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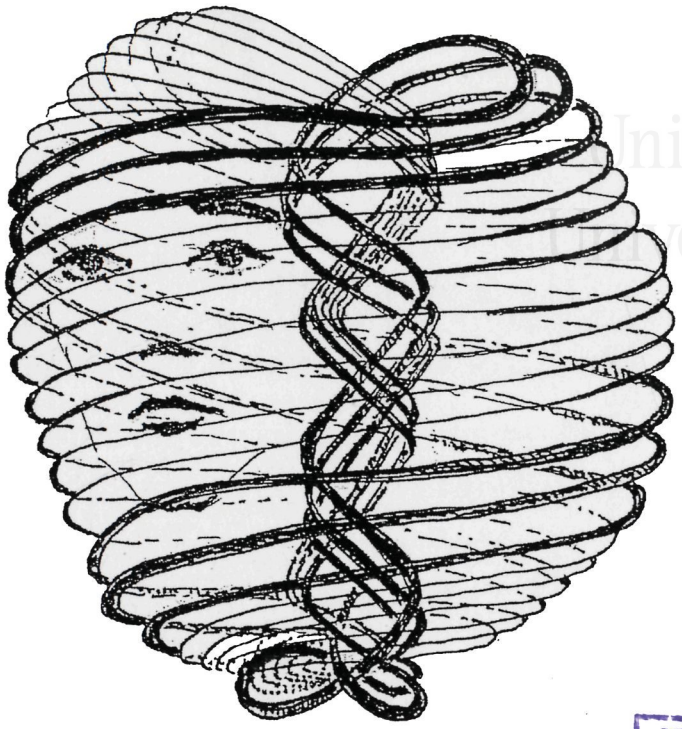

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Ab-initio molecular electronics within mean-field methods

Memoria que,
para optar al grado de
Doctor,
presenta
Yamila García Martínez

Universitat d'Alacant
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sense els meus avis
sen a súa españa
con mis padres
con mi isla

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Introduction

The scope of this thesis

(...) *El mundo era tan reciente, que muchas cosas carecían de nombre, y para mencionarlas había que señalarlas con el dedo* [1].[1] (...). Molecular Electronics is an emerging area of nanoscience, which studies the electronic properties of materials when confined to dimensions of the order of 10^{-9} meters. It does not belong to physics or chemistry, since the behavior of these nanoscale systems is not necessarily that predicted from the behaviour observed at macroscopic or at the molecular scales. In fact, molecular electronics is by itself a new "world" that bridges two extremes. Within this context, this thesis is intended to be a contribution in the formal statement of some of the current methods and concepts (*or names*), applicable to molecular electronics.

The content of this thesis is determined by the necessity of doing *ab-initio*[2] calculations of the meaningful observables for the systems under analysis [3–5]. At the heart of this problem, lies the many-body interaction governing the behavior of the electronic systems, and restricting the applicability of the *ab-initio* calculations. However, due to the recent progress in Density-Functional Theory [6–8] effective *ab-initio* methods have been developed. It has been shown within DFT that a single-particle theory can be constructed where all the many-body interactions can be included in an effective single-particle potential. Unfortunately, thus far, a feasible algebraic form of this potential is unknown. However, its existence is by itself a motivation for its search. This is the main subject of this thesis.

First, we will explore the analytic form of this potential starting from its origin, the basic works due to Hohenberg, Kohn and Sham [6, 7].

[1] (...) The world was so recent that many things lacked names and in order to indicate them it was necessary to point (...) [2]

[2] Latin expression; *ab*, "from", and *initio*, "the beginning".

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Second, we will fix an algebraic form for this potential which satisfies boundary conditions determined from the interplay between Landauer's formalism to describe elastic electron transport, and the Green's function formalism [9, 10]. This potential, obtained within a *static* route, will be compared with the accepted exact form, obtained within a *time-dependent* route [11, 12].

Third, we will demonstrate the feasibility of our static potential by its implementation in our *ab-initio* code [13,14]. The numerical results will be compared with actual experiments, and used to suggest new ones.

Fourth, since the existence of this potential supports the reliability of single-particle approaches, we will carefully include traditional methods such as Frontier Molecular Orbitals and Lewis pair theories, either to avoid the limitation of *ab-initio* methods to explore some process, or as a claim to recover simplicity, at least, as a matter of communication.

We should point out that our proposal for the effective single-particle potential is exact. This is in contrast with the current approximations made by physicists to deal with problems of extended systems [7, 15], and the empirical approximations made by chemists to deal with problems of isolated molecules [16]. Therefore, this thesis can be considered as the design of an effective single-particle potential for such systems, which results from the placement of *one* or *a few* molecules in between extended systems.

-What is the name for this system?

The answer depends on the context where the question is made. For now we just point to the figure in 1.

Outline

In Chapter 1 the central quantity of this thesis is introduced, the conductance for a single or few molecules in between metallic nanowires. We first show how to obtain the conductance within a static formulation, derived from the scattering approach in conjuction with the Green's function formalism [9, 10]. We also give the time-dependent formalism we use for the calculation of the conductance [18]. Finally, and in order to give conductance values in agreement with real conditions, we go toward chemistry with molecular scale precision, nanochemistry [19]; and define how we simulate the data procesing of an experiment of quantum transport, statistics.

In Chapter 2 the *ab-initio* methods we use throughout this thesis are presented. We

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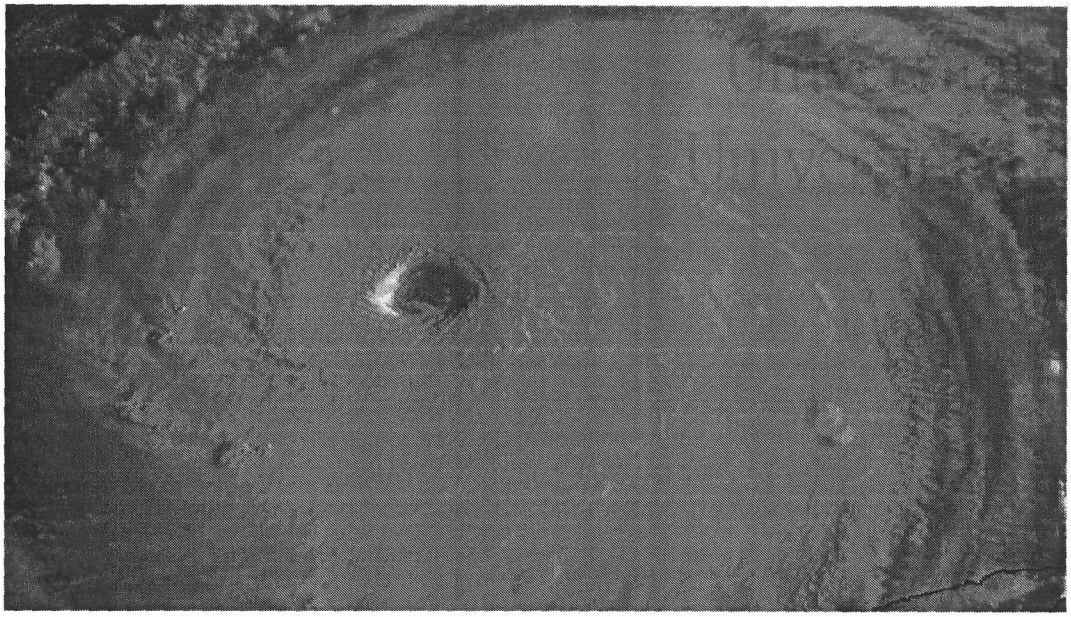

Figure 1: A hydrodynamical representation for the electron flow when a molecular systems is placed in between extended homogenous systems. This hydrodynamical picture to describe electron flow through confined systems has being suggested by recent theoretical works [17]. The photo is of Hurricane Katrina, and was taken far from the center of the storm. (We will return to this subtle point at the end of this thesis.)

begin with the Wave Function methods. However their role in this thesis is restricted in favor of Density-based methods, which are the main object of this chapter. Within this framework, the central quantity of an effective *ab-initio* calculation is introduced: the exchange-correlation potential. The relevance of this entity follows the introduction of the Hohenberg-Kohn-Sham's and Runge-Gross theorems [20], for reducing many-body problems (numerically unsolvable within an *ab-initio* perspective based on wave-function methods) to mean field schemes, [6, 7, 21].

In Chapter 3 the accepted exact and *ab-initio* methodologies for the static quantum transport response characterization are presented. These are developed from a time-dependent formulation of the quantum transport problem, and recovering the static conditions by doing the appropriate limits [18, 22]. The role played by the spatial *locality* as a property of the exchange-correlation potentials is discussed. Precisely, behind this property could be the mathematical answer to the addition of more physics into the initial local time-dependent exchange-correlation potentials, when time-dependent functional methods are applied to quantum transport characterization. This apparently innocuous point, leads to the origin of nonlocal time-dependent exchange-correlation potentials, and defines a whole new field within time-dependent methods: the time-dependent current-density-functional theory [11].

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The Chapter 4 is "the thesis within this thesis". First, the existence of an *ab-initio* methodology for quantum transport, within a static and *ab-initio* density-formulation is discussed. On this basis, the exchange-correlation potential which appears in the mean field formulation of the *ab-initio* problem is fixed, claiming for its canonical construction as a nonlocal functional on position space. Therefore, the local density approximations to this functional, currently in use [15], are left on doubt [23]. Furthermore, the use of these local approximations is the cause of the failure of the traditional density-based method when applied to quantum transport problems [24,25]. We show that, critically, the importance of nonlocality in the approach to the exchange-correlation potential, increases with the electron confinement. This is due to the long rangedness convergence of the Taylor expansion of the electronic density on position space, and the consequent uncontrolled nonlocality of the description of any quantity in terms of the density under this condition. This problem is avoided by introducing a nonlocal contribution to the exchange-correlation potential. The amount of this contribution is derived from ground state calculations of total energies.

The chapters that follow are evoted to giving numerical proofs of the effectiveness of the methodology proposed within this thesis.

In Chapter 5 the first numerical problem is stated: the *ab-initio* calculation of the conductance for a single Hydrogen molecule, when it is placed in between platinum nanocontacts. This system is initially presented as a useful theoretical construction to show, numerically, how the inclusion of nonlocal contributions in the exchange correlation potential do play an important role in the electronic structure of the system, and therefore control the conductance values. At this point, we introduce our method to calculate the conductance value of this system. At the end of the chapter, the same system is analyzed within the time-dependent formulation proposed in chapter 4. The numerical agreement between both results could contribute to open the way for a formal connection between static and time-dependent methods.

In Chapter 6 we present what should be two of the steps in order to establish a connection between theoretical and experimental results. First, we do the chemical analysis of the systems we deal with, and second, we present a simplified statistical analysis of the conductance calculations. For these analyses we select a benchmark set of diatomic molecules interacting with metallic nanocontacts. Based on the results here obtained, the conductance of two of these systems is calculated: platinum nanocontacts in Hydrogen and carbon monoxide environments. These results are presented and compared with their presumably experimental counterparts [26,27].

The final Chapter 7 is devoted to analyzing what is considered a candidate system for manageable molecular electronics [28]. The molecular system is the benzene-1,4-dithiol molecule interacting with gold electrodes. The results presented in this chapter could address the old controversy on the overestimation of the conductance of this system, when

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comparing with experimental results [12, 29, 30]. This overestimation could be due to the use of local approximations for the exchange-correlation potentials in the current *ab-initio* methods.

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At the end of this thesis some appendices are included. From the point of view of the author, the first appendix is a formality, but the rest could contain the basics for the main contribution of this thesis. Appendix B contains a mathematical definition of a local functional, (as far as we know, there is nothing about this in the technical literature). With this definition at hand we should address the old controversies on when a functional is local, sufficiently local, or nonlocal [15, 23, 31–33]. In addition to this apparently abstract definition, in appendix C we establish a connection between the mathematical definition of local functional and an unsolvable problem within density-functional theory: the calculation of the electronic structure of systems where the density is strongly nonhomogenous. By the way, this is the behaviour in the confined systems we assume we are going to deal with in molecular electronics.

Appendix D is a summary of the implementation schemes we developed in this thesis. It is a comparison of the feasibility of our static proposal and the time-dependent methods. From our point of view, the static method we suggest entails fewer uncertainties than the time-dependent route.

Appendix E is an example on how we could, based in a weighty theoretical basis, return to explain all the results we obtain (and even more) at a level understandable by high-school students. We recover Frontier Molecular Orbitals and Lewis pair theories, based on the existence of an effective single-particle theory, if the nonlocal exchange-correlation potential is determined.

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Part I

Theoretical background

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Chapter 1

Electronic transport theory

Overview

This chapter is devoted to introduce two methods for the calculation of the zero-voltage and zero-temperature electronic conductance, defined as,

$$G = \lim_{V \to 0} \frac{\partial I}{\partial V} \tag{1.1}$$

This quantity describes the linear response of the electronic current, $I = I(V)$, to an external potential, V, for a system initially in equilibrium[1].

The methodologies employed to calculate the conductance could be either time-independent, such as the static method treated in section 1.1, or time-dependent, like the dynamic method outlined in section 1.2. Both formulations will be useful to discuss the proposals for an accurate *ab-initio* static methodology for the calculation of the conductance (chapters 3 and 4) which is the central point of this thesis. However, the appealing to dynamical formulations, which yields the quantity we are looking for on the limiting static equilibrium conditions, is motivated considering that almost all the progress is been gained within the context of time-dependent formulations [18, 34–36].

Finally, the typical setup to be studied in this thesis is sketched in the figure 1.1. Technically speaking, the central region is a constriction to the electron current driven by the electrodes. Physically, the constrictions are defined such that their transverse dimensions are smaller than the Fermi wavelength in the electrodes. For metals this implies that

[1] Equilibrium is defined as stationary states such that $I(V) = \lim_{t \to \infty} I(t, V)$, where t is the time coordinate.

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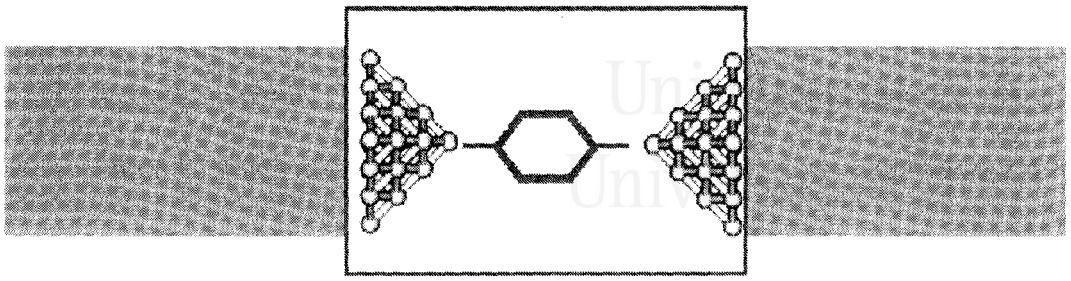

Figure 1.1: Schematic sketch of the theoretical setup described throughout this thesis. The central region contains one or few molecules and a finite part of the macroscopic electrodes, it is connected with the infinite large metallic electrodes.

we have to control the size of the constrictions at the nanometer scale, since the Fermi wavelength for metals is of the order of the atomic diameter [10]. Therefore, the quantum nature of the systems bridging the metals can not be avoided. Geometrically, the constrictions can be realized by placing nanoscaled systems in between metallic wires. Examples of currently used nanoscaled systems are, single molecules, single atoms, molecular strands, atomic wires, etc ... [29, 37]. In this thesis we are mainly concerned about a single or few molecules bridging metallic electrodes. In this respect, section 6 is intended to introduce the concepts and routes we follow to fix the atomic and electronic configurations which are basic for the understanding of an actual *ab-initio* quantum transport simulation through the systems discussed in this thesis.

1.1 An static approach to the conductance

The basic idea of the static-phenomenological approach, also known as Landauer's formalism [9, 10, 37], is to relate the macroscopic current with the transmission coefficient of a finite region, the mesoscopic device, and the distribution functions for the current carriers in connected reservoirs, the electrodes.

The figure 1.2 is an scheme, simple but enough, to introduce the geometrical objects we use to develop a phenomenological transport formalism. The mesoscopic device is connected to macroscopic electrodes by a set of leads, which allow us to inject currents and fix voltages. Throughout the leads the electrons freely propagate, as plane waves along the longitudinal direction, while its transversal momentum is quantized due to lateral confinement (m-labeled), thus a set of incoming and out-coming modes can be defined. For the derivation of the Landauer's formula, it is convenient to introduce creation and annihilation operators ($a^\dagger$ and a) which create and destroy an incoming electron on mode

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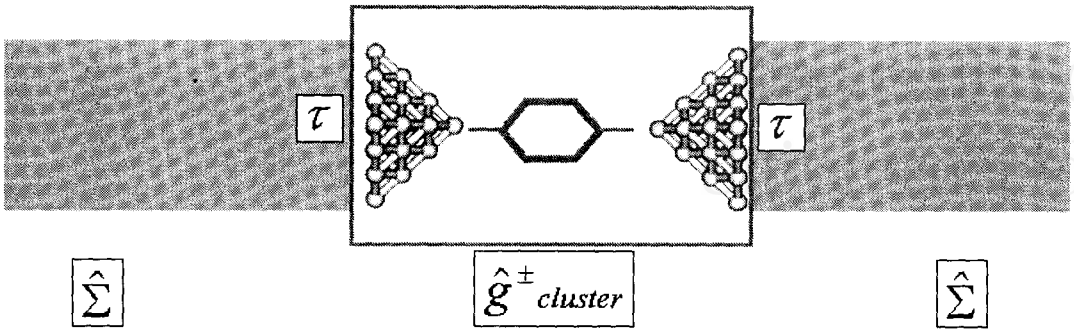

Figure 1.2: Schematic representation of the quantities involve in the scattering formulation of the conductance problem. The details are discussed in the main text.

m in lead α with energy ε. Similarly, we introduce creation and annihilation operators for the outgoing states ($b^{\dagger}$ and b). Thus, population of incoming and out-coming states is fixed by the occupation numbers. The mode m in lead α with energy ε, $N_e^{\alpha,m}(\varepsilon)$, can be represented as,

$$N_e^{\alpha,m}(\varepsilon) =< a_{m\alpha}^{\dagger}(\varepsilon)a_{m\alpha}(\varepsilon) > - < b_{m\alpha}^{\dagger}(\varepsilon)b_{m\alpha}(\varepsilon) > \tag{1.2}$$

Within this picture, the current is the result of the imbalance between the occupation of the electron states-modes,

$$I_{m\alpha} = \frac{2e}{h}\int_{-\infty}^{\infty} d\epsilon \left[< a_{m\alpha}^{\dagger}(\epsilon)a_{m\alpha}(\epsilon) > - < b_{m\alpha}^{\dagger}(\epsilon)b_{m\alpha}(\epsilon) >\right] \tag{1.3}$$

Now, some assumptions are made in order to obtain the total current, I. First, we **assume** that there is **not correlation among single-electron conducting channels**, thus the net current will be considered as the sum of the contribution of each channel, I_m,

$$I = \sum_m I_m \tag{1.4}$$

and using the scattering matrix, s, to establish a relationship between a and b operators,

$$b_{m\alpha} = \sum_{n\beta} \left[s_{\alpha\beta}^{\dagger}\right]_{mn} a_{n\beta} \tag{1.5}$$

thus the net current in the lead α is,

$$I_\alpha = \frac{2e}{h}\int_{-\infty}^{\infty} d\epsilon \left[(N_e^{\alpha} - R_{\alpha\alpha})f_\alpha - T_{\alpha\beta}f_\beta\right] \tag{1.6}$$

where $f_{\alpha\beta}$ are the distribution functions for the electrons in the leads, and R, T refer to the reflexion and transmission matrices. In further approximations the $f_{\alpha\beta}$ are associated with **the Fermi distributions for a free-electron gas**, obtaining, the net current in lead α given by,

$$I_\alpha = \frac{2e}{h}\int_{-\infty}^{\infty} d\epsilon\, T_{\alpha\beta}\left(f_\alpha - f_\beta\right) \tag{1.7}$$

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Now, we consider the **linear response conductance**, which is given by,

$$G = \frac{2e^2}{h} \int_{-\infty}^{\infty} d\epsilon \, \frac{\partial f}{\partial \epsilon} T_{\alpha\beta} \tag{1.8}$$

Finally, at the limit of zero temperature (the one we are interested about as is stated in equation (4.18)) this expression give as the well known Landauer formula,

$$G = \frac{2e^2}{h} Tr \;\; T\left(\varepsilon_{Fermi}\right) \tag{1.9}$$

where the conductance is strictly related with the trace of the transmission matrix evaluated at the Fermi level.

In further mathematical steps, it is common the calculation of the transmission matrix using Green's function methods. This is the procedure we follow for the numerical implementation of the transport method and it is going to be discussed in the next section.

1.1.1 Conductance calculation within Green's functions technique

The conductance, as given by equation (1.9), can also be rewritten by expressing the transmission operator within Green's functions technique. This is done through the following relation [10],

$$\hat{T}\left(\epsilon\right) = \hat{\Gamma}_L \, \hat{g}^{+}\left(\epsilon\right) \hat{\Gamma}_R \, \hat{g}^{-}\left(\epsilon\right) \tag{1.10}$$

Here, $g^{\pm}\left(\epsilon\right)$ are Green's functions defines as,

$$g^{\pm}\left(\epsilon\right) = \left[\epsilon \pm i\eta - \hat{H} - \hat{\Sigma_L}^{\pm} - \hat{\Sigma_R}^{\pm}\right]^{-1} \tag{1.11}$$

where $\hat{H}$ is the Hamiltonian operator for the finite conductor and $\Sigma_{L/R}$ are the self-energies for the left and right electrodes, L and R labeled. The $\Gamma(\epsilon)_{L/R}$ are related with the self-energies describing the electrodes, $\Sigma_{L/R}$, as,

$$\hat{\Gamma_{L/R}} = i\left[\hat{\Sigma}^{-}_{L/R} - \hat{\Sigma}^{+}_{L/R}\right] \tag{1.12}$$

The $\Sigma_{L/R}$ take into account the effect of the electrodes on the conductor, upon the knowledge of the Hamiltonian characterizing the electrodes, $\hat{H}_{\infty}$, and its coupling with the conductor, $\tau_{L/R}$. Therefore, $\Sigma_{L/R} = \Sigma_{L/R}\left(\hat{H}_{\infty}, \tau\right)$ (see the figure 1.2). At this point, the static methodology for the calculation of the conductance we are going to use is defined, the scattering approach linked to the Green's functions technique.

Before ending with this transport formalism, some keen hypothesis which have been made should be remarked (In black color in the previous text.). Those approaches must be taken into account when comparing transport characteristics with experiments. Furthermore,

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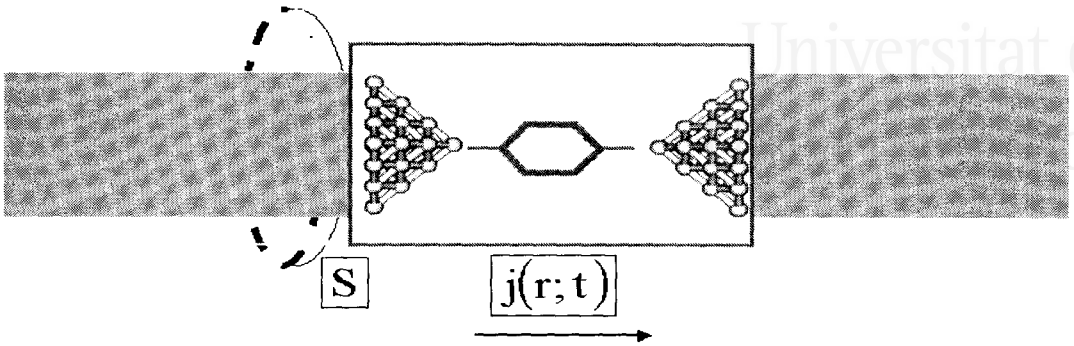

Figure 1.3: Schematic sketch of the quantities used in the main text in correspondence with the theoretical system we are describing. Its significance is discussed in the main text.

and this is the point we are going to discuss in chapter 4, since the scattering theory is an approach to the transport description from phenomenological point of view, its hypothesis are made without a rigorous justification and then, the role these do play when charge transport mechanism is studied under real conditions is not at all clear [18, 38, 39]. For instance, events such as electron correlations, chemical activity, heating, decoherence, and finite temperature effects must be carefully examined. In this thesis, all of these events are going to be mentioned. However, the attention will be focused mainly on the first one of the previous features, the analysis of electron-electron interactions in the implementation of the scattering approach for molecular devices. In this systems, due to a confinement situation for the electronic states, we are intending to show that the electron-electron interactions could play an important role in the calculation of electronic response, very noticeable when all the rest of the events are frozen.

1.2 A time-dependent approach to the conductance

In contrast to the static approach previously introduced, in this section an alternative picture for quantum transport description is proposed relying in time-dependent simulations [18]. From the point of view of Todorov and Diventra, this method gives us a formally exact time-dependent description of the many-electron current within a one-electron picture. From the point of view of the "*ab-initio* community", the current density and the electronic density are central ($n \equiv n(\mathbf{r};t)$, $\mathbf{j} \equiv \mathbf{j}(\mathbf{r};t)$) since these are the key quantities for the exactness of this theory within an *ab-initio* context. This statement could be shared after reading the next two chapters. Now, a summary of the main ideas of this method is introduced.

The total time-dependent current, by definition of $\mathbf{j}(\mathbf{r},t)$, is derived from the following

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integral expression,

$$I(t) \stackrel{\text{def}}{=} \int_{\mathbf{S}} d\mathbf{S} \cdot \mathbf{j}(\mathbf{r};t) \tag{1.13}$$

where $\mathbf{S}$ is a closed surface. (See the figure 1.3). The surface $\mathbf{S}$ is closed in the vacuum, and the vacuum is taken sufficiently far from the boundaries of the system, to enable us to ignore any contributions to the surface integral over the closed surface it defines. Then, using the Gauss's theorem this integral representation through the closed surface, can be replaced by the volume integral of the divergence of $\mathbf{j}(\mathbf{r};t)$,

$$I(t) = \int_{\mathbf{r}} d\mathbf{r} \ \nabla \cdot \mathbf{j}(\mathbf{r};t) \tag{1.14}$$

Now, with the perspective in mind of using this expression in the context of *ab-initio* calculations[2], the functional relation between $j(\mathbf{r};t)$ and the electronic density of the interacting system, $n_{interacting}(\mathbf{r};t)$, known as the continuity equation, is introduced,

$$\nabla \cdot \mathbf{j}(\mathbf{r};t) = -\frac{\partial n(\mathbf{r};t)}{\partial t} \tag{1.15}$$

Then, invoking the N-representability of the systems we are dealing with, the total current within the TDDFT can be expressed as[3],

$$I(t) = -\int_{\mathbf{r}} d\mathbf{r} \ \frac{\partial n_{non-interacting}(\mathbf{r};t)}{\partial t} \tag{1.16}$$

or,

$$I(t) = \int_{\mathbf{r}} d\mathbf{r} \ \nabla \cdot \mathbf{j}_{\mathbf{non-interacting}}(\mathbf{r};t) \tag{1.17}$$

The schemes based in the equation (1.16), are labeled as TDDFT transport theories. The schemes based in the equation (1.17), are labeled as Time-Dependent Current-Density-Functional transport theories, TDCDFT. In chapter 3, we are going to proof that for the systems we are dealing with, this scheme will be a necessity since an exact treatment within a TDDFT scheme, in practice, does not exist.

Finally, going back to the central quantity of this thesis (the conductance defined in equation (E.3)), we need to proof a result which is not at all obvious. Necessarily, we must show that an stationary current can be developed, even when the systems are treated as non-interacting. This proof will mark a difference with the static approach where instead of a proof, an assumption is made to proceed through this formal step. Due to its importance, the next part of this section will be devoted to enter in this scheme. But before

[2]In chapter 4 is shown that an exact *ab-initio* theory can be constructed, at least in principle, using the electronic density as a basic variable.

[3]The N-representability of the systems we are dealing with, is the basic hypothesis of the mean-field scheme design within density functional theories, section 2.3. In few words, it means that the interacting electron system can be mapped in a non-interacting electron system, with the same charge density ($n(\mathbf{r};t) \rightarrow n_{non-interacting}(\mathbf{r};t)$). Even when through this map we cannot guarantee the exactness of any other electronic quantity, using this identity and substituting the continuity equation (1.15) for the non-interacting system , we can support the exact formal map: $\mathbf{j}(\mathbf{r};t) \rightarrow \mathbf{j}_{\mathbf{non-interacting}}(\mathbf{r};t)$. In addition to this argument, this map was rigorously proved by Vignale [22]. (Both publications are dated on 2004.)

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going in details, we remark that this assumption is the source of discussions in the "*ab-initio* quantum transport" community, referred as the thermodynamic inconsistency of the scattering approach [18, 36]. Therefore, by construction, the evolution of $\mathbf{j}_{\mathbf{non-interacting}}$ through steady states is going to be guaranteed, and this allow us to define a conductance within this theory using the following expression for the total current,

$$I_{stationary} = \lim_{t\to\infty} I(t) \tag{1.18}$$

then, back in equation (E.3),

$$G = \lim_{V\to 0}\lim_{t\to\infty} \frac{\partial I(t,V)}{\partial V} \tag{1.19}$$

Analytic insight is necessary to support the exact formal derivation of the static conductance going through this time-dependent limit. This discussion is left to section 4.3.

1.2.1 The exactness of a mean-field quantum transport description

In this part of the section we give a short overview of the proof given by Di Ventra and Todorov to show that the limit introduced through equation (4.17) exists. In the original work [18], it is made a constructive proof of the existence of such limit, by identifying a functional whose minimization within the space of interacting electron states defines an instantaneous steady state. Physically, the existence of such limit leads to a proof of the existence of a direct mapping between the exact, true, and many body -current in an stationary state, and the knowledge of mean-field quantities, for instance the ground state electronic density,$n(\mathbf{r};t)$, and to assure that the description of the transient response to an external perturbation for a molecular system between the electrodes surfaces is possible within time-dependent transport simulations.

The scheme relies on the modeling of the whole system sketched in the figure 1.3 as closed in terms of thermodynamic requirements, and the not discussed selection of the dynamical laws contained in the Schrödinger equation. No further considerations are made in terms of the construction of a functional, which once minimized provides the steady-state exact current, I.

First of all, an stationary state is defined as,

$$\forall\ \mathbf{S} \quad \left[\frac{dI(t)}{dt} = 0\right] \tag{1.20}$$

Now, the whole formalism is summarized in the next paragraphs [18].

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As stated in equation (3.2) the total current across a junction can be calculated in terms of **S** and **j** (**r**,t). Conceptually, this model enables us to assume that all electrons are bound within a finite surface crossing the nanojunction, so that the charge and current densities are enough small outside this surface, at all times. Since, for the description of $\mathbf{j}(\mathbf{r},t)$ a quantum dynamical scheme is chosen, this quantity should be expressed as,

$$\mathbf{j}(\mathbf{r},t) = \langle \Psi\left(t\right) \mid \hat{\mathbf{j}} \mid \Psi(t)\rangle \tag{1.21}$$

where $\hat{\mathbf{j}}$ and $\mid \Psi(t) >$ are the many-body current-density operator and many-body state vector, respectively. The $\Psi(t)$-state-vectors are defined upon the acceptance of the time-dependent Schrödinger equation in describing the evolution of the system,

$$i\hbar \frac{d \mid \Psi(t)\rangle}{dt} = H \mid \Psi(t)\rangle \tag{1.22}$$

In this equations, H is the Hamiltonian of the system, many-body by construction, and $\mid \Psi(0)\rangle = \mid \Psi_0$ is an initial condition, which could be nicely considered as a parameter for the objectives we have. At this point, a variational procedure is proposed for the calculation of **j** as follows.

First, a new functional is defined, which is enough to describe temporal variations in the current as is detailed discussed in the original reference [18],

$$B = \int_{\bigcup} d\mathbf{r} \ \left(\frac{\partial n(\mathbf{r},t)}{\partial t}\right)^2 \tag{1.23}$$

where $\bigcup$ means an integration through all the space.

By using the continuity equation (1.15), the B-functional can be rewritten as,

$$B = \int_{\bigcup} d\mathbf{r} \ \left(\nabla \cdot \mathbf{j}\right)^2, \tag{1.24}$$

so that, B is written as a functional of the many-body current density $\mathbf{j}(\mathbf{r};t)$.

The next step pass through the following expansion,

$$\mid \Psi(\mathbf{r};t) > = \sum \ c_i \mid_i > \tag{1.25}$$

where c_i are the expansion coefficients of the $N-$bound states, $\mid \Psi_i >$.

The expansion above is substituted in the canonical definition of **j**, expression (1.21), and thence into (1.24). Therefore, the functional which is going to be minimized can be build in terms of the variational parameters c_i,

$$B\left[\{c_i\}\right] = \sum_{i,i',i'',i'''} c_i^* c_i' c_i''^* c_i''' \int_{\bigcup} d\mathbf{r} \ \left(\nabla \cdot \mathbf{j}_{ii'}(\mathbf{r};t)\right) \cdot \left(\nabla \cdot \mathbf{j}_{i''i'''}(\mathbf{r};t)\right) \tag{1.26}$$

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where remarkably, $\mathbf{j}_{ii'}$ is a single-particle quantity. The next step is the definition of the constraints for the minimization.

The systems is thermodynamically closed, therefore the conservation of the total energy, E, and the number of particles (electrons), N must be imposed to the total current,

$$E = \sum_i c_i^* c_i E_i \tag{1.27}$$

$$1 = \sum_i c_i^* c_i \tag{1.28}$$

$$I_{stationary} = \sum_{i,i'} c_i^* c_{i'} \int_{\mathbf{S}} d\mathbf{S} \cdot \mathbf{j}_{ii'}$$

As a result of this constrained minimization procedure, the instantaneuos many-body states, expressions (6.1), can be determined, enough to define the exact-many-body total current density $\mathbf{j}$, and subsequently the exact (many-body) total current I,

$$I_{stationary} = \sum_{i,i'} c_i^* c_{i'} \int_{\mathbf{S}_{junction}} d\mathbf{S} \cdot \mathbf{j}_{ii'}(\mathbf{r}) \tag{1.29}$$

The messages to be gotten from this expression, at least in the context of this thesis, is that the stationary current can de exactly defined in terms of a single-particle quantity $\mathbf{j}_{ii'}$. Physically, the result can be stated as the capability of any system to be driven to stationary-states mean-field represented, by a direct propagation of time-dependent many-body states.

Finally, the main results from this section are summarized. In the first part, the total current, $I \equiv I(t)$ is being related with quantities which can are exactly defined within *ab-initio* schemes. Then, an stationary theory is being constructed from the knowledge of the time-dependent current,

$$I_{stationary} = \lim_{t \to \infty} I(t) \tag{1.30}$$

Those two results will be invoked in chapter 3, and therefore are among the building blocks of the methodology for the exactification of electronic transport calculations we propose in this thesis.

1.3 Nanochemistry

The formalism underpinning the *effectiveness* of any exact quantum transport methodology is called nanochemistry. (...) In its broadest terms, the defining feature of nanochemistry is the utilization of synthetic chemistry to make nanoscale building block of different size and shape, composition and surface structure, charge and functionality (...) [19]. In the context of an effective quantum transport methodology, and this is one of the claims

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within this thesis, nanochemistry is defined as a necessity. The necessity of fixing an architecture at the nanoscale before start with any quantum transport calculation, which may play a foremost role. In other words, the development of the tools for defining the position of the atomic nucleus, $\mathbf{R_I}$, in such a way that allow the calculation of the electronic quantities which enter in the method chosen, figures 1.2 and 1.3. If we pass from bulk materials to that in the nanoscale, the driving forces for molecule organization are going to be essentially dictated by the quantum evolution of the system. It implies, a chemical description of the system at hand based on the mean values of the corresponding quantum operators.

The chemical analysis we made in this thesis, requires the proper definition of energies in the extended systems we are studying. Therefore, some essential points should be clarified for a consistent methodology.

The expecting values of the total Hamiltonian determines the total energy surface, E_{total}. (In the next chapter the methods for its calculation are discussed.) Thus, the first assumption we do is, that the systems evolve towards a set of *lower* free energy and so then, greater structural stability. Since our systems are in the nearby of zero temperature limit, their evolution could be determined fulfilling the following two conditions,

$$\begin{aligned} \mathbf{F} &= \mathbf{0} \\ \nabla \mathbf{F} &> \mathbf{0} \end{aligned} \tag{1.31}$$

This set represents the stability for the force conjugate to the position of the nucleus, $\mathbf{F} = \mathbf{F}(\mathbf{R}_I)$, and defines the space of most probable states. The set of equations above introduced, could be considered as an obvious first-principles route, but unfortunately, in practical calculations it is an impossible task, due to numerical cost. Therefore, it is left only as a mathematical assignment, and the whole $\mathbf{R}_i$-space (the reaction path) is not analyzed. Due to this limitation, currently we must extrapolate the concepts of ordinary/traditional chemistry to this nano level without rigorous basis. In fact, there are not doubts, the doors are open to formalization of a new field, nanochemistry[4]. A new field which must be completed with an statistical analysis, if the quantity in point should be compared with real measurement. This will be the subject of the next lines.

Once the space of more probable states is defined an statistical analysis is recommended, to introduce the statistical correlation among chemical events, and to model the uncertainties in the mean values we fixed. In this thesis we use a Gaussian statistics. This distribution is the first simple attempt to made an statistical analysis of the conductance measurements. Therefore, the conductance is the variable, and its mean value, G_0 , would be those calculated for each selected configuration. The variance, σ_I, will be a parameter in our model.

$$f(G) = \sum_I P_I^{max} \frac{1}{\sigma_I \sqrt{2\pi}} e^{-\frac{(G-G_0)^2}{(2\sigma_I)^2}} \tag{1.32}$$

[4]This topic will be taken up again in the presentation of numerical results in chapters 6 and 7.

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Here the I label represents a collection of different atomic configurations, defined as solutions of 1.31. This will be enough for "drawing" the theoretical histograms.

At this point we can stablish a direct comparison between our results and those provided by the experimentalists, since present day experimental quantum transport measurements are given in a form of histograms [5].

Summarizing, to approach the desirable mapping between theoretical an experimental results, our proposal is, that an statistical analysis (from a theoretical point of view) should also be made [40].

[5]Experimental histograms are a collection of a set of conductance values, derived from the analysis of the corresponding $I.vs.V$ curves.

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Chapter 2

Ab-initio methods

Overview

In theoretical Molecular Electronics we already know our "theory of everything": the *ab-initio* calculation. This consists on the calculation of the quantities involved in quantum electronic transport as the expectation values of corresponding operators on a basis of the total wave functions, Ψ. These wave functions are defined through the differential Schrödinger eigenvalue equation [33][1],

$$\hat{H}_{ab-initio}\,\Xi\left(\mathbf{x_1},\ldots,\mathbf{x_N};\mathbf{R_1},\ldots,\mathbf{R_M}\right)=E_{ab-initio}\,\Xi\left(\mathbf{x_1},\ldots,\mathbf{x_N};\mathbf{R_1},\ldots,\mathbf{R_M}\right) \quad (2.1)$$

Here, $E_{ab-initio}$ is the total energy for the systems of electrons and nuclei, and $\hat{H}_{ab-initio}$ is its full non-relativistic *ab-initio* molecular Hamiltonian[2],

$$\hat{H}_{ab-initio}=\hat{T}_I+\hat{T}_i+\hat{U}_{I-J}+\hat{V}^{ext}_{J-i}+\hat{U}_{i-j} \quad (2.2)$$

This Hamiltonian contains the following contributions: the kinetic energy operator for the nuclei, $\hat{T}_I$,

$$\hat{T}_I=-\frac{\hbar^2}{2M_I}\sum_I\nabla^2 \quad (2.3)$$

the kinetic energy operator for the electrons, $\hat{T}_i$,

$$\hat{T}_i=-\frac{\hbar^2}{2m_e}\sum_i\nabla_i^2 \quad (2.4)$$

[1]The quantum description of the system is now restricted to static situations, which is the main frame of this thesis. However, the generalization to time-dependent contexts will be done in section 2.56. Henceforth, the $\mathbf{x}$-space includes the spatial and spin coordinates for the electrons, $\mathbf{x}=(\mathbf{r},\sigma)$

[2]The strict analysis of the role played by the relativistic effects is beyond the scope of this work. Presumably, its effects on the problems we analyze can be accounted as an average within the pseudopotential approximations ([41] and section2.1.)

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the potential energy operator due to interactions between nuclei, $\hat{U}_{I-J}$,

$$\hat{U}_{I-J} = \frac{1}{2}\sum_{I\neq J}\frac{Z_I Z_J e^2}{\mid \mathbf{R_I} - \mathbf{R_J} \mid} \tag{2.5}$$

the coulomb electron-ion interaction, $\hat{V}^{ext}_{J-i}$,

$$\hat{V}^{ext}_{J-i} = -\sum_{i}\frac{Z_I e^2}{\mid \mathbf{r_i} - \mathbf{R_i} \mid} \tag{2.6}$$

and the Coulomb electron-electron interaction, $\hat{U}_{i-j}$,

$$\hat{U}_{i-j} = \frac{1}{2}\sum_{i\neq j}\frac{e^2}{\mid \mathbf{r_i} - \mathbf{r_j} \mid} \tag{2.7}$$

In order to be able to solve this atomic problem for any system larger than an atom with one electron, various approximations need to be made. Thus, the subject of this chapter is a summary of the methodologies in use, *ab-initio* labeled and only *ab-initio* rooted.

2.1 The "standard" approximations

This section is devoted to describe some approximations routinely used in *ab-initio* calculations. The approximations selected in this section are not going to be central in the discussions presented in chapters 3 and 4. Nevertheless, in order to clearly define the building blocks of this thesis, and in support of further discussions, a quick overview of these approximations is recommended.

2.1.1 The adiabatic or Born-Oppenheimer approximation

The adiabatic or Born-Oppenheimer approximation, allows us to consider that the nucleus are nearly fixed with respect to electron motion. This approximation relies the fact that the relation between the nuclear and electron masses is $\sim \frac{1}{1836}$, thus the kinetic energy of the nuclei can be treated as a perturbation in the total Hamiltonian, expression (2.2). As a result of this approximation the *ab-initio* problem, equations (2.1) and (2.2), can be rewritten as:

$$\hat{H}\,\Psi(\mathbf{x_1},\ldots,\mathbf{x_N}) = E\,\Psi(\mathbf{x_1},\ldots,\mathbf{x_N}) \tag{2.8}$$

where the Hamiltonian (2.2), has been replaced by,

$$\hat{H} = \hat{T}_i + \hat{U}_{I-J} + \hat{V}^{ext}_{J-i} + \hat{U}_{i-j} \tag{2.9}$$

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which depend upon the nuclear positions as parameters. Since Ψ is now a purely electronic wave function, it is constrained by the following antisymmetry condition,

$$\Psi(\mathbf{x_1}, \ldots, \mathbf{x_i}, \ldots, \mathbf{x_j}, \ldots, \mathbf{x_N}) = -\Psi(\mathbf{x_1}, \ldots, \mathbf{x_j}, \ldots, \mathbf{x_i}, \ldots, \mathbf{x_N}) \tag{2.10}$$

Throughout this work we are going to choose (2.8) as the *full electronic-problem*. This assumption is by far the most widespread way in which the *ab-initio* methods have been applied. It is indeed the first step away from the real *ab-initio* calculation.

2.1.2 Basis sets

For purposes of studying the numerical solutions of equation (2.8), expansions of

$$\Psi = \Psi(\mathbf{x_1}, \ldots, \mathbf{x_N}) \tag{2.11}$$

need to be made. Choosing an expansion of this quantity the concepts of single-particle orbitals[3], and basis sets are necessarily introduced. We start with the definition of single-particle orbitals.

A single-particle orbital, φ_j, is a function of a single-particle position. Thus, it describes the spatial distribution of the single-particle, such that $\int d\mathbf{r} \mid \varphi_i(\mathbf{r}) \mid^2$ is the probability of finding such a particle in the volume element, $d\mathbf{r}$, surrounding $\mathbf{r}$.

Using this concept any function of $\mathbf{x}$, particularly the overall wavefunction, $\Psi(\mathbf{x_1}, \ldots, \mathbf{x_N})$, can be obtained. Particularly the many-electron wave function, $\Psi(\mathbf{x_1}, \ldots, \mathbf{x_N})$, can be obtained as a product of single-particle orbitals. (For instance, as a Hartree product, as an Slater determinant, etc ... [42, 43].)

A basis set is is a set of functions used to create the single-particle orbitals, which are expanded as a linear combination of such functions with the weights or coefficients to be determined. Thus, the basis set is defined through the following expansion,

$$\varphi_i(\mathbf{r}) = \sum_j c_{i,j} f_j(\mathbf{r}) \tag{2.12}$$

The selection of f_j as Plane Waves, Slater or Gaussian type orbitals labeled the methods in use. In this work we will use Gaussian orbitals [44]. This selection for f_j leads to simpler integral evaluations than Slater orbitals or Plane Waves, and this is the numerical reason which lies besides this selection.

[3]Currently, referred as "the orbitals"

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2.1.3 Pseudopotentials

A pseudopotential is used to simplify the representation of the ion, thus eliminating the need to describe the orbitals of the possibly too many core electrons. This is done replacing the strong Coulomb potential of the nuclei and the tightly bounded core electrons, N_{core}, by an effective ionic potential. Thus, the pseudopotential, $\hat{V}_i^{pseudo}$, acts on the defined valence electrons,

$$N_{valence} = N - N_{core} \tag{2.13}$$

Therefore, if a pseudopotential scheme is used, the N-electrons problem stated through equations (2.8), (2.9), and (2.10); is replaced as follows[4] ,

$$\hat{H}\ \Psi\left(\mathbf{x_1}, \ldots, \mathbf{x_{N_{valence}}}\right) = E\ \Psi\left(\mathbf{x_1}, \ldots, \mathbf{x_{N_{valence}}}\right) \tag{2.15}$$

where the electron-nuclei interactions, $\hat{V}_{I-i}$ in equation (2.9), is being replaced by an effective potential of the N_{core} -electrons and the nuclei, $\hat{V}_i^{pseudo}$. Therefore, the final Hamiltonian is,

$$\hat{H} = \hat{T}_i + \hat{U}_{I-J} + \hat{V}_i^{pseudo} + \hat{U}_{i-j} \tag{2.16}$$

The use of pseupotentials allows a simplification of electronic structure calculations. Even when the pseudopotential operator, $\hat{V}_i^{pseudo}$, is a more complex object than the ion-electron potential, the fact that it is weaker and smoother has greater advantages, conceptually and computationally [45].

Finally, in this thesis we are not going to analyze the effect of basis set selections, adiabatic or pseudopotentials approximations, in the *ab-initio* electron transport methodology chosen. However, the calculations need to be simplified, and these approximations are *routinely* used. For this reason, in each calculation presented (chapters 5, 6 and 7), the "standard" approximations are indicated.

2.2 Wave Function Methods

As was explained in the introductory chapter, in this thesis the *ab-initio* methods used for determining electronic structures are mainly based on the Density-Functional Theory (DFT), instead of wave function calculations. Nevertheless, this section is basic for the understanding of further discussions within DFT, since some essential concepts to put forward this novel methodology are rooted in the Wave Function schemes. Some of them are central for this thesis, the locality as a mathematical concept in physics, and the

[4]The wave-function of the pseudoelectrons remains constrained by the antisymmetry condition,

$$\Psi\left(\mathbf{x_1}, \ldots, \mathbf{x_i}, \ldots, \mathbf{x_j}, \mathbf{x_{N_{valence}}}\right) = -\Psi\left(\mathbf{x_1}, \ldots, \mathbf{x_j}, \ldots, \mathbf{x_i}, \mathbf{x_{N_{valence}}}\right) \tag{2.14}$$

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xc-potentials as a function to map the many-electron problem in a mean-field electron problem. Therefore, in the next part of this section the fundamentals of the Wave Function methodologies are summarized.

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2.2.1 The Hartree-Fock Method

The foundations of the Wave Function calculations lay on the methodology proposed after the works of Hartree (1928) and Fock (1930), known as Hartree-Fock method, (HF) [46,47]. This method introduce a calculation scheme which is a self-consistent iterative variational procedure to calculate an *approximated* wave function for which the expectation value of the *exact* electronic molecular Hamiltonian is minimum[5].

The essential approximation of the HF method is that for a ground-state electronic system, the electrons can be assigned to a set of non-interacting molecular orbitals. Considering that electrons are fermions, the antisymmetry principle must be filled, therefore, the following determinantal-Slater representation is proposed for the wave function [43],

$$\Psi = \mid \varphi_1 (\mathbf{x_1}) \dots \varphi_N (\mathbf{x_N}) \rangle \tag{2.17}$$

To give us freedom to vary the molecular orbitals to best suit the molecule in question, each molecular orbital is expanded in terms of a set of basis functions as is proposed in the relations (2.12). To find out the values of the coefficients c_i that gives the best molecular orbitals, the following variational procedure for the total energy is applied [47].

The total energy is minimized with respect to all the degrees of freedom, with the restriction that the wave function has the form of a Slater's determinant, and provided that it is normalized,

First, the exchange potential is introduced, $\hat{v}_x$. Mathematically, $\hat{v}_x$ is given by a nonlocal function in the $\mathbf{r}$-space. In few words, it is a quantity which is necessarily defined in terms of two points in the coordinates of the electron system, $\mathbf{r_1}$ and $\mathbf{r_2}$. (For a definition of a nonlocal function a look of the appendix B is recommended.) Physically, this analytic property is connected with the consideration of an Slater's determinant in the proposal for the trial wave functional, when the minimization procedure is done. This observation is derived from a direct comparison with the original Hartree's work [42], only improved by Fock [46], with the addition of this constriction to the wave function. Therefore, the nonlocal $\hat{v}_x(\mathbf{r})$ could contains information derived from the exclusion principle. In addition to this statement, we emphasize, than an strict proof of the connection between nonlocality

[5]The wave function, chose as Slater's type, is written as a determinant of spin-orbitals [43].

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in $\hat{v}_x(\mathbf{r})$, and the fulfillment of the exclusion principle in the most general system, is not known to us.

Second, the concept of correlation energy is presented. The total energy obtained within this HF scheme is not the exact ground state energy. (One Slater determinant does not provide enough variational freedom to expand the entire Hilbert space of a set of fully interacting fermions.) So then, the difference between the exact total ground state energy and the HF energy is defined as the correlation energy,

$$E^{correlation} = E - E_{HF} \tag{2.19}$$

This correlation energy, as can be mathematically expected, is always negative. Furthermore, it is physically interpreted as a consequence of the artificial overlap of the electron clouds inherent to the single-determinantal wave function approximation. The electrons are thus on the average a little further apart than estimated by the HF method, an important consideration in regards the physical interpretation of numerical results. So that, neglecting electron correlation can lead to large deviations from experimental results. A number of approaches to this weakness, which limit the exactness of the HF method, are collectively called post-HF methods. These have been devised to include electron correlation into a multi-determinantal electron wave function. Some of these are going to be used in this thesis at most as references for conceptual frames, or for comparison of selected numerical calculations. Therefore, here we state the fundamental ideas behind the post-HF self-consistent approaches to the complete active space we are going to use, the Configuration Interaction, Coupled Cluster and Möller-Plesset Perturbative theory (in [48] and references therein).

2.2.2 The exactification of the Wave Function: post-Hartree Fock methods

A very brief summary of the post-HF methods, or many-body corrections, used in this thesis is presented:

- Configuration interaction (CI) [47] , is a linear variational method for solving the nonrelativistic Schrödinger equation, (2.8), improving the HF proposal. Mathematically, the configuration interaction describes the linear combination of Slater determinants used for the wave function,

$$\Psi = \sum_{I=0} c_I \Psi_I \tag{2.20}$$

  where Φ_I represents the terms involving I-excitations with respect to a reference function, which usually is the HF determinant. It provides, within the space spanned by the one-particle basis set, a framework to approach the exact solution of the

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electronic problem. As can be noted, this extension is conceptually very simple, but numerically very expensive. Thus, we mention it only for the conceptual values. For numerical calculations and still within Wave-Function methods, we are going to choose other methodologies which are presented below.

- Coupled cluster (CC) [44] ,is a numerical technique used for describing many-body systems. It is now one of the most prevalent methods in quantum chemistry that includes electronic correlation. CC theory proceeds by imposing an *ansatz* on the wave function,

$$\mid \Psi\rangle = e^{\hat{T}} \mid \Psi_0\rangle \tag{2.21}$$

where $\mid \Psi_0\rangle$ is an appropriate reference function of some sort, i.e. it can be a state function in HF space, and $\hat{T}$ is the cluster operator, written in the form,

$$\hat{T} = \hat{T}_1 + \hat{T}_2 + \hat{T}_n + \ldots \tag{2.22}$$

Here, the $\hat{T}_1$ is the operator of all single excitations, $\hat{T}_2$ is the operator of all double excitations and so forth. Usually the notations for coupled cluster methods begin with CC and subsequent letters indicated the level in which the excitations are shortened. In some cases, brackets are used if the excitation term referred is calculated based on perturbation theory. For example, throughout this thesis the highest level of coupled-cluster method is, CCSD[T]. It means that a coupled-cluster calculation is made, including simples and doubles excitations, and the triple excitations are calculated within perturbation theory.

- Møller-Plesset perturbation theory (MP) [49], is an implementation of perturbation theory, which provides a method for adding excitations to the HF wavefunction, $\mid \Psi_{HF}\rangle$, therefore including the effect of electron correlation.

  In MP theory, the unperturbed HF Hamiltonian operator, $\hat{H}_{HF}$ is extended by adding a small perturbation $\hat{V}$,

$$\hat{H} = \hat{H}_{HF} + \lambda \hat{V}. \tag{2.23}$$

Here, λ is an arbitrary parameter. If the perturbation is sufficiently small, according to the quantum perturbation theory [47], the improved wavefunction and energy can be expressed as a power series in λ,

$$\begin{aligned} \mid \Psi\rangle &= \lim_{n\to\infty} \sum_{i=0}^{n} \lambda^i \mid \Psi^{(i)}\rangle \\ E &= \lim_{n->\infty} \sum_{i=0}^{n} \lambda^i E_i \end{aligned} \tag{2.24}$$

The substitution of this expressions for $\mid \Psi >$ and E in the electronic Shrödinger equation (2.15), give as the wave functions and energies at the level defined by the value of n-sum. This information is summarized in the notation used for Moller-Plesset Methods, MPn. It is standard the implementation of n up to $4-$order. (This will be the highest level of our calculations.)

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Finally, we must remark that all the quantities discussed within HF theory are easy to obtain if we compare with those proposed within the exact-wave function methods. The correlation energy is a very difficult quantity to calculate, from a computational point of view, even for very small systems. This is because the correlation energy is directly related to the degrees of freedom in the Hilbert space, which must be spanned in a $4N$-multidimensional space, where N is the number of particles in the system. This "exponential wall" is the motivation for the development of other *ab-initio* electronic structure calculation schemes, for instance, the Density-Functional Theory [20].

2.3 Static Density-Functional Theory: DFT

Density-functional Theory (DFT) is a feasible and exact quantum mechanical methodology to investigate the electronic structure of many interacting particles considering the electronic density as the single basic variable. The fundamental premise of DFT is that **the many-body electronic wavefunction can be replaced by the ground state electronic density as the basic quantity**. Therefore, the knowledge of a single particle quantity, the ground state electronic density, determines all the properties of the system, whether it is in a ground or excited state [33]. Whereas the many-body wavefunction is dependent on $4N-$ variables, four variables for each of the $N-$ electrons, the ground state electronic density is only a function of four variables and is a simpler quantity to deal with, both conceptually and practically. This section is devoted to sketch the proof of this statement, the first Hohenberg-Kohn theorem, (HK) [6], and subsequent works which made manageable this theorem, the Kohn-Sham methods, (KS) [7]. Before reading this section a review of the appendix A is recommended, since there a quick view of the density matrices definitions is presented, the central quantities of DFT.

2.3.1 The Hohenberg-Kohn theorems

The starting point of Hohenberg-Kohn (HK) theorems, (1964) [6], is the hypothesis that a knowledge of the ground-state density, $n(\mathbf{r})$, for any electronic system (with or without interactions) uniquely determines the system. This hypothesis is stated and proved within the context of the first-HK theorem: *the ground-state density $n(\mathbf{r})$ of a bound-system of interacting electrons in some external potential $v^{ext}(\mathbf{r})$ determines this potential uniquely, (up to a physically meaningless additive constant)*, ,

$$n(\mathbf{r}) \iff v^{ext}(\mathbf{r}) \tag{2.25}$$

From the existence of the mapping above presented, it is concluded that the $v^{ext}(\mathbf{r})$, in the Hamiltonian (2.8), is fully determined from the knowledge of $n(\mathbf{r})$.

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Remarkably, it follows that the many-body wavefunctions for all states, ground $s = 0$ and excited s $\neq 0$, $\Psi^s = \Psi^s(\mathbf{x_1}, ..., \mathbf{x_N})$ could be determine as $\Psi^s = \Psi^s[n(\mathbf{r})]$. Therefore, the ground-state density determines the expectation value of **any** electronic operator ($\hat{O}$),

$$O[n] = < \Psi[n] |\hat{O}| \Psi[n] > \tag{2.26}$$

An important consequence of this one-to-one mapping between the many-body wave function and the density is that the $4N-$ dimension electronic problem could be, in principle, reduced to a $4-$ dimensional one. That is, one scalar function of the position such as $n(\mathbf{r})$, in principle, determines all the information in the many-body wavefunctions. There are not doubts of numerical advantages of this mapping within the context of *ab-initio* calculations. Nevertheless, its manageability, or more precisely, the functional relation required to extract any general property, equation (**??**), are generally unknown. Thus, the first HK theorem should be considered as a theorem of existence.

The second HK theorem is a theorem for the construction of the total energy, E, and the ground state electronic density, $n(\mathbf{r})$: *A universal functional (F_{HK} in the next paragraphs) for the total electronic energy, initially defined through the equation (2.8), in terms of the electronic density, can be built valid for a any external potential, and the total ground state energy of such system is the global minimum of this functional evaluated at the exact ground state electronic density.* Within this scheme a route to formally calculate $n(\mathbf{r})$ and total-energies, see equation (2.27), is justified using the variational Rayleigh-Ritz principle [50]. This proof of the theorem starts using the expression which express the total electronic energy as a functional of $n(\mathbf{r})$,

$$E[n(\mathbf{r})] = \int d\mathbf{r}\ \ v^{ext}(\mathbf{r}) n(\mathbf{r}) + F_{HK}[n(\mathbf{r})] \tag{2.27}$$

in this expression, a new functional containing the electron-electron interactions and the total kinetic energy is included, F_{HK},

$$F_{HK}[n(\mathbf{r})] = \frac{1}{2} \int d\mathbf{r} d\mathbf{r}'\ \ \frac{n(\mathbf{r}) n(\mathbf{r}')}{\mid \mathbf{r} - \mathbf{r}' \mid} + \frac{1}{2} \int d\mathbf{r}\ \ \nabla_{\mathbf{r}} \nabla_{\mathbf{r}'} n_1(\mathbf{r}, \mathbf{r}')|_{\mathbf{r}=\mathbf{r}'} + \frac{1}{2} \int d\mathbf{r} d\mathbf{r}'\ \ \frac{C_2(\mathbf{r}, \mathbf{r}')}{\mid \mathbf{r} - \mathbf{r}' \mid} \tag{2.28}$$

Here C_2 is the two-particle correlation function defined in terms of the one- and two-particle density matrices as,

$$C_2(\mathbf{r}, \mathbf{r}') = n_2(\mathbf{r}, \mathbf{r}'; \mathbf{r}, \mathbf{r}') - n_1(\mathbf{r}, \mathbf{r})\ \ n_1(\mathbf{r}', \mathbf{r}') \tag{2.29}$$

The first term in (2.28) is explicitly known in terms of the electronic density.

In what follows, the second HK theorem is analogous to the variational principle for wavefunctions, but in the space of electronic densities. It states that for any given non-negative trial density, $n_{trial}(\mathbf{r}) > 0$, that integrates to the correct number of electrons, N,

$$\int d\mathbf{r}\ n_{trial}(\mathbf{r}) = N \tag{2.30}$$

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and the true ground state energy, (E_0) , is constrained by the relation,

$$E_0 = min_{n(\mathbf{r})} E[n(\mathbf{r})] \tag{2.31}$$

This provides a route for solving equations (2.31) if $F[n]$ is a known functional form.

A subtle point to be mentioned is that associated with the $v-$ representability problem. This deals with the definition of the density for any external potential. An electronic density is called $v-$ representable if it is associated with the antisymmetric ground state wavefunctions of the Hamiltonian (2.8). This is a non-trivial assumption. (Detailed discussions are included in [31, 33, 51].) Nevertheless, in this work we are going to assume that all our densities are $v-$ representable.

Finally, the real manageability of the HK theorems comes after the Kohn and Sham works (1965), the first approach which provide a way to make approximate ground state functionals for real systems of many electrons [7]. Due to its importance, this subject will be discussed in the next part of this section.

2.3.2 The Kohn-Sham method

The proof of the Hohenberg-Kohn theorem is not constructive, hence the form of the functional F_{HK} in equation (??) is not known. It is only after the advent of the Kohn and Sham works, when the Hohenberg-Kohn Theory became manageable, through an exact formalism for the calculation of the total electronic energy as a functional of the electronic density.

Based on the work of Hohenberg and Kohn, Kohn and Sham take up the total ground-state energy in terms of electronic density [7]. In their notation, this $E[n(\mathbf{r})]$ is,

$$E[n(\mathbf{r})] = \int d\mathbf{r}\ \ v^{ext}(\mathbf{r})n(\mathbf{r}) + \int d\mathbf{r}\ \ v^{Hartree}n(\mathbf{r}) + G[n(\mathbf{r})] \tag{2.32}$$

where $v^{Hartree}$ is,

$$v^{Hartree}[n](\mathbf{r}) = \frac{1}{2}\int d\mathbf{r}'\ \ \frac{n(\mathbf{r})n(\mathbf{r}')}{\mid \mathbf{r} - \mathbf{r}' \mid} \tag{2.33}$$

where $G[n(\mathbf{r})]$ is expressed as,

$$G[n(\mathbf{r})] = T_s[n(\mathbf{r})] + E_{xc}[n(\mathbf{r})] \tag{2.34}$$

In the expression above $T_s[n(\mathbf{r})]$ is the kinetic energy of a system of noninteracting electrons with density $n(\mathbf{r})$ and $E_{xc}[n(\mathbf{r})]$ is defined as the xc-energy contribution of an interacting system with density $n(\mathbf{r})$. This energy is included in the last two terms in the expression (??,

$$E_{xc}[n(\mathbf{r})] = \frac{1}{2}\int d\mathbf{r}\ \ \nabla_{\mathbf{r}}\nabla_{\mathbf{r}'}n_1(\mathbf{r},\mathbf{r}')|_{\mathbf{r}=\mathbf{r}'} + \frac{1}{2}\int d\mathbf{r}d\mathbf{r}'\ \ \frac{C_2(\mathbf{r},\mathbf{r}')}{\mid \mathbf{r} - \mathbf{r}' \mid} - T_s[n(\mathbf{r})] \tag{2.35}$$

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The E_{xc} is unknown in terms of the electronic density. Special attention should be paid to this quantity. This is the central of this thesis, and without doubts its finding as an algebraic expression of the density is central for almost all the works within the fundamentals of the *ab-initio* density-based methods, ([31,33] and references therein).

The first Kohn and Sham ***ansatz***, the hypothesis where the theory relies, is that the system of interacting particles can be represented by a system of non-interacting particles but interacting densities; and in such mapping the electronic density remains unchanged. As Kohn and Sham did, we proceed assuming the validity of this *anzats*[6].

In what follows, the derivation of the equations which leads to the exact total electronic energy and total electronic density is introduced as in the original paper by Kohn and Sham [7]. Due to the stationary property of the total energy functional, (expression 2.32), its minimization is subject to the constraint,

$$\int d\mathbf{r}\ \ \delta n\left(\mathbf{r}\right) = 0 \tag{2.36}$$

Therefore, the following equation is obtained,

$$\int d\mathbf{r}\ \ \delta n\left(\mathbf{r}\right)\left[\frac{\delta T_s\left[n\right]}{\delta n} + v^{ext} + v^{Hartree} + \frac{\delta E_{xc}[n\left(\mathbf{r}\right)]}{\delta n\left(\mathbf{r}\right)}\right] \ = \ 0 \tag{2.37}$$

Thus, for a given external potential and xc-energy functional we can obtain the electronic density which satisfies this condition (2.37) by solving the $i-$coupled mean-field equations:

$$[-\frac{1}{2}\nabla^2 + v^{ext} + v^{Hartree} + \frac{\delta E_{xc}[n\left(\mathbf{r}\right)]}{\delta n\left(\mathbf{r}\right)}]\,\varphi_i = \varepsilon_i\,\varphi_i \tag{2.38}$$

where the referred $N-$electrons are described through single-particle orbitals, $\varphi_i\left(\mathbf{r}\right)$, subject to the constrain,

$$n(\mathbf{r}) = \sum_{\sigma}\sum_{i=1}^{N_\sigma} \mid \varphi_i^{\sigma}(\mathbf{r}) \mid^2 \tag{2.39}$$

Equations (2.38) and (2.39) constitute a set of coupled mean-field equations for single-quasiparticles, which provide a route for finding the exact ground state density and energy, by finding the expression of the xc-energy functional. The functional derivative of E_{xc} defines the xc-potential, v_{xc} (the definition of functional derivative is in the appendix B)

$$v_{xc}[n](\mathbf{r}) = \frac{\delta E_{xc}[n(\mathbf{r})]}{\delta n(\mathbf{r})} \tag{2.40}$$

If the $v-$representability in a non-interacting electronic system is accepted, this set of equations, (2.38), (2.39), and (4.9), provide a variational framework for the exactification of the total energy and the electronic density of the original many body interacting system. The accuracy relies on the definition of the xc-energy, $E_{xc}[n(\mathbf{r})]$, or equivalently the xc-potential functional, $v_{xc}[n](\mathbf{r})$, which are unknown for the most general situations as will be discussed in the next part of this section.

[6]A A rigorous proofs of its exactness is done within the topic of $v-$ representativity for the non-interacting density which ,apparently, is not central for this thesis. For details on this discussion references in [51,52] could be checked.

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2.3.3 The Local Density Approximation: LDA methods

The central track doing a practical Kohn-Sham scheme lies on the definition of $E_{xc}[n(\mathbf{r})]$, or equivalently, $v_{xc}[n](\mathbf{r})$. Several works are being doing in this line [15, 16, 53–55].

First, a careful distinction should be made between the mean-field Kohn-Sham scheme and the LDA[7]. The Kohn-Sham method is formally exact, and the LDA is an approach strictly valid only for a non-interacting *homogenous electron gas*. In other words, further extensions of this treatment for general electronic densities are not justified, as will be discussed in chapter 4, pointing to the central line of this thesis. Nevertheless, since almost all the DFT methods are rooted in the LDA, its presentation will be useful in terms of introducing some basic concepts.

In the LDA scheme the $E_{xc}[n(\mathbf{r})]$ functional is given by [6],

$$E_{xc}[n(\mathbf{r})] = \int d\mathbf{r}\ n(\mathbf{r})\epsilon_{xc}\left(n(\mathbf{r})\right). \tag{2.41}$$

The functional derivative of this expression give us the xc-potential, $v_{xc}(n(\mathbf{r}))$, which could be written as,

$$v_{xc}(n(\mathbf{r})) = \epsilon_{xc}\left(n\left(\mathbf{r}\right)\right) + n(\mathbf{r})\frac{\partial \epsilon_{xc}\left(n(\mathbf{r})\right)}{\partial n(\mathbf{r})} \tag{2.42}$$

In the expressions above, $\epsilon_{xc}\left(n(\mathbf{r})\right)$ is the xc-energy per electron of a *homogenous electron gas* of density $n(\mathbf{r}) = constant$, which is discussed within the theories of the *homogeneous electron gas* [56]. In this thesis, the only thing that matters, is that ϵ_{xc} is defined, and therefore constrained, to a finite algebraic function of $n(\mathbf{r})$, $[\epsilon = \epsilon_{xc}\left(n(\mathbf{r})\right)]$. Equivalently, ϵ_{xc} is a local functional of the density (in the appendix B the formal definition of locality is stated) and thenceforth it is local in the $\mathbf{r}$-space,

$$\forall\ \mathbf{r} \neq \mathbf{r}' \quad [\epsilon_{xc}(\mathbf{r}, \mathbf{r}') = \epsilon_{xc}(\mathbf{r})] \tag{2.43}$$

Physically, it means that the $\epsilon_{xc}(\mathbf{r})$, could be obtained without consider causal effects in the $\mathbf{r}$-space.

The first improvements upon the LDA were made in the context of what is known as Generalized Gradient Approximations (GGA's) [15]. These GGA methods can be summarized in the following expressions for $E_{xc}[n(\mathbf{r})]$ and $v_{xc}[n(\mathbf{r}]$,

$$E_{xc}\left[n(\mathbf{r})\right] = \int d\mathbf{r}\ n(\mathbf{r})\epsilon_{xc}\left(n(\mathbf{r}), \nabla n(\mathbf{r}), \nabla^2 n(\mathbf{r}), ..., \nabla^i n(\mathbf{r})\right) \tag{2.44}$$

$$v_{xc}\left[n(\mathbf{r})\right] = \epsilon_{xc}\left(n(\mathbf{r}), \nabla n(\mathbf{r}), \nabla^2 n(\mathbf{r}), ..., \nabla^i n(\mathbf{r})\right) + n(\mathbf{r})\left[\sum_{k=1}^{i}(-1)^i \frac{d^i}{d\mathbf{r}^i}\frac{\partial \epsilon_{xc}}{\partial n(\mathbf{r})}\right] \tag{2.45}$$

[7] In the specialized literature the works based in LDA plus the Kohn-Sham scheme, are often labeled as Kohn-Sham methods [33, 36]. From our point of view, it is a confusing label. It should be the basis of the nonjustified map of LDA inconsistency to an inability of the mean-field Kohn-Sham scheme.

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These two forms defining $E_{xc}[n(\mathbf{r})]$ and $v_{xc}[n(\mathbf{r})]$, have a common analytic property, both are local in the **r**-space. Henceforth, all the works rooted in any of those two approaches, LDA or GGA's, are going to be labeled as **Local Density-Functional Theories, Local-DFT**. This analytic property, the local dependence on the **r**-space, will be sufficient for showing in the next chapters the non validity of Local-DFT for the most general situations we could deal with.

A sketch of the main results contained in this section are shown in the sketch that follows,

$$n(\mathbf{r}) \quad \overset{\text{HK}}{\Longleftrightarrow} \quad v^{ext}(\mathbf{r}) \quad \overset{\text{KS}}{\Longleftrightarrow} \quad v^{meanfield}\ [v_{xc}(\mathbf{r})] \tag{2.46}$$

HK and KS made reference to the canonical Hohenberg-Kohn and Kohn-Sham works [6,7].

2.4 Time-Dependent Density-Functional Theory: TDDFT

In this section, a short overview of some results obtained within Time-Dependent Density-Functional Theory, (TDDFT), is given.

2.4.1 The Runge-Gross theorems

TDDFT extends the concepts of static DFT to time-dependent situations. Its origins dates back to the works developed by Runge and Gross (1984) [21]. The central quantities of TDDFT are the time-dependent single particle- and current- densities, ($(n \equiv n(\mathbf{r},t)$ and $\mathbf{j} \equiv (\mathbf{r},t)$). These are defined as an extension of the expressions (A.4) and (1.21) previously introduced. This generalization is made replacing the wave function vectors obtained from the stationary Schrödinger equation for the time-dependent wave function vectors obtained from the time-dependent Schrödinger equation,

$$i\hbar \frac{\partial \Phi(t)}{\partial t} = \hat{H}(t)\ \Phi(t), \qquad \Phi_{(t_0)} = \Phi_0. \tag{2.47}$$

First, it is proven within TDDFT, that the single particle potential $v^{ext} = v^{ext}(\mathbf{r},t)$ leading to a given $n(\mathbf{r},t)$ is uniquely determined, so that the corresponding map is invertible [21],

$$n(\mathbf{r},t) \Longleftrightarrow v^{ext}(\mathbf{r},t). \tag{2.48}$$

In other words, the Hamiltonian in (2.47), is fully determined from the knowledge of $n(\mathbf{r},t)$. Using this result the calculation of any time-dependent operator could be, in principle, defined in terms of the $n(\mathbf{r},t)$. The success in the context of quantum transport, is that

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the current-density is well defined in terms of the $n(\mathbf{r},t)$ using a set of hydrodynamical equations. (For the detailed discussion of this topic see section 1.2 in chapter 1.) The success in the context of this thesis, is that the conductance can be determined as a limit of the corresponding time-dependent quantity, which is only $(\mathbf{r},t)$- dependent.

For the calculation of the $n(\mathbf{r},t)$ a mean-field route analogous to the one proposed by Kohn and Sham within stationary DFT is developed, section 2.3.3. In a time-dependent context, the variational principle for the total electronic energy cannot be applied. Instead, a minimal principle can be defined on the following action integral,

$$A = \int_{t_0}^{t_1} dt \ \ < \Phi(t) \mid i\frac{\partial}{\partial t} - \hat{H}(t) \mid \Phi(t) > \tag{2.49}$$

as stated by Runge and Gross [21]. Therefore, the exact time-dependent electronic density could be computed from the Euler equation,

$$\frac{\delta A}{\delta n(\mathbf{r},t)} = 0. \tag{2.50}$$

The scheme for the calculation of $n(\mathbf{r},t)$ is defined as follows,

$$n(\mathbf{r},t) = \sum \phi_j^*(\mathbf{r},t)\phi_j(\mathbf{r},t) \tag{2.51}$$

where the single-particle orbitals $\phi_j(\mathbf{r},t)$ fulfill the time-dependent Shrödinger equation,

$$\left(i\frac{\partial}{\partial t} + \frac{1}{2}\nabla^2)\phi_j(\mathbf{r},t)\right) = v_{eff}[n](\mathbf{r},t) \ \ \phi_j(\mathbf{r},t) \tag{2.52}$$

with an effective single-particle potential given by,

$$v_{eff}[n](\mathbf{r},t) \ \ \Phi_j(\mathbf{r},t) = v(\mathbf{r},t) + v^{Hartree}(\mathbf{r},t) + \frac{\delta A_{xc}[n(\mathbf{r},t)]}{\delta n(\mathbf{r},t)} \tag{2.53}$$

At this point a practical and exact mean-field route for the calculation of $n(\mathbf{r},t)$ is devised. Nevertheless, it should be emphasized, that like in the case of static DFT, practical calculations demands an expression for the dynamical single-particle xc-potential , $v_{xc} \equiv v_{xc}[n](\mathbf{r},t)$,

$$v_{xc}[n](\mathbf{r},t) = \frac{\delta A_{xc}[n(\mathbf{r},t)]}{\delta n(\mathbf{r},t)} \tag{2.54}$$

Its first definition is the subject of the next paragraphs. Like in the case of the static xc-potential, its finding is the essence of a very active field [36, 57].

2.4.2 The Adiabatic Local Density Approximation: ALDA methods

The simplest approximation one can make for this potential is the adiabatic local density approximation (ALDA), which is a generalization of the LDA approximation introduced

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in the context of static DFT, see section 2.3.3. In the ALDA approximation the static LDA xc-kernel is used, equation (2.41), but replacing the static density, $n(\mathbf{r})$ by the time-dependent density, $n(\mathbf{r},t)$,

$$v_{xc}[n](\mathbf{r},t) = \epsilon_{xc}(n(\mathbf{r}),t) + n(\mathbf{r},t)\frac{\partial \epsilon_{xc}(n(\mathbf{r},t))}{\partial n(\mathbf{r},t)} \tag{2.55}$$

Just like in the case of static DFT, we want to remark the local dependence on $n(\mathbf{r},t)$, for such xc-potential. The first extension to this approximations where done in the same line as in LDA potentials, doing gradients terms of the electronic density in the expression for the kernel. Therefore, all the methodologies based on this sort of mathematical constructions are going to be labeled as Local-TDDFT.

An sketch of the main results obtained in this section are shown in this scheme,

$$n(\mathbf{r};t) \quad \overset{\text{RG}}{\Longleftrightarrow} \quad v^{ext}(\mathbf{r};t) \quad \overset{\text{RG}}{\Longleftrightarrow} \quad v^{meanfield}\ [v_{xc}[n](\mathbf{r};t)] \tag{2.56}$$

where RG made reference to the Runge-Gross works [21]. A comparison with the representation in 2.46 is recommended.

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Part II

Present Theories

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Chapter 3

An *ab-initio* time-dependent electronic transport theory

Overview

In this chapter the attention is focused in the efficient and accurate design of xc-potentials, $v_{xc} = v_{xc}(\mathbf{r}, t)$. As was shown in section 1.2, this quantity could be controlling an *ab-initio* time-dependent direct access to the conductance. The following scheme is a representation of this *ab-initio* route,

$$v_{xc}(\mathbf{r};t) \overset{\text{RG}}{\Longleftrightarrow} n(\mathbf{r};t) \overset{\text{TD}}{\Longleftrightarrow} \mathbf{j}(\mathbf{r};t) \overset{\text{LIM}}{\Longleftrightarrow} G \tag{3.1}$$

The notation RG denotes the Runge-Gross theorem applied to the non-interacting problem (in reference [21] and section 2.4); the TD denotes the Todorov and Di Ventra theorem (in reference [18] and section 1.2). The arrow labeled LIM provides a connection between the time-dependent and the static systems, through the limit we do to recover the central quantity within this thesis, the conductance, equation (E.3). Therefore, in principle, the finding of $v_{xc} = v_{xc}(\mathbf{r}, t)$ determines the conductance of the full many-body system.

The first section of this chapter is devoted to discuss the capacity of the xc-potential locally defined on the space of the electronic densities, $v_{xc} = v_{xc}[n(\mathbf{r};t)]$, for describing linear current response for the systems we want to investigate, *one* or *few* molecules bridging metallic nanowires. Based on the derivation of the xc-potential as a functional of the time-dependent electronic density, due to Gross and Kohn [58]. It is shown that *a consistent xc-potential construction in terms of a local functional of the electronic density, to deal with the most general systems, is not formally justified.* This mathematical inability is in agreement with the own physical nature of the systems studied, as will be identified in this

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section. In few words, the arguments given are intended to formally question the validity of any local density approximation for the xc-potential due to the inability to capture nonlocal physical effects.

In the second section, the locality problem is circumvented and completely eliminated. This is done by upgrading TDDFT to describe the xc-potential in terms of the electronic and the current densities, $v_{xc} = v_{xc}[n(\mathbf{r};t), \mathbf{j}(\mathbf{r};t)]$ [11, 59]. This generalized TDDFT, where the electronic and the current densities are used as basic quantities, is labeled as Time-Dependent Current-Density-Functional Theory, (TDCDFT). A bird's-eye view of the fundamentals of TDCDFT and the main references for this theory are given in this section, considering its importance as a formal basis for the application of the *ab-initio* methods to quantum transport problems.

From these two sections, some fundamental results for the application of time-dependent density-based formalisms to transport problems are obtained. Due to its importance within the context of this thesis these are stressed in the next paragraph.

A single-particle formulation of the linear response problem exists. Its manageability relies on the construction of the xc-potential, $v_{xc} = v_{xc}[n](\mathbf{r};t)$. Generally, the analytic form of this functional is not known. However, as a first step some of its properties can be obtained. These can be identified from the exact treatment of the Runge-Gross theorem [21]. In this thesis we are concerned about the following property, the locality of the xc-potential (An extended discussion of the locality property is included in the appendix B and references therein.). As it will be shown in these two sections, for the most general system, *necessarily, the xc-potential is nonlocally defined in the* $\mathbf{r}$*-space.*

Finally, in section 3.3 and in the same line as Sai. *et al.* [12], the static limit is recovered,

$$\lim_{\omega \to 0} F^{dyn}(\omega) = F^{sta} \tag{3.2}$$

where $F = F^{dyn}(\omega)$ is any well-behaved function defined in the ω-space. Physically, ω describes the frequency of the excitation. Therefore, $F(\omega)\,|_{\omega \neq 0}$ must be interpreted as a dynamical quantity, F^{dyn}; and $F(\omega)\,|_{\omega=0}$ must be interpreted as the corresponding static quantity, F^{sta}. This generic limit will be enough to obtain some properties of the static xc-potential, v_{xc}^{sta}, starting from its exact dynamical counterpart, v_{xc}^{dyn}. Then, from the knowledge of the exact static xc-potential, the exact static conductance could be derived. Summarizing, in this section, the quantity we are interested in this thesis, will be determined starting from mean-field time-dependent simulations.

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3.1 The conductance within TDDFT

As mentioned in the introduction of the chapter, this section is devoted to discuss a formal derivation of the xc-potential, $v_{xc} = v_{xc}[n(\mathbf{r};t)]$, since, as was pointed out in sections 2.4 and 1.2, this quantity is sufficient to complete a mean-field and time-dependent *ab-initio* route for electronic transport calculations. At the end of the section, we will have to resign ourselves to deal with exact analytic forms of $v_{xc} = v_{xc}[n(\mathbf{r};t)]$ only for systems of *almost constant* and *slowly varying densities*, which are not the ones we are interested in either.

However, the form here introduced for the xc-potential, equation (3.9), will be useful in the context of this thesis. Explicitly, the equation (3.9) claims for *a nonlocal field defining the xc-potential in the most general electronic system.* The next paragraphs are devoted to proof this fact.

The response of any electronic system to an external potential, $v = v(\mathbf{r};t)$, is fully described by its electronic density, $n(\mathbf{r};t)$ (this is one of the contents of the Runge-Gross theorem [21]). Therefore, the $v(\mathbf{r};t)$ and $n(\mathbf{r};t)$ are conjugate variables. For convenience, the following expressions for $v(\mathbf{r};t)$ and $n(\mathbf{r};t)$ are introduced,

$$\begin{aligned} v(\mathbf{r};t) &= v^0(\mathbf{r}) + v^1(\mathbf{r};t) \\ n(\mathbf{r};t) &= n^0(\mathbf{r}) + n^1(\mathbf{r};t) \end{aligned} \tag{3.3}$$

where the $0-$superindex indicates a ground state quantity, and the $1-$superindex indicates a time-dependent quantity. This separation will be useful in further discussions. In the linear response regime, $v^1(\mathbf{r};t) << v^0(\mathbf{r})$, and the expressions above can be rewritten as,

$$\begin{aligned} v(\mathbf{r};t) &= v^0(\mathbf{r}) + v^1(\mathbf{r};\omega)\, e^{-i\omega t} + c.c \\ n(\mathbf{r};t) &= n^0(\mathbf{r}) + n^1(\mathbf{r};\omega)\, e^{-i\omega t} + c.c \end{aligned} \tag{3.4}$$

these two expressions above, should be enough to mathematically enclose the physics in the *vicinity* of the static regime. This is the zone to characterize, before going to the static limit, the one we are interested in this thesis for define the conductance.

As was showed in section 2.4, the two quantities above can be coupled and solved through a set of mean-field equations. In this line of analysis, the following hypothesis is made; the existence of a map for the system above described in a single-electron system, where all the electron-electron interactions are replaced by an effective potential, $v^{eff}(\mathbf{r};t)$, and the static and time-dependent densities do not change[1], $n^0(\mathbf{r})$ and $n^1(\mathbf{r};\omega)$. After some elementary manipulations, the following expressions for the effective potential and the electronic density are,

$$\begin{aligned} v_{eff}(\mathbf{r};t) &= v^0_{eff}(\mathbf{r}) + v^1_{eff}(\mathbf{r};\omega)\, e^{-i\omega t} + c.c \\ n(\mathbf{r};t) &= n^0(\mathbf{r}) + n^1(\mathbf{r};\omega)\, e^{-i\omega t} + c.c \end{aligned} \tag{3.5}$$

[1]This *anzats* could be considered as a plausible map if the proof of Leeuwen is accepted (in [52] and references therein).

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here, the effective potentials, $v^0_{eff}(\mathbf{r})$ and $v^1_{eff}(\mathbf{r};\omega)$, are of the form,

$$\begin{aligned} v^0_{eff}(\mathbf{r}') &= v^0(\mathbf{r}) + \int d\mathbf{r}' \frac{n_0(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} + v^0_{xc}(\mathbf{r}) \\ v^1_{eff}(\mathbf{r}';\omega) &= v^1(\mathbf{r},\omega) + \int d\mathbf{r}' \frac{n_1(\mathbf{r}',\omega)}{|\mathbf{r}-\mathbf{r}'|} + v^1_{xc}(\mathbf{r},\omega) \end{aligned} \tag{3.6}$$

In the expressions above, the first two potentials are the external and the Hartree potentials, explicitly represented. The remaining term, in both expressions, are the obscure xc-potentials, the static is $v^0_{xc}(\mathbf{r})$ and the time-dependent is $v^1_{xc}(\mathbf{r};\omega)$. Definitively, these two xc-potentials are the building blocks of an effective *ab-initio* electronic transport theory.

In the line of the method followed by Gross and Kohn a new formal representation of the v_{xc} is introduced [58]. Its novelty is established by a direct comparison with the v_{xc} derived in the section 2.4. Its ability is that it could give light to defining an analytic form for the general v_{xc}.

Firstly, it is *assumed* that $v^0_{xc}(\mathbf{r})$ could be known. So then, the problem associated with its definition is not treated, and therefore the finding of v_{xc} rests on the definition of $v^1_{xc}(\mathbf{r},\omega)$. Then, they assume the validity of the transformations (3.3), (3.17), (3.5), (3.6) and introduce the density response functions to formally connect the perturbing xc-potentials, $v^1_{xc}(\mathbf{r};\omega)$, with the electronic densities. These transformations are made as follows,

$$n_1(\mathbf{r};\omega) = \int d\mathbf{r}' \chi(\mathbf{r},\mathbf{r}';\omega)\, v_1(\mathbf{r}';\omega) \tag{3.7}$$

where $\chi(\mathbf{r},\mathbf{r}';\omega)$ denotes the exact, in principle many body, density response function and,

$$n_1(\mathbf{r};\omega) = \int d\mathbf{r}' \chi_{KS}(\mathbf{r},\mathbf{r}';\omega) v^{eff}(\mathbf{r}';\omega) \tag{3.8}$$

where $\chi_{KS}(\mathbf{r},\mathbf{r}';\omega)$ is the effective single-particle density response. At this point, Gross and Kohn derive $v_{1,xc}(\mathbf{r};\omega)$,

$$v^1_{xc}(\mathbf{r};\omega) = \int d\mathbf{r}' f_{xc}(\mathbf{r},\mathbf{r}';\omega) n_1(\mathbf{r}';\omega) \tag{3.9}$$

where $f_{xc}(\mathbf{r},\mathbf{r}';\omega)$ is a compact term, known as the kernel of the transformation. It is defined as follows,

$$f_{xc}(\mathbf{r},\mathbf{r}';\omega) = \chi^{-1}_{KS}(\mathbf{r},\mathbf{r}';\omega) - \chi^{-1}(\mathbf{r},\mathbf{r}';\omega) - \frac{1}{|\mathbf{r}-\mathbf{r}'|} \tag{3.10}$$

Therefore, provided that the inverse response functions $\chi^{-1}_{KS}(\mathbf{r},\mathbf{r}';\omega)$ and $\chi^{-1}(\mathbf{r},\mathbf{r}';\omega)$ exist, a new expression for $v^1_{xc}(\mathbf{r},\omega)$ is being obtained, equation (3.9).

As was mentioned in the introduction of this section, for initially *almost constant* or *slowly varying* systems explicit expressions for $v^1_{xc}(\mathbf{r},\omega)$ are also derived by Gross and Kohn [58]

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(The definitions of *almost constant* or *slowly varying* systems is discussed in the appendix C.). Without enter in details of their derivation, a common between the two limit forms for $v^1_{xc}(\mathbf{r},\omega)$ obtained in [58], should be remarked, the field where $v^1_{xc}(\mathbf{r},\omega)$ is defined. It is local in the position space (for details see the original work [58]). Now, if it is considered that $v_{0,xc}(\mathbf{r})$ is also local in the position space, then the resulting $v_{xc}(\mathbf{r},\omega)$ will also obey the same analytic property. As far as we know, this is the work which formally supports the construction of local expressions for $v_{xc}(\mathbf{r},\omega)$.

At this point, we must remark the following three partial conclusions. First, through equation (3.9), we have a new route to derive $v_{xc}(\mathbf{r},\omega)$ in addition to the canonical definitions given within the *ab-initio* time-dependent formalism,

$$v_{xc} = \frac{\delta}{\delta n} A_{xc} \tag{3.11}$$

Further details can be found in section 2.56.

Second, the expression (3.9) is enough to justify a nonlocal relationship between $n_1(\mathbf{r}',\omega)$ and $v^1_{xc}(\mathbf{r},\omega)$ in the most general electronic system. If not further assumptions are made, using the equations (3.5) and (3.6), this nonlocality should be extended to the relation between the $n(\mathbf{r}',t)$ and the $v_{xc}(\mathbf{r},\omega)$. Remarkably, this analytic property cannot be directly appreciated if we look at the canonical definition given by equation (3.11), taken from section 2.56. Finally, local constructions of $v_{xc}(\mathbf{r},\omega)$ is only justified for initially *almost constant* or *slowly varying* systems.

As will be shown in the next part of this section, the nonlocality in any quantity, for instance the $v_{xc}(\mathbf{r},\omega)$, must be directly related with the behavior of the electronic density, since this is the basic quantity of the *ab-initio* mean-field theory. The next part point to control this mathematical essence. (No general proof of the existence of such relation is known to us, although it is formally established in two special cases, e.g., *almost constant* and *slowly varying* electronic densities). In addition to this "subtle" relationship, the next part of this section should not be read as a final proof of the necessity of nonlocality for an exact mean field theory in terms of $v_{xc}(\mathbf{r},\omega)$. It should be interpreted as a formal proof of the non fulfillment of the hypothesis required by current methodologies [32, 60], for constructing local approximations for v_{xc} in the systems we are dealing with, one or few molecules between metallic nanowires.

3.1.1 A connection between nonlocality and electronic confinement

The "novel and Nobel" work of Hohenberg and Kohn, supports the full characterization of an interacting electronic system in terms of the spatial behavior of its ground state electronic density [6]. This is of prime importance for any thesis within density functional

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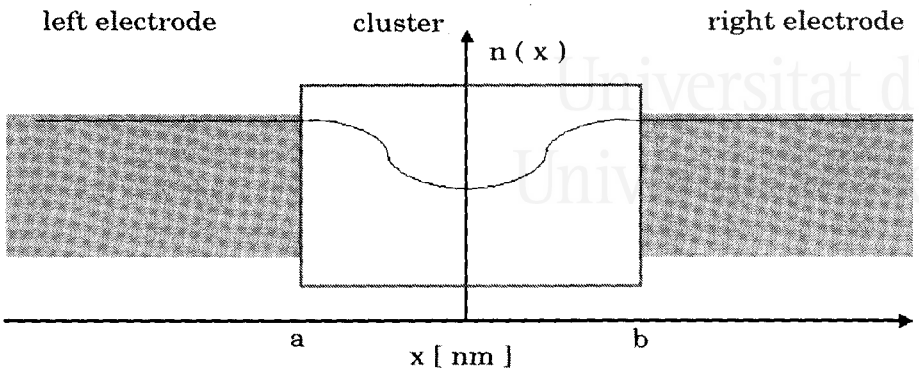

Figure 3.1: Schematic diagram of the *expected* constriction, due to one or few molecules in between a metallic nanocontact.

theory (before reading this part a review of some of the concepts summarized in appendices A, B and C is recommended). All the following developments, are constrained to an exact frame only for two cases, the "*almost homogenous*" and "*slowly varying*" electronic densities [6, 7]. With this fact in mind, the next steps of this section are devoted to show that the most general of our systems, one or few molecules bridging metallic electrodes, should not be enclosed in any of these two categories. Therefore, models making these assumptions must be used cautiously. Pointing in this line, a single electron model potential is selected to describe the effect of a molecular contact as follows (see the figures 3.1 and 3.2)

$$V(x) = \begin{cases} -V_0 & \text{if } \mid x \mid < a \\ 0 & \text{if } \mid x \mid > a \end{cases} \tag{3.12}$$

This potential represents a confinement to the electron flow through the x-direction. The extended molecule[2]. , the responsible for this behavior, is turned in a one-dimensional quantum well of length $L = 2a$ and a finite potential V_0, which results from the difference between the chemical potentials of the isolated molecule, and the chemical potential of the bulk metal. This simple model should suffice to capture the essential physics of the problem.

The ground state and even wave function is defined such that [3],

$$\psi(x) = \begin{cases} A\cos k_1 x & \text{if } \mid x \mid \leq a \\ Be^{\left(\sqrt{\frac{2m\mid E\mid}{\hbar^2}}\right)\mid x\mid} & \text{if } \mid x \mid \geq a \end{cases} \tag{3.13}$$

[2]The extended molecule is defined as the interested molecular system with an small part of the metallic cluster, in such a way that the effect of the metallic leads is taken into account [61]. Here, it is defined as the geometric zone where the electronic density varies in respect to the constant and macroscopic electronic density, which describes the metallic leads (in [12] for discussion on the macroscopic electronic density).

[3]A detailed solution of this problem could be found in any basic book on Quantum Mechanics. Here, we restrict ourselves to even parities, since we are interested in the ground state, the lowest one of this set.

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The boundary conditions for the wave function will determine the single electron energies through the following transcendental equation,

$$k_1 a = n_1 \pi + \arccos \sqrt{\frac{\hbar^2}{2mV_0}}\, k_1 \tag{3.14}$$

with $n_1 = 0, 1, \ldots, N < \infty$, and the restriction,

$$0 < \arccos \frac{\hbar^2}{2mV_0}\, k_1 < \frac{\pi}{2} \tag{3.15}$$

We are interested in the ground state, so then the equation (3.14) for $n_1 = 0$ is reduced to,

$$k_1 a = \arccos \sqrt{\frac{\hbar^2}{2mV_0}}\, k_1 \tag{3.16}$$

It can be graphically solved, but in our context what should be remarked is that $k_1 \propto \frac{1}{a}$. In addition to the relation of proportionality between k_1 and V_0 in the equation (3.13), the k_1 could be defined as the confinement,

$$k_1 \propto \frac{V_0}{a} \tag{3.17}$$

This parameter is of fundamental importance in the theoretical discussion of electronic conduction. For a molecule bridging a metallic junction, such as those we are intending to describe, it will suffice to connect the physical notion of electronic confinement with the mathematical concept of local functions, such as the electronic density.

Now we proceed to the calculation of the electronic density. After an elementary operation starting with the expression (3.13), the single particle electronic density is obtained,

$$n(x) = \begin{cases} A^2 \cos^2 k_1 x & \text{if } \mid x \mid \leq a \\ B^2 e^{-2\sqrt{\frac{2m|E|}{\hbar^2}}|x|} & \text{if } \mid x \mid \geq a \end{cases} \tag{3.18}$$

In order to establish a correspondence of this quantity with the concept of locality, a Taylor expansion is done,

$$n(x) = \begin{cases} \frac{A^2}{2} + \frac{A^2}{2}\cos 2k_1 x_0 + \underbrace{\frac{A^2}{2}\sum_{n=1}^{\infty}\frac{(-k_1)^n}{n!}\cos\left(n\frac{\pi}{2} - 2k_1 x\right)|_{x_0}(x-x_0)^n}_{nonlocal} & \text{if } \mid x \mid \leq a \\ A^2 + \underbrace{A^2\sum_{n=1}^{\infty}(-1)^n\frac{(\sqrt{\frac{2m|E|E}{\hbar^2}})}{n!}e^{-2\sqrt{\frac{2m|E|}{\hbar^2}}|x|}|_{x_0}(x-x_0)^n}_{nonlocal} & \text{if } x \geq a \\ A^2 + \underbrace{A^2\sum_{n=1}^{\infty}\frac{(\sqrt{\frac{2m|E|E}{\hbar^2}})}{n!}e^{-2\sqrt{\frac{2m|E|}{\hbar^2}}|x|}|_{x_0}(x-x_0)^n}_{nonlocal} & \text{if } x \leq a \end{cases} \tag{3.19}$$

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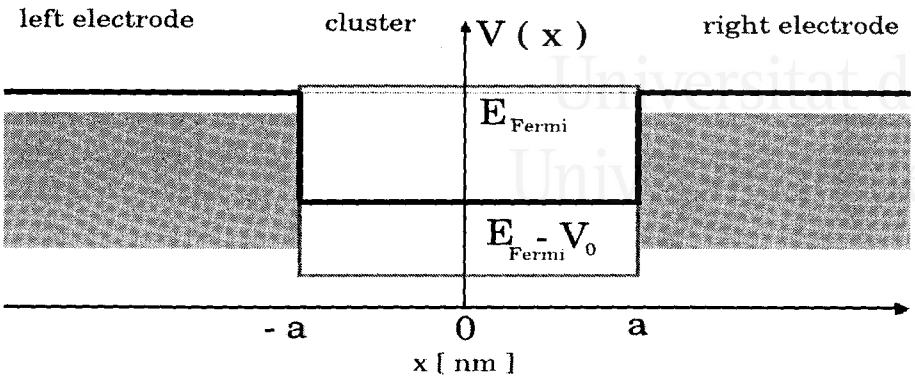

Figure 3.2: Simplified potential profile for a confined system in the x-direction, a finite square quantum well. The $L = 2a$ is the wide of the constriction, and V_0 is the depth of the well.

hence, by direct comparison with the formal expressions for the concept of locality given in the appendix B, the nonlocality of the function $n = n(x)$ is established.

Mathematically, the essential point is that this nonlocality is the source of the long rangedness local convergence. Therefore, the range of $n = n(x)$ will be infinite and the system cannot be defined as initially *homogenous* or *slowly varying*. Then, the reduction of v_{xc} in the expression (3.9) to a local space is not justified.

Physically, the existence of such a series expansion, expression (3.19), wipes out the possibility of a finite range in the algebraic representation of $n = n(x)$. Each term of the series contains information of the $x = x_0$ point, and the point at hand, x. It is also a physical representation of spatial entanglement.

Both interpretations above should be associated with the intuitive notion of spatial causality. In the next section we are going to show how could be circumvented this nonlocality in a feasible manner, and remaining within a time-dependent methodology.

3.2 The conductance within Time-Dependent Current Density-Functional Theory: TDCDFT

In the previous section it is showed that the xc-potential, $v_{xc} = v_{xc}(\mathbf{r}, \omega)$, can be given by local-density approximations in two particular cases, *almost constant* and *slowly varying* density systems. However, for the most general systems, there are some important features of the density behavior that cannot be accounted for in any way by an algebraic finite

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local $v_{xc}(\mathbf{r},\omega)$. A technical fact besides this result (in the previous section illustrated for confined systems), is that the the electronic density is an algebraic function of infinite range in space. Thus, the use of a local function of it will preserve this property, therefore becoming in an uncontrolled approximation (more insights in this mathematical in the appendixes B and ??). This problem can be circumvented by working with the current density as a basic variable, instead or, in addition to the electronic density. This is the essence of the Time-Dependent Current-Density-Functional Theory, TDCDFT [11, 62]. The fundamental reasons because this could be the basic of an exact mean field transport theory are two, as is discussed in the next paragraphs.

First, the relationship between the longitudinal density current, $j(\mathbf{r},t)$, and the electronic density is nonlocal. This is due to its relation through an integral expression as results from the continuity equation (1.15),

$$j(\mathbf{r},t) = \frac{1}{4\pi}\int d\mathbf{r}'\frac{n_1(\mathbf{r}';t)}{\mid \mathbf{r}-\mathbf{r}' \mid} \tag{3.20}$$

thus, a local function of the current density is sufficient to implicitly define a nonlocal function of the electronic density, and include all its physical effects.

The second is a theorem of sufficiency proved by Vignale [22]. It states that *two vector potentials that produce the same current density starting from the same initial state of a many-particle system must necessarily coincide up to a gauge transformation.* From there, it follows that the map from vector potentials to current densities is invertible. This theorem is analogous to the one proved by Runge and Gross for time-dependent densities [21]; and the theorem Hohenberg and Kohn for ground-state densities [6]. The difference of the Vignale's theorem is that the current density is established as a basic variable. Its success lies in that it goes **straight ahead to support an exact mean field theory of electronic transport in interacting systems**. In other words, the $\mathbf{j}(\mathbf{r},t)$ produced from a non-interacting system is identical to one describing the many body interacting system, and therefore, it is enough to formally define a construction of an exact transport theory in a mean-field frame. With all these premises, the xc-potentials are defined in the field of local $\mathbf{j}(\mathbf{r},t)$ and $n(\mathbf{r},\omega)$,

$$v_{xc}(\mathbf{r},\omega) = v_{xc}(n(\mathbf{r},\omega),\mathbf{j}(\mathbf{r},t) \tag{3.21}$$

To derive the functional relation we use the expression for the electric field contribution associated with the xc-effects, which was derived from many-body calculations by Vignale, Ullrich and Conti in [59]. In their notation, this field is,

$$E_\alpha(\mathbf{r},\omega) = E_\alpha^{ALDA}(\mathbf{r},\omega) - \frac{1}{en}\partial_\beta\sigma_{\alpha\beta}(\mathbf{r},\omega) \tag{3.22}$$

where the electric field contributions are split off in two terms. The first is the ALDA part (for details on the ALDA approximation see the section 2.4) and the second term is a dynamical contribution to this ALDA term [4]. This dynamical contribution is the

[4]The first term is also wrongly referred as the static contribution and the second as the one resulting from dynamical considerations

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correction to the local static electric field and is expressed as,

$$E_{\alpha}^{dynamical}(\mathbf{r},\omega) = -\frac{1}{en}\partial_{\beta}\sigma_{\alpha\beta}(\mathbf{r},\omega) \tag{3.23}$$

Here $n \equiv n_0(\mathbf{r}$ is the ground state density for the electron liquid. The general xc-stress tensor also derived in [59] is,

$$\sigma_{\alpha\beta}(\mathbf{r},\omega) = \eta(n;\omega)(\partial_{\beta}u_{\alpha} + \partial_{\alpha}u_{\beta} - \frac{2}{3}\nabla\cdot\mathbf{u}\delta_{\alpha\beta}) + \zeta(n;\omega)\nabla\cdot\mathbf{u}\delta_{\alpha\beta} \tag{3.24}$$

here $\mathbf{u} = \frac{\mathbf{j}}{n_0}$ is the velocity field and $\eta(n;\omega)$ and $\zeta(n;\omega)$ are the viscoelastic coefficients [5].

3.3 The conductance from TDCDFT

In this section the static limit is recovered, expression (E.4). In principle, this limit is enough to verify the existence of dynamical corrections to any *local* static theory. In addition, the dynamical corrections to the local xc- potential should be the basic for an exact and static mean field quantum transport theory. Therefore, provided one knows this function, and for a strictly finite and isolated system, the many-body total current and therefore the conductance, could be given exactly starting from the mean field picture introduced by Todorov and Di Ventra [18].

The static limit can be obtained from the time-dependent electric field, equation (4.11), and doing the appropriate integrals. Within this frame [12], as will be sketched in the next paragraphs obtain a correction to the real space form of the static local xc- potential,

$$v_{xc}^{DFT-corrections}(\mathbf{r},\omega=0) = v_{xc}^{dynamic}(\mathbf{r},\omega=0) \tag{3.25}$$

it was properly interpreted as a correction to static local DFT calculation due to the inclusion of dynamical effects. This discussion will be taking up again at the end of the section.

To obtain the explicit form for corrections on the xc- potential, the xc- dynamical part of the electric field the integral is done between the two points, a and b where the electronic density varies[6] (see the figure 3.1)

$$v_{xc}^{dynamic}(\omega=0) = -\frac{4I}{3e^2A_c}\int_a^b \eta\frac{(\partial_x n)^2}{n^4}dx' \tag{3.26}$$

Considering this dynamical contribution to the total potential, the total current is written as,

$$I = G^{static-local-DFT}(v + v_{xc}^{dynamic}(\mathbf{r},\omega=0)) \tag{3.27}$$

[5] At this point we proceed without enter in the expressions of these quantities. In the appendix D.2 and in the thesis by M. van Faassen some discussions are made [63].

[6] This two points defines the wide of the set U in the figure B.3, when it is reduced to one dimension.

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In agreement with the labels used in the original reference [12], the dynamical resistance concept is being introduced, even in the static limit,

$$R^{dynamic} = R^{dynamic}(\mathbf{r}, \omega = 0) = \frac{v_{xc}^{dynamic}(\mathbf{r}, \omega = 0))}{I} \tag{3.28}$$

then the electronic current is rewritten as,

$$I = G^{static-local-DFT}(v + R^{dynamic} I) \tag{3.29}$$

Therefore, the many-body static conductance is expressed as,

$$G^{many-body} = \frac{G^{static-local-DFT}}{1 + G^{static-local-DFT} \cdot R^{dynamic}} \tag{3.30}$$

The significance of this expression is two fold. First, there we note a non null correction for the conductance obtained within local-DFT. Second, this correction is the mathematical implication of a nonlocal field for the xc-potential, expression (3.26), which are physically interpreted as the mathematical expression of the inability of local DFT to describe non homogeneous electronic systems. Further insights in these issues would be gained after reading the next chapter.

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Chapter 4

An *ab-initio* stationary electronic transport theory

Overview

In this chapter we describe the conductance through molecular bridges, within an *ab-initio* and static Density-Functional Theory, DFT. The basic concepts, which are necessary to build up this frame, were introduced in the previous chapters and are summarized in the next two paragraphs.

In chapter 1, the central quantity of this thesis was defined, the conductance. Next, the scattering approach was presented as an effective alternative to quantify this conductance. The validity of the scattering approach, is the first piece we are going to use in support of the existence of an static electronic transport methodology. It should be remarked, as was mentioned in chapter 1, that the assumptions made within the scattering approach, and therefore its validity, are not free of discussions among the community working for quantum transport characterization [18, 36]. However, it is not the objective of this thesis to enter in this debate by one transparent reason. Mathematically (and considering physics as a mathematical statement of any intuitive idea) there are no doubts on the validity of the constructions made within the scattering approach [39, 64]. Moreover, and as far as we know, the arguments for the failures of the scattering approach to do transport calculations, rest on the non agreement between the scattering approach based on predictable *ab-initio* methods and its, presumably, experimental counterparts.

In chapter 2, the *ab-initio* mean field density based methodology we use throughout this thesis presented, the canonical Hohenberg-Kohn's theorems in conjunction with the Kohn-

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Sham's scheme. These two blocks are going to be sufficient to support the **existence** of an exact mean field *ab-initio* static electronic transport methodology. Its manageability is discussed in the first section of this chapter. Along this line, the effectiveness of the mean field *ab-initio* static electronic transport methodology is going to be transfered to the finding of the exact xc-potential, $v_{xc} = v_{xc}[n](\mathbf{r})$. An algebraic expression for this quantity cannot be derived from an exact treatment. However, practical approximations are currently used [65]. Mostly, those approximations are based on the restricted and not justified version of DFT, wrongly known as Kohn-Sham theory, where the $v_{xc} = v_{xc}[n](\mathbf{r})$ is defined over the space of local electronic densities. Therefore, it is reduced to a local functional on the position space. In this thesis, **the nonlocal space defining the exact** $v_{xc} = v_{xc}[n](\mathbf{r})$ will be recovered and introduced in practical functionals. The analysis presented in the section 4.1, and also the numerical and experimental results presented in the following chapters 5, 6, and 7, will support the dramatic role this apparently innocuous algebraic property would play in the *ab-initio* quantum transport calculations through molecular bridges.

Section 4.2 presents a practical scheme for the manageability of the theory previously introduced. In a few words, it is a section for design. The design of xc-potentials, roughly extending the space of currently used DFT's frames.

Section 4.3 is devoted to proof our thesis using the fact that the static situation could be also attained as a time-dependent limit. The discussions are based on the results introduced in chapter 3. Although it seems an obvious choice, it is important to remark that these time-dependent methodologies are used in this thesis for two reasons. First, time-dependent methods are a common trend among the quantum transport community, and therefore any work which use these methods will fancy itself as a novel candidate for credibility. The second is a more science based reason, and is stated in the next paragraph.

There is no doubt, the conductance as defined through the expression (1.1), is the static limit of its time-dependent counterpart, the expression (1.19). Furthermore, an exact manageable theory exists for time-dependent situations [11, 18, 66]. Therefore, any exact static theory must be obtained when considering the right limits. So then, the matching between the results obtained within an static treatment and those obtained from a time-dependent method, are a necessary condition for the validity of any approach to such theories. The comparison presented in this section is not going to be complete, since algebraic identities are not going to be established. Nevertheless, it should shed light in the darkness covering the problem we are dealing with, the space defining the xc-potential for an exact mean field *ab-initio* static electronic transport methodology for one or few molecules bridging metallic nanowires [67].

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4.1 The conductance within local-DFT

This section is devoted to support the existence of a route for the *ab-initio* calculation of the conductance within the static density-functional theory, DFT 2.3.

The conductance is expressed as (for details see section 1.1)

$$G = \frac{2e^2}{h} Tr \;\; T\left(\varepsilon_{Fermi}\right) \tag{4.1}$$

where T is the transmission matrix. Using Green's function techniques it is transformed to the form,

$$T\left(\epsilon\right) = \Gamma_L \, g^{+} \, \Gamma_R \, g^{-} \tag{4.2}$$

enclosing the building blocks of this method, the self-energies $\Sigma^{\pm}_{L(R)}$, and the expecting values of the Hamiltonian of the finite conductor, $\hat{H}$, as will be shown with the next relations,

$$\Gamma_{L(R)} = i\left[\Sigma^{+}_{L(R)} - \Sigma^{-}_{L(R)}\right] \tag{4.3}$$

$$g^{\pm}\left(\epsilon\right) = \left[\epsilon \pm i\eta - \hat{H} - \hat{\Sigma_L}^{\pm} - \hat{\Sigma_R}^{\pm}\right]^{-1} \tag{4.4}$$

For an *ab-initio* DFT of the scattering approach, it is recommended to split the problem into two separate subproblems, and to consider solutions in two groups. One must be related with the quantities representing a finite system and the other group, with the quantities representing infinite systems. The reason is that for the effectiveness of DFT, a necessary condition is that the system to be described must be thermodynamically closed, therefore finite, section 2.3. So then, in principle the calculation of H as $H = H\left[n(\mathbf{r})\right]$, where $n(\mathbf{r})$ is the ground state electronic density is justified based on the Hohenberg-Kohn theorems [6,33]. In contrast, the calculation of $\Sigma^{\pm}_{L}$ as $\Sigma^{\pm}_{L} \equiv \Sigma^{\pm}_{L}\left[n(\mathbf{r})\right]$ is not justified. To rule out this inconsistency with the *ab-initio* DFT selected, an alternative point of the quantum transport is proposed considering the following facts,

1. The H and the Γ_L are the result of an arbitrary geometric division of the infinite system (see the figure 4.1). So then, and for a formal discussion, $T\left(\epsilon\right)$ could be expressed as an index quantity,

   $$T_I\left(\epsilon\right) = \Gamma_{L_I} g^{+}_{I} \Gamma_{R_I} g^{-}_{I} \tag{4.5}$$

   where the subindex I represents an infinite set of geometric arrangements, which in principle, should gives us the $\hat{T}\left(\epsilon\right)$.

2. The $\hat{T}_I\left(\epsilon\right)$ is a finite physical quantity, since it has a finite value, regardless of which is the I subindex. In principle, we could define a convergence of $T_I\left(\epsilon\right)$ in terms of a growing I, based on the capacity for determining an exact $H \equiv H\left[n(\mathbf{r})\right]$ and the

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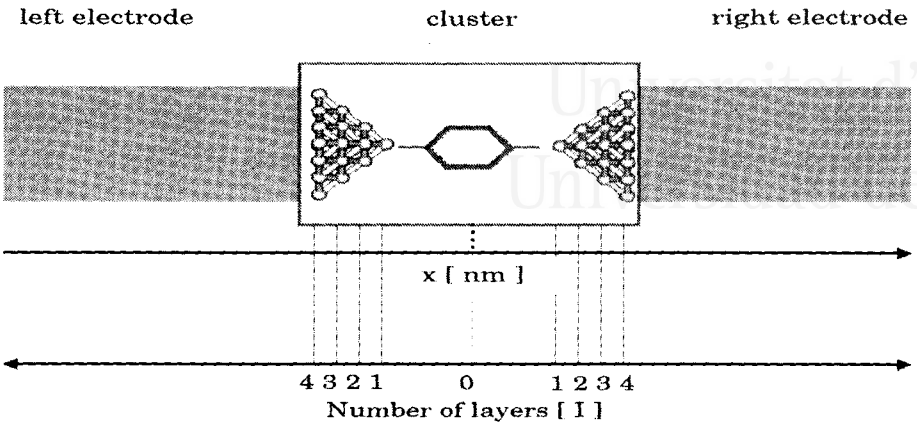

Figure 4.1: Schematic representation of the I-partition for a finite system constructions within the scattering picture.

non existence of $\Sigma_L^{\pm} = \Sigma_L^{\pm}[n(\mathbf{r})]$. This abstract construction permits the search of $T_I(\epsilon)$ upon the knowledge of $H = H[n(\mathbf{r})]$ and the non rigorous definition of $\Sigma_L^{\pm}$. It will imply,

$$T(\epsilon) = \lim_{I \to \infty} T_I(\epsilon) \tag{4.6}$$

In fact, this limiting situation is unpractical and its value is restricted to a formal result, *the calculation of $T_I(\epsilon)$ in terms of the density could be restricted to the calculation of H in terms of the density, which is supported with the thesis of existence of any quantity as a functional of the electronic density in a closed system.*

For our practical calculations, we did the following approach to the previous exact result. The ∞ is understand as such size, where the model used for $\Sigma_L^{\pm}$ does not affect the value of the transmission. In terms of the microscopical parameters we can look at the minimal finite system, $I_{minimal}$, as such defined so that the coupling to the leads do not affect the electronic structure on the extended molecule. In actual numerical calculations it imply the inclusion in the finite system of a piece of the metallic leads, at least to include the screening length of the electrodes in the molecular bridges. This is physics behind the definition of the concept of *the extended molecule* [68]. So then, the sizes for our finite cluster must belong to the following set (A-set in the figure 4.2)

$$\left(\text{size}_{\text{molecule}} + \text{size}_{\text{screening length of the metal}} \, , \, \infty\right) \tag{4.7}$$

This expression defines a minimal size for the finite cluster we could choose, where the leads are being considered, by construction, as perturbations to electronic states in the molecular bridge. From then on, the *ab-initio* density based calculation will be restricted to the Hamiltonian of this set of cluster sizes, H_A and parameterized calculations will be done for the self energies. In this thesis the attention is centered in H_A, therefore the methods deployed for the self energies calculations are presented as an appendix D.3.

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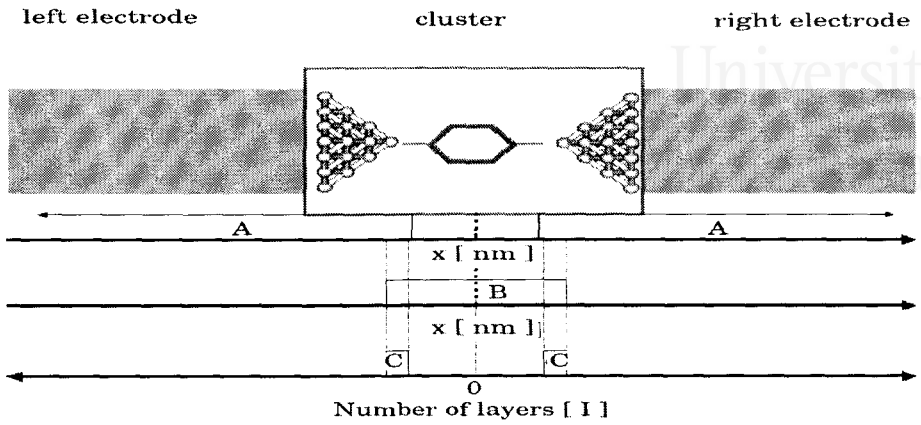

Figure 4.2: Allowed sizes for the systems to be treated within the methodology in this thesis proposed. The minimal size is fixed by the quantum transport method we choose. The maximal size is fixed by the *ab-initio* mean-field method we propose. (The details are in the main text).

Now, and from the basic Hohenberg-Kohn theorem we state the following, *an exact conductance as a functional of the ground state electronic density, and in a mean-field scheme based on the* $v_{xc} = v_{xc}[n](\mathbf{r})$ *exists.* Therefore, for the definition of the conductance two steps are sufficient; first, the definition of xc-potential, $v_{xc} = v_{xc}[n](\mathbf{r})$; and second, the finding of the functional relation between the conductance and the xc-potential, $G = G[v_{xc}[n](\mathbf{r})]$. (In agreement with the scattering approach this second step can be replaced by the finding of the functional relation between the Green's function in a non interacting electron system and the xc-potential, $g = g[v_{xc}[n](\mathbf{r}))$. Summarizing, the following scheme is a representation of such route,

$$n(\mathbf{r}) \overset{\text{HK-KS}}{\Longleftrightarrow} v_{xc} = v_{xc}[n](\mathbf{r}) \overset{\text{HK}}{\Longrightarrow} g = g(v_{xc}) \overset{\text{Scattering}}{\Longrightarrow} G = G(g) \tag{4.8}$$

The first equivalence is due to the Hohenberg-Kohn and Kohn-Sham works [6,7]. The second implication is a result of the Hohenberg-Kohn theorem for the existence of the Green's function, and finally the introduction of the scattering approach for the conductance is made. At this point, it should be accepted that a manageable $v_{xc} = v_{xc}[n](\mathbf{r})$ could be the basis of an exact quantum transport method.

Up to now, the algebraic expression of this xc-potential is explicitly unknown. However, insights into its algebraic expression are gained if we replace an step in the original Kohn-Sham's work, if we go beyond the Local Density Approximation for the xc-potential, $v_{xc} = v_{xc}[n](\mathbf{r})$. In addition to this formal mathematical requirement, the corrections we will propose, contain physics that pertains to a truly nonlocal spatial problem. This will be the subject of the next part of this section and points to the main contribution within this thesis.

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4.1.1 The LDA in the Kohn-Sham scheme: a practical solution or a trap?

The xc-potential is by definition the functional derivative of the xc-energy [7],

$$v_{xc}[n](\mathbf{r}) \stackrel{\text{def}}{=} \frac{\delta}{\delta n(\mathbf{r})} E_{xc}[n(\mathbf{r})] \tag{4.9}$$

The Local Density Approximation to the xc-potential within the Kohn-Sham scheme (The LDA is enclosed in the expression (2.3) for xc-energy in the original paper [7]) reverts this initial exact mean field theory for interacting electrons to an approximate theory [52,69].

The LDA for E_{xc} results in the following expression for $v_{xc} = v_{xc}[n](x)$[1],

$$v_{xc}^{LDA} = (-1)^i \frac{d^i}{dx^i} \left(\underbrace{i \frac{\partial^{(i-1)}}{\partial n^{(i-1)}} \epsilon_{xc}[n(x)]}_{\text{local}} + \underbrace{n \frac{\partial^i}{\partial n^i} \epsilon_{xc}[n(x)]}_{\text{local}} \right) \tag{4.10}$$

The foundations of this approximation were given in the original work, it is supported in the behavior of the electronic gas, as *almost constant* or *slowly varying* in terms of its electronic density[2] (in reference [7] and appendix C) However, our hypothesis is that the conductance through molecular bridges, the problem we are interested in, is not consistent with the LDA, due to the relationship between the nonlocal space of $v_{xc} = v_{xc}[n(x]$ and the own nature of the systems we are dealing with captured by the electronic density, $n = n(x)$. Our intention, is that the discussions presented in this chapter and the numerical results that follow, will proof this hypothesis and turn it as the main thesis of this work.

The exact expression for the xc-energy within the mean-field KS scheme is derived using the original HK's work [6]. Using their notation it is written as,

$$E_{xc}[n(x)] = \frac{1}{2} \int dx \, \nabla_x \nabla'_x n_1(x,x') \mid_{x=x'} + \frac{1}{2} \int dx dx' \frac{C_2(x,x')}{\mid x - x' \mid} - T_s \tag{4.11}$$

therefore, doing the functional derivative (in reference [52] and appendix B the formula for the functional derivative is included) we can obtain a formal expression for the exact $v_{xc} = v_{xc}[n](x)$,

$$v_{xc}^{exact} = \underbrace{\frac{(-1)^i}{2} \frac{d^i}{dx^i} \frac{\partial^i}{\partial n^i} \left(\nabla_x \nabla_{x'} n_1(x,x') \right) \mid_{x=x'}}_{\text{local}} + \underbrace{\frac{\partial^i}{\partial n^i} \int dx' \frac{C_2(x,x')}{\mid x - x' \mid}}_{\text{nonlocal}} + \underbrace{\frac{\delta T_s}{\delta n(x)}}_{\text{local}} \tag{4.12}$$

[1] Henceforth, $n(\mathbf{r})$ will be restricted to 1-dimension, x, for avoiding tedious functional derivatives in the main text. This restriction will suffice to capture the essential physics of the problem we are dealing with. With the LDA label we are enclosing GGA or any of such approximations where the $\epsilon = \epsilon_{xc}[n(x)]$ [15,52,67]. Therefore, it is expressed in terms of local electronic densities. This will be enough to capture the essential features of the problem.

[2] It has been turns out that the LDA give extremely useful results for most applications even for systems which do not fulfill this condition [33].

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It is not the desirable, algebraic form in terms of $n(x)$, the one which could be introduced in the self consistent scheme devised by Kohn and Sham to determine v_{xc} and $n(\mathbf{r})$, section 2.3. However, even if this expression (4.12) is obscure in terms of constructing $v_{xc} = v_{xc}[n](x)$, it is enough to derive one of the analytical properties of the exact xc-potential, its canonical nonlocality in the x-space. The importance of this algebraic property, is that it is sufficient to state that the the exact xc-potential cannot be approached with the routinely used LDA approximations, expression (4.10), by an inconsistency in the own definition. (This topic is more rigorously discussed in the appendix B, and references therein). The field defining both functions are different, therefore the functions by construction cannot be identical. Therefore, any attempt to design an exact xc-potential must go beyond the LDA approximations.

In the remainder of this section, we want to address the connection between the nonlocal character of the xc-potential and the non homogeneity of the electronic system. This is done using for the electronic density of the many electron system, the same model introduced in section 3.1. Now, we must go back to the nonlocal term in the expression (4.12). Its existence is determined by the non null value of $C_2(x, x')$, the two-particle correlation function (its definition is included in the appendix A). Therefore, we must express this in terms of the confinement parameters. A derivation of $C_2(x, x')$ in terms of the confinement parameters is straightforward. One finds,

$$C_2(x, x') \propto n(x)\ n(x') \tag{4.13}$$

The essential point is that $C_2(x, x')$ is an infinite Taylor expansion in terms of x and x' for confined systems, as such modeled in section 3.1[3], and the dependence of this infiniteness in terms of the confinement. It is this feature that will enable us to construct a **local** and **finite** algebraic approach of the xc-potential in the $x-$ space.

However, directly related to the lack of sufficiently strict convergence of this Taylor's series for the electronic density, is the fact that v_{xc} exists. Therefore we could approach the xc-potential with a finite expansion, as much as we want, but obeying the fulfillment of the nonlocality properties of the exact expansion. Without room for discussion, this statement is mathematically valid. Too much space could be left for the physics behind this property [65, 67]. (The appendixes C and B could be reviewed). The numerical calculations presented in the final chapters of this thesis contribute to support the role the skip of this analytic property could play in current *ab-initio* density based transport calculations.

As a summary of this section, the common assignment of DFT as a local theory within the mean field scheme is not justified, and could be the source of the drastic messages announcing the DFT failure [23, 70, 71] . Furthermore, the derivations from the original theorems leads to the nonlocal field definition of $v_{xc} = v_{xc}[n](\mathbf{r})$ for the most general

[3]Without proof, and only as an observation we want to remark that confined systems are always described by transcendental functions, so then infinite Taylor's expansions. Therefore its algebraic local expansions are infinite, or equivalently the nonlocality cannot be controlled by finite expansions.

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systems. In the next section we will return to the more general problem of determining the conductance in terms of v_{xc}.

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4.2 The conductance within nonlocal-DFT

The inclusion of the nonlocality in the approach to the true xc-potential is done in accordance with the following scheme.

A linear combination of two terms is proposed. One of the terms is local and the other one is nonlocal in the position space, **r**-space[4],

$$v_{xc}[n(\mathbf{r}'),n(\mathbf{r})] = a\cdot\underbrace{F_1[n(\mathbf{r})]}_{\text{local}} + b\cdot\underbrace{F_2[n(\mathbf{r}'),n(\mathbf{r})]}_{\text{nonlocal}} \tag{4.14}$$

The proposal of this linear dependence is formally exact. for design what is known as hybrid functionals. Becke showed that it is the starting point for a proper approach to the exact xc-potential, starting from the adiabatic connection formula [16, 72–75].

To define the expansions the two constants a and b must be fixed. In this line, we use two boundary conditions for $v_{xc} = v_{xc}\left[n\left(\mathbf{r}'\right), n\left(\mathbf{r}\right)\right]$. These are chosen in accordance with the physical problem we are dealing with. These are strictly connected with the analytic properties of the Hamiltonian we need to define the conductance as a functional of the Green's function of the non interacting electron system, expressions (4.3) and (4.1). In agreement with the single effective one electron picture described by this Green's function, its two poles must coincide with the ionization and electron affinities energies, IP and EA [56]. These two conditions can be expressed as,

$$v_{xc}\left[n\left(\mathbf{r}'\right), n\left(\mathbf{r}\right)\right]|_{a,b} \Longrightarrow\ g^{\pm}\left(IP\right) = \infty\ \ \wedge\ \ g^{\pm}\left(EA\right) = \infty \tag{4.15}$$

For practical calculations, the parameters a and b are derived in a self consistent scheme (see the appendix D for computational details). Remarkably, this self consistent scheme is based on the calculation of the ionization and electron affinities energies within wave function methods. These wave function methods provide a frame for the exact approach to the calculation of these total energies.

Therefore we design an xc-potential which yields, at least, a right description in the vicinity of HOMO[5] and LUMO[6] single particle orbitals. In the context of our quantum transport calculations, the success of this method, is based on how close the physical Fermi surface

[4] In practical calculations, F_1 is any of the available local DFT functionals, section 2.3.3, and F_2 is the Fock exchange, expression (??).

[5] Highest Occupied Molecular Orbital

[6] Lowest Unoccupied Molecular Orbital

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is from these two orbitals[7]. The conductance, as is discussed in section 1.1, is determined by the alignment of the HOMO and LUMO of the molecular bridge with the Fermi level of the leads, resulting in a final Fermi surface. In cases where a "neck" is presented in the r-space we should expect a singularity in the Fourier transform of the physical Fermi surface. Precisely, this neck-singularity, will determine the conductance of the system. Based on this fact, we must do the adjustment to guarantee that the physical Fermi surface is correct at the neck. Therefore, to do this adjustment, we must search for a finite cluster such that the HOMO and LUMO belong to the molecular bridge. This "neck" in the scheme will determine a maximal size in the set of the finite system (B set in the figure 4.2)

$$\left(\text{size}_{\text{molecule}} \, , \, \text{size}_{\text{molecule}} + \, \text{size}_{\text{decay length of the molecule}}\right) \tag{4.16}$$

In those cases where the intersection of this set with the set defined through the expression (4.7) is not empty (C-set in the figure 4.2) the scheme here introduced for defining nonlocal functionals can be used, and the extended molecule should be defined as the atomic system included in this range. This intersection will not be null, since generally, the screening length of the metals is smaller than the decay length of the molecular system[8]. Therefore, and apart from the approximations we did, the method here presented turns out to be an improvement to the most traditional LDA methods applied to quantum transport through molecular bridges.

4.3 The conductance within nonlocal-DFT and within TD-CDFT: common points

In this section we compare the results obtained within nonlocal DFT with the results obtained from time-dependent current-density based methods, TDCDFT (section 4.17). The formality is nothing else than a mathematical return to the physical static conditions doing a limit. This limit is based on the following facts,

1. There are not doubts, that for any continuous time-dependent quantity, $f(t,k) = f_1^{dynamical} + f_0^{statical}$, its static counterpart, $f_0(k) = f_0^{statical}$ can be defined as,

$$\lim_{t\to\infty} f(t) = f_0 \tag{4.17}$$

   where all the other set of variables which are used to define the function remains constant. A measurable quantity, such as, the current density or the conductance, fulfill this condition.

[7]The physical Fermi surface may be defined as the surface in the Fourier transformed r-space which separates occupied from unoccupied single electron states. It is a well-defined physical quantity within static theories, and is sufficient to describe the linear response of an electronic system [?].

[8]For metals, the screening lengths are of the order of interatomic distances [?, 76]. Here, the decay length is defined as the maximum size for which the local density of states, projected on the HOMO- or LUMO-state of the finite cluster, is due to the molecular system.

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2. It is guaranteed the existence of a single effective electron system in the vicinity (as close as we need) of any interacting many electron time-dependent system (in [52] and references therein).

3. In the work of Vignale [22], it is shown that the map from the exact many electron density current, $\mathbf{j}(\mathbf{r},t)$, to the density current calculated within a single electron picture is invertible. The important of this formality for the application of the mean field schemes within density based theories to transport problems is an obvious. It is stated as the following limit to redefine the conductance (expression (1.1)) from time-dependent quantities.

$$G = \lim_{V\to 0}\lim_{t\to\infty}\frac{\partial}{\partial V}\int_{\mathbf{S}} d\mathbf{S}\ \cdot \mathbf{j}^{noninteracting} \tag{4.18}$$

If it is accepted, considering the unicity of the conductance, and taking up the discussion on the existence of the conductance, from the section 4.1, we could guarantee that **the Green's function of the non interacting system gives us the exact conductance.** The scheme that follows is a summary of the route here presented for the construction of the conductance,

$$\mathrm{n}\ (\mathbf{r};t) \overset{\mathrm{RG}}{\Longleftrightarrow} v_{xc} = v_{xc}\left[n\right](\mathbf{r};t) \overset{\mathrm{TD}}{\Longrightarrow} G = G\left[v_{xc}\right]$$

$$\mathrm{G}\ \left[v_{xc}[n]\,(\mathbf{r};t)\right] \overset{\mathrm{Vignale}}{\Longrightarrow} G^{NI}\left[v_{xc}[n]\,(\mathbf{r};t)\right]$$

$$\lim_{t\to\infty} G^{NI}\left[v_{xc}[n]\,(\mathbf{r};t)\right] \overset{\mathrm{scattering}}{\Longrightarrow} G^{NI}\left(g^{NI}\left[v_{xc}[n]\,(\mathbf{r})\right]\right)$$

(Here, NI is the label for constructions in non interacting systems. The rest of the labels are included in the list of acronyms)

Finally, we enter in a subtle non solved point within this thesis. From the work here presented we cannot derive a formal mathematical relation between the time-dependent corrections, expression (3.26), and our Fock exchange correction, expression (4.14). However, at least, they are **nonlocal functionals of the electronic density**. This common property, is a point in support of its possible algebraical connection. The fundamental physical relation between both corrections is now clear for us, in both cases they are beside beside the causal effects inclusion when non homogenous systems are described in terms of the electronic density.

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Part III

APPLICATIONS

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Chapter 5

Conductance of platinum nanocontacts bridged by a Hydrogen molecule

Overview

In this chapter we study the conductance of platinum nanowires connected to the *extended molecule*: Pt_2H_2. A diagram of such system is,

$$Pt \overset{0.17nm}{\underline{\quad}} H \overset{0.091nm}{\underline{\quad}} H \overset{0.17nm}{\underline{\quad}} Pt \tag{5.1}$$

This benchmark system is sufficient to put into action the method described in the previous chapter for the calculation of the conductance through quantum systems[1].

In the first section of this chapter, the role that the approximations to the xc-potential are playing in current *ab-initio* electronic transport calculations is showed. This section should be enough to address the differences among theoretical groups, presumably doing *ab-initio* calculations [24, 25, 77]. Also, it should be enough to justify the outline of the rest of the chapter. It contains a methodology that could be implemented in order to leave behind uncertainties in the selection of the xc-potential, and finally, how could we go beyond the current practical limitations of density-functional methods, due to the use of local xc-potentials. This is done as follows.

In section 5.2, the methodology described in section 4.2 is emlpoyed and a nonlocal xc-

[1]The selection of this geometry could respond to the *ab-initio* simulation of the interaction between a platinum nanowire and a Hydrogen molecule, as will be discussed in the next chapter.

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potential is devised. First, the influence of the xc-potential approximations in the active[2] electronic structure of the extended molecule is studied, taking into account that the correct active electronic structure in the extended molecule is of prime importance for a right quantum transport outcome (see section 4.2 for details). Furthermore, we use this as a boundary condition for our central problem, the construction of a manageable approach to the exact xc-potential. With this xc-potential we can perform quantum transport calculations within a static and *ab-initio* mean field method.

In the last section, and in support of our static calculations, we present the results obtained for the conductance through this benchmark system, within the time-dependent and *ab-initio* methodology described in section 4.17.

5.1 Role of nonlocal-DFT in the electronic structure

The extended molecule system, the Pt-H_2-Pt, fulfills the geometric conditions to be examined with our methodology for *ab-initio* mean field conductance characterization. It means that the size of the extended molecule, is included in the interval defined by the intersection of the intervals stated in 4.16 and 4.7. To prove that we did the analysis that follows.

The physical lengths that we must look at to give a meaning to this model are, the size of the molecular bridge, the decay length of the molecular bridge, and the screening length of the metal. The assignment is the one that gets (we follow the notation introduced in section 4.2)

$$\begin{aligned} \text{size}_{\text{molecular bridge}} &= d_{\text{H-H}} \\ \text{size}_{\text{decay of the molecular bridge}} &\sim \lambda_{\text{metal}} \sqrt{\frac{\epsilon_{\text{Fermi}}^{\text{metal}}}{\epsilon_{\text{Fermi}}^{\text{molecule}}}} \\ \text{size}_{\text{screening length of the metal}} &\sim 10^{-1}\ \text{nm} \end{aligned} \tag{5.2}$$

All the expressions above are estimations to made manageable the "abstract" method introduced in the section 4.2[3].

At this point, the Pt-H_2-Pt system is the input for the *ab-initio* quantum transport scheme we have implemented (details in the appendix D.2). The xc-potential we used in the

[2]The active electronic structure is the label we use for the HOMO and LUMO single-particle orbitals. As was discussed in section ??, these two orbitals are the ones involved in the final conductance value.

[3]However, even when we do not have a roughly method to proof the validity of the above estimations, an argument in its favor could be that, presumably, it works; as is shown in the next chapters when we contrast our numerical results with experimental measurements.

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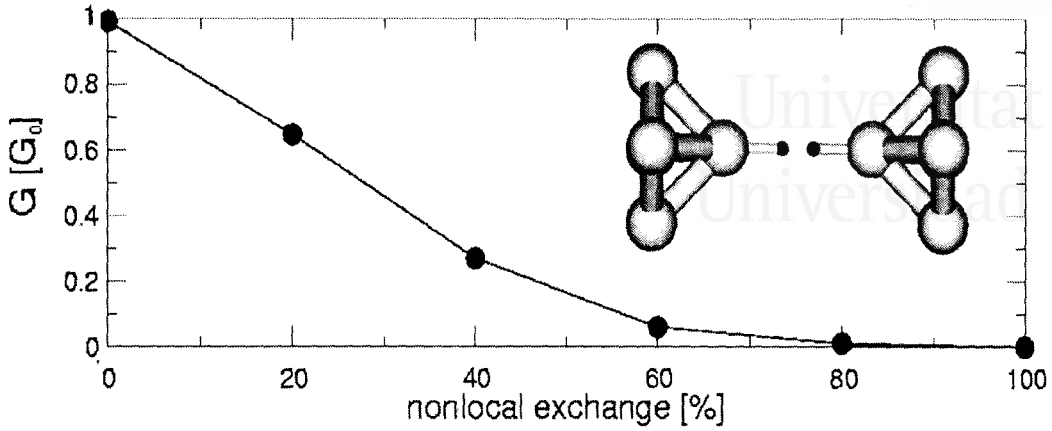

Figure 5.1: Reduction of the conductance due to the progressive substitution of the local xc-potential by a nonlocal contribution. The inset shows the extended molecule bridging the platinum electrodes. G_0 is the quantum of conductance, $G_0 = \frac{2e^2}{h}$.

calculations here presented was the one that follows,

$$v_{xc}[n(\mathbf{r}'), n(\mathbf{r})] = (1-a) \cdot F_1[n(\mathbf{r})] + a \cdot F_2[n(\mathbf{r}'), n(\mathbf{r})] + b \tag{5.3}$$

where F_1 is the GGA functional known as PW91 [78], and F_2 is the Fock exchange potential, equation ??. The a range is between 0 and 1, and b is keep constant and equal to zero. The first result we present is the conductance value as a function of the a parameter in xc-potential, see the figure 5.1. This curve should be enough to claim for attention to the xc-potential in use.

The first point of the curve in the figure 5.1 is the conductance calculated with zero nonlocal xc-potential contribution[4]. This type of calculations are a common train among the *ab-initio* quantum transport community. From our point of view, without formal arguments for its validity [24, 25]. To explain this dependence of the conductance, we must look at the electronic structure of the active electronic structure as a function of the xc-potential contribution, since there will be a microscopical correspondence with the behavior sketched in the figure 5.1. Furthermore, in the control of this dependence will be the practical solution for the problem we are dealing with, the finding of the exact, or less rigorously, an approach to the xc-potential for the *ab-initio* mean field quantum transport calculations. This will be the subject of the next section.

[4]Practical calculations where done using different LDA and GGA xc-potentials. The differences are not noticeable in the scales we are working.

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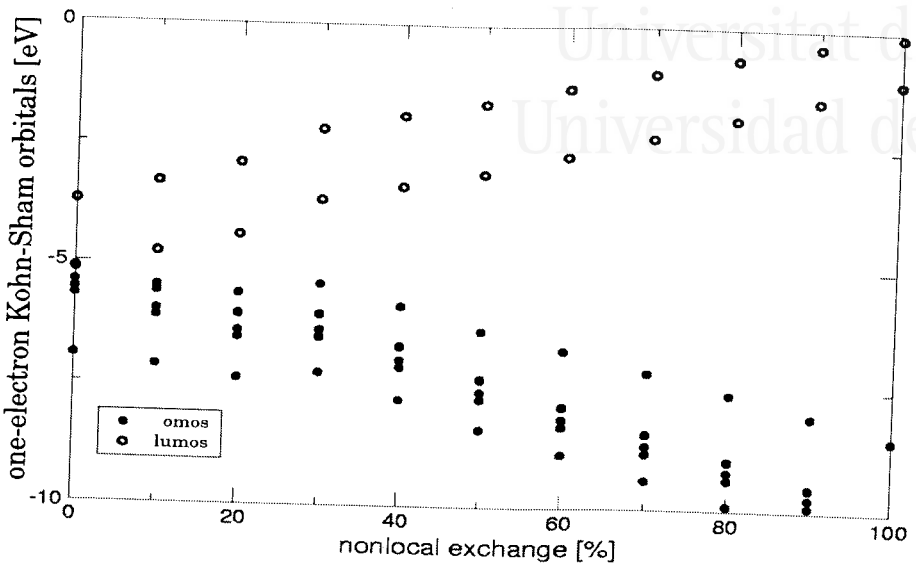

Figure 5.2: HOMO and LUMO position in the energy space as a function of the nonlocal contribution in the xc-potential. The a parameter is that in equation 5.3.

5.2 Design of an effective nonlocal-DFT for the calculation of the conductance

In this section we show how do we improve the xc-potential (how do we put more physics into it) to approach the exact ground state electronic structure of the extended molecule. Mathematically, it means how do we find the Green's function of a non interacting electronic system in order to approach the exact conductance.

The active single particle electronic state for the extended molecule system as a function of the nonlocality in the xc-potential, is represented in the figure 5.2. This result is not surprising[5]. Physically, the addition of the nonlocal exchange through the Fock terms, helps to correctly considerate the Pauli exclusion principle, and therefore include the Pauli repulsion in electron orbitals. Mathematically, we cannot support this behavior.

To find out our approach for the xc-potential the contour problem in 5.3 is rewritten as follows,

$$v_{xc}[n(\mathbf{r}'), n(\mathbf{r})] = (1-a)\cdot F_1[n(\mathbf{r})] + a\cdot F_2[n(\mathbf{r}'), n(\mathbf{r})] + b \tag{5.4}$$

and the two boundary condition for **a** and **b** are,

$$\epsilon_{HOMO}\,|_{v_{xc}} - \epsilon_{LUMO}\,|_{v_{xc}} \;=\; GAP \tag{5.5}$$

[5]This effect is well known in molecules and bulk semiconductors.

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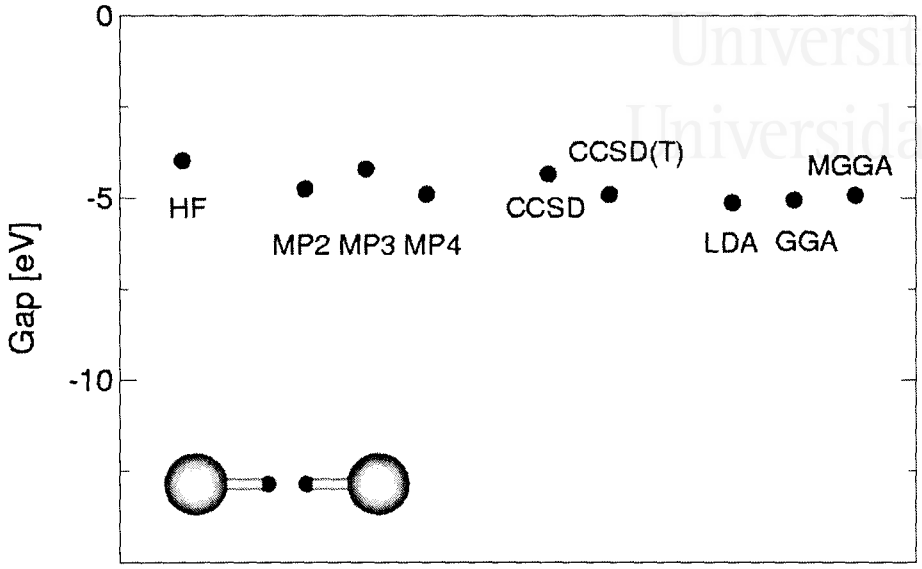

Figure 5.3: Ground state total-energy calculations for the estimation of the energetic distance between the HOMO and LUMO orbitals, the GAP. It is calculated as: $E_{gap} = 2\,E_0\,(N) - E_0\,(N+1) - E_0\,(N-1)$.

$$\epsilon_{HOMO}\,|_{v_{xc}}\,/\epsilon_{LUMO}\,|_{v_{xc}} \;=\; IP/EA$$

The first condition is used to determine a and the second for determining b. This algorithm leads to gain in computational efficiency, if we compare with the one sketched through equations 5.3.

For the tip system selected the value we obtain for **a** is ~ 0.6 and for **b** is ~ 0.0. With these two parameters the xc-potential can be fixed and introduced in the scheme for the calculation of the conductance as is explained in the flowcharts, of the appendix D.2. Finally, we get a conductance value $\sim 0.2\,G_0$, which remarkably, is a correction of almost an order of magnitude if we compare with the conductance calculated with a local xc-potential. As was remarked in the section 4.2, our scheme for the calculation of the conductance, is not free of approximations. The main two are the consideration of a linear form proposed for the xc-potential, and then the criterion for the selection of the extended molecule. Actually, we are not ready to go beyond these uncertainties. Therefore, we cannot estimate the error in the value of the conductance we are proposing.

At this point, what we suggest is a comparison with the time-dependent method for the calculation of the conductance. Surprisingly (or not) both results agree fairly well. This will be the subject of the next section.

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5.3 Nonlocal-TDDFT and TDCDFT for the calculation of the conductance

In this section we want to test the performance of the nonlocal DFT corrections, proposed within this thesis, to the local conductance. This is done by a numerical comparison with the well accepted time-dependent corrections to the local conductance proposed by Sai.et.al [12] (a summary of the original work is in section 4.17).

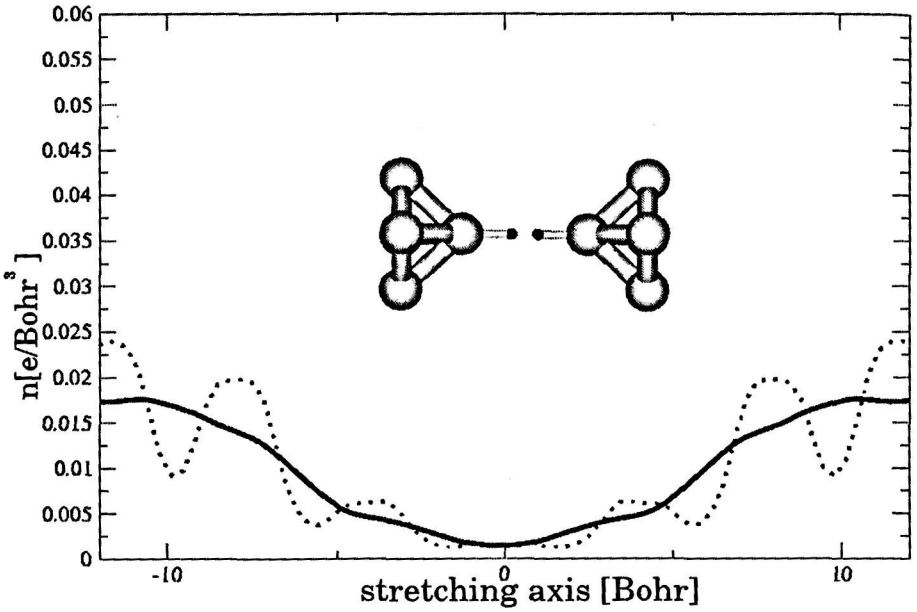

Figure 5.4: Electron density profile after planar average [dashed line] and three-dimensional average of the microscopic density for the system included in the inset. [Details in the main text].

An extended discussion on how do we implement the methodology proposed by Sai.et.al, is presented in the appendix D[6] . From the analysis there presented, we should note that the evaluation of the time-dependent corrections to the local conductance cannot be done without fixing some parameters for the system at hand. Those are, the average free electron density in the metal, $n = n(\infty)$; the interplanar distance in the metallic electrodes, Δ; and the Fermi energy in the metal, ϵ_F. Here, we restrict to present the parameters we choose for the extended molecule Pt-H_2-Pt.

To estimate the free electron density in the bulk, we use the following expression,

$$n(\infty) = \frac{\rho_{Pt}\ N_A\ N_{valence}}{M_{Pt}}\ a_0^3 \tag{5.6}$$

[6]From our point of view, this route is not free of ambiguities, due to the necessity of making estimations for too many microscopical parameters, such as the viscoelastic coefficients [63].

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here $N_{valence}$ is the number of free electrons in the platinum. The estimation of this parameter is not at all obvious. Therefore, we made the following *ad hoc* approximation. The number of free electrons in platinum coincides with the number of the experimental conductance in units of G_0 [79]. On this basis, we take the number of valence electrons $N_{valence} \sim 2$. The rest of the quantities involved in the expression 5.6, are read from tables[7].

With all these parameters the macroscopic electron density can be calculated for the extended molecule. The result is shown in the figure 5.4. Finally, to evaluate the dynamical corrections, these parameters are included in the scheme described in the section D.2.

Within this frame, a non zero dynamical correction to the conductance is predicted. Furthermore, this corrections are as great as, to reduce the conductance to $G \sim 0.02\ G_0$, which agrees well with the prediction we made within nonlocal Fock corrections to DFT.

[7]The bulk density for platinum is $\rho_{Pt} = 21.46\ \frac{g}{cm^3}$, the Avogadro's number is $N_A = 6.02\ 10^{23}\ mol^{-1}$ and, the molar mass for platinum is $M_{Pt} = 195.08\ \frac{g}{mol}$. The interplanar distance in the platinum electrodes with a 001 arrangement is $\Delta = 26$ nm [76]. The Fermi energy in the metal is ~ 5.6 eV [80].

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Chapter 6

An approach to *ab-initio* chemistry-based molecular electronics

(...) small is different (...)[1]

Overview

The ability to understand the relationship between the dynamics of the *extended molecule*, and its conductance properties is central to our appreciation of the quantum transport and applications. This chapters is intended to contribute to the first step in the way to "draw" this connection. It means, the definition of the dynamical atomic configurations of the systems composed of *one* or *few* molecules interacting with metallic nanocontacts. The method developed is an attempt to do *ab-initio* chemistry based molecular electronics. Its use is justified with an accepted fact: the experience gained from traditional macroscopical chemistry cannot be roughly extrapolated to our *extended molecules*. However, since the rules of physics are known, we can use them to create model environments, such as the *ab-initio* simulations. This is the alternative we choose.

With this idea in mind, this chapter points to a prime concern, the introduction of the

[1]This simple and therefore beautiful statement, is used when the knowledges of traditional chemistry are going to be extended to chemistry-based molecular electronics. From systems in the order of $\sim 10^{23}$ interacting molecules to systems where the interactions can be reduced to *one* of *a few* interacting molecules [4,81].

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concept of an inTeraction tIp comPlex, TIP [82]. It is used to refer the novel atomic arrangement in the tip of our metallic systems.

As a first approximation, the TIP could be considered identical to the *extended molecule* defined in section 4.1. However, this is not strictly necessary. The extended molecule was defined as a geometrical construction for the design of a feasible electronic transport method. The TIP should be interpreted in a more chemical context. The main difference is that the TIP has a well-defined atomic structure[2]. The TIP could be viewed as the product of the reaction of the atomic-tip of metal, $\text{Metal}_{\text{tip}}$, and molecules in gas state. The model reaction to be studied is

$$\text{Metal}_{(\text{tip})} \quad + \quad \text{Molecule}_{(\text{gas})} \implies \text{TIP} \tag{6.1}$$

Henceforth, all the numerical analysis are done using the quantum chemistry code Gaussian [78] and in each case the *ab-initio* tools will be mentioned. The scheme presented in section 6 for what we define as nanochemistry is partially implemented in this package within an *ab-initio* framework. The total force on the nuclei, $\mathbf{F}$, is defined as[3],

$$\mathbf{F} = -\int d\mathbf{r} n(\mathbf{r}) \frac{\partial V_{J-i}^{ext}(\mathbf{r})}{\partial \mathbf{R_I}} - \frac{\partial U_{I-J}}{\partial \mathbf{R_I}} \tag{6.2}$$

This expression is known as the Feynman's theorem (1939) [84]. Here, it follows that the force depends only on the density of the electrons and the position of the other nuclei[4]. The success of this electrostatic theorem is that it defines the density based functional for the force on a nuclei. In other words, the dynamical stability of the nuclei is given explicitly in terms of the electronic density, an static parameter. Moreover, it is independent of the kinetic energy of the electrons, and the keen unknown xc-potential.

This chapter is outlined as follows.

In the the first two sections, the interaction of a benchmark set of diatomic molecules with metallic tips is analyzed. First, we study Hydrogen interacting with the transition metals, nickel, palladium and platinum. The interests on these TIPs is well justified. It is in response to the growing demand of development of experimental, and *ab-initio* methods for an effective description of these candidates for a fuel cell economy [85]. Then, we analyze carbon monoxide interacting with platinum. In the second section, oxygen and nitrogen monoxide interacting with platinum tips are briefly studied. The TIPs obtained for these two molecular systems are similar to those derived for Hydrogen and carbon monoxide concerning the atomic configurations. The inclusion within this thesis of these magnetic molecules is done only to contribute to further analyses of magnetism in the TIPs.

[2]It should be considered as an hybrid of the traditional coordination complex and the reaction intermediate concepts [83]

[3]The notation agrees with those introduced in section 2.

[4]The Feynman's theorem points to a manageable DFT result, 26 years before its establishment.

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Finally, the last section is intended to deploy our method in an *ab-initio* quantum transport characterization of actual platinum nanowires in Hydrogen and carbon monoxide environments. The significance of this actual characterization, is that it joins three lines of work. The first is the *ab-initio* quantum transport method within this thesis proposed. The second is the required chemical analysis of the TIPs, and finally, the unavoidable statistical analysis of the results. This section should be read as the state-of-the-art of our way towards an effective comparison of theoretical methods with experimental results.

6.1 Basics

The approach here developed towards an *ab-initio* chemistry based molecular electronics, is organized to address the following issues,

1. Is thermodynamically favorable the formation of the TIP?.

   The gain in the total energy, is the concept which allows us to predict if a reaction is thermodynamically favorable. However, even though if the reaction is thermodynamically favorable, there is no clear evidence that the reaction occurs. Therefore, in addition, the kinetic of the reaction should be studied, and the activation barriers must be determined.

2. How many molecules are assembled in the TIP?

   This question is addressed using the thermodynamical and kinetical concepts already mentioned.

3. How the configuration of the TIP can evolve during an experimental realization, for instance, a mechanically controlled break junction, (MCBJ)?

   This question is intended to made a simulation of the experiments we refer in this chapter, through the analysis of the stability of the TIP when the leads are pulled apart.

In each case the *ab-initio* results could be contrasted with qualitative analyses based on the Frontier Molecular Orbitals Theory, presented in the appendix E.

6.1.1 A Hydrogen molecule towards platinum tips

The main subject of this part, is the chemistry behind proposal of a controlled deposition for a single Hydrogen molecule in between platinum tips, proposed by Smit.*et.al* [26].

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If we assume that the main feature that marks the difference between the two conductance measurements presented in the figure 6.1 is due to the addition of Hydrogen, we can assure that the Hydrogen molecule has, at least, *affected* the contact. In better words,

"By far the best proof is experience"[5].

However, how is it chemically possible is not obvious at temperatures near zero Kelvin degrees[6].

The figure 6.2 is a barrier less reaction path for a single Hydrogen molecule to a platinum nanowires obtained within an *ab-initio* simulation [86]. The reaction coordinate is the distance between the center of mass of the molecule and the axis of the nanocontact, d. As is noticed, there is no activation barrier, and the gain in energy is more than zero. These two conditions, are sufficient to justify the existence of the TIP configuration that appears in the figure 6.3-left. (The stability of this TIP could be explained considering the closed shell configurations represented in the inset of the figure 6.3, in comparison with the open shell configuration expected for the platinum tip, see **??**. See the appendix E.)

The next step is the simulation of a break junction process. The evolution of the TIP is analyzed through the curves such as those presented in the figure 6.4. This curve is enough to state that an additional configuration could appears in a MCBJ process. In this case, the two Hydrogen atoms lies in the axis of the nanocontact. This TIP configuration is included in the figure 6.3-right. However, an extended analysis considering different initial conditions has been done, which support this result [87].

6.1.2 Hydrogen in between nickel and palladium tips

Here, a few results for Hydrogen molecules interacting with nickel and palladium tips are presented. The value of these calculations is no more than give an *ab-initio* support to our chemical intuition see the appendix E, and open the doors for future works.

The two configurations presented in the figure 6.3 for Hydrogen are studied upon the interaction with nickel and palladium [88]. The nickel and platinum tips behave similarly. They can "dissociate" the Hydrogen molecule. In contrast, the palladium tips behave as noble metal in the interaction with the Hydrogen molecule. This could be derived from the comparison of the bonding distances in between the two Hydrogen atoms, included

[5] Francis Bacon, 1561-1626.

[6] The experiments are done at temperatures $\sim$ 4 Kelvin and the conductance measurements at 10 mV [26].

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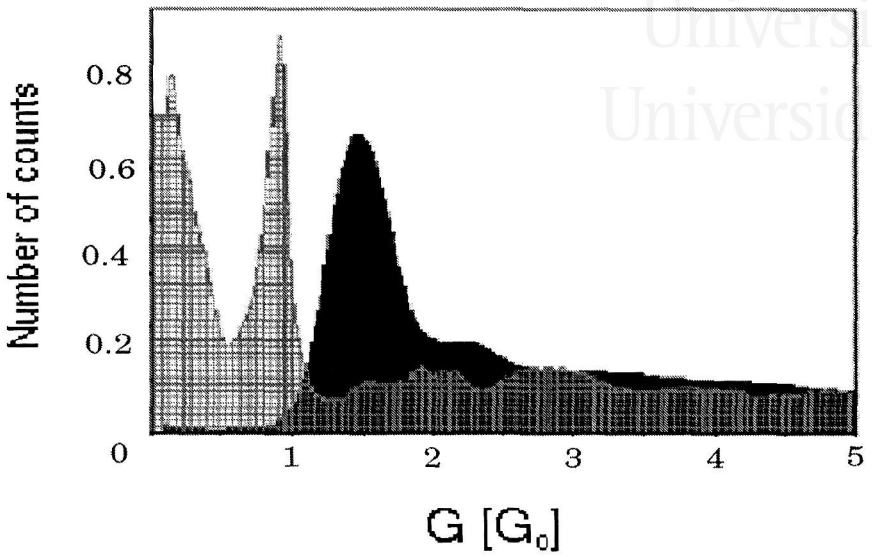

Figure 6.1: Experimental conductance histograms obtained for clean platinum and platinum in a Hydrogen atmosphere. The black curve corresponds to the measurements for a pure platinum nanocontact, and the grey curve was recorded when Hydrogen was added. For experimental details see [26].

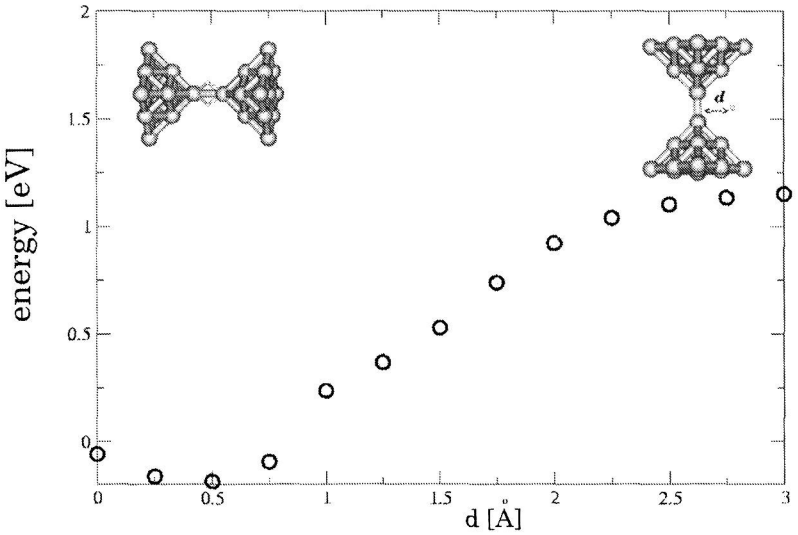

Figure 6.2: *Ab-initio* simulation of the reaction path for a single Hydrogen molecule towards a platinum nanocontact. The total energy of a finite cluster is calculated for different values of the reaction coordinate, d. The inset is a picture of the finite cluster used in the simulation [86].

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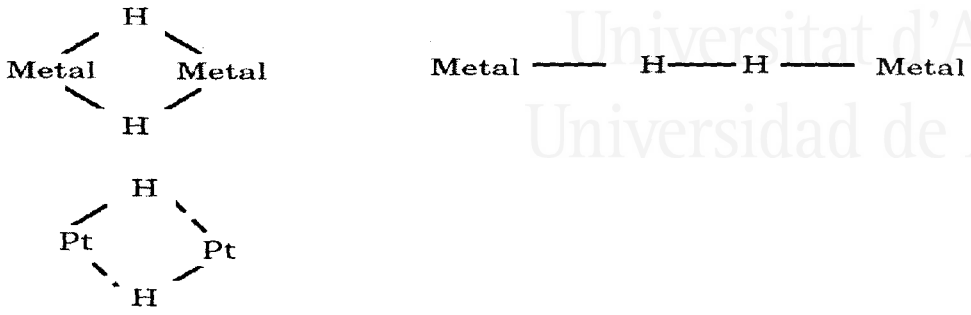

Figure 6.3: Geometric configurations obtained due to the *ab-initio* simulation of the interaction of the selected metallic tips with a Hydrogen molecule. In each case, the bonding distances are included in table 6.1 and 6.2. The configuration in the left is labeled as T_1, and the configuration in the right is labeled as L_1. It should be pointed out, that for nickel and platinum tips, the lowest energy configuration corresponds with structures where the Hydrogen atoms are deviated from the transverse to the stretching axis. The lengths of this metal-H_1 bonds and the metal-H_2 terminal bonds are slightly different, for instance in $Pt2H_2$ Tips, they are $\sim$ 0.166 and 0.182 nm, respectively. It makes as think on structures similar to the diborane compound [?], and a similar bonding mechanism. Thus the Pt_2H_2 ring is held together with four electrons, which low the energy of the TIP, and leaving only two "free" electrons in a higher energy level (see the molecular orbital diagram in the figure E.4). Further details on such atomic arrangements are given in [87].

Table 6.1: Bonding distances for Hydrogen interacting with nickel, palladium and platinum tips in the T_1 configurations obtained within our *ab-initio* simulations. Henceforth, the errors regarding the *ab-initio* calculations of chemical bonds are in second significant digits. To find out this error, we analyze variations in respect to cluster sizes, random initial and constraint conditions, basis sets and different xc-potentials, computational details in [86, 88]].

$Metal_{tip}$	distance $(Metal_{tip} - H)[nm]$	distance (H - H) [nm]
Ni	0.15	0.19
Pd	0.18	0.08(7)
Pt	0.17	0.19

Table 6.2: Bonding distances for Hydrogen interacting with nickel, palladium and platinum tips in the L_1 configurations.

$Metal_{tip}$	distance $(Metal_{tip} - H)[nm]$	distance (H - H) [nm]
Ni	0.15	0.10
Pd	0.18	0.08(2)
Pt	0.17	0.087

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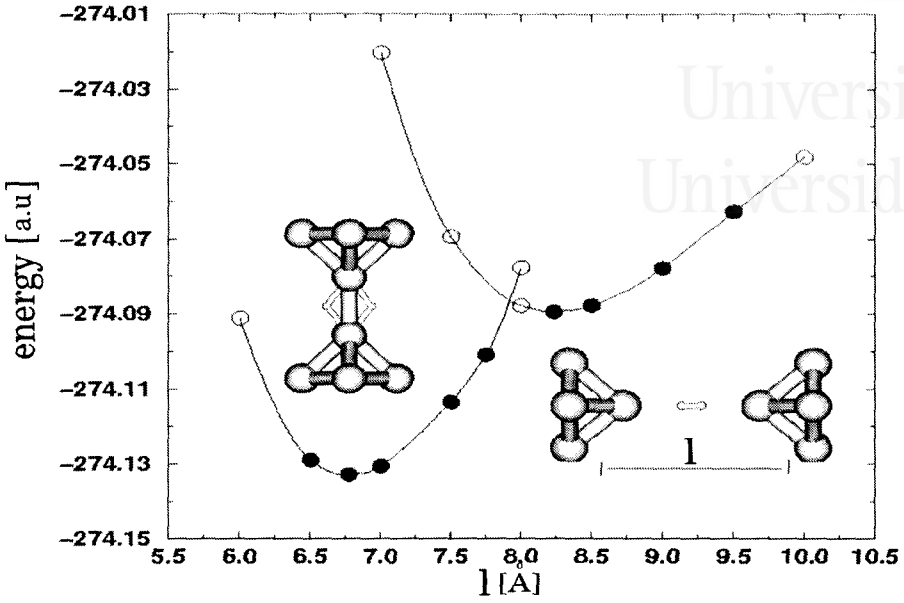

Figure 6.4: Total energy of a H_2 molecule in a Pt nanocontact versus distance between electrodes (outer planes). Blue circles correspond to the H atoms positioned along the stretching axis, z, in molecular form (see right inset) and black circles correspond to the H atoms positioned on the plane perpendicular to the stretching axis (see left inset). Empty symbols have been added as a guide to the eye which correspond to restricted relaxations where the H atoms are forced to stay on the stretching-axis (blue or less black) or on the plane perpendicular to it (black). Arrows indicate configurations for which vibrational mode frequencies closest to the experiment are obtained.

in the tables 6.1 and 6.2, with the distance of the isolated Hydrogen molecule $\sim$ 0.076 Å. The Frontier Molecular Orbitals structure of nickel and platinum could be sufficient to explain this behavior as is discussed in the appendix E.

6.1.3 Carbon monoxide in between platinum tips

In the analysis here presented, it is assumed that the carbon monoxide molecules could arrive to the platinum tips. Therefore, the single molecule deposited in between the platinum tips, is the starting point for the simulations [89]. More in the context of the *ab-initio* simulations, we are avoiding the very expensive analyses of the existence of a reaction path assuming that the differences between the experimental conductance results showed in the figure 6.5 are due to the deposition of carbon monoxide in the platinum tip.

The TIP configurations are presented in the figure 6.6. The main result, and the one

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is going to be remarkable in the context of this Thesis, is that for carbon monoxide, the platinum tips are less selective than for Hydrogen. The platinum tip act as a center for the polymerization of the carbon monoxide, contrasting with the single molecule deposition we obtain for Hydrogen. This chemical selectivity will be shown through the histograms for conductance measurements in the last section "drawn". This behavior could also be explained considering the polarization of the bond in the carbon monoxide, as is discussed in the appendix E.

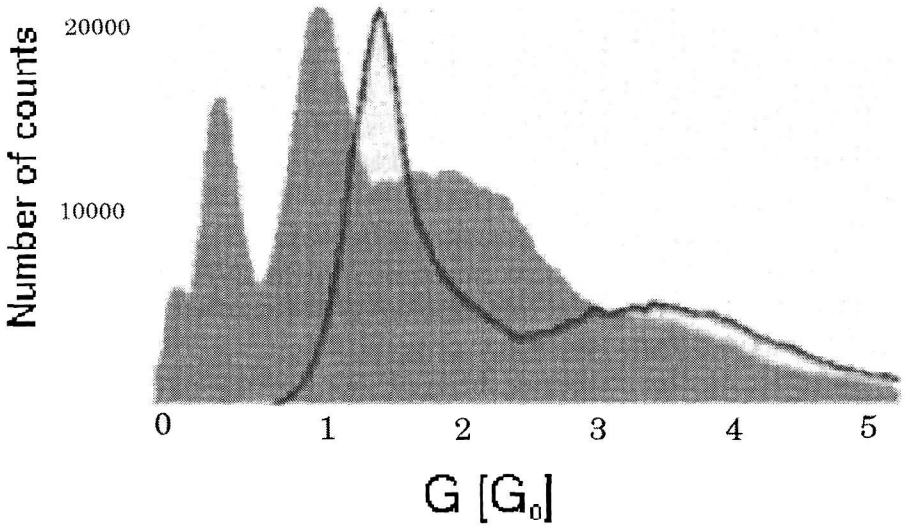

Figure 6.5: Experimental conductance histograms obtained for clean platinum and platinum in a carbon monoxide atmosphere. The black curve corresponds to the measurements for a pure platinum nanocontact, and the grey curve was recorded when carbon monoxide was added. The experimental results were provided by [90].

Table 6.3: Bonding distances for carbon monoxide interacting with platinum tips in the T_1, T_2, and L_1 configurations.

TIP	distance (Pt-C) [nm]	distance (C-O) [nm]	distance (Pt-Pt) [nm]
T1	0.21	0.11	0.26
T2	0.21	0.11	0.28
L1	0.18	0.11	0.58

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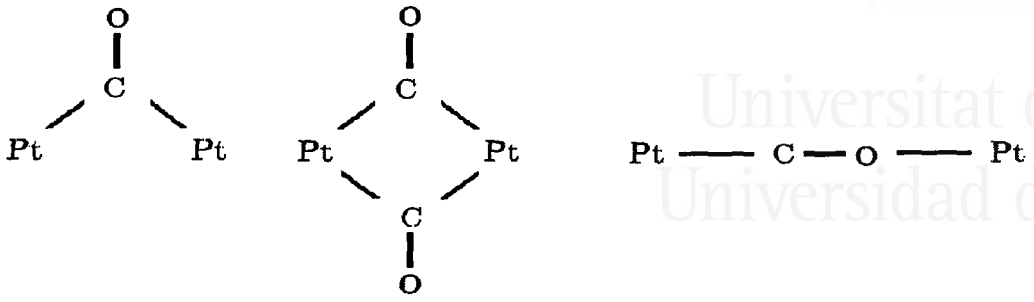

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Figure 6.6: Geometric configuration obtained due to the *ab-initio* simulation of the interaction of the platinum metallic tip with one and two carbon monoxide molecules. In each case, the bonding distances are included in table 6.3. The configuration in the left is labeled as T_1, the one in the center of the figure as T_2, and the configuration in the right is labeled as L_1.

6.2 Nitrogen monoxide and oxygen in between platinum tips

Finally, we mention the results for nitrogen monoxide and oxygen molecules, interacting with platinum tips. These two systems are well suited candidates for study the evolution of molecular magnetism upon reaction with metallic nanocontacts. More in the context of this thesis (but less attractive) they are accepted candidates for comparison with the results for Hydrogen and carbon monoxide in reaction with platinum tips since the electronic structures have similarities. It is done in the appendix E, where the analysis of the frontier molecular orbitals is expected to be enough to claim for the study of magnetism in these tips.

The TIPs obtained appears in the figure 6.7 and 6.8 [91]. The oxygen molecule is "dissociated" by the platinum tips, like the Hydrogen molecule. Also, for bigger distances between the platinum tips we observe that the oxygen molecule could lie in the stretching axis.

For nitrogen monoxide the behavior is similar to that of carbon monoxide, the platinum tips should act as a polymerization center, and more than one molecule is expected to be deposited in between the platinum tips. (In the appendix E more details are included.)

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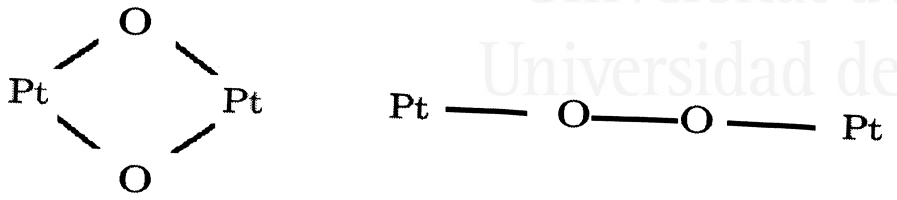

Figure 6.7: Geometric configuration obtained due to the *ab-initio* simulation of the interaction of the platinum metallic tip with oxygen molecules. In each case, the bonding distances are included in table 6.4. The configuration in the left is labeled as T_1, and the configuration in the right is labeled as L_1.

Table 6.4: Bonding distances for oxygen interacting with platinum tips in the T_1 and L_1 configurations.

TIP	distance (Pt-O) [nm]	distance (O-O) [nm]
T1	0.21	0.25
L1	0.19	0.13

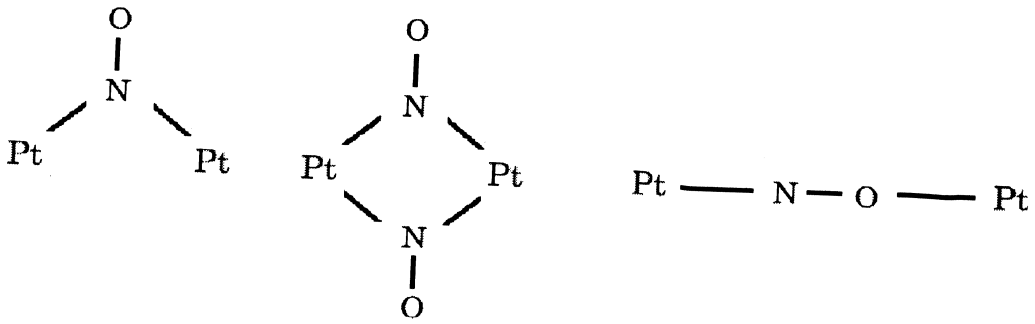

Figure 6.8: Geometric configuration obtained due to the *ab-initio* simulation of the interaction of the platinum metallic tip with one and two nitrogen monoxide molecules. In each case, the bonding distances are included in table 6.5. The configuration in the left is labeled as T_1, the one in the center of the figure as T_2, and the configuration in the right is labeled as L_1.

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Table 6.5: Bonding distances for nitrogen monoxide interacting with platinum tips in the T_1, T_2, and L_1 configurations.

TIP	distance (Pt-N) [nm]	distance (N-O) [nm]	distance (Pt-Pt) [nm]
T1	0.20	0.11	0.28
T2	0.21	0.11	0.31
L1	0.18	0.11	0.53

6.3 Platinum nanocontacts in Hydrogen and carbon monoxide environments: an attempt to *ab-initio* simulations of conductance measurements

The TIP structures selected are those indicated through tables 6.1 and 6.3. The schemes of the atomic structures are in the figures 6.3 and 6.6. The statistical analysis is done following the scheme introduced in the section 1.3, and the quantum transport method described in chapter 4.

With all this in mind, we report numerical calculations intended to describe the electrical response of Hydrogen and carbon monoxide molecules added to platinum nanocontacts, by the analysis of the following Gaussian distribution function,

$$f(G) = \sum_I P_I^{max} \frac{1}{\sigma_I \sqrt{2\pi}} e^{-\frac{(G-\langle G_I \rangle)^2}{(2\sigma_I)^2}} \tag{6.3}$$

where σ is the standard deviation, and, G_I is the expected value, in an assumed *statistical* record of individual measurements [40]. In the case of conductance measurements of platinum nanocontacts in a Hydrogen environment, we propose I = 2 in the model equation 6.3. This value is directly related with the number of events we are considering in the simulation of the break junction experiments. P_I^{max} is the probability-weight of a single I-event, if chemical correlations among them are taken into account. We consider that,

$$P_1^{\max} = P_2^{\max} \tag{6.4}$$

since the two configurations exist in a simulation of a break junction process, see the figure 6.4 or, (in other words), the two events are not chemically correlated. (From the simulated stretching curves, such as this indicated in the figure 6.4, we observe that the two configurations can exist in a break junction process).

In the model 6.3, the standard deviation, σ_I, could be related with the existence of different microstates around the average I affecting the mean value of the conductance, $\langle G_I \rangle$. As a first approximation, we could considered that it as proportional to the stability of the I-microstates, thus, proportional to the coupling strength. The coupling of the molecules

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to the metal is modeled as the highest relative change in the internal vibrational mode, ω_0,

$$\text{coupling} = \frac{\Delta\ \omega_0}{\omega_0} \tag{6.5}$$

The results are included in table 6.6 and the computational details in [92].

The mean values of the conductance are calculated following two routes. The difference between both routes is in regards of the local and nonlocal character of the xc-potentials. The conductance results appears in table 6.6.

This quantitive analysis is enough to sketch the histograms for the simulation of conductance measurement of the break junction of a platinum wire in Hydrogen environment, see the figure 6.9.

Table 6.6: Conductance measurements of platinum nanocontacts in Hydrogen atmosphere. Numerical parameters for the *ab-initio* simulation of an experimental histogram.

TIP label	$P^{max}H_2$	$\frac{\Delta\omega_0}{\omega_0}$	$G_{\text{local-DFT}}$	$G_{\text{nonlocal-DFT}}$
T_1	1	0.63	2.18	0.97
L_2	1	0.51	0.99	0.18

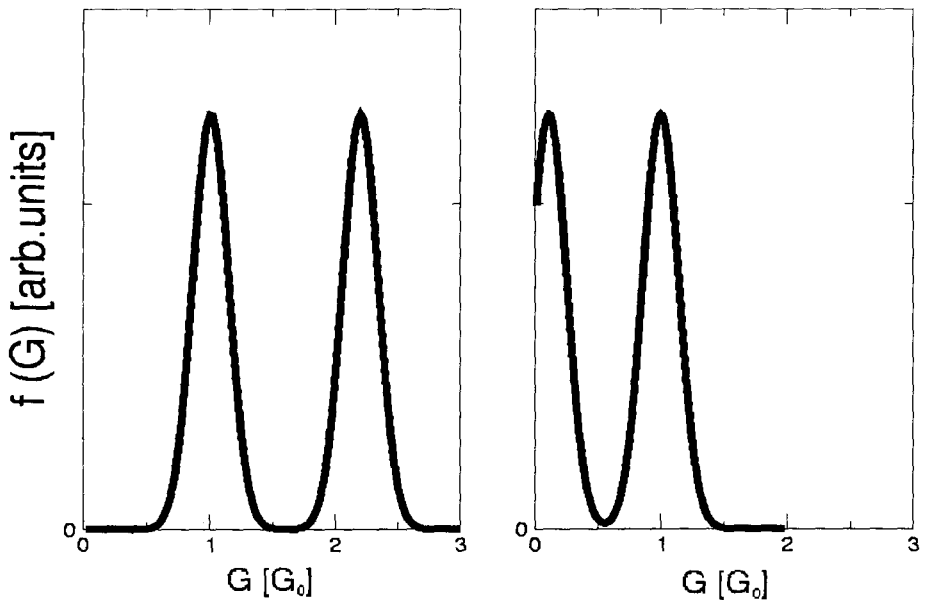

Figure 6.9: Theoretical histogram for the conductance measurements of platinum nanocontacts in a Hydrogen environment. The details are included in the main text.

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For carbon monoxide environment, the same analysis is done. In this case I is limited to $I_{max} = 3$ in the model equation 6.3, even when more configurations than those indicated in the figure 6.6 are allowed. For the probabilities of the configurations sketched in the figure 6.6 we did the following model,

$$\begin{aligned} (P_1^{\max})^2 &= P_2^{\max} \\ P_3^{\max} &= P_1^{\max}(1 - P_1^{\max} \end{aligned} \tag{6.6}$$

Statistically, the TIP events labeled as "1" and "2" are not independent. They respond to the following constriction. If the stretching is slow enough as to permit the presence of another carbon monoxide molecule in the vicinity of the neck, then this molecule will be also bounded. The second condition is related with the picture that the TIP label as "3" will exists if and only if, the TIP-1 exists and the TIP labeled as "2" is not formed.

The analysis of the standard deviations in each TIP conductance simulation, and the mean value of the conductance, where similar to those did for Hydrogen. The results are summarized in table 6.7.

The theoretical histograms are represented in the figures 6.10. Naively, the agreement of "nonlocal simulations" with experimental results can be established, see also the figures ?? and 6.5-right.

Finally, we should point out two messages.

The distribution function plots in each case, either the theoretical simulations or the experimental proposals, show how the *chemistry could be mapped in an electronic response.* The number of peaks correspond with the most stable configurations, and the relative height among them is modulated by the number of times each configuration could appear. More in the context of this Thesis, these two sets, support previous messages concerning the role of nonlocality in the xc-potentials in use. *There are noticeable distinctions in the conductance values depending on the use of local or nonlocal xc-potentials.* When nonlocal xc-potentials are employed the conductance values are reduced. Furthermore, when nonlocal xc-potentials are employed, the experimental results are matched[7].

[7] We should admit that this result turns out to be surprising, since as is showed through the presentation of numerical results there are many approximations to made manageable the *ab-initio* methods.

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Table 6.7: Conductance measurements of platinum nanocontacts in carbon monoxide atmosphere. Numerical parameters for the *ab-initio* simulation of an experimental histogram.

TIP label	$P^{max}CO$	$\frac{\Delta\omega_0}{\omega_0}$	$G_{local\text{-}DFT}$	$G_{nonlocal\text{-}DFT}$
1	0.8	0.16	1.89	1.03
2	0.64	0.04	1.30	0.51
3	0.264	0.07	0.21	0.16

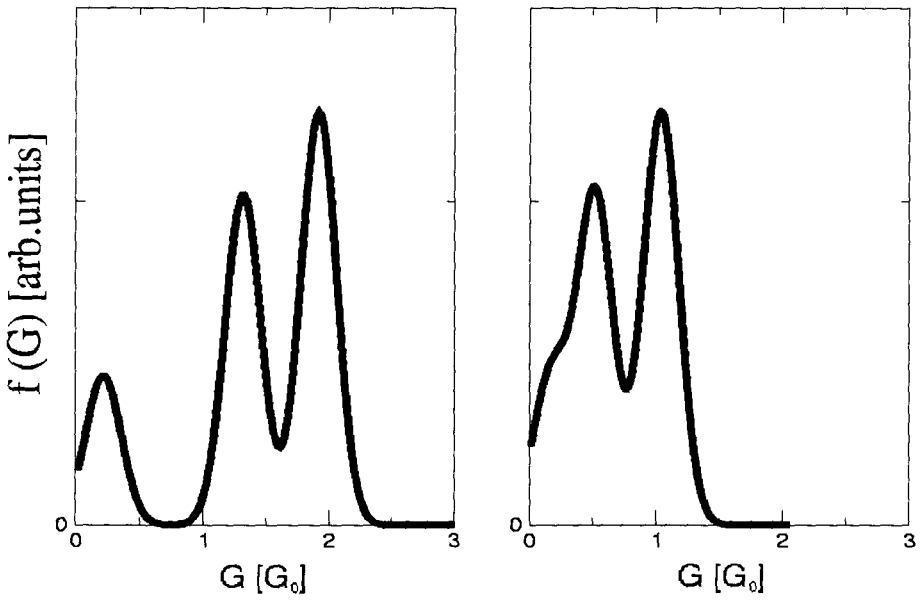

Figure 6.10: Theoretical histogram for the conductance measurements of platinum nanocontacts in carbon monoxide environment. The details are included in the main text.

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Chapter 7

Towards Molecular Electronics: benzene-1,4-dithiolate in between gold surfaces

Overview

This is a brief chapter devoted to show how the effectiveness of our *ab-initio* methods could be deployed in an accepted candidate for real molecular electronics: the benzene-1,4-dithiol molecule. The attention is focused in the study of this system upon its interaction with two gold surfaces. Due to chemical interactions at gold-sulfur surfaces, when the benzene-1,4-dithiol is adsorbed on gold surfaces, the hydrogens of the thiol terminations desorbs, given us the remaining "molecule" in the TIP, the benzene-1,4-dithiolate, (BDT).

The possibilities of BDT as a basic unit in molecular devices was discussed by Reed *et al.* [93]. In addition, experimental measurements have been done on this system by the group of Tao [29]. Our concern is that among theoretical groups, there is a agreement in the conductance values calculated for this system [12, 68, 94–97]. The main scope of this chapter is to address the differences among theoretical proposals to the different approaches used for the xc-potentials.

In the first section, the TIP configurations we propose for BDT molecules interacting with gold surfaces are discussed. This analysis is done within a restricted *ab-initio* simulations framework, and taking up the standard chemical analysis for studying the stability of organic molecules and their bonding capabilities.

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In the second section our *ab-initio* quantum transport scheme is deployed on the TIPs we propose. Upon the simple statistical analysis we explain in section ??, we compare our theoretical results with its admitted experimental counterparts [29].

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7.1 Discussion of geometrical configurations

There are not doubts on the adsorbtion capabilities of BDT molecules with metal surfaces [98–100]. Furthermore, it is an experimental evidence. The well-defined peaks in the conductance histograms for clean gold nanocontacts, $\sim 1G_0$, disappear when the gold nanocontacts are made in solutions of benzene-1,4-dithiol (see the figure 7.1). This is a signal of the substantial adsorbtion of BDT in gold surfaces.

However, there are not clear evidences on which are the possible configurations of the TIPs. In this respect, a considerable amount of theoretical simulations are being done [30,94,97–100]. As far as we know, there is not consensus among theoretical proposals. The molecular geometry calculations here presented, are a contribution to show that the model for the gold surface interacting with BDT, is determinant for the final TIP configurations.

We performed geometry optimizations for two model gold surfaces, the single atom contact and the slab surface contacts[1]. The final geometric configurations for the TIPs are sketched in the figure 7.2 [101].

In order to simulate a controlled break junction for gold wires in a BDT solution, and taking into account, the high tendency of the BDT to be adsorbed by gold surfaces we made the following assumption. The TIP structure sketched in the figure 7.2 and table 7.1, is going to be selected as the most probable in a sufficiently slow break junction experiment[2]. Moreover, we assume that the concentration of molecules is high enough to allow the deposition of more than one molecule bridging the gold surfaces. Therefore, the configurations where more than one BDT unit bridge the gold surfaces are plausible to exist. In such cases the planarity of the benzene ring and the strong repulsion between the π electron clouds, should dictate the relative position between BDT molecules[3]. This possible set of configurations, is schematically showed in the figure 7.3.

Finally, we cannot consider our calculations as conclusive for modeling interactions between the experimental-obscure gold nanocontacts, and BDT molecules. Nevertheless,

[1]The slabs were taken simulating Au (111) surfaces. The range of gold clusters we use were, $Au_3 - BDT - Au_3$ and $Au_6 - Au_3 - BDT - Au_3 - Au_6$.

[2]The experimental measurements here reported were carried out using gold surfaces in a 1 mM benzene-1,4-dithiol solution [29].

[3]We do not analyze within an *ab-initio* framework the possible configurations due to numerical costs.

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the knowledge of the experimental framework and the chemical activity of both systems is enough to predict that the *hollow* structure is the most probable configuration, and parallel configurations on hollow, are also possible, figures 7.2 and 7.3. These set of geometries are our candidates to carry out the *ab-initio* quantum transport simulations.

Table 7.1: Selected geometric distances for the systems above presented. First, the distance for the gold point contacts (surfaces), distance (Au-Au). Second, between the adsorbed molecule and gold, distance (Au-S).

TIP	distance (Au-Au) [nm]	distance (Au-S) [nm]
Au-BDT	0.88	0.23
$Au_3 - BDT$	0.82	0.20

7.2 *Ab-initio* simulations of conductance measurements

In this section we study the conductance of the TIP system sketched in the figure ??. The route here deployed for the *ab-initio* calculation of the conductance is widely explained in chapter 4.

In the figure 7.4 we show the evolution of the energetic positions for the HOMO and LUMO orbitals in correspondence with the addition of nonlocal contribution to the xc-potential. This microscopical picture is the enough to explain the conductance evolution when nonlocality is included in the practical xc-potentials, see the figure 7.5.

To find out the right amount of nonlocal contribution, in accordance with the methodology we are proposing, the HOMO and LUMO positions are fixed to the Ionization Potential and Electron Affinity of the selected TIP. The way to approach the exact solution is to invoke hierarchical correlated *ab initio* methods as Möller-Plesset perturbation (MP) and Coupled-Cluster (CC) theories (DFT calculations are shown for comparison). The corresponding results are presented in the figure 7.6.

The central result is that a finite nonlocal correction to the xc-potentials is enough to reproduce the right HOMO and LUMO position of the TIP under study. With this nonlocal correction proposed within our static methodology, a finite correction to the conductance calculation is obtained This correction is in agreement with the one derived from calculation within TDCDFT, also a nonlocal theory for xc-potentials [12]. Remarkably, both methodologies, TDCDFT and the one proposed within this thesis, match the experimental values for the single TIP conduction.

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Finally, and considering the chemical analysis we did in the previous section, the existence of one, two or more molecules bridging the metallic surfaces are considered as individual and equally probable events. In other words, the existence of a single molecule TIP do not affect the formation of more single molecule TIPs, this is the meaning of individual or not correlated events. The non correlation or equal probabilities is an assumption considering that the break junctions are made sufficiently slow, to admit more than one molecule bridging the metallic surfaces. This information is used to construct theoretical histograms for a direct comparison with its experimental counterpart, figure ??. The histograms we made are presented in the figure 7.7. The comparison between both set of histograms, could be appreciated as a numerical claim for the main thesis within this thesis, *the nonlocal quantum transport calculations drastically reduce the local density-based quantum transport calculations* and at least for the benchmark systems in this thesis analyzed, we could within a nonlocal density-based framework, reproduce the experimental results.

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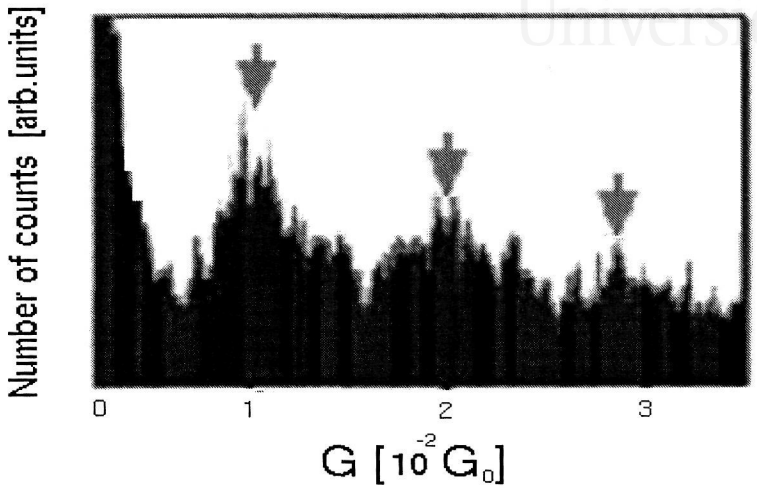

Figure 7.1: Experimental conductance histogram of BDT junctions of gold surface. For experimental details see [29].

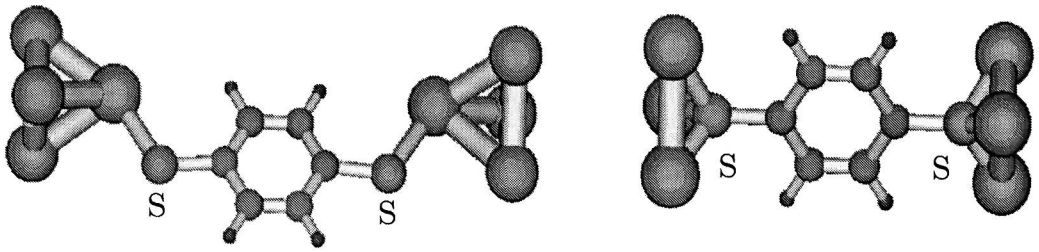

Figure 7.2: *Ab-initio* simulation of geometrical configurations for a single BDT junction of a gold nanocontact, Au-BDT TIP (left) and a gold surface, Au_3-BDT TIP (right). The sulfur atoms, indicated in the figure, stick the molecule to the gold nanocontact (or the surface). For computational details see [101].

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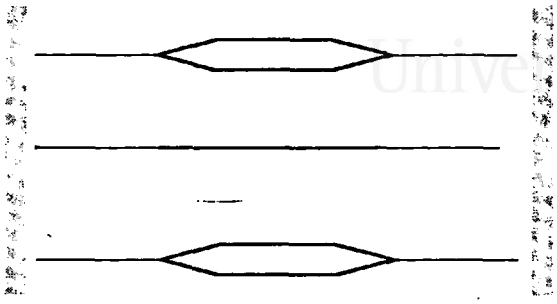

Figure 7.3: Geometric configurations of BDT bridging gold surfaces. The straight line is a representation of the gold surface. The BDT molecules are deposited singly under the present deposition conditions. They are isolated on the gold substrates and there is no appreciable interaction among them. This set of configurations is not calculated within *ab-initio* methods. Fairly well, our *ab-initio* quantum transport methodology on this set of structures, gives results similar to the experimental reported.

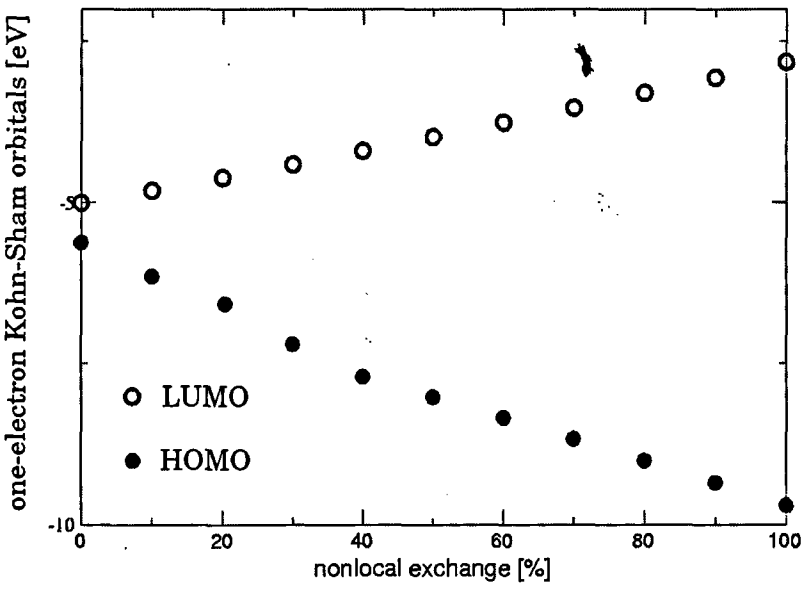

Figure 7.4: HOMO and LUMO position in the energy space as a function of the local contribution in the xc-potential. The "a" parameter is that in the equation 5.3.

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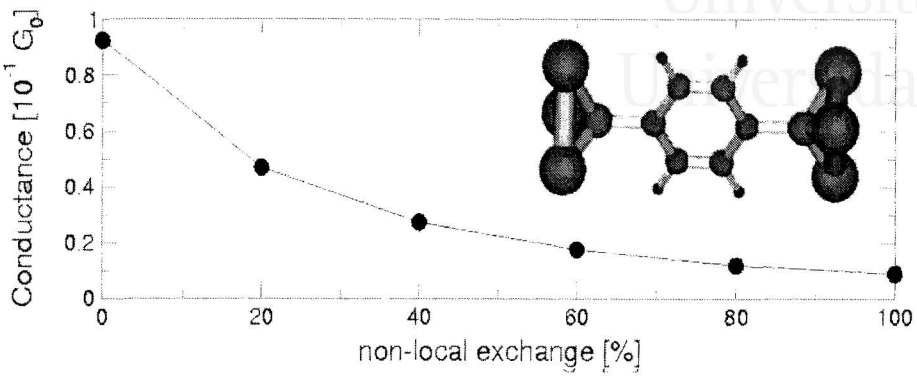

Figure 7.5: Reduction of the conductance due to the progressive substitution of the local xc-potential potential by a nonlocal contribution. The inset shows the TIP bridging the gold electrodes. G_0 is the quantum of conductance, $G_0 = \frac{2e^2}{h}$.

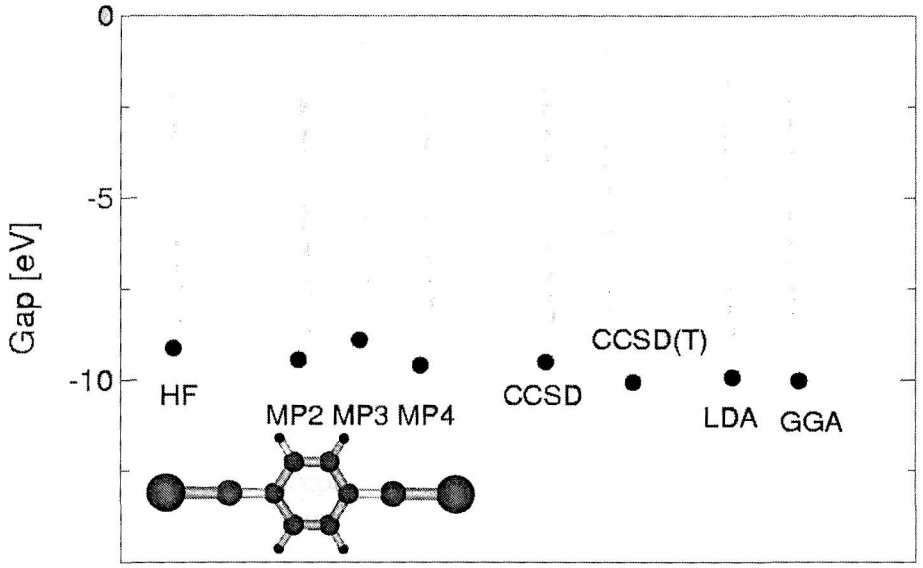

Figure 7.6: Ground state calculations for the energetic distance between the HOMO and LUMO orbitals, the GAP. It is calculated as: $E_{gap} = 2\,E_0\,(N) - E_0\,(N+1) - E_0\,(N-1)$.

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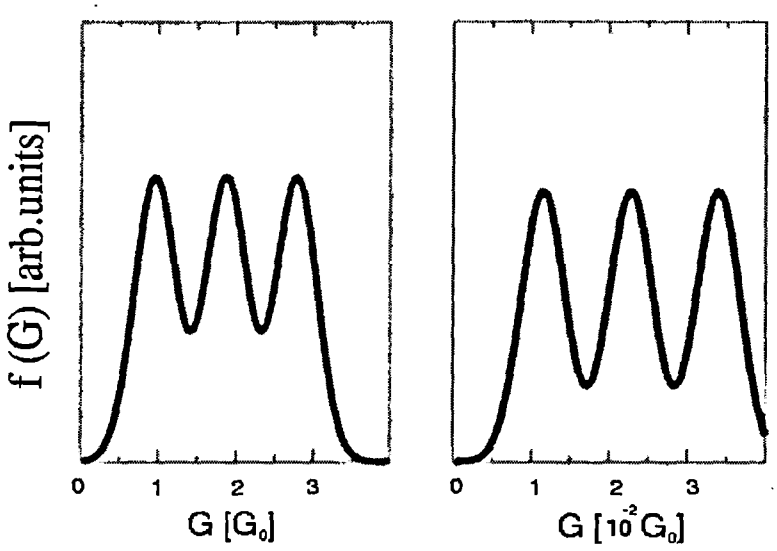

Figure 7.7: Theoretical histogram for the conductance measurements of BDT junctions of gold surfaces. (The details are included in the main text.)

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Outlook

Main results

Sometimes, beside an *ab-initio* calculation thesis a cooking class is expected. Nevertheless, despite this pressure, this *ab-initio* research is intended to find its way within the contributions that actually claim a rigorous, and therefore effective application of the *ab-initio* methodologies ([5,33,70,102] and references therein). In this line, the main results obtained in this thesis are summarized in the next paragraphs.

First, in contrast to recent theoretical works [18, 39], we support the existence of an *ab-initio* density-based theory to approach the quantum transport characterization. Its effectiveness relies on the definition of the exchange-correlation potential to account for the many-body interactions in an equivalent single-particle problem [6,67].

Second, we fix an algebraic form for the exchange-correlation potential that fulfills two boundary conditions. The analytic definition of the exchange-correlation potential serves as an excuse to formally define the local character of a functional. This subtle mathematical point, led us to divide present *ab-initio* density-based research in two groups: the local and nonlocal functional based. As far as we know, there are not previous formal definitions which permit this separation (in a consistent manner). Furthermore, this subtle mathematical point pertains to the consideration of a truly physical problem: the nearsightedness [103]. This concept is roughly connected with the behavior of electrons in many-electron systems, and its importance is enhanced when the electrons are confined, the physical situation we assume we deal with in molecular electronics. Therefore, we address the corrections to *ab-initio* density-based quantum transport calculations to the use of nonlocal exchange-correlation potentials.

Third, we study the effect of the inclusion of nonlocality in the quantum transport features of some benchmark systems. We observe a drastic reduction of the conductance values due to the addition of nonlocal contributions to the exchange-correlation potentials. The

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control of the amount of nonlocality is central in the route we propose to approach the exact exchange-correlation potential. This piece, in conjunction with the calculation of the geometric structures of the molecular bridges, and a model for a statistical analysis, is used to make theoretical histograms for a direct comparison with experimental ones. Their matching (as far as we know, not obtained with the use of local exchange-correlation potentials) should be interpreted as the demonstration of an old problem in physics: nonlocality and its role in a present-day technological challenge: the measurement of the electronic response of molecular bridges. Our theoretical, *ab-initio* and static density-based, results are compared with those obtained when the *ab-initio* time-dependent density-based methodologies are implemented. The agreement between static and time-dependent results, opens up the possibility of formally justifying a connection between the two theories. Nevertheless, an analytic connection could be already established, in both methodologies the exchange-correlation potential is a nonlocal quantity on the space of coordinates.

Fourth, we use traditional concepts from chemistry and physics to explain some aspects which cannot be explained with present *ab-initio* methods. For instance, the reaction mechanisms, bonding preferences, and single-conducting channels formation in some of the systems studied, were some of the issues explained.

Issues we have not covered

We have seen that by appropriately describing an analytic property of a potential, we can get quantitative conductance properties in *good* agreement with actual experimental results. However, we now outline four of the issues that we have not analyzed in this thesis.

First, even when we state a mathematical relation between the static and time-dependent corrections to the potential: the nonlocality, we do not establish an explicit relation between both corrections.

Second, based on the original work on density-functional theory [6], the potential we are approaching is universal and the design route we propose, apparently does not lead to a universal functional. This is very much an open line of research.

Third, all the theoretical methods here developed are based in unaccepted *a priori* assumptions; for instance, the zero-temperature behavior, crystal arrangements on the leads, the non existence of electron-phonon interactions, etc... In order to develop theoretical framework for real molecular electronics all these effects should be carefully included.

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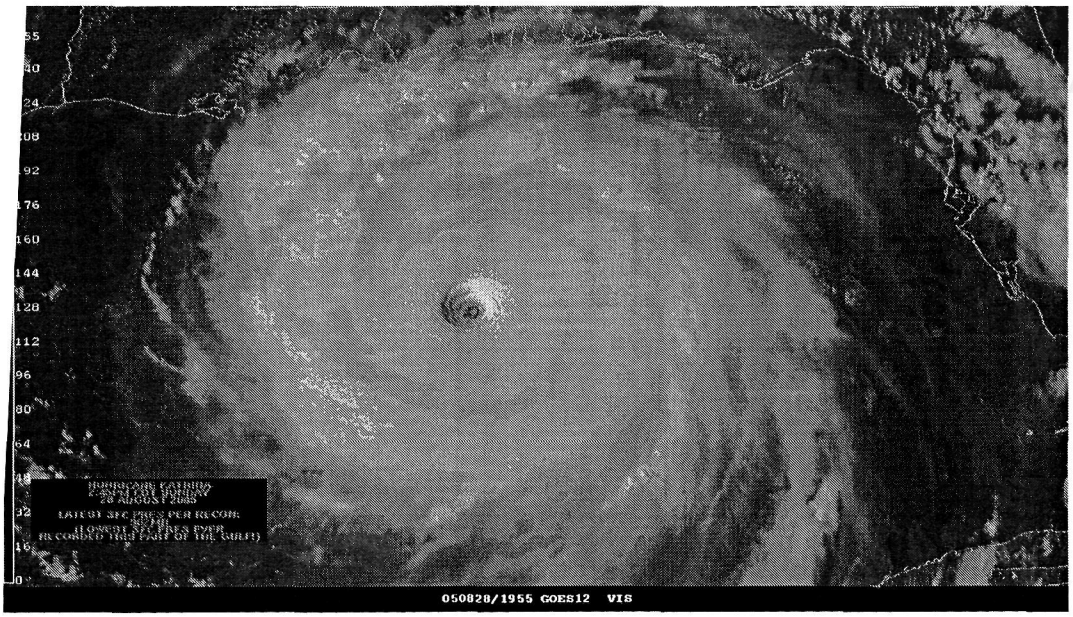

Figure 7.8: A hydrodynamical representation for the electron flow when a molecule placed in between an extended homogenous system. This hydrodynamical picture should be enough to motivate a discussion concerning the role of the systems surrounding the molecule, in the quantization of the electron flow through the molecular system: the main subject of this thesis. (The photo is of Hurricane Katrina and was taken sufficiently far from the center of the storm, but closer than in the case sketched in the introduction of this thesis.)

Fourth, some of the concepts used to describe the systems we are dealing with, are rough extrapolations of the concepts used in physics and chemistry. Their validity is questionable. For instance, the screening length of the bulk metal, the decay length of the isolated molecule, and the "interaction tip complex" as a label to enclose the chemical qualities of the systems we are considering.

We hope that the result of this thesis will be confirmed by further research.

Now, back in the question presented at the end of the introduction of this thesis:

-What is the name for this system? -Pointing to the figure in 7.8.

It should be some of the physics to put into the figure 1, for an effective representation of the systems defined by *one* or *few* molecules in between an extended system, or more simply and cautiously: *this* system -it is necessary to point [2].

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(...) There's Plenty of Work at the Bottom (...)[4]

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[4]Inspired in the title of a lecture given by physicist Richard Feynman in 1959: There's Plenty of Room at the Bottom

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Part IV

Appendices

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Appendix A

Density matrices

This is an appendix for the rough definition of the density matrices, without referring to its physical interpretation.

A.1 Definitions

The mathematical expressions for density matrices are obtained as follows [51, 104]:

For a finite N-dimensional Hilbert space, the N-order density operator is defined as,

$$\hat{\Gamma}^N = \sum_j a_j \mid \Psi_j \rangle \langle \Psi'_j \mid \tag{A.1}$$

where the coefficients a_j are non-negative and add up to one, representing the proportion of the ensemble being in the pure $j-$state. Thus, this represents a statistical mixture of pure states.

Subsequent integrations of the expression above, lead to reduced density matrices. In this work we are going to use the *second-* and the *first-order* density matrices.

The *second-* order density matrix is defined as,

$$n_2\left(\mathbf{r}'_1, \mathbf{r}'_2; \mathbf{r}_1, \mathbf{r}_2\right) = N\left(N-1\right) \int d\sigma_1 d\sigma_2 \int d\mathbf{x}_3 \ldots d\mathbf{x}_N \, \Gamma^N\left(\mathbf{x}_1, \mathbf{x}_2, \ldots, \mathbf{x}_N; \mathbf{x}'_1, \mathbf{x}'_2 \ldots, \mathbf{x}_N\right) \tag{A.2}$$

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and the *first-order* density matrix is by construction,

$$n_1(\mathbf{r_1}, \mathbf{r'_1}) = \frac{1}{N-1} \int d\mathbf{r_2}\, n_2(\mathbf{r'_1}, \mathbf{r_2}; \mathbf{r_1}, \mathbf{r_2}) \tag{A.3}$$

The *zero* order density matrix is associated with the probability of finding a single particle in the vicinity of $\mathbf{r_1}$, commonly known as the electronic density. It is obtained doing $\mathbf{r_1} = \mathbf{r'_1}$ in the expression for the first order density matrix, expression (A.3). Since this is the central quantity of this thesis it is explicitly stated ($\mathbf{r_1} = \mathbf{r}$),

$$n(\mathbf{r}) = N \int d\sigma_1 \int d\mathbf{x_2} \ldots d\mathbf{x_N}\, \Psi(\mathbf{r}, \mathbf{x_2}, ..., \mathbf{x_N})\ \ \Psi^*(\mathbf{r}, \mathbf{x_2}, ..., \mathbf{x_N}) \tag{A.4}$$

A.2 The total energy in terms of density

The total energy as a density functional is (the notation agrees with the one introduced in chapter 2),

$$\begin{aligned} E[n(\mathbf{r})] &= \int d\mathbf{r}\, v_{ext}(\mathbf{r})\, n(\mathbf{r}) + \frac{1}{2} \int d\mathbf{r} d\mathbf{r'}\, \frac{n(\mathbf{r})\, n(\mathbf{r'})}{\mid \mathbf{r} - \mathbf{r'} \mid} + G[n(\mathbf{r})] \\ G[n(\mathbf{r})] &= \frac{1}{2} \int d\mathbf{r}\, \nabla_{\mathbf{r}} \nabla_{\mathbf{r'}} n_1(\mathbf{r}, \mathbf{r'}) \mid_{\mathbf{r}=\mathbf{r'}} + \frac{1}{2} \int d\mathbf{r} d\mathbf{r'}\, \frac{C_2(\mathbf{r}, \mathbf{r'})}{\mid \mathbf{r} - \mathbf{r'} \mid} \end{aligned} \tag{A.5}$$

where $C_2 \equiv C_2(\mathbf{r}, \mathbf{r'})$ is the two-particle correlation function defined in terms of the one- and two- particle density matrices as,

$$C_2(\mathbf{r}, \mathbf{r'}) = n_2(\mathbf{r}, \mathbf{r'}; \mathbf{r}, \mathbf{r'}) - n_1(\mathbf{r}, \mathbf{r})\, n_1(\mathbf{r'}, \mathbf{r'}) \tag{A.6}$$

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Appendix B

Mathematical miscellanies

Some of the mathematical definitions developed in this appendix may seem meaningless at first, but I consider this the scientific route to supporting the main hypothesis of this dissertation: that nonlocal functionals are necessary for an effective mean-field description of quantum transport. Furthermore, for me this appendix is a belated tribute to Eddy Jimnez, professor of Mathematical Analysis in the Faculty of Physics at the University of Havana. I will always miss his ability to articulate the logical essence of a problem.

This appendix provides an overview of some formal mathematical concepts and rules. The emphasis is on the conceptual ideas rather than on rigorous definitions or proofs. The issues addressed are related with the concept of functional [105, 106]. First, its definition is presented. Then, the functional derivative is introduced. It is done for technical reasons, since this property is routinely used in this work. Finally, the concept of local functional in a set is presented, [106].

The "locality" requires an explicit definition due to the central role it could play in the physical problem discussed within this thesis. From our point of view, this property is very often used in the works within density-functional theories without a rigorous basis [31]. The main proof of this sentence is the contradictory treatment of this definition in the technical literature [15, 23, 31, 32, 72, 107].

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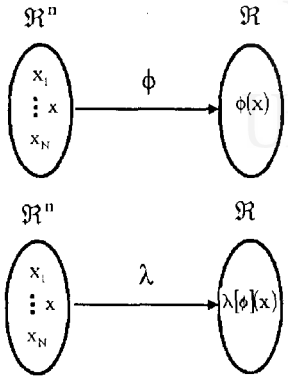

Figure B.1: The illustrations above show the connected X- space with $\phi(\mathbf{x})$ through the ϕ- function and the functional λ connecting the ϕ- function space with the $\lambda[\phi](\mathbf{x})$. As is indicated in the top of the picture, for the most general cases the mapping is done in the sequence that follows, $\Re^n \rightarrow \Re \rightarrow \Re$.

B.1 Definition of functional

Lets consider a space of fields F, and take $F \subset C^\infty(\Re^n)$. (Here $C^\infty(\Re^n)$ is the mathematical notation for the set of infinitely differentiable functions on $\Re^n$.) Then, the field $\phi \in F$ with $\mathbf{x} \in \Re^n$ is denoted as, $\phi = \phi(\mathbf{x})$. The map is,

$$\phi : \ \Re^n \rightarrow \Re \tag{B.1}$$

Then, a functional can be defined as any map from F to some other set. (Usually, this is the real numbers.) The most common definition of functional is limited to the real-valued functionals. It means, $\lambda \in \Re$, when we give it a field $\phi \in F$ and a point $\mathbf{x} \in \Re^n$. It is denoted as $\lambda = \lambda[\phi](\mathbf{x})$. The associated map is given by,

$$\lambda : \ F \rightarrow \Re \tag{B.2}$$

In this thesis we are interested in the most general definition of functional. The functional defined as a function-valued function. It means, $\mu \in \Re$ and is denoted as $\mu = \mu[\phi](\mathbf{x})$. The map behind this definition is,

$$\mu : \ F \rightarrow C^\infty(\Re^n) \tag{B.3}$$

In this case μ gives a number when we give it a field $\phi \in F$ and a point $\mathbf{x} \in \Re^n$, [1].

[1] In the next appendix this notation is going to be "map" to the space of positions, the electronic density as the function to deal with, and finally, the exchange-correlation potential as the functional.

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B.1.1 Functional derivative

If λ is a functional of ϕ, and ϕ is a function on the U-space, with $U \subset \Re^n$ and $\mathbf{x} \in \Re^n$ then, the functional derivative of λ in respect to ϕ is denoted as,

$$\frac{\delta}{\delta\,\phi(\mathbf{x})}\lambda[phi](\mathbf{x}) \tag{B.4}$$

such that,

$$lim_{\epsilon\to 0}\frac{\lambda[\phi(\mathbf{x})+\epsilon\tau(\mathbf{x})]-\lambda[\phi(\mathbf{x})]}{\epsilon} = \int d\mathbf{x}\,\frac{\delta\lambda}{\delta\phi(\mathbf{x})}\tau(\mathbf{x}) \tag{B.5}$$

for any *compactly supported* $\tau(\mathbf{x}) \in C^{\infty}(\Re^n)$, therefore $\tau(\mathbf{x}) = 0$ for large $\mathbf{x}$. This means that we avoid boundary terms at infinity. This definition (which is a generalization of the directional derivative, carries information on the rate of functional changes) when the function $\phi = \phi(\mathbf{x})$ changes by a small amount.

The rules used to find out the functional derivatives of functionals are similar to those used for finding the ordinary derivative. However, a very useful relation in the context of this thesis is now shown.

For $\lambda[\phi]$-functionals which can be written as an integral in U-space and $U \subset \Re^n$,

$$\lambda[\phi(\mathbf{x})] = \int d\mathbf{x}\,\xi(\mathbf{x},\phi(\mathbf{x}),\nabla^{(1)}\phi(\mathbf{x}),\nabla^{(2)}\phi(\mathbf{x}),\ldots,\nabla^{(N)}\phi(\mathbf{x})) \tag{B.6}$$

the functional derivative is constructed according to the rule [52, 108],

$$\frac{\delta\lambda}{\delta\phi(\mathbf{x})} = \sum_{i=0}^{N}(-1)^i\nabla^i\ \frac{\partial\xi}{\partial(\nabla^i\phi(\mathbf{x}))} \tag{B.7}$$

For 1−D systems it is reduced to,

$$\frac{\delta\lambda}{\delta\phi(x)} = \sum_{i=0}^{N}(-1)^i\frac{d^i}{dx^i}\frac{\partial\xi}{\partial\phi^{(i)}} \tag{B.8}$$

with $\phi^{(i)}(x)$ defined as,

$$\phi^{(i)}(x) = \frac{d^i\phi(x)}{dx^i} \tag{B.9}$$

B.2 Definition of local functionals

Two definitions for local functionals are given as follows:

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i- definition μ is local if for **any point** $\mathbf{x} \in U \subset \Re^n$, and fields ϕ and ϕ', if there exists a neighborhood $U \subset \Re^n$ of $\mathbf{x}$ such that

$$\phi\,|_U = \phi'\,|_U \quad \Longrightarrow \quad \mu[\phi](\mathbf{x}) = \mu[\phi'](\mathbf{x}) \tag{B.10}$$

This means that $\mu[\phi](\mathbf{x})$ is determined by the values of ϕ arbitrarily close to $\mathbf{x}$.

ii-definition [equivalent to the definition above introduced] μ is local if for **any open set** $U \subset \Re^n$ and fields ϕ and ϕ',

$$\phi\,|_U = \phi'\,|_U \quad \Longrightarrow \quad \mu[\phi]\,|_U = \mu[\phi']\,|_U \tag{B.11}$$

This means that $\mu[\phi]\,|_U$ is determined by the values of ϕ in a arbitrarily set U.

In addition to the definitions given above, a more abstract but simpler manner to enclose local functionals is the one that follows,

A functional $\lambda[\phi]$ is local if it is given by the integral,

$$\lambda[\phi] = \int_{\Re^n} d\mathbf{x}\, \mu[\phi](\mathbf{x}) \tag{B.12}$$

of a local functional $\mu: \quad F \rightarrow C^{\infty}(\Re^n)$.

The functionals which do not fulfill any of these two conditions in the algebraic fields where they are defined are called nonlocal functionals. In other words, it means that the definition of the functional in a finite set of the whole algebraic field is not enough to determine the functional. A graphical representation of a local and a nonlocal field is sketched in the figure **??**. It could be useful to understand the functionals we discuss throughout this thesis.

The figure B.2 is an scheme of the functionals enclosed in the form that follows,

$$\mu = \mu[\phi(\mathbf{x}), \nabla^1\phi(\mathbf{x}), \ldots, \nabla^i\phi(\mathbf{x})] \quad i < \infty \tag{B.13}$$

These class of functionals are known as gradient corrected functionals. They are read as local functionals on $\Re^n$ or nonlocal functionals in an arbitrary small set, $\epsilon \subset \Re^n$. The second example is showed in the figure B.3 and defined as,

$$\mu = \int_{U \subset \Re^n} d\mathbf{x}\, \Phi(\phi\,(\mathbf{x})) \quad \wedge \quad \Phi(\mathbf{x}) \text{ is not an analytic integrable function} \tag{B.14}$$

This class of functionals are known as integral functionals. They could be read as local functionals on $\Re^n$ or nonlocal functionals in a fixed and finite set, $U \subset \Re^n$. The last example takes key interest in this work. It is showed in the figure **??**, and it is defined as,

$$\mu = \mu\,[(\phi(\mathbf{x_1}), \ldots, \phi(\mathbf{x_i})] \quad \wedge \quad \{\mathbf{x_1}, \ldots, \mathbf{x_i}\} \quad \in \quad \Re^n \tag{B.15}$$

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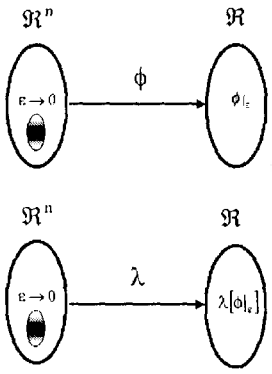

Figure B.2: Schematic representation of gradient corrected functionals on $\Re^n$. The shadow in the algebraic fields, indicates the elements which are necessary to define a single valuation of the functional on $\Re^n$.

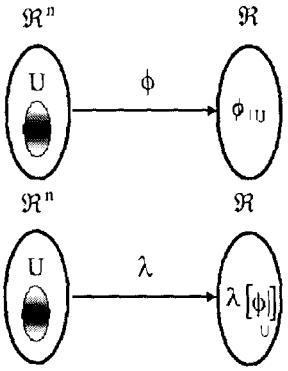

Figure B.3: Schematic representation of integral functionals on $\Re^n$. The shadow in the algebraic fields, indicates the elements which are necessary to define a single valuation of the functional on $\Re^n$.

This class of functionals are known as fully nonlocal functionals. They are read as nonlocal functionals on the whole algebraic field where the functional is defined, in this example $\Re^n$. The differences between these three definitions would be the basic of the physics discussed in the appendix C and the building block of this thesis.

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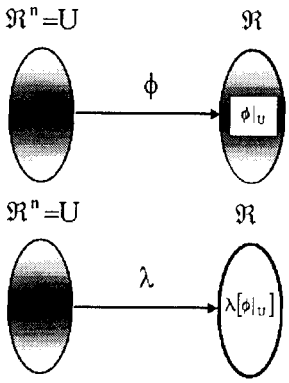

Figure B.4: Schematic representation of fully nonlocal functionals on $\Re^n$. The shadow in the algebraic fields, indicates the elements which are necessary to define a single valuation of the functional on $\Re^n$.

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Appendix C

On the density field

This appendix provides the connection we need between the "abstract" mathematical concept introduced in the appendix B, the local functionals, and the basic quantity of this thesis, the electronic density and the xc-potential "functionals" . Our proposal, is that the careful inclusion of this property, plays an important role in the *ab-initio* quantum transport method proposed within this thesis.

C.1 The electronic density as a basic quantity: "few" remarks

The main goal of this appendix is to define a connection between the concept of local functionals, and the maps we are interested in this thesis,

$$\mathbf{r} \Longrightarrow n(\mathbf{r}) \Longrightarrow v_{xc}[n](\mathbf{r}) \tag{C.1}$$

with $\mathbf{r}$ we denote the position space, $n(\mathbf{r})$ refers to the electronic density and $v_{xc}[n](\mathbf{r})$ is the xc-potential. (All these quantities are defined in the main text of this thesis).

We begin by introducing the current labels used by physicists in the analysis of the electronic densities over the space of coordinates. Mathematically, we are analyzing an algebraic field over the space of coordinates.

Here is a subtle remark. In our physical problem, this algebraic field is the assignment of a real quantity (the electronic density and then the xc-potential) to every point in space (or, more generally, spacetime). This algebraic field is thus viewed as extending throughout a

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large region of space so that its influence is all-pervading and the strength of a field usually varies over a region [109]. In our mathematical problem, the space of fields is the set of infinitely differentiable functions on $\Re^n$, defined by the functional or *the function-valued-function*, introduced in the previous appendix. In each case, we determine its strength by the inverse of the radius of the subset U, where the entity at hand is local. In what follows, we show how these concepts could be addressed to shed light in the controversial problem of the requirement of nonlocal $v_{xc} = v_{xc}[n](\mathbf{r})$ to describe electron-electron interactions in strongly inhomogeneous systems: *one* or *few* molecules bridging metallic leads.

In agreement with the notation used in the seminal work on DFT [6, 7], any electronic density should be enclosed in the following categories,

$$n(x) = \begin{cases} n_0 + n_1(x) & \text{with } \frac{n_1(x)}{n_0} << 1 \\ \varphi(\frac{x}{x_0}) & \text{with } x_0 \to \infty \\ \text{otherwise} \end{cases} \tag{C.2}$$

The first of the above lines corresponds with the definition of *almost constant* density systems, and the second agrees with the original definition of *slowly varying* systems [6]. The third absent event is surely the most striking, and unfortunately, it contains the systems we are dealing with in molecular electronics.

Since the electronic density is continuous in all the space where it is defined, $\{\mathbf{r}\} \in U \subset \Re^n$, it can be written as (we recover the abstract notation introduced in the appendix B to make easier the further comparisons)

$$n(x; x_0) = n(x_0) + \sum_{i=1}^{\infty} \frac{1}{i!} \frac{\partial^i n(x)}{\partial x^i}|_{x_0}(x - x_0)^i \tag{C.3}$$

equivalently,

$$n(x) = n(x_0) + \underbrace{\sum_{i=1}^{\frac{1}{i!}} \frac{\partial^i n(x)}{\partial x^i}|_{x_0}(x - x_0)^i}_{nonlocal} + \underbrace{R_J(x_0, x)}_{nonlocal} \tag{C.4}$$

In the expression above $R_J(x_0, x)$ is the nonlocal remainder in a Taylor's expansion. Here it is related with the error we introduce when the functions in use are necessarily truncated at a nonlocal finite serie, $i = J < \infty$.

The conditions in C.2 can be rewritten $\forall\{x, x_0\} \in \Re^n$ as,

$$n(x) \Longrightarrow \begin{cases} \frac{R_1(x_0,x)}{n(x_0)} = 0 \\ \frac{R_n(x_0,x)}{n(x_0)} << 1 \\ \frac{R_n(x_0,x)}{n(x_0)} \to 0 \end{cases} \tag{C.5}$$

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Generally, in molecular electronics, the problems to deal with are enclosed in the third category as will be discussed in what follows.

We consider that the physical systems we are dealing with are confined in the x-direction (see the figures 3.1 and 3.2). If this is true, then the electronic density will be represented by a transcendental function (not formal proof of this statement is known to us). All what follows, could be illustrated with the academic model introduced in the subsection 3.1.1 to analyze the physics behind a description based on the electronic density of a confined system,

$$n(x) = \sin C\,x \tag{C.6}$$

where C is a constant due to the confinement. (In section 3.1 of the main text a model is used to assign a meaning to this confinement.)

Due to the existence of a finite C the systems we are describing are enclosed in the third set of the definition C.5. Therefore, the basic quantity we are considering in any density based theory is nonlocal in the $\Re^n$- space.

So then, for the systems we are dealing with, the electronic density can be defined as follows,

$$n(x, a_i\mid_{i\in[0,J]}, R_J) = a_0 + \sum_{i=1}^{J} \frac{a_i}{i!}(x - x_0)^i + R_J(x; x_0) \quad a_i \propto C \tag{C.7}$$

or,

$$n(x; x_0, R_J) = n(x_0) + \sum_{i=1}^{J} \frac{1}{i!}\frac{\partial^i n}{\partial x}\mid_{x=x_0} (x - x_0)^i + R_J(x; x_0) \tag{C.8}$$

Both forms are equivalent Taylor's expressions for density defined in C.6. They differ in the number of variables required for their definition.

If we try to define a functional on these set of functions, we obtain what follows,

$$v_{xc}[n](x; a_i\mid_{i\in[0,J]}, R_J) = \underbrace{v_{xc}(x, a_i\mid_{i\in[0,J]})}_{local} + v_{xc}(R_J(x; x_0)) \tag{C.9}$$

or,

$$v_{xc}[n](x; x_0, R_J) = \underbrace{v_{xc}(x, x_0)}_{nonlocal} + v_{xc}(R_J(x; x_0)) \tag{C.10}$$

The definition in C.9 enclose a local finite gradient expansion. However, its exactness relies on the definition of a finite not controlled set of parameters, $a_i\mid_{i\in[0,J]} \propto C$. This finite proposal of v_{xc}, could be the basic for the gradient corrected approximations. The inclusion of the remainder could lie besides the LDA + U corrections [110]. (These two interpretations are not formally supported since the formal basis of these techniques goes beyond our knowledge).

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The definition C.10 is the construction we are proposing within this thesis. Its exactness relies in the definition of a nonlocal functional v_{xc} on $U \subset \Re^n$ and the inclusion of the remainder is controlled. This control is based on an unquestionable fact. The construction of the v_{xc} is done within a route, where we can guarantee the exactness of the quantities we are interested in, the HOMO and LUMO positions and, thenceforth the conductance.

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Appendix D

Numerical implementations for calculating the conductance

In this appendix we sketch the flowcharts for the implementation of the *ab-initio* quantum transport methodologies used within this thesis. In the last two sections two possible lines of development in the actual codes are discussed. First, the study of the scope of the models in use to compute the conductance within the dynamical method proposed by Sai. *et al.* [12]. Then, the role that the self-energies are playing within the basis sets transformation is suggested to control the numerical effectivity within our static method [10] and chapter 4.

D.1 Flowcharts of the codes developed in this thesis

The two flowcharts indicated in the figures D.1 and D.2, are used throughout this thesis to calculate the conductance. The first of the two schemes corresponds to the time-dependent route in the limit of static conditions, which is used for comparison with our static proposal, either within the theoretical frames (chapters 3 and 4) or within the purely numerical algorithms (chapters 5 and 7). The second is the static method, which is the central of this work.

The quantities involve in the time-dependent route are discussed in the main part of this thesis. Here, we enter in details of actual implementation of the dynamical resistance, appealing for transparency towards an *ab-initio* method. It is done in the next section.

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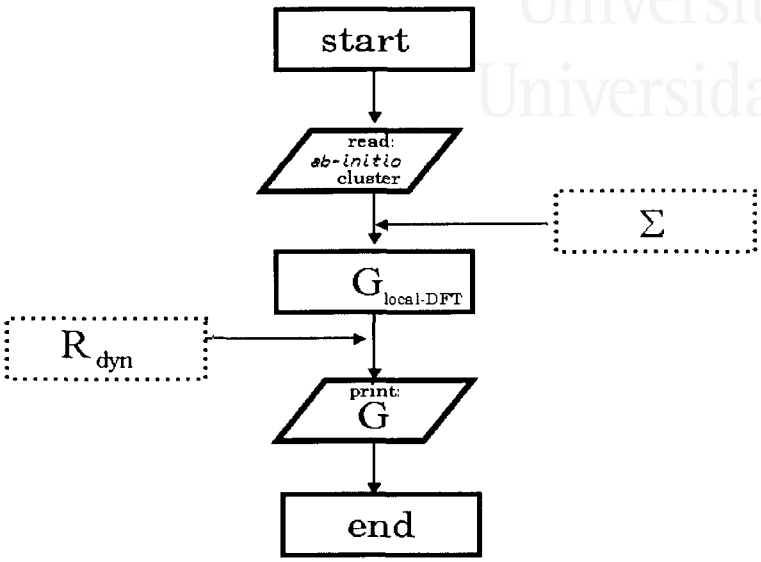

Figure D.1: Flowchart of the time-dependent based-quantum transport method we are using. It is devised as an interface with the Gaussian quantum chemistry code. First, we restrict the calculation of the conductance to local exchange-correlation potential, G_{-DFT}. So then, in principle the corrections that permit the derivation of the exact conductance, are controlled through the addition of the dynamical resistance, R_{dyn}.

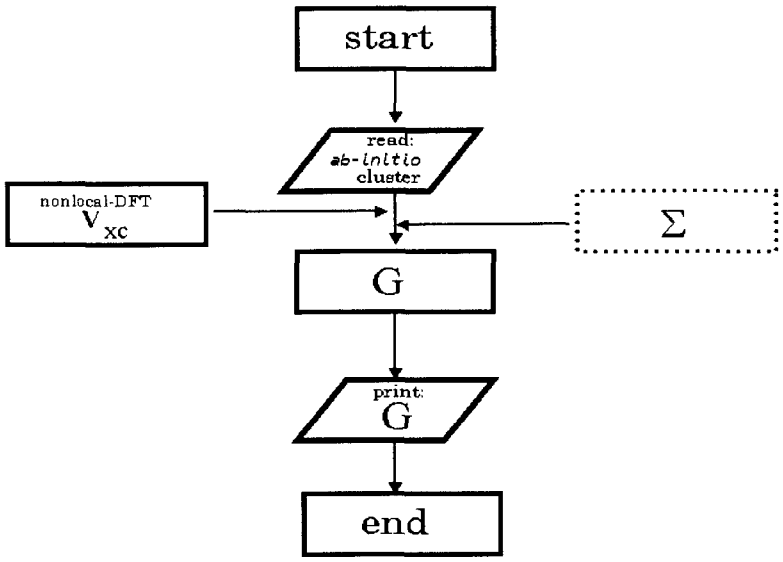

Figure D.2: Flowchart of the static quantum transport method we are using. It is devised as an interface with the Gaussian quantum chemistry code [78]. The boxes enclosing the xc-potential, v_{xc}, the self-energy, Σ, and the conductance,G; corresponds to implementations done in our group [13, 14, 111]. This thesis is a contribution in the line of design of the exact v_xc

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With the same intention, the model we use for the calculation of the self-energy, Σ, is discussed in the final section. It is based in a parameterization of a Bethe lattice construction extensively discussed in [14]. Here, we limit ourselves to present the transformation of these self-energies to a non-orthogonal basis, (the ones we use for the calculations of the quantities in the finite systems), considering the necessity of possible works to study the numerical corrections in regards to this transformation.

D.2 Estimation of the parameters involved in the time-dependent nonlocal corrections to the conductance

The dynamical and nonlocal correction to the calculation of the conductance within TDDFT can be expressed as (see reference [112] and section 4.17 for details),

$$G = \frac{G_{static-local-DFT}}{1 + G_{static-local-DFT} R^{dynamic}} \tag{D.1}$$

where $R^{dynamic}$ is,

$$R^{dynamic} = \frac{4}{3e^2 A_c} \int_x^{x'} dx \ \eta \frac{(\partial_x n)^2}{n^4} \tag{D.2}$$

in accordance with the model developed by Sai. *et al.* [12].

Therefore, quantities for be modeled and numerically computed are,
i. The contact radius, A_c.
ii. The viscoelastic coefficient, η.
iii. The electronic density, $n(x)$ (electrodes are placed lying in the x-axis, parallel to the current flow), and finally
iv. The upper/lower limit for the x-axis-zone where electronic density varies must be fixed, x'/x.

A_c—. The contact area is defined as a circle in the y,z-plane centered in the x-axis,

$$A_c = \pi \ < r_c >^2 \tag{D.3}$$

and $< r_c >^2$ is defined as,

$$< r_c >^2 = min_z \frac{\int dydz \ (x^2 + y^2) n(x,y,z)}{\int dydz \ n(x,y,z)} \tag{D.4}$$

η—. The viscosity for the electron liquid is modeled as Sai *et al.* [12],

$$\eta = \frac{\hbar}{120} \left[\frac{k_{Fermi}}{\pi \ a_0} \right]^{\frac{3}{2}} \tag{D.5}$$

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If this model for η is accepted, the only parameter is the wave vector for the electrons at the Fermi level, k_{Fermi}. Apart from some constants, $k_F = k_{Fermi}(\epsilon_{Fermi})$ and ϵ_{Fermi} can be considered equal to the Fermi energy. The numerical value of ϵ_{Fermi} is taken from band structure calculations reported in [80].

$n(x)$—. In order to keep the best agreement with the model proposed by Sai *et al.* [12] and trying to remain within an *ab-initio* procedure we proceed as follows:

1. We make a self-consistent calculation of the electronic density in a region containing the narrowest zone of the junction -bounded by x and x' in the x-axis–. The output is $n \equiv n(x, y, z)$

2. A planar average is made as follows,

$$n = \frac{\int dydz \;\; n(x, y, x)P(x, y, z)}{\int dydz \;\; P(x, y, z)} \tag{D.6}$$

In this way n is dimensionally reduced, $n \equiv n(x)$.

The simplest way to define $P = P(x, y, z)$ would be,

$$P(x, y, z) = \begin{cases} 1 & \text{if } n(x, y, z) > cutoff \\ 0 & \text{otherwise} \end{cases} \tag{D.7}$$

In this expression $cutoff$ is defined as the *smallest* isoelectronic surface which contains the total charge of the cluster, (N). Then,

$$N = \int_0^{V|_{n(x,y,z)=cut}} dxdydz \;\; n(x, y, z) \tag{D.8}$$

3. Once we have the result of this planar average, $n = n(x)$, a macroscopic average is made in order to eliminate the meaningless atomic oscillations,

$$n = \frac{\int_{x-\frac{\Delta}{2}}^{x+\frac{\Delta}{2}} dx \;\; n(x)}{\Delta} \tag{D.9}$$

where the first and simplest approximation for Δ is the interplanar distance in the bulk/electrodes. This is the $n = n(x)$ we are going to use in the equation D.2.

x *and* x'—.

These atomic-electronic parameters must fulfill two conditions. They must coincide with the entrance to the zone where the atomic arrangements differ from the volumetric one, and also as a consequence these points indicate the zone where $n(x)$ is not constant on the x-axis. The figure 3.1 should give as a geometric representation of these two points.

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D.3 Discussion on the self-energies calculations

In this section the transformation of the self-energies to nonorthogonal basis is made. It is presented as a possible line of improvement of the numerical methodology used throughout this work. The concept of self-energy is presented in chapter 1 for the analysis of the semi-infinite systems. In this thesis, the The details on the calculations of the self-energies are included in [14]. Here, we limited to sketch how can we extend this self-energy calculated in an orthogonal basis set, to nonorthogonal basis sets.

In this section, the finite structure is going to be labeled as the unitary cell. (0). and the notation with uppercase/lowercase letters is used to indicate a matrix represented in orthogonal/nonorthogonal basis sets.

D.3.1 The self-energies in an orthogonal basis set

The wave function, (Ψ), for a general infinite system such as these represented in 1.2 is,

$$[H_\infty - EI] \quad \Psi = 0 \tag{D.10}$$

where H_∞ is an infinite matrix.

The Green's function (G) from its standard definition is,

$$[-H_\infty + EI] \quad G = I \tag{D.11}$$

where,

$$H_\infty = \begin{vmatrix} \cdots & \cdot & \cdot & \cdot & \cdot & \cdot & \cdots \\ \cdots & \cdot & \cdot & \cdot & \cdot & \cdot & \cdots \\ \cdots & V^\dagger & H_0 & V & 0 & 0 & \cdots \\ \cdots & 0 & V^\dagger & H_0 & V & 0 & \cdots \\ \cdots & 0 & 0 & V^\dagger & H_0 & V & \cdots \\ \cdots & \cdot & \cdot & \cdot & \cdot & \cdot & \cdots \\ \cdots & \cdot & \cdot & \cdot & \cdot & \cdot & \cdots \end{vmatrix} \tag{D.12}$$

Therefore, the Green's function is an infinite matrix,

$$G = \begin{vmatrix} \cdots & \cdot & \cdot & \cdot & \cdot & \cdot & \cdots \\ \cdots & \cdot & \cdot & \cdot & \cdot & \cdot & \cdots \\ \cdots & G_{n-1,n-2} & G_{n-1,n-1} & G_{n-1,n} & G_{n-1,n+1} & G_{n-1,n+2} & \cdots \\ \cdots & G_{n,n-2} & G_{n,n-1} & G_{n,n} & G_{n,n+1} & G_{n,n+2} & \cdots \\ \cdots & G_{n+1,n-2} & G_{n+1,n-1} & G_{n+1,n} & G_{n+1,n+1} & G_{n+1,n+2} & \cdots \\ \cdots & \cdot & \cdot & \cdot & \cdot & \cdot & \cdots \\ \cdots & \cdot & \cdot & \cdot & \cdot & \cdot & \cdots \end{vmatrix} \tag{D.13}$$

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For the computation of Green's functions the Hamiltonian must be truncated, and this is be done introducing the self-energies (Σ) formalism [10].

The infinite Hamiltonian is expressed as follows,

$$H = \begin{vmatrix} H_L - \Sigma & H_{L,0} & 0 \\ H_{L,0}^{\dagger} & H_0 & H_{0,R} \\ 0 & H_{0,R}^{\dagger} & H_R - \Sigma \end{vmatrix} \tag{D.14}$$

this Hamiltonian corresponds with a geometry as such in the figure D.3.

The dimensions (DIM) of H_0, and V, are related with the number of atoms in the unitary cell (N_{atoms}), and the extension of the basis sets (N_{basis}), used to describe the electronic states, $DIM = N_{atoms} x N_{basis}$.

For the calculation of Σ the expressions D.13 and D.12 are substituted in D.21. Considering transfer relations among Green's functions,

$$G_{n,n} = T\ G_{n-1,n} \tag{D.15}$$

where T is the transfer matrix.

Straightforward, the following relation is obtained,

$$V^{\dagger} G_{n-1,n+1} + (E_0 - E) T G_{n-1,n+1} + V T^2 G_{n-1,n+1} = 0 \tag{D.16}$$

equivalent to,

$$V^{\dagger} + (E_0 - E) T + V T^2 = 0 \tag{D.17}$$

If we define selfenergies as,

$$\Sigma = V\,T \tag{D.18}$$

then, the Dyson equation is obtained [113],

$$V\,[(E - E_0) - \Sigma]^{-1}\ \ V^{\dagger} = \Sigma \tag{D.19}$$

and the Green's function of the whole systems is,

$$G\,(E)^{1,2} = [EI - H_0 - 2\Sigma]^{-1} \tag{D.20}$$

D.3.2 The self-energies in a non-orthogonal basis sets

The "appearance" of the overlap matrix, $S_{i,j} = \langle \Psi_i \mid \Psi_j \rangle$ in equations D.10 and D.21 is the key point in the derivation that follows. These equations are transformed to,

$$[-h_{\infty} + \varepsilon S I]\ \ g = I \tag{D.21}$$

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Then, we express the overlap matrix as,

$$S_\infty = \begin{vmatrix} \cdots & \cdot & \cdot & \cdot & \cdot & \cdot & \cdots \\ \cdots & \cdot & \cdot & \cdot & \cdot & \cdot & \cdots \\ \cdots & S_1^\dagger & S_0 & S_1 & 0 & 0 & \cdots \\ \cdots & 0 & S_1^\dagger & S_0 & S_1 & 0 & \cdots \\ \cdots & 0 & 0 & S_1^\dagger & S_0 & S_1 & \cdots \\ \cdots & \cdot & \cdot & \cdot & \cdot & \cdot & \cdots \\ \cdots & \cdot & \cdot & \cdot & \cdot & \cdot & \cdots \end{vmatrix} \tag{D.22}$$

the Hamiltonian is,

$$h_\infty = \begin{vmatrix} \cdots & \cdot & \cdot & \cdot & \cdot & \cdot & \cdots \\ \cdots & \cdot & \cdot & \cdot & \cdot & \cdot & \cdots \\ \cdots & \cdot & \cdot & \cdot & \cdot & \cdot & \cdots \\ \cdots & 0 & v^\dagger & \varepsilon_0 & v & 0 & \cdots \\ \cdots & \cdot & \cdot & \cdot & \cdot & \cdot & \cdots \\ \cdots & \cdot & \cdot & \cdot & \cdot & \cdot & \cdots \\ \cdots & \cdot & \cdot & \cdot & \cdot & \cdot & \cdots \end{vmatrix} \tag{D.23}$$

and the generalized Green's function is,

$$g = \begin{vmatrix} \cdots & \cdot & \cdot & \cdot & \cdot & \cdot & \cdots \\ \cdots & \cdot & \cdot & \cdot & \cdot & \cdot & \cdots \\ \cdots & g_{n-1,n-2} & g_{n-1,n-1} & g_{n-1,n} & g_{n-1,n+1} & g_{n-1,n+2} & \cdots \\ \cdots & g_{n,n-2} & g_{n,n-1} & g_{n,n} & g_{n,n+1} & g_{n,n+2} & \cdots \\ \cdots & g_{n+1,n-2} & g_{n+1,n-1} & g_{n+1,n} & g_{n+1,n+1} & g_{n+1,n+2} & \cdots \\ \cdots & \cdot & \cdot & \cdot & \cdot & \cdot & \cdots \\ \cdots & \cdot & \cdot & \cdot & \cdot & \cdot & \cdots \end{vmatrix} \tag{D.24}$$

We proceed as previously done in orthogonal basis. Therefore, the reduced Hamiltonian is written,

$$h_{reduced} = \begin{vmatrix} h_l - \sigma & h_{l,0} & 0 \\ h_{l,0}^\dagger & h_0 & h_{0,r} \\ 0 & h_{0,r}^\dagger & h_r - \sigma \end{vmatrix} \tag{D.25}$$

Then, we apply the same transfer relations,

$$g_{n,n} = t \quad g_{n,n+1} \tag{D.26}$$

and, if we proceed as we did in orthogonal basis, the obtaining of Dyson equation is straightforward,

$$\left(v^\dagger - \varepsilon\, S_1^\dagger\right) + (\varepsilon_0 - \varepsilon\, S_0)\, t + (v - \varepsilon\, S_1)\, t^2 = 0 \tag{D.27}$$

an equation which is mathematically identical to D.17. Then, if we define a selfenergy σ as,

$$\sigma = v\ t \tag{D.28}$$

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The Dyson equation in a nonorthogonal basis will be,

$$(v - \varepsilon S_1) \ \ (\varepsilon S_0 - \varepsilon_0 - \sigma)^{-1} \ \ \left(v^{\dagger} - \varepsilon S_1^{\dagger}\right)^{\dagger} = \sigma \tag{D.29}$$

and the generalized Green's function are,

$$g(\varepsilon) = [\varepsilon \, I - h_0 - 2\sigma]^{-1} \tag{D.30}$$

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Appendix E

Understanding chemistry within mean-field theories

This appendix is devoted to understand chemical bonding and quantum transport features on the basis of "elementary" physical concepts from molecular orbital theories, such as the Frontier Molecular Orbitals and the Lewis pairs theories. If we recover these single-electron descriptions is by one transparent but controversial reason: *The single-electron orbitals derived from a density-functional approach are perfectly suited for use in molecular orbital theories* [52, 114].

The investigations on chemical bonds are done on the TIP structures discussed in the chapter 6. We show how the understanding of the electronic structure evolution of such reactant system can help recognize certain features of the experimental results, either for the geometric structures of the TIP, or for the quantum transport characteristic of the "infinite" system.

E.1 Frontier Molecular Orbitals theory based on a Kohn-Sham scheme

In this section the electronic structure of the TIPs is made based on the Frontier Molecular Orbitals theory [115]. It will be used to explain the bonding and the transport mechanisms. In the analysis here presented we have in mind a reaction such as these guiding the chapter 6,

$$\mathrm{Metal}_{(\mathrm{tip})} \quad + \quad \mathrm{H}_{2(\mathrm{gas})} \implies \mathrm{TIP} \tag{E.1}$$

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The selected metals are nickel, palladium and platinum.

E.1.1 A Hydrogen molecule attacking transition metal tips

The figure E.1 depicts the HOMO-LUMO occupancy in the isolated Hydrogen molecule. In the figures E.2 and E.3 the same simplified analysis is presented for three metals tips: nickel, palladium and platinum.

In terms of chemical bonding, we could justify a chemical bonding for the Hydrogen molecule to nickel and platinum tips. It could be explained in terms of a donor-acceptor mechanism. The Hydrogen molecule could transfer its electrons to the nickel and platinum tips, which has incomplete shell structures. This process results in a frontier molecular orbital scheme for the nickel and platinum tips as such presented in figure E.4. A noticeable difference between nickel and platinum is in the symmetry of the single-electron states involved in the bonding mechanism. We should expect that the d-character on the frontier orbitals on platinum will be less than the d-character of the frontier orbitals on nickel[1]. Based on these statements we feel free to make the following proposal. Experimental results on the chain length formations upon addition of Hydrogen contrasted with experimental investigations on the clean metallic tips ([116] and references therein) should help as to confirm, (or not), this loss of symmetry in the states of the metal tips. It could greatly benefit the credibility of the theoretical predictions.

In addition to the discussion above presented, the electron transfer to the Hydrogen molecule in supports of a bonding mechanism, is not justified from our *ab-initio* calculation of the LUMO position, which places this single-particle orbital over the vacuum level, and therefore claims for the instability of such structure[2], H_2^-.

In contrast with these two very reactive metallic tips, we should not expect a strong chemical bond of Hydrogen with palladium. Therefore, the interaction between this two systems, could be limited to the physisorption of Hydrogen in between the palladium tips. This prediction is confirmed with our *ab-initio* simulations.

In terms of quantum transport, now we try to contribute to the debate on the answer to the following question [25,26]. What is the role of the Hydrogen molecule in the quantum transport mechanism. Since the LUMO charging of the Hydrogen molecule is not justified, we should expect that the Hydrogen molecule would act as a blocker in the two initial available conducting channels of the nickel and platinum nanocontacts, see figure E.2. (From the point of view of the electrons carrying the current, the molecule kept out of the

[1] The shell structure for a single platinum tip is in the nearby of: $5d^9 6s^1$ and for nickel is in the nearby of: $3d^8$.

[2] As far as we know, there are not experimental reports on the existence of H_2^-

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way through one channel.) This would drastically limit the conductance of these systems to the single-conduction mode, and to the maximum value $G_0 = 2\,\frac{e^2}{h}$.

E.1.2 An oxygen molecule in between platinum tips

The figure E.5 sketches the electronic structure of the oxygen molecule. Here, the main subject is that a simple single-electron picture as this presented, is enough to justify the tendency of platinum tips to chemically bind the oxygen molecule, due to its unpaired electrons and the tendency of platinum to gain electrons. This agrees with the structures we obtain in the *ab-initio* simulations presented in section 6.2.

E.2 Lewis diagrams theory based on a Kohn-Sham scheme

The reliability of the Lewis diagrams for comparison with the most advanced *ab-initio* approach is based on the same arguments given in the head of this appendix.

E.2.1 Carbon and nitrogen monoxide molecules in between platinum tips

The Lewis diagrams for carbon and nitrogen monoxide are represented in figures E.6. The strong polarization of the electron cloud is reflected in the tendency of platinum tips to bind this system, selectively, through the carbon or nitrogen atoms[3]. This simple explanation agrees with the *ab-initio* geometrical pictures presented in chapter 6, in the figures 6.6 and 6.8.

Finally, this appendix is being present mostly as an example of how we could recover simplicity, at least, to communicate the strongest theoretical results besides the actual many-body problems [52, 114]. This should be interpreted as a claim for development of the mean-field Kohn-Sham scheme as a basic for an explanation of the many-body problems in an academic way, at a level admitted by the high school students [82]. More in the context of this thesis, this appendix is a claim for the development of the exact xc-potentials, as the basis of a meaningful density-functional Molecular Orbitals Theory.

[3]Simulations leaving preferences to bind through oxygen atoms were made, for instance, doing the simulation described in [89,91] where the initial condition place the oxygen atoms of the molecules in the nearest point of the stretching axis.

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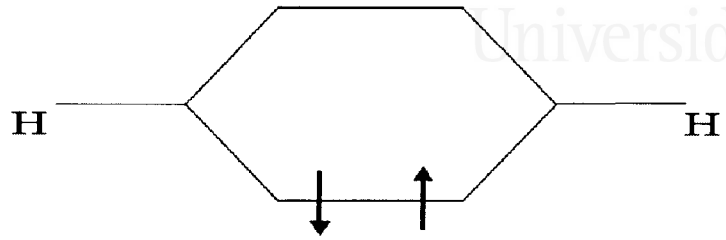

Figure E.1: Diagram for the frontier molecular orbitals of the Hydrogen Molecule.

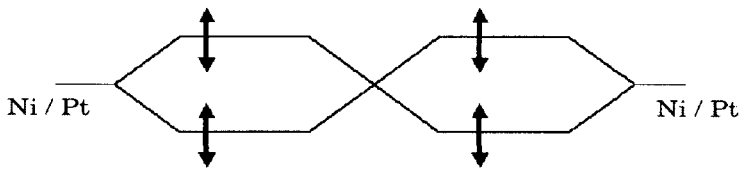

Figure E.2: Diagram for the frontier molecular orbitals of the nickel/platinum tips. (Two nickel/platinum atoms which are perturbed by the semiinfinite nickel/platinum electrodes.) The double arrows indicates that the spin orientation is not determined. This limitation should be meaningless in the analysis here made.

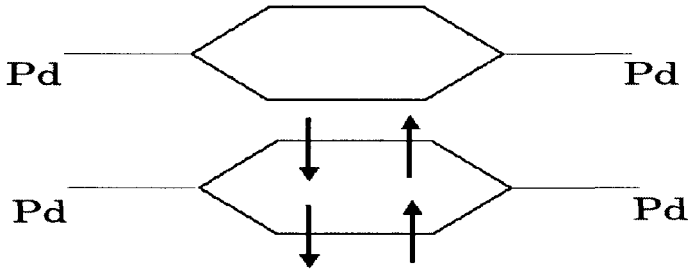

Figure E.3: Diagram for the frontier molecular orbitals of the palladium tip. (Two palladium atoms which are perturbed by the semiinfinite palladium electrodes.)

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In this way we can account for the understanding of chemistry within mean-field theories.

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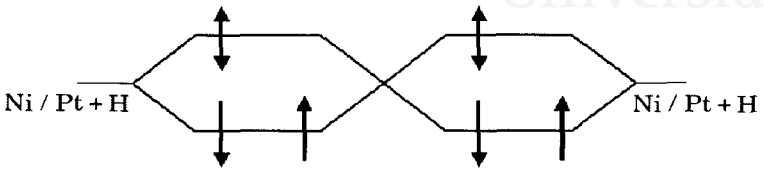

Figure E.4: Diagram for the frontier molecular orbitals of the Pt_2H_2 and Ni_2H_2 Tips.

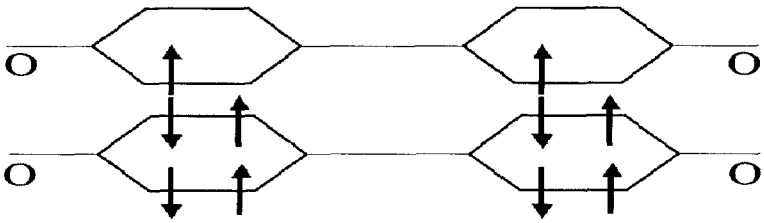

Figure E.5: Diagram for the frontier molecular orbitals of the oxygen Molecule.

Figure E.6: left: Lewis diagram for Carbon monoxide molecule. right:Lewis diagram for carbon monoxide molecule.

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LIST OF ACRONYMS

ALDA	Adiabatic Local Density Approximation
BDT	Benzene-1,4-dithiolate
CCSD[T]	Coupled cluster methods and subsequent letters indicated the level in which the excitations are shorted
DFT	Density-Functional Theory
GGA	Generalized Gradient Approximation
HF	Hartree-Fock
HOMO	Higest Occupied Molecular Orbital
HK	Hohenberg-Kohn theorem, [6]
KS	Kohn-Sham's work, [7]
LDA	Local Density Approximation
LUMO	Lowest Unoccupied Molecular Orbital
MPn	n-order Møller-Plesset perturbation theory
PW91	Perdew and Wang functional
RG	Runge-Gross theorem, [21]
scattering	The scattering approach combined with the Green's function technique, [9, 10]
TD	Todorov and Di Ventra's theorem, [18]
TIP	In**T**eraction t**I**p com**P**lex
TDCDFT	Time-Dependent Current-Density-Functional Theory
TDDFT	Time-Dependent Density-Functional Theory
Vignale	Vignale's theorem, [22]
xc	exchange-correlation

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Resum

- Introducció general [4]

  (...) Quan el món era tan recent, que moltes coses no tenien nom, i per nomenar-les calia indicar-les amb el dit (...)[5] La electrònica molecular és un àrea capdavantera dins del que es coneix com a nanociència. Específicament, l'objectiu d'aquesta electrònica molecular és l'estudi de materials electrònics funcionals confinats a dimensions de l'ordre de 10^{-9} metres que, una vegada aptes per ésser aplicats, podríen contribuir al desig de ser un camp tecnòlogic nou i efectiu: la nanotecnologia. L'electrònica molecular no pot considerar-se una extrapolació de la física o de la química tradicional. Açò és així pel comportament no necesariament previsible dels sistemes nanomètrics que ara s'intenten descriure a partir del comportament dels seus components, quan aquests components formant part dels corresponents sistemes estessos o moleculars. Indiscutiblement, l'electrònica molecular està destinada a ser un nou "món", a connectar amb dos més, fins avui considerats com a extrems. El "món" dels sistemes macroscòpics i el món dels sistemes a l'escala molecular. En aquest context, aquesta tesina intenta ser una contribució al plantejament formal d'alguns dels mètodes més usuals, conceptes (o noms), per ser aplicats tras una electrónica molecular i científica.

- Resum global dels resultats obtinguts

  En aquesta tesina l'atenció està centrada en el desenvolupament d'un mètode eficient i exacte per definir els potencials d'intercanvi i correlació, $v_{xc} = v_{xc}(\mathbf{r}, t)$. Com és a la secció 1.2, aquesta quantitat podria estar controlant un accés directe, *ab-initio*[6] i amb mètodes dependents del temps, a la determinació de la conductància, equació

[4] Aquest resum en catal'a s'inclou més que res per resaltar el valor que tinc per aquesta.les errates pretenen ser un toc de crida per una necessitat cultural de recuperar la llengua que en el seu moment s'intentà fer desaparèixer. És per tant, una petita forma de mostrar el meu gran respecte a aquells que van padèixer aquesta barbàrie. Les errates que aquest text puga contenir, son responsabilitat de l'autor original d'aquest treball. Els valors que d'ací sorgeixen es deuen a C. Ramal-Ballester i a Marisa Cano que ès van deixar la son de costat i *la risa* per traduir la versió original, que per la seva part, hi estava una mica en anglés i una mica en castellà.

[5] Traducció lliure de la versió en castellà [1] de C. Ramal-Ballester

[6] Expresió llatina; *ab-initio*, "des del principi".

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(1.1). Això és la ruta *ab-initio* que es resum en l'esquema següent:

$$v_{xc}(\mathbf{r};t) \overset{\text{RG}}{\Longleftrightarrow} n(\mathbf{r};t) \overset{\text{TD}}{\Longleftrightarrow} \mathbf{j}(\mathbf{r};t) \overset{\text{LIM}}{\Longleftrightarrow} G \tag{E.2}$$

La notació RG denota el teorema de Runge-Gross aplicat al sistema de partícules no interactuants (si és necessari veure [18] i secció 2.4); TD denota el teorema de Todorov i Di Ventra ([18] i secció 2.4). Els límits indicats com a LIM, mostren la conexió matemàtica i contínua, entre el problema dependent del temps i l'estàtic. Basant-se en l'existència d'aquest límit que nosaltres utilitzarem en les teories dependents del temps i en el moment apropiat, es retornarà al nostre problema estàtic, enunciat en un parèntesi que constitueix els paràgrafs següents.

La conductància és, precisament, la quantitat central d'aquesta tesina. Aquesta es pot definir com,

$$G = \lim_{V \to 0} \frac{\partial I}{\partial V} \tag{E.3}$$

el límit indica que ens limitarem a reduir aquesta quantitat al cas del règim en què la diferència de potencial entre els electròdes tendeix a zero. Aquesta quantitat, descriu la resposta lineal del corrent elèctric, $I = I(V)$, a un potencial extern V, per un sistema inicialment en equilibri estàtic[7].

Retornant a les metodologies dependents del temps que nosaltres utilitzem, en la primera secció del capítol 3, es discrepa sobre la capacitat del potencial d'intercanvi i correlació localment definida en l'espai de les coordenades $v_{xc} = v_{xc}[n(\mathbf{r};t)]$,; per descriure la resposta electrònica lineal dels sistemes que s'investiguen en aquesta tesina, *una* o *poques* molècules fent de pont entre elèctrodes metàl·lics. (Al potencial d'intercanvi i correlació s'accedeix amb la densitat electrònica. Aquesta és la definició de funcional de la densitat electrònica aplicada a la quantitat física denominada potencial d'intercanvi i correlació). A partir d'aquest punt el formalisme teòric es desenvolupa com es resum a continuació.

Basats en la derivació del funcional d'intercanvi i correlació de la densitat electrònica dependent del temps desenvolupada per Gross i Kohn [58]; es mostra que *l'existència d'una construcció consistent del potencial d'intercanvi i de correlació com un funcional local de la densitat electrònica dependent del temps per a tractar el més general dels sistemes electrònics, no està formalment justificada.*

Aquesta limitació, només matemàtica, respon a la pròpia naturalesa física dels sistemes estudiats, com s'identifica en l'apartat 3.1.1. En poques paraules, els arguments que aquí es mostren ací, pretenen pasar en doubte de manera intencionada i formal la veracitat de qualsevol aproximació local en la densitat electrónica mitjantçant el potencial d'intercanvi i de correlació degut, com era d'esperar, i podria semblar redundant, a la capacitat de capturar els efectes físics no locals.

A continuació, el problema de la localitat (com és habitual denominar en l'argot científic) es sorteja i s'elimina completament. Això es fa millorant les descripcions basades en la teoria del funcional de la densitat electrònica dependents del temps,

[7] L'equilibri es defineix com els resultats estacionaris tal que, $I(V) = \lim_{t \to \infty} I(t, V)$, on t és la coordenada temporal.

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amb l'introducció de potencials d'intercanvi i de correlació en termes de la densitat electrònica i de la densitat de corrent, $v_{xc} = v_{xc}[n(\mathbf{r};t), \mathbf{j}(\mathbf{r};t)]$ [11, 59].

Aquesta formulació generalitzada de la teoria del funcional de la densitat dependent del temps, és el que coneixem actualment com a teoria del funcional de la densitat electrònica i del corrent, ambdues depenents del temps.

Considerant la importancia que té en com a base formal per l'aplicació dels mètodes *ab-initio* a problemes de transport quàntic, en aquesta tesina, fem una revisió superficial o de colp d'ull d'aquesta teoria.

D'aquestos anàlisis es deriven resultats centrals per a l'aplicació de la teoria del funcional de la densitat depenent del temps als problemes de transport quàntic, que degut a la seva importància trascendental es remarca en el paràgraf que es desenvolupa a continuació.

Existeix una formulació en el context de problemes de partícules independents a la quantificació de la resposta linial existent. Aquesta és manipulable, en tant que es desenvolupen "bases" per a construccions del potencial d'intercanvi i de correlació, $v_{xc} = v_{xc}[n](\mathbf{r};t)$. Generalment, la forma analítica d'aquests funcional no es coneix.

No obstant això, poden ser obtingudes com a primer pas d'algunes de les seves propietats. Aquestes es poden identificar a partir del tractament, amb exactitud, del teorema de Runge-Gross [21].

En aquesta tesina ens preocupem de la propietat següent: la localitat del potencial d'intercanvi i de correlació. (Una extensa discusió de la localitat s'inclou en l'apèndix B.) Com s'intenta mostrar en aquest treball per al sistema físic i/o químic més general que es puga tractar, *necessàriament, el potencial d'intercanvi i de correlació està definit no localment en l'espai de posicions.*

Finalment, en el context dels mètodes depenents del temps estudiats ací i en la línea proposada per Sai *et al.* [12],

$$\lim_{\omega \to 0} F^{dyn}(\omega) = F^{sta} \tag{E.4}$$

on $F = F^{dyn}(\omega)$ es qualsevol funció que es "comporte bé", quan està definida en l'espai de les freqüències, $\omega-$espai. Una vegada que aquest cas límit estàtic és recuperat, es pot donar el pas a la segona contribució teòrica en la tesina.

A partir de la interpretació $F(\omega)\,|_{\omega \neq 0}$ com a una quantitat dinàmica , F^{dyn}; com el seu corrresponent límit estàtic. Aquest límit genèric, serà suficient per obtenir algunes propietats del potencial d'intercanvi i de correlació a partir de la seva contrapart dinàmica, v_{xc}^{dyn}.

A continuació d'ací, i tenint en compte el coneixement del potencial d'intercanvi i correlació exacte i també l'estàtic, la conductància estàtica pot ser derivada. Aquesta conductància és allò que no hem de perdre de vista, per que és la quantitat central per determinar en la tesina.

Resumint, demostrarem aplicando un límit que la quantitat que va motivar el treball de la tesina pot ser determinat a partir de proves de camp mitjà i depenent del temps.

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Allò que constitueix la principal contribució -original- d'aquesta tesina, és presentat en el capítol 4. En aquest apartat es descriu la conductància electrònica *ab-initio* i estàtica, basant-nos en la teoria del funcional de la densitat estàtica, DFT. Els conceptes bàsics que s'han introduit per construir el nostre esquema, i que es desenvolupa a partir de les bases discutides en els capítols 1 y 2, es resumeixen a continuació.

La quantitat central d'aquesta tesina va ser definida en l'expressió (1.1) en el capítol 1. A continuació, la proposta de Landauer com una alternativa exacta i efectiva per quantificar la conductància és presentada [9,117]. La validesa d'aquesta proposta, és la primera peça que nosaltres utilitzarem per sostenir l'existència d'una metodología de transport electrònic estàtic. Ací s'ha de remarcar, com es menciona en el capítol 1, que les hipòtesis fetes dintre del formalisme de Landauer, són qüestionades i són un tema de debat actual dins de la comunitat que treballa en el desenvolupament de mètodes per caracteritzar el transport quàntic [18, 36]. No obstant, això, no és objectiu d'aquesta tesina ficar-se en aquest debat per una raó transparent. Matemàticament (i considerant la física com a l'expressió matemàtica d'una idea intuïtiva), no existeixen dubtes sobre la validesa i la veracitat de les construccions fetes dins del formalisme de Landauer [39,64]. Més encara, i fins on nosaltres tenim coneixement, els arguments en què es basa la proposta d'errates en el formalisme de Landauer per fer càlculs de transport electrònic, existeix el desacord entre formalisme de Landuer amb conjunció amb càlculs *ab-initio*, i la seua presumible contrapartida experimental.

En el capítol 2, fou presentada la metodologia *ab-initio* i de camp mitjà (els teoremes canònics de Hohenberg i Kohn [6] basada en la densitat electrònica que emprem en la tesina. Aquests dos blocs són suficients per a justificar l'existència d'un mètode de camp mitjà *ab-initio*, estàtic i exacte pel desenvolupament d'una metodologia de transport electrònic a nivell quàntic. La seua viabilitat es debatuda a la primera secció d'aquest capítol. Apuntant en aquesta línia, l'efectivitat dels mètodes de camp mitjà, *ab-initio* i estàtics, és directament transferida a la capacitat per a la definició del potencial d'intercanvi i de correlació exacte, $v_{xc} = v_{xc}[n](\mathbf{r})$. Una expressió algebràica per aquesta quantitat no podrà ser derivada d'un tactament exacte, no obstant, pràctiques d'aproximació emprades comunment [65].

Fonamentalment, aquestes aproximacions estan basades en la injustificada i restringida versió de DFT, coneguda erròneament com a teoria de Kohn i Sham, on el potencial d'intercanvi i de correlació es defineix localment sobre l'espai de les densitats electròniques. Per això, aquest potencial d'intercanvi i de correlació es defineix localment sobre l'espai de las densitats electròniques. Per això, est potencial d'intercanvi i de correlació es redueix a un funcional local en l'espai de posicions espacials. En aquesta tesina, l'espai no local de posicions definit per a $v_{xc} = v_{xc}[n](\mathbf{r})$ serà recuperat i introduit en els funcionals per utilitzar-los en càlculs numèrics. Aquesta anàlisi, presentada en la secció 4.1, i la seua eficiència mostrada en els capítols 5, 6, i 7.1, podrà servir de base per enunciar el dramàtic paper que una propietat aparentment inòcua pogués aprofitar-se en càlculs quàntics de transport electrònic aprofitant de "ponts" moleculars confinats per electròdes metàl·lics.

En la secció 4.2 s'ha presentat un esquema pràctic per desenvolupar una manera

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viable de la correció no local que proposem. En poques paraules, és una secció per dissenyar esquemes per expressar funcionals no locals que puguen ser emprats. Aquests són extensions directes del espai en què es defineixen els funcionals locals a l'espai no local.

En la secció 4.3, es mostra la parte de la tesina per que fa a la necessitat de la no localitat. Això és fa emprant la veritat irrefutable de que la situació estàtica es pot obtenir com el límit de la seua corresponent contrapartida dependent del temps. Aquestes demostracions es basen en els resultats introduits en el capítol 3. Tot i que això sembla una opció òbvia, és molt important remarcar i recordar que les teories depenents del temps s'utilitzen en la tesina per dues raons. En primer terme, els mètodes depenents del temps són una moda entre la comunitat que realitza els càlculs de transport quàntic i amb els que qualsevol treball que els utilitza podrà presumir de ser un bon candidat a la credibilitat. El segon motiu, pot ser té un caràcter més científic i, per tant, s'expressa en el paràgraf que continua.

No existeixen dubtes de que la conductància definida a partir de l'expressió (1.1), és el límit estàtic de la seua contrapartida dinàmica, l'expressió (1.19). Més encara, una teoria exacta viable per a situacions depenents del temps existeixen [11, 18, 66]. A més a més, d'això, qualsevol teoria estàtica ha de ser obtesa fent els límits corresponents. A partir d'aleshores, l'acord entre els resultats obtinguts dins d'un tractament estàtic i els que s'obtenen a partir d'un mètode depenent del temps, són una condició necessària per a la validesa de qualsevol proposta d'aquestes teories. La comparació presentada en aquesta secció no serà completa ja que, no s'estableixen identitats algebraiques. No obstant això, aquest intent de comparació pot aportar llum a l'oscuritat que cobreix i "encapota" el problema amb que estem tractant, l'espai necessari per definir el potencial d'intercanvi i de correlació que proveïsca un tipus de metodologia de camp mitjà, al menys exacta, per descriure el transport electrònic des d'*una* o *poques* molècules "pontejant" contactes metàl·lics.

A continuació, resumim els principals resultats numèrics obtinguts en la tesina com a mostra de l'efectivitat (o no) del mètode teòric ací desenvolupat.

El capítol 5, està dirigit a realitzar una anàlisi (la més acurada possible), del càlcul de la conductància per a una molècula d'Hidrogen connectada a electròdes de platí.

En la primera secció d'aquest capítol es mostra, el paper que desenvolupen les aproximacions al potencial dinàmic d'intercanvi i de correlació en els càlculs de transport quàntic i a nivel *ab-initio* que avui en dia es realitzen. Aquesta secció, esperem que siga suficient per justificar les discrepàncies d'opinió que encara existeixen avui dia entre diferents grups teòrics, que presumiblement treballen a nivel *ab-initio* [24, 25, 77]. A més a més, aquesta secció havrà ser suficient per a justificar els resultats que s'enuncien en al que resta d'aquest capítol. Aquesta secció conté una metodologia que podria ser implementada per tal de deixar enrere les coses desconegudes en la selecció del potencial d'intercanvi i correlació. Per acabar, la resta d'aquest capítol ha de ser suficient per a poder mostrar com podríem actuar front les limitacions que tenen algunes de les versions actuals dels mètodes basats en la teoria del funcional de la densitat, com és segons la nostra opinió, l'utilització d'aproximacions locals en l'espai de posicions al potencial de intercanvi i correlació,

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intrínsecament no local. Això es fa com s'indica a continuació.

En la secció 5.2, es desplega la metodologia descrita en la secció 4.2, i es dissenya un potencial no local d'intercanvi i de correlació. En primer lloc, es debat la influència de les diferents aproximacions al potencial d'intercanvi i de correlació en la posició dels orbitals químicament actius HOMO i LUMO. Com s'analitza en la referència [118], aquestos dos orbitals són acceptats com els de major influència en els valors finals de la conductància. Més encara, aquestos són emprats per a fixar les condicions del medi, vàlides per a la construcció d'aproximacions vàlides al potencial d'intercanvi i correlació exacte. Ambaquest potencial (aproximat per una ruta exacta), podem fer càlculs de transport de camp mitjà i *ab-initio* dins d'un formalisme estàtic. Sens dubte, això és tan desitjable dins dels models teòrics que tracten aquesta teoria.

En la última secció, i per comparar amb els nostres càlculs basats en la compatibilitat d'una teoria estàtica, presentem els resultats obtinguts per a la conductància a partir d'aquest sistema model però tras l'implementació dels resultats adiens. En aquest sentit, s'aprècia una acceptable compatibilitat entre els valors de conductància obtinguts.

En el capítol 6 comencem amb una premisa. Els sistemes que estem tractant, degut a les seues dimensions i al confinament, exhibiran comportaments radicalment diferents als estudiats en la química tradicionalment i a aquells que han estat estudiats per la física de l'estat sòlid. Per la importància que tenen les estructures geomètriques per a l'obtenció de valors de conductància comparables amb l'experiment, aquest capítol està reservat a l'experiment, l'estudi del que suposem s'anomenarà: química per a l'electrònica molecular.

Amb aquesta idea, aquest capítol apunta a una precupació primària, de com anomenar als sistemes formats per una o per unes poques molècules "pontejant" electròdes metàl·lics. La nostra solució i proposta és a nomenar-les: TIP[8] En una primera impressió, el TIP pot considerar-se com una etiqueta comercial insignificant (i no pretenem restringir la llibertat de pensament amb una cosa tan trivial que la podria acceptar, fins i tot, un nen). No obstant, això no és estrictament cert. Darrere del TIP pensem contribuir al desenvolupament de debats basats en mètodes tradicionals de la química que ensenyant la seua efectivitat per fer anàlisis qualitatives, i moltes vegades quantitatives, de les posicions geomètriques quan interactuen especies diferents. Per tant, darrere del TIP ha de veure's l'etiqueta per fer debats en un context més químic. El TIP ha de ser considerat com un híbrid entre els tan coneguts i comuns complexos de coordinació i els intermedis de reacció. El TIP és el producte d'una "reacció" entre una punta de metall i les molècules, de vegades, en estat gasós. Per això, el model de reaccions a estudiar es defineix com:

$$\text{Metal}_{(\text{tip})} \quad + \quad \text{Molecule}_{(\text{gas})} \implies \text{TIP} \tag{E.5}$$

A partir d'aleshores, tots els resultats numèrics s'obtenen emprant un codi de la química quàntica GAUSSIAN [78] sobre els sistemes que pertoca. En el que resta d'aquest capítol, s'obtenen els resultats següents.

[8] Aquest acrònim té el seu origen en el nom complet i original en anglés: *in***T***eraction t***I***p com***P***lex*, que significa complex d'interacció de punta.

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En les dues primeres seccions, es duu a terme l'anàlisi de l'interacció química entre un sistema representatiu de molècules diatòmiques i les puntes metàl·liques.

En primer terme, s'estudia l'Hidrogen interactuant amb puntes de metalls de la sèrie de transició (níquel, pal·ladi i platí). L'interés en aquestos TIPs està ben justificat. El seu estudi és una resposta a la creixent demanda del desenvolupament de mètodes experimentals i *ab-inito* per fer una descripció efectiva d'aquestos nous candidats a una economía de fonts d'energia, basats en el desenvolupament de piles de combustible d'Hidrogen [85]. (Aquesta es la raó per a designar a les molècules d'Hidrogen amb la seua exaltació corresponent). Seguidament, nosaltres analitzem el monòxid de carboni interactuant amb el platí. En la secció que ve a continuació, estudiem oxigen i monòxid de nitrogen interactuant amb puntes de platí. El tractament d'aquestos sistemes en aquesta tesina es fa, principalment, per contribuir a futurs anàlisis de l'evolució del magnetisme molecular.

La última secció d'aquest capítol, està dirigida a desplegar allò que seria tota la capacitat de la nostra metodologia. La combinació de la metodologia per la caracterització del transport quàntic, l'anàlisi química, i el senzill model estadístic. Això implica, descriure allò més proper a la realitat les mesures en un sistema. Els elegits vàren ser hidrogen i monòxid de carboni interactuant amb electrodes de platí. Una concordància bona és la que observem.

L'últim capítol d'aquesta tesina és intencionadament breu. Desitgem mostrar l'eficàcia dels mètodes desenvolupats al llarg de la tesina, amb un sistema que siga realment un candidat a l'electrònica molecular. El sistema elegit és un sistema orgànic que sembla que està millor controlat a nivell de laboratori que les molécules diatòmiques anteriorment presentades. Es tracta de la molècula benzè-1,4-ditiol.

L'atenció es centra en l'estudi d'aquest sistema en condicions reals. És a dir, partim d'una disolució d'aquest derivat d'un alcohol (simplement la substitució de l'oxigen per un àtom de sofre) i simulem la seua interacció amb electròdes d'or, que es sumergeixen en aquesta disolució. Degut a les interaccions entre les superficies d'or finals (no necessàriament nanomètriques degut a que el benzè-1,4-ditiol s'adsorbeix molt fàcilment, es forma un TIP que es coneix com a BDT, i que envolta, ara, a un benzè-1,4-ditiolat adherit a dues superfícies d'or.)

Les possibilitats del BDT com a unitat bàsica en sistemes moleculars ha estat discutida per Reed *et al* [93]. Més encara, el grup de Tao [29] ha obtingut resultats experimentals en aquests sistema. (Aquestos resultats no estan lliures de debat, no obstant, així com que no tenim uns altres, ni, segons el nostre coneixement, mostra cap tipus d'errada en aquestos experiments, anem a acceptar-los sense discusió.) En conseqüència, el nostre objectiu principal és, una vegada més, ensenyar la possible causa de discrepància entre els grups teòrics que vàren intentar explicar aquest experiment [12,68,94–97]. I, una vegada més, aquesta discrepància, s'associa a l'utilització de funcionals locals per descriure el potencial d'intercanvi i de correlació.

En una primera secció d'aquest capítol, són estudiades les posibles configuracions, que poden resultar de l'interacció del benzè-1,4-ditiol amb les superficies d'or en disolució. Aquesta anàlisi es limita a un medi de simulacions basades en mètodes *ab-initio*, i recordant conceptes habituals en química per analitzar l'estabilitat i la

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capacitat de l'enllaç de molècules orgàniques quan interactuen amb superficies i/o puntes d'or.

En una segona, i darrera secció, el nostre mètode de transport quàntic i *ab-initio* és emprat en sistemes candidats a TIPs que nosaltres proposem. Per acabar, amb la contrapartida experimental s'observa una concordància (pot ser massa bona per ser creïble).

- Discusió d'aquests resultats

  Desitjablement, amb aquesta tesina hem demostrat que describint apropiadament una propietat analítica, sembla que subtil, podem obtenir valors de conductància que coincideixen en gran manera amb els resultats experimentals actualment en debat [27, 29, 118]. No obstant, fem d'apuntar a alguns dels punts que no s'han pogut explicar dintre d'aquest treball de tesina, i que considerem podríen ser la base per a futures línies d'investigació i un honorable treball (fins i tot per als més humils col·laboradors).

  En primer lloc, encara que nosaltres obtenim una relació matemàtica entre la nostra proposta com a correcció estàtica i les correccions depenents del temps propostes per la comunitat: la no localitat, nosaltres no hem estat capaços d'establir una relació explícita entre ambdues expressions analítiques per aquestes correccions.

  En segon terme, basant-se en el treball original de la teoria del funcional de la densitat [6], el potencial d'intercanvi i de correlació que nosaltres estem proposant hauria de ser universal, i contrastant de la ruta que proposem per dissenyar-lo, aparentment no dou a un funcional universal. Amb això, considerem que aquésta és una línia "bona" oberta a les investigacions en el camp del desenvolupament formal.

  En tercer terme, tots els mètodes teòrics desenvolupats ací estan basats en una veritat inacceptable *a priori*, el comportament assolible a temperatures properes al zero absolut, l'existència d'estructures cristal·lines en els electrodes, la no existència d'interacció electró-fonó, etc... Per tal de desenvolupa un marc teòric per una electrònica molecular realista i efectiva, tots aquests efectes han de ser acuradament inclosos.

  En quart terme, alguns dels conceptes emprats per descriure els sistemes amb que estem tractant són extrapolacions "crues" de conceptes inicialment definits en el context de la química i de la física tradicional i, per això, les seues capacitats són qüestionables. *Verbi gratia*, la longitut d'apantallament en el metall volumètric, la longitut de caiguda en les molècules aïllades i l'etiqueta "complex d'interacció de punta" per a marcar les qualitats químiques que hi estem considerant.

  Per totes aquestes coses, esperem que els resultats obtinguts en aquesta tesina siguen confirmats per investigacions (que es valoren, respecten i s'accepten sense cap mena de discusió supèrflua) en un futur suficientment proper.

- Conclusions finals

  En primer terme, en contrast amb els treballs teòrics recents [18,39], la nostra tesina és que existeix una teoria *ab-initio* vàlida per realitzar una descripció exacta del transport quàntic. A més a més, aquesta teoria té com a variable central, i suficient,

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per a la seua determinació completa, la densitat electrònica del sistema. L'efectivitat d'aquesta teoria, com abans hem indicat des de la formulació inicial d'aquesta, subjau en la definició de potencial d'intercanvi i de correlació [6, 67].

En segon terme, en aquesta tesina es fixa una expresió algebraica pel potencial d'intercanvi i de correlació que es determina com a funció de la posició, fixant les condicions de l'entorn apropiades. La proposta de definició analítica del potencial d'intercanvi i de correlació, ens servei com a excusa per introduir formalment el caràcter local d'un funcional. Fins on nosaltres coneixem, no existeixen definicions formals prèvies a aquesta (almenys alguna prou acceptable). Aquest concepte està indiscutiblement connectat amb el comportament dels electrons, quan les interaccions de molts cossos són importants. Aquesta importància aumenta quan els electrons estan confinats; la situació física que asumim anem a tractar-la en els problemes asociats a l'electrònica molecular.

En tercer terme, hem estudiat l'efecte de la inclusió de la no localitat en els resultats numèrics quan es considera el transport quàntic en un conjunt representatiu de sistemes. Hem observat una reducció dràstrica del valor de la conductància degut a la consideració d'aquestes contribucions no locals en el potencial d'intercanvi i de correlació. Els nostres resultats teòrics, *ab-initio* i basats en la teoria del funcional de la densitat estàtica, són a més a més, comparats amb els que s'obtenen en implementar la metodología *ab-initio* depenent del temps (dinàmica). La semblança entre les dues metodologies, estàtica i dinàmica, obri la porta a la possible connexió explícita entre ambdues metodologies. No obstant això, una connexió analítica ja es pot establir en les dues metodologies, el potencial d'intercanvi i de correlació és una quantitat no local quan es defineix en les coordenades espacials.

En quart terme, hem utilitzat en aquesta tesina conceptes tradicionals de la química i la de física per explicar alguns aspectes que encara no hem pogut explicar des de la perspectiva dels mètodes *ab-initio*. Per exemple, els mecanismes de reacció, les preferencies d'enllaç químic, i la formació d'un únic canal de conducció en alguns dels sistemes estudiats, han estat alguns d'aquestos subtils punts explicats aquesta tesina.

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Agradecimientos

Porque lo hemos hecho juntos

Hoy no quiero estar lejos de la casa y el árbol,
Hoy quisiera estrechar mi ciudad sumergida
(...)¿Qué le voy a enseñar a la suma del viento?
Algo como un recuerdo, una imagen, un beso (...)
[9]

Y le faltó "algo como un dulce abrazo"... en mi caso sentiría el de aquellos padres que dan todo por mi (la mitad de su todo). Porque la otra mitad se la lleva mi hermanita. A la que *las flores maldicen, celosas.* La hermana que se quedará para siempre con el ita, pues aún cuando me supera, esa será la respuesta a su exceso de dulzura para con los que la rodean. Los que la rodean,..., *la familia, la propiedad privada* (montonazo) *y el amor* (otro montonazo).

Sin los drámaticos emails de mi tata y Generoso, satirizando desde una perspectiva que he observado propia de químicos y prácticos, garantizo que esta tesis no estaría aún terminada. Sin los lacónicos emails de mi tío, que sólo me demuestran que existe como es propio de un matemático aunque lo reniegue, esta sobrina maledetta habría perdido la ilusión de abrir el email.

Si a alguien hay que agradecer por responderme aún es a mis primos. Rebeca, por ser capaz de responder con poesía a lo que para ella genero. A Tonito (el enanito chorri), por responder aún cuando le asalte a preguntas sobre la adolescencia y sus complicaciones. *Te conozco.* Eso para Anita, pues aunque no te puedo "ver", creo vas a ser una copia de nuestra abuelita (tarde para que yo le llame abuelita).

Observaba la bodega
donde peleaba y dormía,
con la pupila vidriosa
miraba pasar el día.

[9] Las frases que aparecen en cursivas son resultado de la creación de un poeta de verdad. Para él: esa es la ayuda que necesitaba, usar tu fascinante poesía -que los periodistas exageran- para que cuando deje de ser una adolescente y tenga pocas fuerzas, ... pueda hablar en lenguaje correcto y citar a personas importantes, sin correr otra vez el riesgo de que un profesor de física me suspenda ... (y queda entre nosotros).

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Amigo puede ser quien bien repara
en la musa o engendro que yo aporte.
Amigo, sí, es también quien me soporte,
pero amigo mayor es quien me ampara.

Tengo que agradecer a esos amigos que se hacen mayores y siguen amparando. Los jimaguas: Julito y Mandy, y más de lo mismo: Douglas y Alain. A Pachanga, o Jorge Carlos, por haber estado en momentos (difíciles quizás) pero lo que tendré en cuenta es que era capaz de lanzar por los aires el teléfono móvil cuando le llamaba por muy dura que estuviese la situación.
A Yailén por regalarme una sobrinita y ser cómplice de locuras.

¿A quiénes me deja la Universidad de la Habana, UH?

ay de cúanto se marche, ay de cuánto se quede
(...) ¿A dónde van las palabras qué no se quedaron?
¿A dónde van las miradas que un día partieron?
¿Acaso flotan eternas, como prisioneras de un ventarrón?
¿O se acurrucan, entre las endijas, buscando calor?
¿Acaso nunca vuelven a ser algo? ¿Acaso se van?
¿Y a dónde van? ¿A dónde van?

A Ale y su hermana Marlén que son fuente infinita de cariño, además de físicos, filólogos, etc...
A Erwin, que aún cuidando de su padre me acoge en su actual Lausanne.
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A Fabio porque tenía razón. A la luz del Sol todo el mundo es amigo tuyo, y a veces hacen falta momentos de sombra para distinguir las amistades. -Un momento irrepetible en el muro del cuarto piso de la Facultad de Física-.

¿A quiénes me deja un Instituto Preuniversitario Vocacional de Ciencias Exactas, IPVCE?

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A un Eduardo que es capaz de seguir mostrando al CO_2 como un gas pardo-rojizo, y todo ... por enrollarse. Una Arlheet, nombre de chico en Cuba, que sigue empeñado en anunciar que si una chica le tiene cariño es por su cuerpo de escultura davidiana (me he inventado temporalmente el término, pensando en el David de Miguel Ángel Buonarroti, y que no se entere Arlii!). Esa idea es bastante generalizada en sus semejantes. Pienso en los Ericks, Dovale y Cebrían, Ulises-el bocaza, Dani TV, Ariel el Picolín, David el cortico. A todas esas bestias, con sus emails que ni contesto, a veces por miedo, les agradezco su respeto y compañia.

la cobardía es asunto
de los hombres, no de los amantes

Quizás porque va de mensajes de mujeres a hombres esta poesía .... me vea obligada a hablar de los amigos de fuera de la isla empezando por una mujer ... de Madrid. De María o Marie o Cristina, es la misma, que tanto aportó con su madurez para sumarse de cómplice en las locuras cotidianas e incluso para apoyar la realización de un doctorado. De su Emilio, y los momentos de compartir el lenguaje hispano en estado puro, y sentirlo como una muestra de bella espontaneidad. De mi primita pequeña Carmencita, que sin siquiera tener un título de matemáticas, me ha ayudado a comprender las series de Taylor y a presumir de nanocontactos en la entrada de un cine. A mis tíos, sus padres, y a su abuela, por dejarnos hacer y deshacer en sus propiedades. De Trini, es difícil disimular el cariño para con Trini, que cuando parecía imposible te descubre que hay gente que ofrece lo que no le sobra (y pienso en términos materiales) humanamente, le sobran muchas cosas, y espero que en poco le sobre la más esperada.

Hay locuras para la esperanza
Hay locuras que son poesía,
hay locuras de un raro lugar.
Hay locuras sin nombre,
sin fecha, sin cura,
que no vale la pena curar.

Las locuras podrán ser esperanza, pero en este caso se llama EspeR (sin entrar en detalles pues no podría parar de reír). La poesía la pone un raro lugar donde a pesar de que no se pueda concebir el mar en él (Sabina me está ayudando...), el fugitivo siempre tendrá que regresar a buscar, al menos, a esos amigos que son un: no te rindas! -sólo efectivo si sale con la ternura de Carlitos- o con un "cousin number" para dar nombre a algo, que ya teníamos definido y claro hasta esa nueva denominación, ... o que también dedican una noche fría a explicar la irracionalidad de π y su belleza, la belleza del número π!, ese es Loren.

Dirán que pasó de moda la locura,
dirán que la gente es mala y no merece,
más yo seguiré soñando travesuras
(acaso multiplicar panes y peces).

estoy endeudada con una familia de madrid que me cuidó y no precisamente, multiplicando panes y peces ... multiplicaron locuras, carne Argentina, y un cariño que sólo se les puede pagar luchando contra los Olvidos y Silencios. a mi mariano, la

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mamá alicia, el papá omar y el travieso hermano gustavo.

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Hay que agradecer a todas las personas que han hecho grata la convivencia, Elena, Inma, Ezequiel, Leo, LLuis y Cristian. (No han coincidido temporalmente, sino hubiese sido más breve y hubiese dicho: a los compañeros de la comuna). A todos habrá que recordarles por algo, Elena por sus animales, Inma por sus confidencias (animales también), Ezequiel por su silencio, Leo por la fiesta, LLuis porque... tiene La Moncla más limpia que nadie, y a Cristian porque a pesar se ser casi un niño, $cristian << 2x$ jajajja!, a nivel intelectual y profesional es enorme.

el mundo de un adolescente
un semininño asustado, mirando a la gente
un ángel interrogado

Les debo momentos muy interesantes y dulces a los "adolescentes" a que he dado clases en esta etapa. Sin duda las mejores preguntas han venido de ellos, muchas han servido de inspiración en el trabajo que aquí se expone. Pero más que eso, el cariño y agradecimiento que cotidianamente devuelven, ha tirado para escapar a verles cada tarde, a Iñaki, Manuel, Raquel, Silvia, Clara, Olimpia y Pablo.

"Los hombres no pueden ser más perfectos que el Sol. El Sol quema con la misma luz con que calienta. El Sol, precisamente por ser Sol, tiene manchas. Los desagradecidos no hablan más que de las manchas. Los agradecidos hablan de la luz" [119].

Si bien es cierto que los resultados de cualquier obra humana a nivel *ab-initio* se achacan al esfuerzo personal, en mi caso prefiero dejar a ese nivel las incapacidades de que presumo, y transferir la valía que "esto" pueda tener a la dedicación y esmero de muchas personas admirables.

En primer lugar, esta tesis ha sido dirigida en la distancia por Rolando Pérez-Álvarez, RPA. No necesariamente aproximado según la fase y con apariciones aleatorias (aquí hay un juego de palabras que queda para interpretación libre usando jerga de físicos aburridos). Si estoy en deuda con él es porque desinteresadamente ha estado siempre que le he necesitado, tanto como científico como "padre". Además me siento en deuda con todos los profesores de la Facultad de Física, UH; que con tanta exquisitez, respeto y nivel académico envidiable; literalmente, nos regalaron educación científica. Pienso desde Eddy (ver B) hasta C. Trallero-Giner (director de tesis de Diploma), pasando sin duda por el encanto de Medel (con su física molecular tan didáctica) o de Melquiades (con su mecánica cuántica para suspender ...) o de Carlos Rodríguez (que aún me cuesta ver su facilidad para desarmar un problema de estadística física, y luego decirnos que sólo ha contado estados). Me falta espacio para tantos Otros...

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Quizás el riesgo declarado para con un adolescente, es la facilidad para dejarle huella. Creo que algo tan sútil como dormirse en una clase de definición de orbitales moleculares, de construir orbitales híbridos, etc... todo eso en un IPVCE, fue el inicio de una carrera que aún sugerida no llevé a cabo explícitamente, pero llevo dentro y en esta tesis eché en falta. Agradezco a Andrés Rodríguez por dibujar con sus manos los orbitales más lindos que he visto. (Es que los tuve que soñar y la pasé fatal estudiando para su primer exámen de chícharos, sino es por mi tata que me explica el H_20, etc...) y también su consejo de estudiar químicas en lugar de física que he tenido que retomar, informalmente... (Es que sino de electrónica molecular poco). A Bertica, su compañera y profesora de Español-Literatura, le debo muchos, muchos signos de puntuación que aún pongo al azar. Esta es la rutina a implementar: sacamos una media de cuantas comas, puntos y comas, dos puntos, etc... deben aparecer en una redacción, escribimos con el alma y sin respirar, y luego dispersamos los signos de puntuación para que estéticamente se vean bien. Le agradezco, que no me haya aceptado eso y que como tal me haya penalizado. Se me quedan más profesores, de los que iban en bici, en plan hippies o superelegantes. En cualquier caso la principal moraleja que dejaron, es que hay personas que enseñan y no lo hacen por dinero. Eso los hace maestros.

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Si caemos en la Universidad de Alicante ... debo empezar a agradecer en orden cero a los "viejitos" de la piscina (no sé sus nombres y espero no se enteren que les llamos viejitos), pero les agradezco sus buenos días y el dejar entrar siempre a la cubana a la piscina. A partir de ahí se coge aire para trabajar. Al médico, preferiría no agradecerle, pero nos ha tocado conocernos.

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Ya no te espero
Ya es el tiempo que fascina

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A manos del desespero
Saltando a quien la domina

Debo agradecer también la oportunidad para crecer que me han dado. Crecer y no científicamente. Pero agradezco, y hasta le daría una rosa blanca si la tuviera, a los que me han demostrado que había razón en el que dijo:
Muchachos... Chavales....
"Hay que endurecerce pero sin perder la ternura: jamás!"[10]

Con un poco de amor sobrevivo,
sobrevivo pecado, castigo.
Con un poco de amor yo me salvo,
sólo un poco de amor y soy algo.

Es que me los había guardado para el final ... Esta tesis no hubiese tenido una primera frase sino hubiese sido por la familia que espero haber ganado. Esta familia para mi definida como una transición discontinua, irregular y sorpendente entre Abuela y Andrea, pasando por la más original de las adolescentes. Adolescente que aún puede estar dolida porque Yamila le ganó a su España en 1898. Pero bueno, ni Yamila es Cuba, ni Cuba le ganó a España. Ni España perdió a Cuba. Ese tema es más extenso. Yamila lo único que desea es haberse ganado un sitio en la vida de esa adolescente y de su abuela -si me dejan llamarle abuela-. En cualquier caso, debo demasiado a esa familia. A Fini por mostrarme con su ejemplo que hay que se puede ser mujer y valiente, a Menchu por ser tan madre, a Alicia por enseñarme que trás un "perro verde" se puede esconder una muestra de infinito cariño, a Mari Carmen ... después de traer a la Andreita es difícil recordarle por otra cosa, a Ángela por ser el matiz serio de madre educadora, a Casandra por ser una cómplice compañera, y a la Concha por estar por ahí siempre con mensajes para subir la moral. Y como esa familia no es nada sin sus chicos...

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[10] El autor de esta frase se inmortalizó precisamente por no tener nombre, así que se queda sin ser citado. Esto podría atentar contra el mensaje técnico de esta tesis, pero si es preciso corro ese riesgo.

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equidistant points in this range, (the same analysis of nonlocal contributions presented in chapter {H2). The bonding distances reported have the error in the last number. For that reason, we also state the observation, that the role of the exchange-correlation potential does not seem noticeable in the structures we are analizing. The basis sets are cc-pvtz for Hydrogen atoms and lanl2dz for Nickel, Paladium and Platinum atoms, [78]. The clusters for modeling the tips contains two metal atoms, or the first layer corresponding to a section of the perfect bulk. The Hydrogen molecule in between the metals tips, and lying perpendicular and paralell to the axis of the stretching of the modeled nanocontact, are used as initial condition in the two type of simulations. In case of more that two metal atoms in the simulation, they are fixed to the positions dictated by thelk arrangement.

[89] The calculation were done using the B3LYP functional for the exchange-correlation potential. The basis sets are cc-pvtz for Carbon and Oxigen atoms and lanl2dz for Platinum atoms, [78]. The clusters for modeling the tips contains 10 metals atoms corresponding to two atomic tip sections of the perfect bulk. The Carbon Monoxide molecule in between the metals tips, is placed lying perpendicular and paralell to the axis of the stretching of the modeled nanocontact, as initial condition in the simulations.

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Reunido el Tribunal que suscribe en el día de la fecha acordó otorgar, por UNANIMIDAD **a la Tesis Doctoral de Don/Dña.** Yamila García Martínez **la calificación de** Sobresaliente CUM-LAUDE 10

Alicante 27 **de** Junio **de** 2007

El Secretario, Guillermo Chaple.

El Presidente, Francesc Illas i Riera

UNIVERSIDAD DE ALICANTE
Comisión de Doctorado

La presente Tesis de Dña. Yamila García Martínez **ha sido registrada al Folio** ..... **con el n.º** 1284-223 VA **del registro de entrada correspondiente**

Alicante 27 **de** junio **de** 2007

El Encargado del Registro,

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