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## Taking control of charge transfer : strategic design for solar cells

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## Theory and Computational Methodology

### **2.0.ABSTRACT**

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*This chapter is meant to provide the reader with a general overview of the computational methodology applied throughout this thesis and explain their theoretical basis.*

*The chapter is structured as follows. At first, a general description of the Born-Oppenheimer approximation is presented (section 2.1). Then, an introduction to the theoretical basis of the density functional theory (DFT) method (section 2.2) and a brief discussion on the most commonly used type of approximations for the exchange-correlation functional (section 2.3) are given.*

*The Car-Parrinello Molecular Dynamics method, which unifies DFT and classical MD, is described in section 2.4, while section 2.5 is dedicated to the description of the theoretical basis of Time-dependent DFT (TD-DFT) and linear-response TD-DFT.*

*Finally, in the last two sections of this chapter (2.6 and 2.7), the constrained DFT method, employed in chapter 3 for the electron coupling calculations, and the semiempirical Hückel and Extended Hückel theories are explained. The latter, together with the Car-Parrinello MD method, is central to the work presented in chapter 4 and chapter 5.*

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## 2.1. THE BORN-OPPENHEIMER APPROXIMATION

In its most general form, the time-dependent Schrödinger equation can be written as

$$\hat{H}_{\text{tot}}\Psi = i\hbar \frac{\partial}{\partial t}\Psi, \quad (2.1)$$

where  $\Psi$  is the total wavefunction,  $i$  is the imaginary unit,  $t$  represents the time,  $\hbar$  is the reduced Planck constant, and  $\hat{H}_{\text{tot}}$  is the total Hamiltonian of the system under investigation. The latter contains both the nuclear and electronic kinetic-energy operators, and the potential-energy operators describing particles interactions:

$$\hat{H}_{\text{tot}} = \hat{T}_{\text{nuc}} + \hat{T}_{\text{el}} + \hat{V}_{\text{nuc,nuc}} + \hat{V}_{\text{el,el}} + \hat{V}_{\text{nuc,el}} \quad (2.2)$$

In a more explicit form, for a system with  $N$  nuclei and  $n$  electrons, the nuclear ( $\hat{T}_{\text{nuc}}$ ) and electronic ( $\hat{T}_{\text{el}}$ ) kinetic-energy operators can be written as

$$\hat{T}_{\text{nuc}} = - \sum_{I=1}^N \frac{\hbar^2}{2m_I} \nabla_I^2 \quad (2.3)$$

$$\hat{T}_{\text{el}} = - \sum_{i=1}^n \frac{\hbar^2}{2m} \nabla_i^2 \quad (2.4)$$

The potential-energy operators, describing in order the nucleus-nucleus, electron-electron, and nucleus-electron Coulomb interactions, can be expressed as

$$\hat{V}_{\text{nuc,nuc}} = \sum_{I=1}^N \sum_{J>I}^N \frac{1}{4\pi\epsilon_0} \frac{Z_I Z_J e^2}{|\mathbf{R}_I - \mathbf{R}_J|} \quad (2.5)$$

$$\hat{V}_{\text{el,el}} = \sum_{i=1}^n \sum_{j>i}^n \frac{1}{4\pi\epsilon_0} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|} \quad (2.6)$$

$$\hat{V}_{\text{el,nuc}} = - \sum_{I=1}^N \sum_{i=1}^n \frac{1}{4\pi\epsilon_0} \frac{Z_I e^2}{|\mathbf{R}_I - \mathbf{r}_i|} \quad (2.7)$$

In this notation the capital indexes refer to the nuclei, while the small ones point to the electrons.  $Z_I$  and  $-e$  are the atomic number of the  $I^{\text{th}}$  nucleus, and the electron charge, while  $\mathbf{R}_I$  and  $\mathbf{r}_i$  represent the coordinates of the  $I^{\text{th}}$  nucleus and  $i^{\text{th}}$

electron. Finally,  $\epsilon_0$  is the vacuum permittivity and the masses of nuclei and electrons are respectively referred to as  $m_I$  and  $m$ .

The Schrödinger equation (equation 2.1), combined with the expression of the total Hamiltonian  $\hat{H}_{\text{tot}}$  (equation 2.2), implies a direct dependency of the total wavefunction  $\Psi$  on the entire set of nuclear and electronic coordinates as well as on time,  $\Psi(\mathbf{R}, \mathbf{r}, t)$ .

Unfortunately, an analytical solution of equation 2.1 cannot be found in general. A first simplification of this problem can be achieved by factorizing the wavefunction into terms depending on different variables. In this way it is possible to separate equation 2.1 into simpler equations.

Due to the large mass difference between nuclei and electrons  $m_I \gg m$ , the electrons generally move much faster than the nuclei and can therefore instantaneously respond to changes in the nuclear configuration.

This regime is known as the Born-Oppenheimer (BO) approximation<sup>1</sup> and allows to consider nuclear and electronic motions separately. The total wavefunction can be written as a product between electronic  $\psi_i(\mathbf{r}; \mathbf{R})$  and nuclear  $\chi_i(\mathbf{R}, t)$  wavefunctions, according to

$$\Psi(\mathbf{R}, \mathbf{r}, t) = \sum_{i=1}^{\infty} \psi_i(\mathbf{r}; \mathbf{R}) \chi_i(\mathbf{R}, t). \quad (2.8)$$

The electronic wavefunctions are parametrically dependent on the nuclear coordinates that define the "external" potential energy field  $\hat{V}_{\text{el,nuc}}$  experienced by the electrons. This implies that, if we assume the nuclei to be fixed in a specific nuclear configuration  $\{\mathbf{R}\}$ , we can solve the electronic Schrödinger equation

$$\hat{H}_{\text{el}} \psi_i(\mathbf{r}; \mathbf{R}) = E_{\text{el},i}(\mathbf{R}) \psi_i(\mathbf{r}; \mathbf{R}) \quad (2.9)$$

and calculate the electronic eigenfunctions and eigenvalues that uniquely correspond to that specific geometrical configuration. The electronic Hamiltonian is then defined as  $\hat{H}_{\text{el}} = \hat{H}_{\text{tot}} - \hat{T}_{\text{nuc}}$ , or

$$\hat{H}_{\text{el}} = \hat{T}_{\text{el}} + \hat{V}_{\text{nuc,nuc}} + \hat{V}_{\text{el,el}} + \hat{V}_{\text{nuc,el}}. \quad (2.10)$$

The combination of equation 2.1 and 2.9, solved for a specific electronic wavefunction  $\psi_j$  gives the equation

$$\left(\hat{T}_{\text{nuc}} + E_{\text{el},j}(\mathbf{R})\right) \chi_j(\mathbf{R}, t) + \sum_{i=1}^{\infty} \hat{C}_{ji} \chi_i(\mathbf{R}, t) = i\hbar \frac{\partial}{\partial t} \chi_j(\mathbf{R}, t) \quad (2.11)$$

where

$$\hat{C}_{ji} = \sum_{I=1}^N \frac{\hbar^2}{m_I} \int_{\Omega_{\text{TOT}}} d\mathbf{r} \psi_j^*(\mathbf{r}; \mathbf{R}) \left( -\frac{1}{2} [\nabla_I^2 \psi_i(\mathbf{r}; \mathbf{R})] - [\nabla_I \psi_i(\mathbf{r}; \mathbf{R})] \nabla_I \right) \quad (2.12)$$

Here, and throughout the whole thesis, the integration over the spatial coordinates  $\mathbf{r}$  runs over the entire space  $\Omega_{\text{TOT}}$ .

Due to the large difference between nuclear and electronic masses, in the Born-Oppenheimer approximation the  $\hat{C}_{ji}$  coefficients can be considered negligible and this leads to the effective Schrödinger equation

$$\left(\hat{T}_{\text{nuc}} + E_{\text{el},j}(\mathbf{R})\right) \chi_j(\mathbf{R}, t) = i\hbar \frac{\partial}{\partial t} \chi_j(\mathbf{R}, t). \quad (2.13)$$

This equation shows clearly that the nuclei move on a potential energy surface (PES) given by the  $\hat{H}_{\text{el}}$  expectation value  $E_{\text{el},j}(\mathbf{R})$ .

The Born-Oppenheimer approximation is generally sufficient. However, when two electronic states are close in energy or cross each other, the approximation introduced in equation 2.12 is not applicable and the  $\hat{C}_{ji}$  coefficients have to be, at least in part, calculated.

One way to improve the BO approximation is through the so called *adiabatic correction*<sup>2</sup>. It consists in the introduction of a first order correction to the BO electronic energy to account for nuclear motion. This is done by including only the  $\hat{C}_{ji}$  coefficients of equation 2.12 for which  $i = j$ . These terms are rather easy to calculate, but they usually introduce very small corrections.

More important are the  $\hat{C}_{ji}$  terms for which  $i \neq j$ , also called *nonadiabatic* coupling terms. The inclusion of these terms is essential to study nuclear dynamics in regions where near-degeneracy between different adiabatic states occurs. This is the case for many photochemical reactions. Nonadiabatic crossings are also involved during the photoinduced charge transfer processes which are subject of this thesis.

The most commonly employed methodologies for the description of nonadiabatic dynamics of a system are the Ehrenfest dynamics and the surface hopping

algorithm<sup>3-5</sup>. In Ehrenfest dynamics the nuclei move according to the mean force induced by the time-evolution of the electronic wavefunction. Instead, in surface hopping the electronic wavefunction follows the motion of the nuclei on a specific PES. The transition between two adiabatic states occurs, based on their nonadiabatic coupling, according to a stochastic algorithm.

First principles implementations of these methodologies are currently available. However, their applicability is hampered by high computational costs, which can limit the size of the studied system and the time scale of the simulations.

In this thesis a different strategy is adopted in which a unitary transformation is used to move from an adiabatic to a diabatic description of the system at each time step. The quantum evolution of the electronic wavefunction is performed in the molecular orbital adiabatic base for a fixed set of nuclear coordinates, while the nuclear positions are evolved in the atomic orbital diabatic base.

Together with a semiempirical description of the electronic structure, this method allows for quantum-classical study of heterogeneous electron transfer processes on a time scale of picoseconds.

## 2.2. DENSITY FUNCTIONAL THEORY

Every wavefunction method dedicated to electronic structure calculations is based on the same principles: an initial ansatz for the total wavefunction is proposed, which is progressively optimized through the variational principle to minimize the energy expectation value. The energy is therefore a functional of the electronic wavefunction.

The total wavefunction is, however, a very complicated object, which depends on  $3n$  electronic coordinates, where  $n$  is the number of interacting electrons, and whose complexity increases with the dimension of the system. This implies that the application of such methods becomes computationally infeasible for chemical systems with large  $n$ .

The limited applicability of wavefunction-based methodologies is the main motivation for the success that density functional theory (DFT) is experiencing in the last decades.

Based on a completely different theoretical approach, DFT does not aim for the optimal approximation to the total wavefunction, but rather describes a many-electron system based on its ground state density  $\rho(\mathbf{r})$ , which is a function only of 3 spatial coordinates:

$$\rho(\mathbf{r}_1) = n \int_{\Omega_{\text{TOT}}} d\mathbf{r}_2 \dots d\mathbf{r}_n \int_{s^{\uparrow\downarrow}} |\Psi(\mathbf{r}_1 s_1 \mathbf{r}_2 s_2 \dots \mathbf{r}_n s_n)|^2 ds_1 ds_2 \dots ds_n \quad (2.14)$$

where  $\mathbf{r}_i$  and  $s_i$  indicate the electron coordinates and the spin variables. The integration runs over  $n - 1$  spatial coordinates and all spin variables.

The foundations of this theory were first laid down by Hohenberg and Kohn in 1964<sup>6</sup> through two theorems.

The first theorem states that if the ground state electron density of the system under investigation is known, it is possible to construct the Hamiltonian, determine the wavefunction, and consequently extract any observable of the system. It can be in fact demonstrated that a bijective mapping exists between the nuclear-electron interaction or external potential,  $\hat{V}_{\text{ext}}$ , the ground state electronic wavefunction  $\Psi$ , and the electron density  $\rho$

$$\hat{V}_{\text{ext}} \leftrightarrow \Psi \leftrightarrow \rho \quad (2.15)$$

such that to a particular external potential corresponds a unique electron density, and vice versa.



This relation implies that every observable of the system is a functional of the electron density, including the ground state energy

$$\begin{aligned}
 E[\rho] &= \langle \Psi[\rho] | \hat{T} + \hat{V}_{\text{el,el}} + \hat{V}_{\text{ext}} | \Psi[\rho] \rangle \\
 &= \int_{\Omega_{\text{TOT}}} \rho(\mathbf{r}) v_{\text{ext}}(\mathbf{r}) d\mathbf{r} + F_{\text{HK}}[\rho],
 \end{aligned} \tag{2.16}$$

where

$$F_{\text{HK}}[\rho] = T[\rho] + V_{\text{el,el}}[\rho] \tag{2.17}$$

is a universal density functional independent of the external potential, named Hohenberg-Kohn (HK) functional. It has to be noted that the employed Hamiltonian (equation 2.16) differs from equation 2.2 in the following: i) the kinetic operator involves only the kinetics of the electrons since the nuclei are assumed to be fixed; ii) the nucleus-nucleus term is not included since it is a constant term that can be added to the total electronic energy at a later stage; iii) the electron-nuclear term is described as  $\hat{V}_{\text{ext}}$ , an external potential that could in principle include other contributions than the electrostatic field from the nuclei.

The second HK theorem states that for a given density the corresponding energy functional will have an absolute minimum at the ground state energy  $E_0$ . The exact ground state density  $\rho_0$  is the one associated with the lowest energy, and can be found through the minimization of  $E[\rho]$  according to equation 2.16.

Unfortunately, these theorems do not provide an explicit form for the universal functional  $F_{\text{HK}}[\rho]$ , but merely prove that such a functional exists and, once known, can yield the ground state density  $\rho_0$  and the system properties.

To address this problem, Kohn and Sham postulated in 1965<sup>7</sup> that for every system with  $n$  interacting electrons moving in an external potential  $v_{\text{ext}}$ , a local external potential  $v_s$  exists that acts on an hypothetical reference system of  $n$  non-interacting fermions, in such a way that the density of the non-interacting and interacting systems match, *i.e.*  $\rho_s(\mathbf{r}) = \rho(\mathbf{r})$ .

Since the particles of this reference system do not interact, the exact ground state wavefunction can be described as a single Slater determinant, whose orbitals  $\phi_i$  are obtained by solving the equations

$$\left[-\frac{1}{2}\nabla^2 + v_s(\mathbf{r})\right]\phi_i(\mathbf{r}) = \varepsilon_i\phi_i(\mathbf{r}), \quad (2.18)$$

where only the kinetic energy and the one-body local external potential terms  $v_s(\mathbf{r})$  appear. In equation 2.18, and for the remaining of this chapter, we use atomic units to simplify the notation. The total density of the non-interacting system is therefore obtained as

$$\rho_s(\mathbf{r}) = \sum_{i=1}^n |\phi_i(\mathbf{r})|^2 \quad (2.19)$$

As previously said, an exact form of the energy functional for the interacting system cannot be written since an expression for the electronic kinetic energy and the electron-electron repulsion terms of equation 2.17 are unknown.

However, it is possible to approximate the term for the electron-electron repulsion energy  $V_{\text{el,el}}[\rho]$  as a sum between a classical Coulomb interaction term  $J[\rho]$  and a non-classical part  $V_{\text{NC}}[\rho]$

$$\begin{aligned} V_{\text{el,el}}[\rho] &= J[\rho] + V_{\text{NC}}[\rho] \\ &= \left( \frac{1}{2} \int_{\Omega_{\text{TOT}}} d\mathbf{r}_1 \int_{\Omega_{\text{TOT}}} d\mathbf{r}_2 \left[ \frac{\rho(\mathbf{r}_1)\rho(\mathbf{r}_2)}{r_{12}} \right] \right) + V_{\text{NC}}[\rho] \end{aligned} \quad (2.20)$$

Using the same approach, it is also possible to approximate the kinetic energy functional as the sum between the kinetic energy of the non-interacting system  $T_s[\rho]$  and the kinetic correlation energy term  $T_c[\rho]$

$$T[\rho] = T_s[\rho] + T_c[\rho] = \left( \sum_{i=1}^n \langle \phi_i \left| -\frac{\nabla^2}{2} \right| \phi_i \rangle \right) + T_c[\rho] \quad (2.21)$$

The functional for the total energy can therefore be rewritten as

$$E[\rho] = T_s[\rho] + V_{\text{ext}}[\rho] + J[\rho] + E_{\text{xc}}[\rho] + V_{\text{nuc,nuc}} \quad (2.22)$$

where  $E_{\text{xc}}[\rho] = V_{\text{NC}}[\rho] + T_c[\rho]$  is the exchange-correlation (xc) functional. In equation 2.22 we have now included also the nucleus-nucleus energy term  $V_{\text{nuc,nuc}}$ .

Since the form of  $v_s(\mathbf{r})$  is unknown, so are the electron densities  $\rho_s(\mathbf{r}) = \rho(\mathbf{r})$ , and consequently the orbitals of the non-interacting system  $\{\phi_i\}$ .

Under the constraint that the density is normalized to the number of electrons  $n$ , the minimization of the energy from equation 2.22 with respect to the density leads to the expression of the Kohn-Sham equations

$$\left[ -\frac{\nabla^2}{2} + v_{\text{ext}}(\mathbf{r}) + \int_{\Omega_{\text{TOT}}} \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' + v_{\text{xc}}(\mathbf{r}) \right] \phi_i(\mathbf{r}) = \varepsilon_i \phi_i(\mathbf{r}) \quad (2.23)$$

where the potential  $v_{\text{xc}}(\mathbf{r})$  depends on the approximation chosen for the functional  $E_{\text{xc}}[\rho]$  (see section 2.3).

The self-consistent solution of equations 2.23 leads to a set of one-electron orbitals  $\{\phi_i(\mathbf{r})\}_n$  that generate the electron density for the interacting system

$$\rho(\mathbf{r}) = \sum_{i=1}^n |\phi_i(\mathbf{r})|^2 \quad (2.24)$$

### 2.3. EXCHANGE-CORRELATION FUNCTIONALS

The exact form of  $E_{xc}[\rho]$  in the Kohn-Sham formalism is unknown and has to be approximated. Therefore, the quality of the DFT results depends on how accurately this functional is approximated.

The Local Density Approximation (LDA) is an approximation for the exchange-correlation term in which it is assumed that the system behaves locally as a uniform electron gas:

$$E_{xc}^{LDA}[\rho] = \int_{\Omega_{TOT}} \varepsilon_{xc}^{hom}(\rho(\mathbf{r})) \rho(\mathbf{r}) d\mathbf{r}. \quad (2.25)$$

Here,  $\varepsilon_{xc}^{hom}(\rho(\mathbf{r}))$  is the exchange-correlation energy per particle of the uniform electron gas of charge density  $\rho(\mathbf{r})$ . This function is most commonly parametrized based on the very accurate results obtained from Quantum Monte Carlo calculations on homogeneous electron gases at different densities<sup>8-12</sup>.

The LDA is most suited for the treatment of systems with slow-varying densities, such as metals and semiconductors. However, it has been proved to perform poorly for molecular systems where the electron density is strongly inhomogeneous.

To account for the non-homogeneity of the electron density, a first approximation of the xc-functional  $E_{xc}[\rho]$  beyond LDA must include not only the information about the local density  $\rho(\mathbf{r})$  at a particular position  $\mathbf{r}$ , but also about the gradient of the density at that position:  $\nabla\rho(\mathbf{r})$ . This approximation takes the name of Generalized Gradient Approximation (GGA)

$$E_{xc}^{GGA}[\rho, \nabla\rho] = \int_{\Omega_{TOT}} \varepsilon_{xc}^{hom}(\rho(\mathbf{r})) \rho(\mathbf{r}) d\mathbf{r} + \int_{\Omega_{TOT}} F_{xc}[\rho(\mathbf{r}), \nabla\rho(\mathbf{r})] \rho(\mathbf{r}) d\mathbf{r} \quad (2.26)$$

Here  $F_{xc}[\rho(\mathbf{r}), \nabla\rho(\mathbf{r})]$  is the factor which depends on the approach adopted in writing the xc-functional. In fact, several different GGA functionals have been developed to address specific requirements. Among the most popular GGA xc-functionals we can mention: BP (exchange functional from Becke<sup>13,14</sup>, and correlations according to Perdew<sup>15</sup>), PBE<sup>16</sup> (both exchange and correlation parts developed by Perdew, Burke and Ernzerhof) and BLYP (exchange functional according to Becke<sup>13</sup>, and the Lee-Yang-Parr correlation functional<sup>17</sup>).

Another class of approximation to  $E_{xc}[\rho]$  for DFT are the so called hybrid

functionals, in which a fraction of exact Hartree-Fock (HF) exchange energy is added to the exchange and correlation from pure DFT functionals.

The exact HF exchange is calculated in terms of the Kohn-Sham orbitals as

$$E_x^{\text{HF}} = -\frac{1}{2} \sum_{i,j}^{\text{occ}} \int_{\Omega_{\text{TOT}}} d\mathbf{r}_1 \int_{\Omega_{\text{TOT}}} d\mathbf{r}_2 \phi_i^*(\mathbf{r}_1) \phi_j^*(\mathbf{r}_1) \frac{1}{r_{12}} \phi_i(\mathbf{r}_2) \phi_j(\mathbf{r}_2) \quad (2.27)$$

and their general form is

$$E_{\text{xc}}^{\text{hybrid}} = cE_x^{\text{HF}} + (1 - c)E_x^{\text{DFT}} + E_c^{\text{DFT}} \quad (2.28)$$

where  $c$  is the coefficient that determines the extent by which the HF and the DFT exchange are mixed. A variety of hybrid functionals have been developed where the amount of HF exchange energy included varies.

A remarkably popular hybrid functional is the xc-functional B3LYP (Becke<sup>13</sup>, 3 parameters, Lee-Yang-Parr<sup>17</sup>), which is defined as

$$E_{\text{xc}}^{\text{B3LYP}} = c_0 E_x^{\text{HF}} + (1 - c_0) E_x^{\text{S}} + c_x E_x^{\text{B88}} + (1 - c_c) E_c^{\text{VWN}} + c_c E_c^{\text{LYP}} \quad (2.29)$$

where  $c_0 = 0.20$ ,  $c_x = 0.72$ ,  $c_c = 0.81$ . These parameters control the ratio between the Becke 88 (B88)<sup>13</sup> and Slater (S)<sup>18</sup> exchange functionals, the Lee-Yang-Parr (LYP)<sup>17</sup> and Vosko-Wilk-Nusair (VWN)<sup>9</sup> correlation functionals, and the Hartree-Fock (HF) integral.

GGA and hybrid functionals are very effective in describing properties depending on short-range effects of the exchange and correlation energy terms. However, they are unsuccessful in describing properties where the long-range behavior of the xc-potential is important, such as the description of charge transfer excitations or the polarizability of extended conjugated systems. The reason behind this failure can be found in the local character of their xc-potentials, which induces a qualitatively wrong asymptotic behavior of the exchange potential<sup>19-22</sup>.

To overcome this problem, the class of the long-range corrected (LC) functionals has been developed. The basic idea of these functionals is to achieve a correct asymptotic behavior by partitioning the electron repulsion operator into short and long-range terms. At short range, the GGA exchange is maintained while the exact HF exchange is asymptotically introduced via a range-separated Coulomb attenuation method which ensures a smooth transition between the two different

ranges<sup>19-22</sup>.

A particular LC-functional which has been widely used to study charge-transfer excitations is CAM-B3LYP<sup>19</sup>. In chapter 3 of this thesis, we make use of this functional to compute charge-transfer excitations and optimize excited state geometries, within the framework of time-dependent DFT (TD-DFT, see section 2.5).

## 2.4. CAR-PARRINELLO MOLECULAR DYNAMICS

The Car-Parrinello Molecular Dynamics<sup>23</sup> (CPMD) method was proposed in 1985 to unify classical MD simulations with DFT methods.

In this approach the nuclei move, according to classical mechanics, in an electron-induced effective potential, which is computed by solving the electronic time-evolving problem “on the fly”.

In the Car-Parrinello MD, the electronic degrees of freedom are treated as fictitious dynamical variables. Their evolution is carried on in parallel with the ionic dynamics, avoiding however energy exchange between the two subsystems.

The energy of the electronic subsystem can be considered a functional of the one-particle orbitals set  $\{\psi_i\}$ . Therefore, given an appropriate Lagrangian<sup>24</sup>, the derivative of the electronic energy with respect to the orbitals yields the forces acting on the orbitals and the electrons can be evolved as classical particles.

The Lagrangian postulated by Car and Parrinello takes the form

$$\begin{aligned} \mathcal{L}_{CP} = & \sum_{I=1}^N \frac{1}{2} M_I \dot{R}_I^2 + \sum_{i=1}^n \frac{1}{2} \mu_i \langle \dot{\psi}_i | \dot{\psi}_i \rangle - E^{KS}[\{R_I\}, \{\psi_i\}] \\ & + \sum_{i,j=1}^n \lambda_{ij} (\langle \psi_i | \psi_j \rangle - \delta_{ij}) \end{aligned} \quad (2.30)$$

The first and the second terms of equation 2.30 are the classical kinetic energy of the nuclei and the fictitious kinetic energy of the KS electronic orbitals, respectively.  $E^{KS}[\{R_I\}, \{\psi_i\}]$  is the Kohn-Sham energy density functional, while the last term in the Lagrangian is the constraint needed to impose the orthonormality of the KS orbitals.

Like in classical mechanics, the Car-Parrinello equations of motion are obtained from the Euler-Lagrange equations

$$M_I \ddot{R}_I(t) = -\nabla_I E^{KS}[\{R_I\}, \{\psi_i\}] \quad (2.31)$$

$$\mu_i \ddot{\psi}_i = -\frac{\partial E^{\text{KS}}[\{R_I\}, \{\psi_i\}]}{\partial \psi_i^*} + \frac{\partial}{\partial \psi_i^*} \sum_{i,j=1}^n \lambda_{ij} (\langle \psi_i | \psi_j \rangle - \delta_{ij}) \quad (2.32)$$

In this notation, each dot on  $\dot{R}_I$  and  $\ddot{\psi}_i$  indicates a time derivative of the function. Here  $\mu$  is a fictitious mass assigned to the electrons. The value of  $\mu$  is chosen small enough to maintain adiabaticity; that is, to avoid significant energy transfer between nuclei and electrons.

According to the Car-Parrinello equations of motion, the nuclei evolve in time at a physical temperature proportional to their kinetic energy  $\sum_{I=1}^N \frac{1}{2} M_I \dot{R}_I^2$ . At the same time, to ensure that during time evolution they remain close to the Born-Oppenheimer surface, the electrons are maintained at a fictitious temperature which is low compared to the physical nuclear temperature, and proportional to their kinetic energy  $\sum_{i=1}^n \frac{1}{2} \mu_i \langle \dot{\psi}_i | \dot{\psi}_i \rangle$ . Therefore, if the electronic wavefunction has been optimized for an initial nuclear configuration, the electronic subsystem will remain close to its energy minimum along the MD trajectory.

In order for the electrons to remain at low temperature while following the motion of the nuclei along the dynamics, no energy transfer has to occur between the electronic and the nuclear subsystems. This adiabatic separation can be achieved if the lowest electronic frequency  $\omega_{\text{el}}^{\text{min}}$  is much higher than the highest nuclear frequency  $\omega_{\text{nuc}}^{\text{max}}$ ; that is, if there is no substantial overlap in the frequency domain of the two subsystems.

The electronic frequency spectrum is inversely proportional to the square root of the fictitious mass  $\mu$ :  $\omega_{\text{el}}^{\text{min}} \propto (E_{\text{gap}}/\mu)^{1/2}$ , where  $E_{\text{gap}}$  is the electronic energy difference between the lowest unoccupied and the highest occupied orbital.

Since the  $E_{\text{gap}}$  and  $\omega_{\text{nuc}}^{\text{max}}$  values are inherently correlated to the properties of the system,  $\mu$  is the only parameter that can be decreased to increase  $\omega_{\text{el}}^{\text{min}}$ , and consequently the  $\omega_{\text{el}}^{\text{min}} - \omega_{\text{nuc}}^{\text{max}}$  separation. However, increasing  $\omega_{\text{el}}^{\text{min}}$  implies also decreasing the maximum time step applicable in a simulation since  $\Delta t^{\text{max}} \propto \mu^{1/2}$ . Therefore, the value of  $\mu$  has to be chosen in order to provide the largest possible time step, while conserving adiabaticity. A  $\mu$  value of 400 a.u. is used for all the CPMD simulations presented in this thesis.

#### **2.4.1. Periodic boundary conditions and plane wave basis set**

In MD the simulation box is repeated in space using periodic boundary conditions (PBC) to mimic macroscopic systems and minimize surface effects. PBC can also be

used when simulating an isolated molecule, provided that the dimension of the box is large enough to avoid spurious interactions between periodic images.

Within the context of chapter 4 of this thesis, PBC are used to simulate an infinite slab of TiO<sub>2</sub> functionalized with a molecular chromophore. Due to the presence of the chromophore, the unit cell of the crystal cannot be taken as the simulation box. Instead, a supercell has to be used. Its dimension must be large enough to, on one side, avoid spurious interactions between the chromophore images, while also accurately describe the density of states of the TiO<sub>2</sub> surface. In chapter 5, PBC are used to simulate a molecular complex in an explicit water environment.

PBC are used within the CPMD program, allowing the expansion of the orbitals as linear combinations of plane wave (PW) basis functions:

$$\psi_i(\mathbf{r}) = \frac{1}{\sqrt{\Omega_{SC}}} \sum_{\mathbf{G}}^{G_{max}} c_i(\mathbf{G}) \exp[i\mathbf{G}\mathbf{r}]. \quad (2.33)$$

Here, the plane wave basis function

$$f_{\mathbf{G}}^{PW}(\mathbf{r}) = \frac{1}{\sqrt{\Omega_{SC}}} \exp[i\mathbf{G}\mathbf{r}] \quad (2.34)$$

is expressed in terms of the reciprocal lattice vectors  $\mathbf{G}$ .  $\Omega_{SC}$ , which is included in the normalization factor  $1/\sqrt{\Omega_{SC}}$ , represents the volume of the supercell. It has to be noted that equation 2.34 does not show any dependency on the nuclear positions  $\{R_I\}$ , since the plane waves are originless functions delocalized over the entire space. This allows to control the accuracy of the calculations with an energy cutoff,  $E_{cut} = \frac{1}{2}G_{max}^2$  (in a.u.), which determines the number of plane waves used. Increasing this parameter, increases the largest reciprocal lattice vector included in the finite expansion of equation 2.33.

Fast Fourier transform algorithms can be used to move from the real to the reciprocal space, and vice versa. Consequently, the different terms in the energy functional can be more easily evaluated in one or the other space, depending on the efficiency of the calculation.

Additionally, since the PW functions are originless, the Pulay forces are zero, which greatly facilitates the calculation of nuclear forces.

A disadvantage of using PW functions is that to describe the electrons at a decreasingly small distance from the nucleus, requires a large increase in the PW basis set, making therefore their use unpractical. To solve this problem, a distinction



between core and valence electrons is made when using PW functions. It is assumed that the core electrons are practically inert. This allows to take the core electrons out of the explicit calculation, by replacing them with smooth and nodeless potentials called pseudopotentials<sup>25-28</sup>.

### **2.5. TIME-DEPENDENT DENSITY FUNCTIONAL THEORY (TD-DFT)**

Crucial for the study of photochemical processes is the description of the excited electronic states. In 1984 Runge and Gross generalized the density functional formalism for time-dependent systems<sup>29</sup>, thus paving the way for efficient calculations of excited state properties for large molecular systems.

The Runge-Gross theorem considers an arbitrary system which evolves under the influence of a time dependent external potential  $v(\mathbf{r}, t)$ . As in the first HK theorem, they proved that a bijective map exists between the time-dependent external potential  $v(\mathbf{r}, t)$  and the time-dependent electron density  $\rho(\mathbf{r}, t)$ , as well as the time-dependent total wavefunction:  $v(\mathbf{r}, t) \leftrightarrow \Psi(t) \leftrightarrow \rho(\mathbf{r}, t)$ .

It follows that every observable of the system is a unique functional of the density at time  $t$ :

$$O[\rho_t](t) = \langle \Psi[\rho](t) | \hat{O}(t) | \Psi[\rho](t) \rangle \quad (2.35)$$

Again, the time-dependent density of the interacting system  $\rho(\mathbf{r}, t)$  can be calculated as the density of a non-interacting system  $\rho_s(\mathbf{r}, t)$  under the influence of the local potential  $v_s(\mathbf{r}, t)$

$$\rho(\mathbf{r}, t) = \rho_s(\mathbf{r}, t) = \sum_{i=1}^n |\phi_i(\mathbf{r}, t)|^2 \quad (2.36)$$

where  $\phi_i(\mathbf{r}, t)$  are the non-interacting single particle KS orbitals obtained by solving the time-dependent Kohn-Sham equations of the non-interacting system

$$i \frac{\partial}{\partial t} \phi_i(\mathbf{r}, t) = \left( -\frac{\nabla^2}{2} + v_s[\rho](\mathbf{r}, t) \right) \phi_i(\mathbf{r}, t) \quad (2.37)$$

The time-dependent single particle KS potential is again written as

$$v_s[\rho](\mathbf{r}, t) = v_{\text{ext}}(\mathbf{r}, t) + \int_{\Omega_{\text{TOT}}} \frac{\rho(\mathbf{r}', t)}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' + v_{\text{xc}}[\rho](\mathbf{r}, t) \quad (2.38)$$

where the first and the second term on the right hand side of the equation are, respectively, the external time-dependent field and the Hartree potential, while  $v_{\text{xc}}[\rho](\mathbf{r}, t)$  is the exchange-correlation potential. The latter has to be approximated since its exact form is unknown.

TD-DFT describes the interaction of an arbitrary system, *e.g.* a molecule, with a time-dependent external field. If the effect of the external field on the system is sufficiently small in the sense that it does not disrupt completely the ground state system's structure, then the system response can be more efficiently described with a perturbative method, rather than explicitly solving iteratively the TDKS equations.

This is the case for the determination of properties like excitation energies and polarizabilities, which are obtained through the linear response of the ground state density while avoiding the explicit evaluation of the excited states.

### 2.5.1. Linear response TD-DFT

A time-dependent external potential  $v_{\text{ext}}(\mathbf{r}, t)$  acting on a system, such as an electromagnetic field, induces a time-dependent change in the electron density of the system.

We assume that the external potential acting on the system has the form

$$v_{\text{ext}}(\mathbf{r}, t) = \begin{cases} v_0(\mathbf{r}) & ; t \leq t_0 \\ v_0(\mathbf{r}) + v_1(\mathbf{r}, t) & ; t > t_0 \end{cases} \quad (2.39)$$

This means that at  $t \leq t_0$  the system is subject solely to the potential imposed by the nuclei  $v_0(\mathbf{r})$  in its ground state, and that its electron density is  $\rho_0(\mathbf{r})$ . At  $t > t_0$ , the perturbation  $v_1(\mathbf{r}, t)$  is switched on, leading to a total external potential  $v_{\text{ext}}(\mathbf{r}; t) = v_0(\mathbf{r}) + v_1(\mathbf{r}, t)$ . The variation in the total external potential will induce a variation in the electron density of the system.

Using perturbation theory, the effect of a variation in the external field  $v_1$  on any system's observable, and thus also on  $\rho(\mathbf{r}, t)$ , can be represented as a Taylor series

$$\rho(\mathbf{r}, t) = \rho_0(\mathbf{r}) + \rho_1(\mathbf{r}, t) . \quad (2.40)$$

In linear response only the first order term in the density perturbation  $\rho_1(\mathbf{r}, t)$  is

considered<sup>30</sup>. It can be defined as

$$\rho_1(\mathbf{r}, t) = \int_0^\infty dt' \int_{\Omega_{\text{TOT}}} \chi(\mathbf{r}t, \mathbf{r}'t') \delta v_1(\mathbf{r}', t) d\mathbf{r}' \quad (2.41)$$

where

$$\chi(\mathbf{r}t, \mathbf{r}'t') = \left. \frac{\delta \rho(\mathbf{r}, t)}{\delta v_1(\mathbf{r}', t')} \right|_{v_0} \quad (2.42)$$

takes the name of linear response function.

In TD-DFT, the density of a system of interacting electrons can be obtained from a KS system for which the electrons do not interact. Consequently, the linear electron density change  $\rho_1(\mathbf{r}, t)$  induced by the perturbation acting on the interacting system can be calculated as the response of the non-interacting KS system:

$$\rho_1(\mathbf{r}, t) = \int_0^\infty dt' \int_{\Omega_{\text{TOT}}} \chi_s(\mathbf{r}t, \mathbf{r}'t') v_{s,1}(\mathbf{r}', t') d\mathbf{r}' \quad (2.43)$$

Here  $\chi_s(\mathbf{r}t, \mathbf{r}'t')$  is the linear response function of the non-interacting system evaluated at the unperturbed density, while  $v_{s,1}(\mathbf{r}', t)$  is the effective time-dependent potential evaluated as the first order perturbation of the external potential acting on the KS system.

Moving to a non-interacting framework makes possible to write  $\chi_s$  in terms of the unperturbed stationary KS orbitals as

$$\chi_s(\mathbf{r}, \mathbf{r}'; \omega) = \lim_{\eta \rightarrow 0^+} \sum_{i,k=1}^K (f_k - f_i) \frac{\phi_i(\mathbf{r}) \phi_k^*(\mathbf{r}) \phi_i^*(\mathbf{r}') \phi_k(\mathbf{r}')}{\omega - (\varepsilon_i - \varepsilon_k) + i\eta} \quad (2.44)$$

where  $f_i$  is the occupation number of the ground-state KS orbital  $\phi_i$ ,  $\varepsilon_i$  its energy,  $\eta$  is a positive infinitesimal, and  $\omega$  is the frequency of the external perturbation field. The summation of equation 2.44 runs over all the  $K$  occupied and unoccupied orbitals of the system. It has to be noted that for convenience, in equation 2.44 the KS density response function has been written in the Lehmann representation by

Fourier transformation into the frequency domain.

To solve equation 2.43, an expression for the first order variation of the time-dependent KS potential has to be given.

The exchange-correlation kernel is defined as the functional derivative of the xc-potential with respect to the ground state density  $\rho_0$ . It is defined as:

$$f_{xc}[\rho_0](\mathbf{r}t, \mathbf{r}'t') = \left. \frac{\delta v_{xc}[\rho](\mathbf{r}, t)}{\delta \rho(\mathbf{r}', t')} \right|_{\rho=\rho_0} \quad (2.45)$$

Therefore, for any given  $v_1$  it is possible to write the expression for the time-dependent KS potential as

$$v_s(\mathbf{r}, t) = v_1(\mathbf{r}, t) + \int_{\Omega_{TOT}} \frac{\rho_1(\mathbf{r}', t)}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' + \int_{t_0}^t dt' \int_{\Omega_{TOT}} d\mathbf{r}' f_{xc}[\rho_0](\mathbf{r}t, \mathbf{r}'t') \rho_1(\mathbf{r}', t'). \quad (2.46)$$

Again, the exact form of equation 2.45 is unknown and has to be approximated. The simplest approximation for this kernel is the Adiabatic LDA (ALDA). The term adiabatic derives from the assumption that the electron density of the system readjusts instantaneously to a variation in the external field, thus reducing the kernel dependency only to local density and time:  $f_{xc}[\rho_0](\mathbf{r}, t)$ .

By applying equation 2.46 and 2.44 into equation 2.43, it is obtained an exact representation of the linear response of the interacting system density to the effective time-dependent perturbation.

TD-DFT has proven to provide accurate excitation energies as long as low-energy transitions involving valence states are investigated.

TD-DFT has become a standard tool for the characterization of molecular systems, particularly if designed for optical applications.

With the development of more and more sophisticated exchange-correlation functionals that can account for long-range correction (see section 2.3), TD-DFT is assuming an ever growing role in studying photoinduced charge transfer processes.

## 2.6. CONSTRAINED DENSITY FUNCTIONAL THEORY

The process of electron transfer (ET) from a donor (D) to and acceptor (A) state is a nonadiabatic process whose description has been proven computationally challenging<sup>31,32</sup>.

In this context, given a donor-acceptor (D-A) system, the objective is to calculate the rate of electron transfer between them (*i.e.*  $D - A \xrightarrow{k_{ET}} D^+ - A^-$ ).

In 1956, R.A. Marcus proposed a theory<sup>33</sup> (see section 1.4 of this thesis) to estimate the rate of such a process through the expression

$$k_{ET} = \frac{2\pi}{\hbar} \langle |H_{ab}|^2 \rangle (4\pi k_B T \lambda)^{-1/2} \exp \left[ \frac{(\Delta G^0 + \lambda)^2}{4\lambda k_B T} \right], \quad (2.47)$$

where  $H_{ab}$  is the coupling between the donor and the acceptor states ( $\psi_d$  and  $\psi_a$ , respectively),  $\Delta G^0$  is the driving force of the process, and  $\lambda$  is the reorganization free energy. Among these three parameters, essential for  $k_{ET}$  calculations,  $H_{ab}$  is the one proven more challenging to accurately estimate since it requires the use of expensive wavefunction based *ab initio* methods<sup>34</sup>. In principle, DFT-based methods could also be used as less computationally intensive alternatives for such tasks. However, their results are often biased by the electron delocalization error of commonly used exchange-correlation approximations<sup>35,36</sup>.

Inspired by previous works<sup>37-39</sup> on DFT-based methods in which the energy is minimized under certain density constraints, Van Voorhis and collaborators have recently proposed a new approach for calculating  $H_{ab}$ ,  $\Delta G^0$  and  $\lambda$  from charge-localized diabatic states. Due to their localized nature, the use of these states strongly reduces the electron delocalization error previously mentioned.

Constrained DFT (CDFT) methods allow the construction of the two diabatic states  $D - A$  and  $D^+ - A^-$  and thus the computation of the parameters in equation 2.47. This is done by minimizing the KS energy functional  $E^{KS}[\rho]$  under the constraint that the charge difference between D and A is equal to a certain value  $N_c$ . The purpose is to find that particular external potential associated to a ground-state corresponding to the constrained state<sup>40</sup>.

The minimization is carried out by using a Lagrange multiplier as

$$W[\rho, V_c] = E^{KS}[\rho] + V_c \left( \int_{\Omega_{tot}} w(\mathbf{r}) \rho(\mathbf{r}) d\mathbf{r} - N_c \right), \quad (2.48)$$

where  $W[\rho, V_c]$  is the energy functional for the constrained state,  $E^{KS}[\rho]$  is the KS energy functional and  $V_c$  is the Lagrange multiplier used to enforce the constraint

$$\int_{\Omega_{\text{tot}}} w(\mathbf{r})\rho(\mathbf{r})d\mathbf{r} = N_c. \quad (2.49)$$

Here,  $w(\mathbf{r})$  is the weight function that defines the partition of the electron density between donor and acceptor.

Making equation 2.48 stationary for normalized orbitals yields

$$\left[ -\frac{\nabla^2}{2} + v_{\text{ext}}(\mathbf{r}) + \int_{\Omega_{\text{tot}}} \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' + v_{\text{xc}}(\mathbf{r}) + V_c w_c(\mathbf{r}) \right] \psi_i(\mathbf{r}) = \varepsilon_i \psi_i(\mathbf{r}), \quad (2.50)$$

which is the same as equation 2.23, except for the last term in the effective Hamiltonian, which represents the constraint potential.

For every  $V_c$  then exists a unique set of orbitals  $\{\psi_i\}$  that can be used to calculate the system's electron density associated with that specific constraint potential. This implies that  $W$  is itself a function of  $V_c$ . It can be shown<sup>40</sup> that  $W(V_c)$  is a concave function, which has only one stationary point of maximum. Therefore, it can be optimized with respect to  $V_c$ , to find the potential value that produces the constrained ground state density.

The optimization procedure involves a double loop which proceeds as follows: i) an initial set of orbitals is used to construct the KS Hamiltonian; ii) an initial value is assigned to the constraint potential to build the total effective Hamiltonian and solve equation 2.50; iii) the first and second derivative of  $W$  with respect to  $V_c$  are calculated to optimize the potential. Since to every new potential corresponds a new electron density, the process is restarted from point (i) and is iterated until it converges self consistently. Self-consistency is considered reached when the total deviation of the constraint with respect to  $N_c$  is lower than  $10^{-5}$ .

Once  $V_c$  is found for both diabatic states, then the calculation of  $\Delta G$ ,  $\lambda$  and  $H_{ab}$  can be done assuming the validity of Marcus theory. A detailed mathematical description of the procedures leading to these parameters can be found in the literature<sup>34,40,41</sup>.

## 2.7. SEMI-EMPIRICAL METHODS: Hückel and Extended Hückel Method

One of the first semi-empirical methods to be proposed was the Hückel Molecular Orbital (MO) theory in 1930. Introduced by Erich Hückel, this method is intended for studying planar conjugated hydrocarbon systems.

In the Hückel MO method one of the central assumptions is that the general properties of a conjugated hydrocarbon molecule are determined by its  $\pi$ -electron MOs. This allows to disregard all the  $\sigma$ -electrons in a molecule, and simply treat  $\sigma$ -bonds as the backbone on which  $\pi$ -electrons delocalize. This approximation is made possible by the planarity of a conjugated molecule. In a planar molecule, in fact,  $\sigma$  and  $\pi$  molecular orbitals are respectively symmetric and anti-symmetric with respect to reflection in the molecular plane. Consequently, the  $\sigma$  and  $\pi$  orbitals are orthogonal and can be treated independently from each other. Despite its simplicity, this method is able to predict the effects of delocalization on orbital stability and identify whether a specific structure will or will not be aromatic. However, due to the strong approximations introduced, its applicability is limited solely to planar systems.

To overcome the limitations presented by the Hückel MO theory, in 1963<sup>42</sup> Roald Hoffmann developed the Extended Hückel theory (EHT). Differently from Hückel MO theory, in the EHT method not only the  $\pi$  but all the valence electrons are considered. This enlargement of basis set allows the determination of molecular energies and structures, transition states and energy barriers.

In the EHT formalism, the total electronic wavefunction for a system with  $n$  valence electrons is described as a product of one-electron wavefunctions  $\psi_j(\mathbf{r}_j)$

$$\Psi_{\text{EHT}} = \psi_1(\mathbf{r}_1)\psi_2(\mathbf{r}_2)\dots\psi_j(\mathbf{r}_j)\dots\psi_n(\mathbf{r}_n). \quad (2.51)$$

In turn, these one-electron molecular orbitals can be written as linear combinations of normalized valence atomic orbitals  $\varphi_\nu$

$$\psi_j = \sum_{\nu=1}^K c_{\nu j} \varphi_\nu \quad (2.52)$$

In the EHT, the basis set is formed by Slater-type orbitals (STOs) chosen to represent the valence orbitals of the atoms in the molecule. Once the molecular orbitals are constructed, it is possible to calculate the total energy of the system as the sum of the one-electron energies  $\varepsilon_j$ , which can be evaluated by applying the effective one-electron Hamiltonian  $\hat{h}_{eff}$  to the one-electron molecular orbital  $\psi_j$

$$\hat{h}_{eff}\psi_j = \varepsilon_j\psi_j \quad (2.53)$$

The  $\hat{h}_{eff}$  describes the interaction of an electron with the rest of the molecule. However, the exact expression of this Hamiltonian is not needed in EHT.

The crucial step in obtaining the eigenfunctions for an effective Hamiltonian is the construction of the secular determinant

$$\begin{vmatrix} H_{11} - ES_{11} & H_{12} - ES_{12} & \cdots & H_{1K} - ES_{1K} \\ H_{21} - ES_{21} & H_{22} - ES_{22} & \cdots & H_{2K} - ES_{2K} \\ \vdots & \vdots & \ddots & \vdots \\ H_{K1} - ES_{K1} & H_{K2} - ES_{K2} & \cdots & H_{KK} - ES_{KK} \end{vmatrix} = 0 \quad (2.54)$$

To solve this equation it is necessary to calculate a series of overlap ( $S_{\mu\nu}$ ) and resonance integrals ( $H_{\nu\mu}$ ). The solution to the first problem is rather simple. Since we know the form and the position of the atomic orbitals, their overlap can be readily evaluated as a function of interatomic distances. The diagonal resonance integral  $H_{\mu\mu}$  is called Coulomb integral and represents the kinetic and potential energy of an electron in a specific atomic orbital  $\varphi_\mu$ . Its value is parametrized against a specific reference value, which is usually taken as the negative of the orbital ionization potential. On the contrary, the off diagonal resonance integral  $H_{\mu\nu}$  describes the energy of an electron in the region where the orbitals  $\varphi_\mu$  and  $\varphi_\nu$  overlap. This term can be approximated as

$$H_{\mu\nu} = \frac{1}{2} k_{\mu\nu} (H_{\mu\mu} + H_{\nu\nu}) S_{\mu\nu} \quad (2.55)$$

Equation 2.55 indicates that  $H_{\mu\nu}$  is proportional to the energy of the atomic orbitals involved, and to the extent of their overlap. The term  $k_{\mu\nu}$  is an empirical factor usually assumed equal to 1.75, which takes the name of Wolfsberg-Helmholtz constant.

Through the application of these conventions it is possible to solve the secular equation and obtain qualitatively correct energy values and wavefunctions for the molecular orbitals of the investigated system. However, since EHT is not a self-consistent method, it is not able to generate potential energy surfaces accurately. Therefore, it is best applied in combination with structures or trajectories obtained



from higher levels of theory. This is the strategy adopted in chapter 4 and 5 of this thesis.

## 2.8. REFERENCES

- (1) Born, M.; Oppenheimer, R. Zur Quantentheorie Der Molekeln. *Ann. Phys.* **1927**, *389* (20), 457–484.
- (2) Handy, N. C.; Yamaguchi, Y.; Iii, H. F. S. The Diagonal Correction to the Born–Oppenheimer Approximation: Its Effect on the Singlet–triplet Splitting of CH<sub>2</sub> and Other Molecular Effects. *J. Chem. Phys.* **1986**, *84* (8), 4481–4484.
- (3) Ehrenfest, P. Bemerkung Über Die Angenäherte Gültigkeit Der Klassischen Mechanik Innerhalb Der Quantenmechanik. *Z. Für Phys.* **1927**, *45*, 455–457.
- (4) Fischer, S. A.; Chapman, C. T.; Li, X. Surface Hopping with Ehrenfest Excited Potential. *J. Chem. Phys.* **2011**, *135* (14), 144102.
- (5) Tully, J. C.; Preston, R. K. Trajectory Surface Hopping Approach to Nonadiabatic Molecular Collisions: The Reaction of H<sup>+</sup> with D<sub>2</sub>. *J. Chem. Phys.* **1971**, *55* (2), 562–572.
- (6) Hohenberg, P.; Kohn, W. Inhomogeneous Electron Gas. *Phys. Rev.* **1964**, *136* (3B), B864–B871.
- (7) Kohn, W.; Sham, L. J. Self-Consistent Equations Including Exchange and Correlation Effects. *Phys. Rev.* **1965**, *140* (4A), A1133–A1138.
- (8) Ceperley, D. M.; Alder, B. J. Ground State of the Electron Gas by a Stochastic Method. *Phys. Rev. Lett.* **1980**, *45* (7), 566–569.
- (9) Vosko, S. H.; Wilk, L.; Nusair, M. Accurate Spin-Dependent Electron Liquid Correlation Energies for Local Spin Density Calculations: A Critical Analysis. *Can. J. Phys.* **1980**, *58* (8), 1200–1211.
- (10) Perdew, J. P.; Wang, Y. Accurate and Simple Analytic Representation of the Electron-Gas Correlation Energy. *Phys. Rev. B* **1992**, *45* (23), 13244–13249.
- (11) Perdew, J. P.; Zunger, A. Self-Interaction Correction to Density-Functional Approximations for Many-Electron Systems. *Phys. Rev. B* **1981**, *23* (10), 5048–5079.
- (12) Cole, L. A.; Perdew, J. P. Calculated Electron Affinities of the Elements. *Phys. Rev. A* **1982**, *25* (3), 1265–1271.
- (13) Becke, A. D. Density-Functional Exchange-Energy Approximation with Correct Asymptotic Behavior. *Phys. Rev. A* **1988**, *38* (6), 3098–3100.
- (14) Becke, A. D. Density-functional Thermochemistry. III. The Role of Exact Exchange. *J. Chem. Phys.* **1993**, *98* (7), 5648–5652.
- (15) Perdew, J. P. Density-Functional Approximation for the Correlation Energy of the Inhomogeneous Electron Gas. *Phys. Rev. B Condens. Matter* **1986**, *33* (12), 8822–8824.
- (16) Perdew, J. P.; Burke, K.; Ernzerhof, M. Generalized Gradient Approximation Made Simple. *Phys. Rev. Lett.* **1996**, *77* (18), 3865–3868.
- (17) Lee, C.; Yang, W.; Parr, R. G. Development of the Colle-Salvetti Correlation-Energy Formula into a Functional of the Electron Density. *Phys. Rev. B* **1988**, *37* (2), 785–789.
- (18) Slater, J. C. A Simplification of the Hartree-Fock Method. *Phys. Rev.* **1951**, *81* (3), 385–390.
- (19) Yanai, T.; Tew, D. P.; Handy, N. C. A New Hybrid Exchange–correlation Functional Using the Coulomb-Attenuating Method (CAM-B3LYP). *Chem. Phys. Lett.* **2004**, *393* (1–3), 51–57.
- (20) Rohrdanz, M. A.; Martins, K. M.; Herbert, J. M. A Long-Range-Corrected Density Functional That Performs Well for Both Ground-State Properties and Time-Dependent Density Functional Theory Excitation Energies, Including Charge-Transfer Excited States. *J. Chem. Phys.* **2009**, *130* (5), 054112.
- (21) Tawada, Y.; Tsuneda, T.; Yanagisawa, S.; Yanai, T.; Hirao, K. A Long-Range-Corrected Time-Dependent Density Functional Theory. *J. Chem. Phys.* **2004**, *120* (18), 8425–8433.

- (22) Kobayashi, R.; Amos, R. D. The Application of CAM-B3LYP to the Charge-Transfer Band Problem of the Zincbacteriochlorin–bacteriochlorin Complex. *Chem. Phys. Lett.* **2006**, *420* (1–3), 106–109.
- (23) Car, R.; Parrinello, M. Unified Approach for Molecular Dynamics and Density-Functional Theory. *Phys. Rev. Lett.* **1985**, *55* (22), 2471–2474.
- (24) Sprik, M.; Ciccotti, G. Free Energy from Constrained Molecular Dynamics. *J. Chem. Phys.* **1998**, *109* (18), 7737–7744.
- (25) Phillips, J. C. Energy-Band Interpolation Scheme Based on a Pseudopotential. *Phys. Rev.* **1958**, *112* (3), 685–695.
- (26) Phillips, J. C.; Kleinman, L. New Method for Calculating Wave Functions in Crystals and Molecules. *Phys. Rev.* **1959**, *116* (2), 287–294.
- (27) Hellmann, H. A New Approximation Method in the Problem of Many Electrons. *J. Chem. Phys.* **1935**, *3* (1), 61–61.
- (28) Hellmann, H.; Kassatotschkin, W. Metallic Binding According to the Combined Approximation Procedure. *J. Chem. Phys.* **1936**, *4* (5), 324–325.
- (29) Runge, E.; Gross, E. K. U. Density-Functional Theory for Time-Dependent Systems. *Phys. Rev. Lett.* **1984**, *52* (12), 997–1000.
- (30) Gross, E. K.; Maitra, N. T. Introduction to TDDFT. In *Fundamentals of Time-Dependent Density Functional Theory*; Springer, 2012; pp 53–99.
- (31) Duncan, W. R.; Prezhdo, O. V. Theoretical Studies of Photoinduced Electron Transfer in Dye-Sensitized TiO<sub>2</sub>. *Annu. Rev. Phys. Chem.* **2007**, *58*, 143–184.
- (32) Eshuis, H.; Voorhis, T. van. The Influence of Initial Conditions on Charge Transfer Dynamics. *Phys. Chem. Chem. Phys.* **2009**, *11* (44), 10293–10298.
- (33) Marcus, R. A. On the Theory of Oxidation-Reduction Reactions Involving Electron Transfer. I. *J. Chem. Phys.* **1956**, *24* (5), 966–978.
- (34) Oberhofer, H.; Blumberger, J. Electronic Coupling Matrix Elements from Charge Constrained Density Functional Theory Calculations Using a Plane Wave Basis Set. *J. Chem. Phys.* **2010**, *133* (24), 244105–244105 – 10.
- (35) Cohen, A. J.; Mori-Sánchez, P.; Yang, W. Insights into Current Limitations of Density Functional Theory. *Science* **2008**, *321* (5890), 792–794.
- (36) Zhang, Y.; Yang, W. A Challenge for Density Functionals: Self-Interaction Error Increases for Systems with a Noninteger Number of Electrons. *J. Chem. Phys.* **1998**, *109* (7), 2604–2608.
- (37) Akai, H.; Blügel, S.; Zeller, R.; Dederichs, P. H. Isomer Shifts and Their Relation to Charge Transfer in Dilute Fe Alloys. *Phys. Rev. Lett.* **1986**, *56* (22), 2407–2410.
- (38) Dederichs, P. H.; Blügel, S.; Zeller, R.; Akai, H. Ground States of Constrained Systems: Application to Cerium Impurities. *Phys. Rev. Lett.* **1984**, *53* (26), 2512–2515.
- (39) Prezhdo, O. V.; Kindt, J. T.; Tully, J. C. Perturbed Ground State Method for Electron Transfer. *J. Chem. Phys.* **1999**, *111* (17), 7818–7827.
- (40) Wu, Q.; Van Voorhis, T. Direct Optimization Method to Study Constrained Systems within Density-Functional Theory. *Phys. Rev. A* **2005**, *72* (2), 024502.
- (41) Wu, Q.; Voorhis, T. V. Extracting Electron Transfer Coupling Elements from Constrained Density Functional Theory. *J. Chem. Phys.* **2006**, *125* (16), 164105.
- (42) Hoffmann, R. An Extended Hückel Theory. I. Hydrocarbons. *J. Chem. Phys.* **1963**, *39* (6), 1397–1412.

