

Worksheet 2: Density functional theory and solid state physics

Maofeng Dou, Kartik Jain, and Maria Fyta

Institute for Computational Physics, University of Stuttgart

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General remarks

- Deadline for the report is **Wednesday, 15 May 2019, 13:00**.
- In this worksheet, you can get **a maximum of 23 points**.
- The report should be written as though it would be read by a fellow student who attends the lecture, but does not do the tutorials.
- To hand in your report, send it to your tutor via email: Maofeng Dou (mdou@icp.uni-stuttgart.de).
- For the report, please use the **PDF format** (unfortunately, MS Word doc/docx files are not accepted) and include graphs and images. We recommend using LATEX. A good template for a report is available online.
- The report should be **5–10 pages long**.
- The worksheets are to be solved in **groups of two or three** people.

1 Introduction

In this worksheet, you will first tackle a couple of theoretical tasks concerning density functional theory (DFT). The files required for this tutorial can be found in the archive templates.zip which can be downloaded from the lecture's homepage.

2 Short Questions - short answers (5 points)

Task (5 points)

- Q1: What do the Kohn-Sham equations describe?
- Q2: When is it useful to use DFT compared to Hartree-Fock? Give reasons for your choice.
- Q3: What is the main difference between LDA and GGA density functionals?
- Q4: Why can regular LDA- or GGA-type density functionals not describe long-range van-der-Waals type interactions?
- Q5: Which minimum output frequency is needed to describe a vibrational mode of 3000 cm⁻¹?

3 Local spin-density approximation and Thomas-Fermi energy of hydrogen atom (5 points)

The local spin-density (LSD) approximation introduces a new variable to our density functional, namely the spin density $m(\mathbf{r})$. The spin density is defined as the difference between individual densities for α and β spin as $m(r) = \rho^{\alpha(r)} - \rho^{\beta(r)}$. Introducing spin densities allows for a more complete description of the physics in our systems. It is also necessary to correctly describe systems with unpaired electrons, i.e., radicals like the hydrogen atom. The corresponding kinetic energy is defined as:

$$T_s[\rho^\alpha, \rho^\beta] = \sum_{i\sigma} \int dr \phi_{i\sigma}^*(r) \left(-\frac{1}{2}\nabla^2\right) \phi_{i\sigma}(r), \quad (1)$$

where $\phi_{i\sigma}$ are spatial parts to the spin orbitals $\psi(\mathbf{r}s) = \phi_{i\sigma}(\mathbf{r})\sigma(s)$ and the $\sigma(s)$ are spin eigenfunctions. Here and throughout the text, we use atomic units. We write for convenience $T_s^0[\rho] = T_s[\frac{1}{2}\rho, \frac{1}{2}\rho]$. The superscript 0 indicates completely paired spin densities, i.e., $m(\mathbf{r}) = 0$ everywhere. This kinetic energy is, however, not generally equal to the exact Kohn-Sham kinetic energy $T_s[\rho]$, $T_s[\rho] \neq T_s^0[\rho]$. A specific example is the case of an odd number of electrons. For all of our following calculations, we use the Thomas-Fermi density functional. It is one of the earliest density functional theoretical descriptions available. The Thomas-Fermi kinetic energy density functional T_{TF} for an electron density $\rho(\mathbf{r})$ (without spin) is given by:

$$T_{TF} = C_F \int d\mathbf{r} \rho^{\frac{5}{3}}(\mathbf{r}), \quad (2)$$

with

$$C_F = \frac{3}{10}(3\pi^2)^{\frac{2}{3}}. \quad (3)$$

Task (5 points)

- Derive the general formula for the kinetic energy functional in terms of kinetic energies for the spin-unpolarized case: $T_s[\rho^\alpha, \rho^\beta] = \frac{1}{2}T_s^0[2\rho^\alpha] + \frac{1}{2}T_s^0[2\rho^\beta]$.
- Use the Thomas-Fermi kinetic-energy density functional as an approximation to $T_s^0[\rho^{\alpha/\beta}]$ and calculate the energy of a hydrogen atom with in the local density approximation and the local spin-density approximation. Note that for the 1s ground state of the hydrogen atom $\int \rho_{1s}^{\frac{5}{3}}(\mathbf{r}) d\mathbf{r} = 0.1007$. Compare your value to the exact value for the hydrogen atom.

4 Quantum mechanical calculations using SIESTA (13 points)

We already calculated the properties of molecules using Hartree-Fock approximation in the worksheet 1. In this one, we will calculate the electronic structures of different solid state materials by means of density functional theory using SIESTA.

4.1 Running the simulations

4.1.1 Prepare files for simulation

The files required for simulation include input file (.fdf) and pseudopotential file (.psf). Examples for diamond are provided in the templates.zip archive. You will see input files for diamond (diamond-opt.fdf, diamond-structure.fdf, C-basis.fdf, and C.psf), SIESTA executable (siesta) and post-processing tools (utils). For graphene and graphite, only the structure files are provided, please **adapt** the input files of diamond to that of graphene and graphite yourself.

The main input file (.fdf) contains all the simulations parameters, like atomic coordinates, basis set, functional, k-mesh, cutoff and so on in the flexible data format (fdf). Brief expiation of the input parameters is provided in the .pdf file. Please note:

- fdf labels are case insensitive, and characters - . in a data label are ignored. Thus, LatticeConstant and lattice constant represent the same label.
- All text following the # character is taken as comment.
- Logical values can be specified as T, true, .true., yes, F, false, .false., no. Blank is also equivalent to true.
- The input files allow the inclusion of other fdf files to keep a structured and simple to read fdf file. In the example files, we split the fdf file into diamond-structure.fdf which contains the information about crystal structure, C-basis.fdf which contains information about the basis set and diamond-scf.fdf file which contains the rest for SCF simulation. The diamond-structure.fdf and C-basis.fdf are called through **%include** block in the diamond-scf.fdf file.

For the **diamond-structure.fdf** file, the important parameters are:

- LatticeConstant: this is to define the scale of the lattice vectors.
- LatticeVectors: they are read as a matrix CELL, each vector being one line, e.g. first, second, and third line define the vector of a, b, c of diamond, respectively (diamond is cubic, so a=b=c).
- NumberOfSpecies: number of different atomic species in the simulation (e.g. 1 for diamond).

- `NumberOfAtoms`: number of atoms in the simulation (e.g., 8 for diamond).
- `ChemicalSpeciesLabel`: specifies the different chemical species that are present (e.g. first number 1 is the species number, the second one is the atomic number, and the last one is the desired label).
- `AtomicCoordinatesFormat`: specify the format of the atomic positions in input, in our structure files, all coordinates are in the unit of Å and in cartesian coordinate.
- `AtomicCoordinatesAndAtomicSpecies`: specify the positions and Cartesian coordinate of atoms.

For details of the input and output parameters, please refer to the SIESTA manual. The manual for SIESTA can be found here:

<https://departments.icmab.es/leem/siesta/Documentation/Manuals/siesta-4.0.pdf>

The pseudopotential file for C (`C.psf`) is in the template, you can also download it from the SIESTA website:

<https://departments.icmab.es/leem/siesta/Databases/Pseudopotentials/periodictable-gga-abinit.html>

4.1.2 Run SIESTA

The SIESTA program is installed at directory `/group/allatom/siesta`. For convenient, the SIESTA executable and tools to analyse results are provided in template. Run SIESTA executable by typing:

```
siesta < diamond-scf.fdf > diamond-scf.out
```

Here, `diamond-scf.fdf` and `diamond-scf.out` is the name of the input and output file, respectively. The version is compiled without support for MPI, thus it runs in a single thread only.

4.1.3 Output files

SIESTA generates several output files, the most important ones for our tutorial are:

- `*.out` contains the output information.
- `*.EIG` contains the eigenvalues of the Kohn-Sham Hamiltonian.

- *.DM contains the density matrix to allow a restart.
- *.DOS density of states.
- *.xyz contains coordinates, easy to read by VMD, VESTA or others.
- *.ANI contains the coordinates of every MD step.
- *.bands contains the k point coordinates (in a.u.) and the corresponding band energies (in eV).
- *.RHO valence pseudocharge density at the mesh.

4.1.4 Restart

SIESTA is able to restart from not finished simulations or to calculate some further properties using an existing simulation. Therefore one has to define, in the fdf file, which files it should use, like

```
MD. UseSaveXV true
```

which tells SIESTA to overwrite the atomic coordinates defined in the fdf file with, if present, the coordinates written in the XV file.

4.2 DFT and solid state materials

Solid state materials include metals, semiconductors, ceramics and molecule crystals. How the structures of these materials affect their electrical, mechanical, optical, and magnetic properties, is what solid state researchers seek to understand. In addition, solids at the nanoscale behave differently compared to that in larger dimensions.

Elemental carbon materials take numerous forms including graphite, carbon nanotube, graphene, carbon black, activated carbon, fullerene and diamond. These forms differ greatly in the structure, properties, and fabrication method. The applications of these carbon forms include electronic, electromagnetic, electrochemical, environmental and biomedical applications.

In this section you will choose diamond and graphene as example, learn how to calculate the electronic structures of solid state materials and understand how the crystalline structures and dimensions affect their electronic structures.

Task (6 points)

- Optimize the lattice constant of diamond using PBE functional and compare with the experimental measurement.
- With the optimized lattice constant, calculate and plot the density of state (DOS) of diamond (use the Fermi level as reference in plotting).
- Extract the calculated band-gap energy (E_g) and compared it with the experimental measurement. Explain why PBE functional underestimates the band-gap of diamond (shortly in your own words).

Note:

SIESTA uses a finite 3D grid for the calculation of some integrals and the representation of charge densities and potentials. Its fineness is determined by its plane-wave cutoff (MeshCutoff in diamond-scf.fdf). It means that all periodic plane waves with kinetic energy lower than this cutoff can be represented in the grid without aliasing. In turn, this implies that if a function (e.g. the density or the effective potential) is an expansion of only these plane waves, it can be Fourier transformed back and forth without any approximation.

In addition, unlike the molecules we calculated in worksheet 1, the materials to be calculated in this worksheet are all periodic systems (at least in one dimension). Therefore, integrals in real space over the system are replaced by integrals over the first Brillouin zone in reciprocal space using Bloch's theorem. In SIESTA (and most DFT softwares for solid), such integrals are performed by summing the values of the integrated (e.g., the charge density) at a finite number of points in the Brillouin zone, called the k-point mesh. Therefore, choosing a sufficiently dense mesh of integration points and cutoff energy is crucial for the convergence of the results. **It is recommended to perform convergence test before conducting your simulations for the task, for example:**

- Perform a series of self-consistent calculation (also called static calculation) with different cutoff energy (Meshcutoff in the diamond-scf.fdf), e.g. from 50 to 350 Ry with increments of 50 Ry and converge to total energy to about 0.01 eV/atom.
- With the converged cutoff energy, perform calculations with different k-mesh (%kgrid_Monkhorst_Pack block) and converge to total energy to about 0.01 eV/atom.

Hits:

- There are different ways to optimize the lattice constant, we recommend use the equation-of-state approach. To do so, you need to perform a series of calculations at different volumes for a crystal (diamond is a cubic crystal, so you can simply change the lattice constant a within the range of $\pm 5\%$). Thereafter, fit the energy-vs-volume curves with either polynomial of various degree or other types of equation of state to obtain the corresponding equilibrium volume and lattice constant.
- For DOS, generally a finer grid of k-mesh is required, it is therefore more efficient to restart from a SCF calculation, for details, please see page 75 on the manual of SIESTA.

Task (7 points)

- Calculate the binding energy of bilayer-graphene (assume AB stacking) and graphite using PBE functional and compare the differences.
- Repeat the task of binding energy calculation with van der Waals functional and explain the differences of the results from PBE and vdW functional.
- Calculate the DOS of graphene, bilayer-graphene, and graphite using vdW functional and explain the difference (shortly in your words).

Notes:

- Since you already learned how to perform convergence test in the previous task, in this task, the lattice constants and atom positions of graphene and graphite in the graphene.xyz and graphite.xyz are already optimized for you. You do not need to optimize them any more.
- For graphene and bilayer-graphene, the cell size in the direction perpendicular to graphene surface should be large enough to avoid the influences of periodic images.