Advanced Materials Modeling
Homework 2, due date 17.04
Topic: Introduction

Notes: *In multiple choice problems explain your answer. Add references if needed. Upload solution as a single file "YourName.pdf" or "YourName.zip".*

1. Derive the dependence of total energy $E_{\text{tot}}(N)$ of a system on the number of electrons between two integer values.
Hint: Minimize the total energy

$$E_{\text{tot}} = p_N E_N + p_{N+1} E_{N+1} + p_{N-1} E_{N-1} \,,$$

where p_i is the probability of charge state i, with respect to p_i under the following constraints:
condition of convex dependence on *integer N*:

$$E_{N+1} + E_{N-1} > 2E_N \,;$$

the normalization condition

$$p_N + p_{N+1} + p_{N-1} = 1 \,;$$

and the fixed charge constraint

$$p_N N + p_{N+1}(N+1) + p_{N-1}(N-1) = N + \omega \,,$$

where ω is the fractional charge.

2. Prove Janak's theorem:

$$\frac{\partial E[f, n]}{\partial f_i} = \varepsilon_i \,,$$

where $E[f, n]$ is the total energy depending on occupations f and electron density $n(\mathbf{r})$, and ε_i is the energy of the ith Kohn-Sham eigenstate.
Hint:

$$E[f, n] = -\frac{1}{2} \sum_i f_i \langle \psi_i | \nabla^2 | \psi_i \rangle + \int d^3 r \, V_{\text{ext}}(\mathbf{r}) n(\mathbf{r}) + \frac{1}{2} \int d^3 r d^3 r' \frac{n(\mathbf{r}) n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + \int d^3 r \, V_{\text{XC}}(\mathbf{r}) n(\mathbf{r}) \,,$$

$$n(\mathbf{r}) = \sum_i f_i |\psi_i(\mathbf{r})|^2 \,,$$

$$\int d^3 r |\psi_i(\mathbf{r})|^2 = 1 \,,$$

and Kohn-Sham equations:

$$-\frac{1}{2} \nabla^2 \psi_i(\mathbf{r}) + V_{\text{ext}}(\mathbf{r}) \psi_i(\mathbf{r}) + \left(\int d^3 r' \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \right) \psi_i(\mathbf{r}) + V_{\text{XC}}(\mathbf{r}) \psi_i(\mathbf{r}) = \varepsilon_i \psi_i(\mathbf{r}) \,.$$

Also, consider ψ_i and V_{XC} as independent of f_i (PARTIAL derivative with respect to f_i!).

3. Mark all correct statements:
Hartree-Fock method

(A) includes correlation

(B) is exact

(C) is self-interaction free

(D) generally underestimates band gaps

4. Mark all correct statements:
DFT with LDA functional

(A) includes correlation

(B) prefers electron delocalization

(C) is self-interaction free

(D) generally underestimates band gaps

5. Mark all correct statements:
For exact DFT functional

(A) KS gap is equal to observable gap

(B) highest occupied Kohn-Sham state energy does not depend on occupation $0 < f < 1$

(C) the total energy of a system is a non-linear function of particle number between integer occupations