Report for Worksheet 1: Calculate solid crystalline materials using density functional theory

Markus Baur and David Beyer

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Contents

1 Short Questions –Short Answers

- **A1**:

- **A2**: Because the energy density functional of a given system is minimized by the electron density of the ground state (Hohenberg-Kohn theorem II), we can also obtain the ground state energy by describing a given system as a system of non-interacting particles in an effective potential with the same electron density. The one-particle differential equations for these ficitious particles are obtained by minimizing the energy functional and are known as Kohn-Sham equations. The Kohn-Sham equations have the form of one-particle Schrödinger equations with the difference that the effective potential depends on the electron density. The effective potential appearing in the Kohn-Sham equations contains the external potential, electron repulsion and a term accounting for the exchange correlation.

- **A3**: LDA stands for local density approximation. In the LDA, the exchange-correlation energy is a local functional of the electron density $n(\mathbf{r})$, this means that it only depends on the value at each point separately. We can thus write it as an integral which contains no derivatives of the density. GGA stands for generalized gradient approximation, as the name suggest, the energy functional not only depends on the electron density but also on its derivatives. This means that in contrast to LDA the exchange-correlation energy for GGA is not a local, but a semilocal functional of the electron density.

- **A4**: The van-der-Waals interaction is effectively caused by longe-range correlations of the electrons. Because LDA and GGA are (semi-)local approximations to the exchange correlation energy functional, they cannot account for this non-local effect.

- **A5**: Because we don't know the exact exchange correlation energy functional, we have to use approximations like LDA or GGA. These (semi-)local approximations cause the so-called self-interaction error: the effective potential appearing in the Kohn-Sham equations

depends on electron density, this means that every fictious electron will also interact with itself through its own density.

2 Quantum Mechanical Calculations using CP2K

The following section deals with DFT-calculations for diamond.

2.1 Converging the Cutoff Energy

In order to find an appropriate cutoff energy, we ran calculations with different values of the cutoff energy (between 50 and 450 Rydberg). REL_CUTOFF was set to 60 Rydberg. Figure 1 shows the computed total energies as a function of the cutoff energy. We can clearly see that the total energy sharply decreases when the cutoff energy is increased from 50 Ry to 100 Ry. However, a further increase in the cutoff energy does not change much. Because of this, we used a cutoff energy of 100 Ry in the following simulations.
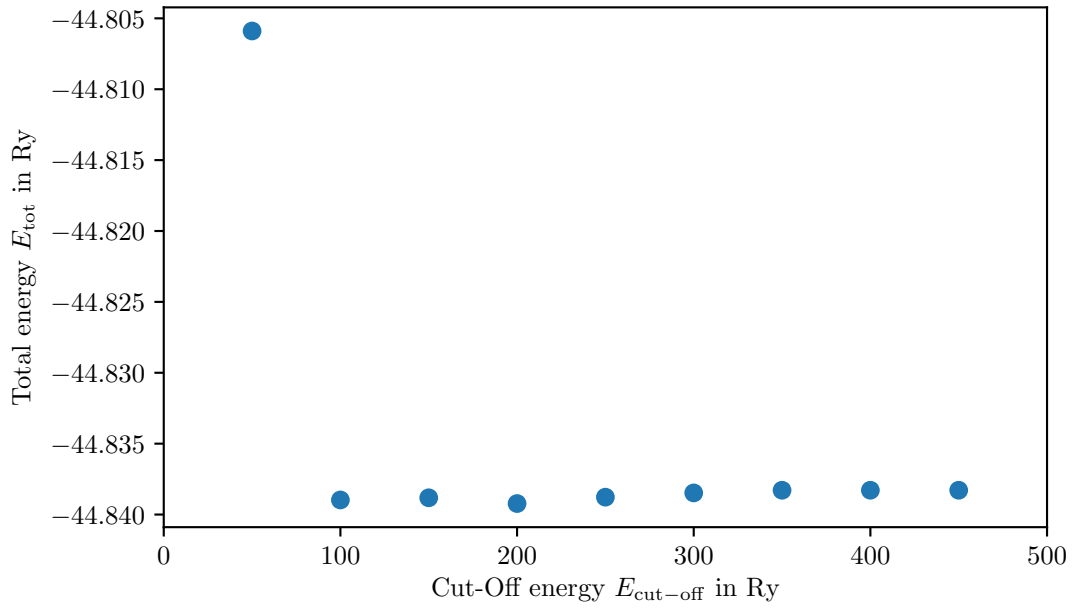

Figure 1: Plot of the calculated total energy for different cutoff energies.

2.2 Optimzing the Lattice Constant

To optimize the crystal structure, we ran calculations with the RUN_TYPE GEO_OPT and different values of the lattice constant. We could then determine the equilibirium lattice constant using a fit.

2.2.1 PBE Functional

Figure 2 shows the calculated total energy as a function of the volume $V = a^3$ of the unit cell. It is easy to see that there is a minimum. In order to determine the corresponding equilibrium volume, we fitted the quadratic function

$$f(V) = a + b \cdot (V - V_{\text{eq}})^2 \tag{1}$$

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to the calculated values, this is also shown in the plot. The obtained fit parameters are

$$a = -44.9809763 \, \text{Ry} \tag{2}$$

$$b = 7.72048911 \cdot 10^{-4} \, \frac{\text{Ry}}{\text{Å}^6} \tag{3}$$

$$V_{\text{eq}} = 50.7015415 \, \text{Å}^3. \tag{4}$$

The equilibrium lattice constant can be calculated from V_{eq} and is given by

$$a_{\text{eq}} = \sqrt[3]{V_{\text{eq}}} \approx 3.70 \, \text{Å}. \tag{5}$$

This value is about 3% larger than the experimental value of $a_{\text{eq,exp.}} \approx 3.57 \, \text{Å}$[1], which means that PBE overestimates the lattice constant. PBE is a GGA functional which is known to overestimate lattice constants.

Figure 3 shows a visualization of the primitive unit cell of diamond which was created using the software VMD (Visual Molecular Dynamics). The structure was taken from the simulation with the equilibrium lattice constant determined above.
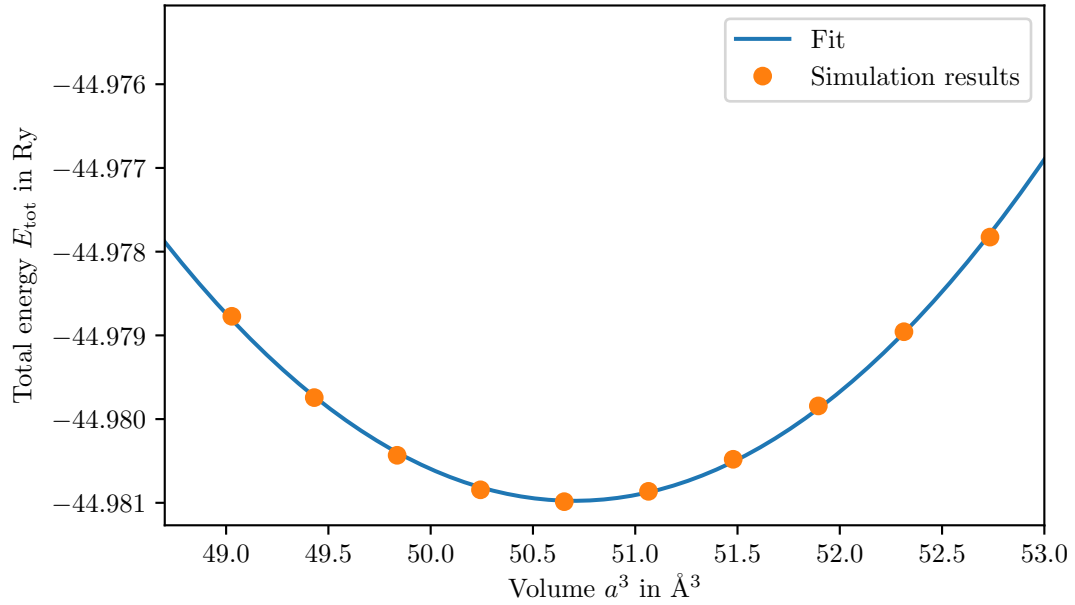

Figure 2: Plot of the calculated total energy (using the PBE functional) as a function of the volume of the unit cell. The fit-function which is also shown is a parabola which was fitted to the obtained values in order to determine the equilibrium lattice constant.

2.2.2 LDA Functional

In order to use the LDA functional we have to change the input at two places /the exchange correlation functional and the potential):

```
&XC
    &XC_FUNCTIONAL LDA
    &END XC_FUNCTIONAL
&END XC
```

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[1]http://lampx.tugraz.at/ hadley/ss1/crystalstructure/structures/diamond/diamond.php, accessed on April 30, 2020 at 22:00
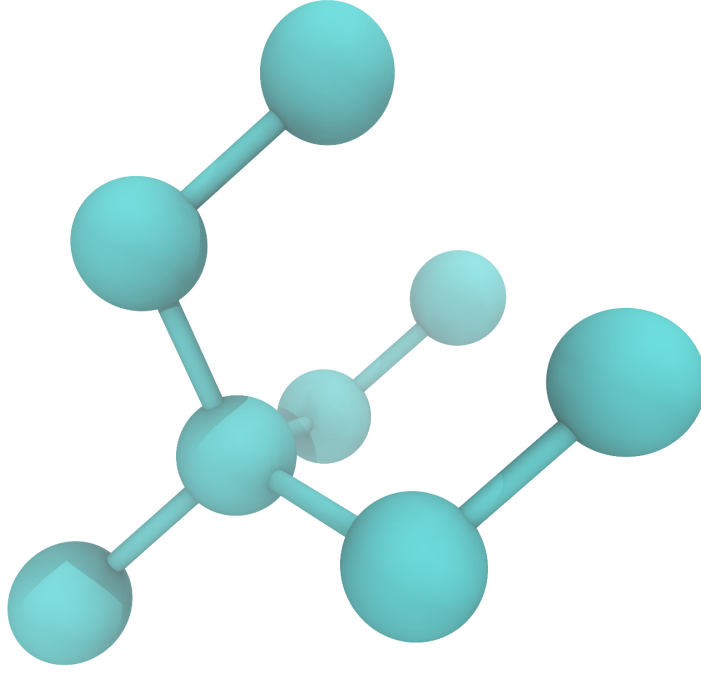
Figure 3: Visualization of the crystal structure of diamond. The shown selection corresponds to the primite unit cell.

```
&KIND C
    POTENTIAL GTH-PADE-q4
    BASIS_SET DZVP-MOLOPT-SR-GTH
&END KIND
```

Figure 4 shows the calculated total energy as a function of the volume $V = a^3$ of the unit cell. It is easy to see that there is a minimum. In order to determine the corresponding equilibrium volume, we fitted the quadratic function

$$f(V) = a + b \cdot (V - V_{\mathrm{eq}})^2 \tag{6}$$

to the calculated values, this is also shown in the plot. The obtained fit parameters are

$$a = -45.1151414 \, \mathrm{Ry} \tag{7}$$

$$b = 1.01386118 \cdot 10^{-3} \, \frac{\mathrm{Ry}}{\mathrm{Å}^6} \tag{8}$$

$$V_{\mathrm{eq}} = 48.4645445 \, \mathrm{Å}^3. \tag{9}$$

The equilibrium lattice constant can be calculated from V_{eq} and is given by

$$a_{\mathrm{eq}} = \sqrt[3]{V_{\mathrm{eq}}} \approx 3.65 \, \mathrm{Å}. \tag{10}$$

This value is about 2% larger than the experimental value of $a_{\mathrm{eq,exp.}} \approx 3.57 \, \mathrm{Å}$[2] but smaller than the value which was obtained using PBE. This is rather unexpected since LDA methods normally tend to underestimate lattice constants.

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[2]http://lampx.tugraz.at/ hadley/ss1/crystalstructure/structures/diamond/diamond.php, accessed on April 30, 2020 at 22:00
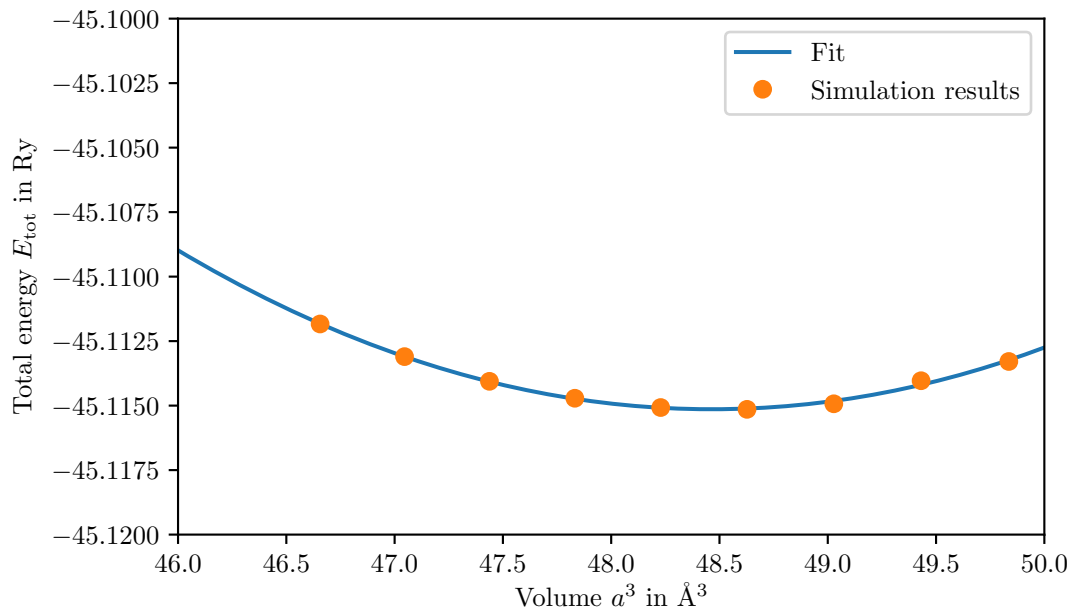
Figure 4: Plot of the calculated total energy (using the LDA functional) as a function of the volume of the unit cell. The fit-function which is also shown is a parabola which was fitted to the obtained values in order to determine the equilibrium lattice constant.

2.3 Electronic Structure Calculation

In order to calculate the projected density of states, we ran a calculation with $4 \times 4 \times 4 = 64$ copies of the unit cell.[3] The calculation was performed using PBE and the equilibrium lattice constant which was determined in the previous exercise. We used the following input file:

```
&GLOBAL
    PROJECT_NAME diamond_PDOS
    RUN_TYPE ENERGY
    PRINT_LEVEL MEDIUM
&END GLOBAL

&FORCE_EVAL
  METHOD QS
  STRESS_TENSOR NONE
  &DFT
      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 100
          REL_CUTOFF 60
      &END MGRID
       &SCF
```

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[3]Similar to the example provided on the website: https://www.cp2k.org/exercises:2017__uzh__cmest:pdos

```
                 ADDED_MOS 50
                 &DIAGONALIZATION
                    ALGORITHM STANDARD
                    EPS_ADAPT 0.01
                 &END DIAGONALIZATION
                 &SMEAR  ON
                    METHOD FERMI_DIRAC
                    ELECTRONIC_TEMPERATURE [K] 300
                 &END SMEAR
                 &MIXING
                    METHOD BROYDEN_MIXING
                    ALPHA 0.2
                    BETA 1.5
                    NBROYDEN 8
                 &END MIXING
            &END SCF
            &XC
                 &XC_FUNCTIONAL PBE
                 &END XC_FUNCTIONAL
            &END XC
            &PRINT
                 &PDOS
                    NLUMO -1
                    FILENAME ./diamond_pdos
                 &END
            &END PRINT
      &END DFT

      &SUBSYS
        &CELL
            A 3.7 0.0000 0.0000
            B 0.00000000 3.7 0.00000
            C 0.00000000 0.000000 3.7
            PERIODIC XYZ
            MULTIPLE_UNIT_CELL 4 4 4
        &END CELL
        &TOPOLOGY
          MULTIPLE_UNIT_CELL 4 4 4
          COORD_FILE_NAME diamond_fd3m.xyz
          COORD_FILE_FORMAT xyz
        &END TOPOLOGY
        &KIND C
            POTENTIAL GTH-PBE
            BASIS_SET DZVP-MOLOPT-SR-GTH
        &END KIND
      &END SUBSYS
&END FORCE_EVAL
```

Figure 5 shows a plot of the obtained PDOS for the carbon orbitals. Figure 6 shows a PDOS which combines the contributions of all orbitals and was smoothed/smeared by convolving it with a Gaussian.[4] The band gap which makes diamond an insulator is clearly visible.

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[4]This was done using two Python scripts which are provided on the CP2K website: https://wiki.wpi.edu/images/images/b/b7/Pdos.txt and https://wiki.wpi.edu/images/images/4/41/Get-smearing-pdos.txt
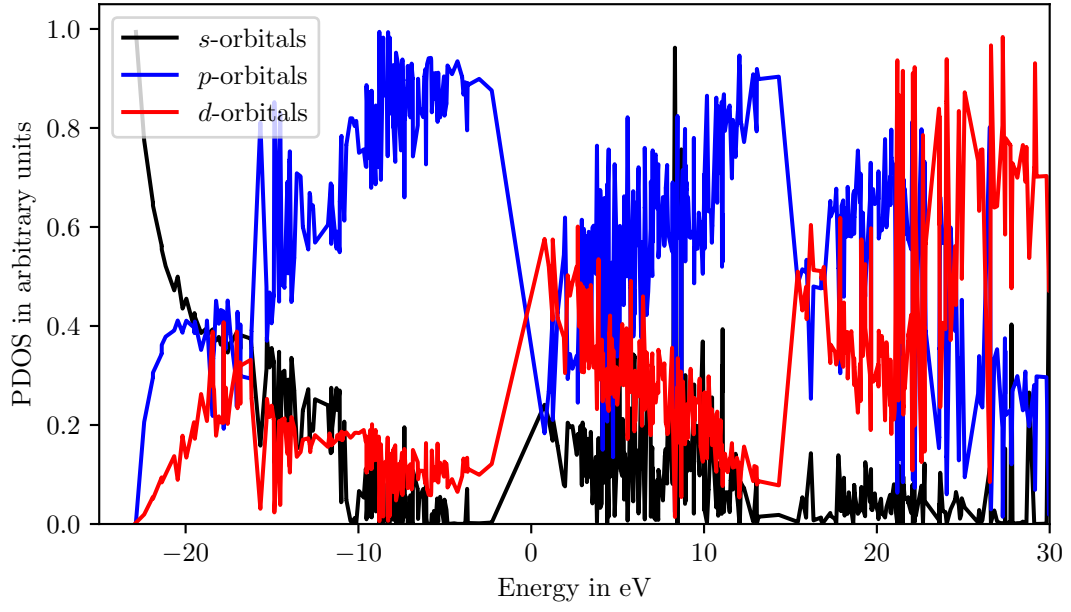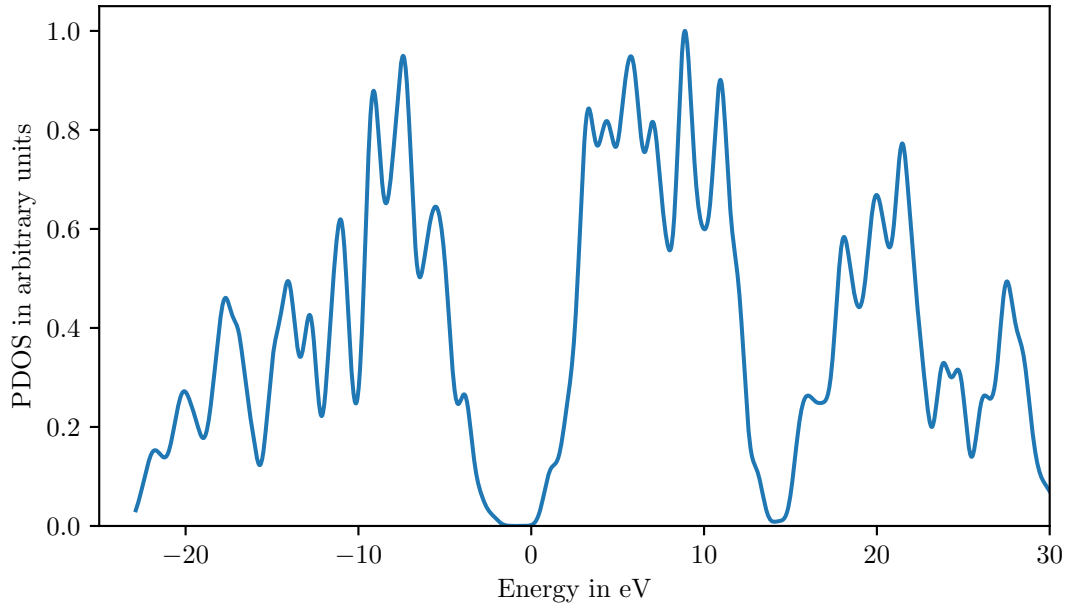
Figure 5: PDOS of diamond.

Figure 6: Combined and smeared PDOS of diamond.