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Nattino, F.

Citation

Nattino, F. (2015, October 28). *Ab initio molecular dynamics calculations on reactions of molecules with metal surfaces*. Retrieved from https://hdl.handle.net/1887/35980

Author: Nattino, Francesco
Title: Ab initio molecular dynamics calculations on reactions of molecules with metal surfaces
Issue Date: 2015-10-28

Chapter 2

Ab Initio Molecular Dynamics for Modeling Gas-Surface Reaction Dynamics

The aim of this chapter is to introduce the theoretical framework of *ab initio* molecular dynamics (AIMD) and to show how this technique can be employed to study gas-surface reactions. In Section 2.1 the AIMD method is presented, followed by a brief description of the electronic structure method employed, namely density functional theory (DFT, Section 2.2). The AIMD implementation to study gas-surface reaction dynamics is then described in Section 2.3, and the description of the most important observables computed concludes this chapter (Section 2.4).

2.1 The *Ab Initio* Molecular Dynamics Technique

The term *ab initio* molecular dynamics has been used in literature to refer to a large variety of techniques [1]: molecular dynamics simulations involving a pre-calculated *ab initio* based potential energy surface (PES), but also methods that calculate the relevant features of the PES (energy, forces) on the fly, i.e. during the dynamical evolution of the nuclei; wave function based methods, but also techniques that exploit density functional theory (DFT); techniques in which the Kohn-Sham (KS) DFT equations are diagonalized at each time-step while evolving the nuclear positions (Born-Oppenheimer molecular dynamics), but also methods in which the KS orbitals are classically propagated together with the nuclear positions (Car-Parrinello molecular dynamics [2]). Despite the variety of techniques which have been named AIMD in the past, this term is nowadays generally used as a synonym of Born-Oppenheimer molecular dynamics (BOMD) and we will use it with this meaning in the rest of the thesis.

2.1.1 Deriving Born-Oppenheimer Molecular Dynamics

The equations that govern the AIMD technique can be derived from the time-dependent Schrödinger equation, which describes the time evolution of a molecular system whose state is defined by the wave function $\Psi(\{\mathbf{r}_i\}, \{\mathbf{R}_I\}, t)$:

$$i\frac{\partial}{\partial t}\Psi(\{\mathbf{r}_i\}, \{\mathbf{R}_I\}, t) = \hat{H}\Psi(\{\mathbf{r}_i\}, \{\mathbf{R}_I\}, t). \tag{2.1}$$

Here $\{\mathbf{r}_i\}$ and $\{\mathbf{R}_I\}$ represent the sets of electronic and nuclear degrees of freedom, respectively. Note that atomic units have been used in Equation 2.1, and will be used in the rest of this chapter. $\hat{H}$ is the full Hamiltonian of the system and can be written in the following way:

$$\begin{aligned}\hat{H} = &-\sum_I \frac{1}{2M_I}\nabla_I^2 - \sum_i \frac{1}{2}\nabla_i^2 + \\ &-\sum_{i,I}\frac{Z_I}{|\mathbf{r}_i - \mathbf{R}_I|} + \sum_{j>i}\frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} + \sum_{J>I}\frac{Z_I Z_J}{|\mathbf{R}_I - \mathbf{R}_J|}.\end{aligned} \tag{2.2}$$

The first two terms represent the kinetic energy of the nuclei and the electrons, respectively. The third term represents the (attractive) interaction between electrons and nuclei. The last two terms represent the (repulsive) interaction between electrons and between nuclei, respectively. M_I and Z_I are the mass and the nuclear charge of the I-th nucleus, respectively. The Hamiltonian in equation 2.2 can also be written as:

$$\hat{H} = -\sum_I \frac{1}{2M_I} \nabla_I^2 + \hat{H}_e, \tag{2.3}$$

where $\hat{H}_e$ is the so-called clamped-nuclei Hamiltonian, the eigenstates of which depend parametrically on $\{\mathbf{R}_I\}$:

$$\hat{H}_e \psi_k(\{\mathbf{r}_i\}; \{\mathbf{R}_I\}) = E_k(\{\mathbf{R}_I\}) \psi_k(\{\mathbf{r}_i\}; \{\mathbf{R}_I\}). \tag{2.4}$$

Here, the $\psi_k(\{\mathbf{r}_i\}; \{\mathbf{R}_I\})$'s are known as adiabatic electronic states. Using these states, we can formulate an *ansatz* for $\Psi(\{\mathbf{r}_i\}, \{\mathbf{R}_I\}, t)$:

$$\Psi(\{\mathbf{r}_i\}, \{\mathbf{R}_I\}, t) = \sum_k \psi_k(\{\mathbf{r}_i\}; \{\mathbf{R}_I\}) \chi_k(\{\mathbf{R}_I\}, t). \tag{2.5}$$

Inserting this *ansatz* into Equation 2.1, multiplying it from the left by $\psi_k^*(\{\mathbf{r}_i\}; \{\mathbf{R}_I\})$ and integrating it over the electronic coordinates lead to a set of differential equations describing the nuclear motion. These equations are coupled through terms which arise from the action of the nuclear kinetic energy operator on $\psi_k(\{\mathbf{r}_i\}; \{\mathbf{R}_I\})$. Neglecting these coupling terms is the basis of the adiabatic (or Born-Huang) approximation [3]. Such neglect is equivalent to considering only one term into the expansion of Equation 2.5, typically the electronic ground state:

$$\Psi(\{\mathbf{r}_i\}, \{\mathbf{R}_I\}, t) \approx \psi_0(\{\mathbf{r}_i\}; \{\mathbf{R}_I\}) \chi_0(\{\mathbf{R}_I\}, t). \tag{2.6}$$

We can then introduce a further approximation and neglect all the terms arising from the action of the nuclear kinetic energy operator on $\psi_0(\{\mathbf{r}_i\}; \{\mathbf{R}_I\})$. This approximation is known as the Born-Oppenheimer (BO) approximation [4]. Both the adiabatic and the BO approximations are based on the consideration that the motion of the electrons and the nuclei occurs on different time-scales due to the large mass mismatch between the two particles. After applying the BO approximation, Equations 2.1 and 2.4 can be rewritten in the following way:

$$\left[-\sum_I \frac{1}{2M_I}\nabla_I^2 + E_0(\{\mathbf{R}_I\})\right]\chi_0(\{\mathbf{R}_I\},t) = i\frac{\partial}{\partial t}\chi_0(\{\mathbf{R}_I\},t), \tag{2.7a}$$

$$\hat{H}_e\psi_0(\{\mathbf{r}_i\};\{\mathbf{R}_I\}) = E_0(\{\mathbf{R}_I\})\psi_0(\{\mathbf{r}_i\};\{\mathbf{R}_I\}). \tag{2.7b}$$

The first equation describes the time evolution of the nuclei and contains the BO potential energy surface $E_0(\{\mathbf{R}_I\})$, obtained by solving the electronic time-independent Schrödinger equation for the ground state (Equation 2.7b).

At this stage we can introduce a further approximation for the nuclei and assume that they behave like classical point particles. It can be shown that taking the classical limit of Equation 2.7a leads to Newton's equation of motion:

$$M_I\ddot{\mathbf{R}}_I = -\nabla_I E_0(\{\mathbf{R}_I\}). \tag{2.8}$$

Therefore, the time-dependent problem of Equation 2.1 can be reduced to a time-independent electronic structure problem, with the time dependence remaining implicit in the time evolution of the nuclear positions: $\{\mathbf{R}_I\} = \{\mathbf{R}_I(t)\}$. Equation 2.8 can be integrated over time while solving concurrently the time-independent electronic Schrödinger equation, from which the forces $F_I = -\nabla_I E_0(\{\mathbf{R}_I\})$ are calculated for a specific fixed nuclear configuration $\{\mathbf{R}_I\}$. Since $E_0(\{\mathbf{R}_I\})$ is the Born-Oppenheimer potential energy surface, this approach is known as Born-Oppenheimer molecular dynamics.

2.1.2 The Hellmann-Feynman Forces

An efficient scheme for evaluating the forces acting on the nuclei is crucial for performing AIMD. We can write the following expression for the forces:

$$\begin{aligned} F_I &= -\nabla_I E_0(\{\mathbf{R}_I\}) = -\nabla_I\left\langle \psi_0 \middle| \hat{H}_e \middle| \psi_0 \right\rangle = \\ &= -\left\langle \nabla_I\psi_0 \middle| \hat{H}_e \middle| \psi_0 \right\rangle - \left\langle \psi_0 \middle| \hat{H}_e \middle| \nabla_I\psi_0 \right\rangle - \left\langle \psi_0 \middle| \nabla_I\hat{H}_e \middle| \psi_0 \right\rangle. \end{aligned} \tag{2.9}$$

According to the Hellmann-Feynman theorem [5,6], the first two terms in Equation 2.9 vanish, provided that ψ_0 is an eigenfunction of $\hat{H}_e$:

$$F_I^{HF} = -\left\langle \psi_0 \middle| \nabla_I \hat{H}_e \middle| \psi_0 \right\rangle . \tag{2.10}$$

This theorem is also valid if ψ_0 is not an eigenfunction of $\hat{H}_e$ but only in the limit of a complete basis set expansion for ψ_0. For incomplete basis sets, in addition to the Hellmann-Feynman force F_I^{HF} (Equation 2.10), two other terms have to be considered when computing the force F_I [7, 8]. One term arises from the action of the nuclear derivative on the basis functions, and it is generally known as Pulay force. This contribution, however, is exactly zero if a basis set of non-atom-centered functions is employed (e.g. plane waves, see also Section 2.2.2), provided that the number of basis functions is kept fixed during the calculation. The second contribution is related to the way in which the electronic structure problem is solved to find the electronic ground state of the system. In Kohn-Sham DFT, the Kohn-Sham equations are solved iteratively until a certain convergence threshold is reached (see also Section 2.2). This means that the ground state electron density is not exactly self-consistent, and the same is true for the KS potential, which leads to a 'non-self-consistency' (NSC) contribution to the forces. This contribution, however, can be made arbitrarily small by setting tighter convergence criteria. Furthermore, schemes exist to estimate and approximately correct for the NSC contribution [7–9].

2.1.3 Alternative Dynamical Methods

In Section 2.1 we have seen that the time-dependent problem of Equation 2.1 can be reduced to the time-independent problem of finding the electronic ground state solution for a fixed nuclear configuration and the time evolution of the nuclear positions (Equation 2.8). The electronic and nuclear problems can in principle be solved in two separate steps: first one calculates the BO potential energy surface (PES) for various nuclear configurations, and then one employs the pre-calculated PES for running the nuclear dynamics. Note that only the first of these two steps is computationally expensive, while the integration of the nuclear equations of motion is relatively cheap. Therefore, the implementation of this approach allows for the computation of a large number of nuclear dynamics calculations, and a long time propagation in these. The drawback of this strategy is that the PES has to be represented by a continuous function, which means that a suitable functional form has to be employed to fit or interpolate the pre-calculated points of the PES. For molecules interacting with a metal surface, state-of-the-art PESs typically describe up to six degrees of freedom (DOFs), i.e. all the molecular DOFs for a diatomic [10–18]. The PES of systems like CH_4 + metal surfaces, where in principle a large number of molecular degrees of freedom (15) has to be modeled together with the relevant surface phonons, has been described so far only by using dynamical approximations or model potentials (e.g. reactive force-fields) [19–21].

The methods discussed so far exploit the classical approximation for the nuclei. Quantum effects could also play a role in gas-surface reactions. For instance, classical mechanics is not able to describe tunneling and does not guarantee zero point energy (ZPE) conservation. Such effects are especially relevant for reactions involving light atoms, like hydrogen, and at conditions such as low collision energies. Quantum dynamical methods have been used to solve directly Equation 2.7a [15, 22–24]. These methods are computationally expensive because they have to deal with the nuclear wave function. Therefore, the number of DOFs that can be explicitly modeled is limited. Moreover, a continuous representation of the PES is still needed by these methods.

2.2 Density Functional Theory

The electronic structure method which is mostly used in conjunction with AIMD is density functional theory (DFT), due to its relatively low computational cost and its favorable scaling ($\propto n^3$, where n is the number of electrons in the system, which compares to $\propto n^4$ or worse for wave function-based methods). The groundwork of DFT has been laid by Hohenberg and Kohn (HK) [25], who demonstrated that for a system constituted by n electrons in an external potential generated by the nuclei the ground state wave function is uniquely determined by the electron density. Therefore, the electron density defines all the properties of the system. Furthermore, HK demonstrated that the energy corresponding to any electron density other than the ground state density is larger than the ground state energy, giving a criterion for guiding the search of the ground state density. Note that in the original paper by HK, the demonstration was restricted only to non-degenerate ground states, while this restriction was lifted in later formulations of DFT [26].

Kohn and Sham (KS) [27] suggested a strategy for putting DFT into practice. Their approach involves a fictitious system constituted by non-interacting electrons. The exact ground-state wave function of such a system can be represented by a Slater determinant. The one-electron wave functions $\phi_i(\mathbf{r})$ (the KS orbitals) that compose such a determinant can be determined through the following set of equations:

$$\left[-\frac{1}{2}\nabla^2 + V_S(\mathbf{r})\right]\phi_i(\mathbf{r}) = \epsilon_i\phi_i(\mathbf{r}). \tag{2.11}$$

Here $V_S(\mathbf{r})$ is an effective potential, the KS potential, and ϵ_i is the orbital energy. In the first term in the brackets we recognize the one-electron kinetic energy operator. The KS orbitals can be used to construct the electron density of the non-interacting system according to:

$$\rho_S(\mathbf{r}) = \sum_i |\phi_i(\mathbf{r})|^2 . \tag{2.12}$$

The KS potential is crucial to connect the real system, i.e. the system with interacting electrons, to the fictitious system (with non-interacting electrons). In fact, it can be shown that $\rho_S(\mathbf{r})$ equals the ground state density of the real system $\rho_0(\mathbf{r})$ if the KS potential is set in the following way:

$$V_S(\mathbf{r}) = -\sum_I \frac{Z_I}{|\mathbf{r}-\mathbf{R}_I|} + \int d\mathbf{r}' \frac{\rho(\mathbf{r})}{|\mathbf{r}-\mathbf{r}'|} + V_{XC}(\mathbf{r}). \tag{2.13}$$

In the first term we recognize the electron-nuclei interaction potential. The second term is the Hartree potential, which gives rise to the classical part of the electron-

electron interaction energy (the electrostatic repulsion). The last term is the exchange-correlation potential, defined as the functional derivative of the exchange-correlation energy $E_{XC}[\rho(\mathbf{r})]$ with respect to the electron density:

$$V_{XC}(\mathbf{r}) = \frac{\delta E_{XC}[\rho(\mathbf{r})]}{\delta \rho(\mathbf{r})}. \tag{2.14}$$

The exchange-correlation energy represents the collection of all the energy terms of which the exact expression is unknown, i.e. the non-classical part of the electron-electron interaction and the difference between the kinetic energy of the real system and the kinetic energy of the non-interacting system. By substituting the expression of $V_S(\mathbf{r})$ into Equation 2.11 we obtain the so-called KS equations. Note that $V_S(\mathbf{r})$ depends on the density (and therefore on the orbitals ϕ_i) through the Hartree potential, therefore the KS equations have to be solved iteratively. The expression of the energy as a function of the electron density has the following form:

$$\begin{aligned} E[\rho] = &- \frac{1}{2}\sum_i \langle\phi_i| \nabla^2 |\phi_i\rangle - \sum_I \int \frac{Z_I}{|\mathbf{r} - \mathbf{R}_I|}\rho(\mathbf{r})d\mathbf{r} + \\ &+ \int d\mathbf{r} \int d\mathbf{r}' \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + E_{XC}(\mathbf{r}) + \sum_{J>I} \frac{Z_I Z_J}{|\mathbf{R}_I - \mathbf{R}_J|}. \end{aligned} \tag{2.15}$$

Note that we have added the nuclei-nuclei interaction (last term), that contributes to the energy of the system as a mere constant for a given nuclear configuration. The fictitious non-interacting system is therefore used to represent at least the part of the kinetic energy for which we have an analytical expression, which involves the KS orbitals.

2.2.1 The Exchange-Correlation Functional

If the exact expression of $E_{XC}[\rho(\mathbf{r})]$ was known, the KS equations would lead to the exact ground state energy of the system. However, only approximations are available for this energy term. Using the local density approximation (LDA) the electrons of the system are assumed to behave as a uniform electron gas on a positive background. For such a system, $E_{XC}[\rho(\mathbf{r})]$ can be written in the following way:

$$E_{XC}^{LDA}[\rho(\mathbf{r})] = \int \rho(\mathbf{r})(\varepsilon_X(\rho(\mathbf{r})) + \varepsilon_C(\rho(\mathbf{r})))d\mathbf{r}, \tag{2.16}$$

where $\varepsilon_X(\rho(\mathbf{r}))$ and $\varepsilon_C(\rho(\mathbf{r}))$ are the exchange and the correlation energies per electron for a given electron density $\rho(\mathbf{r})$, respectively. An analytical expression exists for $\varepsilon_X(\rho(\mathbf{r}))$ [28, 29]:

$$\varepsilon_X(\rho(\mathbf{r})) = -\frac{3}{4}\left(\frac{3}{\pi}\rho(\mathbf{r})\right)^{\frac{1}{3}}, \tag{2.17}$$

while $\varepsilon_C(\rho(\mathbf{r}))$ can be calculated very accurately using analytical expressions [30, 31] which have been fitted to quantum Monte Carlo calculations [32].

Unfortunately, the LDA fails quite dramatically in reproducing properties like barrier heights for molecule-surface reactions (see for instance Refs. [33, 34]). If the gradient of the density is included in the expression of $E_{XC}[\rho(\mathbf{r})]$ in addition to the density itself we obtain the so-called generalized gradient approximation (GGA):

$$E_{XC}^{GGA}[\rho(\mathbf{r})] = \int f[\nabla\rho(\mathbf{r}), \rho(\mathbf{r})]d\mathbf{r}. \tag{2.18}$$

All the traditional GGA functionals employ an expression for the exchange-correlation energy E_{XC}^{GGA} in which this term is split into an exchange and a correlation contribution, E_X^{GGA} and E_C^{GGA}, respectively, as for the LDA. Furthermore, the exchange part of E_{XC}^{GGA} is always expressed in the following way [35–38]:

$$E_X^{GGA} = \int \rho(\mathbf{r})\varepsilon_X(\rho(\mathbf{r}))F(s)d\mathbf{r}, \tag{2.19}$$

where $F(s)$ is generally called exchange enhancement factor, and s is the so-called reduced density gradient:

$$s = \frac{|\nabla\rho|}{2(3\pi^2)^{1/3}\rho^{4/3}(\mathbf{r})}. \tag{2.20}$$

The exponent of the density at the denominator is such that s is dimensionless. We note in passing that Peverati and Truhlar use Equation 2.19 to define the GGA [39], since all the traditional GGA functionals exploit such an expression for the exchange part of E_{XC}^{GGA}. In addition, Peverati and Truhlar define the non-separable gradient approximation (NGA) according to which a functional of the electron density and its gradient is employed to represent both exchange and correlation in a non-separable term [39, 40].

One example of $F(s)$ is the following function, which constitutes the exchange enhancement factor for the PBE exchange-correlation functional [36]:

$$F^{PBE}(s) = 1 + \kappa - \frac{\kappa}{1 + \mu s^2/\kappa}, \tag{2.21}$$

where κ and μ are derived from physical constants (not semiempirical parameters). The RPBE exchange-correlation functional [37] differs from the PBE functional only in the expression of $F(s)$:

$$F^{RPBE}(s) = 1 + \kappa \cdot \left(1 - e^{-\mu s^2/\kappa}\right). \tag{2.22}$$

Various expressions have been proposed for E_C^{GGA}. Functionals like PW91 [35] and (R)PBE [36, 37] employ an expression for E_C^{GGA} based on the free-electron gas correlation:

$$E_C^{GGA} = \int \rho(\mathbf{r}) \left(\varepsilon_C(\rho(\mathbf{r})) + H[\nabla\rho(\mathbf{r}), \rho(\mathbf{r})]\right), \tag{2.23}$$

where H represents the gradient contribution to E_C^{GGA}. H differs from functional to functional, and is parameter-free for both PW91 and (R)PBE. The LYP correlation functional [41], on the other hand, is derived from the expression of the correlation energy for an helium atom based on wave function methods [42].

GGA functionals generally present a mean absolute error (MAE) in describing gas-phase reaction barrier heights of about 5 kcal/mol [43], the lowest value so far being obtained by the MOHLYP2 functional (MAE = 3.8 kcal/mol) [39, 43]. The MAE has not yet been determined for gas surface reactions but many examples are known in which a chemically accurate description (to within 1 kcal/mol) of the barrier heights was not achieved with regular GGA functionals (see for instance Refs. [15, 44, 45]).

The research of more accurate exchange-correlation functionals led to the formulation of functionals which take the Laplacian of the electron density $\nabla^2\rho(\mathbf{r})$ and the (non-interacting) kinetic energy density $\tau = \sum_i |\nabla\phi_i|^2$ into account (meta-GGA and meta-NGA functionals) and functionals that include a part of exact Hartree-Fock exchange (hybrid functionals). Meta-GGA, meta-NGA and in particular hybrid functionals are computationally more expensive than GGA functionals. For this reason their use in molecule-surface reactions has been scarce so far.

A limitation of regular GGA functionals is that they are not able to accurately describe long-ranged interactions such as van der Waals (vdW) forces. Different approaches have been developed to mimic these interactions using conventional KS-DFT. According to the methods of Grimme [46,47] and Tkatchenko and Sheffler [48] a dispersion potential in the form of a pairwise force field is added to the KS energy. Langreth, Lundqvist and coworkers, on the other hand, proposed a non-local correlation functional able to approximately account for dispersion interactions [49,50]. An efficient implementation of this correlation functional has recently appeared [51]. Functionals including this correlation have been recently tested in the field of gas surface reaction dynamics showing a moderate improvement over regular GGA functionals [44,52].

A semi-empirical approach to the unknown exchange-correlation functional is the so-called specific reaction parameter (SRP) approach. In its original version developed by Truhlar and coworkers [53,54] for gas-phase reactions, one or a few parameters in the exchange-correlation functional are fitted to a set of experimental data in order to make the functional optimal for describing a specific reaction; the fitted functional is then tested against other sets of experimental data for the same system. Díaz et al. [15,16] applied a novel implementation of this approach to a gas-surface reaction by fitting a weighted average of two GGA density functionals to a single set of experimental data sensitive to the minimum barrier height for H_2 + Cu(111). It has been shown that this new semi-empirical functional is able to reproduce various experimental data for the H_2 + Cu(111) system with chemical accuracy, and that this functional is transferable to another crystal face of the same metal, i.e. Cu(100) [55,56].

2.2.2 Plane wave DFT

As mentioned above, DFT is very often employed in conjunction with AIMD due to the favorable scaling of this electronic structure method with system size. Furthermore, in combination with a periodic slab approach, DFT is very suitable for representing an infinite surface. For periodic systems, the natural basis for the expansion of the KS orbitals consists of plane waves:

$$\phi_j(\mathbf{r},\mathbf{k}) = N\sum_{\mathbf{G}} c_{j\mathbf{Gk}} e^{i(\mathbf{k}+\mathbf{G})\cdot\mathbf{r}}. \tag{2.24}$$

Here j labels the KS orbitals, $\mathbf{G}$ is a reciprocal lattice vector, $\mathbf{k}$ is a vector in the first Brillouin zone, $c_{j\mathbf{Gk}}$ is an expansion coefficient and N a normalization factor. When performing actual calculations the first Brillouin zone has to be sampled by a discrete grid of points (the k-points) and the plane wave expansion of Equation 2.24 has to be truncated. The size of the basis set is generally specified further by a single parameter, i.e. the maximum kinetic energy E_{cut} that can be represented by a basis function. In formulas, the plane wave $e^{i(\mathbf{k}+\mathbf{G})\cdot\mathbf{r}}$ is included in the basis set if :

$$\frac{1}{2}\left|\mathbf{k}+\mathbf{G}\right|^2 < E_{cut}. \tag{2.25}$$

The use of a plane wave basis set brings a number of advantages. First, Pulay forces, which arise in the evaluation of the forces when using an (incomplete) localized basis set, automatically vanish, significantly simplifying the evaluation of $-\nabla_I E_0(\{\mathbf{R}_I\})$ (see also Section 2.1). Also, a basis set superposition error does not arise in the context of plane waves, since plane waves are non-atom-centered functions homogeneously distributed in the space. Furthermore, computational advantages arise from the fact that plane wave derivatives in real space correspond to simple multiplications in reciprocal space, and efficient algorithms exist to connect the real and the reciprocal space (Fast Fourier Transforms, FFTs).

One of the drawbacks of the use of plane waves is that the energy converges slowly with basis set size when trying to represent core electron atomic orbitals, which are rapidly varying functions due to their localization near the nucleus, and valence electron orbitals in the proximity of the nuclei, which can assume an highly-oscillating behaviour. Core electrons, however, do not significantly affect the chemistry of atoms and molecules, since the rearrangement of the valence electrons is mainly responsible for bonding. Therefore, they can be replaced by effective potentials named pseudopotentials [57, 58]. Furthermore, pseudopotentials can also be used to account for relativistic effects. Moreover, the pseudopotentials can be chosen such that the pseudized wave functions are smoother than the corresponding all-electron wave functions at short distances from the nuclei, while they reproduce the all-electron wave functions beyond a certain cut-off radius.

Another drawback of plane waves is that the basis-set size automatically increases with the unit cell size, regardless of the number of atoms in the unit cell. This means that the need to include a large vacuum space in the unit cell to minimize the ‘artificial’ interactions between periodic images, automatically translates in a large basis set size.

2.3 The AIMD Implementation

AIMD has been employed to investigate gas-surface reactions since the early 90’s [59–61]. However, the computational cost of AIMD limited these first studies to a few explorative trajectories. With the growth of computational power and the development of efficient algorithms, the use of AIMD to perform statistically relevant calculations for gas-surface reactions has recently become possible [62].

Ultimately, an AIMD study of a molecule-surface reaction can be divided into three steps:

- the choice of the trajectories’ initial conditions;
- the time propagation of the trajectories;
- the analysis of the computed trajectories.

These steps are now discussed below.

2.3.1 The Choice of the Initial Conditions

The way in which the initial positions and the velocities are assigned to the nuclei at the starting point of the trajectories is discussed separately for the surface atoms and for the molecule.

2.3.1.1 The Surface

As we already mentioned, the surface is modeled with a periodic slab. The atomic positions are chosen in such a way that the periodic repetition of a suitably chosen unit cell reproduces the desired surface structure. In the implementation used, the unit cell has to include a large vacuum space in order to minimize the interaction between periodic images of the slab, and of the molecule with the periodic replica of the slab it interacts with. The length of the vacuum space in the cell, the surface unit cell size and the number of atomic layers are all parameters for which convergence needs to be tested with respect to the properties of interest.

The initial conditions of the surface atoms are chosen with the aim of studying the effect that surface temperature and surface atom motion have on the dissociation probability of molecules on metal surfaces. Surface temperature can influence the dissociation probability in various ways. First, local lattice deformations caused by the thermal motion of surface atoms can affect the reaction barrier heights as known, for instance, for the dissociation of CH_4 on metals, where the outward displacement of the surface atom below the dissociating molecule significantly lowers the energy of the transition state [63, 64]. The dissociation barrier heights can also be affected by the thermal expansion of the whole lattice [65, 66], as observed for H_2 on Cu(111), where the d-band of the metal is up-shifted with increased surface strain [67]. Finally, the surface can act as a heat bath, and help to stabilize an adsorbate by subtracting an excess of kinetic energy from the impinging molecule through recoil. This last effect is expected to be the more significant the larger the ratio between the mass of the molecule and the mass of the surface atoms is, due to the larger efficacy of the energy transfer as predicted by the Baule model [68, 69].

In order to investigate the role that surface atom motion plays in each system investigated, we have performed three types of calculation. In the first type of calculations we simulate an ideal surface keeping the atoms fixed in their equilibrium positions, neglecting all the surface temperature effects (lattice distortion, thermal expansion) and surface atom motion effects (recoil). In the second type of calculations surface temperature effects are included, but the surface atoms are kept fixed in their (distorted) initial position, blocking the energy transfer to the surface. Surface deformation, surface atom motion and the expansion of the lattice constant to mimic the thermal expansion of the lattice are all effects included in the third and last kind of calculations performed. Displacements and velocities are assigned to surface atoms by sampling the initial configuration from long differently-initialized equilibration runs.

2.3.1.2 The Molecule

The molecules' initial conditions are chosen on the basis of the experiments that we want to simulate. The positions and the velocities of each atom define the initial position of the center of mass of the molecule, its orientation, the collision energy, and the (initial) quantum state. Concerning the molecule's initial position, the lateral displacement is chosen randomly in order to uniformly sample the surface unit cell plane with the impacting molecule's center of mass. The initial distance from the surface is chosen in an area where the molecule-surface interaction is negligible. The initial translational and rotational energies are set by assigning the corresponding velocities to the atoms. The rotational phase of the molecule is randomly sampled. The molecules are chosen to be isotropically oriented if the experimental conditions that we want to simulate do not require a specific rotational alignment. The vibrational coordinates are chosen such that normal vibrational coordinates and momenta sample classical microcanonical distributions. Note, however, that we exploit the quasi-classical trajectory (QCT) method, which means that vibrational zero-point energy is imparted to the molecules. If rotational alignment effects are investigated, the initial orientation of the molecule and of its angular momentum are sampled in accordance with the experimental distributions.

2.3.2 The Time Propagation

The time propagation of the trajectories has been carried out using the DFT and molecular dynamics code VASP [9, 70–73]. Once the forces are calculated from the optimized electron density, the nuclear positions are updated according to a propagator of the leapfrog form:

$$\mathbf{v}_I(t + {}^{\Delta t}\!/_2) = \mathbf{v}_I(t - {}^{\Delta t}\!/_2) + \mathbf{a}_I(t)\Delta t, \tag{2.26a}$$

$$\mathbf{R}_I(t + \Delta t) = \mathbf{R}_I(t) + \mathbf{v}_I(t + {}^{\Delta t}\!/_2)\Delta t. \tag{2.26b}$$

Here $\mathbf{v}_I$ and $\mathbf{a}_I$ are the velocity and the acceleration of the I-th nucleus, respectively, and Δt is the time-step chosen for the integration. Note that in contrast to the standard implementation of the leapfrog algorithm, the algorithm presented here propagates first the velocities and then the positions. Note also that the algorithm presented in Equations 2.26(a-b) is not self-starting, and that the velocities at time $t = -{}^{\Delta t}\!/_2$ have to be supplied together with the positions at time $t = 0$ to VASP when starting an AIMD calculation. The leapfrog propagator is equivalent to the Velocity Verlet algorithm [74], with the only difference being an half time-step stagger between positions and velocities in the former. However, the velocities at the times at which positions are available can be easily computed as:

$$\mathbf{v}_I(t) = \frac{\mathbf{R}_I(t - \Delta t) + \mathbf{R}_I(t + \Delta t)}{2\Delta t}. \tag{2.27}$$

Both the leapfrog and the Velocity Verlet algorithms are time-reversible and symplectic. These properties allow for a good conservation of total energy and other constants of motion such as linear and angular momentum. The truncation error in the leapfrog propagator is of the order of Δt^3 for a single time-step, while the global error, i.e. the error associated with the propagation for a finite time $T = n\Delta\mathrm{t}$, with n integer, is of the order of Δt^2, as for the Velocity Verlet algorithm.

2.3.3 The Analysis of the Trajectories

After the propagation over a certain number of time-steps, the trajectories are analyzed to determine whether a specific outcome has been reached. This outcome can be, for instance, the dissociation of the molecule, and its verification can be monitored through a suitable operational definition. For instance, we can monitor whether the distance between two fragments of the molecule becomes larger than a certain value, in which case we may consider the outcome of the trajectory as reaction. Given the slab approach employed, the periodic boundary conditions have to be taken into account when analyzing the computed trajectories. In case that no outcome has been reached yet, the trajectories can be further propagated in time.

Note that a single trajectory usually does not give information that can be directly compared to experimental observables, but that it is only from the statistical analysis of a set of trajectories that we can extract physically relevant data.

2.4 The Computation of Observables

In this subsection we describe two observables that we have computed with AIMD. Further details will be given for each specific system in the following chapters.

2.4.1 The Initial State-Selected Reaction Probability

The initial state-selected reaction probability $R_{v,J}(E,\Theta,\Phi)$ is the dissociation probability for molecules initially prepared in a specific quantum state (v,J) and with a specific collision energy E, averaged over impact site on the surface and molecular orientation. The dissociation probability can also depend on the polar and the azimuthal angles defining the direction with which the molecules approach the surface, Θ and Φ, respectively.

As a consequence of the multidimensionality of the PES that describes the molecule-surface interaction, each molecule approaching the surface experiences a different interaction depending on the path that it follows. A first rough estimate of the reaction probability for molecule-surface systems can be based on a (static) analysis of a pre-calculated PES, assuming that the molecules maintain their initial orientation and impact site on the surface, and that they follow the minimum energy path in the remaining degrees of freedom. Such a static model, for instance the hole model [75, 76], does not include any dynamical effects, such as steering, and cannot be used to describe experiments in which the dependence of the reactivity on the energy disposed in various molecular degrees of freedom is far from statistical. A dynamical model is therefore required to investigate such properties.

The initial state-selected reaction probability $R_{v,J}$ can be estimated by running a set of AIMD trajectories. The initial conditions of all the trajectories are chosen to model a specific initial quantum (rovibrational) state and a specific initial collision energy. $R_{v,J}$ can then be estimated as the ratio between the number of reactive events observed and the total number of simulated trajectories. Experimentally, $R_{v,J}$ has been determined for H_2 [77] and D_2 [78] reacting on Cu(111) from desorption experiments through application of the principle of detailed balance. $R_{v,J}$ can also be measured in adsorption experiments by using a laser to prepare the reacting molecules in a specific initial quantum state (see for instance Refs. [24,79]). Special care, however, has to be taken to discard the reactivity contribution coming from molecules not excited by the laser, and to deconvolute the dissociation probability from the velocity distribution of the molecular beam (see also Section 2.4.2).

2.4.2 Simulation of Molecular Beam Adsorption Experiments

The molecular beam technique is a powerful experimental method to study the dynamics of gas-surface reactions. A basic molecular beam apparatus consists of a gas chamber connected to a ultra high vacuum (UHV) chamber through a small orifice. The expansion of the gas through the orifice produces a beam of molecules, in which the number of collisions between particles is very low. The molecular beam can be directed towards a well-cut single crystal, and the sticking probability determined through various experimental techniques. Molecular beam experiments are very popular in surface science because they allow for a relatively high control of the physical properties of the molecules in the beam, such as their velocity or their vibrational and rotational state.

The sticking probability measured in a molecular beam experiment can be related to the initial state-selected reaction probabilities $R_{v,J}(E, \Theta, \Phi)$ through the following expression:

$$S_0(v_s, \alpha, T_n, \Theta, \Phi) = \sum_{v,J} F_{v,J}(T_n) \int_{E=0}^{\infty} R_{v,J}(E, \Theta, \Phi) f(v_s, \alpha, E) dE. \tag{2.28}$$

Note that we left the dependence of S_0 on Θ and Φ explicit. Experimental conditions are such that the polar angle Θ is usually accurately determined, while the azimuthal angle Φ, the determination of which requires the knowledge of the orientation of the beam with respect to the surface crystal directions, is often not known. The simulation of experiments in which Φ has not been determined is frequently performed by averaging over all the possible azimuthal orientations, i.e. by integrating the rhs of Equation 2.28 over Φ between 0 and 2π. The energy integral in Equation 2.28 includes the translational energy distribution of the molecules in the beam $f(v_s, \alpha, E)$. This distribution can be expressed as a function of two parameters, i.e. the stream velocity v_s and the width parameter α. These parameters can be obtained by determining the translational energy distribution from fits to recorded time-of-flight (TOF) measurements of the beam. In the velocity domain, this distribution has the following form [80]:

$$f'(v_s, \alpha, v) dv = N_v \exp\left[-\left(\frac{v - v_s}{\alpha} \right)^2 \right] v^3 dv. \tag{2.29}$$

Here N_v is a normalization factor. The same distribution can also be expressed in the energy domain [80]:

$$f(v_s, \alpha, E) dE = N_E \exp\left[-4E_s \left(\frac{\sqrt{E} - \sqrt{E_s}}{\Delta E_s^2} \right)^2 \right] E dE, \tag{2.30}$$

where N_E is a normalization factor, $E_s = \frac{1}{2} m v_s^2$ and $\Delta E_s = 2E_s\alpha/v_s$. The presence of various rovibrational states in the beam is taken into account by the sum in Equation

2.28. The contribution of each quantum state to the overall reactivity is weighted by the corresponding Boltzmann factor $F_{v,J}(T_n)$:

$$F_{v,J}(T_n) = N \cdot g_v \cdot g_J \cdot \exp\left(-\frac{E(v,J)}{k_b T_n}\right). \tag{2.31}$$

Here N is a normalization factor, g_v and g_J are the vibrational and the rotational degeneracy factors, respectively, $E(v,J)$ is the internal energy of the rovibrational state (v,J) and k_b is the Boltzmann constant. For molecular hydrogen, the rotational degeneracy factor is equal to $g_J = d_{op} \cdot (2J+1)$, where d_{op} is a factor that accounts for the ortho-para population ratio (3:1 for H_2 and 2:1 for D_2, at room temperature). In Equation 2.31 we are assuming the same rotational and vibrational temperatures for the molecules in the beam, both being equal to the nozzle temperature T_n. However, the rotational degrees of freedom might cool down during the expansion from the nozzle. To model this effect, a lower rotational temperature can be employed for calculating the Boltzmann population of the rotational states.

In order to simulate a molecular beam experiment and to calculate the corresponding sticking probability with AIMD a Monte Carlo integration is performed over the collision energies and the rovibrational states. The initial conditions are randomly selected by sampling the experimental translational energy distribution and the Boltzmann distribution of states and the sticking probability is estimated as the ratio between the number of reactive events observed N_r and the total number of trajectories simulated N_{tot}:

$$p = \frac{N_r}{N_{tot}}. \tag{2.32}$$

It is also important to adequately estimate a confidence interval for p. The set of possible outcomes (reaction or scattering) for N_{tot} simulated trajectories obeys a binomial distribution. According to the central limit theorem, this distribution approaches a Gaussian for large N_{tot}. Thus, under this condition, the confidence interval for the binomial proportion p can be estimated as for data normally distributed around the sample mean p with standard deviation of the mean $\sigma = \sqrt{p(1-p)/N_{tot}}$ [81]. The lower limit l and the upper limit u of the c confidence interval can therefore be written as:

$$l = p - z_{1-\frac{1}{2}(1-c)} \cdot \sqrt{\frac{p(1-p)}{N_{tot}}}, \tag{2.33a}$$

$$u = p + z_{1-\frac{1}{2}(1-c)} \cdot \sqrt{\frac{p(1-p)}{N_{tot}}}, \tag{2.33b}$$

where z_k is the k percentile of a standard normal distribution (e.g. for 95% confidence interval, $c = 0.95$, $z_{1-\frac{1}{2}(1-c)} = z_{0.975} = 2$). This interval, known as normal approximation interval or Wald interval, can be used whenever N_{tot} is large and p is far from both 0 and 1.

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