

Turning chemistry into information: from calculations to data

Sergio P. García Carrillo, Moisés Álvarez, Núria López[†]

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1 Introduction

Computational chemistry is nowadays ubiquitous and finds applications in Chemistry, Biology, Physics, Materials Science and Nanotechnology. As the applications grow and the access to massive computers and robust codes[1] extends worldwide structural data, spectroscopic fingerprints,[2] general properties can be generated as databases for molecules, nanostructures and materials. The ultimate applications can range from environmental detection through spectroscopy to data mining for materials in Catalysis and Electrocatalysis. And yet, most of the purpose-oriented calculations are directly not saved (general case in Materials and Heterogeneous Catalysis) or presented as infinite xyz coordinate listing in Supplementary files in pdf formats. Only lately the relevance of keeping this data in the form of databases has been realized. Most of the systems though have emerged in Materials Science for which the Genome. . . . Data is mostly unlinked to the particular works and thus the traceability (who, when, what) and fairness (functional, accessible, iXX, recyclable) is lost.

A second problem emerges from the requirement of human intervention in very routinely tasks, thus error prone and with multiple deficiencies when trying to generate dense (non-sparse) datasets. This are particularly required should statistical learning techniques[3, 4] be applied as sparse datasets are biased towards a particular type of successful event, exactly what SL algorithms need to avoid to ensure their robustness. The repetitiveness has been addressed by different groups by the use of scripts of different level of sophistication. However, the emergence of new frameworks that can steer

the tedious tasks and generate/check/upload to a database significant data blocks of the phase spaces provides the right tools into the avoidhuman concepts. Generation is thus no longer the important area but rather checking unusual cases and analysis will be the focus of the research in computational chemistry in the next years. This will on one side increase our abilities in identifying outliers that can be crucial to particular performance (and identification of new families of molecules and compounds with particularly appealing properties), to refine the analytics, to incorporate graph theory[5] and other encodings like SMILES[6] to be able to transfer active patterns irrespective of the nature of the compound (solid, enzymatic, molecular).

The new editorial platforms like Authorea, can also integrate the benefits of this systematic approaches. The process of reading documents has severely changed since the establishment of the world-wide web and the availability of more than one instance simultaneously running. Reading in the 21st century means a completely different experience than it was for at least 500 years as the meta- and linked data are accessible and are consulted almost simultaneously with the primary source. New ways of acquiring information can thus now benefit from viewers that can

integrate the content while being interactive and improving the reception of complex (for instance 3D) information in a more adequate manner.

Our manuscript tries to address all these new challenges in computational chemistry and with the overall idea of transforming the results into a true information science that can be search, analyzed and mined ensuring the transferability in different fields.¶Paste¶

In this paper we propose an automated procedure to overcome the different drawbacks associated with the repetitive processes included in the study of large reaction networks. A framework that combines Fireworks,[7] VASP,[8, 9] ioChem-BD[10] and ad-hoc developed software has been built to fully automate the study of reaction networks over different metals. This framework allows to transfer all the relaxed species and transition states obtained for a metal slab to another slab of a different metal as well as to automatically prepare and perform the pertinent DFT calculations using the generated geometries for the new slab.

2 Computational Details

DFT calculations have been performed using Vienna **ab-initio** Simulation Package (VASP). [8, 9]. Generalized Gradient Approximation with the Perdew-Burke-Ernzerhof functional (GGA-PBE) have been used to obtain the exchange-correlation energy term. Inner electrons have been represented using the Projector Augmented Wave (PAW) [11] with a cut-off energy of 450 eV. For generating the K-points a Γ -centered mesh have been generated using the Monkhorst-Pack method. Improved dimer method have been employed to locate the transition states. [12]

Fireworks [7] is a free software package that allows to manage, build and run workflows, in this project it has been used to built and configure the ties between the different steps of our calculations. Also, it allows to track the status of active workflows and stops the process if one of the steps fails, allowing to completely restart the process or continuing the step after the application of the needed changes.

Software written in Python and Bash has been developed in our lab and used to script the preparation, transfer and checking processes. Developed Python libraries and scripts focus on geometry manipulation and input/output parsing, while Bash scripts intend to manage the files related to the calculations, and control the execution of VASP.

The framework has been tested using a reaction network composed by 9 different metals, 8 of them with p(3x3)-(111) fcc packing and 1 of them with p(3x3)-(0001) hcp packing. Hcp metal has serve as the "ansatz" host for the rest of the metals. Both packings share similar surfaces, containing the same type of adsorption sites. The two lowest layers have been frozen and a vacuum of 15 Å has been applied to all metal slabs.

A total of 12 organic species composed by 2 to 5 atoms and 8 transition states have been evaluated with our method. For the minimum energy relaxations, different adsorption sites have been calculated for every metal/species combination while for the transition states only one adsorption site has been tested. The species were first obtained manually for the hcp metal and then recalculated for the other metals using our framework.

Figures included on this paper were made with Cytoscape, 3Dmol and Plotly.[13–15]

3 Results and Discussion

3.1 Transfer algorithm

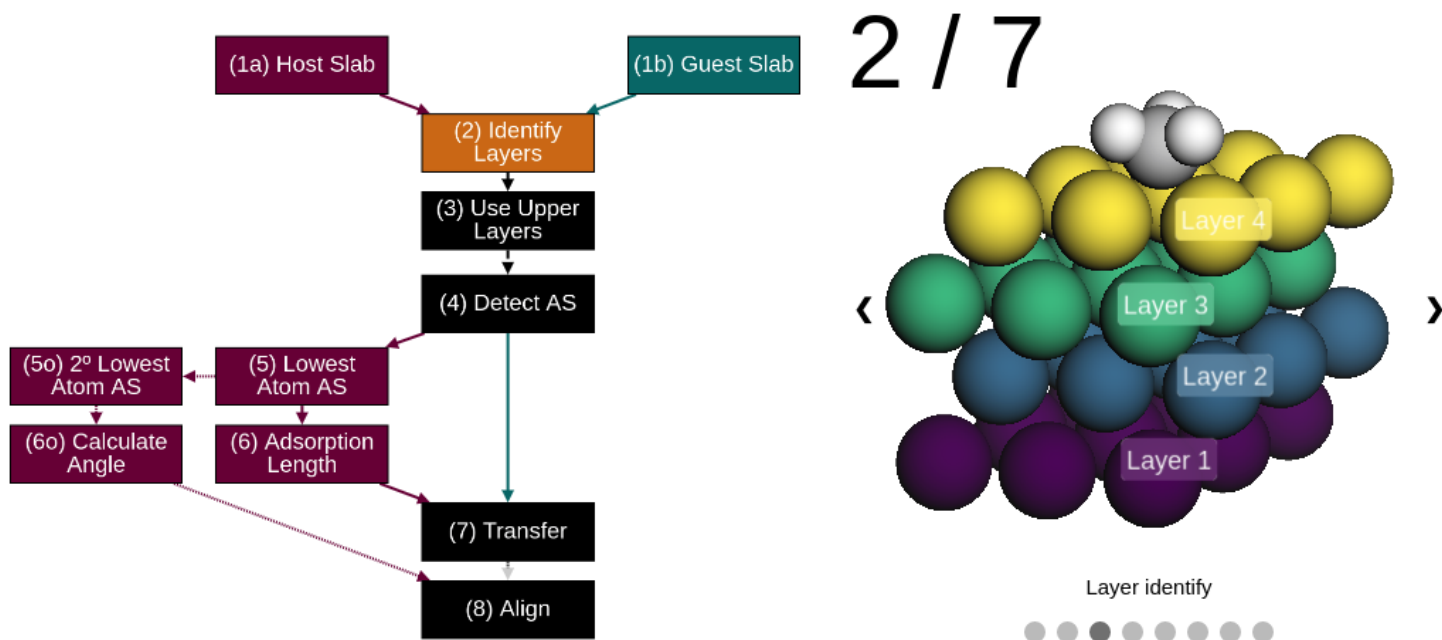


Figure 1: Interactive diagram containing the steps that the transfer algorithm performs. While some of the steps only use the data from the host slab, the first 5 steps are applied concurrently to both slabs.

A transfer algorithm that performs a relocation of an adsorbed molecule in metal surface to a similar metal surface has been developed. Automatic transfer of adsorbed species between similar metallic surfaces allow not only to save a considerable amount time during the geometry production but also to classify accurately the generated models.

Figure 1 depicts the procedure of the algorithm. Having two different metal slabs, a host with an adsorbed molecule (1a) and a guest consisting on an empty metal slab (1b), the transfer algorithm works as follow: First, identifies the layers (2) for both slabs and selects the highest layer.(3) Then, searches for all the possible adsorption sites (4) on both surfaces. Once the adsorption sites have been identified, the algorithm associates the nearest adsorption site with the lowest atom of the adsorbed molecule in the host

slab.(5) In the next step, the adsorption length is computed employing the distance between the assigned site and the lowest atom of the adsorbate. However, in some molecules the lowest atom is not perfectly aligned with the adsorption site. To overcome this issue, the shift between both is also computed in this step.(6) Lastly, the algorithm transfers the molecule to a similar site in the guest surface, taking into account the adsorption site type and maintaining the adsorption length.(7) As an optional step, the algorithm can be setted to identify the nearest adsorption site of the second lowest (5o) atom and compute the angle between both (6o), this information will be used to rotate the molecule around the z axis of the lowest atom to preserve its original alignment.(8)

Transfer algorithm apply different methods to find the possible adsorption sites. For the fcc and hcp holes detection, Voronoi tetrahedron method [16] is used to disclose the bonds between the atoms of the upper layer, to then search for cycles of three atoms. Differentiation between hcp and fcc holes is achieved projecting the triangle formed by the cycles in the lower layer and searching for atoms inside this space. Once the bonds are defined, bridge and top positions are trivial to find.

After a few tests, further improvements were integrated to the transfer algorithm. An analysis of the difference between the adsorption length in the different metals were used to apply a correction in the adsorption length of the new slab.

3.2 Workflow design

Geometries generated using the transfer algorithm are not optimized and require further DFT calculations to obtain a full description of the reaction network. To address this problem two different workflows have been developed and embedded in the framework: one for the minimum energy relaxation (**MER**) and another for the transition state search (**TSS**). Both workflows use the transfer algorithm as first step to generate a new metal slab with the desired adsorbate, then, different Bash scripts prepare and run the pertinent DFT calculations using VASP.

While the workflow to search relaxed geometries only generates a single geometry, the TS workflow generates three unique geometries with different rotations along the z axis of the lowest atom. A partial relaxation involving a small number of ionic steps is performed to the three structures, allowing to relax the atoms of the molecule with high initial forces and preventing

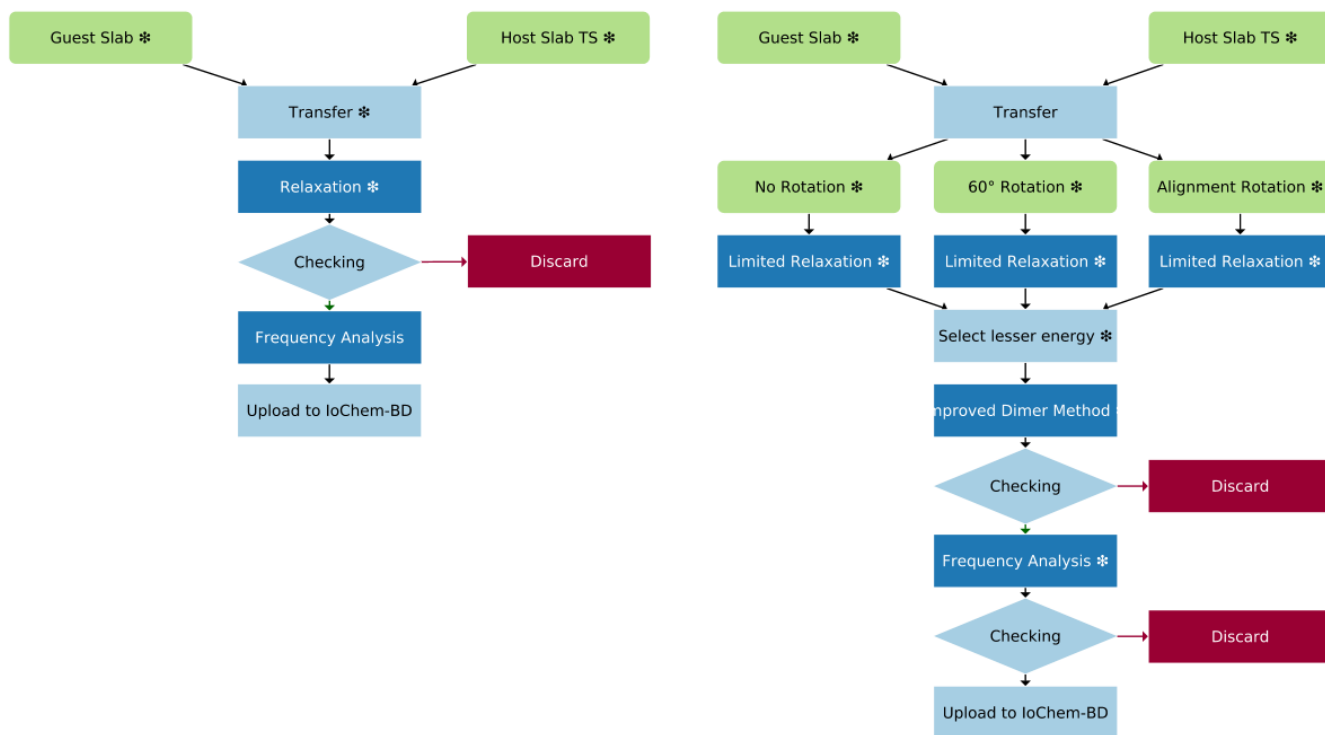


Figure 2: Interactive flux diagram showing the required steps for the relax and TS processes. DFT calculations are depicted with an square and script are marked with a circle. Clicking the different points will show the status of the structure at this point.

the transition state to fall into a minimum energy point. The best candidate along the relaxed structures is selected using a lowest energy criteria, in the next step, the chosen candidate is used as the starting geometry in an improved dimer method calculation. Selection steps are unnecessary for the MER workflow due to the efficiency of the minimum energy point relax algorithms in front of the transition search ones. Thus, for MER workflow the generated geometry is directly used as starting point for the minimum energy search calculation.

Errors of different nature can occur during the calculation steps, also the geometry obtained after the calculation may be chemically meaningless, then, it is important to manage errors with care. To address this issues, a checking algorithm is applied to the results of the calculations, search-

ing for inconsistencies through the calculation steps. Additionally, to verify that no bond breaking occurred during the relaxations a bond identification algorithm is used. This algorithm uses the Voronoi tetrahedron method to identify the bonds of the molecule, and then uses graph theory to find disconnected graphs. If the calculation passes the checking, a frequency calculation is launched.

3.3 Storing data

Due to the large number of calculations that compose this type of reaction networks it is mandatory to sort and store the results orderly. IoChem-BD provides the essential tools to perform the last step of our project: convert our results into organized data. Shell client of IoChem-BD allows to easily upload the generated output files to a private server. Once uploaded, it transform, parse and store the results to grant a clear presentation and easy access to the uploaded data.

Consequently, as the final step of both workflows, the results of the DFT calculations are uploaded to ioChem-BD as well as the frequency calculations performed at the end of the workflows. For the TS workflow, the dimer method is uploaded while for the MER workflow the relaxation method is uploaded.

Once all the calculations finish, the stored data is published in the public IoChem-BD server to easily share the obtained information with other researchers. Moreover, it generates interactive figures that serve as a great support to understand complex molecules.

3.4 Test and results

Both workflows presented solid results, applying correctly the procedure for the different species (see Figure 3). Almost 88% of the minimum energy relaxations and 56% of the transition states converged at the first attempt without issues. Additional steps were required for 0.1% of the relaxed models and 27% of the transition states. The rest required manual preparation and supervision to obtain the expected result.

Relaxations that needed additional steps were uncommon and most of them converged after a few more optimization steps. However, TS searches are more inclined to this outcome and the solution required a different approach. Most of the TS searches achieved the convergence replacing the host

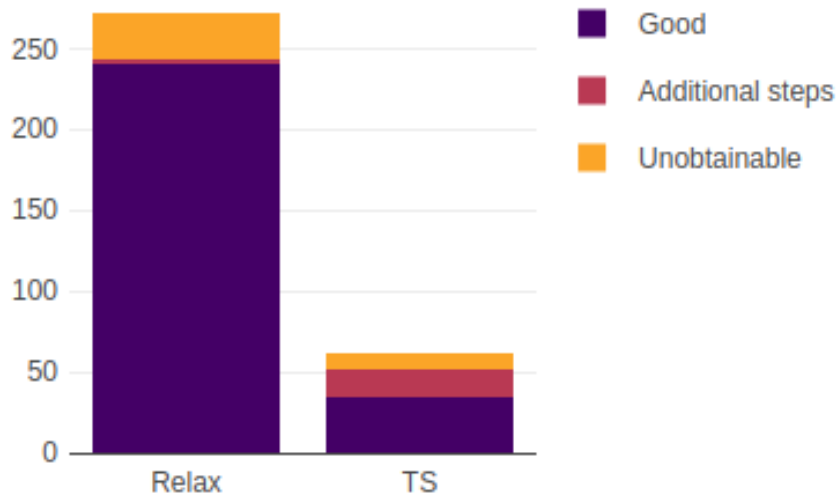


Figure 3: Efficiency of the Relax and TS workflows.

slab with a chemically similar metal slab and restarting the workflow. Still, a small fraction only required a few more optimization steps.

In the case of relaxations, most of the unobtainable structures fell into a different adsorption sites during the calculation, while only few of them ended the calculation with a broken bond. Differently, all the unobtainable transition states ended with a broken bond and more precise methods as the Nudged-Elastic Band (NEB) [17, 18] have been required to obtain the geometries.

4 Conclusions

Our framework has proven to successfully automate two different kind of molecular transfers through similar metals.

It has not been possible to achieve a flawless success rate with our method. However it is possible to classify the different error cases obtained during our study and fuse the solutions as additional steps for our workflows.

IoChem-BD eases the obtention of published reaction networks. In combination with our framework, simplifies the exploration known reaction networks within new metals, reducing the needed human time to check only the not converged structures.

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