

## Chapter 2

# Computational Methods

*We are perhaps not far removed from the time when we shall be able to submit the bulk of chemical phenomena to calculation.*

Joseph Louie Gay-Lussac (1888)

The aim of this chapter is not just to make a general description of the computational methods used in this thesis (as it is usually the case), but also to try to provide an overview of what quantum mechanics is, and how do we use it to study chemical reactions. In particular, the first part of this chapter will be devoted to make a brief introduction on the origin and some basic concepts of quantum mechanics. In general, this is a part that is usually skipped by the Ph.D. candidates probably because they are not experts on it, or just because collecting the main ideas of quantum mechanics in a reasonable space is a harsh work. Honestly, I would probably be in the first group. However, when I started “doing bibliography” for this chapter, I found something that changed my mind. Specifically, it was a sentence from one of most brilliant physicists, Richard Feynman, who said: “*I think I can safely say that nobody understands quantum mechanics*”. Obviously, this sentence comforted me and was what prompted me to write and include this first part of the chapter. In any case, I am aware that there may be people that may know much more about quantum mechanics than I do, and that might not agree with some aspects of this first part of the chapter. To those, I sincerely apologize.

In the second part of this chapter, I will explain how we, computational chemists, apply quantum mechanics to the study of chemical reactions, which are the approximations that we do, and how do we obtain valuable information by means of applying these approximations.

Finally, in the last part of this chapter, I will briefly describe the methods that I have used during this thesis. This last part is probably the part that involves more mathematical equations, but don't worry about it because I will only include the most important ones. Furthermore, my intention in this last part of the chapter is not to do an exhaustive description of the methods, but to provide a comprehensive view of the original concepts, approximations and ideas that are behind them.

## 2.1 Quantum Mechanics Basis

### 2.1.1 Origin and Basic Concepts

As we go deeper into the microscopic world, classical mechanics laws start failing and do not provide the good results that they are used to. This impossibility of reproducing some observations by means of classical mechanics is a consequence of the so-called *quantum realm*, which is a term applied in Physics that refers to the scales where quantum mechanical effects become important.<sup>1</sup> This fact, in particular, was what led to the development of quantum mechanics in the first half of 20th century. However, it is important not to forget that, despite the differences between classical and quantum mechanics, they are not independent. In fact, according to the *correspondence principle* between classical and quantum mechanics, all objects obey the laws of quantum mechanics, and classical mechanics is just an approximation for large systems (or a statistical quantum mechanics of a large collection of particles). Thus, classical and quantum mechanics provide the same answer when the systems under study become large. These conditions under which quantum and classical mechanics agree are commonly known as the *correspondence limit* or *classical limit*.

One of the basic concepts derived from quantum mechanics is the *discretization of magnitudes* (e.g. energy), which states that magnitudes can only have discrete values or *quantized* values. Other derived basic concepts are the *wave-particle duality*, which postulates that all particles exhibit both wave and particle properties, and the *uncertainty principle*. This last principle, formulated by Werner Heisenberg in 1927, [1] states a fundamental limit on the accuracy with which certain pairs of physical properties of a particle, such as position and momentum, can be simultaneously known. In other words, the more precisely one property is measured, the less precisely the other can be determined. Thus, quantum mechanics only provides a range of probabilities of where a particle might be given its momentum and momentum probability. This range of probabilities are described by the *wavefunction* ( $\Psi$ ) and depends on the quantum state at the “instant” of the measurement. Hence, uncertainty is indeed involved in the value. Nevertheless, there are certain states that are associated with a definite value of a particular measured property (i.e. *observable*); these states are the *eigenstates* of the observable. Unfortunately, usually a system is not in an eigenstate of the observable that we are interested in. However, if we measure the observable, the wavefunction will instantaneously be an eigenstate of that observable. This process, known as *wavefunction collapse*, has been a much debated process but due to the lack of space, time, and deeper knowledge, it will not be further discussed in this thesis.

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<sup>1</sup> Interestingly, these scales are typically distances of 100 nm or less, which is (and not coincidentally) the same scale as Nanotechnology.

### 2.1.2 The Schrödinger Equation

With a role similar to *Newton's second law* in classical mechanics, the *Schrödinger equation* in quantum mechanics describes how the wavefunction evolves in time:

$$i\hbar \frac{\partial}{\partial t} \Psi(x, t) = H \Psi(x, t) \quad (2.1)$$

In this last equation,  $H$  is the *Hamiltonian*, an operator that generates the time evolution of quantum states and provides the value for the total energy of the system. By analogy with classical mechanics, this operator is generally expressed as the sum of the operators for the kinetic ( $T$ ) and potential ( $V$ ) energies<sup>2</sup>:

$$H = T + V \quad (2.2)$$

As with all the operators, there are a series of states that are eigenstates of the Hamiltonian, whose eigenvalues correspond to the energies of those states. In fact, if we assume that the Hamiltonian does not contain time,<sup>3</sup> the spatial and time dependences of the wavefunction for these states can be treated separately:

$$\Psi(x, t) = f(t) \Psi(x) \quad (2.3)$$

Then, if the wavefunction  $\Psi(x)$  is an eigenstate of the Hamiltonian, the Eq. (2.1) can be written as:

$$i\hbar \frac{1}{f(t)} \frac{\partial f(t)}{\partial t} = \frac{1}{\Psi(x)} H \Psi(x) = E \quad (2.4)$$

where the constant  $E$  that appears in this equation is the total energy of the system in the quantum state described by the wavefunction.

Now, if we isolate the two function parts of Eq. (2.4) we obtain the following two equations:

$$f(t) = e^{-iEt/\hbar} \quad (2.5)$$

and

$$H \Psi(x) = E \Psi(x) \quad (2.6)$$

This last Eq. (2.6) is usually called *time-independent Schrödinger equation* to distinguish it from Eq. (2.1), commonly named *time-dependent Schrödinger equation*.

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<sup>2</sup> In this general definition of the Hamiltonian, relativistic effects are neglected. These effects are normally negligible for the first three rows in the periodic table (i.e.  $Z < 36$ ), but become important for the fourth and fifth rows, and for transition metals. Other operators such as the ones describing spin-orbit, orbit-orbit, or spin-spin couplings are also neglected because their contributions are, in most cases, rather small.

<sup>3</sup> This implies that the total energy of the system remains constant; thus, the system is conservative.

It is interesting to note that Eq.(2.6) can also be seen as the spatial part of the time-dependent Schrödinger equation (2.1), because the time dependency is always an exponential function of the type represented in the Eq.(2.5).

Hence, the eigenstates of the Hamiltonian are of the type:

$$\Psi(x, t) = e^{-iEt/\hbar} \Psi(x) \quad (2.7)$$

Importantly, these eigenstates have the peculiarity that they produce probability distributions that are independent of time and, accordingly, their properties do not depend on it either. For this reason, they are called *stationary states*. Among these stationary states, the one with the lowest energy value is commonly known as the *ground state* and the other ones as *excited states*.

In general, most of the methods used for the study of chemical reactions focus on the resolution of the time-independent Schrödinger equation (2.6). Thus, from now on, we will refer to this last equation simply as “*Schrödinger equation*”, unless otherwise specified.

## 2.2 Theory Applied to Reactivity

After having summarized the origin and some of the basic concepts of quantum mechanics in the previous section, the next step is to understand how quantum mechanics is applied to the study of chemical reactions.

The application of quantum mechanics to the study of reactivity results in very complex equations, which have led to the appearance of multiple approximations. These approximations allow obtaining approximate values for many properties of molecules. However, their acceptance without having checked their validity can occasionally lead to cases where they are not valid and, consequently, to incorrect results. On the other hand, the no acceptance of approximations, even when they are valid, restricts the study to only very small systems though, in such cases, we have the certainty of obtaining the correct results. Hence, when facing chemical problems, the choice (or not) of these approximations is crucial.

This section, in particular, will be devoted to summarize which are the common approximations that we use when applying quantum mechanics for studying chemical reactions, and how do we obtain valuable information of these reactions by means of these approximations. It should be said, however, that this section does not intend to be exhaustive on the theoretical methods to study reactivity, but just to introduce how do we approach to such analysis.

### 2.2.1 The Born-Oppenheimer Approximation and the Concept of Electronic Structure

The *Born-Oppenheimer* approximation is probably the approximation that has been most successfully applied in Theoretical Chemistry. In general terms, we could say that it allows the decomposition of the Schrödinger equation in two parts: one part that describes the electronic wavefunction for a fixed nuclear geometry, and the other part that describes the nuclear wavefunction, where the energy from the electronic wavefunction plays the role of a potential energy. This is, however, a very generalized description of this approximation, so let us go into a more detailed description of it.

The Born-Oppenheimer approximation is based on the following two assumptions:

- *The wavefunction can be separated by the product of an electronic wavefunction and a nuclear wavefunction:*

$$\Psi_{tot}(R, r) = \Psi_{el}(R, r) \Psi_{nuc}(R) \quad (2.8)$$

( $R$  and  $r$  denote the nuclear and the electronic coordinates, respectively).

- *The electronic wavefunction depends parametrically<sup>4</sup> on the coordinates of the nuclei, but not on their momenta.*

The basis for these two assumptions is the high mass ratio between nuclei and electrons, which reflects in a much faster movement of the electrons compared to the nuclei. In general, we can safely say that this is a very good approximation because for the lightest nuclei, the *proton* or  $^1H$ , that ratio is:  $\frac{m^1H}{m_{e^-}} \approx 1836$ .

The Born-Oppenheimer approximation consists of two steps that we will discuss below. First, let us start by writing the Schrödinger equation for a given molecule:

$$H_{tot} \Psi_{tot}(R, r) = E_{tot} \Psi_{tot}(R, r) \quad (2.9)$$

The total Hamiltonian,  $H_{tot}$ , in Eq.(2.9) is:

$$H_{tot} = T_{tot} + V_{tot} = (T_{el} + T_{nuc}) + (V_{ne} + V_{ee} + V_{nn}) \quad (2.10)$$

where  $T_{el}$  and  $T_{nuc}$  stand for the kinetic energy of electrons and nuclei, respectively,  $V_{ne}$  stands for the coulombic attraction between electrons and nuclei, and  $V_{ee}$  and  $V_{nn}$  stand for the coulombic repulsion between electrons and between nuclei, respectively.

Now, assuming that nuclei move much more slowly than electrons, and that the latter are moving in the potential of fixed nuclei, it results that the term corresponding to the nuclear kinetic energy can be dropped from Eq.(2.10) and that the repulsion between the nuclei can be considered to be constant. At this point, we can define the *electronic Hamiltonian* as:

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<sup>4</sup> By *parametrically* we mean that for different arrangements of the nuclei, the electronic wavefunction is a different function of the electronic coordinates.

$$H_{el} = T_{el} + (V_{ne} + V_{ee} + \underbrace{V_{nn}}_{const}) = T_{el} + V \quad (2.11)$$

Then, if we apply this electronic Hamiltonian to the electronic wavefunction, we obtain the electronic state of the molecule by solving the equation:

$$(T_{el} + V)\Psi_{el}(R, r) = U_n(R)\Psi_{el}(R, r) \quad (2.12)$$

where  $U_n$  is the sum of the electronic energy and the potential energy of the nuclei, for a fixed nuclear coordinates. This dependence of  $U_n$  on the nuclear coordinates means that for each nuclear positions, we will have a different electronic wavefunction and a different electronic energetic spectrum. The resolution of this Eq. (2.12) is the first of the two steps in the Born-Oppenheimer approximation.

Once the electronic Schrödinger equation (2.12) has been solved, the second step is to solve the complete Schrödinger equation. For this step, we just have to apply the complete Hamiltonian (2.10) to the nuclear wavefunction:

$$(T_{nuc} + T_{el} + V)\Psi_{nuc}(R) = E_{tot}\Psi_{nuc}(R) \quad (2.13)$$

Then, as the electrons move much faster than the nuclei, it is a reasonable approximation to replace the electronic Hamiltonian by its average value. This generates a nuclear Hamiltonian for the motion of the nuclei in the average potential of the electrons, which transforms Eq. (2.13) into:

$$(T_{nuc} + U_n(R))\Psi_{nuc}(R) = E_{tot}\Psi_{nuc}(R) \quad (2.14)$$

This potential  $U_n$ , also known as *adiabatic potential*, comes from the resolution of the electronic Schrödinger equation (2.12) and, as above mentioned, corresponds to the sum of the electronic energy and the coulombic repulsion between the nuclei, for a fixed nuclear arrangement. This adiabatic potential calculated for a large number of nuclear geometries is known as *potential energy surface (PES)*.

Overall, in the Born-Oppenheimer approximation, the nuclei move on a potential energy surface obtained by solving the electronic Schrödinger equation. This assumption of the nuclei moving on a potential energy surface was, in particular, what led to the development of methods aimed at solving the electronic Schrödinger equation. These methods are broadly referred to as *electronic structure calculations*, and allow obtaining molecular properties that result very useful in the study of chemical reactions.

### 2.2.2 The Potential Energy Surface (PES)

As previously stated, the potential energy surface (PES) is nothing else than the terms  $U_n$  that one obtain in the Born-Oppenheimer approximation by solving the

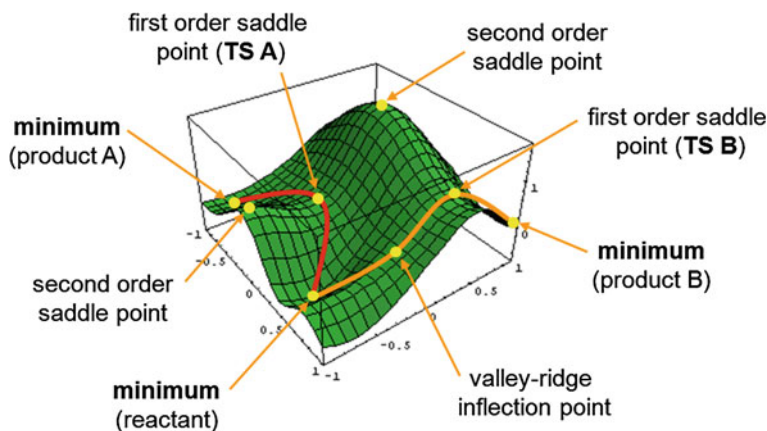


Fig. 2.1 Example of a 3D-representation of an arbitrary *PES*

electronic Schrödinger equation (2.12) for a set of fixed nuclear coordinates. Hence, once the electronic Schrödinger equation has been solved for all the possible nuclear configurations, the complete *PES* is known. Unfortunately, the construction of the complete *PES* for molecules containing more than 3–4 atoms is virtually impossible given that it is a  $3N-6$  dimension space, where  $N$  is the number of atoms.

Hence, a general strategy in computational chemistry consists in restricting the calculations to the chemically interesting part of the *PES*, which usually allows extracting useful information. The most interesting points from the chemical perspective are, in general, the points on the *PES* where the energy is stationary with respect to the nuclear coordinates. Particularly, those that are minima and first-order saddle points (Fig. 2.1).

The energy minima give us an idea of the expected nuclear configuration of a molecular structure, and are potentially observables as stable products or reaction intermediates. On the other hand, the first-order saddle points (or *transition states*, *TSs*) are points on the *PES* that are minima in all directions but one, which are maxima. Furthermore, the energy of these transition states provide an estimation of the reaction rate when going from one minimum to another one. Thus, the reaction minima and the transition states that relate these minima are usually the stationary points on the *PES* that we look for when we are interested in the reaction mechanism and/or the kinetics of a particular reaction. Finding these stationary points, however, is frequently not trivial<sup>5</sup> and requires the choice of an appropriate methodology, which entails a right balance between accuracy and computational cost. This choice of the methodology includes the selection of the level of theory (e.g. Molecular Mechanics, Quantum Mechanics, *QM/MM*), the method (e.g. Force Field, Hartree-Fock, *DFT*, *MP2*), the basis sets (e.g. double- $\zeta$ , pseudo-potentials, polarization functions), the

<sup>5</sup> Some of us even think that the location of transition states can be considered as an “art”.

chemical model (i.e. the simplification, or not, of parts of the system), and the solvent (e.g. continuum model, explicit solvent molecules).

Once the energy minima and the corresponding transition states have been located, then we obtain a potential energy profile from which we can extract the reaction energy ( $\Delta E$ ) and the energy barrier(s) ( $\Delta E^\ddagger$ ). It is important to remark that these potential energies are only valid for one molecule and not for an ensemble of molecules, as it is the case in a real reaction. Thus, if we want to calculate a thermodynamic property and compare its value with the experimental one, we have to use statistical thermodynamics in order to estimate this thermodynamic property for the whole ensemble of molecules. This is a lengthy process and thus, it will not be discussed here. However, if you have further interest in it, there are excellent books on statistical mechanics where you can find a detailed description of it [2–4].

As we will see in the next chapters, one of the most common thermodynamic properties that we compute for its further comparison with the experimental value is the *Gibbs energy* in solution ( $G_s$ ).<sup>6</sup> Generally, this thermodynamic magnitude is estimated by computing the entropic contributions for the solute in gas phase (i.e. in vacuum). This, of course, is a rough approximation, but normally provides good results except for associative and dissociative processes. In these last cases, the results through this approximation are not so good mainly because, in gas phase, the translational and rotational contributions to the entropy are overestimated. This overestimation stems from the fact that, in solution, the molecules are surrounded by the solvent and consequently, they can not freely move and rotate as they do in gas phase. Hence, the computation of dissociative processes in condensed phases, such as the dissociation of one molecule into two fragments, results to be more favorable than what they really are. On the contrary, the computation of associative processes turn out to be less favorable than what they are. On this issue, several approaches have been developed and proposed in the last decades [5, 6]. For example, some authors [7–9] have proposed to only consider the vibrational contribution to the entropy, but if the previous approximation overestimates the entropy, this one underestimates it. Another approximation is the one proposed by Ziegler et al. [10–12] and based on the *Wertz model* [13]. This approximation, however, requires the knowledge of reference quantities, which sometimes might be not available.<sup>7</sup> On the other hand, Martin et al. [14] proposed simulating the condensed phase by computing the Gibbs energies in gas phase at high pressure. More specifically, the authors suggested that the computation of the Gibbs energies at the pressure:  $p = \rho_W RT$ , is a good estimation.<sup>8</sup> This is also a rough approximation because it involves the modification of the standard state

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<sup>6</sup> When we talk about “experimental Gibbs energies”, we should be aware that these are not truly experimental values, since there is no “*Gibbs-meter*” that enables measuring this thermodynamic property. In fact, these experimental Gibbs energies are always based on theoretical models. Thus, even though we use the term “experimental Gibbs energies”, they are as theoretical as the ones that we compute.

<sup>7</sup> This approximation in the case of solvation entropies in water states that they can be approximated in qualitative discussions as 50 % of the gas phase entropy, with the opposite sign.

<sup>8</sup> In this formula,  $\rho_W$  is the experimental density of the solvent,  $R$  is the ideal gas constant, and  $T$  is the temperature.



( $T = 298.15\text{ K}$ , and  $p = 1\text{ atm}$ ) but, somehow, it allows simulating the constraints imposed by the solvent over the free movement of the molecules.

Obviously, apart from all these approximations, there are other methods that, in principle, provide better Gibbs energy values (e.g. molecular dynamics simulations, Monte-Carlo-based methods). These methods, however, are too computationally demanding and thus, they are normally restricted to small systems.

### 2.2.3 Approximate Resolution of the Schrödinger Equation

In the case of one-electron systems, like in the  $H_2^+$  molecule, the electronic Schrödinger equation (2.12) can be solved exactly; however, this is not the case when we are in front of many-electron systems. Typically, we say that this impossibility of solving exactly this equation is because the Schrödinger equation is a *many-body interacting* problem. But, what does it exactly mean? Well, this means that, as a consequence of the electron-electron repulsive interactions, we can not solve the problem of  $N$ -interacting electrons as a sum of  $N$  one-electron problems. In order to overcome this issue, several methods have been developed, which, by means of different approximations, deal with this electronic problem. These methods aimed at solving the electronic Schrödinger equation can be classified in two well differentiated classes: the methods that are based on the wavefunction, and the methods that are based on the electron density. Among the first class of methods, probably the most important one is the *Hartree-Fock (HF)* method, since most of the precise methods are based on corrections to this method. As far as the methods based on the electron density is concerned, these methods have received special attention and are being increasingly used due to the good results that they provide at a reasonable computational cost.

In this thesis, all the calculations have been performed using methods based on the electron density. Thus, the following section will be exclusively devoted to describe these methods, and the approximations that there are behind them.

## 2.3 The Density Functional Theory (DFT)

In the methods based on the wavefunction, the resolution of the electronic Schrödinger equation (2.12) implies the computation of the wavefunction for a given nuclear coordinates, which is a function of  $3N$  spatial coordinates plus  $N$  spin variables, where  $N$  is the number of electrons. This, in the systems that we are usually interested in, where there are many atoms and many more electrons, becomes a very complicated problem. But, is there any other formulation that allows simplifying this problem? The answer is *yes*. This alternative formulation is the so-called *Density Functional Theory (DFT)* and is based on the calculation of electronic properties from the electron density, instead of from the wavefunction. This formulation has the main

advantage that the electron density depends only on the three spatial coordinates ( $x$ ,  $y$ ,  $z$ ), which simplifies considerably the problem.

The electron density  $\rho(\vec{r})$  is defined as the multiple integral over the spin variables of all the electrons and over all but one of the spatial coordinates,

$$\rho(\vec{r}_1) = N \int \cdots \int |\Psi(\vec{x}_1, \vec{x}_2, \dots, \vec{x}_N)|^2 ds_1 d\vec{x}_2 \dots d\vec{x}_N \quad (2.15)$$

where

$$d\vec{x}_i = ds_i d\vec{r}_i$$

The electron density represents the probability of finding any of the  $N$  electrons within the volume element  $d\vec{r}_1$  but with arbitrary spin, while the other  $N-1$  electrons have arbitrary positions and spin in the state represented by  $\Psi$ . Thus, strictly speaking  $\rho(\vec{r})$  is a probability density although, in practice, it is commonly known simply as electron density. Furthermore, since the electrons are indistinguishable, the probability of finding any electron at that position is just  $N$  times the probability for one particular electron. Therefore, we can say that  $\rho(\vec{r})$  is a non-negative function of only three spatial coordinates that vanishes at infinity and integrates to the total number of electrons:

$$\rho(\vec{r} \rightarrow \infty) = 0, \quad (2.16)$$

$$\int \rho(\vec{r}_1) d\vec{r}_1 = N \quad (2.17)$$

### 2.3.1 The Hohenberg-Kohn Theorems

The density functional theory as we know it today was born in 1964 with the appearance of the seminal paper of Hohenberg and Kohn [15]. In this paper, the authors stated two theorems that now represent the major theoretical bedrock of *DFT*. Quoting directly from the Hohenberg and Kohn's paper, the first theorem states:

*“The external potential  $V_{ext}(\vec{r})$  is (to within a constant) a unique functional of  $\rho(\vec{r})$ ; since, in turn,  $V_{ext}(\vec{r})$  fixes  $H$  we see that the full many-particle ground state is a unique functional of  $\rho(\vec{r})$ ”.*

The authors demonstrated this first theorem by proving by *reductio ad absurdum* that there can not be two different  $V_{ext}(\vec{r})$ <sup>9</sup> that result in the same ground state electron density; or what is the same, the ground state density uniquely specifies the external potential  $V_{ext}(\vec{r})$ . A direct consequence derived from this first principle is that all the ground state properties of a system are defined by its electron density.

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<sup>9</sup> This external potential is the potential that the nuclei exert over the electrons.

On the other hand, given that the complete ground state energy is a functional<sup>10</sup> of the ground state electron density so must be its individual components. Thus, the expectation value for the energy of the system can be written as<sup>11</sup>:

$$E[\rho] = T[\rho] + V_{ee}[\rho] + V_{ne}[\rho] \quad (2.18)$$

Now, if we separate the terms that are dependent on the external potential and those which are *universal* or independent on it, we arrive at

$$E[\rho] = \underbrace{T[\rho] + V_{ee}[\rho]}_{\text{independent}} + \underbrace{V_{ne}[\rho]}_{\text{dependent}} = F_{HK}[\rho] + \int \rho_r V_{ne} d\vec{r} \quad (2.19)$$

where the independent terms have been collected into a new quantity, the *Hohenberg-Kohn functional*,  $F_{HK}[\rho]$ :

$$F_{HK}[\rho] \equiv T[\rho] + V_{ee}[\rho] \quad (2.20)$$

According to the Eq. (2.19), if we know  $F_{HK}[\rho]$ , then we can solve the Schrödinger equation exactly. Moreover, it is noteworthy to note that since this is a functional that is completely independent of the system, it applies equally well to the hydrogen atom as to huge molecules such as the *DNA*! Unfortunately, things usually are not as easy as they seem, and this case will not be an exception. Here, the main problem is that the exact form of the functional  $F_{HK}[\rho]$  is not known. Hence, the pursuit of the explicit expression for this unknown functional is the major challenge in the *DFT* and, at the same time, represents the weakest point of this theory.

Up to this point, we have seen that the ground state density is, in principle, sufficient to obtain all the properties of interest. However, how can we know that a certain density is indeed the ground state density that we are looking for? Well, here is where the second Hohenberg-Kohn theorem takes part. This second theorem states:

*The functional  $F_{HK}[\rho]$ , which provides the ground state energy of the system, provides the lowest energy if and only if the input density is truly the ground state density.*

This statement is nothing else than applying the variational principle established for wavefunctions, to the present case:

$$E_0 \leq E[\tilde{\rho}] = T[\tilde{\rho}] + V_{ee}[\tilde{\rho}] + V_{ne}[\tilde{\rho}] \quad (2.21)$$

In this last equation, the density  $\tilde{\rho}(\vec{r})$  represents a trial density that defines a trial external potential, a trial Hamiltonian, and a trial wavefunction, and leads to an energy that is higher than or equal to the exact energy of the system. Thus, in order

<sup>10</sup> A functional is a prescription for producing a number from a function, which in turn depends on variables. Thus, the wavefunction and the electron density are functions, whereas the energy that depends on the wavefunction or the electron density, is a functional.

<sup>11</sup> In this expression, the Born-Oppenheimer approximation has been adopted.

to obtain the exact energy of the system we will have to find the electron density that minimizes the energy,

$$\left[ \frac{\partial E[\rho]}{\partial \rho} \right] = 0 \quad (2.22)$$

Overall, the second Hohenberg-Kohn theorem establishes the variational principle in the *DFT*. However, we have to be aware of what it implies and do not overinterpret this result. Many conventional methods based on the wavefunction, such as the *HF* method, are strictly variational and, consequently, the expectation value of the energy is an indicator of the quality of the trial wavefunction. This means that the lower the energy the better approximated the trial wavefunction to the ground state wavefunction. However, this is not the case in the “real” *DFT*.<sup>12</sup> The variational principle stated by the second Hohenberg-Kohn theorem applies only for the exact functional, which is not known. Thus, the energy provided by a trial functional has absolutely no meaning in that respect.

### 2.3.2 The Kohn-Sham Method

As above mentioned, the ignorance of the exact expression of the functional  $F_{HK}[\rho]$  is undoubtedly the major drawback when trying to solve a system of  $N$  electrons by means of the *DFT*. An alternative to overcome this issue is to use an approximate expression for this functional and solve the  $N$ -electron problem approximately. In fact, if the approximate functional  $F_{HK}[\rho]$  is good enough, we should obtain an energy value close to the exact energy of the system. This aim at obtaining an approximate expression for  $F_{HK}[\rho]$  was what led to the formulation of the *Thomas-Fermi (TF)* and *Thomas-Fermi-Dirac (TFD)* methods [16–18]. These two methods are normally viewed as precursors of modern *DFT*, and further represent the basis of the formulation of the widely known *Kohn-Sham (KS)* method [19]. In particular, this last method is considered as the second major paper of the modern *DFT*, and is based on corrections to the *TF* and *TFD* methods. Thus, let us first start by making a brief summary of these two methods before going into the description of the Kohn-Sham method.

In the *TF* and *TFD* methods, the general expression for the energy functional (2.18),

$$E[\rho] = T[\rho] + V_{ee}[\rho] + V_{ne}[\rho]$$

is approximated as follows: the first term  $T[\rho]$ , which corresponds to the kinetic energy of the  $N$ -electron system, is substituted by the functional corresponding to a non-interacting and uniform electron gas,  $T_{TF}[\rho]$ . On the other hand, the term that stands for the electron-electron repulsion,  $V_{ee}[\rho]$ , is replaced by the classic

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<sup>12</sup> When I say “real” *DFT* I am assuming that the exact expression of the functional  $F_{HK}[\rho]$  is not known.

coulombic repulsion between two electrons,  $J[\rho]$ , and the exchange energy,  $K[\rho]$ .<sup>13</sup> Taking into account all these approximations, the equation for the energy functional  $E[\rho]$  in the *TFD* method can be written as:

$$E_{TFD}[\rho] = T_{TF}[\rho] + J[\rho] + K[\rho] + V_{ne}[\rho] \quad (2.23)$$

With the expression for the energy functional already defined, let us see now how do the terms in (2.23) look like. In the *TF* and *TFD* methods, the terms  $V_{ne}[\rho]$  and  $J[\rho]$  are treated in a completely classical way, so they can be easily obtained from their classical expressions,

$$V_{ne}[\rho] = - \sum_a^M \int \frac{Z_a \rho(\vec{r})}{|R_a - \vec{r}|} d\vec{r} \quad (2.24)$$

$$J[\rho] = \frac{1}{2} \iint \frac{\rho(\vec{r}_1) \rho(\vec{r}_2)}{|\vec{r}_1 - \vec{r}_2|} d\vec{r}_1 d\vec{r}_2 \quad (2.25)$$

where the factor of 1/2 in  $J[\rho]$  allows the integration to run over all space for both variables.

As regards to the terms  $T_{TF}[\rho]$  and  $K[\rho]$ , it can be demonstrated that their expressions for a non-interacting uniform gas of electrons are:

$$T_{TF}[\rho] = C_F \int \rho^{5/3}(\vec{r}) d\vec{r} \quad (2.26)$$

$$K[\rho] = -C_x \int \rho^{4/3}(\vec{r}) d\vec{r} \quad (2.27)$$

with

$$C_F = \frac{3}{10} (3\pi^2)^{2/3} = 2.8712 \quad (2.28)$$

$$C_x = \frac{3}{4} \left( \frac{3}{\pi} \right)^{1/3} = 0.7386 \quad (2.29)$$

Hence, introducing the expressions for  $T_{TF}[\rho]$ ,  $J[\rho]$ ,  $K[\rho]$ , and  $V_{ne}[\rho]$  into the equation for the energy functional  $E[\rho]$  (2.23), we obtain that the expression for the energy functional in the *TFD* method is given by:

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<sup>13</sup> This exchange energy term is only added in the *TFD* method.

$$\begin{aligned}
E_{TFD}[\rho] = & \underbrace{C_F \int \rho^{5/3}(\vec{r}) d\vec{r}}_{T_{TF}[\rho]} + \underbrace{\frac{1}{2} \iint \frac{\rho(\vec{r}_1) \rho(\vec{r}_2)}{|\vec{r}_1 - \vec{r}_2|} d\vec{r}_1 d\vec{r}_2}_{J[\rho]} \\
& - \underbrace{C_x \int \rho^{4/3}(\vec{r}) d\vec{r}}_{K[\rho]} - \underbrace{\sum_a^M \int \frac{Z_a \rho(\vec{r})}{|R_a - \vec{r}|} d\vec{r}}_{V_{ne}[\rho]} \quad (2.30)
\end{aligned}$$

This expression (2.30) but without the term  $K[\rho]$  corresponds to the energy functional in the  $TF$  method.

To summarize, with the  $TF$  and  $TFD$  methods all the terms included in the energy functional (2.30) are explicit functionals of the electron density, which simplifies considerably the problem of the  $N$ -electron system. However, these two methods fail miserably in many cases, mainly because the approximation that these models do for the kinetic energy term is rather simple. Here was when, in 1965, Kohn and Sham [19] realized that if we are not able to accurately determine the kinetic energy through an explicit functional of the density, we should concentrate on calculating as much as we can the true kinetic energy exactly. Thus, their basic idea was to obtain from a Slater determinant<sup>14</sup> the exact kinetic energy of a non-interacting reference system with the same density as the real one (i.e. the interacting system),

$$T_S = -\frac{1}{2} \sum_i^N \langle \varphi_i | \nabla^2 | \varphi_i \rangle \quad (2.31)$$

Of course, the kinetic energy of this non-interacting system is not equal to the kinetic energy in the real system, even if both systems share the same density. In order to account for this and the other approximations present in the universal functional  $F_{HK}[\rho]$  (Eq. 2.20), Kohn and Sham collected all the necessary corrections into a new term  $E_{XC}$ , so that the expression for  $F_{HK}[\rho]$  becomes:

$$F[\rho] = T_S[\rho] + J[\rho] + E_{XC}[\rho] \quad (2.32)$$

This term  $E_{XC}[\rho]$  is known as *exchange-correlation energy*, and is defined as:

$$E_{XC}[\rho] \equiv (T[\rho] - T_S[\rho]) + (V_{ee}[\rho] - J[\rho]) \quad (2.33)$$

The two first terms in  $E_{XC}[\rho]$  correct the difference between the true and the approximate kinetic energies, while the last two terms correct the difference between the classical electron-electron interaction  $J[\rho]$  defined in (2.25) and the real one.

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<sup>14</sup> A Slater determinant is an antisymmetrized product of  $N$  one-electron wavefunctions (*spin orbitals*). In this determinant, the columns are the one-electron wave functions while the electron coordinates are along the rows.

Thus, we can say that the exchange-correlation energy  $E_{XC}[\rho]$  is the functional that contains everything that is unknown.

Introducing the expression (2.32) into (2.19), we can write down the expression for the energy functional of the real system as:

$$\begin{aligned}
 E[\rho(\vec{r})] &= T_S[\rho] + J[\rho] + E_{XC}[\rho] + V_{ne}[\rho] \\
 &= -\frac{1}{2} \sum_i^N \langle \varphi_i | \nabla^2 | \varphi_i \rangle + \frac{1}{2} \iint \frac{\rho(\vec{r}_1)\rho(\vec{r}_2)}{|\vec{r}_1 - \vec{r}_2|} d\vec{r}_1 d\vec{r}_2 \\
 &\quad + E_{XC}[\rho] - \sum_a^M \int \frac{Z_a \rho(\vec{r})}{|R_a - \vec{r}|} d\vec{r}
 \end{aligned} \tag{2.34}$$

Now, introducing into this last equation the restriction that the electron density resulting from the summation of the moduli of the squared orbitals  $\varphi_i$  exactly equals the ground state density of our real system of interacting electrons,

$$\rho(\vec{r}) = \sum_i^N \sum_s |\varphi_i(\vec{r}, s)|^2 = \rho_0(\vec{r}) \tag{2.35}$$

and imposing the constraint that the orbitals  $\varphi_i$  have to be orthonormal,

$$\begin{aligned}
 \int \varphi_i(\vec{r})^* \varphi_j(\vec{r}) &= \delta_{ij} \\
 \delta_{ij} &= 1 \quad i = j \\
 \delta_{ij} &= 0 \quad i \neq j
 \end{aligned} \tag{2.36}$$

we finally arrive to the Kohn-Sham equations:

$$\underbrace{\left(-\frac{1}{2}\nabla^2 + v_{eff}\right)}_{h_{KS}} \varphi_i = \varepsilon_i \varphi_i \tag{2.37}$$

where  $h_{KS}$  is the Kohn-Sham monoelectronic hamiltonian and the term  $v_{eff}$  is the *effective potential*, which is defined as:

$$v_{eff}(\vec{r}) = \int \frac{\rho(\vec{r}_2)}{r_{12}} d\vec{r}_2 + V_{XC}(\vec{r}_1) - \sum_a^M \frac{Z_a}{r_{1a}} \tag{2.38}$$

In this last equation, the only term that is unknown is the potential  $V_{XC}$  due to the exchange-correlation energy  $E_{XC}$ . This potential is simply defined as the functional derivative of  $E_{XC}$  with respect to the electron density:

$$V_{XC} \equiv \frac{\partial E_{XC}}{\partial \rho} \quad (2.39)$$

It is very important to realize that if the exact forms of  $E_{XC}$  and  $V_{XC}$  were known, the Kohn-Sham method would provide the exact energy. Unfortunately, this is not the case. Furthermore, since the effective potential depends on the electron density, the Kohn-Sham Eqs. (2.37) have to be solved in an iterative way. For this process, we define a trial electron density from which we can calculate the effective potential through Eq. (2.38). Then, with this effective potential we solve the Kohn-Sham Eqs. (2.37) and obtain the orbitals  $\varphi_i$ , which are introduced into the Eq. (2.35) resulting in a new electron density. This process is iteratively repeated until the difference between this new electron density and the trial density satisfies the desired convergence criterion. Once this is done, the energy can be easily computed from Eq. (2.34) using the converged electron density.

Another important point that should be remarked is that unlike the *HF* method, where the approximation is introduced right from the start,<sup>15</sup> the Kohn-Sham method is in principle exact! The approximation in this last method only comes into play when we choose an explicit form of the unknown exchange-correlation functional  $E_{XC}$  and the corresponding potential  $V_{XC}$ . Therefore, the difference between *DFT* methods stem from the form of these unknown functionals.

### 2.3.3 Exchange-Correlation Functionals

The form of exchange-correlation functionals is often designed to have a certain limiting behavior (e.g. including the uniform electron gas limit), and fitting parameters to known accurate data. A common approach in the design of these functionals consists in splitting them into two parts: the exchange part  $E_X$ , and the correlation part  $E_C$

$$E_{XC}[\rho] = E_X[\rho] + E_C[\rho] \quad (2.40)$$

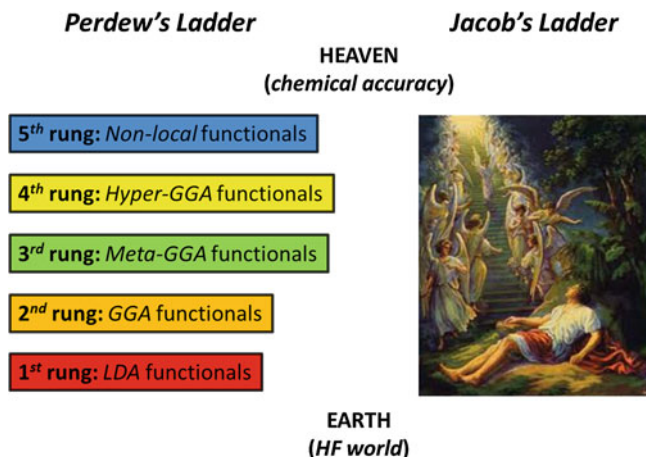
These exchange and correlation parts are normally calculated separately by means of different approximations and then, combined into the exchange-correlation functional. Based on these approximations, John P. Perdew presented by analogy with the biblical referent of *Jacob's ladder* [20], his particular vision of which are the rungs to be climbed in the *DFT* for going from the Earth (i.e. the *HF* world) to Heaven (i.e. the chemical accuracy) (Fig. 2.2).

According to Perdew, the main advantage of the *DFT* is that we can go up or down this ladder of functionals depending on our necessities. In principle, going up this ladder involves an improvement of the results but also, an increase in the computational cost. Thus, when choosing an exchange-correlation functional, we

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<sup>15</sup> In the *HF* method the wavefunction is assumed to be a single Slater determinant, which therefore, can never provide the true solution.





**Fig. 2.2** Graphical representation of the “Perdew’s functionals ladder” (*left*) and the Jacob’s Ladder (*right*)

should arrive to a good compromise between accuracy and computational cost. It is important, however, to keep in mind that despite of this general classification of functionals, the typical one million dollar question “*which is the best functional?*” does not have a unique answer, and needs to be settled for each particular case by comparing the performance of functionals with experiments or high-level wave mechanics calculations.

In the next pages, I will briefly describe the different types of exchange-correlation functionals that appear in the Perdew’s ladder (Fig. 2.2), and which are the approximations that are behind them.

### Local Density and Local Spin Density Approximations (LDA/LSDA)

The *local density approximation (LDA)* constitutes the simplest way of representing the exchange-correlation functional. In particular, this approximation assumes that the density can be locally treated as a uniform electron gas. The general expression for the functional  $E_{XC}$  in the *LDA* is:

$$E_{XC}^{LDA}[\rho] = \int f(\rho)d\vec{r} = E_X^{LDA}[\rho] + E_C^{LDA}[\rho] \quad (2.41)$$

The exchange part in a uniform electron gas is nothing else that the exchange functional that we met in the Thomas-Fermi-Dirac method (2.27). Thus, the exchange energy  $E_X$  in this *LDA* approximation is also given by:

$$E_X^{LDA}[\rho] = -\frac{3}{4} \left( \frac{3}{\pi} \right)^{1/3} \int \rho^{4/3}(\vec{r}) d\vec{r} \quad (2.42)$$

As far as the correlation part  $E_C^{LDA}$  is concerned, no such explicit expression for this term is known. However, there are highly accurate numerical quantum Monte-Carlo simulations of the uniform electron gas [21] from which several authors have derived analytical expressions by means of sophisticated interpolation schemes. One of the most widely used representations for this term is the one developed by Vosko, Wilk, and Nusair (VWN) [22].

In the *LDA*, the total density is considered to be the sum of  $\alpha$  and  $\beta$  spin densities. This assumption is satisfied in closed-shell systems, but not in open-shell systems. If we extend the *LDA* to the latter case, we arrive to the so-called *local spin density approximation (LSDA)*. The exchange energy in this *LSDA* is:

$$E_X^{LSDA}[\rho] = -(2)^{1/3} \frac{3}{4} \left( \frac{3}{\pi} \right)^{1/3} \int [\rho_\alpha^{4/3} + \rho_\beta^{4/3}] d\vec{r} \quad (2.43)$$

Despite the simplicity of these *LDA* or *LSDA* approximations, it has been proven that they can deliver results with a similar accuracy than those obtained with the *HF* method. However, we should not get overexcited about these results because a look at energetical properties, such as bond energies, immediately shows that the performance of these approximations is rather poor. Hence, there is still a long way to go in the development of exchange-correlation functionals before the chemical accuracy can be reached. The next step on this way is the introduction of the gradient of the density, which takes us to the next rung of the Perdew's ladder (Fig. 2.2): the *generalized gradient approximation (GGA)* functionals.

## The Generalized Gradient Approximation (GGA)

Probably the most logical and intuitive way of improving the *LDA*-based functionals is to try to account for the non-homogeneity of the true electron density. A first approximation to this aim is to consider that exchange and correlation energies not only depend on the electron density, but also on its derivatives. This, in particular, represents the basis of the *generalized gradient approximation (GGA)* functionals.<sup>16</sup> The general expression for the exchange-correlation functional in the *GGA* is:

$$E_{XC}^{GGA}[\rho] = \int f(\rho, \nabla \rho) d\vec{r} = E_X^{GGA}[\rho] + E_C^{GGA}[\rho] \quad (2.44)$$

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<sup>16</sup> These functionals are sometimes referred to as non-local functionals in order to distinguish them from the *LDA* ones. However, it is more appropriate to consider them as local functionals because they depend only on the density (and derivatives) at a given point, and not on a space volume as the *HF* exchange energy.

The exchange part in this approximation can be expressed as:

$$E_X^{GGA}[\rho] = E_X^{LDA}[\rho] - \sum_{\sigma} \int F(s_{\sigma}) \rho_{\sigma}^{4/3}(\vec{r}) d\vec{r} \quad (2.45)$$

where  $F$  is a function whose argument is the *reduced density gradient* for spin  $\sigma$ ,<sup>17</sup>

$$s_{\sigma}(\vec{r}) = \frac{|\nabla \rho_{\sigma}(\vec{r})|}{\rho_{\sigma}^{4/3}(\vec{r})} \quad (2.46)$$

In general, most of the *GGA* exchange functionals are developed following two main philosophies. The first one, initiated with the formulation of the *GGA* exchange functional  $B$  (or  $B88$ ) by Becke [23], is based on fitting empirical parameters usually considering experimental data for a set of atoms or model molecules. Some examples of *GGA* exchange functionals that follow this philosophy are the  $PW91$  [24–27], the  $OPTX$  ( $O$ ) [28, 29], and the modified Perdew-Wang ( $mPW$ ) functional [30]. On the other hand, the second philosophy considers that the development of exchange functionals should be based on principles derived from quantum mechanics. Examples of *GGA* exchange functionals following this second philosophy are the  $B86$  functional from Becke [31], the  $P$  functional from Perdew [32], and the  $PBE$  functional from Perdew, Burke, and Ernzerhof [33].

Regarding the *GGA* correlation functionals, these have an even more complicated analytical form than the exchange functionals. Thus, I will merely enumerate some of the most commonly used correlation functionals. For example, it is worth highlighting the correlation counterpart of the exchange functional  $P$  from Perdew ( $P$  or  $P86$ ) [32], the  $LYP$  functional from Lee, Yang and Parr [34], and the parameter-free correlation functional  $PW91$  from Perdew and Wang [24–27]. In principle, all the correlation functionals could be combined with any of the exchange functionals, but in practice, only some combinations are currently in use.

### Meta-GGA Functionals

According to Perdew's ladder (Fig. 2.2), the next rung corresponds to the *meta-GGA* functionals [35]. The difference between this third rung and the previous one (i.e. the *GGA* rung) is that this type of exchange-correlation functionals expands *GGA* to include further the kinetic energy density  $\tau$  (i.e. the Laplacian of the occupied orbitals) and/or the Laplacian of the density  $\nabla^2 \rho(r)$ .

$$\tau(\vec{r}) = \frac{1}{2} \sum_i^{occupied} |\nabla \varphi_i(\vec{r})|^2 \quad (2.47)$$

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<sup>17</sup> The term  $s_{\sigma}$  can be understood as a local inhomogeneity parameter.

Thus, the *meta-GGA* functionals are functionals of the density, the gradient of the density, and the kinetic energy density.

$$E_{XC}^{meta-GGA}[\rho] = \int f(\rho, \nabla\rho, \tau) d\vec{r} \quad (2.48)$$

Some examples of this type of functionals are the exchange-correlation functionals *B98* [36], *TPSS* [37], *VSXC* [38] and the correlation functional *KCIS* [39–42].

### The Adiabatic Connection: Hybrid Functionals

Keeping up with the quest for a most accurate exchange-correlation functional, another appropriate strategy is to use the exact exchange energy calculated with the *HF* method and the Kohn-Sham orbitals, and rely on approximate functionals only for the part that *HF* misses, i.e. the electron correlation (2.49). The exchange-correlation functionals based on this strategy are commonly known as *hybrid functionals*.

$$E_{XC} = E_X^{exact} + E_C^K \quad (2.49)$$

The connection between these two components of the exchange-correlation energy is achieved by means of the so-called *adiabatic connection formula* (ACF),

$$E_{XC}[\rho] = \int_0^1 E_{ncl}^\lambda[\rho] d\lambda \quad (2.50)$$

where  $\lambda$  is the *coupling strength parameter* (with values between 0 and 1), and  $E_{ncl}$  is nothing else than the non-classical contribution to the electron-electron interaction for different values of  $\lambda$ . In particular, at the integration limit  $\lambda = 0$ , we are dealing with a non-interacting system and accordingly,  $E_{ncl}^{\lambda=0}$  is composed of exchange only. Hence, this limiting case (i.e.  $\lambda = 0$ ) simply corresponds to the exact exchange. On the other hand, at  $\lambda = 1$ , the non-classical contributions are those of the fully interacting system, which contains both exchange and correlation terms. This interacting exchange-correlation is not known and therefore, has to be approximated by any  $E_{XC}$  functional.

The simplest approximation to solve the Eq. (2.50) is to assume that  $E_{ncl}^\lambda$  is a linear function in  $\lambda$ , and use the *LDA* exchange-correlation functional for  $E_{ncl}^{\lambda=1}$ . This approximation leads to the so-called *half-and-half* (*HH*) combination proposed by Becke [43], in which a 50 % of exact exchange and a 50 % of *LDA* exchange is included.

$$E_{XC}^{HH} = \frac{1}{2} E_X^{\lambda=0} + \frac{1}{2} E_X^{\lambda=1} \quad (2.51)$$

One of the most widely used variants of this combination is the *BHandHLYP* [23, 34, 43], which has been shown to deliver particularly good results for radical systems [44–47].

$$E_{XC}^{BHandHLYP} = \frac{1}{2}E_X^{exact} + \frac{1}{2}E_X^{LSDA} + \frac{1}{2}\Delta E_X^{B88} + E_C^{LYP} \quad (2.52)$$

During the same year than the proposal of the *HH* combination and following the same scheme, Becke developed one of the most famous hybrid functionals, i.e. the *Becke 3 parameter functional (B3)* [48]. For this functional, the expression for the exchange-correlation is given by:

$$E_{XC}^{B3} = aE_X^{exact} + (1-a)E_X^{LSDA} + b\Delta E_X^{B88} + E_C^{LSDA} + c\Delta E_C^{PW91} \quad (2.53)$$

where  $a$ ,  $b$ , and  $c$  are parameters that weigh the various terms in this *B3* functional. In particular, these three parameters were chosen to optimally reproduce a set of properties such as total energies, atomization and ionization energies, and proton affinities. The resulting values for these parameters are:  $a = 0.20$ ,  $b = 0.72$ , and  $c = 0.81$ . Note that in this functional, the parameter  $a$  determines the amount of exact exchange (i.e. 20 %).

The substitution of the correlation terms in this *B3* functional (2.53) by the correlation functional *LYP* was proposed by Stevens et al. [49], and gave birth to the appearance of the widely known *B3LYP* functional.<sup>18</sup>

$$E_{XC}^{B3LYP} = aE_X^{exact} + (1-a)E_X^{LSDA} + b\Delta E_X^{B88} + cE_C^{LYP} + (1-c)E_C^{VWN} \quad (2.54)$$

Since its appearance in 1994, the *B3LYP* functional has experienced an unprecedented success to the point that, in the last years, it has been by far the most popular and most widely used functional. This hegemony, however, is presently getting lost mainly because *B3LYP* (as most of the functionals) fails in certain aspects, such as the bad description of non-covalent interactions (e.g. van der Waals interactions) and the underestimation of energy barriers [50, 51]. Thus, new functionals and/or correction terms have been developed to overcome these lacks. Among these new functionals one could highlight the appearance of the “*MXX*” series of functionals of Truhlar et al. which have shown to provide satisfactory results. The first of these series of functionals are the *M05* functionals [52–54], which consist of two functionals: the *M05* [52] and the *M05-2X* [53]. In particular, the *M05* functional (with 28 % of exact exchange) is recommended by the authors for reactivity studies involving metals, while the *M05-2X* functional (with 56 % of exact exchange) is recommended for reactivity studies without metals. The second of these series are the *M06* functionals [54–57], which includes four functionals: the *M06* functional [55] (with 27 % of exact exchange), the *M06-2X* functional [55] (with 54 % of exact exchange), the *M06-L* functional [56] (without exact exchange), and the *M06-HF* functional [57] (with 100 % of exact exchange). At present, the last of these series of functionals are the *M08* functionals, which includes the *M08-HX* functional (with 52.23 % of

<sup>18</sup> In this functional, since the *LYP* functional contains a local part besides of the correction to the gradient, the term  $E_C^{VWN}$  is also added in order to subtract this local part. This last term corresponds to the *LSDA*-based correlation functional derived from Vosko, Wilk, and Nusair [22].

exact exchange) and the *M08-SO* functional (with 56.79% of exact exchange) [58], and the *M11* functional [59].

Unlike the *B3LYP* functional, where the non-covalent interactions are not well described, most of Truhlar’s “*MX*” functionals are designed in order to provide a good description of these interactions. This, in particular, is carried out by means of implicit parametrization of these functionals. However, there are other ways of improving the description of non-covalent interactions in *DFT* [60–63]. Among them, probably the most popular and in fashion strategy up to date is the method of dispersion correction (*DFT-D*), commonly known as *Grimme’s dispersion correction* [60]. This correction consists in the addition to the Kohn-Sham energy of a dispersion energy term defined as:

$$E_{disp} = -s_6 \sum_{i=1}^{N_{at}-1} \sum_{j=i+1}^{N_{at}} \frac{C_6^{ij}}{R_{ij}^6} f_{dmp}(R_{ij}) \quad (2.55)$$

where  $N_{at}$  is the number of atoms in the system,  $C_6^{ij}$  denotes the dispersion coefficient for atom pair  $ij$ ,  $s_6$  is a global scaling factor that only depends on the density functional used,  $f_{dmp}$  is a damping function, and  $R_{ij}$  is an interatomic distance. Recently, some additional corrections to this dispersion term have been added resulting in a considerably improvement of the performance of these dispersion corrected density functionals [64–66].

## Hyper-GGA Functionals

Going another rung up in the Jacob’s ladder of functionals (Fig. 2.2) we arrive to the level of the *hyper-GGA* functionals. Some books and articles define the *hyper-GGA* functionals as functionals that include exact exchange. This definition, however, is rather incomplete because it does not specify whether a functional that includes part of exact exchange (e.g. hybrid functionals) can be considered as a *hyper-GGA* functional or not. On the other hand, there are many articles and books that consider that the term *hyper-GGA* applies to functionals that include part of exact exchange. Thus, according to this last definition, hybrid functionals can be considered as *hyper-GGA* functionals. Honestly, I have to recognize that even after having surfed the literature looking for the exact meaning of this *hyper-GGA* term, its exact definition remains still not clear for me. In fact, in my humble opinion, its general definition entails certain ambiguity. In any case, this is just a mere question of nomenclature and has no further relevance, but it is interesting to see how this term can lead to two different concepts.

Importantly, even though the *hyper-GGA* functionals appear as the last rung in the Perdew’s ladder (Fig. 2.2), there is still another rung before reaching the chemical accuracy. This last level corresponds to fully *non-local functionals*, which includes the exact exchange and refines the correlation part by evaluating part of it exactly.

Examples of this last type of functionals are the *generalized random phase approximation (RPA)* [67–72] and the *interaction strength interpolation (ISI)* [73].

### 2.3.4 Self-Interaction Error

Apart from the problem of the ignorance of the exact form of the exchange-correlation functional, there is one more typical problem in the *DFT* methods: the so-called *self-interaction error*. Probably the easiest way of understanding this error is to consider the particular case of a one-electron system and compare the energies obtained with the Kohn-Sham method and the *HF* method, which is free of self-interaction errors. Let us first start by the *HF* method.<sup>19</sup>

In the *HF* method, the electronic energy of the system is given by:

$$E_{HF} = \sum_{i=1}^N \varepsilon_i - \frac{1}{2} \sum_{i=1}^N \sum_{j=1}^N (J_{ij} - K_{ij}) \quad (2.56)$$

where  $\varepsilon_i$  is the energy of the electron  $i$ , and  $J$  and  $K$  are the coulombic and exchange integrals, respectively. In a mono-electronic system, since there is no electron-electron repulsion, the terms  $J$  and  $K$  in (2.56) are equal with opposite sign, which leads to the complete cancellation of the self-interaction of the electron  $i$ .

On the other hand, in the Kohn-Sham scheme (2.34),

$$E[\rho(\vec{r})] = T_S[\rho] + J[\rho] + E_{XC}[\rho] + V_{ne}[\rho]$$

the term  $J[\rho]$

$$J[\rho] = \frac{1}{2} \iint \frac{\rho(\vec{r}_1)\rho(\vec{r}_2)}{|\vec{r}_1 - \vec{r}_2|} d\vec{r}_1 d\vec{r}_2$$

is also different from zero because it contains the spurious interaction of the density with itself, but in this case, does not cancel completely with  $E_{XC}$ . This no complete cancellation stems from the approximate expressions we have to do for the unknown term  $E_{XC}$ . A solution to this problem is the *self-interaction corrected (SIC)* form of approximate functionals suggested by Perdew and Zunger [77].

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<sup>19</sup> For the lack of time and space, the expression for the electronic energy in the *HF* method has not been derived in this thesis. Even so, I will use this expression in order to explain the concept of self-interaction error. Details on the derivation of this equation can be found in many books on general quantum chemistry [74–76].

## 2.4 Computation of Solvent Effects

In general, most of the chemical reactions are carried out in the presence of a solvent, which can, in some cases, be crucial for the final outcome of the reaction (e.g. stabilizing species, acting as a reactant). Thus, when studying chemical reactions, an appropriate description of solvent effects is highly recommended. But, how do we introduce solvent effects into calculations? One alternative for evaluating solvent effects is to consider individual solvent molecules explicitly. This alternative, however, involves dealing with a higher number of molecules, which increases the number of degrees of freedom and therefore, the computational cost. Furthermore, other problems that can arise related to this alternative are, for example, which is the number of molecules that should be included, and where should they be placed.<sup>20</sup> Hence, this alternative is normally used only in specific cases where the solvent actively participates in the reaction, and provided they were not too computationally demanding.

A more affordable alternative is to treat the solvent as a continuous medium with the commonly named *continuum methods*. Among this type of methods, probably the most widely used is the *Self-Consistent Reaction Field (SCRF)* [78], which considers the solvent as a uniform polarizable medium with a dielectric constant  $\epsilon$ , and with the solute placed in a suitable shaped hole in the medium. In this method, the electric charge distribution of the solute polarizes the medium, which in turn acts back on the solute, thereby producing an electrostatic stabilization. This process is iteratively repeated until the mutual polarization between the solute and solvent achieves the self-consistency.<sup>21</sup>

The solvation “free” energy<sup>22</sup> in the *SCRF* method can be calculated as a sum of different energy contributions:

$$\Delta G_{\text{solvation}} = \Delta G_{\text{cav}} + \Delta G_{\text{disp}} + \Delta G_{\text{rep}} + \Delta G_{\text{elec}} \quad (2.57)$$

In this expression, the  $\Delta G_{\text{cav}}$  term corresponds to the energetic cost that is needed to create the cavity for the solute and thus, this term is always positive. On the other hand, the  $\Delta G_{\text{disp}}$  term is associated with the dispersive interactions between solute and solvent, and contributes positively to the solvation. In contrast, the  $\Delta G_{\text{rep}}$  term is associated with the repulsive interactions between solute and solvent, and is always positive. Finally, the term  $\Delta G_{\text{elec}}$  is a stabilizing term that accounts for the electrostatic interactions between the solute and solvent.

Within the *SCRF* method, we can distinguish between different models depending on several features:

<sup>20</sup> To overcome this issue one should use methods such as molecular dynamics or Monte-Carlo-based methods.

<sup>21</sup> This is the reason for the name of this method.

<sup>22</sup> Even though it is generally considered as a Gibbs energy, it is really not, because entropic terms are not included.



- How the size and shape of the cavity is defined.
- How the dispersion contributions are calculated.
- How the charge distribution of the solute is represented.
- How the solute is described (i.e. classically or quantumly).
- How the dielectric constant is described.

In this thesis, the models that have been used for all the calculations are the widely known *polarizable continuum model (PCM)* [79], and the recently developed *SMD* model [80]. These two models define the cavity for the solute as the union of a series of interlocking spheres centered on the atoms and differ only in that the latter includes the radii and non-electrostatic terms as suggested by Truhlar and coworkers. Other variants of the *PCM* model are, for example, the *Isoelectronic-PCM (IPCM)*, which uses a static isodensity surface for the cavity, and its improved version *self-consistent isodensity-PCM (SCI-PCM)* [81].

In all *PCM* methods, the radii of the spheres used to create the cavity can be further defined in different ways, but in the course of this thesis only the two most common radii have been employed: the *UA0* and *UFF*. These two radii use the united atom topological model applied on atomic radii of the *UFF* force field for heavy atoms and only differ in how the spheres for hydrogen atoms are described. More specifically, in the *UA0* radii the hydrogen atoms are enclosed in the sphere of the heavy atom to which they are bonded, while in the *UFF* radii they have individual spheres.

In a compromise between good description of solvent effects and computational cost, combinations of discrete (i.e. with explicit solvent molecules) and continuum methods are a good alternative. An example of combination of these methods is to consider explicitly the first solvation sphere, and treat the rest with a continuous method. This combination is commonly referred to as *discrete-continuum* methods and has been used in some parts of the present thesis.

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