

Hexagonal Boron Nitride

Group 2A and 2B

1 Input set-up

Hexagonal boron nitride has a layered structure similar to graphite. Within each layer, boron and nitrogen atoms are bound by strong covalent bonds, whereas the layers are held together by weak van der Waals forces. The experimental lattice parameters are $a = 4.716$ bohr and $c/a = 2.582$.

- generate an input file for an SCF computation: you should decide which pseudopotential you will use (norm-conserving, ultrasoft, PAW) and the approximation for the exchange-correlation potential (LDA, PBE, PBE-sol).
- visualize your crystal structure with the software XCRYSDEN. This will help you understand if you are going to simulate the correct system or not with the input file you have written!

2 Convergence tests - bulk

- Set a sufficiently high grid sampling in k-space (e.g. $6 \times 6 \times 2$) and vary the value of E_{cut} . Be careful that you must also change the value of E_{rho} if you are using US or PAW pseudopotentials! Then plot the total energy per atom as a function of E_{cut} . We say that the energy is converged when its variations are ≤ 1 mRy. What is your converged E_{cut} ?
- Now set E_{cut} to the value which assures convergence as found at precedent point. Vary the k-point grid and plot the total energy per atom as a function of the number of k-points. What is your converged k-point grid?

3 Vacuum convergence - monolayer

The standard way to calculate surface properties from first-principles is a supercell representing an infinite two-dimensional system oriented to expose the facet of interest, separated from periodic images by a large vacuum. The vacuum distance between repeated images should be increased until there is no more interaction between adjacent slabs. For a converged, clean system in vacuum, the surface energy can be defined as:

$$\gamma = \frac{1}{2A}(E_{slab} - NE_{bulk})$$

where A is the surface area of the unit cell, E_{slab} is the energy of the supercell, E_{bulk} is the bulk energy per atom and N is the number of atoms in the supercell.

- In the input files set `assume_isolated = 2D` : Total energy, forces and stresses are computed in a two-dimensional framework. Linear-response calculations are done on top of a self-consistent calculation with this flag will automatically be performed in the 2D framework as well.
- Increase the vacuum until γ is converged. Start from the atomic thickness + 10 bohr, which should be a safe estimate. Notice that since that, if you are using crystal coordinates, you should also rescale them. Usually a vacuum of ~ 10 Å should be enough to guarantee converged surface properties.
- Now relax ions+lattice parameters as done in the bulk: only in-plane stresses make sense and one should use `cell_dofree=2Dxy` in a `vc-relax` calculation. What is the new lattice parameter? what are the new ions' positions? Compare both the theoretical lattice parameter and the theoretical bulk modulus with their experimental counterparts. What is the error? What is the cause?

4 Electronic structure

Starting from either the theoretical relaxed structure or the experimental structure, both with the converged parameters:

- Perform a band computation and extract the electronic dispersion relation. From this you can get an estimate of the direct/indirect energy band gap: compare with the experimental one, what is the error? Moreover, by fitting band minima or maxima with a parabola you can extract the effective masses of carriers.
- Perform a non-self consistent computation with increasing value of the k-point grid and extract the electron density of states until convergence is reached. Plot the converged result and discuss if the system can be considered free-electron like.

5 Vibrational properties

- Perform a convergence test for phonons at $q = \Gamma$: change the k-grid in the SCF cycle and for each case perform a phonon computation until convergence of phonon frequencies is reached.
- With the converged k-grid, perform a phonon computation on a coarse grid of q-points, for example you can start with $3 \times 3 \times 1$. Extract the phonon dispersion relation and the phonon density of states. From this you can fit acoustic modes with lines, whose slope will give you the sound velocity. Moreover, from the density of states you can get an estimate of both the Debye and Einstein temperature.
- Now increase the grid of q-points and see if phonon dispersion relation and density of states change.