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

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1. Questions on the lecture material (9 points)

a) **[3 pts]** Give the expression of the density-functional Hartree energy $E_\text{H}[n]$. Is it a universal functional of the density? Within the local density approximation (LDA), a density functional $S[n]$ is written as $S[n] = \int d\mathbf{r}\ s(n(\mathbf{r}))n(\mathbf{r})$, where s is a *function* of the density at position $\mathbf{r}$. Is $E_\text{H}[n]$ an LDA-type functional?

b) **[3 pts]** Does the Hartree functional describe the two-electron repulsion in molecules and solids exactly? If not, what are the missing contributions (discuss briefly their physical meaning)?

c) **[3 pts]** We consider, for simplicity, the expression in *one dimension* of the Kohn–Sham (KS) potential at the LDA level of approximation: $v_\text{LDA}^\text{KS}(x) \equiv v(x) + \int dx'\ \dfrac{n(x')}{|x' - x|} + \dfrac{\partial \varepsilon_\text{xc}(n)}{\partial n}\bigg|_{n=n(x)}$, where $v(x)$ is the nuclear potential with periodicity a [*i.e.*, $v(x+a) = v(x)$] in the extended system under study. We know from Bloch's theorem that, when the two-electron repulsion is neglected, the (one-electron) solutions to the Schrödinger equation can be written as $\varphi_{l,k}(x) = e^{ikx} \times u_{l,k}(x)$ where l is a quantum number and $u_{l,k}(x)$ has the periodicity a of the lattice. Does Bloch's theorem also hold for the KS orbitals? **Hint:** Show that the density $n(x) \equiv \displaystyle\sum_{l,k}^{\text{occupied}} |\varphi_{l,k}(x)|^2$, and therefore the KS-LDA potential, is periodic. Conclude.

2. Problem: Hohenberg–Kohn theorem for N-centered ensembles (12 points)

The purpose of this exercise is to prove that the fundamental gap is a functional of the so-called N-centered ensemble density. The formulation of a Kohn–Sham density-functional theory (KS-DFT) in this context is then contemplated.

Let us consider an $\mathcal{N}$-electron system where $\mathcal{N}$ **can take three different positive integer values:** N (which is the so-called central number of electrons), $N - 1$, or $N + 1$. The corresponding normalized ground-state wavefunctions $\Psi_\mathcal{N}$ fulfill the regular Schrödinger equation $\boxed{\hat{H}[v]\Psi_\mathcal{N} = E_\mathcal{N} \times \Psi_\mathcal{N},}$ where the

$\mathcal{N}$-electron Hamiltonian operator reads $\boxed{\hat{H}[v] = \hat{T} + \hat{W}_{\text{ee}} + \sum_{i=1}^{\mathcal{N}} v(\mathbf{r}_i)\times}$, $\hat{T}$ and $\hat{W}_{\text{ee}}$ being the kinetic and two-electron repulsion energy operators, respectively, and $v(\mathbf{r})$ is the local nuclear potential.

a) **[2 pts]** Let us consider a potential $v'(\mathbf{r})$ that differ from $v(\mathbf{r})$ by more than a constant. We denote $\Psi'_{\mathcal{N}}$ and $E'_{\mathcal{N}}$ the $\mathcal{N}$-electron ground-state wavefunction and energy that are obtained by solving the Schrödinger equation with the Hamiltonian $\hat{H}[v']$. Show that $\Psi'_{\mathcal{N}}$ cannot be solution to the Schrödinger equation with the Hamiltonian $\hat{H}[v]$. **Hint**: Assume that $\hat{H}[v]\Psi'_{\mathcal{N}} = \mathscr{E}'_{\mathcal{N}}\Psi'_{\mathcal{N}}$ and deduce that $\left(\hat{H}[v] - \hat{H}[v']\right)\Psi'_{\mathcal{N}} = (\mathscr{E}'_{\mathcal{N}} - E'_{\mathcal{N}}) \times \Psi'_{\mathcal{N}} = \sum_{i=1}^{\mathcal{N}}\left(v(\mathbf{r}_i) - v'(\mathbf{r}_i)\right) \times \Psi'_{\mathcal{N}}$, thus leading to $v(\mathbf{r}) - v'(\mathbf{r}) = (\mathscr{E}'_{\mathcal{N}} - E'_{\mathcal{N}})/\mathcal{N}$ when $\mathbf{r}_1 = \mathbf{r}_2 = \ldots = \mathbf{r}_{\mathcal{N}} = \mathbf{r}$. Conclude.

b) **[1 pt]** Explain briefly, in the light of question 2. a), why $\langle\Psi'_{\mathcal{N}}|\,\hat{H}[v]\,|\Psi'_{\mathcal{N}}\rangle > E_{\mathcal{N}}$.

c) **[1 pt]** Let ξ be a real number in the range $0 \leq \xi \leq 1/2$. We denote $E(\xi)$ the so-called N-centered ensemble energy, which is defined as follows: $\boxed{E(\xi) = \xi \times (E_{N+1} + E_{N-1}) + (1 - 2\xi) \times E_N}$. Explain why the slope $\dfrac{dE(\xi)}{d\xi}$ of the N-centered ensemble energy, which is referred to as the fundamental gap, characterizes the ability of the system under study to conduct electricity.

d) **[1 pt]** Show that, according to question 2. b),

$$\xi\left(\langle\Psi'_{N+1}|\,\hat{H}[v]\,|\Psi'_{N+1}\rangle + \langle\Psi'_{N-1}|\,\hat{H}[v]\,|\Psi'_{N-1}\rangle\right) + (1 - 2\xi)\langle\Psi'_N|\,\hat{H}[v]\,|\Psi'_N\rangle > E(\xi). \tag{1}$$

e) **[2 pts]** We now introduce the so-called N-centered ensemble density:

$$n(\mathbf{r}) = \xi \times \left(n_{\Psi_{N+1}}(\mathbf{r}) + n_{\Psi_{N-1}}(\mathbf{r})\right) + (1 - 2\xi) \times n_{\Psi_N}(\mathbf{r}). \tag{2}$$

Show that, according to Eq. (1), $\boxed{E'(\xi) + (v - v'|n') > E(\xi)}$, where $(v|n) \equiv \int d\mathbf{r}\, v(\mathbf{r})n(\mathbf{r})$; $E'(\xi)$ and n' are the N-centered ensemble energy and density generated from the potential v', respectively.

f) **[1 pt]** Similarly we have $\boxed{E(\xi) + (v' - v|n) > E'(\xi)}$. Show that it is absurd to assume that the densities n and n' are equal. Conclude.

g) **[2 pts]** Let $F^{\xi}[n'] = E'(\xi) - (v'|n')$. Show that, for a fixed ξ value, $F^{\xi}[n']$ is a universal functional of the N-centered ensemble density n' and prove, by referring to question 2. e), the following variational principle: $E(\xi) = \min_{n'}\left\{F^{\xi}[n'] + (v|n')\right\}$.

h) **[2 pts]** Explain how, in the light of the previous questions, one could derive a Kohn–Sham DFT for N-centered ensembles. How different and useful would it be compared to the regular (N-electron) formulation of KS-DFT?