NANO266 Lab 4 - Al surfaces

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1 Introduction

In this lab, we will look surface calculations with PWSCF.

2 Initial setup

By this stage, you should already have everything set up. Make sure you are in the lab4 folder by doing:

cd <path/to/repo>/labs/lab4

3 Running calculations

You will still be running the calculations using the queues on Comet. However, it is important to note that surface calculations can take much longer than bulk calculations. It is therefore imperative that you perform these calculations prudently. It is very easy to burn through all the allocated CPU time if you are not careful.

4 Q1 (20 points): The (100) surface of Al

We will first start by calculating the energy of the (100) surface in Al. You need to perform a convergence with respect to both slab and vaAlum size. Use an energy cutoff of 30 Ry with a k-point grid of $16 \times 16 \times 1$.

1. Start by first finding the equilibrium structure of fcc Al. You have already done this in lab 3, but we are going to do this again using the SCF method, i.e., by plotting the equation of state of energy versus the lattice parameter. Converge your lattice parameter to within 0.001 angstroms. For reference, the experimental lattice parameter

is 4.05 angstroms. A template file `Al.100.bulk.pw.in.template` has already been provided. Please use the `scf.py` script to perform these calculations. As usual, please scan with a fairly coarse grid (e.g., 0.01 increments) before performing scans with a more dense grid near the minimum energy. Record down the lattice parameter in Bohr and energy in Ry.

2. Using the lattice parameter you obtained in part 1, perform a calculation of the Al (100) surface. A sample `Al.100.surf.pw.in.template` file has been provided to you, as well as a `fcc_surf_gen.py` (type `fcc_surf_gen.py -h` for help). Start by typing:

   ```
   python fcc_surf_gen.py --a 7.65 --miller "100" --k 16 --nslab 3 --nvac 3
   ```

The output should be something like the following:

```
 &CONTROL
  calculation = 'relax' ,
  outdir = './tmp' ,
  prefix = 'Al_100_3_3',
  pseudo_dir = './' ,
  tprnfor = .True.,
  tstress = .True.,
 /
 &SYSTEM
  ibrav = 6,
  celldm(1) = 7.65,
  celldm(3) = 6,
  nat = 12,
  ntyp = 1,
  ecutwfc = 30,
  ecutrho = 150,
  occupations = 'smearing',
  smearing = 'cold',
  degauss = 0.025,
 /
 &ELECTRONS
  diagonalization = 'david',
  conv_thr = 1.D-6,
  mixing_beta = 0.3,
  mixing_mode = 'local-TF'
 /
 &IONS
  ion_dynamics = 'bfgs',
 /
ATOMIC_SPECIES
  Al   26.98  Al.pbe-n-van.UPF
ATOMIC_POSITIONS crystal
```

```
  Al 0.0 0.0 0.0
  Al 0.5 0.5 0.0
  Al 0.5 0.0 0.0833333333333
  Al 0.0 0.5 0.0833333333333
  Al 0.0 0.0 0.166666666667
  Al 0.5 0.5 0.166666666667
  Al 0.5 0.0 0.25
  Al 0.0 0.5 0.25
  Al 0.0 0.0 0.333333333333
  Al 0.5 0.5 0.333333333333
  Al 0.5 0.0 0.416666666667
  Al 0.0 0.5 0.416666666667
K_POINTS automatic
  16 16 1   0 0 0
```

There are several important things to note about this input file:

- The `calculation` parameter has been set to `relax`. This allows the atoms to move, but fixes the cell shape.
- The `ibrav` tag has been set to 6, which is a tetragonal cell. To perform a surface calculation, we are extending the cell in the c-direction and removing atoms. So we are breaking symmetry in that direction.
- The `celldm(3)` parameter is set to 6. This means that we have constructed a supercell where the c lattice parameter is 6 $\times$ that in the a and b directions.
- In the ATOMIC_POSITIONS section, note the c fractional coordinate of each atom. The conventional fcc cell has four atoms. Look at how each group of four atoms are related to each other by a translation in the c direction. It is absolutely critical that you understand that the c fractional coordinate depends on **both your slab size as well as your vacuum size**!

You can write the output to a file by giving it the `--outfile` option:

```
python fcc_surf_gen.py --a 7.65 --miller "100" --k 16 --nslab 3 --nvac 3 --outfile Al10
```

To do this question, vary nslab and nvac and look at how the energies change with nslab and nvac. Start by keeping nslab = 2 and vary nvac between 1 and 4. Get a value of nvac that gives a reasonable convergence of surface energies (say 0.01 Jm $^{-2}$). Note that the surface energy is given by:

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

where E_{slab} is the energy of the slab, E_{bulk} is the energy per atom of bulk Al, and N is the number of atoms in the slab.

Using the converged value of nvac, vary your nslab between 1 and 6. Again, determine the value of nslab that converges the surface energies to 0.01 Jm $^{-2}$. Do not exceed `nslab = 6` for this exercise.

Report your final surface energy in Jm $^{-2}$. Also discuss how the atoms at the surface has relaxed and comment on why.

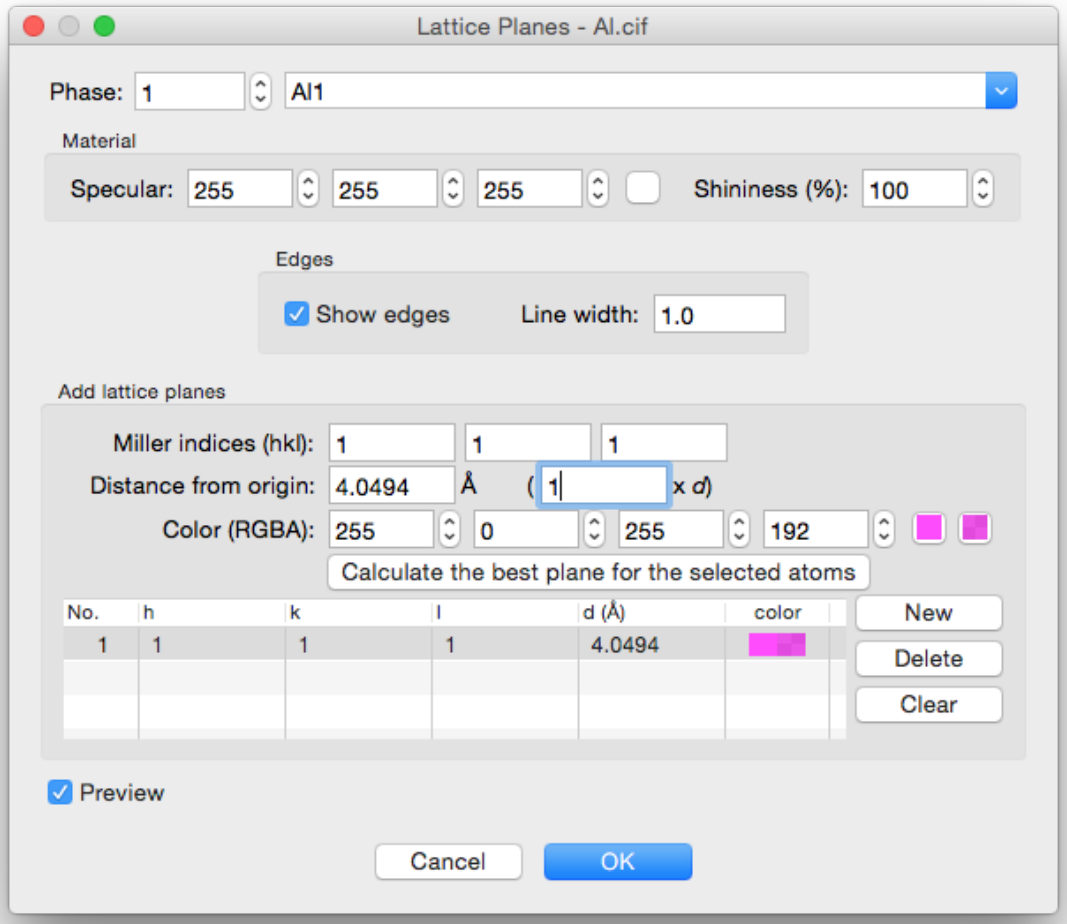
5 Q2 (30 points): The (111) surface of Al

We will now explore the (111) surface of Al. For this, we need to first get our slab structure. Unlike the (100) surface that is simply along the cubic crystallographic axes, getting the (111) surface involves some work.

The first thing to note is that the fcc structure is in fact a stacking of hexagonally close-packed atoms along the [111] direction.

We will now show you how you can use VESTA (http://jp-minerals.org/vesta/en/) to generate any surface structure. First download and install VESTA for your platform. Here is the step by step guide to creating the Al (111) surface.

- Step 1: Open the `Al.cif` in VESTA. This is the standard `fcc` conventional unit cell of Al.
- Step 2: Let us now first insert the (111) lattice plane into the crystal for easier visualization. Go to `Edit->Lattice Planes`. Click new, then type in (111) for your Miller indices and set your `d` to 1. Your dialog box should look something like the figure below:



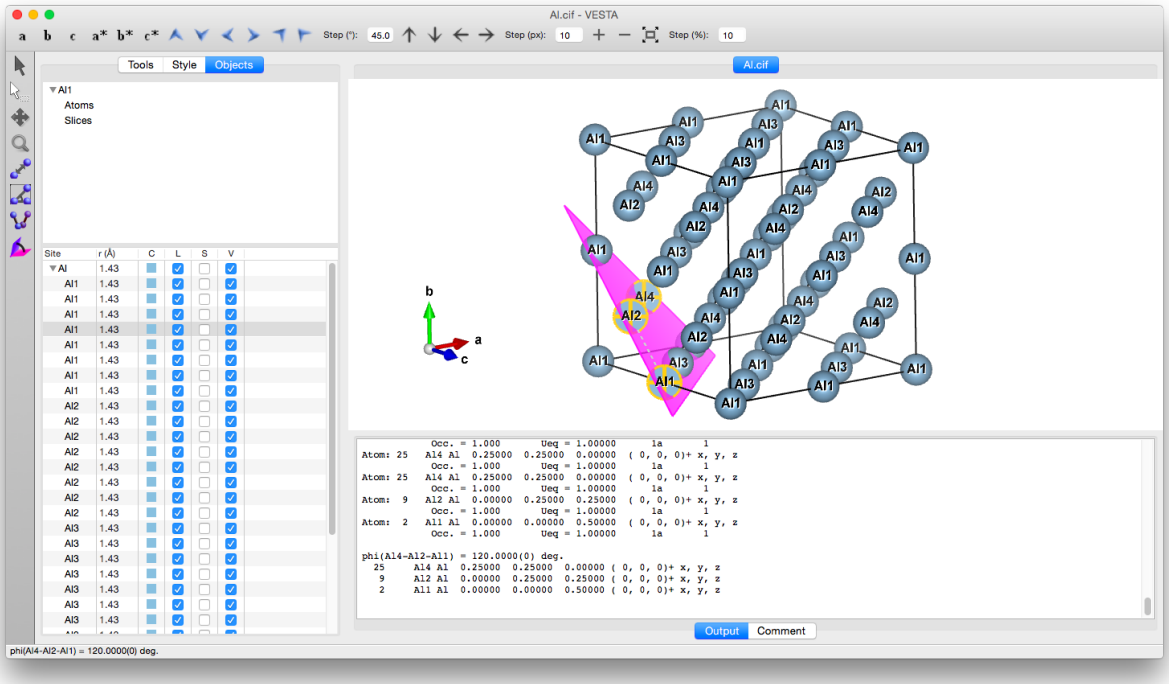
- Step 3: Click `Ok`. You will see that a lattice plane has been drawn in your crystal. Go to `Edit->Edit Data->Unit Cell`. Click `Remove symmetry` and then hit `Apply`. We need to break symmetry before we can create the slab. Then go to the `Structure Parameters` tab and assign different labels for each of your atoms. This makes it easier to identify the atoms later. Hit `Apply` again.

- Step 4: The next step is to generate a larger unit cell as we are going to "cut" the crystal in a different orientation that goes beyond the limits of the unit cell. Go back to the `Unit Cell` tab. Click on `Options` and then enter 2 for all the diagonal elements of the rotation matrix. That generates a

$$2 \times 2 \times 2$$

supercell of your crystal. Click `Ok` for all the warnings. Click `Ok` until you close all dialog boxes and see a larger version of the Al cell.

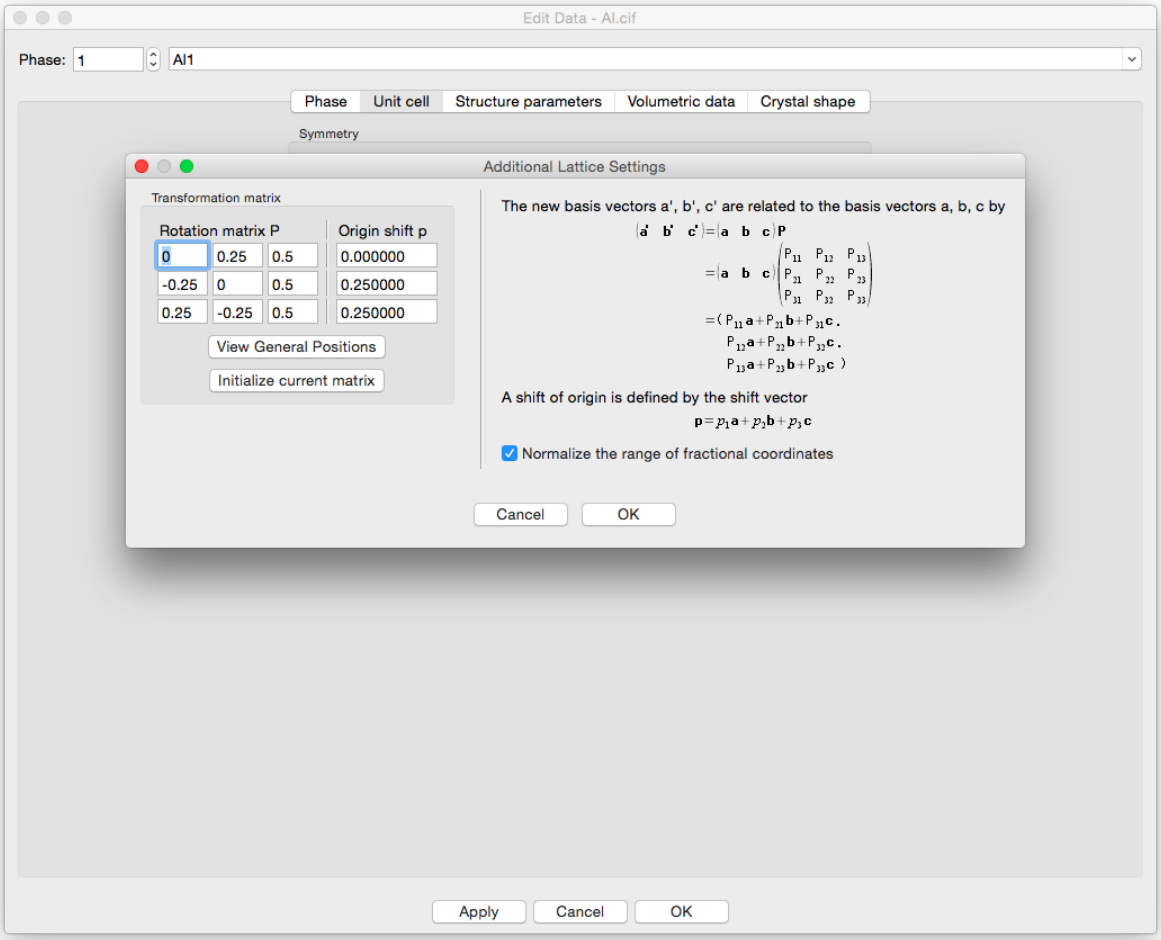
- Step 5: Click on `Objects` and check the `L` (label) for the topmost Al. All the Al atoms should now be labeled.



- Step 6: We are going to now redefine our lattice vectors so that our **a** and **b** lattice vectors are within the (111) plane and our **c** lattice vector is non-parallel (ideally normal to the plane). To do this, we can observe that we can define atom `Al2` in the figure above to be the origin, and set our new $\mathbf{a}'$ to be the vector connecting `Al2` and `Al1`, and $\mathbf{b}'$ to be the vector connecting `Al2` and `Al4`. Using the VESTA atom picker, we can determine that the crystal coordinates of the atoms to be:

$$\mathbf{r}_{\mathbf{Al4}} = (0.25, 0.25, 0)$$
$$\mathbf{r}_{\mathbf{Al2}} = (0, 0.25, 0.25)$$
$$\mathbf{r}_{\mathbf{Al1}} = (0, 0, 0.5)$$

- Step 7: Go to `Edit->Unit Cell` again, and click `Options`. We then need to enter our rotation matrix and origin shift to the values we have determined in the previous step. Note the way the lattice vectors are transformed based on the documentation (the vectors are in a row format and the matrix is defined in columns). For the last column, we set it (0.5, 0.5, 0.5), since we have already doubled our cell in all directions (see figure below). Click `Ok`. Then go to the `Structure Parameters` tab. You will find that there are a lot of duplicate atoms due to the mapping of supercell atoms onto each other. Just click `Remove duplicate atoms` and you should be left with three unique atoms.



- Step 8: Click `Ok` until you end up in the crystal. You will find that you now have a hexagonal cell and the (111) lattice plane is now parallel to your **a** and **b** lattice vectors. Export the atom position to a file using `File->Export Data`. Choose the VASP POSCAR format, even though we will not be using VASP for our calculations.

Using the coordinates (e.g., viewing the POSCAR file in a text editor), you will need to modify the `fcc_surf_gen.py` to work for the (111) lattice plane. Look at `Al.111.bulk.pw.in.template` and `Al.111.surf.pw.in.template`. Note that we are now using a hexagonal Bravais lattice setting.

Repeat your calculations of surface energy in Q1 for the (111) lattice plane. You do not need to search for the optimal lattice parameters again. You need to work out the appropriate hexagonal lattice parameters based on your optimal cubic lattice parameters. Use a $16 \times 16 \times 1$ k-point grid for your slab calculations. Also, you may perform your calculations using 2 vacuum layers and 3 slab layers. There is no need to redo the convergence study.

Report your final (111) surface energy for Al in Jm $^{-2}$. Discuss how the atom at the surface has relaxed and comment on why the relaxtion occurs the way it does.

Comment on the difference in surface energy between the (100) and (111) surface. Which one is lower in energy? Can you provide a likely physical reason for the relative stabilities of the surfaces?

6 Q3 (50 points): Binding energy of H atom on Al

In the final question, we will investigate the adsorption of a hydrogen atom on the Al (111) surface. As this is a final question of the course, you should have enough experience with calculations by now. We will keep only provide a few guidelines, and you will be responsible for creating the necessary input files, either manually or using VESTA, and performing the calculations.

The binding energy of an H atom on a surface is given by:

$$E_b = E(\text{slab + H}) - E(\text{slab}) - \frac{1}{2}E(\text{H}_2)$$

To calculate this, you need to perform calculations of a slab with the H atom, as well as the energy of H2 gas. To do the latter in periodic boundary conditions, you need to do a "particle in a box" calculation, i.e., you create a big enough simulation box (typically, sizes $\sim$10 angstroms should be sufficient, but you need to do your own tests), and put your H2 molecule in a non-symmetry position, and perform a calculation that allows atomic positions but not cell volumes to relax.

For the slab + H calculation, you will need to investigate the different absorption sites on the Al surface. For the (111) hexagonal surface, there are three high symmetry sites - the `on top'' site above an Al atom, the`bridge" site between two nearest neighbor Al atoms, and the "hollow" site between three nearest neighbor Al atoms. There are 2 such hollow sites to be considered. The stacking in the direction is given by the A-B-C-A-B-C sequence. Assuming the surface ends with a 'C' plane, the hollow-site will either correspond to a 'A'-plane hollow site or 'B' pane hollow site. You will need to create simulation cells to model each of them. Note that you will need to extend your unit cell in the **a** and **b** directions as well to ensure that H atoms in neighboring periodic images are not too close to each other. Use a reasonable sized cell, and scale your k-point grid accordingly. Because we are comparing relative energies between different sites rather than absolute binding energies, you do not need to use very large cells. The calculations should be doable using a single processor. If your calculations are taking too long, rethink your supercell and k-point grid.

Report all your binding energies in eV. Discuss the relative binding energies of H on the different sites, and whether the results are in line with your chemical intuition. Can you estimate the diffusion coefficient for H on the Al(111) surface?