

DFT Midterm, Sample Solution

Elements: Be,N

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

Preliminary Questions (2 points):

- *What is the space group number? What is the underlying Bravais lattice?*

The space group number is 225 (Fm-3m). The underlying Bravais lattice is fcc.

- *How many inequivalent Wyckoff positions are occupied? What is their multiplicity? Are they fixed or free? What is the point group?*

There are 2 inequivalent Wyckoff positions (4a and 4b). They both have multiplicity 4
The point group is m-3m for both.

- *What is the difference between space and point group?*

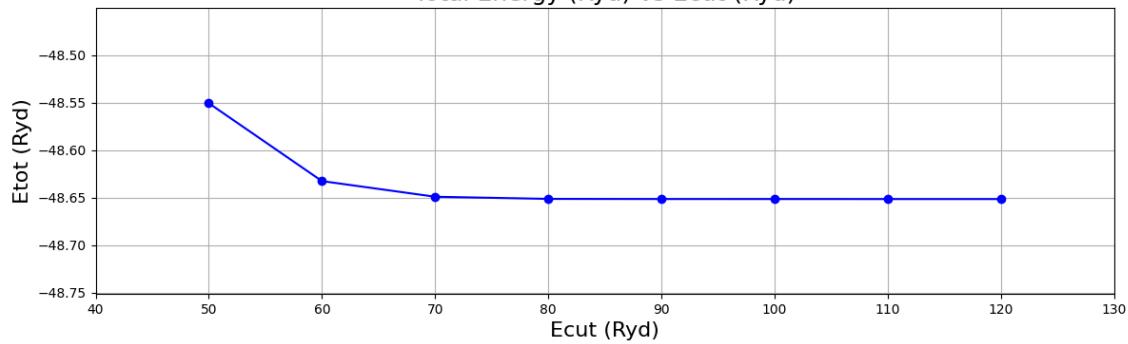
Point groups represent the set of symmetry operations (e.g., rotations, reflections, and inversions) that leave a single point fixed, describing the rotational symmetry of an object without considering translational symmetry. They apply to isolated objects in space (atoms, molecules) as well as to points in a crystal. **Space groups** include not only the symmetry operations of point groups but also translational symmetry elements such as lattice translations, glide planes, and screw axes. In 3 dimensions, there are 230 distinct space groups, which can be obtained combining the 32 crystallographic point groups with the 14 Bravais lattices.

Convergence Tests (6 points):

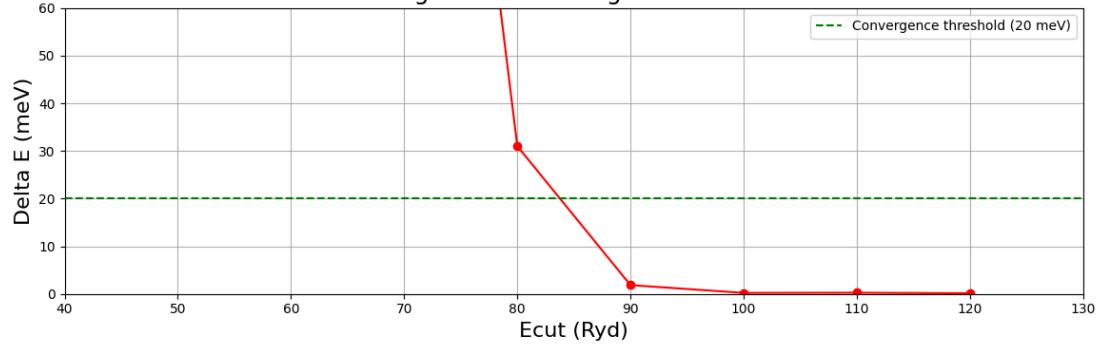
- *Once you have verified that your input file is correctly set up, run all convergence tests required to attain an accuracy on the total energy of at least 10 meV/atom. Produce a separate plot for each convergence test, with a short explanation (max 50 words for each plot).*

The plots below show the convergence of the calculated total energy with respect to the kinetic energy cutoff (number of planewaves) and grid for reciprocal space integration. Calculations are carried out for increasingly larger values, at regular intervals. A calculation is considered converged when the total energy difference between a calculation with a given parameter and one with increased parameter is lower than a set threshold, i.e. 20 meV (10 meV/atom) in the present case. The green lines mark the threshold.

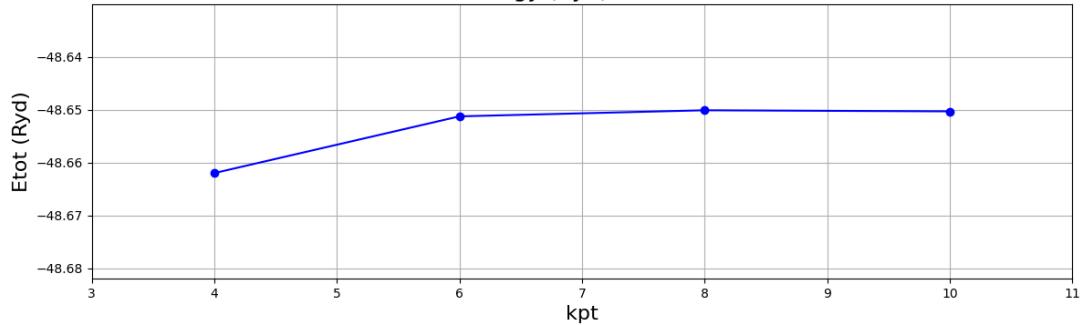
Total Energy (Ryd) vs Ecut (Ryd)



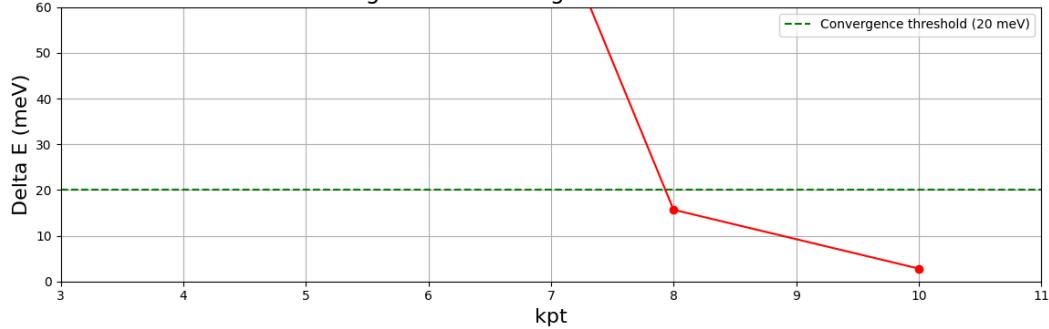
Convergence Monitoring: Delta E vs Ecut



Total Energy (Ryd) vs mesh size



Convergence Monitoring: Delta E vs mesh size



NB: Points are subtracted for unreadable graphs (too large scale), lack of explicit convergence criteria, lack of description, figures not included in the text).

2.2 Structural Relaxation:

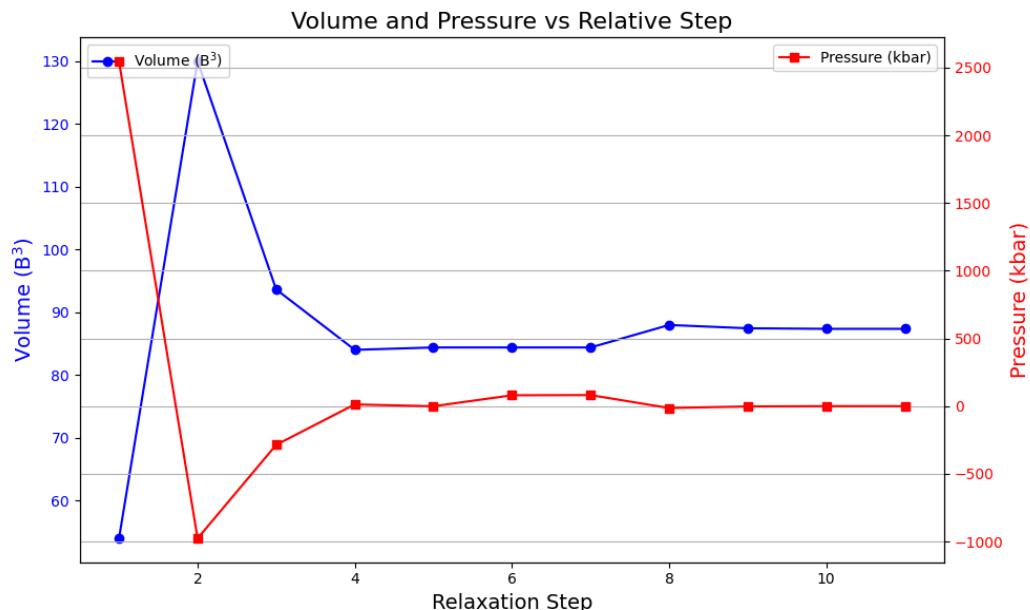
- Explain briefly (max 100 words) what is meant by structural relaxation, and how quantum espresso computes forces acting on individual atoms and on the unit cell (pressure/stress) - (2 points).

Thermodynamically stable and metastable structures correspond to global and local minima of the potential energy surface, i.e. the generalized potential energy hypersurface in the space of atomic coordinates. In a minimum, all forces and stresses acting on atoms are zero. In a structural relaxation, atomic positions and unit cell parameters are progressively modified to minimize forces and stress, using ad-hoc algorithms, such as the conjugate-gradient methods. Quantum Espresso computes forces and stresses applying the Hellmann-Feynmann theorem to derivatives of the total energy with respect to atomic displacements and cell deformations, respectively.

- 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 point).

The initial pressure is 2545 kbar (254 GPa). This means that for P=0 the final volume will be considerably larger.

- Provide a plot that you would use to monitor the structural relaxation, with a short description, explaining which quantities you decided to monitor and why (3 points).



The plot below shows the evolution of the predicted volume and pressure as a function of iteration (I am plotting two consecutive relaxation runs). The figure clearly shows that there are larger oscillations at the beginning, and then both values converge.

NB: Use of wrong criteria/plots, such as Enthalpy, Energy, Pressure vs Volume and not relaxation step considerably reduces the points - these quantities define the Equation of State, but do not offer any hint on whether the relaxation is converging.

- 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 (**4 points**).

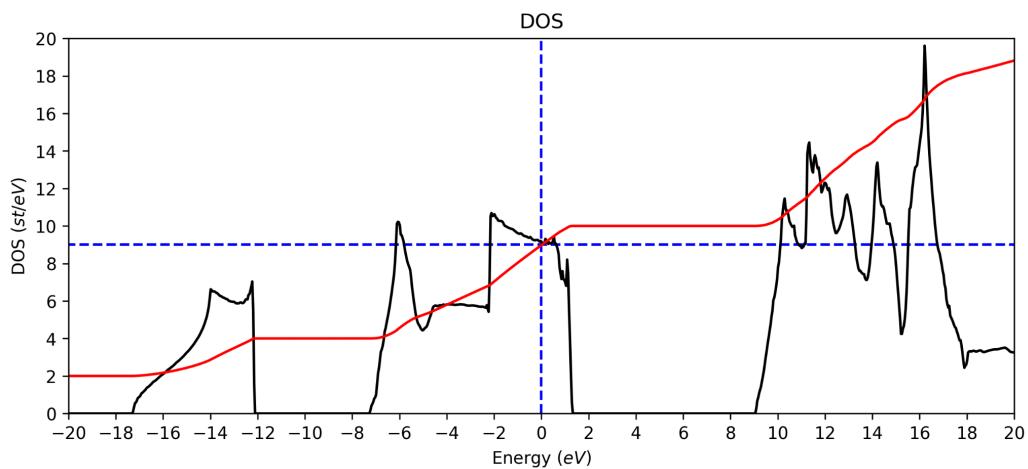
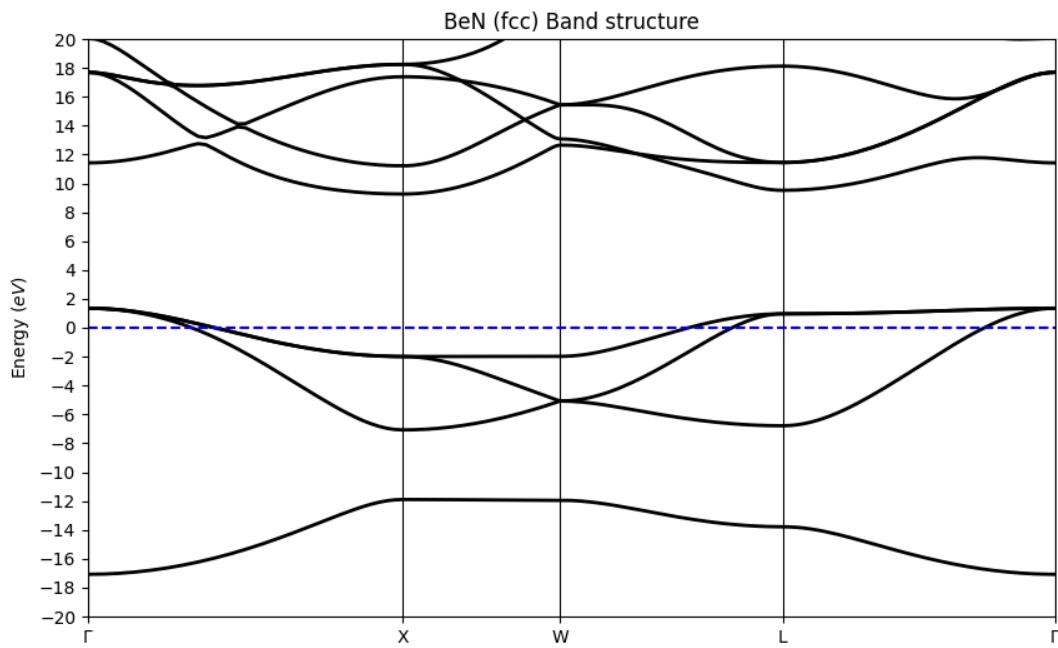
In my case the final equilibrium volume is **87.5373 B³** and the corresponding lattice constant is **7.044 B**. Note that I had to perform two consecutive relaxation runs to achieve convergence because the starting structure was too far from 0 pressure.

NB: Points are awarded/reduced for incorrect structural relaxation.

2.3 Electronic Structure:

- Compute the electronic band structure and Density of States of your AB crystal. A list of special k points for the fcc crystal is provided in the Appendix (**4 points**).

The figures below show the calculated band structure of BeN and the corresponding Density of States (DOS) in an energy interval of ± 20 eV around the Fermi level. Energies have been rescaled with respect to the Fermi level.



Based on your plots, answer the following questions: (4 points total).

- How many bands are filled in your system? Is this consistent with the number of valence electrons?

The number of valence electrons is 9 (5 from N and 4 from Be, which includes semicore electrons). There are 2 fully filled bands (the semicore band of Be is well below EF), and three more bands cross the Fermi level. This is fully consistent with the number of valence electrons, as each band can accommodate 2 electrons (one per spin).

- Are there any semicore states in your system? What are they? Why can you have/not have semicore states in a DFT/psp calculation? (max. 100 words)

Yes, the Be pseudopotential includes semicore electrons. These states are located well below in energy compared to valence states, but may participate in the bonding in some particular cases (like high-pressure phases). Including semicore states makes a pseudopotential “harder” but also more transferable.

- Is your system a metal or an insulator? How can you answer this question based on your results?

My system is a metal since it has an odd number of electrons. The band structure is consistent with this, as there is no gap at the Fermi level.

3.1 Construction of the Conventional Cell:

- What are the lattice constant and volume of the conventional cell? What is their relation to the fcc one? (1 point)

The lattice constant of the primitive and conventional cell is the same, but the volume of the conventional cell (simple cubic) is 4 times larger than the fcc one.

Primitive cell:

$$\mathbf{R}_1 = a(0, \frac{1}{2}, \frac{1}{2})$$

$$\mathbf{R}_2 = a(\frac{1}{2}, 0, \frac{1}{2})$$

$$\mathbf{R}_3 = a(\frac{1}{2}, \frac{1}{2}, 0)$$

Conventional cell:

$$\mathbf{R}_1 = a(1, 0, 0)$$

$$\mathbf{R}_2 = a(0, 1, 0)$$

$$\mathbf{R}_3 = a(0, 0, 1)$$

- How many atoms are there in the conventional cell? How many formula units? What is the difference? (1 point)

The conventional cell contains 4 formula units (BeN), and hence 8 atoms.

- Write down the coordinates of all atoms in the conventional cell, and explain how you obtained them. (2 points)

There are 8 atoms in the conventional cell; their coordinates can be obtained by summing the basis vectors of the fcc lattice in the conventional cell to the Wyckoff positions of the two atoms in the primitive cell, and translating back all coordinates to the Wigner Seitz cell (i.e. 1 0 0 translates back to 0 0 0 etc).

Be1 0,0,0

N1 0 0 ½

Be2 ½ ½ 0

N2 ½ ½ ½

Be3 ½ 0 ½

N3 ½ 0 0

Be4 0 ½ ½

N4 0 ½ 0

- *How many A nearest neighbours does each B atom have? (and vice-versa). What is their relative distance? (1 point)*

Each A/B atom has 6 n.n. of B/A type, at $a/2$, along the 6 +/- cartesian directions.

- *Setup a self-consistent input file for quantum espresso. Run the self-consistent calculation and explain how you can make sure that your conventional cell is correctly set up, based on your previous results in the primitive fcc cell. (2 points)*

To check whether the unit cell is correctly set up, apart from visualizing the structure and measuring interatomic distances, one should check that physical observables remain unchanged. For example, the energy/atom, pressure and forces on the atoms, the electronic DOS should remain the same.

3.2 Vacancies:

- *What is the concentration of vacancies in the structure you just set up? What is the number of electrons? Why? (1 point)*

There is one vacancy/unit cell, i.e. $\frac{1}{8}$ atoms. The number of electrons is $4 \times 9 - 4 = 32$ valence electrons.

- *Compute the forces/stresses acting on the structure with the vacancy. How large are they? Is this result expected? Why? (2 points)*

The stress is around 8 GPa, and isotropic. This indicates that the lattice would contract, if allowed to relax. The result is expected since removing one atom generates a void in the structure, which the system tries to compensate by reducing the volume.

Forces on all atoms are zero. This is to be expected since the atoms surrounding the vacancy are placed symmetrically around it, and hence all interatomic forces cancel by symmetry. To simulate what happens in a true physical system, one would have to introduce a random displacements on all atoms and let the structure relax.

- *Produce a 2D plot of the charge density of the cubic conventional cell with and without vacancies, using the attached script (4 points).*

The two plots are attached below. The charge localization is typical of a ionically-bonded structure, with charge localizing on the cations. Introducing a vacancy creates a

perturbation of the local symmetry, and the charge density distribution becomes more elongated

