

Computational Solid State Physics

2nd Midterm (DFT)

Solutions of the Midterm Exam, December 22nd 2025

For this examples I will employ as elements: A= Ni, B=Si.

1 Electronic properties of hypothetical AB compounds in the B_2 structure, ground-state structure:

1.1 Initial Structure Setup and Convergence of the Relevant Input Parameters:

The structural parameters of the B_2 structure are reported in the Appendix. Before setting up the calculation, answer the following questions:

- Q1 How many inequivalent Wyckoff positions are occupied? What is their multiplicity? Are these positions fixed or free? What is the point group? (To answer these questions you may consult the Bilbao Crystallographic Server entry attached to this document.) - **2 pts.**
- Q2 If A and B were the same element, what type of crystal structure would you obtain? What would be the corresponding space group? - **1 pt.**
- Q3 What types of symmetry operations can a space group contain? - **2 pts.**

Answers:

- A1 There are two inequivalent Wyckoff positions, i.e. $(1a)$ and $(1b)$, both with multiplicity one and point group $m - 3m$. Both positions are *fixed* because there are no free coordinates.
- A2 I would obtain a bcc lattice - space group 229.
- A3 A space group combines lattice translations with point-group symmetry operations. This means it may contain: identity, translations, inversion, rotations (2-, 3-, 4-, 6- fold), mirror reflections, screw rotations and glide plane reflections.

Using the structural data provided in the Appendix, set up an initial input file for a Quantum ESPRESSO calculation of your AB binary compound in the CsCl crystal structure. The input file should contain all parameters required to perform a standard self-consistent calculation. For the initial setup, assume a cubic lattice constant $a = 6.0$ a.u..

Since at this stage you cannot know whether the system you are setting up will be a metal or an insulator, it is safer to use an occupation method that can handle both cases. We will employ the Methfessel–Paxton smearing method, which is computationally efficient and numerically stable, with a fixed smearing value of 0.04 Ry. Therefore, the &SYSTEM section of the input file must include the following keywords: `occupations = 'smearing', smearing = 'mp', degauss = 0.04`.

Once you have verified that your input file is correctly set up, perform all convergence tests required to achieve a total-energy accuracy of at least 20 meV/atom. Produce a separate plot for each convergence test, accompanied by a brief explanation (maximum 50 words per plot). - **5 points.**

Solution:

The two panels in Fig. 1 show convergence tests of the total energy with respect to the plane-wave cutoff energy (**ecut**) and the density of the k -point grid (**kpt**). These parameters control, respectively, the number of plane waves used to expand the Kohn–Sham states and the number of k points used to approximate Brillouin-zone integrals. Increasing either parameter improves the accuracy of the calculation at the expense of a higher computational cost.

The red horizontal line indicates the convergence threshold of 20 meV/atom required by the exercise. Based on the results shown, the total energy can be considered converged for **ecut** values above 100 Ry and for **kpt** grids larger than $6 \times 6 \times 6$.

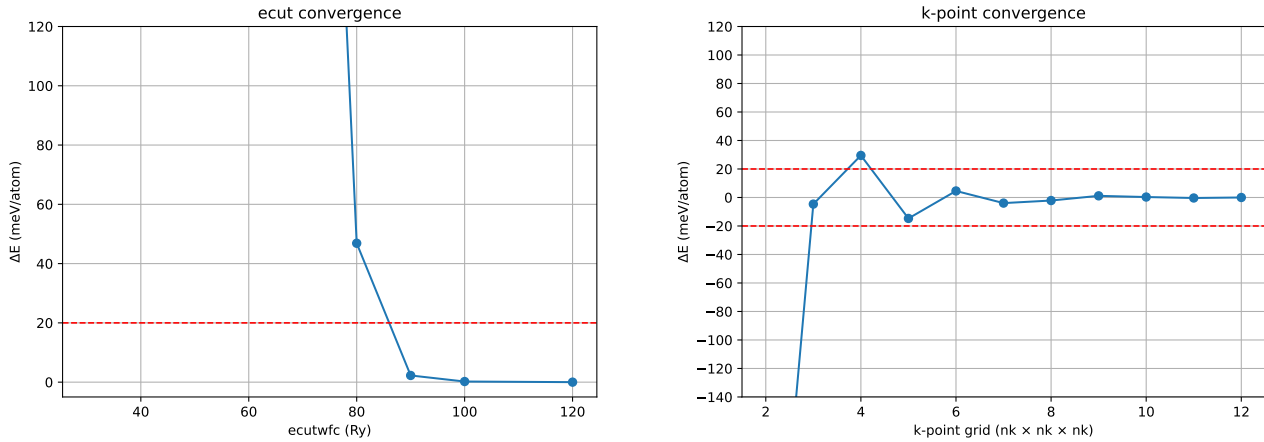


Figure 1: Convergence of the total energy with respect to the plane-wave cutoff (left) and the k -point grid density (right). The red line marks the 20 meV/atom threshold.

*Points are deducted for wrong/unreadable scale/units (MeV instead of meV), wrong convergence threshold (the text was specifying 20 meV/atom, i.e. 40 meV on the total energy, wrong setup of the input file - wrong **ibrav** or lattice constant).*

1.2 Finding the ground-state structure

In the second part of the exercise we will relax the crystal structure of the AB crystal to the hypothetical ground-state structure at ambient pressure, and compute the corresponding electronic properties.

- Q1 Explain briefly (max 100 words) what is meant by structural relaxation, and what are the steps that **Quantum ESPRESSO** needs to carry out to perform one - **1 pt.**
- Q2 What is the theoretical pressure calculated by **Quantum ESPRESSO** for the initial structure you set up? What are the forces acting on the atoms? Do you expect your final volume to be larger or smaller than the initial one? - **1 pt.**
- Q3 How many total steps did you need to find the equilibrium structure? - **3 pts.**
- Q4 Once you are sure that your calculation has reached the theoretical equilibrium volume, write down the final value of the volume and the corresponding lattice constant. - **1 pt.**

Answers:

- A1 Structural relaxation is the process of finding the atomic positions (and possibly the cell parameters) that minimize the total energy of a system, corresponding to zero forces and, if allowed, zero stress. In Quantum ESPRESSO, the steps are: starting from an initial structure, the electronic ground state is solved self-consistently; atomic forces (and stress) are computed via the Hellmann–Feynman theorem; atomic positions (and/or the cell) are updated using an optimization algorithm (e.g. BFGS); the procedure is iterated until forces and stresses fall below chosen convergence thresholds.
- A2 For a lattice constant of 6 $a.u.$ Quantum Espresso predicts a negative pressure of 259.03 kbar. The stress tensor is isotropic because the system is cubic. There are no forces acting on the atoms because the atoms sit in high-symmetry positions. Since the pressure is negative and relatively large, I expect that the crystal will relax to a smaller lattice constant.
- A3 To find the equilibrium structure QE employed 6 relaxation steps, starting from the initial structure with a volume of $216 (a.u.)^3$. A second relaxation starting from the converged structure ran for a single iteration. Fig. 2 shows the evolution of the volume and pressure as a function of relaxation step.
- A4 The final volume is $155.8743 (a.u.)^3$, corresponding to a lattice constant of $5.3817 a.u.$ (2.8479 \AA).

2 Strain:

In the second part of the exercise you will simulate the effect of epitaxial strain by contracting the in-plane lattice constants a, b , and allowing the out-of-plane lattice constant c to relax.

Formally, the effect of strain is described by a strain tensor $\hat{\varepsilon}$, with components ε_{ij} ($i, j = 1, \dots, 3$), which relates the strained (\mathbf{a}'_i) and unstrained (\mathbf{a}_i) lattice vectors through

$$\begin{pmatrix} \mathbf{a}'_1 \\ \mathbf{a}'_2 \\ \mathbf{a}'_3 \end{pmatrix} = (\mathbf{I} + \hat{\varepsilon}) \begin{pmatrix} \mathbf{a}_1 \\ \mathbf{a}_2 \\ \mathbf{a}_3 \end{pmatrix} = \begin{pmatrix} 1 + \varepsilon_{xx} & \varepsilon_{xy} & \varepsilon_{xz} \\ \varepsilon_{yx} & 1 + \varepsilon_{yy} & \varepsilon_{yz} \\ \varepsilon_{zx} & \varepsilon_{zy} & 1 + \varepsilon_{zz} \end{pmatrix} \begin{pmatrix} \mathbf{a}_1 \\ \mathbf{a}_2 \\ \mathbf{a}_3 \end{pmatrix}. \quad (1)$$

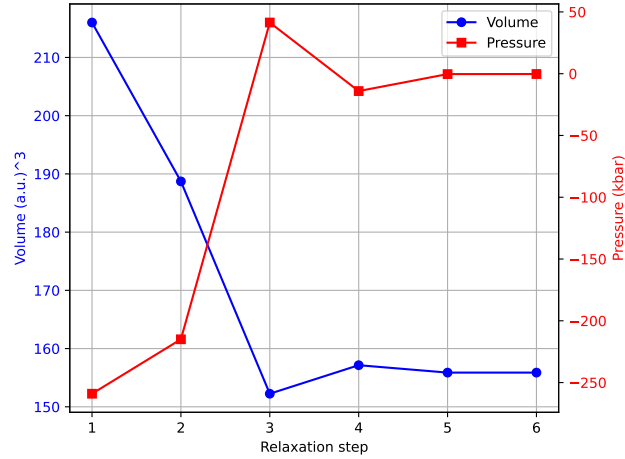


Figure 2: Volume and Pressure vs relaxation step.

The diagonal components of the strain tensor describe *normal* strains ($\varepsilon_{xx}, \varepsilon_{yy}, \varepsilon_{zz}$), corresponding to relative elongations or contractions along the Cartesian axes, while the off-diagonal components describe *shear* strains ($\varepsilon_{xy}, \varepsilon_{xz}, \varepsilon_{yz}$), corresponding to changes in the angles between the lattice vectors. A strain deformation introduces a *stress* in the crystal. The stress response is described by a stress tensor $\hat{\sigma}$, whose diagonal components $\sigma_{xx}, \sigma_{yy}, \sigma_{zz}$ describe normal stresses (pressure), while the off-diagonal components describe shear stresses.

The stress tensor is related to the derivative of the total internal energy of the crystal with respect to strain deformations through

$$\sigma_{ij} = \frac{1}{V} \frac{\partial E}{\partial \varepsilon_{ij}}, \quad (2)$$

where E is the total energy of the system, V is the volume, and ε_{ij} are the components of the strain tensor.

In this exercise you will compute the total energy and the stress tensor of your hypothetical AB crystal for different values of *biaxial in-plane strain* $\varepsilon_{xx} = \varepsilon_{yy} = \varepsilon = -0.02, -0.04, \dots, -0.16$, and use these results to detect possible supersoft behavior.

- Q1 Set up a calculation corresponding to a 10% biaxial in-plane strain $\varepsilon = -0.10$, modifying the Quantum ESPRESSO input file as follows: In the `&SYSTEM` section, set `ibrav=0` (custom-defined Bravais lattice), without modifying the value of the in-plane lattice constant. After the `ATOMIC_POSITIONS` block introduce a `CELL_PARAMETERS` block, containing the definitions of the three lattice vectors:

```
CELL_PARAMETERS (alat)
0.9000000000 0.0 0.0
0.0 0.9000000000 0.0
0.0 0.0 1.00000000
```

Here, `alat` indicates that the lattice vectors are expressed in units of a . The above choice corresponds to a 10% negative in-plane strain

Run a self-consistent calculation for this structure, and write down the value of the volume, total energy, and stress tensor.

Answer the following questions (100 words): What are the values of the three diagonal components of the stress tensor? Are they positive/negative? Why? What do you expect will happen if you let the unit cell relax in the out-of-plane (z) direction? - **3 pts.**

- Q2 Now, relax the crystal in the z direction, while keeping the a, b lattice constants fixed, with a `vc-relax` calculation. To relax the cell only along z , add the instruction `cell_dofree = 'z'` to the `&CELL` section of the input file. Write down the final value of the volume and lattice constant.

Answer the following questions (100 words): Has the unit cell expanded/contracted in the c direction? What happened to the volume? Is this expected/unexpected, based on the values of the stress tensor you computed before? **Hint:** Also in this case, to make sure your relaxation has really converged, run a second relaxation starting from the relaxed structure.

- Q3 Repeat the operations described for different values of the in-plane biaxial strain $\varepsilon_{xx} = \varepsilon_{yy} = \varepsilon = -0.02, -0.04, \dots, -0.16$. Keep track of the values of in-plane strain, volume, c/a ratio, total energy, and of the three components of the stress tensor.

- Q4 Produce three plots of the energy vs. strain, in-plane stress vs. strain, and c/a ratio vs. strain. In a normal crystal, for small strains the E vs. ε curve is approximately parabolic. In a *supersoft* material, on the other hand, the energy vs. strain has a minimum for a finite value of $\varepsilon \neq 0$, which means that the cubic B_2 structure is so strongly metastable that a relatively small in-plane deformation is enough to destabilize it towards a tetragonal structure.

Based on your plots, answer the following questions (100 words): Where is the minimum of your energy vs. ε curve? Is your AB crystal supersoft? What happens to the c lattice constant when you apply strain? Why? Are the behaviour of energy vs. strain and stress vs. strain consistent with the definitions in Eqs. (1)–(2)?

NB: It may not be possible to determine precisely the position of the minimum, if the E vs. strain curve is too flat. In this case, do not overconverge the calculation but briefly discuss what the problem is and how you would in principle solve it if you had enough time.

- Q5 **Bonus question, only if you have finished everything else:**

Construct a cubic cell with the same lattice constant corresponding to $\varepsilon = -0.10$.

Answer the following questions: What is the theoretical value of the pressure? Is it smaller/larger than the value of the in-plane stress for the same in-plane lattice constant? Why? What does this say about the elastic behaviour of epitaxially grown crystals?

Solutions:

- A1 The stress tensor is diagonal, with in-plane $\sigma_{xx} = \sigma_{yy} = 525.71$ kbar and out-of-plane $\sigma_{zz} = 636.11$ kbar components. The sign of the σ_{ii} is consistent with the fact that we have compressed the crystal; we expect that, if we allowed the c lattice constant to relax, the crystal would expand in that direction to release part of the applied strain.

NB: The numerical values of the stress components depend on the specific choice of the in-plane lattice parameters A and B . However, the appearance of off-diagonal or negative stress components would indicate an incorrectly defined input structure, as such behavior is not physically consistent with the applied strain.

- A2 The unit cell relaxed to zero stress in the c direction in 12 iterations, performed over two relaxation runs. The unit cell expanded in the c direction to release stress, leading to a final volume of $149.4425 \text{ (a.u.)}^3$, which is 18 % larger than the starting value. This was expected, since the σ_{zz} component of the stress tensor was positive.
- A3 Constrained relaxations were run for several values of negative in-plane stress, until the out-of-plane components of the stress tensor was less than 1.0 kbar. The results are summarized in table 1.

Strain	V (a.u.) ³	c/a	Energy (Ry)	σ_{xx} (kbar)	σ_{zz} (kbar)
0.00	155.8743	1.0000000000	-344.08143294	-0.22	-0.22
-0.02	157.3872	1.0723734694	-344.08251168	-39.69	1.01
-0.04	156.2810	1.1332302083	-344.08434416	-41.30	0.04
-0.06	154.1604	1.1907340426	-344.08573799	-18.28	-0.15
-0.08	152.1706	1.2536967391	-344.08593173	13.06	0.20
-0.10	149.4140	1.3148900000	-344.08410315	72.54	0.50
-0.12	146.3442	1.3776943182	-344.07915088	149.85	1.07
-0.14	143.0597	1.4429372093	-344.07033371	244.16	0.30
-0.16	139.4954	1.5098976190	-344.05670047	364.35	0.34
-0.18	135.8435	1.5806024390	-344.03690637	520.63	0.38
-0.20	132.1209	1.6554912500	-344.00919554	718.88	0.33

Table 1: Structural and energetic properties as a function of applied in-plane strain.

- A4 Fig 3 shows the behaviour of the Energy vs strain, in-plane stress vs strain and c/a ratio vs strain.

The energy (left) exhibits a negative curvature around $\varepsilon = 0$ and a shallow minimum around $\varepsilon \simeq -0.08$. Consistently, the in-plane component of the stress tensor (center) is initially negative, crosses zero around $\varepsilon \simeq -0.075$, i.e. close to the position of the energy minimum, and becomes positive at larger compressive strain. This indicate that the crystal is "supersoft", i.e. it has a tendency of the system to undergo a tetragonal distortion under small applied strain.

Tighter convergence parameters may shift the results quantitatively, but the qualitative behavior is robust; the current energy and stress accuracy is not sufficient to locate the minimum with sufficient precision.

The right panel shows that the tetragonal distortion provides a mechanism to partially release the in-plane strain: as the in-plane lattice parameter is reduced, the crystal responds by expanding along the out-of-plane direction, to partially compensate the volume compression.

- A5 A cubic crystal with the same lattice constant as the $\varepsilon = -0.10$ strained cell has a volume of $113.6324 \text{ (a.u.)}^3$ and an isotropic stress tensor corresponding to a pressure of 1084.73 kbar (108.5 GPa). This value is more than one order of magnitude larger than the in-plane stress of the strained crystal (72.54 kbar), which corresponds to a significantly larger volume of 149.41 (a.u.)^3 . The total energy is also substantially higher in the cubic case.

This comparison clearly shows that out-of-plane lattice expansion is a highly effective mechanism to release in-plane strain and minimize the internal energy of the crystal.

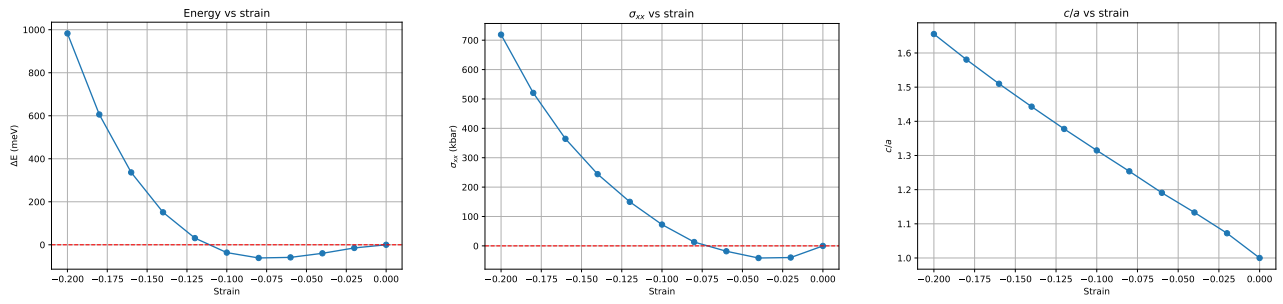


Figure 3: (Left) ΔE vs strain. (Center) σ_{xx} vs strain. (Right) c/a vs strain.

3 Appendix

3.1 Structural Parameters:

Chemical Formula: AB

Space Group (Lattice): **221** (cubic), **123** (tetragonal).

Atomic coordinates (*WyckoffPositions*): A ($1a$) B ($1b$)

3.2 Crystal structure:

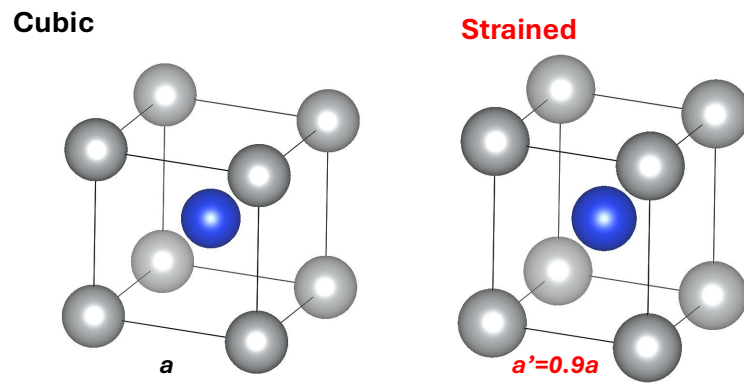


Figure 4: (Left) CsCl crystal structure, undistorted (left) and with a -10% in-plane strain.

3.3 Combinations of element pairs for each student:

St. Number	Element A	Element B	St. Number	Element A	Element B
1	Sc	Al	31	Fe	Si
2	Ti	Si	32	Co	P
3	V	P	33	Ni	Al
4	Cr	Al	34	Cu	Si
5	Mn	Si	35	Zn	P
6	Fe	P	36	Sc	Si
7	Co	Al	37	Ti	P
8	Ni	Si	38	V	Al
9	Cu	P	39	Cr	Si
10	Zn	Al	40	Mn	P
11	Sc	P	41	Fe	Al
12	Ti	Al	42	Co	Si
13	V	Si	43	Ni	P
14	Cr	P	44	Cu	Al
15	Mn	Al	45	Zn	Si
16	Fe	Si	46	Sc	Al
17	Co	P	47	Ti	Si
18	Ni	Al	48	V	P
19	Cu	Si	49	Cr	Al
20	Zn	P	50	Mn	Si
21	Sc	Si	51	Fe	P
22	Ti	P	52	Co	Al
23	V	Al	53	Ni	Si
24	Cr	Si	54	Cu	P
25	Mn	P	55	Zn	Al
26	Fe	Al	56	Sc	P
27	Co	Si	57	Ti	Al
28	Ni	P	58	V	Si
29	Cu	Al	59	Cr	P
30	Zn	Si	60	Mn	Al

Table 2: List of assigned AB combinations for each student.