

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

Alessandro Lovo, mat. 1236048

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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 centered 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.1.1.0.0.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 increase the 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 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 `4ecutwfc`. In fig 2 one can see that with `ecutwfc` = 80 Ry 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.

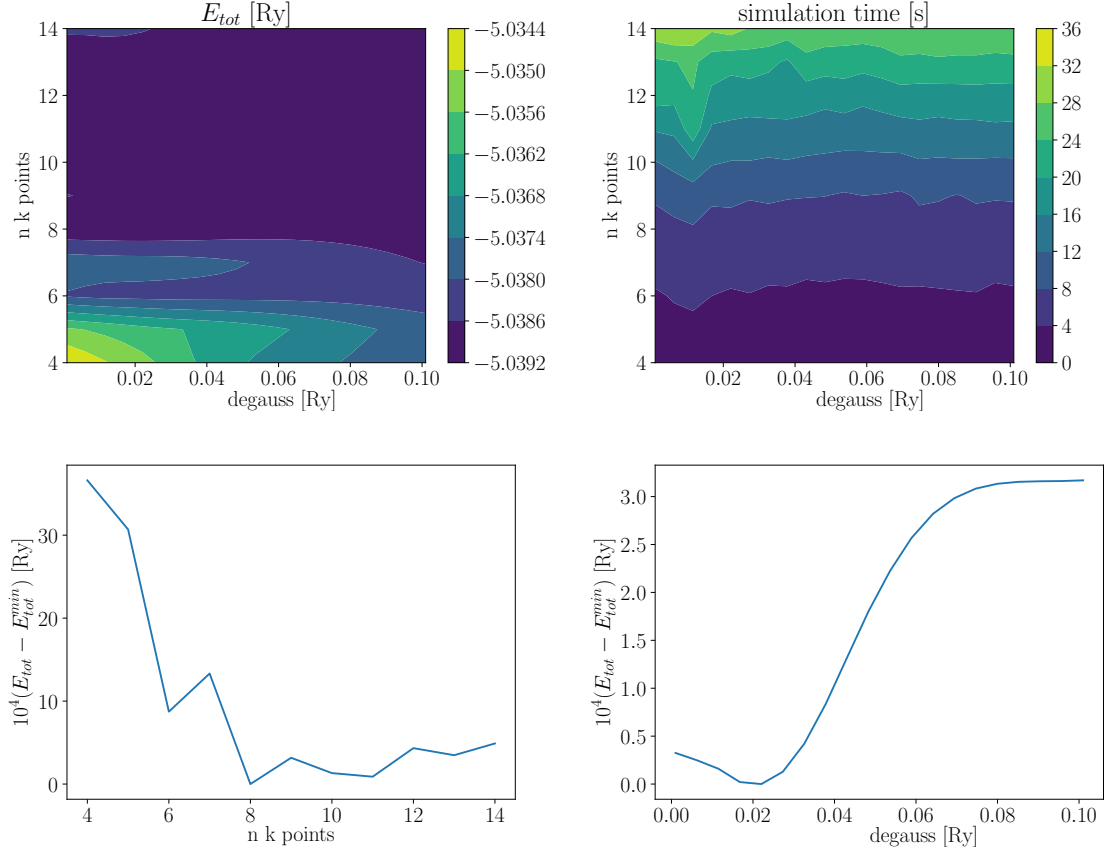


Figure 1: Behavior of the total energy and the simulation time as a function of the number of k points and of the amount of smearing. Simulations performed on the relativistic pseudopotential, but with the other the results are very similar.

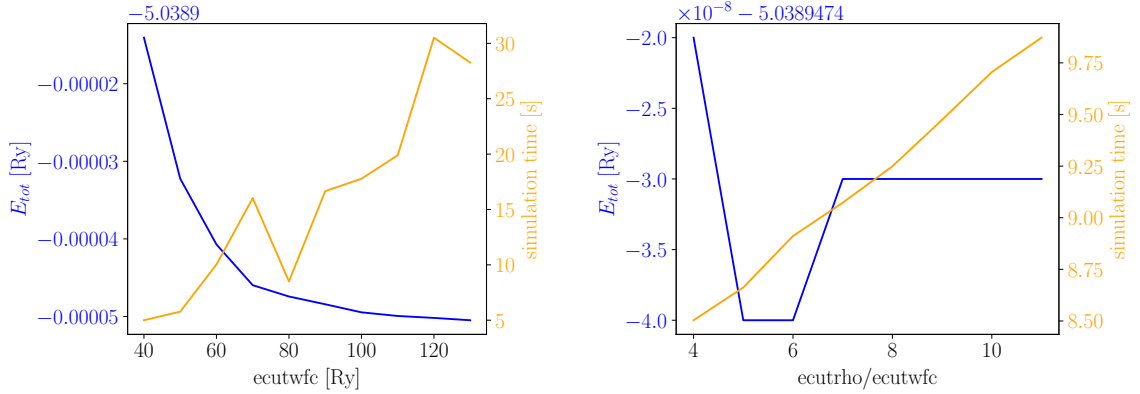


Figure 2: Total energy and simulation time as a function of the two energy cutoffs.

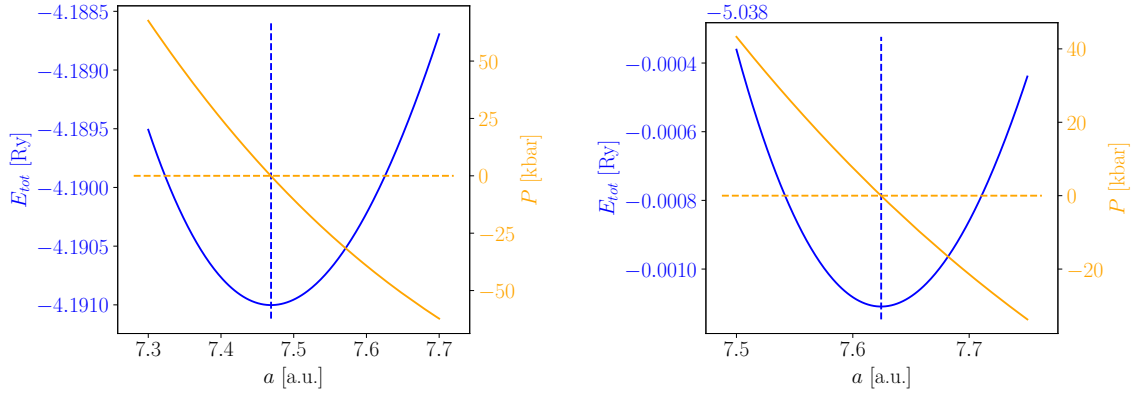


Figure 3: Behavior of the total energy and pressure as a function of the lattice constant for the non relativistic and relativistic pseudopotential respectively.

	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.

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 $\Delta z_{n,n+1} = \frac{z_{n+1} - z_n}{(z_{n+1} - z_n)_{bulk} - 1}$, $n \in 0, 1, \dots, \frac{n_{layers} - 1}{2}$ 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 computation 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).

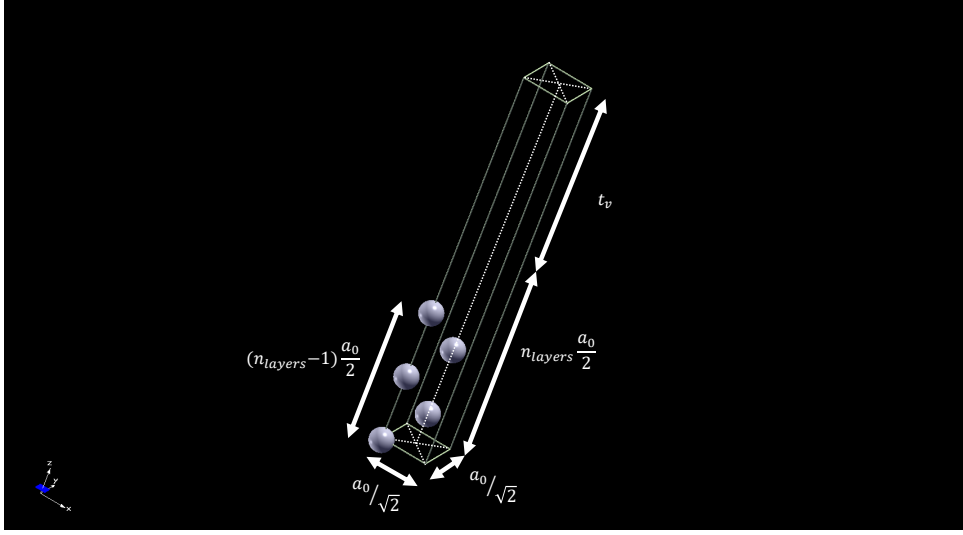


Figure 4: Schematics of the unit cell with 5 layers. t_v is defined in such a way that if $t_v = 0$ atoms do not overlap, namely if $t_v = 0$ and n_{layers} is even, one recovers the bulk crystal.

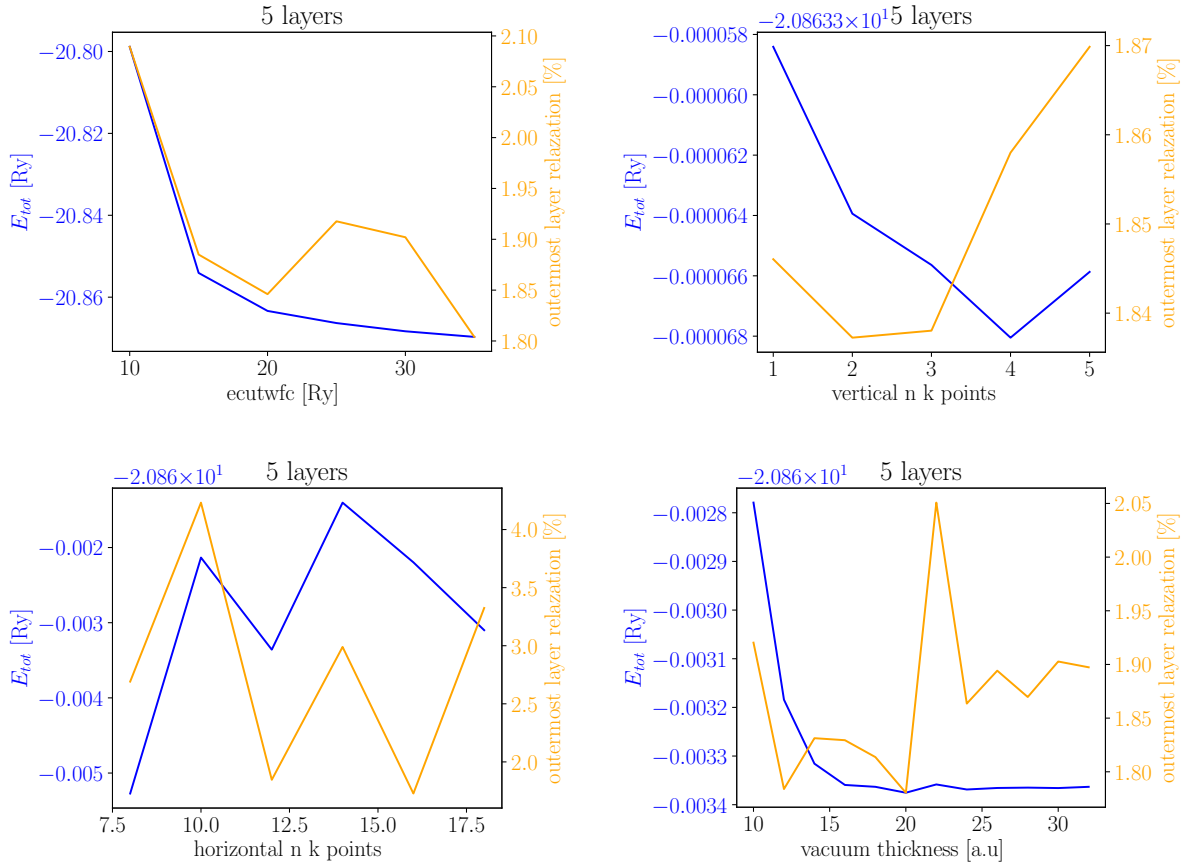
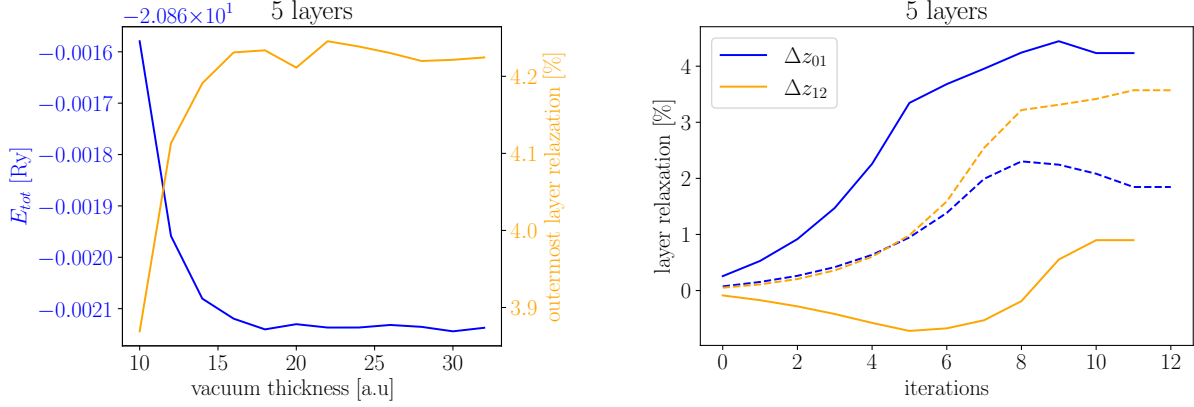


Figure 5: Behavior of the total energy of the system and the relaxation of the outermost layer varying the simulation parameters.

From by doing some more computations one can see that increasing `ecutwfc` does not improve the results 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 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. If one plots the relaxation 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. 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. On the other hand the 11-layered system exhibits a more weird behavior (figs 9, 10).

Source	n_{layers}	n_k^h	t_v [a.u.]	Δz_{01} [%]	Δz_{12}	Δz_{23}	Δz_{34}	Δz_{45}
This work	5	10	18	4.23	0.90			

Table 2

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 *Multilayer relaxation of the Al(100) and Al(110) surfaces: an ab initio pseudopotential study* <https://www.sciencedirect.com/science/article/pii/S0368204800003625>

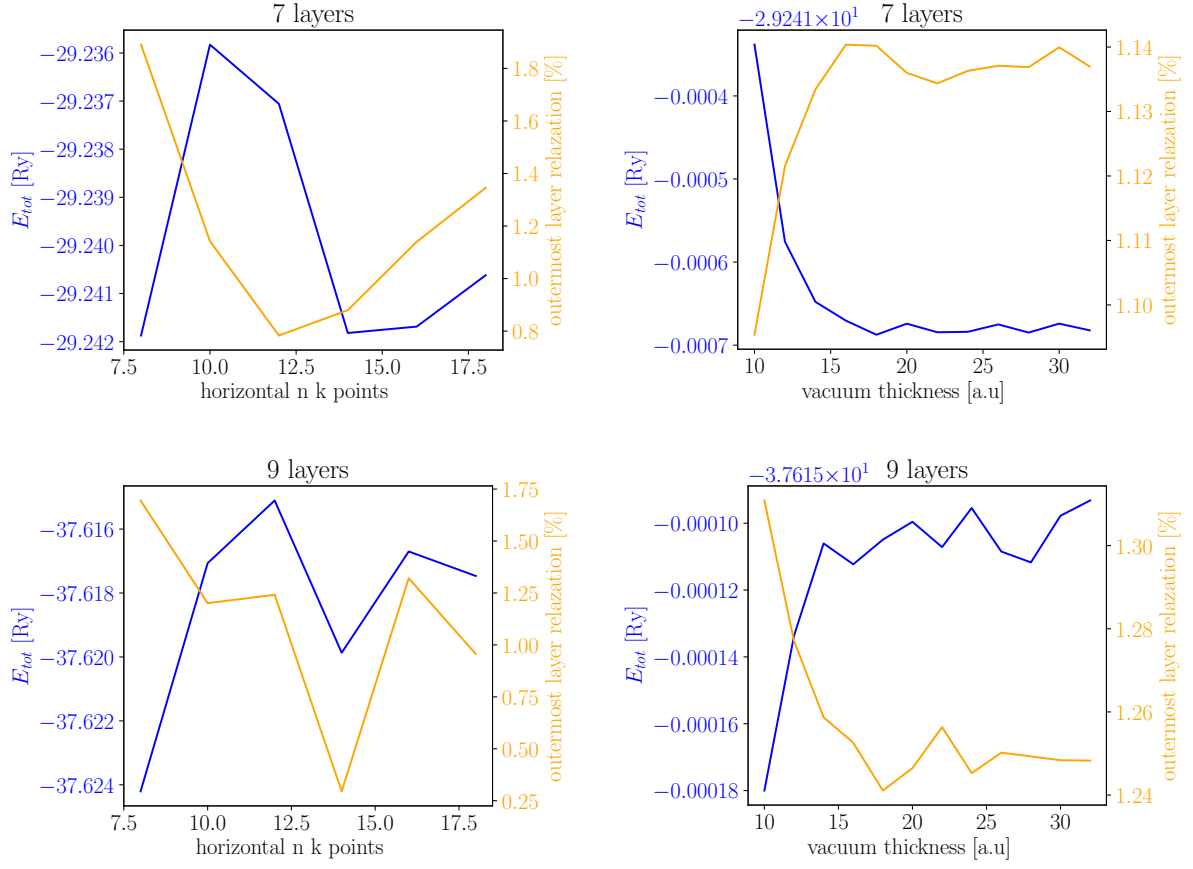


Figure 7: Dependence of total energy and Δz_{01} on t_v, n_k^h for the 7 and 9-layered system.

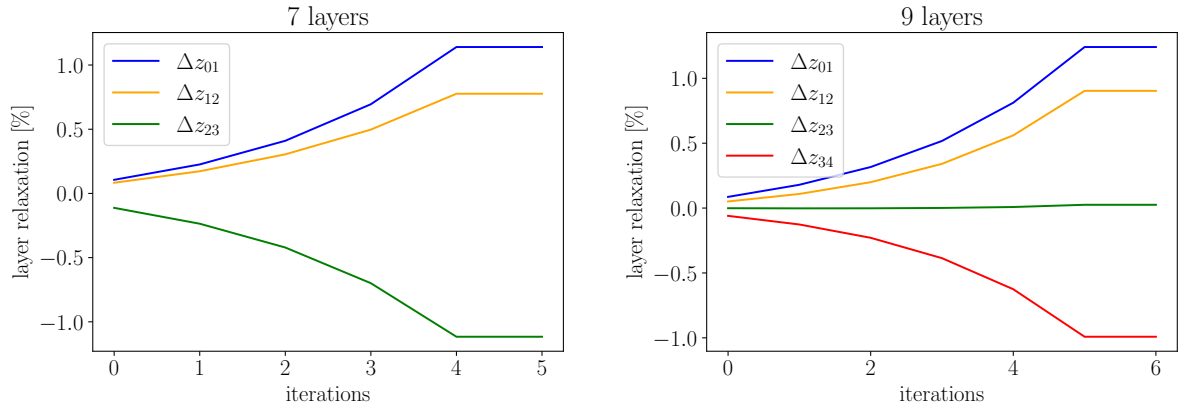


Figure 8: Relaxation of the 7 and 9 layered systems

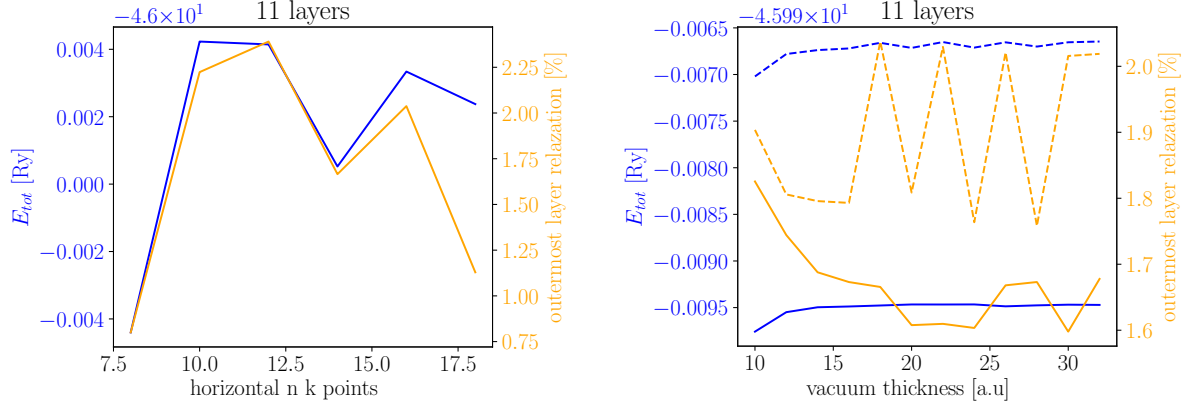


Figure 9: In the second plot the solid line refers to $n_k^h = 14$ and the dashed one to $n_k^h = 16$

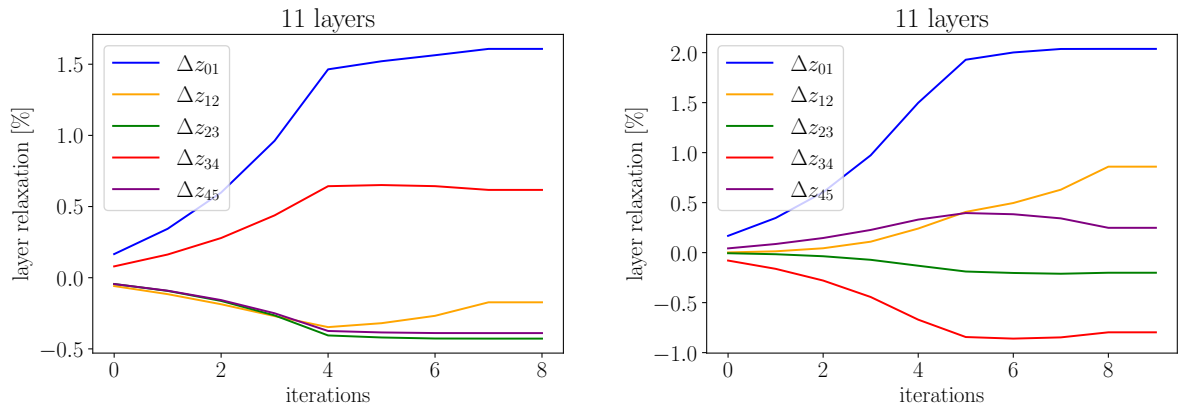


Figure 10: Relaxation of the layers at $n_k^h = 14$ and $n_k^h = 16$ respectively.