Determining elastic constants of graphene using density functional theory

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Contents

Chapter 1

Introduction

Numerical simulations using density functional theory have become a very powerful tool in solid state physics to predict the properties of materials. Its applications range from analyzing the influence of trace impurities in metals to studying the potential phases of hydrogen in the core of gas giants. In this thesis DFT calculations are used to study the elastic behavior of graphene. Graphene is a material that only consists of one plane of carbon atoms arranged in a hexagonal structure, it forms a two dimensional crystal. Graphene has been studied intensively in recent years since it has exceptional electronic properties [1], but it also has extraordinary mechanical properties such as the highest tensile strength ever measured [2]. The aim of this thesis is to determine the elasticity tensor of graphene. The elasticity tensor fully describes the behavior of a material under elastic deformation. For graphene, when only considering in-plane deformations, the elasticity tensor has three independent components. The DFT code used in this thesis was the Vienna ab initio simulation package (VASP) [3][4], which allows two approaches to solve the task at hand. The first is to calculate the total energy of a unit cell as a function of strain, the second is to calculate the stresses acting on the unit cell as a function of strain. These two approaches allow for a consistency check of the results.

Chapter 2

Theory

2.1 Density functional theory

Density functional theory is a method to calculate the ground state energy and the corresponding electron density of a many electron system. DFT rests on two fundamental theorems by Hohenberg and Kohn. These are [5]:

- The ground state energy from Schrödinger's equation is a unique functional of the electron density

- The electron density that minimizes the energy of the overall functional is the true electron density corresponding to the full solution of the Schrödinger equation

The first theorem states that any ground state electron density uniquely corresponds to a ground state energy. The second one states that the electron density that minimizes the energy is the actual ground state electron density, and therefore the minimum of energy also is the actual ground state energy. One important quantity in this theory is the electron density. Since in many electron systems the individual electrons are indistinguishable, it is convenient to only consider the total electron density instead of the wavefunctions of the individual electrons. What makes this formulation so convenient is the fact that the electron density only depends on three coordinates, while the whole set of individual electron wavefunctions of a many electron system with N electrons depends on $3N$ coordinates. Another important quantity used in DFT is the functional that associates the total ground state energy with the ground state electron density. Unfortunately, the exact form of this functional is not known, and therefore only approximations are available. A common way of writing down this functional is splitting

it into two parts, the "known" interactions and the exchange-correlation functional

$$E[n(\vec{r})] = E_{known}[n(\vec{r})] + E_{XC}[n(\vec{r})] \tag{2.1}$$

The "known" part consists of the following terms

$$E_{known}[\psi_i] = -\frac{\hbar^2}{2m}\sum_i \int \psi_i^*\nabla^2\psi_i d^3r + \int V(\vec{r})n(\vec{r})d^3r + \frac{e^2}{2}\int\int\frac{n(\vec{r})n(\vec{r'})}{|\vec{r}-\vec{r'}|}d^3r d^3r' + E_{ion} \tag{2.2}$$

The terms are, in order, kinetic energy of the electrons, Coulomb interaction between electrons and nuclei, Coulomb interaction between pairs of electrons and Coulomb interaction between pairs of nuclei. The exchange-correlation functional shall be discussed later. Another crucial contribution to density functional theory are the so-called Kohn Sham equations. These single particle equations make it possible to calculate the individual electron wavefunctions ψ and subsequently the electron density. The Kohn Sham equation are defined as follows

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + V(\vec{r}) + V_H(\vec{r}) + V_{XC}(\vec{r})\right]\psi_i(\vec{r}) = \epsilon_i\psi_i(\vec{r}) \tag{2.3}$$

At first glance these equations are very similar to single particle time independent Schrödinger's equation. The Hamilton operator consists of the kinetic energy of the electrons, the Coulomb potential of the atomic nuclei, the Hartree potential and the the exchange-correlation contribution. The Kohn-Sham equations yield single particle wavefunctions that can be used to calculate the electron density $n(\vec{r})$

$$n(\vec{r}) = 2\sum_i \psi_i^*(\vec{r})\psi_i(\vec{r}) \tag{2.4}$$

Here the factor 2 is a consequence of the Pauli exclusion principal. The Hartree potential describes the interaction between the individual electron and the total electron density. It is defined as follows

$$V_H(\vec{r}) = e^2\int\frac{n(\vec{r'})}{|\vec{r}-\vec{r'}|}d^3r' \tag{2.5}$$

This potential leads to two important implications. First, this form includes a self-interaction contribution, since the individual electron is also part of the electron density. This is of course unphysical and is usually compensated for in the exchange correlation part. Second, in order to solve these equations in the first place one needs to start off with a trial electron density, the Kohn Sham equations are therefore well suited for iterative calculations. The exchange-correlation contribution is defined as a functional

derivative of the exchange-correlation energy

$$V_{XC}(\vec{r}) = \frac{\delta E_{XC}[n(\vec{r})]}{\delta n(\vec{r})} \qquad (2.6)$$

Now in order to actually solve a many electron problem using DFT the following steps are performed iteratively:

1. Define a trial electron density

2. Solve the Kohn Sham equations for the individual electron wavefunctions using the trial electron density

3. Calculate the new electron density using the individual wave functions

4. If the trial electron density and the calculated one are identical, they are the actual ground state electron density. However, if they are different the trial electron density needs to be updated in some way and the process begins again at step 2.

This process eventually leads to a solution that is self-consistent. In order to actually solve the equations the exchange correlation functional needs to be defined. As mentioned before the exact form of this functional is not known. The only case for which the exact form of the exchange contribution to the functional can be determined analytically is for the uniform electron gas, the correlation energy still needs to be determined numerically. A simple approximation for the general case is to simply use the exchange correlation functional of the uniform electron gas as a functional of the actual electron density.

$$V_{XC}^{LDA}(\vec{r}) = \int n(\vec{r}) e_{XC}^{electrongas}(\vec{r}) d^3 r \qquad (2.7)$$

This functional only depends on the local electron density, hence the name local density approximation or LDA. Another approach to find an approximate form of the exchange correlation functional is to also include the gradient of the electron density and not just the local density. There are many approximations of this type but they are all collectively called generalized gradient approximations or GGA [5].

2.2 Hooke's law

The elastic deformations of solids due to forces acting on them can be described using Hooke's law. The central idea behind this law is that stress is proportional to strain. It generally only applies for cases with small deformations. The range of strain where it applies is generally called the elastic domain. Beyond this domain higher order effects

become dominant and materials that are deformed to this point usually are damaged and obtain permanent deformation that remains even after the stress has been relieved. When studying the behavior of materials under strain it is very important to make sure that one always stays within the domain for which the used theory applies. For Hooke's law this would be the elastic domain. This is particularly important when working with simulations, since there is no obvious sign of leaving the elastic domain like there is with actual experiments, where a sample will attain a permanent deformation or break altogether. The simplest form of Hooke's law is the equation describing an elastic spring with spring constant k

$$F = -k \cdot x \tag{2.8}$$

This equation simply translates the central axiom of Hooke's theory, that strain is proportional to stress, into mathematical form. The general form of Hooke's law describes continuous elastic materials. Here every point in the material can be subject to stretching in one direction, compression in another direction and shearing all at the same time. In order to properly describe this, it is necessary to define stress and strain as tensors of 2nd rank and the elasticity tensor now is of rank four

$$\sigma_{ij} = \sum_k \sum_l \gamma_{ijkl} \epsilon_{kl} \tag{2.9}$$

The elasticity tensor γ has a total of 81 components, but since the strain tensor, the stress tensor and the elasticity tensor itself are all symmetric, at most 21 of those 81 components are independent. Additional symmetries, for example of the crystal structure, further reduce the number of independent components. Note that this is a local theory, meaning that for every point in a material any of these tensors might be different. Therefore describing extended bodies using this equation can prove to be quite a challenge [6].

2.3   Elastic Energy

Every elastic deformation is associated with a change of energy. Energy can be stored in a spring by compressing it and it can be released again by letting the spring expand back to its equilibrium state. Such a system can be described very easily using the simplest form of Hooke's law that was already discussed before

$$F = -k \cdot x \tag{2.10}$$

In order to determine the energy associated with a system like this, one has to integrate the above equation with respect to the deflection x. Doing so gives the following equation

$$E = \frac{1}{2}k \cdot x^2 \qquad (2.11)$$

This equation might be simple but it points out two important properties of the elastic energy. First it is proportional to the elastic constant, second it is proportional to the square of the strain. We will see that these two properties also apply for the more general case. This equation would include lower order terms if a deflection x equal to zero would not correspond to the equilibrium state. For continuous materials the equation describing the elastic energy for a general deformation of a two-dimensional material is as follows

$$E = E_0 + A_0 \sum_i \sum_j \sigma_{ij}\epsilon_{ij} + \frac{A_0}{2} \sum_i \sum_j \epsilon_{ij} \cdot \left(\sum_k \sum_l \gamma_{ijkl}\epsilon_{kl}\right) \qquad (2.12)$$

Here all quantities, stress strain and elasticity are in tensor form and identical to the quantities used in the general case of Hooke's law. Note that unlike in the case of a simple spring here lower order terms are included [6].

2.4 Voigt notation

We have seen that in the most general case of Hooke's law the elastic behavior of a material is described by a rank 4 tensor, which can be quite cumbersome. A simple method to simplify the notation of Hooke's law is the Voigt notation. Here the fact that all tensors are symmetric is used to rewrite the rank 2 tensors as Vectors with six components and the elasticity tensor as six by six matrix. The usual convention to rewrite the tensors is as follows

$$\begin{pmatrix} \sigma_{11} & \sigma_{12} & \sigma_{13} \\ \sigma_{12} & \sigma_{22} & \sigma_{23} \\ \sigma_{13} & \sigma_{23} & \sigma_{33} \end{pmatrix} \rightarrow \begin{pmatrix} \sigma_1 \\ \sigma_2 \\ \sigma_3 \\ \sigma_4 \\ \sigma_5 \\ \sigma_6 \end{pmatrix} := \begin{pmatrix} \sigma_{11} \\ \sigma_{22} \\ \sigma_{33} \\ \sigma_{23} \\ \sigma_{13} \\ \sigma_{12} \end{pmatrix}$$

$$
\begin{pmatrix} \epsilon_{11} & \epsilon_{12} & \epsilon_{13} \\ \epsilon_{12} & \epsilon_{22} & \epsilon_{23} \\ \epsilon_{13} & \epsilon_{23} & \epsilon_{33} \end{pmatrix} \rightarrow \begin{pmatrix} \epsilon_1 \\ \epsilon_2 \\ \epsilon_3 \\ \epsilon_4 \\ \epsilon_5 \\ \epsilon_6 \end{pmatrix} := \begin{pmatrix} \epsilon_{11} \\ \epsilon_{22} \\ \epsilon_{33} \\ 2 * \epsilon_{23} \\ 2 * \epsilon_{13} \\ 2 * \epsilon_{12} \end{pmatrix}
$$

The Voigt notation allows to rewrite Hooke's law in a much more comprehensible manner while still fully describing any system. But there is one drawback with Voigt notation, the new vectors and the elasticity matrix are not tensors anymore. This means that once Voigt notation is applied no coordinate transformation is possible anymore [6].

Chapter 3

Method and Results

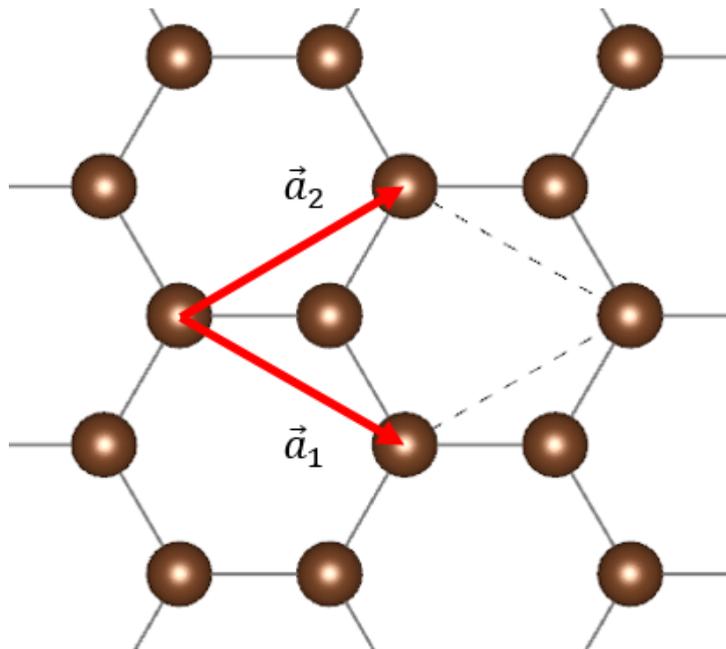## 3.1 Defining elastic constants of graphene

FIGURE 3.1: Structure of graphene, dashed line indicates unit cell

As can be seen in figure 3.1, graphene is a material that forms a two-dimensional layer with a honeycomb like structure. Multiple layers of graphene stacked onto each other form a graphite crystal. In this thesis, only the properties of individual, free standing graphene layers are discussed. The following unit cell vectors describe the structure of

graphene

$$\vec{a}_1 = a \begin{pmatrix} \frac{\sqrt{3}}{2} \\ -\frac{1}{2} \end{pmatrix} \quad \vec{a}_2 = a \begin{pmatrix} \frac{\sqrt{3}}{2} \\ +\frac{1}{2} \end{pmatrix}$$

There are two carbon atoms in the basis at the following fractional coordinates

$$\vec{b}_1 = \begin{pmatrix} 0 \\ 0 \end{pmatrix} \quad \vec{b}_2 = \begin{pmatrix} \frac{1}{3} \\ \frac{1}{3} \end{pmatrix}$$

The lattice constant a was determined by using DFT calculations of the ground state energies for different values of a. The results of these calculations (fig. 3.2) were then fitted to the Birch-Murnaghan equation of state to determine the equilibrium lattice constant.
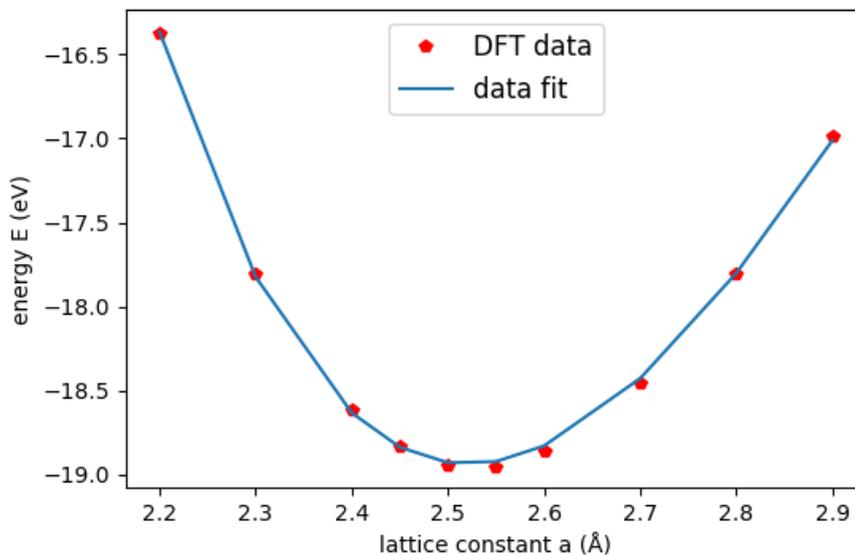

FIGURE 3.2: results of the DFT calculations to determine the lattice constant a

The exchange-correlation functional used in these calculations was the Perdew-Burke-Ernzerhof functional, which is a generalized gradient approximation [7]. GGA functionals are known to yield lattice constants slightly larger then experimental results [8], and indeed the value determined with this method for the lattice constant of graphene is 2.51Å and therefore slightly larger then the experimental result of 2.46Å [9]. For all subsequent calculations $a = 2.51$Å was used.

Since we only consider in plane deformations, the deformation tensor can be described by a symmetric 2×2 matrix.

$$\hat{\delta} = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} + \begin{pmatrix} \epsilon_1 & \epsilon_6 \\ \epsilon_6 & \epsilon_2 \end{pmatrix}$$

Applying Voigt notation then leads to the following form of the strain components ϵ and the elasticity matrix $\hat{\gamma}$

$$\epsilon = \begin{pmatrix} \epsilon_1 \\ \epsilon_2 \\ 2\epsilon_6 \end{pmatrix} \quad \hat{\gamma} = \begin{pmatrix} \gamma_{11} & \gamma_{12} & 0 \\ \gamma_{12} & \gamma_{11} & 0 \\ 0 & 0 & \gamma_{66} \end{pmatrix}$$

Note that because of the symmetries of the hexagonal structure of graphene, some of the components of the elasticity matrix vanish. The three elastic constants γ_{11}, γ_{12} and γ_{66} are the independent components of the elasticity tensor.

To determine the elastic constants, one can apply different, finite but small, deformations and calculate the resulting energy or stress acting on the unit cell. Doing this with multiple magnitudes of strain allows to fit either the equation for total energy or stress with the elastic constants being fit parameters. Since there are three independent elastic constants, at least three different types of deformations are necessary to determine all elastic constants. The three kinds of deformation used here are defined as follows.

Type 1: stretching along x axis

$$\epsilon = \begin{pmatrix} \epsilon_1 \\ \epsilon_2 \\ 2\epsilon_6 \end{pmatrix} \rightarrow \begin{pmatrix} \eta \\ 0 \\ 0 \end{pmatrix}$$

$$\vec{a}_1 = a \begin{pmatrix} \frac{\sqrt{3}}{2} \\ \frac{1}{2} \end{pmatrix} \rightarrow a \begin{pmatrix} \frac{\sqrt{3}}{2}(1+\eta) \\ \frac{1}{2} \end{pmatrix}$$

$$\vec{a}_2 = a \begin{pmatrix} \frac{\sqrt{3}}{2} \\ -\frac{1}{2} \end{pmatrix} \rightarrow a \begin{pmatrix} \frac{\sqrt{3}}{2}(1+\eta) \\ -\frac{1}{2} \end{pmatrix}$$

Type 2: stretching both along x and y axis

$$\epsilon = \begin{pmatrix} \epsilon_1 \\ \epsilon_2 \\ 2\epsilon_6 \end{pmatrix} \rightarrow \begin{pmatrix} \eta \\ \eta \\ 0 \end{pmatrix}$$

$$\vec{a}_1 = a \begin{pmatrix} \frac{\sqrt{3}}{2} \\ \frac{1}{2} \end{pmatrix} \rightarrow a \begin{pmatrix} \frac{\sqrt{3}}{2}(1+\eta) \\ \frac{1}{2}(1+\eta) \end{pmatrix}$$

$$\vec{a}_2 = a \begin{pmatrix} \frac{\sqrt{3}}{2} \\ -\frac{1}{2} \end{pmatrix} \rightarrow a \begin{pmatrix} \frac{\sqrt{3}}{2}(1+\eta) \\ -\frac{1}{2}(1+\eta) \end{pmatrix}$$

Type 3: shearing

$$\epsilon = \begin{pmatrix} \epsilon_1 \\ \epsilon_2 \\ 2*\epsilon_6 \end{pmatrix} \rightarrow \begin{pmatrix} 0 \\ 0 \\ 2*\eta \end{pmatrix}$$

$$\vec{a}_1 = a \begin{pmatrix} \frac{\sqrt{3}}{2} \\ \frac{1}{2} \end{pmatrix} \rightarrow a \begin{pmatrix} \frac{\sqrt{3}}{2} + \frac{\eta}{2} \\ \frac{1}{2} + \frac{\sqrt{3}\eta}{2} \end{pmatrix}$$

$$\vec{a}_2 = a \begin{pmatrix} \frac{\sqrt{3}}{2} \\ -\frac{1}{2} \end{pmatrix} \rightarrow a \begin{pmatrix} \frac{\sqrt{3}}{2} - \frac{\eta}{2} \\ -\frac{1}{2} + \frac{\sqrt{3}\eta}{2} \end{pmatrix}$$

Here η is the magnitude of strain, a dimensionless quantity. Note that these three types are not the only possible choice that would allow to fully define the elastic behavior.

3.2   Method

In order to perform the DFT calculations the VASP program package was used [3][4]. The VASP package allows to calculate the total energy and the stress tensor of any periodic arrangement of atoms. The unit cell vectors and the internal coordinates of the atoms are defined in the POSCAR input file. Further computational parameters are defined in the INCAR, KPOINTS and POTCAR files. Due to the plane wave basis set three dimensional boundary conditions are applied in all three dimensions. In order to treat a two dimensional layer, such as graphene, a large enough vacuum gap is inserted in the z-direction such that the interaction between the individual layers is negligible. The exchange-correlation functional used for the DFT calculations was the PBE functional.

For the DFT calculations the unit cell vectors for the deformed unit cells were calculated for all three types. The strain was chosen to be in the range of -0.05 and 0.05 with a step size of 0.01. Therefore 11 unit cells were calculated for each type, resulting in a total of 33 different unit cells that were used in the DFT calculations. These unit cells were supplied to the VASP software in order to calculate the total energies and the stresses that act on the unit cells. The results for total energies and stresses were then evaluated using two different methods. This allows to later judge the final results in terms consistency. The first method based on total energies is described in Sec. 3.3 while the second method using stresses is discussed in Sec. 3.4.

3.3 Total energy

In solids the total energy associated with an elastic deformation can be expressed using equation 2.12. Applying the definitions of the three deformation types discussed before leads to three different forms of this equation

Type 1

$$E(\eta) = E_0 + A_0\sigma_1\eta + \frac{A_0}{2}\gamma_{11}\eta^2$$

Type 2

$$E(\eta) = E_0 + A_0(\sigma_1 + \sigma_2)\eta + A_0(\gamma_{11} + \gamma_{12})\eta^2$$

Type 3

$$E(\eta) = E_0 + 2A_0\sigma_6\eta + 2A_0\gamma_{66}\eta^2$$

Here A_0 is the area of the unit cell without strain, the lattice constant $a = 2.51\text{Å}$ leads to $A_0 = 5.28\text{Å}^2$. In order to determine them the values for total energy as a function of strain gathered through the DFT calculations can simply be fit by equations of the corresponding form. This is a straight forward fit problem for a polynomial function depending only on one variable, the strain. Note that two elastic constants contribute to the leading order term in deformation of type 2. Therefore it is necessary to first calculate the first elastic constant which appears in deformation type one, and then subtract it from the prefactor gathered by fitting the deformation of type 2 in order determine the second elastic constant γ_{12}. The total energies (symbols) as well as the corresponding fits (lines) for the three deformation types are depicted in Figs. 3.3, 3.4 and 3.5, respectively. The resulting fit parameters, i.e., the elastic constants are summarized in Table 3.1.
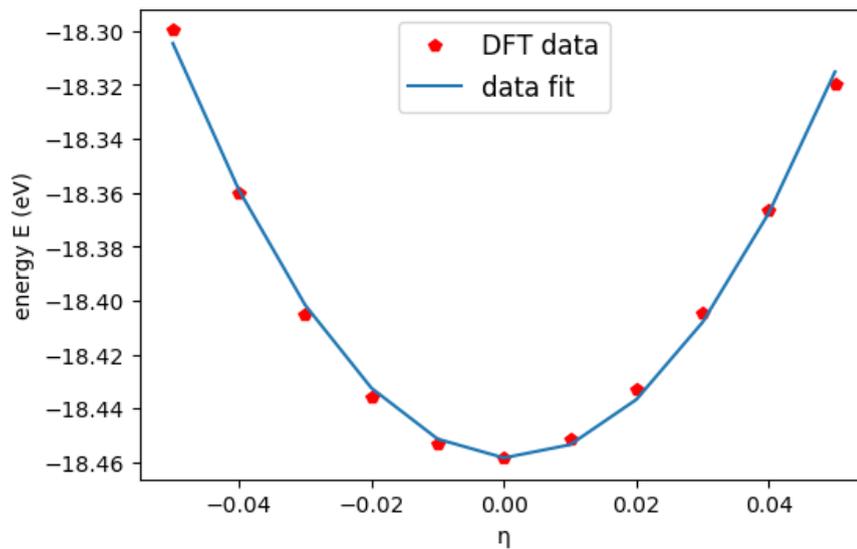
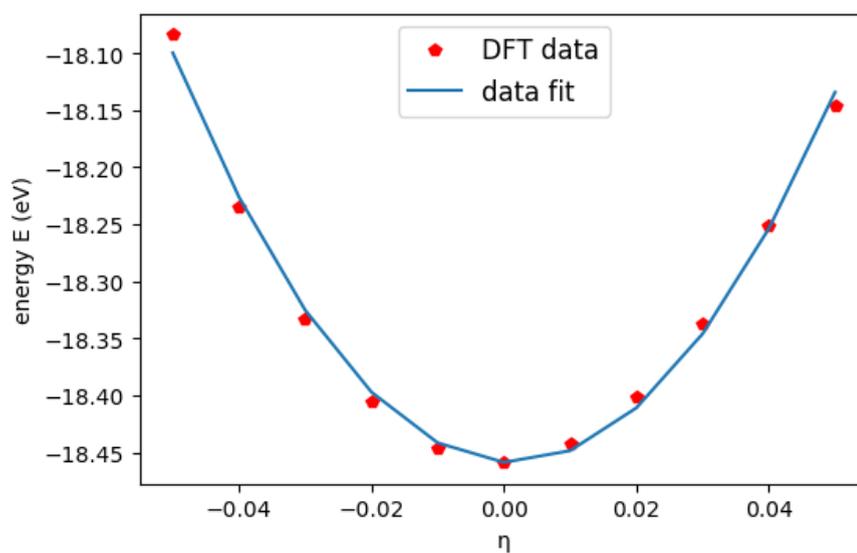FIGURE 3.3: Energies for deformation of type 1
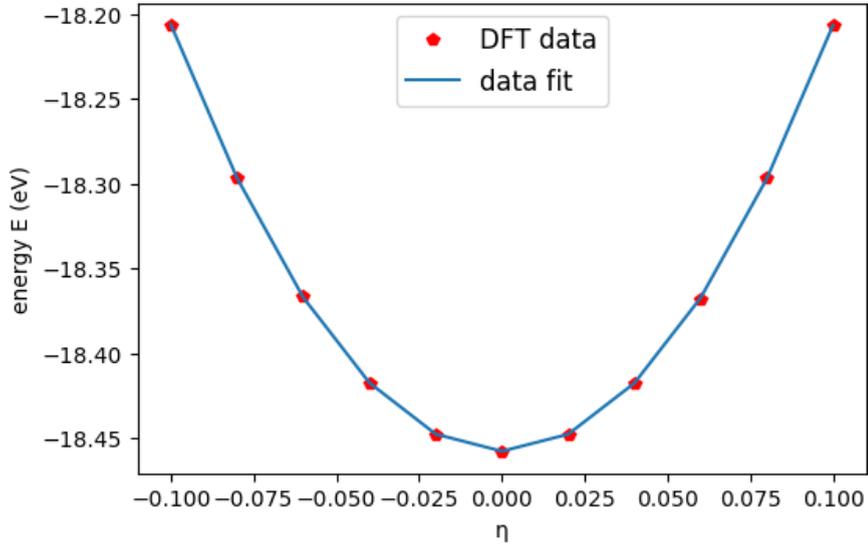

FIGURE 3.4: Energies for deformation of type 2

FIGURE 3.5: Energies for deformation of type 3

TABLE 3.1: Values of elastic constants determined by fitting the energies from the
DFT calculations

Parameter	eV/Å^2
γ_{11}	22.51
γ_{12}	3.39
γ_{66}	9.52

3.4   Stress

The other approach that can be used to determine the elastic constants is to use the
stresses acting on the unit cell. Here three kinds of stresses are relevant, stretching and
compression along the x and y axis in deformation types one and two, and shearing in
y direction in type three. The equation that describes the stresses is as follows

$$\sigma_i = \sum_j \gamma_{ij} \epsilon_j$$

Similar to the method used for the energies applying the deformation type definitions
again leads to three distinct equations that describe the stress for each type

Type 1

$$\sigma_1 = \gamma_{11} \eta$$

Type 2

$$\sigma_1 = (\gamma_{11} + \gamma_{12})\eta$$

Type 3

$$\sigma_3 = \gamma_{66}\eta$$

Again, these are simple scalar equations for the stress as a function of strain. These equations can be used to fit the results of the DFT calculations. Note that in order to solve for γ_{12} one first needs to solve for γ_{11}. As mentioned before, the VASP package can only calculate three dimensional materials and therefore the dimension of stress is defined as force per area. On the other hand, the analogous quantity in a two dimensional material is of dimension force per length. Therefore, in order to obtain the corresponding 2D value of the DFT results one needs to multiply the 3D value by the inter-planar spacing, which was chosen to be twelve times the lattice constant of 2.51Å. The resulting data points are shown as a function of strain η for the three deformation types in figures 3.6 to 3.8 as filled circles. The linear least squares fit is straight forward and yields the elastic constants given in Table 3.2
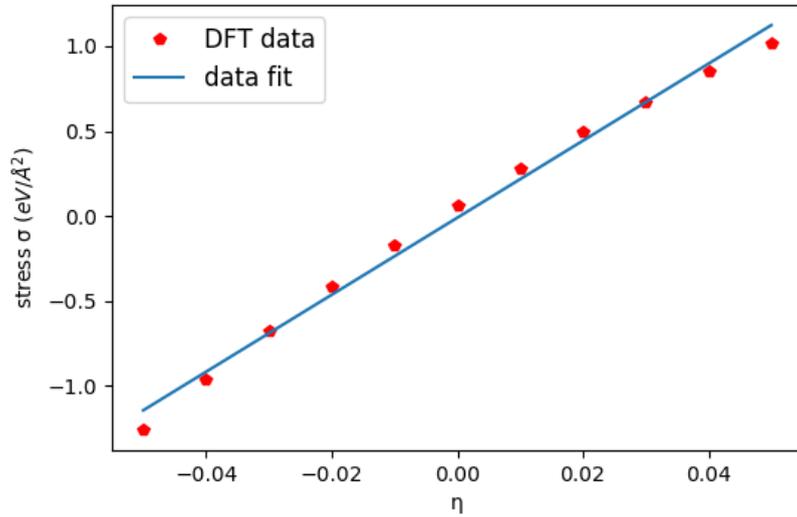

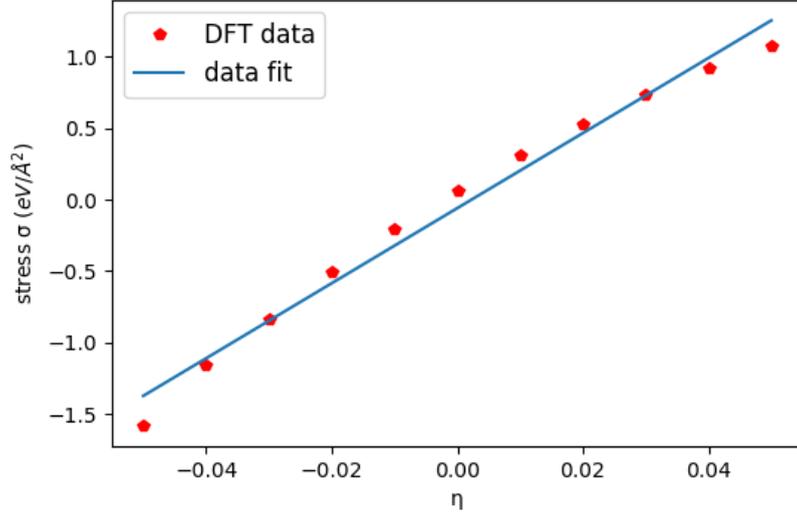FIGURE 3.6: Stresses for deformation of type 1
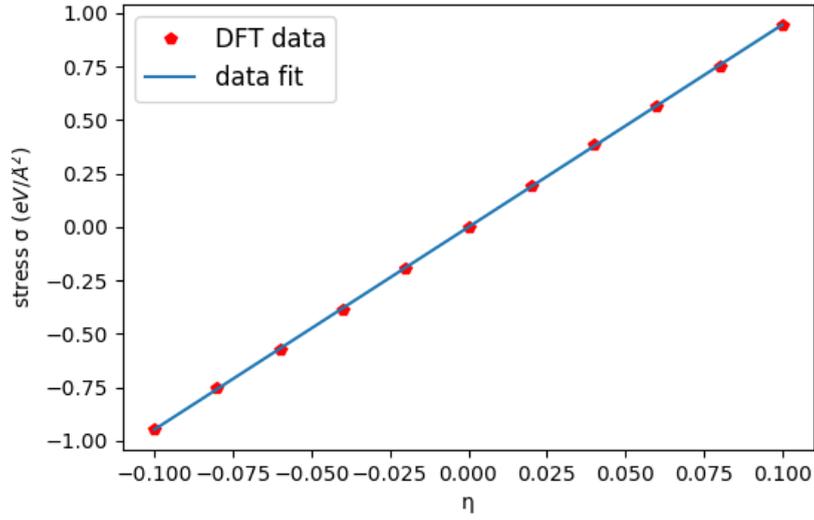
FIGURE 3.7: Stresses for deformation of type 2

FIGURE 3.8: Stresses for deformation of type 3

TABLE 3.2: Values of elastic constants determined by fitting the stresses from the DFT calculations

Parameter	eV/Å^2
γ_{11}	22.68
γ_{12}	3.56
γ_{66}	9.47

Chapter 4

Conclusion

The aim of this thesis was to determine the elastic constants of graphene, which fully describe the in-plane elastic behavior of this material. For this, DFT calculations using the VASP package were performed for several deformed graphene structures. These calculations yielded both values for energy and elastic stress which were evaluated separately. By comparing the results of these two evaluations, it is possible to check for consistency. In order to check the process as a whole and make sure no mistakes were made in the DFT calculations, the results are also compared to those of Michel and Verbeck [10], who have used an alternative approach based on the analysis of experimental values of phonon dispersion to determine the elastic constants of graphene.

TABLE 4.1: Comparison of results gathered through evaluation of energies and stresses, and the results of Michel and Verbeck [10]

Parameter	method 1	method 2	previous work [10]
γ_{11} (eV/Å^2)	22.51	22.68	25.3
γ_{12} (eV/Å^2)	3.39	3.56	5.8
γ_{66} (eV/Å^2)	9.52	9.47	9.8

At first glance, these results are in good agreement with each other. Especially the results of method 1 using energy and method 2 using stress evaluations deviate only slightly from each other. When comparing the results obtained in this thesis with the results of Michel and Verbeck [10] one notices that both γ_{11} and γ_{12} are slightly smaller here. One consequence of the choice of deformation types made in this thesis is that during evaluation γ_{12} is connected to γ_{11} and through deformation type two, therefore an inaccuracy in γ_{11} leads to an inaccuracy in γ_{12}. This effect is even amplified by the fact that the contribution of γ_{11} is much greater than that of γ_{12} in both energy and stress evaluation. Hence, small inaccuracies in the DFT calculations can lead to significant

inaccuracies for γ_{12}. This problem could be avoided by choosing a different deformation of type two where only γ_{12} contributes. Another potential source of inaccuracies in the DFT calculations is the used exchange-correlation functional. The used PBE functional is known to yield values for the bulk modulus which are smaller than experimental results [11]. Since a smaller bulk modulus corresponds to smaller elastic constants, this might explain why the results of this thesis are somewhat smaller than those of Michel and Verbeck [10].

Bibliography

[1] A. H. Castro Neto, F. Guinea, N. M. R. Peres, K. S. Novoselov, and A. K. Geim. The electronic properties of graphene. *Rev. Mod. Phys.*, 81:109–162, Jan 2009. doi: 10.1103/RevModPhys.81.109. URL https://link.aps.org/doi/10.1103/RevModPhys.81.109.

[2] C. Lee, X. Wei, J. W. Kysar, and J Hone. Measurement of the elastic properties and intrinsic strength of monolayer graphene. *Science*, 2008.

[3] G. Kresse and J. Furthmüller. Efficient iterative schemes for ab initio total-energy calculations using a plane-wave basis set. *Phys. Rev. B*, 54:11169, 1996.

[4] G. Kresse and D. Joubert. From ultrasoft pseudopotentials to the projector augmented-wave method. *Phys. Rev. B*, 59:1758–1775, 1999. doi: 10.1103/PhysRevB.59.1758.

[5] David Sholl and Janice Steckel. *Density Functional Theory - A Practical Introduction.* John Wiley & Sons, Inc., 2009.

[6] Christian Weißmantel and Claus Hamann. *Grundlage der Festkörperphysik.* Johann Ambrosius Barth Verlag, 1995.

[7] J. P. Perdew, K. Burke, and M. Ernzerhof. Generalized Gradient Approximation Made Simple. *Phys. Rev. Lett.*, 77:3865–3868, 1996. doi: 10.1103/PhysRevLett.77.3865.

[8] Philipp Haas, Fabien Tran, and Peter Blaha. Calculation of the lattice constant of solids with semilocal functionals. *Phys. Rev. B*, 79(8):085104, 2009. doi: 10.1103/PhysRevB.79.085104.

[9] Daniel R. Cooper, Benjamin D'Anjou, Nageswara Ghattamaneni, Benjamin Harack, Michael Hilke, Alexandre Horth, Norberto Majlis, Mathieu Massicotte, Leron Vandsburger, Eric Whiteway, and Victor Yu. Experimental review of graphene. *ISRN Condensed Matter Physics*, 2012:56, 2012. doi: 10.5402/2012/501686. URL http://dx.doi.org/10.5402/2012/501686.

[10] K. H. Michel and B. Verberck. Theory of the elastic constants of graphite and graphene. *physica status solidi (b)*, 245(10):2177–2180, 2008. doi: 10.1002/pssb. 200879604. URL `https://onlinelibrary.wiley.com/doi/abs/10.1002/pssb.200879604`.

[11] Gabor I. Csonka, John P. Perdew, Adrienn Ruzsinszky, Pier H. T. Philipsen, Sebastien Lebegue, Joachim Paier, Oleg A. Vydrov, and Janos G. Angyan. Assessing the performance of recent density functionals for bulk solids. *Phys. Rev. B*, 79(15): 155107, 2009. doi: 10.1103/PhysRevB.79.155107.