Student ID number or First name/NAME:

Density functional theory of extended systems (M1 course)

March 2024 – Duration of the exam: *40 minutes*

READ CAREFULLY WHAT FOLLOWS: The exam consists of an essay (see below) AND an exercise (turn the page!). You are expected to **write directly on this exam paper**. Do NOT forget to write your first name/NAME or your student ID number (see above).

Essay **[13 pts] Discuss the major differences between density functional theory (DFT) computations for molecular and extended periodic systems**. *You are expected to discuss in your essay the impact of periodicity on the construction of the Kohn–Sham (KS) orbitals and their energies, by referring to Bloch's theorem, the concept of band structure and how it can be related to the molecular orbital energy diagram of quantum chemistry.* **Finally, explain what the fundamental gap is, its physical significance, and its connection with the KS band gap.**

Exercise [7 pts]

The (so-called N-centered) ensemble energy of ground N-electron, cationic, and anionic states, $E^\xi = \xi\left(E_0^{N+1} + E_0^{N-1}\right) + (1-2\xi)E_0^N = E_0^N + \xi\Omega_g$, *is an affine function of the ensemble weight ξ, which varies in the range $0 \leq \xi \leq 1/2$, Ω_g being the fundamental gap of the system under study. Like in regular N-electron ground-state DFT, the Hartree-exchange-correlation (Hxc) energy of the ensemble can be described by a density functional $E^\xi_{\rm Hxc}[n]$ which, for a fixed density n, now varies with ξ. It can be shown that the fundamental and Kohn–Sham (KS) band gaps are linked by the following relation,* $\boxed{\Omega_g = \frac{dE^\xi}{d\xi} \overset{exact}{=} \varepsilon_{\rm L} - \varepsilon_{\rm H} + \left.\frac{\partial E^\xi_{\rm Hxc}[n]}{\partial \xi}\right|_{\xi=0, n=n_0^N}}$, *where n_0^N denotes the reference N-electron ground-state density. The Hartree-exchange (Hx) part of the Hxc functional can be conveniently decomposed as follows in terms of the conventional (ξ-independent) Hartree functional* $E_{\rm H}[n] = \frac{1}{2}\int d\mathbf{r}\int d\mathbf{r}'\,\frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}$, $\boxed{E^\xi_{\rm Hx}[n] = E_{\rm H}[n] + E^\xi_{\rm x}[n]}$. *It can be shown that the ensemble exchange functional satisfies, for any value of ξ, the following uniform coordinate scaling relation,* $\boxed{E^\xi_{\rm x}[n_\gamma] \overset{exact}{=} \gamma E^\xi_{\rm x}[n]}$, *with $\gamma > 0$ and $n_\gamma(\mathbf{r}) = \gamma^3 n(\gamma\mathbf{r})$.*

Why is it not trivial to compute fundamental gaps in DFT?

We investigate in the following the possibility to approximately correct the KS band gap by $\boxed{(1)}$ *neglecting the ξ dependence of the ensemble correlation functional and* $\boxed{(2)}$ *using the following local density approximation (LDA) to the ensemble exchange energy,*

$$E^\xi_{\rm x}[n] \overset{\rm LDA}{\approx} -\frac{3}{4}\left(\frac{3}{\pi}\right)^{\frac{1}{3}}(1+C\xi)\int d\mathbf{r}\left(n(\mathbf{r})\right)^\beta. \tag{1}$$

Determine the value of the exponent β for which the above functional satisfies the exact uniform coordinate scaling relation.

The fundamental gap $\Omega_g^{H_2}$ of the simple two-electron hydrogen molecule H_2 can be evaluated accurately along with its ground-state density $n_0^{H_2}(\mathbf{r})$ and the corresponding KS HOMO-LUMO gap $\varepsilon_{\rm L}^{H_2} - \varepsilon_{\rm H}^{H_2}$. **Explain why the parameter C in the functional of Eq. (1) could be evaluated numerically as follows,** $C = -\frac{4}{3}\left(\frac{\pi}{3}\right)^{\frac{1}{3}}\frac{\left(\Omega_g^{H_2} - \varepsilon_{\rm L}^{H_2} + \varepsilon_{\rm H}^{H_2}\right)}{\int d\mathbf{r}\left(n_0^{H_2}(\mathbf{r})\right)^{\frac{4}{3}}}$. **What do you expect from the resulting LDA functional's performance in the description of the fundamental gap of materials?**