

CHAPTER 2

Theoretical Approach and Computational Details

This chapter is an overview of the first-principles-based theoretical chemistry of current use, without any attempt at rigour in the mathematical description. After a short introduction, section 2.2 describes the elementary topics and mathematical formulation of the well-known Hartree–Fock approximation, the density functional theory and the role of the basis set. Section 2.3 revisits the strong and weak points of both theories in a comparative fashion. In section 2.4 we present the general characteristics of the functionals used in the framework of calculations arising from first-principles theories. It also contains computational details of this particular study. Finally, in section 2.5, the reader shall meet a few important tools for analysis in theoretical chemistry. The features derived from these tools are studied in becoming chapters.

2.1. Introduction to Quantum Chemistry

After the birth of the Quantum Mechanics in the early 1900's, the application of the new quantum concepts to the study of atomic and molecular systems experienced a growing acceptance. Some semi-empirical approximations were developed in a first stage, like the Hückel model for calculating the orbital energies of organic molecules or, at a higher level, the extended-Hückel method, both making use of empirical parameters. First-principles quantum mechanical methods are, on the other hand, aimed at solving the Schrödinger equation with neither an approximation nor additional parameters. That is, to solve equation (1) *ab initio*:

$$H\Psi = E\Psi \quad (1)$$

$$H = -\frac{1}{2}\nabla_i^2 - \sum_{i=1}^N \sum_{A=1}^M \frac{Z_A}{r_{iA}} + \sum_{i=1}^N \sum_{j>1}^N \frac{1}{r_{ij}} \quad (2)$$

where H is the full time-independent electronic Hamiltonian. The first term is the electronic kinetic energy, the second one is the electron-nucleus coulombic attraction, and the third one accounts for the electron-electron repulsion. Even though, theoreticians realised that the exact solution of (1) is only attainable for monoelectronic systems, so only when Ψ describes the motion of one electron (hydrogen-like systems). However, the interest on monoelectronic systems amongst the scientific community is rare, and the efforts to obtain accurate results for polyelectronic systems started soon. Therefore, approximate methods were developed in order to obtain an estimate for the energy of the system and other molecular magnitudes. In a way, especially in a first stage of this new theory, the main problem was the complicated way to find the solution to the equations arising from that theory. The fundamentals for the modern methods of computation were established during the 1930-50's. Since the decade of 1960's, with the introduction of the primitive computing machines, the development of more and more efficient algorithms for solving the equations involved in the motion of electrons allowed to obtain the first relevant results.

Many-body theories are those aimed at describing in a mathematical way the motion (or the behaviour, in general) of more than two interacting particles. Models of increasing complexity have been developed attempting to reproduce as better as possible the features of molecules. In section 2.2

we present a few basic aspects of the mathematical formulation used throughout the text without any attempt at completeness or rigor. For this purpose a vast literature is available.¹⁻³ Only the most outstanding aspects of the theory are discussed, those that are necessary for further understanding of the performance of the model and the accuracy and meaning of the results.

2.2. Fundamentals of Computational Chemistry

2.2.1. The Hartree-Fock approximation

The wavefunction-based *ab initio* methods were the preferred ones to be used for solving the Schrödinger equation until the late 80's. The starting point for all of them is the Hartree-Fock (HF) approximation. Let us consider some of the basic ideas underlying this method. A simple antisymmetric wavefunction, used to describe the ground state of an N -electron system, is constructed with one-electron spin orbitals, χ_i (exact solutions of (1)) to form a single determinant, also called Slater determinant, represented as

$$\Psi_0 = |\chi_1 \chi_2 \dots \chi_N\rangle \quad (3)$$

The variational principle can find the best wavefunction of this form, simply forcing it to give the lowest possible energy

$$E_0 = \langle \Psi_0 | H | \Psi_0 \rangle \quad (4)$$

E_0 is the lowest expected value for the energy of the ground state taking Ψ_0 as the reference function. The flexibility in the wavefunction can be introduced choosing the spin orbitals. Obviously, the better the approximation to Ψ_0 , the lower the energy. So, an improvement of the wavefunction by means of better spin orbitals always leads to an energy closer to the exact result. This is the basis of the variational principle and has a great relevance, especially for more complex wavefunction-based methods. So, if we minimise E_0 with respect to the χ_i 's we obtain the

Hartree–Fock equation, thus determining the optimal spin orbitals. This is again an eigenvalue problem of the form

$$f_i \chi(\mathbf{x}_i) = \varepsilon_i \chi(\mathbf{x}_i) \quad (5)$$

with

$$f(i) = -\frac{1}{2} \nabla_i^2 - \sum_{A=1}^M \frac{Z_A}{r_{iA}} + v^{HF}(i) \quad (6)$$

and

$$v^{HF}(i) = \sum_b J_b(i) - K_b(i)$$

v^{HF} is the two-electron term of the Fock operator, $f(i)$. So, the $v^{HF}(i)$ is the average potential experienced by the i -th electron due to the presence of the other $N-1$ electrons. J_b is a *local* operator accounting for the classical Coulomb repulsion that each electron experiences by the effect of the remaining $N-1$ electrons, and K_b is the attractive exchange term. This one has no simple classical interpretation because is concerned with the spin of particles, and arises due to the antisymmetric nature of the determinantal wavefunction. The exchange operator is *non-local* and is approximated as a mean-field, averaged effect of the mutual interaction of the electrons of the same spin. In terms of the spin orbitals, these contributions are written in the form

$$J_b(1)\chi_a(1) = \left[\int \chi_b^*(2) r_{12}^{-1} \chi_b(2) d\mathbf{x}_2 \right] \chi_a(1), \text{ Coulomb}$$

$$K_b(1)\chi_a(1) = \left[\int \chi_b^*(2) r_{12}^{-1} \chi_a(2) d\mathbf{x}_2 \right] \chi_b(1), \text{ Exchange}$$

It will be shown below the importance of these two expressions in the evolution of computational chemistry.

Introduction of basis sets

In 1951, Roothaan⁴ introduced the use of a set of spatial basis functions to solve the differential equations of the HF approximation. Thus, the differential equations were converted into a set of algebraic equations that could be solved by matrix techniques. A given basis set is formed by an

ensemble of functions that describe the motion of the electrons in space. The choice of the basis set is very important since it governs the correct functioning of the machinery of calculation. Lots of basis sets are available nowadays. They were developed with the aim of improving the behaviour of electrons by stressing some characteristics. It is not the goal of this text to discuss exhaustively those sets. It is worth showing the two types of functions that are of most common use for computation. Their mathematical differences are of much importance in the implementation for computation. The Slater-type orbitals (STO) are defined, in general, as

$$\varphi^{STO} = Nx^l y^m z^n e^{-\zeta r}$$

whereas Gaussian-type orbitals (GTO) are

$$\varphi^{GTO} = Nx^l y^m z^n e^{-\zeta r^2}$$

x , y and z describe the angular part of the orbital, and the ζ factor, which affects the exponential radial function, fixes how much contracted the orbital is.

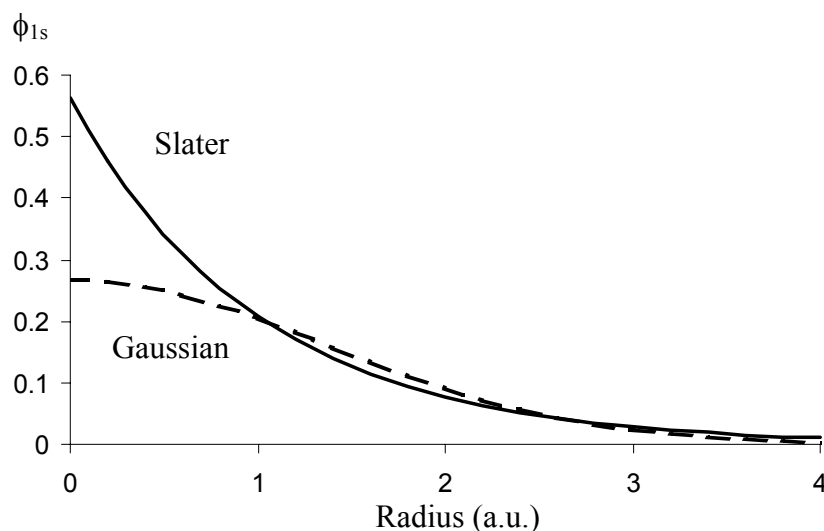


Figure 1.1. Comparison of a Slater function with $\zeta = 1.0$, and a single Gaussian function ($\alpha = 0.27095$) for a 1s orbital.

The only difference between STO's and GTO's is the dependence with r of the exponential term. Even though, this has dramatic implications in the treatment of data. GTO's enable the efficient calculation of molecular multi-center integrals by an analytical procedure. On the other hand, STO's, which are used in a few computational chemistry packages like ADF, MOPAC and others, are more adequate for numerical integration since no efficient analytical algorithms are known yet. Even though, and as a general rule, the accuracy achieved by a single STO is similar to that of about three GTOs. This fact arises from the behaviour of each type of orbital in the $r \rightarrow 0$ region. STOs are advantageous from this point of view since they reproduce very well the necessary conditions of electronic behaviour around a nucleus. They are actually the exact solutions of the Schrödinger equation for the hydrogen atom. Contrarily to wavefunction-based methods, where Gaussian-type functions are commonplace (because of the advantages they offer to the calculation of four-centre-two-electron integrals), there is no need of combinations or contractions of functions to reproduce the cusp behaviour at $r \rightarrow 0$. See Figure 1.1 for comparison of Slater- and Gaussian-type functions.

Another type of functions, not so extended amongst the theoretical community but employed under certain circumstances in DFT calculations, is the so-called plane-waves. They are sometimes used in periodic calculations since they implicitly contain the features of periodic boundary conditions.

Every basis set can be classified in terms of the quality. It depends on the number of functions describing each atomic orbital. The simple rule is "more is better". But, recalling in the mathematical shape of GTO's and STO's, with the angular and the radial parts, we can carefully choose the shape of these orbitals. If we increase the number of functions by varying the exponential factor ζ , we get simple- ζ , double- ζ , ... n ζ basis sets. This factor governs how much *diffuse* is each function. The second characteristic describes the angular part of the function. That is, the complexity of the nodal structure of ϕ_i , and it is sometimes required for introducing some additional electronic correlation. For a better description of the electronic structure, ϕ_i 's with different values of ζ and polarisation functions may be used. Of course, the more extended the basis is, the more time-demanding the calculation becomes, but the better the result is. Even though, with the

fast evolution of hardware and mathematical algorithms implemented, large basis sets are routinely used.

The essence of the HF approximation is, thus, to replace the complicated expression for the many-electron problem by a one-electron, mean-field formulation of the electronic repulsion. Provided that the averaged field for the i -th electron depends itself on all the spin orbitals, the HF equation must be solved iteratively. Such a procedure is the Self-Consistent-Field (SCF) method.⁵ This is a typical eigenvalue problem. The procedure for solving it yields a set of eigenvalues with an associated set of eigenvectors, which is the sequence of molecular orbitals. The HF method determines the best single-determinant wave function. At this level of theory, the improvement of the wavefunction is linked to the quality of the basis set.

It is worth mentioning that the HF method itself does not properly account for the Coulomb hole. It is associated to the repulsion that two electrons experience for being charged particles. This is the main failure of this approximation since the motion of the electrons is then poorly described. In fact, the HF wavefunction only incorporates the exchange hole, which arises from the nature of fermions. It is also known as the Fermi hole. Consequently, it gives too much importance to electron pairing and to ionic structures. On average, two electrons are closer at the HF level than they should be.

One way to improve the pioneering but modestly accurate electronic description introduced with the HF approximation is to enlarge the trial wavefunction or to make it more flexible. This is possible by means of two strategies. One is the perturbation method, and the other is the configuration interaction (CI) method. They constitute the post-HF methods, which were developed with the main goal of introducing electronic correlation. They are, in general, very computationally demanding since the number of variables to handle grows very fast as we enlarge Ψ . Most of the CI techniques developed for introducing the correlation effects to get better energies and wavefunctions use the *brute force*, in the sense that, in general, they use larger (linear combination of N -electron Slater determinants) trial functions. The CI methods make use of a multi-determinantal trial wave function, which can be formulated as

$$|\psi_0\rangle = c_0 |\Phi_0\rangle + \sum_{i=1} c_i |\Phi_i\rangle$$

where Φ_0 is a Slater determinant and the Φ_i terms represent other electronic configurations, with an associated weight, c_i , each. These terms in the above expression are the expansion of the *uncorrelated* function. If no truncation were made, we would obtain the exact solution Ψ_0 within the chosen basis set—the so-called Full Configuration Interaction (FCI) solution. In fact, the application of CI techniques is restricted to small systems due the extraordinary scaling with the molecular size. Furthermore, the convergence of the correlation effects with the size of the trial function is slow. Computational chemists apply some variants of such CI techniques daily, but rarely to medium or large systems.

2.2.2. Density functional theory

Hohenberg-Kohn theorems and Kohn-Sham formulation

Let us now introduce an alternative way for describing the many-electron problem. It is formulated introducing the electron correlation *locally*. This idea constitutes the fundamental idea of Density Functional Theory (DFT). This theory is based on the assumption that the ground state electronic density, ρ_0 , contains all the information of the chemical system. Such a method was built on the basis of the famous first Hohenberg–Kohn theorem,⁶ which states that there is a one-to-one correspondence between an external potential (the nuclear field) $v(\mathbf{r})$, the particle density $\rho(\mathbf{r})$ and the ground state wavefunction, $\Psi(\mathbf{r})$. This is, indeed, a consequence of the variational principle. In addition, the energy of the ground state is a functional of $\rho(\mathbf{r})$,

$$E[\rho] = T[\rho] + V[\rho] + W[\rho]$$

with

$$T = -\frac{1}{2} \nabla^2(i); \quad V = -\sum_{i=1}^N \sum_{A=1}^M \frac{Z_A}{r_{iA}}; \quad W = \sum_{i < j}^N \frac{1}{r_{ij}}$$

where T is the electronic kinetic energy, V is the electron-nucleus Coulomb potential, and W is the electron-electron interaction energy. The latter term can be split into two contributions, the classical electron-electron Coulomb

repulsion and the exchange-correlation term, XC , for which the mathematical nature as a functional of ρ is unknown

$$\begin{aligned} W[\rho] &= W_{Coul}[\rho] + W_{XC}[\rho] \\ W_{XC}[\rho] &= W_X[\rho] + W_C[\rho] \end{aligned}$$

W_{XC} contains all the terms remaining from the electron-electron interactions not included in W_{Coul} . The XC part is artificially decomposed into exchange + correlation, although it has no much physical significance. However the theoretical study of both effects seems to be easier in that way. The second Hohenberg-Kohn theorem⁶ predicts that we can apply the variational principle, at a fixed external potential, v , to the electronic density

$$E_v[\rho] = \langle \Psi[\rho] | T + V + W | \Psi[\rho] \rangle \geq E_0$$

Almost all the modern DF-based applications make use of the DFT formulation of Kohn and Sham⁷ (KS). It was postulated the existence of an auxiliary system of *noninteracting* electrons moving in an external and unique potential $v_s(\mathbf{r})$. This potential has the property of having a wavefunction associated yielding exactly the same density than the interacting system. In addition, that wavefunction is a Slater determinant. The exact energy may be written as

$$\begin{aligned} E &= \int \frac{1}{2} \nabla^2 \psi(1) \psi(1) d1 + \int \rho(\mathbf{r}) v(\mathbf{r}) d\mathbf{r} + \frac{1}{2} \int r_{12}^{-1} \Gamma(1, 2) d1 d2 \\ \Gamma(1, 2) &= \rho(1)\rho(2) + \Gamma_{XC}(1, 2) \end{aligned}$$

$\Gamma(1, 2)$ is the correlated probability of finding two electrons at 1 and 2. It is decomposed into the uncorrelated part, $\rho(1)\rho(2)$, and the remainder that accounts for the exchange and correlation parts of the correlated probability.

From this formulation we obtain the KS orbitals, in which the optimisation of the density is a straightforward procedure since it is derived after solving a set of one-electron equations. The problem at this point is that the exact mathematical form connecting the energy and the total electronic density is yet unknown. Hence, approximations should be introduced in order to have an analytic expression to be evaluated. The

primitive XC part of $E[\rho]$ is the central battlefield for theoreticians that try to improve the performance of the model.

Local Density Approximation

Let us discuss here the central model that gave birth to the DFT. It is the simplistic but surprisingly good uniform electron gas approximation (or homogeneous gas model) proposed in the middle 1920's by Thomas and Fermi.⁸ Such a model can be mathematically formulated as an energy functional that accounts for the local value of ρ at each point in space (regardless of any other one). For the homogeneous gas approximation, the first analytic expression obtained for the electron correlation part was reported in the early 80's by Vosko, Wilk and Nusair (VWN)⁹ which fitted energy values obtained from Monte Carlo simulations by Ceperley and Alder.¹⁰ The exchange part of this functional was approximated, in a simple form, with the $X\alpha$ method of Slater¹¹

$$E_{X\alpha}[\rho] = -\frac{9}{8} \left(\frac{3}{\pi} \right)^{\frac{2}{3}} \alpha \int \rho(\vec{r}_i)^{\frac{4}{3}} d\vec{r}_i$$

where α is a semi-empirical adjustable parameter. The XC part of the energy functional within the Local Density Approximation (LDA) consists in these two parts

$$E_{XC}^{LDA} = E_X^{X\alpha} + E_C^{VWN}$$

We will see below that more complex functionals can be proposed.

Generalised Gradient Approximation

The modestly accurate results of the LDA applied to molecules forced the search of more accurate expressions for describing the motion of electrons. The central idea is to take into account not only the value of the electron density at each point in space but also what is the value of its first derivative. This constitutes the so-called *non-local* or generalised gradient approximations, GGA. The gradient corrections are added to the local definition of X and C , thus redefining the E_{XC} and, in most of the cases,

improving the performance of the model. In general, we have that gradient corrections are functionals of the density and of its first derivative:

$$E_{XC}^{NLDA}[\rho] = \int f(\rho, \nabla \rho) d\vec{r}$$

The density gradient is typically included in the form $\frac{|\nabla \rho|^2}{\rho^{\frac{4}{3}}}$.

The *non-local* term, NLDA, together with the LDA part of XC leads to mathematical expressions for the corrected $E_{XC}^{GGA}[\rho]$ functionals

$$E_C^{GGA}[\rho] = E_C^{LDA}[\rho] + E_C^{NLDA}[\rho] \text{ for correlation}$$

$$E_X^{GGA}[\rho] = E_X^{LDA}[\rho] + E_X^{NLDA}[\rho] \text{ for exchange}$$

All the efforts concerned with the development of DFT are aimed at improving and testing the exchange and correlation corrections for the *NLDA* part. There is an inherent problem beneath the current status of the model. Provided that the exact form of $E[\rho]$ is unknown (it is indeed what we are looking for), we can not say much about the performance of the new functionals until they are tested with chemical systems. So, there is no systematic way to get better functionals and, a priori, a new formulation of the E_{XC} part is not better than a previous one. There are many XC expressions in the literature.¹² The functionals enjoying of a spread acceptance nowadays are the Becke¹³ exchange functional and the Perdew¹⁴ and Perdew–Wang¹⁵ correlation functionals. There is a different class of functionals, the so-called hybrid functionals, like the Lee–Yang–Parr¹⁶ (LYP) for correlation that combined with the Becke's three-parameter method (B3),¹⁷ led to the popular B3LYP exchange-correlation functional. They were introduced with the aim of including the exact exchange energy as a contribution from the correct HF exchange. This latter mathematical approach have proven to be accurate for many systems, although somewhat more time demanding than non-hybrid XC functionals like the BP or the BP86. This is so since the calculation of the two-electron integrals in the HF exchange (the bottleneck of quantum chemistry) is avoided.

2.3. DFT vs. HF Methods

Compared to the HF-based methods, the DFT is conceptually more difficult to be improved. The way to account for the correlation effects in the framework of the DFT does not pass through enlarging the trial wavefunction. It is the unknown Hamiltonian that is improved, indeed. As we pointed out before, no systematic procedure is known to date to improve the performance of the model. Luckily, better functionals do not imply more expensive calculations (with the exception of those that include a part of the HF exchange). Thus, new pure (non-hybrid) functionals can be tested regardless of how much time-consuming they are. After more than fifteen years of work concerning the mathematical expression of $E[\rho]$, some conclusions about the performance and current status of the DFT-based methods arise. Here we divide the discussion in three main points: molecular energies, accuracy of the geometries and electronic properties (molecular orbitals structure).

Total Molecular Energies. Care must be taken when we analyse the molecular energies with different functionals. Provided that the variational principle is not applicable in the framework of the DFT (the exact functional connecting E and ρ is unknown), it is impossible to know *a priori* whether a GGA method will give a lower (better) energy than the LDA. Thus, a simpler functional does not imply a worse energy, there is not such a direct connection in DFT energies. Even though, the use of the same functional for the study of relative values of binding energies is, in the context of the accuracy of the functional, perfectly applicable. In this compilation, it is a constant way to evaluate chemical problems to compare pairs of energies to elucidate relative stabilities.

Molecular Geometries. Not much experience has been achieved yet in the calculation of large transition-metal-based clusters compared to the smaller metal-ligand or organic compounds. For these cases, compared to experimental data, LDA and GGA geometries proved to be in better agreement than HF ones. The latter method, in general, overestimates the Metal–Ligand (M–L) distance, which is an effect of the inherent deficiencies in the treatment of electron correlation. On the other hand, equilibrium geometries computed by the LDA tend to be underestimate bond distances. Nevertheless, LDA deviations have been reported smaller

than HF ones. For large systems like polyoxometalates, with many heavy atoms, the performance of the DFT can be considered excellent. Experimental geometries are very well reproduced with medium-size basis sets and GGA functionals, so at low cost. With the BP86 exchange-correlation functionals, some elongation of the LDA-computed bond distances is achieved, thus reducing the average deviation in M–L distances. The inclusion of some exact exchange (HF exchange) in the energy functional (say, by means of the B3LYP) can improve the equilibrium geometries although at a major computational cost.

Electronic Properties. Most of the present work deals with the analysis of electronic properties in terms of molecular orbital energies. The conventionally accepted idea in which electrons are disposed in a well-defined sequence of energetic levels facilitates the rationalisation of plenty of the features of molecular systems. The original idea (or we might say, perhaps, the main goal) of the DFT gets rid off electrons as the basic unit of the machinery. Instead, it makes use of an electron gas. Even though, the current formalism in use (the Kohn–Sham approach) forced the implementation, in density functional-based methods, of molecular orbitals containing the electrons, the KS orbitals. They are trivially connected to the density via

$$\rho(r) = \sum_i |\varphi_{i,KS}|^2$$

After recent reports in favour of the physical significance of the KS orbitals, their use in the context of the density functional scheme is welcome,¹⁸⁻²² and their application for rationalising chemical phenomena is justified. The molecular orbital theory has been routinely used as a tool for the analysis of the electronic structure.

Chemists are being familiarised with the discussion of properties related with the Highest Occupied Molecular Orbital (HOMO) and the Lowest Unoccupied Molecular Orbital (LUMO) and their spatial shape. The linked value HOMO-LUMO (H-L) gap, the energetic separation between both orbitals, is an indicator of the stability of the cluster. Comparison of H-L gaps in various systems is a good guess for advancing the electronic affinity of each one. Must we warn the reader that, in highly charged clusters like those discussed in chapters 4-8, the energy of the molecular

orbitals can be dramatically shifted to unrealistic levels. The fact that the HOMO (or some occupied orbitals) appears at positive energies is a signal of failure of both the DFT and the HF approximation. This energy upshift is indicative of instability and is reflected in the total binding energy, being less negative than it should be. In chapter 7, a way to arrange this error is used to equalise HOMO energies in several clusters, thus giving somewhat comparable orbital energy values and electron transfer energies.

To resume this section, we schematise several considerations concerning the general features, failures and advantages of the HF and the DFT methods.²³

DFT weak points:

- ▶ The DFT energy is not variational with v_{XC} . The HF method was formulated within the framework of an exact Hamiltonian, so the variational principle is applicable. The only way to improve the performance of the DFT is formulating better XC potentials. However, there is no systematic procedure to do that. In wavefunction-based methods, the trial function is enlarged to improve the results. The better the function, the closer we are to the exact result (more correlation energy is included).
- ▶ The complex electronic configurations (those that are clearly multi-determinantal) are troublesome. The mono-determinantal nature of the DFT formalism can not handle them within the framework of the current KS implementation. Post-HF techniques are the tool to be used in such cases.
- ▶ Highly negatively charged molecules display artificially upshifted occupied molecular orbitals. In general, HOMO-LUMO gaps are smaller at the DFT level than in the HF approximation.

DFT strong points:

- ▶ In principle, the DFT formulation only deals with ρ , which depends on 3 variables irrespective of the size of the system. In wavefunction-based methods, like the HF, Ψ is a function of $3N$ variables.
- ▶ Gradient-corrected density functionals applied to POMs far surpass HF in accuracy. The electronic correlation is introduced at low cost, whereas including correlation to the HF method is highly expensive.

- ▶ DFT is cheaper than HF at similar performance.
- ▶ The shape, symmetry and energetic sequence of the KS orbitals coincide with those obtained at the HF level.
- ▶ In principle, DFT can include *all* the electronic correlation, whereas HF can not.
- ▶ The total electronic density is an observable. The wavefunction Ψ is not.
- ▶ Nowadays, it is the method to be used in large systems, like POMs. DFT geometries are proven to be very good. Even with medium-quality basis sets, the experimental geometries are well reproduced. Only double-bonded metal-oxygen distances in POMs are modestly calculated.

Resuming, before the decade of the 80's, the conventional *ab initio* methods were the only way to include correlation effects in quantum calculations. The Density Functional Theory (DFT) represents an alternative way for introducing the electronic correlation effects for solving the electronic Schrödinger equation. In the last fifteen years, the application of the DFT-based methods was popularised amongst the computational chemists since they permit the calculation of systems of medium and large size with low computational cost. Furthermore, the accuracy reached is generally comparable to the expensive post-Hartree–Fock methods. For the large systems studied here, the DFT is the optimal tool to achieve a good accuracy in the results with modest computational demands.

2.4. Computational Details

The density-functional

In order to achieve a general consistency of the work for further comparison of the results, the same computational accuracy was kept to obtain the results presented here. With this policy we can avoid artificial differences due to mere aspects of the calculation. Where a different computational level or method is applied, the motivation for doing that and a detailed explanation are highlighted.

The DFT calculations presented in this thesis were carried out with the ADF package of programs²⁴ (versions 2.3, 1999 and 2000). The local density approximation (LDA) characterised by the homogeneous electron gas exchange (the $X\alpha$ method¹¹) together with the Vosko–Wilk–Nusair⁹

(VWN) parameterisation for correlation were used. The gradient-corrected Becke¹³ and Perdew¹⁴ functionals (BP86 *XC* functional) for exchange and correlation are included, respectively. All these features are resumed in this chapter above.

One way to simplify the computation when heavy atoms are involved passes through discarding some electrons of each atom from first-principles calculations. They are the lowest-lying, internal and most inert ones, or *core* electrons. They can be considered frozen or, otherwise, they can be treated by means of effective core potentials. The energy and orbital sequence of such electrons can be computed in a previous stage of the procedure. In the process of searching the total electron density of the system (ρ or Ψ), they do not account for bonding more than in the extent in which they affect the energy of the *valence* electrons. (Quasi)relativistic corrections are applied to core electrons since their kinetic energy is much larger than that of the valence shells. They were introduced alongside the Pauli formalism with corrected core potentials. The quasirelativistic frozen core shells were generated with the auxiliary program DIRAC,²⁴ included in the ADF package.

The choice of the basis set and the functional utilised in this work has its fundament in the good balance between accuracy and time. Taking the reference of the previous works published by authors concerned with similar systems,²⁵⁻²⁶ STO basis sets of triple- ζ + polarisation quality were used to describe the valence electrons of all the atoms. The electrons treated as frozen core shells are listed in Table 2.1.

Table 2.1. Complete list of the elements appearing in the calculations of chapters 4–8, together with their respective core electrons, classified as p- or d-elements.

<i>p-series</i>		<i>transition-metals</i>	
element	core electrons	element	core electrons
O	1s	Ti, V	1s–2sp
Al, Si, P	1s–2s	Nb, Mo	1s–3spd
Ga, Ge, As	1s–2sp	W	1s–4spd

All the electrons included in the core are described by means of a single Slater-type orbital each.²⁷⁻²⁸

2.5. Tools for Analysis

It was discussed before the importance of the total electronic density, ρ , in the DFT formulation. In principle, all the molecular properties can be extracted from this unique function. Here we briefly point out some outstanding properties derived from ρ that reveal characteristics of the molecular system.

Atomic charge analysis

Although the atomic charge is not an observable magnitude, its values can indicate a tendency if they are properly taken into account in relative terms. There is no experimental chance to measure the charge of an atom in a molecule. Even though, such an analysis can easily link the quantum chemical calculations with concepts like bonding and valence, but a qualitative level. Amongst many other methods for obtaining the atomic charge, the Mulliken population analysis²⁹ is a standard method to have a guess to this magnitude. The net charge of an atom is calculated as follows:

$$q_A = Z_A - \sum_{\mu(A)} (\mathbf{PS})_{\mu\mu}$$

where Z_A is the nuclear charge, \mathbf{P} is the electron density in matrix form and \mathbf{S} represents the overlap matrix between atomic orbitals. Their elements are constructed by

$$P_{\mu\nu} = \sum_a^N C_{\mu a}^\alpha (C_{\nu a}^\alpha)^*$$

$$S_{\mu\nu} = \int \phi_\mu(1)^* \phi_\nu(1) dr_1$$

respectively. $(\mathbf{PS})_{\mu\mu}$ can be interpreted as the number of electrons associated to the atomic orbital ϕ_μ . This partition of the charge is strongly dependent on the basis set, in addition to other serious deficiencies of the method. So, the meaning of absolute values of atomic charge does not make sense. Only for comparing purposes atomic charges might be computed, and some parts of this work make use of this. In a particular case, another method is applied (see chapter 4) for the calculation of atomic charges. It is the CHelpG

method,³⁰ in which atomic charges are calculated to reproduce the same electrostatic potential generated by the electronic density and nuclear distributions in the molecule.

If an unrestricted calculation have been carried out, the spatial parts for α and β electrons are treated separately. For a further population analysis, both sets combined adequately hold information of *spin polarisation*. Apart of the total electric charge attributed to a single atom in a molecule, we can have a guess of the spin polarisation in case of unpaired electrons by means of the same Mulliken population analysis. This will provide the excess of α vs. β electrons in each atom and, consequently, in different regions of the molecule. The mathematical procedure is equivalent to that of the closed-shell restricted case, although two density matrices shall be constructed, one for each set of electrons.

Decomposition of the energy

In many cases, especially when some units take part in a complex molecule, special phenomena can be studied. This is the case of, say, adsorption, encapsulation or coordination. These three cases show at least two fragments: adsorbate + substrate, host + guest or metal + ligand. For the study of these systems, theoreticians can artificially split the molecule in order to compute the energy of the fragments separately. Afterwards, their mutual interaction is computed. Then, a general expression for the total energy is in terms of the energy of the fragments is

$$E(\text{molecule}) = \sum_{i=1}^N E(i) + FIE$$

where $E(i)$ is the energy of the i -th isolated (and thus distorted) and FIE is the energy of interaction between the fragments. The decomposition of the FIE , which accounts for the stabilisation of the whole system when the fragments are united adopting the geometry of the real cluster, can be carried out by means of several strategies. The Constrained Space Orbital Variation (CSOV) method, developed by Bagus,³¹ performs a decomposition of the fragments interaction in various contributions in terms of a given orbital interaction scheme.³²

Another decomposition method of the *FIE* is that formulated by Morokuma³³ and later adapted by Ziegler *et al.* in their Transition State method.³⁴ According to this formulation

$$FIE = SR + OI$$

Here, *SR* is the steric repulsion, consisting of two components: the classical electrostatic interaction between the *N* unperturbed charge distributions of the interacting fragments, and the so-called exchange or Pauli repulsion. This latter term accounts for the 4-electron destabilising interactions between occupied orbitals in the fragments. The orbital interaction (*OI*) term recover the energy variation due to charge transfer between fragments as well as the mutual electronic density polarisation of each fragment as an effect of the presence of the other. With this scheme one can study how fragments affect each other and what is the nature of this interaction, the magnitude of the charge transfer, etc.

In chapter 1 we introduced the clathrate concept associated to a family of POMs as special feature of this set of molecules. For further analysis of clathrate-like frameworks, the interaction between the fragments (say, the *cage* and the *internal ion*) is highly valuable. We will see in chapter 4 how the application of this scheme of decomposition can contribute to unravel highly interesting problems concerning the relative stability of a set of molecules.

Deformation density maps

Somehow related to the previous point there are the Deformation Density Maps,³⁵ DDM in brief. It is a tool for qualitative analysis. The fundamentals of this method lie in the deformation of two electronic densities upon interaction. The calculation of, say, two isolated fragments leads to ρ_1 and ρ_2 , whereas the whole cluster provides ρ_{super} . Obviously, the sum of the densities of the isolates fragments does not equal ρ_{super} , the density of the supersystem. The difference between them is the deformation density,

$$\Delta\rho = \rho_{\text{super}} - (\rho_1 + \rho_2)$$

The magnitude of change, $\Delta\rho$,³⁶ is induced by the mutual polarisation + charge transfer. With DDM we can detect regions of charge accumulation or

charge depletion after interaction. We shall see in chapter 3 how the analysis of a DDM provides information related to the magnitude of the charge accumulation depending on the variation of one fragment.

Molecular electrostatic potential

For the study of fundamental aspects of the molecular structure and the reactivity, the interpretation of molecular electrostatic potentials (MESP) is of much importance. The electrostatic potential is defined as the energy experienced by a positive unitary charge put in position \mathbf{r} in space under the effect of an electric field. The electrostatic potential (EP) is defined at each point of space with

$$V(\mathbf{r}) = \sum_{A=1}^N \frac{Z_A}{|\mathbf{r} - \mathbf{R}_A|} - \int \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d^3r',$$

where \mathbf{r} is a spatial position. The charge distribution of a molecule is composed of the positively charged nuclei and the negative charge density of electrons. Thus, the first term of the sum corresponds to the nuclear contribution (positive charges, Z_A) and the second one to the effect of the negative electronic distribution that is integrated over all space since $\rho(\mathbf{r}')$ is formally a continuous function. The values of $V(\mathbf{r})$ provide information about the electro- or nucleophilicity of the different regions of a molecule.³⁷ Provided that we can calculate the value of $V(\mathbf{r})$ at any point of space, a good way to represent this function in a friendly way is to plot it over a 3-dimensional isodensity surface of the molecule, thus giving a 4-dimensional coloured plot.

The major utilisation of MESP in the present work is concerned with the study of the basicity in Keggin clusters. This is, in some sense, the analysis of an electrophilic attack of an incoming H^+ to form an O–H bond in a cluster. For this purpose, an atomic charge analysis is sometimes proposed but from the discussion carried out before in this section, the latter tool is not as reliable as the MESP function. The reader shall notice in next chapters that the atomic charges of individual nucleophilic centres have shown no correspondence with their respective basicities. This is so for two reasons: the basicity is a property much more complicated than the simple study of the (artificial) atomic charges and, second, the calculation of atomic charges is inherently erroneous.

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