A new approach to explore the energetic landscape of molecular systems

Lionel FOULON (PhD student 2018-2019)

KEYWORDS:

Static Modes, Multi-levels modeling, DFT calculations

CONTEXT

The main barrier to atomic modeling is to identify the atomic event the most feasible and consistent to figure out some molecular mechanism or property. Nevertheless, the exploration of the energetic landscape is greedy in human means and calculation time. To solve this complication, we choose to use the Static Mode approach [1]. This approach is based on deformation induced by a force calculated from the Hessian (see equation 1).

$$-\boldsymbol{F}_i = \frac{\partial \boldsymbol{E}}{\partial \boldsymbol{x}_i} = \sum_{i}^{3N} \boldsymbol{H}_{i,j} \times \boldsymbol{x}_j \tag{1}$$

So, we obtain the elementary deformation for each atoms, named Static Modes, that we can combine in a lot of different ways to create and test atomic events. Our challenge is to use this atomic event to lead DFT calculations. The final ambition of this approach could be to make an automatic procedure (see figure 1) where the user just has to ask a question like « How this bound can be broken ? » and the procedure will propose some atomic events and test it.

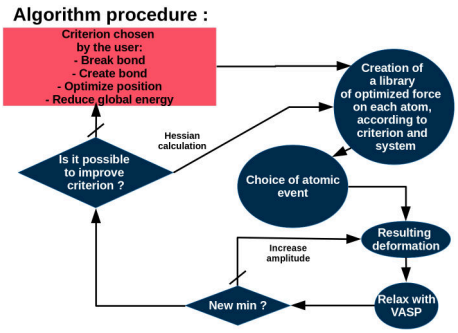


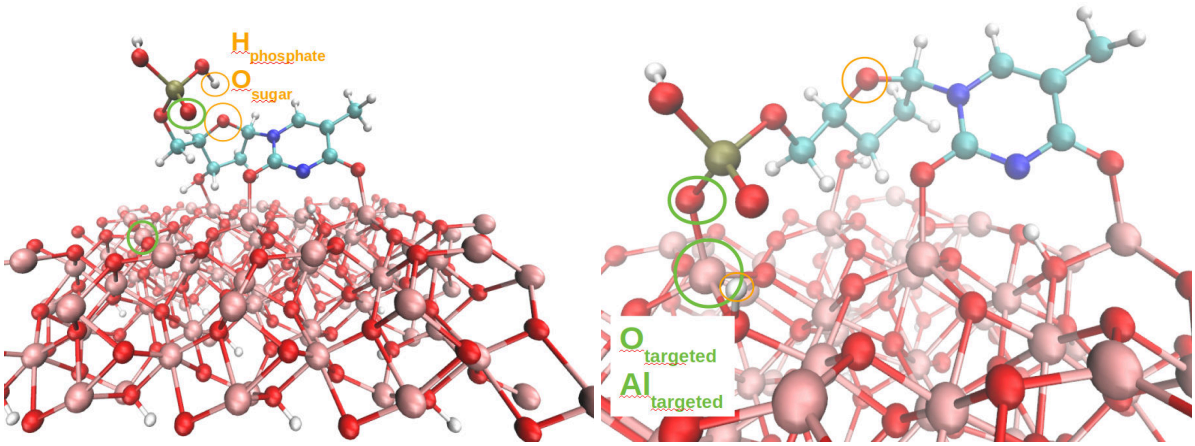
Figure 1. Procedure developed to explore the system with Static Modes

Methodological Development:

Our work is mainly based on the software developed in LAAS (FleXible [lien re direction?9999?]) and precisely how to use Static Modes. So we have tested some strategies and different criterion to create the best atomic event which can correctly guide the DFT calculation. But, depending on what do you want to do and how do you want to orient the exploration, each criterions have its benefits and drawbacks. Then we limit this work to prove that is it possible to find, with Static Modes, a pathway between two local minima previously detected [2] (see figure 2). In practice, to explore our system we follow by hand the procedure in figure 1.

RESULTS

A first loop of exploration starting from the initial position leads to find five new local minima. In a first approach, we assess the relevance of those configurations on geometrical consistent



(a) Initial position of dTMP on Al_2O_3 surface **(b)** Final position of dTMP on Al_2O_3 surface

Figure 2. Grafting mechanism of a fragment of DNA: 2-deoxythymidine-5-monophosphate (dTMP) into a oxidized aluminium surface: Al_2O_3

and the total energy of the system (supply by VASP and corroborate by other calculations from the Hessian). So three minima were selected to deal with exploration in depth. Then three atomic events were find which can lead to the final configuration. The mechanism which seems the most relevant is made up with two atomic events, one apply on the $Oxygen_{sugar}$ to break the $O - H_{Phosphate}$ bound and release the Phosphate group. And the second event on $Phosphate$ to bring the Phosphate group closer to the surface and create the bound $O - Al_{targeted}$. The total energy of minimum state is posted in table 1.

Minimum name	Total system energy	Delta from initial state
Inital position	2244.0452 eV	0.000 eV
Transitional state with OH breacked	2243.9714 eV	+ 0.074 eV
Final position	2246.0643 eV	- 2.019 eV

Table 1: Total energy of minimum state encountered during the mechanism

CONCLUSIONS

Currently the procedure are not autonomous and still need human interventions for some choice and difficult step. But Static Modes is good tool to help the user in this choice. This study demonstrates that this convenient and reacheable approach can guide DFT calculation and reduce the human and the time cost while keeping the absolutely precision of classical exploration.

On the other hand, we currently work on a local field potential to characterize our results. Moreover, take into account the local constraint can drive the choice of the atomic event more quantitative (so this step could be automated). Last, the local view could improve the understanding of the mechanism by visualizing where the constraint is localized and how the system rearranges itself to stabilize it internal constraint.

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