

Chapter 2

Theoretical Foundation

2.1 Introduction

Ab initio calculation of the electronic structure of molecules and solids have become one of the most important tools in solid state physics. These methods allow us to predict some properties (crystal structure, density, molecular geometry, adsorption and cohesive energies, among others) of condensed matter systems without need of any empirical parameters. By this way we can understand and calculate some properties of the systems that are very difficult or even impossible to measure experimentally. We can also gain insight in the origin of some effects that cannot be explained only with experimental data (such as conductance quantization in nanowires, or the origin of the dipole at metal/organic junctions). However, the price to pay is that a lot of computational effort is needed, compared with empirical or semi-empirical models. In order to reduce the computational time, a lot of approximations have been done in order to get the best accuracy/resources ratio. This chapter will guide through the state-of-the-art ab initio techniques necessary (some of them developed during this work) to successfully simulate the systems that have been studied during this thesis.

2.2 Statement of the Problem

Let us consider a system of n nuclei and N electrons. In order to calculate the properties of this system we should solve the following Schrödinger equation.

$$\left(-\sum_{\alpha} \frac{\hbar^2 \nabla_{\alpha}^2}{2M_{\alpha}} - \sum_i \frac{\hbar^2 \nabla_i^2}{2m} + \frac{1}{2} \sum_{\alpha, \beta} \frac{1}{4\pi \epsilon_0} \frac{Z_{\alpha} Z_{\beta} e^2}{|\mathbf{R}_{\alpha} - \mathbf{R}_{\beta}|} + \frac{1}{2} \sum_{i, j} \frac{1}{4\pi \epsilon_0} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|} - \sum_{\alpha, i} \frac{1}{4\pi \epsilon_0} \frac{Z_{\alpha} e^2}{|\mathbf{R}_{\alpha} - \mathbf{r}_i|} \right) \psi(\mathbf{R}_{\alpha}, s_{\alpha}, \mathbf{r}_i, s_i) = E \psi(\mathbf{R}_{\alpha}, s_{\alpha}, \mathbf{r}_i, s_i) \quad (2.1)$$

where $\mathbf{R}_\alpha = (R_{\alpha,x}, R_{\alpha,y}, R_{\alpha,z})$ are the spatial and s_α the spin coordinates of the nucleus α and \mathbf{r}_i are the spatial and s_i the spin coordinates of the electron i . This is a partial differential equation with $3N + 3n$ variables, clearly impossible to solve analytically or even numerically for the simplest system of interest. The first approximation to be done is the Born-Oppenheimer approximation. Due to the big mass difference between the heavy nuclei and the light electrons, we can decouple both equations of motion. The electronic structure relaxation is much faster than nuclei dynamics so we can consider that electrons “see” the ions as if they were frozen. The nuclei dynamics can be treated classically, considering that they are affected by a potential created by the electronic structure ($V(\mathbf{R}_\alpha) = -\nabla E_{gs}[\{\mathbf{R}_\alpha\}]$). So the equation we need to solve now is:

$$\left(-\sum_i \frac{\hbar^2 \nabla_i^2}{2m} + \frac{1}{2} \sum_{\alpha,\beta} \frac{1}{4\pi\epsilon_0} \frac{Z_\alpha Z_\beta e^2}{|\mathbf{R}_\alpha - \mathbf{R}_\beta|} + \frac{1}{2} \sum_{i,j} \frac{1}{4\pi\epsilon_0} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|} - \sum_{\alpha,i} \frac{1}{4\pi\epsilon_0} \frac{Z_\alpha e^2}{|\mathbf{R}_\alpha - \mathbf{r}_i|} \right) \psi(\mathbf{r}_i, s_i) = E \psi(\mathbf{r}_i, s_i) \quad (2.2)$$

that has “only” $3N$ variables. Although this equation seems very similar to (2.1), it is necessary to point out that in this case $\{\mathbf{R}_\alpha\}$ are parameters instead of variables, so for example, the nucleus-nucleus interaction is just a number. However, this equation is still impossible to solve. The main problem is the electron-electron interaction potential ($\hat{V}_{ee} = \frac{1}{2} \sum_{i,j} \frac{1}{4\pi\epsilon_0} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|}$) that mix the position operators of the different electrons. Without this potential, the equation is separable in N equations of 3 variables. Most of the approximations made in order to solve this equation are aimed to transform this term and get separability of the problem. These approximations can be classified in two types: approximations based on the wave function (often used by chemists) or approximations based on the electron density (the most used, where the DFT is the most common). We are going to give the main ideas of the wave function methods on this section and we will explain in detail the DFT in the next one (for extensive monographs see [1–3]).

2.2.1 Hartree Approximation

Hartree approximation is the most simple one. It consists on treating the electron-electron interaction semiclassically, considering that each electron “see” a cloud of negative charge that is the square modulus of the electronic wavefunction.

The deduction of the equation for this approximation is very simple. First it’s necessary to realize that (2.2) can be derived [4] as the equation that makes stationary the following expression:

$$\langle \hat{H} \rangle_\psi = \frac{\langle \psi | \hat{H} | \psi \rangle}{\langle \psi | \psi \rangle} \quad (2.3)$$

The Hartree approximation relies in considering a fully separable solution for the Schrödinger equation $\psi(\{\mathbf{r}_i\}) = \prod_i \phi_i(\mathbf{r})$. Introducing this ansatz on (2.3) we get:

$$\left(-\sum_i \frac{\hbar^2 \nabla_i^2}{2m} + V_{nucl} + \hat{V}_{ee}^H + \hat{V}_{ext} \right) \phi(\mathbf{r}) = \varepsilon_i \phi(\mathbf{r}) \quad (2.4)$$

where $V_{nucl} = \frac{1}{2} \sum_{\alpha, \beta} \frac{1}{4\pi\epsilon_0} \frac{Z_\alpha Z_\beta e^2}{|\mathbf{R}_\alpha - \mathbf{R}_\beta|}$ is the nucleus-nucleus interaction (just a number) and $\hat{V}_{ext} = \sum_{\alpha, i} \frac{1}{4\pi\epsilon_0} \frac{Z_\alpha e^2}{|\mathbf{R}_\alpha - \mathbf{r}_i|}$ is the interaction of the electrons with the electrostatic field created by the nuclei, and \hat{V}_{ee}^H is the so-called *Hartree potential* that has the form of an electronic density cloud interacting with the electron:

$$\hat{V}_{ee}^H = \frac{e^2}{4\pi\epsilon_0} \int d^3\mathbf{r}' \frac{\sum_i |\phi_i(\mathbf{r}')|^2}{|\mathbf{r} - \mathbf{r}'|} \quad (2.5)$$

where the sum is extended over the occupied orbitals. As we need $\{\phi_i\}$ to build \hat{V}_{ee}^H , but only knowing the latter, the former can be obtained, we can only solve this equation in a selfconsistent manner: we choose some initial $\{\phi_i^{in}\}$ that seem not to be too different than the actual ones (for example, if we are calculating the electronic structure of a molecule, the wavefunctions of the free atoms that belong to it, is a good initial set). Then we calculate the Hartree potential and solve the Schrödinger equation, and we get $\{\phi_i^{out}\}$. Then we use this output as a new input (in fact, we use a combination of the $\{\phi_i^{in}\}$ and $\{\phi_i^{out}\}$, to avoid numerical instabilities), and obtain a new output. Use this output again as a new input, and so on. When the input and the output one-electron wave functions are very close to each other, we have found a *selfconsistent* solution, and we can use it to calculate the electronic properties of the system.

This simple approximation neglects *completely* any many-body effect (exchange and correlation), and does not give good numerical results even for systems where exchange and correlation are not very important. Moreover, it is very easy to see that the electronic wavefunction is not anti-symmetric, and we have to introduce the Pauli exclusion principle as an *ad-hoc* hypothesis. Despite the lack of accuracy of this approximation, it is very pedagogical as it introduces the idea of selfconsistency, and in the more sophisticated approximations the electron-electron interaction is of the form: $\hat{V}_{ee} = \hat{V}_{ee}^H$ + other terms.

2.2.2 Hartree-Fock Approximation

The Hartree-Fock (HF) equation can be derived from Eq. (2.3), taking as an ansatz the simplest anti-symmetric wave-function: the Slater determinant:

$$\psi(\mathbf{r}_1, \dots, \mathbf{r}_n) = \frac{1}{\sqrt{n!}} \begin{vmatrix} \phi_1(\mathbf{r}_1) & \dots & \phi_1(\mathbf{r}_n) \\ \vdots & \ddots & \vdots \\ \phi_n(\mathbf{r}_1) & \dots & \phi_n(\mathbf{r}_n) \end{vmatrix} \quad (2.6)$$

If we introduce this expression into (2.3) we get the following integro-differential equation:

$$-\frac{1}{2}\nabla^2\phi_i(\mathbf{r}) + V_{ext}(\mathbf{r})\phi_i(\mathbf{r}) + V_{ee}^H(\mathbf{r})\phi_i(\mathbf{r}) - \sum_j \int d^3\mathbf{r}' \frac{\delta s_{i,j}}{|\mathbf{r} - \mathbf{r}'|} \phi_j^*(\mathbf{r}') \phi_j(\mathbf{r}) \phi_i(\mathbf{r}') = \varepsilon_i \phi_i(\mathbf{r}) \quad (2.7)$$

This equation is considerably more complex than the Hartree one-electron Schrödinger-like equation (and more computationally “expensive” to solve). It is important to remark that it contains a non-local term (the last one), with the advantage of taking into account *exactly* the exchange, but no correlation effects at all, so the electronic repulsion will be overestimated. In order to introduce these effects, we have two choices: introduce them using a perturbative treatment (the Møller-Plesset (MPn) methods) or using a more general ansatz (a linear combination of Slater-like wave-functions) that is the basis of configuration interaction method.

2.2.3 Configuration Interaction

This method allow us to improve the HF results in a systematic (but expensive) way. It is based on the fact that the *exact* solution to the Schrödinger equation is a linear combination of Slater determinants.

$$|\psi\rangle = \sum_i a_i |\phi\rangle$$

where $\{|\phi\rangle\}$ is the infinite set of N -electron Slater determinants. Considering a subset of $\{|\phi\rangle\}$ we obtain better results than using Hartree-Fock (the bigger the subset, the closer to the exact energy). In order to obtain the eigen-energies and eigen-values we calculate the matrix equation:

$$\sum_j H_{ij} a_j = E a_i; \quad \text{where} \quad H_{ij} = \langle \phi_i | \hat{H} | \phi_j \rangle \quad (2.8)$$

This method is very expensive computationally, but the main problem is the scalability, because the time spent solving the equations grows as $N!$ with the number of electrons N , that limits this method for very small systems. It is also not suitable for extended systems (like solids) since for large N , the energy of the system $E \propto N^{1/2}$, violating the thermodynamic limit (unless we take the full—infinite—set of Slater determinants).

2.2.4 Møller-Plesset Perturbation Theory

It is based on time-independent perturbation theory.¹ We consider that we have a hamiltonian of the form $\hat{H} = \hat{H}_0 + \hat{V}$ where $\hat{V} = \hat{H} - \hat{H}_{HF} - \langle \psi_0 | \hat{H} - \hat{H}_{HF} | \psi_0 \rangle$ (ψ_0 is the ground state wave function of \hat{H}_0), and solutions of $\hat{H}_0 = \hat{H}_{HF} + \langle \psi_0 | \hat{H} - \hat{H}_{HF} | \psi_0 \rangle$ are well known. It can be easily shown [5, 6] that corrections to the eigenvalues and energy at first order of perturbation theory are:

$$\begin{aligned} |\psi_i^{(1)}\rangle &= \sum_{j(j \neq i)} \frac{\langle \psi_j^{(0)} | \hat{V} | \psi_i^{(0)} \rangle}{E_i^{(0)} - E_j^{(0)}} |\psi_i^{(0)}\rangle \\ E_i^{(1)} &= \langle \psi_i^{(0)} | \hat{V} | \psi_i^{(0)} \rangle \\ E_i^{(2)} &= \sum_{j(j \neq i)} \frac{\langle \psi_i^{(0)} | \hat{V} | \psi_j^{(0)} \rangle \langle \psi_j^{(0)} | \hat{V} | \psi_i^{(0)} \rangle}{E_i^{(0)} - E_j^{(0)}} \end{aligned} \quad (2.9)$$

The Møller-Plesset methods [7] (MPn) calculate the energy at n -th order of perturbation theory. MP0 (no perturbation) is just Hartree-Fock, MP1 correction is Hartree-Fock also (the first order correction is zero), MP2 uses this second order equation for the energy, MP3 uses the third order and so on.

2.2.5 Pseudopotential

In most of the chemical or solid state physical systems only the valence electrons (i.e. the electrons in the outer shells) contribute to the bonding or band formation. The core electrons are so deep inside the atom, and so strongly bonded by the nucleus that they barely feel other atoms. So it is a waste of time to take into account a huge number of electrons that aren't important for obtaining the electronic properties of the system.

Pseudopotentials [8, 9] are used to avoid the use of core electrons in the calculation. They have the same scattering properties than the system formed by nucleus plus core electrons; and the wave functions of the valence electrons and the potential strength are the same as the all-electron system for a distance greater than some certain radius (r_c). At distances smaller than r_c , the pseudopotential is weaker than the bare nucleus potential (it doesn't diverge at $r = 0$ too), and the valence wave-functions are smoother (they don't need to have any nodes to be orthogonal to the core electrons).

So, not only pseudopotential simplify a N electron system by a $N - N_{core}$ one, it also allow us to work with well behaved and weaker potentials and smoother wave

¹ An excellent introduction of this theory, with some practical examples can be found in [5], Chap. XI.

functions, that numerical methods can handle much more efficiently. Moreover, some methods like plain wave-density functional theory methods (PW-DFT) will need a much smaller basis set in order to describe properly the systems under consideration.

Good pseudopotentials need to have some properties. The most important one is the *transferability*. That means that they have to reproduce the scattering properties of the nucleus plus core electrons in a lot of different chemical environments (isolated atom, molecules, crystals, etc.). It can be achieved just imposing norm conserving (that means that the pseudo-wavefunction integrals need to be the same as the actual ones) [10]. More sophisticated pseudopotentials are non-local (like the ones used in this thesis) and a different potential is used for each angular momentum [11–15]. Recently a new generation of ultra soft pseudopotentials have appeared in the literature. They are not norm-conserving; but they compensate this including different projectors in each angular moment [16, 17].

2.3 Density Functional Theory

The huge amount of theoretical ab initio research of very different materials (metal, semiconductors, organic molecules) in the second half of 20th century relies on the great simplification of the many-body Schrödinger equation due to the DFT and the Kohn–Sham equations [18, 19].

Despite of its known deficiencies (most of them related with the difficulty of finding a suitable exchange and correlation potential, see Sect. 2.3.2), the DFT has better computational resources/accuracy ratio than the other wave-function based methods (Hartree-Fock, configuration interaction, MP2...), so it is the suitable choice for the study of large systems (of more than one hundred, or even one thousand electrons). Although wave-function methods can be systematically improved (unlike DFT), usually don't work on extended systems (HF does not work well in metals, CI does not recover the thermodynamic limit, MP2 diverges for the homogeneous electron gas). That is another reason that encourage to use DFT in condensed matter systems, instead of other methods.

This theory is based on the Hohenberg-Kohn theorem [18]: The energy (and every observable) of a system of interacting electrons in a external potential (\hat{V}_{ext}) is a functional *only* of the electronic density of the system $E = E[\rho(\mathbf{r})]$. Moreover, the minimum of this functional occurs when the electronic density is the electronic density of the ground state of the system ($\rho(\mathbf{r}) = \rho_{gs}(\mathbf{r})$). The proof is very simple.

Let \hat{H} be the following hamiltonian:

$$\hat{H} = \hat{T} + \hat{V}_{ext} + \hat{V}_{ee} \quad (2.10)$$

where \hat{T} is the kinetic energy of the electrons, \hat{V}_{ext} the external potential, and \hat{V}_{ee} the coulomb electron-electron interaction [20]. And let $V = \{\hat{V}_{ext}\}$ be the set of all possible external potentials with the property that the solution of the many-body Schrödinger equation has a non degenerate ground state. If $\Psi = \{|\psi\rangle\}$ is the set of

all the possible ground states of \hat{H} , then we can define the following application:

$$A : V \rightarrow \Psi$$

And if $N = \{\rho(\mathbf{r})\}$ is the set of the electronic densities of $\{|\psi\rangle\}$ $\rho(\mathbf{r}) = \int d^3\mathbf{r}_2 \dots d^3\mathbf{r}_N |\psi(\mathbf{r}, \mathbf{r}_2, \dots, \mathbf{r}_N)|^2$ then we can define another application:

$$B : \Psi \rightarrow N$$

The Hohenberg–Kohn theorem shows us that both applications are bijective. So let's show that A is surjective: If we have \hat{V}_{ext} , and \hat{V}'_{ext} with $\hat{V}_{ext} \neq \hat{V}'_{ext} + C$, and we assume that both have the same ground state

$$\begin{aligned} (\hat{T} + \hat{V}_{ee} + \hat{V}_{ext})|\psi\rangle &= E|\psi\rangle \\ (\hat{T} + \hat{V}_{ee} + \hat{V}'_{ext})|\psi\rangle &= E'|\psi\rangle \end{aligned} \quad (2.11)$$

subtracting both expressions:

$$(\hat{V}_{ext} - \hat{V}'_{ext})|\psi\rangle = (E - E')|\psi\rangle \Rightarrow (\hat{V}_{ext} - \hat{V}'_{ext}) = (E - E') \Rightarrow \hat{V}_{ext} = \hat{V}'_{ext} + C \quad (2.12)$$

that is against original assumption.

The proof of the surjectivity of the second application is the following. Let $|\psi\rangle$ and $|\psi'\rangle$ be two ground states of \hat{H} and \hat{H}' with densities $\rho(\mathbf{r})$ and $\rho'(\mathbf{r})$, that we consider to be the same. Due to both are ground states it is easy to see that:

$$\begin{aligned} E &= \langle \psi | \hat{H} | \psi \rangle < \langle \psi' | \hat{H} | \psi' \rangle = \langle \psi' | \hat{H}' + \hat{V}_{ext} - \hat{V}'_{ext} | \psi' \rangle \Rightarrow \\ E &< E' + \int d^3\mathbf{r} \rho'(\mathbf{r})(V_{ext}(\mathbf{r}) - V'_{ext}(\mathbf{r})) \end{aligned} \quad (2.13)$$

If we repeat this for E' we find an analogous equation with primed and unprimed variables changed. Adding both expressions and taking into account that $\rho(\mathbf{r}) = \rho'(\mathbf{r})$ then:

$$E + E' < E' + E \quad (2.14)$$

that is impossible, so necessarily $\rho(\mathbf{r}) \neq \rho'(\mathbf{r})$.

The consequence of this theorem (as mentioned before) is that every observable, like the energy, is a functional of the density of the system. The definition of the ground state is the state that makes the energy of the hamiltonian a minimum. In the variational analysis language, the ground state is an extremal of the energy functional. This will allow us to deduce the Kohn–Sham equations.

2.3.1 Kohn–Sham Equations

We are going to separate from the energy functional the term due to the external potential:

$$E = E[\rho(\mathbf{r})] = F[\rho(\mathbf{r})] + \int d^3\mathbf{r} V_{ext}(\mathbf{r})\rho(\mathbf{r}) \quad (2.15)$$

where F is an universal functional that does not depend on the external potential. Kohn and Sham wrote, without loss of generality, the density as a sum of some orthonormal functions, $\psi_i(\mathbf{r})$, so that, $\rho(\mathbf{r}) = 2 \sum_{i=1}^{N/2} |\psi_i(\mathbf{r})|^2$ and divided this F functional in three terms with very easy physical interpretations.

$$\begin{aligned} F[\rho(\mathbf{r})] &= T_s[\rho(\mathbf{r})] + E_H[\rho(\mathbf{r})] + E_{xc}[\rho(\mathbf{r})] \quad \text{where} \\ T_s[\rho(\mathbf{r})] &= \sum_{i=1}^{N/2} \int d^3\mathbf{r} \psi_i^*(\mathbf{r}) \left(-\frac{\hbar^2}{2m} \nabla^2 \right) \psi_i(\mathbf{r}) \\ E_H[\rho(\mathbf{r})] &= \int d^3\mathbf{r} d^3\mathbf{r}' \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \\ E_{xc}[\rho(\mathbf{r})] &= F[\rho(\mathbf{r})] - T_s[\rho(\mathbf{r})] + E_H[\rho(\mathbf{r})] \end{aligned} \quad (2.16)$$

It's clear that the T_s term can be considered as the kinetic energy of some hypothetical non-interacting particles, whose wavefunctions are $\psi_i(\mathbf{r})$, the E_H term is Hartree energy, and E_{xc} is the part of energy functional that we don't know. This equation means that we can consider this hypothetical non interacting particles as the electrons of the system, and the energy functional is the one-electron functional $E_{oe} = T_s + E_H + \int d^3\mathbf{r} V_{ext}(\mathbf{r})\rho(\mathbf{r})$, plus a term E_{xc} that contains all the many-body terms that we don't consider in the one-electron functional.

If the ground state is an extremal of the energy functional (the state where the energy is minimum), we can use variational analysis. We have a constraint on the total number of electrons $\int d^3\mathbf{r} \rho(\mathbf{r}) = N$, so we need to use a Lagrange parameter μ , that will be renamed as ε_i . Using the Euler-Lagrange equation:

$$\frac{\delta}{\delta\rho(\mathbf{r})} \left[T_s[\rho(\mathbf{r})] + E_H[\rho(\mathbf{r})] + E_{xc}[\rho(\mathbf{r})] + \int d^3\mathbf{r} V_{ext}(\mathbf{r})\rho(\mathbf{r}) + \varepsilon_i \left(N - \int d^3\mathbf{r} \rho(\mathbf{r}) \right) \right] = 0 \quad (2.17)$$

it is not difficult to get that:

$$\begin{aligned} \frac{\delta T_s[\rho(\mathbf{r})]}{\delta\rho(\mathbf{r})} &= -\frac{\hbar^2 \nabla^2}{2m} \\ \frac{\delta}{\delta\rho(\mathbf{r})} \left[\int d^3\mathbf{r} V_{ext}(\mathbf{r})\rho(\mathbf{r}) \right] &= V_{ext}(\mathbf{r}) \\ \frac{\delta E_H[\rho(\mathbf{r})]}{\delta\rho(\mathbf{r})} &= \int d^3\mathbf{r} \frac{\rho(\mathbf{r})}{|\mathbf{r} - \mathbf{r}'|} = V_{Hartree}(\mathbf{r}) \end{aligned}$$

$$\frac{\delta E_{xc}[\rho(\mathbf{r})]}{\delta \rho(\mathbf{r})} = V_{xc}(\mathbf{r}) \quad (2.18)$$

Putting all together we get [19]:

$$\left(-\frac{\hbar^2 \nabla^2}{2m} + V_{ext}(\mathbf{r}) + V_{Hartree}(\mathbf{r}) + V_{xc}(\mathbf{r}) - \varepsilon_i \right) \psi_i(\mathbf{r}) = 0 \quad (2.19)$$

We need to remember that these equations are *exact*. We haven't made any approximation up to this point. We have decoupled a partial differential equation with $3N$ variables to N partial differential Schrödinger-like equations of 3 variables. We need to remember here, that neither ε_i nor $\psi_i(\mathbf{r})$ have any physical meaning. They don't correspond to the electronic energy levels and considering them as that could result in misinterpretation of the calculation results.

However, this non-physical spectrum (eigen-energies and eigen-wavefunctions) compares reasonably well with the physical one and it is often treated as a reasonable approximation to the exact spectrum. Why these non-physical quantities turn out to be a good approximation for the physical ones?

Quasiparticles

This can be well understood if we introduce the idea of quasiparticles. Imagine that you have a jellium solid: that means, an homogeneous electron gas with an homogeneous positive background to neutralize the system. Then you add an electron to the system at a point \mathbf{r} . What will be the form of the potential created by this electron at a point \mathbf{r}' ?

If the electron does not interact with the electron gas, the potential will be simply $V_{coulomb} = e^2 / (4\pi \varepsilon_0) |\mathbf{r} - \mathbf{r}'|$.

This is considered in one-electron approaches like Hartree or Hartree-Fock. However, if the electron interact with the gas, things are not so simple. Physically, this interaction will repel other electrons on the surroundings (due to Coulomb repulsion and due to the Pauli exclusion principle). That means that the electron will be surrounded by a “lack” of negative charge (that implies a net positive charge due to the positive background, see Fig. 2.1). This is the so-called “exchange-correlation hole” (see Sect. 2.5.1). Now the potential created by the electron will be smaller, due to this exchange-correlation hole will screen the negative charge (see Fig. 2.1). So what will be the potential now? In simple dielectric theory, the potential is calculated using a dielectric constant $\varepsilon = \varepsilon_r \varepsilon_0$. A more accurate form of the potential can be written in a similar way:

$$W(\mathbf{r}, \mathbf{r}', \omega) = \int d\mathbf{r}'' \varepsilon^{-1}(\mathbf{r}, \mathbf{r}'', \omega) V_{coulomb}(\mathbf{r}', \mathbf{r}'') \quad (2.20)$$

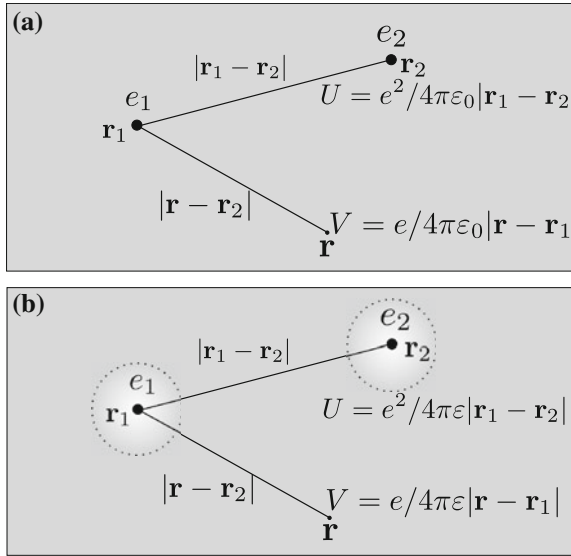


Fig. 2.1 Schematic figure of quasiparticles. In case **a**, there is no interaction of e_1 and e_2 with the surrounding electron gas. In case **b**, interaction between the electrons and the gas is working, creating a charge hole around them, so the effective coulomb interaction of the quasiparticle is lower. This allow to consider quasi-electrons as independent particles, explaining the good agreement of using KS orbitals as quasiparticle orbitals

where $\varepsilon^{-1}(\mathbf{r}, \mathbf{r}'', \omega)$ is the dielectric function. Its properties and different approximations for its calculation belong to the linear response theory in many-body physics. An extensive discussion about it can be found in [21, 22].

So instead of working with bare electrons (and holes), that are the ones that exists physically, we can take the electron and its positive charge cloud and treat it as a whole. This is not an actual particle but a *quasiparticle*. These quasiparticles can be considered, in good approximation, as nearly independent particles. That is the reason why the one-electron picture works pretty well. That is also the reason why, although they don't have in principle any physical meaning, Kohn–Sham eigenfunctions are treated as reliable eigenfunctions of the interacting system. They are the quasiparticle eigenvalues.

Despite this quasiparticle interpretation of the DFT spectra, in order to calculate the energy of the electrons at ground state we need to realize that it is not just $E = 2 \sum_{i=1}^{N/2} \varepsilon_i$ (factor 2 is due to spin multiplicity). There are terms that are not correctly included in this sum. For example, the electron-electron Hartree contribution is counted twice: in Hartree potential for atom i we include the i - j interaction term, and in Hartree potential for atom j we include i - j interaction too. This fact is commonly called 'double counting'. Also, the exchange and correlation energy E_{XC} is not correctly evaluated, because it is considered as $E_{XC} = \int d^3\mathbf{r} \rho(\mathbf{r}) V_{xc}(\mathbf{r})$ that is not true in general. So, the actual total energy is given by:

$$E[\rho(\mathbf{r})] = 2 \sum_{i=1}^{N/2} \varepsilon_i - \frac{1}{2} \int d^3\mathbf{r} d^3\mathbf{r}' \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + E^{xc}[\rho(\mathbf{r})] - \int d^3\mathbf{r} \rho(\mathbf{r}) V_{xc}(\mathbf{r}) \quad (2.21)$$

2.3.2 Exchange and Correlation Functional Approximations

When we want to put DFT in practice, we find a very important problem. We don't know the exact form of E^{xc} and $V_{xc}(\mathbf{r})$. So we need to do *approximations*, and our results will no longer be exact. There are several approximations to calculate the exchange-correlation energy (potential). The most common are:

Local Density Approximation (LDA)

It is the most simple one and it was proposed by Kohn and Sham in [19]. It relies on the approximation that the exchange and correlation interactions are entirely *local*; that means that exchange and correlation energy at the point \mathbf{r} *only* depends on the density at \mathbf{r} . Under this consideration, we can use the exchange-correlation energy for an homogeneous electron gas of density ρ (that is not, however, a trivial calculation [23, 24]) to calculate the E_{xc} functional:

$$E_{xc}[\rho(\mathbf{r})] = \int d^3\mathbf{r} \rho(\mathbf{r}) \varepsilon_{xc}(\rho = \rho(\mathbf{r})) \quad (2.22)$$

where $\varepsilon(\rho = \rho(\mathbf{r})) = f(\rho)$, (the exchange-correlation energy depends *only* on the density at each point).

Surprisingly this naive approximation works *pretty* well. However LDA has some deficiencies that cause systematic failures when computing some properties of the systems, such as:

- Bond lengths in LDA are systematically smaller than the ones found experimentally, i.e. LDA overestimates the attraction between atoms.
- Cohesive energies in LDA are systematically bigger than the ones found experimentally. This is related with the previous failure.
- It does not describe well the magnetic properties of some systems (for example LDA predicts for the iron a paramagnetic FCC structure, instead of the ferromagnetic BCC structure found experimentally).
- It does not describe well weak interactions (hydrogen bonds, Van der Waals interactions, etc.) so it is not suitable for calculations involving water, ice, biological molecules (proteins, DNA...), physisorbed molecules on metals, etc.
- V_{xc}^{LDA} decreases as $-\rho^{1/3}$ for atoms and clusters, instead of $-1/r$. Some anions are not stable in LDA.

Generalized Gradient Approximation (GGA)

This approximation corrects some of the deficiencies of the LDA, because it takes into account not only the density at some point, but also the gradient of the density. So the functional can be expressed as:

$$E_{xc}^{GGA}[\rho(\mathbf{r})] = \int d^3\mathbf{r} \rho(\mathbf{r}) \varepsilon_{xc}[\rho(\mathbf{r}), \nabla \rho(\mathbf{r})] \quad (2.23)$$

The exact form of the functional is found imposing several limits and scale and normalization rules. There are two types of GGA functionals: semiempirical [25, 26] (adjusted to reproduce good results in a big variety of molecules, but fail on non-localized systems) and non-empirical [27] (based on physical arguments, can handle a full variety of systems).

GGA correct some of the problems of LDA but not systematically.

- Reduces the error in formation energies, but not in bond length in molecules.
- It describes better hydrogen bonds.
- Tend (but not systematically) to reduce the error in energies and bond length in solids.
- It stabilizes the BCC magnetic iron.
- It still has some deficiencies: small bulk modulus in semiconductors, open gaps in transition metal oxides, etc.

Other Functionals

There are a full variety of other functionals apart from LDA and GGA. They can include exact exchange or second order derivatives [28], for example Meta-GGA. There are also hybrid methods that mix exact exchange (using Hartree-Fock) with E_{xc} . A new hybrid method is presented in this thesis (in the context of LCAO-OO) and will be carefully explained later (see 2.7.3).

There is an special family of functionals that uses the Kohn–Sham non-physical orbitals as an input, instead of charge density ($E_{xc} = E_{xc}[\{\phi_i(\mathbf{r})\}]$). For a extensive monograph of these functionals see [29].

2.4 The FIREBALL Method

The FIREBALL method is based on the work of Sankey and Niklewski [30]. It is an ab initio local orbital tight-binding method, using a self-consistent version [31] of the Harris-Foulkes functional [32, 33]. It has been implemented in a DFT code called FIREBALL [34, 35].

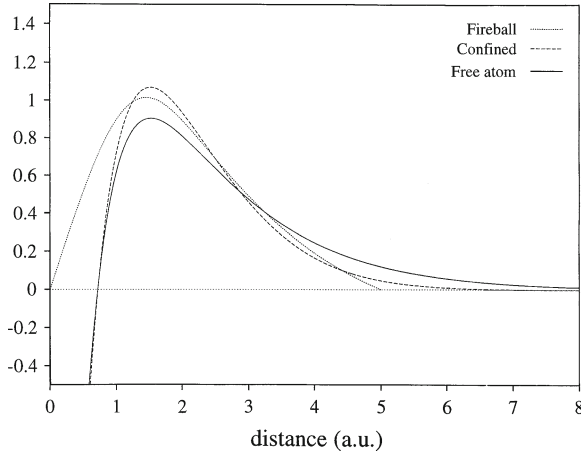


Fig. 2.2 Differences in the radial part of a 3p silicon fireball, free and confined orbitals. Reprinted from [36], Copyright (1998) with permission from Elsevier

2.4.1 Fireball Orbitals

The basis set used in the FIREBALL code are constructed using ‘fireball’ orbitals. They are atomic-like orbitals $\{\phi_{i\alpha}(\mathbf{r}_i)\}$ ($\alpha = nlm$) that are strictly zero beyond a certain cut-off radius (R_C) (Fig. 2.2). So the orbitals used in the code are slightly excited (this is the reason why they are called ‘fireball’ orbitals) but they reproduce better the shape of the orbitals inside a molecule or a lattice (due to orthonormalization they are more confined than free atomic ones). They also have the advantage of being strictly zero beyond R_C , so there are a finite number of interactions between the atoms in our system (even if they are extended systems like solids or surfaces). Although all electron calculations are possible in FIREBALL, usually calculations are carried out using only valence electrons: separable Kleinman–Bylander pseudopotentials [14] are used to take into account the effect of the nucleus and the core electrons.

Before any calculation is done we need to calculate the ‘fireball’ orbitals basis set. We have several degrees of freedom that give us a lot of flexibility in this choice:

- We can choose different R_C for each shell of each atomic species.
- We can choose a minimal basis (only $(2l + 1)$ orbitals for each l quantum number shell): an sp^3 basis or an sp^3d^5 basis.
- We can choose double basis set ($2(2l + 1)$ orbitals for l quantum number); the ground and the first excited wavefunction of the atomic hamiltonian (with the R_C condition) are used. There is no need to use both wavefunctions for all l , so it is possible to use double basis for some l and simple for the others (the use of a $sp^3d^5d^{*5}$ is common [37]).
- We can introduce an confinement potential, so the electronic tails would go smoothly to zero.

- We can mix ground state and excited state orbitals in order to construct an optimized minimal basis set [38]. Or we can even use ground state and excited orbitals from different calculations (such as ground state basis and ground state confined basis or even basis of different atoms).

In order to know if our basis is a good one for the element (or elements) under consideration, some tests are usually carried out: calculation of the lattice parameter of the crystal, bulk modulus, the volume band structure (comparing it with PW-LDA calculations [39]), surface properties, bond lengths, etc.

2.4.2 The Harris Functional

In Sect. 2.3 energy has been calculated using the Kohn–Sham functional, considering the output charge density $\rho^{out}(\mathbf{r})$, obtained after the diagonalization of the hamiltonian. Harris and Foulkes [32, 33] proved that the energy can be calculated approximately without self-consistent process. The Harris functional is formally the same as the Kohn–Sham functional, but using $\rho^{in}(\mathbf{r})$ instead of $\rho^{out}(\mathbf{r})$. The energy difference between the results obtained with the Kohn–Sham and the Harris functionals scale as the second order in the difference between the input and the self-consistent density.

$$E^{Harris} = E^{Kohn-Sham} + O^2(\rho^{in} - \rho^{sc}) \quad (2.24)$$

By this way we can choose an arbitrary input density to do our calculations. In FIREBALL, for computational convenience it has the form:

$$\rho^{in}(\mathbf{r}) = \sum_{i\alpha} n_{i\alpha}^{in} |\phi_{i\alpha}(\mathbf{r} - \mathbf{R}_i)|^2 \quad (2.25)$$

With this form of the input density, and the fact that the orbitals are confined, the hamiltonian matrix elements involve (at most) three center interactions (on the form $\langle \phi(\mathbf{r} - \mathbf{R}_i) | V(\mathbf{r} - \mathbf{R}_j) | \phi(\mathbf{r} - \mathbf{R}_k) \rangle$) and can be tabulated for several distances and angles [30] and interpolated for the distances and angles of our calculations. That means that no matrix elements' integral calculations are made during the simulations. That is one of the reasons why FIREBALL is so fast.

This combination of fireball orbitals and Harris functional works well in dimers and some solids but it fails in surfaces or in systems with big charge transfer between the atoms. In reference [31] a self-consistent version of the Harris functional is presented. In order to maintain the form of the input density in (2.25) to tabulate the interactions, an output $n_{i\alpha}^{out}$ are defined as:

$$n_{i\alpha}^{out} = \sum_n^{occ.} |\langle \psi_n | \phi_{i\alpha} \rangle|^2 \quad (2.26)$$

where ψ_n are the hamiltonian eigenvalues and $\varphi_{i\alpha}$ are the Löwdin orbitals [40]. These orbitals form an orthonormal basis set (the basis set of fireball orbitals is not orthonormal), that is the most similar to the fireball one [41]. These orbitals are calculated via:

$$\varphi_{i\alpha} = \sum_{j\beta} (S^{-1/2})_{i\alpha,j\beta} \phi_{j\beta}; \quad \text{where} \quad (S)_{i\alpha,j\beta} = \langle \phi_{i\alpha} | \phi_{j\beta} \rangle \quad (2.27)$$

The $(S^{-1/2})$ matrix can be calculated by diagonalizing S and then taking the square root of the main diagonal elements [6]. So, we can calculate the $n_{i\alpha}$ numbers in a self consistent way $n_{i\alpha}^{in} = n_{i\alpha}^{out}$. These $n_{i\alpha}$ can be seen as the occupation numbers of the orbitals of our system, linking this approach to the LCAO-OO method, explained in Sect. 2.5.

We need to say here that the use of $n_{i\alpha}^{out}$ has an implicit approximation, due to the actual output density has the form:

$$\rho^{out}(\mathbf{r}) = \sum_{i\alpha,j\beta} n_{i\alpha,j\beta}^{out} \varphi_{i\alpha}^* \varphi_{j\beta}; \quad \text{where} \quad n_{i\alpha,j\beta}^{out} = \sum_n^{occ.} \langle \psi_n | \varphi_{i\alpha} \rangle \langle \varphi_{j\beta} | \psi_n \rangle \quad (2.28)$$

and taking into account only $n_{i\alpha}^{out}$ means that we are considering that the non diagonal elements ($n_{i\alpha,j\beta}^{out}; j\beta \neq i\alpha$) are zero, that in general is not true. Moreover, note that in Eq. 2.28 the wavefunctions are the Löwdin φ instead of the non-diagonal ϕ that we use in (2.25). This is another approximation, motivated by the fact that φ are the orthonormal wavefunctions more similar to ϕ . Other choices for $n_{i\alpha}^{out}$ are available, but this is the one that gives better results.

In practice, for a calculation in FIREBALL there are always three steps. In the first step we calculate the atomic orbitals of the elements that are present at our system. In the second step we calculate and tabulate the two and three center integrals for different hamiltonian matrix elements. In the third step we use the tabulated elements to construct and diagonalize our hamiltonian until we find self-consistent occupation numbers. Then we calculate the energy using the Harris functional and the forces suffered by each atom, that allows us to do molecular dynamics (MD).

2.4.3 Exchange and Correlation

We want to tabulate the exchange-correlation potential as we have done for the Hartree and kinetic energy term. The problem is that this potential is not linear in the density (so if the density has the form $\rho = \sum_i \rho_i$, the potential cannot be written in the form $V^{xc}(\rho) = \sum_i V_i^{xc}(\rho_i)$). Some approximations are done in order to tabulate these interactions. Although LDA and GGA exchange-correlation functionals can be implemented in these approximations, only LDA is available for all approximations at the present version of the code.

The first one, Sankey-Niklewski (SN) approximation [30], is based on a Taylor expansion of exchange-correlation energy and potential. This approximation has been improved adding terms beyond first order Taylor expansion [42, 43].

Sankey–Niklewski

We want to calculate the matrix elements $\langle \phi_{i\alpha} | E_{xc} | \phi_{i\alpha} \rangle$, $\langle \phi_{i\alpha} | V_{xc} | \phi_{j\beta} \rangle$. In the Sankey–Niklewski approximation we just perform a Taylor expansion around an average density $\bar{\rho}_{i\alpha, j\beta}$.

$$\langle \phi_{i\alpha} | E_{xc} | \phi_{i\alpha} \rangle \simeq E_{xc}(\bar{\rho}_{i\alpha, i\alpha}) + \frac{dE_{xc}}{d\rho}(\bar{\rho}_{i\alpha, i\alpha})(\langle \phi_{i\alpha} | \rho | \phi_{i\alpha} \rangle - \bar{\rho}_{i\alpha, i\alpha}) \quad (2.29)$$

$$\langle \phi_{i\alpha} | V_{xc} | \phi_{j\beta} \rangle \simeq V_{xc}(\bar{\rho}_{i\alpha, j\beta})S_{i\alpha, j\beta} + \frac{dV_{xc}}{d\rho}(\bar{\rho}_{i\alpha, j\beta})(\langle \phi_{i\alpha} | \rho | \phi_{j\beta} \rangle - \bar{\rho}_{i\alpha, j\beta}S_{i\alpha, j\beta}) \quad (2.30)$$

In this approximation, the average density is defined as:

$$\bar{\rho}_{i\alpha, j\beta} = \frac{\langle \phi_{i\alpha} | \rho | \phi_{j\beta} \rangle}{\langle \phi_{i\alpha} | \phi_{j\beta} \rangle} = \frac{\rho_{i\alpha, j\beta}}{S_{i\alpha, j\beta}} \quad (2.31)$$

Choosing $\bar{\rho}_{i\alpha, j\beta}$ this way, the second term of the Taylor expansion (that depends on $d^2 E_{xc}/d\rho^2$) is identically zero, and the third term is minimized. Physically it means that the effective density is calculated using *importance sampling*, because the density is weighted more where the bond charge is high.

However this average density lacks for some deficiencies. First of all, it is not defined when the overlap is zero. Moreover, there is no reason why $\rho_{i\alpha, j\beta}$ and $S_{i\alpha, j\beta}$ need to have the same sign, giving unphysical $\bar{\rho}_{i\alpha, j\beta} < 0$. New methods, that correct these deficiencies (that are fatal for transition metals) are needed. We will describe them in the next paragraphs.

Horsfield

An attempt to improve the deficiencies of SN approximation was made by Horsfield [42]. It calculate exchange and correlation using a multi center expansion of density (an idea that will be used in McWEDA also). Different expansions will be made in $\langle \phi_{i\alpha} | V_{xc} | \phi_{j\beta} \rangle$ depending whether $i = j$ or not.

$$\langle \phi_{i\alpha} | V_{xc}[\rho] | \phi_{i\beta} \rangle \simeq \langle \phi_{i\alpha} | V_{xc}[\rho_i] | \phi_{i\beta} \rangle + \sum_{j \neq i} \langle \phi_{i\alpha} | V_{xc}[\rho_i + \rho_j] - V_{xc}[\rho_i] | \phi_{i\beta} \rangle \quad (\text{on-site term}) \quad (2.32)$$

$$\begin{aligned}
\langle \phi_{i\alpha} | V_{xc}[\rho] | \phi_{j\beta} \rangle &\simeq \langle \phi_{i\alpha} | V_{xc}[\rho_i + \rho_j] | \phi_{j\beta} \rangle \\
&+ \sum_{k \neq i, j} \langle \phi_{i\alpha} | V_{xc}[\rho_i + \rho_j + \rho_k] - V_{xc}[\rho_i + \rho_j] | \phi_{j\beta} \rangle \quad (\text{off-site term: } i \neq j)
\end{aligned} \tag{2.33}$$

These integrals can be stored in data tables, just like in the SN approach. Although this approximation is good in many cases, the on-site terms ($i = j$) are not accurate enough for some systems (such as transition metals) and an additional term must be included:

$$\langle \phi_{i\alpha} | \left(V_{xc}[\rho] - V_{xc}[\rho_i] - \sum_{j \neq i} V_{xc}[\rho_i + \rho_j] - V_{xc}[\rho_i] \right) | \phi_{i\beta} \rangle \tag{2.34}$$

Unfortunately these integrals cannot be stored in data tables. Moreover, most of the computational time is spent in calculation of exchange-correlation terms, reducing the efficiency.

McWEDA

A more sophisticated way to improve the SN approximation is the Multi-center Weighted Exchange-correlation Density Approximation (McWEDA), developed by Jelínek and coworkers [43]. This method has been used for all the systems studied in this thesis.

First of all, a new average density is used, using the weighting functions $w_{i\alpha}$ associated with the wavefunctions $\phi_{i\alpha}$ defined this way:

$$\begin{aligned}
\phi_{nlm} &= R_{nl}(r) \Upsilon_l^m(\Omega) \\
w_{nl} &= |R_{nl}(r)| \Upsilon_0^0(\Omega)
\end{aligned} \tag{2.35}$$

so the average density is now:

$$\bar{\rho}_{i\alpha, j\beta} = \frac{\langle w_{i\alpha} | \rho | w_{j\beta} \rangle}{\langle w_{i\alpha} | w_{j\beta} \rangle} \tag{2.36}$$

that does not have the deficiencies of definition (2.31).

We can define a Generalized SN (GSN) approximation where this new $\bar{\rho}_{i\alpha, j\beta}$ is used in the same scheme. However we can go beyond GSN approximation, using the one center matrix element $\langle \phi_{i\alpha} | E_{xc}[\rho_i] | \phi_{j\beta} \rangle$ ($\langle \phi_{i\alpha} | V_{xc}[\rho_i] | \phi_{j\beta} \rangle$) where $\rho_i = \sum_{\alpha} n_{i\alpha}^{in} |\phi_{i\alpha}(\mathbf{r} - \mathbf{R}_i)|^2$. This element will be the most important term in the total exchange-correlation matrix elements so we can write the total exchange-correlation potential as $\langle \phi_{i\alpha} | V_{xc}[\rho_i] | \phi_{j\beta} \rangle$ plus a correction.

$$\langle \phi_{i\alpha} | E_{xc}[\rho] | \phi_{i\beta} \rangle = \langle \phi_{i\alpha} | E_{xc}[\rho_i] | \phi_{i\beta} \rangle + (\langle \phi_{i\alpha} | E_{xc}[\rho] | \phi_{i\beta} \rangle - \langle \phi_{i\alpha} | E_{xc}[\rho_i] | \phi_{i\beta} \rangle) \quad (2.37)$$

$$\langle \phi_{i\alpha} | V_{xc}[\rho] | \phi_{j\beta} \rangle = \langle \phi_{i\alpha} | V_{xc}[\rho_i] | \phi_{j\beta} \rangle + (\langle \phi_{i\alpha} | V_{xc}[\rho] | \phi_{j\beta} \rangle - \langle \phi_{i\alpha} | V_{xc}[\rho_i] | \phi_{j\beta} \rangle) \quad \text{if } i = j \quad (2.38)$$

$$\begin{aligned} \langle \phi_{i\alpha} | V_{xc}[\rho] | \phi_{j\beta} \rangle &= \langle \phi_{i\alpha} | V_{xc}[\rho_i + \rho_j] | \phi_{j\beta} \rangle \\ &+ (\langle \phi_{i\alpha} | V_{xc}[\rho] | \phi_{j\beta} \rangle - \langle \phi_{i\alpha} | V_{xc}[\rho_i + \rho_j] | \phi_{j\beta} \rangle) \quad \text{if } i \neq j \end{aligned} \quad (2.39)$$

From now on we will consider only the potential term (the same ideas hold for the energy one). We will explain now the $i = j$ case (on-site term). $\langle \phi_{i\alpha} | V_{xc}[\rho_i] | \phi_{i\beta} \rangle$ is a one-center integral and can be very easily calculated and tabulated. The correction part (the term between parentheses) is calculated using the GSN approximation (due to this term is a correction of the main one, the GSN correction should be good enough). So the on-site term is written in McWEDA approximation as:

$$\begin{aligned} \langle \phi_{i\alpha} | V_{xc}[\rho] | \phi_{i\beta} \rangle &= \langle \phi_{i\alpha} | V_{xc}[\rho_i] | \phi_{i\beta} \rangle + V_{xc}(\bar{\rho}_{i\alpha,i\beta}) S_{i\alpha,i\beta} + V'_{xc}(\bar{\rho}_{i\alpha,i\beta}) (\langle \phi_{i\alpha} | \rho | \phi_{i\beta} \rangle \\ &- \bar{\rho}_{i\alpha,i\beta} S_{i\alpha,i\beta}) - V_{xc}(\bar{\rho}_{i\alpha,i\beta}^i) S_{i\alpha,i\beta} - V'_{xc}(\bar{\rho}_{i\alpha,i\beta}^i) (\langle \phi_{i\alpha} | \rho_i | \phi_{i\beta} \rangle \\ &- \bar{\rho}_{i\alpha,i\beta}^i S_{i\alpha,i\beta}) \end{aligned} \quad (2.40)$$

where $\bar{\rho}_{i\alpha,i\beta}^i = \langle w_{i\alpha} | \rho_i | w_{j\beta} \rangle / \langle w_{i\alpha} | w_{j\beta} \rangle$. In the off-site case ($i \neq j$) the evaluation of correction part is also done in the GSN approximation so:

$$\begin{aligned} \langle \phi_{i\alpha} | V_{xc}[\rho] | \phi_{j\beta} \rangle &= \langle \phi_{i\alpha} | V_{xc}[\rho_i + \rho_j] | \phi_{j\beta} \rangle + V_{xc}(\bar{\rho}_{i\alpha,j\beta}) S_{i\alpha,j\beta} \\ &+ V'_{xc}(\bar{\rho}_{i\alpha,j\beta}) (\langle \phi_{i\alpha} | \rho | \phi_{j\beta} \rangle - \bar{\rho}_{i\alpha,j\beta} S_{i\alpha,j\beta}) - V_{xc}(\bar{\rho}_{i\alpha,j\beta}^{ij}) S_{i\alpha,j\beta} \\ &- V'_{xc}(\bar{\rho}_{i\alpha,j\beta}^{ij}) (\langle \phi_{i\alpha} | \rho_i + \rho_j | \phi_{j\beta} \rangle - \bar{\rho}_{i\alpha,j\beta}^{ij} S_{i\alpha,j\beta}) \end{aligned} \quad (2.41)$$

where $\bar{\rho}_{i\alpha,j\beta}^{ij} = \langle w_{i\alpha} | \rho_i + \rho_j | w_{j\beta} \rangle / \langle w_{i\alpha} | w_{j\beta} \rangle$. Recently McWEDA approximation has been improved [44], introducing the effect of charge transfer in $\langle \phi_{i\alpha} | V_{xc}[\rho_i] | \phi_{i\beta} \rangle$ and $\langle \phi_{i\alpha} | V_{xc}[\rho_i + \rho_j] | \phi_{j\beta} \rangle$, where ρ_i and ρ_j in practice were considered the neutral density (that makes the atom electrically neutral) instead of the selfconsistent ones. A Taylor expansion is performed around the neutral density ρ_i^0 and ρ_j^0 , and we obtain:

$$\begin{aligned} \langle \phi_{i\alpha} | V_{xc}[\rho_i] | \phi_{i\beta} \rangle &\simeq \langle \phi_{i\alpha} | V_{xc}[\rho_i^0] | \phi_{i\beta} \rangle + \frac{dV_{xc}}{d\rho}[\rho_i^0] (\langle \phi_{i\alpha} | \rho_i - \rho_i^0 | \phi_{i\beta} \rangle \\ \langle \phi_{i\alpha} | V_{xc}[\rho_i + \rho_j] | \phi_{j\beta} \rangle &\simeq \langle \phi_{i\alpha} | V_{xc}[\rho_i^0 + \rho_j^0] | \phi_{j\beta} \rangle + \frac{dV_{xc}}{d\rho}[\rho_i^0 + \rho_j^0] \\ &\langle \phi_{i\alpha} | \rho_i - \rho_i^0 + \rho_j - \rho_j^0 | \phi_{j\beta} \rangle \end{aligned} \quad (2.42)$$

This has corrected some deficiencies in the energy using extended basis sets, but work on this direction is still in progress. In this thesis there is also some progress in extending McWEDA to the local spin density approximation (LSDA), see Appendix C for details.

2.4.4 Molecular Dynamics and Structure Relaxation

FIREBALL can calculate the energy and the atomic forces acting on our system, so it can be employed as a MD code. Moreover, because of the storage of integrals in data tables make the code very fast, MD simulations can be performed in a reasonable amount of time.

The forces can be calculated as the derivative of the total energy given by the Harris functional:

$$\begin{aligned} \mathbf{F}_i = -\frac{\partial E_{Tot}}{\partial \mathbf{R}_i} = & -\frac{\partial}{\partial \mathbf{R}_i} (2 \sum_i^{occ} \varepsilon_i) - \frac{\partial}{\partial \mathbf{R}_i} \left(\frac{1}{2} \sum_{j,k} \frac{Z_j Z_k e^2}{|\mathbf{R}_j - \mathbf{R}_k|} - \frac{1}{2} \int d^3\mathbf{r} d^3\mathbf{r}' \frac{\rho_{in}(\mathbf{r}) \rho_{in}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \right) \\ & - \frac{\partial}{\partial \mathbf{R}_i} (E^{xc}[\rho_{in}(\mathbf{r})] - \int d^3\mathbf{r} \rho_{in}(\mathbf{r}) V_{xc}[\rho_{in}(\mathbf{r})]) = -\frac{\partial E_{BS}}{\partial \mathbf{R}_i} - \frac{\partial (E_{ion-ion} - E_{ee})}{\partial \mathbf{R}_i} - \frac{\partial (\delta U_{xc})}{\partial \mathbf{R}_i} \end{aligned} \quad (2.43)$$

A variation of the Hellman-Feynman theorem [45–47] is used to compute the band structure force. This way, the derivatives with respect to the atomic positions of the matrix elements $\frac{\partial}{\partial \mathbf{R}_i} \langle i\alpha | H | j\beta \rangle$ can be easily calculated using the tabulated interactions and taking the derivative of the interpolation polynomials.

Using forces, not only we can do MD, but also we can relax the systems and find the minimum energy positions of the atoms. There are two main ways of calculating them in FIREBALL: dynamical quenching and conjugate gradients.

Dynamical Quenching

This is a pure MD method for relaxing atomic positions of our system. It is based on energy conservation. When the nuclei are in a minimum of potential energy they have a maximum of kinetic energy. So, if we calculate the kinetic energy of the system we can use it to know when we are in a potential energy minimum.

The mechanism of dynamical quenching is the following one: we have some initial guess of the atomic positions of our system. Then we do MD, taking care of the kinetic energy of the nuclei. Usually it increases (that means that the atomic positions are moving towards a potential energy minimum), but when we find a MD step where the kinetic energy is smaller than the previous one; then potential energy has increased, that means that we have passed through a potential energy minimum. If we don't do anything, the system will go by, or at best, it will begin to oscillate

around the energy minimum. In order to avoid that, a *quenching* is done, that means that all atomic positions are frozen. In the following MD step, we allow the atoms to move, and the kinetic energy begin to increase again, when it begins to decrease, we freeze the atoms again, and then allow to move again, and then freeze, and so on. When the forces (and the difference of potential energy between one step and the previous one) are lower than a tolerance value, we consider that the system is relaxed.

There is a more sophisticated variant of dynamical quenching. It consist on comparing the sign of the components of the velocity of each atom ($v_{i,x}$, $v_{i,y}$, $v_{i,z}$) and the analog components of the forces ($F_{i,x}$, $F_{i,y}$, $F_{i,z}$). If they are different, the component of this atom is frozen (that means that the velocity component is set to zero). By this way, we gain specifickness. Instead of frozen all atoms at a time, we can freeze only the velocity atom components that are moving each atom away from the energy minimum.

Conjugate Gradients

This method is not so based on physical arguments, but in functional analysis of several variables. We should consider the energy E as a function of several variables (that can be treated as a vector \mathbf{X}) $E = E(\mathbf{X})$. In our case, the variables will be the atomic positions ($\mathbf{X} = \{\mathbf{R}_\alpha\}$). If we want to reach a minimum, we want to go through the fastest direction (i. e. the direction where the function varies more quickly). This direction is given by the gradient. If the initial positions of the system are given by $\mathbf{X} = \mathbf{X}_1$ then:

$$\mathbf{g}_1 = - \left(\frac{\partial E}{\partial \mathbf{X}} \right)_{\mathbf{X}=\mathbf{X}_1} = \{\mathbf{F}_\alpha\} \quad (2.44)$$

So, the gradient can be calculated using the forces given by FIREBALL. The subindex 1 means that is the first iteration. Now that we know the direction we want to move, we want to find the minimum along this direction. The equation of the line along this direction is:

$$\mathbf{X}_2 = \mathbf{X}_1 + b_1 \mathbf{g}_1 \quad (2.45)$$

Calculating the energy for several values of \mathbf{X}_2 (b_1) we can interpolate the minimum position.

Now that we have \mathbf{X}_2 , we can calculate the gradient \mathbf{g}_2 and find the minimum of $\mathbf{X}_3 = \mathbf{X}_2 + b_2 \mathbf{g}_2$ and get \mathbf{X}_3 , \mathbf{g}_3 and continue until we get the minimum of our system.

The problem of this method is that each line is orthogonal to the line of the previous step, so we will need a lot of steps to find the minimum. We can use *conjugate* gradients. In this case the new direction is not orthogonal to the previous one, but a direction given by a linear combination of the old and new gradient. This way there will not be sudden changes of direction, and each step will have some

‘memory’ of the previous steps. A more in depth discussion of conjugate gradients can be found on [48, 49].

This technique has the advantage of being really fast to relax the system. However, it has two handicaps. The first one is that, by construction, it will find the *local* minimum of our system closer to the original atomic positions, even if a more deeper minimum (or even the absolute one) is also close to the original atomic positions. However, the dynamical quenching explores better the phase space of the system and is able to find deeper minima.

The other problem is that due to the inherent approximations in FIREBALL, the minimum of the forces and of the energy sometimes does not coincide (but the difference is very small for the systems studied in this work). So sometimes, the gradient of the energy does not point to the energy minimum, and the program can go crazy because internal checks of the code. That is the reason why, we have used dynamical quenching in this thesis.

2.5 LCAO-OO Method

The Linear Combination of Atomic Orbitals - Orbital Occupancies (LCAO-OO) method is a variation of DFT based on second quantization Hubbard-like hamiltonians (see appendix A, B and [50]) that relies on the orbital occupancies $n_{i\sigma}$ instead of the charge density [51–53]. It is extensively analyzed in [52], including the proof of Hohenberg–Kohn theorem in terms of orbital occupancies. It combines the simplicity of DFT-like techniques with the power of a second quantized hamiltonian. By this way, sophisticated exchange-correlation functionals, or many-body calculations can be made in a intuitive way.

Equation 2.2 can be written in second quantization and atomic units as:

$$\hat{H} = \sum_{i\sigma} (\varepsilon_{i\sigma} + V_{ii}^{psp}) \hat{n}_{i\sigma} + \sum_{i,j \neq i,\sigma} (t_{ij} + V_{ij}^{psp}) \hat{c}_{i\sigma}^\dagger \hat{c}_{j\sigma} + \sum_{ijkl,\sigma\sigma'} O_{lk}^{ij} \hat{c}_{i\sigma}^\dagger \hat{c}_{j\sigma'}^\dagger \hat{c}_{k\sigma'} \hat{c}_{l\sigma} \quad (2.46)$$

where V_{ij}^{psp} is the pseudopotential of the core electrons and the nuclei and:

$$\begin{aligned} \varepsilon_i &= \int d^3\mathbf{r} \phi_i^*(\mathbf{r}) \left(-\frac{1}{2} \nabla^2 + \sum_{\alpha} \frac{Z_{\alpha}}{|\mathbf{R}_{\alpha} - \mathbf{r}|} \right) \phi_i(\mathbf{r}) \\ t_{ij} &= \int d^3\mathbf{r} \phi_i^*(\mathbf{r}) \left(-\frac{1}{2} \nabla^2 + \sum_{\alpha} \frac{Z_{\alpha}}{|\mathbf{R}_{\alpha} - \mathbf{r}|} \right) \phi_j(\mathbf{r}) \\ O_{lk}^{ij} &= \int d^3\mathbf{r} d^3\mathbf{r}' \phi_i^*(\mathbf{r}) \phi_j^*(\mathbf{r}') \frac{1}{|\mathbf{r} - \mathbf{r}'|} \phi_k(\mathbf{r}') \phi_l(\mathbf{r}) \end{aligned} \quad (2.47)$$

This is the complete many-body hamiltonian of the system. The first two parts correspond to one-electron terms while the last one contains the many-body terms of

the system. We can rewrite the hamiltonian in a more physically meaningful manner, and retain only important terms. The hamiltonian is written now as:

$$\begin{aligned}
\hat{H} = & \sum_{i\alpha\sigma} (\varepsilon_{i\alpha\sigma} + V_{i\alpha,i\alpha}^{psp}) \hat{n}_{i\alpha\sigma} + \sum_{\substack{i\alpha\sigma,i\beta \\ i\alpha \neq i\beta}} (t_{i\alpha,j\beta} + V_{i\alpha,j\beta}^{psp}) \hat{c}_{i\alpha\sigma}^\dagger \hat{c}_{j\beta\sigma} + \\
& + \frac{1}{2} \sum_{\substack{i\alpha\sigma,i\beta\sigma' \\ i\alpha\sigma \neq i\beta\sigma'}} U_{i\alpha,i\beta} \hat{n}_{i\alpha\sigma} \hat{n}_{i\beta\sigma'} - \frac{1}{2} \sum_{\substack{i\alpha\sigma,i\beta \\ i\alpha \neq i\beta}} U_{i\alpha,i\beta}^x \hat{n}_{i\alpha\sigma} \hat{n}_{i\beta\sigma} + \\
& + \frac{1}{2} \sum_{\substack{i\alpha\sigma,j\beta\sigma' \\ i \neq j}} J_{i\alpha,j\beta} \hat{n}_{i\alpha\sigma} \hat{n}_{j\beta\sigma'} - \frac{1}{2} \sum_{\substack{i\alpha\sigma,j\beta \\ i \neq j}} J_{i\alpha,j\beta}^x \hat{n}_{i\alpha\sigma} \hat{n}_{j\beta\sigma} \\
& + \sum_{\substack{i\alpha\sigma,j\beta,k\gamma\sigma' \\ i\alpha \neq j\beta \\ k\gamma\sigma' \neq i\alpha\sigma, j\beta\sigma}} h_{k\gamma,i\alpha j\beta} \hat{n}_{k\gamma\sigma'} \hat{c}_{i\alpha\sigma}^\dagger \hat{c}_{j\beta\sigma} - \sum_{\substack{i\alpha\sigma,j\beta,k\gamma \\ i\alpha \neq j\beta \\ k\gamma \neq i\alpha, j\beta}} h_{k\gamma,i\alpha j\beta}^x \hat{n}_{k\gamma\sigma} \hat{c}_{i\alpha\sigma}^\dagger \hat{c}_{j\beta\sigma} \\
& + \frac{1}{2} \sum_{\substack{i\alpha\sigma,j\beta\sigma \\ k\gamma\sigma' l\delta\sigma' \\ \text{all different}}} O_{l\gamma,k\delta}^{i\alpha,j\beta} \hat{c}_{i\alpha\sigma}^\dagger \hat{c}_{j\beta\sigma'} \hat{c}_{k\gamma\sigma'} \hat{c}_{l\delta\sigma}
\end{aligned} \tag{2.48}$$

where the Latin indexes run in all the atoms of the system, and the Greek ones in the orbitals of each atom, and

$$\begin{aligned}
U_{i\alpha,i\beta} &= \int d^3\mathbf{r} d^3\mathbf{r}' |\phi_{i\alpha}(\mathbf{r})|^2 \frac{1}{|\mathbf{r} - \mathbf{r}'|} |\phi_{i\beta}(\mathbf{r}')|^2 \\
U_{i\alpha,i\beta}^x &= \int d^3\mathbf{r} d^3\mathbf{r}' \phi_{i\alpha}^*(\mathbf{r}) \phi_{i\beta}^*(\mathbf{r}') \frac{1}{|\mathbf{r} - \mathbf{r}'|} \phi_{i\alpha}(\mathbf{r}') \phi_{i\beta}(\mathbf{r}) \\
J_{i\alpha,j\beta} &= \int d^3\mathbf{r} d^3\mathbf{r}' |\phi_{i\alpha}(\mathbf{r})|^2 \frac{1}{|\mathbf{r} - \mathbf{r}'|} |\phi_{j\beta}(\mathbf{r}')|^2 \\
J_{i\alpha,j\beta}^x &= \int d^3\mathbf{r} d^3\mathbf{r}' \phi_{i\alpha}^*(\mathbf{r}) \phi_{j\beta}^*(\mathbf{r}') \frac{1}{|\mathbf{r} - \mathbf{r}'|} \phi_{i\alpha}(\mathbf{r}') \phi_{j\beta}(\mathbf{r}) \\
h_{k\gamma,i\alpha j\beta} &= \int d^3\mathbf{r} d^3\mathbf{r}' |\phi_{k\gamma}(\mathbf{r})|^2 \frac{1}{|\mathbf{r} - \mathbf{r}'|} \phi_{i\alpha}^*(\mathbf{r}') \phi_{j\beta}(\mathbf{r}') \\
h_{k\gamma,i\alpha j\beta}^x &= \int d^3\mathbf{r} d^3\mathbf{r}' \phi_{k\gamma}^*(\mathbf{r}) \phi_{i\alpha}^*(\mathbf{r}') \frac{1}{|\mathbf{r} - \mathbf{r}'|} \phi_{j\beta}(\mathbf{r}') \phi_{k\gamma}(\mathbf{r})
\end{aligned} \tag{2.49}$$

Despite of the formidable form of this hamiltonian, we can give an easy physical interpretation to all of this terms, taking into account the form of the integrals in (2.49). $J_{i\alpha,j\beta}$ ($U_{i\alpha,i\beta}$) is just the electrostatic interaction of the charge cloud in orbital α of atom i with the cloud in orbital β of atom j (i). Note that $U_{i\alpha,i\alpha}$ is the interaction of two electrons in the same orbital with spin up and down (that is usually not well considered in DFT). The term $h_{k\gamma,i\alpha j\beta}$ takes into account how the hopping between $i\alpha$ and $j\beta$ varies due to the interaction with an electron placed in $k\gamma$. Finally, the last

$O_{l\gamma,k\delta}^{i\alpha,j\beta}$ term takes into account the effect on the hopping between $i\alpha\sigma$ and $l\delta\sigma$ due to a transition of an electron going from $k\gamma\sigma'$ to $j\beta\sigma'$

For further discussion we are going to ignore terms of order greater than two ($h_{k\gamma,i\alpha j\beta}^{(x)}$, $O_{l\gamma,k\delta}^{i\alpha,j\beta}$) and the exchange terms ($U_{i\alpha,i\beta}^x$, $J_{i\alpha,j\beta}^x$), since they are not critical neither for theoretical nor for numerical reasons. This way we will be able to see the main physics of this model avoiding large formulas that obscure what we are really doing. For calculations taking into account all the terms see [52, 54].

2.5.1 Local Density LCAO-OO

We can make a local density (LD) approach to our LCAO-OO hamiltonian. We only need to write the energy of the system in terms of the occupation numbers $n_{i\alpha\sigma}$: $E = E[\{n_{i\alpha\sigma}\}]$. We can split this functional in one-electron and many body terms $E = E[\{n_{i\alpha\sigma}\}] = E^{OE}[\{n_{i\alpha\sigma}\}] + E^{MB}[\{n_{i\alpha\sigma}\}]$. Then, using a variation of the Kohn–Sham theorem [51, 52, 55] we can introduce the following effective hamiltonian.

$$\hat{H}^{eff} = \sum_{i\alpha\sigma} (\varepsilon_{i\alpha\sigma} + V_{i\alpha,i\alpha}^{psp} + V_{i\alpha\sigma}^{MB}) \hat{n}_{i\alpha\sigma} + \sum_{i\alpha,j\beta \neq i\alpha\sigma} (t_{i\alpha,j\beta} + V_{i\alpha,j\beta}^{psp}) \hat{c}_{i\alpha\sigma}^\dagger \hat{c}_{j\beta\sigma} \quad (2.50)$$

where

$$V_{i\alpha\sigma}^{MB} = \frac{\partial E^{MB}[\{n_{i\alpha\sigma}\}]}{\partial n_{i\alpha\sigma}} \quad (2.51)$$

Hartree and Exchange Functionals

The problem now is to find a many-body energy functional that depends on orbital occupancies $E^{MB}[\{n_{i\alpha\sigma}\}]$ instead of charge density. The case of the Hartree term can be easily derived just noting that the charge density can be written in function of occupation numbers $\rho(\mathbf{r}) = \sum_{i\alpha\sigma,j\beta\sigma} n_{i\alpha\sigma,j\beta\sigma} \phi_{i\alpha}^*(\mathbf{r}) \phi_{j\beta}(\mathbf{r})$, where $n_{i\alpha\sigma,j\beta\sigma} = \langle \hat{c}_{i\alpha\sigma}^\dagger \hat{c}_{j\beta\sigma} \rangle$, and that the Hartree energy is given by:

$$E_H = \frac{1}{2} \int d^3\mathbf{r} d^3\mathbf{r}' \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \quad (2.52)$$

Introducing the density in terms of the occupation numbers we get:

$$\begin{aligned}
E_H = & \frac{1}{2} \sum_{\substack{i\alpha\sigma, j\beta \\ k\gamma\sigma', l\delta}} O_{k\gamma, l\delta}^{i\alpha, j\beta} n_{i\alpha\sigma, j\beta\sigma} n_{k\gamma\sigma', l\delta\sigma'} \simeq \frac{1}{2} \sum_{\substack{i\alpha\sigma, i\beta\sigma' \\ i\alpha\sigma \neq i\beta\sigma'}} U_{i\alpha, i\beta} n_{i\alpha\sigma} n_{i\beta\sigma'} \\
& + \frac{1}{2} \sum_{\substack{i\alpha\sigma, j\beta, \sigma' \\ i \neq j}} J_{i\alpha, j\beta} n_{i\alpha\sigma} n_{j\beta\sigma'}
\end{aligned} \tag{2.53}$$

and the exchange energy can be written as²

$$\begin{aligned}
E_X = & -\frac{1}{2} \sum_{\substack{i\alpha\sigma, j\beta \\ k\gamma\sigma, l\delta}} O_{k\gamma, l\delta}^{i\alpha, j\beta} n_{i\alpha\sigma, l\delta\sigma} n_{k\gamma\sigma, j\beta\sigma} \simeq -\frac{1}{2} \sum_{\substack{i\alpha\sigma, i\beta \\ \alpha \neq \beta}} U_{i\alpha, i\beta} n_{i\alpha\sigma, i\beta\sigma} n_{i\beta\sigma, i\alpha\sigma} \\
& - \frac{1}{2} \sum_{\substack{i\alpha\sigma, j\beta \\ i \neq j}} J_{i\alpha, j\beta} n_{i\alpha\sigma, j\beta\sigma} n_{j\beta\sigma, i\alpha\sigma}
\end{aligned} \tag{2.54}$$

we need to note here that this is the *exact* exchange (considering $U_{i\alpha, i\beta}^x = J_{i\alpha, j\beta}^x = h_{k\gamma, i\alpha j\beta} = h_{k\gamma, i\alpha j\beta}^x = 0$), not the LD exchange approximation (the functional (2.54) does not depend on $\{n_{i\alpha\sigma}\}$ but on $\{n_{i\alpha\sigma, j\beta\sigma}\}$). In order to get a LD-like exchange approximation we use the following sum rule:

$$\begin{aligned}
\sum_{j\beta} n_{i\alpha\sigma, j\beta\sigma} n_{j\beta\sigma, i\alpha\sigma} &= n_{i\alpha\sigma} \\
\sum_{j\beta \neq i\alpha} n_{i\alpha\sigma, j\beta\sigma} n_{j\beta\sigma, i\alpha\sigma} &= n_{i\alpha\sigma} (1 - n_{i\alpha\sigma})
\end{aligned} \tag{2.55}$$

Using the sum rule (2.55) we can write the exchange energy as:

$$E_X[\{n_{i\alpha\sigma}\}] = -\frac{1}{2} \sum_{i\alpha\sigma} J_{i\alpha\sigma}^{eff} n_{i\alpha\sigma} (1 - n_{i\alpha\sigma}) \tag{2.56}$$

where the effective interaction $J_{i\alpha\sigma}^{eff}$ can be calculated as:

$$J_{i\alpha\sigma}^{eff} = \frac{\sum_{j\beta \neq i\alpha} J_{i\alpha, j\beta} |n_{i\alpha\sigma, j\beta\sigma}|^2 + \sum_{\beta \neq \alpha} U_{i\alpha, i\beta} |n_{i\alpha\sigma, i\beta\sigma}|^2}{\sum_{j\beta \neq i\alpha} |n_{i\alpha\sigma, j\beta\sigma}|^2 + \sum_{\beta \neq \alpha} |n_{i\alpha\sigma, i\beta\sigma}|^2} \tag{2.57}$$

The physical meaning of this equation is very simple: is just the interaction between the electron density at site i $n_{i\alpha\sigma}$, and its exchange hole $(1 - n_{i\alpha\sigma})$ (see the discussion about quasiparticles in Sect. 2.3.1 for the physical origin of this hole).

This form of the exchange energy depends explicitly on the occupation numbers, and can be used as an LD exchange energy. Later in this text (see Sect. 2.7.3) we

² See, for example, [56], Sect. 4.7.

discuss how to use this result to create local orbital hybrid functionals within the FIREBALL code.

Correlation Functional

We can assume correlation effects modify the exchange hole in such a way that it is not localized outside the orbital $i\alpha\sigma$, but a fraction $f_{i\alpha\sigma}$ ($0 < f_{i\alpha\sigma} < 1$) of the hole is transferred back to the site $i\alpha\sigma$. This $f_{i\alpha\sigma}$ is related to the fact that Hartree-Fock approximation (exact exchange and no correlation) does not take into account the screening of the potential (see Sect. 2.3.1). Correlation energy can thus be written as:

$$E_C = -\frac{1}{2} \sum_{i\alpha\sigma} f_{i\alpha\sigma} (U_{i\alpha,i\alpha} - J_{i\alpha\sigma}^{eff}) n_{i\alpha\sigma} (1 - n_{i\alpha\sigma}) \quad (2.58)$$

so the exchange-correlation functional reads as:

$$E_{XC}[\{n_{i\alpha\sigma}\}] = -\frac{1}{2} \sum_{i\alpha\sigma} f_{i\alpha\sigma} U_{i\alpha,i\alpha} n_{i\alpha\sigma} (1 - n_{i\alpha\sigma}) - \sum_{i\alpha\sigma} (1 - f_{i\alpha\sigma}) J_{i\alpha\sigma}^{eff} n_{i\alpha\sigma} (1 - n_{i\alpha\sigma}) \quad (2.59)$$

We have now all the terms of the many-body functional, and can write the effective hamiltonian (2.50) as:

$$\hat{H}^{eff} = \sum_{i\alpha\sigma} (\varepsilon_{i\alpha\sigma} + V_{i\alpha,i\alpha}^{psp} + V_{i\alpha\sigma}^H + V_{i\alpha\sigma}^{xc}) \hat{n}_{i\alpha\sigma} + \sum_{\substack{i\alpha,j\beta \neq i\alpha \\ \sigma}} (t_{i\alpha,j\beta} + V_{i\alpha,j\beta}^{psp}) \hat{c}_{i\alpha\sigma}^\dagger \hat{c}_{j\beta\sigma} \quad (2.60)$$

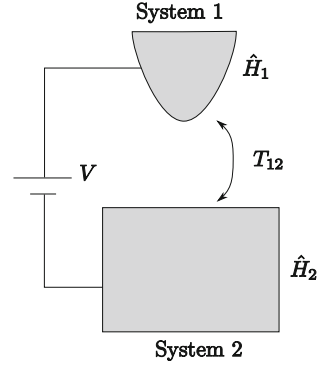
where

$$\begin{aligned} V_{i\alpha\sigma}^H &= \frac{\partial E_H[\{n_{i\alpha\sigma}\}]}{\partial n_{i\alpha\sigma}} \\ V_{i\alpha\sigma}^{xc} &= \frac{\partial E_{XC}[\{n_{i\alpha\sigma}\}]}{\partial n_{i\alpha\sigma}} \end{aligned} \quad (2.61)$$

and the ground state energy:

$$\begin{aligned} E &= \sum_n^{occupied} \varepsilon_n + E_H[\{n_{i\alpha\sigma}\}] + E_{xc}[\{n_{i\alpha\sigma}\}] - \sum_{i\alpha\sigma} (V_{i\alpha\sigma}^H + V_{i\alpha\sigma}^{xc}) \hat{n}_{i\alpha\sigma} \\ &= \sum_n^{occupied} \varepsilon_n - E_H[\{n_{i\alpha\sigma}\}] + E_{xc}[\{n_{i\alpha\sigma}\}] - \sum_{i\alpha\sigma} V_{i\alpha\sigma}^{xc} \hat{n}_{i\alpha\sigma} \end{aligned} \quad (2.62)$$

Fig. 2.3 Scheme of a system partitioned in order to calculate the electrical conductance from 1 to 2



2.6 Calculation of Transport Properties

In this thesis we have analyzed the transport properties of molecular electronic devices at the nanoscale (see Sect. 4.3). A brief introduction to the theory used to calculate these properties will be given in this section.

2.6.1 Current Equation

From a theoretical point of view, let's start with a system that can be divided in two interacting subsystems like the one shown in Fig. 2.3 (this can be the case of an STM, where the tip and sample are the respective subsystems). The Hamiltonian can be written in second quantization as:

$$\hat{H} = \hat{H}_1 + \hat{H}_2 + \hat{H}_{1,2} \quad (2.63)$$

where

$$\begin{aligned} \hat{H}_1 &= \sum_{ij} \varepsilon_i \hat{n}_i + t_{ij} (\hat{c}_i^\dagger \hat{c}_j + \hat{c}_j^\dagger \hat{c}_i) \\ \hat{H}_2 &= \sum_{\alpha\beta} \varepsilon_\alpha \hat{n}_\alpha + t_{\alpha\beta} (\hat{c}_\alpha^\dagger \hat{c}_\beta + \hat{c}_\beta^\dagger \hat{c}_\alpha) \\ \hat{H}_{1,2} &= \sum_{i\alpha} t_{i\alpha} (\hat{c}_i^\dagger \hat{c}_\alpha + \hat{c}_\alpha^\dagger \hat{c}_i) \end{aligned} \quad (2.64)$$

(Latin indexes run over the orbitals in system 1 and Greek ones over orbitals in system 2).

Now consider that we apply an external potential V to one of the electrodes. Now an irreversible current will flow from one system to the other. In order to calculate the

current through the system we will need non-equilibrium techniques. We are going to use Keldysh formalism, that is explained in appendix Sect. A.2.4, to get the current through the system. The interaction hamiltonian $\hat{H}_{1,2}$ will be treated as a perturbation of $\hat{H}_0 = \hat{H}_1 + \hat{H}_2$ + external potential. One may think that is more “physical” to consider the perturbation as the external potential, but calculations from this point of view will be more complex, and no current will flow neither there is not external potential nor interaction between subsystems.

When we add the perturbation $\hat{H}_{1,2}$, we can calculate the current that appears using the Keldysh formalism. First of all, we are going to deduce the form of the current operator \hat{J} in second quantization. A good guess is that it will be proportional to a product of an operator that creates one electron in subsystem 2 and annihilates it on subsystem 1, that is $\hat{J}_{\alpha i} \propto \hat{c}_{\alpha}^{\dagger} \hat{c}_i$. We need to consider inverse current from subsystem 2 to 1, so the form of the current operator in second quantization will be:

$$\hat{J}_{\alpha i} = \lim_{\tau \rightarrow 0} A_{\alpha i} \hat{c}_{\alpha}^{\dagger}(t + \tau) \hat{c}_i(t) - A_{i\alpha} \hat{c}_i^{\dagger}(t + \tau) \hat{c}_{\alpha}(t) \quad (2.65)$$

In order to know the value of $A_{i\alpha}$ we will use the continuity equation:

$$\frac{\partial \hat{\rho}_{ii}}{\partial t} = \sum_{\alpha} \hat{J}_{\alpha i}; \quad \text{where} \quad \hat{\rho}_{ii} = \hat{c}_i^{\dagger}(t) \hat{c}_i(t) = \lim_{\tau \rightarrow 0} \hat{c}_i^{\dagger}(t + \tau) \hat{c}_i(t) \quad (2.66)$$

on the other hand, making use of the equation of motion of the operator $\hat{\rho}_{ii}$ (Eq. A.10) we can find that:

$$\frac{\partial \hat{\rho}_{ii}}{\partial t} = -i/\hbar [\hat{\rho}_{ii}, \hat{H}] = \lim_{\tau \rightarrow 0} \sum_{\alpha} -i/\hbar (t_{\alpha i} \hat{c}_{\alpha}^{\dagger}(t + \tau) \hat{c}_i(t) - t_{i\alpha} \hat{c}_i^{\dagger}(t + \tau) \hat{c}_{\alpha}(t)) \quad (2.67)$$

So comparing equations (2.65) and (2.67), we deduce that $A_{\alpha i} = -it_{\alpha i}/\hbar$. Now, in order to know the value of the current from system 1 to system 2 at the ground (non-equilibrium) perturbed state $|\Psi_{0,H}\rangle$ we need to calculate the following sandwich:

$$\begin{aligned} I(t) &= e \sum_{i\alpha} \langle \Psi_{0,H} | \hat{J}_{\alpha i} | \Psi_{0,H} \rangle \\ &= e \lim_{\tau \rightarrow 0} \sum_{i\alpha} -i/\hbar (t_{\alpha i} \langle \Psi_{0,H} | \hat{c}_{\alpha}^{\dagger}(t + \tau) \hat{c}_i(t) | \Psi_{0,H} \rangle - t_{i\alpha} \langle \Psi_{0,H} | \hat{c}_i^{\dagger}(t + \tau) \hat{c}_{\alpha}(t) | \Psi_{0,H} \rangle) \\ &= e \lim_{\tau \rightarrow 0} \sum_{i\alpha} t_{\alpha i} G^{+-}(i, t + \tau, \alpha, t) - t_{i\alpha} G^{+-}(\alpha, t + \tau, i, t) \\ &= e \lim_{\tau \rightarrow 0} \text{Tr}[\mathbb{T}_{21} \mathbb{G}_{12}^{+-}(t + \tau, t) - \mathbb{G}_{21}^{+-}(t + \tau, t) \mathbb{T}_{12}] \end{aligned} \quad (2.68)$$

where we have used the matrix form of the Green-Keldysh function (see Appendix A.2.4).

2.6.2 Stationary Current

Usually we are interested in the stationary regime. In that case, G^{+-} only depends on time difference τ so we can work with the Fourier transform:

$$\lim_{\tau \rightarrow 0} G^{+-}(i, \alpha, \tau) = \frac{1}{h} \lim_{\tau \rightarrow 0} \int_{-\infty}^{\infty} dE G^{+-}(i, \alpha, E) e^{iE\tau/\hbar} = \frac{1}{h} \int_{-\infty}^{\infty} G^{+-}(i, \alpha, E) dE \quad (2.69)$$

If we rewrite (2.68) in the energy space, and we consider that there is no spin dependence on the hamiltonian we can just add a factor 2 and we get [57]:

$$I = \frac{2e}{h} \int_{-\infty}^{\infty} dE \text{Tr}[\mathbb{T}_{21} \mathbb{G}_{12}^{+-}(E) - \mathbb{G}_{21}^{+-}(E) \mathbb{T}_{12}] \quad (2.70)$$

In our case, we are interested in rewrite (2.70) as a function of the unperturbed green functions of the subsystems ($G_{1,2}^0$). Using Dyson equation (A.48) it can be done easily getting [58, 59]:

$$I = \frac{4\pi e^2}{h} \int_{-\infty}^{\infty} dE \text{Tr}[\rho_{22}(E) \mathbb{D}_{22}'(E) \mathbb{T}_{21} \rho_{11}(E - eV) \mathbb{D}_{11}^a(E - eV) \mathbb{T}_{12}] (f_1(E - eV) - f_2(E)) \quad (2.71)$$

where

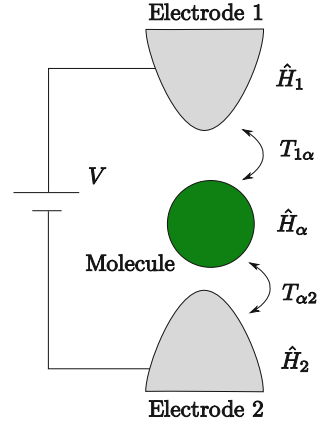
$$\begin{aligned} \rho_{22}(E) &= -\frac{1}{\pi} \text{Im}[\mathbb{G}_{22}^{0,r}(E)], \quad \rho_{11}(E - eV) = -\frac{1}{\pi} \text{Im}[\mathbb{G}_{11}^{0,r}(E - eV)] \\ \mathbb{D}_{11}^a(E - eV) &= [\mathbb{I} - \mathbb{T}_{12} \mathbb{G}_{22}^{0,a}(E) \mathbb{T}_{21} \mathbb{G}_{11}^{0,a}(E - eV)]^{-1} \\ \mathbb{D}_{22}'(E) &= [\mathbb{I} - \mathbb{T}_{21} \mathbb{G}_{11}^{0,r}(E - eV) \mathbb{T}_{12} \mathbb{G}_{22}^{0,r}(E)]^{-1} \\ f_1(E - eV) &= 1 / \left(\exp\left(\frac{E - eV}{k_B T}\right) + 1 \right), \quad f_2(E) = 1 / \left(\exp\left(\frac{E}{k_B T}\right) + 1 \right) \end{aligned} \quad (2.72)$$

We remember here that the voltage was included in the unperturbed subsystems; as it is shown explicitly in (2.71).

The denominators $\mathbb{D}_{22}'(E)$ and $\mathbb{D}_{11}^a(E - eV)$ can be seen as renormalizers of the hopping matrices: $\mathbb{T}_{12}' = \mathbb{D}_{11}^a(E - eV) \mathbb{T}_{12}$, and they take into account the backscattering that tends to saturate the current. This interpretation is clear if we make the series expansion of the denominator:

$$\mathbb{T}_{12}' = \mathbb{D}_{11}^a \mathbb{T}_{12} = \mathbb{T}_{12} + \mathbb{T}_{12} \mathbb{G}_{22}^a \mathbb{T}_{21} \mathbb{G}_{11}^a \mathbb{T}_{12} + \dots \quad (2.73)$$

Fig. 2.4 Scheme of a system divided in three parts in order to calculate the electrical conductance from 1 to 2 (Color figure online)



However, in this work we are interested on differential conductance $g = dI/dV$, in particular when $V \rightarrow 0$. We will consider the electronic temperature as zero (that is a good approximation in metals at room temperature). Using (2.71) we get for that particular case.

$$g = \left(\frac{dI}{dV} \right)_{V \rightarrow 0} = \frac{4\pi e^2}{\hbar} \text{Tr}[\rho_{22}(E_F) \mathbb{T}'_{21} \rho_{11}(E_F) \mathbb{T}'_{12}] \quad (2.74)$$

This conductance can be interpreted as a coherent sum of conductance channels. The analogy with Landauer formalism, based on conductance channels [60] is clear if we write (2.74) in the form

$$g = \frac{4\pi e^2}{\hbar} \text{Tr}[\mathbb{t} \mathbb{t}^+] \quad (2.75)$$

where $\mathbb{t} = 2\pi \rho_{11}^{1/2}(E_F) \mathbb{T}'_{12} \rho_{22}^{1/2}(E_F)$ is the transmission matrix of the system. In order to know the character of different channel and the contribution of orbitals to that channel we can just diagonalize $\mathbb{t} \mathbb{t}^+$.

2.6.3 Conductance with Two Electrodes

However, for some systems (like a C_{60} molecule between two gold tips, studied in Sect. 4.3), it is more natural to divide the system in three subsystems instead of only two. This option, that was not available in the standard conductance module of FIREBALL has been implemented during this thesis. In Fig. 2.4 we can see the division of such that system.

In that case we can use previous results, if we consider the system $(\alpha + 2)$ as the previous system 2. In order to do that, we need first to calculate ρ and \mathbb{G} of the $(\alpha + 2)$ system. The density of states (DOS) is [20]:

$$\rho_{\alpha\alpha}^0 = \mathbb{G}_{\alpha\alpha}^{r,0} \mathbb{T}_{\alpha 2} \rho_{22}^0 \mathbb{T}_{2\alpha} \mathbb{G}_{\alpha\alpha}^{a,0} \quad (2.76)$$

with (2.76) and (2.74) and taking into account that $\mathbb{T}'_{12} = [\mathbb{I} - \mathbb{T}_{12} \mathbb{G}_{22}^{0,a} \mathbb{T}_{21} \mathbb{G}_{11}^{0,a}]^{-1} \times \mathbb{T}_{12} = \mathbb{T}_{12} [\mathbb{I} - \mathbb{G}_{22}^{0,a} \mathbb{T}_{21} \mathbb{G}_{11}^{0,a} \mathbb{T}_{12}]^{-1}$ we get:

$$g = \frac{4\pi e^2}{\hbar} \text{Tr}[\mathbb{T}_{\alpha 1} \rho_{11}^0 \mathbb{T}_{1\alpha} [\mathbb{I} - \mathbb{G}_{\alpha\alpha}^{r,0} \mathbb{T}_{\alpha 1} \mathbb{G}_{11}^{r,0} \mathbb{T}_{1\alpha}]^{-1} \rho_{\alpha\alpha}^0 [\mathbb{I} - \mathbb{T}_{\alpha 1} \mathbb{G}_{11}^{a,0} \mathbb{T}_{1\alpha} \mathbb{G}_{\alpha\alpha}^{a,0}]^{-1}] \quad (2.77)$$

and realizing that

$$\mathbb{G}_{\alpha\alpha}^r = [\mathbb{I} - \mathbb{G}_{\alpha\alpha}^{r,0} \mathbb{T}_{\alpha 1} \mathbb{G}_{11}^{r,0} \mathbb{T}_{1\alpha}]^{-1} \mathbb{G}_{\alpha\alpha}^{r,0} = [(\mathbb{G}_{\alpha\alpha}^{r,0})^{-1} - \mathbb{T}_{\alpha 1} \mathbb{G}_{11}^{r,0} \mathbb{T}_{1\alpha}]^{-1} \quad (2.78)$$

we can rewrite (2.77) as:

$$g = \frac{4\pi e^2}{\hbar} \text{Tr}[\mathbb{T}_{\alpha 1} \rho_{11}^0 \mathbb{T}_{1\alpha} \mathbb{G}_{\alpha\alpha}^r \mathbb{T}_{\alpha 2} \rho_{22}^0 \mathbb{T}_{2\alpha} \mathbb{G}_{\alpha\alpha}^a] \quad (2.79)$$

Let's see the physics of this equation. First of all, if we define $\Sigma_{\alpha\alpha}^{(i)} = \mathbb{T}_{\alpha i} \rho_{ii}^0 \mathbb{T}_{i\alpha}$ we get:

$$g = \frac{4\pi e^2}{\hbar} \text{Tr}[\Sigma_{\alpha\alpha}^{(1)} \mathbb{G}_{\alpha\alpha}^r \Sigma_{\alpha\alpha}^{(2)} \mathbb{G}_{\alpha\alpha}^a] \quad (2.80)$$

that is just the Fisher-Lee equation for the electrical conductance [61]. We can also define a effective hopping $\mathbb{T}'_{12} = \mathbb{T}_{1\alpha} \mathbb{G}_{\alpha\alpha}^r \mathbb{T}_{\alpha 2}$, and introduce it in (2.79). Using the cyclic property of the trace we recover (2.74). Finally, we can connect this with the Landauer formalism [60] defining:

$$\mathfrak{t} = 2\pi \rho_{11}^{1/2} \mathbb{T}'_{12} \rho_{22}^{1/2} = 2\pi \rho_{11}^{1/2} \mathbb{T}_{1\alpha} \mathbb{G}_{\alpha\alpha}^r \mathbb{T}_{\alpha 2} \rho_{22}^{1/2} \quad (2.81)$$

We have checked that the conductance does not depend too much on the division of the system (in two or three) as it should be, because the physical conductance should not depend on how we calculate it.

2.7 Corrections of DFT Deficiencies

Although DFT in its LDA and GGA approximation is usually reliable enough for most applications, its well known failures make its application meaningless for some systems unless we correct these problems. Here we have focused in metal/organic

interfaces; so the significant deficiencies of DFT-LDA (and GGA) we have to overcome are the absence of Van der Waals (vdW) interaction in these functionals and the underestimation of the gap (the last one is a failure of DFT itself, because it is only a ground state theory). In this section we are going to describe the techniques developed in this thesis to deal with these deficiencies.

2.7.1 Weak Chemical and Van der Waals Interaction

Here we adapt the discussion about long-range forces in [62] (Copyright 2011 American Institute of Physics).

Weakly interacting systems, such as some metal/organic interfaces like benzene/Au(111) and TTF/Au(111), cannot be characterized accurately in a standard DFT formalism. The reason is that the vdW interaction is nonlocal and long-range, while exchange-correlation functionals in standard DFT methods are (semi)local and short range, with a typical exponential decay (as stated in Sect. 2.3.2). Due to the importance of this interaction (not only for interfaces but also for carbon nanotubes or biological systems, for instance), a lot of effort has been directed in recent years to develop a practical DFT approach that properly takes into account vdW interactions for these systems (see, e.g. references [63–68]).

In order to accurately determine the vdW interaction between two subsystems (the metal and the adsorbed molecules, in our thesis) we have used here an extension of the LCAO- S^2 +vdW formalism, previously developed for noble gases and graphitic materials [69–71]. We consider that the exchange and correlation is correctly taken into account within each subsystem (metal and organic molecule) but the LDA-like exchange and correlation between subsystems is not well considered, so we take it away, and introduce later with a better approximation. That means, in a first step we consider:

$$V_{xc}[\rho_M + \rho_O] = V_{xc}[\rho_M] + V_{xc}[\rho_O] \quad (2.82)$$

where ρ_M and ρ_O are the electron density of the metal and organic molecule respectively. So we define an electron density for each subsystem and approximate the LDA exchange-correlation energy as the sum of the exchange-correlation energies for the different subsystems. This can be done easily within McWEDA scheme.

After that we introduce the exchange correlation between subsystems in a way that takes into account the dispersive forces. In order to reproduce Van der Waals energy we have used the following simple but correct atom-atom form:

$$E_{vdW}(R) = -f_D(R)C_6/R^6 \quad (2.83)$$

where R is the distance between atoms, and the factor $f_D(R)$ eliminates the vdW contribution for short distances [65, 66, 72]. We are going to use two different damping factors common in literature. The first one has the form $f_D(R) = 1 - \exp(-\alpha(R/R_c)^8)$ [65], where R_c is the sum of covalent radii and $\alpha = 7.5 \times 10^{-4}$ is

Table 2.1 LDA and exact gaps for organic molecules studied in this thesis and some inorganic semiconductors

Gap/molecule	Benzene	C ₆₀	TTF	PTCDA	Si	Ge
LDA gap	4.7	1.6	2.6	1.6	0.55	0
Exact	10.39	4.95	6.3	4.7	1.17	0.74

chosen to reproduce the c lattice constant of graphite. The second one has the form $f_D(R) = 1/(1 + \exp(-d(R/R_{vdW}) - 1))$ [66] where $d = 20$ and R_{vdW} is the sum of Van der Waals radii of the elements under consideration [66]. A similar approach although with different radii can be found in [72]. The choice of the damping factor $f_D(R)$ changes less than 0.2 \AA the value of the adsorption distance of molecules [62, 73]. However the adsorption energy is clearly affected (changes of around 100 % are found). But as we are interested in electronic structure properties in this thesis (where only distance between both subsystems is important) and as we have used simple basis for our calculations (so adsorption energies are not very reliable), we consider that this method has a good balance between accuracy and computational cost for our needs.

2.7.2 Underestimation of the Gap

The obtention of an accurate semiconductor gap is critical to understand the metal/organic interfaces as will be shown in Chap. 3. As stated before, DFT is unable to give a correct gap, even if we know the exact exchange-correlation functional, because it is a ground state theory. However, in systems where electrons are not strongly correlated, the quasiparticle image is still valid and we can consider that the distance between the eigenvalue of the highest occupied molecular orbital (HOMO) and the eigenvalue of the lowest unoccupied molecular orbital (LUMO) are a first approximation for the real transport gap.

Unfortunately, this approximation is not good even for systems with low correlation. In Table 2.1 we can see the difference between the LDA gaps and the experimental ones. In molecules, the transport gap is considered as the difference between ionization (IE) and affinity (A) energies $E_g^t = IE - A$ for the experimental case and as $E_g = \varepsilon_{LUMO} - \varepsilon_{HOMO}$ for LDA.

Table 2.1 shows that the difference between LDA and experimental gap can be more than 100 % (and even predict that some well known semiconductors are metals). The main reason for this underestimation is the fact that this naive approximation does not take into account the SIC, due to the interaction of the new electron (hole) in the LUMO (HOMO) and the pre-existing charge (Fig. 2.5). In the next subsection we present some corrections developed during this thesis. They rely on a parameter (β in hybrid functionals, U in scissor operator) that cannot be calculated in a straightforward manner. Moreover, in metal/organic interfaces there is an additional effect that

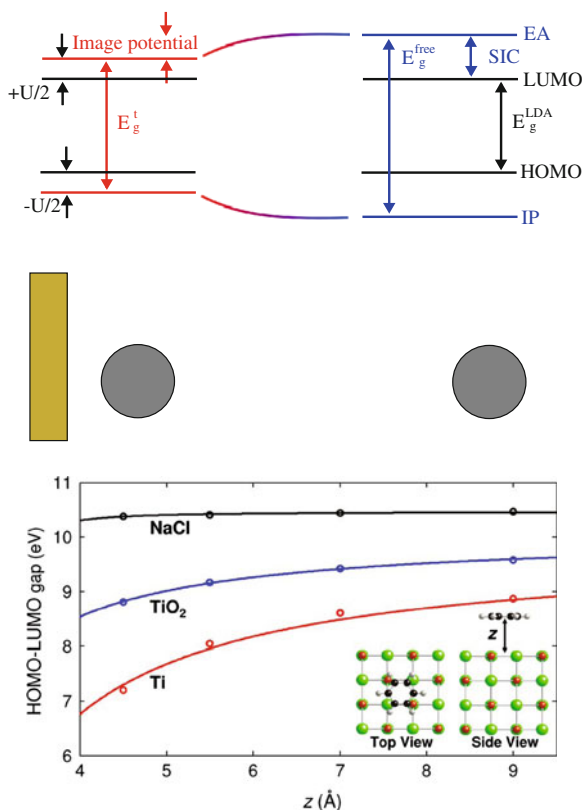


Fig. 2.5 *Up* Scheme of the different effects that determine the actual gap of an organic molecule over a surface. The LDA gap gives an underestimated and surface distance independent gap. At large distances, SIC opens the gap and gives the measured gas phase gap. However, when the molecule approaches to a metallic surface, the effect of the image potential tends to reduce the organic gap. *Down* Dependence of the benzene gap with distance when it is approaching different surfaces. Reprinted from [74] Copyright (2009) by the American Physical Society (Color figure online)

does not appear in bulk semiconductors or gas phase molecules: the image potential. This can be understood classically considering that the introduction of a charge in a molecule over a metal (creating an ion) will have, as a response, an image charge inside the metal in order to get a constant potential in the metal surface, disturbing the molecular spectra (Fig. 2.5). In Chaps. 3 and 4, we will show an easy but reliable way to calculate the gap taking into account these effects, and then getting a value for these unknown parameters (β and U).

2.7.3 Hybrid HF-LDA Functional

In this thesis we have developed and introduced in FIREBALL an hybrid HF-LDA functional (see Sect. 5.6 and [75] for a practical use of it) based on the LCAO-OO approach. Hybrid functionals have been mentioned at the end of Sect. 2.3.2, but here we present a large discussion.

Standard hybrid hamiltonians are based on the adiabatic connection [76, 77]. The derivation of these kind of functionals is based on “turning on” adiabatically the electron-electron interaction. Let’s consider the following many-electron hamiltonian:

$$\hat{H}_\lambda = \hat{T} + \hat{V}_{ext,\lambda} + \lambda \hat{V}_{ee} \quad (2.84)$$

where $0 \leq \lambda \leq 1$ and $\hat{V}_{ext,\lambda}$ is an external potential that depends on λ . When $\lambda = 1$ we obtain the physical system, so $\hat{V}_{ext,1} = \hat{V}_{ion}$. For every $0 \leq \lambda < 1$, \hat{H}_λ gives the exact ground state electronic density of the physical system (but not the exact physical wave function). If we denote $|\psi_\lambda\rangle$ as the normalized antisymmetric wavefunction that minimizes the expectation value of $\hat{T} + \lambda \hat{V}_{ee}$, the exchange-correlation energy of the physical system is given by:

$$E_{xc}[\rho(\mathbf{r})] = \int_0^1 E_{xc,\lambda}[\rho(\mathbf{r})] d\lambda \text{ where } E_{xc,\lambda}[\rho(\mathbf{r})] = \langle \psi_\lambda | \hat{V}_{ee} | \psi_\lambda \rangle - E_H[\rho(\mathbf{r})] \quad (2.85)$$

Becke [78] considered that integral (2.85) can be calculated using trapezoidal rule, and he took the following energies for the edge points: The HF exact exchange energy when $\lambda = 0$ and the LDA exchange correlation energy when $\lambda = 1$. So in a first approximation:

$$E_{XC} \simeq \frac{1}{2} E_X^{exact} + \frac{1}{2} E_{XC}^{LDA} \quad (2.86)$$

Better results can be obtained if we consider other values of the fraction of HF exchange and LDA exchange-correlation. By the mean value theorem, there exists a value β that makes the following equation *exact*:

$$E_{XC} = \beta E_X^{exact} + (1 - \beta) E_{XC}^{\lambda=1} \quad (2.87)$$

Our approach, although leads to very similar results is based on a different assumption. In the LCAO-OO method, the local density-like $E_X^{LD}[\{n_{i\alpha\sigma}\}]$ and exact-like $E_X^{HF}[\{n_{i\alpha\sigma}, j\beta\sigma}\}]$ form of the exchange functional are the same, as long as $J_{i\alpha\sigma}^{eff}$ have been calculated using the formula (2.57), so $E_{XC} = \beta E_X^{HF} + (1 - \beta) E_{XC}^{LD}$ is exact for all β . But this is no longer true for the functional derivatives (i.e. potentials), so the exchange potential $V_X = \beta V_X^{HF} + (1 - \beta) V_X^{LD}$ does depend on the value of β . In appendix B is pointed out that the size of the gap depends critically on the exchange potential, so the value of β can be used to determine it.

In our case β has been tuned to obtain $E_g = E_g^{LDA} + U$ where U is calculated following the ideas of Sect. 4.2.1. The exchange-correlation potential is derived using Eqs. (2.54), (2.56) and (2.61). We obtain:

$$\begin{aligned} (V_X^{LD-OO})_{i\alpha\sigma,j\beta\sigma} &= -J_{i\alpha\sigma}^{eff} \left(\frac{1}{2} - n_{i\alpha\sigma} \right) \delta_{i\alpha,j\beta} \\ (V_X^{HF-OO})_{i\alpha\sigma,j\beta\sigma} &= -U_{i\alpha,i\beta} n_{i\alpha\sigma,i\beta\sigma} \delta_{i,j} - J_{i\alpha,j\beta} n_{i\alpha\sigma,j\beta\sigma} \end{aligned} \quad (2.88)$$

Implementation in FIREBALL

The FIREBALL method does not calculate exchange and correlation using LCAO-OO but using McWEDA, that is an approximation to the LDA exchange and correlation. So in order to take the LDA exchange away we have just subtracted to V_{XC}^{McWEDA} the V_X^{LD-OO} part (Eq. 2.88). Then we add V_X^{HF-OO} , so the exchange-correlation matrix elements are:

$$(V_{XC}^{hybrid})_{i\alpha\sigma,j\beta\sigma} = (V_{XC}^{McWEDA})_{i\alpha\sigma,j\beta\sigma} - \beta (V_X^{LD-OO})_{i\alpha\sigma,j\beta\sigma} + \beta (V_X^{HF-OO})_{i\alpha\sigma,j\beta\sigma} \quad (2.89)$$

The values of $U_{i\alpha,i\beta}$ and $J_{i\alpha,j\beta}$ have been calculated using the program *gcluster* [52].

Molecule Interacting with a Metal

The Hartree-Fock approximation does not usually work properly on metals, so in the case of a molecule interacting with a metal, the former will be treated via hybrid functional, while the latter via standard DFT (that means that the matrix elements $V_{i\alpha,j\beta}^{XC}$, where i or j (or both) are index of metallic atoms, will be calculated with standard McWEDA LDA approximation).

It is necessary to take into account that, for a molecule interacting with a surface, the sum rule (2.55) is no longer true, because only a fraction α of the exchange-correlation hole is inside the molecule, so the sum rule needs to be written now as:

$$\sum_{\substack{j\beta; i \neq j \\ i, j \in \text{molecule}}} n_{i\alpha\sigma,j\beta\sigma} n_{j\beta\sigma,i\alpha\sigma} = \alpha_{i\alpha\sigma} n_{i\alpha\sigma} (1 - n_{i\alpha\sigma}) \quad (2.90)$$

So E_X^{LD-OO} and V_X^{LD-OO} reads now as:

$$\begin{aligned}
E_X^{LD-OO}[\{n_{i\alpha\sigma}\}] &= -\frac{1}{2} \sum_{i\alpha\sigma} J_{i\alpha\sigma}^{eff} \alpha_{i\alpha\sigma} n_{i\alpha\sigma} (1 - n_{i\alpha\sigma}) \\
(V_X^{LD-OO})_{i\alpha\sigma, j\beta\sigma} &= -\alpha_{i\alpha\sigma} J_{i\alpha\sigma}^{eff} \left(\frac{1}{2} - n_{i\alpha\sigma}\right) \delta_{i\alpha, j\beta}
\end{aligned} \tag{2.91}$$

The V_X^{HF-OO} part remains unchanged (we didn't use the sum rule (2.55) to deduce it).

As we will see in Chap. 5 the value of α is very high in the case of aromatic compounds adsorbed on metals. For pentacene/Au(111) this value is greater than 0.9, while in first tests in benzene/Au(111) $\alpha \sim 0.7$ –0.9. These values depends on the σ or π character of the orbitals (the π orbitals have a lower α due to its greater interaction with the metal surface).

2.7.4 Koopmans' Shift

In this section we present another method to correct the underestimation to the LDA gap. This method relies on Koopmans' theorem [79] and estimates the SIC error.

The actual transport energy gap (E_g^t) is the difference between the ionization (IE) and affinity (A) energies:

$$\begin{aligned}
IE &= E[N - 1] - E[N] \\
A &= E[N] - E[N + 1] \\
E_g^t &= IE - A = E[N + 1] + E[N - 1] - 2E[N]
\end{aligned} \tag{2.92}$$

If we consider $-\varepsilon_{HOMO}$ (the energy of the HOMO) as IE and $-\varepsilon_{LUMO}$ (the energy of the LUMO) as A following the spirit of Koopmans' theorem [79], we obtain the underestimated DFT gap. In order to correct it we have to take into account somehow the SIC. Here we consider that this electron (hole) is described by the Kohn–Sham LUMO (HOMO) eigen-wavefunction, neglecting the electron relaxation effects. This self-interaction is introduced as a correction for the LUMO (HOMO) eigen-energy δA (δIE).

In the LCAO-OO scheme, the orbital occupancies of the $N + 1$ ($N - 1$) system can be computed from the N occupancies, neglecting electron relaxation, as:

$$\begin{aligned}
n_{i\alpha\sigma}^{N+1} &= n_{i\alpha\sigma}^N + \delta n'_{i\alpha\sigma}; n_{i\alpha\sigma}^{N-1} = n_{i\alpha\sigma}^N - \delta n_{i\alpha\sigma} \quad \text{where} \\
\delta n'_{i\alpha\sigma} &= |\langle \phi_{i\alpha} | LUMO_N \rangle|^2; \delta n_{i\alpha\sigma} = |\langle \phi_{i\alpha} | HOMO_N \rangle|^2
\end{aligned} \tag{2.93}$$

For the sake of simplicity we are going to focus on the change of electron affinity due to the extra electron, and consider its spin is upwards. It is just [80]:

$$\begin{aligned}
A = E[N] - E[N + 1] = & \varepsilon_{N+1}^{o.e.} + \frac{1}{2} \sum_{\substack{\alpha, \beta \\ \alpha \neq \beta}} U_{i\alpha, i\beta} (n_{i\alpha\uparrow}^N + \delta n'_{i\alpha\uparrow}) (n_{i\beta\uparrow}^N + \delta n'_{i\beta\uparrow}) + \\
& + \frac{1}{2} \sum_{\alpha, \beta} U_{i\alpha, i\beta} (n_{i\alpha\uparrow}^N + \delta n'_{i\alpha\uparrow}) n_{i\beta\downarrow}^N + \frac{1}{2} \sum_{\substack{\alpha, \beta \\ i \neq j}} J_{i\alpha, j\beta} (n_{i\alpha\uparrow}^N + \delta n'_{i\alpha\uparrow}) (n_{j\beta\uparrow}^N + \delta n'_{j\beta\uparrow}) + \\
& + \frac{1}{2} \sum_{\substack{\alpha, \beta \\ i \neq j}} J_{i\alpha, j\beta} (n_{i\alpha\uparrow}^N + \delta n'_{i\alpha\uparrow}) n_{j\beta\downarrow}^N - \frac{1}{2} \sum_{i\alpha} J_{i\alpha\uparrow}^{eff} (n_{i\alpha\uparrow}^N + \delta n'_{i\alpha\uparrow}) (1 - n_{i\alpha\uparrow}^N - \delta n'_{i\alpha\uparrow}) \\
& - \frac{1}{2} \sum_{i\alpha\uparrow} f_{i\alpha\uparrow} (U_{i\alpha, i\alpha} - J_{i\alpha\uparrow}^{eff}) (n_{i\alpha\uparrow}^N + \delta n'_{i\alpha\uparrow}) (1 - n_{i\alpha\uparrow}^N - \delta n'_{i\alpha\uparrow}) \\
& - \left[-\frac{1}{2} \sum_{\substack{\alpha, \beta \sigma \\ i\alpha\uparrow \neq i\beta\sigma}} U_{i\alpha, i\beta} n_{i\alpha\uparrow}^N n_{i\beta\sigma}^N + \frac{1}{2} \sum_{\substack{\alpha, \beta \\ i \neq j}} J_{i\alpha, j\beta} n_{i\alpha\uparrow}^N n_{j\beta\sigma}^N \right. \\
& \left. + \frac{1}{2} \sum_{i\alpha} J_{i\alpha\uparrow}^{eff} n_{i\alpha\uparrow}^N (1 - n_{i\alpha\uparrow}^N) + \frac{1}{2} \sum_{i\alpha} f_{i\alpha\uparrow} (U_{i\alpha, i\alpha} - J_{i\alpha\uparrow}^{eff}) n_{i\alpha\uparrow}^N (1 - n_{i\alpha\uparrow}^N) \right]
\end{aligned} \tag{2.94}$$

we can group terms that, that are linear in $\delta n'_{i\alpha\uparrow}$, and quadratic in $\delta n'_{i\alpha\uparrow}$. With some math we obtain:

$$A = E[N] - E[N + 1] = \varepsilon_{N+1}^{o.e.} + \frac{\partial(E_H + E_X)}{\partial n_{i\alpha\uparrow}} \delta n'_{i\alpha\uparrow} + \delta A[O(\delta n'^2_{i\alpha\uparrow})] \tag{2.95}$$

It is obvious that the terms linear in $\delta n'_{i\alpha\uparrow}$ are already taken into account on ε_{LUMO}^{DFT} . So the first non-vanishing correction terms are of second order in $\delta n_{i\alpha\uparrow}$. These values for the ionization ($IE = -\varepsilon_{HOMO} + \delta IE$) and affinity ($A = -\varepsilon_{LUMO} + \delta A$) can be written as [80]:

$$\begin{aligned}
\delta IE = & \frac{1}{2} \sum_{i \neq j} J_{i\alpha, j\beta} \delta n_{i\alpha\uparrow} \delta n_{j\beta\uparrow} + \frac{1}{2} \sum_{\alpha \neq \beta} U_{i\alpha, i\beta} \delta n_{i\alpha\uparrow} \delta n_{i\beta\uparrow} \\
& + \frac{1}{2} \sum_{i\alpha} J_{i\alpha}^{eff} \delta n_{i\alpha\uparrow}^2 + \frac{1}{2} \sum_{i\alpha} f_{i\alpha} (U_{i\alpha, i\alpha} - J_{i\alpha}^{eff}) \delta n_{i\alpha\uparrow}^2 \\
\delta A = & -\frac{1}{2} \sum_{i \neq j} J_{i\alpha, j\beta} \delta n'_{i\alpha\uparrow} \delta n'_{j\beta\uparrow} - \frac{1}{2} \sum_{\alpha \neq \beta} U_{i\alpha, i\beta} \delta n'_{i\alpha\uparrow} \delta n'_{i\beta\uparrow} \\
& - \frac{1}{2} \sum_{i\alpha} J_{i\alpha}^{eff} \delta n'^2_{i\alpha\uparrow} - \frac{1}{2} \sum_{i\alpha} f_{i\alpha} (U_{i\alpha, i\alpha} - J_{i\alpha}^{eff}) \delta n'^2_{i\alpha\uparrow}
\end{aligned} \tag{2.96}$$

It has been found that this approximation gives good results [80, 81] for the gaps of a variety of π -conjugated organic molecules, in particular, the results are better for larger molecules, due to electron relaxation effects become less important.

This Koopmans' shift can be used not only for the HOMO and LUMO but for all the molecular levels, we only need to change in (2.93) $\delta n_{i\alpha\sigma} = |\langle \phi_{i\alpha} | HOMO_N \rangle|^2$ by $\delta n_{i\alpha\sigma} = |\langle \phi_{i\alpha} | LEVEL_N \rangle|^2$ where $|LEVEL_N\rangle$ is the eigen-wavefunction of the level we want to correct.

So the Koopmans' shift is a good way to improve the underestimation of DFT gap. In particular we can combine it with the scissor operator (see next section) in order to get an improved hamiltonian to calculate, among other things, transport or density of states.

2.7.5 Scissor Operator

We have shown how the Koopmans' shift can deal with the underestimation of the DFT gap, including self energy terms. In Sects. 3.6 and 4.2.1 we will see a method to estimate the gap of our molecules interacting with a metal surface. In this thesis, in order to obtain this corrected HOMO-LUMO gap in our hamiltonian (and play with the relative alignment between organic molecules and metals, as in Chap. 5) we have used the scissor operator. If $|\mu_i\rangle$ ($|v_i\rangle$) are the empty (occupied) molecular orbitals of the isolated, but deformed, molecule (with the actual geometry of the molecule on the surface) then the scissor operator read as:

$$\hat{O}^{scissor} = \sum_{\mu_i} (\varepsilon + \Delta) |\mu_i\rangle \langle \mu_i| + \sum_{v_i} (\varepsilon - \Delta) |v_i\rangle \langle v_i| \quad (2.97)$$

where Δ acts on a different way on the occupied (empty) molecular states, and therefore changes the value of the energy gap, and ε move all molecular orbitals in the same direction. This scissor operator allow us not only to include SIC in the gas phase molecule, but also to tune the gap and the relative alignment between metal and molecular levels in the case of a molecule interacting with a surface.

The case of a molecule over a surface deserves some comments. Although $|\mu_i\rangle$ ($|v_i\rangle$) are defined for the isolated molecule and we shouldn't use them when it is interacting with the metal, we obtain that this approximation works very well (see Chaps. 4 and 5) as long as the deformed molecule geometry (instead of the gas phase one) is used.

We can rewrite it in the fireball atomic basis, in order to introduce it in our hamiltonian. Equation (2.97) reads then:

$$\begin{aligned}
O_{ij}^{scissor} &= \sum_k \Delta_k \langle i | \Psi_k \rangle \langle \Psi_k | j \rangle = \sum_k \Delta_k \langle i | \left(\sum_l c_{kl} | l \rangle \right) \left(\sum_m c_{km}^* \langle m | \right) | j \rangle \\
&= \sum_{k,l,m} \Delta_k c_{kl} c_{km}^* \langle i | l \rangle \langle m | j \rangle \\
O_{ij}^{scissor} &= \sum_{k,l,m} \Delta_k c_{kl} c_{km}^* S_{il} S_{mj}
\end{aligned} \tag{2.98}$$

where $\Delta_k = \varepsilon - \Delta$ for $k \in$ occupied levels and $\Delta_k = \varepsilon + \Delta$ for $k \in$ empty levels and Ψ_k are the eigenvectors of the energy eigenvalues.

2.8 Other Methods for Correcting the Gap

As we have said, the underestimation of the DFT gap is the most important problem for the systems that we are studying on this thesis. In the previous section, we explained the methods used here to deal with this failure. For the sake of completeness, a couple of state-of-the-art methods will be shown. Moreover, they can be inspiring later for some approximations

2.8.1 GW Method

GW Form of Selfenergy

The GW method relies on many-body green functions and self-energy formalism (Sect. A.2). It provides a way to calculate the self-energy in a reasonably amount of time with good accuracy. The deduction of the form of the selfenergy can be found on [82]. The form in time space and energy space is just.

$$\begin{aligned}
\Sigma^{GW}(\mathbf{r}, \mathbf{r}', \tau) &= i\hbar G_0(\mathbf{r}, \mathbf{r}', \tau) W(\mathbf{r}, \mathbf{r}', \tau) \\
\Sigma^{GW}(\mathbf{r}, \mathbf{r}', \omega) &= \frac{i\hbar}{2\pi} \int_{-\infty}^{\infty} d\omega' G_0(\mathbf{r}, \mathbf{r}', \omega + \omega') W(\mathbf{r}, \mathbf{r}', \omega') e^{i\omega'\tau}
\end{aligned} \tag{2.99}$$

where $W(\mathbf{r}, \mathbf{r}', \omega)$ is the screened coulomb interaction, in (2.20). The reason for the name of the method is now clear. It is important to say that this is an improvement with respect to the HF form of the self-energy $\Sigma^{HF}(\mathbf{r}, \mathbf{r}') = i\hbar G_0(\mathbf{r}, \mathbf{r}', 0^-) V_{coulomb}(\mathbf{r}, \mathbf{r}')$, because the screened potential $W(\mathbf{r}, \mathbf{r}', \omega)$ is considerably smaller than the coulomb potential. Besides it introduces dynamic effects since it is energy dependent. To sum up GW selfenergy takes into account exchange and a part of the correlation trough the screening potential.

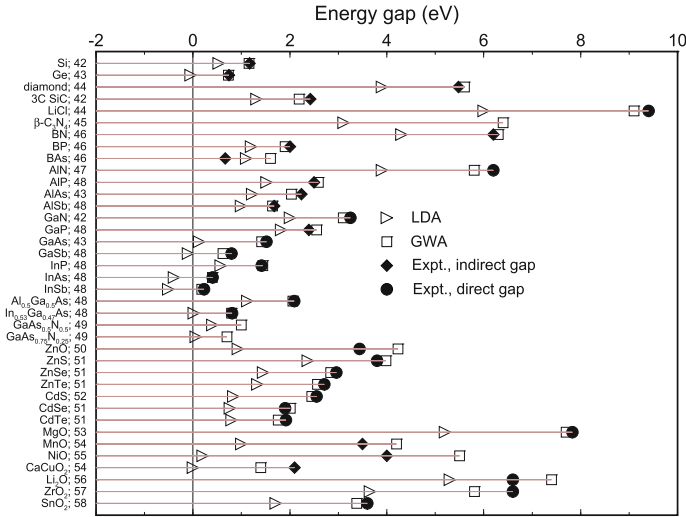


Fig. 2.6 Comparison of characteristic direct and indirect LDA, GW and experimental gap for a big variety of semiconductors. The numbers after the chemical symbols are the references for those values in [83]. Reprinted from [83], Copyright (2000) with permission from Elsevier (Color figure online)

Practical Implementation

It can be demonstrated [83] that the quasiparticles energy in the GW approximation can be calculated using formula:

$$\varepsilon_i^{GW} = \varepsilon_i^{KS} + \frac{1}{Z_i} \langle \phi_i^{KS} | \Sigma^{GW}(\omega_i^{KS}) - V_{xc} | \phi_i^{KS} \rangle \quad \text{where} \quad (2.100)$$

$$Z_i = 1 - \langle \phi_i^{KS} | \frac{1}{\hbar} \frac{\partial \Sigma^{GW}(\omega_i^{KS})}{\partial \omega} | \phi_i^{KS} \rangle$$

where we have assumed that the self-energy correction to the Kohn–Sham potential $\Sigma^{GW}(\mathbf{r}, \mathbf{r}', \omega) - V_{XC}(\mathbf{r})\delta(\mathbf{r} - \mathbf{r}')$ is small and we can use first-order perturbation theory. Moreover, we have considered that $\omega_i^{GW} - \omega_i^{KS} = \varepsilon_i^{GW}/\hbar - \varepsilon_i^{KS}/\hbar$ is small so we can perform a Taylor expansion around ω_i^{KS} . This approximation means that we don't need to compute explicitly the temporal dependence of Σ^{GW} .

So in practice, we first have to know the dielectric function $\varepsilon^{-1}(\mathbf{r}, \mathbf{r}'', \omega)$. We can calculate it using polarization matrix and random phase approximation (RPA) [84, 85], that is accurate but very expensive computationally, or calculate it using plasmon models [83, 86, 87]. Moreover, the exchange and correlation parts of Σ^{GW} are separated (the screened potential W is rewritten as $W = V_{coulomb} + (W - V_{coulomb})$), because the exchange part can be calculated analytically.

As can be seen in Fig. 2.6, GW approximation leads to really good results if we compare gap energies calculated using this method with the experimental results, or, at least it gives better results than LDA. The main problem of this method is that it is much more costly computationally than DFT, even if approximations for the dielectric function are used.

2.8.2 LDA+U Method

The origin of this method is to try to improve standard LDA functional for band systems where coulomb repulsion on localized orbitals introduces an important source of correlation, such as transition metal oxides, where we have delocalized electrons in s and p bands (where LDA works pretty well) and electrons localized in metal d bands, where the electron-electron repulsion U is important.

The LDA+U method is introduced as a functional that treats delocalized electrons correlation in a LDA fashion, and localized ones in a Hubbard-like way. If we take the standard Hubbard hamiltonian (A.8), the underlying idea of LDA+U is simple.

$$\begin{aligned} \hat{H} = & \underbrace{\sum_i \varepsilon_0 \hat{n}_{i\sigma} - \sum_i t (\hat{c}_{i+1\sigma}^\dagger \hat{c}_{i\sigma} + \hat{c}_{i\sigma}^\dagger \hat{c}_{i+1\sigma})}_{\text{delocalized, one electron}} + \underbrace{\sum_i U \hat{n}_{i\uparrow} \hat{n}_{i\downarrow}}_{\text{localized, correlation}} \\ E[\rho(\mathbf{r})] = & E^{LDA}[\rho(\mathbf{r})] + E^U[\{n_{i\alpha\sigma}, i\beta\sigma\}] \end{aligned} \quad (2.101)$$

Note that E^U is a functional of the occupation numbers instead of density. This is because this is the natural language in a Hubbard-like approach to localized electrons. We also need to include a double counting term that takes out the electron correlation already taken into account in LDA.

We are going to summarize here the basic formulas of the method. For a complete description of the method see references [88, 89]. Consider a transition metal with d orbitals where we have imposed spherical symmetry, then the simplest E^U repulsive term one can write is $E^U = \frac{1}{2} U^{eff} \sum_{m \neq m'} n_m n_{m'}$, where m, m' are the magnetic numbers of the d electrons, U^{eff} is calculated as in (2.49), but using the screened coulomb potential W (2.20) instead of the unscreened one. The double counting term E^{dc} , that takes out the interaction taken into account in LDA can be written as $E^{dc} = \frac{1}{2} U^{eff} N(N-1)/2$ (where $N = \sum_i n_i$). So this simplified LDA+U functional can be written as:

$$E = E^{LDA} + E^U - E^{dc} = E^{LDA} + \frac{1}{2} U^{eff} \sum_{m \neq m'} n_m n_{m'} - \frac{1}{2} U^{eff} N(N-1)/2 \quad (2.102)$$

The atomic energies are now (using Janak's theorem [90]):

$$\varepsilon_m^{LDA+U} = \frac{\partial E}{\partial n_m} = \varepsilon_m^{LDA} + U^{eff} \left(\frac{1}{2} - n_m \right) \quad (2.103)$$

This means that the LDA eigenvalues are shifted by $-U^{eff}/2$ if the level is filled ($n_m = 1$) and by $+U^{eff}/2$ if the level is empty ($n_m = 0$).

This method is closely related to our LCAO-OO approach. First of all, a more complete description of the method includes not only Hartree-like corrections but also exchange-like ones, as well as non-diagonal occupations $n_{m,m'}$ [89]. The simplified model explained here correspond to the particular case of [89] where $n_{m,m'}^\sigma = n_m^\sigma \delta_{m,m'}$, $U = \langle m, m' | V_{ee} | m, m' \rangle$ and the other $\langle m, m' | V_{ee} | m', m'' \rangle$ terms are zero. Moreover, the matrix elements involved in E^U calculation in [89] are nothing but the ones in (2.49), and the form of the functional can be derived using a mean-field approximation of the LCAO-OO Hamiltonian (2.50) (approximating all the operators $\hat{n}_{i\alpha\sigma}$ by its mean values $n_{i\alpha\sigma}$).

A point of caution with the LCAO-OO method analogy has to be taken. In this case the electron-electron potential V_{ee} is not the bare one but the screened one (so $f_{i\alpha\sigma}$ is not needed anymore to take into account correlation). This converts LDA+U in a post-HF theory. This screened potential relates the LDA+U method with the GW one. The relationship between this method and GW and HF ones is extensively studied in [91].

In Sect. 3.6 the ideas of Cococcioni et al. [92] are used to extend this method from metal transition oxides to organic molecules over metal surfaces.

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