Exam in theory of extended systems (*part 2*)

March 2019

one-hour exam

Neither documents nor calculators are allowed.

The grading scale might be changed.

2. Problem: Ionization potential in density-functional theory (16 points)

Let us consider both interacting ($\lambda = 1$) and non-interacting ($\lambda = 0$) $\mathcal{N}$-electron systems where $\mathcal{N}$ is either equal to N (the system is then referred to as *neutral*) or $N - 1$ (it is then referred to as *ionized*). Their normalized ground-state wavefunctions $\Psi_{\mathcal{N}}^{\lambda,\xi}$ fulfill the following Schrödinger-like equation,

$$\left(\hat{T} + \lambda \hat{W}_{\text{ee}} + \sum_{i=1}^{\mathcal{N}} v^{\lambda,\xi}(\mathbf{r}_i) \times \right) \Psi_{\mathcal{N}}^{\lambda,\xi} = E_{\mathcal{N}}^{\lambda,\xi} \Psi_{\mathcal{N}}^{\lambda,\xi}, \quad \text{with} \quad \mathcal{N} = N \text{ or } N - 1. \tag{1}$$

The additional parameter ξ is a *weight* that will be assigned to the ionized state in the following. The local potential $v^{\lambda,\xi}(\mathbf{r})$ is adjusted such that the so-called ensemble density $n^{\lambda,\xi}(\mathbf{r})$, which is a weighted sum of neutral and ionized densities, ***does not vary with ξ and λ***:

$$n^{\lambda,\xi}(\mathbf{r}) = \left[1 - \frac{(N-1)\xi}{N} \right] \times n_{\Psi_N^{\lambda,\xi}}(\mathbf{r}) + \xi \times n_{\Psi_{N-1}^{\lambda,\xi}}(\mathbf{r}) = n(\mathbf{r}) \quad \forall \lambda, \forall \xi. \tag{2}$$

a) **[1 pt]** Verify that, by construction, the ensemble density integrates to the number N of electrons in the neutral system: $\int d\mathbf{r} \, n^{\lambda,\xi}(\mathbf{r}) = N$.

Since $\int d\mathbf{r} \, n_{\Psi_N^{\lambda,\xi}}(\mathbf{r}) = N$ and $\int d\mathbf{r} \, n_{\Psi_{N-1}^{\lambda,\xi}}(\mathbf{r}) = N - 1$ it comes

$$\int d\mathbf{r} \, n^{\lambda,\xi}(\mathbf{r}) = \left[1 - \frac{(N-1)\xi}{N} \right] \times N + \xi \times (N-1) = N. \tag{3}$$

b) **[2 pts]** Let us consider the $\xi = 0$ limit of the theory.

How would you name the local potentials $v^{\lambda=1,\xi=0}(\mathbf{r})$

This is the nuclear potential, i.e. the local potential in the real interacting ($\lambda = 1$) system.

and

$v^{\lambda=0,\xi=0}(\mathbf{r})$?

This is the Kohn–Sham potential, i.e. the local potential in the fictitious noninteracting ($\lambda = 0$) system.

Are they uniquely defined by the density constraint in Eq. (2) ?

Yes (up to a constant), according to the (first) Hohenberg–Kohn theorem.

c) **[0.5 pt]** We introduce the following density functionals,

$$
\begin{aligned}
F^{\lambda,\xi}[n] &= \left[1 - \frac{(N-1)\xi}{N}\right] \times \left\langle \Psi_N^{\lambda,\xi}\middle|\hat{T} + \lambda\hat{W}_{\mathrm{ee}}\middle|\Psi_N^{\lambda,\xi}\right\rangle + \xi \times \left\langle \Psi_{N-1}^{\lambda,\xi}\middle|\hat{T} + \lambda\hat{W}_{\mathrm{ee}}\middle|\Psi_{N-1}^{\lambda,\xi}\right\rangle, \\
E_{\mathrm{Hxc}}^{\xi}[n] &= F^{\lambda=1,\xi}[n] - F^{\lambda=0,\xi}[n].
\end{aligned}
\tag{4}
$$

Are they universal ?

Yes they are. The reason is that, for given λ and ξ values, the ground-state wavefunctions $\Psi_N^{\lambda,\xi}$ and $\Psi_{N-1}^{\lambda,\xi}$ can be determined from the density n. Since $\hat{T}$ and $\hat{W}_{\mathrm{ee}}$ are universal operators, the functional $F^{\lambda,\xi}[n]$ is universal, so is the difference $F^{\lambda=1,\xi}[n] - F^{\lambda=0,\xi}[n]$.

d) **[2 pts]** Show that conventional (N-electron) KS-DFT is recovered from Eqs. (2) and (4) when $\xi = 0$.

When $\xi = 0$, the ensemble density reduces to an N-electron (pure) ground-state density $n = n_{\Psi_N^{\lambda,\xi=0}} \equiv n_{\Psi_0} = n_{\Phi^{\mathrm{KS}}}$ where $\Psi_0 \equiv \Psi_N^{\lambda=1,\xi=0}$ and $\Phi^{\mathrm{KS}} = \Psi_N^{\lambda=0,\xi=0}$.

How would you name the functionals $F^{\lambda=1,\xi=0}[n]$

This is the universal Hohenberg–Kohn functional $F[n]$.

, $F^{\lambda=0,\xi=0}[n]$,

This is the noninteracting kinetic energy functional $T_{\mathrm{s}}[n]$

and $E_{\mathrm{Hxc}}^{\xi=0}[n]$?

This is the conventional Hartree-exchange-correlation functional $E_{\mathrm{Hxc}}[n]$.

Which energy contributions do they describe?

$F[n]$: kinetic and two-electron repulsion energies of the true (interacting) system in its pure N-electron ground state with density n.

$T_{\mathrm{s}}[n]$: kinetic energy of the fictitious noninteracting KS system in its pure N-electron ground state with density n.

$E_{\mathrm{Hxc}}[n]$: Hartree density-functional energy (from classical electrostatics), exchange energy (due to the antisymmetrization in the KS determinant), and the correlation energy which is the difference in total energy between the true (interacting) system and the KS system.

e) **[2 pts]** Deduce from Eqs. (1) and (2) that $F^{\lambda,\xi}[n] = \left[1 - \frac{(N-1)\xi}{N}\right] \times E_N^{\lambda,\xi} + \xi \times E_{N-1}^{\lambda,\xi} - \int d\mathbf{r}\, v^{\lambda,\xi}(\mathbf{r})n(\mathbf{r})$.

For $\mathcal{N} = N$ or $N-1$,

$$
\begin{aligned}
E_{\mathcal{N}}^{\lambda,\xi} &= \left\langle \Psi_{\mathcal{N}}^{\lambda,\xi} \middle| \hat{T} + \lambda \hat{W}_{\text{ee}} + \sum_{i=1}^{\mathcal{N}} v^{\lambda,\xi}(\mathbf{r}_i) \times \middle| \Psi_{\mathcal{N}}^{\lambda,\xi} \right\rangle \\
&= \left\langle \Psi_{\mathcal{N}}^{\lambda,\xi} \middle| \hat{T} + \lambda \hat{W}_{\text{ee}} \middle| \Psi_{\mathcal{N}}^{\lambda,\xi} \right\rangle + \left\langle \Psi_{\mathcal{N}}^{\lambda,\xi} \middle| \sum_{i=1}^{\mathcal{N}} v^{\lambda,\xi}(\mathbf{r}_i) \times \middle| \Psi_{\mathcal{N}}^{\lambda,\xi} \right\rangle \\
&= \left\langle \Psi_{\mathcal{N}}^{\lambda,\xi} \middle| \hat{T} + \lambda \hat{W}_{\text{ee}} \middle| \Psi_{\mathcal{N}}^{\lambda,\xi} \right\rangle + \int d\mathbf{r}\, v^{\lambda,\xi}(\mathbf{r}) n_{\Psi_{\mathcal{N}}^{\lambda,\xi}}(\mathbf{r}),
\end{aligned} \tag{5}
$$

so that

$$
\begin{aligned}
&\left[1 - \frac{(N-1)\xi}{N} \right] \times E_{N}^{\lambda,\xi} + \xi \times E_{N-1}^{\lambda,\xi} \\
&= F^{\lambda,\xi}[n] \\
&\quad + \int d\mathbf{r}\, v^{\lambda,\xi}(\mathbf{r}) \times \left(\left[1 - \frac{(N-1)\xi}{N} \right] \times n_{\Psi_{N}^{\lambda,\xi}}(\mathbf{r}) + \xi \times n_{\Psi_{N-1}^{\lambda,\xi}}(\mathbf{r}) \right) \\
&= F^{\lambda,\xi}[n] + \int d\mathbf{r}\, v^{\lambda,\xi}(\mathbf{r}) n(\mathbf{r}),
\end{aligned} \tag{6}
$$

thus leading to

$$
F^{\lambda,\xi}[n] = \left[1 - \frac{(N-1)\xi}{N} \right] \times E_{N}^{\lambda,\xi} + \xi \times E_{N-1}^{\lambda,\xi} - \int d\mathbf{r}\, v^{\lambda,\xi}(\mathbf{r}) n(\mathbf{r}). \tag{7}
$$

f) **[1.5 pts]** Prove that $\dfrac{\partial E_{\mathcal{N}}^{\lambda,\xi}}{\partial \xi} = \displaystyle\int d\mathbf{r}\, \frac{\partial v^{\lambda,\xi}(\mathbf{r})}{\partial \xi} n_{\Psi_{\mathcal{N}}^{\lambda,\xi}}(\mathbf{r})$ where $\mathcal{N} = N$ or $N-1$.

According to the Hellmann–Feynman theorem (see below),

$$
\begin{aligned}
\frac{\partial E_{\mathcal{N}}^{\lambda,\xi}}{\partial \xi} &= \left\langle \Psi_{\mathcal{N}}^{\lambda,\xi} \middle| \sum_{i=1}^{\mathcal{N}} \frac{\partial v^{\lambda,\xi}(\mathbf{r}_i)}{\partial \xi} \times \middle| \Psi_{\mathcal{N}}^{\lambda,\xi} \right\rangle \\
&= \int d\mathbf{r}\, \frac{\partial v^{\lambda,\xi}(\mathbf{r})}{\partial \xi} n_{\Psi_{\mathcal{N}}^{\lambda,\xi}}(\mathbf{r}).
\end{aligned} \tag{8}
$$

Hint: prove the Hellmann–Feynman theorem, $\dfrac{\partial E_{\mathcal{N}}^{\lambda,\xi}}{\partial \xi} = \left\langle \Psi_{\mathcal{N}}^{\lambda,\xi} \middle| \dfrac{\partial \hat{H}^{\lambda,\xi}}{\partial \xi} \middle| \Psi_{\mathcal{N}}^{\lambda,\xi} \right\rangle$ where $\hat{H}^{\lambda,\xi} = \hat{T} + \lambda \hat{W}_{\text{ee}} + \sum_{i=1}^{\mathcal{N}} v^{\lambda,\xi}(\mathbf{r}_i) \times$, and conclude.

Since $E_{\mathcal{N}}^{\lambda,\xi} = \left\langle \Psi_{\mathcal{N}}^{\lambda,\xi} \middle| \hat{H}^{\lambda,\xi} \middle| \Psi_{\mathcal{N}}^{\lambda,\xi} \right\rangle$ [see Eq. (1)], it comes

$$
\begin{aligned}
\frac{\partial E_{\mathcal{N}}^{\lambda,\xi}}{\partial \xi} &= \left\langle \frac{\partial \Psi_{\mathcal{N}}^{\lambda,\xi}}{\partial \xi} \middle| \hat{H}^{\lambda,\xi} \middle| \Psi_{\mathcal{N}}^{\lambda,\xi} \right\rangle + \left\langle \Psi_{\mathcal{N}}^{\lambda,\xi} \middle| \hat{H}^{\lambda,\xi} \middle| \frac{\partial \Psi_{\mathcal{N}}^{\lambda,\xi}}{\partial \xi} \right\rangle + \left\langle \Psi_{\mathcal{N}}^{\lambda,\xi} \middle| \frac{\partial \hat{H}^{\lambda,\xi}}{\partial \xi} \middle| \Psi_{\mathcal{N}}^{\lambda,\xi} \right\rangle \\
&= E_{\mathcal{N}}^{\lambda,\xi} \left\langle \frac{\partial \Psi_{\mathcal{N}}^{\lambda,\xi}}{\partial \xi} \middle| \Psi_{\mathcal{N}}^{\lambda,\xi} \right\rangle + E_{\mathcal{N}}^{\lambda,\xi} \left\langle \Psi_{\mathcal{N}}^{\lambda,\xi} \middle| \frac{\partial \Psi_{\mathcal{N}}^{\lambda,\xi}}{\partial \xi} \right\rangle + \left\langle \Psi_{\mathcal{N}}^{\lambda,\xi} \middle| \frac{\partial \hat{H}^{\lambda,\xi}}{\partial \xi} \middle| \Psi_{\mathcal{N}}^{\lambda,\xi} \right\rangle \\
&= E_{\mathcal{N}}^{\lambda,\xi} \underbrace{\frac{\partial}{\partial \xi} \left[\underbrace{\left\langle \Psi_{\mathcal{N}}^{\lambda,\xi} \middle| \Psi_{\mathcal{N}}^{\lambda,\xi} \right\rangle}_{=1} \right]}_{=0} + \left\langle \Psi_{\mathcal{N}}^{\lambda,\xi} \middle| \frac{\partial \hat{H}^{\lambda,\xi}}{\partial \xi} \middle| \Psi_{\mathcal{N}}^{\lambda,\xi} \right\rangle \\
&= \left\langle \Psi_{\mathcal{N}}^{\lambda,\xi} \middle| \frac{\partial \hat{H}^{\lambda,\xi}}{\partial \xi} \middle| \Psi_{\mathcal{N}}^{\lambda,\xi} \right\rangle.
\end{aligned}
\tag{9}
$$

g) **[1.5 pts]** Deduce from Eq. (2) and questions 2. e) and 2. f) that $\dfrac{\partial F^{\lambda,\xi}[n]}{\partial \xi} = E_{N-1}^{\lambda,\xi} - \dfrac{(N-1)}{N} \times E_N^{\lambda,\xi}$.

$$
\begin{aligned}
\frac{\partial F^{\lambda,\xi}[n]}{\partial \xi} &= E_{N-1}^{\lambda,\xi} - \frac{(N-1)}{N} \times E_N^{\lambda,\xi} + \left[1 - \frac{(N-1)\xi}{N} \right] \times \frac{\partial E_N^{\lambda,\xi}}{\partial \xi} + \xi \times \frac{\partial E_{N-1}^{\lambda,\xi}}{\partial \xi} - \int d\mathbf{r} \, \frac{\partial v^{\lambda,\xi}(\mathbf{r})}{\partial \xi} n(\mathbf{r}) \\
&= E_{N-1}^{\lambda,\xi} - \frac{(N-1)}{N} \times E_N^{\lambda,\xi} + \int d\mathbf{r} \, \frac{\partial v^{\lambda,\xi}(\mathbf{r})}{\partial \xi} \times \left(\underbrace{\left[1 - \frac{(N-1)\xi}{N} \right] n_{\Psi_N^{\lambda,\xi}}(\mathbf{r}) + \xi n_{\Psi_{N-1}^{\lambda,\xi}}(\mathbf{r})}_{=n(\mathbf{r})} \right) \\
&\quad - \int d\mathbf{r} \, \frac{\partial v^{\lambda,\xi}(\mathbf{r})}{\partial \xi} n(\mathbf{r}) \\
&= E_{N-1}^{\lambda,\xi} - \frac{(N-1)}{N} \times E_N^{\lambda,\xi}.
\end{aligned}
\tag{10}
$$

h) **[1 pt]** Let $I_N = E_{N-1}^{\lambda=1,\xi=0} - E_N^{\lambda=1,\xi=0}$ denote the exact ionization potential of a given N-electron system. We denote ε_N the HOMO energy (where HOMO stands for *highest occupied molecular orbital*) that would be obtained by applying standard KS-DFT to the latter system. Explain why $\varepsilon_N = -\left(E_{N-1}^{\lambda=0,\xi=0} - E_N^{\lambda=0,\xi=0} \right)$.

In the noninteracting system ($\lambda = 0$) [$\xi = 0$ means that the latter system is the conventional N-electron KS one], total energies are simply obtained by summing up the energies of the occupied orbitals, i.e.

$$
E_{N-1}^{\lambda=0,\xi=0} \equiv \sum_{p=1}^{N-1} \varepsilon_p,
\tag{11}
$$

and

$$E_N^{\lambda=0,\xi=0} \equiv \sum_{p=1}^{N} \varepsilon_p, \tag{12}$$

thus leading to

$$E_N^{\lambda=0,\xi=0} - E_{N-1}^{\lambda=0,\xi=0} = \varepsilon_N. \tag{13}$$

i) **[1.5 pts]** Let $C_N = \dfrac{1}{N}\left(E_N^{\lambda=1,\xi=0} - E_N^{\lambda=0,\xi=0}\right)$. Is C_N expected to be equal to zero in the exact theory ? Justify your answer by considering the exact (interacting) energy decomposition used in KS-DFT.

We consider here the particular case where $\xi = 0$, which corresponds to conventional KS-DFT. The KS system is expected to reproduce the true (interacting) density n [i.e. $n^{\lambda=0,\xi=0}(\mathbf{r}) = n^{\lambda=1,\xi=0}(\mathbf{r}) = n(\mathbf{r})$], not the energy. Therefore, there is no reason to expect C_N to be equal to zero. A more detailed answer would be:

$$E_N^{\lambda=0,\xi=0} = T_s[n] + \int d\mathbf{r}\; v^{\mathrm{KS}}[n](\mathbf{r})n(\mathbf{r}), \tag{14}$$

and

$$E_N^{\lambda=1,\xi=0} = F[n] + \int d\mathbf{r}\; v_{\mathrm{ne}}[n](\mathbf{r})n(\mathbf{r}), \tag{15}$$

where $v_{\mathrm{ne}}[n]$ is the local (nuclear) potential in the true (interacting) system with ground-state density n, thus leading to

$$E_N^{\lambda=1,\xi=0} - E_N^{\lambda=0,\xi=0} = E_{\mathrm{Hxc}}[n] - \int d\mathbf{r}\; \left(\underbrace{v^{\mathrm{KS}}[n](\mathbf{r}) - v_{\mathrm{ne}}[n](\mathbf{r})}_{\dfrac{\delta E_{\mathrm{Hxc}}[n]}{\delta n(\mathbf{r})}}\right)n(\mathbf{r}). \tag{16}$$

Since $N = \int d\mathbf{r}\; n(\mathbf{r})$, we obtain the final expression

$$C_N = \frac{E_{\mathrm{Hxc}}[n] - \int d\mathbf{r}\; \frac{\delta E_{\mathrm{Hxc}}[n]}{\delta n(\mathbf{r})} n(\mathbf{r})}{\int d\mathbf{r}\; n(\mathbf{r})}. \tag{17}$$

The latter quantity is known as Levy–Zahariev shift in potential [M. Levy and F. Zahariev, Phys. Rev.

Lett. 113, 113002 (2014)]. If the universal Hxc functional could be simplified as follows:

$$E_{\mathrm{Hxc}}[n] \rightarrow \int d\mathbf{r}\, \epsilon_{\mathrm{Hxc}} \times n(\mathbf{r}) = N\epsilon_{\mathrm{Hxc}}, \qquad (18)$$

where the Hxc energy per particle ϵ_{Hxc} is considered as density-independent, then we would have $\frac{\delta E_{\mathrm{Hxc}}[n]}{\delta n(\mathbf{r})} \rightarrow \epsilon_{\mathrm{Hxc}}$ and $C_N \rightarrow 0$. In general, ϵ_{Hxc} is a functional of the density [see, for example, the particular case of a uniform electron gas], so that $C_N \neq 0$.

j) **[1.5 pts]** Deduce from Eq. (4) and questions 2. g), 2. h), and 2. i) that $I_N = -\varepsilon_N - C_N + \left.\dfrac{\partial E_{\mathrm{Hxc}}^{\xi}[n]}{\partial \xi}\right|_{\xi=0}$.

According to Eq. (10),

$$
\begin{aligned}
\frac{\partial E_{\mathrm{Hxc}}^{\xi}[n]}{\partial \xi} &\equiv \frac{\partial F^{\lambda=1,\xi}[n]}{\partial \xi} - \frac{\partial F^{\lambda=0,\xi}[n]}{\partial \xi} \\
&= E_{N-1}^{\lambda=1,\xi} - \frac{(N-1)}{N} \times E_N^{\lambda=1,\xi} - \left(E_{N-1}^{\lambda=0,\xi} - \frac{(N-1)}{N} \times E_N^{\lambda=0,\xi} \right),
\end{aligned}
\qquad (19)
$$

which gives, when $\xi = 0$,

$$
\left.\frac{\partial E_{\mathrm{Hxc}}^{\xi}[n]}{\partial \xi}\right|_{\xi=0} = \underbrace{\frac{1}{N}\left(E_N^{\lambda=1,\xi=0} - E_N^{\lambda=0,\xi=0} \right)}_{C_N} + \underbrace{\left(E_{N-1}^{\lambda=1,\xi=0} - E_N^{\lambda=1,\xi=0} \right)}_{I_N} - \underbrace{\left(E_{N-1}^{\lambda=0,\xi=0} - E_N^{\lambda=0,\xi=0} \right)}_{\varepsilon_N}
$$

$$(20)$$

k) **[1.5 pts]** The following fundamental question naturally arises in KS-DFT: *Can we interpret the energy of the HOMO as minus the ionization potential of the true (interacting) system under study?* Explain why this question is of primary importance, for example, in the field of nanotechnology,

   The ability of a material to lose (and gain) an electron characterizes its conductivity.

   and bring an answer in the light of question 2. j).

   As readily seen from Eq. (20), the deviation of the true ionization potential from the KS one [the latter is equal to $-\varepsilon_N$], can be evaluated as follows:

$$I_N - \left(-\varepsilon_N \right) = -C_N + \left.\frac{\partial E_{\mathrm{Hxc}}^{\xi}[n]}{\partial \xi}\right|_{\xi=0}. \qquad (21)$$

As none of the quantities on the right-hand side of Eq. (21) are expected to be equal to zero, in the general case, we conclude that, in principle, the true and KS ionization potentials should not be expected to match.