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**Many-body perturbation theory and
maximally-localized Wannier functions: a
combined tool for first-principles
electronic structure and quantum
transport calculations**

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Abstract

Nowadays, quantum mechanic simulations are widely used to predict the properties of matter at the nanoscopic level with great accuracy. Many-body perturbation theory (MBPT), which can describe complex phenomena such as electron interactions, is amongst the most advanced techniques in this field. This methodology is, however, highly demanding in computational resources. In this manuscript, we propose a low-cost and accurate method for atomistic calculations: the combination of MBPT and maximally-localized Wannier functions (MLWFs). This effective approach is used in the calculation of excited states and transport properties of nano-materials and solids.

In the field of quantum transport, experimental measurements and theoretical calculations tend to disagree for the conductance of a single molecule contacted to metallic leads. We found that many-body effects, which are missing in the most popular theoretical approaches, can partially explain this discrepancy. Second, the bandstructure of gold has been revisited. Since the 70's, it has been observed that the theoretical prediction and the experimental measurement of the position of the electronic bands disagree. Within our approach, this long-standing disagreement has been solved. Third, we used MBPT and MLWFs to predict the electronic properties of other materials (zircon, hafnion and Ge and Si nanowires), in particular, accurate bandstructures, which can be useful in the interpretation of photo-emission experiments. The results of this thesis point to the importance of many-body effects to simulate the properties of matter at the nanoscale and to the importance of MLWFs as a cheap solution for large scale calculations.

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List of Acronyms

ARPUS angleresolved ultraviolet photoelectron spectroscopy

ASIC atomic self-interaction correction

BDA benzene-diamine

BDT benzene-dithiol

BDT-h benzene-dithiolate at hollow geometry

BDT-p benzene-dithiolate at pyramid geometry

BDT-n benzene-dithiol non-disorbed

BO Born-Oppenheimer

BZ Brillouin zone

DFT density functional theory

CD contour deformation

CH Coulomb-hole

CHSX Coulomb-hole and screened-exchange

EA electron affinity

EAs electron affinities

FCC face centered cubic

FQ first quantization

GGA generalized gradient approximation

GW *GW* approximation

HF Hartree-Fock

HK Hohenberg-Kohn
HVB highest valence band
HOMO highest occupied molecular orbital
IBZ irreducible Brillouin zone
IP ionization potential
KS Kohn-Sham
LCB lowest conduction band
LCR left lead-channel-right lead
LDA local density approximation
LDOS local density of states
LL Levy-Lieb
LUMO lowest unoccupied molecular orbital
MBPT many-body perturbation theory
MLWF maximally-localized Wannier function
MO molecular orbital
MPM molecular projectors model
NSCF non-self-consistent field
NW nanowire
OEP_x exact-exchange optimized effective potential
PBE Perdew, Burke and Ernzerhof
PDOS projected density of states
PL principal layer
PPM plasmon-pole model
QM quantum mechanics
QP quasiparticle
QPSCGW quasiparticle self-consistent *GW*

SAM self-assembled monolayer

SIC self-interaction corrected potential

SX screened-exchange

SO spin-orbit

SQ second quantization

SR scalar-relativistic

TDDFT time-dependent DFT

VBM valence band maxima

WDA weighted density approximation

XC exchange-correlation

3PM three projectors model

Nomenclature

$A_{mn}^{(\mathbf{k})}$	Initial guess matrix for MLWFs
$\hat{a}$	Annihilation operator
χ_0	Independent particle polarizability
$\hat{a}^\dagger$	Creation operator
Δ	Scissors operator shift
$\mathbf{E}$	Electric field
E_{H}	Hartree energy
ϵ_i	The i^{th} eigen energy
E_{xc}	Exchange and correlation energy
$\mathcal{G}$	Conductance
Γ	Vertex function
$\Gamma_{R/L}$	Coupling matrices
$\mathcal{G}_0$	Conductance quantum
$\hat{H}$	Hamiltonian
$\mathbf{j}$	Current density
λ	Wavelength
λ_F	De Broglie wavelength
$\mathcal{A}$	Spectral function
$M_{mn}^{(\mathbf{k},\mathbf{b})}$	Overlap matrix for MLWFs
ν	Frequency

Ω	Unit-cell volume
$\hat{\psi}$	Wave field operator
Ψ	Wave-function
ρ_q	Charge density
$\mathbf{r}, \mathbf{R}$	Position operator
Σ	Self-energy
σ	Conductivity
τ_m	Momentum relaxation time
$\tilde{\chi}$	Irreducible polarizability
ε	Dielectric function
φ	Single-particle wave-function
v_{eff}	Effective potential
v_{H}	Hartree potential
$\hat{V}_{\text{ext}}$	Total external potential operator
$\hat{V}_{\text{int}}$	Electron-electron interaction potential operator
v_{xc}	Exchange-correlation potential
$\mathcal{W}_n$	Wannier function labeled by n
c	Speed of light
E	Energy
e	Elementary charge
E_F	Fermi energy
G	Green's function
h	Planck's constant
I	Conductance
L_ϕ	Phase-relaxation length
M	Number of conducting modes

m	Mass
n	Density
n_0	Ground state density
p	Momentum
S	Spread functional
T	Kinetic energy
$T(E)$	Transmittance
$t_i, \tilde{t}_i$	Transfer matrices
$u_{n\mathbf{k}}$	Periodic part of the wave function
W	Screened coulomb interaction
$\mathcal{G}(E=0)$	Zero-bias conductance

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Introduction

The aim of the present manuscript is to show how the combination of maximally-localized Wannier functions (MLWFs) and many-body perturbation theory (MBPT) provides a powerful tool for the calculation of excited states and transport properties of nano-materials and solids. On the one hand, MLWFs constitute a minimal and localized basis set, which provides a bridge between tight-binding approaches and *ab initio* methods. MLWFs are used in a large number of applications, including linear-scaling approaches, interpolation of matrix-elements, and quantum transport calculations, among others. On the other hand, MBPT is nowadays the standard theory to predict bandwidths and band-gaps of materials at the nano-level. The combination of these two theories has allowed us to tackle some interesting problems in the field of quantum mechanics simulations.

This work started with the development and implementation of interfaces between the computer codes ABINIT [1], Wannier90 [2] and WanT [3]. ABINIT deals with DFT and MBPT calculations. Wannier90 allows one to obtain MLWFs and to compute transport properties. WanT is dedicated to the calculations of transport properties with MLWFs. These interfaces allow us to use MLWFs together with DFT/MBPT in the simulation of material properties.

Chapter 1 provides the theoretical background. In section 1.2, we introduce the density functional theory (DFT). This popular method is widely used in the computational physics and computational chemistry communities. It is exact in principle for the ground state properties of the system. However, it presents difficulties related to the practical approximations for the exchange-correlation (XC) energy when it comes to treating certain properties, such as interatomic distances or van der Waals forces. Moreover, DFT does not formally provide a theoretically justified framework to compute excited states or optical properties. In section 1.3, we introduce the MBPT. This theory accounts for many-body correlation effects and provides a direct access to electronic excitations. Therefore, it is more appropriate than DFT for excited state

properties, such as optical and transport properties. In section 1.4, we provide a brief introduction to MLWFs. We describe the methods to calculate them and how they can be used to interpolate matrix elements. Finally, section 1.5 is dedicated to quantum transport. We start from the classical approaches, such as the Drude conductivity, explaining some of the important concepts of transport. Then, we explain in more details the quantum approaches for mesoscopic systems (the scale of such materials is between the atomic size [a few atoms] and a few microns). We end the chapter, with the WanT approach, a practical method to simulate the transport properties of mesoscopic systems with MLWFs.

Chapter 2 is devoted to understand many-body effects in the transport properties of molecular nano-junctions (single molecules connected to metal leads). At the DFT level, the geometrical details and total energy of the junctions are well described. However, the zero-bias conductance can be overestimated by up to three orders of magnitude [4]. We found that many-body corrections, in weak coupling regimes, reduce the zero-bias conductance, improving the agreement with the experiments. The conductance change is due to changes in the wavefunctions in both the metal and the molecule regions. Therefore, many-body effects are crucial to determine the metal-molecule hybridizations (wavefunctions) and the zero-bias conductance.

We use our MBPT results to evaluate the applicability of a model self-energy frequently proposed in the literature [5, 6]. This operator shifts the molecular orbitals (MOs) in the junction, modifying the metal-molecule hybridizations and reducing the zero-bias conductance. Although the results obtained with this model are usually in agreement with the experiments, we find that they are not in agreement with the MBPT results. With respect to the MBPT results, the model corrections shift the MOs too much. And, even if we refine the model to predict the same shifts as in the *ab initio* calculations, the model is not accurate enough to predict the conductance of these junctions.

Chapter 3 is dedicated to revisiting the electronic band structure of solid gold, which has been extensively studied from the 70's on. Since that decade, it has been observed that the theoretical prediction and the experimental measurement of the position of the occupied 5*d* bands disagree by a rigid shift of ~ 0.35 eV [7, 8, 9]. Moreover, it was expected that standard many-body corrections, within the G_0W_0 technique, could account for this shift, as in other noble metals [10, 11].

In section 3.2, we use this system to test different approximations within the G_0W_0 theory. First, we study the effect of semicore states in the G_0W_0 calculations. We find that they need to be included to obtain accurate bandstructures. Second, we study the validity of the PPM (by

comparing with the results obtained using the contour deformation (CD) integration technique) to evaluate the corrections at different frequencies. In fact, the validity of the PPM for d states has been questioned for other metals. Here, we find, in contrast, that the PPM produces reasonable results.

Globally, we find that G_0W_0 corrections negligibly modify the occupied bands. Quite surprisingly, a self-consistent many-body approach, which corrects not only the DFT eigenvalues, but also the DFT eigenfunctions, is required to lower the $5d$ bands, improving the agreement with the experiments (as explained in section 3.3). This is very similar to what has been found for the molecular junctions. These results show the importance of correcting the DFT wavefunctions by MBPT methods to predict the electrical properties for this metal. In section 3.4 and section 3.5, we analyze in detail the effect of MBPT self-energy corrections in the wavefunctions of gold. In section 3.6, we study the effect of vertex corrections (electron-hole correlations). These account for only a change in the absolute value of the Fermi level, whereas, the bandstructure is negligibly modified. Finally, in section 3.7, we evaluate the spin-orbit (SO) effect in the quasiparticle bandstructure of gold.

In chapter 4, we use MLWFs and quasiparticles to predict the electrical properties of other materials (zircon, hafnon and Ge and Si nanowires). This is not the main subject of this thesis, but a secondary work done in collaboration with other researchers. In section 4.1, zircon and hafnon, two promising materials for the industry of transistors, are studied in detail. The motivation of this work is to provide accurate bandstructures, which can be useful in the interpretation of photo-emission experiments. We find that the band structure of both materials is very similar within MBPT and DFT except for the band gap opening, the increase in the dispersion of the bands, and a slight displacement of the valence-band maximum away from the Γ point within MBPT. In section 4.2, Si and Ge nanowires are studied within the G_0W_0 approximation. The effectiveness of recently developed techniques in speeding up the convergence of the QP calculations is demonstrated. The QP bandstructures are also obtained using the MLWFs interpolation technique. From the QP results, we assess the correctness of the commonly applied scissor-shift correction. Dispersion changes are observed, which are also reflected in changes in the effective band masses calculated taking into account quasiparticle corrections.

Finally, we summarize our results. We draw some conclusions about our work and develop some perspectives for future investigations.

Chapter 1

Background theory

1.1 Introduction

Matter at the macroscopic level is governed by classical mechanics. However, when matter reaches small proportions of only a few nanometers (at the nanoscale), it presents special properties which cannot be explained by classical mechanics. At the nanoscale, quantum mechanics, is needed.

In this theory, electrons behave at the same time as particles and as waves. Hence, a wave-like equation called the Schrödinger equation needs to be solved to find the wave-function of the system, from which electric, optical and transport properties of a material can be calculated. This can be only solved analytically for very simple systems such as the hydrogen atom. For more complex systems, numerical methods are needed.

Finding the solution of the Schrödinger equation for solids is an enormous task. There is an infinite number of atoms and an infinite number of interacting electrons which move at high speeds with different trajectories. The solution of the Schrödinger equation for periodic systems is possible thanks to the Bloch's theorem. This states that the wavefunction of an electron in a periodic system can be written as the product of a plane wave and a periodic function.

Density functional theory

The many-body problem can be further simplified within the density functional theory (DFT). It is based on the works of Kohn, Hohenberg and Sham [12, 13]. The HK theorem states that the ground state of a many-electron system is uniquely determined by its electron density. This reduces the many-body problem of N electrons and 3 spatial coor-

ordinates each to only 3 spatial coordinates. Thanks to the KS formalism, the complicated system of interacting electrons in an external potential is mapped onto to a fictitious system of non-interacting electrons in an external potential.

The DFT is an exact theory for the ground state of the system. However, the exchange-correlation potential (V_{xc}), which accounts for electron-electron interactions is unknown and it has to be approximated. The most common approximations are the local density approximation (LDA), already introduced in the seminar paper of W. Kohn [12], and the generalized gradient approximation (GGA) [14]. The LDA is based upon exact exchange and correlation energy for a uniform electron gas. It is a local approximation in the sense that it only depends on the density at the coordinate at which it is evaluated. The GGA is also a local approximation but it also depends on the gradient of the density.

The DFT-LDA/GGA has an enormous success in the simulation of properties of solids and nano-materials. Despite this success, there are still difficulties in the treatment of interacting electrons. More fundamentally, the applicability of the DFT to find electric, optic and transport properties can be questioned. Being a ground state theory, there is no formal justification to interpret the DFT energies as addition or removal energies of the many-body system. As a result, the DFT-LDA/GGA optical gaps are systematically underestimated and the transport properties can also disagree with the experimental measurements. This will be discussed in details in section 1.2.

Many-body perturbation theory

An alternative approach is the so called many-body perturbation theory (MBPT). It is an excited state theory in the sense that the addition and removal of electrons are treated within the Green's functions formalism. Here the non-interacting electrons picture (in DFT) is changed to one of interacting quasiparticles (QPs). QP energies have a direct connection to addition or removal energies due to the definition of the Green's function. However, the many-body equation has never been implemented for real systems due to its difficulty and further approximations are needed.

In the *GW* approximation of Hedin [15], electron-electron interactions are treated by a non-local, frequency dependent and non-hermitian operator. The QP energies using this approximation are in closer agreement with the experimental measurements than the DFT eigenvalues. This method has been studied extensively in molecules, solids and hybrid systems. Nowadays, it has been established as an accurate and

robust technique to study the properties of materials at the nano-scale. In section [1.3](#), we will be dealing with MBPT.

Maximally-localized Wannier functions

The electronic ground state of a periodic system is usually represented by delocalized Bloch waves. Though this choice is widely used in electronic structure calculations, alternative representations also exist. For instance, these can be changed into a set of localized Wannier-functions [16]. These Wannier functions are non-unique due to the arbitrariness of the transformation matrix. This gauge of freedom can be further exploited if one chooses the unitary matrix which maximally localizes the Wannier functions, and hence obtaining maximally-localized Wannier functions [17]. These have numerous advantages: they constitute a minimal basis for large scale calculations, they are connected to the Berry phase theory, they can be used as an interpolation tool, and they are solid-state physics equivalent to localized molecular orbitals studied in chemistry. An overview of MLWFs is provided in section 1.4.

Quantum transport

MLWFs can be used to construct real-space Hamiltonians containing only a minimal number of elements. These compact Hamiltonians can be employed in quantum transport calculations within tight-binding-like methods. In section 1.5, we introduce the concepts behind quantum transport and a practical approach to calculate the transport properties of materials using MLWFs.

1.2 The density functional theory (DFT)

1.2.1 Total energy calculations

In 1924, Louis de Broglie proposed the idea that particles behave as waves. This is founded on the ideas of Albert Einstein and Max Planck. When joining Planck's expression for the quantization of the energy $E = h\nu$ to the Einstein's relativity formula $E = mc^2$ the de Broglie equation $\lambda = h/p$ is obtained. This formula states that electromagnetic radiation has a particle nature (momentum) and wave characteristics (wavelength).¹ The de Broglie equation is the basis of wave mechanics.

Erwin Schrödinger associated the classical equation for waves to the de Broglie's particle waves. With this aim he developed his famous (we

¹Here h is the Planck's constant, ν is the light frequency, λ is the light wavelength, c is the speed of light and p is the particle's momentum.

use here the time-independent form) *Schrödinger equation*:

$$\hat{H}\Psi = E\Psi. \quad (1.1)$$

Max Born gave the wave-function Ψ a wider meaning. He named it a probability wave because the modulus squared of the wavefunction $|\Psi(\mathbf{r})|^2$ is the probability of finding the particle at position $\mathbf{r}$. Moreover, from the wavefunction all physical properties can be obtained, *i.e.*, any observable $\mathcal{O}$ as the position and the momentum can be easily obtained from the expectation value $\langle\Psi|\mathcal{O}|\Psi\rangle$, and many other properties can be derived from them. Thus, it is extremely important to obtain the wave function Ψ in order to get other physical properties of the system.

One of the main quantities to find is the total energy of the system E_{tot} because of the fact that it is related to the wavefunction by an eigenvalue equation, the Schrödinger equation. E_{tot} can be obtained from Ψ by the following general expression:

$$E_{\text{tot}} = \frac{\langle\Psi|\hat{H}|\Psi\rangle}{\langle\Psi|\Psi\rangle}. \quad (1.2)$$

The Hamiltonian $\hat{H}$ for a system of N interacting electrons and nuclei is

$$\begin{aligned} \hat{H} = & -\frac{1}{2} \sum_i \nabla_i^2 + \sum_{i,I} \frac{Z_I}{|\mathbf{r}_i - \mathbf{R}_I|} + \frac{1}{2} \sum_{i \neq j} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} \\ & - \sum_I \frac{1}{2M_I} \nabla_I^2 + \frac{1}{2} \sum_{I \neq J} \frac{Z_I Z_J}{|\mathbf{R}_I - \mathbf{R}_J|}, \end{aligned} \quad (1.3)$$

where the lower case indices i and j run over the N electrons. We use upper case indices I and J denote ions. Hence R_I and r_i are the position of ions and electrons, respectively. Z and M are the atomic charge and atomic mass, respectively. For simplicity, the atomic units, $\hbar = m_e = e = 1$, are adopted.

The problem of solving Eq. (1.3) is formidable. A common simplification is the Born-Oppenheimer (BO) approximation, in which the nuclei are treated as static. This assumption is justified by the difference in masses between the nuclei and the electrons in a solid. Since the kinetic energy (T) is inversely proportional to the mass ($T = p^2/(2m)$), it follows that, the kinetic energy of the nuclei in a solid is usually much smaller than the one of the electrons. (protons and neutrons have a mass 1837 times greater than that of an electron). Hence, electrons move at higher velocities than the nuclei, which can be considered as being static with respect to the electrons. Hence, the problem is reduced to a system of electrons moving along frozen nuclei. If the ions are at rest the

Hamiltonian can be rewritten as: ²

$$\hat{H} = \hat{T} + \hat{V}_{\text{ext}} + \hat{V}_{\text{int}}, \quad (1.4)$$

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

$$\hat{T} = -\frac{1}{2} \sum_i \nabla_i^2. \quad (1.5)$$

$\hat{V}_{\text{ext}}$ is the total external potential experienced by an electrons due to the nuclei,

$$\hat{V}_{\text{ext}} = \sum_{i,I} \frac{Z_I}{|\mathbf{R}_I - \mathbf{r}_i|}, \quad (1.6)$$

$\hat{V}_{\text{int}}$ is the electron-electron interaction,

$$\hat{V}_{\text{int}} = \frac{1}{2} \sum_{i \neq j} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}. \quad (1.7)$$

The last term in Eq. (1.4) dramatically complicates the solution of the Schrödinger Equation (Eq. (1.1)). It accounts for particle interactions which are difficult to treat.

The second order differential Equation of Eq. (1.1) can only solved exactly for systems with one or two electrons. For system with a macroscopic number of electrons, the solution of this equation is out of reach and further approximations are needed.

Different approximations were proposed in the last century to solve the Schrödinger equation. For instance, it is approximated by a variational approach using a Slater (antisymmetric by construction) determinant of single particle wavefunctions in the HF method. However, a single determinant is not enough to describe exact wavefunctions. Nevertheless, the HF approximation and its variants are still used to determine the properties of materials specially in the quantum chemistry community.

In 1964, Hohenberg and Kohn (HK) set the basis of the density functional theory (DFT) with the theorem that the ground state of a many-electron system is uniquely determined by an electron density [13]. This reduces the many-body problem of N electrons with 3 spatial coordinates each to only 3 spatial coordinates for the density.

²The last term in Eq. (1.3) is neglected because it is simply a constant, usually called the Madelung energy. This constant can be calculated by using the Ewalds method [18].

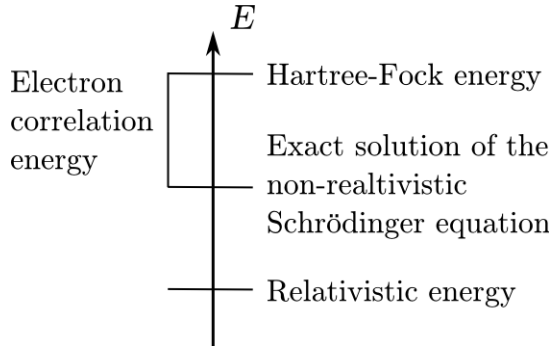


Figure 1.1: Schematic representation of the electron correlation energy, which is equal to the Hartree-Fock energy minus the energy obtained by solving the non-relativistic Schrödinger equation under the Oppenheimer approximation.

The DFT is a highlight in the history of quantum simulations. It provides a simple approach to obtain the total energy of the system using as fundamental degree of freedom a single quantity, the ground state density. In this section, an introduction to the main concepts in the DFT is given. The section is organized as follows. In section 1.2.2, a brief introduction to the Hartree-Fock method is given to illustrate the concepts of exchange and correlation energies. In section 1.2.3, the HK theorems are revised. In section 1.2.4, the KS approximation, which maps the complex many-body system to an ideal system of non-interacting electrons, is introduced. Finally, in section 1.2.5, the success and failures of the DFT are briefly summarized.

1.2.2 Hartree-Fock (HF) method

Because of the fact that electrons are fermions, the wavefunction must be antisymmetric under exchange of any two electrons. That is, each electron has a unique set of quantum numbers. The antisymmetry of the wavefunctions produces a separation among electrons having the same spin orientation. Moreover, these separations cause a reduction of the Coulomb energy of the system. The reduction of the energy due to the antisymmetry of the wavefunctions is known as the *exchange energy*.

In the HF approximation, the wavefunction is approximated by a Slater determinant. By means of a variational approach, a set of N -coupled equations for the N orbitals is derived. The HF wavefunction is obtained by solving these equations. However, a single determinant is not enough to describe exact wavefunctions. In this case this approximation does not take into account the *electron correlation*. Therefore, the total energy calculation will be slightly different from the exact solution of the Schrödinger equation given by 1.1. The difference between both solutions

is known as the *electron correlation energy*.³

Fig. 1.1 shows the differences among energies calculated by different methods. The lowest energy is the energy calculated by relativistic equations, and, the use of non-relativistic equations leads to a higher energy value. Moreover, when introducing the HF approximation the energy obtained is slightly higher than the exact solution of the Schrödinger equation. The difference between the HF energy and the energy obtained by the non-relativistic Schrödinger equation is the *electron correlation energy*.

1.2.3 The Hohenberg-Kohn (HK) theorems

In 1964, Hohenberg and Kohn (HK) proposed an approach to deal with the ground state of an interacting gas in an external potential v_{ext} [13]. It is an exact ground state theory of many-body systems which is applicable to any system of interacting particles. It is based in two theorems which together set the basis of the DFT [21, 13].

Theorem 1. *For any system of interacting particles in an external potential $v_{\text{ext}}(\mathbf{r})$, the potential $v_{\text{ext}}(\mathbf{r})$ is determined uniquely, except for a constant, by the ground state particle density $n_0(\mathbf{r})$.*

In other words, it states that the ground state Hamiltonian is fully determined, except by a constant shift, by the ground state density $n_0(\mathbf{r})$. Hence, all ground state properties are determined by a single quantity, $n_0(\mathbf{r})$.

Theorem 2. *There exists a universal functional of the density, $F[n(\mathbf{r})]$, valid for any external potential $v_{\text{ext}}(\mathbf{r})$. The exact ground state energy of the system, associated with v_{ext} , is the minimum value of the expression $E[n] = F[n] + \int d^3\mathbf{r} v_{\text{ext}}(\mathbf{r})n(\mathbf{r})$. The density $n(\mathbf{r})$ that minimizes the functional is the exact ground state density n_0 .*

An energy functional $E[n]$ exists, such that its minimum determines the exact ground density $n_0(\mathbf{r})$ and ground state energy $E_0 = E[n_0]$.

The energy functional $E[n]$ can be defined by the Levy-Lieb (LL) formulation as:

$$\begin{aligned} E[n] &= \min_{\Psi \rightarrow n(\mathbf{r})} \langle \Psi | \hat{H} | \Psi \rangle \\ &= \min_{\Psi \rightarrow n(\mathbf{r})} \left[\langle \Psi | \hat{T} | \Psi \rangle + \langle \Psi | \hat{V}_{\text{int}} | \Psi \rangle \right] + \int d^3\mathbf{r} v_{\text{ext}}(\mathbf{r})n(\mathbf{r}) \\ &= F[n] + \int d^3\mathbf{r} v_{\text{ext}}(\mathbf{r})n(\mathbf{r}). \end{aligned} \quad (1.8)$$

³ It was Per-Olov Löwdin who made numerous studies on the HF approximation and coined the term *correlation energy* [19, 20].

The LL reformulation eliminates the restriction of the HK formalism to non-degenerate ground states [21]. Moreover, the $F[n]$ functional is defined for any density $n(\mathbf{r})$ derivable from a wavefunction Ψ . It does not depend on an external potential as the original HK formulation. In Eq. (1.8), $E[n]$ is explicitly a functional of the density and the ground state is found by minimizing $E[n]$.

The Hohenberg and Kohn theorems change the initial problem of minimizing a Hamiltonian of $3N$ -dimensional trial functions into a simpler problem of minimizing $E[n]$ with respect to a 3-dimensional function $n_0(\mathbf{r})$. Moreover, the works of Levy and Lieb generalize the HK formulation to degenerate ground states and clarifies its physical meaning. However, the form of the functional $F[n]$ remains unknown. Altogether, the complicated problem of dealing with interacting electrons remains and further approximations are needed.

1.2.4 The Kohn-Sham (KS) equations

The DFT has become a practical theory only after the work of Kohn-Sham in 1965 [22]. In the Kohn-Sham (KS) approach, the original interacting many-body problem is mapped onto a simpler auxiliary system which can be solved numerically. The auxiliary system consists of independent particles moving in an effective potential v_{eff} . The auxiliary system is fictitious, in the sense, that it does not exist. However, the assumption is made that the ground state density of the auxiliary system is equal to the corresponding density of the interacting many-body system.

The density of the auxiliary system is, thus, the sum of non interacting single particle wavefunctions

$$n(\mathbf{r}) = \sum_i |\varphi_i(\mathbf{r})|^2, \quad (1.9)$$

the independent particle kinetic energy T_s is

$$T_s[n] = \frac{1}{2} \sum_i |\nabla \varphi_i(\mathbf{r})|^2. \quad (1.10)$$

The ground state energy functional becomes:

$$E_s[n] = T_s[n] + \int d\mathbf{r} v_{\text{eff}}(\mathbf{r})n(\mathbf{r}). \quad (1.11)$$

In order to find the ground state density of the interacting system, the energy functional is, hence, minimized with respect to n .

Within the KS method, $E_s[n]$ is decomposed in the following terms:

$$E_s[n] = T_s[n] + \int d\mathbf{r} v_{\text{ext}}(\mathbf{r})n(\mathbf{r}) + E_H[n] + E_{\text{xc}}[n], \quad (1.12)$$

where the Hartree energy, E_H , is

$$E_H[n] = \frac{1}{2} \int \int d^3\mathbf{r} d^3\mathbf{r}' \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}. \quad (1.13)$$

This accounts for a classical Coulomb interaction of the electron density $n(\mathbf{r})$ with itself. The system contains non-interacting electrons, but an interacting density. The last term E_{xc} is the so-called *exchange-correlation* energy which is formally defined as:

$$E_{\text{xc}}[n] = F[n] - T_s[n] - E_H[n]. \quad (1.14)$$

The simple auxiliary system treats the exchange and correlation into $E_{\text{xc}}[n]$, which is unknown.

The solution of the KS auxiliary system is a minimization problem with respect to the density. The variation of the energy functional with respect to the orbitals,

$$\frac{\delta E_s}{\delta \varphi_i^*(\mathbf{r})} = \frac{\delta T_s}{\delta \varphi_i^*(\mathbf{r})} + \left[\frac{\delta E_{\text{eff}}}{\delta n(\mathbf{r})} \right] \frac{\delta n(\mathbf{r})}{\delta \varphi_i^*(\mathbf{r})} = 0,$$

with the orthonormalization constrain of $\langle \varphi_i | \varphi_j \rangle = \delta_{i,j}$, leads to a Schrödinger-like equation:

$$\begin{aligned} \left[-\frac{1}{2} \nabla^2 + v_{\text{eff}}(\mathbf{r}) \right] \varphi_i(\mathbf{r}) &= \epsilon_i \varphi_i(\mathbf{r}) \\ \left[-\frac{1}{2} \nabla^2 + v_{\text{ext}}(\mathbf{r}) + v_H([n], \mathbf{r}) + v_{\text{xc}}([n], \mathbf{r}) \right] \varphi_i(\mathbf{r}) &= \epsilon_i \varphi_i(\mathbf{r}) \end{aligned} \quad (1.15)$$

with the Hartree potential v_H and the exchange-correlation potential v_{xc} defined as:

$$v_H([n], \mathbf{r}) = \frac{\delta E_H}{\delta n(\mathbf{r})}, \text{ and, } v_{\text{xc}}([n], \mathbf{r}) = \frac{\delta E_{\text{xc}}}{\delta n(\mathbf{r})}. \quad (1.16)$$

Eqs. (1.9)-(1.15) are the so-called KS equations. The effective potential $v_{\text{eff}}(n(\mathbf{r}))$ depends on the density, which is obtained from the wavefunctions, and hence from solving the equations. Therefore, the equations need to be solved self-consistently. Starting from a trial density, the effective potential ($v_{\text{eff}} = v_{\text{ext}} + v_H + v_{\text{xc}}$) is constructed. A new density is then obtained from Eqs. (1.9)-(1.15). This procedure is

repeated until the total energy or v_{eff} converges to some value within a given tolerance.

All quantities in the KS equations are known except for the exchange correlation potential v_{xc} . In fact, the DFT accuracy depends on the approximations to this functional. The most popular approximation to v_{xc} is the local density approximation (LDA). This was already proposed in the seminal paper of KS [22] as a local contribution taken from the homogeneous electron gas theory,

$$E_{\text{xc}}^{\text{LDA}} = \int d^3\mathbf{r} n(\mathbf{r}) \epsilon_{\text{xc}}^{\text{hom}}(n(\mathbf{r})), \quad (1.17)$$

where $\epsilon_{\text{xc}}^{\text{hom}}(n(\mathbf{r}))$ is the exchange and correlation energy per electron for a homogeneous electron gas of density n .

A refinement of the LDA, is the generalized-gradient approximation (GGA) [14]. Here, the XC functional also depends on the density gradient,

$$E_{\text{xc}}^{\text{GGA}} = \int d^3\mathbf{r} f[n(\mathbf{r}), \nabla n(\mathbf{r})], \quad (1.18)$$

where the $f[n(\mathbf{r}), \nabla n(\mathbf{r})]$ is a general functional and there exist several forms of it already in use.

In comparison with LDA, GGA improves the treatment of structural energy differences, atomization energies, energy barriers and total energies [14]. In particular, the ground state of 3d transition metals is better described within GGA [23]. However, some properties are in better agreement with experiments in LDA due to cancellation of errors. For example, the graphite interplanar distance is largely overestimated within GGA [24], while it is in almost perfect agreement with the experiments within LDA [25, 26].

1.2.5 DFT in real systems

The DFT has an enormous impact on the quantum chemistry and physics communities. It has been successful in describing ground state properties (structural parameters, total energies, ...) of a wide range of materials. Even though, the ground state density is exact within DFT, there are intrinsic problematics of this theory and other failures due to the approximations to the XC potential.

Among the intrinsic problems of the DFT theory we can cite:

- The Kohn-Sham eigenstates are those of the auxiliary system, and not those of the real system. Hence, they are just mathematical objects which do not have a physical meaning.

- Different sets of wavefunctions can have the same state density.
- The DFT is a ground state theory and excited states cannot be described. Hence, an excited state theory such as time-dependent DFT (TDDFT) or MBPT is required to model, for instance, optical and transport properties.
- The energy bandwidths are expected to be underestimated even with the unknown exact XC potential, because of derivative discontinuities of the exchange-correlation energy. To know more on this refer to Ref. [27].

Some of the failures due to the usual approximations to the XC potential (LDA and GGA) are

- The fundamental band gap is systematically underestimated in semiconductors and insulators by about 30% to 40% [28, 29]. This is the well known *band-gap problem*. Note that even if the exact XC energy were known, there would be an underestimation of the gap due to derivative discontinuities of the XC energy [27].
- Inter-band gaps in metallic systems can be also underestimated [10, 11].
- The long range form of the usual XC approximations does not have the correct decay. Hence, low-coupling systems dominated by Van der Waals (vdW) interactions are out of reach for these theories. However, recently theoretical works have successfully included vdW interactions within DFT with more sophisticated XC functionals [30, 31].

Some of the problematics cited here are overcome with more appropriate theories such as the MBPT and TDDFT. MBPT treats explicitly electron correlations, as will be explained in the following sections.

1.3 Many-body perturbation theory (MBPT): the *GW* approximation

As seen in the previous section, the DFT is a ground state theory, which successfully predicts the structural and other ground state properties of the system. However, it has some limitation when it comes to simulating optical, transport and other excited state properties of the system.

A more appropriate technique is the so called many-body perturbation theory (MBPT), where the excited state of the system is obtained as a perturbation with respect to a known reference system (usually the ground state of the system). In particular, we will discuss here only the *GW* approximation. MBPT is based in the Green's function formalism, which gives access to the ground state of the system such as DFT does. Moreover, it also enables the computation of the excitation spectra of the system. In fact, the poles of the Green's function are the excitation energies of the system.

In MBPT the exchange and correlation energies are treated by a non-local, frequency dependent and antihermitian operator, usually named as the self-energy operator, $\hat{\Sigma}(\omega, \mathbf{r}, \mathbf{r}')$. This is a much more complex operator than the local exchange-correlation potential $\hat{V}_{xc}(\mathbf{r})$ in the Kohn-Sham equations.

The evaluation of such a complex operator is, hence, highly demanding of computing resources and several approximations to this self-energy are usually employed. In this section, we give an introduction to the *GW* formalism and to the most common approximations to it. In section 1.3.1, a brief introduction to second quantization is given. This is the basis to understand the equations behind MBPT. In section 1.3.2, an overview of Green's functions is provided. In section 1.3.3, the spectral representation of the Green's functions is presented. This representation clarifies its physical meaning. In section 1.3.4, the Green's functions for interacting and non-interacting systems is given with the aim of understanding the implications of many-body interactions. In section 1.3.5, the quasiparticle equation is introduced. This is the homologous of the KS equation in MBPT. In section 1.3.6, the Hedin's equations are introduced. These are a closed set of equations used to solve the many-body problem. In section 1.3.7, we introduce the *GW* approximation. In section 1.3.8, CHSX, a static approximation to *GW* is reviewed. In section 1.3.9, the standard *GW* technique, the so-called G_0W_0 is introduced. The success and failures of this technique are discussed in section 1.3.10. In section 1.3.11, a more refined *GW* approximation, the QPSCGW technique, is reviewed. In section 1.3.12, the integration technique known as the plasmon-pole model (PPM) is introduced. For convenience, in section 1.3.13, we provide a summary of the MBPT approximations used in this work.

1.3.1 Second quantization

Historically, quantum physics first dealt only with the quantization of the motion of particles, the surrounding environment being treated

with classical fields (e.g. electrical or magnetic). In this original form, denoted first quantization (FQ), particles are associated to wavefunctions which are the solution of the Schrödinger equation. This wavefunction can be a single-particle function φ or a many-particle function Ψ for a fixed number of particles. Later, it was found that also the fields are quantized and the particles themselves got represented by quantum fields, leading to the development of quantum field theory, also called second quantization (SQ). The particle field is associated to an operator $\hat{\psi}(\mathbf{r}, t)$ that creates or destroys the particle at particular point in space. SQ greatly simplifies the description of many-interacting particles.

The field operator is defined in terms of single particle eigenstates φ_k as

$$\hat{\psi}(\mathbf{r}, t) = \sum_{\mathbf{k}} \hat{a}_{\mathbf{k}} \varphi_{\mathbf{k}}(\mathbf{r}) \quad (1.19a)$$

$$\hat{\psi}^\dagger(\mathbf{r}, t) = \sum_{\mathbf{k}} \hat{a}_{\mathbf{k}}^\dagger \varphi_{\mathbf{k}}^*(\mathbf{r}) \quad (1.19b)$$

where $\hat{a}_{\mathbf{k}}^\dagger$ ($\hat{a}_{\mathbf{k}}$) is known as the *creation (annihilation) operator* because it creates (destroys) an electron at a particular state $\mathbf{k}$. This definition implies that a quantized wavefunction creates or destroys a wave-packet centered at $\mathbf{r}$. It sets the main difference between classical fields and quantum fields, the appearance of particles. In other words, a quantum field is no longer thought as a continuous field but as an entity that is composed of discrete particles.

The formalism of SQ is useful for the description of many-body systems where the number of particles may change due to dynamics. It is a powerful tool to treat manybody effects. It uses creation and annihilation operators which change the number of particles. Therefore, it is useful to describe Green's functions in terms of addition and of removal particles from the system, as it will be shown in the following sections.

A more complete review of SQ can be found elsewhere in Refs. [32, 33, 34].

1.3.2 Green's functions formalism

In mathematics, Green's functions are used to solve inhomogeneous differential equations of the form:

$$L(q_1, q_2, \dots, q_N)G(q_1, q_2, \dots, q_N) = - \prod_i \delta(q_i - q'_i), \quad (1.20)$$

where L is a linear combination of differential operators acting on distributions at the generalized coordinates q_i (this can be space and/or

time variables). Green's functions are named after its creator, the mathematician George Green.

The time-dependent Schrödinger equation,

$$\left(-i\frac{\delta}{\delta t} + \hat{H}(\mathbf{r})\right) \Psi(\mathbf{r}, t) = 0,$$

can be changed to a Green's functions problem for the differential operator $L = -i\frac{\delta}{\delta t} + \hat{H}(\mathbf{r})$, such that

$$\left(-i\frac{\delta}{\delta t} - \hat{H}(\mathbf{r})\right) G(\mathbf{r}, \mathbf{r}'; t, t') = -\delta(\mathbf{r}, \mathbf{r}')\delta(t - t'). \quad (1.21)$$

A solution to Eq. (1.21) is the so-called single-particle Green's function

$$G(\mathbf{r}, t; \mathbf{r}', t') = -i \langle \Psi_0 | \mathcal{T} \left\{ \hat{\psi}(\mathbf{r}, t) \hat{\psi}^\dagger(\mathbf{r}', t') \right\} | \Psi_0 \rangle, \quad (1.22)$$

where, $\mathcal{T}$ is the time-ordering operator

$$\mathcal{T} \left\{ \hat{\psi}(\mathbf{r}, t) \hat{\psi}^\dagger(\mathbf{r}', t') \right\} = \begin{cases} \hat{\psi}(\mathbf{r}, t) \hat{\psi}^\dagger(\mathbf{r}', t') & , \quad t > t' \\ -\hat{\psi}^\dagger(\mathbf{r}', t') \hat{\psi}(\mathbf{r}, t) & , \quad t < t' \end{cases}.$$

That is,

$$\begin{aligned} G(\mathbf{r}, \mathbf{r}'; t, t') = & -i \langle \Psi_0 | \hat{\psi}(\mathbf{r}, t) \hat{\psi}^\dagger(\mathbf{r}', t') | \Psi_0 \rangle \Theta(t - t') \\ & + i \langle \Psi_0 | \hat{\psi}^\dagger(\mathbf{r}', t') \hat{\psi}(\mathbf{r}, t) | \Psi_0 \rangle \Theta(t' - t), \\ \Theta(t) = & \begin{cases} 1 & , \quad t > 0 \\ 0 & , \quad t < 0 \end{cases} \end{aligned} \quad (1.23)$$

Therefore, for $t > t'$ the Green's function represents the propagation of a particle from point $(\mathbf{r}', t')$ to point $(\mathbf{r}, t)$. For $t < t'$, it represents the propagation of a hole.

The Green's function is the main quantity to find because many relevant properties of the system can be calculated from it. In particular, the expectation value of any particle observable in the ground state, the ground state of the system and the excitation spectra of the system. The last point will be more clear when we revise the Green's function in a different representation in the following section.

1.3.3 The spectral representation

The Green's function can be represented in the spectral representation which clarifies its physical interpretation. Starting with Eq. (1.23),

by introducing the closure relation, $\sum |\Psi_M^s\rangle\langle\Psi_M^s| = 1$, where $|\Psi_M^s\rangle$ is the excited state s of a system of M particles,

$$\begin{aligned} G(\mathbf{r}, \mathbf{r}'; t, t') = & - i\Theta(t - t') \sum_s \langle\Psi_0|\hat{\psi}(\mathbf{r}, t)|\Psi_{N+1}^s\rangle\langle\Psi_{N+1}^s|\hat{\psi}^\dagger(\mathbf{r}', t')|\Psi_0\rangle \\ & + i\Theta(t' - t) \sum_s \langle\Psi_0|\hat{\psi}^\dagger(\mathbf{r}', t')|\Psi_{N-1}^s\rangle\langle\Psi_{N-1}^s|\hat{\psi}(\mathbf{r}, t)|\Psi_0\rangle, \end{aligned} \quad (1.24)$$

where we have used the fact that due to the creation-annihilation operators only the terms for $N + 1$ and $N - 1$ electrons survive in the first and second terms of the equation, respectively.

By introducing the Heisenberg picture for the wave field operator, $\hat{\psi}(\mathbf{r}, t) = e^{i\hat{H}t}\hat{\psi}(\mathbf{r})e^{-i\hat{H}t}$, and by setting $\tau = t - t'$,

$$\begin{aligned} G(\mathbf{r}, \mathbf{r}'; \tau) = & - i\Theta(\tau) \sum_s \langle\Psi_0|\hat{\psi}(\mathbf{r})|\Psi_{N+1}^s\rangle \\ & \times \langle\Psi_{N+1}^s|\hat{\psi}^\dagger(\mathbf{r}')|\Psi_0\rangle e^{i(E_N^0 - E_{N+1}^s)\tau} \\ & + i\Theta(-\tau) \sum_s \langle\Psi_0|\hat{\psi}^\dagger(\mathbf{r}')|\Psi_{N-1}^s\rangle\langle\Psi_{N-1}^s| \\ & \times \hat{\psi}(\mathbf{r})|\Psi_0\rangle e^{-i(E_N^0 - E_{N-1}^s)\tau}, \end{aligned} \quad (1.25)$$

which can be rewritten in a more compact form as,

$$\begin{aligned} G(\mathbf{r}, \mathbf{r}'; \tau) = & -i \sum_s f_s(\mathbf{r}) f_s^*(\mathbf{r}') \exp(-i\epsilon_s \tau) \\ & \times [\Theta(\tau)\Theta(\epsilon_s - \mu) - \Theta(-\tau)\Theta(\mu - \epsilon_s)], \end{aligned} \quad (1.26)$$

where μ is the chemical potential of the system, the Lehman amplitudes f_s and the eigenvalues ϵ_s are

$$f_s(\mathbf{r}) = \begin{cases} \langle\Psi_0|\hat{\psi}(\mathbf{r})|\Psi_{N+1}^s\rangle, & \epsilon_s = E_{N+1}^s - E_N^0, \quad \text{if } \epsilon_s \geq \mu \\ \langle\Psi_{N-1}^s|\hat{\psi}(\mathbf{r})|\Psi_0\rangle, & \epsilon_s = E_N^0 - E_{N-1}^s, \quad \text{if } \epsilon_s < \mu \end{cases} \quad (1.27)$$

The Lehman amplitudes connect the Ψ_0 state to the excited states Ψ_{N+1}^s and Ψ_{N-1}^s states by a creation and annihilation of one electron, respectively. Notice that the eigenvalues $\epsilon_s = E_{N+1}^s - E_N^0$ and $\epsilon_s = E_N^0 - E_{N-1}^s$ correspond to the addition and removal energies of one electron, which are measured directly in photo-emission experiments.

In the general case, the Lehman amplitudes $f_s(\mathbf{r})$ are not normalized and they are not linearly independent. However, they fulfill the completeness rule

$$\sum_s f_s(\mathbf{r}) f_s^*(\mathbf{r}') = \langle\Psi_0|\hat{\psi}(\mathbf{r})\hat{\psi}^\dagger(\mathbf{r}') + \hat{\psi}^\dagger(\mathbf{r}')\hat{\psi}(\mathbf{r})|\Psi_0\rangle = \delta(\mathbf{r} - \mathbf{r}'). \quad (1.28)$$

After a temporal Fourier transform of Eq. (1.26), the Green's function can be rewritten in the Lehman or spectral representation as:

$$G(\mathbf{r}, \mathbf{r}', \omega) = \sum_s \frac{f_s(\mathbf{r}) f_s^*(\mathbf{r}')}{\omega - \epsilon_s - i\eta \operatorname{sgn}(\mu - \epsilon_s)}, \quad (1.29)$$

where η is an infinitesimal positive number. From Eqs. (1.29) and (1.27), it is clear that the poles of the Green's function are the addition and removal energies of the system.

Taking the imaginary part of Eq. (1.29), the spectral function is found,

$$\pm A(\mathbf{r}, \mathbf{r}'; \omega) = \frac{1}{\pi} \operatorname{Im} (G(\mathbf{r}, \mathbf{r}'; \omega)) = \pm \sum_s f_s(\mathbf{r}) f_s^*(\mathbf{r}') \delta(\omega - \epsilon_s). \quad (1.30)$$

The right side of the equation shows that the spectral function is a sort of density of available states. It is weighted by the Lehman amplitudes f_s (f_s^*), which give the probability to find the system in an excited state with $N + 1$ ($N - 1$) electrons, after the addition (removal) of an electron. The spectral function is, hence, connected directly with important quantities measured experimentally.

The Green's function can be expressed in terms of the spectral function, in the so-called *spectral representation*:

$$G(\mathbf{r}, \mathbf{r}'; \omega) = \int_{-\infty}^{E_F} d\omega' \frac{A(\mathbf{r}, \mathbf{r}'; \omega')}{\omega - \omega' - i\eta} + \int_{E_F}^{\infty} d\omega' \frac{A(\mathbf{r}, \mathbf{r}'; \omega')}{\omega - \omega' + i\eta} \quad (1.31)$$

This states that the spectral function itself contains the same amount of information than the Green's function.

1.3.4 Interacting and non-interacting spectral function

In the non-interacting picture, the spectral function has a simple form

$$\pm A(\mathbf{r}, \mathbf{r}'; \omega) = \pm \sum_i \varphi_i(\mathbf{r}) \varphi_i^*(\mathbf{r}') \delta(\omega - \epsilon_i), \quad (1.32)$$

where φ_i are non-interacting wavefunctions with energies ϵ_i . Hence, the matrix element $A_{ii}(\omega)$ is simply a delta peak centered at ϵ_i ,

$$A_{ii}(\omega) = \langle \varphi_i(\mathbf{r}) | A(\mathbf{r}, \mathbf{r}'; \omega) | \varphi_i(\mathbf{r}) \rangle = \delta(\omega - \epsilon_i). \quad (1.33)$$

In fact, A_{ii} gives the amplitude of the oscillations at frequency ω when adding or removing a particle from the ground state in the state ϕ_i . The form of A_{ii} in the non-interacting and interacting cases is shown in

Fig. 1.2 taken from Ref. [35]. While in the non-interacting case, $A_{ii}(\omega)$ is a delta peak indicating that this state is stable; in the interacting case, $A_{ii}(\omega)$ presents a finite width, indicating that the state presents a life-time. That is, this excited state oscillates for some time before the system goes back to its ground state. These states are known as *quasiparticles*. A second peak may appear in the interacting case, this is a typical satellite plasmon peak. This is interpreted as an excited state made by a quasiparticle plus a plasmon.

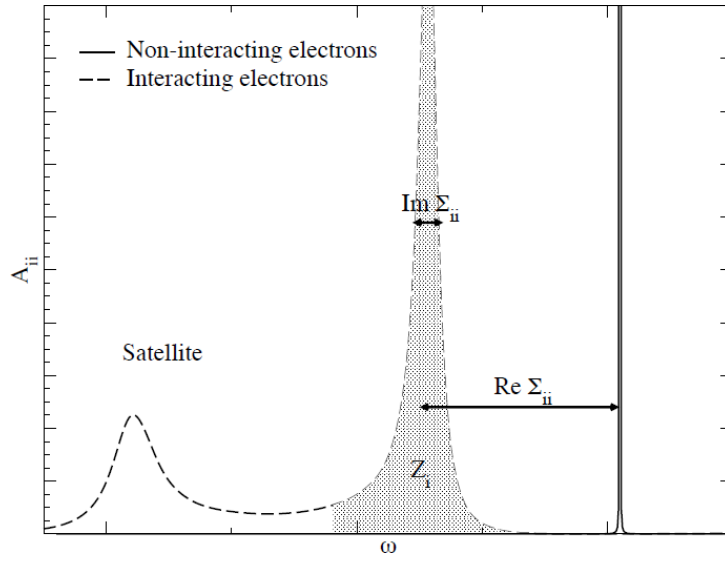


Figure 1.2: Schematic representation of the spectral function $A_{ii}(\omega)$. In the non-interacting case $A_{ii}(\omega)$ is a delta peak. In the interacting case, the matrix elements have a width and a satellite peak may appear. Taken from Ref. [35].

1.3.5 The quasiparticle equation

As in DFT, where we have a closed set of KS equations, in MBPT, the quasiparticle equation has to be solved. In this equation, a self-energy operator $\Sigma(\mathbf{r}, \mathbf{r}', \omega)$ contains the particle correlations. This object is more complicated than the local $v_{xc}(\mathbf{r})$ of the KS theory, giving rise to complex poles and particle life-times.

The Dyson equation connects the Green's function of the non interacting system, G_0 , to $G(1, 2)$. It is written as

$$G(1, 2) = G_0(1, 2) + \int d(3, 4) G_0(1, 3) \Sigma(3, 4) G(4, 2), \quad (1.34)$$

where Σ is the self-energy operator, a non-hermitian, non-local and frequency-dependent operator. In this section, we adopt a different nomenclature, where integer numbers denote time and position. For example, $G(1, 2) = G(\mathbf{r}, \mathbf{r}'; t, t')$.

By introducing the equation of motion for G , the so called *quasiparticle equation* is obtained,

$$\left[-\frac{\nabla^2}{2} + v_{\text{ext}}(\mathbf{r}) + v_{\text{H}}(\mathbf{r}) \right] \varphi_s(\mathbf{r}, \omega) + \int d\mathbf{r}' \Sigma(\mathbf{r}, \mathbf{r}', \omega) \varphi_s(\mathbf{r}', \omega) = \epsilon_s(\omega) \varphi_s(\mathbf{r}, \omega), \quad (1.35)$$

where $\epsilon_s(\omega)$ are the poles of the Green's function, which give the addition and removal energies of the system. Due to the complex form of Σ , the poles $\epsilon_s(\omega)$ are now complex energies.

Here all the exchange and correlation is contained in the self-energy. And, as in the DFT case, we need to find a suitable approximation Σ . Notice that the quasiparticle equation reduces to the Hartree equation when $\Sigma = 0$, to the HF one when $\Sigma = iGv$ (where v is the bare Coulomb potential), and to the KS equation when $\Sigma = v_{\text{xc}}(\mathbf{r})$. This explains the fact that usually DFT calculations are in good agreement with MBPT ones, given that $v_{\text{xc}}(\mathbf{r})$ is a good approximation to $\Sigma(\mathbf{r}, \mathbf{r}', \omega)$.

1.3.6 The Hedin's equations

Similarly to the DFT, in which $v_{\text{xc}}(\mathbf{r})$ is approximated, in MBPT we have to find a suitable expression for the self-energy Σ . A solution is given in a set of equations proposed by Hedin [15], where Σ is implicitly defined:

$$\begin{aligned} \Sigma(12) &= i \int G(13) \Gamma(324) W(41) d(34); \\ W(12) &= v(12) + \int v(13) \tilde{\chi}(34) W(42) d(34); \\ \tilde{\chi}(12) &= -i \int G(13) G(41) \Gamma(342) d(34); \\ \Gamma(123) &= \delta(12) \delta(13) + \int \frac{\delta \Sigma(12)}{\delta G(45)} G(46) G(75) \Gamma(673) d(4567), \end{aligned} \quad (1.36)$$

where Γ is known as the vertex function, $\tilde{\chi}$ is the irreducible polarizability and W is the dynamical screened potential. The latter is defined as:

$$W(12) = \int d3 v(13) \varepsilon^{-1}(32), \quad (1.37)$$

where ε is the dielectric function of the system.

The Hedin Eqs. (1.36) together with the Dyson Eq. (1.34) form a closed set of equations which should be solved self-consistently. Starting from a given Σ and G , Γ is calculated. Then, $\tilde{\chi}$ is evaluated, followed by W and finally Σ . At this step, a new G is found, and this procedure is repeated until convergence in G is reached. This is sketched in the Hedin's pentagon in Fig. 1.3

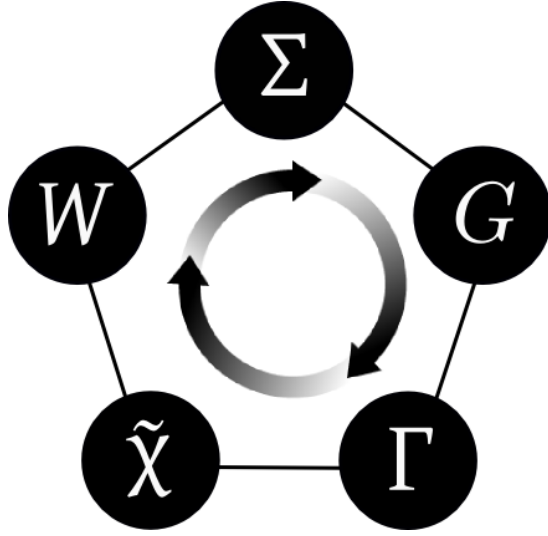


Figure 1.3: Schematic representation of the solution of the Hedin's equation.

1.3.7 The GW approximation

The Green's function of the interacting system, $G(12)$, cannot be calculated exactly for real systems and further approximations are needed. A common approximation is to neglect vertex effects by setting $\Gamma(123) = \delta(12)\delta(13)$, and to perform only one iteration of the Hedin's pentagon in the so-called GW approximation [36]. Within this approximation, the self-energy becomes:

$$\Sigma(12) = iW(1^+2)G(12), \quad (1.38)$$

which gives the name to this approach. Moreover, the screened interaction reduces to,

$$W(12) = v(12) + \int d(34)W(13)\tilde{\chi}(34)v(42) \quad (1.39)$$

Finally, the irreducible polarizability becomes

$$\tilde{\chi}(12) = -iG(12)G(21) \equiv \chi_0(12), \quad (1.40)$$

where χ_0 is the independent particle polarizability.

1.3.8 The CHSX approximation

Performing a Fourier transform from time to energy, the GW self-energy in Eq. (1.38) can be rewritten as

$$\Sigma(\mathbf{r}, \mathbf{r}'; \omega) = \frac{i}{2\pi} \int d\tau W(\mathbf{r}, \mathbf{r}'; \tau) G(\mathbf{r}, \mathbf{r}'; \tau) e^{i\omega\tau}. \quad (1.41)$$

If the screened potential is static,

$$W(\mathbf{r}, \mathbf{r}'; \tau) = \frac{1}{2\pi} W(\mathbf{r}, \mathbf{r}'; \omega = 0) \delta(\tau) \quad (1.42)$$

the integral in Eq. (1.41) becomes

$$\Sigma(\mathbf{r}, \mathbf{r}'; \omega) = \frac{i}{2\pi} \int d\tau W(\mathbf{r}, \mathbf{r}'; \omega = 0) G(\mathbf{r}, \mathbf{r}'; \tau) \delta(\tau + \eta) e^{i\omega\tau}, \quad (1.43)$$

where η is a small positive number.

Introducing the definition of the Green's function in Eq. (1.26), and neglecting the contributions from the unoccupied states (first term in Eq. (1.26)), the self-energy becomes:

$$\Sigma_{\text{SX}}(\mathbf{r}, \mathbf{r}') = -W(\mathbf{r}, \mathbf{r}'; \omega = 0) \langle \Psi_0 | \hat{\psi}^\dagger(\mathbf{r}') \hat{\psi}(\mathbf{r}) | \Psi_0 \rangle, \quad (1.44)$$

where the frequency dependency was dropped due to the fact that all of the terms $e^{i(\omega - \epsilon_s)\eta} \rightarrow 1$, when $\eta \rightarrow 0$. This is the so-called screened-exchange (SX) approximation, whose name comes from the fact that it contains only a screened-exchange term. This approximation is similar to the HF approximation, but the bare Coulomb interaction v is replaced by a statically screened Coulomb interaction $W = v\epsilon^{-1}$.

This approximation can be improved when introducing a simple modification, which leads to an additional Coulomb hole term [36]. The screened Coulomb interaction in Eq. (1.39),

$$W(12) = v(12) + \int d(34) W(13) \tilde{\chi}(34) v(42),$$

can be split in two terms: the Coulomb part v , which is instantaneous, and the polarizable part W_p , which has some frequency dependency: $W = v + W_p$. By assuming that W is sharply peaked in τ , the self-energy becomes:

$$\begin{aligned} \Sigma(\mathbf{r}, \mathbf{r}'; \omega) &= \frac{i}{2\pi} \int d\tau [v(\mathbf{r}, \mathbf{r}') \delta(\tau + \eta) \\ &+ W_p(\mathbf{r}, \mathbf{r}'; \omega = 0) \delta(\tau)] G(\mathbf{r}, \mathbf{r}'; \tau) e^{i\omega\tau}, \end{aligned} \quad (1.45)$$

the first term is the HF term, and the second one contains contributions from the occupied states as well since we removed η from its delta function. From this definition and using the relations, $\delta(\tau)\Theta(\tau) = \delta(\tau)\Theta(-\tau) = \frac{1}{2}\delta(\tau)$ ⁴, the self-energy is

$$\begin{aligned} \Sigma(\mathbf{r}, \mathbf{r}') = & - \langle \Psi_0 | \hat{\psi}^\dagger(\mathbf{r}') \hat{\psi}(\mathbf{r}) | \Psi_0 \rangle v(\mathbf{r}, \mathbf{r}') + \frac{1}{2} \left[\langle \Psi_0 | \hat{\psi}(\mathbf{r}) \hat{\psi}^\dagger(\mathbf{r}') | \Psi_0 \rangle \right. \\ & \left. - \langle \Psi_0 | \hat{\psi}^\dagger(\mathbf{r}') \hat{\psi}(\mathbf{r}) | \Psi_0 \rangle \right] W_p(\mathbf{r}, \mathbf{r}'; \omega = 0), \end{aligned} \quad (1.46)$$

by adding and subtracting $\frac{1}{2}\langle \Psi_0 | \hat{\psi}^\dagger(\mathbf{r}') \hat{\psi}(\mathbf{r}) | \Psi_0 \rangle W_p(\mathbf{r}, \mathbf{r}'; \omega = 0)$,

$$\begin{aligned} \Sigma(\mathbf{r}, \mathbf{r}') = & - \langle \Psi_0 | \hat{\psi}^\dagger(\mathbf{r}') \hat{\psi}(\mathbf{r}) | \Psi_0 \rangle W(\mathbf{r}, \mathbf{r}'; \omega = 0) \\ & + \frac{1}{2} \langle \Psi_0 | \left[\hat{\psi}(\mathbf{r}) \hat{\psi}^\dagger(\mathbf{r}') + \hat{\psi}^\dagger(\mathbf{r}') \hat{\psi}(\mathbf{r}) \right] | \Psi_0 \rangle W_p(\mathbf{r}, \mathbf{r}'; \omega = 0) \\ = & - \langle \Psi_0 | \hat{\psi}^\dagger(\mathbf{r}') \hat{\psi}(\mathbf{r}) | \Psi_0 \rangle W(\mathbf{r}, \mathbf{r}'; \omega = 0) \\ & + \frac{1}{2} \delta(\mathbf{r} - \mathbf{r}') W_p(\mathbf{r}, \mathbf{r}'; \omega = 0), \end{aligned} \quad (1.47)$$

where we have used the completeness relation in Eq. (1.28). The first term is the SX term and the second one is known as the Coulomb-hole (CH) term,

$$\Sigma_{\text{CH}}(\mathbf{r}, \mathbf{r}') = \frac{1}{2} \delta(\mathbf{r} - \mathbf{r}') W_p(\mathbf{r}, \mathbf{r}'; \omega = 0). \quad (1.48)$$

The CH term accounts for a classical response of the medium after the addition of a point charge (electron or hole). This classical term is still a crude approximation from the quantum point of view. The treatment of the Coulomb-hole term in quantum-mechanics basis is found in the *GW* approximation, however, it is harder to evaluate.

Eq. (1.47), is known as the Coulomb-hole and screened-exchange (CHSX) approximation, which is static with only contributions from occupied states. This contains more physics than the SX approximation, and it is of a great interest due to the fact that it is much simpler to evaluate than the *GW* approximation.

1.3.9 The G_0W_0 approximation in practice: a perturbative approach

Fully self-consistent *GW* has been successfully applied in simple systems as jellium and model systems [37, 38]. Recently, it has been per-

⁴ The δ function is placed in between the Θ functions to obtain these relations.

formed on molecules [39, 40] and solids [41]. However, the error due to the approximations used in these works remains unknown⁵.

In general, the solution of the GW equations is still an impressive work from the practical point of view and further approximations are usually employed.

The standard GW approach is the so-called one-shot G_0W_0 technique. Here, the QP equations are solved in a perturbative way starting from the KS equations and stopping at the first iteration.

The static version of the QP equation (1.35),

$$\left[-\frac{\nabla^2}{2} + v_{\text{ext}}(\mathbf{r}) + v_{\text{H}}(\mathbf{r}) \right] \varphi_i^{\text{QP}}(\mathbf{r}) + \int d\mathbf{r}' \Sigma(\mathbf{r}, \mathbf{r}', \epsilon_i^{\text{QP}}) \varphi_i^{\text{QP}}(\mathbf{r}') = \epsilon_i^{\text{QP}} \varphi_i^{\text{QP}}(\mathbf{r}),$$

presents similarities to the KS equation (1.15),

$$\left[-\frac{1}{2}\nabla^2 + v_{\text{ext}}(\mathbf{r}) + v_{\text{H}}(\mathbf{r}) \right] \varphi_i^{\text{KS}}(\mathbf{r}) + v_{\text{xc}}(\mathbf{r}) \varphi_i^{\text{KS}}(\mathbf{r}) = \epsilon_i^{\text{KS}} \varphi_i^{\text{KS}}(\mathbf{r}),$$

where φ_i^{QP} and φ_i^{KS} are the QP and KS eigenstates, with eigenenergies ϵ_i^{QP} and ϵ_i^{KS} , respectively. The non-Hermitian part of Σ , which give rise to QP life times and imaginary eigenvalues, is usually neglected.

Assuming that $\varphi^{\text{QP}} \approx \varphi^{\text{KS}}$, premultiplying both equation by $(\varphi_i^{\text{KS}}(\mathbf{r}))^*$, and integrating over $\mathbf{r}$,

$$\langle \varphi_i^{\text{KS}}(\mathbf{r}) | \Sigma(\epsilon_i^{\text{QP}}) | \varphi_i^{\text{KS}}(\mathbf{r}) \rangle - \langle \varphi_i^{\text{KS}}(\mathbf{r}) | v_{\text{xc}} | \varphi_i^{\text{KS}}(\mathbf{r}) \rangle = \epsilon_i^{\text{QP}} - \epsilon_i^{\text{KS}}. \quad (1.49)$$

Since Σ has to be evaluated at the QP energy, which is unknown, we can Taylor expand it around the KS energy, and stop at the first order getting:

$$\Sigma(\epsilon_i^{\text{QP}}) \approx \epsilon_i^{\text{KS}} + (\epsilon_i^{\text{QP}} - \epsilon_i^{\text{KS}}) \left. \frac{\partial \Sigma(\omega)}{\partial \omega} \right|_{\omega=\epsilon_i^{\text{KS}}}. \quad (1.50)$$

By substituting Eq. (1.50) into Eq. (1.49), one can obtain

$$\epsilon_i^{\text{QP}} = \epsilon_i^{\text{KS}} + Z \left[\langle \varphi_i^{\text{KS}}(\mathbf{r}) | \Sigma(\epsilon_i^{\text{KS}}) | \varphi_i^{\text{KS}}(\mathbf{r}) \rangle - \langle \varphi_i^{\text{KS}}(\mathbf{r}) | v_{\text{xc}} | \varphi_i^{\text{KS}}(\mathbf{r}) \rangle \right] \quad (1.51)$$

⁵ Two strong approximations in the works of Refs. [39, 40] can be cited: (1) They use a molecular orbitals (MOs) basis set, a non-systematic basis set, whose completeness at the GW level is difficult to test. (2) The Green's functions are calculated along the imaginary axis. Therefore, to find the QP energies these have to be analytically continued to the real axis. The latter approximation is also used in Ref. [41].

with the normalization factor,

$$Z = \left[1 - \langle \varphi_i^{\text{KS}} | \frac{\partial \Sigma(\omega)}{\partial \omega} \Big|_{\omega=\epsilon_i^{\text{KS}}} | \varphi_i^{\text{KS}} \rangle \right]^{-1}. \quad (1.52)$$

Eq. (1.51) is known as the G_0W_0 approximation, this is a diagonal approximation in the sense that only the diagonal matrix elements of the self-energy (Σ_{ii}) are needed. Hence, only the KS energies are corrected.

1.3.10 Success and failures of the G_0W_0 approximation

This technique has an enormous impact in the physics community and nowadays it is the standard technique to calculate more accurate gaps in solids. Initial calculations done mostly in homogeneous s -electrons and p -electrons such as Si, Ge and diamond showed that the G_0W_0 gaps were in agreement with the experiments within 0.1 eV [42]. In these systems, it was found that the QP wavefunction has more than 99.9% overlap with the KS wavefunction, explaining the accuracy of the calculations.

Years later, it was found that G_0W_0 slightly underestimates the band-gaps of solids [43, 44], as shown in the left panel of Fig. 1.4. In some systems, such as rare-earths, correlated systems and d - and f -electron semiconductors among others, the disagreement with the experiments is bigger [44, 45, 46, 47, 48]. For example, in f -electron systems such as ErAs and in d -electron systems such as InAs, InSb and InN, G_0W_0 predicts narrow-gap insulators in qualitative structure with DFT-LDA but in disagreement with experiments [47].

Moreover, G_0W_0 presents a starting point dependency: different gaps are reported for the same system within G_0W_0 for different XC potentials. For instance, the G_0W_0 gap for the d -electron InN semiconductor in the wurzite phase ranges from 0.02 to 1.6 eV depending on the XC potential; it is 0.02-0.05 eV [49, 50], 0.7-1.0 eV [51, 52] and 1.6 eV [53, 54] when starting from LDA, exact-exchange optimized effective potential (OEPx) and self-interaction corrected potential (SIC), respectively.

1.3.11 The quasi-particle self-consistent GW (QPSCGW) approximation

The quasiparticle self-consistent GW (QPSCGW) method of Kotani *et al.* [45] successfully eliminates the starting point dependency of G_0W_0 . Moreover, it improves the agreement with the experimental band-gaps.

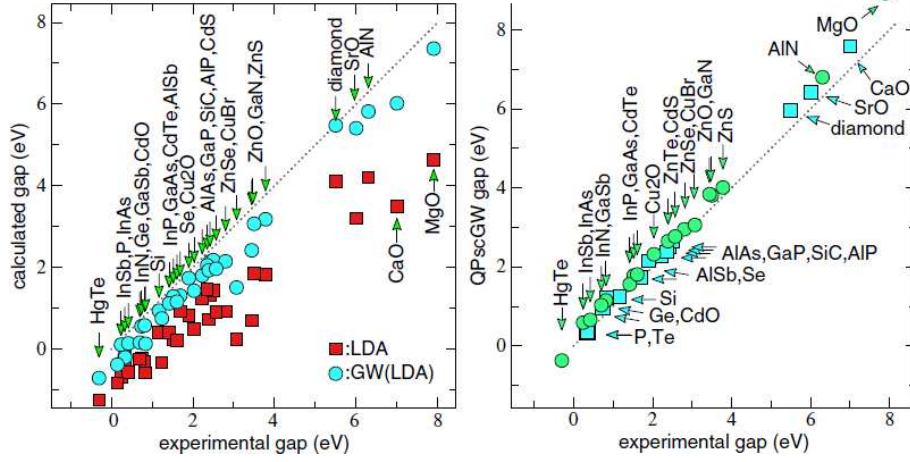


Figure 1.4: GW gaps in solids. Left: Calculated LDA (red squares) and G_0W_0 (cyan circles) gaps vs. experimental gaps. Right: Calculated QPSCGW vs. experimental gaps: the calculated gaps for Zinc-blende compounds are shown in circles, and all others are shown in squares. Taken from Ref. [44].

This method is based on the KS equation, with the XC potential obtained from a G_0W_0 calculation:

$$\begin{aligned} v_{xc} &= \text{Re}[\Sigma(\epsilon_i)] \\ &= \frac{1}{2} \sum_{ij} |\varphi_i\rangle \{ \text{Re}[\langle \varphi_i | \Sigma(\epsilon_i) | \varphi_j \rangle] + \text{Re}[\langle \varphi_i | \Sigma(\epsilon_j) | \varphi_j \rangle] \}, \quad (1.53) \end{aligned}$$

where $\text{Re}[\Sigma(\epsilon_i)]$ is the Hermitian part of $\Sigma(\epsilon_i)$. These new KS equations are then solved self-consistently: starting from v_{xc}^{LDA} , Σ is determined through a G_0W_0 calculation, which determines a new v_{xc} and this is repeated until convergence is reached. At each step, the KS wavefunctions are changed via the non-diagonal elements of Σ . Finally, in some way, the KS states evolve into QP states.

For some systems, the QPSCGW gaps are in better agreement with the experiments than the corresponding G_0W_0 ones, as shown in Fig. 1.4. The QPSCGW gaps are substantially improved in most of the different kinds of materials: alkali metals, semiconductors, insulators, transition metals, transition metal oxides, magnetic insulators and rare earth compounds. Nevertheless, for a few materials the less refined G_0W_0 technique predicts better gaps (see, for instance, the diamond case in the figure).

1.3.12 The plasmon-pole model (PPM)

The expression of Σ within the GW approximation,

$$\Sigma(\mathbf{r}, \mathbf{r}'; \omega) = \frac{i}{2\pi} \int d\omega' W(\mathbf{r}, \mathbf{r}'; \omega') G(\mathbf{r}, \mathbf{r}'; \omega + \omega') e^{i\eta\omega'},$$

contains an integration over an infinite number of frequencies ω' . In practice, this integral is approximated using the plasmon-pole model (PPM), or the more robust contour deformation (CD) method, among others.

The PPM is based in the observation that the largest contribution to $\text{Im}[\epsilon^{-1}(\mathbf{q}, \omega)]$ comes from the sharp peak due to the plasmon pole excitations in the system. Here $\text{Im}[\epsilon^{-1}(\mathbf{q}, \omega)]$ is approximated by a delta peak in frequency, assuming that all of the contribution comes from the plasmon pole excitation, neglecting all possible contributions from electron-hole formation.

The basic expression of the PPM is,

$$\text{Im} \epsilon^{-1}(\mathbf{q}, \omega) = B(\mathbf{q}) \delta(\omega - \omega_{\mathbf{G}, \mathbf{G}'}(\mathbf{q})), \quad (1.54)$$

where $B(\mathbf{q})$ and ω define the width and position of the plasmon peak, respectively. The real part of $\epsilon^{-1}(\mathbf{q}, \omega)$ is obtained from the imaginary part using the Kramers-Kronig relation.

Several plasmon-pole models exist, named after their corresponding authors: Hybertsen-Louie [42], Godby-Needs [55], Von der Linden-Horsch [56] and Engel-Farid [57] (see Ref. [58] for more details). Among these techniques, the PPM of Godby-Needs provides band-gaps with a better agreement with the experiments [59].

A more robust integration technique is the contour deformation (CD) method. Here, the integral over the real axis frequency in Eq. (1.41) is transformed into an integral over a contour in the complex plane plus contributions from outside this contour (see Ref. [58] for more details). Within this method, $W(\omega)$ is, hence, evaluated at only a few real and imaginary frequencies.

1.3.13 Summary of MBPT approximations

The standard MBPT approach to correct the DFT eigenvalues is the single-shot G_0W_0 approximation. Here, the QP equations are solved in a perturbative way starting from the KS equations and stopping at the first iteration. The QP energies within G_0W_0 are obtained from Eq. (1.51) as

$$\epsilon_i^{\text{QP}} = \epsilon_i^{\text{KS}} + Z [\langle \varphi_i^{\text{KS}} | \Sigma(\epsilon_i^{\text{KS}}) | \varphi_i^{\text{KS}} \rangle - \langle \varphi_i^{\text{KS}} | v_{xc} | \varphi_i^{\text{KS}} \rangle],$$

with the normalization factor,

$$Z = \left[1 - \langle \varphi_i^{\text{KS}} | \frac{\partial \Sigma(\omega)}{\partial \omega} \Big|_{\omega=\epsilon_i^{\text{KS}}} | \varphi_i^{\text{KS}} \rangle \right]^{-1}.$$

Beyond G_0W_0 , various self-consistent approaches are used to compute the QP quantities. In GW_0 , only G is updated self-consistently. Here, starting from the KS quantities, a G_0W_0 cycle is done first to find a new set of eigenvalues ϵ^{QP} and W_0 . Keeping W_0 constant, the QP equations are solved self-consistently updating ϵ^{QP} at each iteration. This step is repeated until convergence is reached. GW_0 generally predicts band-gaps in better agreement with the experimental data than G_0W_0 does. To illustrate, in the work of Ref. [43], G_0W_0 and GW_0 were used to obtain the band gap for a series of semiconductors, insulators and noble gas solids. For GW_0 , the mean absolute relative error with respect to the experiments was 5%, whereas for G_0W_0 the corresponding error was 10%. The agreement with experiments was almost perfect for most of the materials, except for materials with shallow d states, such as GaAs, GaN, and ZnO, where the gaps were underestimated. In general, GW_0 predicts band-gaps in remarkably good agreement with the experimental data for semiconductors and insulators (except for systems with shallow d states) at a low price, since W_0 is calculated only once.

In the quasiparticle self-consistent GW (QPSCGW) method, the QP quantities are obtained self-consistently following a set of modified KS equations. Here V_{xc} is found via Eq. (1.53) as

$$v_{xc} = \frac{1}{2} \sum_{ij} |\varphi_i\rangle \{ \text{Re}[\langle \varphi_i | \Sigma(\epsilon_i) | \varphi_j \rangle] + \text{Re}[\langle \varphi_i | \Sigma(\epsilon_j) | \varphi_j \rangle] \}.$$

A useful static approximation to the GW method, is the Coulomb-hole and screened-exchange (CHSX) approximation. As in the HF approximation, the contributions from the unoccupied states are neglected. Here, the self-energy is given by Eq. (1.47):

$$\begin{aligned} \Sigma(\mathbf{r}, \mathbf{r}') &= -\langle \Psi_0 | \hat{\psi}^\dagger(\mathbf{r}') \hat{\psi}(\mathbf{r}) | \Psi_0 \rangle W(\mathbf{r}, \mathbf{r}'; \omega = 0) \\ &\quad + \frac{1}{2} \delta(\mathbf{r} - \mathbf{r}') W_p(\mathbf{r}, \mathbf{r}'; \omega = 0), \end{aligned}$$

where the first term accounts for a classical response of the medium after the addition of a point charge (electron or hole) and the second term accounts for a static exchange.

Beyond the GW approximation, extra electron-hole correlations can be included through the vertex term Γ in the $G\Gamma W$ approximation [60].

In this work, we use this approach within the different GW approximations. For instance, $G_0W_0\Gamma$ refers to the G_0W_0 approximation plus the Γ term. Similarly, QPSCGWT ($GW_0\Gamma$) refers to the QPSCGW (GW_0) approximation including the Γ term at each iteration.

1.4 Maximally-localized Wannier functions (MLWFs)

The electronic structure of a periodic system is represented using Bloch states. A Bloch wave or Bloch state is the wavefunction of a particle in a periodic potential. These waves are by nature periodical and delocalized in space. In 1937, Gregory Wannier proposed a set of localized orbitals, known as Wannier functions [16]. These can be obtained from the Bloch states of the system by means of a unitary transformation. Wannier functions have a big impact on many areas of the physics community, due to their localization and to the fact that they represent a minimal basis set. Nevertheless, Wannier functions are non-unique. There is a freedom of choice of the unitary transformation matrix from Bloch to Wannier representation.

This gauge freedom was further exploited by N. Marzari and D. Vanderbilt, who proposed a set of uniquely defined and maximally localized Wannier functions (MLWFs) [17]. These are the solid-state equivalent of the Boys formulation for localized molecular orbitals in chemistry [61]. They are based on a localization algorithm which finds the optimal unitary matrix which best localizes the Wannier functions. This algorithm is independent of the initial electronic basis set, and it can be extended to QP states [62].

MLWFs are useful in numerous applications. Their spread and center is connected to the chemical nature of the system. For instance, they can provide a deep understanding of the bonding nature and the kind of coordination. In fact, MLWFs can be interpreted as a classical picture of localization of an electron (or electron pair) in the system, or a local density associated to an electron. This connects the MLWFs to the modern theory of polarization, which directly relates the Wannier centers to the macroscopic polarization [63]. Moreover, this classical interpretation connects the MLWFs centers and spreads to force field classical methods [64], including the calculation of van-der-Waals interactions [24]. Besides the above points, MLWFs present exponential localization, which allows for efficient interpolation of Hamiltonians, Fermi surfaces, and other operators [65]. MLWFs are also used as a minimal basis set to construct tight-binding like Hamiltonians for large scale

calculations. These include ballistic transport [66], strongly-correlated electrons [67, 68], electron-phonon coupling [69] and even G_0W_0 calculations [70], among others.

The section is organized as follows: In section 1.4.1, the Bloch theorem is introduced. In section 1.4.2, a formal introduction to Wannier functions is presented. In section 1.4.3, the uniquely defined set of MLWFs is introduced. In section 1.4.4, the procedure to obtain MLWFs from Bloch functions is presented. In section 1.4.5, the particular case of MLWFs for entangled bands is commented. In section 1.4.6, the initial guess, one of the practical issues of the procedure to obtain MLWFs, is explained. Finally, in section 1.4.7, the interpolation technique based on MLWFs, one of the common applications of MLWF, is introduced.

1.4.1 Bloch's theorem

An electron in a periodic potential $V(\mathbf{r})$ (*e.g.*, in a crystal) is governed by the Schrödinger equation of the form

$$\left(\frac{1}{2}\nabla^2 + V(\mathbf{r})\right)\varphi(\mathbf{r}) = E\varphi(\mathbf{r}), \quad (1.55)$$

where $V(\mathbf{r})$ has the translational symmetry of the lattice, $V(\mathbf{r} + \mathbf{R}) = V(\mathbf{r})$.

The Bloch theorem states, that the solution of Eq. (1.55) has the following form:

$$\varphi_{\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}}u_{\mathbf{k}}(\mathbf{r}), \quad (1.56)$$

where $u_{\mathbf{k}}$ has the periodicity of the potential, $u(\mathbf{r} + \mathbf{R}) = u(\mathbf{r})$, and $\mathbf{k}$ is the wave vector, a quantity related to the momentum of the particle. The state $\varphi_{\mathbf{k}}$ of the form of Eq. (1.56), is known as a Bloch wave or Bloch state.

Figure 1.5 shows a graphical representation of a Bloch wave. The dashed curve represents a free wave $e^{i\mathbf{k}\cdot\mathbf{r}}$. The solid curve represents the Bloch wave, in which the wavefunction is modulated by $u_{\mathbf{k}}(\mathbf{r})$. This implies that in a crystal an electron propagates like a free particle, but the wavefunction amplitude is modulated by $u_{\mathbf{k}}(\mathbf{r})$.

The Bloch function $\varphi_{\mathbf{k}}(\mathbf{r})$ is delocalized throughout the crystal. That is, the electron is not confined around any particular atom, but it has a non-zero probability to be anywhere in the solid.

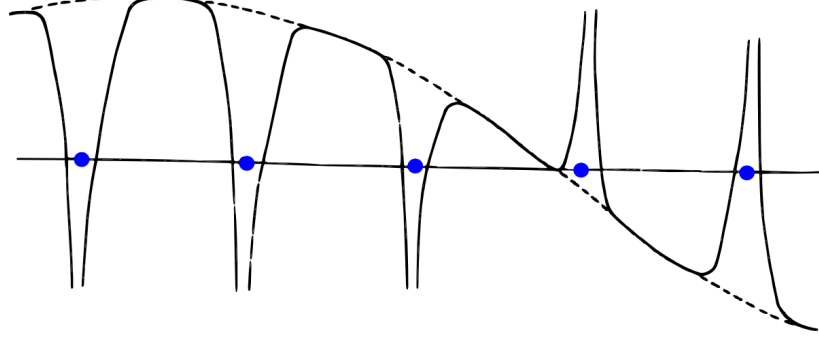


Figure 1.5: Graphical representation of a Bloch wave. The dashed curve represents the wave $e^{i\mathbf{k}\cdot\mathbf{r}}$. The solid curve represents the Bloch wave, which is modulated by $u_{\mathbf{k}}(\mathbf{r})$. The blue dots represent atom centers along a line.

1.4.2 Wannier functions

Starting from Bloch functions $\varphi_{n\mathbf{k}}$, Wannier functions, $\mathcal{W}_{n\mathbf{k}}$, can be obtained by a unitary transformation of the following form:

$$\mathcal{W}_{\mathbf{R}n}(\mathbf{r}) = \frac{\Omega}{(2\pi)^3} \int_{BZ} d\mathbf{k} e^{-i\mathbf{k}\cdot\mathbf{R}} e^{i\phi_n(\mathbf{k})} \varphi_{n\mathbf{k}}(\mathbf{r}), \quad (1.57)$$

where $\mathbf{R}$ are lattice vectors in real space, Ω is the unit-cell volume, and $e^{i\phi_i(\mathbf{k})}$ is a non-unique phase factor. When instead of a single band n , a set of N Bloch bands are to be transformed, this phase factor becomes a unitary matrix, $U_{mn}^{(\mathbf{k})}$ of dimension $N \times N$. Therefore, the general expression to transform Bloch functions to Wannier functions is:

$$\mathcal{W}_{\mathbf{R}n}(\mathbf{r}) = \frac{\Omega}{(2\pi)^3} \int_{BZ} d\mathbf{k} e^{-i\mathbf{k}\cdot\mathbf{R}} \sum_{m=1}^N U_{mn}^{(\mathbf{k})} \varphi_{m\mathbf{k}}(\mathbf{r}). \quad (1.58)$$

Similarly, the Bloch functions can be written in terms of Wannier functions as follows:

$$\varphi_{m\mathbf{k}}(\mathbf{r}) = \frac{\Omega}{(2\pi)^3} \int_{BZ} d\mathbf{k} e^{i\mathbf{k}\cdot\mathbf{R}} \sum_{n=1}^N (U_{mn}^{(\mathbf{k})})^\dagger \mathcal{W}_{\mathbf{R}n}(\mathbf{r}). \quad (1.59)$$

The non-uniqueness of $U_{mn}^{(\mathbf{k})}$ or $\mathcal{W}_{\mathbf{R}n}$ can be exploited to find the $U_{mn}^{(\mathbf{k})}$ in such a way that the resulting Wannier functions have a desired form.

1.4.3 Maximally-localized Wannier functions

In 1997, N. Marzari and D. Vanderbilt [17] proposed a method to reduce the arbitrariness of $U_{mn}^{(\mathbf{k})}$ by choosing the transformation matrix

which best minimizes the spread functional,

$$S = \sum_{n=1}^N [\langle \mathcal{W}_{0n} | r^2 | \mathcal{W}_{0n} \rangle - |\langle \mathcal{W}_{0n} | \mathbf{r} | \mathcal{W}_{0n} \rangle|^2], \quad (1.60)$$

The unique set of Wannier functions obtained with the $U_{mn}^{(\mathbf{k})}$ which minimizes the spread functional are named maximally-localized Wannier-functions (MLWFs).

There are several consequences of choosing this transformation matrix:

1. MLWFs are uniquely defined.
2. MLWFs look like the molecular-orbitals studied in chemistry. MLWFs are referred to as the solid state equivalent to the chemistry molecular orbitals. Although, there is no formal proof of this assumption, it is generally accepted.
3. MLWFs present an exponential localization. This conjecture has been demonstrated in 1D [12, 71, 72] and in 2D and 3D [73].
4. MLWFs are real. This conjecture has no formal proof, however, it is supported by empirical experience. In general, the $\text{Re}(\mathcal{W}_n)/\text{Im}(\mathcal{W}_n)$ ratio is taken as a criteria to tell how "good" the Wannier functions are after the minimization of the spread S .

1.4.4 Procedure

By substituting the general expression for a Wannier function, Eq. (1.58), into the spread functional, Eq. (1.60), the matrix elements of the position $\mathbf{r}$ and its second moment r^2 can be expressed in terms of $u_{n\mathbf{k}}$ [71],

$$\langle \mathcal{W}_{0n} | \mathbf{r} | \mathcal{W}_{0n} \rangle = i \frac{\omega}{(2\pi)^3} \int d\mathbf{k} \langle u_{n\mathbf{k}} | \nabla | u_{n\mathbf{k}} \rangle, \quad (1.61)$$

$$\langle \mathcal{W}_{0n} | r^2 | \mathcal{W}_{0n} \rangle = i \frac{\omega}{(2\pi)^3} \int d\mathbf{k} \langle u_{n\mathbf{k}} | \nabla_{\mathbf{k}}^2 | u_{n\mathbf{k}} \rangle. \quad (1.62)$$

These two equations are needed to express the spread S in terms of the matrix elements of ∇^2 and ∇ . Hence, once these derivatives have been calculated, one can proceed with the minimization of S , without the need for any other quantity.

Since the integrations in Eq. (1.58) are approximated by sums in the BZ on Monkhorst pack grids of $\mathbf{k}$ -points. The only ingredient needed to

calculate these gradients and Lapacians are the matrix elements between Bloch orbitals at neighboring $\mathbf{k}$ -points,

$$M_{mn}^{(\mathbf{k},\mathbf{b})} = \langle u_{m\mathbf{k}} | u_{n,\mathbf{k}+\mathbf{b}} \rangle, \quad (1.63)$$

where $\mathbf{b}$ are vectors connecting the $\mathbf{k}$ -points to its nearest neighbors.

After some algebra, the matrix elements of the position operator and its second moment can be expressed in term of this matrix as [17]

$$\langle \mathcal{W}_{0n} | \mathbf{r} | \mathcal{W}_{0n} \rangle = -\frac{1}{N} \sum_{\mathbf{k},\mathbf{b}} w_{\mathbf{b}} \mathbf{b} \operatorname{Im} \ln M_{mn}^{(\mathbf{k},\mathbf{b})} \quad (1.64)$$

$$\begin{aligned} \langle \mathcal{W}_{0n} | r^2 | \mathcal{W}_{0n} \rangle &= -\frac{1}{N} \sum_{\mathbf{k},\mathbf{b}} w_{\mathbf{b}} \left\{ \left[1 - |M_{mn}^{(\mathbf{k},\mathbf{b})}|^2 \right] \right. \\ &\quad \left. + \left[\operatorname{Im} \ln M_{mn}^{(\mathbf{k},\mathbf{b})} \right]^2 \right\} \end{aligned} \quad (1.65)$$

Since all of the required quantities are now expressed in terms of the overlaps $M_{mn}^{(\mathbf{k},\mathbf{b})}$, this matrix becomes the central quantity in the formalism. After the $M_{mn}^{(\mathbf{k},\mathbf{b})}$ matrix is constructed the minimization of the spread performed as explained in Ref. [17].

The fact, that the formalism is based on the overlap matrix, makes this procedure independent on the initial basis used to express the Bloch orbitals. That is, the procedure can be used with plane-waves, localized orbitals or hybrid basis.

1.4.5 Entangled bands

The general procedure introduced in the preceding section applies only to composite bands, a set of bands which is isolated in energy from other bands. When Wannier functions are constructed for entangled bands, a set of bands which is not isolated, a *disentangling* procedure is used [74].

For the isolated-group case, S can be divided in $S = S_I + \tilde{S}$, where S_I is invariant with respect to the choice of U . That is, S_I is calculated directly from $M_{mn}^{(\mathbf{k},\mathbf{b})}$ and only $\tilde{S}$ is optimized to find the MLWFs.

For entangled bands, we need to extract N MLWFs from $N_{\mathbf{k}} > N$ Bloch bands. First, a subspace of N Bloch-like functions, $\tilde{\phi}$, is constructed for each $\mathbf{k}$ point,

$$\tilde{\phi}_{n\mathbf{k}}(\mathbf{r}) = \sum_{m=1}^{N_{\mathbf{k}}} D_{mn}^{(\mathbf{k})} \varphi_{m\mathbf{k}}(\mathbf{r}), \quad (1.66)$$

where $D_{mn}^{(\mathbf{k})}$ is $N_{\mathbf{k}} \times N$. A new overlap matrix is constructed as $M'^{\mathbf{k},\mathbf{b}} = D^{(\mathbf{k})} \dagger M^{(\mathbf{k},\mathbf{b})} D^{(\mathbf{k}+\mathbf{b})}$. Then, S_I is minimized with respect to $D^{(\mathbf{k})}$ in a self-consistent procedure [74].

S_I , in a sense, measures the smoothness of connections along neighboring $\mathbf{k}$ -points. Thus, by minimizing S_I , a subspace with a minimum of mismatch at neighboring $\mathbf{k}$ -points is chosen. Hence, we can disentangle a subspace of well-localized bands of a given character inside a given energy window.

After the minimization of S_I , a new Hamiltonian is obtained as

$$H'_{mn}(\mathbf{k}) = \sum_{l=1}^{N_{\mathbf{k}}} D_{lm}^{*(\mathbf{k})} \epsilon_{\mathbf{k}l} D_{ln}^{(\mathbf{k})}. \quad (1.67)$$

This Hamiltonian contains only $N \times N$ elements, thus, we can start the *wannierization* procedure from it as in the isolated-bands case. After a diagonalization of this new Hamiltonian, a new set of eigenvalues $\tilde{\epsilon}_{m\mathbf{k}}$ and eigenvectors $\tilde{\varphi}_{m\mathbf{k}}(\mathbf{r})$ are obtained. These are used to obtain the Wannier functions as,

$$\mathcal{W}_{\mathbf{R}n}(\mathbf{r}) = e^{i\phi} \frac{\Omega}{(2\pi)^3} \int_{BZ} d\mathbf{k} e^{-i\mathbf{k}\cdot\mathbf{R}} \sum_{m=1}^N \tilde{U}_{mn}^{(\mathbf{k})} \tilde{\varphi}_{m\mathbf{k}}(\mathbf{r}), \quad (1.68)$$

where the term $e^{i\phi}$ is an arbitrary overall phase, which is, generally, not zero for disentangled bands. The MLWFs are, hence, obtained from the minimization of $\tilde{S}$ with respect to $\tilde{U}$ as in the isolated case. Finally, the rotation matrix for entangled bands is simply $U = \tilde{D}\tilde{U}$. Eq. (1.68) is the general expression for Wannier functions. For isolated bands, U is simply equal to $\tilde{U}$.

In Fig. 1.6 we show the 5-*d* bands of gold bulk obtained with MLWFs. These were disentangled from the 6-*s* bands. The *d* bands, being highly localized, can be disentangled by minimizing S_I . The Wannier interpolated bandstructure (red lines) with the technique introduced in section. 1.4.7. are in good agreement with the bandstructure calculated explicitly by a non-self-consistent field calculation (black points). Along the $\Gamma - X$ and $L - \Gamma$ paths, there are interpolated bands which do not correspond to the bands calculated explicitly. This disagreement results from the disentangling procedure. During this procedure, the subspace of 5*d* bands is extracted from hybridized 5*d* and 6*s* bands, moreover, a smoothness of the 5*d* subspace is imposed along neighboring $\mathbf{k}$ -points, resulting in band regions which do not coincide with the bands calculated explicitly (these regions smoothly connect the subspace of 5*d* bands).

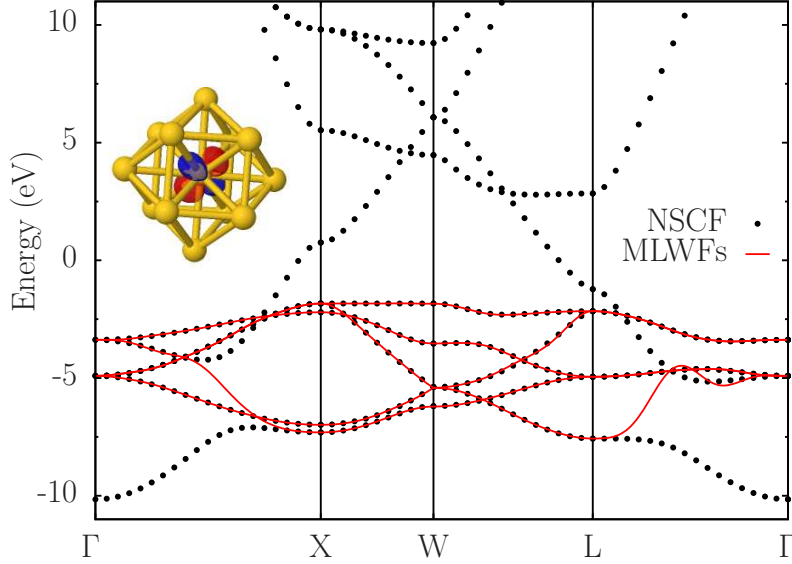


Figure 1.6: 5d bands of gold bulk (red lines) interpolated with MLWFs. The bandstructure obtained with a NSCF calculation is shown in black points. A representative 5d MLWF is shown as an inset.

1.4.6 Initial guess

The minimization of the spread S is started by an initial guess. This is done by starting on chemically motivated initial functions. A set of N guiding functions $g_n(\mathbf{r})$ are constructed, having an appropriate center and chemical character, such as s , p or sp^3 among others. Then, a $N_{\mathbf{k}} \times N$ matrix $A_{mn}^{(\mathbf{k})}$ is constructed as:

$$A_{mn}^{(\mathbf{k})} = \langle \varphi_{m\mathbf{k}} | g_n \rangle. \quad (1.69)$$

After an orthonormalization procedure, the $A_{mn}^{(\mathbf{k})}$ is used to form a starting approximation to $U_{mn}^{(\mathbf{k})}$.

The starting guess is quite important to obtain Wannier functions for entangled bands, conduction bands and metallic systems. The shape of the Wannier functions depends strongly on the initial shape of the guiding functions. To illustrate in Fig. 1.7, different Wannier functions for the lowest $N > 4$ silicon bulk bands are shown. They correspond to different starting points. When starting from a random initial guess, there is a high probability to find 8 sp^3 -backward Wannier functions, with $S = 2.56 \text{ \AA}^2$, (see Fig. 1.7a). They do not correspond to chemical orbitals. Another initial guess can lead to 8 sp^3 -forward Wannier

functions (see Fig. 1.7b), with $S = 2.95 \text{ \AA}^2$, corresponding to the chemical sp^3 orbitals. One can also find 4 sp^3 -forward on one Si atom and 4 sp^3 -backward Wannier functions on the other one. Moreover, 4 bonding (see Fig. 1.7c) plus 4 anti-bonding (see Fig. 1.7d) Wannier functions can also be found. These have a spread of 1.70 and $5.09 \text{ \AA}^2$, respectively. Therefore, the MLWFs associated to the lowest $N > 4$ bands of silicon are the 8 sp^3 -backwards Wannier functions. Alternatively, the MLWFs associated to the isolated valence-manifold ($N = 4$) are the 4 bonding Wannier functions.

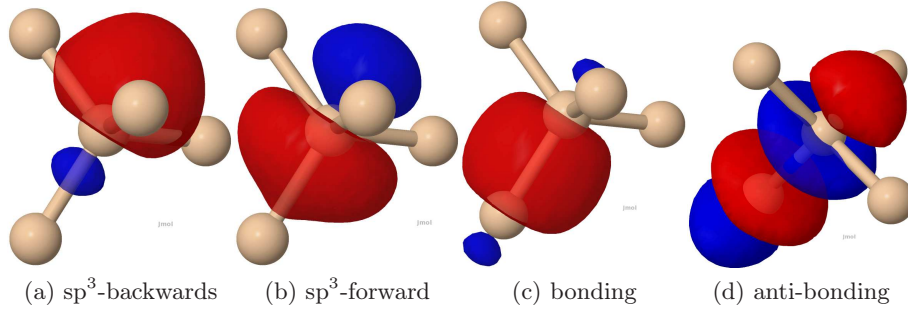


Figure 1.7: Wannier functions for silicon: red and blue colors indicate opposite isovalues. silicon atoms in the FCC tetrahedra are represented by brown spheres.

1.4.7 Interpolation of matrix-elements

The high localization of MLWFs makes them a powerful interpolation tool [65]. The matrix elements, $\mathcal{O}_{mn}^{\mathbf{k}} = \langle \varphi_{m\mathbf{k}} | \hat{\mathcal{O}} | \varphi_{n\mathbf{k}} \rangle$, of a given operator $\hat{\mathcal{O}}$, can be interpolated to arbitrary $\mathbf{k}$ -points, whenever $\mathcal{O}_{mn}$ present a fast-decay in real space.

First, the operator is converted into Wannier basis,

$$\mathcal{O}_{mn}^{\mathcal{W}(\mathbf{k})} = \sum_{j=1}^{N_{\mathbf{k}}} \sum_{i=1}^{N_{\mathbf{k}}} U_{im}^{\dagger}(\mathbf{k}) \mathcal{O}_{ij}(\mathbf{k}) U_{jn}(\mathbf{k}). \quad (1.70)$$

Then, it is Fourier transformed into real space,

$$\mathcal{O}_{mn}^{\mathcal{W}}(\mathbf{R}) = \frac{1}{N_{kp}} \sum_{\mathbf{k}} e^{-i\mathbf{k} \cdot \mathbf{R}} \mathcal{O}_{mn}^{\mathcal{W}}(\mathbf{k}), \quad (1.71)$$

where N_{kp} is the number of $\mathbf{k}$ -points in the irreducible Brillouin zone (IBZ).

Then, the operator can be obtained for any arbitrary $\mathbf{k}'$ point, with an inverse Fourier transform,

$$\mathcal{O}_{mn}^{\mathcal{W}(\mathbf{k}')} = \sum_{\mathbf{R}} e^{i\mathbf{k}\cdot\mathbf{r}} \mathcal{O}_{mn}^{\mathcal{W}}(\mathbf{R}). \quad (1.72)$$

Finally, it is rotated back into Bloch space, as follows,

$$\mathcal{O}_{ij}^{(\mathbf{k}')} = \sum_{n=1}^N \sum_{m=1}^N U_{im}^{(\mathbf{k}')} \mathcal{O}_{mn}^{\mathcal{W}(\mathbf{k})} U_{jn}^{\dagger(\mathbf{k}')}. \quad (1.73)$$

In order to find the U at $\mathbf{k}'$, the above procedure is repeated with $\mathcal{O} = \hat{H}$, then the rotation matrices are found such that $U^{\dagger(\mathbf{k}')} H^{\mathcal{W}(\mathbf{k}')} U^{(\mathbf{k})} = H^{\mathbf{k}'}$. However, for diagonal operators in Bloch space, such as the Hamiltonian, $\mathcal{O}_{mn}^{\mathcal{W}(\mathbf{k}')}$ in Eq. (1.72) is simply diagonalized.

This leads to a very rapid and efficient interpolation algorithm. In particular, information about $\mathbf{k}$ -points connectivity is kept due to the $M_{mn}^{(\mathbf{k},\mathbf{b})}$ matrices. Moreover, this technique is not limited to DFT quantities, but also, it is applicable to GW quantities [62].

1.5 Quantum transport

In physics, transport phenomena refer to processes involving motion of matter. These include momentum, energy and mass transfer. Transport, is hence, a wide concept. In this section, however, we use this general term to refer to only electronic transport.

Starting from a classical approach, charge transport in macroscopic systems is governed by the *Ohm's law*

$$V = RI, \quad (1.74)$$

where V is the applied voltage, R is the *resistance* of the material and I is the current.

When matter approaches the nanoscale, special properties of matter start to appear, and one has to rely on quantum mechanics. Different approaches are used to simulate the transport on mesoscopic and nanoscale systems, such as the Landauer approach and the Kubo formalism, among others.

The purpose of this section is to introduce the preliminary concepts of electronic transport at the nano-level. The section is organized as follows. In section 1.5.1, we deal with the Drude model, a classical approach. In section 1.5.2, we introduce the concept of ballistic regime.

Here, the quantization of the conductance is also explained. In section 1.5.3, the Landauer formula, an approach for the ballistic regime, is explained. In section 1.5.4, the Landauer formulation for the non-zero temperature case is derived. In section 1.5.5, the Landauer-Büttiker formalism, a more general approach, is introduced. Finally, a practical *ab initio* approach to calculate the transport properties within the Landauer-Büttiker formalism is explained in section 1.5.6.

1.5.1 The Drude model

From the classical point of view, the electrical current can be seen as a consequence of an applied electric field, *i.e.*, the current is the response to the field. The *current density* $\mathbf{j}$ along a macroscopic conductor is proportional to the applied electric field $\mathbf{E}$,

$$\mathbf{j} = \sigma \mathbf{E}, \quad (1.75)$$

where σ is the *conductivity*. Assuming that the conductor is uniform with *resistivity* $\rho = 1/\sigma$, area A and length L ; the conductance, $\mathcal{G}$, is given by,

$$\mathcal{G} = \frac{1}{R} = \sigma \frac{A}{L}. \quad (1.76)$$

This relation only holds for *ohmic conductors*, those obeying the Ohm's law in Eq. (1.74). This is the case of macroscopic conductors, however, this is not always true for mesoscopic systems (systems with intermediate size between microscopic and macroscopic systems) and this is not true for nanoscopic systems (systems measuring a few-nanometers). A conductor shows ohmic behavior if its dimensions are much larger than three *characteristic lengths*: (1) the phase relaxation length, (2) the De Broglie wavelength and (3) the mean free path.

To understand these microscopic quantities, consider electrons traveling with an average velocity v in a crystal as sketched in Fig. 1.8. Electrons undergo scattering events; collisions with other electrons, or scattering from phonons, or from other particles.

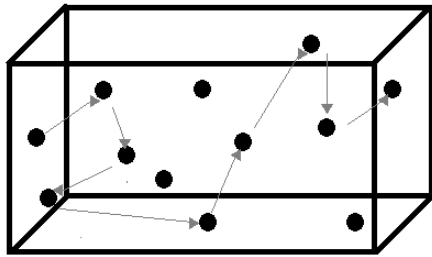


Figure 1.8: Schematic representation of the path an electron follows inside a crystal. The trajectory changes at the dots due to scattering events.

The *momentum relaxation time*, τ_m , is defined as the time that an electron travels before it loses its initial momentum. The corresponding distance, $L_m = v_F \tau_m$, is known as the *mean free path*, which is given by

$$L_m = v_F \tau_m = \frac{\hbar k_F}{m} \tau_m, \quad (1.77)$$

where v_F is the Fermi velocity, and k_F is the corresponding momentum. The corresponding wavelength $\lambda_F = 2\pi/k_F$ is the *De Broglie wavelength* for electrons with momentum k_F or the *Fermi wavelength*. In general, the *De Broglie wavelength* of a given particle, atom or molecule with momentum k is defined as $\lambda = 2\pi/k$.

The *phase-relaxation length*, L_ϕ , is the average distance which an electron travels before it loses its initial phase. The *phase-relaxation time* is thus $\tau_\phi = L_\phi/v_F$. τ_ϕ has some relation with τ_m , but these are very different concepts. For instance, an electron can experience momentum changes due to collisions, but keeping the same phase. For example, in low-mobility semiconductors, $\tau_\phi \gg \tau_m$ [75].

In the Drude model, these microscopic quantities are related to the macroscopic current density by,

$$\mathbf{j} = \frac{m}{ne^2\tau_m} \mathbf{E}, \quad (1.78)$$

where n is the electron density and e is the elementary charge. The Drude model in Eq. (1.78) results in semiclassical reformulation of the Ohm's law in Eq. (1.74).

1.5.2 The ballistic regime

Transverse modes

When conductors reach the characteristic lengths cited above (non-ohmic conductors), the conductance flows along a number M of transverse modes (or magneto-electric subbands). These are analogous to the transverse modes of electromagnetic waveguides.

Consider a quantum wire confined in the transverse y -direction, subject to a confining potential $U(y)$. The Hamiltonian for this system is,

$$H = \frac{(i\nabla^2 + \mathbf{A})^2}{2} + U(y). \quad (1.79)$$

With the vector potential $\mathbf{A} = (y\mathbf{B}, 0, 0)$ and a parabolic potential of the form $U(y) = 1/2 \omega_0^2 y^2$, the solution of the Schrödinger equation is well known (see Ref. [75]). The wavefunctions can be expressed in form of plane waves,

$$\psi_k(x, y) = e^{ikx} \phi(y), \quad (1.80)$$

where the transverse function $\phi(y)$ satisfy the equation,

$$\left[\frac{(k + y\mathbf{B})^2}{2} + \frac{p_y^2}{2} + U(y) \right] \phi(y) = E\phi(y), \quad (1.81)$$

where $p_y \equiv -i\partial/\partial y$.

This choice of magnetic field and potential U , gives a harmonic oscillator problem for the transverse eigenfunctions $\phi(y)$, with eigenenergies,

$$E_n(k) = (n + \frac{1}{2})\omega_{c0} + \frac{k^2}{2} \frac{\omega_0^2}{\omega_{c0}^2}, \quad (1.82)$$

where $\omega_{c0}^2 \equiv \omega_c^2 + \omega_0^2$ and $\omega_c \equiv \mathbf{B}$ (in atomic units). Thus obtaining magnet-electric subbands labeled by n . They can be reduced to magnetic subbands (Landau levels) when $U=0$, or to electric subbands when $\mathbf{B}=0$. The dispersion relation E vs. k is sketched in Fig. 1.9. In narrow conductors, the different transverse modes are well separated in energy such as electron waveguides.

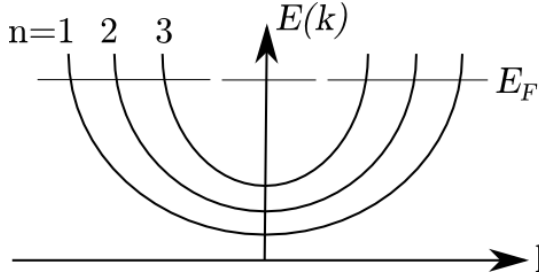


Figure 1.9: Dispersion relation $E(k)$ vs. k . for magneto-electric subbands n in a parabolic potential.

The group velocity for a particular mode n is

$$v_n(k) = \frac{\partial E_n(k)}{\partial k} = k \frac{\omega_0^2}{\omega_{c0}^2}. \quad (1.83)$$

Hence, for unconfined electrons ($U=0$), the group velocity $v_n(k)$ equals 0. That is, electrons in a magnetic field will circulate in orbits and they will not move in any particular direction. This result shows that the quantum confinement is a necessary condition for the transport.

Quantized conductance

When a conductor reaches a length $L = 2\lambda_F$, the conductance is quantized,

$$\mathcal{G} = M \frac{2e^2}{h} = M\mathcal{G}_0 \quad (1.84)$$

where $\mathcal{G}_0 = 77.5\mu S$ is the *quantum of conductance*, and M is the number of transverse modes. In this regime, electrons are not scattered, an electron which enters the conductor has a probability to be transmitted equal to one. This is known as the *ballistic* regime.

Experimentally it has been confirmed that the conductance is quantized in the works of Refs. [76, 77], as shown in Fig. 1.10.

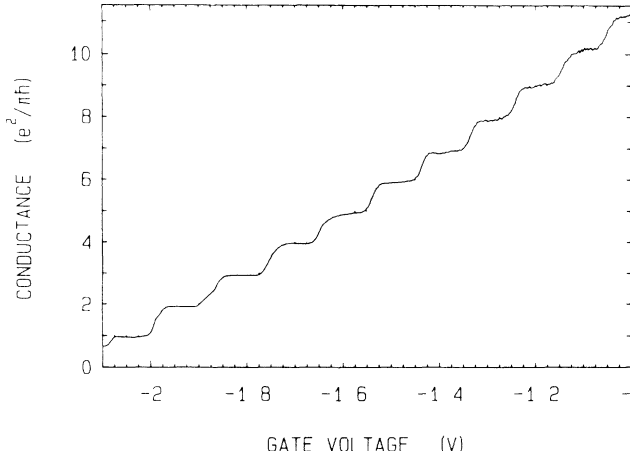


Figure 1.10: Experiment showing that the conductance of a ballistic conductor is quantized. The gate varies reducing M at constant steps. Taken from Ref. [76].

1.5.3 The Landauer conductance

With respect to the Ohm's law, two main corrections are introduced: (1) there is an interface resistance which does not depend on the conductor length L ; and (2) the conductance is quantized, and depends on the number of modes M .

Consider the setup in Fig 1.11: A conductor is attached to the contacts by two leads. The concepts of contacts, leads and conductor require a brief introduction:

- The *channel* or *conductor* region in this regime has a finite number of modes M and a given transmittance T . For the ballistic regime $T = 1$. That is, an electron which enters the channel from the left lead has a probability to be transmitted to the right lead equal to one.
- The *contacts* are considered as external to the system. These are large reservoirs of an infinite number of modes.
- The *leads* are the intermediate part between the contacts and the channel. These allow one to connect the channel to the contacts. The number of modes here is finite.

The Landauer conductance is

$$\mathcal{G} = \mathcal{G}_0 MT. \quad (1.85)$$

For *ballistic* conductors $T = 1$ and we obtain Eq. (1.84). When $T \neq 1$, scattering events can occur in the channel in the *diffusive* regime.

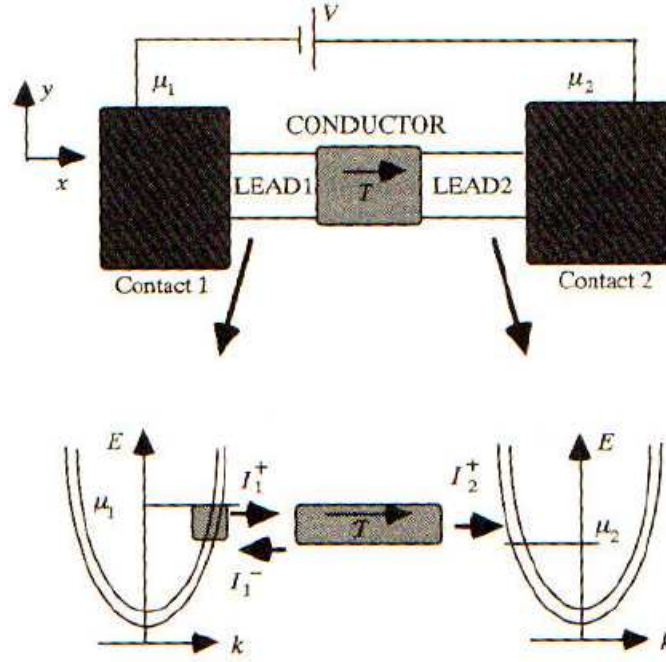


Figure 1.11: (a) Schematic representation of conductor consisting of two contacts and a central conducting region. The conductor is connected to the contacts by two leads. (b) Schematic representation of the energy levels of the conductor and the leads. The chemical potentials of the leads μ_1 and μ_2 are indicated by horizontal lines. Taken from Ref [75].

In this formalism the contacts are assumed to be *reflectionless*. That is, electrons can enter the contacts from the conductor with negligible probability of being reflected. This hypothesis is supported by theoretical calculations in Ref [78]. With respect to Fig. 1.11 (b), states $+k$ in the left lead are occupied only by electrons coming from the left contact, and vice versa, states $-k$ in the right lead are occupied only by electrons coming from the right contact. Hence, these states on the left lead must have the same chemical potential of the left lead μ_1 , whereas, the corresponding states on the right lead have a chemical potential μ_2 .

Due to this assumptions, in the zero-temperature limit, electrons will only flow for states with energy between μ_1 and μ_2 , since states $-k$ and

$+k$ are only filled with electrons within this range of energies. This is shown in Fig 1.12. Each mode, N , has a dispersion relation, $E(N, k)$ with a cut-off energy $\epsilon_N = E(N, k = 0)$, below which the mode cannot propagate. For a number M of conducting modes at an energy E , we have,

$$M(E) = \sum_N \Theta(E - \epsilon_N), \quad (1.86)$$

where Θ is a step function. Since we have non-interacting modes, we can calculate the current for each mode separately and then sum them all to find the total current.

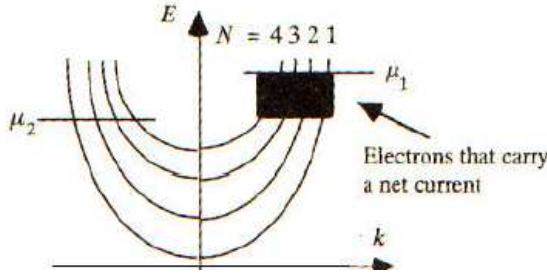


Figure 1.12: Only modes labeled by N with energy between μ_1 and μ_2 carry net current.

Assuming a conductor of length L , with a uniform density n of electrons moving with a velocity v , the current for a single mode is $I = env$. If the states of the system are occupied by a given distribution $n = \sum_k f(E)/L$, it follows that

$$\begin{aligned} I &= env \\ &= \frac{e}{L} \sum_k v f(E) \\ &= \frac{e}{L} \sum_k \frac{1}{\hbar} \frac{dE}{dk} f(E), \end{aligned} \quad (1.87)$$

where we used the definition of the group velocity $v = (dE/dk)/\hbar$. For a continuous number of wave vectors k , the sum in Eq. (1.87) can be approximated by an integral, ($\sum_k \rightarrow 2 \text{ spin} \times (L/2\pi) \int dk$), and hence

$$\begin{aligned} I &= \frac{e}{L} \frac{2L}{2\pi} \int \frac{dk}{\hbar} \frac{dE}{dk} f(E) \\ &= \frac{2e}{h} \int_{\epsilon}^{\infty} f(E) dE, \end{aligned} \quad (1.88)$$

where ϵ is the cutoff energy for that particular mode. For multiple M modes, we have,

$$I = \frac{2e}{h} \int_{\epsilon}^{\infty} f(E) M(E) dE. \quad (1.89)$$

Assuming that $M(E)$ is a constant function over $\mu_1 > E > \mu_2$, this formula can be simplified,

$$I = \frac{2e}{h} M \frac{\mu_1 - \mu_2}{e}, \quad (1.90)$$

with $V = (\mu_1 - \mu_2)/e$ and $\mathcal{G} = I/V$,

$$\mathcal{G} = \frac{2e^2}{h} M. \quad (1.91)$$

In general, T is not necessarily the unity (diffusive regimes), hence, the conductance in Eq. (1.91) becomes the Landauer formula in Eq. (1.85),

$$\mathcal{G} = \frac{2e^2}{h} MT.$$

1.5.4 Non-zero temperature

The Landauer formula in the preceding section was derived for the zero-temperature case and assuming that current just flows in a single channel (from one lead to the other). T was supposed to be constant in the energy range $\mu_1 > E > \mu_2$.

The current can flow in multiple channels (for example, from lead 1 to lead 2 and vice versa). Moreover $\bar{T} = MT$ is different for each channel. With a procedure similar to that of the preceding section, it can be easily verified that the total current is [75],

$$I = \int (E) dE = \int \frac{2e}{h} \bar{T}(E) [f_1(E) - f_2(E)], \quad (1.92)$$

where $f_1(E)$ and $f_2(E)$ are the electron distributions for lead 1 and lead 2, respectively.

When the bias $(\mu_1 - \mu_2)$ is much smaller than $k_B T$, where $k_B T$ is the Boltzmann constant times the temperature, the current is proportional to the applied bias. This is known as the linear response. Assuming a small deviation from the equilibrium state,

$$\delta I = \frac{2e}{h} \int \left([\bar{T}(E)]_{\text{eq}} \delta[f_1 - f_2] + [f_1 - f_2]_{\text{eq}} \delta[\bar{T}(E)] \right) dE. \quad (1.93)$$

The second term is zero at equilibrium ($f_1 = f_2$), and the first term can be rewritten using the first term of a Taylor expansion as:

$$\delta[f_1 - f_2] \approx [\mu_1 - \mu_2] \left[\frac{\partial f}{\partial \mu} \right]_{\text{eq}} = \left[-\frac{\partial f}{\partial E} \right]_{\text{eq}} [\mu_1 - \mu_2]. \quad (1.94)$$

Therefore, the non-zero temperature linear response conductance is

$$\mathcal{G} = \frac{\delta I}{(\mu_1 - \mu_2)/e} = 2 \frac{e^2}{h} \int \bar{T}(E) \left(-\frac{\partial f}{\partial E} \right)_{\text{eq}} dE. \quad (1.95)$$

At low temperatures the Fermi distribution is a Heaviside function, whose derivative is a Dirac delta function, thus,

$$\mathcal{G} = \frac{2e^2}{h} \bar{T}(E_F)_{\text{eq}}. \quad (1.96)$$

This is evaluated at equilibrium indicating that the linear response is an equilibrium property.

1.5.5 Landauer-Büttiker formalism

The above expression can be generalized for multi-terminal devices thanks to the Büttiker formalism. The main idea here is to treat all of the terminals on equal footing, and simply sum over all terminals (labeled by p and q). The current becomes,

$$\begin{aligned} I_p &= \int i_p(E) dE; \\ i_p(E) &= \frac{2e}{h} \sum_q [\bar{T}_{qp}(E) f_p(E) - \bar{T}_{pq}(E) f_q(E)], \end{aligned} \quad (1.97)$$

where $\bar{T}_{qp}(E)$ is the average transmission from p to q at energy E times the number of modes in that channel.

Following a procedure similar to the one shown in the precedent section, the linear response current for a multi-terminal conductor is,

$$\begin{aligned} I_p &= \sum_q \mathcal{G}_{pq} [(f_p - f_q)/e], \text{ where} \\ \mathcal{G}_{pq} &= \frac{2e^2}{h} \int \bar{T}_{pq}(E) \left(-\frac{\partial f}{\partial E} \right)_{\text{eq}} dE. \end{aligned} \quad (1.98)$$

For low temperatures, it gives

$$\mathcal{G}_{pq} = \frac{2e^2}{h} \bar{T}_{pq}(E_F). \quad (1.99)$$

1.5.6 The Landauer-Büttiker formalism from Green's functions.

The Landauer Büttiker formalism is widely used to simulate the transport properties at equilibrium. The applications range from 1D conductors such as nanowires, or nanotubes, to 3D conductors such as molecular junctions with two or more contacts.

At the *ab initio* level, it is a practical formalism thanks to the Fisher–Lee relation, which connects the Landauer expression to the Green's function formalism. The transport properties of a given material can, thus, be simulated by finding the Green's function of the system within DFT or MBPT. In sections 1.5.7–1.5.10, we introduce the Fisher–Lee relation and we review the Green's function formalism.

1.5.7 Retarded and Advanced Green's functions

Coming back to section 1.3, the Green's function of the system contains all ground state plus the excited states of the system. The time-independent version the Green's function in Eq. (1.21) is

$$\left(E - \hat{H}(\mathbf{r})\right) \hat{G}(\mathbf{r}, \mathbf{r}', E) = -\delta(\mathbf{r}, \mathbf{r}'). \quad (1.100)$$

It can be interpreted as the response of the system due to an excitation at point $\mathbf{r}$.

For a system of N non-interacting wavefunctions φ_i , the Green's function in Eq. (1.29), can be rewritten as

$$\hat{G}(\mathbf{r}, \mathbf{r}', E) = \sum_i \frac{\varphi_i(\mathbf{r})\varphi_i^*(\mathbf{r}')}{E - \epsilon_i - i\eta \operatorname{sgn}(\mu - \epsilon_i)}, \quad (1.101)$$

where η is an infinitesimal positive number. This expression contains two separate Green's functions of the form,

$$\hat{G}^r(\mathbf{r}, \mathbf{r}', E) = \sum_i \frac{\varphi_i(\mathbf{r})\varphi_i^*(\mathbf{r}')}{E - \epsilon_i + i\eta}, \text{ and} \quad (1.102)$$

$$\hat{G}^a(\mathbf{r}, \mathbf{r}', E) = \sum_i \frac{\varphi_i(\mathbf{r})\varphi_i^*(\mathbf{r}')}{E - \epsilon_i - i\eta}. \quad (1.103)$$

These are known as the retarded $\hat{G}^r$ and advanced $\hat{G}^a$ Green's functions. The former corresponds to outgoing waves that originate at the point of excitation, whereas the latter corresponds to incoming waves that disappear at the point of excitation. These functions present the following relation:

$$\hat{G}^a = \left(\hat{G}^r\right)^\dagger. \quad (1.104)$$

In general, these are defined as:

$$\hat{G}^r(\mathbf{r}, \mathbf{r}', E) = \left(E - \hat{H}(\mathbf{r}) + i\eta \right)^{-1} \quad (1.105)$$

$$\hat{G}^a(\mathbf{r}, \mathbf{r}', E) = \left(E - \hat{H}(\mathbf{r}) - i\eta \right)^{-1} \quad (1.106)$$

From here on we will refer to the retarded Green's function as just the "Green's function".

1.5.8 Green's functions of the left lead–channel–right lead (LCR) system

The systems considered here have a special layout known as the left lead–channel–right lead (LCR) geometry, which consists of a left-lead (L), a central conducting region (C) and a right lead (R) as shown in Fig. 1.13. In theory, the leads should be infinite; but in practice, they are semi-infinite due to the self-energy matrix $\Sigma^{L/R}$ as explained along this section.

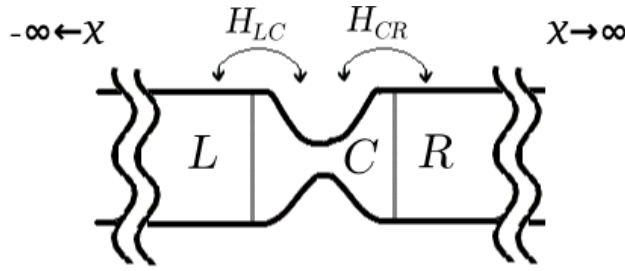


Figure 1.13: Schematic representation of an LCR conductor. The central region C is coupled to the leads via H_{LC} and H_{CR} .

Due to this special geometry, the Hamiltonian can be partitioned into different components:

$$\hat{H} = \hat{H}_L + \hat{H}_R + \hat{H}_C + \hat{H}_{LC} + \hat{H}_{LC}^\dagger + \hat{H}_{CR} + \hat{H}_{CR}^\dagger. \quad (1.107)$$

Here the subindices L , R and C indicate the left, right and central regions, respectively. The elements with two indices, such as LC or CR , are the interaction terms between the corresponding two regions.

With this partition the Schrödinger equation can be expressed as,

$$\begin{bmatrix} \hat{H}_L & \hat{H}_{LC} & 0 \\ \hat{H}_{LC}^\dagger & \hat{H}_C & \hat{H}_{CR}^\dagger \\ 0 & \hat{H}_{CR} & \hat{H}_R \end{bmatrix} \begin{bmatrix} |\varphi_L\rangle \\ |\varphi_C\rangle \\ |\varphi_R\rangle \end{bmatrix} = E \begin{bmatrix} |\varphi_L\rangle \\ |\varphi_C\rangle \\ |\varphi_R\rangle \end{bmatrix},$$

where the states, labeled by $L/R/C$, are single particle eigenstates of the left-lead/right-lead/central-region. That is, they are solutions of the

Schrödinger Equation: $\hat{H}_{L/R/C}|\varphi_{L/R/C}\rangle = E|\varphi_{L/R/C}\rangle$. The interaction terms between the left and right leads are zero in Eq. (1.5.8), since we assume that there is no coupling between the left and right leads. That is, an electron cannot tunnel from one lead to the other.

From Eq. (1.5.8), one can easily obtain,

$$\hat{H}_L|\varphi_L\rangle + \hat{H}_{LC}|\varphi_C\rangle = E|\varphi_L\rangle, \quad (1.108)$$

$$\hat{H}_R|\varphi_R\rangle + \hat{H}_{CR}|\varphi_C\rangle = E|\varphi_R\rangle, \quad (1.109)$$

$$\hat{H}_{LC}^\dagger|\varphi_L\rangle + \hat{H}_C|\varphi_C\rangle + \hat{H}_{CR}^\dagger|\varphi_R\rangle = E|\varphi_C\rangle. \quad (1.110)$$

Using the definition of the Green's functions in Eq. (1.106), Eq. (1.108) and Eq. (1.109), can be expressed as

$$\begin{aligned} |\varphi_L\rangle &= \hat{G}_L(E)\hat{H}_{LC}|\varphi_C\rangle \\ |\varphi_R\rangle &= \hat{G}_R(E)\hat{H}_{CR}|\varphi_C\rangle. \end{aligned} \quad (1.111)$$

By substituting Eqs. (1.111) into Eq. (1.110),

$$\left(E - \hat{H}_C - \hat{\Sigma}_L(E) - \hat{\Sigma}_R(E)\right)|\varphi_C\rangle = 0, \quad (1.112)$$

where the operators,

$$\hat{\Sigma}_L(E) \equiv \hat{H}_{LC}^\dagger \hat{G}_L(E) \hat{H}_{LC}; \quad (1.113)$$

$$\hat{\Sigma}_R(E) \equiv \hat{H}_{CR}^\dagger \hat{G}_R(E) \hat{H}_{CR}, \quad (1.114)$$

are known as the *self-energy* operators of the leads. These can be seen as effective Hamiltonians which arise from the coupling of the conductor with the leads.

The eigenstates ϵ_i of the conductor region C , are modified due to the presence of the leads by the self-energies of the leads. This results in a renormalization of the eigenstates; a net shift, plus a broadening of the states as shown in Fig. 1.14. At the same time, the poles of Green's functions are imaginary as discussed in section 1.3.4, leading to lifetimes for the electrons. These can be interpreted as the electron lifetime to scatter from the central regions to the leads.

Finally, from Eq. (1.112), and the definition of the Green's function in Eq. (1.106), one can obtain the Green's function of the conductor coupled to the leads:

$$\hat{G}_C(E) = \left(E - \hat{H}_C - \hat{\Sigma}_L(E) - \hat{\Sigma}_R(E) \pm i\eta\right)^{-1}. \quad (1.115)$$

At this point, we still have not obtained a practical solution to find the Green's function of the system. Two main problematics arise: (1)

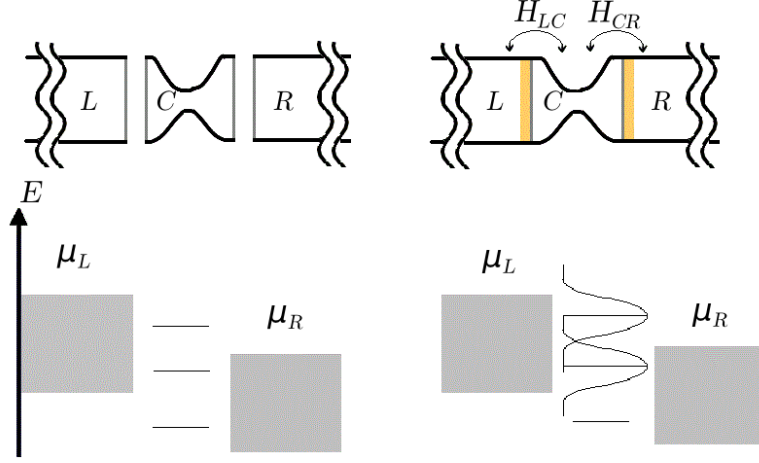


Figure 1.14: Schematic representation of a conductor (top) and its energy levels (down). At the left, the conductor is not coupled to the leads. At the right, the conductor is coupled to the leads, hence, its eigenstates are broadened and shifted.

we do not know an explicit formula to calculate the self-energies of the leads, and (2) the leads are semi-infinite, which means that the matrix elements G_{mn} and H_{mn} for the leads do not have a finite number of elements. These two problems are going to be discussed in the next section.

1.5.9 The transfer-matrices

In the previous section, we have seen that the Green's function of the conductor region is modified by the self-energies, of the leads. However, we still do not know how to calculate the latter. An efficient method to do it is to introduce the transfer matrices T and $\bar{T}$, within the principal layers approach [79, 80].

A principal layer (PL) constitutes the minimal stacking unit for building up the final system. In this case, we refer to a periodic bulk system. For example, in Fig. 1.15 we show that a PL for Au(111) consists of 3 gold layers.

From the general expression of the Green's function in Eq. (1.100),

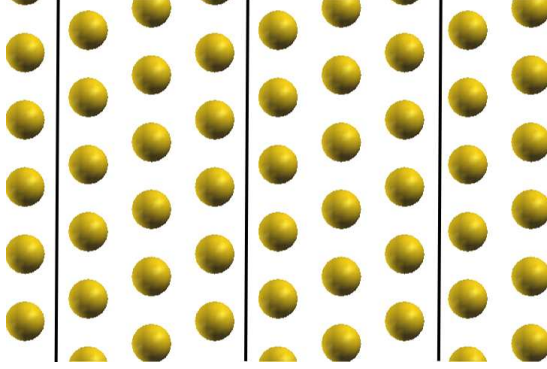


Figure 1.15: Schematic representation of principal layers for gold (111). Au atoms are represented by yellow spheres. Each PL, the basic unit of repetition to construct the crystal, consists of 3 gold layers.

one can obtain a series of matrix equations within the PL approach,

$$\begin{aligned} (E - H_{00})G_{00} &= I + H_{01}G_{10} \\ (E - H_{00})G_{10} &= I + H_{01}^\dagger G_{00} + H_{01}G_{20} \\ &\vdots \end{aligned} \quad (1.116)$$

$$(E - H_{00})G_{n0} = I + H_{01}^\dagger G_{n-1,0} + H_{01}G_{n+1,0}, \quad (1.117)$$

where I is the identity matrix, $\hat{H}_{mn}$ and G_{mn} are matrices of *finite* size, and the subindices m, n denote the corresponding layer. In a bulk system $H_{00} = H_{11} = \dots$ and $H_{01} = H_{12} = \dots$.

Defining,

$$\begin{aligned} t_0 &= (E - H_{00})^{-1} H_{01}^\dagger, \\ \tilde{t}_0 &= (E - H_{00})^{-1} H_{01}, \end{aligned} \quad (1.118)$$

the general expression of Eq. (1.117) can be written as,

$$G_{n0} = (E - H_{00})^{-1} \left(H_{01}^\dagger G_{n-1,0} + H_{01} G_{n+1,0} \right), \quad n \geq 1 \quad (1.119)$$

$$= t_0 G_{n-1,0} + \tilde{t}_0 G_{n+1,0}. \quad (1.120)$$

By substituting $G_{n-1,0}$ and $G_{n+1,0}$ using Eq. (1.119) into Eq. (1.120), a similar expression is found. By doing this iteratively, the following expression is found:

$$G_{n0} = t_i G_{n-2^i,0} + \tilde{t}_i G_{n+2^i,0}, \quad n \geq 2^i. \quad (1.121)$$

where t_i and $\tilde{t}_i$ are defined as:

$$t_i = (I - t_{i-1} \tilde{t}_{i-1} - \tilde{t}_{i-1} t_{i-1})^{-1} t_{i-1}^2, \quad (1.122)$$

$$\tilde{t}_i = (I - t_{i-1} \tilde{t}_{i-1} - \tilde{t}_{i-1} t_{i-1})^{-1} \tilde{t}_{i-1}^2. \quad (1.123)$$

These are evaluated recursively starting from t_0 and $\tilde{t}_0$ in Eq. (1.118). The process is repeated until $t_n, \tilde{t}_n \leq t_{\text{cut}}$, where t_{cut} is a small number.

Evaluating Eq. (1.121) with $n = 2^i$, one can find,

$$\begin{aligned} G_{10} &= t_0 G_{00} + \tilde{t}_0 G_{20} \\ G_{20} &= t_1 G_{00} + \tilde{t}_1 G_{40} \\ &\vdots \\ G_{2^n,0} &= t_n G_{00} + \tilde{t}_n G_{2^{n+1},0}. \end{aligned} \quad (1.124)$$

The first equation of the series can be rewritten using the subsequent equations. By substituting G_{20} of the second equation into the first one, and so on, one can obtain,

$$\begin{aligned} G_{10} &= t_0 G_{00} + \tilde{t}_0 G_{20} \\ &= (t_0 + \tilde{t}_0 t_1) G_{00} + \tilde{t}_1 G_{40} \\ &\vdots \\ &= (t_0 + \tilde{t}_0 t_1 + \tilde{t}_0 \tilde{t}_1 t_2 + \dots + \tilde{t}_0 \dots \tilde{t}_{n-1} t_n) G_{00} + \tilde{t}_n G_{2^{n+1},0}. \end{aligned} \quad (1.125)$$

This is done until $t_n, \tilde{t}_n \leq t_{\text{cut}}$, at that stage we can neglect the second term of the Eq. (1.125), to obtain:

$$G_{10} = T G_{00}, \quad (1.126)$$

where,

$$T = t_0 + \tilde{t}_0 t_1 + \tilde{t}_0 \tilde{t}_1 t_2 + \dots + \tilde{t}_0 \dots \tilde{t}_{n-1} t_n. \quad (1.127)$$

This result is quite important, since from the knowledge of the matrix T one can obtain G_{10} from G_{00} incorporating the effects of 2^n layers.

If instead of starting this procedure for $n \rightarrow \infty$ being a positive number, one starts expanding n for negative values up to $n \rightarrow -\infty$. Then, one can find,

$$G_{00} = \bar{T} G_{10}; \quad (1.128)$$

$$\bar{T} = \tilde{t}_0 + t_0 \tilde{t}_1 + t_0 t_1 \tilde{t}_2 + \dots + t_0 \dots t_{n-1} \tilde{t}_n. \quad (1.129)$$

T and $\bar{T}$ are known as the *transfer matrices*, which allow to calculate all of the matrix elements of G once G_{00} is known.

Taking the last term of Eq. (1.117), setting $n \rightarrow \infty$, and using the relations in Eq. (1.126) and Eq. (1.128),

$$(E - H_{00})G_{n0} - H_{01}G_{n+1,0} - H_{01}^\dagger G_{n-1,0} = I \quad (1.130)$$

$$(E - H_{00} - H_{01}T - H_{01}^\dagger \bar{T})G_{n,0} = I, \quad (1.131)$$

which can be generalized to get all elements G_{mn} . For instance, for $n = 0$, $G_{00} = G_{11} = \dots = G_{nn}$. Hence, we can find the diagonal matrix elements of the bulk Green's function as:

$$G_{nn} = (E - H_{00} - H_{01}T - H_{01}^\dagger \bar{T} \pm i\eta)^{-1}. \quad (1.132)$$

1.5.10 The Fisher-Lee relation

The transmission function can be expressed in terms of the Green's function, thanks to the *Fisher-Lee relation*,

$$\bar{T}(E)_{pq} = \text{tr} \left[\hat{\Gamma}_p \hat{G}_C^r \hat{\Gamma}_q \hat{G}_C^a \right], \quad (1.133)$$

where p and q denote two different contacts, and

$$\hat{\Gamma}_{L,R}(E) = i \left[\hat{\Sigma}_{L,R}^r(E) - \hat{\Sigma}_{L,R}^a(E) \right] = -2\text{Im} \left\{ \hat{\Sigma}_{L,R}^r(E) \right\} \quad (1.134)$$

are known as the *coupling functions*, since they couple the conductor to the leads.

The Green's function gives also the *spectral density of states*:

$$N(E) = -\frac{1}{\pi} \text{Im} [\text{Tr}(G_c(E))] \quad (1.135)$$

1.5.11 The WanT methodology

Along this section, we describe a practical method to obtain the conductance of a material, namely the WanT scheme [66]. This is based on the method developed in Refs. [81, 82, 83].

1.5.12 Transmission through a bulk system

Within the PL approach, it is straightforward to find the self-energies and the Green's functions of a bulk system. Assuming that the Hamiltonian matrix elements of the conductor are equal to those of the principal layer:

$$H_C \equiv H_{00}, \quad (1.136)$$

where we denote the matrix elements of a given operator $\hat{\mathcal{O}}$ by simply $\mathcal{O}$.

By comparing Eq. (1.115) to Eq. (1.132), one can identify:

$$\Sigma_L(E) = H_{01}^\dagger \bar{T} \pm i\eta, \quad \Sigma_R(E) = H_{01}^\dagger T \pm i\eta. \quad (1.137)$$

Hence, the Green's function of the system can be found directly from Eq. (1.132):

$$G_C(E) = (E - H_{00} - H_{01}T - H_{01}^\dagger \bar{T} \pm i\eta)^{-1}. \quad (1.138)$$

By substituting Eqs. (1.137) into Eq. (1.134),

$$\Gamma_L(E) = -2\text{Im} \left\{ H_{01}^\dagger T + i\eta \right\}, \quad \Gamma_C(E) = -2\text{Im} \left\{ H_{01} \bar{T} + i\eta \right\}. \quad (1.139)$$

By doing this, the matrices $\Sigma_{L,R}$ and G_C have finite size. Thus, we arrive to a practical methodology to evaluate the conductance of a bulk system, where the only ingredients are H_{00} and H_{01} (the transfer functions are also obtained from these matrices).

1.5.13 Transmission through a LCR system

Following the path as in the bulk system, we can find the Green's functions of the leads as if they were almost isolated bulk systems [84, 85]. *i.e.*,

$$H_L = H_{00}^L + (H_{01}^L)^\dagger \bar{T} \quad \text{and} \quad (1.140)$$

$$H_R = H_{00}^R + H_{01}^R T. \quad (1.141)$$

Due to the geometry of the system, H_L includes only effects from the PLs $n = -1$ to layer $n \rightarrow -\infty$. Hence, it is only coupled with $\Sigma_L^L = (H_{01}^L)^\dagger \bar{T}$. On the other hand, H_R is only coupled with principal layers at the right hand side.

Thus, the Schrödinger equation (Eq. (1.5.8)) becomes,

$$\begin{bmatrix} H_{00}^L + (H_{01}^L)^\dagger \bar{T} & H_{LC} & 0 \\ H_{LC}^\dagger & H_C & H_{CR}^\dagger \\ 0 & H_{CR} & H_{00}^R + H_{01}^R T \end{bmatrix} \begin{bmatrix} |\varphi_L\rangle \\ |\varphi_C\rangle \\ |\varphi_R\rangle \end{bmatrix} = E \begin{bmatrix} |\varphi_L\rangle \\ |\varphi_C\rangle \\ |\varphi_R\rangle \end{bmatrix}. \quad (1.142)$$

From Eq. (1.142), it is straightforward to find a Green's function in the form of Eq. (1.115):

$$G_C(E) = (E - H_C - \Sigma_L(E) - \Sigma_R(E) \pm i\eta)^{-1},$$

by setting:

$$\Sigma_L(E) = H_{LC}^\dagger \left(E - H_{00}^L - (H_{01}^L)^\dagger \bar{T} \pm i\eta \right)^{-1} H_{LC} \quad (1.143)$$

$$\Sigma_R(E) = H_{CR} \left(E - H_{00}^R - H_{01}^R T \pm i\eta \right)^{-1} H_{CR}^\dagger. \quad (1.144)$$

The transmission can be obtained via the Landauer formula [Eq. (1.85)] and the Fisher-Lee relation [Eq. (1.133)].

The formulas here were developed for 1D systems, such as nanowires, nanotubes, etc. For 3D systems, the formulas can be generalized thanks to the introduction of principal layers. A crystal is modeled at an infinite number of $\mathbf{k}_{\parallel}$, defined as $\mathbf{k}$ -points perpendicular to the transport direction. At each $\mathbf{k}_{\parallel}$, the crystal can be modelled as being a one-dimensional chain of principal layers (n) [86]. This is schematized in Fig. 1.16. This procedure reduces the problem to system of non-interacting 1D chains, one for each $\mathbf{k}_{\parallel}$. This can be reduced to a finite sum over the BZ, giving to each $\mathbf{k}_{\parallel}$ a weight, $w_{\mathbf{k}_{\parallel}}$. Therefore, the transmittance for a 3D system is:

$$\bar{T}(E) = \sum_{\mathbf{k}_{\parallel}} w_{\mathbf{k}_{\parallel}} \bar{T}_{\mathbf{k}_{\parallel}}(E) \quad (1.145)$$

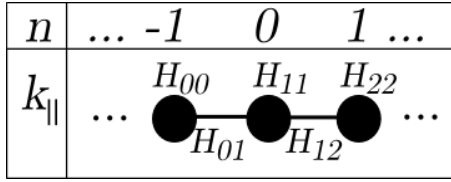


Figure 1.16: For each $\mathbf{k}_{\parallel}$, a crystal can be represented by an infinite 1D chain of principal layers (n). The circles represent principal layers, with Hamiltonians $H_{00}, H_{11}, \dots$. The lines connecting them represent the interaction terms $H_{10}, H_{12}, \dots$.

Chapter 2

Transport properties of molecular junctions from many-body perturbation theory

2.1 Introduction

A single BDT molecule attached to gold leads is among the most studied systems in quantum transport. Since the conductance of this molecule was first measured in the pioneering work of Reed *et al.* [87], this system has been studied extensively by both experimental [88, 89, 90, 91] and theoretical groups [4, 92, 93, 6, 94, 95, 96, 97, 98]. Initially, there was some disagreement between different experimental measurements by up to three orders of magnitude [87, 99, 100]. Nowadays, a consensus has been reached on the value of $0.011 \mathcal{G}_0$ for the zero-bias conductance using the mechanically controllable break junctions technique [88] and the break junction technique [89]. Unfortunately, these experimental strategies to measure the conductance are blind to the geometrical configuration of the junction. In view of this uncertainty, a lot of hope is placed in *ab initio* calculations to determine the atomistic details of the junction. However, there are still open issues on the theoretical side as well, in particular, related to the validity of approximations frequently used within DFT.

Among the most common studied geometries of this system are the hollow geometry (BDT-h) in which the sulfur atom sits at the same distance from 3 surface Au atoms, the pyramid geometry (BDT-p) in which the S atom is position at the top of an extra Au adatom, and the

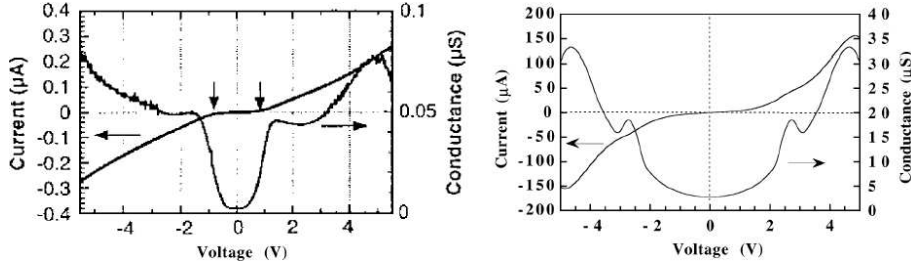


Figure 2.1: Comparison between the experimental and the theoretical I/V characteristics of a benzenedithiolate molecule as a function of the external bias applied to the metallic contacts (taken from Ref. [4]).

non-dissociative Hydrogen geometry (BDT-n) which is similar to BDT-p apart from two extra H atoms bonded to each S atom which are considered not dissociate during the adsorption process. With the *ab-initio* studies of Sellers *et al.*, it was found that the preferred binding site for the -thiol radical is the hollow site [101, 102]. Thereafter, numerous contradicting studies pointed out different adsorption sites [103, 104, 105, 106, 107]. Only recently, it has been found both theoretically and experimentally that the situation in which the H atoms are not-dissociated (BDT-n) is possible and energetically favorable [108, 109].

Initial theoretical calculations were done within DFT for BDT-h or, more simply, for a BDT molecule with featureless jellium leads. The zero-bias conductance was found to be $\sim 0.038\text{--}0.452 \mathcal{G}_0$ [4, 97, 94, 95, 96]. The different conductance values can partly be explained by the different geometries used in these works. In fact, the BDT-h conductance is strongly dependent on the microscopic geometrical details of the junction. In particular, in Ref. [93], it was shown that it can range from 0.16 to 0.77 $\mathcal{G}_0$ for different molecule-metal distances. Recent works indicate that it is also the case for BDT-p. Here, the calculated $\mathcal{G}(E=0)$ is 0.38 – 0.86 $\mathcal{G}_0$ [93, 108]. On the other hand, BDT-n presents a weaker molecule-metal bonding motif, which explains the smaller variation in the calculated $\mathcal{G}(E=0)$: it ranges from 0.02 to 0.06 $\mathcal{G}_0$ [108, 110].

The BDA molecule has emerged as an attractive system since its low bias conductance is reproducible [111, 112, 5]. A zero-bias conductance of 0.006 – 0.007 $\mathcal{G}_0$ was consistently found by different experimental groups [112, 5, 113, 114]. Nevertheless, in the works of Refs. [113, 114], two lower conductance regimes attributed to different binding configurations were also found. The DFT zero-bias conductance presents small variations with small changes to the geometry: the $\mathcal{G}(E=0)$ value is 0.021 to 0.046 $\mathcal{G}_0$ [5, 6, 110].

Early comparisons between the experimental and theoretical $\mathcal{G}(E=0)$ for BDT showed a disagreement of about two orders of magnitude, as shown in Fig. 2.1. However, more recent works show a smaller disagreement between the experimental and theoretical results [115]. The calculated values for the zero-bias conductance for BDT-h, BDT-p, BDT-n and BDA in recent works are shown in Table 2.1. For BDT-p, $\mathcal{G}(E=0)$ can be a factor of 80 bigger than the experimental value of 0.011 $\mathcal{G}_0$. This geometry presents the higher conductance among the studied systems, followed by BDT-h, in which the disagreement with the experiment can be up to a factor of 70. For the junctions presenting weaker metal-molecule coupling (BDT-n and BDA), an order-of-magnitude agreement with the consensus experimental values (0.011 $\mathcal{G}_0$ for BDT and 0.007 $\mathcal{G}_0$ for BDA) is found, however, the theoretical conductance is higher than the experimental one by at least a factor of 2 and 3, for BDT-n and BDA, respectively.

Calculated DFT conductance		
Junction	Zero-bias conductance $\mathcal{G}_0$	Reference
BDA	0.02 - 0.05	[5, 6, 110, 116]
BDT-n	0.02 - 0.05	[108, 110]
BDT-h	0.16 - 0.77	[93, 110]
BDT-p	0.38 - 0.86	[93, 108]
Experimental conductance		
Junction	Zero-bias conductance $\mathcal{G}_0$	Reference
BDT	0.0040- 0.011	[87, 88, 89]
BDA	0.0001- 0.007	[112, 5, 113, 114]

Table 2.1: Zero-bias conductance of a single BDA/BDT molecule. The calculated DFT conductance is shown at the top. For BDT, several geometries are considered: BDT-n, BDT-p and BDT-h, see the text. The experimental conductance is shown at the bottom. In the experiments, the geometry of the junctions is unknown and different conductance traces have been reported for the same molecule, indicating different bonding motifs. However, a consensus has been reached on the value of 0.011 and 0.007 $\mathcal{G}_0$ (in bold) for BDT and BDA, respectively.

Many explanations have been proposed for such a discrepancy. For example, arguing an uncertainty over the experimental junction structure, the sensitiveness to the contact geometry was investigated [92, 108]. More fundamentally, it has been found that the zero-bias conductance

may vary by several orders of magnitude when using different exchange-correlation (XC) energy functionals [117, 93]. Moreover, the DFT lack of derivative discontinuity was shown to be a source of significant errors in weakly coupled systems [118]. In fact, the validity of using DFT to treat electron interactions in the Landauer formalism has also been questioned [119], and it is believed that a many-body theory should be better suited. Indeed, the DFT eigenstates do not have a formal direct connection to the quasiparticle (QP) states.

Recently, many-body perturbation theory (MBPT) calculations [15] have been used in combination with the Landauer formalism to study the conductance of a simple gold monoatomic chain [120]. The applicability of this method to more complex systems, as realistic three dimensional junctions, is extremely difficult and hence very limited, especially when using plane-waves. Therefore, a simpler approach relying on a model self-energy [5, 6], based on projectors onto molecular orbitals, has been applied to molecular junctions with some success. Nevertheless, a formal justification of this model is still lacking.

In this section, we refer to $\overline{\text{CHSX}}_0$ as only one iteration of the CHSX approximation introduced in section 1.3.8. The diagonal version of this operator is called as simply CHSX_0 . This only modifies the DFT eigenvalues, similarly to the G_0W_0 approximation.

In this work, the effect of electron-electron interactions on the zero-bias conductance is investigated for the BDT and BDA molecules attached to gold electrodes. Several self-energy corrections obtained from many-body perturbation theory are considered. (i) The QP corrections to the DFT eigenvalues are computed within the G_0W_0 and the CHSX_0 approximation for the complete molecular junctions and the resulting QP energies are used in the Landauer approach. These diagonal self-energy corrections are found not to modify significantly the zero-bias conductance. (ii) The DFT eigenfunctions are corrected within the $\overline{\text{CHSX}}_0$ approximation.

For the junctions with lower coupling (BDT-n and BDA), the zero-bias conductance is found to decrease within $\overline{\text{CHSX}}_0$ by a factor of 1.7 (1.4) towards the experimental evidence for BDT-n (BDA). A comparison of the original and the updated local DOS (LDOS) at the Fermi level shows that both the molecule and the gold regions are modified. In particular, it is found that the change of the zero-bias conductance is triggered by a decrease of the molecular character and an increase of the $e_g(d_{z^2})$ character of the wavefunctions on the gold atoms.

For the junctions with stronger coupling (BDT-p and BDT-h), even a modification of the wavefunctions within $\overline{\text{CHSX}}_0$ is found not to change the initial DFT conductance. However, an analysis of the updated and

initial LDOS shows important modifications of the wavefunctions. In particular, it is found a decrease of the molecular character and a relocalization of the wavefunctions on the gold atoms.

These results, show the importance of off-diagonal elements of the self-energy operator to correct the wavefunctions of metal-molecule junctions in both the molecule and metal regions. In low coupling junctions, many-body corrections are important to reduce the zero-bias conductance towards the experimental evidence.

The calculation of a $N \times N$ self-energy operator, for a system with N bands at each $\mathbf{k}$ -point, is expensive in computing resources. Therefore, a cheaper approach would be highly desirable. To this end, a new model-self energy operator is proposed and studied. Its parameters are fitted from the diagonal self-energy matrix elements. However, a careful analysis indicates that the model results are not in agreement with the *ab initio* calculations. Moreover, this conclusion also applies for other model self-energies based on MOs.

The chapter is organized as follows. In section 2.2, the BDA and BDT molecules in the gas phase are studied. This is an important preliminary step to study later the molecules in contact with metal leads. In section 2.3, the geometry of the molecular junctions is studied at the DFT level. In section 2.4, the molecular orbitals of the molecule in the junction are studied. These hybridize with the gold states, experiencing substantial changes. In section 2.5, the conductance of these junctions is studied at the DFT level. In section 2.6, the effect of the classical model self-energy introduced in Refs. [5, 6] is studied more thoroughly. In section 2.7, *GW* corrections are applied to the DFT Hamiltonian of these junctions. The effect of this *ab initio* self-energy is compared to the one of the model self-energy introduced previously. In section 2.8, the *GW* results are used to fit a model operator based on molecular projectors. Finally, in section 2.9, the conclusions of this work are exposed.

Part of the work related to this chapter is explained in more details in the Appendices: The technical details of the calculations of this chapter are shown in appendix A.1. Cell-size convergence issues at the *GW* level are shown in appendix B. Moreover, the details to obtain the classical model parameters of section 2.6 are explained in appendix C.

2.2 The benzene-diamine (BDA) and benzene-dithiol (BDT) molecules in gas phase

The electronic levels of isolated molecules are underestimated by the DFT within the LDA or the GGA due to the approximations to the

unknown XC potential (V_{xc}) and to the lack of derivative discontinuity of the XC energy, as explained in Section 1.2.5. The standard technique to correct the molecular levels is the so-called G_0W_0 approximation (see section 1.3.13).

In this section, we study the BDT and BDA molecules in the gas phase at the DFT, G_0W_0 and CHSX₀ levels. The geometries were relaxed in a supercell including 20 Å of vacuum. These are shown in Fig. 2.2. The BDA molecule has the two NH₂ groups out-of-plane; one of which points upwards while the other points backwards. We find that the in-plane solution is a local minima for this molecule. The other two molecules are in-plane.

In particular, the BDT (thiol) geometry in Fig. 2.2b agrees well with experimental data obtained by electron diffraction [121]. The C-C bond distance is 1.399 ± 0.003 Å in experiment and our calculations give 1.39-1.40 Å. In fact, the C-C bonds for the *ortho*- and the *para*-position can hardly be distinguished experimentally. The C-S bond distance is measured to be 1.775 ± 0.004 Å while the simulations lead to 1.77 Å. For BDA our theoretical geometry agrees well with the experimental measurements of Ref. [122]: The C-C lengths for the *ortho*- and the *para*-position are, 1.39 and 1.40 Å respectively, which are in good agreement with the experimental values (1.399 ± 0.003 and 1.392 ± 0.006 Å). The dihedral angle between the phenyl plane and the terminated H-N-H plane is calculated to be 42.9°, in close agreement to the experimental value of 44.4°.

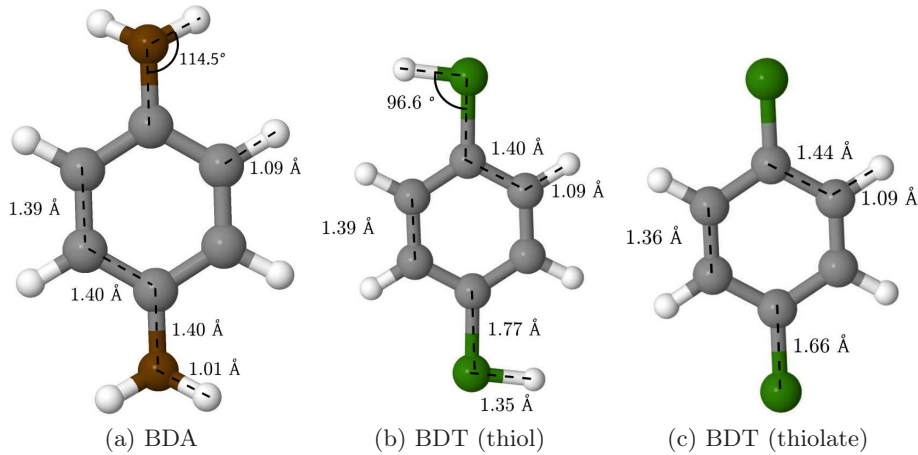


Figure 2.2: Geometry of molecules in gas phase. The sulfur, nitrogen, hydrogen and carbon atoms are represented by green, brown, white and gray spheres, respectively.

For the GW calculations, the Ismail-Beigi cutoff technique [123] is used to accelerate the convergence with respect to the supercell size (see section 4.2.2 for more details on this technique). In the GW method, due to the introduction of a charge in the calculation, the cell-size convergence is rather slow as discussed in appendix B.

The GGA, G_0W_0 and $CHSX_0$ gaps calculated in this work and those found in the literature are shown in Table 2.2. The corresponding HOMO and LUMO energy levels are also shown.

Molecule	Orbital	DFT-GGA [eV]			
		Ours	Ref. [116]	Ref. [5]	Ref. [110]
BDA	HOMO	-4.2	-4.2	-3.8	-4.1
	LUMO	-1.0	-1.0	-0.6	-0.9
	Gap	3.2	3.2	3.2	3.2
BDT thiol	HOMO	-4.9			-5.1
	LUMO	-1.5			-1.3
	Gap	3.5			3.8
BDT thiolate	HOMO	-5.5			-5.7
	LUMO	-4.9			-5.1
	Gap	0.7			0.6

Molecule	Orbital	G_0W_0		$CHSX_0$	HF	ΔSCF	Exp.
		Ours	^a	Ours	^a	^a	
BDA	HOMO	-5.9	-6.2	-6.8	-7.2	-6.8	-6.83 ^b
	LUMO	3.2	2.9	3.0	3.9	2.3	
	Gap	9.2	9.1	9.8	11.1	9.1	
BDT thiol	HOMO	-6.4	-6.9	-7.4	-8.0	-7.5	7.8 ^c , 8.6 ^d
	LUMO	2.2	2.2	2.1	3.3	1.3	
	Gap	8.7	9.1	9.6	11.3	8.8	
BDT thiolate	HOMO	-6.9	-7.9	-8.3	-8.6	-8.3	
	LUMO	-1.8	-2.3	-1.6	-1.6	-2.7	
	Gap	5.1	5.6	6.7	7.0	5.6	

^a Ref. [110]. ^b Ref. [124]. ^c Ref. [125]. ^d Ref. [126].

Table 2.2: Molecular levels for the isolated BDA and BDT molecules. The calculated levels at the GGA level are shown in the table at the top. The calculated levels beyond GGA (G_0W_0 , $CHSX_0$, HF and ΔSCF) are shown in the table at the bottom. Our results (bold numbers) and others (regular numbers) are shown. The experimental data is also included.

For the BDA molecule, the DFT-GGA results are in good agreement with those of Refs. [5, 6, 110], and they are in excellent agreement with

those of Ref. [116]. For the BDT molecule, the DFT-GGA results are also in good agreement with the literature [110]. For all of the systems, the G_0W_0 results agree within 0.5 eV with those of Ref. [110]. Moreover, the HOMO energy for BDT (thiol) is -6.4 eV within G_0W_0 which compares well with the value of -6.5 eV previously found within the MP2 method [127].

The Δ SCF results of Ref. [110] are included to validate our results. The Δ SCF technique predicts highly accurate ionization potentials (IPs) and electron affinities (EAs) for molecules [21]. Compared to the Δ SCF gaps, DFT-GGA always underestimates the gaps. The best agreement with the Δ SCF method is obtained with the G_0W_0 technique. In contrast, CHSX₀ overestimates the gaps: the CHSX₀ gaps are found to be halfway between the Δ SCF and the HF results of Ref. [110], as expected.

Only a few experimental measurements of the energy levels for these molecules can be found in the literature [125, 126, 124]. The gap for BDT (thiol) is 7.8 eV as determined by electron scattering experiments [125]. The value of 8.6 eV obtained from photo-emission and inverse-photoemission experiments on a similar molecule (biphenyl-dimethyldithiol) is usually used as a reference for the BDT gap [126]. These two experimental values are in good agreement with the 8.7 eV gap obtained within G_0W_0 .

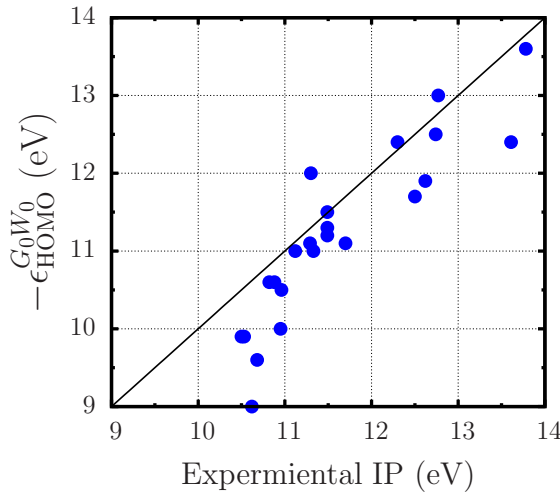


Figure 2.3: G_0W_0 HOMO energy vs. experimental IP for a series of 27 molecules. Data taken from Ref. [128].

For the BDA molecule, we could not find the experimental gap in the literature. The experimental IP is 6.83 eV [124]. This value is not in agreement with our G_0W_0 IP of 5.9 eV. However, in G_0W_0 the absolute position of the individual levels may not correspond to the experiments. For instance, as shown in Fig. 2.3, a comparison of the G_0W_0 -GGA HOMO energy and the experimental IP for a series of 27 molecules shows

discrepancies as large as ~ 1.5 eV. This disagreement might be due to the missing vertex effects in the G_0W_0 theory.

2.3 Geometry of the junctions

The junctions considered here are BDA and BDT attached to Au (111) electrodes. These are among the most studied systems in quantum transport. The BDT molecule is often used as a benchmarking model. However, its conductance is strongly dependent on the geometry of the molecule [94, 95, 129]. On the other hand, the BDA molecule emerged as an attractive molecule for theoretical calculations since its low bias conductance is stable with moderate changes to the geometry [111, 112, 5]. To account for different hybridizations and bonding motifs, three BDT geometries are considered here: BDT-h, BDT-p and BDT-n. Benzenedithiol may lose its hydrogen atoms at the thiol-group during the absorption process, thus becoming benzenedithiolate. The thiolate group can adsorb at several sites on the Au surface, here we just considered two of the most studied ones: the hollow site (BDT-h) and the pyramid site (BDT-p). At the hollow site, the sulfur atom adsorbs at the same distance from 3 Au atoms, and hence, binding with all 3. At the pyramid site, the sulfur atom adsorbs on the top of an extra Au adatom forming a pyramid on the surface. The thiolate group (BDT-n) can also adsorb in several sites: the BDT molecule can attach directly to the gold surface or to a gold adatom. Nevertheless, a comparison of the binding energies in these two systems reveals that the latter is the most stable, with a difference in the binding energy of ~ 0.4 eV per molecule [108]. Moreover, recent STM experiments point out that BDT molecules attach to the gold surface via gold adatoms [130, 131]. Therefore, for BDT-n we consider a system in which the molecule adsorbs to gold adatoms, similarly to BDT-p. On the other side, the diamine group (BDA) only adsorbs to an extra Au adatom [5], explaining the reproducibility of its zero-bias conductance.

For the atomic relaxation, a 2×2 surface cell is adopted for the Au (111) surface with seven atomic layers in the electrodes. This corresponds to highly-packed junctions, with a molecule-molecule distance of only ~ 3 Å. Nevertheless, experimental and theoretical works show that alkanethiols can form densely-packed self-assembled monolayers (SAMs) on Au(111) [132, 98, 133, 134]. The relaxed geometries are shown in Fig. 2.4. They agree with previous theoretical predictions [6, 116, 108, 93]. The tilt angle (angle between the normal to the Au surface and the direction X-X joining the two contact atoms X=N for BDA or S

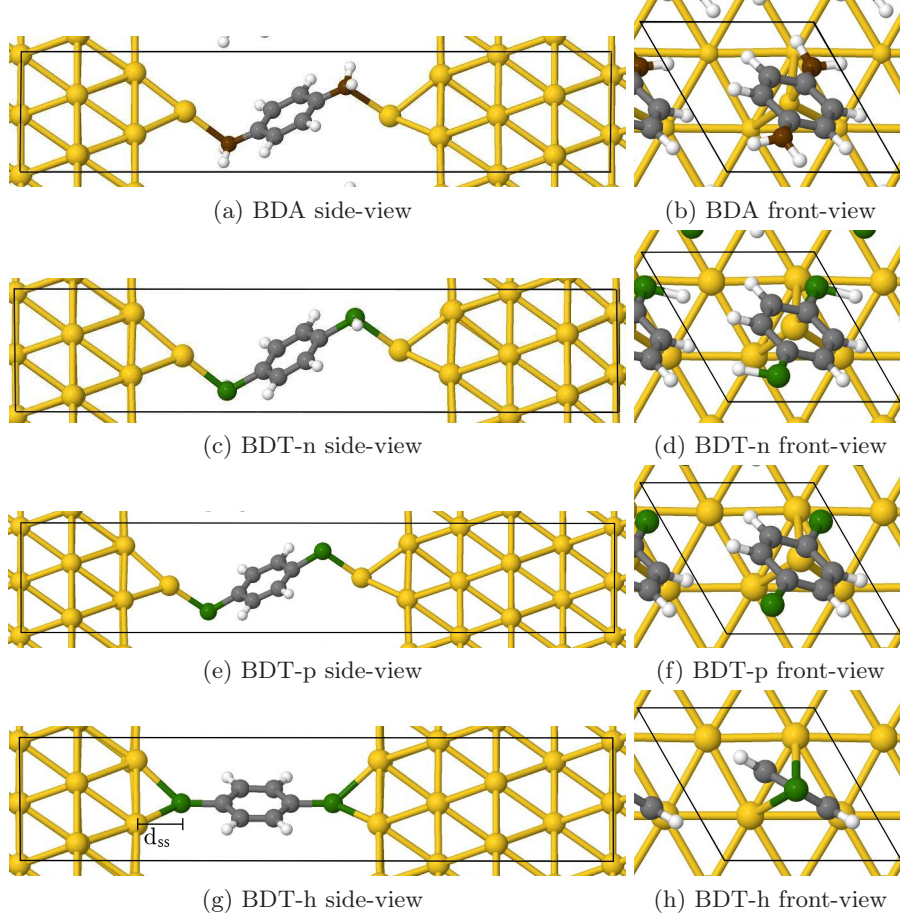


Figure 2.4: BDA and BDT attached to gold (111). The BDA geometry [(a) side and (b) front views], the BDT-n geometry [(c) side and (d) front views], the BDT-p geometry [(e) side and (f) front views], and the BDT-h geometry [(g) side and (h) front views] are shown. For clarity, just one gold layer is shown in the front views. The Au, C, S, N, and H atoms are represented by yellow, gray, green, brown, and white spheres, respectively. The unit cell is represented by black lines.

for BDT) measures 29° , 32° , 31° and 0° for BDA, BDT-n, BDT-p and BDT-h, respectively. Moreover, the Au-X distance is 2.4, 2.5, 2.3 and 2.6 Å for BDA, BDT-n, BDT-p and BDT-h, respectively. For BDT-p, the Au-S distance, d_{ss} , as shown in Fig. 2.4g is 2.0 Å.

The BDA and BDT junctions, although being almost identical systems, present very different bonding motifs due to their anchoring groups. In the thiol case, the sulfur atoms form covalent bonds with the Au

atoms. Hence, the conductance changes considerably with small changes of the geometry. The conductance change with respect to the geometry can be as large as a factor of three for this system [93]. In contrast, in the BDA case, the amino group donates its lone pair to form Au-N bonds with an undercoordinated Au adatom [112]. The bonding is through the 6s gold orbital. Due to the isotropy of this orbital, the low bias conductance is almost not affected by small changes in the bond lengths or angles [111, 112, 5].

2.4 Molecular orbitals in the junction

The shape of $\mathcal{G}(E)$ for a molecular junction is usually interpreted in terms of the molecular orbitals (MOs) (the orbitals driving the conductance) of the isolated molecule. In particular, the projected density of states (PDOS) on the MOs is a quantity used to explain the conductance spectrum. The PDOS on a given MO m is defined as

$$\text{PDOS}_m(E) = \sum_n \langle \varphi_m^{\text{mol}} | \varphi_n^{\text{sys}} \rangle \delta(E - E_n), \quad (2.1)$$

where n runs over the states of the junction, φ_n^{sys} , with energy E_n and the delta function is usually replaced by a gaussian function with a given smearing factor.

The molecular orbitals, φ_m^{mol} , in Eq. (2.1) can be defined in two different ways:

- (i) First, we compute the real-space Hamiltonian of the whole junction. Then we extract the part corresponding to the basis elements (Wannier functions) that are localized on the molecule only. This restricted Hamiltonian is then diagonalized¹. Here, the resulting MOs are linear combinations of the MLWFs localized on the molecule.
- (ii) We do a ground state calculation of the molecule in gas phase.

The MOs obtained with method (i) are shown in Fig. (2.5). All the junctions are considered here. The MOs obtained with method (ii) are shown in Fig. (2.6). For BDT, the thiol and thiolate species are considered. The MOs obtained with method (i) provide a chemical insight on the nature of the molecule-metal bonds (see Fig. 2.5). For instance, for BDA, the HOMO presents a clear bonding character, binding the N atom to the Au adatom.

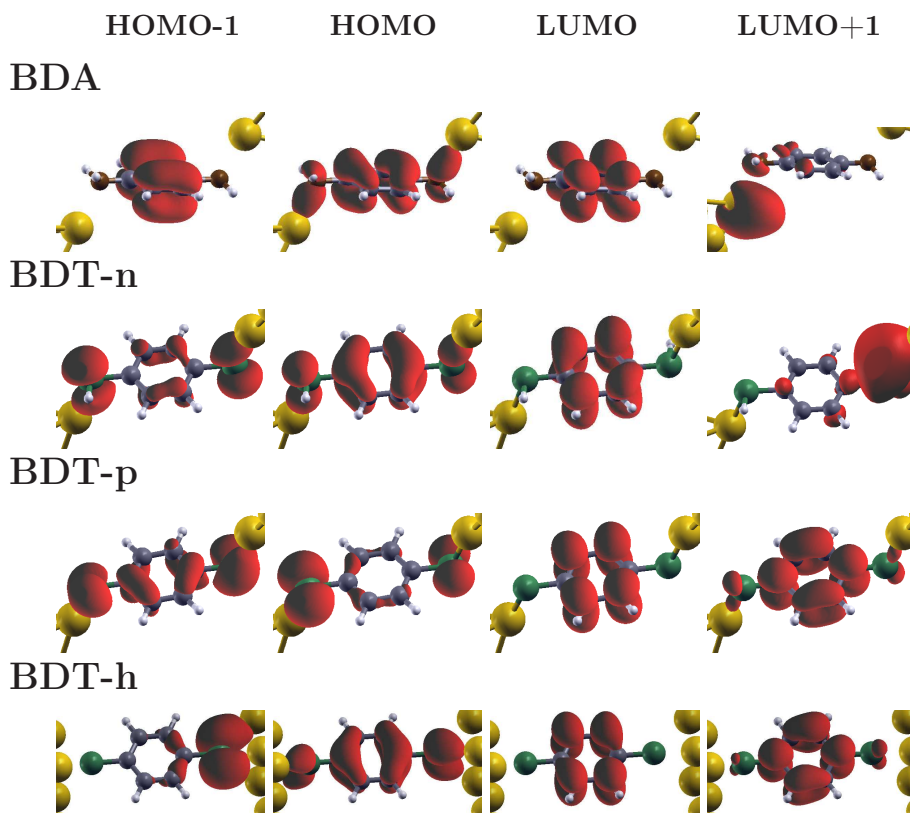


Figure 2.5: Electronic density of the molecular orbitals for BDA/BDT (red isosurfaces), as obtained by method (i) [see the text]. The hydrogen, carbon, nitrogen and sulfur atoms are represented by white, gray, brown and green spheres, respectively.

For BDA, the molecular orbitals obtained within method (i) (Fig. 2.5) are similar those obtained within method (ii) (Fig. 2.6), except for the hybridized HOMO and LUMO+1. To illustrate, these hybridized orbitals in Fig. 2.5 contain some extra-density along the molecule-gold bonds, which is not clear if it belongs to the molecule or to gold. The same is observed for BDT-n, and it is expected in other systems presenting weak molecule-gold coupling. Given the different results between the two methods, there is an arbitrariness on the definition of the hybridized molecular orbitals in the junctions. **In principle, these should not be considered as isolated molecular orbitals.** That is, the molecule

¹This procedure is valid just when the basis elements are localized. Moreover, the molecule should be very weakly hybridized with the metal, so that it can be considered an independent system similar to the molecule in gas phase.

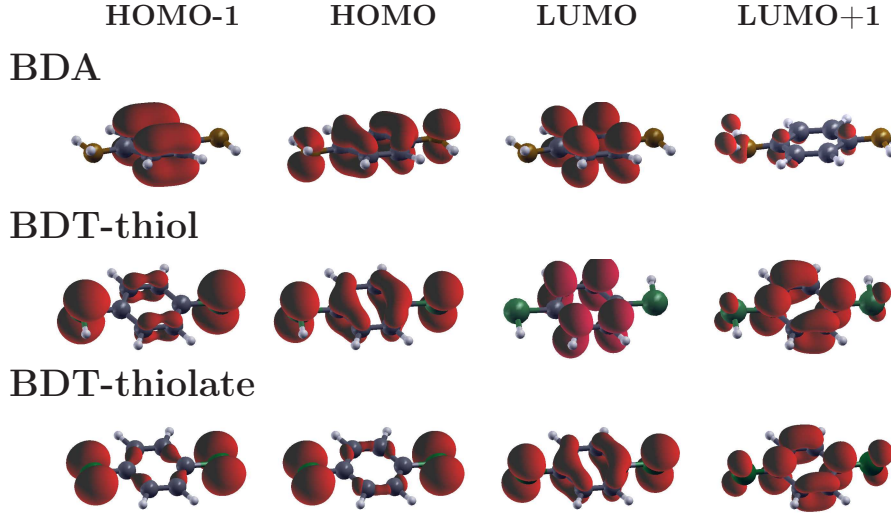


Figure 2.6: Density of molecular orbitals for the molecules in gas phase (red isosurfaces), as obtained by a ground state calculation of the isolated molecule (method (ii)) The hydrogen, carbon, nitrogen and sulfur atoms are represented by white, gray, brown and green spheres, respectively.

and gold should not be considered as separate sub-systems even in weak coupling regimes.

For BDT-p, the non-hybridized molecular orbitals (LUMO/LUMO+1) obtained within method (i) resemble to those of the BDT-thiol molecule obtained within method (ii). However, those which are hybridized with gold (HOMO-1/HOMO) are quite different depending on the method used. For BDT-h, we observe similar results: the HOMO, LUMO and LUMO+1 obtained within method (i) correspond to those obtained within method (ii). However, the hybridized HOMO-1 and HOMO-2 (not-shown here) don't. Similar trends are expected in systems with a similar coupling regime.

The PDOS on the MOs in $e^-/\text{cell}/\text{eV}/(2 \text{ spins})$ for BDA, BDT-h, BDT-n and BDT-p is shown in Fig. 2.7. For BDA (a) and BDT-n (b) the PDOS with φ_m^{mol} calculated with both methods (i) and (ii) [panels (1) and (2) respectively] is shown.

For BDA and BDT-n, the two methods give similar PDOS as a result of the low coupling regime of these junctions. Differences are seen in the shape and heights of the hybridized HOMO and LUMO+1. As an example, the LUMO+1 is shifted and presents a different shape for BDT-n. These discrepancies are expected due to the fact that the MOs as obtained within the two methods are different, as discussed before.

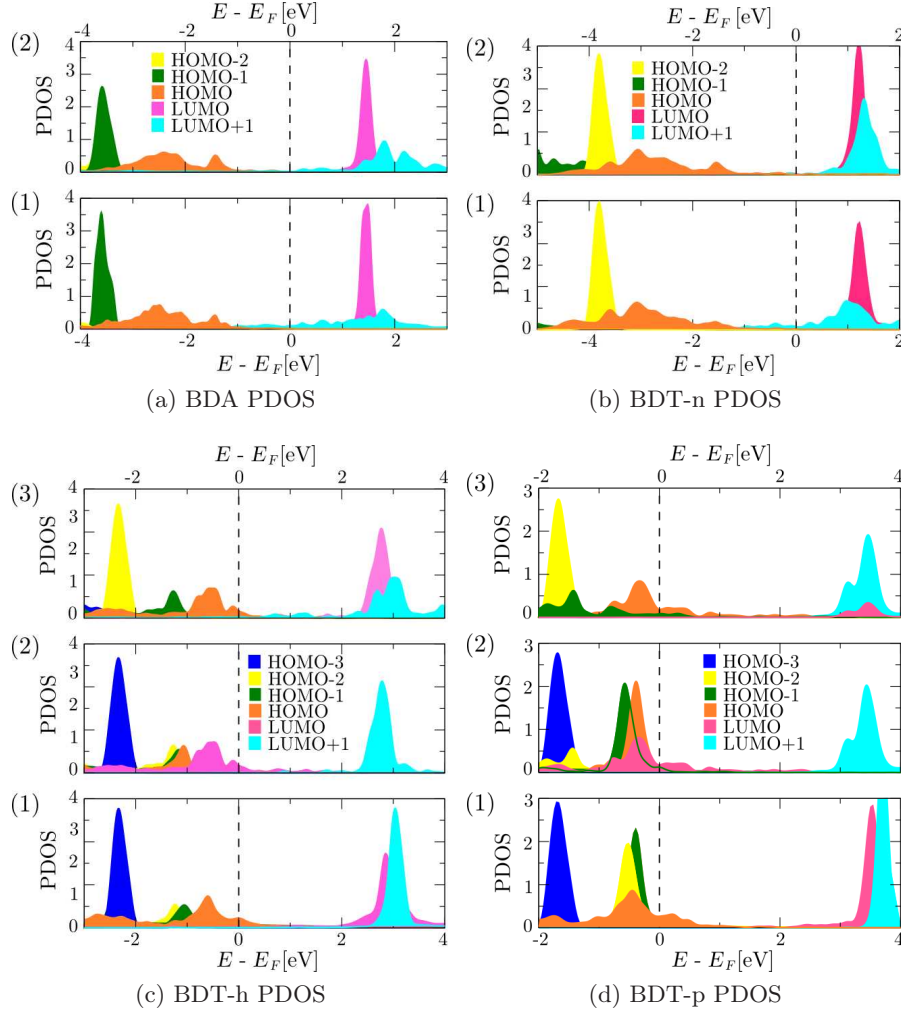


Figure 2.7: PDOS on the MOs as a function of the energy (the Fermi energy E_F is set to zero) in $e^-/\text{cell}/\text{eV}/(2 \text{ spins})$ for BDA (a), BDT-n (b), BDT-h (c) and BDT-p (d). The corresponding contributions from the HOMO-3 (blue), the HOMO-2 (yellow), the HOMO-1 (green) the HOMO (orange), the LUMO (pink), and the LUMO+1 (cyan) are shown. For BDA and BDT-n, panels (1) and (2) show the PDOS obtained within method (i) and (ii), respectively. For BDT-h and BDT-p, panel (1) shows the PDOS obtained within method (i), while panels (2) and (3) show the PDOS calculated within method (ii), for the thiolate and thiol molecule, respectively.

For BDT-h and BDT-p [Fig. 2.7c and Fig. 2.7d] the correspond-

ing PDOS is also shown. Several versions of this PDOS are reported. Panel (1) shows the PDOS obtained by method (i); while panels (2) and (3) show the PDOS obtained by method (ii) applied to the thiol- and thiolate-molecules in the gas phase, respectively.

For these stronger-coupling systems, the resulting PDOS is highly dependent on the method used to get φ_m^{mol} . For instance, for BDT-h (Fig. 2.7c) in the range of -2 eV to 0 eV, the number of peaks vary depending on the method used: three, four and two peaks appear in panel (1), (2) and (3), respectively. In fact, in these junctions, some MOs strongly mix with gold and they do not resemble to those of the isolated molecule, as discussed before. Therefore, we find that it is inappropriate to refer to individual orbitals in this coupling regime, and from now on, we will not do so. We will only refer to individual MOs in the weakly-coupled systems (BDA and BDT-n). For the rest of this chapter, we will only use method (i) to obtain the PDOS on the MOs and on the molecule.

2.5 The DFT conductance

The DFT conductance is shown in the top panels of Fig. 2.8 for (a) BDA, (b) BDT-n, (c) BDT-h and (d) BDT-p. The corresponding PDOS on the MOs obtained within method (i) [see section 2.4] are shown in the bottom panels of Fig. 2.8. For BDT-h and BDT-p, only the total PDOS on the molecule is shown, due to the fact that the MOs were strongly modified via hybridizations with the metal states, as previously discussed.

The conductance shape is consistent with the PDOS on the molecule. the peaks on the conductance can be assigned to one or more MOs. For instance, for BDA, the peaks at -1.5, 2.8 and 1.2 eV are assigned to the highest occupied molecular orbital (HOMO), lowest unoccupied molecular orbital (LUMO) and LUMO+1, respectively. For BDT-n, the peak at -1.7 eV is assigned to HOMO, whereas, the one at 1.2 eV is due to both the LUMO and the LUMO+1. For BDT-p and BDT-h, the conductance main peaks can also be identified with peaks in the PDOS.

A summary of the zero-bias conductance for these junctions is shown in Table 2.3, in which, the results of other works are also reported. Our calculated DFT-GGA zero bias conductances are in good agreement with previous calculations. For instance, the zero-bias conductance ($\mathcal{G}(E=0)$) is 0.018 $\mathcal{G}_0$ for BDA. This result is close to the 0.021, 0.024 and 0.028 $\mathcal{G}_0$ found in Refs. [110, 6, 116], respectively. It is about one half of the value of 0.046 $\mathcal{G}_0$ calculated in Ref. [5]. However, the latter was obtained aver-

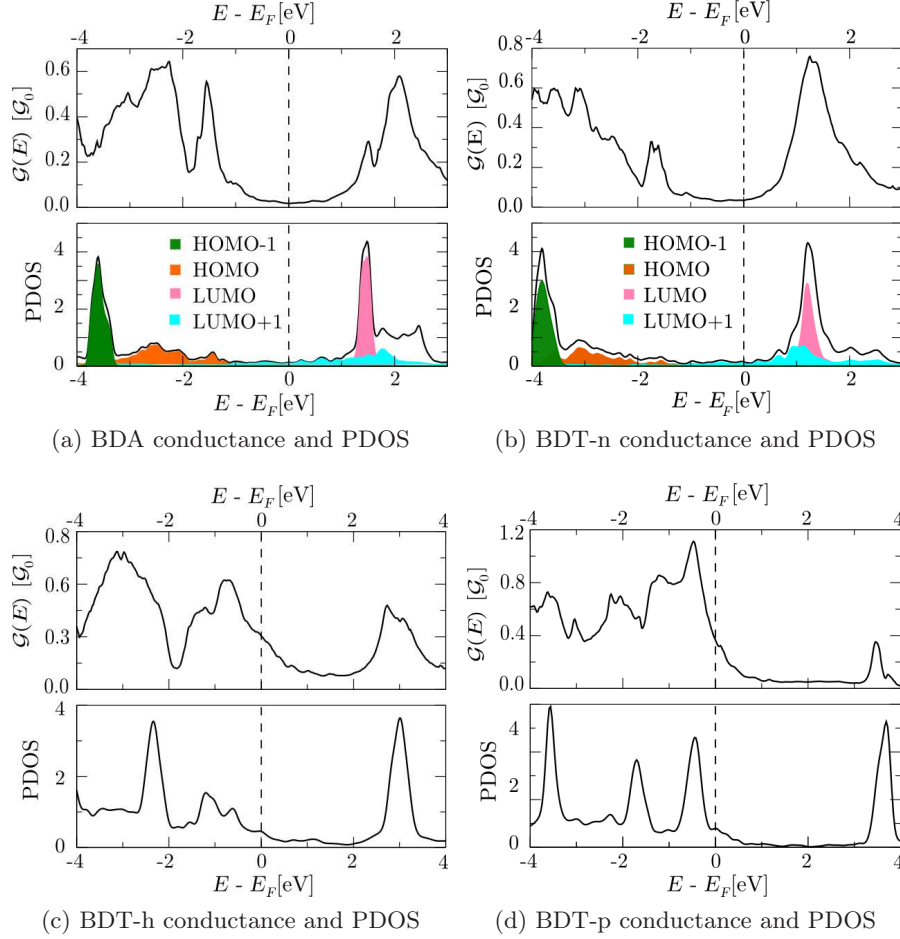


Figure 2.8: Conductance (top) and PDOS on the molecule (bottom) as a function of the energy (the Fermi energy E_F is set to zero) for BDA (a), BDT-n (b), BDT-h (c) and BDT-p(d). The total PDOS (black) and the corresponding contributions from the HOMO-2 (yellow), HOMO-1 (green), the HOMO (orange), the LUMO (pink), and the LUMO+1 (cyan) are shown.

aging the conductance of 15 different geometries². For BDT-n, $\mathcal{G}(E=0)$ is

² These geometries have different Au-N bond lengths, and in general the Au-N length is bigger than ours. These systems contain a number of 6 to 8 total nearest neighbors at the Au binding sites, while our system contains just six. In the supporting information of Ref. [5], it can be read that the conductance is $0.031 \mathcal{G}_0$ for the geometry which is closer to ours (In this geometry, the total number of nearest-neighbors is 6 and the Au-N distance is $2.44 \text{ \AA}$). This conductance value is in a better agreement with ours.

0.034 $\mathcal{G}_0$ in agreement with the value of 0.02 and 0.054 $\mathcal{G}_0$ found in Refs. [108, 110], respectively. For BDT-h, $\mathcal{G}(E=0)$ equals 0.305 $\mathcal{G}_0$ with $d_{ss}=2.0\text{\AA}$, in agreement with the literature. The conductance for this junction varies more with the distance d_{ss} , for example, in Ref. [93], $\mathcal{G}(E=0)$ equals 0.23 $\mathcal{G}_0$ and 0.32 $\mathcal{G}_0$ with $d_{ss}=1.9\text{\AA}$ and $2.1\text{\AA}$, respectively. A $\mathcal{G}(E=0)$ value of 0.28 $\mathcal{G}_0$ was found in Refs. [135, 110, 136], with a slightly more compact geometry: in their calculations the Au-S distance is $\sim 2.45\text{\AA}$ and the Au surface-surface distance is $9.68\text{\AA}$, while in ours these distances are $2.6\text{\AA}$ and $10.1\text{\AA}$, respectively. For BDT-p, $\mathcal{G}(E=0)$ equals 0.365 $\mathcal{G}_0$ in agreement with the value of 0.43 $\mathcal{G}_0$ of Ref. [93].

Junction	DFT-GGA/LDA $\mathcal{G}(E=0)$ [$\mathcal{G}_0$]	
	Ours	Others
BDA	0.018	0.021 ^a , 0.024 ^b , 0.028 ^c , 0.046 ^d
BDT-n	0.034	0.054 ^a , 0.023 ^e
BDT-h	0.305	0.28 ^a , 0.23-0.32 ^f , 0.278 ^g
BDT-p	0.365	0.43 ^f

^a Ref. [110, 135], ^b Ref. [6], ^c Ref. [116], ^d Ref. [5], ^e Ref. [108],
^f Ref. [93] and ^g Ref. [136].

Table 2.3: DFT zero-bias conductance for BDA, BDT-n, BDT-h and BDT-p. The calculated DFT-GGA/LDA conductance is shown: our results and those found in the literature are included. For BDT-h, only a few recent works were selected with similar geometries to ours. All of these works use DFT-GGA except for Ref. [93] which uses DFT-LDA.

In summary, the DFT-GGA zero-bias conductance in our calculations is 0.018 $\mathcal{G}_0$ and 0.034-0.365 $\mathcal{G}_0$ for BDA and BDT, respectively (see Table 2.3). For BDA, the DFT value is a factor of 3 higher than the experimental value of 0.006 $\mathcal{G}_0$ [5, 112]. For BDT, the experimental conductance is 0.011 $\mathcal{G}_0$ [88, 89]. This is a factor of 3 higher than the DFT value of 0.034 $\mathcal{G}_0$ (for BDT-n), and an order of magnitude higher than the DFT values of 0.305 and 0.365 $\mathcal{G}_0$ for BDT-h and BDT-p, respectively. Hence, the DFT conductance is higher than the experimental one by at least a factor of 3. This DFT drawback is well known and it has been discussed in several occasions.

2.6 Classical model corrections to the DFT Hamiltonian

It is well known that the DFT-LDA/GGA overestimates the zero-bias conductance of weakly coupled systems (by at least a factor of three) compared to experimental measurements (see section 2.5). Many explanations have been proposed for such a discrepancy. In particular, the validity of using DFT to treat electron interactions has been questioned. In general, the DFT eigenvalues do not correspond to the QP energies. Furthermore, the zero-bias conductance may vary by more than an order of magnitude when using different XC functionals [117, 93].

Many-body corrections beyond DFT have been studied more recently [5, 6]. A model self-energy correction operator ($\Delta\Sigma$) was introduced to correct the DFT XC potential. This operator is basically a one-projector model (MPM) over the molecular orbitals with the following form:

$$\Delta\Sigma^{\text{MPM}} = \sum_m^{\text{occ.}} -\Delta|\varphi_m^{\text{mol}}\rangle\langle\varphi_m^{\text{mol}}| + \sum_m^{\text{empty}} \Delta|\varphi_m^{\text{mol}}\rangle\langle\varphi_m^{\text{mol}}|, \quad (2.2)$$

where m runs over the orbitals of the DFT isolated molecule, φ_m^{mol} , (the first term runs over the occupied bands and the second one runs over the empty bands) and Δ is the scissor-operator shift to be applied. This model modifies the DFT wavefunctions since it contains off-diagonal elements. In this thesis, for the sake of comparison, the diagonal version of this model is also considered:

$$\begin{aligned} \Delta\Sigma^{\text{MPM}} &= \sum_i \left(\sum_m^{\text{occ.}} -\Delta|\varphi_i^{\text{sys}}\rangle w_{i,m} \langle\varphi_i^{\text{sys}}| \right. \\ &\quad \left. + \sum_m^{\text{empty}} \Delta|\varphi_i^{\text{sys}}\rangle w_{i,m} \langle\varphi_i^{\text{sys}}| \right), \\ w_{i,m} &= |\langle\varphi_i^{\text{sys}}|\varphi_m^{\text{mol}}\rangle|^2, \end{aligned} \quad (2.3)$$

with φ_i^{sys} being the i^{th} Bloch state of the junction. This will only modify the DFT eigenvalues as in the G_0W_0 approximation.

The value of Δ is obtained in a two step procedure as sketched in Fig. 2.9. First, the correction to the DFT HOMO level of the molecule in the gas phase (Δ^{gas}) is computed either from a ΔSCF calculation or, more simply, by matching the experimental value. For instance, for the HOMO, $\Delta^{\text{gas}} = \text{IP} - E_{\text{DFT}}^{\text{HOMO}}$. Second, the presence of the metallic surface is taken into account through a classical image-charge (IC)

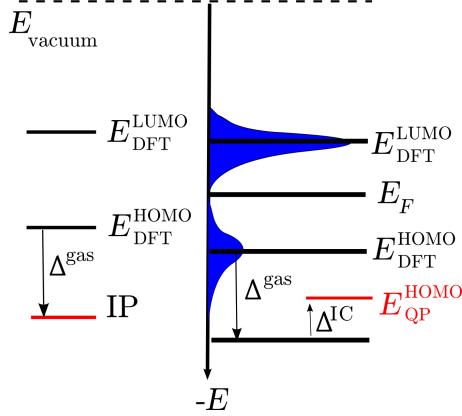


Figure 2.9: Procedure to obtain Δ in the MPM. Left: the HOMO and LUMO DFT levels of the molecule in gas phase are represented by horizontal lines. Δ^{gas} is the correction to the DFT HOMO level. Right: The molecular levels are broadened with the presence of the metallic surface (blue peaks). The correction to the DFT HOMO level in the presence of the surface is reduced by Δ^{IC} with respect to the gas phase.

model leading to a reduction of Δ compared to the gas phase. That is, $\Delta = \Delta^{\text{gas}} - \Delta^{\text{IC}}$, with Δ^{IC} being the reduction of the gap in the presence of the metallic surface as observed in calculations within the G_0W_0 approximation [137, 138] (see right panel of Fig. 2.9). In principle, the shift for the LUMO level should be obtained by a similar procedure with Δ^{gas} being calculated with the electron affinity (EA) as $\Delta^{\text{gas}} = \text{EA} + E_{\text{LUMO}}^{\text{DFT}}$. However, in these systems the corrections to the HOMO and the LUMO levels are found to be similar [5, 6]. Moreover, the same Δ value is used for all molecular orbitals [5, 6]. This is reasonable when orbitals other than the HOMO and LUMO are located far away from the Fermi level so that they have a negligible influence on the zero-bias conductance. However, in this work we found that **the LUMO+1 is as important as the HOMO for the conductance at zero-bias** (see Fig. 2.8). Hence, the applicability of this methodology can be questioned. Moreover, this model is not applicable to the -thiol groups, due to their relatively strong binding motifs [6]. Hence, it was just applied to the weaker binding systems: BDA and BDT-n.

	$E_{\text{HOMO}}^{\text{DFT}}$	IP	Δ^{gas}	Δ^{IC}	Δ
BDA	-4.2	6.97	-2.77	0.79	1.98
BDT-n	-5.0	7.59	-2.59	0.78	1.81

Table 2.4: Calculated parameters for the $\overline{\text{MPM}}$ in eV (see text).

The results of the calculations to find Δ are shown in Table 2.4. The IP of the isolated molecule is found with the formula $\text{IP} = E(N-1) -$

$E(N)$, where $E(N-1)$ is the total energy of the system with a charge of 1 e and $E(N)$ is the corresponding energy of the neutral system³ Possible spin polarization is explicitly taken into account in our calculations. The calculations are repeated by varying the cell dimensions by steps of 10 a.u. The energy of the molecule for an infinite box is then extrapolated with a cubic fitting using correction procedure proposed by Makov and Payne [139]. The calculated IP is 6.97 (7.59) eV for BDA (BDT-n). The results are close to the experimental IP of 6.8 eV for BDA [124]⁴. With this value for the IP, Δ^{gas} is -2.77 (-2.29) eV. The image charge energy Δ^{IC} can be estimated to be ~ 0.79 (0.78) eV for BDA (BDT-n) (see appendix C). Hence, $\Delta = 1.98$ (1.81) eV for BDA (BDT-n). Here we use the rounded value of 2.0 eV for both systems.

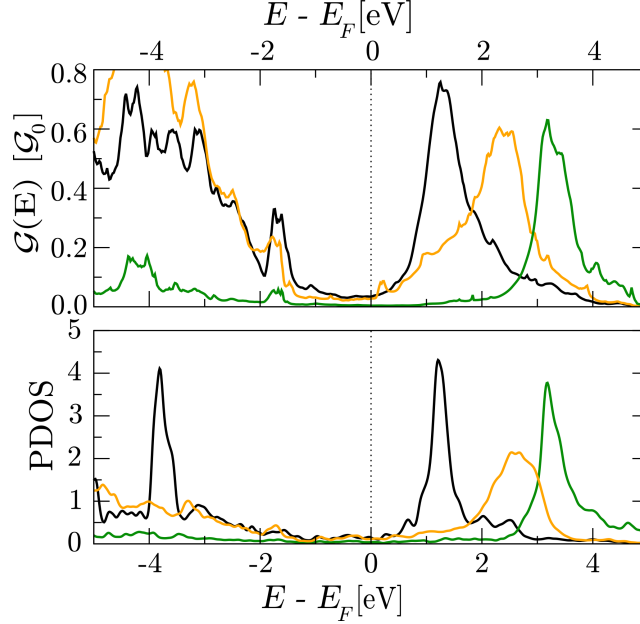


Figure 2.10: MPM conductance (top) and the corresponding PDOS on the molecule (bottom) for BDT-n. The $\overline{\text{MPM}}$ (green) and diagonal MPM (orange) results are shown. The DFT (black) results are also shown. The Fermi level is indicated by a dashed vertical line.

The conductance $\mathcal{G}(E)$ within the MPM and the $\overline{\text{MPM}}$ approximations are shown in Fig. 2.10 for BDT-n. The corresponding PDOS on the molecule obtained within method (i) [see section 2.4] are shown in

³ One could use the experimental IP whenever it is known: with this choice of IP, the resulting Δ is the same as ours for BDA, *i.e.*, ~ 2.0 eV [5].

⁴The experimental IP of BDT-n is not available in the literature.

the bottom panel. As expected, the $\overline{\text{MPM}}$ operator mainly shifts the PDOS peaks (molecular orbitals) by 2 eV apart from the Fermi level. This effect is due to the form of $\Delta\Sigma^{\overline{\text{MPM}}}$, *i.e.*, the operator is similar to a scissors shift with $\Delta = 2$ eV (see Eq. (2.2))⁵. The molecular orbitals are not rigidly shifted as in a scissors operator, but their shape is also modified via a change of the metal-molecule hybridizations (see, for instance, the regions below E_F in the PDOS). In fact, the operator is changing the hybridizations in an unphysical way. As an effect of these shifts, the PDOS at 0 eV is decreased considerably leading to a decrease in $\mathcal{G}(E=0)$. The $\overline{\text{MPM}}$ zero-bias conductance is $0.004 \mathcal{G}_0$. The reduction is of a factor of 8.5 (4.5) with respect to DFT, however, $\mathcal{G}(E=0)$ ends up to be smaller than in the experimental measurements of 0.011 (0.007) $\mathcal{G}_0$ for BDA (BDT-n).

The MPM model is also shifting the PDOS peaks apart from the Fermi level. However, the shifts are smaller than those of the $\overline{\text{MPM}}$ model⁶. In particular, the HOMO (its DFT maxima are at -1.6 eV and at -2.5 eV⁷) is shifted just -0.2 eV while the LUMO (its DFT maxima is at 1.5 eV) is shifted +1.5 eV. In fact, the MPM shifts depend on the weights of the different states of the system on the molecular orbitals ($w_{i,m}$) as can be seen explicitly in Eq. (2.3). The molecular states which are less hybridized with the metal ($w_{i,m}$ is almost 1) are shifted more than those with more hybridization. For example, the LUMO is shifted significantly more than the HOMO. Hence, the hybridized states, which drive the conductance, are less shifted here than in the $\overline{\text{MPM}}$ case. As a direct consequence, $\mathcal{G}(E=0)$ is reduced by much less than in the $\overline{\text{MPM}}$ case. The zero-bias conductance is 0.017 (0.027) $\mathcal{G}_0$, which accounts for a reduction of 0.9 (0.8) with respect to DFT for BDA (BDT-n).

The MPM conductance presents numerous instabilities leading to spurious peaks in $\mathcal{G}(E)$ [see, for instance, the small peaks close to 0.25

⁵ The $\overline{\text{MPM}}$ operator is not strictly speaking a scissors operator. A scissors operator is defined as an operator which shifts the eigenvalues corresponding to a given set of Bloch states. Here, the MOs are hybridized with gold, and this is achieved by changing the metal-molecule hybridizations. $\overline{\text{MPM}}$ is shifting only the Hamiltonian elements localized on the molecule. That is, it is modifying the metal-molecule hybridizations to shift only the Hamiltonian elements localized on the molecule.

⁶ The $\overline{\text{MPM}}$ model shifts the MOs more than the diagonal MPM via a change in the metal-molecule hybridizations. This is clear in the PDOS on the LUMO+1 for BDT-n in Fig 2.10: the maxima of the LUMO+1 is shifted by 1.4 eV and by 2 eV within MPM and $\overline{\text{MPM}}$. This can be confusing since the diagonal part of the two models is equal, and hence the eigenvalues shifts are equal. However, since the MOs in the junctions are hybridized with gold, a change in the hybridizations can shift the PDOS on the MOs (we refer to a shift of the PDOS peaks to as a shift of the MOs).

⁷The hybridized orbitals are adsorbed over a large range of energies. Therefore the PDOS on these orbitals may show more than one peak.

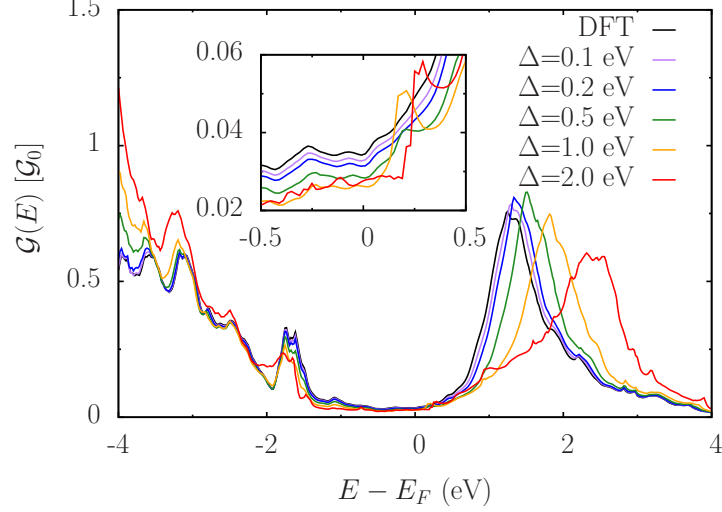


Figure 2.11: MPM conductance of BDT-n with respect to the energy $E - E_F$. E_F is placed at 0 eV. Several Δ values are used: 0.1 eV (purple), 0.2 eV (blue), 0.5 eV (green), 1.0 eV (orange) and 2.0 eV (red). The DFT conductance (black) is also shown.

eV in the inset and the small peak at 1 eV, among others]. In fact, the MPM is a non-localized correction to the DFT Hamiltonian in Wannier basis. That is, it shifts the Hamiltonian elements localized on the molecule together with those ones localized on gold⁸. A modification of the gold elements of the Hamiltonian induces errors in the Landauer formalism: the Hamiltonian on the extended-molecule has to match the lead Hamiltonians, to obtain the transfer matrices in the Landauer formalism. Since, the MPM shifts the gold elements of the extended-molecule Hamiltonian, this does not match anymore the lead Hamiltonians. As a result, instabilities in the conductance appear.

The noise in the conductance within the MPM is shown more clearly in Fig. 2.11. Here, the conductance is calculated for BDT-n within the MPM for different Δ values. For small Δ ($\Delta < 1$), the conductance is not noisy (there is no notorious jitter in the spectra) and the zero-bias conductance is reduced with respect to DFT proportionally to Δ (see the inset). For larger Δ ($\Delta \geq 1$), the conductance is subject to noise

⁸ The diagonal MPM shifts the Bloch orbitals of the system $\varphi_{\text{mol}}^{\text{sys}}$ as can be seen in Eq. (2.3). Therefore, a shift of a Bloch orbital with mixed molecule-metal character results in a shift of the Wannier functions localized in both the molecule and the metal.

and it is manifested in small peaks along the spectra. A similar behavior is observed for the BDA geometry.

In summary, the $\overline{\text{MPM}}$ model effectively reduces the DFT conductance. The $\overline{\text{MPM}}$ zero-bias conductances are even smaller than the experimental measurements. In contrast, the MPM model just slightly decreases the zero-bias conductance due to the weight factor $w_{i,m}$. Moreover, whenever Δ is larger than 1 eV⁹, the MPM conductance presents instabilities coming from noise entering the Landauer formalism. These results show that only the full $\overline{\text{MPM}}$ effectively reduces the zero-bias conductance even in these weakly coupled junctions via a change of the wavefunctions.

2.7 *GW* corrections to the DFT Hamiltonian

In the standard single-shot G_0W_0 approach, the self-energy is approximated using the DFT electronic structure: The QP corrections to the DFT eigenvalues are determined using first-order perturbation theory considering only the diagonal elements of Σ in the space of the DFT orbitals φ_i^{sys} of the contacted-molecule system. In order to calculate the first order correction to the DFT wavefunctions, the off-diagonal elements of Σ are needed also. Currently, such calculations are out of reach for the systems considered here. Nevertheless, a full diagonalization can be performed if a further simplified self-energy is considered. For this purpose, the Coulomb-hole screened-exchange approach [42], which is a static approximation to the *GW* self-energy, is adopted here. For more details, see section 1.3.13.

The *GW* results are found to be similar for BDA and BDT-n. However, the results are different for BDT-h and BDT-p. Hence, BDA and BDT-n are treated in section 2.7.1, whereas, BDT-h and BDT-p are treated in section 2.7.2. In section 2.7.1 we also include a comparison with the results of MPM and $\overline{\text{MPM}}$.

2.7.1 BDA and BDT-n

The values of the zero-bias conductance $\mathcal{G}(E=0)$ calculated with these different approaches are reported in Table 2.5 for BDA and BDT-n. The complete energy dependence of the conductance $\mathcal{G}(E)$ is also given in Fig. 2.12 and Fig. 2.13 for BDA and BDT-n respectively. The cor-

⁹Here we found that instabilities in the conductance start to appear for $\Delta \geq 1$ eV for both systems BDA and BDT-n. However, this value is system dependent.

responding PDOS on the molecule obtained within method (i) [see section 2.4] are shown in the bottom panels of Fig. 2.13 and Fig. 2.12.

	DFT	G_0W_0	CHSX ₀	$\overline{\text{CHSX}}_0$	MPM	$\overline{\text{MPM}}$	Expt.
BDA	0.018	0.019	0.019	0.013	0.017	0.004	0.006 ^a
BDT-n	0.034	0.036	0.037	0.020	0.027	0.004	0.011 ^b

^aRefs. [5, 112]. ^bRefs. [88, 89].

Table 2.5: Zero-bias conductance $\mathcal{G}(E=0)$ in $\mathcal{G}_0$ units calculated with different approaches (see text) for the two systems.

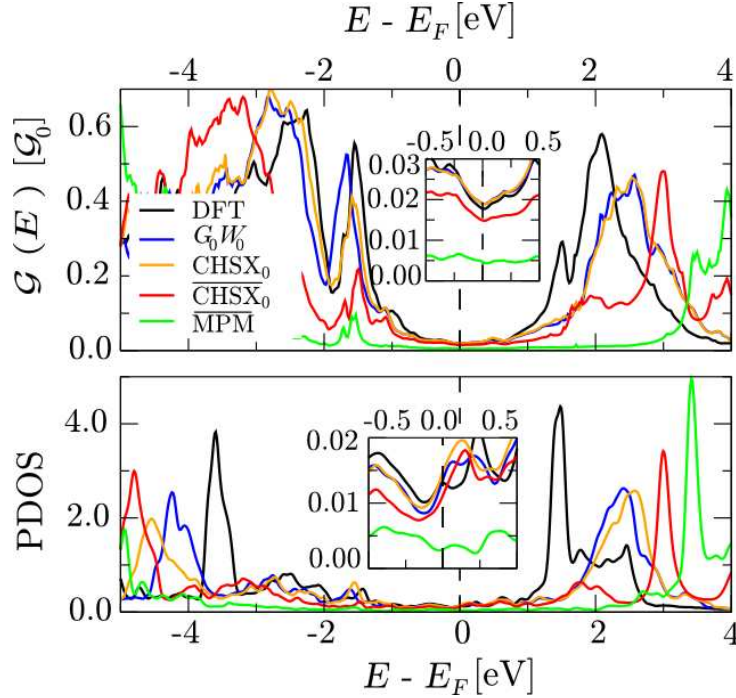


Figure 2.12: Conductance (top) and PDOS on the molecule (bottom) in $e^-/eV/\text{cell}/(2 \text{ spins})$ as a function of the energy (the Fermi energy E_F is set to zero) for BDA. Different approaches are considered: DFT (black), G_0W_0 (blue), CHSX₀ (orange), $\overline{\text{CHSX}}_0$ (red), and $\overline{\text{MPM}}$ (green). For each panel, an inset provides a zoom around the Fermi energy.

As expected, the G_0W_0 corrections to the DFT eigenvalues open the gap between the occupied and unoccupied molecular-like levels, as can be seen by the displacement of the peaks in the PDOS (bottom

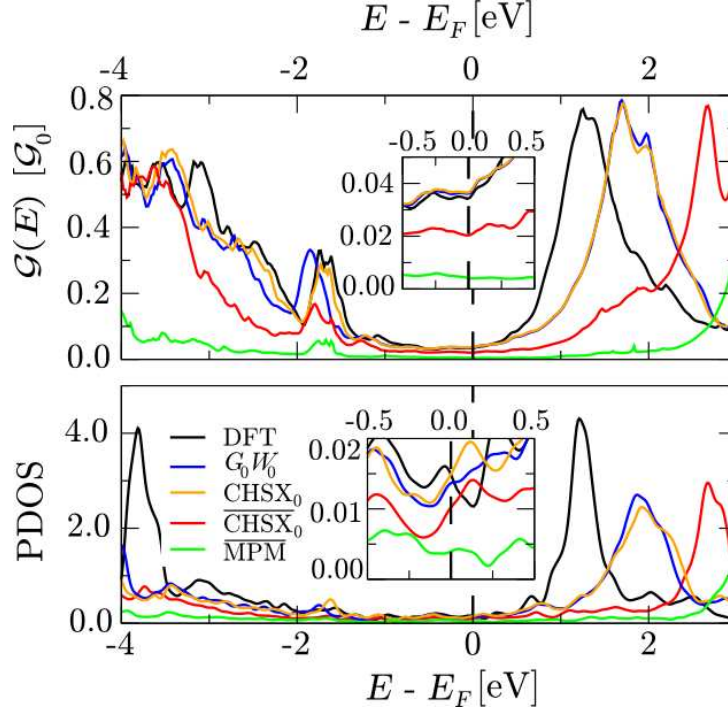


Figure 2.13: Conductance (top) and PDOS on the molecule (bottom) in $e^-/\text{eV}/\text{cell}/(2 \text{ spins})$ as a function of the energy (the Fermi energy E_F is set to zero) for BDT-n. Different approaches are considered: DFT (black), G_0W_0 (blue), CHSX_0 (orange), $\overline{\text{CHSX}}_0$ (red), and $\overline{\text{MPM}}$ (green). For each panel, an inset provides a zoom around the Fermi energy.

panel) and in the conductance (top panel) in Fig. 2.12 and Fig. 2.13. This opening of the gap is much smaller than the one obtained for the isolated molecule (5.5 eV). In particular, the gap between the HOMO and LUMO+1 is increased only by 0.5 eV. The presence of the metallic surface can be estimated to account for a reduction of 2 eV with respect to the isolated molecule (see appendix C). More importantly, the G_0W_0 corrections depend on the weights of the different states of the system on the molecular orbitals $w_{i,m} = |\langle \varphi_i^{\text{sys}} | \varphi_{i,m}^{\text{mol}} \rangle|^2$.

To clarify this point, the G_0W_0 corrections ($\Delta \Sigma^{G_0W_0} = E^{G_0W_0} - E^{DFT}$) are shown in Fig. 2.14 for BDA (a) and BDT-n (b). The PDOS on the MOs obtained within method (i) [see section 2.4] are also shown (bottom panels). Moreover, the corrections corresponding to bands with more than 5 % of molecular character are also shown (yellow points). The molecular character of a given band i is defined as $\sum_m^{\text{mol}} w_{i,m} \times 100\%$. In these Figures the corrections are mainly along simple lines, with slope

given by the metal character of the states. At certain energies, there are abrupt deviations from these lines. These regions coincide with the peaks of the PDOS. Indeed, the corrections depend on the weights: the bigger the weight (the higher the PDOS) the stronger the correction.

Due to the dependence of $\Delta\Sigma^{G_0W_0}$ on $w_{i,m}$, and hence on the wavefunctions, the opening on the gap does not lead to a reduction of $\mathcal{G}(E=0)$. In particular, these weights are quite small around the Fermi level for the very hybridized HOMO and LUMO+1, which drive the zero-bias conductance. Hence, if the DFT wavefunctions are not updated, the resulting G_0W_0 zero-bias conductance will be very close to the DFT one. In contrast, the values of $w_{i,m}$ are higher for the more localized LUMO and HOMO-1, which influence the conductance at larger biases. Thus, the effect of the QP corrections on the energies is mostly visible for $\mathcal{G}(E \neq 0)$.

As a confirmation, the CHSX approximation also does not modify $\mathcal{G}(E=0)$ despite the fact that it usually leads to bigger gaps than those obtained with the G_0W_0 approach. Moreover, the use of closed-packed geometries in the G_0W_0 calculations is not affecting this conclusion (see appendix B for details). These findings point to the importance of the quality of the wavefunctions around E_F .

When updating not only the eigenenergies but also the wavefunctions by the CHSX approximation, $\mathcal{G}(E)$ is reduced by a factor 1.4 (1.7) in the direction of the experimental value reaching 0.013 (0.020) $\mathcal{G}_0$ for BDA (BDT-n). The agreement with experiments would probably be further improved if one could afford to perform calculations with (i) more than one step in the self-consistency loop on the wavefunctions; (ii) more realistic geometries, such as those depicted in Ref. [5]; and (iii) a higher number of gold layers entering the Landauer formula. Furthermore, the results depend somehow on the flavor of the GW self-energy and on the degree of self-consistency adopted, as very recently observed in Ref. [110].

In Ref. [110], both self-consistent GW and non-self consistent $\overline{G_0W_0}$ (including off-diagonal elements for the self-energy) calculations have been performed also on the BDA and BDT-n junctions. A direct comparison with our results is not straightforward since the packing regimes, contact geometries, and methodologies used in both studies are slightly different. Regarding the packing regimes, our plane-wave calculations only allow us to use a 2×2 surface unit cell while it is a 4×4 cell in Ref. [110]. This changes the molecule-molecule distance (it is ~ 3 Å and ~ 8 Å for a 2×2 and a 4×4 surface unit cell, respectively). It is well known that GW is highly sensitive to long-range Coulomb interactions (see Appendix B). Regarding the contact geometries, in the present work, the attachment of the molecule to the leads is modeled by an adatom

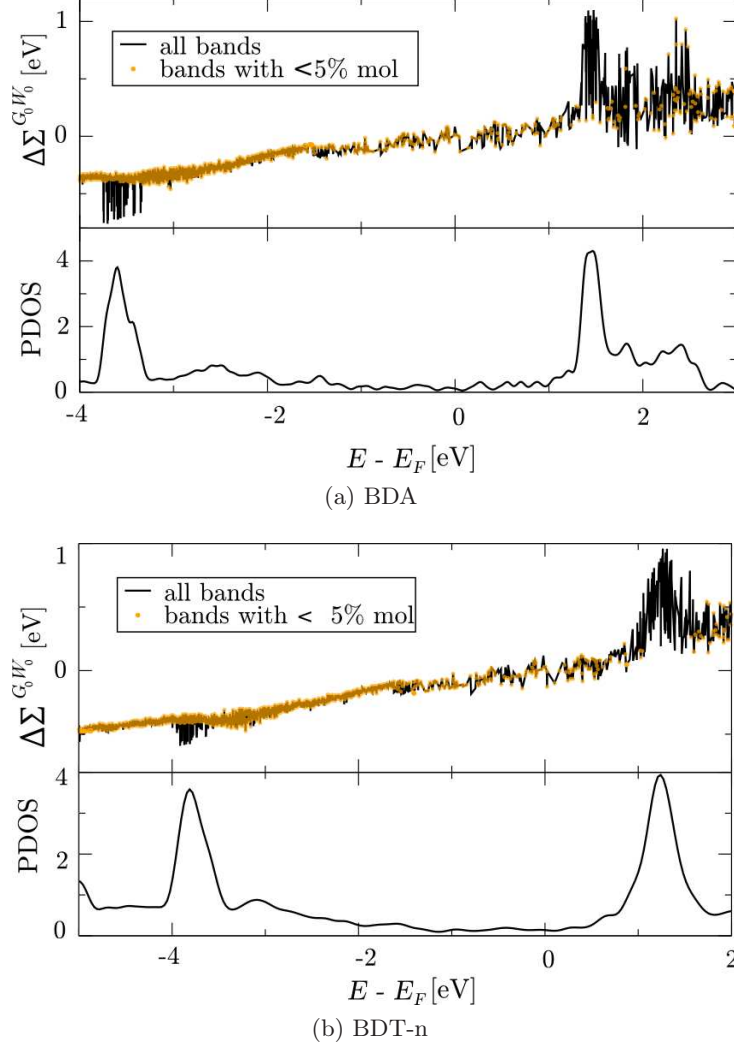


Figure 2.14: $\Delta\Sigma^{G_0W_0} = E^{G_0W_0} - E^{\text{DFT}}$ (top) and PDOS on the molecule (bottom) with respect to the DFT energy $E - E_F$ for BDA (a) and BDT-n (b). On top, the black lines are the G_0W_0 corrections in eV for all $\mathbf{k}$ -points in the IBZ. The yellow circles represent just the corrections for bands with less than 5% of molecular character (see the text).

connected to a flat surface, whereas pyramid-like tips are adopted in Ref. [110]. With respect to a flat surface, a pyramid-like tip is placing the surface farther away from the molecule, reducing the screened-potential at the molecule. Regarding the methodologies, both the self-energy and the polarizability extend over the whole junction (molecule and leads) in

our calculations, while they are limited to the molecule and a few atoms of the leads in Ref. [110]. Finally, our wavefunctions are expanded on a plane-wave basis-set, while a localized basis-set is used in Ref. [110]. The basis convergence for a non-systematic localized basis-set (in a systematic basis-set the completeness of the basis is improved by simply adding more elements to the basis, as is the case for plane-wave basis) is not easy to study and the error magnitude in the QP quantities coming from an incomplete localized basis-set is unknown. Moreover, in our work we updated the Fermi level while in Ref. [110] the Fermi level is kept at the DFT value. We found that this is crucial since a non-self-consistent GW approach is a non-conserving approximation. The absolute position of the MOs after one GW iteration is meaningless if the Fermi level is not updated, that is, the shifts of the MOs are relative to the shifts of the gold states. For example, if the HOMO is shifted by -2 eV with respect to the Fermi level, the conductance is highly reduced, but if at the same time the gold states are shifted by the same value, then the conductance is not affected and only the Fermi level is changed. The most meaningful comparison is between their $\overline{G_0W_0}$ results and our findings for $\overline{\text{CHSX}}_0$. It turns out that they observe a reduction of the conductance by a factor 2.6 (3.4) for BDA (BDT-n) with respect to DFT, while the reduction is 1.4 (1.7) in our case.

The PDOS on the molecule (Fig. 2.12 and Fig. 2.13) shows that $\overline{\text{CHSX}}$ corrections contribute to further separate the unoccupied and occupied molecular-like orbitals (PDOS on the molecule peaks). Since the eigenenergies are only affected at the second order compared to CHSX, this increased opening of the gap is to be attributed to modifications of the metal-molecule hybridizations. To gain more insight on the changes of the wavefunctions, the local density of states (LDOS) is computed in an energy window of 0.8 eV around the Fermi level E_F :

$$\text{LDOS}(\mathbf{r}) = \int_{E_F-0.4\text{eV}}^{E_F+0.4\text{eV}} \sum_i |\varphi_i^{\text{sys}}(\mathbf{r})|^2 \delta(E - E_i) dE. \quad (2.4)$$

The effect of the off-diagonal elements of Σ can be analyzed by plotting the difference between the $\overline{\text{CHSX}}$ and CHSX LDOS, as shown in Fig. 2.15a. Two main changes can be identified. First, *the molecular character is reduced*. This charge transfer does not take place in space (it is less $0.02e^-$ from the molecule to the gold leads) but in energy: the molecular orbitals being shifted away from E_F (see the PDOS in Fig. 2.12 and in Fig. 2.13). Second, *the $e_g(d_{z^2})$ character increases on gold atoms* (see the typical ring shaped red lobes on the gold atoms). For the Au adatoms, the z direction of the $e_g(d_{z^2})$ orbital is oriented along

the Au-N bonding direction. For the atoms of the next gold layer, it changes though it is still conditioned by the Au-N direction. Since there is not a noticeable reduction of the gold character in other directions and no molecule-gold charge transfer, this increase of the $e_g(d_{z^2})$ character can be mainly due to a transfer of electrons from lower energies to the E_F region due to the complete diagonalization of the self-energy corrected Hamiltonian. In contrast, the difference between the CHSX₀ and DFT LDOS (see Fig. 2.15b) is negligible on the molecule, which explains their similar zero-bias conductance. However, there is an increase of the LDOS on the gold atoms without any preferred direction. Since CHSX₀ is not modifying the wavefunctions, this is due to Bloch states shifted from outside the energy window to inside this region. Nevertheless, this shifting of bands does not have an important effect on the conductance in this region as shown in the insets of Figs. 2.12 and 2.13. That is, CHSX₀ is negligibly modifying the conductance, and hence the molecule-gold resonances at this region.

Finally, the self-energy is also modeled by the $\overline{\text{MPM}}$ of section. 2.6, which includes off-diagonal elements, using $\Delta=2$ eV. The $\overline{\text{MPM}}$ leads to an effective opening of the gap between the unoccupied and occupied molecular-like orbitals (PDOS on the molecule peaks) which is much bigger (~ 4 eV) than the one obtained with the $\overline{\text{CHSX}}$ approximation (~ 2 eV). As a result, the $\overline{\text{MPM}}$ conductance is much lower than in any of the fully *ab initio* approaches. This discrepancy can be attributed to some limitations in both the fully *ab initio* calculations and the model ones. On the one hand, the use of highly-packed geometries considerably increases the screening and reduces the size of the corrections obtained within the fully *ab initio* calculations. Nevertheless, the use of the $\overline{\text{CHSX}}$ approximation, which is known to overestimate the experimental gaps, may partially compensates this reduction. On the other hand, two main drawbacks can be pointed out for the model calculations: (i) the classical image charge model is not always appropriate in predicting the individual shifts [138]; (ii) many-body effects on the gold region as observed in our calculations within the $\overline{\text{CHSX}}$ approximation.

In summary, we have demonstrated that a self-energy operator leading to the mere correction of the eigenenergies (such as the G_0W_0 or CHSX approximations) is not enough to change the initial DFT zero-bias conductance. In contrast, when updating also the wavefunctions (such as obtained by the $\overline{\text{CHSX}}$ approximation), the conductance is reduced, improving the agreement with the experiment. The conductance change can be attributed to both a reduction of the molecular character and an increase of the $e_g(d_{z^2})$ gold character. Finally, the disagreement between the $\overline{\text{MPM}}$ and *ab initio* calculations originates from the value of

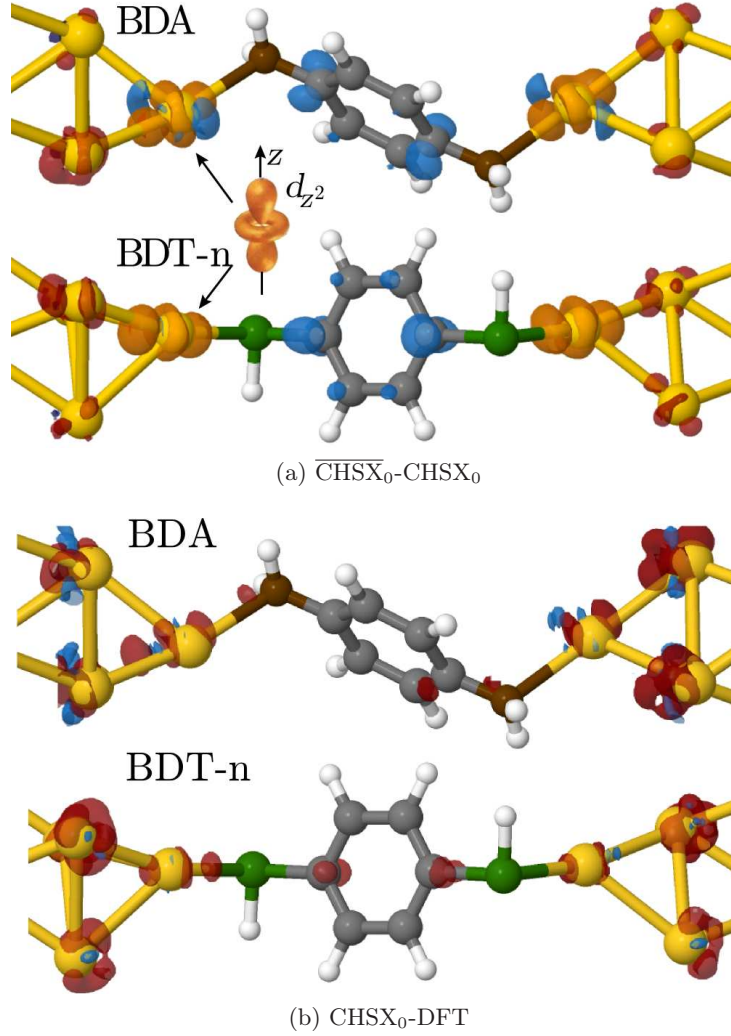


Figure 2.15: Difference between the $\overline{\text{CHSX}}_0$ and the CHSX_0 LDOS (a) and between the CHSX_0 and the DFT LDOS (b) calculated in an energy window of 0.8 eV around the Fermi level for BDA (top) and BDT-n (bottom). Four isovalues are represented: $+4\rho$ in orange, $+1\rho$ in dark red, -1ρ in dark blue, and -4ρ in light blue, with $\rho = 4 \times 10^{-4}$ (6×10^{-4}) $e^-/\text{\AA}^3$ in BDA (BDT-n). The Au, C, N, S, and H atoms are represented by yellow, gray, brown, green, and white spheres, respectively.

the scissor-operator shift Δ and from the wavefunction changes on the gold atoms.

2.7.2 Benzenedithiolate at hollow geometry (BDT-h) and at pyramid geometry (BDT-p)

The values of the zero-bias conductance $\mathcal{G}(E=0)$ calculated with these different approaches are reported in Table 2.6 for BDT-h and BDT-p. The complete energy dependence of the conductance $\mathcal{G}(E)$ is also given in Fig. 2.16 (for BDT-h) and Fig. 2.17 (for BDT-p). The corresponding PDOS on the molecule obtained within method (i) [see section 2.4] are shown in the bottom panels of Fig. 2.16 and Fig. 2.17

	DFT	G_0W_0	CHSX ₀	$\overline{\text{CHSX}}_0$	Expt.
BDT-h	0.305	0.297	0.305	0.270	0.011 ^a
BDT-p	0.365	0.389	0.396	0.362	

^aRefs. [88, 89].

Table 2.6: Zero-bias conductance $\mathcal{G}(E=0)$ in $\mathcal{G}_0$ units calculated with different approaches (see text) for the two systems.

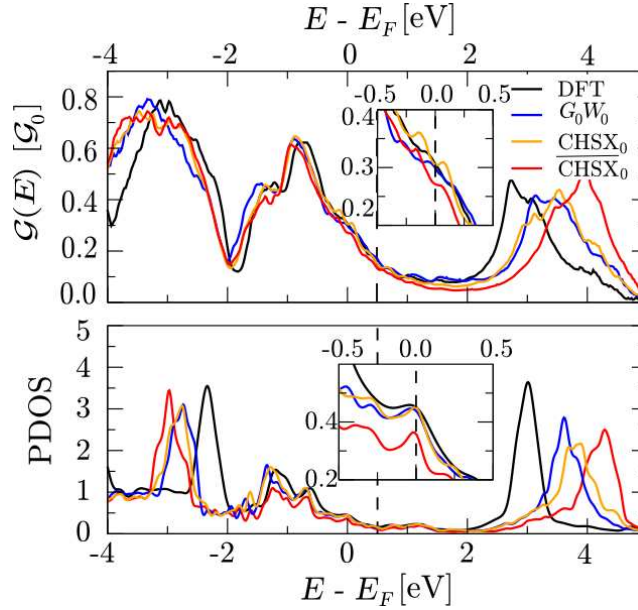


Figure 2.16: Conductance (top) and PDOS on the molecule (bottom) in $e^-/\text{eV}/\text{cell}/(2 \text{ spins})$ as a function of the energy (the Fermi energy E_F is set to zero) for BDT-h. Different approaches are considered: DFT (in black), G_0W_0 (in blue), CHSX₀ (in violet) and $\overline{\text{CHSX}}_0$ (in red). For each panel, an inset provides a zoom around the Fermi energy.

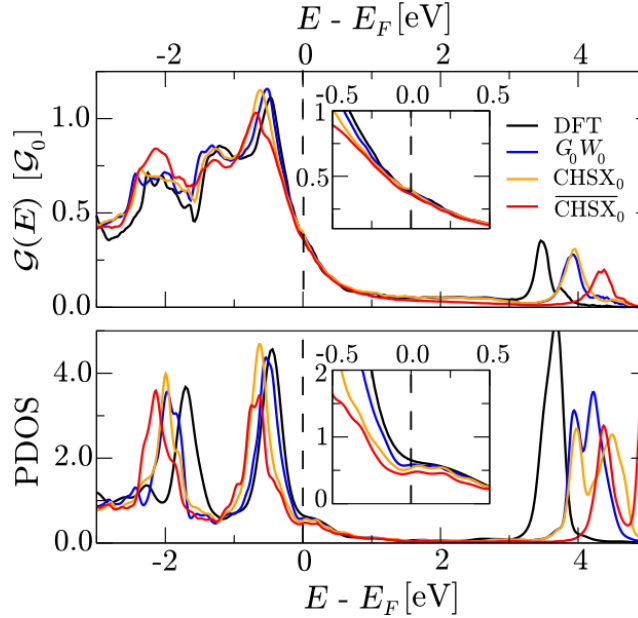


Figure 2.17: Conductance (top) and PDOS on the molecule (bottom) in e^2/h as a function of the energy (the Fermi energy E_F is set to zero) for BDT-p. Different approaches are considered: DFT (in black), G_0W_0 (in blue), CHSX_0 (in violet) and $\overline{\text{CHSX}}_0$ (in red). For each panel, an inset provides a zoom around the Fermi energy.

As expected, the G_0W_0 corrections to the DFT eigenvalues open the gap between the occupied and unoccupied molecular-like levels, as can be seen by the displacement of the peaks in the PDOS (bottom panel) and in the conductance (top panel) in Figs. 2.16 and 2.17. The opening of the gap is of ~ 0.9 (0.5) eV for BDT-h (BDT-p). Moreover, the corrections mainly shift unoccupied bands: the shifts are of ~ -0.2 (-0.1) eV, and $\sim +0.7$ ($+0.3$) eV for the occupied and unoccupied molecular-like levels, respectively, for BDT-h (BDT-p).

The CHSX_0 corrections to the DFT eigenvalues also open the DFT gap. In particular, the shifts are of ~ -0.1 (-0.2) eV, and $\sim +1.0$ ($+0.4$) eV for the occupied and unoccupied molecular-like levels, respectively, for BDT-h (BDT-p). As expected, these gaps are slightly higher than the corresponding G_0W_0 gaps. In fact, CHSX_0 is known to give bigger gaps than G_0W_0 .

In general, diagonal GW corrections are not leading to a reduction of $\mathcal{G}(E=0)$, consistently with the G_0W_0/CHSX_0 results for BDA and BDT-n in section 2.7.1. Indeed, the corrections are negligibly modifying

the PDOS on the molecule at the vicinities of Fermi.

The $\overline{\text{CHSX}}_0$ corrections to the DFT eigenfunctions and eigenvalues further open the gap. Here the shifts are of ~ 0.1 and ~ 1.4 (0.8) eV for BDT-h (BDT-p), for the occupied and unoccupied molecular-like levels. These shifts are mostly on the unoccupied levels, which are far from the Fermi level. Indeed, the total PDOS on the molecule is only considerably modified at energies less than 0 eV and bigger than 2 eV, for the two systems. Hence, the conductance is mainly modified at energies far from the Fermi level. In particular, $\mathcal{G}(E=0)$ is 0.270 and 0.362 $\mathcal{G}_0$ for BDT-h and BDT-p, respectively. This accounts for a reduction of a factor of 1.1 with respect to DFT for BDT-h, whereas for BDT-p the zero-bias conductance remains at its initial DFT value.

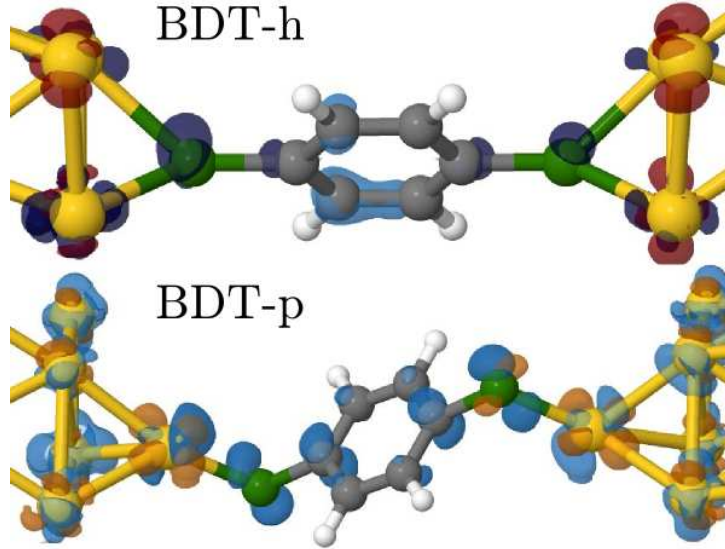


Figure 2.18: Difference between the $\overline{\text{CHSX}}_0$ and the CHSX_0 LDOS calculated in an energy window of 0.8 eV around the Fermi level for BDT-h (top) and BDT-p (bottom). Four isovalues are represented: $+4\rho$ in orange, $+1\rho$ in dark red, -1ρ in dark blue, and -4ρ in light blue, with $\rho = 5 \times 10^{-4}$ (6×10^{-4}) $e^-/\text{\AA}^3$ in BDT-h (BDT-p). The Au, C, S, and H atoms are represented by yellow, gray, green, and white spheres, respectively.

The negligible effect on the zero-bias conductance of the quasiparticle corrections for these systems can be partially explained by the fact that the corrections are mainly modifying the unoccupied molecular-like levels which do not play an important role close to the Fermi level. More important, at the Fermi level region there are complex changes

on the wavefunctions, as explained later, but the zero-bias conductance remains almost unchanged. In fact, when only updating the Hamiltonian elements on the molecule (similar to what is done in Ref. [110]), $\mathcal{G}(E=0)$ is slightly reduced (by a factor of 1.2 [1.5] for BDT-p [BDT-h]), nevertheless, when modifying also the Hamiltonian elements on gold, $\mathcal{G}(E=0)$ goes back to the DFT value. This indicates that the wavefunction changes on gold and on the molecule have the opposite effect on the conductance, therefore, the zero-bias conductance is almost unchanged.

To show the effect of the self-energy on the wavefunctions, in Fig. 2.15b we show the $\overline{\text{CHSX}}_0$ -CHSX₀ LDOS for BDT-h (top) and BDT-p (bottom) in an energy window of 0.8 eV around the Fermi level. The LDOS difference shows important wavefunction modifications in both the molecule and the gold regions (similar to BDA and BDT-n). In both systems, we find a relocation of the wavefunctions on the gold regions close to the metal surfaces. That is, the LDOS is augmented mainly along the gold bonds, and it is reduced in the opposite directions. This effect is more clear for BDT-p, specially on the gold adatoms (see light blue and orange lobes). Such wavefunction changes due to many-body corrections are not unexpected: a similar renormalization effect has been observed in vanadium dioxide [140]. In the molecule region, the LDOS is reduced (light blue lobes), as expected.

More fundamentally, it is known that the zero-bias conductance is successfully treated by the DFT in combination with the Landauer approach in strong coupling regimes [120, 141]. These two systems presenting stronger binding regimes than BDT-n, might be better suited by the Landauer-DFT formalism. However, this is only due to cancellation of errors, since DFT is not predicting the correct wavefunctions. This hypothesis is only based on our $\overline{\text{CHSX}}_0$ results, however, the effect of self-consistency within CHSX remains unknown. Other works in the literature show contradictory results for BDT-h. A self-consistent QP approach, applied only to the molecule part of the Hamiltonian in Ref. [110], indicates that the effect of *GW* corrections in BDT-h is even augmenting the DFT conductance¹⁰. On the other hand, the work of Ref. [93], shows that improving the DFT MOs description within the atomic self-interaction correction (ASIC) XC functional is shifting the

¹⁰ In Ref. [110], it is found that self-consistent *GW* increases the zero-bias conductance due to a modification of the conductance peaks for BDT-h. The "HOMO" peak is moved towards the Fermi-level, which ends up almost at the maxima of the "HOMO" peak. However, their results should be checked with a more rigorous method since their HF conductance for this system does not show the standard features. In particular, the Fermi level is not located in the middle of the "HOMO" and the "LUMO" peaks, but it is just below (in energy) of the "HOMO" peak!

conductance peaks far from the Fermi level, reducing $\mathcal{G}(E=0)$. Due to these contradictory results, more research is required to know whether or not QP effects are important in these systems. For example, a self-consistent MBPT approach, such as CHSX (or QPSCGW) within our methodology, could solve this controversy.

2.8 Partial *ab initio* model corrections to the DFT Hamiltonian

Many-body effects are crucial in the determination of the molecule-metal hybridizations in molecular junctions as seen in the previous section. The main drawback of *ab initio* calculations is the computation time that they usually require. Inspired by the classical model of section 2.6, we study the viability of simple model corrections to predict results in agreement with the *ab initio* calculations. The idea behind this model is to avoid calculating the off-diagonal elements of Σ within $\overline{\text{CHSX}}_0$ or $\overline{G}_0\overline{W}_0$. That is, we aim to have a simple method to obtain a full Σ operator by calculating only explicitly the diagonal elements of the self-energy. Contrary to what was expected, the model results are not accurate enough to be used in quantum transport calculations. Large discrepancies between *ab initio* and model calculations indicate that many-body effects are complex in these systems, and they cannot be accounted for by simple models based on molecular projectors, as it will be explained along this section.

We propose a model which obtain its parameters from the diagonal $G_0W_0(\text{CHSX}_0)$ results through a fitting procedure. $\Delta\Sigma$ contains projectors to the MOs as well as 2 other terms with projectors to the gold states. Hence, it is named 3 projectors model, $\overline{3\text{PM}}$. This self-energy has the following form:

$$\begin{aligned}\Delta\Sigma^{\overline{3\text{PM}}} &= \sum_i^{\text{mol}} \Delta_i |\varphi_i^{\text{mol}}\rangle \langle \varphi_i^{\text{mol}}| \\ &+ \sum_j^{\text{lead}} [\alpha_1(\epsilon_j^1 - E_F + \beta_1)] |\varphi_j^1\rangle \langle \varphi_j^1| \\ &+ \sum_l^{d,\text{lead}} [\alpha_2(\epsilon_l^2 - E_F + \beta_2)] |\varphi_l^2\rangle \langle \varphi_l^2|,\end{aligned}\tag{2.5}$$

where the first term is similar to Eq. (2.2), $|\varphi_j^1\rangle$ and ϵ_j^1 are the j^{th} eigenstate and eigenvalue of an ideal system with just the metal states.

Similarly, $|\varphi_l^2\rangle$ and ϵ_l^2 are those of an ideal system with just the Au 5d bands. E_F is the Fermi level and α_1 , β_1 , α_2 and β_2 are the model parameters. Here the corrections for a given band are coming from two main sources: its molecular character and its metal character. The later has an additional contribution given that the 5d states have a different correction. The diagonal version in Bloch space of this model is also considered:

$$\begin{aligned}\Delta\Sigma^{3\text{PM}} &= \sum_n^{\text{sys}} \sum_i^{\text{mol}} |\varphi_n^{\text{sys}}\rangle \Delta_i |\langle \varphi_n^{\text{sys}} | \varphi_i^{\text{mol}} \rangle|^2 \langle \varphi_n^{\text{sys}}| \\ &+ \sum_n^{\text{sys}} \sum_j^{\text{lead}} |\varphi_n^{\text{sys}}\rangle [\alpha_1(\epsilon_j^1 - E_F + \beta_1)] |\langle \varphi_n^{\text{sys}} | \varphi_j^1 \rangle|^2 \langle \varphi_n^{\text{sys}}| \\ &+ \sum_n^{\text{sys}} \sum_l^{d,\text{lead}} |\varphi_n^{\text{sys}}\rangle [\alpha_2(\epsilon_l^2 - E_F + \beta_2)] |\langle \varphi_n^{\text{sys}} | \varphi_l^2 \rangle|^2 \langle \varphi_n^{\text{sys}}|,\end{aligned}\tag{2.6}$$

where φ_n^{sys} is the n^{th} Bloch state of the junction.

The model parameters can be fitted from the G_0W_0 or from the CHSX₀ results in the $3\text{PM-}G_0W_0$ or in the 3PM-CHSX_0 approximations, respectively. First, the *ab initio* corrections are computed as: $\Delta\Sigma^{G_0W_0} = E^{G_0W_0} - E^{\text{DFT}}$ or $\Delta\Sigma^{\text{CHSX}_0} = E^{\text{CHSX}_0} - E^{\text{DFT}}$, where $E^{G_0W_0}$, E^{CHSX_0} and E^{DFT} are the eigenenergies with respect to E_F at the G_0W_0 , CHSX₀ and DFT approximations, respectively. Second, the model parameters are obtained with a least square fitting to minimize the following functional

$$\mathcal{F}[\{\Delta_i\}, \alpha_1, \beta_1, \alpha_2, \beta_2] = \frac{1}{2} \sum_n (\Delta\Sigma_{nn}^{3\text{PM}} - \Delta\Sigma_n^{G_0W_0})^2. \tag{2.7}$$

Alternatively, when the fitting is done over the CHSX₀ quantities, $\Delta\Sigma_n^{\text{CHSX}_0}$ replaces $\Delta\Sigma_n^{G_0W_0}$ in Eq. (2.7).

To achieve good results, the value of the parameters related to gold (α_1 , β_1 , α_2 and β_2) are fitted first, focusing on the states with mainly gold character. Hence, the first term in Eq. (2.6) is assumed to be negligible. The procedure is as follows:

1. The energy range of interest is separated in two regions according to the dominant gold character. In the first region, the states present mostly gold 6s and 6p character, whereas, in the second region, they essentially show 5d character. The many-body corrections present a different slope in these two regions, as shown in Fig. 2.19.

2. In the first region, the matrix elements $\Delta\Sigma_{nn}^{G_0W_0}$ ($\Delta\Sigma_{nn}^{\text{CHSX}_0}$) are fitted to the second term of Eq. (2.6) in order to find α_1 and β_1 .
3. In the second region, the second and third terms dominate in Eq. (2.6). The second term is fixed by the value of α_1 and β_1 determined previously. The difference between the matrix elements and the second term is fitted to the third term of Eq. (2.6) to obtain α_2 and β_2 .

Notice that lower in energy, the corrections may show a different slope from the two previous ones. However, we are not interested in that energy range.

For BDA, for instance, the first (with $6s$ and $6p$ states) and second (with $5d$ states) regions go from -1.6 to 3 eV and from -3.5 to -1.6 eV, respectively. The dominance of the d character in the second region can be clearly seen in the DOS, as shown in Fig. 2.19. In the first region, the fitting is done over 1470 points to find a straight line defined by α_1 and β_1 (see pink line in Fig. 2.19). The fitting is satisfactory with a standard deviation of only 0.05 eV. In the second region, the fitting is done over 6688 points to find a second line defined by α_1 , α_2 , β_1 and β_2 (see orange line in Fig. 2.19). This time the fitted values have a standard deviation of only 0.04 eV.

After finding the parameters related to gold, the individual shifts Δ_i are obtained by the fitting procedure to the full Eq. (2.6). To obtain good results, it is important to weight the states by their amount of molecular character. Fig. 2.20 shows a comparison of $\Delta\Sigma_{nm}$ calculated with G_0W_0 and 3PM- G_0W_0 . The model matrix elements are in good agreement with the *ab initio* ones, with an average absolute difference of less than 0.2 eV for most of the bands, as shown in the figure. As a validation test, the PDOS on the MOs predicted by the model should agree well with the *ab initio* results, as shown in Fig. 2.21.

The model parameters are shown in Table 2.7 for BDA and BDT-n, only. For BDT-h and BDT-p, this model is not applicable since it relies on the MOs of the isolated molecule, which are strongly modified in these junctions due to the presence of the metal (see section 2.4).

2.8.1 The diagonal three-projectors model (3PM)

In Fig. 2.21 the PDOS to the HOMO (left) and LUMO (right) is shown for BDA (top) and BDT (bottom) as calculated by different approaches: DFT (black lines), G_0W_0 (blue lines), and 3PM (red lines). The PDOS peaks corresponding to the HOMO and the LUMO are just slightly shifted by the G_0W_0 corrections. Moreover, the peaks change

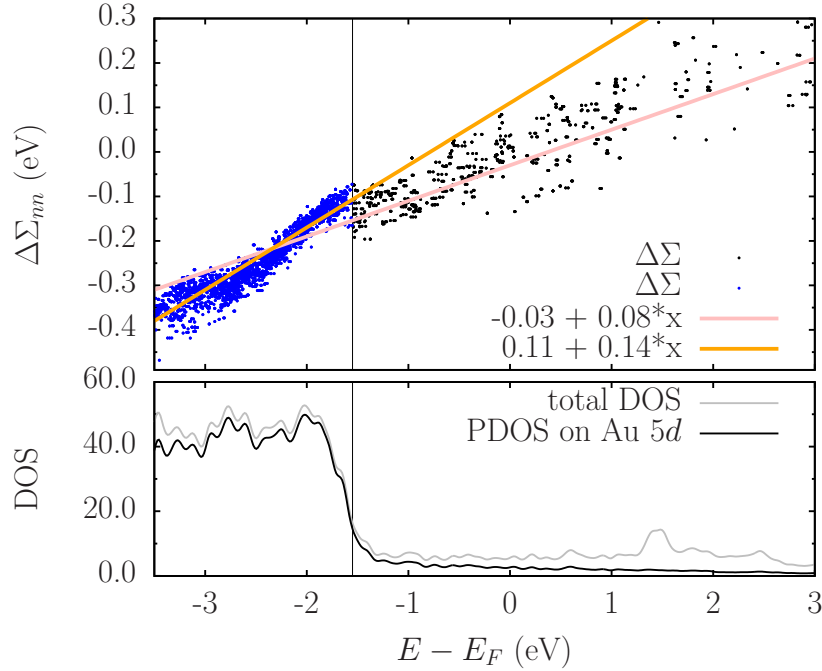


Figure 2.19: Gold parameters for 3PM. Two regions are defined from -3.5 to -1.6 eV and from -1.6 to 3 eV, respectively (they are separated by a vertical line). For BDA, the matrix elements of $\Delta\Sigma_{nn}^{G_0W_0}$ are shown (on top) in eV. The matrix elements with more than 90% of gold character in the first region are shown in black dots, whereas those with more than 90% of gold 5d character in the second region are shown in blue dots. The pink and orange lines are the two fitted lines (defined by $\alpha_1, \beta_1, \alpha_2$ and β_2). On the bottom, the PDOS on the 5d gold states (black line) and the total DOS (gray line) are shown in elec./eV/cell.

in shape. For both systems, the PDOS peaks are well predicted by the model, that is, the blue and red lines are almost on top of each other.

Fig 2.22 shows the conductance (top) and PDOS on the molecule (bottom) for BDT-n. Several approaches are shown: DFT (solid black), G_0W_0 (solid blue) and the diagonal 3PM- G_0W_0 (dashed green). At first glance, the 3PM- G_0W_0 results are almost on top of the G_0W_0 ones. In particular, the position of the PDOS peaks are, in a rough way, well predicted by the model. When zooming at the Fermi level region (see the insets), small differences appear in the PDOS. While the model lowers the DFT PDOS at this region, the *ab initio* correction reaccommodates the bands in a complex way: the PDOS just above E_F is higher than in DFT, whereas the one below E_F is lower.

	$\overline{3\text{PM-CHSX}_0}$ [eV]				$\overline{3\text{PM-}G_0W_0}$ [eV]			
	α_1	β_1	α_2	β_2	α_1	β_2	α_2	β_2
BDA	0.07	0.00	0.25	2.57	0.09	-0.35	0.06	2.35
BDT-n	0.06	-4.42	0.23	3.05	0.09	0.30	0.05	2.24

	Δ_i in $\overline{3\text{PM-CHSX}_0}$ [eV]			Δ_i in $\overline{3\text{PM-}G_0W_0}$ [eV]		
	HOMO	LUMO	LUMO+1	HOMO	LUMO	LUMO+1
BDA	-1.0	1.2	0.1	-0.5	1.0	0.4
BDT-n	-0.8	0.8	0.8	-0.5	0.7	0.6

Table 2.7: $\overline{3\text{PM}}$ model parameters

These small differences in the PDOS, have a direct consequence in the zero-bias conductance. The $3\text{PM-}G_0W_0$ conductance is $0.029 \mathcal{G}_0$, slightly lower than the DFT value of $0.034 \mathcal{G}_0$. However, the G_0W_0 conductance is $0.036 \mathcal{G}_0$, almost equal to the DFT value. Hence, the zero-bias conductance predicted by the model is slightly lower than the *ab initio* one, despite the fact that the position of the HOMO and LUMO peaks are well predicted by the model. Similar results are observed for BDA and for 3PM-CHSX_0 [the calculated $\mathcal{G}(E=0)$ within the different approaches here are shown in table 2.8 and the 3PM-CHSX_0 results are shown in the following section: in Figs. 2.23 and 2.24 along with the $\overline{3\text{PM-CHSX}_0}$ results].

Based on these results, we can cite some problems related to the 3PM .

1. The model PDOS on the molecule is only in rough agreement with the G_0W_0 results. In fact, the microscopic details at the Fermi level region are not recovered.
2. Due to this small discrepancy, the zero-bias conductance predicted by the model is often slightly lower than in the *ab initio* case.
3. More fundamentally, φ_m^{mol} , (the main quantity of the model) is not well defined, as explained in section 2.4.

2.8.2 The full three-projectors model ($\overline{3\text{PM}}$)

The 3PM-CHSX_0 (dashed blue lines) and $\overline{3\text{PM-CHSX}_0}$ (dashed red lines) results are shown in Fig. 2.23 for BDA. The full *ab initio* CHSX_0 (solid blue lines) and $\overline{\text{CHSX}_0}$ (solid red lines) results are also shown. The corresponding results for BDT-n are shown in Fig. 2.24. Moreover, the

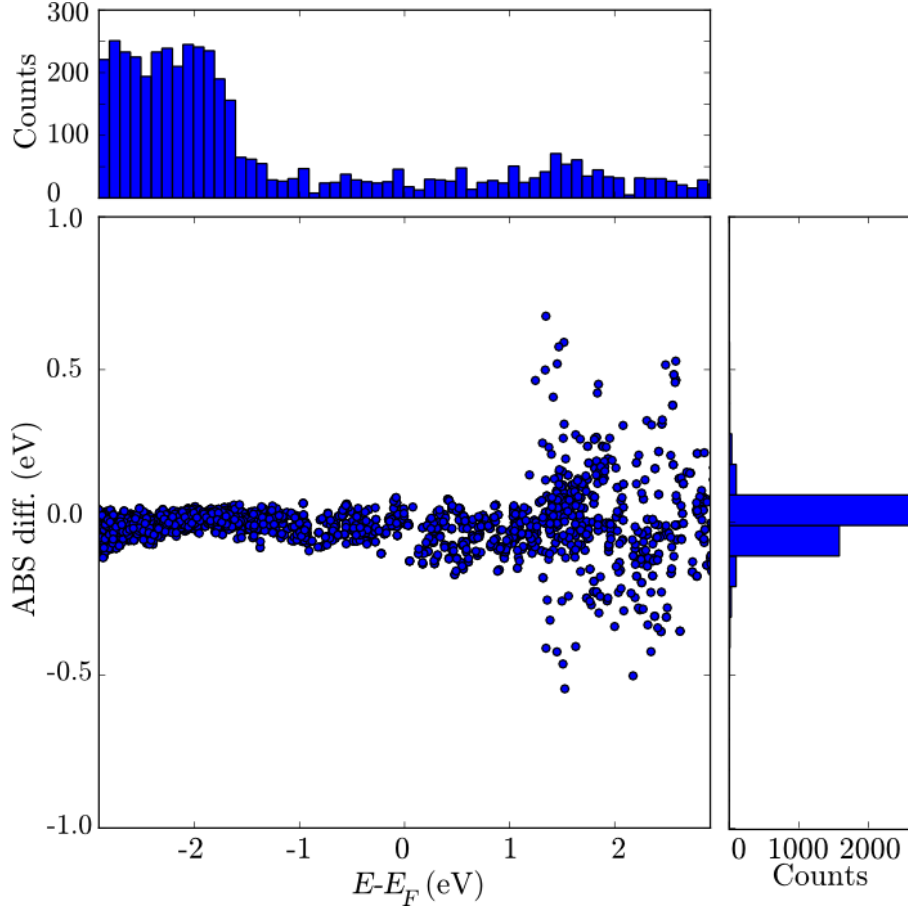


Figure 2.20: 3PM vs. G_0W_0 corrections. Absolute difference in eV between the diagonal matrix elements of $\Delta\Sigma_{nn}$ as calculated within G_0W_0 and within 3PM- G_0W_0 , for BDA.

values for the zero-bias conductance as calculated within the models and within the *ab initio* methods are shown in Table 2.8.

For the diagonal 3PM-CHSX₀ results, we found the same trends as for those of the 3PM- G_0W_0 . In particular, the PDOS on the MOs are in rough agreement with the *ab initio* results. The position of the peaks agree well, however, there are small differences in the PDOS which are important for the conductance. These findings were already commented in the previous section.

The PDOS on the molecule calculated within $\overline{\text{CHSX}}_0$ and $\overline{\text{3PM-CHSX}}_0$ are in poor agreement for most of the energy range (see the dashed and solid red lines in Fig. 2.23 and Fig. 2.24). For instance, the

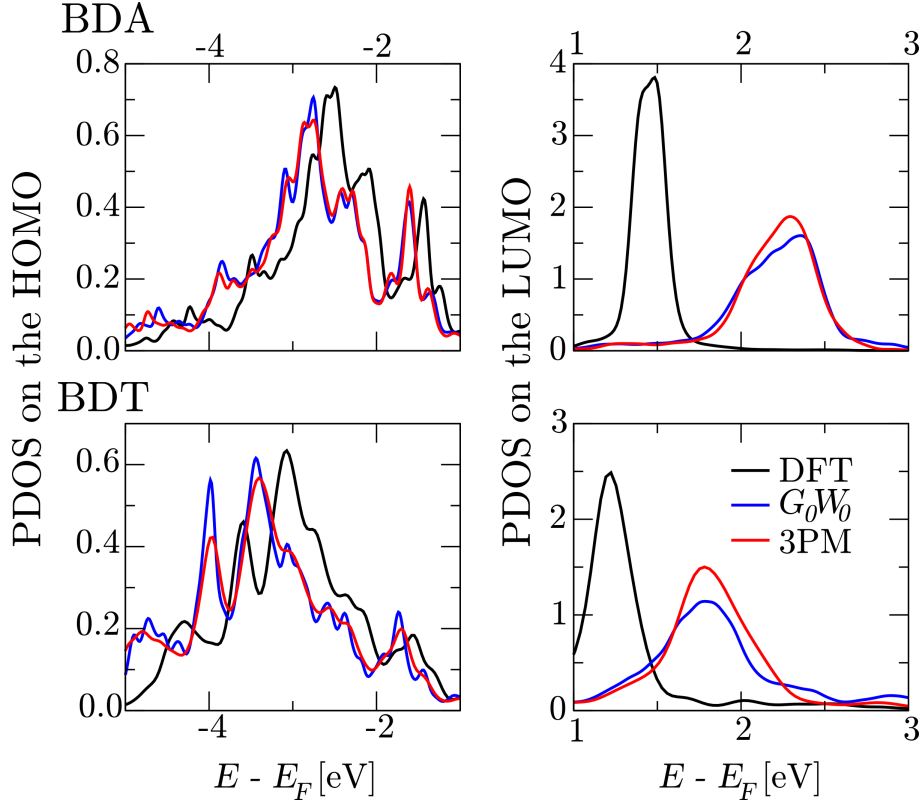


Figure 2.21: PDOS on the HOMO (left) and LUMO (right) in arb. units for BDA (top) and BDT-n (bottom). The DFT (black), G_0W_0 (blue) and 3PM- G_0W_0 (red) results are shown (see text).

position of the LUMO peak is 2.7 eV (2.0 eV) within the model, whereas it is 3.0 eV (2.7 eV) within the *ab initio* method, for BDA (BDT-n). That is, the diagonal 3PM-CHSX₀ predicts the MOs positions in agreement with CHSX₀, while the full $\overline{3PM}$ -CHSX₀ results are not consistent with the $\overline{CHSX_0}$ ones. This implies that **the off-diagonal elements of 3PM are quite different from the *ab initio* ones.**

The resulting $\overline{3PM}$ -CHSX₀ conductance for BDA is 0.013 $\mathcal{G}_0$, in excellent agreement with the $\overline{CHSX_0}$ result, however, this is just a lucky coincidence as discussed afterwards. On the other hand, the model conductance for BDT-n is 0.009 $\mathcal{G}_0$, a factor of 2 smaller than the $\overline{CHSX_0}$ value of 0.02 $\mathcal{G}_0$. This is a direct consequence of the disagreement in the PDOS on the molecule.

The disagreement between the results obtained within $\overline{3PM}$ -CHSX₀ and CHSX₀ for BDT-n has important implications. The position of

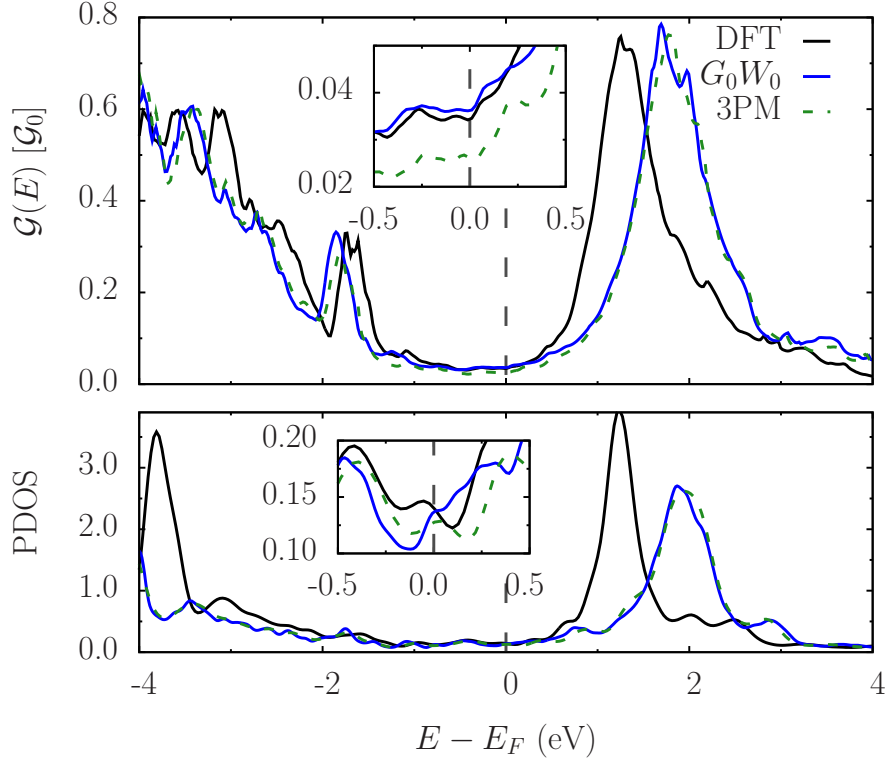


Figure 2.22: Conductance (top) and the corresponding PDOS on the molecule (bottom) for BDT-n. The DFT (solid black), G_0W_0 (solid blue) and 3PM- G_0W_0 (dashed green) results are shown. Two insets show zoom over the area close to the Fermi level (E_F), which is placed at 0 eV as indicated by a dashed vertical line.

the occupied MOs close to the Fermi level, such as the HOMO, are in agreement within the two methods, whereas, the position of the partially unoccupied LUMO+1 is ~ 2.0 eV within the model, and ~ 3.0 eV within the *ab initio* calculation. The molecular-shift Δ_i associated to this orbital in the model is ~ 0.8 eV, moreover, to place the maxima of the LUMO+1 at 3.0 eV, one needs a shift of ~ 1.5 eV. Hence, one could think that the *ab initio* operator is shifting twice the LUMO+1, with respect to the model. Since the zero-bias conductance for this system is driven mainly by the HOMO and the LUMO+1, within the reasoning of the model calculations, one could expect a smaller $\mathcal{G}(E=0)$ within $\overline{\text{CHSX}}_0$ than within $\overline{3\text{PM-CHSX}}_0$, (the bigger the shifts, the smaller the $\mathcal{G}(E=0)$). However, the result is the opposite: the model conductance is about one half of the *ab initio* one. This unexpected result is explained by the fact

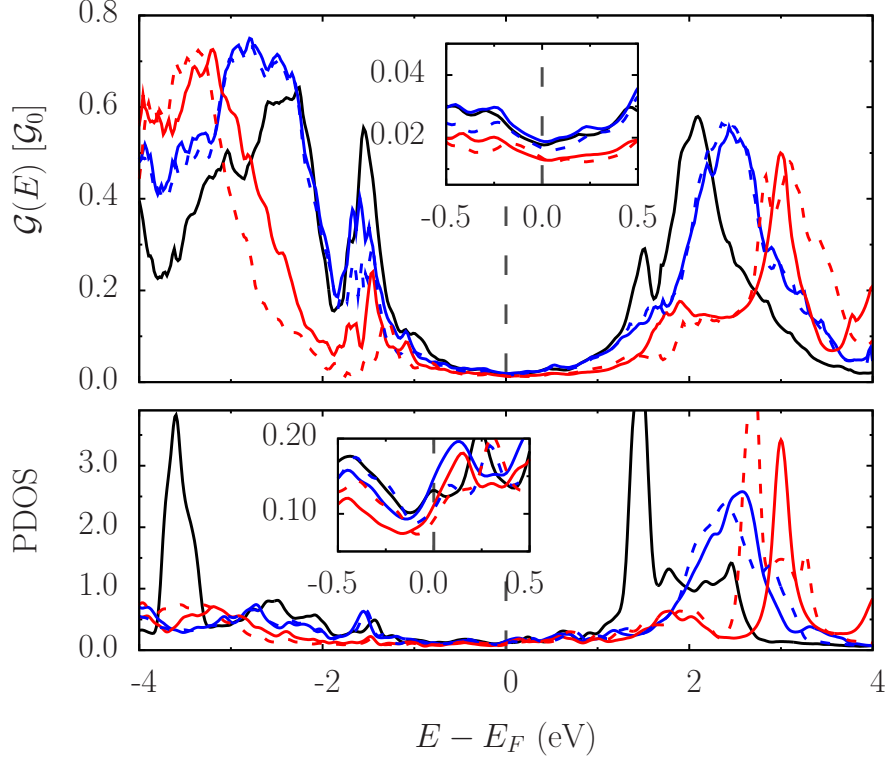


Figure 2.23: Conductance (top) and the corresponding PDOS on the molecule (bottom) for BDA. The *ab initio* results; DFT (solid black lines), $\overline{\text{CHSX}}_0$ (solid blue lines) and $\overline{\text{CHSX}}_0$ (solid red lines), and the model results; 3PM- $\overline{\text{CHSX}}_0$ (dashed blue lines) and 3PM- $\overline{\text{CHSX}}_0$ (dashed red lines), are shown. Two insets show zoom over the area close to the Fermi level (E_F), which is placed at 0 eV as indicated by a dashed vertical line.

that in the model calculations the PDOS on the molecule at the vicinities of the Fermi level is substantially smaller than the corresponding PDOS obtained within $\overline{\text{CHSX}}_0$, as shown in the inset of Fig. 2.24. Therefore, **the PDOS changes at 0 eV (wavefunction changes) due to many-body interactions are not well described by models based on molecular orbitals.** This conclusion is in line with the findings of Ref. [110]¹¹.

¹¹ In Ref. [110], many-body corrections were studied for the same junctions as in our work. Self-consistent and one-shot *GW* self-energies were used to correct the DFT Hamiltonian on only the molecule. They compared their *GW* results to those with the MPM with Δ_i chosen to put the PDOS peaks at the same position that the *GW* results. They found that model corrections were in disagreement with the *ab*

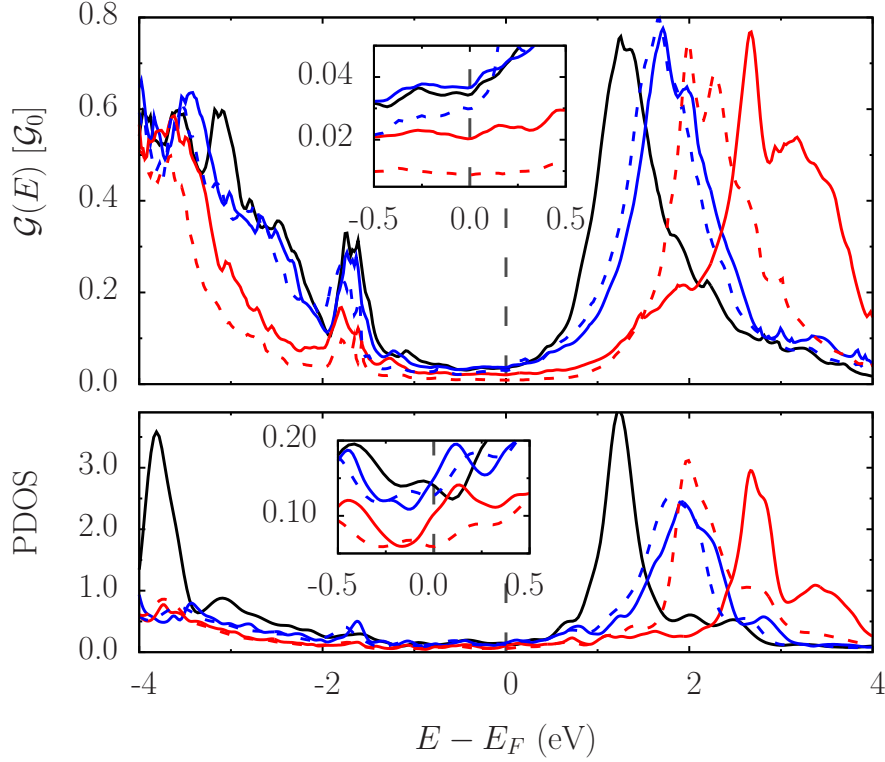


Figure 2.24: Conductance (top) and the corresponding PDOS on the molecule (bottom) for BDT-n. The *ab initio* results; DFT (solid black lines), $\overline{\text{CHSX}}_0$ (solid blue lines) and $\overline{\text{CHSX}}_0$ (solid red lines), and the model results; 3PM- $\overline{\text{CHSX}}_0$ (dashed blue lines) and 3PM- $\overline{\text{CHSX}}_0$ (dashed red lines), are shown. Two insets show zoom over the area close to the Fermi level (E_F), which is placed at 0 eV as indicated by a dashed vertical line.

To evaluate more rigorously the accuracy of the model calculations, we calculate the relative and absolute error in the conductance (in an energy window of 4 eV around the Fermi level) within the model calculations with respect to the *ab initio* results [absolute error= (model value - *ab initio* value), relative error= absolute error / *ab initio* value $\times$ 100]. This is shown in Table 2.9. In this energy range, the diagonal model conductances agree with the *ab initio* ones with an absolute (relative) error of 0.014 G_0 to 0.03 G_0 , (11% to 30% of the DFT value), depending on the system. Notice that 30% of error is as large as the many-body *ab initio* corrections [the $\overline{\text{CHSX}}_0$ corrections are $\sim$ 30% (41%) of the DFT value in

initio ones, due to different decays in the conductance peaks.

	DFT	G_0W_0	CHSX ₀	$\overline{\text{CHSX}}_0$	Expt.
BDA	0.018	0.019	0.019	0.013	0.006 ^a
BDT-n	0.034	0.036	0.037	0.020	0.011 ^b

^aRefs. [5, 112]. ^bRefs. [88, 89].

	3PM		$\overline{3\text{PM}}$	
	G_0W_0	CHSX ₀	G_0W_0	CHSX ₀
BDA	0.015	0.017	0.011	0.013
BDT-n	0.026	0.029	0.012	0.009

Table 2.8: Zero-bias conductance $\mathcal{G}(E=0)$ in $\mathcal{G}_0$ units calculated with different approaches (see text) for the two systems.

	Absolute and relative error		
	G_0W_0 vs.	CHSX ₀ vs.	$\overline{\text{CHSX}}_0$ vs.
	3PM- G_0W_0	3PM-CHSX ₀	$\overline{3\text{PM}}$ -CHSX ₀
BDA	11%, 0.014 $\mathcal{G}_0$	13%, 0.017 $\mathcal{G}_0$	29%, 0.020 $\mathcal{G}_0$
BDT-n	18%, 0.020 $\mathcal{G}_0$	26%, 0.030 $\mathcal{G}_0$	57%, 0.046 $\mathcal{G}_0$

Table 2.9: Absolute and relative error in the calculated conductance from -2 eV to 2 eV within the model calculations with respect to the *ab initio* results (see text).

this energy window]. What is more, the full model conductance presents big errors with respect to the $\overline{\text{CHSX}}_0$ results: 0.020 $\mathcal{G}_0$ (0.046 $\mathcal{G}_0$) [29% (57%)] for BDA (BDT-n). That is, the error can be even larger than the magnitude of the *ab initio* corrections. Hence, the conductance as predicted by the diagonal or full model is not reliable.

2.8.3 The shape of Σ

As seen in the previous section, the model results are not in line with the *ab initio* calculations. Two models were introduced in this chapter: the $\overline{\text{MPM}}$ in section 2.6 and the $\overline{3\text{PM}}$ in section 2.8. These two models are assuming that many-body effects are mainly shifting the molecular orbitals by a given Δ_i value. This is obtained by a classical image-charge model in the $\overline{\text{MPM}}$, whereas this is fitted from the *ab initio* many-body results in the $\overline{3\text{PM}}$. In this section, we study the validity of

models based on molecular projectors by analyzing Σ as obtained from $\overline{\text{CHSX}}_0$ ($\Sigma^{\overline{\text{CHSX}}_0}$).

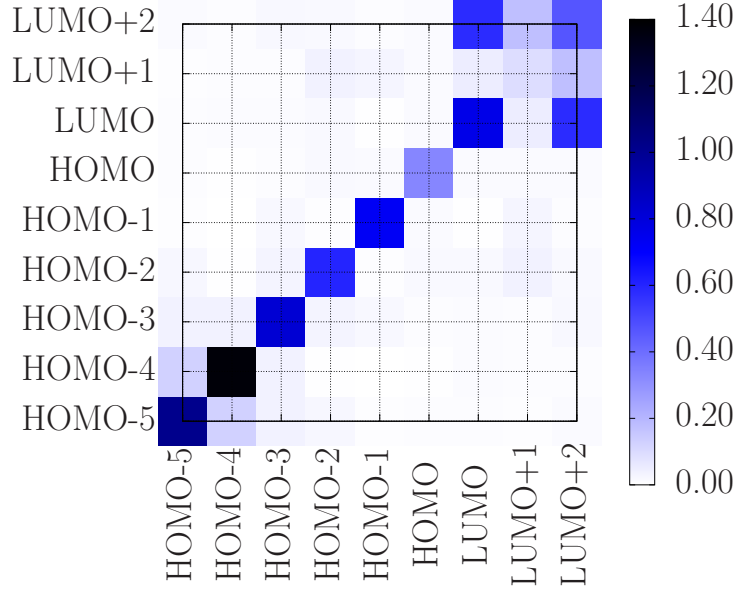


Figure 2.25: Matrix elements of $\Sigma^{\overline{\text{CHSX}}_0}$ in molecular orbital basis for BDT-n (see text). The absolute value in eV is shown for an arbitrary $\mathbf{k}$ -point.

At the end of a $\overline{\text{CHSX}}_0$ calculation, we have the matrix elements of $\Sigma_{mn}^{\overline{\text{CHSX}}_0}$ between pairs of Bloch states of the system, labeled by m and n . These can be used to obtain the matrix elements of $\Sigma_{j,\ell}^{\overline{\text{CHSX}}_0}$ between two molecular orbitals labeled by j and ℓ by using the closure relation, $\sum_m |\varphi_m^{\text{sys}}\rangle \langle \varphi_m^{\text{sys}}| = 1$, as

$$\langle \varphi_j^{\text{mol}} | \Sigma^{\overline{\text{CHSX}}_0} | \varphi_\ell^{\text{mol}} \rangle = \sum_{m,n} \langle \varphi_j^{\text{mol}} | \varphi_m^{\text{sys}} \rangle \langle \varphi_m^{\text{sys}} | \Sigma^{\overline{\text{CHSX}}_0} | \varphi_n^{\text{sys}} \rangle \langle \varphi_n^{\text{sys}} | \varphi_\ell^{\text{mol}} \rangle \quad (2.8)$$

Using this formula and defining the MOs with MLWFs (method (ii) in section 2.4), we calculate the matrix elements of $\Sigma_{j,\ell}^{\overline{\text{CHSX}}_0}$ for BDT-n. We analyze this junction, since we obtained the larger discrepancies between model and *ab initio* calculations in this system in section 2.8.2. Fig. 2.25 shows the absolute value of $\langle \varphi_j^{\text{mol}} | \Sigma^{\overline{\text{CHSX}}_0} | \varphi_\ell^{\text{mol}} \rangle$ at an arbitrary $\mathbf{k}$ -point¹² for BDT-n. Only the elements corresponding to MOs close to the Fermi level are shown. The diagonal elements of this matrix indicate a simple

¹²For most of the $\mathbf{k}$ -points we found similar results.

shift of the orbitals, whereas the off-diagonal elements indicate changes in the hybridization. The matrix is diagonal for some orbitals (see for example, the HOMO-3 to the HOMO). Nevertheless, off-diagonal elements indicate strong changes in the hybridization, as is the case for the LUMO, LUMO+1 and LUMO+2. This clearly indicates that **self-energy *ab initio* corrections are not only shifting the MOs, but also mixing them, which cannot be accounted for with models based on molecular projectors.**

2.9 Conclusions

In section 2.2 we studied the BDT (-thiol and -thiolate) and the BDA molecules in gas phase. The geometrical parameters were obtained within DFT in remarkably good agreement with the experimental data.

It is well known that the molecule band gaps are largely underestimated by the DFT theory and that an excited states theory such as MBPT is better suited for this. By means of G_0W_0 calculations we corrected the DFT eigenenergies. The G_0W_0 gaps, shown in section 2.2, were in good agreement with those obtained by a Δ SCF calculation, which is known to predict with good accuracy the band-gaps of these kind of molecules. On the other hand, when correcting the DFT eigenenergies within CHSX₀, the resulting gaps were about 1 eV bigger than the corresponding G_0W_0 gaps. This was expected since CHSX₀ is well known to predict bigger gaps than G_0W_0 .

In section 2.3, we studied four molecular junctions at the DFT level. In particular, we calculated the geometrical details of these systems. Our results were in agreement with previous theoretical studies and with the experimental measurements.

In these junctions, the MOs hybridize with metal states. By means of DFT calculations, in section 2.4, we found that the MOs in the junctions experienced important changes, due to metal-molecule hybridizations. For the systems with lower coupling, (BDA and BDT-n), the hybridized orbitals still resembled those of the isolated molecule, although, an important mixing with gold states was observed. For the systems with stronger coupling (BDT-p and BDT-n), the hybridized orbitals did not resemble anymore those of the isolated molecule. In fact, the concept of MOs in these junctions is ambiguous *i.e.*, the MOs in these junctions are not well defined. Due to this reason, the PDOS on the molecule was found to depend on the method used to obtain the MOs. For example, in BDT-n and BDT-p, we calculated the PDOS with three different sets of MOs, which resulted in three different spectra.

In section 2.5, we calculated the DFT conductance for the molecular junctions. Our results were in agreement with previous findings. In particular, the value of the zero-bias conductance was higher than the experimental evidence by at least a factor of 3, as it has been found by many other groups.

In section 2.6, we applied classical model corrections to the DFT Hamiltonian. The full $\overline{\text{MPM}}$ modifies the wavefunction of the system, and hence the metal-molecule hybridizations. The calculated $\overline{\text{MPM}}$ zero-bias conductance ended up to be even lower than the experimental evidence. The diagonal MPM reduced just slightly the DFT conductance, due to the weights factor, $w_{i,m}$ entering in the definition of the operator. The resulting conductance presented noise due to instabilities in the calculation of the transfer matrices entering the Landauer formalism.

In section 2.7, we applied *ab initio* corrections to the DFT Hamiltonian. G_0W_0 or CHSX_0 corrections to only the DFT eigenvalues did not modify the initial DFT zero-bias conductance for all of the envisioned systems. This result was in agreement with the diagonal classical corrections of section 2.6. For the systems with lower coupling, BDA and BDT-n, a modification of the metal-molecule hybridizations, and hence of the wavefunctions, via a $\overline{\text{CHSX}}_0$ self-energy operator resulted in a decrease of the zero-bias conductance. Thus, the agreement with the experiment was improved. The conductance change was attributed to both a decrease of the molecular character and an increase of the $e_g(d_{z^2})$ gold character, as shown in section 2.7.1.

In section 2.7.1, we also compared the $\overline{\text{MPM}}$ and $\overline{\text{CHSX}}_0$ results. They presented strong disagreements, which originated mainly from the value of the scissor-operator shift Δ , and from the wavefunction changes on the gold atoms.

For BDT-p and BDT-h, even a first $\overline{\text{CHSX}}_0$ iteration was found not change considerably the initial DFT zero-bias conductance, although important changes in the wavefunctions and PDOS on the molecule (metal-mol hybridizations) were observed. That is, DFT predicted the correct zero-bias conductance due to cancellation of errors.

In section 2.8, a more refined model based on the classical $\overline{\text{MPM}}$ was introduced to determine the viability of model corrections based on molecular projectors. With respect to the *ab initio* results, the model was imprecise in determining the conductance: the relative error in the conductance was often even higher than the *ab initio* many-body corrections, as explained in section 2.8.2. By analyzing the matrix elements of $\Sigma^{\overline{\text{CHSX}}_0}$, we found that *ab initio* corrections were not simply shifting the MOs as the models assume. In fact, important MOs hybridizations were observed, which cannot be accounted for with models based on molecular

projectors, such as the $\overline{3PM}$ and the $\overline{MPM}$.

In summary, many-body effects were important to describe the MOs for the isolated molecules and the wavefunctions (metal-molecule hybridizations) for the molecular junctions. Due to the complex nature of the wavefunction changes, only *ab initio* many-body approaches were reliable to predict the conductance of these junctions.

Chapter 3

The bandstructure of gold from first-principles

3.1 Introduction

The theoretical determination of the bandstructure of gold has been an open issue for more than four decades. Early works from the 70's [142, 7, 143] focused on relativistic effects which are responsible for its yellow color. Thereafter, the bandstructure of Christensen and Seraphin [142] has been used to interpret photoemission experiments. Recently, a few discussions on this topic appeared in the literature. The cohesive energy in noble metals was shown to contain large terms arising from dispersion forces, such as Van der Waals interactions [144], indicating the importance of many-body correlations for closed shell d electrons. Moreover, the experimental work of R. Courths *et al.* [8] using angle-resolved photoemission and the theoretical work of P. Romaniello *et al.* [9] using time-dependent current DFT, confirmed previous findings [7]. The occupied $5d$ bands agree well with the experimental measurements if they are shifted down by ~ 0.35 eV. For the same purpose, the unoccupied $6sp$ bands must be shifted up by ~ 0.7 eV. *i.e.*, the theoretical interband gap ($5d$ - $6sp$ gap) is smaller than the experimental one by ~ 1 eV.

Similar discrepancies were encountered in other noble metals when calculating the bandstructure with DFT within the LDA or the GGA. To solve these deviations, quasiparticle corrections to the DFT eigenvalues have been applied with great success. For instance, in silver and copper, the G_0W_0 approach corrects the DFT interband gap in a remarkably good agreement with the experiments [10, 11].

The standard G_0W_0 approach is a first order-perturbation theory which only modifies the DFT eigenvalues. Its validity comes from the

assumption that the DFT wavefunctions are close to the QP ones. Therefore, it sometimes fails to predict the correct band widths and inter-band gaps in metals. Moreover, its results depend on the starting DFT bandstructure [145]. In general, the use of this approximation must be considered with care. To overcome these deficiencies, the quasiparticle self-consistent GW (QPSCGW) approximation was proposed and applied to several systems [45, 44, 146]. In fact, it predicts more accurate band-widths in solids than G_0W_0 does [146].

In this chapter, the bandstructure of gold is calculated from MBPT to elucidate the role of correlations and to provide a more reliable theoretical bandstructure to interpret the experimental findings. Different approximations are considered here (see section 1.3.13). It is found that G_0W_0 corrections shift the unoccupied bands by ~ 0.2 eV while leaving the $5d$ occupied bands unmodified. At this point, an analysis of the standard techniques used within G_0W_0 is provided. The effect of semicore orbitals and the validity of the plasmon-pole model (PPM) (see section Ref. 1.3.12) are investigated more thoroughly. Beyond G_0W_0 , self-consistency on the wavefunctions is required to lower the $5d$ bands by ~ 0.35 eV and to shift further the unoccupied bands by ~ 0.1 eV towards the experimental results. Finally, vertex effects account for small corrections of no more than 0.1 eV. The remaining disagreements might be explained by the lack of a unified relativistic many-body approach [147, 148, 149].

The chapter is organized as follows. In section 3.2, the bandstructure within the G_0W_0 approach is shown. The role of semicore orbitals and the validity of the PPM are discussed here. In section 3.3, the bandstructure within the QPSCGW method is calculated. A comparison of the QP bandstructure within different approaches is included. In section 3.4, the QP and DFT wavefunctions are analyzed with MLWFs. This gives an insight on the chemical composition of the bands. In section 3.5, the QP and DFT densities are compared to explain the difference between their bandstructures. In section 3.6, electron-hole interactions are included in the GW formalism to determine their effect in the bandstructure of gold. In section 3.7, the spin-orbit (SO) corrections at the DFT level are revised. At the GW level, they are included in the bandstructure to compare it to the experimental measurements. Finally, in section 3.8, the conclusions of this work are given. The technical details of the calculations are shown in the appendix A.2.

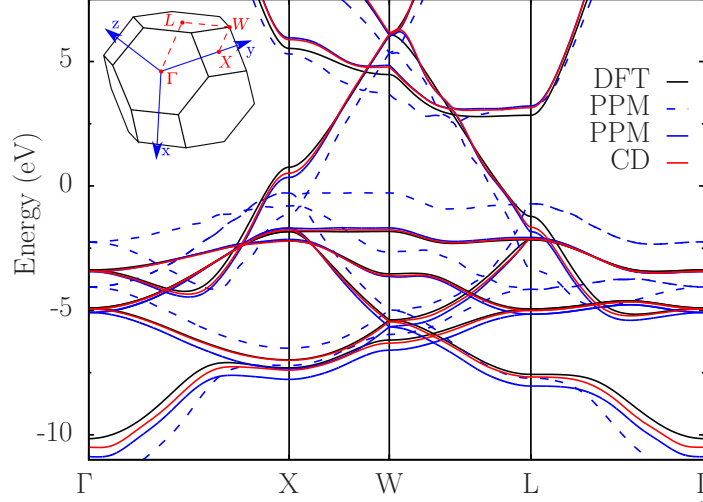


Figure 3.1: Calculated bandstructure of gold within DFT (solid black lines) and G_0W_0 . Several approximations are considered within G_0W_0 . PPM with- (solid blue lines) and without- (dashed blue lines) semicore orbitals, and CD with semicores (solid red lines). The corresponding Brillouin zone is shown as an inset.

3.2 The G_0W_0 bandstructure of gold

The aim of this section is to show the QP bandstructure of gold within the G_0W_0 approach and to clarify the effect of its standard approximations. First, special emphasis is put in understanding the role of semicore orbitals which are very important at the QP level. Second, the validity of the PPM is researched more thoroughly. The PPM is believed to be unstable in the presence of d -metals due to the oscillatory behavior of $\epsilon_{GG'}^{-1}(q, \omega)$ [10]. To illustrate, in Ref. [10], it is explained that the presence of flat d bands just below the Fermi level implies strong transitions in $\epsilon_{GG'}^{-1}(q, \omega)$. For small values of G and G' , the behavior of this function cannot always be approximated by a single-pole function. Thus, the PPM parameters might be unstable. To clarify this issue, the bandstructures obtained with the PPM and the more robust contour deformation (CD) integration technique (see section 1.3.12) are compared.

Fig. 3.1 shows the bandstructure of gold as calculated within DFT and G_0W_0 . The DFT bandstructure is found to be in agreement with previous calculations [9]. Within G_0W_0 , several approximations are considered: the bandstructure is calculated with and without semicore orbitals in the pseudopotential, moreover, the PPM and CD integration

techniques are used.

The semicore orbitals have a negligible effect in the DFT eigenvalues. However, they are important at the GW level. Indeed, when they are excluded (dashed blue lines), the $5d$ bands are shifted up while the $6sp$ bands are shifted down in a non-homogeneous way. This leads to a reduction of the $5d$ - $6sp$ interband gap. This effect is alarming at the proximities of the X point, where the lowest empty band is shifted by -1.7 eV while the top-most $5d$ band is shifted by $+1.1$ eV leading to an inversion on the band ordering. This unphysical shifting of bands is solved by including the exchange contributions from the $5d$ to the $5s$ and $5p$ semicore orbitals (solid blue lines). Although the semicore states are energetically separated from the $5d$ states by ~ 50 eV, they become important at the GW level due to their spatial overlap with these occupied states [150, 10, 35].

The G_0W_0 bandstructure within the PPM (solid blue lines) and within the more robust CD integration method (solid red lines) are shown in a comparative basis (here semicores are included). For bands located at most 5 eV from the Fermi level, both methods give the same results within 0.1 eV. This is true for most of the $\mathbf{k}$ -points except for those close to the X and the L points, where the deviations can be as big as 0.2 eV. As expected within the PPM, larger discrepancies start to appear further away from Fermi due to the strong oscillations of $\Sigma(\omega)$. Hence, the PPM remains a good approximation for this particular system.

3.3 Self-consistency effects within the QPSCGW approximation

The aim of this section is to find the best QP bandstructure within the GW theory. Here, several approximations beyond G_0W_0 are considered. First, the bandstructure is calculated with a single G_0W_0 renormalization of the DFT eigenvalues. Second, the QPSCGW mixing of the wavefunctions is used. Finally, vertex effects are included in the GW approaches. At each step, an explanation of the important many-body effects is provided.

Fig. 3.2 shows the bandstructure at different approaches: DFT (in black), G_0W_0 (in red), QPSCGW (in blue). The band-widths at the more symmetric $\mathbf{k}$ -points can also be read in Table 3.1. Here all many-body calculations are made within the CD integration method.

The G_0W_0 bandstructure (red lines) is almost on top of the DFT one (black lines). Actually, the G_0W_0 corrections are negligibly modifying the $5d$ manifold of bands; their shape, position and band-widths are kept

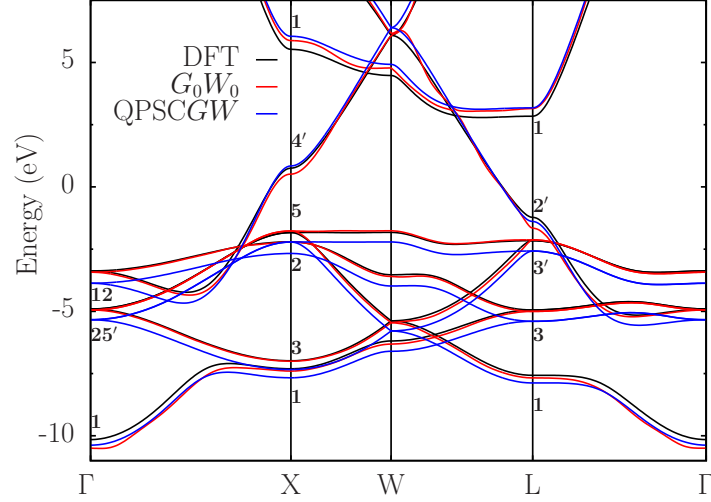


Figure 3.2: Calculated bandstructure of gold. Several approximations are used: DFT (in black), G_0W_0 (in red) and QPSCGW (in blue). Here all many-body calculations are made within the CD method.

as in the DFT case. On the other hand, the bottommost occupied band 1 is shifted down by ~ 0.4 eV, while the first unoccupied band 1 is shifted up by ~ 0.2 eV. Hence, the G_0W_0 interband gap ($5d$ - $6sp$ gap) remains ~ 0.8 eV smaller than the experimental evidence.

When mixing the wavefunctions within the QPSCGW approach the interband gap is opened by ~ 0.6 eV with respect to DFT. The $5d$ bands are shifted by ~ -0.35 eV, whereas the $6sp$ bands are shifted by $\sim +0.3$ eV. This shows that correcting the DFT wavefunctions is important in this system to obtain a more accurate QP bandstructure.

3.4 MLWFs analysis of the QP and DFT eigenstates

In this section a MLWFs analysis is used to compare the DFT $5d$ bands with the corresponding QPSCGW ones. To this end, the $5d$ MLWFs are obtained together with the $6s$ MLWF. These are shown in Fig. 3.3. The occupied bands have a mixed s and d character and it is necessary to extract the six MLWFs together to obtain localized functions with the required character¹. The localized $5d$ MLWFs are

¹ As an alternative, one can extract only the $5d$ MLWFs. However, the interpolated bandstructure will contain bands which do not coincide with the bands calculated

	DFT	G_0W_0	QPSCGW
$\Gamma_1 \rightarrow \Gamma_{25'}$	5.2	5.6	5.0
$\Gamma_{25'} \rightarrow \Gamma_{12}$	1.5	1.5	1.5
$X_3 \rightarrow X_2$	4.8	4.8	4.7
$X_5 \rightarrow X'_4$	2.6	2.3	3.1
$X'_4 \rightarrow X_1$	4.8	5.4	5.2
$L_3 \rightarrow L'_3$	2.8	2.9	2.8
$L'_3 \rightarrow L'_2$	0.9	0.5	1.2
$L'_2 \rightarrow L_1$	4.0	4.8	4.6

Table 3.1: Calculated band-widths of gold within DFT and GW in eV. Different approaches are considered (see the text).

similar to the atomic orbitals of the isolated atom. The less localized $6s$ -like MLWFs presents a strong bonding character. Its center is at the middle point among four gold atoms forming a tetrahedron.

To compare the $5d$ orbitals as predicted by the QPSCGW and DFT approximations, the PDOS on the MLWFs is calculated. Fig. 3.4 shows the PDOS at the QPSCGW (solid lines) and DFT (dashed lines) approximations. The PDOS on all the $5d$ (black), on the $5d_{xz}$ (red), on the $5d_{yz}$ (orange), and on the $5d_{z^2}$ (blue) MLWFs are also shown. For symmetry reasons, the PDOS on the $5d_{xy}$ and $5d_{x^2-y^2}$ MLWFs (not shown here) are equal to the ones on the $5d_{yz}$ and $5d_{z^2}$ MLWFs, respectively. The Fermi level is placed at 0 eV and -0.35 eV for the QP and the DFT cases respectively, in order to match the PDOS peaks.

The DFT PDOS is almost equal to the QPSCGW one when this rigid shift is applied. Hence, the hybridizations and positions of the $5d$ orbitals are notably well predicted in DFT. Moreover, the DFT $5d$ bandwidths in Table 3.1 are equal to the QPSCGW ones within 0.1 eV. Actually, it is known that the DFT bandstructure agrees quantitative almost perfectly with the experimental measurements, if one applies a rigid shift of -0.35 eV and +0.4 eV for the occupied and empty bands, respectively [8].

3.5 Analysis of the QP and DFT wavefunctions

In this section, the QP and DFT wavefunctions are compared to understand the effect of many-body corrections. It is found that mixing of the DFT wavefunction within the QPSCGW theory produces rota-

explicitly (see Fig. 1.6), as explained at the end of section 1.4.5.

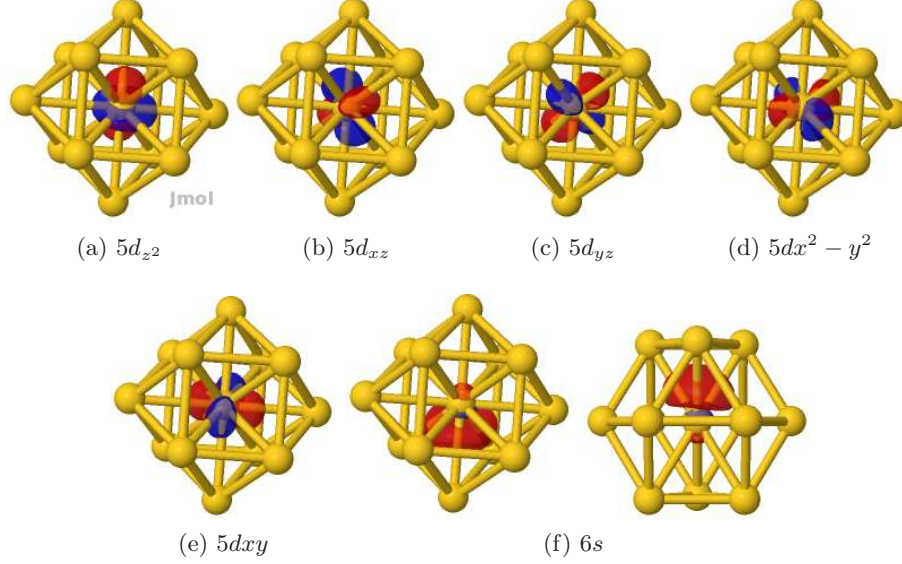


Figure 3.3: MLWFs of gold: red and blue colors indicate opposite iso-values. Gold atoms in the FCC lattice are represented by yellow spheres.

tions and small relocalizations of the wavefunctions. These changes are $\mathbf{k}$ -point and band dependent.

In Fig. 3.5, the projection of the QP wavefunction on the DFT one at the L and A $\mathbf{k}$ -points is plotted [panel (a)] to show the band mixings at these sample points. The A point, with reduced coordinates (0.5,0.3,0.1), is a random low symmetry $\mathbf{k}$ -point. The QP and the DFT modulus of the wavefunction, $|\varphi_{\mathbf{k}n}|^2$, for band 4 at the L point are shown in panel (b), and panel (c) respectively. Finally, in panel (d), the QP modulus of the wavefunction minus the DFT one for band 6 at the A point is shown. Regardless of the $\mathbf{k}$ -point, the biggest mixings are always found among degenerate bands (see top panel). These strong band mixings give rise to rotations of the wavefunction associated to the individual bands. For example, the QP modulus of the wavefunction associated to band 4 in the L point [panel (c)] is equal to the DFT one [panel (b)] within a simple rotation around the center of the gold atom. In fact, this band is $\sim 50\%$ mixed with its degenerate band 5, whose wavefunction rotates in the opposite direction. Other degenerate band wavefunctions also rotate along different directions. These rotations (mixing of degenerate bands) do not have an important effect in the bandstructure ².

²This is confirmed by the fact that mixing of the occupied bands and only 5 unoccupied bands within QPSCGW is negligibly modifying the initial DFT $5d$ -bands,

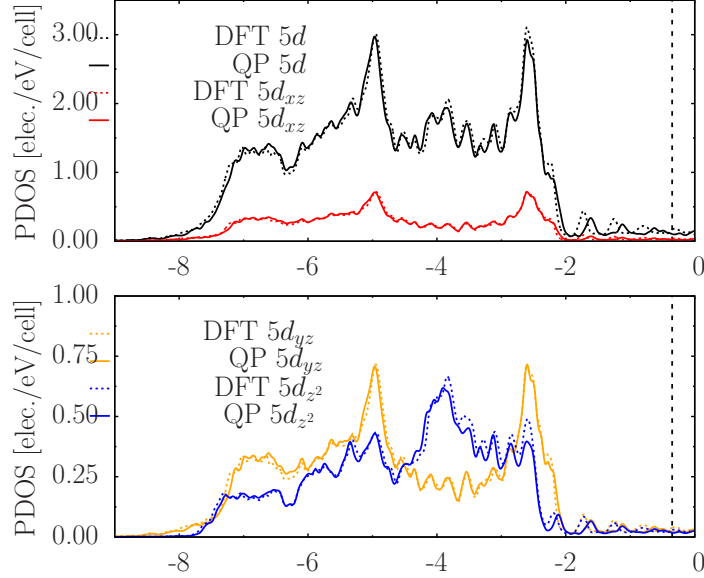


Figure 3.4: PDOS on the MLWFs of gold. The QPSCGW (solid lines) and DFT (dashed lines) PDOS on the MLWFs is shown. Top graph: the total PDOS on all the 5d MLWFs (black) and the 5d_{xz} MLWFs (red) are shown. Bottom graph: the PDOS on the 5d_{yz} (orange) and the 5d_{z²} MLWFs (blue) are shown. The QPSCGW and DFT Fermi levels are at 0 eV and -0.35 eV (dashed vertical line), respectively.

More important, numerous small hybridizations occur among the occupied bands and higher empty bands [see panel (a)]. This is more evident in low-symmetry $\mathbf{k}$ -points, such as the A point [see panel (a)]. These small hybridizations change slightly the wavefunctions. To show this, we calculate the difference between the modulus of the wavefunctions at the QP and DFT levels. This is done for the first unoccupied band at $\mathbf{k} = \text{A}$. For this particular band and $\mathbf{k}$ -point, a relocation of the wavefunction is observed; the 5d character is reduced (blue lobes) while the 6s character close to the atom is slightly augmented (red lobes). We found that the nature of these small changes are $\mathbf{k}$ -point and band dependent.

These small modifications of the wavefunction modify the $\Sigma_{ii} = \langle \varphi_i | \Sigma | \varphi_i \rangle$ and Hartree potential $V_{ii}^H = \langle \varphi_i | V^H | \varphi_i \rangle$ matrix elements entering the QP equation. In particular, the relative change of the matrix elements of the 5d bands with respect to those of the first unoccupied

such as G_0W_0 .

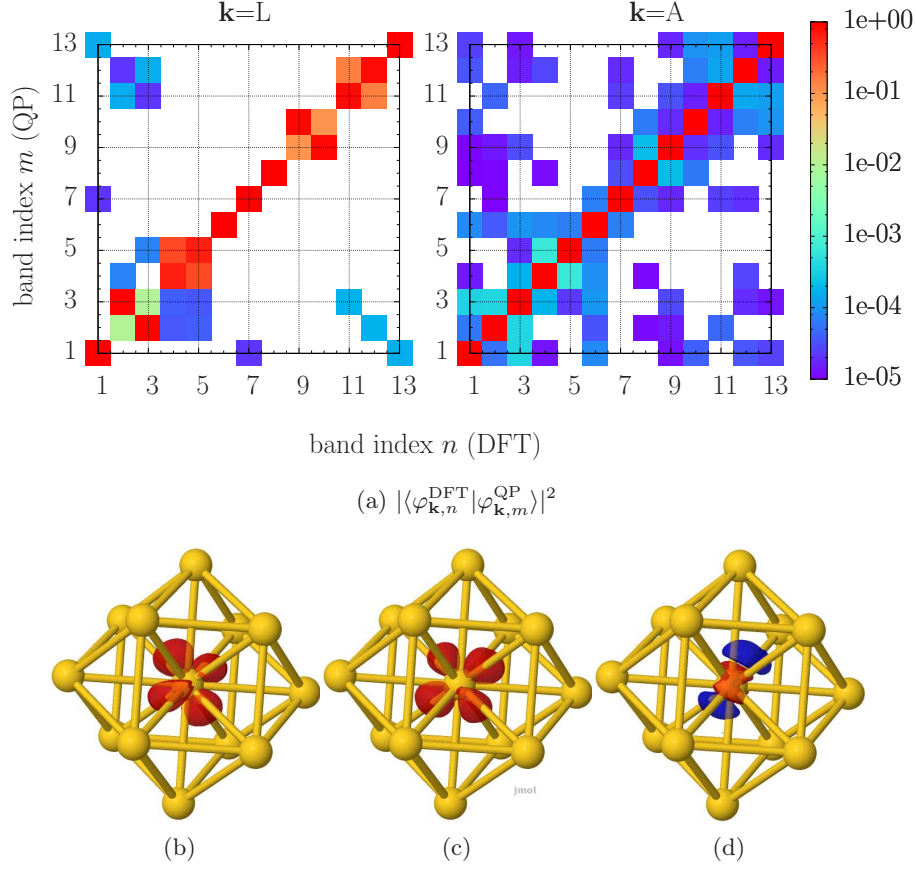


Figure 3.5: DFT band mixings at the QPSCGW level. Panel (a): Modulus of the projection of the QP wavefunction on the DFT one at the L (left) and A (right) $\mathbf{k}$ -points. The A point is a non-predefined point with reduced coordinates (0.5,0.3,0.1). The DFT and QP densities for band 4 at $\mathbf{k}$ -point L are shown in panel (b), and panel (c) respectively. The QP minus the DFT densities for band 6 at $\mathbf{k}$ -point A is shown in panel (d). Gold atoms in the FCC lattice are represented by yellow spheres. The density is represented by red ($+1\rho$) and blue (-1ρ) isosurfaces, with $\rho = 6 \times 10^{-4} e^-/\text{\AA}^3$. In panel (d), an extra factor of 20 is used.

band is ~ 0.35 eV. Therefore, the origin of the -0.35 eV rigid shift of the $5d$ bands comes from small differences in the QP wavefunctions which change the Σ_{ii} and V_{ii}^H matrix elements.

	G_0W_0	$G_0W_0\Gamma$	QPSCGW	QPSCGWT
$\Gamma_1 \rightarrow \Gamma_{25'}$	5.6	5.6	5.0	5.1
$\Gamma_{25'} \rightarrow \Gamma_{12}$	1.5	1.5	1.5	1.5
$X_3 \rightarrow X_2$	4.8	4.8	4.7	4.7
$X_5 \rightarrow X'_4$	2.3	2.3	3.1	3.1
$X'_4 \rightarrow X_1$	5.4	5.4	5.2	5.2
$L_3 \rightarrow L'_3$	2.9	2.9	2.8	2.8
$L'_3 \rightarrow L'_2$	0.5	0.5	1.2	1.2
$L'_2 \rightarrow L_1$	4.8	4.8	4.6	4.5

Table 3.2: Band-widths of gold in eV within GW with- and without-vertex effects (see the text).

3.6 Vertex effects in the bandstructure of gold

In the QP equation, electron-hole interactions are taken into account via the vertex term Γ . These are neglected in the GW formalism by setting $\Gamma = \delta$. Additional electron-hole correlation effects can be added by using an approximate vertex term [60].

Vertex effects can be included in the G_0W_0 and in the QPSCGW approaches. These approximations will be referred to as $G_0W_0\Gamma$ and QPSCGWT, respectively. At the one-shot level, vertex effects usually account for rigid shifts in the absolute QP eigenenergies while the QP energies relative to E_F are not changed (see for instance R. Shaltaf et al. [59]). At the self-consistent level, vertex effects are important in the determination of the band-gaps of semiconductors. In fact, when they are included, the band-gaps are within a few percent of the experimental values [151]. In the case of metals, their effect is unknown.

In this section, the effect of vertex corrections in the bandstructure of gold is studied within $G_0W_0\Gamma$ and QPSCGWT. The vertex effects are included as in Ref. [60], in the self-energy and in W . Non-local vertex corrections only in W were also considered [152, 153]. However, these only shift the bands with respect to the local vertex corrections. *i.e.*, the local and non-local vertex approaches predict the same bandstructures and only the absolute value of the Fermi level is changed. It is found that $G_0W_0\Gamma$ only accounts for a rigid shift of the absolute position of the QP bands (only E_F is shifted) as in other systems. On the other hand, the self-consistent approach slightly changes the bandstructure. However, these changes are very small (~ 0.1 eV).

In Table. 3.2, the bandwidths obtained within different GW approximations are shown. G_0W_0 and $G_0W_0\Gamma$ give the same bandwidths within

0.01 eV. This was expected since the Γ corrections at this level are mainly a rigid shift of all bands. Moreover, the QPSCGW and QPSCGWT approximations predict almost the same bandstructure; the bandwidths are equal within 0.1 eV.

3.7 Spin orbit effects in the bandstructure of gold

To fully take into account the relativistic effects at the DFT level, the Dirac equation should be solved. Alternatively, the scalar-relativistic (SR) equation captures most of the Dirac physics; the Darwin and mass-velocity terms omitting the SO term [154, 155, 156]. Therefore, as a standard approach, the SR equation is solved and the SO effects are added afterwards.

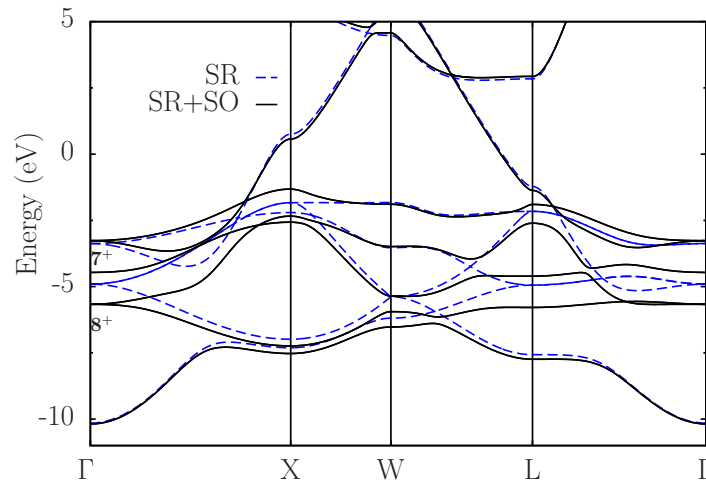


Figure 3.6: Calculated bandstructure of gold at the DFT level. The SR and fully-relativistic (scalar plus spin-orbit effects) are shown with dashed blue lines and solid black lines, respectively. The Fermi levels are at 0 eV.

In the case of gold, most of the relativistic effects in the bandstructure come from the SR terms. The SO term mainly accounts for band splittings [142, 9], as shown in as shown in Fig. 3.6. To show the SO effect on the wavefunction, the modulus of the projection of the SR wavefunction on the fully relativistic one (SR+SO) is calculated at the Γ point. This is shown in Fig. 3.7. The projections are close to 1 for the occupied bands 1, 5 and 6, that is, these bands are almost unaffected by the SO term. However, the d bands 2, 3 and 4 are strongly changed by the SO

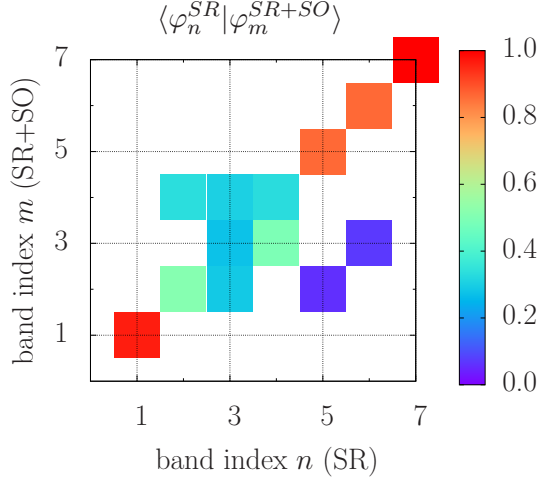


Figure 3.7: Modulus of the projection of the fully relativistic wavefunction (SR+SO) on the SR one.

term. Indeed, they form the $\Gamma_{25'}$ state at the SR case which is split into the Γ_{7+} and Γ_{8+} states by the SO term. Similar effects are observed in other $\mathbf{k}$ points as explained elsewhere [9].

The SO effects at the many-body level should, in principle, be calculated within a relativistic GW approach [147, 148, 149]. However, this theory has not yet been applied to real systems and its effect remains unknown. Therefore, SO effects are added *graphically* to the QPSCGW bandstructure to compare it to the experimental evidence. This is done in a two step procedure:

1. We compute a Σ^{SO} from the DFT and DFT + SO bandstructures. It is quite crudely as the difference between the energies calculated with SO (E_i^{SO}) and those without SO (E_i), $\Sigma_i^{\text{SO}} = E_i^{\text{SO}} - E_i$, for band and $\mathbf{k}$ point index i .
2. We add Σ^{SO} to the GW bandstructure.

Fig. 3.8 shows the DFT (solid black lines) and the QPSCGW (dashed red lines) bandstructures with spin-orbit (SO) effects. The experimental bandstructure along the $L \rightarrow \Gamma$ $\mathbf{k}$ -path of R. Courths *et al.* [8] is also shown. The QP occupied bands are in good agreement with the experiment with an average error of 0.07 eV. A disagreement of ~ 0.4 eV in the unoccupied bands still remains. This discrepancy can be attributed the unknown effect of a generalized relativistic-many-body theory [147, 149]. Note that, in principle, van der Waals interactions are important to determine the atomic distance in noble metals [144]. Here, we simply use the experimental lattice constant to avoid this difficulty.

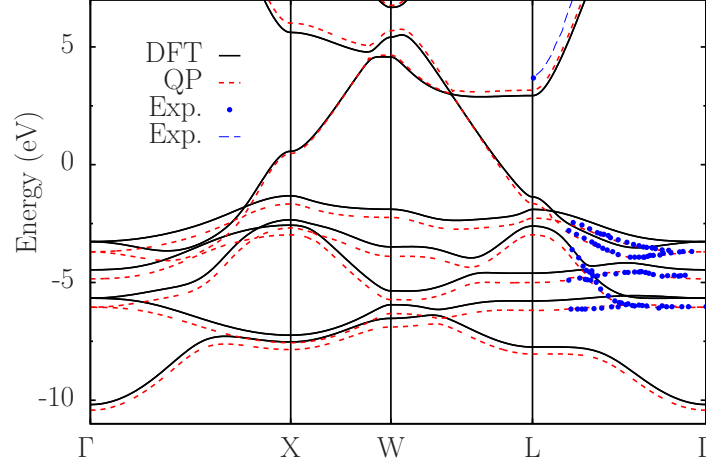


Figure 3.8: Calculated bandstructure of gold. Several approximations are used: DFT + SO (solid black lines) and QPSCGW + SO (dashed red lines). The blue dots represent the experimental measurements of R. Courths *et al.* (Ref. [8]). The dashed blue line gives the experimental final-band consistent with all data points from ARPUS in Refs. [8, 157, 158] and from low-electron reflectance in Ref. [159], taken from Ref. [8].

3.8 Conclusions

In summary, we have studied the bandstructure of gold within several approximations to the MBPT self-energy. The single-shot G_0W_0 corrections to the DFT eigenvalues are shifting the empty bands by ~ 0.35 eV while leaving intact the $5d$ occupied bands. We found that it is crucial to update also the DFT wavefunctions to improve the agreement with the experiments. Self-consistency in the wavefunctions, within the QPSCGW approximation, shifted down the occupied $5d$ bands by ~ 0.35 eV. This shift was due to modifications of the wavefunctions. These produced a change of the Σ_{ii} and V_{ii}^H matrix elements, which enter the QP equation.

Within the G_0W_0 approximation, we have studied the effect of semi-core states. These had a negligible effect in the DFT eigenvalues, however, they were crucial at the GW level. Indeed, when they were excluded, the $5d$ bands were shifted up while the $6sp$ bands were shifted down in a non-homogeneous way, leading to a reduction of the $5d$ - $6sp$ interband gap.

By a careful comparison of the G_0W_0 bandstructures obtained within the PPM or the more robust CD technique. We found that the PPM remained a valid approximation for this metal. For bands located at at most 5 eV from the Fermi level, both methods give the same results within 0.1 eV.

Furthermore, we studied the effect of vertex corrections at the $G_0W_0\Gamma$ and QPSCGW Γ levels. Besides a change of the absolute value for the Fermi level, vertex effects change little or almost nothing the bandstructure, as observed in other systems.

Chapter 4

Electronic properties of novel materials and nanowires

This chapter is dedicated to the study the electronic properties of various materials of technological relevance for future applications. This work was carried in collaboration with other researchers. Our main contribution was mainly to compute MBPT bandstructures using MLWFs. This work involved the testing and debugging of our recently implemented interface within Wannier90 and the GW capabilities of ABINIT [1]. The results shown in this chapter have already been published in the literature in Refs. [160, 161]. This chapter is organized as follows: section 4.1.1 is dedicated to study the electronic properties of zircon and hafnon, and in section 4.2 we study the electronic properties of Ge and Si nanowires.

4.1 Zircon and hafnon

4.1.1 Introduction

Zircon (ZrSiO_4) and hafnon (HfSiO_4) are materials of technological relevance. Due to their durability and ability to host large quantities of long-lived actinides, they are used for nuclear waste disposal [162]. Moreover, they both possess high dielectric constants and large energy gaps which made them emerge as high- κ gate dielectric materials in MOS technology [163, 164, 165, 166]. Due to the similarity of the physical and chemical properties of Zr and Hf, the structural and electronic properties of zircon and hafnon are very much alike. At ambient conditions, they present a body-centered tetragonal crystal structure (space group $I41/amd$, No. 141) with 2 formula units $M\text{SiO}_4$ $M=(\text{Hf},\text{Zr})$ in

the primitive cell. In this structure, each $M=(\text{Hf,Zr})$ atom is bonded to eight O atoms, while each Si atom is bonded to four O atoms so that each O atom is bonded to two $M=(\text{Hf,Zr})$ and one Si atoms. At higher pressure, zircon and hafnion stabilize in a scheelite structure (space group $I_{41/a}$, No. 88), with a Bravais lattice which is also body-centered tetragonal with the same number of atoms as in the low-pressure phase. Various properties of hafnion and zircon have been investigated within the DFT: pressure induced phase-transition [167, 168], properties of point defects [169, 170, 171], dynamical, electronic, and dielectric properties [172, 173, 174]. In these studies, DFT proved to be successful in reproducing many experimental results. However, it is well known that DFT fails to give a reliable estimation of the electronic energy gap [27, 175]. Such an excited-state property can be accessed directly through the MBPT formalism [176]. Today MBPT is considered a reliable and well established method for electronic band-structure calculations, which makes it an ideal choice for energy gap prediction when little experimental information is available. Experimentally, a direct measure of the energy gap of zircon and hafnion in their crystalline phase is still missing [171, 177]. In practice, the value of 6.5 – 7.0 eV, which has been extrapolated from measurements on $(\text{MO}_2)_x(\text{SiO}_2)_y$ disordered alloys grown on Si [178, 179, 180], is often considered as the reference [163, 171, 177]. This can be reasonably questioned given the structural difference between amorphous alloys and single crystal phases. On the other hand, values ranging from 5.0 to 7.7 eV have been reported for the Kohn-Sham energy gap, as calculated within the LDA and weighted density approximation (WDA) [171, 177]. However, these values are subject to the above mentioned criticisms and cannot be considered as reliable. The aim of this work is to provide a more accurate prediction of the energy band gap of zircon and hafnion based on MBPT. The precise knowledge of energy band gap and the associated many-body corrections with respect to the standard DFT approach is crucial for band-offset calculations [171, 59]. Our results will hopefully reduce the uncertainty present in the literature. In section 4.1.2, we present and discuss the band structure obtained within DFT-LDA and GW approximations. In section 4.1.3, we present the conclusions of this work. The detail of the calculations are shown in appendix A.3. The results of this work are already published [161].

4.1.2 Results

Starting from the set of DFT-LDA eigenvalues and eigenfunctions calculated on a homogeneous grid of $4 \times 4 \times 4$ $\mathbf{k}$ -points, the QP corrections

are computed for the same set of $\mathbf{k}$ -points. Different GW approximations are considered here, namely, G_0W_0 , GW_0 , $G_0W_0\Gamma$ and $GW_0\Gamma$ introduced in section 1.3.13. Then, the quasiparticle corrections are interpolated for the high-symmetry segments of the Brillouin zone (BZ) using MLWFs as described in section 1.4.7. In order for the interpolation to be really advantageous, the real-space representation $|H_{nm\mathbf{R}}^{\mathcal{W}}|$ of the DFT-LDA and GW Hamiltonians needs to have a sufficient fast decay with $|\mathbf{R}|$. In principle, this decay should be monitored for each pair of n, m indices individually. Alternatively, a global view on the decay can be obtained by summing the square of the matrix elements for the group of bands under consideration:

$$V_{\mathbf{R}}^H = \sum_{n,m} |H_{nm\mathbf{R}}^{\mathcal{W}}|^2 = \sum_{n,m} |\langle \mathcal{W}_{n\mathbf{R}} | H | \mathcal{W}_{m\mathbf{O}} \rangle|^2 \quad (4.1)$$

and taking the square root of this sum. Interestingly, it can be shown that $V_{\mathbf{R}}^H$ is nothing but $Tr[HP_{\mathbf{R}}HP_0]$ where $P_{\mathbf{R}}$ is the projection operator onto the corresponding group of MLWFs attached to the vector $\mathbf{R}$:

$$P_{\mathbf{R}} = \sum_n |\mathcal{W}_{n\mathbf{R}}\rangle \langle \mathcal{W}_{n\mathbf{R}}|. \quad (4.2)$$

As illustrated in Fig. 4.1, $\sqrt{V_{\mathbf{R}}^H}$ decays exponentially showing that the $\mathbf{k}$ -points grid used in the Wannier interpolation is indeed sufficient. The

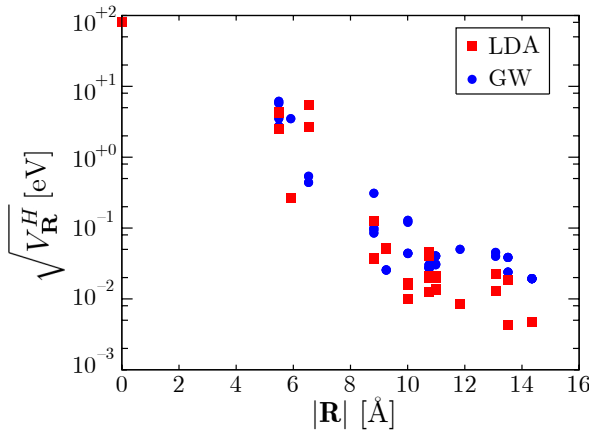


Figure 4.1: Global decay of the real space representation of the DFT-LDA (blue circles) and GW (red squares) Hamiltonians as a function of the lattice vector size $|\mathbf{R}|$ measured by $\sqrt{V_{\mathbf{R}}^H}$ for all the valence bands.

GW_0 band structure along the high-symmetry lines of the BZ (using the notation of Ref. [181]) is reported in Fig. 4.2 for hafnion and zircon. The band structure is similar for both materials, with valence bands consisting of four well separated manifolds (labeled with the Roman numbers I–IV starting from the lowest in energy). The typical corresponding

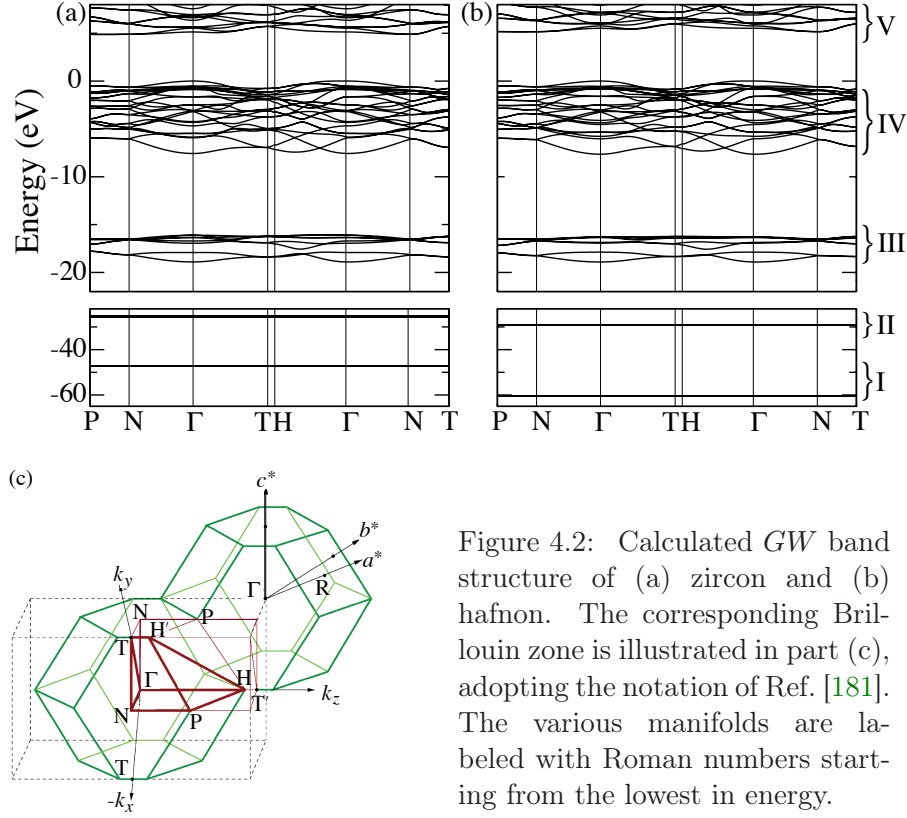


Figure 4.2: Calculated GW band structure of (a) zircon and (b) hafnon. The corresponding Brillouin zone is illustrated in part (c), adopting the notation of Ref. [181]. The various manifolds are labeled with Roman numbers starting from the lowest in energy.

MLWFs are reported in Fig. 4.3, allowing us to identify the chemical character of the orbitals. The first two manifolds (I and II, consisting of two and six bands, respectively) are associated to one $4s$ and three $4p$ orbitals centered on the two Zr (one $5s$ and three $5p$ for Hf) atoms, respectively. These bands do not show any significant dispersion and, accordingly, the atomic s and p orbitals on the metal atoms are not hybridized. For these two manifolds, the only significant difference between zircon and hafnon is a shift of the Hf s and p bands by about 10 eV down with respect to their Zr analogs.

The MLWFs associated to manifold III (consisting of eight bands) show mainly s character with their center located close to one of the eight oxygen atoms. In fact, the s -like orbital is elongated in the direction of the nearest silicon atoms and its center is shifted accordingly, as illustrated in Fig. 4.3. This indicates a mixing of the O $2s$ orbitals with the Si $3p$ ones. The manifold IV (consisting of 24 bands) covers the last set of valence bands which show the largest dispersion. The

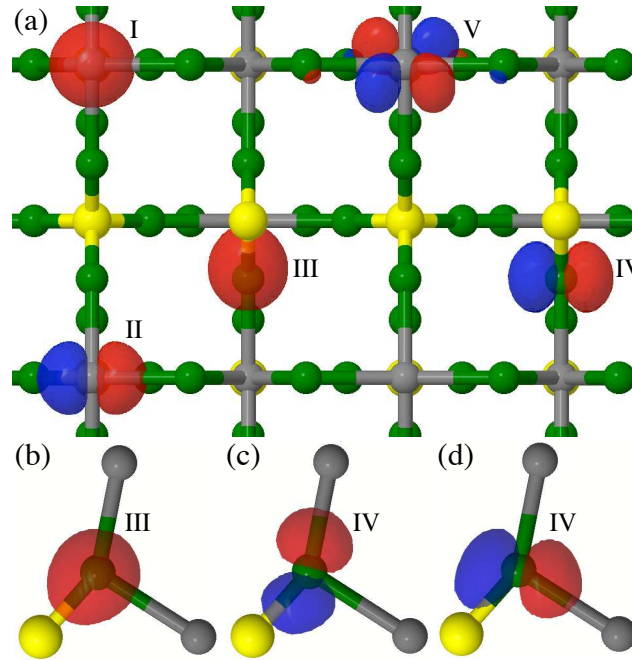


Figure 4.3: Isosurfaces of the MLWFs of zircon: Red and blue colors indicate opposite isovalues. The O atoms are colored in dark green, Zr atoms in gray, and Si atoms in yellow. The different manifolds are labeled with Roman numbers according to Fig. 4.2. Different views of the crystal are represented: (a) top view (perpendicular to the tetragonal axis, i.e., the [001] direction) and [(b)-(d)] side view (perpendicular to the [100] or [010] directions, which are equivalent). For the latter, the focus is on an O atom and its three nearest neighbors, two Zr atoms and one Si atom, all lying in the same plane.

corresponding MLWFs are O $2p$ orbitals with some mixing with Si $3p$ and Zr $4p$ (Hf $5p$) orbitals, indicating that these electrons are involved in the bonds formation. For each of the eight O atoms, one of the three $2p$ -like orbitals [Fig 4.3(a)] is oriented perpendicular to the plane formed by the O atom and its three nearest neighbors, two Zr atoms and one Si atom. This orbital does not show mixing with other atomic orbitals, it corresponds to a lone pair on the O atom. The other two $2p$ -like orbitals [Figs. 4.3(c) and 4.3(d)] lie in the plane formed by the O atom and its neighbors and show significant mixing with Si $3p$ and Zr $4p$ (Hf $5p$) orbitals. The associated electrons are responsible for the bonding. Finally, the MLWFs associated to manifold V (consisting of the 14 lowest conduction bands) essentially correspond to Zr $4d$ (Hf $5d$) orbitals with

Table 4.1: HVB and LCB at high symmetry points with their corresponding many-body corrections within GW_0 and $GW_0\Gamma$ for both zircon and hafnon

k point		ZrSiO ₄			HfSiO ₄		
		LDA	GW_0	$GW_0\Gamma$	LDA	GW_0	$GW_0\Gamma$
Γ	HVB	0.0	-0.7	-0.5	0.0	-0.7	-0.5
	LCB	5.1	+2.1	+2.4	5.5	+1.9	+2.2
P	HVB	-0.5	-0.7	-0.4	-0.5	-0.8	-0.5
	LCB	4.9	+2.0	+2.3	5.2	+2.1	+2.4
N	HVB	-0.7	-0.7	-0.4	-0.6	-0.8	-0.4
	LCB	4.9	+2.0	+2.3	5.2	+2.1	+2.4
T	HVB	-0.8	-0.6	-0.3	-0.9	-0.7	-0.5
	LCB	5.7	+2.2	+2.4	5.9	+2.3	+2.6
H	HVB	-0.7	-0.6	-0.3	-0.8	-0.7	-0.5
	LCB	5.6	+2.3	+2.4	5.9	+2.4	+2.6

an important mixing with orbitals originating from all the other atoms, as shown in Fig. 4.3(a).

In Table 4.1, the quasiparticle corrections with respect to the DFT-LDA values are reported for the highest valence band (HVB) and the lowest conduction band (LCB) for both zircon and hafnon. The results computed both within GW_0 and $GW_0\Gamma$ are presented for five high-symmetry **k** points in the BZ. GW_0 is used here, since it predicts band-gaps in remarkably good agreement with the experimental data and because it is less expensive than QPSCGW (see section 1.3.13). It is worth mentioning that only the P and Γ points correspond to the wavevector grid points for which direct GW calculations are performed. For these two points, the calculated quasiparticle corrections and those resulting from the Wannier interpolation differ by less than 0.01 eV. For zircon, the complete band structures, which are obtained using the Wannier interpolation, are presented in Fig 4.4.

For both materials, the effect of many-body corrections (see Table 4.1) is to lower the highest valence band and to raise the lowest conduction band. For zircon, the lowering of the HVB ranges from 0.6 to 0.7 eV depending on the **k**-point, while the raising of LCB extends between 2.0 and 2.3 eV. For hafnon, the trend is about the same as for zircon. The HVB is lowered by 0.7–0.8 eV, whereas the LCB is shifted up by 1.9–2.4 eV. Moreover, the dispersion of the top valence bands is increased by about 0.6 eV with respect to DFT-LDA [see Fig 4.4]. Finally, the valence band maxima (VBM) location is also affected. In

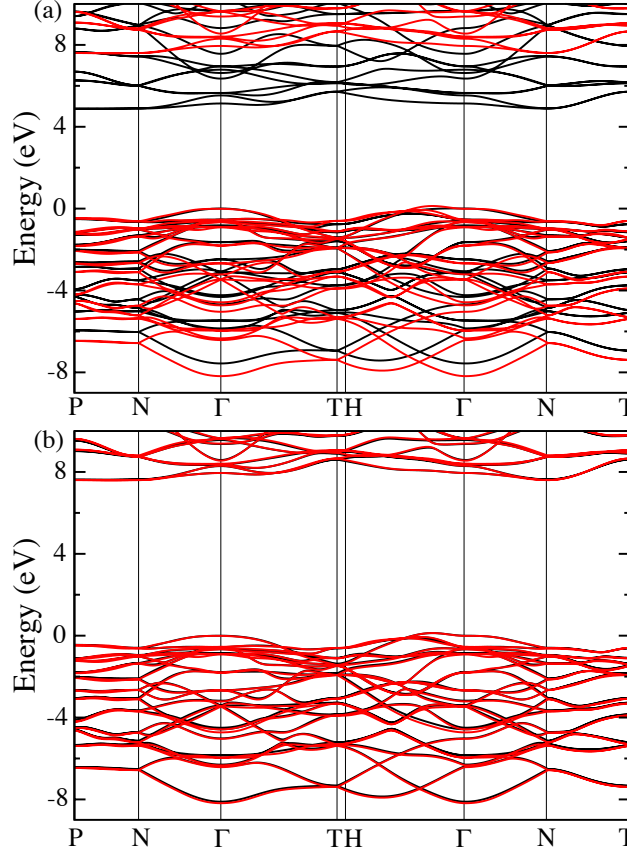


Figure 4.4: Bandstructure of zircon: comparison between (a) GW_0 (red) and DFT-LDA (black) (b) GW_0 (red) and $GW_0\Gamma$ (black).

DFT-LDA, the VBM is located at about one tenth of the $\Gamma - H$ symmetry line, away from the Γ point. It is very close in energy with respect to the value at the Γ point. The effect of many-body corrections [see Fig. 4.4] is (i) to push the VBM further away from the Γ point at about one-fourth of the Γ -H segment and (ii) to increase the difference in energy between the VBM and the Γ point. Such an effect could not have been identified without resorting to the Wannier interpolation. Note that the many-body corrections do not alter the location of the conduction band minimum.

The calculated quasiparticle gaps are 7.6 and 8.0 eV within GW_0 (7.7 and 8.1 eV within $GW_0\Gamma$) for zircon and hafnion, respectively. These values are much larger than those obtained in DFT-LDA (4.87 for zircon and 5.12 eV for hafnion). They are also significantly larger than the experimental estimations of 6.5–7.0 eV, which are based on measurements

on amorphous $(\text{MO}_2)_x(\text{SiO}_2)_y$ grown on Si [178, 179, 180]. Given the differences in the bonding and the coordination numbers between such disordered alloys and the single crystals, such a variation in the gap can be considered as reasonable. Finally, it is worth noting that the calculated quasiparticle gaps are also slightly higher than the values of 7.0 and 7.7 eV obtained for zircon and hafnon, respectively, within DFT-WDA [171, 177]. Though the WDA is supposed to work better than the LDA/GGA, it still suffers from the limitations of DFT calculations. For both materials, the quasiparticle corrections to the HVB are smaller within GW_0 than within $GW_0\Gamma$. But, at the same time, the corrections to the LCB are larger. The effect of the vertex corrections is thus basically to shift the bands rigidly by 0.3 eV. Thus, once the VBM is set to zero, the GW_0 and $GW_0\Gamma$ band structures can hardly be distinguished, as illustrated in Fig. 4.4(b) for zircon. This trend has been noticed before for other materials [59, 60].

4.1.3 Conclusions

The electronic band structure of two high- κ materials, namely, zircon and hafnon, have been investigated within GW and $GW\Gamma$ approximations. The quasiparticle band structure has been calculated using Wannier interpolation scheme. The band structure of both materials is very similar within MBPT and DFT-LDA except for the band gap opening, the increase in the dispersion of the bands, and a slight displacement of the valence-band maximum away from the Γ point within MBPT. Many-body effects account for an opening of the band-gap of ~ 2.7 and ~ 2.8 eV for zircon and hafnon, respectively.

On the other hand, both MBPT approximations, GW and $GW\Gamma$, yield almost the same value for the energy gap. The resulting band-structures are also very similar. These results show the small effect of the vertex corrections in these systems.

4.2 Ge and Si nanowires

4.2.1 Introduction

Nanowires are one-dimensional structures that have shown a promising prospective to be used as building blocks for future applications. Wires consisting of the semiconductor species Si and Ge are particularly interesting due to their compatibility with current semiconductor industry. Since Ge nanowires (NWs) can be grown on silicon substrates [182, 183, 184], they could be used in devices fabricated within

silicon based technology. Prototype applications such as field-effect transistors [185], p-n diodes [186, 187] sensors for chemical and biological substances [188, 189] and solar cells [190] have already been realized.

These nanowires can be grown using standard vapor-liquid-solid growth methods [191]. The growth of thin wires has also been reported. For Si, these are mainly oriented along the [110] direction [184], while for Ge both the [111] and [110] directions are reported [192, 193]. In this work, we focus on the [110] direction since it has been shown to be the dominant experimental growth direction for the smallest nanowires [184].

Motivated by the possibilities of these nanowires, several theoretical *ab initio* studies have been already performed in order to investigate the wire properties. The structural and electronic properties of bare and passivated nanowires have been studied within DFT and semiempirical methods in Refs. [194, 195]. The properties of doped nanowires have also been extensively studied [196, 197, 198, 199]. In Refs. [200, 201], the phonon bandstructures of Si/Ge nanowires were calculated. From the results of these calculations, it was found that the wires were stable also when doped either with B or P, except for highly-doped thin NWs. The effect of confinement on the acoustic modes was also studied in Ref. [201]. A thorough overview of the performed theoretical studies can be found in the review paper by Rurali [202].

The knowledge of how the size of the band gap depends on the specific structure is very important, as this determines in part the properties of the wires. The standard *ab initio* DFT calculations using approximate functionals to model the exchange-correlation energy, such as the LDA or GGA, tend to underestimate the size of this band gap by as much as 50% [203]. This is a well-known shortcoming of these functionals, which do not properly take into account the many-body effects due to electron-electron interactions, as explained in section 1.2.5. In contrast, MBPT provides a formal ground for evaluating the experimentally observed QP bandstructures.

MBPT has already been applied to study Si and Ge NWs [203, 204, 205, 206] and Si chains [207]. In these works, G_0W_0 corrections to the bandstructure are calculated first in order to study the optical properties. Many-body effects have been important to open the fundamental gap, improving the agreement with the experimental data, and big excitonic effects were also found in the optical response of these systems. [206, 208, 209, 210]. MBPT was also used to include interface-induced correlation effects in the calculation of transport properties in SiNW metal-oxide-semiconductor field-effect transistors [211].

It is often assumed that the QP corrections cause a uniform shift of all the conduction bands, so that a global constant energy change (the

so-called scissor shift) is applied to these bands using the QP corrections obtained only in one $\mathbf{k}$ -point. This assumption has been very commonly used in the literature for these systems [203, 204, 205, 208, 209, 210]. However, the validity of the scissors operator technique has not been studied.

Some of the technical aspects on the QP calculations are given by Palummo *et al.* [212]. In particular, the convergence with respect to the $\mathbf{k}$ -point sampling within a one-dimensional BZ is discussed. Moreover, an underestimation of 0.3 eV was obtained when long-range tail of the Coulomb potential was not cut-off beyond a certain distance (even for a lateral unit cell of 30 Bohr). The importance of truncating the long-range Coulomb interaction in order to ensure the convergence of 0.1 eV in the G_0W_0 band gaps has also been pointed out in Ref. [206].

In this work, we (i) calculate the QP corrections for Si- and Ge-[110] oriented nanowires at the Γ point (as these nanowires have a direct band gap), (ii) calculate the complete QP bandstructures, (iii) assess the correctness of applying a scissor shift, and (iv) study the effective electron and hole masses, calculated both within standard DFT and including QP corrections.

The first part of this work addresses the convergence issues related to the one-dimensional nature of the nanowires, as illustrated by the test case of a 0.5 nm Ge nanowire (consisting of six Ge and eight passivating H atoms). The main parameters that need to be converged are the number of bands (including a large number of empty bands), the number of $\mathbf{k}$ -points along the periodic direction, and the size of the unit cell in the directions perpendicular to the wire, i.e., the amount of vacuum separating the wire from its periodically repeated images. We aim at a global accuracy of 0.01 eV on the band energies, with a maximal tolerance of 0.002 eV for the convergence with respect to the number of $\mathbf{k}$ -points, the number of bands, and the cell size separately. Several techniques recently introduced to solve the aforementioned convergence problems arising in G_0W_0 calculations are discussed and applied to the test system.

In the second part, the calculated QP corrections are used to obtain the complete bandstructures employing an interpolation technique based on MLWFs. The resulting bandstructures are compared with the corresponding DFT-LDA results and the reliability of a scissor-shift operator is discussed. Finally, the electron and hole masses are calculated and compared both at the DFT-LDA and MBPT levels. Our results are obtained with the ABINIT code [1] using a plane-wave basis set and norm-conserving pseudopotentials [213]. This work was published in Ref. [160].

4.2.2 Speeding up the convergence

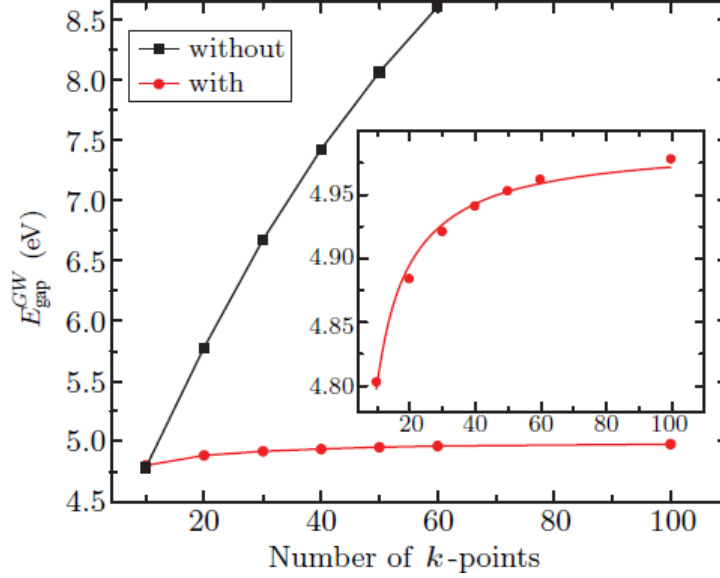


Figure 4.5: Convergence of the QP gap with respect to the number of k -points with (in red) and without (in black) Ismail-Beigi cutoff for the 0.5 nm Ge nanowire. Inset: Zoom of the convergence with Ismail-Beigi cutoff. The squares and circles represent the calculated values, while the lines show the best fit with Eq. (4.8).

The first parameter leading to convergence problems is the number of k -points employed for sampling the Brillouin zone. As can be seen from Fig. 4.5 (black curve), the value of the QP corrected band gap for the 0.5 nm Ge nanowire increases when increasing the number of k -points in the irreducible part of the Brillouin zone. There is no sign of convergence (even with 100 k -points the curve still shows a linear slope). This lack of convergence is due to the presence of a long-range Coulomb interaction between the periodically repeated images of the wire. Indeed, in contrast with DFT-LDA calculations in which the wire is neutral (and thus, the convergence is not problematic), GW calculations involve the addition of an electron (or a hole) to the wire. The resulting charge is not screened completely by the passivating hydrogen layer, hence, there remains a long-range Coulombian interaction between neighboring cells. In fact, the size of the unit cell that would be required to render the spurious electrostatic interaction negligible would be extremely large and the analysis could not be handled with the present computing resources. A possible approach for overcoming this problem consists in introducing

a truncation in real space of the Coulomb interaction beyond a certain radius, so that the number of interacting replicas is eliminated. The modified expression equals the bare Coulomb term in the region of interest, and is chosen so that the truncation can be efficiently performed in Fourier space. Several techniques have been used in the literature in order to accelerate the convergence (e.g., the one by Ismail-Beigi [123] or the one by Rozzi *et al.* [214]). In this work, we use the Ismail-Beigi approach, in which the Coulomb term v is replaced by a truncated interaction v_c . Explicitly

$$W_{\mathbf{G}\mathbf{G}'}(\mathbf{q}) = \epsilon_{\mathbf{G}\mathbf{G}'}^{-1}(\mathbf{q})v_c(\mathbf{q} + \mathbf{G}') \quad (4.3)$$

$$\epsilon_{\mathbf{G}\mathbf{G}'}(\mathbf{q}) = \delta_{\mathbf{G}\mathbf{G}'} - v_c(\mathbf{q} + \mathbf{G}')\chi_{\mathbf{G}\mathbf{G}'}^0(\mathbf{q}), \quad (4.4)$$

where the truncated Coulomb interaction for a wire oriented along the z axis is given by

$$v_c(\mathbf{r}) = \frac{\Theta(x, y)}{|\mathbf{r}|} \quad (4.5)$$

in which $\Theta(x, y)$ is one when x and y are inside the Wigner-Seitz unit cell, and 0 otherwise (the interested reader is referred to Ref. [123] for a more complete discussion of this cutoff technique). The interaction in real space has infinite extent along the z axis and its Fourier transform is given by

$$v_c(\mathbf{k}) = \int dx dy \Theta(x, y) 2K_0(|k_z|\rho) \cos(k_x x + k_y y), \quad (4.6)$$

where $\rho = (x^2 + y^2)^{1/2}$ and $K_0(z)$ is the modified Bessel function. Since the integral is of finite extent, the only diverging term in the limit $k_z \rightarrow 0$ originates from K_0 and behaves as

$$-2\ln(|k_z|) \int dx dy \Theta(x, y) \cos(k_x x + k_y y). \quad (4.7)$$

When $\sqrt{k_x^2 + k_y^2} \neq 0$ the divergence vanishes, as the projection of k in the xy plane is a reciprocal lattice vector. The expression is singular only if the Γ point is approached along the periodic dimension. This singularity is, however, milder than the one presented by the bare Coulomb term and can be accurately and efficiently treated via standard quadrature techniques. It is worth noting that the cutoff radius depends only on the geometrical setup of the supercell, hence no additional convergence parameters are needed.

The effect of the Ismail-Beigi cutoff technique on the convergence can be clearly seen in Fig. 4.5 (red curve). A detailed view of the convergence

graph in the case of the Ismail-Beigi approach is shown in the inset of Fig. 4.5. Here, we also fitted the values of the band gap as a function of the number of $\mathbf{k}$ -points used, with the form

$$E_{\text{gap}}^{GW}(N_{\mathbf{k}}) = E_{\text{gap}}^{GW}(\infty) + \frac{A}{N_{\mathbf{k}}}, \quad (4.8)$$

where $N_{\mathbf{k}}$ is the number of irreducible $\mathbf{k}$ -points, $E_{\text{gap}}(\infty)$ is the value of the band gap when an infinite number of $\mathbf{k}$ -points is taken into account, and A is a fitting parameter. We have not tried other fitting functional forms.

For what concerns the convergence with respect to the number of bands, the extrapolar method [215] allows one to decrease (by around ten times) the number of unoccupied bands that have to be used to converge the G_0W_0 calculations. Reducing the number of empty states is of fundamental importance since it leads to an important decrease both in CPU time and memory requirements. Strictly speaking, a well-converged GW calculation should take into account a number of states similar to the Hilbert space dimensionality, which is infinite. In practice, the number of basis functions is truncated to handle them computationally. In a plane-wave based approach, the number of basis functions is very large, thus rendering GW calculations extremely CPU demanding. To improve the convergence, the eigenenergies of states not explicitly treated are replaced by a common energy, determined from the highest computed state and the single parameter ΔE (which is the energy added to the energy of the highest treated band). The contribution of the states that are not explicitly considered in the calculation are taken into account by means of the closure relation

$$\sum_{i>N_b} |i\rangle\langle i| = \mathbf{1} - \sum_{i\leq N_b} |i\rangle\langle i|, \quad (4.9)$$

where N_b is the number of treated bands. The value of the parameter ΔE might be adjusted to provide the fastest convergence. It is worth stressing, however, that for the calculation of the polarizability, it is possible to obtain an optimal value for by monitoring the fulfillment of a particular sum rule (see Ref. [215] for details).

The convergence of the G_0W_0 number of states at fixed ΔE is shown in Fig. 4.6(a). In this figure, the same number of bands and the same value of ΔE is used both for the screening and the subsequent self-energy calculation. When the extrapolar technique is used, we find that the band gap is converged with a total of 180 bands (within 0.1 eV and for $\Delta E=1$ Ha). Such a level of convergence is not obtained when the

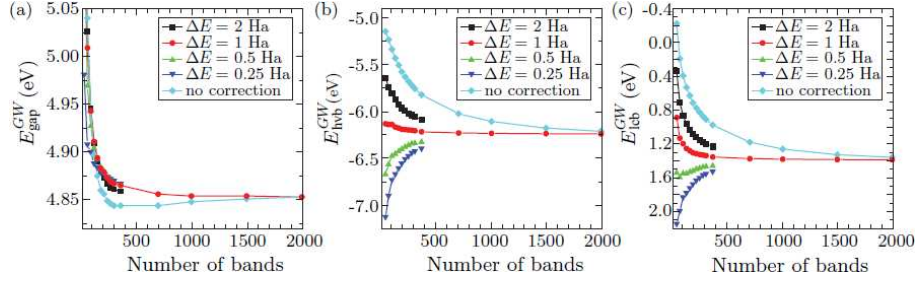


Figure 4.6: Convergence of (a) the band gap $E_{\text{gap}}^{\text{GW}}$, (b) the highest valence band $E_{\text{hvb}}^{\text{GW}}$, and (c) the lowest conduction band $E_{\text{lcb}}^{\text{GW}}$ with respect to the number of bands in the calculation for the 0.5 nm Ge nanowire. The convergence is shown for different values of the parameter ΔE (see text).

extrapolar technique is not used. For a small number of bands, it seems that the calculation using the extrapolar technique is converging toward another value for the band gap, compared to the calculations without using the technique. However, when the number of bands is increased further, both approaches converge toward the same value. The reduction from 2000 bands to 180 bands influences both memory requirements and CPU time substantially.

In the present case, the best value to take for ΔE is 1 Ha, leading to the fastest convergence, with the smallest slope in the convergence graphs. From Fig. 4.6, it is also clear that the convergence of the band gap is faster than the convergence of the individual parts (band energies of the highest valence $E_{\text{hvb}}^{\text{GW}}$ and lowest conduction band $E_{\text{lcb}}^{\text{GW}}$), which is an effect of the cancellation of errors and which confirms that energy differences converge faster than the individual components. This technique is not limited to one-dimensional (or more generally, low dimensional) systems, but it can also be used in bulk systems.

Finally, the convergence with respect to the interwire distance and thus of the lateral size of the unit cell, is performed. Here, we use the previously discussed extrapolar technique with $\Delta E = 1$ Ha. This convergence for the value of the band gap, with (red dots) and without (black squares) the Ismail-Beigi cutoff, is shown in Fig. 4.7. Without cutoff, a huge unit cell would be required to converge the band gap because of the Coulomb interaction. In contrast, convergence is already achieved for a lateral unit cell size of 26 bohrs with the Ismail-Beigi cutoff. Please note that, in the inset, the scale of the y axis is such that the differences between two successive labels is 0.001 eV, which is

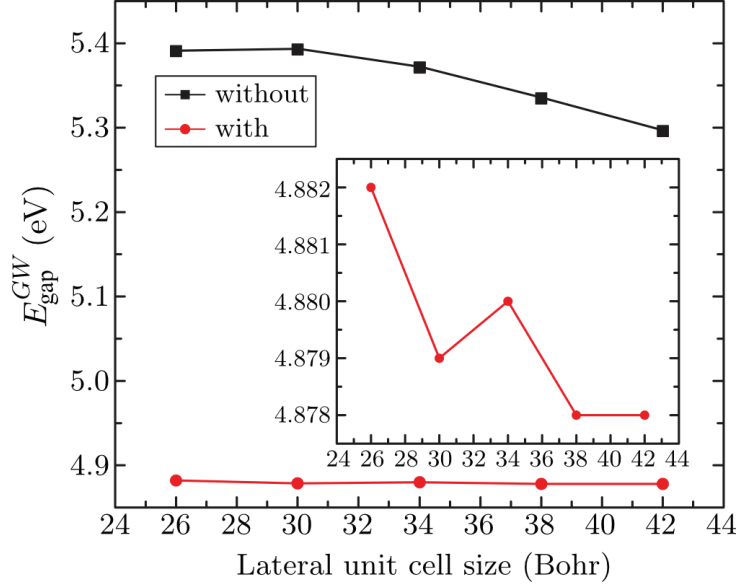


Figure 4.7: Convergence of the band gap E_{gap}^{GW} with respect to the size of the unit cell in the directions perpendicular to the wire with (in red) and without (in black) Ismail-Beigi cutoff for the 0.5 nm Ge nanowire. Inset: Zoom of the convergence with Ismail-Beigi cutoff.

smaller than the desired accuracy. With this combination of numerical techniques, we were able to compute efficiently the QP band gap of 0.5 and 1.2 nm Si and Ge nanowires, and of the 1.6 nm Si nanowire. The obtained DFT-LDA values, the QP results, and the size of the QP corrections are shown in Table 4.2. These corrections are larger for the 0.5 nm nanowire than for the 1.2 and 1.6 nm nanowires. These values are comparable to the values previously reported in literature, which are also reported in Table 4.2. Experimental results for these wire sizes are not available, as the experimental wires have larger diameters.

4.2.3 Bandstructures and effective masses

Here we use the MLWFs scheme to interpolate bandstructures (see section 1.4.7)¹. We first find the smallest initial $\mathbf{k}$ -point mesh needed

¹ The MLWFs that we use are random, that is, they do not correspond to chemical orbitals. They are just a localized basis useful to interpolate bandstructures. An alternative method to interpolate bandstructures without resorting to MLWFs is the Shirley technique [217].

Wire diameter		$E_{\text{gap}}^{\text{DFT}}$	$\Delta E_{\text{gap}}^{\text{GW}}$	$E_{\text{gap}}^{\text{GW}}$	Literature (theory)
	(nm)				
Ge	0.5	2.76	2.11	4.87	4.50 ^a
	1.2	1.57	1.41	2.98	3.01 ^b
Si	0.5	3.20	2.35	5.55	5.00 ^c
	1.2	1.70	1.62	3.32	3.12 ^d ; 3.20 ^c ; 3.40 ^e
	1.6	1.14	1.18	2.31	2.20 ^c ; 2.32 ^d ; 2.33 ^e

^a Ref. [204]; ^b Ref. [208]; ^c Ref. [203]; ^d Ref. [216]; ^e Ref. [205]

Table 4.2: Calculated gaps for Ge and Si nanowires. The band gap (in eV) for different wires as calculated within DFT-LDA ($E_{\text{gap}}^{\text{DFT}}$) and MBPT ($E_{\text{gap}}^{\text{GW}}$). The QP corrections ($\Delta E_{\text{gap}}^{\text{GW}} = E_{\text{gap}}^{\text{GW}} - E_{\text{gap}}^{\text{DFT}}$) are also given. The last column shows previously reported values for the QP band gap

to obtain good bandstructures at the DFT-LDA level. For this mesh, the QP corrections are subsequently calculated. These are then used to interpolate the bandstructures based on the MLWFs. The latter are the same as in DFT-LDA, since the G_0W_0 approximation uses the DFT-LDA wavefunctions and only corrects the eigenenergies.

Fig. 4.8 shows the DFT-LDA bandstructure of the 0.5 nm Ge nanowire interpolated using MLWFs. The latter are obtained using a disentanglement procedure [74] setting an inner window from the bottom of the lowest valence band to a value of 5 eV and an outer window to 6 eV. In Fig. 4.8(a) the MLWFs were obtained using an initial (unshifted) $1 \times 1 \times 5$ $\mathbf{k}$ -point grid in the full Brillouin zone, corresponding to three symmetry inequivalent $\mathbf{k}$ -points. The $\mathbf{k}$ -point grid is unshifted so that it contains the Γ point needed to calculate the band gap in the G_0W_0 calculations. The eigenenergies at these three points are indicated by red dots. It is clear that the interpolation is wrong in this case. In Fig. 4.8(b), a finer $\mathbf{k}$ -point grid was used, containing six inequivalent $\mathbf{k}$ -points corresponding to an unshifted $1 \times 1 \times 10$ grid. The agreement with the eigenenergies obtained directly from non-self-consistent calculations (blue dots) is excellent, as can be observed from Fig. 4.8(c).

If the QP corrected eigenenergies are available for the same $\mathbf{k}$ -point mesh, the corresponding bandstructure can also be obtained by interpolation, as shown in Fig. 4.9(a) (black lines). The obtained QP bandstructures can be used to study the validity of the commonly applied scissor shift. The latter aims to correct the DFT-LDA bandstructures by rigidly shifting all conduction bands in such a way that the band gap reaches the calculated G_0W_0 value (or the experimental one if available).

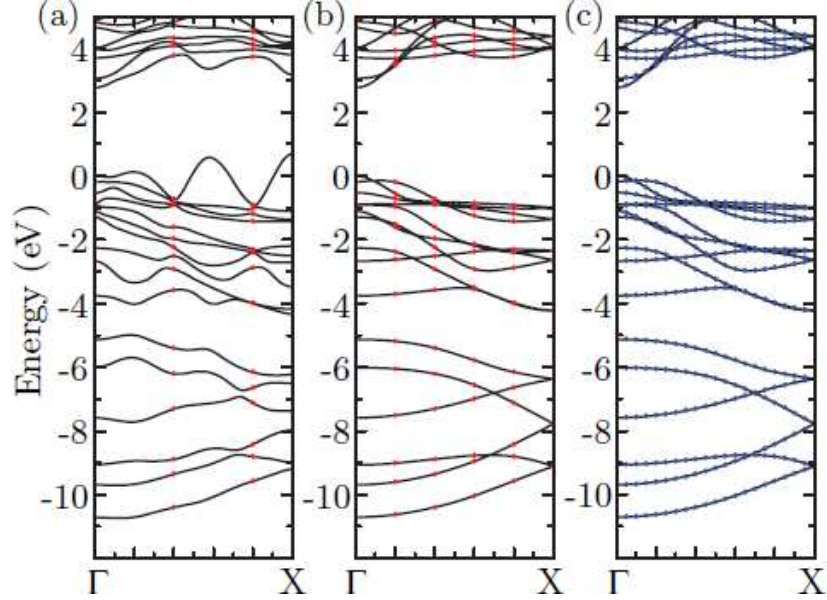


Figure 4.8: Interpolated DFT-LDA bandstructure (solid black lines) of the 0.5 nm Ge nanowire. The interpolations obtained using unshifted $1 \times 1 \times 5$ and $1 \times 1 \times 10$ grids are represented in panels (a) and (b), respectively. The red dots are the eigenenergies obtained directly using non-self-consistent calculations for the $\mathbf{k}$ -points belonging to the grids. In panel (c), the interpolation obtained with the unshifted $1 \times 1 \times 10$ is compared with additional non-self-consistent calculations (blue dots).

Such an approach clearly neglects all curvature differences between the DFT-LDA and QP bandstructures. As we now have the full QP bandstructure, we can test the validity of this approach. This is done in Fig. 4.9(a), where the red lines are the interpolated scissor-shifted DFT-LDA bandstructures. As can be seen from the zoom around the region close to the band gap shown in Fig. 4.9(b), this approach is only valid for $\mathbf{k}$ -points close to the Γ point and for bands close to the highest valence and lowest conduction band. One also observes that the gap between the highest valence and lowest conduction band in other $\mathbf{k}$ -points is underestimated in spite of the applied scissor shift: the highest valence band is too high in energy, while the lowest conductance band is too low in energy. The QP corrections are clearly not uniform, in contrast with what is implicitly assumed in the scissor-shift approach. To check if the curvatures near the Γ point, i.e., the hole and electron effective masses, are different in the QP corrected case as compared to the DFT-

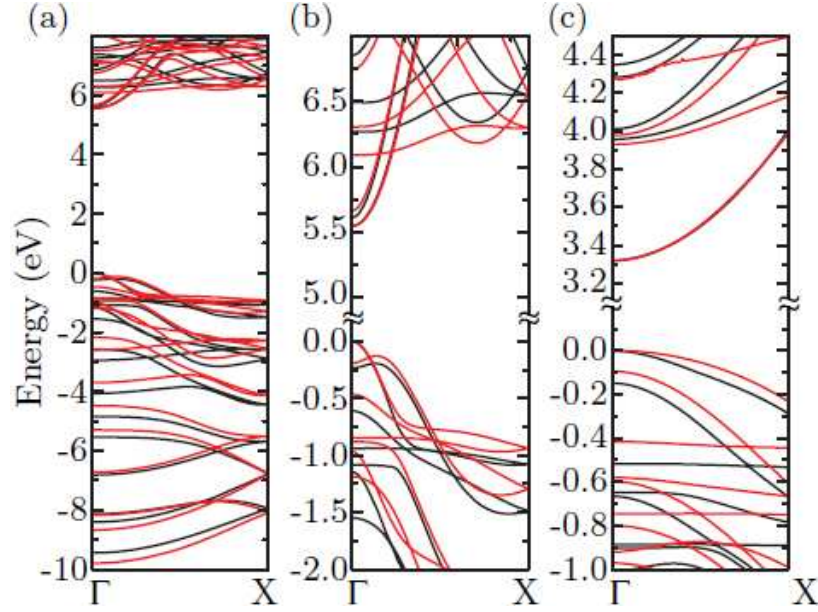


Figure 4.9: Interpolated QP (black) and scissor-shifted DFT-LDA (red) bandstructures of the 0.5 nm [(a) and (b)] and 1.2 Si nanowires. Panels (b) and (c) show a zoom of the region around the band gap.

LDA case, these were calculated by fitting a quadratic curve for small $\mathbf{k}$ -points. From these calculations, shown in Table 4.3, one can observe that the curvature is not always the same, e.g., the curvature of the highest valence band (thus corresponding to the hole effective mass) for the Ge nanowires or for the 1.6 nm Si nanowire differs significantly. This is visible in Fig. 4.9(c), where a detailed zoom of the bandstructure near the band gap is shown for the 1.2 nm Si nanowire. The curvature of the highest valence band (thus corresponding to the hole effective mass) is different for the interpolated QP (black) and scissor-shifted DFT-LDA (red) bandstructures. The values for the electron effective masses in the DFT-LDA and QP corrected cases are very similar, indicating that for these thin nanowires the lowest conduction band is shifted rigidly close to the Γ point. The fact that the corrections to the band masses are larger for the holes than for the electrons has also been observed in bulk systems [218].

Diameter(nm)		m_e^{DFT}	m_h^{DFT}	m_e^{QP}	m_h^{QP}
Ge	0.5	0.10	-0.12	0.11	-0.29
	1.2	0.12	-0.33	0.09	-0.18
Si	0.5	0.27	-0.16	0.22	-0.16
	1.2	0.13	-0.54	0.13	-0.19

Table 4.3: The calculated effective hole and electron masses (expressed in units of the electron mass) for Si and Ge nanowires, calculated within DFT-LDA and using QP corrections.

4.2.4 Conclusions

In this section, we have presented a systematic convergence study of the G_0W_0 calculations for one-dimensional nanowires. It was shown that it is necessary to use a cutoff of the Coulomb interactions to achieve convergence. The application of the extrapolar technique leads to an important reduction in the number of empty states by a factor of 10. The rule of thumb to take an amount of empty bands equal to ten times the number of occupied bands is also valid in the case of nanowires. By using an interpolation scheme based on maximally localized Wannier functions, we found that accurate bandstructures can be obtained. From these, it was demonstrated that applying a scissor shift to the DFT-LDA bandstructure leads to substantial differences with respect to the G_0W_0 results, when one compares the bandstructures at $\mathbf{k}$ -points away from the Γ point or for bands with lower (higher) energies than the highest valence (lowest conduction) band. This might lead to noticeable differences in the optical spectra. Significant differences can also be observed close to Γ , depending on the diameter and composition of the wire, as is evident from the calculated effective masses.

Conclusions

The calculation of material properties using MBPT is very expensive in terms of computing resources (CPU time, memory, disk space). Hence, sometimes it can become unaffordable. One of the most consuming parts is the evaluation of matrix elements at a large number of $\mathbf{k}$ -points. In this thesis, MLWFs were used in conjunction with MBPT as an accurate and efficient technique to determine the electrical and transport properties of nanomaterials and solids. Indeed, we have used MLWFs to interpolate the MBPT Hamiltonian, reducing the number of $\mathbf{k}$ -points where it has to be evaluated explicitly, and hence saving computing resources. Moreover, MLWFs are also used as a basis set for quantum transport calculations and other large-scale calculations. Several practical applications have been presented.

Chapter 1 has been dedicated to present the theoretical background. In section 1.2, we have introduced the density functional theory (DFT), a popular method widely used in the computational physics and computational chemistry communities. It is exact in principle for the ground state properties of the system. However, it presents intrinsic limitations to treat electronic excitations and other problems due to the approximations usually used for the XC energy functional. In section 1.3, we have introduced the MBPT. Since this theory provides a direct access to electronic excitations, it is more appropriate than DFT for transport properties, among others. In section 1.4, we have provided a practical introduction to MLWFs. In particular, we have described the basic formalism and the interpolation technique based on MLWFs. Finally, section 1.5 has been dedicated to quantum transport focusing in the nanoscopic regime.

In chapter 2, we have used MLWFs together with MBPT to study the transport properties of molecular junctions. We found that it is crucial to update not only the DFT eigenvalues but also the DFT wavefunctions to correct the metal-molecule hybridizations, and hence to correct the zero-bias conductance. On the other hand, we have also found that *ab initio* self-energy operators modify the metal-molecule hybridizations in

a complex way, which cannot always be accounted for with model self-energies based on molecular projectors. Our results have emphasized the importance of (1) the wavefunctions in molecular junctions, and (2) the atomistic detail needed for the calculation of transport properties of these materials.

Chapter 3 has been dedicated to our calculations of the bandstructure of solid gold within MLWFs and MBPT. We have found that G_0W_0 , the standard method to correct the interband gaps in noble metals, negligibly modifies the DFT eigenvalues. In contrast, mixing of the DFT eigenfunctions within QPSCGW showed to open the interband gap, improving the agreement with the experimental measurements. This result has pointed out the importance of correcting the DFT wavefunction to predict the electronic properties of this material. This is very similar to what was observed for the molecular junction.

Finally, chapter 4 has been dedicated to the use of MLWFs and MBPT to predict the bandstructures of various materials (zircon, hafnon, Si and Ge nanowires). For zircon and hafnon, we saw that the band structure of both materials is very similar within MBPT and DFT-LDA except for the band gap opening, the increase in the dispersion of the bands, and a slight displacement of the valence-band maximum away from the Γ point within MBPT. On the other hand, the inclusion of vertex effects resulted in just a rigid shift of all bands, which only accounts for a change in the absolute value of the Fermi level. For the Si and Ge nanowires, we have investigated within the G_0W_0 approximation, focusing on the techniques used to speed up the convergence of the QP calculations. The validity of the scissor-shift operator has been studied through a comparison with the QP results. This simple operator showed not to predict the atomistic detail of the bandstructures. Dispersion changes have been observed, which were also reflected in changes in the effective band masses calculated taking into account quasiparticle corrections.

As one of the general conclusions, we would like to emphasize that, in both the molecular junctions and gold bulk, the wavefunctions play a crucial role in the determination of their electrical and transport properties. Standard many-body techniques which only correct the DFT eigenvalues are, hence, insufficient. In particular, in gold G_0W_0 did not modify the inter-band gap ($5d$ - $6sp$ gap), and in the junctions the MOs gap was just slightly opened leading to a negligible effect in the zero-bias conductance. These results point out the importance of self-consistent many-body techniques, such as CHSX and QPSCGW in the modeling of electrical and transport properties of nano-scale materials and solids.

A series of limitations can be highlighted in our transport calcula-

tions.

- Our transport calculations were limited to four junctions. It would be necessary to study other systems to analyze whether or not our conclusions can be generalized.
- The conclusions that the wavefunctions are important for the transport properties of molecular junctions were derived from results obtained using only one iteration in the self-consistency loop. Thus, the effect of reaching complete self-consistency with our many-body method remains unknown.
- Our partly self-consistent calculations (with $\overline{\text{CHSX}}_0$) were performed approximating the self-energy at the CHSX level. More accurate self-consistent *GW* techniques, going beyond CHSX, such as QPSCGW, might further improve the agreement with the experiments.

These limitations clearly indicate some directions for future work that could be started right away. Furthermore, in our transport calculations, we have only considered the static conductance at the ballistic regime. This only give us access to one experimental observable, the zero-bias conductance. The out-of-equilibrium phenomena at the many-body level is a long-term perspective of this work. Beyond the Landauer approach, the Keldysh formalism could bring new light in the field of quantum transport. However, it is still too early to think about this, and more research is still needed to understand first the transport at the zero-bias regime.

Limitations can obviously be identified in our calculations on solid gold.

- The MBPT bandstructure was interpolated using an initial grid of $10 \times 10 \times 10$ $\mathbf{k}$ -points. However, this grid is insufficient to calculate other material properties, such as the optical properties. Since, we used a self-consistent *GW* approach, the evaluation of the *GW* corrections on a denser $\mathbf{k}$ -mesh is prohibitive in terms of computing resources. The *GW* corrections scale as $N_{\mathbf{k}}^2$, with respect to the number of $\mathbf{k}$ -points ($N_{\mathbf{k}}$). Hence, it would be important to implement an interpolation technique for the QP wavefunctions to then calculate other material properties in a denser $\mathbf{k}$ -mesh. This technique could be based on MLWFs, following the schema of Ref. [65], or using the Shirley method [217], among other methodologies.
- At present, the *GW* code in ABINIT [1] is not generalized to treat spinors. Hence, spin-orbit (SO) corrections to the MBPT

bandstructure were included just graphically (as explained in section 3.7). The treatment of spin-orbit effects at the GW level is not a trivial work. In fact, a set of generalized GW equations should be considered as already discussed in Refs. [148, 149, 147]. The effect of a fully relativistic GW formalism remains unknown, and it is important to achieve in the future.

The results of this work have shown that MLWFs are a powerful tool to interpolate MBPT Hamiltonians. As a perspective of this work, MLWFs could be used to interpolate other MBPT operators. This is important to speed up the GW calculations, converging at a lower cost the number of $\mathbf{k}$ -points needed to be treated explicitly.

Appendix A

Technical details of the calculations

In this appendix, we provide the technical details for the calculations performed in this work. In section A.1, the details for the calculations on molecular junctions (in chapter 2) are shown. In section A.2, the details for the calculations on gold bulk (in chapter 3) are discussed. In section A.3, the details for the calculations on zircon and hafnion (in chapter 4.1) are shown.

A.1 For the molecular junctions

In this section, we provide the technical details for the calculations on molecular junctions (in chapter 2). The DFT and MBPT calculations are performed using the ABINIT package [1]. The XC energy is approximated by the Perdew, Burke and Ernzerhof (PBE) functional [14]. Norm-conserving pseudopotentials [213] are used. For gold, these include the $5s$ and $5p$ semicore states which are crucial for the MBPT calculations [10]. The wavefunctions are expanded on a plane-wave basis set up to kinetic energy cutoff of 30 Ha. The corresponding MLWFs are obtained following the procedure of Ref. [62] with the WANT package [3]. These are used in the transport calculations which are performed also with WANT.

Two systems are considered: BDA and BDT attached to gold electrodes. For BDT, we consider a system in which the H atoms remain attached to the thiols after the molecule has being absorbed to the Au surfaces. Therefore, this geometry is referred to as BDT-H.

For the atomic relaxation, a 2×2 surface cell is adopted for the Au (111) surface with seven atomic layers in the electrodes. For the MBPT

calculations, three gold layers are removed. This guarantees an affordable computational cost without compromising the calculated conductance¹ despite the rather packed geometry (with ~ 3.1 Å between the repeated images of the molecules). All the parameters of the calculations are converged to ensure an error smaller than $0.001 \mathcal{G}_0$ on the zero-bias conductance $\mathcal{G}(E=0)$. Hence, a $8 \times 8 \times 3$ grid of $\mathbf{k}$ points is adopted to sample the Brillouin zone. The QP corrections are calculated explicitly for 210 bands at 96 irreducible $\mathbf{k}$ -points including ~ 300 bands in the calculations.

For the MBPT calculations, the GW approximation is adopted for the self-energy Σ , neglecting vertex corrections [15]. In principle, Σ is a non-hermitean, non-local and frequency-dependent operator. The non-hermitian part of Σ is ignored, assuming infinite QP lifetimes; while the non-locality is fully taken into account. Different flavors are then considered for the GW self-energy. In the standard single-shot G_0W_0 approach, the self-energy is approximated using the DFT electronic structure; and, the QP corrections to the DFT eigenvalues are determined using first-order perturbation theory considering only the diagonal elements of Σ in the space of the DFT orbitals φ_i^{sys} of the contacted-molecule system (see section 1.3.9). Here, the frequency dependence is obtained using the plasmon pole model of Godby and Needs [55]. Moreover, the Coulomb-hole and screened-exchange (CHSX) introduced in section 1.3.8, which is a static approximation to the GW self-energy, is adopted here.

A.2 For gold bulk

In this section, the technical details for the calculations on gold bulk (in chapter 3) are shown. The ground state and GW calculations are performed using the ABINIT code [1]. The unit cell consists of a FCC lattice with one gold atom and the experimental lattice constant of 7.71 bohrs [219]. The XC energy is approximated by the PBE functional [14]. Scalar-relativistic norm-conserving pseudopotentials are used [220, 221].

Two pseudopotentials are employed to elucidate the role of semicore states; The first one contains 11 valence electrons ($5d^{10}, 6s^1$) while the second contains 19 electrons ($5s^2, 5p^6, 5d^{10}, 6s^1$). The plane-waves basis set is expanded up to a cut-off energy of 30 Ha when no semicores are

¹ For the BDT geometry, it was explicitly checked that using a 3×3 surface cell and 7 layers of gold does not change significantly the transport properties at the DFT and G_0W_0 levels. Note also that, for both systems, the coupling self-energies (between the system to ideal infinite leads) are calculated at the DFT level in order to limit the effect of some errors introduced by the use of only four gold layers.

included and 50 Ha when they are. The BZ is sampled using a shifted grid of $10 \times 10 \times 10$ $\mathbf{k}$ -points following the Monkhorst-Pack scheme [222].

In the GW calculations a number of parameters are chosen to ensure a convergence of 0.01 eV in the QP energies. A total of 100 bands are used. To evaluate W , 59 plane waves and 145 $\mathbf{q}$ -vectors in the irreducible BZ are considered. The PPM by Godby and Needs [55] is used here because it gives the best agreement with more robust integration methods [59]. In the CD method, a total of 6 and 20 frequencies are evaluated in the imaginary and real axis, respectively. All self-consistent GW calculations are made with semicore orbitals and within the CD method. Moreover, a total of 40 bands are mixed, including the semicore orbitals, in ~ 120 iterations to achieve the desired accuracy. Vertex effects are included within the standard del-Sole approximation [60, 223, 224]. Non-local vertex corrections only in W were also considered [152, 153].

The QP bandstructures are interpolated with the use of MLWFs with the Wannier90 code [2] as explained elsewhere [65, 62]. In the bandstructure interpolation, a total of 9 MLWFs were extracted from the KS bands with a frozen window covering up to 10 eV above the Fermi level (excluding the semicore bands) in the disentangling procedure [74] as shown in Fig A.1. These MLWFs are the six functions shown in section 3.4 and 3 extra $6p$ -like MLWFs (not shown here).

In all cases, the Fermi level is obtained by integrating the density of states (DOS), calculated with an interpolated grid of $30 \times 30 \times 30$ $\mathbf{k}$ -points using MLWFs and a low Gaussian smearing of 0.005 hartrees. At the DFT level, it was verified that the Fermi levels obtained with a grid of $30 \times 30 \times 30$ and $60 \times 60 \times 60$ interpolated $\mathbf{k}$ -points are equal within 0.01 eV. At the GW level, it is expected that this $\mathbf{k}$ -grid is also converged to obtain the Fermi level.

A.3 For zircon and hafnon

In this section, the technical details for the calculations on zircon and hafnon (in chapter 4.1) are shown. All the ground-state and GW calculations are performed using the ABINIT code [1]. The MLWFs were obtained with Wannier90 [2]. The MLWFs for GW QPs were obtained with the procedure in Ref. [62], as implemented in ABINIT and as explained in Ref. [1]. The ion-electron interaction is approximated by highly transferable extended norm-conserving pseudopotentials [220]. The pseudopotentials are constructed considering the following states as valence ones: Hf($5s, 5p, 5d, 6s$), Zr($4s, 4p, 4d, 5s$), Si($3s, 3p$), and O($2s, 2p$). The wavefunctions are expanded onto a planewave basis setup to a ki-

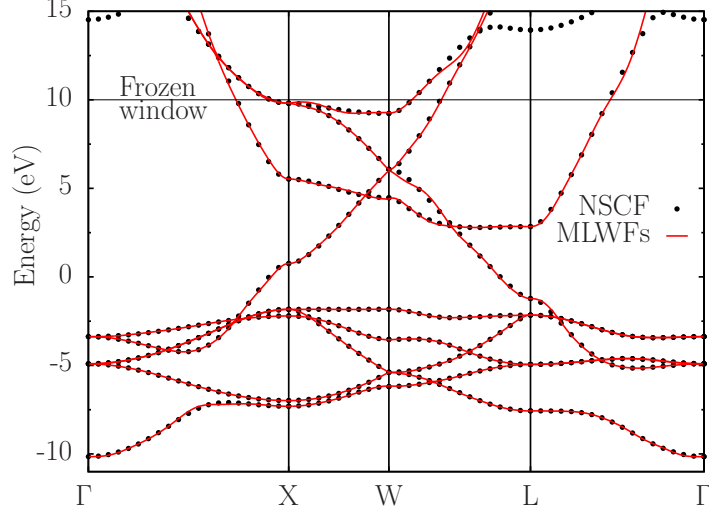


Figure A.1: Calculated bandstructure of gold. The DFT bandstructure obtained by a NSCF calculation is shown with black points. The corresponding MLWFs interpolated one is shown with red lines. The Fermi levels are at 0 eV. The position of the frozen window in the disentangling procedure is shown with a horizontal line at 10 eV.

netic energy cutoff of 30 hartree. The BZ integration is performed using a special $4 \times 4 \times 4$ wave vector grid sampled within the Monkhorst-Pack scheme [222]. The dielectric matrix is calculated using the Adler-Wiser expression [225] summing over 300 bands. We find that using a matrix size of 345×345 plane waves to represent the dielectric matrix is enough to account for inclusion of local field effects and to achieve convergence of quasiparticle energies. The self-energy is obtained by summing over 24 special $\mathbf{q}$ vectors in the IBZ, and over 400 bands. For the *GW* calculations, approximate vertex corrections have been included following the method proposed in Ref. [60].

All the calculations are performed with the low-pressure body-centered tetragonal structure. In this structure, both $M = (\text{Hf}, \text{Zr})$ and Si atoms are located at high-symmetry positions $(0, \frac{3}{8}, \frac{1}{4})$ and $(0, \frac{1}{4}, \frac{3}{8})$ on the $4a$ and $4b$ Wyckoff sites, respectively. The O atoms occupy the $16h$ Wyckoff sites at $(0, u, v)$, where u and v are internal parameters. The theoretical parameters used throughout all the calculations are identical to those reported in Ref. [173]. These are shown in Table A.1.

	Zircon		Hafnon	
	Theory	Expt.	Theory	Expt.
a	6.61	6.57	6.54	6.61
c	5.97	5.96	5.92	6.00
u	0.0672	0.0655	0.0645	0.0646
v	0.1964	0.1948	0.1945	0.1967
Volume	130.42	128.63	126.60	131.08
$d(\text{Si-O})$	1.62	1.61	1.61	1.62
$d(\text{M-O})$	2.14	2.10	2.10	2.13
	2.27	2.24	2.24	2.27
$\angle(\text{O-Si-O})$	97°	97	97	97
	116	117	116	116

Table A.1: Structural parameters of hafnon and zircon. The lengths are in Å. This table was taken from Ref. [173]. The theoretical results for zircon are those of Refs. [172, 173]. The experimental data are taken from Ref. [226] for hafnon, and from Ref. [227] for zircon.

Appendix B

Molecule-molecule interactions at the G_0W_0 level

In DFT calculations, the Schrödinger equation is usually solved for periodic systems within the Bloch's theorem (see section 1.4.1). For non-periodic systems, a supercell is employed. Here, the unit cell in the calculation contains also a large vacuum size to prevent spurious interactions among neighboring cells. To illustrate, a supercell for the BDT molecule is shown in Fig. B.1. The cells should be sufficiently large so that a molecule will not interact with its periodic image at a neighboring cell [228].

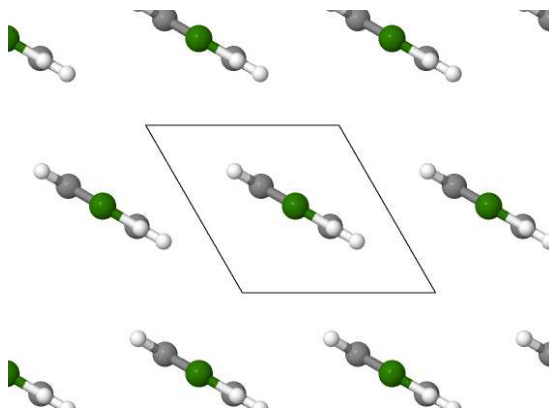


Figure B.1: Supercell of BDT in gas phase. The sulfur, carbon and hydrogen atoms are represented by green, gray and white spheres respectively. The unit cell is represented by black lines.

In total energy calculations of neutral systems within DFT, the convergence of the electronic levels with respect to the cell size is achieved with relatively small unit cells. On the other hand, in GW calculations the system becomes charged due to a test-charge in the calculation of the screening. As a result, convergence is achieved with much larger supercells. In such cases, the Ismail-Beigi cutoff [123] can be employed

to artificially cut the spurious interactions with neighboring cells. For example, Fig. B.2 shows the convergence for the value of the G_0W_0 band gap of a Ge nanowire, with (red dots) and without (black squares) the Ismail-Beigi cutoff. Without cutoff, a huge unit cell would be required to converge the band gap because of the Coulomb interaction. In contrast, convergence is already achieved for a lateral unit cell size of 26 bohrs with the Ismail-Beigi cutoff.

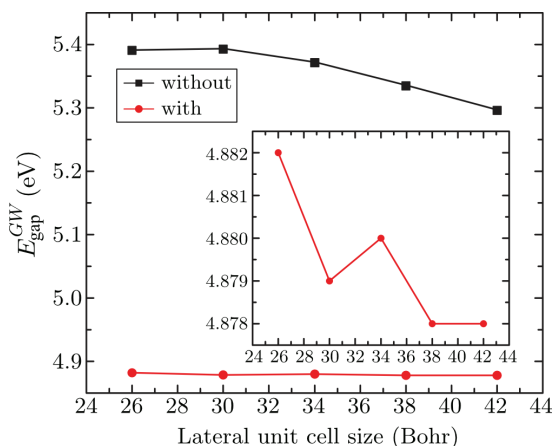


Figure B.2: Convergence of the G_0W_0 band gap with respect to the size of the unit cell in the directions perpendicular to the wire with (in red) and without (in black) Ismail-Beigi cutoff for the 0.5 nm Ge nanowire. Inset: zoom of the convergence with Ismail-Beigi cutoff. For more information see chapter 4.2.

In chapter 2, G_0W_0 calculations were done for molecular junctions in closed-packing regimes (with a molecule-molecule distance of ~ 3 Å). It was found that G_0W_0 self-energy corrections to the DFT Hamiltonian were negligibly modifying the zero-bias conductance in this packing regime.

In this appendix, the electronic levels of BDT molecule in gas phase is studied at the DFT and G_0W_0 levels. Special emphasis is put in the convergence of the cell-size in the calculations. Moreover, the effect of the cell-size is also studied in the conductance of benzene-dithiolate at hollow geometry (BDT-h) (see chapter 2) at the DFT and G_0W_0 levels. It is found that G_0W_0 self-energy corrections do not modify the initial DFT zero-bias conductance in despite of the packing regime.

An hexagonal supercell (shown in Fig. B.1) is used. Different cell-sizes are considered with a molecule-molecule distance of 3.1, 5.5 and 8.3 Å, corresponding to that one for the BDT-h junction with a coverage of $c(2 \times 2)$, $c(3 \times 3)$ and $c(4 \times 4)$, respectively.

Table B.1 shows the DFT and G_0W_0 gaps as a function of the molecule-molecule distance, for BDT in the gas phase. The DFT gap convergence is reached with a distance of 5.5 Å, however, the DFT gap is less than one half of the experimental value. On the other hand, the

G_0W_0 gap convergence is very slow: a molecule-molecule distance of 8.3 Å is not enough to converge the gap within 0.1 eV (see Table B.1). The converged G_0W_0 gap is 8.7 eV (obtained with the Ismael-Beigi cutoff technique and a supercell including 20 Å of vacuum), in agreement with the experimental gap of 8.6 eV [126] and 7.8 eV [125].

Distance [Å]	Gap [eV]		Experimental gap	
	DFT	G_0W_0	Gap [eV]	Ref.
3.1	3.0	6.9	7.8	[125]
5.5	3.4	8.2	8.6	[126]
8.3	3.4	8.4		

Table B.1: Fundamental gap for BDT. The DFT and G_0W_0 gaps with respect to the molecule-molecule distance (left panel) and the experimental gaps (right panel) are shown.

The BDT-h conductance within DFT (black) and G_0W_0 (red) for c(2x2) (dashed lines) and c(3x3) (solid lines) coverages are shown in Fig B.3. The details of the calculations can be found in appendix A.1. The c(2x2) and c(3x3) DFT results are in qualitative agreement with each other: the position of the peaks and the zero-bias conductance agree well. However, the conductance peaks are slightly higher for the c(3x3) system. Moreover, the conductance has a steeper decay around the 1 eV region in the c(3x3) system.

The G_0W_0 corrections on the DFT eigenvalues are changing the conductance at energies $E \neq 0$, while the zero-bias conductance is kept at the DFT value. This result confirms the findings of section 2.7; *ab initio* diagonal corrections, such as G_0W_0 , are negligibly modifying the zero-bias conductance of this junction.

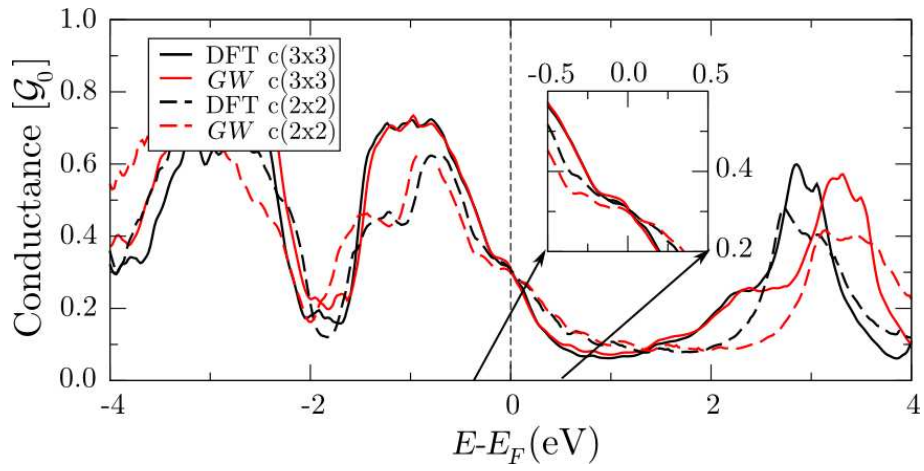


Figure B.3: BDT-h conductance with respect to the energy at several Au coverages is shown. The Fermi level, E_F , is set to zero. The c(2x2) (dashed lines) and c(3x3) (solid lines) results are shown within DFT (black) and G_0W_0 (red). An inset shows a zoom over the zero-bias region.

Appendix C

Image-charge surface effects on an adsorbed molecule

In this appendix, we detail the procedure used to obtain the image-charge correction for the models studied in Section 2.6.

The QP gap of an isolated molecule adsorbed near a metal surface is decreased due to image charge effects as observed in G_0W_0 calculations [137]. Image charge effects refer to the influence on the molecular levels of an induced polarization of the metal surface due the presence of the charged molecule. That is, the charged molecule induces a polarization on the metal surface, which changes the potential energy of the molecule.

The image-charge energy, Δ^{IC} , is evaluated classically by using point charges from a Bader or a Mlliken analysis [6]. The charge density of the molecule, $\rho_q(\mathbf{r})$, is discretized in N point charges located at $\mathbf{r}_i$

$$\rho_q(\mathbf{r}) = \sum_{i=1}^N Q_i \delta(\mathbf{r} - \mathbf{r}_i) \quad (\text{C.1})$$

In this work, to estimate the charge distribution on the molecule $Z(\mathbf{r})$, the gas phase Bader analysis from a charged spin polarized calculation is employed. The distribution of unpaired spin up charges is used following the procedure of Ref. [6]. The atomic charges are shown in Table C.1 together with the envisioned geometries in this work, which can be also seen in Fig. C.1. The geometries of the molecules are taken from the junctions of Section 2.3. *i.e.*, the molecule orientation with respect to the surface, the molecule bond lengths and angles and the gold-molecule distances are those of the molecular junctions.

For BDA, the charge distribution is in good agreement with that one of Ref [6], obtained by a Mlliken analysis. In Ref. [6], the geometry of

BDA					BDT				
	Coordinates [Å]			Q_i [e^-]		Coordinates [Å]			Q_i [e^-]
	x_i	y_i	z_i			x_i	y_i	z_i	
N1	3.98	2.00	2.04	0.000	S1	4.99	2.37	2.15	0.000
C1	5.25	1.78	1.46	0.319	C1	6.51	1.51	1.83	0.086
C2	5.92	0.57	1.69	0.095	C2	7.13	1.76	0.60	0.219
C3	5.82	2.70	0.59	0.091	C3	7.06	0.58	2.71	0.197
C4	7.03	2.44	-0.02	0.094	C4	8.23	-0.07	2.37	0.221
C5	7.14	0.31	1.07	0.092	C5	8.30	1.10	0.26	0.198
C6	7.71	1.24	0.20	0.317	C6	8.85	0.17	1.14	0.085
N2	8.98	1.01	-0.35	0.000	S2	10.38	-0.66	0.83	0.000

Table C.1: Geometry and charge distribution for the BDA and BDT molecules.

the isolated molecule is used, hence, their results are slightly different from ours. In particular, the charge of the carbon atoms bonded to the nitrogen atoms (C1 and C6) is $0.32 e^-$ in our work, while it is split among the nitrogen and carbon atoms in Ref. [6] (it is 0.23 and $0.15 e^-$ for the N and C atoms, respectively). Nevertheless, we found that these differences have a negligible effect on the image-charge energy ¹.

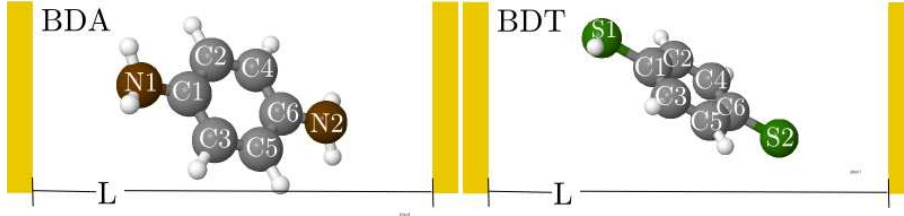


Figure C.1: The BDA (left) and BDT (right) isolated molecules between two parallel metal surfaces separated by a distance L . The hydrogen, carbon, sulfur and nitrogen atoms are represented by white, gray, green and brown spheres, respectively.

The total potential gained by approaching the charged molecule to

¹ For BDA, the image-charge energy is either 0.79 eV or 0.92 eV when calculated with our parameters or those of Ref. [6], respectively. There is negligible difference between these two values given the approximate nature of the classical image-charge approach.

the metal surface is [6]

$$\Delta^{\text{IC}} = \int \int \frac{\rho_q(\mathbf{r}) \rho_q^{\text{ind}}(\mathbf{r}')}{\|\mathbf{r} - \mathbf{r}'\|} d^3\mathbf{r}' d^3\mathbf{r} + \frac{1}{2} \int \int \frac{\rho_q^{\text{ind}}(\mathbf{r}) \rho_q^{\text{ind}}(\mathbf{r}')}{\|\mathbf{r} - \mathbf{r}'\|} d^3\mathbf{r}' d^3\mathbf{r}. \quad (\text{C.2})$$

The first term is the self-energy of the molecule charge density ρ_q due to the charge density induced to the metal surface ρ_q^{ind} , and the second term is the Hartree energy for the charge density ρ_q^{ind} .

The gold surface is approximated by a perfect conductor located at $x = 0$. Moreover, the charges are discretized, so that

$$\Delta^{\text{IC}} = \frac{1}{2} \sum_{i,j=1}^N Q_i Q_j \int d^3\mathbf{r} \frac{\rho_{q(j)}^{\text{img}}(\mathbf{r})}{\|\mathbf{r}_i - \mathbf{r}\|}, \quad (\text{C.3})$$

where $\rho_{q(j)}^{\text{img}}$ is the image charge density in the metal due to a point charge of $1 e^-$ located at $\mathbf{r}_j$ ². If the metallic surface is a perfect conducting surface located at $x = 0$, the charge induced in the metal becomes a series of point charges, hence

$$\rho_{q(j)}^{\text{img}}(\mathbf{r}) = -\delta(x + x_j) \delta(\mathbf{r}^\perp - \mathbf{r}_j^\perp),$$

$$\Delta^{\text{IC}} = -\frac{1}{2} \sum_{i,j=1}^N \frac{Q_i Q_j}{\sqrt{(x_i + x_j)^2 + R_{ij}^2}}, \quad (\text{C.4})$$

where $\mathbf{r}^\perp = y\hat{\mathbf{y}} + z\hat{\mathbf{z}}$ are the components of $\mathbf{r}$ in the yz -plane and $R_{ij} = \|\mathbf{r}_i^\perp - \mathbf{r}_j^\perp\|$.

If the molecule is located between two metal surfaces at $x = 0$ and $x = L$, an infinite series of image charges is produced, analogous to a series of reflections in two parallel mirrors. The image-charge energy

² The deduction of the formulas in this appendix can be found in the supplementary material of Ref [6]. See EPAPS Document No. E-JCPSA6-128-803811. This document can be reached through a direct link in the online article's HTML reference section or via the EPAPS homepage <http://www.aip.org/pubservs/epaps.html>

becomes:

$$\begin{aligned} \rho_{q(j)}^{\text{img}}(\mathbf{r}) = & -\delta(\mathbf{r}^\perp - \mathbf{r}_j^\perp) \sum_{n=1}^{\infty} [\delta(x + x_j - 2nL) \\ & - \delta(x - x_j + 2nL) - \delta(x - x_j - 2nL) \\ & + \delta(x + x_j + 2(n-1)L)], \end{aligned} \quad (\text{C.5})$$

$$\begin{aligned} \Delta^{\text{IC}} = & -\frac{1}{2} \sum_{i,j=1}^N Q_i Q_j \sum_{n=1}^{\infty} \left[\frac{1}{\sqrt{(x_i + x_j - 2nL)^2 + R_{ij}^2}} \right. \\ & - \frac{1}{\sqrt{(x_i - x_j + 2nL)^2 + R_{ij}^2}} - \frac{1}{\sqrt{(x_i - x_j - 2nL)^2 + R_{ij}^2}} \\ & \left. + \frac{1}{\sqrt{(x_i + x_j + 2(n-1)L)^2 + R_{ij}^2}} \right]. \end{aligned} \quad (\text{C.6})$$

The location of the point charges in Eq. (C.5) is sketched on Fig. C.2.

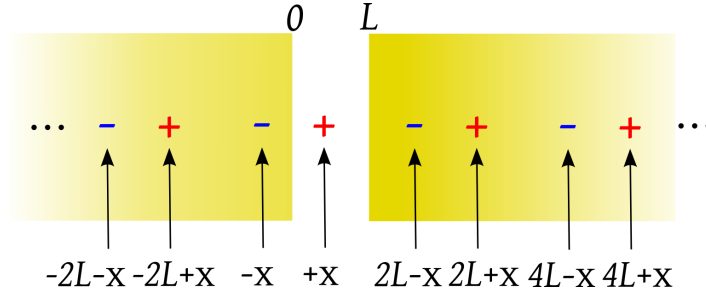


Figure C.2: Location of image charges for two perfectly conducting surfaces at $x = 0$ and $x = L$ originated by a positive charge at $+x$.

In this work the distance L between the two gold surfaces is 13 and 13.4 Å for BDA and BDT, respectively. The image charge energy as calculated using Eq. (C.6) is 0.79 (0.78) eV for BDA (BDT).

List of publications

1. T. Rangel, A. Ferretti, P. E. Trevisanutto, V. Olevano and G.-M. Rignanese, *Transport properties of molecular junctions from many-body perturbation theory*, Phys. Rev. B **4**, 045426 (2011), <http://dx.doi.org/10.1103/PhysRevB.84.045426>.
2. T. Rangel, K. Deniz, P. E. Trevisanutto, V. Olevano, H. Van Swygenhoven, G.-M. Rignanese, *The bandstructure of gold from many-body perturbation theory*, to be submitted.
3. H. Peelaers, B. Partoens, M. Giantomassi, T. Rangel, E. Goossens, G.-M. Rignanese, X. Gonze, and F. M. Peeters, *Convergence of quasiparticle band structures of Si and Ge nanowires in the GW approximation and the validity of scissor shifts*, Phys. Rev. B **83**(4), 045306 (2011), <http://dx.doi.org/10.1103/PhysRevB.83.045306>.
4. X. Gonze, B. Amadon, P.-M. Anglade, J.-M. Beuken, F. Bottin, P. Boulanger, F. Bruneval, D. Caliste, R. Caracas, M. Côte, T. Deutsch, L. Genovese, P. Ghosez, M. Giantomassi, S. Goedecker, D. Hamann, P. Hermet, F. Jollet, G. Jomard, S. Leroux, M. Mancini, S. Mazevet, M. Oliveira, G. Onida, Y. Pouillon, T. Rangel, G.-M. Rignanese, D. Sangalli, R. Shaltaf, M. Torrent, M. Verstraete, G. Zerah and J. Zwanziger, *ABINIT: First-principles approach to material and nanosystem properties*, Comput. Phys. Commun. **180**(12), 2582 (2009), <http://dx.doi.org/10.1016/j.cpc.2009.07.007>.
5. R. Shaltaf, T. Rangel, M. Gruning, X. Gonze, G.-M. Rignanese, and D. R. Hamann, *Electronic properties of zircon and hafnium from many-body perturbation theory*, Phys. Rev. B **79**, 195101 (2009), <http://dx.doi.org/10.1103/PhysRevB.79.195101>.

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