Technische Universität Berlin
Institut für Theoretische Physik
Lecture Course: Prof. Dr. Matthias Scheffler, Dr. Patrick Rinke, Dr. Alex Tkatchenko
Exercises: Dr. Volker Blum

May 02, 2012

http://www.itp.tu-berlin.de/menue/lehre/lv/ss12/
wahlpflichtveranstaltungen/theoretische_festkoerperphysik_i_ii_theoretical_material_science/

Theoretical Material Science: Exercise Sheet 4

Please hand in solutions by: Wednesday, May 09, start of the exercise class

Exercise 9 (4 points): *Kohn-Sham energy functional and self-consistency*
In Kohn-Sham density-functional theory, the total energy is defined as

$$E[n] = T_s[n] + \int d^3r v(\mathbf{r}) \cdot n(\mathbf{r}) + \frac{1}{2} \int d^3r d^3r' \frac{n(\mathbf{r}) n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + E_{xc}[n] \,. \tag{1}$$

Here, the independent-particle kinetic energy T_s refers to the same orbitals $\{\varphi_k\}$ as the electron density n:

$$n(\mathbf{r}) = \sum_k^N |\varphi_k(\mathbf{r})|^2 \,; \quad T_s[n] = -\sum_k^N \int d^3r \varphi_k^*(\mathbf{r}) \frac{\nabla^2}{2} \varphi_k(\mathbf{r}) \,. \tag{2}$$

a) A self-consistent electron density n is defined as one that solves the same Kohn-Sham Hamiltonian $\hat{h}_{\mathsf{KS}}$ that it defines:

$$\hat{h}_{\mathsf{KS}}[n]\varphi_k(\mathbf{r}) = \left\{ -\frac{\nabla^2}{2} + v(\mathbf{r}) + v_{Ha}[n](\mathbf{r}) + v_{xc}[n](\mathbf{r}) \right\} \varphi_k(\mathbf{r}) = \epsilon_k \varphi_k(\mathbf{r}) \tag{3}$$

Prove that the following equality holds for a self-consistent n:

$$E[n] = \sum_k \epsilon_k - \frac{1}{2} \int d^3r v_{Ha}[n](\mathbf{r}) n(\mathbf{r}) - \int d^3r v_{xc}[n](\mathbf{r}) n(\mathbf{r}) + E_{xc}[n] \tag{4}$$

b) Let an arbitary electron density $n^{(0)}$ define a Kohn-Sham Hamiltonian $\hat{h}_{\mathsf{KS}}[n^{(0)}]$. In general, the resulting density is

$$n^{(1)}(\mathbf{r}) = \sum_{k=1}^N |\varphi_k(\mathbf{r})|^2 \neq n^{(0)}(\mathbf{r}) \,. \tag{5}$$

The Kohn-Sham energy functional of the non-selfconsistent *input* density $n^{(0)}$ is then defined through $E_{\mathsf{KS}}[n^{(0)}] := E[n^{(1)}]$. Show that

$$\begin{aligned} E_{KS}[n^{(0)}] &= \sum_k \epsilon_k - \int d^3r \{ v_{Ha}[n^{(0)}](\mathbf{r}) - \frac{1}{2} v_{Ha}[n^{(1)}](\mathbf{r}) \} n^{(1)}(\mathbf{r}) \\ &- \int d^3r v_{xc}[n^{(0)}](\mathbf{r}) n^{(1)}(\mathbf{r}) + E_{xc}[n^{(1)}] \end{aligned} \tag{6}$$

The preceding expression are the real link between the sum of eigenvalues of the effective single-particle equation of density functional theory, and of the many-electron total energy. Evidently, the two are not equal – the corrections to the sum of eigenvalues are also called "double-counting corrections". As you can see, care must be taken to use consistent definitions when faced with non-selfconsistent densities.

Exercise 10 (4 points): *Hellmann-Feynman-Theorem*
The Hellmann-Feynman theorem states that the "forces" on atoms in the Born-Oppenheimer approximation, i.e. the total energy derivative with respect to atomic positions, are due to pure classical electrostatics. Thus, all explicit quantum mechanical terms vanish exactly, and only the electrostatic interaction between the nuclei (the external potential $v(\mathbf{r})$), and the electron density $n(\mathbf{r})$ survives:

$$\frac{\partial E_\nu[n, \{\mathbf{R}_I\}]}{\partial \mathbf{R}_J} = \int \frac{\partial v(\mathbf{r}, \{\mathbf{R}_I\})}{\partial \mathbf{R}_J} n(\mathbf{r}, \{\mathbf{R}_I\}) d^3\mathbf{r}$$

Starting from density-functional theory, prove that this equation is indeed valid when the electron density $n(\mathbf{r})$ is the fully self consistent result.

Please turn over!⟶

Exercise 11 (4 points): *Ionization potential and symmetry breaking.*
This task is an addition to the computational exercise number 8, for free atoms. As before, the below questions are just a "skeleton" – please refer to the accompanying, more detailed script for more information.

a) In exercise 8, we addressed free atoms with an implicit assumption that their ground state is spherically symmetric. In fact, in Hartree-Fock theory as well as DFT, this is usually not the case. Follow the detailed instructions in the exercise to break the symmetry of the Si atom in Hartree-Fock theory. What does the density look like?

b) A classic measurable property of atoms is the ionization potential, tabulated, e.g., at http://en.wikipedia.org/wiki/Ionization_energy .
For the Si atom, use the total energy difference between the neutral and +1 charged atoms to compute the ionization potential in Hartree-Fock theory. Compare your results to the experimental value, and to the highest occupied single-particle eigenvalues of the neutral Si atom. What do you find? How good is Koopman's theorem? If you had used the symmetric atoms of the previous exercise, how good would the result have been?

- **Webpage of the lecture:**
  http://www.itp.tu-berlin.de/menue/lehre/lv/ss12/
  wahlpflichtveranstaltungen/theoretische_festkoerperphysik_i_ii_theoretical_material_science/
  http://th.fhi-berlin.mpg.de/sitesub/lectures/spring_2012/
- **Lecture:** Tue. & Wed., 10:00 h -12:00 h (sharp!) in room EW 203, TU Berlin
- **Exercise:** Wed., 14:00 h in room EW 229
- **Literature:**
  - Ashcroft, Mermin, David: Solid state physics, Saunders College, Philadelphia, 1981
  - Kittel: Quantum theory of solids, Wiley, New York, 1963
  - Ziman: Principles of the theory of solids, Cambridge University Press, Cambridge, 1964
  - Ibach, Lueth: Solid-state physics: an introduction to principles of materials science, Springer, Berlin, 1995
  - Madelung: Festkörpertheorie, Springer, Berlin, 1972
  - Scherz: Quantenmechanik, Teubner, Stuttgart, 1999
  - Dreizler, Gross: Density functional theory: an approach to the quantum many-body problem, Springer, Berlin, 1990
  - Parr, Yang: Density-functional theory of atoms and molecules, Oxford University Press, Oxford, 1994
  - Anderson: Basic notations of condensed matter physics, Benjamin/Cummings, London, 1984
  - Marder: Condensed matter physics, Wiley, New York, 2000
  - Martin: Electronic Structure, Cambridge University Press, Cambridge, 2004
  - Kohanoff: Electronic Structure Calculations for Solids and Molecules: Theory and Computational Methods, Cambridge University Press, Cambridge, 2006
- **"Übungsschein"-criteria:**
  - Regular and active participation in the exercises
  - Presentation of homework tasks and
  - 50% of the homework points.
  - Active participation in computational exercises
- **Consultation hours:**
  - Prof. Dr. Matthias Scheffler, Dr. Alex Tkatchenko, Dr. Patrick Rinke: by appointment
  - Dr. Volker Blum: Available Wed. 16:00 (after the exercise class) or by appointment