
Surface Adsorption on Interstellar Ice I_h

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Abstract

This abstract explains what happens. Benchmark, adsorption, maybe something about the interstellar playground.

1 Introduction

Interstellar chemistry is the key ingredient to understanding the molecular abundancies in our universe. While the formation of atoms takes place in stars[?], their further reaction and therefore the composition of molecular compounds in space largely happens in interstellar clouds. With modern telescopes it is possible to measure the molecular abundancies in the interstellar medium (ISM) to a high degree of accuracy. It became evident that the reaction rates governing the formation of molecules can not properly be explained by gas phase chemistry alone. A prominent theory to mend this discrepancy is to consider the contribution of surface reaction on interstellar dust grains. The dust has been measured[?], so the question is not so much if the reaction happens but rather to quantify its effect.

At temperatures as low as in cold interstellar clouds (between 10 and 100 K), the grains are covered in ices, most prominently H_2O and CO . In the case of water, one faces *amorphous solid water* (ASW), but at very low temperatures one may find a state close to the crystalline I_h state of frozen water.

Various works have already considered surface reactions. (Here we will cite some experimentalists).

The research described above typically chose a model to describe the processes taking place in the experiment and adjusted simulation data – including parameters like the diffusion coefficient – to fit the experimental data. That would mean: if surface reaction processes are the key to filling the gap between observed and predicted reaction rates, the input parameters might be good approximations to the actual coefficients. This is a legit approach since one can not easily think of other processes than surface and gas phase reactions to lead to molecular formation. However, there is not yet a proper *ab initio* theoretical calculation of surface diffusion. This means that evaluating the parameters found in simulation is a very difficult task – there is neither a recommended value nor are there any error bars to such a value. This work tries to make a first step toward the accurate simulation of surface adsorption, diffusion and reaction

of small molecules on interstellar ices. Its aim is to establish a model of crystalline I_h water in which simulations can be carried out. The main mathematical tool for describing the chemistry of this surface is a subdomain treated by *density functional theory* (DFT) within a bigger domain where the interaction is modelled by *molecular mechanics* (MM). The two domains are coupled by a QM/MM coupling scheme.

We will describe the theory underlying the model in the next section. Section 3 then describes the benchmarking we performed on smaller test systems to determine the best functionals and basis sets to use for the actual system. After that, we give our results for adsorption energies in Section 4 and finally there will be concluding remarks and an outlook on possible further application for our findings in Section 5.

2 Theoretical Background

This section focuses on the theoretical framework of the ice surface model. We introduce the main chemical nomenclature in Section 2.1 and then proceed to the mathematical ideas behind DFT in Section 2.2. After that, Section 2.3 will explain how we describe the MM interaction of the system and how QM and MM are coupled by the QM/MM procedure.

2.1 Different Types of Energy

We will consider the *interaction energy* between two molecular species X and Y. We call the system of both molecules X – Y. We also consider the *adsorption energy* of a molecule X on the ice surface S. We call this system s-X. If not declared otherwise, all appearing energies are electronic ground state energies. We will describe the interaction energy first.

Consider a system of two molecules X and Y. We can calculate the energy of the isolated molecule X to be E_X and the energy of the isolated molecule Y to be E_Y . We can also calculate the energy of the full system X – Y, which will in general depend on the distance and the orientation of the two molecules, to be

E_{X-Y} . Then, the interaction energy between the two molecules is the energy given by

$$E_{X-Y}^{int} := E_{X-Y} - E_X - E_Y. \quad (1)$$

We did not include spatial dependency of E_{X-Y} into the above definition. A map $(R_{X-Y}, \Omega_X, \Omega_Y) \mapsto E_{X-Y}^{int}$ with the center of mass separation R_{X-Y} and the molecular orientation Ω_X and Ω_Y is called the *potential energy surface* (PES) of the intermolecular interaction. It may also contain internal deformations of the molecule.

However, one does often speak of the interaction energy of two molecules without further specification of a point on the PES. This is usually a reference to the minimum geometry of $X-Y$, that is the global minimum of E_{X-Y} and therefore E_{X-Y}^{int} . If the interaction between X and Y were purely repulsive, that is $E_{X-Y}^{int} > 0$ for all geometries, the global minimum would not be well-defined since it requires infinite separation of X and Y in an arbitrary direction. However, the algorithms we use will converge to a local minimum around the initial geometry we specify, by which we will then classify the strength of the repulsion. Even for attractive potentials, that is potentials where $E_{X-Y}^{int} < 0$ for some geometries, we are not able to determine whether the potential energy minimum we find is the global minimum or within what error its energy is to the global minimum.

The adsorption energy is mostly similar. There, we have the energy of the isolated species E_X and the energy minimum of the surface E_S . If we denote the system of the surface with the adsorbed molecule X by $s-X$ and its energy minimum by E_{s-X} , we define the adsorption energy to be

$$E_{s-X}^{ads} := E_{s-X} - E_X - E_S. \quad (2)$$

Again, we did not include the dependency of E_{s-X} and E_S on the respective geometries. We even specified that we will consider the individual geometry of minimum energy here. This is quite sensible because the surface geometry of the system $s-X$ (surface + molecule) may be different from the system S of the surface alone when comparing energy minima. For a fixed value of E_S , we could again consider a PES of the type $(\mathbf{r}_i)_i \mapsto E_{s-X}^{ads}$, where the vector \mathbf{r}_i is the coordinate of the i -th atom in $s-X$, $1 \leq i \leq N$ for some N . The different energy minima of this map to E_{s-X}^{ads} are called *binding geometries*, and the position of the center of mass of the molecule X in a binding geometry is called a *binding site*. Exploring binding sites and the strength of the binding E_{s-X}^{ads} can be useful to simulation. The superscripts on E^{int} and E^{ads} may be ignored if it is sufficiently clear which energy is meant.

We also want to introduce a third type of energy, the *zero-point (vibrational) energy*. We describe it for some general system A that may contain any arrangement of atoms. For all calculations we do, we will work with fixed values for the atomic

coordinates \mathbf{r}_i , $1 \leq i \leq N$ for some $N \in \mathbb{N}$. That description can only be accurate if the atoms were classical particles. However, if we want to allow for them to be quantum objects, we need to include uncertainty into their position. This is usually done by including the zero-point vibrational energy of the atoms. It is computed from the *Hessian* matrix \mathbf{H} of the system,

$$\mathbf{H}(\mathbf{r}_1, \dots, \mathbf{r}_N) := \left(\frac{\partial^2 E}{\partial \mathbf{r}_i \partial \mathbf{r}_j}(\mathbf{r}_1, \dots, \mathbf{r}_N) \right)_{1 \leq i, j \leq N} \quad (3)$$

by

$$E^{ZPE} = E + \frac{1}{2} \text{tr}[\mathbf{H}] = E + \Delta E^{ZPE}, \quad (4)$$

where $\text{tr}[\mathbf{H}]$ is the *trace* of the matrix \mathbf{H} , that is the sum of the eigenvalues of \mathbf{H} . In the harmonic approximation, which should be accurate for the vibrational ground state, the eigenvalues of \mathbf{H} are proportional to the eigenfrequencies of the system. We call the term ΔE^{ZPE} the *zero-point (vibrational) energy correction*.

We will always use the superscript in E^{ZPE} if we want to denote energies that are corrected with ΔE^{ZPE} in (4).

2.2 Methods of Quantum Chemistry

We already saw a few different energy expressions so far. The accurate calculation of these is naturally vital to anything we want to do in this work. We now want to focus on the methods of quantum chemistry which will be used to describe the quantum mechanical part of our system.

For a system with a time-independent potential V , one usually looks for solution of the *time-independent Schrödinger equation*

$$\hat{H}|\Psi\rangle = E|\Psi\rangle. \quad (5)$$

This equation holds for all non-relativistic quantum mechanical particles. Within the *Born-Oppenheimer* approximation, one can separate the dynamics of the atomic cores from the dynamics of the electrons. We will treat the cores in a more or less classical way, therefore we will for now focus on solving the Schrödinger equation for $N < \infty$ electrons, that is the Hamiltonian of our system is

$$\hat{H} = - \sum_{i=1}^N \frac{\hbar^2}{2m_e} \nabla_i^2 + \frac{e^2}{4\pi\epsilon_0} \sum_{1 \leq i < j \leq N} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} + V(\mathbf{r}^N). \quad (6)$$

\mathbf{r}_i is the space coordinate of electron i and ∇_i^2 is the *Laplace operator* applied to the three coordinates contained in \mathbf{r}_i . The electrons move in an external potential V given by the core geometry and movement, where \mathbf{r}^N is the vector containing all

electron coordinates. We will have for $K < \infty$ atomic cores

$$V(\mathbf{r}^N) = - \sum_{A=1}^K \frac{\hbar^2}{2m_A} \nabla_A^2 + \frac{e^2}{4\pi\epsilon_0} \sum_{A=1}^K \sum_{B=1}^K \frac{Z_A Z_B}{|\mathbf{R}_A - \mathbf{R}_B|} - \frac{e^2}{4\pi\epsilon_0} \sum_{A=1}^K \sum_{i=1}^N \frac{Z_A}{|\mathbf{R}_A - \mathbf{r}_i|}. \quad (7)$$

Here, Z_A is the atomic number of atom A and \mathbf{R}_A is the coordinate of it with corresponding ∇_A^2 . We can separate V into a core-core (cc) and an core-electron (ce) potential

$$V(\mathbf{r}^N) = V_{cc} + V_{ce}(\mathbf{r}^N) \quad (8)$$

with

$$V_{ce}(\mathbf{r}^N) = \sum_{i=1}^N \tilde{V}(\mathbf{r}_i) = - \frac{e^2}{4\pi\epsilon_0} \sum_{A=1}^K \sum_{i=1}^N \frac{Z_A}{|\mathbf{R}_A - \mathbf{r}_i|}. \quad (9)$$

There will be more than one solution to (5), so one can construct the set of all solutions $\{|\Psi_i\rangle | i \in \mathbb{N}_0\}$ with corresponding energy eigenvalues E_i . $\{|\Psi_i\rangle\}$ always is the complete basis of some \mathbb{C} -vector space \mathcal{H}_a , where the subscript a denotes anti-symmetry according to the *Pauli principle*

$$\begin{aligned} \langle \mathbf{x}_1, \dots, \mathbf{x}_l, \dots, \mathbf{x}_k, \dots, \mathbf{x}_N | \Psi_i \rangle \\ = \Psi_i(\mathbf{x}_1, \dots, \mathbf{x}_l, \dots, \mathbf{x}_k, \dots, \mathbf{x}_N) \\ = -\Psi_i(\mathbf{x}_1, \dots, \mathbf{x}_k, \dots, \mathbf{x}_l, \dots, \mathbf{x}_N), \end{aligned} \quad (10)$$

where we used $\mathbf{x}_i = (\mathbf{r}_i, s_i)$ for orbital coordinates \mathbf{r}_i and the spin coordinate s_i .

If $\mathcal{H}_a \subseteq \mathcal{L}^2$, which is usually the case, the set of solutions can be chosen orthonormal $\langle \Psi_i | \Psi_j \rangle = \delta_{ij}$. The set of solutions is usually not finite and the set of eigenvalues (energies) E_i of \hat{H} is not necessarily bounded from above. But there is always a minimum energy, denoted by E_0 , which we call the (*electronic*) *ground state energy*. The corresponding eigenvector $|\Psi_0\rangle$ is the (*electronic*) *ground state*. They can both be obtained by the variational ansatz

$$\begin{aligned} E_0 &= \min_{|\Psi\rangle} \{ \langle \Psi | \hat{H} | \Psi \rangle \}, \\ |\Psi_0\rangle &= \arg \min_{|\Psi\rangle} \{ \langle \Psi | \hat{H} | \Psi \rangle \}. \end{aligned} \quad (11)$$

Note that while E_0 is unique, there may be multiple possibilities for $|\Psi_0\rangle$, although we will not consider that case.

Now, equation (5) has a variety of equivalent counterparts. One of them is the key to the approach of DFT. When multiplying (5) by the bra $\langle \Psi |$, one can interpret the resulting energy as a (non-linear) functional of the wavefunction by

$$E : \mathcal{H}_a \rightarrow \mathbb{R}, \quad E[|\Psi\rangle] = \langle \Psi | \hat{H} | \Psi \rangle, \quad (12)$$

which would mean that the ground state energy can be found by minimizing the functional $E[|\Psi\rangle]$ according to (11). But so far,

the minimization of said functional only differs in semantics from the task of minimizing the energy expectation value.

A truly new task arises from considering the *electron density* ρ instead of the wave function Ψ . The two approaches are related, since the ground state electron density is given by

$$\rho(\mathbf{x}_1, \dots, \mathbf{x}_N) = |\Psi_0(\mathbf{x}_1, \dots, \mathbf{x}_N)|^2, \quad (13)$$

This N -electron density describes the probability of finding the system in a state within a small volume of $d\mathbf{x}_1 \cdots d\mathbf{x}_N$ around $(\mathbf{x}_1, \dots, \mathbf{x}_N)$. The N -electron density can be reduced to the one-electron density by

$$\rho(\mathbf{r}_1, s_1) = \int d\mathbf{x}_2 \cdots \int d\mathbf{x}_N |\Psi_0(\mathbf{x}_1, \dots, \mathbf{x}_N)|^2, \quad (14)$$

where the integrals run over the full spin-orbit space for all particles but the first.

For a system of N electrons, Hohenberg and Kohn[?] were able to show that the ground state one-electron density uniquely determines the Hamiltonian except for the addition of a constant, and that conversely there is a functional of the density that has its minimal value at the one-electron ground state density, and for which the minimum value is the ground state energy. Therefore, the task of solving the Schrödinger equation (5) is reduced to the task of finding the minimum of this density functional.

The problem here is that not much is known about the nature of this density functional. The popular ansatz by Kohn and Sham[?] is

$$\begin{aligned} E[\rho] &= V_{cc} + \int d\mathbf{r} \tilde{V}(\mathbf{r}) \rho(\mathbf{r}) + \frac{e^2}{2} \int d\mathbf{r} \int d\mathbf{r}' \frac{\rho(\mathbf{r}) \rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \\ &+ T[\rho] + E_{xc}[\rho] \end{aligned} \quad (15)$$

2.3 Molecular Mechanics and QM/MM

3 Benchmarking

4 Adsorption on the Ice Surface

4.1 The Surface Model

4.2 Results

5 Conclusion

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