40-minute **exam: Density functional theory of extended systems**

a) [**2.5 pts**] We consider, for simplicity, the expression in *one dimension* of the Kohn–Sham (KS) potential at the local density level of approximation (LDA): $v_{\mathrm{LDA}}^{\mathrm{KS}}(x) \equiv v(x) + \left. \dfrac{\partial e_{\mathrm{xc}}(n)}{\partial n} \right|_{n=n(x)} + \displaystyle\int dx' \, \dfrac{n(x')}{|x'-x|}$, 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 $\varphi(x) \equiv \varphi_{j,k}(x) = e^{\mathrm{i}kx} \times u_{j,k}(x)$ where k is a given wave number value, j is a quantum number, and $u_{j,k}(x)$ is a function of the position x that has the periodicity a of the lattice. Does Bloch's theorem also hold for the KS orbitals? **Hint:** Explain why the density $n(x) \equiv \displaystyle\sum_{j,k}^{\mathrm{occupied}} |\varphi_{j,k}(x)|^2$ is periodic. Deduce the periodicity of the KS-LDA potential and conclude.

b) [**3 pts**] The fundamental energy gap of an N-electron system is evaluated from its neutral (N), anionic ($N+1$), and cationic ($N-1$) ground-state energies as follows: $E_g = E_{N+1} + E_{N-1} - 2E_N$. Modelling the fundamental gap of materials accurately is of primary importance for condensed matter physicists. Why? Show that, in the particular case of non-interacting electrons, the fundamental gap, the so-called optical gap, and the HOMO-LUMO gap $\varepsilon_{\mathrm{L}} - \varepsilon_{\mathrm{H}}$ boil down to the same quantity. Does this statement hold true for real (interacting) electronic systems? Why?

c) [**2.5 pts**] It can be shown that the true fundamental gap can be evaluated exactly from the KS gap as follows,

$$E_g = \varepsilon_{\mathrm{L}}^{\mathrm{KS}} - \varepsilon_{\mathrm{H}}^{\mathrm{KS}} + \left[\left. \frac{\partial E_{\mathrm{xc}}^{\xi}[n]}{\partial \xi} \right|_{n=n_N} \right]_{\xi=0}, \tag{1}$$

where n_N denotes the N-electron ground-state density and $E_{\mathrm{xc}}^{\xi}[n]$ is the so-called N-centered ensemble exchange-correlation (xc) density functional. The latter describes the xc energy contribution to the N-centered ensemble energy $E^{\xi} = \xi E_{N+1} + \xi E_{N-1} + (1-2\xi)E_N$, where the ensemble weight ξ varies in the range $0 \leq \xi \leq 1/2$. Do standard xc functionals like LDA or PBE have an explicit dependence in ξ? Can this be problematic for evaluating the fundamental gap of semiconductor materials, for example?

d) [**3 pts**] We define as $E_{\mathrm{c}}^{\xi}[n] \approx 0$ and $E_{\mathrm{x}}^{\xi}[n] \approx (B + C\xi) \int d\mathbf{r} \, n^{\beta}(\mathbf{r})$ the ensemble *exchange-only* LDA functional, where the exponent β as well as the constant coefficients B and C are *a priori* unknown. Explain how we could determine B and β by considering the $\xi = 0$ limit of the theory. The coefficient C might be determined by applying Eq. (1) to a simple system like the helium atom. How would you proceed? Would the resulting functional be applicable to extended systems? In your opinion, how useful/successful would such a functional be?