

Advanced Materials Modeling

Homework 2 solution

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.

Solution:

From the equation

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

we obtain:

$$p_{N+1} - p_{N-1} = \omega.$$

Then from equation

$$p_N + p_{N+1} + p_{N-1} = 1$$

we can express p_{N+1} and p_{N-1} via p_N :

$$p_{N-1} = 0.5(1 - p_N - \omega), p_{N+1} = 0.5(1 - p_N + \omega).$$

Substituting this into

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

and rearranging terms we get:

$$E_{\text{tot}} = p_N E_N + (1 - p_N - \omega) \frac{1}{2} (E_{N-1} + E_{N+1}) + \omega E_{N+1}.$$

This now needs to be minimized with respect to p_N . Note that taking the derivative and setting it to zero does not work in this case, because it is a linear problem, and the minimum is at an end point defined by constraints on p_i : $0 \leq p_i \leq 1$. Since

$$E_{N+1} + E_{N-1} > 2E_N$$

(condition of convex dependence on N), and $(1 - p_N - \omega) \geq 0$ (remember the expression of p_{N-1} via p_N and that $p_{N-1} \geq 0$), we obtain that E_{tot} is minimized when

$$p_N = 1 - \omega.$$

This gives the final dependence of E_{tot} on ω :

$$E_{\text{tot}} = (1 - \omega) E_N + \omega E_{N+1}.$$

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 i th Kohn-Sham eigenstate.

Solution:

By taking partial derivative of

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

with respect to f_i (remember that ψ_i and V_{XC} are considered independent of f_i), we obtain:

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

From

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

we obtain:

$$\frac{\partial n(\mathbf{r})}{\partial f_i} = |\psi_i(\mathbf{r})|^2 .$$

With this, the derivative becomes:

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

which can be re-written as:

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

Taking into account the Kohn-Sham equations:

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

and remembering that

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

we arrive at

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

3. Mark all correct statements:

Hartree-Fock method

- (A) includes correlation
- (B) is exact
- (C) is self-interaction free
- (D) generally underestimates band gaps

Solution:

(C)

Hartree-Fock method does not include correlation by definition. It is an approximation, so it is not exact. It is self-interaction free, because exchange term cancels self-interaction term. Hartree-Fock method overestimates 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

Solution:

(A), (B), (D)

LDA functional includes correlation, calculated for a uniform electron gas with the same local density. It prefers delocalization due to self-interaction error. It is not self-interaction free, because the approximate exchange-correlation functional does not cancel self-interaction terms in the Hartree energy. LDA generally underestimates the 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

Solution:

(B)

Due to derivative discontinuity, the KS gap for exact functional is not the same as the observable gap, calculated as the difference between electron affinity and ionization energy. The highest occupied KS state does not depend on occupation for exact functional, because the energy depends linearly on occupation and the derivative of the total energy with respect to occupation is equal to the energy of the highest occupied state (Janak's theorem). The total energy of the system is a linear function of occupation, as proven above.