M1 course, February 2023, *Lecturer: E. Fromager*

40-minute exam: Density functional theory of extended systems

a) [**3 pts**] *We consider, for simplicity, the expression in one dimension of the Kohn–Sham (KS) potential at the local density level of approximation (LDA):* $v^{\mathrm{KS}}_{\mathrm{LDA}}(x) \equiv v(x) + \left.\dfrac{\partial e_{\mathrm{xc}}(n)}{\partial n}\right|_{n=n(x)} + \displaystyle\int dx'\, \dfrac{n(x')}{|x'-x|}$, *where* $v(x)$ *is the nuclear potential with periodicity* a *[i.e.,* $v(x+a) = v(x)$*] of 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* $\varphi(x) \equiv \varphi_{j,k}(x) = \mathrm{e}^{\mathrm{i}kx} \times u_{j,k}(x)$ *where* k *is a given continuous wave number value,* j *is a (discrete) quantum number, and* $u_{j,k}(x)$ *is a function of the position* x *that has the periodicity* a *of the lattice. The orbital energies are denoted* $\varepsilon_j(k)$*.* Explain the concept of band structure on that basis. Does Bloch's theorem hold also for the KS orbitals? **Hint:** Explain why the total electronic density is periodic. Deduce the periodicity of the KS-LDA potential and conclude.

b) [**3 pts**] The Hartree (H) density-functional energy reads $E_{\mathrm{H}}[n] = \dfrac{1}{2}\displaystyle\int d\mathbf{r} \int d\mathbf{r}'\, \dfrac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}$. What is its physical meaning? Does it provide an exact description of the electronic repulsion energy? The Hartree functional can be rewritten as $E_{\mathrm{H}}[n] = \displaystyle\int d\mathbf{r}\, \epsilon_{\mathrm{H}}[n](\mathbf{r}) n(\mathbf{r})$, where $\epsilon_{\mathrm{H}}[n](\mathbf{r})$ is the density-functional Hartree energy per electron evaluated at position $\mathbf{r}$. Give the mathematical expression of $\epsilon_{\mathrm{H}}[n](\mathbf{r})$ and explain why the exact Hartree functional is *not* a local density functional.

c) [**2 pts**] Let us consider the following local density approximation to the Hartree functional $E_{\mathrm{H}}[n] \overset{\mathrm{LDA}}{\approx} C \displaystyle\int d\mathbf{r}\, n^{\delta}(\mathbf{r})$, where the prefactor C and the exponent δ are constant. Show that a value of δ can be determined from the *exact* uniform coordinate scaling constraint $E_{\mathrm{H}}[n_\gamma] = \gamma E_{\mathrm{H}}[n]$, which holds for any $\gamma > 0$ and where $n_\gamma(\mathbf{r}) = \gamma^3 n(\gamma\mathbf{r})$.

d) [**4 pts**] Let $E^N(\xi) = \xi\left(E_0^{N+1} + E_0^{N-1}\right) + (1-2\xi)E_0^N$ denote the so-called N-centered ensemble energy (with ensemble weight ξ in the range $0 \leq \xi \leq 1/2$) of a given electronic system, where $E_0^{\mathcal{N}}$ is the $\mathcal{N}$-electron ground-state energy of the latter. What is the physical meaning of the derivative $\left.\frac{dE^N(\xi)}{d\xi}\right|_{\xi=0}$? It can be shown that, in the vicinity of $\xi = 0$,

$$E^N(\xi) = \xi\left(\mathcal{E}_0^{N+1} + \mathcal{E}_0^{N-1}\right) + (1-2\xi)\mathcal{E}_0^N + E^{\xi}_{\mathrm{Hxc}}[n] - \int d\mathbf{r}\, v_{\mathrm{Hxc}}[n](\mathbf{r}) n(\mathbf{r}), \tag{1}$$

where $E^{\xi}_{\mathrm{Hxc}}[n]$ is the (ξ-dependent) N-centered Hxc ensemble functional, $v_{\mathrm{Hxc}}[n](\mathbf{r})$ and $n(\mathbf{r})$ are the (ξ-independent) Hxc potential and N-electron ground-state density, respectively, and $\mathcal{E}_0^{\mathcal{N}}$ is the ground-state energy of the *non-interacting* $\mathcal{N}$-electron KS system. Explain why the KS ionization potential $\mathcal{E}_0^{N-1} - \mathcal{E}_0^N$ and electron affinity $\mathcal{E}_0^N - \mathcal{E}_0^{N+1}$ are trivially obtained from the KS HOMO (ε_{H}) and LUMO (ε_{L}) energies. Deduce from Eq. (1) an expression of $\left.\frac{dE^N(\xi)}{d\xi}\right|_{\xi=0}$ in terms of the latter energies. Comment on the result and its practical implications regarding the computation of material properties with DFT methods.