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. Also to compensate for the creation of artificial energy gaps due to the finite size of the system one can smear the energy levels. The smearing 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.).
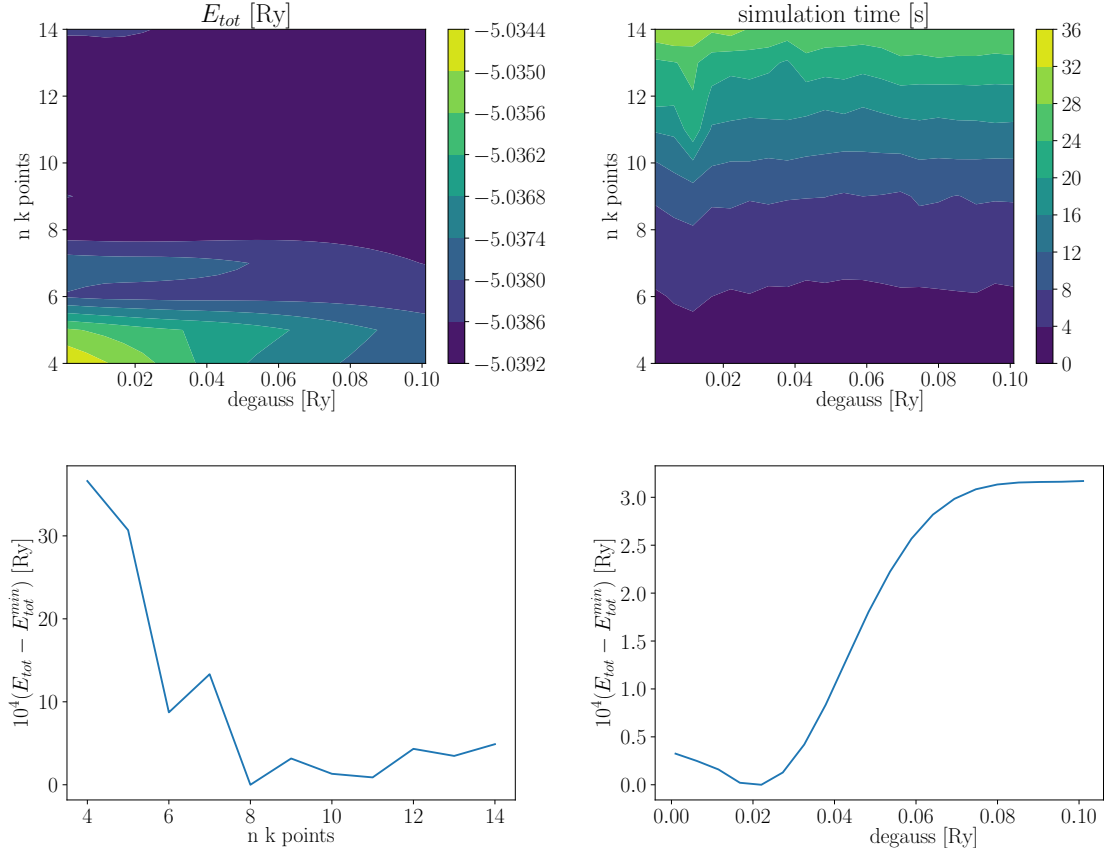
Figure 1: Behavior of the total energy and the simulation time as a function of the number of k points and of the amount of smearing. These plots come from simulations performed on the relativistic pseudopotential, but with the other the results are very similar.

Energy cutoffs The orbitals for the electrons 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` $= 80$ Ry the error on the energy is of the order of 10^{-7} Ry. With this setting the effect of the cutoff on the density is negligible and so the default value is used.
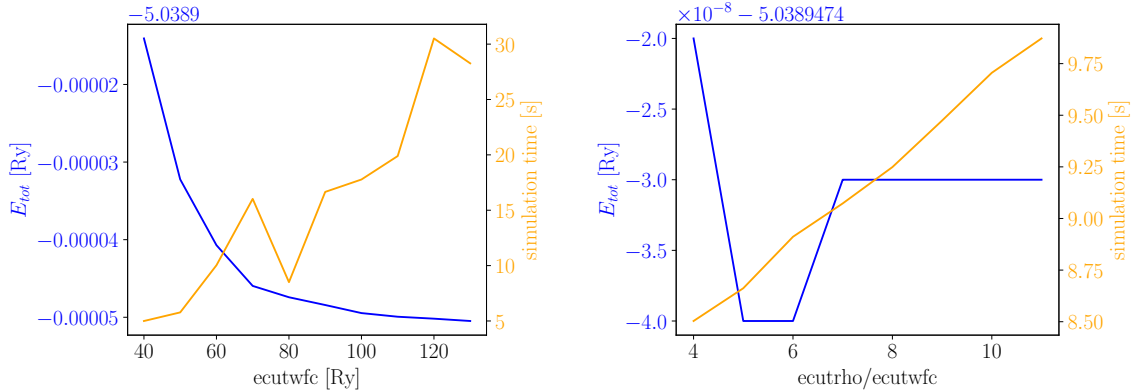

Figure 2: Total energy and simulation time as a function of the two energy cutoffs.

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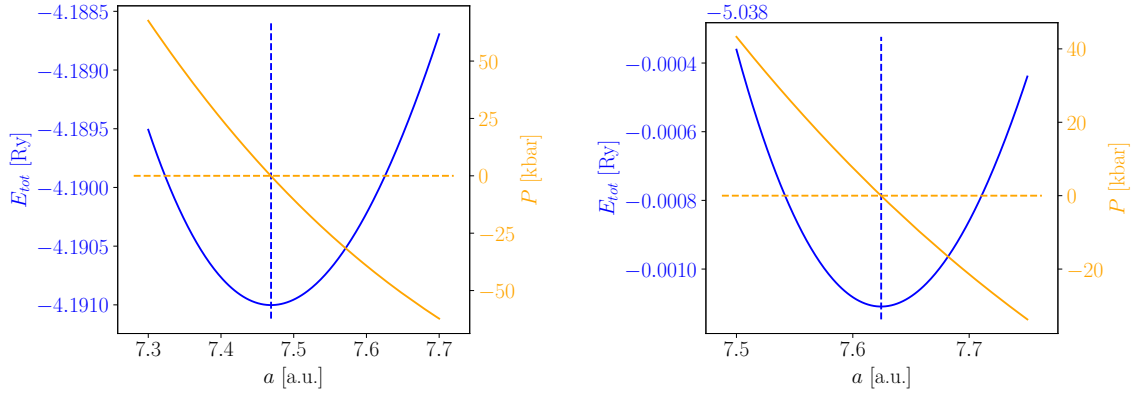
Figure 3: Behavior of the total energy and pressure as a function of the lattice constant for the non relativistic and relativistic pseudopotential respectively.

	$a_0 \, [a.u.]$	$K_0 \, [kbar]$	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

better agrrement with the experimental lattice constant.

3 Surface relaxation

3.1 Unit cell

To simulate a surface in a periodically repeated system one has to simulate slabs separated by a layer of vacuum along the z axis with thickness t_v. The slab will be composed by an odd number of layers where the atoms of the central layers are fixed while the others are free to move. Due to the periodicity of the crystal it is sufficient to put in the unit cell a single atom per layer (fig 4). The starting configuration will have the atoms spaced with the bulk lattice constant found above and the layer relaxation will be expressed as $\Delta z_{n,n+1} = \frac{z_{n+1}-z_n}{(z_{n+1}-z_n)_{bulk}} - 1$, $n \in 0, 1, \ldots, \frac{n_{layers}-3}{2}$ where the outermost layer is numbered with 0.

3.2 Optimization of the simulation parameters

To obtain meaningful results one has first to see how the simulation parameters affect the relaxation. By doing some trials one finds that there is no big dependence on `degauss` and `ecutrho`, so one can fix them at `degauss` $= 0.02$ Ry, `ecutrho/ecutwfc` $= 4$, and study the dependence on `ecutwfc`, t_v and the mesh of k points used for sampling the Brillouin zone, which, due to the symmetry of the unit cell has n_k^h k points in the x and y direction and n_k^v in the z direction. Since the unit cell is elongated on the z axis the Brillouin zone will be squeezed along the z axis meaning that $n_k^v < n_k^h$. Also for now the computations are performed with the non-relativistic pseudopotential. Starting with 5 layers and `ecutwfc` $= 20$ Ry, $t_v = 25$ a.u., $n_k^v = 1$, $n_k^h = 12$ one can try to vary each of these parameters and see how the system responds (fig 5).
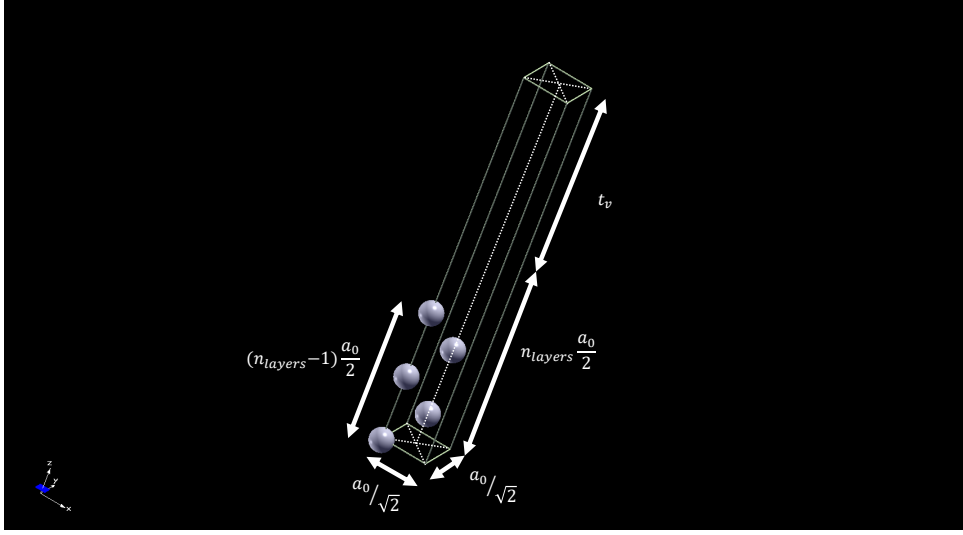
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Figure 4: Schematics of the unit cell with 5 layers. t_v is defined in such a way that if $t_v = 0$ atoms do not overlap, namely if $t_v = 0$ and n_{layers} is even, one recovers the bulk crystal.
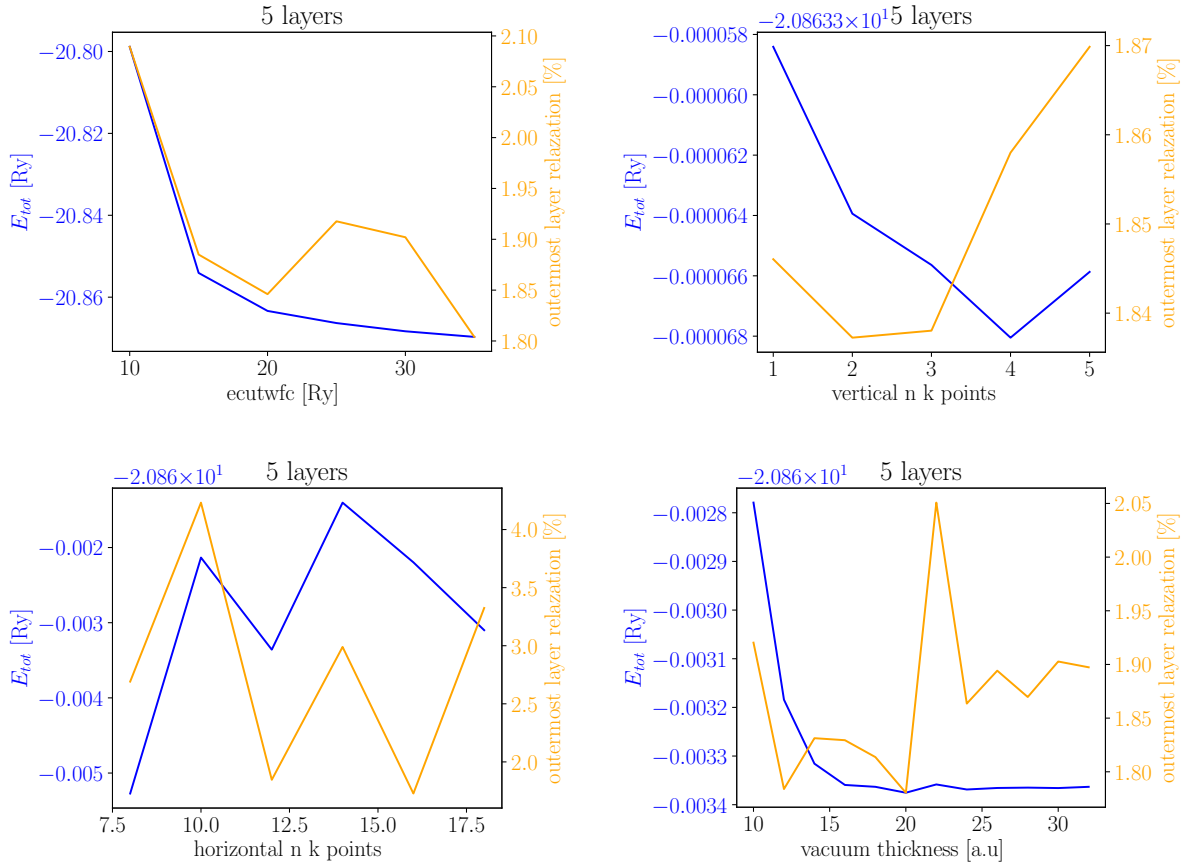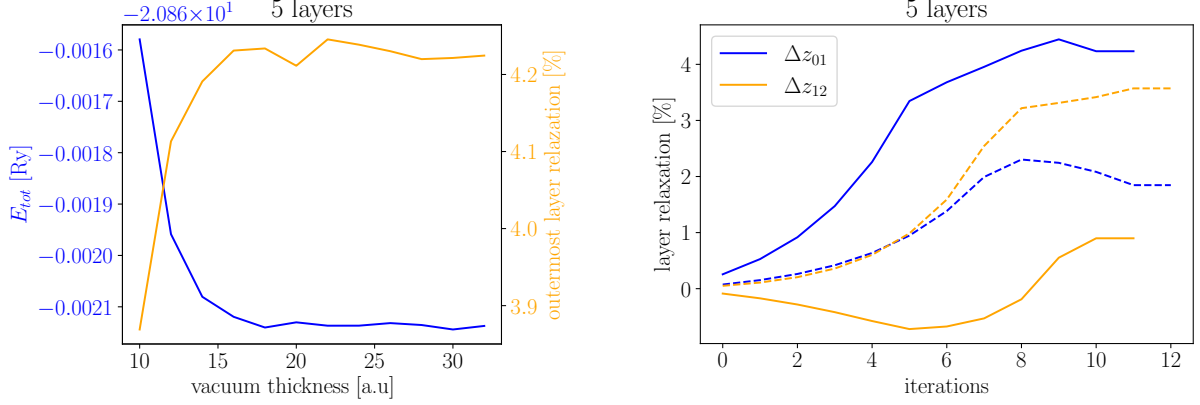

Figure 5: Behavior of the total energy of the system and the relaxation of the outermost layer varying the simulation parameters.

By doing some more computations one can see that increasing `ecutwfc` does not reduce the oscillations with respect to the other parameters, simply increasing the simulation time. For this reason henceforth `ecutwfc = 20` Ry. At this point one can notice that the effect of varying n_k^v is negligible with respect to the one of varying n_k^h, so it reasonable to use $n_k^v = 1$. From fig 5 one can see that for $t_v > 25$ a.u. the system seems to converge, while changes in n_k^h induce quite high fluctuations in the relaxation

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results. Also the choice of this parameter heavily affects the behavior of Δz_{01} with respect to t_v. If one uses $n_k^h = 10$, he obtains fig 6(a) where the trend in Δz_{01} seems more natural than the one at $n_k^h = 12$ (fig 5). Also if one plots the realxation of the layers at the two different values for n_k^h (fig 6(b)) one can notice that for $n_k^h = 12$ the result is quite odd, namely the inner layer relaxes more than the outer one, so this analysis of the relaxation can be then another criterion for choosing the proper set of simulation parameters.

(a) Behavior of total energy and Δz_{01} with respect to t_v with 10 horizontal n k points.

(b) Relaxation of the layers during the simulation. Solid line with $t_v = 18$ a.u., $n_k^h = 10$; dashed line with $t_v = 25$ a.u., $n_k^h = 12$

Figure 6: Results of the 5-layered system

3.3   More layers

The same process of optimization performed on the 5-layered system has been done on systems with 7, 9 and 11 layers, obtaining the following. For the 7 and 9-layered systems there is a nice behavior in the relaxation along iterations (fig 8) and in the behavior with respect to the vacuum thickness (fig 7). On the other hand the 11-layered system exhibits a more weird behavior (figs 9, 10). For this last system the simulations with $n_k^h = 14$ induce less fluctuation with respect to t_v and so are more reliable.

It is here interesting to notice that in these simulations one expects that if n_k^h or t_v are increased, the results should get better with the only drawback of a longer simulation. On the other hand one can observe that actually this is not always true, maybe because the higher precision amplifies unphysical charachteristics of the pseudopotential yielding a meaningless outcome. All the results are reported in tab 2.

n_{layers}	n_k^h	t_v [a.u.]	Δz_{01} [%]	Δz_{12}	Δz_{23}	Δz_{34}	Δz_{45}
5	10	18	4.23	0.90			
7	16	18	1.14	0.77	-1.12		
9	12	18	1.24	0.90	0.03	-0.99	
11	14	18	1.66	-0.02	-0.42	0.56	-0.39

Table 2: Results of the relaxation with non-relativistic pseudopotential.

3.4   Comparison with theory and experiments

In the work by Zheng et al. [5] they study the relaxation of the 9-layered Al 100 surface via ab initio methods comparing their results with theoretical predictions and experimental data. In tab 3 are
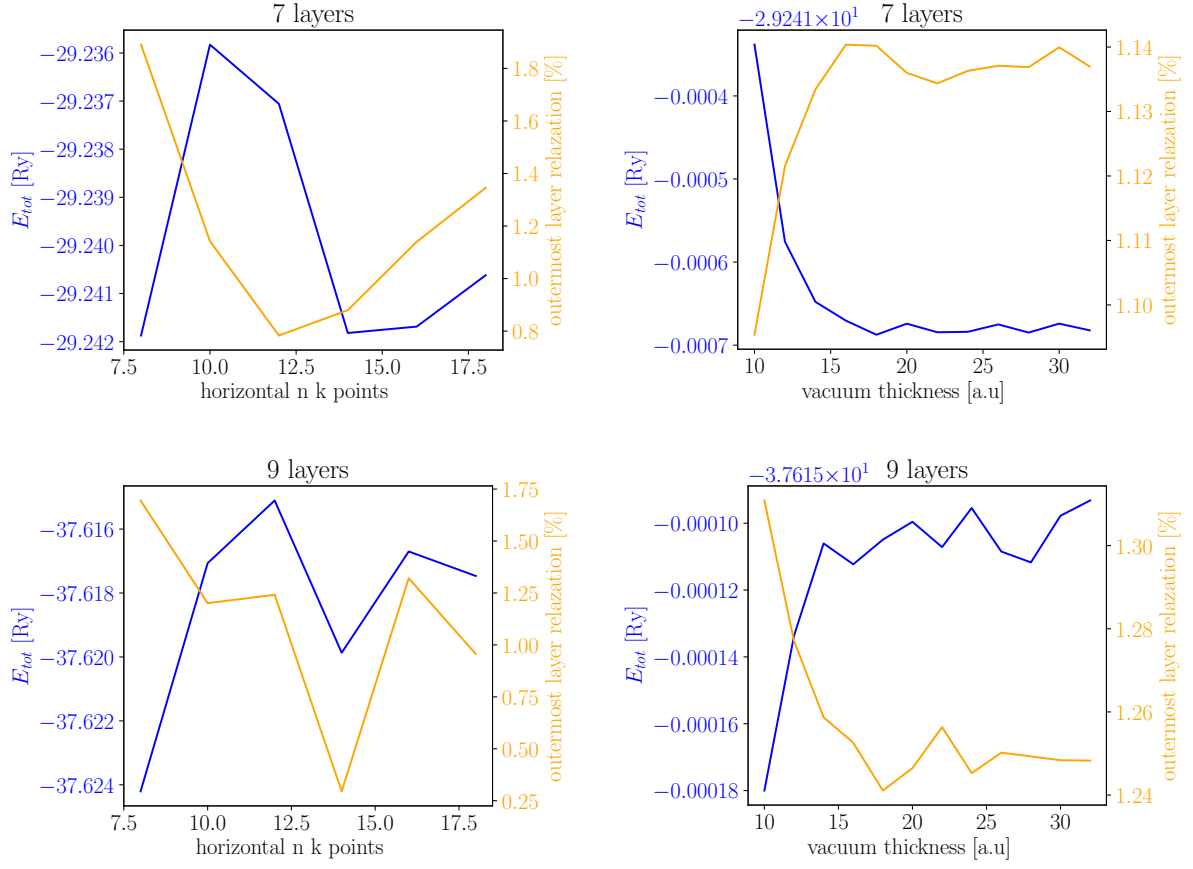
Figure 7: Dependence of total energy and Δz_{01} on t_v, n_k^h for the 7 and 9-layered system.
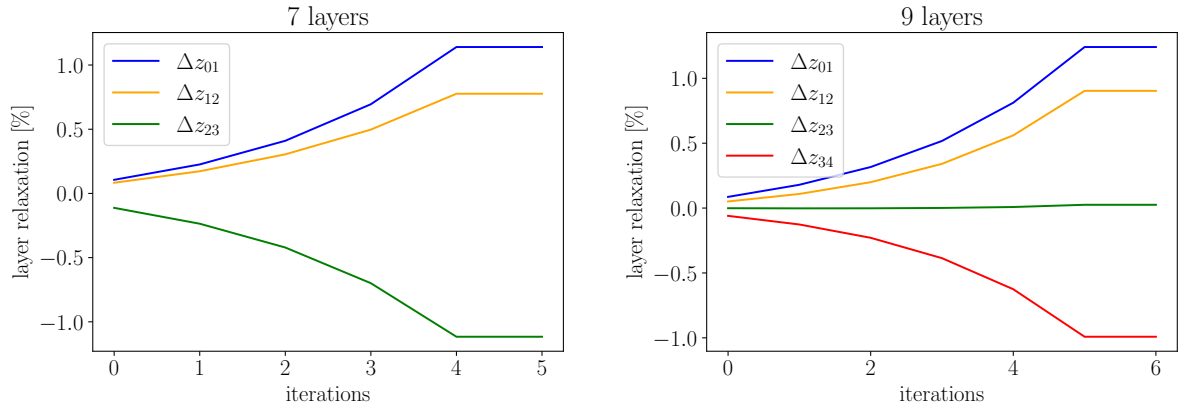

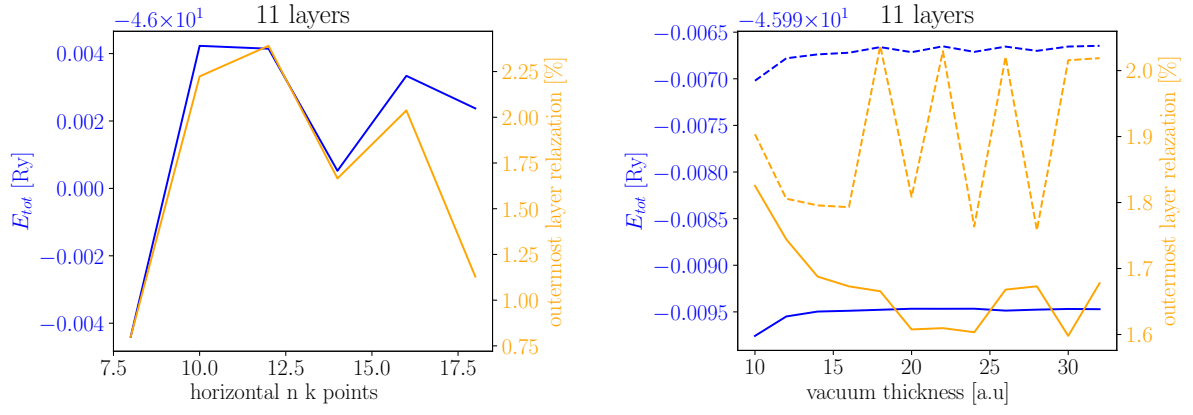Figure 8: Relaxation of the 7 and 9 layered systems

Figure 9: In the second plot the solid line refers to $n_k^h = 14$ and the dashed one to $n_k^h = 16$
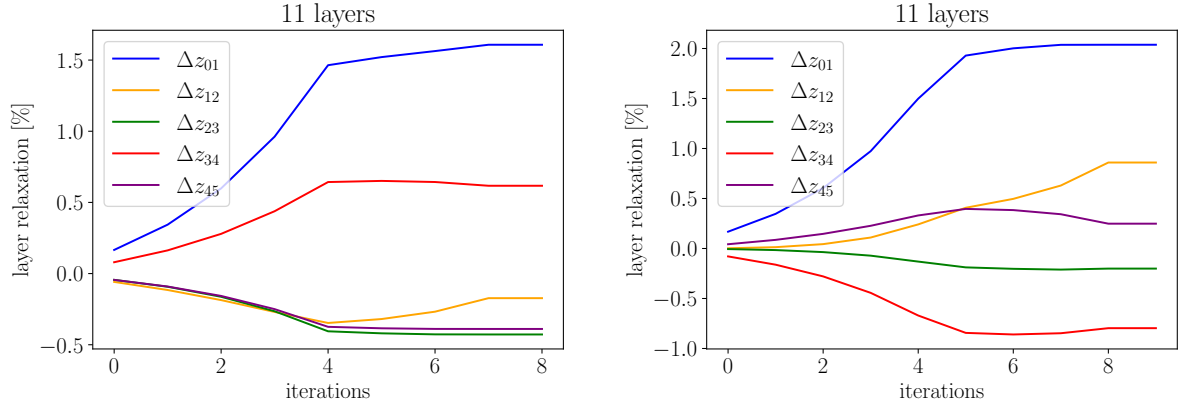

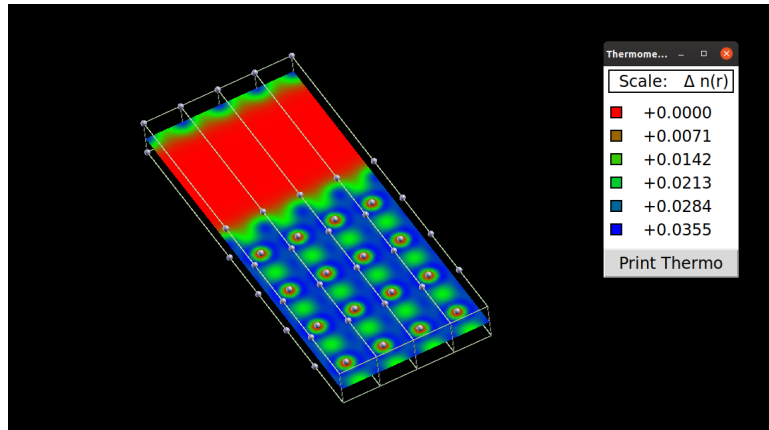Figure 10: Relaxation of the layers at $n_k^h = 14$ and $n_k^h = 16$ respectively.

Figure 11: Section of the electronic density for the 9-layered system after the relaxation with non relativistic pseudopotential.

reported the results they found compared with the ones obtained here, where the coputations have been performed also using the relativistic pseudopotential.

Most of the surfaces of fcc crystals relax inward, however, as experiments show, the Al 100 surface exhibits an anomalous outward relaxation. Interestingly, the data obtained with the non-relativistic pseudopotential agree with the experiments while the relativistic ones predict a more standard, but wrong, inward relaxation despite estimating better the bulk lattice constant.

	Δz_{01} [%]	Δz_{12}	Δz_{23}	Δz_{34}	method
This report	1.24	0.90	0.03	-0.99	ab initio non-relativistic pseudopotential
	-2.79	-4.03	-2.26	-3.93	ab initio relativistic pseudopotential
Zheng et al.	1.89	4.12	2.96	2.94	ab initio
Theory	0.79	0.06	0.01	0.00	MEAM [6]
	-4.9	-2.24	-2.25	-2.39	EAM [8]
Experiment [7]	1.8				

Table 3: Comparison between different caluclation of the relaxation of the 9-layered system.

4 Conclusion

After understanding the effect of the simulations parameters it has been possible to estimate bulk properties such as the lattice constant and the bulk modulus of the Aluminium crystal. On the other hand, the estimation of the relaxation of the Al 100 surface has proven to be more tricky in the proper choice of the simulation parameters, expecially the number of k points used to sample the Brillouin zone. However despite these difficulties it has been possible to obtain a result that has a quite nice agreement with experimental data.

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 *Equation of state for solids* https://doi.org/10.1063/1.3686399

[5] J.C. Zheng et al. *Multilayer relaxation of the Al(100) and Al(110) surfaces: an ab initio pseudopotential study* https://www.sciencedirect.com/science/article/pii/S0368204800003625. The following are indirect references from this work:

[6] J. Wan, Y.L. Fan, D.W. Gong, S.G. Shen, X.Q. Fan, Model. Simul. Mater. Sci. Eng 7 (1999) 189

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[8] F. Jona, D. Sondericker, P.M. Marcus, J.Phys. C: Solid State Phys. 13 (1980) L155