



ÉCOLE POLYTECHNIQUE
FÉDÉRALE DE LAUSANNE

First-principles calculations of the electronic properties of materials: The case study of bulk magnesium oxide

Lab 2

Atomistic and Quantum Simulations of Materials

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Spring semester 2022

In this report several properties of fcc Magnesium Oxide are studied by performing several DFT calculations. The software Quantum Espresso has been used.

1 Problem 1

The first goal is to study the convergence of the total energy of bulk MgO with respect to the cutoff energy E_{cut} . Indeed, the wavefunction is expressed as a finite expansion of plane waves.

$$\psi_{n,\mathbf{k}}(\mathbf{r}) = \sum_{|\mathbf{k}+\mathbf{G}| \leq G_{cut}} c_{n,\mathbf{k}+\mathbf{G}} e^{i(\mathbf{k}+\mathbf{G}) \cdot \mathbf{r}} \quad (1)$$

The cutoff energy then is the kinetic energy related to the cutoff reciprocal lattice vector G_{cut} , as shown in (2), which corresponds to the largest wave vector of the plane waves used in the expansion.

$$E_{cut} = \frac{\hbar^2}{2m} G_{cut}^2 \quad (2)$$

Obviously, the more terms are considered in the expansion, so the larger is E_{cut} , the better is the approximation of the wavefunction, even if the exact one can't be exactly calculated. Indeed an infinite summation would be required and it is not computable.

1.1 Task A

The calculations are first performed by using the conventional unit cell, which is a face centred cubic cell with 8 atoms and a lattice parameter of a_0 , where a_0 is the Bohr radius, equal to 0.5291 \AA and also called atomic unit.

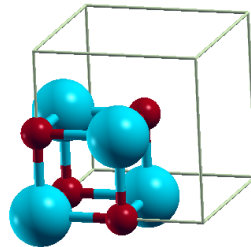


Figure 1: Conventional unit cell of bulk MgO.

The energy cutoff has been varied in a range of $[10 \text{ Ry} - 150 \text{ Ry}]$, with a step of 10 Ry , while all the other variables remained fixed. More precisely 4 \mathbf{k} points have been used to sample the Brillouin zone in each direction and the lattice parameter has been set equal to $8 a_0$, as already said before. The convergence of the energy has been defined as in (5).

$$E_{true} - E_{atom} \leq E_{threshold} \quad (3)$$

where the value of E_{true} is unknown but can be approximated with the one corresponding to the largest cutoff used, if the convergence is reached there. Indeed it is the most precise between the calculated values. It's also important to say that convergence is reached only when one E_{atom} satisfies (5) and all the following values (with bigger cutoff) do as well. The threshold used is $5 \text{ meV/atom} = 0.000367 \text{ Ry/atom}$.

Table 1 shows the collected values for the energy per atom and the difference between each value and E_{true} , which in this case has been approximated by the energy computed by using a cutoff energy of 150 Ry , indeed the convergence seems to be reached for that value. By observing the values of $E_{true} - E_{atom}$, and comparing them to the energy threshold, it is possible to see that the convergence is first reached for $E_{cutoff} = 70 \text{ Ry}$.

The same values have also been plotted to allow a quicker analysis of the trend of the energy of the ground state with respect to the cutoff energy. This trend will be discussed in the next section (Problem 1 - Task B). A plot of $E_{true} - E_{atom}$ can be useful as well for later analysis (Figure 3).

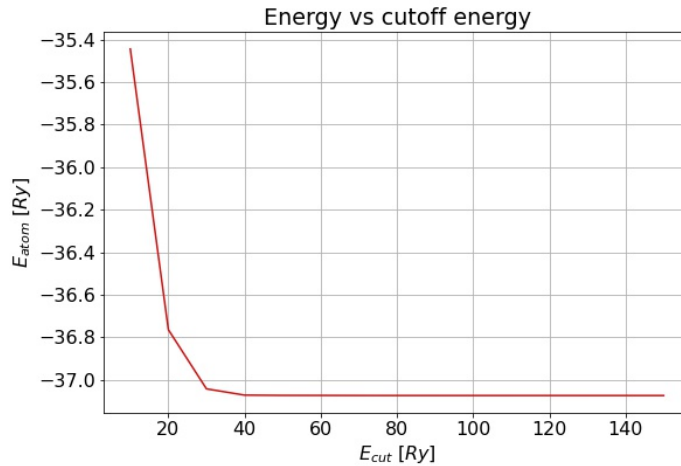


Figure 2: Energy per atom of the lattice as a function of the cutoff energy. Parameters of the DFT calculation (conventional fcc unit cell): 4 \mathbf{k} sampling points, lattice parameter equal to $8 a_0$.

E_{cut} [Ry]	E_{atom} [Ry]	$E_{true} - E_{atom}$ [Ry]
10	-35.444557	1.62e+00
20	-36.764061	3.09e-01
30	-37.042079	3.14e-02
40	-37.071529	1.97e-03
50	-37.072749	7.55e-04
60	-37.072941	5.64e-04
70	-37.073278	2.26e-04
80	-37.073420	8.44e-05
90	-37.073441	6.40e-05
100	-37.073449	5.55e-05
110	-37.073471	3.38e-05
120	-37.073491	1.39e-05
130	-37.073501	3.40e-06
140	-37.073504	4.26e-07
150	-37.073505	/

Table 1: Values obtained from DFT calculations with different cutoff energies. In the columns from left: cutoff energy, correspondent energy per atom of the lattice, difference between that energy per atom and the one in the last line, assumed to be the true energy of the system (in order to check the convergence). All the energies are expressed in Rydbergs.

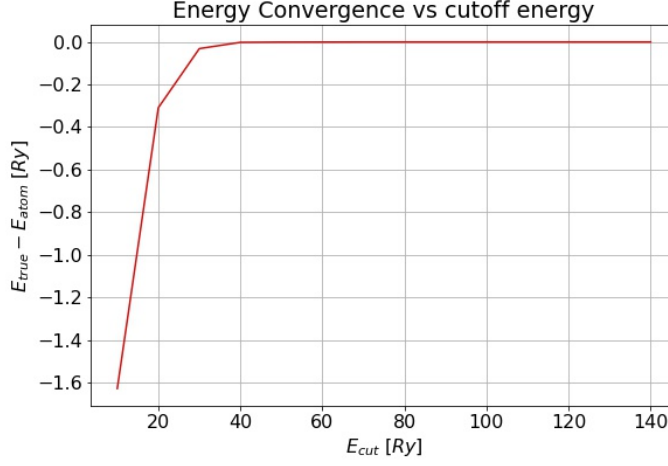


Figure 3: Difference between approximated true energy (energy with $E_{cut} = 150 \text{ Ry}$) and energy per atom of the lattice as a function of the cutoff energy. Parameters of the DFT calculation (conventional fcc unit cell): 4 \mathbf{k} sampling points, lattice parameter equal to $8 a_0$.

1.2 Task B

As it is possible to observe in Figure 2, the energy per atom of the lattice as a function of the cutoff energy decreases monotonically. It means that the more terms are considered in the expansion, the more accurate is the value of the computed energy.

In particular, for small values of the cutoff energy the decrease is sharp. This means that we are excluding terms with a significant weight from the expansion, and the approximation of the energy can be easily improved by adding few more terms. Instead, for higher values of the cutoff energy, and especially close to convergence, the curve is only slightly descendent because the truncation is only excluding terms which have small weights, and a 'good' approximation of the energy has already been found. This means that, as already said before, the more terms are used in the expansion, the better is the approximation of the wavefunction. This trend was then expected.

Although it's important to remember that all the terms, independently from their weights, are necessary to reconstruct the exact wave function and they are an infinite amount. This is why the curve is always decreasing and it doesn't have a stationary point. It is a consequence of the fact that it's always possible to add more terms to the expansion but only when they are infinite the energy will reach its minimum. Then the problem is that an infinite sum is not computable, so that the minimum (considered as the

stationary point, and not the lowest computed value) can't be seen in this curve.

Another important observation is that such a curve is difficult to interpret due to the fact that absolute energies themselves do not have a physical meaning. Indeed they can be arbitrarily shifted upwards or downwards without affecting the description of the system. In addition, there aren't lots of experimental values that can be used as reference to set the origin of the scale. The computation of this quantity is then not really useful because we can't obtain information about the system from it.

1.3 Task C

The same calculation has been performed by using the primitive cell instead of the cubic conventional as before. The primitive cell is defined as the smallest unit cell that contains only one lattice point, while the conventional one may contain more than one lattice point. The primitive unit cell of bulk MgO contains only two atoms, as shown in Figure 4.

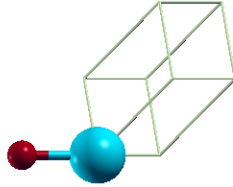


Figure 4: Primitive unit cell of bulk MgO.

The lattice parameter is always set equal to $8 a_0$, and the number of \mathbf{k} sampling points to 4. The obtained values for the energy per atom with respect to the cutoff energy are exactly the same as before (see Figure 5) indeed the two descriptions are identical from a mathematical point of view. Then, as expected, the usage of a different unit cell is not affecting the convergence of the energy of the lattice, which is still reached for a value of $E_{cut} = 70 Ry$. (Tables and plots relative to the convergence of the energy computed by using the primitive unit cell with respect to the cutoff are then not reported for obvious reasons.)

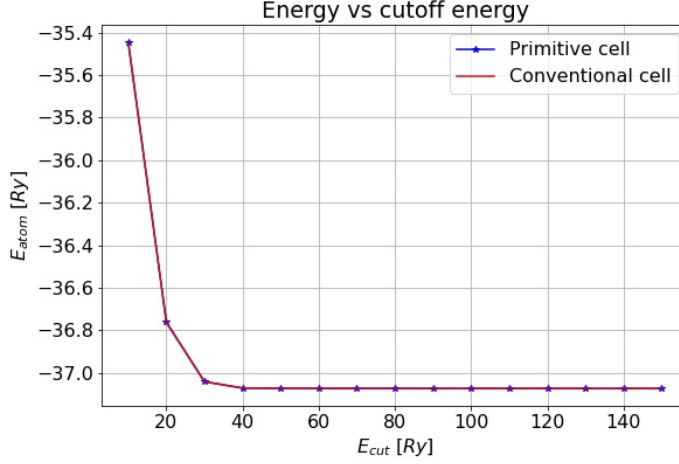


Figure 5: Energy per atom as a function of the cutoff energy for both primitive and conventional unit cell. Parameters of the DFT calculations: 4 \mathbf{k} sampling points, lattice parameter equal to $8 a_0$.

It is known that there is an infinite number of unit cells that can be chosen to describe a crystal system, and all of them provide a correct description thanks to periodic boundary conditions. However, the choice of the unit cell is fundamental in some cases because it determines important features of the calculation that needs to be performed.

The first thing we can observe is the different dimension and number of atoms and electrons contained in the unit cell. As explained before, MgO primitive unit cell contains only two atoms, while the conventional one has 4 times this amount. As a consequence, the calculation that uses a primitive cell is cheaper from a computational point of view: it has smaller dimensions implying a faster computation of the FFT.

On the other hand the primitive unit cell is more difficult to conceptualize and to interpret. Sometimes the symmetry of the system is not obvious by looking at the primitive cell and in such cases the conventional one is preferred. This last one indeed is easier to imagine repeated in the three directions of the space creating the crystal lattice. It captures the full symmetry of the structure.

The choice between these two different unit cells depends also on the type of properties we want to know about the system. Indeed, if a quantity is strictly related to the symmetry of the system, like the bulk modulus or the elastic constants, the conventional cell needs to be used because it's the one able to catch that symmetry.

2 Problem 2

Now the goal is to test the convergence of forces with respect to the cutoff energy. After the observations made in the previous exercise about the unit cell, here the calculations have been performed by using the primitive cell, to make the calculation more efficient from a computational point of view. The other parameters are set always to the same values: lattice parameter equal to $8 a_0$ and 4 \mathbf{k} sampling points. To be able to see the forces, a displacement of $+0.05$ (fractional coordinates) has been applied in the z direction to the Magnesium ion. In this way the symmetry of the system is broken and the forces are not cancelling out.

The adopted definition of convergence is shown in Equation 4, where, as for the energy case, the term F_{true} is not known but it's approximated by the best computed value, which in this case corresponds to the one with $E_{cut} = 150 Ry$.

$$F_{true} - F_n \leq F_{threshold} \quad (4)$$

As for energies, also here convergence is reached only when Equation (4) is satisfied for F_n and also for all the others that follow. Convergence is not reached if F_n satisfies (4) but also only one between F_{n+1} , F_{n+2} , ... doesn't. The threshold for convergence in this case is set to $F_{threshold} = 10 meV/\text{\AA} = 0.000389 Ry/Bohr$.

Because the displacement is in z direction, the forces acting on the atoms are only visible in that direction while they are still null in x, y directions. As shown in Table 2 the convergence is reached for $E_{cutoff} = 30 Ry$.

E_{cut} [Ry]	$F_{z,Mg}$ [Ry/Bohr]	$F_{true} - F_{z,Mg}$ [Ry/Bohr]
10	0.099064	4.18e-02
20	0.053369	3.88e-03
30	0.057021	2.30e-04
40	0.057340	8.79e-05
50	0.057283	3.08e-05
60	0.057287	3.57e-05
70	0.057270	1.79e-05
80	0.057258	6.67e-06
90	0.057258	5.92e-06
100	0.057254	2.80e-06
110	0.057253	1.09e-06
120	0.057252	4.60e-07
130	0.057248	4.03e-06
140	0.057251	9.70e-07
150	0.057252	/

Table 2: Values obtained from DFT calculations with different cutoff energies. In the columns from left: cutoff energy, correspondent force acting on the displaced Mg ion in z direction, difference between the force of that line and the force in the last line which is assumed to be true (in order to check the convergence).

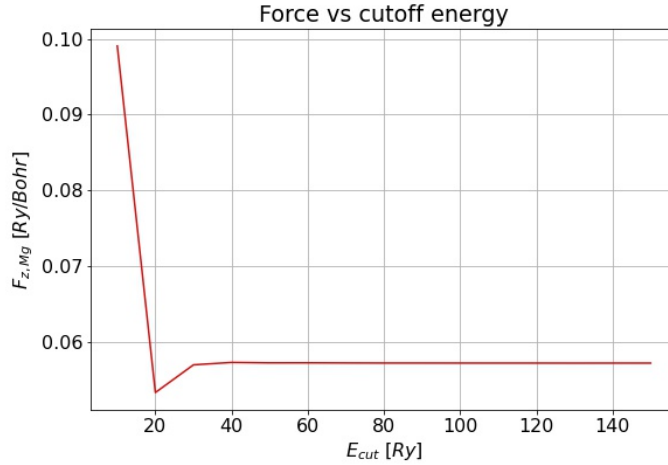


Figure 6: Energy per atom of the lattice as a function of the cutoff energy. Parameters of the DFT calculation (primitive fcc unit cell): 4 \mathbf{k} sampling points, lattice parameter equal to $8 a_0$.

It's important to say that with respect to the previous exercise, in this case the computed quantities are more interesting. It's easier indeed to extract properties about the system from them. Forces are computed with respect to a precise reference value and they can't be scaled arbitrarily as it can be done with energies. There are also more experimental values to compare the results with. Forces have then more physical sense and it's also easier for us to interpret them.

The convergence of forces has a behaviour with respect to the cutoff energy which is different from the one described before for energies. The difference between the approximation of F_{true} and the computed forces oscillates and then tends to zero for high cutoff energies (Figure 7). The reason of this is discussed more in details later in Problem 6, for the moment we limit our observation to the fact that forces need a smaller value of E_{cut} to converge, as shown also in Figure 7.

It's also possible to observe that due to the fact that an atom has been moved, the symmetry of the structure is not conserved anymore and the system is not at equilibrium. Indeed it is not in the minimum of the energy curve and by comparing the absolute energies computed here, where an atom has been displaced, and the ones of the previous problem, for same values of the cutoff energy the first ones are higher than the second ones.

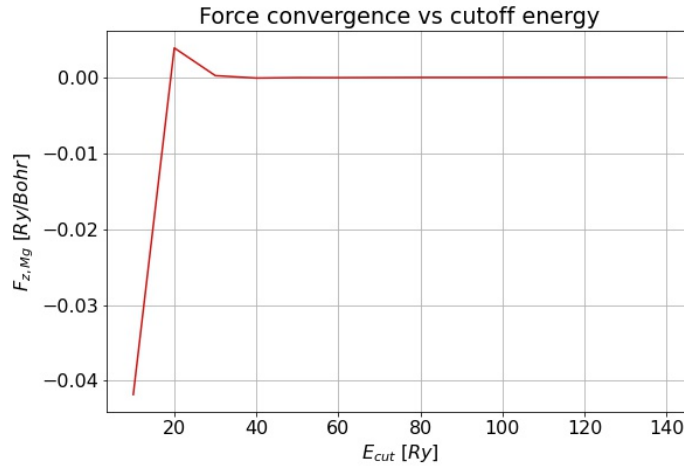


Figure 7: Difference between approximated true energy (energy with $E_{cut} = 150$ Ry) and energy per atom of the lattice as a function of the cutoff energy. Parameters of the DFT calculation (primitive fcc unit cell): 4 \mathbf{k} sampling points, lattice parameter equal to $8 a_0$.

3 Problem 3

It is also possible to study the convergence of the total energy of the lattice as a function of the size of the \mathbf{k} points mesh in the reciprocal space. Uniform Monkhorst-Pack mesh has been used. The calculation of the energy indeed requires the evaluation of many integrals in the reciprocal space, which are converted into summations over discrete, and so finite, \mathbf{k} points. This fact obviously has an impact on the exactness of the calculation: if more points are used, the summation better approximates the integral and the calculated energy is closer to the exact one.

3.1 Task A

Here the cutoff energy and the lattice parameter have been set to $E_{cutoff} = 70Ry$, as found in the first problem, and the lattice parameter is again $8 a_0$. The Brillouin zone has been sampled in 4 different ways, by using 2, 4, 6 and 8 sample points in each direction. Obviously the total sample points are respectively 8, 64, 216, 512 but due to the symmetry of the system some of these are equivalent and only a reduced number of 'irreducible' \mathbf{k} points can be used to calculate all the quantities. In this way the computational effort is significantly reduced. The definition of convergence is the same as in Problem 1, so it's given by (5) where E_{true} is approximated by the value found by using 8 \mathbf{k} points. Also the threshold is set to the same value $E_{threshold} = 0.000367 Ry/atom$.

The computed values are reported in Table 3, together with respective energies per atom of the lattice and convergence evaluation. As it is possible to see the convergence is reached for a sampling of $6 \times 6 \times 6$ points in the Brillouin zone.

$\mathbf{k} \text{ points}$	<i>Irreducible \mathbf{k} points</i>	$E_{atom} [Ry]$	$E_{true} - E_{atom} [Ry]$
$2 \times 2 \times 2$	3	-37.040411	3.28e-02
$4 \times 4 \times 4$	8	-37.072783	4.97e-04
$6 \times 6 \times 6$	16	-37.073264	1.67e-05
$8 \times 8 \times 8$	29	-37.073280	/

Table 3: Number of sampling points in the reciprocal space (in each direction), correspondent number of irreducible points, energy per atom and evaluation of convergence (difference of the energy with the approximated true energy in the last line).

The difference $E_{true} - E_{atom}$ is plotted in Figure 8. As in Problem 1, this quantity tends monotonically to zero without any oscillation.

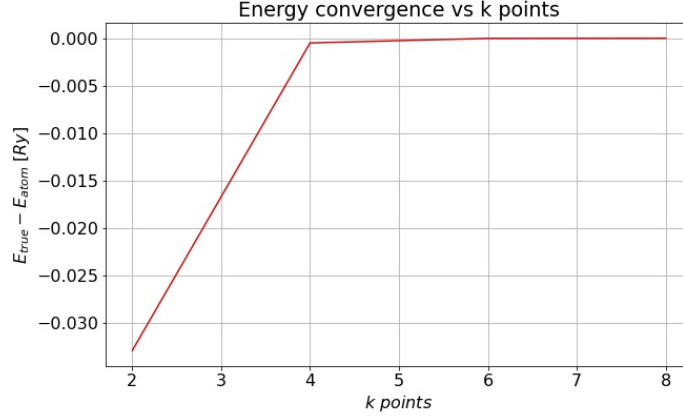


Figure 8: Difference between approximated true energy (energy with 8 \mathbf{k} sampling points) and energy per atom of the lattice as a function of the number of \mathbf{k} points in each direction. Parameters of the DFT calculation (primitive fcc unit cell): $E_{cut} = 70 Ry$, lattice parameter equal to $8 a_0$.

3.2 Task B

Always from Table 3 it is possible to observe that the energy per atom of the lattice is always decreasing while the number of \mathbf{k} sampling points is increasing. This trend was expected because, as it is in general known, a finer sampling of the domain of the integral allows to calculate the quantity of interest more precisely. Indeed, if the integrand is evaluated in more points, more information about it are known and its integral can be better approximated. As the number of sampling points goes to infinite, the calculation stops being in the form of a discrete summation and becomes a real integral which gives the exact result. Then the more \mathbf{k} sampling points are collected, the more precise is the calculation of the energy.

4 Problem 4

We now want to study the convergence of the forces with respect to the \mathbf{k} sampling points in the reciprocal space. As it has been done in Problem 2, to be able to see the forces, a displacement has been applied to one of the atoms of the unit cell. In particular the Magnesium atom of the primitive unit cell has been displaced by $+0.05$ (fractional coordinates) in the z direction. The lattice parameter is set to $8a_0$ and the cutoff energy to $70Ry$, as found in Problem 1. The convergence is defined as in Problem 2 by Equation 4 and

the threshold is $F_{threshold} = 10 meV/\text{\AA} = 0.0003889 Ry/Bohr$.

Table 4 shows the obtained values of the force which acts on the Magnesium ion in the z direction.

\mathbf{k} points	Irreducible \mathbf{k} points	$F_{z,Mg}$ [Ry/Bohr]	ΔF [Ry/Bohr]
$2 \times 2 \times 2$	3	0.05060063	6.86179e-03
$4 \times 4 \times 4$	8	0.05727013	1.92290e-04
$6 \times 6 \times 6$	16	0.05745342	9.00000e-06
$8 \times 8 \times 8$	29	0.05746242	/

Table 4: Number of sampling points in the reciprocal space (each direction), correspondent number of irreducible points, force acting on Mg ion in z direction and evaluation of convergence (difference between the force with the force in the last line).

The convergence is reached for a sampling of 4 \mathbf{k} points in each direction. It's possible to notice that in this case the convergence is reached for a smaller number of \mathbf{k} points than the amount needed to get convergence of the energies (see Problem 6).

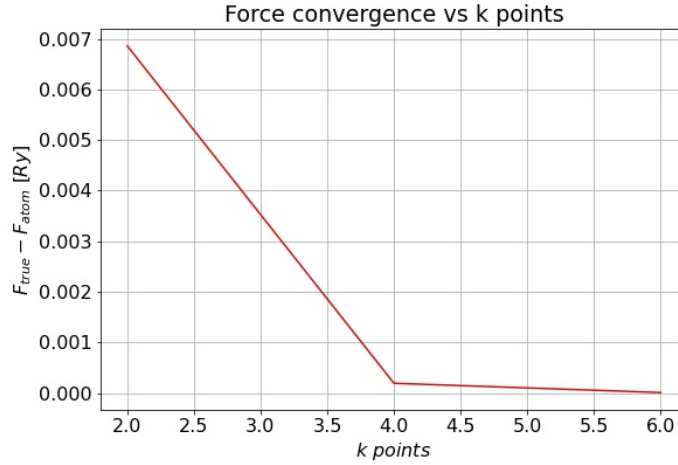


Figure 9: Difference between approximated true force acting on a Mg ion in the z direction (with 8 \mathbf{k} sampling points) and force as a function of the number of \mathbf{k} points in each direction. Parameters of the DFT calculation (primitive fcc unit cell): $E_{cut} = 70 Ry$, lattice parameter equal to $8 a_0$.

5 Problem 5

So far, only absolute energies have been calculated, even if it's known that they have no physical meaning and their scales can be arbitrarily shifted. Then we are interested in calculating total energy differences between two crystals, which are the only ones with physical meaning. In particular we want to study again the convergence with respect to the cutoff energy. We consider two MgO crystals with different lattice parameters: $a_1 = 8 a_0$, $a_2 = 8.094 a_0$. We compute the energies for both the systems varying the cutoff energy in the range $[10 Ry - 150 Ry]$ by using a step of $10 Ry$, where 6 \mathbf{k} sampling points are used (as found before for the convergence of the energy with respect to the number of sampling points). Then the difference between the energies of the two systems is taken by considering the values obtained for the same cutoff energy. The convergence is defined as in Equation ?? but by taking into account energy differences instead of absolute energies, so that

$$\Delta E_{true} - \Delta E_n \leq E_{threshold} \quad (5)$$

where $\Delta E_n = E_{1,n} - E_{2,n}$ and $\Delta E_{true} = E_{1,true} - E_{2,true}$ where $E_{1,n}$ and $E_{2,n}$ are approximated as the values found with the highest cutoff energy $E_{cut} = 150 Ry$. The threshold is set, once again, to $E_{threshold} = 0.000367 Ry/atom$.

It's possible to see in Table 5 that the convergence is reached for a value of the energy cutoff equal to $40 Ry$ and as shown in Figure 10 the difference between a value of ΔE and the best approximation of the true one oscillates for small values of the cutoff and tends to zero for higher values.

E_{cut} [Ry]	$E_{1,n}$ [Ry]	$E_{2,n}$ [Ry]	ΔE_n [Ry]	$\Delta E_{true} - \Delta E_n$ [Ry]
10	-35.434705	-35.460509	0.025804	-2.65e-02
20	-36.761412	-36.763493	0.002081	-2.77e-03
30	-37.041891	-37.040624	-0.001266	5.69e-04
40	-37.071498	-37.070816	-0.000681	-1.55e-05
50	-37.072736	-37.072045	-0.000691	-5.91e-06
60	-37.072929	-37.072233	-0.000696	-5.55e-07
70	-37.073264	-37.072568	-0.000695	-1.82e-06
80	-37.073407	-37.072710	-0.000696	-6.40e-07
90	-37.073428	-37.072731	-0.000696	-4.95e-07
100	-37.073436	-37.072739	-0.000696	-3.65e-07
110	-37.073458	-37.072761	-0.000697	1.00e-08
120	-37.073478	-37.072781	-0.000697	1.65e-07
130	-37.073488	-37.072791	-0.000697	-7.00e-08
140	-37.073491	-37.072794	-0.000697	-5.50e-08
150	-37.073492	-37.072795	-0.000697	/

Table 5: Values obtained from DFT calculations with different cutoff energies. In the columns from left: cutoff energy, energy per atom of the crystal with lattice parameter $a_1 = 8 a_0$, energy per atom of the crystal with lattice parameter $a_2 = 8.094 a_0$, difference between the energies of the two crystals, difference between each difference value and the one in the last line (in order to check the convergence). All the energies are expressed in Rydbergs.

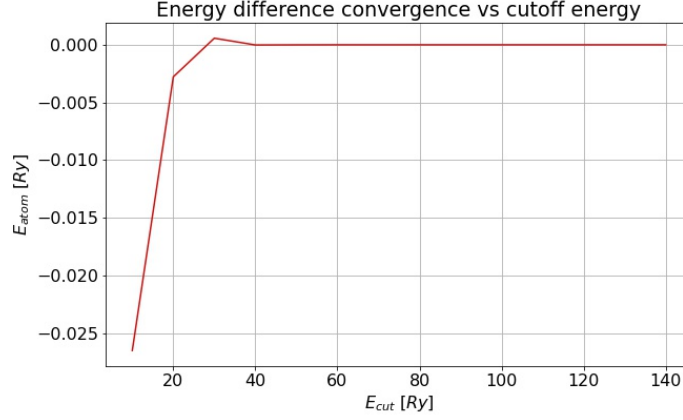


Figure 10: Difference between approximated ΔE_{true} (found by using energies with $E_{cutoff} = 150$ Ry) and energy difference per atom ΔE_n as a function of the cutoff energy. Parameters of the DFT calculation (primitive fcc unit cell): 6 \mathbf{k} sampling points, lattice parameter equal to $8 a_0$.

6 Problem 6

The comparison of the results obtained from all the previous exercises provides interesting information. To resume, two different types of convergence have been studied:

- with respect to the cutoff energy (energies, forces and total energy differences)
- with respect to the number of \mathbf{k} points in the reciprocal space mesh (energies, forces)

By looking at the first type of convergence, the total absolute energy of MgO lattice converged for a value of $E_{cut} = 70$ Ry, the forces for a smaller value of 30 Ry, while the total energy difference between two crystals converged at 40 Ry. It's clear that force and energy difference require a far smaller value of the cutoff energy to converge with respect to the cutoff energy than absolute energy. It's possible to justify this behaviour by thinking about the procedure that it's done in order to calculate these quantities. Absolute energies calculated through DFT calculations are always affected by an error, which depends on the fact that the exchange term in the Kohn-Sham equations is not known. Then the approximations adopted in order to solve the problem introduce a difference between the computed value for absolute energy and

the real one (that can't be known). Absolute energies are then always affected by an error that also can't be properly estimated. On the other hand if energy differences are taken into account, the procedure to calculate them obviously involves the operation of taking the difference between two absolute energies. As a consequence, due to the fact that the two energies are calculated in the same way (but for two crystals with only slightly different properties), we can assume that the committed errors in the two calculations are similar, at least in magnitude. The difference operation introduces a partial cancellation of such errors. Then the convergence with respect to the energy cutoff can be reached faster for energy differences than for absolute energies. The same justification can be adopted also for force. This quantity is computed by taking the gradient of the absolute energy per atom of the lattice, which means that also in this case a difference between absolute energies is performed. Then, for what already said before, the errors that affect the absolute energies are somehow cancelling out and the error committed in estimating forces is smaller. This allows a faster convergence of the forces with respect to the energy cutoff than absolute energies.

The second type of convergence studied is, as already said, with respect to the number of sampling points in the Brillouin zone, in each direction due to the symmetry of the system. Absolute energies converge for a value of 6 \mathbf{k} points while forces converge if a grid with 4 \mathbf{k} sampling points is used. A finer grid in the reciprocal space allows to compute more precisely the integrals in the Brillouin zone that are needed to calculate quantities such as energies and forces. However, the same explanation as before can be adopted to justify the different convergence, indeed also in this case the calculation of forces allows the errors present in the computation of absolute energies to cancel out.

7 Problem 7

7.1 Task A

So far, the approximative value of $8 a_0$ of the lattice parameter has been used (because we know it is close to the experimental one). Now we are interested in calculating the theoretical equilibrium lattice parameter of MgO. Usually, as already explained before, the quantities of interest are forces and energy differences, so the cutoff energy and the number of \mathbf{k} points are set to the values found in the previous exercises, which guarantee the convergence of forces and energy differences with respect to these two parameters, so $E_{cut} = 40Ry$ and $4 \times 4 \times 4$ \mathbf{k} points are used.

In order to find the equilibrium lattice parameter the energy of the system has been calculated for different values of the lattice parameter, more specifically by varying it by $0.05 a_0$ in range $[7.55 a_0; 8.5 a_0]$. The expected result is a curve with a minimum, which obviously corresponds to the lowest energy. The correspondent lattice parameter is then the equilibrium lattice parameter of the system.

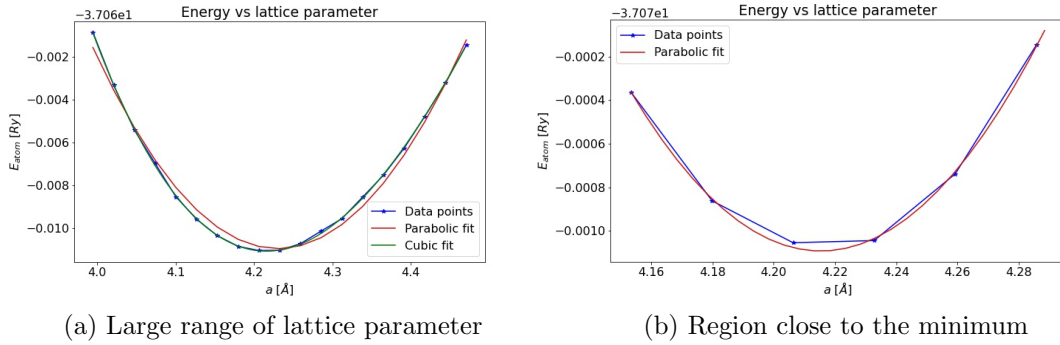


Figure 11: Data points of the energy per atom of the lattice as a function of the lattice parameter, parabolic fit and cubic fit of the data.

From Figure 11(a) it's evident that a parabolic fit of the curve in this case is not good indeed the curve is shifted right, while a cubic fit is able to capture correctly the trend of the energy. This is due to the fact that far from the minimum some anelastic effects become relevant and only polynomials of degree higher than 2 are able to describe the anharmonicity of the potential. However the parabolic approximation of the potential can be considered good very close to the minimum, indeed by looking closer to that region, it's possible to see that a quadratic fit is good (see Figure 11(b)). Then, by looking at the quadratic fit of the data close to the minimum, the theoretical equilibrium lattice parameter is equal to 4.213 Å .

This value is very close to the experimental one, which is 4.21 Å , indeed the error is only 0.07% . This indicates a significant accuracy of the DFT method used.

7.2 Task B

We want now to calculate another important property of MgO which is the bulk modulus B , a measure of the stiffness of the material. It's possible to do it through the derivation of a simple equation starting from (6) and (7).

$$B = -V_0 \frac{\partial P}{\partial V} \quad (6)$$

$$P = -\frac{\partial E}{\partial V} \quad (7)$$

where V_0 is the equilibrium volume of the system, equal to the cube of the equilibrium lattice parameter.

By substituting (7) in (6) the following new relation is obtained to describe the bulk modulus.

$$B = V_0 \frac{\partial^2 E}{\partial V^2} \quad (8)$$

In order to find the value of the bulk modulus is then necessary to know the energy as a function of the cell volume, which is simply obtained as the cube of the lattice parameter. To do this, some calculations have been performed by using the conventional unit cell of MgO. Indeed we are now interested in studying a property of the system which involves the volume of the fcc cubic cell and is then related to the symmetry unit of the system, it's then necessary to be able to easily describe the symmetry and, as already said in Problem 1, this can be done only through the usage of the conventional unit cell.

As shown in Equation (8) the bulk modulus is related to the energy of the unit cell as a function of the cell volume. Then, it's possible to expand the energy as a function of the cell volume with a second order Taylor expansion around the equilibrium volume V_0 . The value of the bulk modulus can be recognized inside the expansion (by inverting Equation (6) we have $\frac{\partial^2 E}{\partial V^2} = \frac{B}{V_0}$). A quadratic fit of the energy curve is then performed in order to find the second order polynomial which describes the energy and it must be equal to the Taylor expansion, so that two equations for the coefficients involving B and V_0 are obtained as shown below.

$$\begin{aligned} E(V - V_0) &= E(V_0) + (V - V_0) \left. \frac{\partial E}{\partial V} \right|_{V=V_0} + \frac{1}{2} (V - V_0)^2 \left. \frac{\partial^2 E}{\partial V^2} \right|_{V=V_0} \\ &= E(V_0) + \frac{1}{2} (V - V_0)^2 \left. \frac{\partial^2 E}{\partial V^2} \right|_{V=V_0} \\ &= E(V_0) + \frac{BV_0}{2} - BV + \frac{B}{2V_0} V^2 \end{aligned} \quad (9)$$

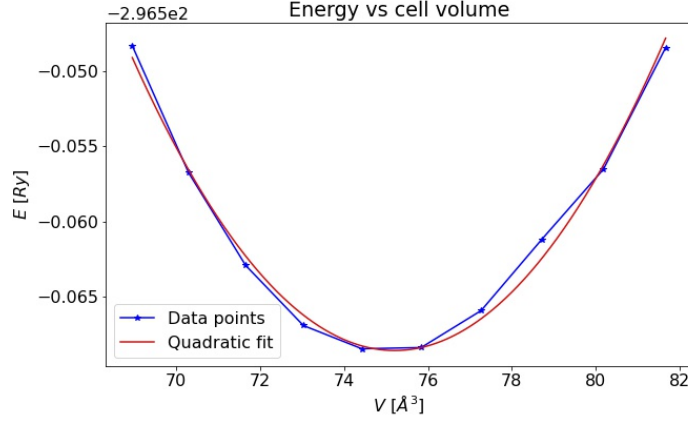


Figure 12: Data points of the energy of the cell as a function of the cell volume and parabolic fit.

In Figure 12 the quadratic polynomial which fits the curve is $E(V) = -293.763 - 1.105 \cdot 10^{-2} V + 1.088 \cdot 10^{-5} V^2$, then the equations that let us to determine B and V_0 are the following ones.

$$\begin{cases} -1.105 \cdot 10^{-2} = -B \\ +1.088 \cdot 10^{-5} = \frac{B}{2V_0} \end{cases} \quad \begin{cases} B = 0.0110509 \text{ Ry/Bohr}^3 = 162.635 \text{ GPa} \\ V_0 = 507.736 \text{ Bohr}^3 = 75.205 \text{ Å}^3 \end{cases} \quad (10)$$

7.3 Task C

Another way to calculate the bulk modulus is through the fit of an Equation of state, here the third-order Birch-Murnaghan isothermal equation of state is used.

$$E(V) = E_0 + \frac{9V_0B}{16} \left\{ \left[\left(\frac{V_0}{V} \right)^{\frac{2}{3}} - 1 \right]^3 B' + \left[\left(\frac{V_0}{V} \right)^{\frac{2}{3}} - 1 \right]^2 \left[6 - 4 \left(\frac{V_0}{V} \right)^{\frac{2}{3}} \right] \right\} \quad (11)$$

The same range of volumes of the previous section has been used, and it was equal to $[465.484 \text{ Å}^3 ; 551.368 \text{ Å}^3]$, which corresponds to values of the lattice parameter in range $[7.75 \text{ Å} ; 8.2 \text{ Å}]$. Although in this case less points are considered so that the energy step is larger and possible high order effects are avoided. The calculated data points are then fitted through the use of

the executable **ev.x** with the third-order Birch-Murnaghan equation of state. Table 6 reports the values found through the fit.

$V[a_0^3]$	$E_{calculated}[Ry]$	$E_{fit}[Ry]$	$\Delta E[Ry]$
465.48	-296.54834	-296.54834	-0.00000
483.74	-296.56291	-296.56291	0.00000
502.46	-296.56844	-296.56844	-0.00000
521.66	-296.56591	-296.56591	0.00000
541.34	-296.55653	-296.55653	-0.00000

Table 6: In the columns from left to right: volume of the cubic cell, energy of the conventional unit cell calculated through DFT calculation, evaluation of the fit with the third-order Birch-Murnaghan equation of state (11) in the volume data points, difference between the DFT energy and the energy of the fit.

The best values of bulk modulus, its derivative and equilibrium volume are then the followings.

$$\begin{aligned}
 B &= 162.0 \text{ GPa} \\
 B' &= 4.93 \text{ GPa}/\text{\AA}^3 \\
 V_0 &= 74.92 \text{ \AA}^3
 \end{aligned} \tag{12}$$

As it is possible to see the difference between the fit and the energy data points is almost zero, indeed $\chi^2 = 0.5910 \cdot 10^{-13}$, and it means that the approximation of the trend is really accurate.

7.4 Task D

To summarize, in Task B and C, two different values for the bulk modulus have been calculated: $B_B = 162.635 \text{ GPa}$ and $B_C = 162.0 \text{ GPa}$. As it is possible to see, they are very close to each other, they are different for only 0.39% with respect to B_C which means that both the approaches give a good estimation of this property of the system.

These values must be compared also with the known experimental value, which can be found to be $B_{exp} = 162.5 \text{ GPa}$ in [1]. The fit of the second order Taylor expansion of the energy gives a value for the bulk modulus very close to the experimental value, indeed by taking B_{exp} as reference value, the relative error between B_{exp} and B_B is 0.083%. On the other hand the fit with the third order Birch-Murnaghan equation of state gives a discrepancy

between B_{exp} and B_B also very small even if it's larger than the previous one, more precisely it's equal to 0.30%. Then it's possible to observe that both the fits of the energy curve as a function of the cell volume are accurate methods to get information about the system, like the bulk modulus. It was expected that the fit with an equation of state like the third-order Birch-Murnaghan one would have been more accurate than a simple quadratic fit because it's able to capture a more complex behaviour. Instead in this case, also because the range considered is very close to the minimum of the curve, the quadratic fit seems to perform better if compared with experimental values. The results can be also compared with some other calculated values found in the literature. For example, more recently it has been estimated from more complicated calculations that the bulk modulus of MgO is equal to 157.37 GPa [2]. In this case the discrepancy between the values found here and that one is higher, 2.94% for B_B and 3.34% for B_C . In general the values that have been found in the present calculations are in good accordance with the experimental and calculated values found in the literature.

8 Problem 8

The last problem concerns the calculation of the elastic constants of MgO. At each deformation of a material corresponds a variation of its energy, then the calculation of the energy of the system before and after the application of a certain strain is needed in order to calculate the answer of the material to a certain strain. The conventional unit cell has been used instead of the primitive one. Indeed in this case we are interested in the variation of the energy of the unit of symmetry of the system when it is subject to a deformation, and it can be represented only by the conventional cell.

In the whole problem a value of 50 Ry for the energy cutoff has been used, which is higher than the one found in the previous studies. Indeed in this case we need to collect more precise values if we want to get good results. The sampling in the Brillouin zone has been done by using 4 \mathbf{k} points in each direction.

As known due to the cubic symmetry of the system the elastic constants matrix is composed by only three elements: C_{11} , C_{12} and C_{44} , which appear as shown below.

$$C = \begin{pmatrix} C_{11} & C_{12} & C_{12} & 0 & 0 & 0 \\ C_{12} & C_{11} & C_{12} & 0 & 0 & 0 \\ C_{12} & C_{12} & C_{11} & 0 & 0 & 0 \\ 0 & 0 & 0 & C_{44} & 0 & 0 \\ 0 & 0 & 0 & 0 & C_{44} & 0 \\ 0 & 0 & 0 & 0 & 0 & C_{44} \end{pmatrix} \quad (13)$$

In order to calculate them a strain needs to be applied to the system, so that also the lattice parameters of the unit cell become different and they can be defined as $\mathbf{a}'_1, \mathbf{a}'_2, \mathbf{a}'_3$ and calculated starting from the previous lattice parameters $\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3$ and the strain tensor $\hat{\varepsilon}$, as shown below (where \hat{I} is the identity matrix with in three dimensions).

$$\begin{pmatrix} \mathbf{a}'_1 \\ \mathbf{a}'_2 \\ \mathbf{a}'_3 \end{pmatrix} = \begin{pmatrix} \mathbf{a}_1 \\ \mathbf{a}_2 \\ \mathbf{a}_3 \end{pmatrix} (\hat{I} + \hat{\varepsilon}) = \begin{pmatrix} a_0 & 0 & 0 \\ 0 & a_0 & 0 \\ 0 & 0 & a_0 \end{pmatrix} (\hat{I} + \hat{\varepsilon}) \quad (14)$$

where a_0 is the equilibrium lattice parameter (the same symbol has been used to express the Bohr unit $a_0 = 0.5291 \text{ \AA}$ but it's clearly possible to understand to which one it's referred to by the context). The energy of the distorted unit cell can then be found through Equation (15), where in our case the applied transformations are all conserving the volume of the unit cell, so that $\Delta V = 0$ and the formula can be simplified.

$$\begin{aligned} E &= E_0 - P(V_0) \Delta V + \frac{1}{2} V_0 \sum_{i=1}^6 \sum_{j=1}^6 C_{ij} e_i e_j \\ &= E_0 + \frac{1}{2} V_0 \sum_{i=1}^6 \sum_{j=1}^6 C_{ij} e_i e_j \end{aligned} \quad (15)$$

where E_0 is the energy of the undistorted lattice and V_0 its respective volume, $P(V_0)$ the pressure of the undistorted lattice at volume V_0 , C_{ij} the elastic constants of the lattice and e_i, e_j the elements of the strain tensor.

8.1 Task A

First we focus on the calculation of the elastic constants C_{11} and C_{12} . In order to do this a tetragonal strain needs to be applied, and it's in the following form.

$$\hat{\varepsilon} = \begin{pmatrix} x & 0 & 0 \\ 0 & -x & 0 \\ 0 & 0 & \frac{x^2}{1-x^2} \end{pmatrix} \quad (16)$$

The new lattice parameters are then calculated by inserting (16) inside Equation (14) and the following result is obtained.

$$\begin{pmatrix} \mathbf{a}'_1 \\ \mathbf{a}'_2 \\ \mathbf{a}'_3 \end{pmatrix} = \begin{pmatrix} a_0(1+x) & 0 & 0 \\ 0 & a_0(1-x) & 0 \\ 0 & 0 & \frac{a_0}{1-x^2} \end{pmatrix} \quad (17)$$

$$\begin{aligned} |\mathbf{a}'_1| &= a_0(1+x) \\ |\mathbf{a}'_2| &= a_0(1-x) \\ |\mathbf{a}'_3| &= \frac{a_0}{(1-x^2)} \end{aligned} \quad (18)$$

The distorted unit cell is defined in the input file for the calculations as an orthorhombic unit cell, and not a cubic anymore because as it is possible to see from (18) the dimension is not anymore the same in all the three directions. An orthorhombic unit cell needs 3 parameters in order to be defined correctly.

$$\begin{aligned} \text{celldm}(1) &= |\mathbf{a}'_1| = a_0(1+x) \\ \text{celldm}(2) &= |\mathbf{a}'_2| / |\mathbf{a}'_1| = \frac{(1+x)}{(1-x)} \\ \text{celldm}(3) &= |\mathbf{a}'_3| / |\mathbf{a}'_1| = \frac{1}{(1+x)(1-x^2)} \end{aligned} \quad (19)$$

At this point, different values of the deformation x are considered and the energy of each deformed structure is calculated. A range of $[-0.1; 0.1]$ with 13 equally spaced points has been used for x .

It is more convenient to define the energy difference between the deformed structure and the cubic one, which has energy E_0 . By doing this it is possible to find the following relation:

$$\Delta E(x) = \Delta E(-x) = V_0 (C_{11} - C_{12}) x^2 \quad (20)$$

The computed values for the energy variation are fitted with a polynomial of the type ax^2 , where the best value of the coefficient is $a = 8.3 \text{ Ry}$.

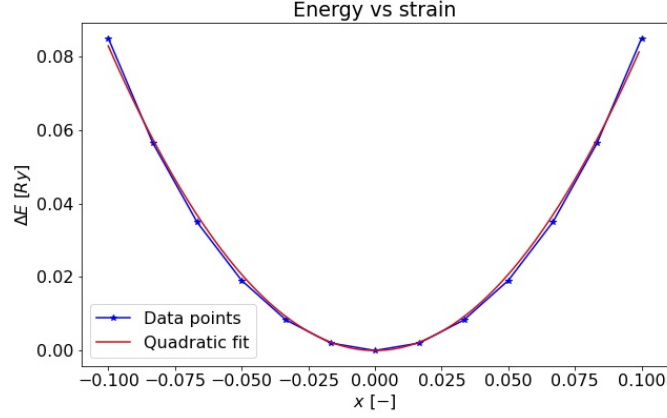


Figure 13: Data points of the difference between the energy of the distorted orthorhombic cell and the energy of the undistorted cell E_0 as a function of the deformation x .

From Equation (20) and the value of the coefficient a of the fit is possible to obtain a value for the difference $C_{11} - C_{12}$ and together with Equation (21), it's possible to get the values of the two elastic constants we are interested in.

$$B = \frac{1}{3}(C_{11} - 2C_{12}) \quad (21)$$

$$\begin{cases} C_{11} - C_{12} = \frac{a}{V_0} \\ B = \frac{1}{3}(C_{11} - 2C_{12}) \end{cases} \quad \begin{cases} C_{11} = B + \frac{2}{3}\frac{a}{V_0} \\ C_{12} = B - \frac{1}{3}\frac{a}{V_0} \end{cases} \quad (22)$$

By inserting the values found previously for the bulk modulus, the equilibrium volume and the coefficient of the quadratic fit, the obtained values for the first two elastic constants are

$$\begin{cases} C_{11} = 323.024 \text{ GPa} \\ C_{12} = 82.440 \text{ GPa} \end{cases} \quad (23)$$

8.2 Task B

To calculate the last elastic constant of MgO, a different deformation of the cubic cell is needed, and it is described by the following strain tensor

$$\hat{\varepsilon} = \begin{pmatrix} 0 & \frac{x}{2} & 0 \\ \frac{x}{2} & 0 & 0 \\ 0 & 0 & \frac{x^2}{4-x^2} \end{pmatrix} \quad (24)$$

As it has been done before, also here the new lattice parameters are calculated through Equation (14).

$$\begin{pmatrix} \mathbf{a}'_1 \\ \mathbf{a}'_2 \\ \mathbf{a}'_3 \end{pmatrix} = \begin{pmatrix} a_0 & a_0 \frac{x}{2} & 0 \\ a_0 \frac{x}{2} & a_0 & 0 \\ 0 & 0 & \frac{a_0}{1-\frac{x^2}{4}} \end{pmatrix} \quad (25)$$

$$\begin{aligned} |\mathbf{a}'_1| &= a_0 \sqrt{1 + \frac{x^2}{4}} \\ |\mathbf{a}'_2| &= a_0 \sqrt{1 + \frac{x^2}{4}} \\ |\mathbf{a}'_3| &= \frac{a_0}{1 - \frac{x^2}{4}} \end{aligned} \quad (26)$$

In this case the deformed cell can be described by a monoclinic Bravais lattice, and it needs the following 4 parameters to be defined appropriately.

$$\begin{aligned} \text{celldm}(1) &= |\mathbf{a}'_1| = a_0 \sqrt{1 + \frac{x^2}{4}} \\ \text{celldm}(2) &= |\mathbf{a}'_2| / |\mathbf{a}'_1| = 1 \\ \text{celldm}(3) &= |\mathbf{a}'_3| / |\mathbf{a}'_1| = \frac{1}{(1 - \frac{x^2}{4}) \sqrt{1 + \frac{x^2}{4}}} \\ \text{celldm}(4) &= \frac{\mathbf{a}'_1 \cdot \mathbf{a}'_2}{|\mathbf{a}'_1| |\mathbf{a}'_2|} = \frac{x}{1 + \frac{x^2}{4}} \end{aligned} \quad (27)$$

Then the procedure is the same as before, a set of energies is collected for different values of the deformation x in the range $[-0.1; 0.1]$. The difference between the energy of the deformed monoclinic structure and the equilibrium energy is equal to Equation (28) plotted and fitted by the polynomial bx^2 .

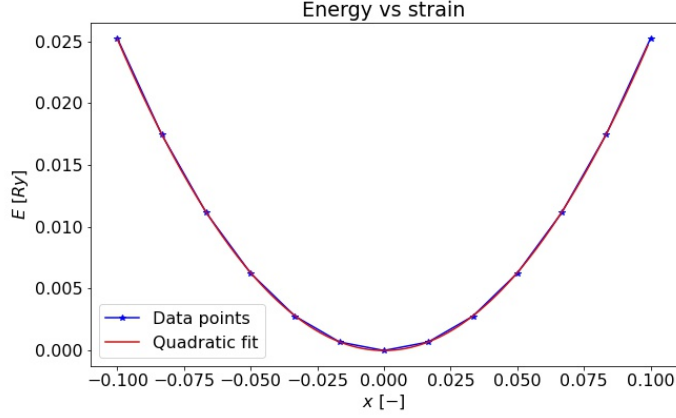


Figure 14: Data points of the difference between the energy of the distorted monoclinic cell and the energy of the undistorted cell E_0 as a function of the deformation x .

where the best fit is given by the polynomial with $b = 2.518 \text{ Ry}$.

Starting from (15) it's possible to find the relation below for the energy difference where the strain tensor has been defined as (24).

$$\Delta E(x) = \Delta E(-x) = \frac{1}{2} V_0 C_{44} x^2 \quad (28)$$

Then by comparing the coefficient of the fit and the coefficient of the equation is possible to directly find the value of the elastic constant C_{44} .

$$C_{44} = \frac{2b}{V_0} = \frac{2 \cdot 2.518 \text{ Ry}}{75.205 \text{ \AA}^3} = 146.017 \text{ GPa} \quad (29)$$

8.3 Task C

To summarize, the values found for the three elastic constants of MgO are $C_{11} = 323.024 \text{ GPa}$, $C_{12} = 82.440 \text{ GPa}$ and $C_{44} = 146.017 \text{ GPa}$. Our last aim is then to compare these values with the experimental ones found in the literature.

Lots of studies have been done about the properties of MgO at different temperatures and pressures but here the calculations have been performed at standard conditions, which means at 300 K and 1 atm . Under these conditions, experimentally it has been found that $C_{11} = 300 \text{ GPa}$, $C_{12} = 94 \text{ GPa}$ and $C_{44} = 147 \text{ GPa}$ [3]. Then it's possible to see immediately that the calculated values are similar to these ones but the accordance is not really accurate for the first two values, indeed the relative errors are respectively

7.7% and 12.2%, while for the elastic constant C_{44} the error is only 0.68%. Other values found in different studies are also reported in order to analyse the results more critically. In [1] it's possible to find that the experimental values of the elastic constants are $C_{11} = 297.0 \text{ GPa}$, $C_{12} = 95.2 \text{ GPa}$ and $C_{44} = 155.7 \text{ GPa}$. All of them are very close to the ones already found, which confirm the good approximation of these quantities. However only the constant C_{44} has been found to have an higher value, which means that our approximation wasn't very good. At the end [4] at a temperature of 300 K gives values of $C_{11} = 295.9 \text{ GPa}$, $C_{12} = 95.4 \text{ GPa}$ and $C_{44} = 153.9 \text{ GPa}$ which are still very close to the previous ones but farer away from the ones calculated here in Problem 8.

To conclude the calculation that has been done for the elastic constants of MgO doesn't give very precise results, even if they are of the same order of the experimental values.

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