In silico study of reaction mechanisms and design principles for water oxidation catalysts

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Chapter 2:

Theoretical Methods

2.1 Introduction

In this chapter a brief description of the theoretical methods and approximations used in this thesis is presented. In the first place, the Born-Oppenheimer approximation will be summarized, followed by a short introduction to Density Functional Theory and a discussion on the exchange-correlation functionals. Finally an overview of the *ab-initio* molecular dynamics theory will be given, together with the recent implementation of the metadynamics approach for describing events that are rare on the time scale of molecular dynamics simulations.

2.2 Born-Oppenheimer Approximation

The time-dependent Schrödinger equation,

$$\hat{H}\,\Psi(\mathbf{r},\mathbf{R},t) = i\hbar\frac{\partial\Psi(\mathbf{r},\mathbf{R},t)}{\partial t}, \qquad (2.1)$$

is a non-relativistic description of the system and it is only valid when the velocity of the particles is small in comparison with the speed of light. Since $\hat{H}$ is not time dependent for the molecular complexes of interest in this thesis, the equation **2.1** can be simplified to the time-independent Schrödinger equation

$$\hat{H}\,\Psi(\mathbf{r},\mathbf{R}) = E\Psi(\mathbf{r},\mathbf{R}). \qquad (2.2)$$

Following the Born interpretation of the wavefunction, Ψ has to satisfy the normalization condition [1]

$$\langle \Psi \mid \Psi \rangle = 1. \qquad (2.3)$$

The Hamiltonian contains kinetic and potential energy terms and can be written as

$$\begin{aligned} \hat{H} = \quad & \hat{T}_{\mathrm{N}}(\mathbf{R}) + \hat{T}_{\mathrm{e}}(\mathbf{r}) + \hat{V}_{\mathrm{N-N}}(\mathbf{R}) \\ & + \hat{V}_{\mathrm{e-e}}(\mathbf{r}) + \hat{V}_{\mathrm{e-N}}(\mathbf{r},\mathbf{R}) \end{aligned} \qquad (2.4)$$

where $\hat{T}_{\mathrm{N}}(\mathbf{R})$ is the kinetic energy operator for the nuclei,

$$\hat{T}_{\mathrm{N}} = -\frac{\hbar^2}{2}\sum_{I}^{N}\frac{1}{M_I}\left(\frac{\partial^2}{\partial X_I^2}+\frac{\partial^2}{\partial Y_I^2}+\frac{\partial^2}{\partial Z_I^2}\right), \qquad (2.5)$$

and $\hat{T}_{\mathrm{e}}(\mathbf{r})$ is the electronic kinetic energy operator

$$\hat{T}_{\mathrm{e}} = -\frac{\hbar^2}{2}\sum_{i}^{n}\frac{1}{m}\left(\frac{\partial^2}{\partial x_i^2}+\frac{\partial^2}{\partial y_i^2}+\frac{\partial^2}{\partial z_i^2}\right). \qquad (2.6)$$

The potential energy part consists of the nuclear-nuclear repulsion, the electron-electron repulsion and the electron-nuclear attraction, written respectively as

$$\hat{V}_{\mathrm{N-N}} = \frac{1}{4\pi\varepsilon_0}\sum_{I}^{N}\sum_{J>I}^{N}\frac{Z_I Z_J e^2}{R_{IJ}}, \qquad (2.7)$$

$$\hat{V}_{\text{e–e}} = \frac{1}{4\pi\varepsilon_0}\sum_{i}^{n}\sum_{j>i}^{n}\frac{e^2}{r_{ij}} \qquad (2.8)$$

and

$$\hat{V}_{\text{e–N}} = -\frac{1}{4\pi\varepsilon_0}\sum_{i}^{n}\sum_{I}^{N}\frac{Z_I e^2}{r_{iI}}. \qquad (2.9)$$

Since the mass of the nuclei is much larger than the mass of the electrons, it can be assumed to a good approximation that the electronic distribution in a system depends only on the positions of the nuclei and not on their velocities. In the Born-Oppenheimer approximation this physical fact is used to separate the Schrödinger equation into an equation for the electronic wavefunction and one for the nuclear wavefunction. The electronic Schrödinger equation is written as

$$\hat{H}_{\text{e}}\Psi_{\text{e}}(\mathbf{r};\mathbf{R}) = E_{\text{eff}}(\mathbf{R})\Psi_{\text{e}}(\mathbf{r};\mathbf{R}), \qquad (2.10)$$

where the electronic Hamiltonian $\hat{H}_{\text{e}}$ is

$$\hat{H}_{\text{e}} = \hat{T}_{\text{e}}(\mathbf{r}) + \hat{V}_{\text{e–e}}(\mathbf{r}) + \hat{V}_{\text{e–N}}(\mathbf{r},\mathbf{R}) + \hat{V}_{\text{N–N}}(\mathbf{R}) \qquad (2.11)$$

and the electronic wavefunction $\Psi_{\text{e}}(\mathbf{r};\mathbf{R})$, as well as the electronic energy $E_{\text{eff}}(\mathbf{R})$, depend only parametrically on the nuclear positions which are considered fixed.

The electronic energy $E_{\text{eff}}(\mathbf{R})$ plays the role of an effective potential in the nuclear Schrödinger equation,

$$\hat{H}_{\mathrm{N}}\chi_{\mathrm{N}} = (\hat{T}_{\mathrm{N}}(\mathbf{R}) + E_{\mathrm{eff}}(\mathbf{R}))\chi_{\mathrm{N}}, \qquad (2.12)$$

and is usually called the potential energy surface (PES).

2.3 Density Functional Theory

As the wave function for an *N*-electron system is a function of 3*N* independent spatial variables, solving the electronic Schrödinger equation (**2.10**) using traditional *ab-initio* quantum chemistry approaches, such as configuration interaction (CI), becomes computationally very demanding for large molecular complexes. Density functional theory (DFT) offers a valuable alternative that is computationally more efficient than *ab-initio* methods and yet is quite accurate. This theory is based on the Hohenberg-Kohn theorem [2] showing that it is possible to use just the electronic density to calculate the ground-state energy E_0. Hence the complexity of the problem decreases drastically, since the electronic density is a function of only three coordinates, and is independent of the number of electrons. Given an external potential $v_{\mathrm{ext}}(\mathbf{r})$, the total electronic energy can be expressed as a functional of the electron density $\rho(\mathbf{r})$,

$$E \equiv E_v[\rho(\mathbf{r})] \equiv \int v_{\text{ext}}(\mathbf{r})\rho(\mathbf{r})d\mathbf{r} + F[\rho(\mathbf{r})], \quad (2.13)$$

where $F[\rho(\mathbf{r})]$ is an universal functional and the integral runs over the entire space. For molecular systems the external potential $v_{\text{ext}}(\mathbf{r})$ is usually the potential generated by the nuclei (see equation **2.9**).

The Hohenberg-Kohn theorem also proves that a variational principle for the energy functional holds: For any density, the energy given by the corresponding energy functional is never smaller than the ground-state energy, and the ground-state energy is obtained only using the exact ground-state electron density.

The total energy functional can be written as a sum of different terms:

$$E_v[\rho] = T[\rho] + V_{\text{e-N}}[\rho] + V_{\text{e-e}}[\rho], \quad (2.14)$$

where $T[\rho]$ is the electronic kinetic energy, $V_{\text{e-N}}[\rho]$ is the energy due to the electron-nuclear attraction, and $V_{\text{e-e}}[\rho]$ is the electron-electron repulsion energy, which can be decomposed into classical Coulomb and non-classical contributions:

$$V_{\text{e-e}}[\rho] = J[\rho] + V_{\text{e-e}}^{\text{nc}}[\rho]. \quad (2.15)$$

While $V_{\text{e-N}}[\text{r}]$ and $J[\rho]$ can be calculated in terms of the electron density as

$$V_{\text{e-N}}[\rho] = \int v_{\text{ext}}(\mathbf{r})\rho(\mathbf{r})d\mathbf{r} \quad (2.16)$$

and

$$J[\rho] = \int \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r} d\mathbf{r}', \qquad (2.17)$$

the explicit form for the kinetic energy functional and the non-classical electron-electron repulsion energy are unknown. In order to simplify the calculations of the kinetic energy term, Kohn and Sham proposed to compute $T_s[\rho]$, which is the kinetic energy for a set of independent particles. This term can be easily written in terms of a set of orbitals, known as the Kohn-Sham orbitals. The remaining unknown part of the kinetic energy $T_c[\rho]$ is the kinetic correlation energy, which leads to

$$T[\rho] = T_c[\rho] + T_s[\rho]. \qquad (2.18)$$

The $T_c[\rho]$ contribution of the kinetic energy is then combined with the non-classical electron-electron repulsion term in the exchange-correlation functional,

$$E_{xc}[\rho] = T_c[\rho] + V_{ee}^{nc}[\rho], \qquad (2.19)$$

and the energy functional can be rewritten as

$$E_v[\rho] = T_s[\rho] + V_{e\text{-}N}[\rho] + J[\rho] + E_{xc}[\rho]. \qquad (2.20)$$

2.4 Exchange-Correlation functionals

The exact form of the exchange-correlation functional is unknown and therefore the main approximation in DFT is in the treatment of this

functional. One of the first proposed approximations is the local density approximation (LDA) in which the system is treated locally as a uniform electron gas using

$$E_{\mathrm{xc}}^{\mathrm{LDA}}[\rho] = \int e_{\mathrm{xc}}(\rho(\mathbf{r}))\rho(\mathbf{r})d\mathbf{r}\,, \qquad (2.21)$$

where the exchange-correlation energy function $e_{\mathrm{xc}}(\rho)$ has been calculated with high accuracy from quantum Monte Carlo for the homogeneous electron gas [3]. The LDA approximation turned out to work well for metals and semiconductors [4]. However, it performs poorly for molecules, especially in predicting binding energies. This is no surprise since the electron density in molecular systems is highly inhomogeneous. To improve the exchange-correlation functional also the knowledge of the gradient of the density is included in the generalized gradient approximation (GGA):

$$E_{\mathrm{xc}}^{\mathrm{GGA}}[\rho,\nabla\rho] = \int f(\rho(\mathbf{r}),\nabla\rho(\mathbf{r}))d\mathbf{r}\,. \qquad (2.22)$$

More recently a new generation of functionals, the meta-GGA functionals, have been proposed including also the Laplacian of the density [5, 6]:

$$E_{\mathrm{xc}}^{\mathrm{mGGA}}[\rho,\nabla\rho,\nabla^2\rho] = \int f(\rho(\mathbf{r}),\nabla\rho(\mathbf{r}),\nabla^2\rho(\mathbf{r}))d\mathbf{r}\,. \qquad (2.23)$$

The GGA functionals that are mostly used in this thesis are the BLYP, which combines the exchange functional of Becke with the correlation functional of Lee, Yang and Parr [7, 8], and the OPBE, which combines the OPTx exchange with the PBE correlation part [9]. The choice of the OPBE functional is justified by previous work where it has been shown to give an accurate description for transition metal complexes [10, 11].

Other functionals that are broadly used are the hybrid functionals. In these functionals part of the exact Hartree-Fock exchange energy is mixed with the GGA functional, according to

$$E_{\mathrm{xc}}^{\mathrm{hybrid}}[\rho] = E_{\mathrm{xc}}^{\mathrm{GGA}}[\rho,\nabla\rho] + c_{\mathrm{x}}\left(E_{\mathrm{x}}^{\mathrm{HF}}[\rho] - E_{\mathrm{x}}^{\mathrm{GGA}}[\rho]\right) \qquad (2.24)$$

The c_x parameter determines the mixing between the Hartree-Fock and GGA exchange. Two hybrid functionals used in this thesis are the B3LYP and B3LYP*, which differ in the amount of exact exchange, 20% for B3LYP and 15% in B3LYP* [10].

2.5 Gaussian-plane waves method

The expression for the total electronic energy in the Kohn-Sham formulation of DFT is shown in equation **2.22**. Within the Gaussian-plane waves (GPW) approach [11] the electronic density ρ is defined

by two different representations. The first one is based on a set of atom centred contracted Gaussian functions with the density matrix $P_{\mu\nu}$:

$$\rho(\mathbf{r}) = \sum_{\mu=1,\nu=1}^{K} P_{\mu\nu}\varphi_{\mu}(\mathbf{r})\varphi_{\nu}(\mathbf{r}), \qquad (2.25)$$

where K is the total number of contracted Gaussian basis functions, φ_μ, defined as

$$\varphi_{\mu}(\mathbf{r}) = \sum_{m=1}^{M} C_{m\mu} g_m(\mathbf{r}), \qquad (2.26)$$

in which g_m (**r**) are the M primitive Gaussian functions used in the linear combination. The introduction of atomic pseudopotentials removes the core electrons from the calculation.

In order to evaluate the density dependent terms, $J[\rho]$ and $E_{xc}[\rho]$, the second representation is used, in which the density is expanded in an auxiliary set of plane waves:

$$\tilde{\rho}(\mathbf{r}) = \frac{1}{\Omega} \sum_{\mathbf{G}}^{\mathbf{G}\,\max} \tilde{\rho}(\mathbf{G}) e^{i\mathbf{G}\cdot\mathbf{r}}, \qquad (2.27)$$

where the sum over the **G** vectors extends up to a maximum value, $\mathbf{G}_{max}$, which depends on the plane waves energy cutoff, and Ω is the volume of the cell.

The expansion coefficients $\tilde{\rho}(\mathbf{G})$ are such that $\tilde{\rho}(\mathbf{r})$ is equal to $\rho(\mathbf{r})$ on a regular grid in the unit cell. The difference $|\rho(\mathbf{r})- \tilde{\rho}(\mathbf{r})|$ goes to zero as the energy cutoff goes to infinity.

Using this dual representation the KS energy expression [2, 12], showed in equation **2.22**, within the GPW framework is defined as

$$\begin{aligned} E(\rho) = & \sum_{\mu\nu}^{\mathrm{K}} P_{\mu\nu} \left\langle \varphi_\mu(\mathbf{r}) \left| -\frac{1}{2}\nabla^2 \right| \varphi_\nu(\mathbf{r}) \right\rangle \\ & + \sum_{\mu\nu}^{\mathrm{K}} P_{\mu\nu} \left\langle \varphi_\mu(\mathbf{r}) \left| V_{\mathrm{loc}}^{\mathrm{PP}}(\mathbf{r}) \right| \varphi_\nu(\mathbf{r}) \right\rangle \\ & + \sum_{\mu\nu}^{\mathrm{K}} P_{\mu\nu} \left\langle \varphi_\mu(\mathbf{r}) \left| V_{\mathrm{nl}}^{\mathrm{PP}}(\mathbf{r},\mathbf{r}') \right| \varphi_\nu(\mathbf{r}') \right\rangle \\ & + 2\pi\Omega \sum_{\mathbf{G}}^{\mathbf{G}\max} \frac{\tilde{\rho}^*(\mathbf{G})\,\tilde{\rho}(\mathbf{G})}{\mathbf{G}^2} + E_{\mathrm{xc}}[\rho(\mathbf{r})] + \frac{1}{2}\sum_{I\neq J}^{N} \frac{Z_I Z_J}{|R_{IJ}|}. \end{aligned} \tag{2.28}$$

$V_{\text{e-N}}[\rho]$ is described by norm-conserving pseudopotentials with a potential split in a local part $V_{\mathrm{loc}}^{\mathrm{PP}}(\mathbf{r})$ and a fully non-local part $V_{\mathrm{nl}}^{\mathrm{PP}}(\mathbf{r},\mathbf{r}')$.

2.6 Molecular Dynamics

Molecular dynamics [13, 14] is a well established method to study thermodynamic properties of complex many-particle systems at finite temperature. The idea is to evolve in time the atoms in the system according to the classical equations of motion to closely match the microscopic evolution of the system. Macroscopic thermodynamic

properties of the system can then be computed based on the ergodic hypothesis that the statistical ensemble averages are equal to time averages along the trajectory of the system.

Similar analyses can be performed with *ab-initio* molecular dynamics, in which the explicit calculation of the electronic structure is used to compute potential energies and forces [15]. A significant advantage of *ab-initio* molecular dynamics is that no parameterization of an empirical potential is needed and that systems can be simulated when unexpected chemical events take place.

In this section a brief overview of two different AIMD methods used in this thesis will be given, the Car-Parrinello Molecular Dynamics, used in the CPMD program [16], and the Born-Oppenheimer Molecular Dynamics, used in the CP2K software package [17].

2.6.1 Car-Parrinello Molecular Dynamics

The main idea of this approach [18] is the treatment of the electronic degrees of freedom, the KS orbitals ψ_i, as fictitious classical dynamical variables, taking advantage of the time scale separation between the fast electronic and slow nuclear motion to avoid energy exchange between them. The Car-Parrinello Lagrangian contains the nuclear kinetic energy, the fictitious electronic kinetic energy and the potential energy

$$L_{\mathrm{CP}} = \sum_{I=1}^{N} \frac{1}{2} M_I \dot{\mathbf{R}}_I^2 + \frac{1}{2}\mu \sum_{i=1}^{n} \int \left| \dot{\psi}_i(\mathbf{r}) \right|^2 d\mathbf{r} - E_v[\psi_i, \mathbf{R}] + \sum_{i=1,\, j=1}^{n} \Lambda_{ij} \left(\langle \psi_i | \psi_j \rangle - \delta_{ij} \right) \tag{2.29}$$

with the orbitals subject to the holonomic constraints of orthonormality. The potential energy, $E_v[\psi_i, \mathbf{R}]$ is given by eq. **2.22**. A fictitious mass, μ, is assigned to the electronic degrees of freedom and can be tuned to ensure the adiabaticity.

The Newtonian equations of motion are obtained from the associated Euler-Lagrange equations, and the corresponding Car-Parrinello equations are

$$M_I \ddot{\mathbf{R}}_I = -\nabla_I E_v[\psi, \mathbf{R}] \tag{2.30}$$

and

$$\mu \ddot{\psi}_i = -\frac{\delta E_v}{\delta \langle \psi_i |} + \sum_{j=1}^{n} \Lambda_{ij} \psi_j \,. \tag{2.31}$$

These equations can be solved numerically through standard finite difference algorithms used in molecular dynamics, such as the Verlet algorithm [19, 20]. The constant of motion in the Car-Parrinello dynamics is

$$E_{\mathrm{cons}} = \sum_{I=1}^{N} \frac{1}{2} M_I \dot{\mathbf{R}}_I^2 \tag{2.32}$$

$$+\frac{1}{2}\sum_{i=1}^{n}\mu\left\langle\dot{\psi}_i\middle|\dot{\psi}_i\right\rangle+E_\upsilon[\psi_i,\mathbf{R}].$$

The fictitious electronic mass is chosen in such a way to ensure that the lowest electronic frequency exceeds the highest frequency of the nuclei. In this way energy transfer from the nuclear to the electronic subsystem is avoided at least on the time scale of the AIMD simulations. The choice of the fictitious electronic mass will then also determine the choice of the time step in the numerical algorithm. A typical time step in Car-Parrinello MD simulations is 0.1 fs.

2.6.2 Born-Oppenheimer Molecular Dynamics

An alternative approach for *ab-initio* MD is to solve self-consistently the electronic structure for *each* molecular dynamics step given the set of nuclear positions at that particular instant in time. Thus, the electronic structure part represents the self-consistent solution of the KS equations, if we use DFT for computing the forces on the nuclei. Then these forces are used to propagate only the nuclear positions at the next time step in the classical molecular dynamics. Since in the BOMD approach the electronic degrees of freedom are not propagated in time, the choice of the time step is limited only by the nuclear characteristic frequencies and therefore can be usually 5 to 10 times larger than in CPMD. On the other hand in BOMD the electronic ground state has to be reached in each molecular dynamics step and the efficiency of this approach will strongly depend on the speed of convergence in the self-

consistent loop.

2.6.3 Metadynamics

Ab-initio molecular dynamics methods have been successfully applied during the last decades for different problems from materials science to biochemistry [21]. However, the main limitation of this approach is that it is still limited to processes occurring within a few tens of picoseconds. This will be particularly relevant if one is interested in studying chemical reactions, since these will usually not take place spontaneously on such a short time scale. Typically energy barriers of many kcal/mol need to be overcome. Several strategies have been developed to face this problem and the metadynamics method, introduced by Laio and Parrinello [22], appears to be one of the most efficient and robust solutions. The metadynamics method introduces a biasing potential in a collective variable space that influences the "real" dynamics. The collective variables selected to explore the configuration space of interest can be different parameters: from distances or angles to coordination numbers or the formation of a hydronium. The selection of the appropriate collective variables is a crucial point in obtaining accurate results with this technique.

The biasing potential is built in such a way to disfavour the configurations already visited and to facilitate the exploration of regions of the configuration space that are statistically unlikely. In all the work presented in this thesis the history dependent potential is

constructed as a sum of Gaussians, along distances as collective variables, according to

$$V_G\left(s(x),t\right) = \int_0^t d\tau \frac{h}{\tau_g} \exp\left[- \frac{\left(s(x) - s(x(\tau))\right)^2}{2w^2} \right], \quad (2.33)$$

where *h* is the height and *w* the width of the Gaussian bias potential, and τ_g^{-1} the frequency of deposition.

Moreover, the same bias potentials used to escape from the energy minima, will eventually converge to the free-energy profile, *F(s)*, along the chosen reaction coordinate. Therefore this method not only allows to find reaction pathways, but also to estimate reaction free-energies and activation barriers.

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