiv -\frac{\nabla_{\mathbf{r}}^2}{2} + \left(v_{\text{ne}}(\mathbf{r}) + v_{\text{Hxc}}^{\text{LDA}}\left[n_{\Phi_0}\right](\mathbf{r})\right)\times \tag{5}$$

f) **[1.5 pts]** It can be shown that $\left.\dfrac{\partial D_{pq}(\boldsymbol{\kappa})}{\partial \kappa_{lm}}\right|_{\boldsymbol{\kappa}=0} = (\mathrm{n}_l - \mathrm{n}_m) \times (\delta_{mp}\delta_{lq} + \delta_{lp}\delta_{mq})$ where $\mathrm{n}_l$ and $\mathrm{n}_m$ denote the occupation numbers of the orbitals $\phi_l$ and $\phi_m$ in the KS determinant $\Phi_0$, respectively. Explain then, by using Eq. (5), why the following condition is fulfilled by the minimizing KS orbitals,

$$(\mathrm{n}_l - \mathrm{n}_m) \times \left\langle\phi_l\middle|\hat{f}^{\text{KS}}\middle|\phi_m\right\rangle = 0. \tag{6}$$

g) **[2 pts]** Conclude from Eq. (6) that the minimizing KS orbitals fulfill the following (so-called KS) equations $\hat{f}^{\text{KS}}\phi_p(\mathbf{r}) = \varepsilon_p\phi_p(\mathbf{r})$ [**Hint:** distinguish cases where $\phi_l$ and $\phi_m$ are occupied or unoccupied in $\Phi_0$]. What is the expression for the local KS potential at the LDA level of approximation ?

h) **[1 pt]** How would you implement, in practice, the optimization of the KS orbitals ?

# Optimization of KS orbitals through orbital rotations

a) The exact functional of the density $E_{Hxc}[n]$ should use the value of the density everywhere in space to deliver the exact Hxc energy. At the LDA level of approximation we have

$$E^{LDA}_{Hxc}[n] = E_H[n] + \underbrace{E^{LDA}_{xc}[n]}_{\int dr\, \underbrace{e_{xc}(n(r))}}$$

local xc energy that uses the value of the density only at the considered position r (not elsewhere)

**Comment:** In the exact theory

$$E_{xc}[n] = \int_0^1 \frac{d}{d\lambda}\left(E_{xc}[\lambda n]\right) d\lambda$$

$$= \int_0^1 \int dr\, n(r) \frac{\delta E_{xc}[\lambda n]}{\delta n(r)} d\lambda$$

$$\Rightarrow E_{xc}[n] = \int dr\, \underbrace{n(r) \int_0^1 d\lambda \frac{\delta E_{xc}[\lambda n]}{\delta n(r)}}$$

exact local xc energy → functional of the density (and not only function of $n(r)$).

b) Optimizing $\Phi$ consists in optimizing the orbitals that are occupied in $\Phi$. This can be achieved by orbital rotation which gives in second quantization $|\Phi\rangle \equiv |\Phi(\kappa)\rangle = e^{-\hat{\kappa}}|\Phi_0\rangle$ where $\kappa$ controls the orbital rotation. Therefore

$\hat{\kappa} = -\hat{\kappa}^\dagger$ !

$$\min_{\Phi} \longrightarrow \min_{\kappa}$$

$$\langle\Phi|\hat{h}|\Phi\rangle \longrightarrow \langle\Phi(\kappa)|\hat{h}|\Phi(\kappa)\rangle = \langle\Phi_0|\left(e^{-\hat{\kappa}}\right)^\dagger \hat{h}\, e^{-\hat{\kappa}}|\Phi_0\rangle$$

$$= \langle\Phi_0|e^{\hat{\kappa}}\hat{h}\, e^{-\hat{\kappa}}|\Phi_0\rangle = \sum_{pq} h_{pq} \underbrace{\langle\Phi_0|e^{\hat{\kappa}}\hat{E}_{pq}e^{-\hat{\kappa}}|\Phi_0\rangle}_{D_{pq}(\kappa)}$$

$$n_{\Phi} \longrightarrow n_{\Phi(\kappa)} = n(\kappa)$$

c) The minimum is reached when $\Phi = \Phi_0$ i.e. when $K=0$

d) $$E_{Hxc}^{LDA}[n(K)] = \frac{1}{2}\int dr\int dr' \, \frac{n(K,r)\, n(K,r')}{|r-r'|} + \int dr \, e_{xc}(n(K,r))$$

$$\Rightarrow \frac{\partial E_{Hxc}^{LDA}[n(K)]}{\partial K_{lm}} = \frac{1}{2}\int dr\int dr' \, \frac{\partial n(K,r)}{\partial K_{lm}} \, \frac{n(K,r')}{|r-r'|}$$

$$+ \boxed{\frac{1}{2}\int dr\int dr' \, \frac{n(K,r)}{|r-r'|} \, \frac{\partial n(K,r')}{\partial K_{lm}}} \qquad r \leftrightarrow r'$$

$$+ \int dr \, \frac{\partial n(K,r)}{\partial K_{lm}} \times \left.\frac{\partial e_{xc}(\nu)}{\partial \nu}\right|_{\nu = n(K,r)}$$

$$= \int dr \, \underbrace{\left[\int dr' \, \frac{n(K,r')}{|r-r'|} + \left.\frac{\partial e_{xc}(\nu)}{\partial \nu}\right|_{\nu = n(K,r)}\right]}_{v_{Hxc}^{LDA}[n(K)](r)} \times \frac{\partial n(K,r)}{\partial K_{lm}}$$

Since $n(K=0) = n_{\Phi_0}$ it comes

$$\boxed{\left.\frac{\partial E_{Hxc}^{LDA}[n(K)]}{\partial K_{lm}}\right|_{K=0} = \int dr \, v_{Hxc}^{LDA}[n_{\Phi_0}](r) \left.\frac{\partial n(K,r)}{\partial K_{lm}}\right|_{K=0}}$$

e) $$\left.\frac{\partial E^{LDA}(K)}{\partial K_{lm}}\right|_{K=0} = \sum_{pq} h_{pq} \left.\frac{\partial D_{pq}(K)}{\partial K_{lm}}\right|_{K=0} + \int dr \, v_{Hxc}^{LDA}[n_{\Phi_0}](r) \times \sum_{pq} \phi_p(r)\,\phi_q(r) \left.\frac{\partial D_{pq}(K)}{\partial K_{lm}}\right|_{K=0}$$

$$= \sum_{pq}\Big(h_{pq} + \underbrace{\int dr \, \phi_p(r)\, v_{Hxc}^{LDA}[n_{\Phi_0}](r)\, \phi_q(r)}_{\langle \phi_p | v_{Hxc}^{LDA}[n_{\Phi_0}] \times | \phi_q \rangle}\Big) \left.\frac{\partial D_{pq}(K)}{\partial K_{lm}}\right|_{K=0}$$

↳ local (multiplicative) potential operator.

Since $h_{pq} = \langle \phi_p | \hat{h} | \phi_q \rangle$ it comes

$$\boxed{\left.\frac{\partial E^{LDA}(\kappa)}{\partial \kappa_{\ell m}}\right|_{\kappa=0} = \sum_{pq} \langle \phi_p | \hat{f}^{KS} | \phi_q \rangle \left.\frac{\partial D_{pq}(\kappa)}{\partial \kappa_{\ell m}}\right|_{\kappa=0}}$$

where $\hat{f}^{KS} = \hat{h} + v^{LDA}_{Hxc}[n_{\Phi_0}] \times \equiv -\frac{1}{2}\nabla^2_{r} + \left[v_{ne}(r) + v^{LDA}_{Hxc}[n_{\Phi_0}](r)\right]\times$

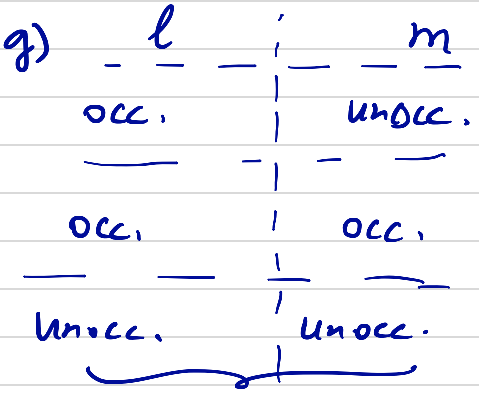
f) The minimum is reached when $\kappa = 0$. Therefore, the following stationarity condition is fulfilled

$$0 = \left.\frac{\partial E^{LDA}(\kappa)}{\partial \kappa_{\ell m}}\right|_{\kappa=0} = \Big(\underbrace{\sum_{pq} f^{KS}_{pq} \left(\delta_{mp}\delta_{\ell q} + \delta_{\ell p}\delta_{mq}\right)}_{f^{KS}_{m\ell} + f^{KS}_{\ell m} = 2 f^{KS}_{\ell m}}\Big) \times (n_\ell - n_m)$$

($\hat{f}^{KS}$ is hermitian and we use real algebra)

Thus leading to $\boxed{f^{KS}_{\ell m}(n_\ell - n_m) = 0}$

g)



$f^{KS}_{\ell m}(n_\ell - 0) = 0 \rightarrow f^{KS}_{\ell m} = 0$

$\uparrow$ 1 or 2 (depends if we have an open or closed shell)

$f^{KS}_{\ell m}(2 - 2) = 0 = 0\,!$ no condition

↳ in the simplest case (closed shell)

$f^{KS}_{\ell m}(0 - 0) = 0 = 0\,!$

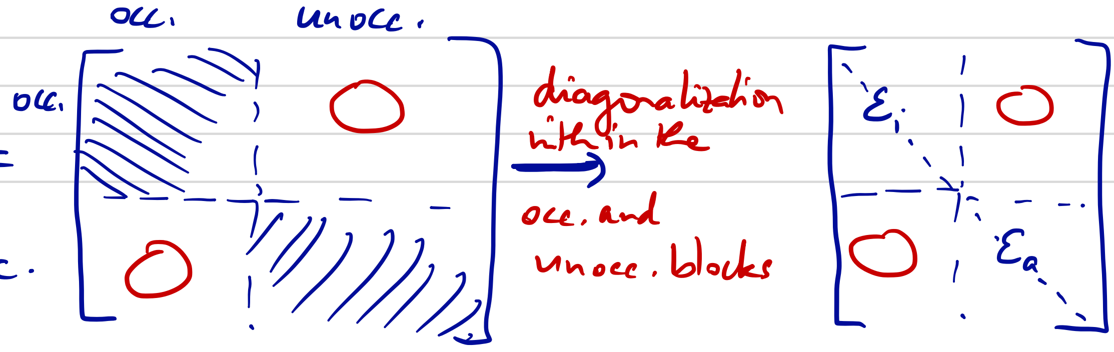
no condition

We know we can rotate the occupied orbitals without changing the energy in that case.

Same thing for the unoccupied orbitals.

Summary :

$[\hat{f}^{KS}] =$



Conclusion: We can find minimizing (KS) orbitals that fulfill

$$\hat{f}^{KS}\phi_p(r) = \mathcal{E}_p\,\phi_p(r)$$

$$\Leftrightarrow \left[-\frac{1}{2}\nabla_r^2 + \underbrace{\left(v_{ne}(r) + v_{Hxc}^{LDA}[n_{\Phi_0}](r)\right)}_{\text{KS potential at the LDA level of approximation.}}\times\right]\phi_p(r) = \mathcal{E}_p\,\phi_p(r) \quad (A)$$

h) Solution 1: Solve Eq. (A) self-consistently. The self-consistency comes from the KS potential (through the density). Indeed

$$n_{\Phi_0}(r) = n(\kappa=0,r) = \sum_{pq}\phi_p(r)\,\phi_q(r)\underbrace{D_{pq}(\kappa=0)}_{\delta_{pq}\,n_p}$$

$$\overset{\text{closed-shell}}{=} 2\sum_i^{occ.}\left(\phi_i(r)\right)^2 = n_{\Phi_0}(r)$$

Solution 2: Newton-method. Desire also the hessian matrix elements

$$E^{[2]} \equiv \frac{\partial^2 E^{LDA}(\kappa)}{\partial\kappa_{no}\,\partial\kappa_{\ell m}}$$

and then expand through second order in $\kappa$:

$$E^{LDA}_{\rightarrow 2}(\kappa) = E^{LDA}(\kappa=0) + \left(E^{[1]}\right)^T\kappa + \frac{1}{2}\kappa^T E^{[2]}\kappa\,.$$

$\neq 0$ (because $\kappa=0$ gives here a non-converged solution)

Find the Newton step $\kappa_+$ such that $\left.\frac{\partial E^{LDA}_{\rightarrow 2}(\kappa)}{\partial\kappa}\right|_{\kappa_+} = 0 \Leftrightarrow \boxed{E^{[2]}\kappa_+ = -E^{[1]}}$

and iterate until $E^{[1]} = 0$.