

One-hour exam: Density functional theory and extended systems

General questions

- a) [3 pts] According to Bloch’s theorem, any one-electron solution to the Schrödinger equation of a one-dimensional (1D) lattice can be written as $\varphi(x) \equiv e^{ikx}u_j(k, x)$, where the index j refers to an energy level $\varepsilon_j(k)$ that is determined for a fixed and real k value, and $u_j(k, x)$ is periodic in the position x , with the same periodicity as the lattice. Is $\varphi(x)$ also periodic in x ? What about its density? What is the major difference, in terms of orbital energy diagram, between a molecule and an extended system?
- b) [3 pts] Is an orbital energy diagram supposed to give, in general, an exact description of the electronic structure? Does it make a difference if this diagram is constructed within Kohn–Sham density-functional theory (KS-DFT)? Why do physicists use the density or the Green function as basic variable, rather than the many-body wave function, when they model the electronic structure of materials?
- c) [4 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 the non-interacting KS system, the gap can be evaluated solely from the HOMO ($\varepsilon_H^{\text{KS}}$) and LUMO ($\varepsilon_L^{\text{KS}}$) energies. Is the band gap of KS-DFT supposed to match the fundamental gap of the true (interacting) material? If not, where does the difference come from?

Exercise: What about a local approximation to the Hartree density functional?

- a) [2 pts] The Hartree (H) energy of an electronic system with density $n(\mathbf{r})$ equals $E_H[n] = \frac{1}{2} \int d\mathbf{r} \int d\mathbf{r}' \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}$. What is its physical meaning? Does the Hartree energy contain any quantum effect?
- b) [3 pts] Let $n_\gamma(\mathbf{r}) = \gamma^3 n(\gamma\mathbf{r})$, where $\gamma > 0$. Prove the exact scaling constraint $E_H[n_\gamma] = \gamma E_H[n]$.
- c) [3 pts] In order to simplify, for a given density n , the evaluation of the Hartree energy, we may consider the following local density approximation (LDA), $E_H^{\text{LDA}}[n] = \int d\mathbf{r} \epsilon_H(n(\mathbf{r}))n(\mathbf{r})$, where the local Hartree energy per electron reads $\epsilon_H(n(\mathbf{r})) = C n^\delta(\mathbf{r})$. We can choose the constant C such that, for example, the functional gives the correct Hartree energy for the helium atom. Which value would you choose for the exponent δ ? Justify your answer in detail.
- d) [2 pts] Explain why $E_H[n]$ is definitely not a local density functional. The good transferability of the LDA introduced in the previous question from the helium atom to other many-electron systems is far from guaranteed, which probably explains why this approximation is never used in practical DFT calculations. Where (in our LDA functional) does this issue of transferability come from?