Chapter 2

Theoretical Framework
Computational Quantum Chemistry

According to classical mechanics, the motion of a particle of constant mass can be described by the following equation:

\[ F = ma = m \frac{d^2x}{dt^2} \]  \hspace{2cm} (2.1)

where \( F \) is the force acting on a particle with mass \( m \), and the acceleration \( a \) is given in terms of position \( x \) and time \( t \). However, since late nineteenth and early twentieth centuries, it was discovered that classical mechanics does not describe correctly the behavior of small particles such as atomic nuclei or electrons due to the implications of the mass of such particles (see Figure 2.1). The behavior of these particles began to be described by a set of laws now known as quantum mechanics. This set of laws came from the study of phenomena such as the photoelectric effect, the black body radiation, the wave-particle duality, among others; which could not be explained by classical physics. As a consequence of the wave-particle duality described by De Broglie in 1927, Werner Heisenberg proposed the uncertainty principle. This principle states that the measurement itself of a molecular property in a system introduces an uncontrollable disturbance in the system. In general, the description of atomic and subatomic particles through this set of postulates is the cornerstone of quantum mechanics and, in turn, these have been used in the determination of the molecular behavior.

![Figure 2.1 The double-slit experiment.](image-url)
2.1 The Schrödinger equation

The Schrödinger equation\(^{230}\) is a mathematical expression that represents the energy \(E\) of a particle which depends on the wavefunction of such an entity.

\[
\hat{H}\psi(r_1, r_2, \ldots, r_N) = E\psi(r_1, r_2, \ldots, r_N)
\]

wherein \(\psi\) is the wavefunction and \(\hat{H}\) is the Hamiltonian of the system. This latter is expressed as follows:

\[
\hat{H} = -\frac{\hbar^2}{2}\sum_A \frac{1}{m_A} \nabla_A^2 - \frac{\hbar^2}{2}\sum_i \frac{1}{m_i} \nabla_i^2 + \sum_B \sum_{A<B} \frac{Z_A Z_B e^2}{4\pi \varepsilon_0 r_{AB}} - \sum_i \sum_A \frac{Z_A e^2}{4\pi \varepsilon_0 r_{iA}}
\]

\[
+ \sum_j \sum_{i<j} \frac{e^2}{4\pi \varepsilon_0 r_{ij}}
\]

or well,

\[
\hat{H} = \hat{T}_N + \hat{T}_e + \hat{V}_{NN} + \hat{V}_{eN} + \hat{V}_{ee}
\]

The first two terms of the Hamiltonian correspond to the kinetic energy of nuclei \(A\) and electrons \(i\); then the following terms describe the interactions between nuclei \(A\) and \(B\), nuclei \(A\) and electrons \(i\), and electrons \(i\) and \(j\); respectively. Many calculations of molecular wavefunctions are based on the separation of the electronic Hamiltonian first formulated by Born and Oppenheimer.\(^{231}\) The nuclear kinetic energy terms are omitted and the remaining quantum operator is a Hamiltonian of electrons only. The stationary nuclei enter to the problem only as generators of an electric potential in which the electrons move in a quantum mechanical way. Within this framework, the molecular Hamiltonian has been simplified to the so-called electronic Hamiltonian including internuclear repulsion that operates only on functions of the electronic coordinates:\(^{229}\)

\[
\hat{H}_{elect} = \hat{T}_e + \hat{V}_{NN} + \hat{V}_{eN} + \hat{V}_{ee}
\]

2.2 Molecular orbitals

According to the molecular orbital (MO) theory, MOs are formed by the interaction of atomic orbitals. This approach is useful to generate simple MOs, which can be constructed through a linear combination of atomic orbitals (LCAO). Some assumptions have to be taken into consideration:

(i) MOs are formed by the overlap of atomic orbitals.
(ii) Atomic orbitals significantly interact each other if they are energetically similar.
(iii) When two atomic orbitals overlap, they interact with each other to form two MOs; those are the bonding and antibonding orbitals.
Like a pair of electromagnetic waves, atomic orbitals can interact either in or out of phase as schematized in Figure 2.2. When the atomic orbitals are in phase, an accumulation of electron density occurs, which is equivalent to an increase in negative charge in the region of overlap between the cores. This generates an increase in the intensity of the attraction between the electronic charge and atomic nuclei involved in the bond. Since electrons in a MO have lower potential energy than they have in isolated atoms, the increase in the intensity of attraction is accompanied by a reduction in the kinetic energy of the electrons in the system. This is known as a bonding MO. On the other hand, when two atomic orbitals interact out of phase, the resulting interaction leads to a decrease in negative charge; as a consequence, it creates a decrease in the attraction between the electronic charge and the atomic nuclei. This leads to a greater potential energy which destabilizes the bond between atoms and forms a nodal plane. In this case, electrons are more stable in the atomic orbitals of isolated atoms. This is known as an antibonding MO.²³²

![Figure 2.2 Linear combination of atomic orbitals leading to antibonding Ψ* and bonding Ψ molecular orbitals.](image)

The MO theory differs from the valence bond theory; this latter is based on the Lewis model of valence electrons. However, in several cases, the MO theory predicts the electron density to be located between two nuclei, which represents a chemical bond; thus resembling the main element of the valence bond theory.²²⁹

### 2.3 The Hartree-Fock approximation

The calculation of the Schrödinger equation for atoms with many electrons is complicated through analytical solutions; therefore, different approaches have been developed to solve such a predicament. In this regard, in the Hartree-Fock (HF) approximation wavefunctions are constructed as a LCAO and arranged in a mathematical determinant also known as the Slater determinant.²³³
\[ \psi_{HF}(r_1, r_2, \ldots, r_N) = (N!)^{-1/2} \begin{bmatrix} \phi_1(r_1) & \phi_2(r_1) & \ldots & \phi_N(r_1) \\ \phi_1(r_2) & \phi_2(r_2) & \ldots & \phi_N(r_2) \\ \vdots & \vdots & \ddots & \vdots \\ \phi_1(r_N) & \phi_2(r_N) & \ldots & \phi_N(r_N) \end{bmatrix} \] (2.6)

wherein \( \phi(r) \) is an atomic orbital and \( N \) is the total number of electrons. The energy of the system is obtained by variationally minimizing the HF energy through:

\[ E_{HF} = \min \langle \psi | \hat{H} | \psi \rangle \] (2.7)

Nonetheless, the variational theorem, equation (2.8), states that for a time-independent Hamiltonian operator any trial wavefunction will have an energy expectation value that is greater than or equal to the true ground state wavefunction corresponding to the given Hamiltonian. Because of this, the HF energy is an upper bound to the true ground state energy of a given molecule. In the context of the HF method, the best possible solution is found at the HF limit; i.e. the limit of the HF energy as the basis set approaches completeness.

\[ E_{\psi} = \frac{\langle \psi | \hat{H} | \psi \rangle}{\langle \psi | \psi \rangle} \geq E_{\psi \text{ exact}} \] (2.8)

The HF method can favorably predict the ground state of small non-ionized molecules such as benzene. For large molecules, the accuracy shall depend indirectly on computational resources and the precision of defining atomic orbitals. This method is also a self-consistent field approximation, because wavefunctions are recursively minimized.\textsuperscript{229,234}

### 2.4 Basis sets

A basis set describes the behavior of a wavefunction of a single electron in an atom. That is, it is the solution of the HF equations for an atomic orbital. The first functions of this type were the Slater type functions due to its similarity to the atomic orbitals of the hydrogen atom as depicted in Figure 2.3a:

\[ \phi_i(\zeta, n, l, m; r, \theta, \phi) = N r^{n-1} e^{-\zeta r} Y_{lm}(\theta, \phi) \] (2.9)

here \( N \) is a normalizing constant; \( \zeta \) is a characteristic exponent; \( r, \theta, \) and \( \phi \) are spherical coordinates; \( Y_{lm} \) is a spherical harmonic; \( n, l, \) and \( m \) are respectively the principal, secondary, and magnetic quantum numbers. The geometric form of a Slater type orbital (STO) can be approximated by a sum of Gaussian functions with different exponents and coefficients (Figure 2.3b). Gaussian functions significantly reduce the computational time because the integration of a Gaussian function is faster (in view of the Gaussian product theorem).\textsuperscript{235,236} Gaussian functions are described as follows:

\[ g(\alpha, \beta, \gamma; x, y, z) = N e^{-\alpha x^2} x^\beta y^\gamma z^\gamma \] (2.10)
where $N$ is a normalizing constant; $\alpha$ is a characteristic exponent; $x$, $y$, and $z$ are Cartesian coordinates; and $a$, $b$, and $c$ are exponents. The sum of these exponents, $L = a + b + c$, is related to an $s$-type orbital if $L = 0$; analogously $L = 1$ for $p$-type orbitals, and $L = 2$ for $d$-type orbitals.\(^{237}\)

![Figure 2.3](image)

**Figure 2.3** a) Comparison of Gaussian and Slater type orbitals for the 1s hydrogen orbital.  
b) Contractions of Gaussian functions to a Slater type orbital.

Primitive Gaussian functions are obtained by electronic optimizations of atoms through calculations such as HF or configuration interaction (CI; a post-Hartree-Fock linear variational method). Exponents and coefficients are varied until the lowest total energy of the atoms is reached. Gaussian functions are grouped into levels (they are not the energy levels of an atom). A level is a collection of Gaussian functions that have the same value of $L$. Primitive Gaussian functions are usually contracted as linear combinations for the calculation of atomic or molecular properties. Better results are attained if the coefficients of the Gaussian functions were left free to vary. However, this represents a large computational effort in both hard disk and storage of integrals; as well as the internal memory of the computer. Contraction of Gaussian functions is performed by a curve-fitting. The number of contractions used to represent a STO is called *zeta* and it corresponds to the number of basis sets per orbital (e.g., double zeta, DZ; triple zeta, TZ; and so on). One of the smallest basis sets is STO-3G, which is used by popular semiempirical methods.\(^{238}\) The STO-3G basis set is the result of the contraction of three Gaussian functions and it has been adjusted by the method of least-squares to a STO (see Figure 2.3b).\(^{229,239}\)
2.4.1 Pople functions

For valence orbitals, sometimes more basis sets are assigned to the rest of the orbitals; these are known as split valence (SV) basis sets. In the Pople convention, the nature of SV basis set is emphasized following the syntax: \( n \cdot ijG \) or \( n \cdot ijkG \), where \( n \) is the number of primitive functions for internal levels, \( ij \) or \( ijk \) are the number of primitive functions for contractions of the valence level. The notations \( ij \) and \( ijk \) describe basis sets of double and triple zeta quality, respectively. Generally, \( s \)- or \( p \)-type contractions are converted into \( sp \)-type levels. For example, a 4-31G basis set corresponds to 4 primitive functions which represent the internal level; and contractions of 3 and 1 primitive functions represent the valence level. Pople functions can be extended with polarization functions \( d \) in heavy atoms; here an asterisk is added to the basis sets. For instance, the 4-31G* basis set in the case of methane contains 8 functions \( s \)-type, 4 \( p \)-type, and one \( dl4s \) type; where the latter is precisely the polarization function.\(^{240,241}\)

2.4.2 Polarization and diffuse functions

Polarization functions are functions with a value of \( L \) higher than those ones representing the orbitals of the corresponding atom. Polarization functions are important for reaching better precision in reproducing a chemical bond since they improve correlation effects. With the addition of \( d \)-type functions to the basis set, each atom adds up to 5 or 6 functions, while with the addition of \( f \)-type functions there is an increment of 7 or 10 basis functions, which increases the computational time. The exponents of the functions of polarization cannot be obtained from HF calculations because the electrons do not occupy virtual orbitals within this approximation. On the other hand, they are estimated from calculations including correlation. For example, the function of Pople 6-31G(\( d \)), or 6-31G*, adds 6 \( d \)-type functions as the polarization functions. Similarly, 6-31G(\( d,p \)), or 6-31G**, includes additional \( p \)-type polarization functions to the hydrogen atoms. Diffuse functions are very important to describe anions and weak bonds. These functions have small exponents and slowly vanish as a function of the distance to the nucleus. Within the Pople’s notation, they are represented by the sign \(+\).\(^{229,239,240}\)

2.5 Pseudopotentials

First introduced by Hans Hellman\(^{242}\) in 1934, pseudopotentials are approximations that simplify the complex description of the effects of the motion of core electrons; that is, a modified effective potential is introduced in the Schrödinger equation instead of the Coulomb potential term in order to describe non-valence electrons of an atom together with its nucleus.
2.5.1 Effective core potentials

In most cases, the internal atomic levels are not significantly affected by changes in the chemical bond. This has motivated the development of effective core potentials (ECPs) which enable the treatment of internal electron levels as an average potential instead of actual particles. ECPs are not orbitals, but modifications to the Hamiltonian operator made with the aim to improve the computational performance. Relativistic effects are also added, which are important in transition metals and heavy atoms. For the rest of the electrons, as well as the valence electrons, basis sets optimized for each type of ECP are included. ECPs are generally published as parameters of the following expression:

\[
ECP = \sum_{i=1}^{M} d_i r^{n_i} e^{-\zeta_i r^2}
\]  

(2.11)

here \( M \) is the number of terms in the expression, \( d_i \) is a coefficient for each term, \( r \) is the distance to the nucleus, and \( n_i \) and \( \zeta_i \) are exponents at the \( i \)-th term. To specify an ECP, it is necessary to include the number of internal electrons that are going to be replaced by the ECP, the angular-momentum quantum number \( l \), and the number of terms in the Gaussian polynomial expansion.\(^{243,244}\) This strategy is implemented in the Gaussian09 computational package used in this thesis.\(^{245}\)

2.5.2 The frozen core approximation

The frozen core approximation (FCA) is an alternative method that uses a frozen core to optimize the computational resources by reducing the size of the basis set. In view of the fact that core atomic orbitals are practically unaltered during the formation of a bond, the quality of the calculations remains unchanged by using the FCA;\(^{246,247}\) which represents savings in the computational time. Unlike ECP, a FCA calculation is indeed an all-electron calculation. FCA also allows the calculation of total charge density and potential in the valence and in the core region.

In the FCA, the valence basis set used in the self-consistent field equations is explicitly orthogonalized to the frozen core. Thus, a series of auxiliary core functions, \( \chi^\text{core} \), are added to the valence basis set. One \( \chi^\text{core} \) per frozen core orbital is therefore included. A valence function is replaced by a linear combination as follows:

\[
\chi^\text{valence} \rightarrow \chi^\text{valence} + \sum_{\mu} c_{\mu\nu} \chi^\text{core} \nu
\]  

(2.12)

Coefficients \( c_{\mu\nu} \) are obtained from the condition that each such modified valence function is orthogonal to each frozen core orbital. The frozen core orbitals are taken from very accurate single-atom calculations with large STO basis sets. This approach can be executed in the Amsterdam Density Functional computational package used in the current thesis.\(^{248,249}\)
2.6 Density functional theory

The density functional theory (DFT) represents an alternative to conventional *ab initio* methods to solve the Schrödinger equation. According to DFT, the energy of a many-electron system can be expressed from the electron density $n(r)$. The function of $n(r)$ depends on three spatial variables $x, y, z$; while polyelectronic wavefunctions require three variables for each one of the $N$ electrons in the molecular system. This reduction in the number of variables results in a reduction of computing time for a procedure based on DFT as compared to post-HF methods.\(^{250}\)

2.6.1 The Hohenberg-Kohn theorems

DFT is formally based on the theorems formulated by Hohenberg and Kohn in 1964.\(^{251,252}\) The first theorem states that there is a one-to-one relationship between the external potential $v_{\text{ext}}(r)$ and the ground state density, and hence the total energy is a unique functional of $n(r)$. The energy functional $E[n(r)]$ referred in the first Hohenberg-Kohn theorem can be written in terms of $v_{\text{ext}}(r)$ in the following way:

$$E[n(r)] = \int n(r)v_{\text{ext}}(r)dr + F[n(r)] \quad (2.13)$$

where $F[n(r)]$ is unknown; although it is a universal functional of $n(r)$. Accordingly, assuming a nondegenerate ground state, the Hamiltonian for the system can be written in the following way: the electron wavefunction $\Psi$ that minimizes the energy expectation value gives the ground-state energy.

$$E[n(r)] = \langle \Psi | H | \Psi \rangle \quad (2.14)$$

then, the Hamiltonian can be written as:

$$\hat{H} = \hat{F} + \hat{V}_{\text{ext}}$$ \quad (2.15)

$$\hat{F} = \hat{T}_e + \hat{V}_{ee}$$ \quad (2.16)

The electron operator $\hat{F}$ is the same for all $N$-electron systems; as a result, $\hat{H}$ is completely defined by $N$ and $v_{\text{ext}}(r)$. The proof of the first theorem is remarkably simple and proceeds by *reductio ad absurdum*. Let us consider two external potentials, $v_{\text{ext},1}(r)$ and $v_{\text{ext},2}(r)$ which differ by more than a constant, that give rise to the same density $n_0(r)$. The corresponding Hamiltonians, $\hat{H}_1$ and $\hat{H}_2$, will therefore have different ground-state wavefunctions, $\Psi_1$ and $\Psi_2$, which give $n_0(r)$. The variational principle then leads to:

$$E_1^0 < \langle \Psi_2 | \hat{H}_1 | \Psi_2 \rangle = \langle \Psi_2 | \hat{H}_2 | \Psi_2 \rangle + \langle \Psi_2 | \hat{H}_1 - \hat{H}_2 | \Psi_2 \rangle$$

$$= E_2^0 + \int n_0(r)[v_{\text{ext},1}(r) - v_{\text{ext},2}(r)]dr \quad (2.17)$$
here $E_1^0$ and $E_2^0$ are the ground-state energies of the corresponding Hamiltonians. An equivalent expression of equation 2.17 is obtained by interchanging the subscripts; which leads to the inequality:

$$E_1^0 + E_2^0 < E_2^0 + E_1^0$$

(2.18)

which is a contradiction and, as a result, the ground-state density uniquely determines $v_{ext}(r)$ within an additive constant. To sum up, the electrons determine the positions of the nuclei in a system and all ground-state electronic properties because $v_{ext}(r)$ and $N$ completely define the Hamiltonian of the system.

The second theorem states that the ground state energy can be obtained variationally: the density that minimizes the total energy is the exact ground-state density. The proof of this theorem is given as follows:

$$n(r) \rightarrow v_{ext}(r)$$

(2.19)

and given that $v_{ext}(r)$ and $N$ determine $\hat{H}$ and $\Psi$, the expectation value of $\hat{F}$ is also a functional of $n(r)$:

$$F[n(r)] = \langle \Psi | \hat{F} | \Psi \rangle$$

(2.20)

then

$$E_v[n'(r)] = \int n'(r)v_{ext}(r)dr + F[n'(r)]$$

(2.21)

where $E_v[n'(r)]$ is a $v$-representable\textsuperscript{253,254} energy functional for which $v_{ext}(r)$ is unrelated to another density $n'(r)$. The variational principle leads to:

$$\langle \Psi' | \hat{F} | \Psi' \rangle + \langle \Psi' | \hat{V}_{ext} | \Psi' \rangle > \langle \Psi | \hat{F} | \Psi \rangle + \langle \Psi | \hat{V}_{ext} | \Psi \rangle$$

(2.22)

$$\int n'(r)v_{ext}(r)dr + F[n'(r)] > \int n(r)v_{ext}(r)dr + F[n(r)]$$

(2.23)

and therefore the variational principle of the second Hohenberg-Kohn theorem is obtained:

$$E_v[n'(r)] > E_v[n(r)]$$

(2.24)

### 2.6.2 The fundamental equation

Minimizing the functional of the energy with respect to $n(r)$, $\delta E_v[n(r)] = 0$, should be performed ensuring conservation of the $N$-representability\textsuperscript{254} during the optimization process. This is done by introducing the restriction:

$$\int n(r)dr - N = 0$$

(2.25)
through the Lagrange's method of undetermined multipliers. In order to do so, an electron density function is constructed so that:

\[
\delta \left[ F[n(r)] + \int n(r)v_{ext}(r)dr - \theta \left( \int n(r)dr - N \right) \right] = 0 \tag{2.26}
\]

\[
\delta \left[ E_v[n(r)] - \theta \left( \int n(r)dr - N \right) \right] = 0 \tag{2.27}
\]

here \( \theta \) is a Lagrange multiplier. By using the definition of the derivative of a functional it is obtained:

\[
\int \frac{\delta E_v[n(r)]}{\delta n(r)} \delta n(r)dr - \theta \int \delta n(r)dr = 0 \tag{2.28}
\]

\[
\int \left\{ \frac{\delta E_v[n(r)]}{\delta n(r)} - \theta \right\} \delta n(r)dr = 0 \tag{2.29}
\]

thus providing the condition of a restricted minimization and giving the value of \( \theta \) at the minimum. Then, the fundamental equation of DFT is expressed as:

\[
\frac{\delta E_v[n(r)]}{\delta n(r)} = \frac{\delta F[n(r)]}{\delta n(r)} + v_{ext}(r) = \theta \tag{2.30}
\]

### 2.6.3 The Kohn-Sham equations

The fundamental equation in DFT provides a formula for minimizing energy and thereby determines \( n(r) \) of the ground state. A problem arises when the expression that relates the electronic Hamiltonian with \( n(r) \) is not exactly known; particularly the exact functional form of the kinetic energy. In contrast, the kinetic energy is easily calculated if the wavefunction is known. To solve this predicament, Kohn and Sham considered a system of \( N \) non-interacting electrons as a reference system moving under the influence of \( v_{ext}(r) \). In this system, the fundamental equation of DFT, considering the exact kinetic energy of non-interacting electrons \( T^{KS}_e \), is:

\[
\frac{\delta E_v[n(r)]}{\delta n(r)} = \frac{\delta T^{KS}_e[n(r)]}{\delta n(r)} + v_{ext}(r) = \mu \tag{2.31}
\]

given that

\[
E_v[n(r)] = T^{KS}_e[n(r)] + \int n(r)v_{ext}(r)dr \tag{2.32}
\]

On the other hand, in a real system electrons interact each other so that the energy is:

\[
E_v[n(r)] = T_e[n(r)] + \int n(r)v_{ext}(r)dr + V_{ee}[n(r)] \tag{2.33}
\]
Here the integral term corresponds to \( V_{en}[n(r)] \) and it refers to the functional of the classical potential energy between nuclei and electrons, and \( V_{ee}[n(r)] \) is the interaction between electrons. The value of \( T_e \) is not the same as \( T_e^{KS} \).

The greatest contribution of Kohn and Sham was the demonstration for the first time that the electronic Hamiltonian can be separated in terms of kinetic, Coulomb-repulsion and exchange-correlation energies; that is:

\[
E_v[n(r)] = T_e^{KS}[n(r)] + V_{en}[n(r)] + J_{ee}[n(r)] + (T_e[n(r)] - T_e^{KS}[n(r)])
\]

\[+ (V_{ee}[n(r)] - J_{ee}[n(r)]) \]

(2.34)

with the Coulomb term given by:

\[
J_{ee}[n(r)] = \frac{1}{2} \int \frac{n(r)n(r')}{|r - r'|} \, drdr'
\]

(2.35)

In the equation 2.34, \((T_e[n(r)] - T_e^{KS}[n(r)])\) is the difference between the kinetic energy of the real and the reference systems. On the other hand, the exchange-correlation contribution is given by \((V_{ee}[n(r)] - J_{ee}[n(r)])\). These two contributions are usually grouped into a single term as \( E_{xc}[n(r)] \):

\[
E_{xc}[n(r)] = (T_e[n(r)] - T_e^{KS}[n(r)]) + (V_{ee}[n(r)] - J_{ee}[n(r)])
\]

(2.36)

\( E_{xc}[n(r)] \) contains all contributions to the total energy for which there is no simple expression as a function of \( n(r) \). Then, the energy of the system is:

\[
E_v[n(r)] = T_e^{KS}[n(r)] + V_{en}[n(r)] + \frac{1}{2} \int \frac{n(r)n(r')}{|r - r'|} \, drdr' + E_{xc}[n(r)]
\]

(2.37)

which naturally leads to:

\[
\frac{\delta E_v[n(r)]}{\delta n(r)} = \frac{\delta T_e^{KS}[n(r)]}{\delta n(r)} + v_{ext}(r) + \frac{1}{2} \int \frac{n(r')}{|r - r'|} \, dr' + \frac{\delta E_{xc}[n(r)]}{\delta n(r)} = \mu
\]

(2.38)

taking the exchange-correlation potential as:

\[
V_{xc}(r) = \frac{\delta E_{xc}[n(r)]}{\delta n(r)}
\]

(2.39)

and the Coulomb potential as:

\[
V_{Coul}(r) = v_{ext}(r) + \frac{1}{2} \int \frac{n(r')}{|r - r'|} \, dr'
\]

(2.40)

the following expression is obtained:

\[
\frac{\delta T_e^{KS}[n(r)]}{\delta n(r)} + V_{Coul}(r) + V_{xc}(r) = \mu
\]

(2.41)
\[
\frac{\delta T_e^{KS}[n(r)]}{\delta n(r)} + V_{KS}(r) = \mu
\]  
(2.42)

wherein \( V_{KS}(r) \) is called the Kohn-Sham potential. When comparing equation 2.31 with equation 2.42, wherein \( v_{ext}(r) \) is turned into \( V_{KS}(r) \), it is concluded that the equation to solve a system of interacting electrons is the same as the equation to solve a system of non-interacting electrons.

The equations to be solved in order to find the density of the ground state, \( n_0(r) \), shall be simply the Schrödinger's equation for the system of one electron rewritten as (in atomic units):

\[
\left[-\frac{1}{2} \nabla_i^2 + V_{KS}(r)\right] \phi_i = \varepsilon_i \phi_i
\]  
(2.43)

\[
V_{KS}(r) = V_{en}(r) + \frac{1}{2} \int \frac{n(r')}{|r - r'|} dr' + V_{xc}(r)
\]  
(2.44)

Equations (2.43) and (2.44) are very similar to the HF equations. Orbitals \( \phi_i \) are called Kohn-Sham orbitals; from which \( n(r) \) is calculated as follows:

\[
n(r) = 2 \sum_{i=1}^{N/2} |\phi_i(r)|^2
\]  
(2.45)

where the factor 2 is due to the degeneracy of the spin generated by the assumption that the orbitals are doubly occupied. Like in the HF approximation, the procedure to find solutions starts with trials of MOs from which \( n(r) \) is determined. This trial density, in turn, is used to get the value for \( V_{KS}(r) \); then the equations of eigenvalues and eigenfunctions are solved. The process is iteratively repeated until convergence is reached, which indicates that the ground state energy has been determined.\(^{250}\)

### 2.6.4 The local density approximation

In the local density approximation (LDA), \( E_{xc}[n(r)] \) is a functional that exclusively depends on \( n(r) \) and the correlation-exchange term is usually treated separately. The treatment of the exchange term is based on the assumption that the density hardly varies with position; that is, its derivative with respect to position is approximately zero so that the resulting \( n(r) \) resembles a homogenous electron gas within the Thomas-Fermi theory. On the other hand, the correlation term is not exactly known; therefore, numerical estimations are usually necessary.\(^{255}\) One of the methods used to determine correlation effects is the quantum Monte-Carlo method implemented in a homogeneous gas of non-interacting electrons.\(^{256}\)
In general, for a spin-unpolarized system, a LDA for the exchange-correlation energy is written as:

$$E_{xc}^{LDA}[n] = \int n(r)\varepsilon_{xc}(n)dr$$  \hspace{1cm} (2.46)

where $\varepsilon_{xc}$ is the exchange-correlation energy per particle of a homogeneous electron gas of charge density $n$. The exchange-correlation energy is decomposed into exchange and correlation terms linearly,

$$E_{xc} = E_x + E_c$$  \hspace{1cm} (2.47)

and, consequently, separate expressions for $E_x$ and $E_c$ may be sought. Moreover, $\alpha$-spin and $\beta$-spin electron densities can be included within the LDA method in order to apply the unrestricted formalism of the Kohn-Sham equations, thus providing a treatment of open-shell systems. This approximation is known as the local spin density approximation, LSDA:

$$E_{xc}^{LSDA}[n^\alpha, n^\beta] = \int n(r)\varepsilon_{xc}(n^\alpha, n^\beta)dr$$  \hspace{1cm} (2.48)

### 2.6.5 The generalized gradient approximation

In view of the fact that the model of the homogenous electron gas is ineffective to accurately predict properties of chemical bonds, it was developed a method that introduces density gradients in the description of the exchange-correlation effects. In the latter method, the value of $n(r)$ at each point is taken into account as well as the variation of $n(r)$ around each point. This method is called the generalized gradient approximation (GGA). Under this approach the exchange-correlation energy is redefined including local values of the derivatives of $n(r)$:

$$\varepsilon_{xc}^{GGA}[n(r)] = \varepsilon_{xc}^{LDA}[n(r)] + \Delta\varepsilon_{xc} \left[ \frac{|\nabla n(r)|}{n^{4/3}(r)} \right]$$  \hspace{1cm} (2.49)

Subsequently, quantitative improvements of exchange-correlation functionals have been introduced, thus establishing that the exact exchange-correlation energy satisfies the relation:

$$E_{xc}[n(r)] \geq -1.68 \int n(r)r^{4/3}dr$$  \hspace{1cm} (2.50)

Several density functionals have been developed within the GGA such as the Perdew-Wang (PW91)\textsuperscript{259-262} and Becke (B)\textsuperscript{263} functionals for the calculation of the exchange contribution, and the Lee-Yang-Par (LYP)\textsuperscript{264,265} and Perdew (P86)\textsuperscript{266} for the treatment of the correlation term. Several density functionals were used for the different studies presented in the current thesis; for instance, cycloadditions to carbon nanostructures were quantum-chemically explored via BP86.
2.6.6 Hybrid density functionals

Hybrid density functionals result from the combination of several exchange-correlation functionals, experimental parameters and/or the HF energy. These functionals are based on the adiabatic connection method, wherein $\Psi$ and $v_{\text{ext}}(r)$ is a function of a parameter, $\lambda$, defining the interaction of the particles in a given system. The value of $\lambda$ varies from 0 (the non-interacting system) to 1 (the real system). In non-interacting systems there is no exchange-correlation potential. However, $\lambda = 1$ completely recovers the exchange-correlation potential defined in equation 2.39 as follows:

$$V_{xc}[n(r)] = \int_0^1 \langle \Psi(\lambda)|v_{xc}(\lambda)|\Psi(\lambda)\rangle d\lambda = \int_0^1 V_{xc}(\lambda) d\lambda$$

(2.51)

even though the functional dependence related to $\lambda$ is rather unknown. Nevertheless, the introduction of adjustable parameters led to the hybrid functionals family:

$$V_{xc} = V_{xc}^{HF} + z(V_{xc}^{DFT} - V_{xc}^{HF})$$

(2.52)

for which fail are corrected by the adjustment of a set of parameters $z$. For example, the popular B3LYP functional is defined by:

$$E_{xc}^{B3LYP} = (1 - a_0)E_x^{LSDA} + a_0E_x^{exact} + a_xE_x^{B88} + (1 - a_c)E_c^{VWN} + a_cE_c^{LYP}$$

(2.53)

here $E_x^{exact}$ is the functional calculated from a HF-like expression; and $a_0$, $a_x$, and $a_c$ are parameters which are calculated from experimental energies of atomization. Subsequently, other hybrid functionals have been proposed with the aim of reaching improvements in chemical accuracy; although greater accuracy may require the use of higher order density derivatives.

2.6.7 Long-range corrected density functionals

The introduction of the HF exchange in hybrid functionals not only improves outcomes as compared with LSDA and GGA values but also partially corrects wrong asymptotic behavior of the exchange potential of such functionals, which do not follow a $-r^{-1}$ decay for remote regions of the nucleus as it should occur at the exact exchange. The improvement produced via hybrid functionals is not, however, completely satisfactory and, for example, the B3LYP functional has a behavior of $-0.2 r^{-1}$ which explains its failure in cases involving a more dispersed electron density. This deficiency is corrected by the division of the interelectronic repulsion term of the exchange potential into two regions, one short-range (SR) and the other long-range (LR), following the partitioning scheme developed by Ewald:

$$\frac{1}{r_{12}} = \frac{1 - \text{erf}(\mu r_{12})}{r_{12}} + \frac{\text{erf}(\mu r_{12})}{r_{12}}$$

(2.54)
wherein \( \text{erf} \) is the error function (which is a normalized form of a Gaussian function) and \( \mu \) is a parameter controlling such a function. The first term defines the SR decay followed by the LR decay in the second term; those are described by the functionals \( V_{x}^{SR} \) and \( V_{x}^{LR} \), respectively. The first case is a GGA exchange functional modified to account for an interelectronic term and, in the second case, the long-range exchange is simply calculated with the HF exchange potential.

According to equation 2.54, the exchange when \( r_{12} \rightarrow 0 \) does not include any HF exchange while at infinite distances, \( r_{12} \rightarrow \infty \), all the exchange is exact. Successively, Yanai et al. introduced more flexibility in the scheme of division of the interelectronic repulsion term by adding two parameters that allow the HF contribution to be variable at \( r_{12} \rightarrow 0 \) and \( r_{12} \rightarrow \infty \). This extension is called the Coulomb attenuating method (CAM), and it is expressed as follows:

\[
\frac{1}{r_{12}} = \frac{1 - [\alpha + \beta \text{erf}(\mu r_{12})]}{r_{12}} + \frac{\alpha + \beta \text{erf}(\mu r_{12})}{r_{12}} \tag{2.55}
\]

wherein \( \alpha \) and \( \beta \) control the contribution of the exact exchange as a function of \( r_{12} \). Besides, the authors specifically optimized parameters using BLYP for \( V_{x}^{SR} \) based on the B3LYP functional, which was used for gradient corrections. Meanwhile, choosing the values \( \alpha = 0.2 \) and \( \beta = 0.6 \), the exact exchange contribution varies from 0.2 to 0.6 for \( r_{12} \) leading to the CAM-B3LYP functional. In some cases, CAM-B3LYP and B3LYP produce similar results; although improvements with the former can be observed, for instance, in the description of states characterized by strong charge transfer character.\(^{269}\)

### 2.7 Time-dependent density functional theory

According to the first theorem by Hohenberg-Kohn, it is clear that DFT is a ground-state quantum theory. Nonetheless, it is possible to extend the DFT ideas to the study of excited states by the introduction of a time-dependent (TD) potential. In fact, in 1984 Runge and Gross\(^{272}\) formulated a theorem that assumes the extension of the first DFT theorem to time-dependent systems, in which it is demonstrated that there exists a correlation between a wavefunction, a TD external potential, and the corresponding TD electron density. That is, the TD wavefunction is defined by the density \( \Psi_{n}(r,t) \) so that any TD molecular property such as excitation energies is also a functional of the density, like in DFT.\(^{273}\) This theorem is the foundation of all the TD-DFT methodology.\(^{274}\)

The TD density \( \Psi_{n}(r,t) \) is determined by the minimization of the action-integral functional instead of the energy; this integral is:

\[
A[n(r,t)] = \int_{t_0}^{t_1} \left( \Psi_{n}(r,t) \left| i \frac{\partial}{\partial t} - \hat{H}(r,t) \right| \Psi_{n}(r,t) \right) dt \tag{2.56}
\]

which can be divided into a universal functional and a term that depends on the total external potential and includes the interaction with the nuclei of the system and the TD potential:
\[ A(n(r, t)) = B[n(r, t)] - \int_{t_0}^{t_1} dt \int n(r, t)[V_{eN}(r) + V_t(r, t)]dr \]  
\[ (2.57) \]

here \( V_t(r, t) \) is the TD external potential. The universal functional \( B[n(r,t)] \) is given by:

\[ B[n(r, t)] = \int_{t_0}^{t_1} \left\langle \psi n(r, t) \left| i \frac{\partial}{\partial t} - \hat{T}_e(r) - \hat{V}_{ee}(r) \right| \psi n(r, t) \right\rangle dt \]  
\[ (2.58) \]

### 2.7.1 Kohn-Sham time-dependent density functional theory

In the case of TD-DFT, \( n(r, t) \) can be calculated through a TD Kohn-Sham formulation, where it is defined a reference system of non-interacting electrons under a TD external potential that gives rise to \( n(r, t) \); that is \( v^{TD-KS} \). Therefore, the resulting wavefunction is a Slater determinant from which every orbital is calculated by solving the corresponding mono-electron equation:

\[ i \frac{\partial}{\partial t} \psi(r, t) = \left[ -\frac{1}{2} \nabla^2 + V_{eN}(r) + v^{TD-KS}(r, t) \right] \psi(r, t) \]  
\[ (2.59) \]

thus providing the orbitals of the real system:

\[ n(r, t) = 2 \sum_{i=1}^{N/2} |\phi_i(r, t)|^2 \]  
\[ (2.60) \]

Proceeding exactly as in the original Kohn-Sham formulation, the TD universal functional, analogous to \( F[n(r)] \), is given as follows:

\[ B_{KS}[n(r, t)] = \int_{t_0}^{t_1} \left\langle \psi(r, t) \left| i \frac{\partial}{\partial t} - \hat{T}_e(r) \right| \psi(r, t) \right\rangle dt \]  
\[ (2.61) \]

thus defining the action-integral functional:

\[ A[n(r, t)] = B_{KS}[n(r, t)] - f_{ee}^{TD}[n(r, t)] - V_{eN}^{TD}[n(r, t)] - \frac{1}{2} \nabla^2 \]  
\[ -V_t^{TD}[n(r, t)] - V_{xc}[n(r, t)] \]  
\[ (2.62) \]

here \( f_{ee}^{TD}[n(r, t)] \) and \( V_{eN}^{TD}[n(r, t)] \) has a similar form as their time-independent counterpart. \( V_t^{TD}[n(r, t)] \) is calculated in the same way as \( V_{eN}^{TD}[n(r, t)] \) by using the TD potential. The last term accounts for the exchange-correlation contribution and is defined as:

\[ V_{xc}[n(r, t)] = B_{KS}[n(r, t)] - f_{ee}^{TD}[n(r, t)] - B[n(r, t)] \]  
\[ (2.63) \]

The minimization of the wavefunction using the Euler-Lagrange method leads to the calculation of the spatial orbitals of the reference system by specifying the form of the potential \( v^{TD-KS} \). Then:
\[ i \frac{\partial}{\partial t} \psi(r, t) = \left[-\frac{1}{2} \nabla^2 + V_{en}(r) + V_t(r, t) + \int \frac{n(r', t)}{|r - r'|} + \frac{\delta V_{xc}[n(r, t)]}{\delta n(r, t)} \right] \psi(r, t) \]  

(2.64)

defined by the LR function for the density. Taking advantage of the Kohn-Sham formulation, the response of the density can be expressed through the LR function \( \chi_{KS}(r, r', \omega) \) of the reference system; thus using the already well-established methods to determine wavefunctions. The response of the density is calculated as follows:

\[ \delta n(r, t) = \int \chi(r, r', \omega) V_{ext}(r', \omega) dr' \]  

(2.66)

where the time dependence \( t \) has been substituted by the frequency dependence \( \omega \) associated to an external potential, and \( \chi(r, r', \omega) \) is the LR function for the density. Taking advantage of the Kohn-Sham formulation, the response of the density can be expressed through the LR function \( \chi_{KS}(r, r', \omega) \) of the reference system; thus using the already well-established methods to determine wavefunctions. The response of the density is calculated as follows:

\[ \delta n(r, t) = \int \chi_{KS}(r, r', \omega) V_{eff}(r', \omega) dr' \]  

(2.67)

here, an effective potential is considered to contain all the components of potential energy:

\[ \delta V_{eff}(r', \omega) = \delta V_{eff}(r', \omega) + \int \frac{\delta n(r'', \omega)}{|r' - r''|} dr'' + \delta V_{xc}(r', \omega) \]  

(2.68)
and the solution of these equations can be achieved by density matrix formulations as developed within the HF theory\textsuperscript{276,277} which involves an iterative process. The LR function for a non-interacting system is expressed as follows:

\[
\chi_{KS}(\mathbf{r}, \mathbf{r}', \omega) = \sum_a \sum_{n} n_a \phi_a(\mathbf{r}) \phi_i(\mathbf{r}) \phi_i(\mathbf{r'}) \phi_a(\mathbf{r'}) \left( \frac{1}{(\varepsilon_a - \varepsilon_i) + \omega} + \frac{1}{(\varepsilon_a - \varepsilon_i) - \omega} \right) \tag{2.69}
\]

where \( \phi_i \) is the \( i \)-th Kohn-Sham orbital of energy \( \varepsilon_i \). The introduction of virtual orbitals leads to the inclusion of terms related to monoexcitations.\textsuperscript{274}

### 2.7.3 Excitation energies

The perturbation of interest is an oscillating electric field with frequency \( \omega \), \(|\mathbf{E}| = E_0 \cos(\omega t)\), since it reasonably describes the effect of the electromagnetic radiation of such a frequency. The first-order response of the molecular dipole moment to that perturbation is:

\[
\mathbf{\mu} = \mathbf{\mu}_0 + \mathbf{\alpha}(\omega)\mathbf{E} \tag{2.70}
\]

where \( \mathbf{\mu}_0 \) is the permanent molecular dipole moment and \( \mathbf{\alpha}(\omega) \) is the frequency-dependent polarizability, which describes the response of the dipole moment to the electric field. Once obtained, the first-order response \( \delta n(\mathbf{r}, t) \) can be used to calculate the polarizability:

\[
\alpha_{ij}(\omega) = -2 \int r_j \delta n(\mathbf{r}, \omega) d\mathbf{r} \tag{2.71}
\]

or well,

\[
\alpha(\omega) = \sum_m \frac{f_m}{\omega_m^2 - \omega^2} \tag{2.72}
\]

following divergences (poles) for the values of frequencies corresponding to the exact excitation energies \( (\omega_m) \); therefore, the calculation of excitation energies can be done by means of the polarizability. The probability of transition is provided by the oscillator strength, \( f_m \), which is calculated as:

\[
f_m = \frac{2}{3} (\omega_m) \left[ |\langle \Psi_0 | x | \Psi_m \rangle|^2 + |\langle \Psi_0 | y | \Psi_m \rangle|^2 + |\langle \Psi_0 | z | \Psi_m \rangle|^2 \right] \tag{2.73}
\]

where \( x, y, \) and \( z \) are positional operators.\textsuperscript{274,278}
2.8 Molecular dynamics

There are methods that provide a correct description of macroscopic systems, for which it is necessary to use a sufficiently large number of representative configurations of a potential energy surface. The two most common methods are the Monte-Carlo method and molecular dynamics (MD).\textsuperscript{279–281} The Monte-Carlo method has two main advantages: it is computationally efficient, and it gives comparable results to the MD method for the calculation of thermodynamic properties in equilibrium. In fact, the Monte-Carlo method is also suitable to calculate properties of polymers in solution.\textsuperscript{282} However, this method does not provide information of the velocities of the particles; therefore, dynamic properties cannot be obtained from it. In view of that, MD is the most widely used method in the study of a variety of systems.\textsuperscript{283}

2.8.1 Equations of motion

Classical MD is based on the solution of the Newton’s equations of motion for the trajectory of nuclei under an effective potential, \( V_{\text{eff}}(R) \), caused by the electron cloud along with the interaction between nuclei. This potential is not necessarily described within a quantum-mechanical approach; in fact, it is usually calculated using low-cost computational techniques such as molecular mechanics (MM). However, for systems of large size, \( V_{\text{eff}}(R) \) can be calculated by either \textit{ab initio} or semiempirical methods; as a result, two approaches are distinguished: Born-Oppenheimer molecular dynamics (BOMD) and semiempirical Born-Oppenheimer molecular dynamics (SEBOMD). Quantum dynamics simulations are also possible; i.e. the TD Schrödinger equation is solved for the propagation of nuclear coordinates. Nevertheless, this latter is computationally too expensive even in systems of a few atoms. On the other hand, in some systems it is possible to use hybrid quantum-classical dynamics such as Ehrenfest dynamics.\textsuperscript{283,284}

The Newton’s second law of motion for an atom \( A \) is expressed as follows:

\[
m_A \frac{d^2 r_A}{dt^2} = F_A
\]  
(2.74)

being \( m_A \) the mass of the particle and \( F_A \) the force resulting from all the interactions in which the atom \( A \) is involved; it can be also calculated as:

\[
\frac{\partial E_{\text{MM}}}{\partial r_A} = F_A
\]  
(2.75)

wherein \( E_{\text{MM}} \) is the energy calculated by MM:

\[
E_{\text{MM}} = E_{\text{covalent}} + E_{\text{noncovalent}}
\]  
(2.76)

\[
E_{\text{covalent}} = E_{\text{bond}} + E_{\text{angle}} + E_{\text{dihedral}}
\]  
(2.77)

\[
E_{\text{noncovalent}} = E_{\text{electrostatic}} + E_{\text{Van der Waals}}
\]  
(2.78)
2.8.2 Algorithms

Due to the couplings of the movements of all particles in the system, the equation 2.74 cannot be solved analytically. In view of that, numerical methods are used, which consist in the propagation of movements in accordance with this equation. The algorithm used must meet certain requirements; that is, it must be reversible in time and also the energy ought to be conserved. Algorithms are usually based on the so-called finite difference methods, which perform Taylor series expansions of the position as a function of the time as follows:

\[
r_A(t + \Delta t) = r_A(t) + v_A(t)(\Delta t) + \frac{1}{2!} a_A(t)(\Delta t)^2 + \frac{1}{3!} \frac{d^3 r(t)}{dt^3} \bigg|_t (\Delta t)^3 + \cdots \tag{2.79}
\]

The most common methods use developments of up to cubic order like the Verlet algorithm\(^2\) and its derivatives such as the algorithms velocity-Verlet\(^2\) and leap-frog.\(^2\)

They are mathematically equivalent, but they differ in accuracy and computational efficiency.

The leap-frog algorithm provides better accuracy than the original Verlet algorithm and is equivalent to the velocity-Verlet algorithm if a coupling of pressure or temperature is not included. With the leap-frog algorithm, the positions are calculated at each \(t + \Delta t\) and velocities are computed in the middle of these intervals, \(t + 0.5\Delta t\). The kinetic and potential energies are obtained at intervals differing in \(0.5\Delta t\) ensuring small errors and better efficiency as compared to the velocity-Verlet algorithm (although this latter does provide direct positions and velocities at every step). The integration step (\(\Delta t\)) should be at least one order of magnitude less than the period of the most rapid movements occurring in the system, which are often molecular vibrations involving hydrogen atoms (\(t \sim 10\) fs); therefore, \(\Delta t = 1\) fs should be used in this example. In fact, 1-2 fs are usually used.\(^2\)

2.8.3 Thermodynamic properties

The direct integration of the equations of motion generates paths where energy is conserved, thus resulting in a microcanonical ensemble, the \(NVE\) ensemble. Let us recall that an ensemble is a large collective of systems that, while differing in their microscopic description, is constructed to the bulk as a replica of the real thermodynamic system under study. Then, a system is defined by the number of particles \(N\), volume \(V\), and energy \(E\); magnitudes required to specify the thermodynamic state. The system therefore shall consist of a large number of systems, all of them with the same values \(NVE\), and it must be compatible with the thermodynamic system under consideration. By making use of the averages measured in all the systems, a thermodynamic property \(\langle A \rangle\) can be calculated such as the internal energy, entropy, among others. Particularly, the average value of a thermodynamic property is given by:
\[
\langle A \rangle = \int \int A(r, p) \frac{e^{-E(r, p)/k_B T}}{\int e^{-E(r', p')/k_B T} dr' dp'} dr dp = \lim_{t \to \infty} \frac{1}{t} \int_{t_0}^{t_0 + t} A(\tau) d\tau \tag{2.80}
\]

\[
P = \frac{e^{-E(r, p)/k_B T}}{\int e^{-E(r', p')/k_B T} dr' dp'} \tag{2.81}
\]

here \( r \) and \( p \) respectively correspond to the position coordinates and velocities in the phase space; and \( P \) represents the probability of reaching a configuration. The last equality in equation 2.80 implies that all accessible microstates are equally probable over a long period of time; this last statement is known as the Ergodic hypothesis firstly formulated by Boltzmann.\(^{289}\)

Although conceptually the microcanonical ensemble is accessible and simple, it is extremely difficult to experimentally achieve the necessary conditions to obtain the description of a system under this framework since the energy cannot be directly measured; as a result, to keep the energy as a constant turns out to be problematic. In view of that, experimental data are normally obtained by keeping constant the temperature; thus giving rise to the canonical ensemble or the \( NVT \) ensemble. In some cases, pressure is kept constant instead of volume, which results in the isothermal-isobaric ensemble or the \( NPT \) ensemble. Furthermore, during the simulation, it must be incorporated algorithms able to keep constant the temperature of the experiment and, if necessary, the pressure. With those algorithms, it should be possible to generate either a \( NVT \) or a \( NPT \) thermodynamic ensembles.\(^{283,289}\)

### 2.9 Chemical reactivity with computational quantum methods

During a chemical reaction a rearrangement of molecular bonds occurs. The transition state theory encompasses the understanding of the reorganization of bonds leading to the prediction of the rate of chemical reactions. This theory assumes that the Born-Oppenheimer approximation is valid and the separation of nuclear and electronic movements is possible because they occur at very different time scales. In the conventional form, this theory is linked to the concept of transition state (TS) structure of a hypersurface of potential energy.\(^{290}\)

McIver and Komornicki\(^{291}\) define the structure of a TS as the point on a potential energy surface (PES), depicted in Figure 2.4, that meets the following conditions: (i) it is a stationary point; that is, the energy gradient at this point is zero; (ii) the matrix of force constants (the Hessian matrix) at such a point should have a single negative eigenvalue; and (iii) it should be the point of highest potential energy in a continuous line connecting reactants and products. The location of a TS is completely defined in the PES by the first and second derivatives of the energy with respect to coordinates.\(^{235}\)
In the case of a first-order saddle point, in the Hessian matrix one of the eigenvalues is negative and all the others are positive. Frequencies of harmonic molecular vibrations are related to the force constant matrix according to equation 2.82. The force acting on a harmonic spring depends on the mass \( m \) and the force constant \( k \) and it can be written as:

\[
\vec{F} = m\ddot{x} = m \frac{\partial^2 x}{\partial t^2} = -k\dddot{x}
\]  

This differential equation has only one periodic solution \( x(t) \) with frequency \( \omega \):

\[
\omega = \frac{1}{2\pi} \left( \frac{k}{m} \right)^{1/2}
\]  

Frequencies are related to the Hessian matrix because they are calculated with the mass-weighted eigenvalues \( f^{li}_{m\omega} \) to obtain frequency values \( \omega_i \) and wave numbers \( \bar{\omega}_i \):

\[
\omega_i = \sqrt{f^{li}_{m\omega}} \quad ; \quad \bar{\omega}_i = \sqrt{f^{li}_{m\omega}}
\]  

At a minimum, all force constants are strictly positive. In a TS, however, one constant force is negative, producing a complex number. Then the PES is defined in terms of minima such as reactants or reactant complexes, intermediates, products or product complexes, and maxima corresponding to saddle points; being the TS structure a first-order saddle point.\(^{235,292}\)
### 2.9.1 Population analysis

The population analysis can be used to calculate partial charges of atoms by partitioning the electron density or otherwise the wavefunction in localized charges in nuclei, bond orders, among others. By making use of charge distributions, it can be estimated the fraction of charge in an atom as a function of the probability density. Particularly, the Mulliken population analysis\(^{293}\) is based on orbital overlaps. In contrast, in the Hirshfeld and Voronoi deformation density (VDD) charge analysis, basis functions are not explicitly used, but the flow of electron density from or to an atom due to bond deformation is determined by spatial integration of the deformation density over the atomic Voronoi cell.\(^{294}\) Besides, the natural population analysis (NPA) is useful to obtain occupation numbers and charges. Although MOs are not directly used, NPA uses natural orbitals, which are those eigenfunctions of the first-order reduced density matrix. These natural orbitals are localized and orthogonalized.\(^{295-299}\)

Aspects in geometry such as hybridizations, coordinates, and bond orders have implications in the interactions of electrons with electrophilic species. For example, in the framework of molecular orbital theory, the estimation of the number of bonds between pairs of atoms in a molecule is done by the determination of the bond order, which is directly related to the bond length and energy. In general, a higher bond order corresponds to an increased energy and reduced length. It is also possible to observe a direct relationship with hybridization since the electron density is more approached to the nucleus as the s-orbital character in the hybrid orbital increases, therefore the electrons will be more strongly attracted.\(^{239,240}\) Accordingly, the population analysis is a convenient tool in the prediction and description of chemical reactions.

### 2.9.2 Solvent effects

The most direct strategy to include the solvent at the quantum mechanical approach is to explicitly include a reduced set of solvent molecules in the system. This method has two main problems:

(i) The size of the system is always too small to represent a real solvated medium.
(ii) The computational cost can be enormous as the size of the system increases.

Some alternatives have been developed to properly include solvent effects; that is, classical particles can be used so that they can be sampled by MD or Monte-Carlo calculations.\(^{281,283}\) Furthermore, macroscopic representations of solvents (continuum solvation models) can be also used.\(^{300}\) These methods can reduce the degrees of freedom associated with the molecules of a solvent.

A continuum solvation model is, for instance, the conductor-like screening model (COSMO)\(^ {301}\) in which a cavity around the solute molecule is created and it interacts with the solvent represented by a dielectric (see Figure 2.5). The charge distribution of the solute polarizes the dielectric medium. The response of the dielectric medium is given by the
generation of point charges (polarization) on the surface of the cavity. In contrast to other implementations of continuum medium, in this model the generation of these point charges requires the solution of boundary conditions of the dielectric. For the generation of point charges, it is used the simpler boundary condition for the conductor, which depends on the dielectric constant $\varepsilon_s$ of the solvent that is used. Accordingly, the polarizability of the continuum material is governed by $\varepsilon_s$.

![Schematic representation of a dielectric continuum solvation model. Figure adapted from original reference.](image)

In COSMO, if the solvent is an ideal conductor of the electrostatic potential, then it may be imposed the restriction that the electrostatic potential must be zero at the surface. As a result, it is less sensitive to the size and shape chosen for the cavity. If the charge distribution $q$ on the solute molecule is known, it is possible to calculate the charge $q^*$ on the surface. By using real solvents, it can be assumed that the charge $q$ is a function of $q^*$:

$$q = f(\varepsilon_s) \ q^* \quad (2.85)$$

In turn, the factor $f(\varepsilon_s)$ is a function of the dielectric:

$$f(\varepsilon_s) = \frac{\varepsilon_s - 1}{\varepsilon_s - x} \quad (2.86)$$

wherein $x$ can be either 0.0$^{302}$ or 0.5.$^{303}$ COSMO is more accurate for solvents having a high dielectric constant since a solvent with high values of $\varepsilon_s$ behaves as an ideal conductor. However, in the current thesis not only COSMO was used but also the Polarizable Continuum Model$^{300}$ was another method to treat solvent effects.
2.9.3 The activation strain model

The understanding of chemical reactions and their associated barriers can be attained by the analysis of the reactive fragments participating in the formation or rupture of bonds. In the activation strain model (ASM), also known as distortion/interaction model, the activation energy $\Delta E^\ddagger$ of the TS is given by two main contributions: the strain energy $\Delta E_{\text{strain}}^\ddagger$ and the interaction energy $\Delta E_{\text{int}}^\ddagger$:

$$\Delta E^\ddagger = \Delta E_{\text{strain}}^\ddagger + \Delta E_{\text{int}}^\ddagger$$  \hspace{1cm} (2.87)

The energy required to deform reactants from their equilibrium geometry into the geometry they acquire in the activated complex is defined as the activation strain $\Delta E_{\text{strain}}^\ddagger$. If many reactants, $\Delta E_{\text{strain}}^\ddagger$ is given by the contribution of each deformed structure. The transition state interaction, $\Delta E_{\text{int}}^\ddagger$, is the interaction between the deformed reactants in the TS. The ASM is usually extended along the reaction coordinated $\zeta$ as $\Delta E^\ddagger$ by itself is meaningless. However, if the whole intrinsic reaction coordinate cannot be obtained, the application of the ASM analysis can be conveniently done only at local stationary points.

![Diagram illustrating the activation energy, $\Delta E^\ddagger$, and the activation strain model along a reaction coordinate $\zeta$.](image)

**Figure 2.6** Illustration of the activation energy, $\Delta E^\ddagger$ to the left, and the activation strain model along a reaction coordinate $\zeta$, to the right.
The Electron Transfer Problem

One of the most important phenomena in chemistry, physics, and biology is known as the electron transfer problem.\textsuperscript{311–316} That is, a number of processes involving isolated molecules and supermolecules, ions and excess of electrons in solution, surfaces and interfaces, condensed phase, and solar cells are related to non-radiative and radiative electron transfer (ET). In view of that, theoretical models describing ET have been developed; for instance, Franck and Libby established that the Franck-Condon principle is applicable not only to the vertical radiative processes but also to non-radiative horizontal ET.\textsuperscript{317} Later, Marcus\textsuperscript{318–322} and Hush and coworkers\textsuperscript{323} expressed the need of a readjustment to the electron transfer problem by taking into consideration the coordination shells of reactants in self-exchange reactions and the dielectric medium. These authors demonstrated that a decrease in the energy barrier of a ET process is brought about by the interaction of reactants, which gives rise to the splitting at the intersection of potential surfaces.

\textbf{Figure 2.7} Potential energy diagrams of nonadiabatic and adiabatic intersecting curves during electron transfer.
2.10 The Landau-Zener model

The nonadiabatic ET (see Figure 2.7) between the donor and acceptor centers is treated by the Fermi’s golden rule:324,325

\[ k_{et} = \frac{2\pi V_{ij}^2 FC}{\hbar} \]  

(2.88)

where FC is the Franck-Condon factor which is the nuclear contribution to the transition probability. Given the overlap of the vibrational wavefunction in the ground and excited state, that is the overlap integral \( S_{\sigma',\sigma} \), where \( \sigma' \) and \( \sigma \) respectively refer to the quantum numbers of the ground and excited states, the FC factor can be calculated as the square of nuclear overlap terms:

\[ FC = \sum_{\sigma'} \sum_{\sigma} S_{\sigma',\sigma}^2 \]  

(2.89)

On the other hand, \( V_{ij} \) represents the electronic contribution to the transition probability; it is an electronic coupling term (resonance integral) that depends upon the overlap of electronic wavefunctions in the initial and final states of the process. Furthermore, in the crossing area, the rate constant of the transition \( k_{tr} \) can be written in an Arrhenius-like expression which shall depend on the height of the energy barrier (activation energy, \( E_a \)), the frequency to reach the crossing area (\( \omega \)), and the transition coefficient (\( A \)):

\[ k_{tr} = A \omega e^{-E_a/RT} \]  

(2.90)

The probability \( P \) that a transition in the crossing area will occur is determined by the Landau-Zener formula:326,327

\[ P_{\text{nonadiabatic}} = \exp \left[ -\frac{2\pi V_{ij}^2}{\hbar \nu \frac{\partial}{\partial q} (E_i - E_j)} \right] ; \quad P_{\text{adiabatic}} = 1 - P_{\text{nonadiabatic}} \]  

(2.91)

here \( \hbar \) is the reduced Planck constant; \( \nu \) is the Landau-Zener velocity associated to the nuclear motion given in terms of the perturbation variable \( q, dq/dt \); and the force related to the movement of nuclei is given by the variation of the nonadiabatic crossing states \( E_i \) and \( E_j \) with respect to \( q \) at a certain value of the coordinate \( Q_{tr} \). Equation (2.91) establishes that the ET can be governed by the overlap of electronic wavefunctions in the initial and final states so that \( V_{ij} \) determines the probability of transition. This equation highlights the important role of \( V_{ij} \) in the theory; that is to say, if this value is sufficiently high, then the terms are split with a decrease of the activation barrier and the process occurs adiabatically, \( P_{\text{adiabatic}} \rightarrow 1 \), since \( P_{\text{nonadiabatic}} \rightarrow 0 \). In the nonadiabatic case, \( P_{\text{nonadiabatic}} > 0 \), the interaction between the donor and acceptor in the region of the coordinate \( Q_{tr} \) is nearly negligible. Consequently, the terms practically do not split and \( P_{\text{adiabatic}} \rightarrow 0 \).
2.11 The Marcus model

In the Marcus model,\textsuperscript{318,321,322,328} the deformation of the equilibrium geometry of reactants, products, and solvent is described by identical parabolas defined by the driving force of the process; that is, the standard Gibbs energy $\Delta G_0$ (see Figure 2.8). Within the nonadiabatic regime, in the frame of the Eyring theory of the transition state, the electron transfer rate constant $k_{et}$ is expressed as:

$$k_{et} = \frac{2\pi}{h} V_{ij}^2 \frac{1}{\sqrt{4\pi\lambda k_B T}} \exp \left[ -\frac{(\lambda + \Delta G_0)^2}{4\lambda k_B T} \right]$$

(2.92)

where $k_B$ is the Boltzmann constant, $T$ the temperature, and $\lambda$ is the reorganization energy defined as the energy required to conform bonding and solvent conditions from reactants to products. However, the Marcus equation has to meet some conditions:

i) All reactive nuclear modes such as local nuclear modes, solvent inertial polarization modes, and some other types of collective modes are purely classical. The electronic transition in the ET process is via the minimum energy at the crossing of the initial and final state potential surfaces.

ii) The potential surfaces are essentially parabolic surfaces with insignificant splitting at the crossing area.

iii) Vibrational frequencies and normal modes are the same in the initial and final states (quantum nuclear effects are not included, see Figure 2.9).

![Figure 2.8 Marcus parabola: the driving force as a function of the logarithm of the rate constant of electron transfer.](image)

Experimental and theoretical approaches can be used to measure $\Delta G_0$. For instance, given a fast solvation of photoinduced ET processes, $\Delta G_0$ can be approximated as follows:

$$\Delta G_0 = E_{D/D^+} - (E_{A/A^-} + E_{D^+}) - \frac{e^2}{\varepsilon_s} (r_{D^+} + r_{A^-})$$

(2.93)
where $E_{D/D^+}$ and $E_{A/A^-}$ are the standard redox potential of the donor and acceptor, respectively, $E_{D^*}$ is the energy of the donor excited state, $r_{D^+}$ and $r_{A^-}$ are the radii of the donor and acceptor defined in a two-sphere model, and $\varepsilon_s$ is the medium dielectric constant. In the following subsections, the inclusion of nuclear contributions and the assessment of $V_{ij}$ and $\lambda$ is reviewed.

### 2.12 Electronic and nuclear quantum mechanical effects

Levich et al.\textsuperscript{329}, utilizing the Landau-Zener theory for the intersection crossing area suggesting harmonic one-dimensional potential surface, proposed a formula that includes high-frequency modes (see Figure 2.9) in the low-temperature limit thus describing parabolic nonadiabatic ET:

$$k_{et} = \frac{2\pi}{\hbar} V_{ij}^2 \frac{1}{\sqrt{4\pi\lambda_{ext} k_B T}} \sum_j e^{-S_j^2} \prod_j \exp \left[ -\left( j\omega_j + \lambda_{ext} + \Delta G_0 \right)^2 \right]$$

(2.94)

where $j$ is the number of high-frequency modes $\omega_j$, $\lambda_{ext}$ denote the external reorganization energy, and $S$ is the Huang-Rhys factor which is a function of the nuclei coordinates.\textsuperscript{330–334}

![Figure 2.9](image)

**Figure 2.9** Schematic one-dimensional representation of the intersection between reactant and product vibrational levels. In this example, the optimal overlap of the initial vibrational level of the reactant is given at the 9th level of the product. Figure adapted from original references.\textsuperscript{335,336}

In the case of thermal excitations of the local molecular medium, the inclusion of nuclear degrees of freedom resembles the normal region described by the classical Marcus model. On the other hand, significant deviations are expected in the inverted region. The inverted region cannot be experimentally observed if the stabilization of the ET product occurs faster than the equilibration of the solvent polarization. Moreover, when the ET reaction is very fast in the region of maximum rate (i.e. where $-\Delta G_0 = \lambda$), the process can be controlled by diffusion and, therefore, is no longer dependent on $\lambda$, $V_{ij}$, and $\Delta G_0$.\textsuperscript{336}
2.13 The electronic coupling

The estimation of $V_{ij}$ can be done via several theoretical frameworks. In some studies, the implications of using a particular level of theory, basis set, or methods are discussed in detail. In this section the two-state model for the evaluation of $V_{ij}$ is reviewed.

2.13.1 The Hamiltonian in two-state systems

Let us consider a physical system in which the state space is two-dimensional and assume that, if the system is not externally perturbed, then the Hamiltonian is $\hat{H}_0$. The eigenstates of this Hamiltonian are $|\phi_1\rangle$ and $|\phi_2\rangle$, and the corresponding eigenvalues are $E_1$ and $E_2$; therefore:

$$\hat{H}_0|\phi_1\rangle = E_1|\phi_1\rangle \quad \hat{H}_0|\phi_2\rangle = E_2|\phi_2\rangle \quad \langle \phi_i|\phi_j\rangle = \delta_{ij}$$

(2.95)

An external TD perturbation shall disturb the system so that $\hat{H} = \hat{H}_0 + \hat{W}$. In the $\{|\phi_1\rangle, |\phi_2\rangle\}$ basis $\hat{W}$ is represented by the Hermitian matrix:

$$\hat{W} = \begin{pmatrix} W_{11} & W_{12} \\ W_{21} & W_{22} \end{pmatrix}$$

(2.96)

where $W_{11}$ and $W_{22}$ are real and $W_{12} = W_{21}^*$. Besides, in the same $\{|\phi_1\rangle, |\phi_2\rangle\}$ basis $\hat{H}$ is represented by the matrix:

$$\hat{H} = \begin{pmatrix} E_1 + W_{11} & W_{12} \\ W_{21} & E_2 + W_{22} \end{pmatrix}$$

(2.97)

leading to the eigenvalues (denoted as $E_{\pm}$):

$$E_{\pm} = \frac{1}{2} (E_1 + W_{11} + E_2 + W_{22}) \pm \frac{1}{2} \sqrt{(E_1 + W_{11} - E_2 - W_{22})^2 + 4|W_{12}|^2}$$

(2.98)

and the eigenvectors:

$$|\psi_+\rangle = \cos \left( \frac{\theta}{2} \right) \exp \left( -\frac{i\varphi}{2} \right) |\phi_1\rangle + \sin \left( \frac{\theta}{2} \right) \exp \left( \frac{i\varphi}{2} \right) |\phi_2\rangle$$

(2.99)

$$|\psi_-\rangle = -\sin \left( \frac{\theta}{2} \right) \exp \left( -\frac{i\varphi}{2} \right) |\phi_1\rangle + \cos \left( \frac{\theta}{2} \right) \exp \left( \frac{i\varphi}{2} \right) |\phi_2\rangle$$

(2.100)

having $\tan(\theta) = 2|W_{12}|/(E_1 + W_{11} - E_2 - W_{22})$ and $W_{21} = |W_{12}|e^{i\varphi}$. 
### 2.13.2 Two-state electronic couplings

The assessment of $V_{ij}$ is usually performed by means of the two-state model described in the previous subsection; wherein the Hamiltonian can be written in two different representations:

$$
H = \begin{pmatrix} E_i & V_{ij} \\ V_{ji} & E_j \end{pmatrix} \leftrightarrow \begin{pmatrix} E_1 & 0 \\ 0 & E_2 \end{pmatrix}
$$

(2.101)

Here the first matrix represents the charge-localized nonadiabatic states $i$ and $j$, and the matrix to the right accounts for adiabatic eigenstates (recall that the Hamiltonian matrix is diagonal in the adiabatic representation). Following the definitions given in equations 2.97 and 2.98, the eigenstates $E_1$ and $E_2$ are:

$$
E_{1,2} = \frac{1}{2}(E_i + E_j) \pm \frac{1}{2} \sqrt{(E_i - E_j)^2 + 4|V_{ij}|^2}
$$

(2.102)

which explicitly displays the manner in which nonadiabatic quantities are related to adiabatic state information. The transition state in the ET problem must satisfy the resonant situation $E_i = E_j$; then, from equation 2.102, $|E_1 - E_2| = 2V_{ij}$. In view of that, quantum chemistry codes or experimental data can provide the necessary information for the estimation of ET parameters in the nonadiabatic regime; in this case $V_{ij}$. As a matter of fact, in Table 2.1 the adiabatic representations of two-state quantum operators to evaluate $V_{ij}$ in terms of the dipole moment and charge difference are provided. As a final point, the expected performance of a two-state model for the estimation of $V_{ij}$ can be assessed, and even improved, by comparison with a three-state model as shown by Voityuk; then the two-state model becomes less accurate with the increasing energy difference of the corresponding states.\(^\text{344,345}\)

<table>
<thead>
<tr>
<th>Approach</th>
<th>Charge-localized states</th>
<th>Eigenstates</th>
<th>Electronic coupling</th>
</tr>
</thead>
<tbody>
<tr>
<td>Generalized Mulliken-Hush(^\text{337,346})</td>
<td>$\begin{pmatrix} \mu_i \ 0 \end{pmatrix}$ \begin{pmatrix} 0 \ \mu_j \end{pmatrix}$</td>
<td>$\begin{pmatrix} \mu_1 &amp; \mu_{12} \ \mu_{12} &amp; \mu_2 \end{pmatrix}$</td>
<td>$V_{ij} = \frac{\mu_{12}\Delta E_{12}}{\sqrt{(\mu_1 - \mu_2)^2 + 4\mu_{12}^2}}$</td>
</tr>
<tr>
<td>Fragment charge difference(^\text{347})</td>
<td>$\begin{pmatrix} \Delta q_i \ 0 \end{pmatrix}$ \begin{pmatrix} 0 \ \Delta q_j \end{pmatrix}$</td>
<td>$\begin{pmatrix} \Delta q_1 &amp; \Delta q_{12} \ \Delta q_{12} &amp; \Delta q_2 \end{pmatrix}$</td>
<td>$V_{ij} = \frac{\Delta q_{12}\Delta E_{12}}{\sqrt{(\Delta q_1 - \Delta q_2)^2 + 4\Delta q_{12}^2}}$</td>
</tr>
</tbody>
</table>
2.14 The reorganization energy

The total reorganization energy $\lambda$ is usually decomposed into two terms, the internal reorganization energy $\lambda_{\text{int}}$ and the external reorganization energy $\lambda_{\text{ext}}$, so that $\lambda = \lambda_{\text{int}} + \lambda_{\text{ext}}$.

In Figure 2.10, the schematization of the ET parameters involved in the evaluation of $k_{et}$ is depicted in detail.

**Figure 2.10** Energy diagram for electron transfer including electronic coupling, reorganization, and Gibbs energies.

**Internal reorganization energy**, $\lambda_{\text{int}}$. The energy required to rearrange all the nuclei of the system due to a charge transfer (CT) reaction leading from a neutral state to a charge transfer state (CTS, an electric-charged exciton state characterized by the physical separation of charges between two moieties often identified as the donor and acceptor fragments) is computed as follows:

$$\lambda_{\text{int}} = \frac{1}{2}(E'_{n} - E_{n} + E'_{\text{CTS}} - E_{\text{CTS}})$$  \hspace{1cm} (2.103)

where $E_{n(CTS)}$ is the energy of the neutral (CTS) state computed in the equilibrium geometry of the neutral (CTS) state and $E'_{n(CTS)}$ is the energy of the neutral (CTS) state computed in the equilibrium geometry of the CTS (neutral state). Nevertheless, $\lambda_{\text{int}}$ can be also calculated by considering isolated donor and acceptor fragments as a separated contribution to the internal organization of each fragment:

$$\lambda_{\text{int}} = \lambda_{D} + \lambda_{A}$$  \hspace{1cm} (2.104)

$$\lambda_{D(A)} = \frac{1}{2}(E'_{n} - E_{n} + E'_{\text{ion}} - E_{\text{ion}})$$  \hspace{1cm} (2.105)

where $\lambda_{D(A)}$ is the reorganization energy of either the donor or the acceptor. $E_{n(ion)}$ is the energy of the neutral (ionic) state computed in the equilibrium geometry of the neutral (ionic) state; and $E'_{n(ion)}$ is the energy of the neutral (ionic) state computed in the equilibrium geometry of the ionic (neutral) state.


**External reorganization energy**, $\lambda_{\text{ext}}$. Changes in solvent polarization is one of the parameters that introduces more uncertainty to the estimation of $k_{\text{ct}}$. Some authors set the value of $\lambda_{\text{ext}}$ as an adjustable parameter.\textsuperscript{348,349} On the other hand, the direct evaluation of $\lambda_{\text{ext}}$ can be consistently performed via QM/MM\textsuperscript{350} or a polarizable force field.\textsuperscript{351} Furthermore, in some cases, neither implicit nor explicit solvent models are sufficient enough to reproduce experimental observations and, therefore, different results might be expected.\textsuperscript{352} In the current manuscript, three different approaches were used for the estimation of $\lambda_{\text{ext}}$:

(i) Two-sphere Marcus model, $\lambda_{\text{ext}}(M)$$^\text{318,320,321}$

$$\lambda_{\text{ext}}(M) = \frac{1}{4\pi \varepsilon_0} \Delta \varepsilon^2 \left( \frac{1}{2a_1} + \frac{1}{2a_2} - \frac{1}{R} \right) \left( \frac{1}{\varepsilon_{\text{OP}}} - \frac{1}{\varepsilon_s} \right)$$  \hspace{1cm} (2.106)

where $\varepsilon_0$ and $\Delta \varepsilon$ are respectively the vacuum permittivity and the amount of transferred charge; $a_1$, $a_2$, and $R$ are respectively the donor and acceptor sphere radii and the distance between the sphere centers; and $\varepsilon_{\text{OP}}$ and $\varepsilon_s$ are the optical and zero-frequency dielectric constants of the surrounding media.\textsuperscript{245}

(ii) Non-equilibrium versus equilibrium solvation, $\lambda_{\text{ext}}(E_{\text{noneq}}-E_{\text{eq}})$

The difference between non-equilibrium and equilibrium solvation naturally arises from excited state calculations in solution. That is to say, a very fast process occurs when the solvent polarizes its electron distribution (electronic polarization); but the solvent may be reoriented (dipole polarization; e.g. rotation), which is a much slower process. If the solvent does not have enough time to fully respond, like in a vertical electronic excitation, then the situation is described by non-equilibrium solvation ($E_{\text{noneq}}$). In contrast, if the solvent does have enough time to fully respond to the solute in both ways (electronic and dipole polarizations) then the situation is described by equilibrium solvation ($E_{\text{eq}}$). Accordingly, $\lambda_{\text{ext}}$ is simply the energy difference between $E_{\text{noneq}}$ and $E_{\text{eq}}$.\textsuperscript{245}

(iii) Dynamic polarization response, $\lambda_{\text{ext}}(E_{\text{noneq}}(\omega)-E_{\text{eq}})$

In this approach, $E_{\text{eq}}$ is exactly the same as explained in (ii); that is, the time or frequency ($\omega$) to reach $E_{\text{eq}}$ is such that the electronic and dipole polarizations can be completed. In this regard, molecular movements depend upon $\omega$ of the change of direction of the electric field; in fact, as $\omega$ increases the dipole polarization effect tends to vanish and $\varepsilon_s$ shall be only dependent on the electronic polarization, as a result the non-equilibrium effects shall appear subsequently in the different contributions to the polarization (i.e. orientational, atomic, and electronic polarization). In the case of photon absorption or emission involving electronic transitions, the solute electronic polarization changes so quickly that one can assume $\varepsilon_s = \varepsilon_{\text{OP}} = n^2$ (refractive index). Therefore, only solvent electrons are able to rearrange in order to stay in equilibrium with the solute, while solvent molecular motions are frozen during the process. This situation leads to a non-equilibrium solvation, $E_{\text{noneq}}(\omega)$. Then $\lambda_{\text{ext}}$ is simply the energy difference between $E_{\text{noneq}}(\omega)$ and $E_{\text{eq}}$.\textsuperscript{245,300,353}
2.15 Electron transfer in polyaromatic organic compounds via quantum chemistry methods

Quantum chemistry methods used for the description of phenomena related to the ET problem in polyaromatic organic compounds have been applied at different levels of theory and approaches. For instance, Friend et al.\textsuperscript{354} examined the amount of charge delocalization upon IR absorption for a set of donor-acceptor organic semiconductors, including fullerene derivatives, as computed via the Austin model 1\textsuperscript{355} (AM1) method coupled to a single configuration interaction (SCI) scheme. In a second step of their study they determined CTS with the intermediate neglect of differential overlap\textsuperscript{356} (INDO) method coupled to SCI (active space of 100 occupied and 100 unoccupied molecular orbitals) in presence of a static electric field. Furthermore, Brédas et al.\textsuperscript{357} developed a computational method to evaluate $V_{ij}$ between intramolecular excited states and CTS in the phthalocyanine/perylene-tetracarboxylic-diimide donor-acceptor complex. They computed ground and excited states through the Zerner’s INDO\textsuperscript{358} Hamiltonian coupled to a configuration interaction scheme involving single and double electronic excitations (CISD); although they used the same HF orbital basis set to compute the electronic states of both neutral and charged configurations, thus resulting in a reduced computational cost. Moreover, in the phthalocyanine/perylene donor-acceptor complex, Cornil et al.\textsuperscript{359} analyzed the different parameters affecting $k_{et}$ at different levels of theory such as the AM1 method coupled to a full configuration interaction (FCI) scheme within an active space built from a few frontier electronic levels for the calculation of $\Delta G$ of reactions, AM1/CI for $\lambda_{int}$, and INDO/SCI for $V_{ij}$.

There are also investigations in the field of fullerenes based on Kohn-Sham DFT. For instance, Kanai and Grossman carried out DFT calculations with the aim of studying the electronic structure of the poly(3-hexylthiophene) (P3HT)/$C_{60}$ interface; looking mostly at the extension of electronic excited states and the relative orbital energy alignment.\textsuperscript{360} On the other hand, it has been proposed that excitation energies for CTS may be computed through the constrained density functional theory\textsuperscript{361} (C-DFT), wherein charges +1$e^-$ and -1$e^-$ are respectively restricted to the donor and acceptor moieties so that a self-consistent field solution is searched. Within this framework, Difley and Voorhis determined CTS in two organic heterodimers.\textsuperscript{362} Moreover, Troisi et al. studied the electronic structure and the different parameters affecting $k_{et}$ for several structures of the P3HT/phenyl-$C_{61}$-butyric acid methyl ester (PCBM) interface as computed by unrestricted DFT combined with MD simulations.\textsuperscript{363} TD-DFT has been also another useful tool in the research of the ET problem; for example, Nelson et al.\textsuperscript{364} studied the influence of the chemical structure on excitation energies, oscillator strengths, and electronic structure for a series of oligomer-fullerene blends.