Worksheet 2: Properties of fermions and Density Functional Theory

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Contents

1 Short Questions - Short Answers

Difference between the LDA and GGA approach

LDA is a local approximation of the exchange-correlation functional, which only uses the density . GGA is in a way global, because it uses the gradient of the density as well.

Born-Oppenheimer approximation

From the electrons' point of view the nucleus stand still. Therefore one can neglect the kinetic term of the nucleus in the SE for the electrons.

The nucleus move in the resulting electronic potential.

Simplifications of the Hartree-Fock approach

It's a mean-field approximation.

- Non-correlated, non-interacting electrons (however the fermionic character of electrons is included by the use of the Slater determinant)
- Born-Oppenheimer approximation
- No relativity

Kohn-Sham equation

It is a set of single particle SEs that generates the same density as the SE of interacting particles.

When is it useful to use DFT compared to Hartree-Fock?

DFT is especially useful for huge systems, because the density only depends on the 3 space coordinates. For the tolal wave function of N electrons you would need 3N coordinates, so that more computing time would be needed. Moreover DFT can include correlation of electrons which Hartree-Fock can't do.

2 Theoretical Task: Fermi energy and partition sums

2.1 T1: Grand canonical partition sum for bosons and electrons

Using that $H = \sum_{k=1}^{n} \epsilon_k \hat{n}_k$ and $\sum_{k=1}^{n} \hat{n}_k = N$ it follows:

$$\begin{aligned} Z_{GC} &= Tr(exp(-\beta(H - \mu N))) \\ &= Tr(exp(-\beta \sum_{k=1}^{N} \epsilon_k \hat{n}_k - \mu \sum_{k=1}^{N} \hat{n}_k)) \\ &= Tr(exp(-\beta \sum_{k=1}^{N} (\epsilon_k - \mu) \hat{n}_k)) \\ &= \prod_{k=1}^{N} Tr(exp(-\beta(\epsilon_k - \mu)\hat{n}_k)) \\ &= \prod_{k=1}^{N} \sum_{n_k} exp(-\beta(\epsilon_k - \mu) n_k) \end{aligned}$$

Therefore it follows for Bosons:

$$\begin{aligned} Z_{GC}^{Boson} &= \prod_{k=1}^{N} \sum_{n_k=0}^{\infty} exp(-\beta(\epsilon_k - \mu) n_k) \\ &= \prod_{k=1}^{N} \sum_{n_k=0}^{\infty} exp(-\beta(\epsilon_k - \mu))^{n_k} \\ &= \prod_{k=1}^{N} \frac{1}{1 - exp(-\beta(\epsilon_k - \mu))} \end{aligned}$$

In the last step we have used that Z_{GC} is a geometric series.

For Fermions we make another conjecture, namely that our system of n fermions can be described using n one-fermion-systems. In case of only one fermion being present the product in Z_{GC} runs from 1 to 1 wherefore the only term that remains is:

$$\begin{aligned} Z_{GC}^{1f} &= \sum_{n_k=0}^{1} exp(-\beta(\epsilon_k - \mu) n_k) \\ &= 1 + exp(-\beta(\epsilon_k - \mu) n_k) \end{aligned}$$

Due to our conjecture it follows that

$$Z_{GC}^{Fermion} = \prod_{k=1}^{N} (1 + exp(-\beta(\epsilon_k - \mu) n_k))$$

2.2 T2: Average occupation of a state

$$\begin{aligned}\langle n_i \rangle &= \frac{1}{Z_{GC}} Tr(exp(-\beta(H-\mu N))n_i) \\ &= \frac{1}{Z_{GC}} \sum_{n_1 \dots n_i \dots} \langle \dots, n_i, \dots | exp(-\beta(E-\mu N))n_i | \dots, n_i, \dots \rangle\end{aligned}$$

The trace is calculated using the basis of symmetrisized n-particle states, which allows us to substitute the occurring operators with their eigenvalues. Using that for an interaction free system it is

$$E = \sum_j \epsilon_j n_j$$

it is easy to be seen that:

$$\begin{aligned}\langle n_i \rangle &= \frac{1}{Z_{GC}} \sum_{n_1 \dots n_i \dots} \left\langle \dots, n_i, \dots \left| \frac{\partial exp(-\beta \sum_j n_j(\epsilon_j - \mu))}{\partial(-\beta\epsilon_i)} \right|_{T,V,\mu,\epsilon_i \neq \epsilon_j} \right| \dots, n_i, \dots \right\rangle \\ &= \frac{1}{Z_{GC}} \frac{\partial Z}{\partial(-\beta\epsilon_i)} \Big|_{T,V,\mu,\epsilon_i\epsilon_j} = \frac{\partial}{\partial(-\beta\epsilon_i)} ln(Z_{GC}) \Big|_{T,V,\mu,\epsilon_i\epsilon_j}\end{aligned}$$

Plugging in our Terms Z_{GC}^{Boson} and executing the stated derivative we get:

$$\begin{aligned}\langle n_i^{Boson} \rangle &= -\frac{-exp(-\beta(\epsilon_i - \mu))}{1 - exp(-\beta(\epsilon_i - \mu))} = \frac{1}{exp(\beta(\epsilon_i - \mu)) - 1} \\ \langle n_i^{Fermion} \rangle &= -\frac{exp(-\beta(\epsilon_i - \mu))}{1 + exp(-\beta(\epsilon_i - \mu))} = \frac{1}{exp(\beta(\epsilon_i - \mu)) + 1}\end{aligned}$$

These are the Bose-Einstein resp. Fermi-Dirac statistics .

2.3 T3: Fermi energy

$$\begin{aligned}N &= V \int_0^{\epsilon_F} d\epsilon\, n(\epsilon) \cdot D(\epsilon) \\ &= V \int_0^{\epsilon_F} d\epsilon\, n(\epsilon) \cdot \frac{4\pi}{2} \left(\frac{2m}{h^2}\right)^{3/2} (2s+1)\sqrt{\epsilon}\end{aligned}$$

For $\nu \to \infty$, $\epsilon = \ll \nu \Rightarrow n(\epsilon) = \frac{1}{\exp(\beta(\epsilon-\mu))-1} \to 1$:

$$\begin{aligned}N &= \frac{4V\pi(2s+1)}{2} \left(\frac{2m}{h^2}\right)^{3/2} \int_0^{\epsilon_F} d\epsilon\, \sqrt{\epsilon} \\ &= \frac{4V\pi(2s+1)}{3} \left(\frac{2m \cdot \epsilon_F}{h^2}\right)^{3/2}\end{aligned}$$

Activating the equation towards ϵ_F:

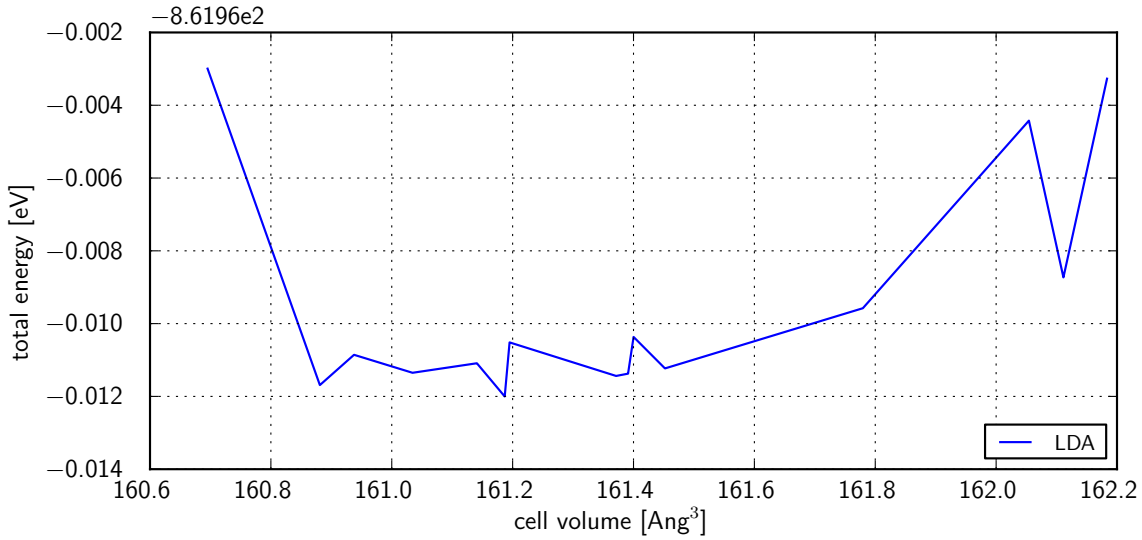
$$\epsilon_F = \left(\frac{3N}{4V\pi(2s+1)}\right)^{2/3} \frac{h^2}{2m} = \frac{\hbar^2}{2m} \left(\frac{6N\pi^2}{2s+1}\right)^{2/3} \tag{1}$$

3 Computational Task: DFT- simulations of silicon

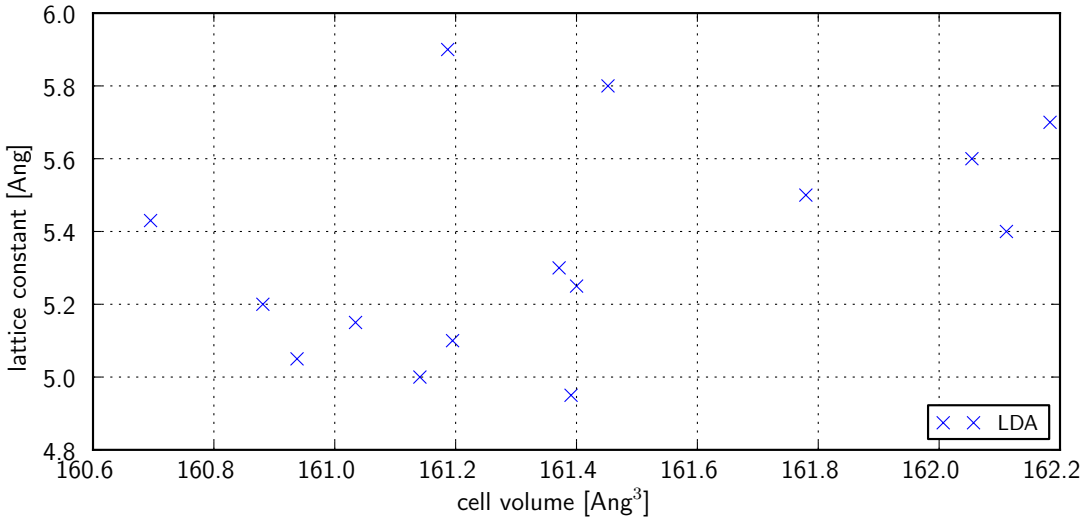
3.1 T1: Energy-Volume curve and lattice constant

For different lattice constants around 5.43 Ang DFT simulations were run. Both total energy and cell volume were taken from the output file and plotted against each other. A second plot shows the dependence between the cell volume and the lattice constant.

3.1.1 LDA



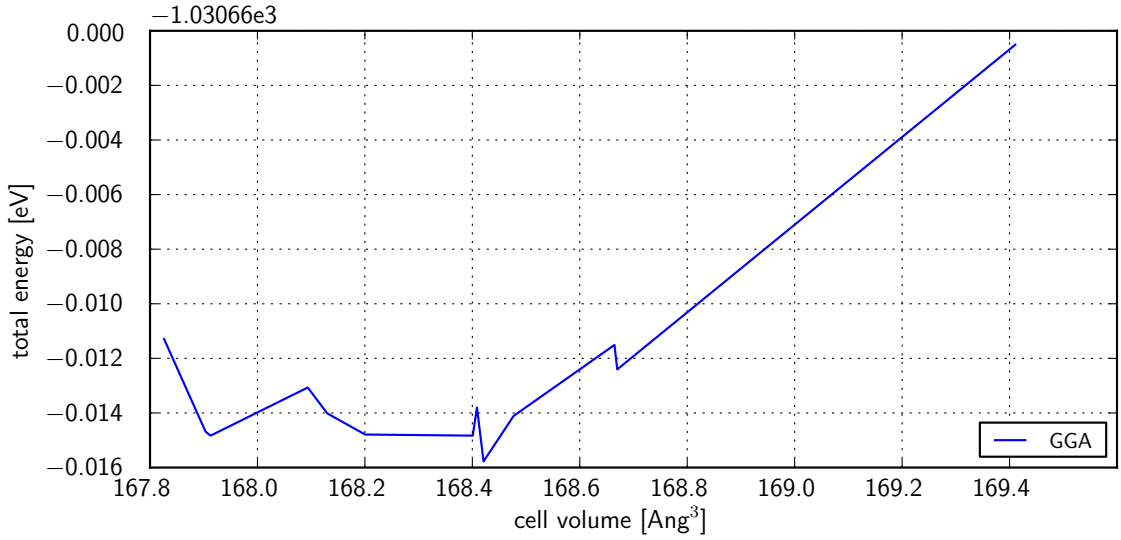
(a) Energy plotted against volume



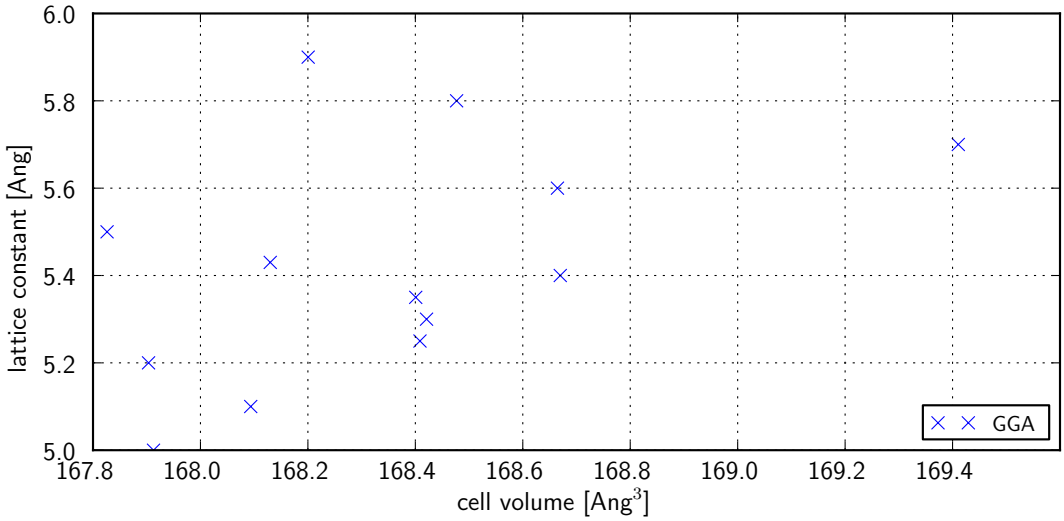
(b) Lattice constant plotted against volume

Figure 1: A lattice constant of around 5.15 Ang corresponds to the lowest total energy. The minima at 5.05 Ang and 5.70 Ang are outlier.

3.1.2 GGA



(a) Energy plotted against volume



(b) Lattice constant plotted against volume

Figure 2: A lattice constant of around 5.30 Ang corresponds to the lowest total energy.

3.1.3 Comparison

The literature value for the lattice constant of silicon is 5.43 Ang. So the errors in the calculation of the lattice constant are as follows:

	value [Ang]	abs. error [Ang]	rel. error [%]
LDA	5.15	0.28	5.1
GGA	5.30	0.13	2.4

3.2 T2: Density of States bulk Silicon

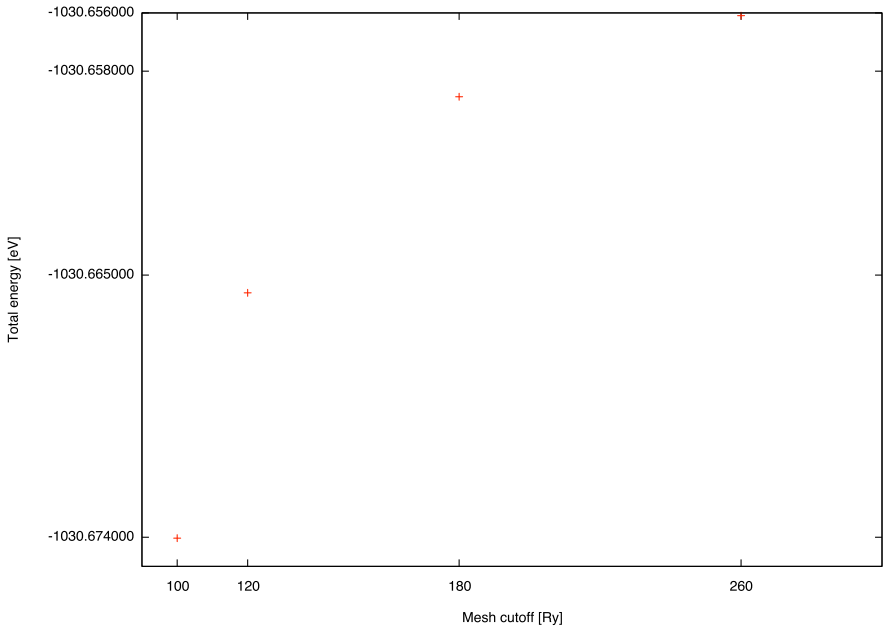


Figure 3: GGA: Total energy depending on the Mesh cutoff

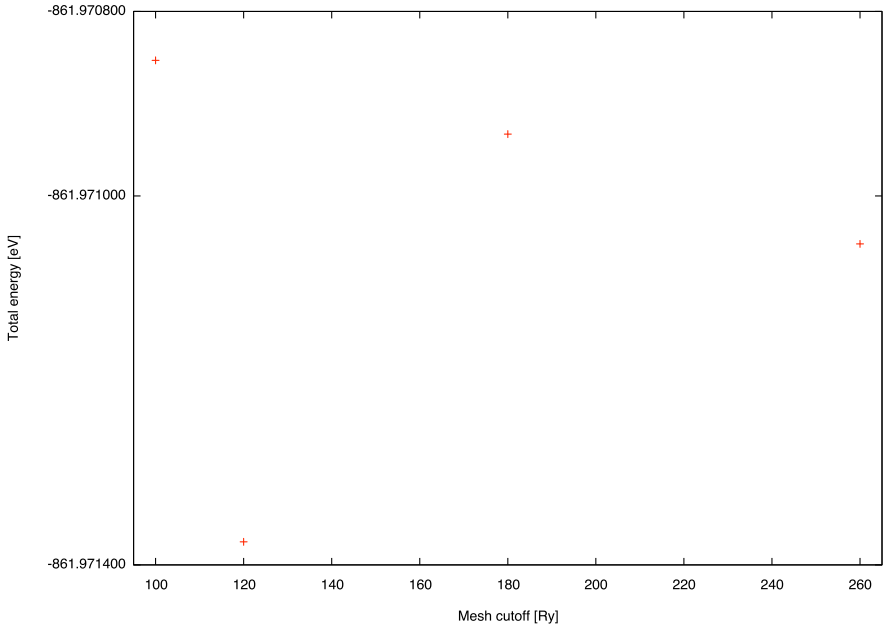


Figure 4: LDA: Total energy depending on the Mesh cutoff

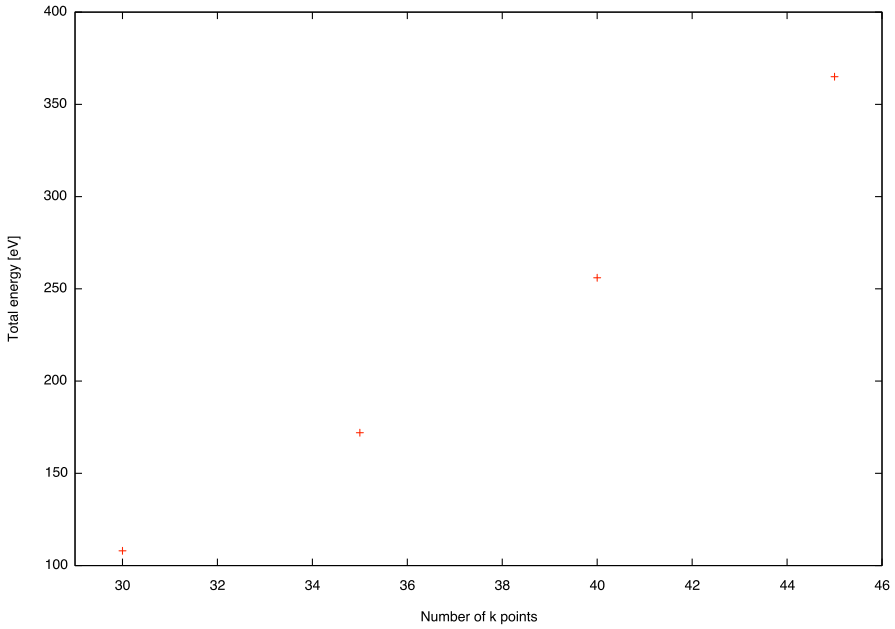


Figure 5: GGA: Total energy depending on the number of k-points

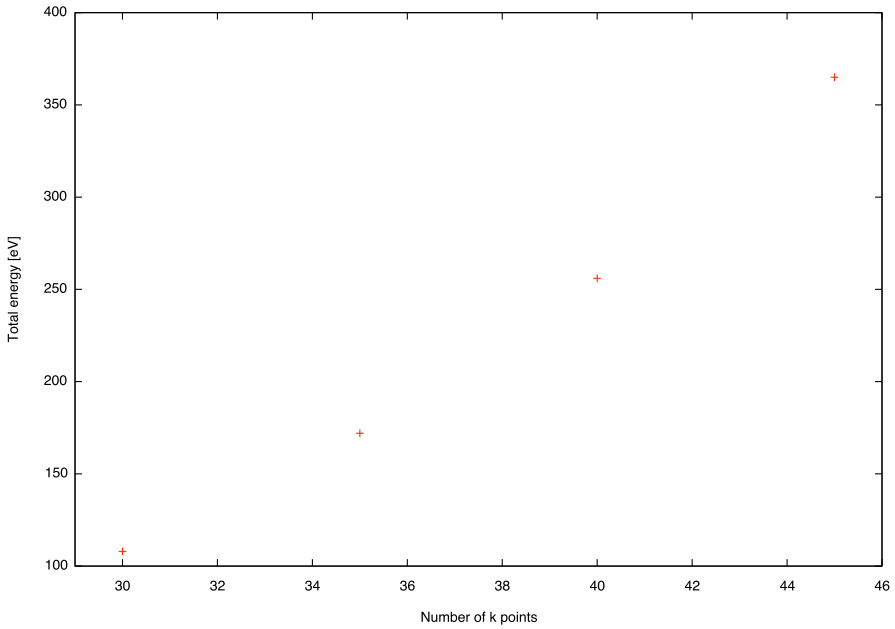
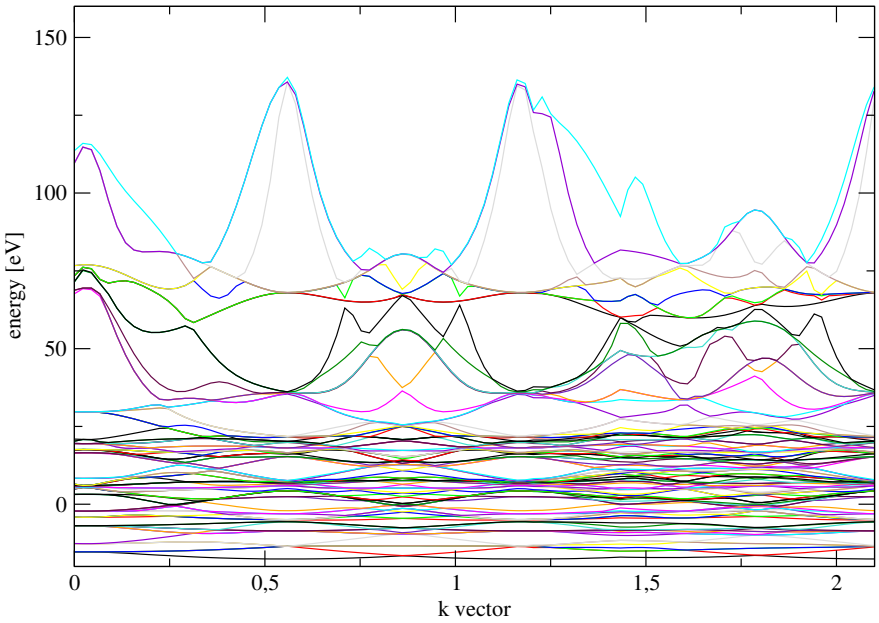


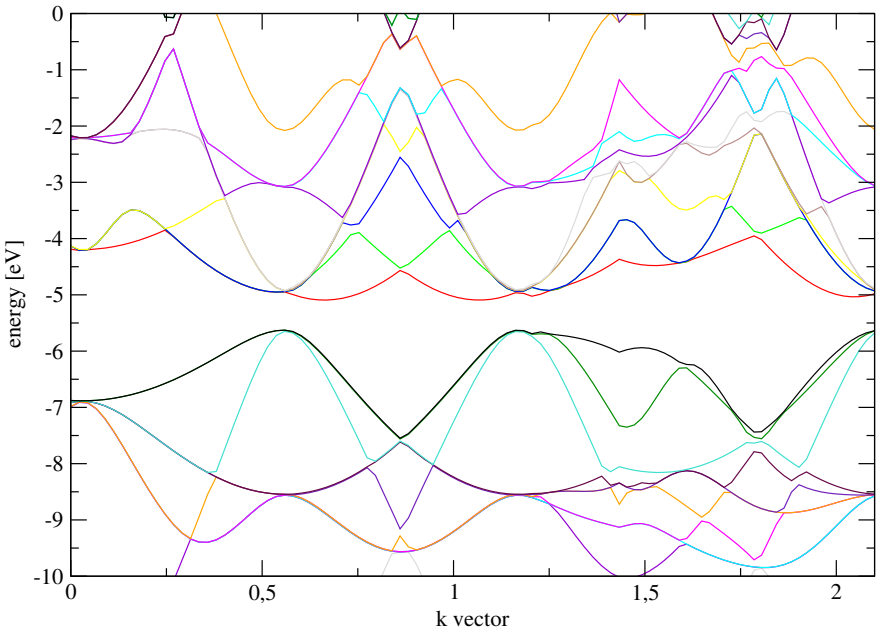
Figure 6: LDA: Total energy depending on the number of k-points

3.3 T3: Band Sructure Analysis of Bulk Silicon

3.3.1 LDA



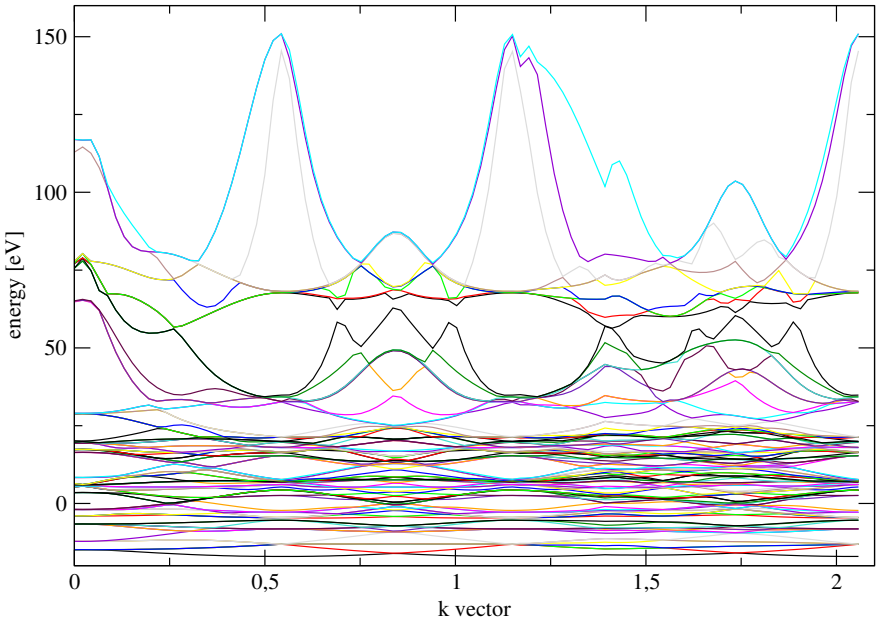
(a) Overview of the band structure



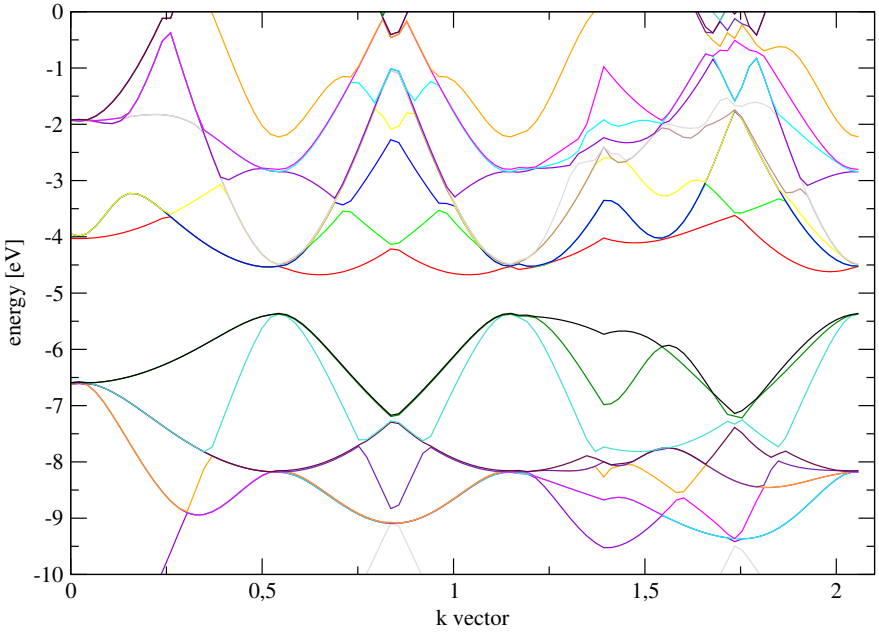
(b) Detailed plot of the band structure around the Fermi energy of $\epsilon_F = -5.338747\,\text{eV}$ (taken from the output file)

Figure 7: Band structure calculated via LDA. A band gap of $\Delta E = 0.61\,\text{eV}$ was determined.

3.3.2 GGA



(a) Overview of the band structure



(b) Detailed plot of the band structure around the Fermi energy of $\epsilon_F = -4.989507\,\text{eV}$ (taken from the output file)

Figure 8: Band structure calculated via GGA. A band gap of $\Delta E = 0.69\,\text{eV}$ was determined.

3.3.3 Comparison

The experimental value for the band gap is $1,1\,\text{eV}$. So both LDA and GGA severely underestimate it. The error for LDA is $45\,\%$ and for GGA $37\,\%$.