Technische Universität Berlin
Institut für Theoretische Physik
Lecture Course: Prof. Dr. Matthias Scheffler, Dr. Christian Carbogno
Exercises: Dr. Christian Carbogno, Henrik Kowalski et al.

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http://www.itp.tu-berlin.de/menue/lehre/lv/ss_2017/pflichtveranstaltungen_masterstudium/theoretische_physik_vi_vertiefung_theoretische_festkoerperphysik_i_ii/

Theoretical Material Science: Exercise Sheet 4

Please hand in solutions by: Tuesday, May 23, start of the exercise class

The following description is only a skeleton description of the task. A more detailed description of the tasks to be performed is provided separately. The actual task will be performed using a general-purpose electronic structure code, installed in a virtual machine (VM). See http://www.itp.tu-berlin.de/fileadmin/a3233/upload/SS17/TMS/Howto_UsingVirtualMachine.pdf for detailed instructions on how to install/use the VM. We will begin the exercise together during class. Any remaining parts should be done as homework.

Exercise 10 (8 points): *Numerical solution of free atoms, using an electronic structure code*

a) Using a so-called "minimal basis" (only one basis function, valid for hydrogen), perform a self-consistent Hartree-Fock calculation for the Hydrogen atom. What are the single-particle energies and total energies? How close are they to the result that you expect? What could be the origin of the difference?

b) Perform the same calculation, except using the "local-density approximation" of Kohn-Sham density functional theory. What do you obtain? Do the results match your expectations?

c) Repeat tasks a) and b), but this time with "basis sets" of increasing size. What are the eigenvalues and total energies, and at which point do you conclude "convergence"?

d) Plot the electron density of the (converged) free Hydrogen atom in three dimensions and visualize the result.

e) Plot the electron density of the (converged) free Hydrogen atom along the x axis (in one dimension), but integrated on a sphere (for a spherical atom, this means $4\pi r^2 n(r)$). At which distance from the nucleus do you find the major part of the electron density?

f) For the Si atom, compare the eigenvalues, total energy, one-dimensional and three-dimensional density in Hartree-Fock theory, and in the local-density approximation. What is the meaning of the order of the eigenlevels, and which differences for the different levels of theory do you observe? Do the results match your expectations? Can you interpret the shape of the 1d density?

Exercise 11 (4 points): *Ionization potential and symmetry breaking.*

a) In exercise 10, 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?

Please turn over!⟶

Exercise 12 (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:

$$\frac{dE_0[n, \{\mathbf{R}_I\}]}{d\mathbf{R}_J} = \frac{\partial E_0[n, \{\mathbf{R}_I\}]}{\partial \mathbf{R}_J} = \int \frac{\partial v(\mathbf{r}, \{\mathbf{R}_I\})}{\partial \mathbf{R}_J} n(\mathbf{r}, \{\mathbf{R}_I\}) d^3\mathbf{r}$$

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.