Study of the relaxation of the Al (100) surface via Ab Initio simulations

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1 Introduction

The aim of this report is use Ab Initio (AI) methods to study the surface of an Aluminium crystal. In order to do this the Quantum Espresso [1] programm will be used to first find the bulk value of the lattice constant for Al and then simulate a surface to study its relaxation from the bulk configuration.

2 Estimation of the bulk lattice constant

The idea to find the equilibrium lattice constant a_0 is to simulate the crystal at different values of a and for each of them compute the pressure P resulting on the system. At this point data can be fitted with the Murnaghan equation of state:

$$P(V; V_0, K_0, k_0') = \frac{K_0}{K_0'}\left(\left(\frac{V}{V_0}\right)^{-K_0'} - 1\right)$$

where V is the volume of the unit cell and V_0 the one at equilibrium, while the bulk modulus is $K = -V\left(\frac{\partial P}{\partial V}\right)_T \approx K_0 + K_0' P$. But to have meaningful results from the simulations one has first to optimize some parameters of the Quantum Espresso (QE) code.

2.1 Optimization of the simulation parameters

Structure of the unit cell Since the crystalline structure of Al is face centerd cubic (fcc) with no basis, it is enough to consider an fcc unit cell with a single Al atom at the origin.

Pseudopotential From all the many pseudopotentials provided in the QE library, here a non relativistic one (`Al.pz-vbc.UPF`) and a scalar-relativistic one (`Al.pbe-nl-rrkjus_psl.1.0.0.UPF`) are tested. With the latter one obtains a better approximation but the simulations take longer.

Number of k points and smearing To sample the first Brillouin zone a grid with `n k points` in each direction is used: the higher the number the more accurate is the result, but also the longer the simulation takes. To mitigate this coarse sampling of the Brillouin zone one can use a smearing of the energy levels whose amplitude is controlled by the variable `degauss`. By monitoring how the total energy behaves with these two parameters one can find a proper value for them: `n k points` $= 8$, `degauss` $= 0.02\,\mathrm{Ry}$ (fig 1 where the two 1D plots are taken at the best value of the other parameter.).

Energy cutoffs The orbitals for the electron are expanded in plain waves, and the number of waves used in the expansion is controlled by the variable `ecutwfc`. Similarly the number of waves used for computing the density is controlled by `ecutrho` which by default is set to 4`ecutwfc`. In fig 2 one can see that with `ecutwfc` $= 80\,\mathrm{Ry}$ error on the energy is of the order of $10^{-7}\,\mathrm{Ry}$. With this setting the effect of the cutoff on the density is negligible and so the default value is used.

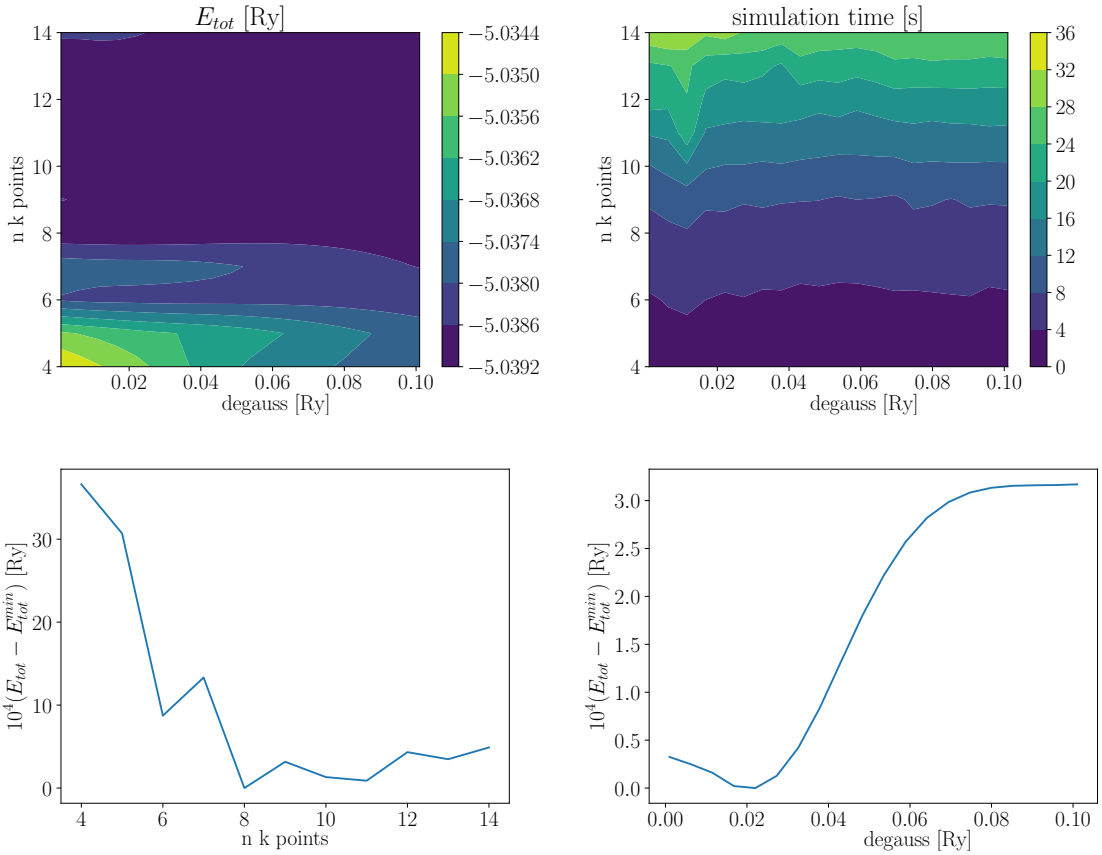

Figure 1: Behavior of the total energy and the simulation time as a function of the number of k points and of the amount of smearing. Simulations performed on the relativistic pseudopotential, but with the other the results are very similar.

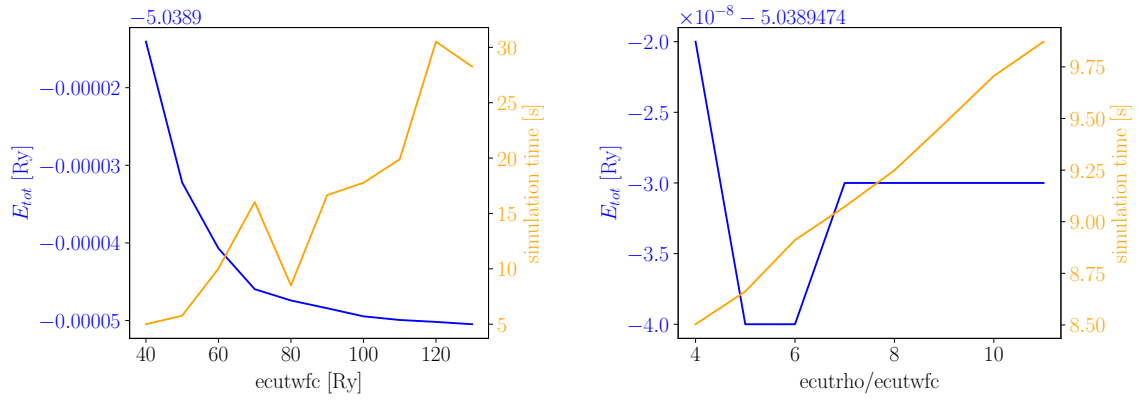

Figure 2: Total energy and simulation time as a function of the two energy cutoffs.

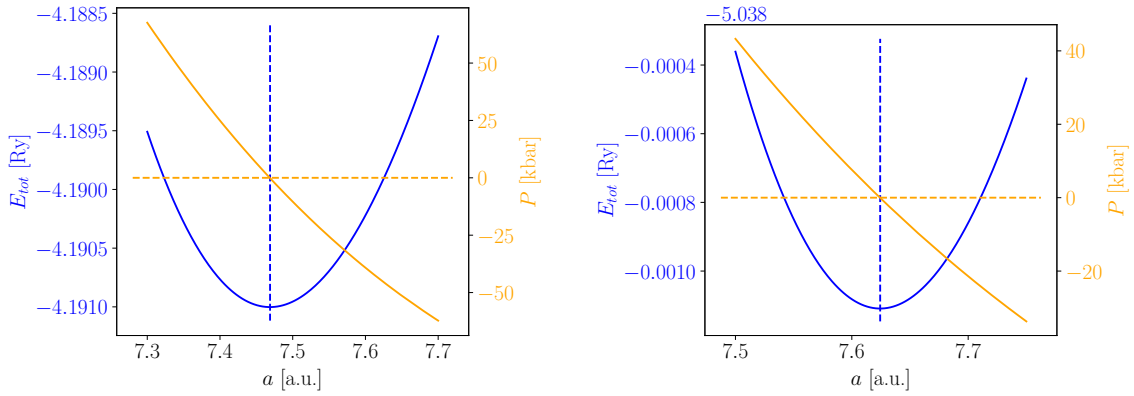

Figure 3: Behavior of the total energy and pressure as a function of the lattice constant for the non relativistic and relativistic pseudopotential respectively.

	a_0 $[a.u.]$	K_0 [kbar]	K_0'
non relativistic	7.46834 ± 0.00004	841.0 ± 0.2	4.73 ± 0.01
relativistic	7.624231 ± 0.000009	775.76 ± 0.06	4.995 ± 0.006
experimental [4]	7.646	721	4.72

Table 1: Results of the fit of the pressure with the two pseudopotentials and corresponding experimental data

2.2 Results

The results of the scanning of the lattice parameter are reported in fig 3 while the results of the fit with with the Murnaghan equation are in tab 1.

References

[1] P. Giannozzi et al. *Quantum Espresso* `http://www.quantum-espresso.org`

[2] Wikipedia *Murnaghan equation of state* `https://en.wikipedia.org/wiki/Murnaghan_equation_of_state`

[3] *Quantum ESPRESSO tutorial: Self-Consistent Calculations,Supercells, Structural Optimization* `http://indico.ictp.it/event/8301/session/95/contribution/528/material/slides/0.pdf`

[4] D.E. Grady *Equatio of state for solids* `https://doi.org/10.1063/1.3686399`