Worksheet 1: Calculate solid crystalline materials using density functional theory

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General remarks

- The tutorial will be given online on the channel: https://unistuttgart.webex.com/meet/maofeng.dou.
- Deadline for the report is Wednesday, 05 May 2020, 13:00.
- In this worksheet, you can get a maximum of 20 points.
- The report should be written as though it would be read by a fellow student who attends the lecture, but is not attending the tutorials.
- In order to hand in your report, send it to your tutor via email: Maofeng Dou (mdou@icp.uni-stuttgart.de).
- For the report, please use a **PDF format** (MS Word doc/docx files will not be accepted) and include graphs and images. We recommend using Lagrant A good template for a report is available online.
- The report should be 4–10 pages long.
- The worksheets are to be solved in **groups of two** people.

1 Introduction

In this tutorial you will calculate fundamental properties of diamond using different exchange correlation functionals. All simulations will be performed with the software package CP2K. CP2K uses the Born-Oppenheimer approximation for structure relaxation and Molecular Dynamics. The files required for this tutorial can be found in the folder named **examples**, which can be downloaded from the ILIAS link for the tutorials (https://ilias3.uni-stuttgart.de/goto_Uni_Stuttgart_crs_1877791.html).

2 Short Questions - short answers (8 points)

Task (8 points)

- Q1: When is it useful to use DFT compared to Hartree-Fock? Give reasons for your choice.
- Q2: Briefly describe the Kohn-Sham equations in your own words.
- Q3: What is the main difference between the LDA and GGA exchange correlation functionals?
- Q4: Why can regular LDA- or GGA-type exchange correlation functionals not describe long-range van-der-Waals type interactions?
- Q5: What is the self-interaction error? (describe in your own words).

3 Quantum mechanical calculations using CP2K (12 points)

In this task, you will calculate the electronic structures of different solid state materials using the density functional theory as implemented CP2K.

3.1 Access to the program

The CP2K program (named cp2k.sopt) is installed at directory: /group/allatom/cp2k/cp2k-5.1/exe/icp2.

You can copy the cp2k.sopt file to your account (e.g., your_home_dir/bin/), and execute it by typing:

cp2k.sopt -i input.inp -o output.out

Remember to add **export PATH=\$HOME/bin:\$PATH** in your bashre file if does not work.

Alternatively, you can install CP2K, which can be download from https://www.cp2k.org/download, in your local computer.

3.2 Prepare input files

The basic files required for simulation include input file (.inp), basis-set file (BASIS_MOLOPT) and the pseudopotential file (GTH_POTENTIALS). An example provided includes:

- the basis set and potential: BASIS_MOLOPT and GTH_POTENTIALS.
- an input example: diamond.inp.
- the diamond crystal structure file: diamond_fd3m.xyz

For details of the input and output parameters, please refer to the CP2K manual: https://manual.cp2k.org/#gsc.tab=0. Note: please choose the version 5.1

3.3 Solid state materials

Solid state materials include metals, semiconductors, ceramics and molecular 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. Carbon materials can assume numerous crystalline allotropes including graphite, carbon nanotube, graphene, carbon black, activated carbon, fullerenes, and diamond. These forms differ greatly in the structure, properties, and fabrication methods. Applications of these carbon allotropes include electronic, electromagnetic, electrochemical, environmental, and biomedical applications. In this section you will model diamond. The goal is to learn how to calculate the electronic structures of solid state materials and understand how the crystalline structures affect their electronic properties.

3.3.1 Converge the cut-off energy

CP2K requires the use of a real-space integration grid to represent the electron density. It uses a multi-grid system for mapping the product Gaussians

```
PROJECT NAME diamond cutoff
  RUN TYPE ENERGY
&END GLOBAL
&FORCE EVAL
 METHOD QS
 STRESS TENSOR NONE
      POTENTIAL_FILE_NAME GTH_POTENTIALS
     BASIS SET FILE NAME BASIS MOLOPT
     &QS
        EPS DEFAULT 1e-10
        EXTRAPOLATION ASPC
        METHOD GPW
     &END QS
     &MGRID
        NGRIDS 4
        CUTOFF LT cutoff
        REL CUTOFF 60
     &END MGRID
     &SCF
          EPS SCF 1E-6
              SCF GUESS ATOMIC
          # SCF GUESS RESTART
         MAX SCF 1
```

Figure 1: Examples for the RUN_TYPE and SCF for cut-off convergence test.

onto the real-space grid(s), so that wide and smooth Gaussian functions are mapped onto a coarser grid than narrow and sharp Gaussians. The electron density is always mapped onto the finest grid. In this section, you will learn how to find the correct settings for obtaining a sufficiently fine integration grid.

We are only interested in the convergence of the integration grid, just looking at the total energy (not the forces) usually suffices. Therefore, set the keyword RUN_TYPE in the &GLOABLE section (Figure 1) to ENERGY, which means only the energies (not forces) of the system are calculated. In addition, set the keyword MAX_SCF in the &SCF section (under &DFT section) to 1 to perform a non self-consistent calculation (Figure 1). This is fine for quickly checking the convergence of the integration grid parameters. Once the calculation is done, the total energy will be printed in the output file. An example of the total energy is shown in Figure 2.

```
eps taylor
                   0.10000E-15
                                                max taylor
                                                                              4
        Update method
                            Time
                                    Convergence
                                                        Total energy
   1 OT DITS
                 0.15F+00 68.4
                                     0.00702751
                                                      -44.7816640147 -1.22E-02
Leaving inner SCF loop after reaching
                                          1 steps.
Electronic density on regular grids:
                                            -31.9999737850
                                                                  0.0000262150
                                                                  -0.0000000028
Core density on regular grids:
                                             31.9999999972
                                              0.0000262122
Total charge density on r-space grids:
Total charge density g-space grids:
                                              0.0000262122
                                                              0.00000008767680
Overlap energy of the core charge distribution:
Self energy of the core charge distribution:
                                                            -106.68006341412169
Core Hamiltonian energy:
                                                              35.01860657106064
Hartree energy:
                                                              41.22301728607503
Exchange-correlation energy:
                                                             -14.34322454534976
Total energy:
                                                             -44.78166401465897
outer SCF iter = 51 RMS gradient = 0.70E-02 energy =
                                                                 -44.7816640147
outer SCF loop FAILED to converge after
                                          51 iterations or
                                                             51 steps
```

Figure 2: Examples for total energy for cut-off convergence test.

Task (2 points)

• Perform a series of non self-consistent calculations with different cutoff energies (CUTOFF under &MGRID section in diamond.inp), e.g. from 50 to 500 Ry with increments of 50 Ry and plot the total energies versus cutoff energies. Choose a cutoff energy you think is reasonable for productive calculation (e.g., with acceptable accuracy and efficiency).

Notes:

- During the simulation, files with *.RESTART.wfn* will be generated. If the simulation crashes and you want restart your calculation, simply change the SCF_GUESS to RESTART (see Figure 1) and resubmit the calculation. CP2K will read the existing wave function file and restart the calculations.
- For your convenience, an example bash script named **gen_cutoff_input.sh** is provided. This will generate the directories with different cut-off energies and copy the required input files (e.g., .xyz, .inp, basis set and potential files) to these directories. Once these directories are generated,

you can run the **run_cutoff_test.sh** script to submit the calculations. (Note: you can write your script or do them manually).

• Scripts for collecting the calculated total energies and checking the convergence are not provided. It is recommended to collect them manually at least for the first task, in order to get familiar with the output results. (Note: you can write your script if your really prefer to do it automatically).

3.3.2 Lattice constant optimization

In this part, you will learn how to optimize a crystal structure. An explicit example is given for diamond. There are different ways to optimize the lattice constants in CP2K. The simplest way is to set RUN_TYPE to CELL_OPT in the .inp file. The best (more accurate) way is to use the equation-of-state approach. In this tutorial, you will use the second approach. Set up and execute a series of calculations for different volumes of crystals. Since diamond is in a cubic lattice (space group: $\mathrm{Fd\bar{3}m}$), you can change the volume by modifying the lattice constant a in the .inp file. Fit the energy-vs-volume curves with either polynomials of different orders or other types of equation-of-states to obtain the corresponding equilibrium volume and lattice constant.

Task (8 points)

- Using the optimized cut-off energy in task 1, calculate the total energies of diamond with different values of lattice constants a (choose at least 5 different a values). Plot the calculated total energies versus volume.
- Fit the energy-vs-volume curve with either polynomials of different orders or other types of equation-of-state to obtain the corresponding equilibrium volume and lattice constant (minimum energy and equilibrium volume).
- Repeat the lattice constant optimization with the LDA functional and to obtain the corresponding equilibrium lattice constant.
- Optimize the geometry of diamond with the equilibrium lattice constant obtained above, plot the crystal structures.
- Compare the lattice constant calculated from LDA and PBE with the experimental measurements and explain why LDA and PBE underestimate/overestimate the lattice constant.

Notes:

- You can prepare the input file for lattice optimization by modifying the example .inp file in the first task. Remember to change the RUN_TYPE to GEO_OPT and comment out MAX_SCF=1.
- The visual analysis of the plots is very important. You should always check them at each step. In particular, if the minimum lies outside the displayed region, the calculation should be restarted with more appropriate values of the initial parameter lattice constants a. The optimal situation is when the minimum of the energy curves is located in the middle of the investigated region. It is recommended to change the values of a within the range of $\pm 1.5\%$ of the equilibrium one.
- If the difference in energy between the calculated points and the fit is larger than the final required accuracy in the energy, the calculation should be restarted with more appropriate computational parameters.

3.3.3 Electronic structures calculation

In the following, the projected density of states (PDOS) is taken as a representative quantity for the electronic properties. Now I guess you already get familiar with the input files of CP2K and therefore you are asked to prepare the input file yourself. The input file can be prepared through modifying the input file of geometry optimization in the previous task. Part of the key parameters for DOS calculation is provided in DOS.inc. You can paste them to the .inp file and modify them when necessary.

Task (2 points)

• With the optimized lattice constant, calculate and plot the projected density of state (PDOS) of diamond, e.g., C-s and C-p orbitals.

Notes:

- Remember to change the RUN_TYPE otherwise you will optimize the geometry again.
- In principle, larger number of k-points should be used for DOS, but that will be time-consuming to run on a desktop. We therefore choose a relative small k-points sampling. Considering the special situation in this year, if some of you have really poor internet connection to the ICP, it is acceptable to use only Γ-point for DOS. But you should be aware the k-points sampling issues.