Advanced Materials Modeling
Homework 2

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

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

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:

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

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

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

and Kohn-Sham equations:

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

Also, consider ψ_i and $V_{\rm XC}$ 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