Real space description of electronic and transport properties of hybrid interfaces

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Notice
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# Contents

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Contents</strong></td>
<td>8</td>
</tr>
<tr>
<td><strong>Introduction</strong></td>
<td>11</td>
</tr>
<tr>
<td><strong>1 Electronic structure within Density Functional Theory</strong></td>
<td>25</td>
</tr>
<tr>
<td>1.1 Density functional theory</td>
<td>25</td>
</tr>
<tr>
<td>1.2 Periodic systems: the Bloch theorem</td>
<td>32</td>
</tr>
<tr>
<td>1.3 The plane wave pseudopotential method</td>
<td>33</td>
</tr>
<tr>
<td><strong>2 Wannier Functions</strong></td>
<td>41</td>
</tr>
<tr>
<td>2.1 Maximally localized Wannier functions</td>
<td>41</td>
</tr>
<tr>
<td>2.2 MLWF from PAW or ultrasoft pseudopotentials</td>
<td>48</td>
</tr>
<tr>
<td>2.3 Polarization of crystalline solids: Wannier functions and Berry phases</td>
<td>67</td>
</tr>
<tr>
<td><strong>3 Transport with maximally localized Wannier functions: the WanT method</strong></td>
<td>73</td>
</tr>
<tr>
<td>3.1 Transport in nanostructures: the Landauer formalism</td>
<td>73</td>
</tr>
<tr>
<td>3.2 Landauer formalism using Green’s functions</td>
<td>76</td>
</tr>
<tr>
<td>3.3 The smearing issue in Green’s functions</td>
<td>82</td>
</tr>
<tr>
<td><strong>4 Applications I: Hybrid silicon–organic interfaces</strong></td>
<td>89</td>
</tr>
<tr>
<td>4.1 First–principles investigation of silicon surfaces: chemisorption of unsaturated carboxylic acids</td>
<td>90</td>
</tr>
<tr>
<td>4.2 <em>Ab initio</em> electron transport through hybrid silicon–organic interfaces</td>
<td>98</td>
</tr>
<tr>
<td><strong>5 Applications II: Semiconductor surfaces and interfaces</strong></td>
<td>107</td>
</tr>
<tr>
<td>5.1 Polarization properties of (1100) and (1120) SiC surfaces from first principles</td>
<td>108</td>
</tr>
<tr>
<td>5.2 Perspectives: electronic transport properties of SiC/AlN interfaces</td>
<td>120</td>
</tr>
<tr>
<td><strong>Conclusions</strong></td>
<td>125</td>
</tr>
<tr>
<td>Full list of publications</td>
<td>127</td>
</tr>
</tbody>
</table>
Abstract

In this thesis we face the issue of calculating electronic transport in hybrid nanostructured interfaces of semiconductors: This class of systems finds possible application in nanoelectronics, or molecular electronics.

Examples are already present in the literature of transport calculation in unrealistic single–molecule junctions, especially on metals, less frequently on semiconductors. In this work we address more realistic extended contacts, where self assembled monolayers on surfaces constitute the active element. For applications in electronics, semiconductor substrates are particularly interesting, allowing for the formation of well ordered covalently bonded layers. Using silicon, one can take advantage of its large technological employment in the existing integrated circuits industry.

We design a prototype system, constituted of an organic monolayer between two silicon surfaces, with the aim of identifying a silicon–based interface, good candidate for having efficient transport properties. Several aspects of the geometrical and electronic structure of interfaces can influence the transport behavior: We address some of them, e.g. the polarization effects, analyzing suitable test cases. In order to accurately treat the transport in truly three–dimensional systems, an appropriate development of the existing theoretical and computational tools has been necessary.

Our main results concern the individuation of a hybrid organic–silicon interface having promising transport characteristics, under proper substrate doping. We demonstrate that surface–molecule bonding strongly affects transport, finding that oxygen termination gives good transport properties for hole transfer.

The developments introduced in the calculation methodology, allow to reliably calculate transport in a new class of nanostructured interfaces, where extended contacts are realized. We plan to study transport properties of further systems as a future development of this work, exploiting the tools and the knowledge achieved up to this point.
Introduction

From micro- to nanoelectronics
The technological development of microelectronics is now approaching its ultimate limit with individual electronic devices having nanoscale dimensions.

In the last three decades the continuous miniaturization and increasing density of the components in an integrated circuit (IC) have been ruled by the Moore’s law \([1]\). This law predicts the exponential growth of the number of transistors per IC, thanks to the shrinking dimensions of the components, and it is based on the observation (originally made in 1965 and then updated in 1975) that this number doubled each couple of years, since the transistor invention. The advantage of having small dimensions stems in the possibility of storing more information on the same chip and in the reduction of the distance between adjacent components of an IC: The closer and the smaller the transistors are, the faster the device is.

The conventional silicon-based microelectronics is founded on the complementary metal–oxide semiconductor (CMOS) transistor technology which is almost mature, because its development is approaching physical, practical and economical limits. Thus the progress is not expected to keep following the Moore’s law for a longer time. The prediction is that the Moore’s trend will start soon to slow down \([2]\).

The ultimate development of microelectronics is nanoelectronics which requires a deep renewal of the current technology: The classical description of the physical phenomena breaks down when reaching the nanoscale, since quantum effects become dominant and have to be taken into account. A new generation of devices which takes advantage of these quantum mechanical effects is that of molecular devices. Molecular electronics, using organic active layers or, at the very ultimate limit, single molecules, is currently explored as a long term alternative for increasing the device density in an IC and continuing Moore’s law, down to the nanometer scale.

Molecular electronics
Molecular electronics is based on the idea that a self assembled monolayer (SAM) or a single molecule between electrodes can play the role of active element in an electronic device. Since the seminal paper by Aviram and
Ratner in the 1974 [3], where they proposed a single organic molecule as a rectifier of electrical current, several examples appeared in the literature: resonant tunneling diodes [4], molecular rectifying junctions [5], organic thin film transistors [6], molecular memory cells [7] are only a few applications that have been presented.

When dealing with molecular–scale contacts, it is fundamental to give a detailed atomistic description of the physical properties of the system: It is crucial to understand the full electronic structure and the chemical nature of the elements involved in the nanocontact. The characterization and manipulation of these structures require experimental and theoretical specific tools. A crucial step in the development of the nanophysics has been the introduction (in the eighties) of the scanning tunneling microscope (STM) and atomic force microscope (AFM) [8], which gave a strong boost to the study of nanoscience. In parallel, appropriate theoretical methods and computational schemes have been developed. The advent of large scale \textit{ab initio} simulations, based e.g. on the density functional theory (DFT) [9], allows to treat details and characteristics of the electronic structure, of the chemical bond and of the electrostatic properties.

However open issues still remained about how to accurately calculate transport in terms of conductance and current in nanoscale systems, which required the development of appropriate computational tools. The first investigations took advantage of the semiclassical theoretical methods already used to reproduce mesoscale experiments, which are based on the solution of the classical Boltzmann equation including effective mass parameters and transition rates from quantum description [10]. In particular the idea that electrical conductance is equivalent to the transmission probability for incoming waves comes from the mesoscopic physics field: This is the key concept of the Landauer approach, used in this thesis to study electronic transport. However, reaching the nanoscale limit, the atomistic description becomes essential in the electronic structure or transport calculations since, differently from the mesoscopic physics, the chemical composition and properties of the materials play an important role [11],[12].

\textit{A bottom–up technique}
Hybrid interfaces are particularly interesting for practical applications in molecular electronics: Functionalization of semiconducting or metallic substrates leads to controllable covalently bonded interfaces and may be profitably exploited for the design of stable hybrid molecular electronic devices. Grafting molecules (both organic and inorganic) allows to tailor the surface properties in a controlled way. One of the most promising ideas of nanoelectronics is to obtain desired functionalities exploiting the ability of the nanosized building blocks to self organize. The usual top–down approach, peculiar of the microelectronics fabrication technology, is thus replaced by the so called bottom–up nanotechnology [13],[14]. Photolithog-
raphy is a fundamental technology for microelectronics: It permits to pattern elementary structures on substrates, which constitute transistors and their interconnections. When reaching the nanoscale (becoming the lengths comparable with the light wavelength), more complex X-rays, electron- or ion-beam lithographic techniques would be required to directly define the structures, which are presently not exploitable for large-scale industrial production. The bottom-up functionalization of surfaces, based on the capability of self-assembling of the molecules, leads to the controlled aggregation of complex structures. Self-assembled monolayers are viewed as a possible route to control in a versatile way the interface properties through the functionalization and have been the subject of intense research in the last two decades [4, 5, 15, 16, 17].

Electronic transport in hybrid interfaces
When dealing with hybrid interfaces, the organization of the molecules on the surface is crucial to determine the transport properties of the system. Transport measures, in terms of conductance or I-V curve, usually done by means of STM microscope, are very sensitive to the interface structural properties, and also their reproducibility strongly depends on the molecule-lead contact, both in single molecule and in extended junctions: Through bond contacts allows for more reproducible measures [17, 18, 19, 20].

Not only the nature and characteristics of molecules (e.g. if they are saturated or conjugated chains [21]) are important, but the transport properties also depend on how the molecules are arranged on the surface: An example is proposed by Venkataraman et al. [22] of a biphenyl molecule between gold electrodes, where the transport is strongly affected by the relative twist angle between the two molecule rings.

The line up of molecular and electrode levels, their broadening and the charge transfer at the interface are fundamental aspects which are determining the transport properties of the system. It is thus really important to do reliable and accurate calculations of transport in such silicon-based molecular devices, having completely understood the structural and electronic properties of the chemically bonded contacts, focusing on the interface effects on the electronic structure [4, 16].

Functionalized silicon surfaces
More numerous are the examples of molecule-metal contacts, however the development of molecular electronics on semiconductors, especially on silicon, is particularly important, because the band gap can be exploited for designing a new class of resonant tunneling devices, with possible application in logic and low power memory [4, 15, 16]. The use of semiconductor rather than metallic substrates is interesting also because a better order of SAMs on the surfaces, with directionally bonded molecules, can be obtained.
Patterning organic molecules on silicon surfaces is in particular feasible: Several examples are given in the literature of well ordered organic monolayers on Si substrates [23,24,25,26]. In fact, among the possible semiconductor surfaces, silicon is largely used in applications: One of the main reasons for using Si is its straightforward technological employment in the existing industrial structures [27,28,29,30].

Most of the seminal studies on functionalized silicon surfaces deal with cleaned reconstructed [14] or oxidized surfaces [31]. However they present practical disadvantages, the former requiring expensive ultra–high vacuum techniques, the latter presenting an insulating layer between the substrate and the adsorbate [27], undesirable for many applications. Numerous recent studies address hydrogenated silicon surfaces: The hydrogen layer hinders surface oxidation and allows the use of cheap wet–chemistry techniques [32,33,16,24,34].

Aliphatic and aromatic organic molecules are the most used for grafting [13]: the choice is driven by the functionality required for the constructed interface. The former are particularly suitable for interlayer construction, while the latter have higher transport efficiency [35].

Order and packing of molecular layers strongly depend on the molecule–surface interactions, related to the surface chemistry and reaction mechanisms [23,36,37]. Si-C and Si-O-C bridges are the most commonly formed on silicon substrates and the characterization of these anchorages is a key point for understanding the functionalization process [27,23,38,39,40,41]. Both Si-C and Si-O-C bonded monolayers show promising transport properties for applications in molecular electronics, thanks to the presence (in particular in the Si-O-C case) of molecular states close to the Fermi energy, that could be involved in coupling with external electrodes [4,5].

**Electronic and transport properties in nanostructures: Theoretical scheme**

The main goal of this thesis is the theoretical investigation of the electronic and transport properties of nanostructured interfaces using a completely *ab initio* real space approach.

The calculations of fundamental electronic properties are performed by means of the density functional theory (DFT) plane wave pseudopotential method [9,42], which is widely used in solid state physics to study real materials from first principles. The use of plane waves as a basis set is particularly convenient: good results can be obtained, simply controlling the accuracy through a cutoff parameter. The number of plane waves necessary to treat the core electrons can be reduced using the pseudopotentials technique. By means of these theoretical tools, electronic properties which are important for transport are analyzed such as band structure and density of states. Significant information can be deduced about the coupling among the different components of a junction and electronic levels possibly involved in transport.
processes can be identified.

Considering the transport properties, the quantum conductance and the I-V characteristic of nanosized contacts are calculated following the Landauer approach, which relates the conduction to the scattering properties \[43\]. The system is divided into lead conductor and lead parts, where the dominant resistance term is due to the scattering at the interface contacts. The scattering properties are calculated using the Green’s functions technique \[44\].

**Maximally localized Wannier functions: a computational tool**

The use of the lattice Green’s functions calculation scheme, requires the representation on a localized basis set: The key connection between the DFT electronic structure, calculated in plane waves, and the Landauer transport is realized by transforming the delocalized Bloch orbitals into maximally localized Wannier functions (MLWFs), in the form proposed by Marzari and Vanderbilt \[15,46,47,48\].

Moreover when dealing with the above presented interfaces, with molecular layers or with the vacuum, we are considering strongly inhomogeneous systems. A spatially defined description is thus crucial: In these cases MLWFs, as a real space basis set, constitute a very useful tool for electronic structure and transport calculations, which allows to understand fundamental physical properties of the different regions that compose the system. In fact MLWFs, being localized and directly coming from the Bloch states, provide a meaningful picture of the chemical bonds and allows to better understand the local properties of the systems, such as the polarization. Polarity effects are crucial when dealing with the electronic structure of materials: The modern theory of polarization makes use of the displacement of the WF’s centers in the definition of the polarization properties of crystalline solids \[49,50,51\].

Through their centers, their extension and their shape, MLWFs, give a description of the electronic structure which is physically insightful. The electronic orbitals can be visualized and located with respect to the positions of the atoms. This concept has been applied in investigating complex crystals \[52\] and disordered solids \[53\] and liquids \[54\].

MLWFs have revealed their usefulness in many applications: examples are reported in the literature of analysis of dielectric response in insulator–insulator or insulator–metal interfaces \[55,56,57\]; studies of the response of the electronic structure to a magnetic field \[58,59\] are presented; an interpretation of photoemission shifts at semiconductor surfaces and interfaces \[60\] is proposed.

The particular properties of MLWFs have also attracted interest from a methodological point of view: This has prompted theoretical work in order to complete the characterization of these functions. A very recent work demonstrates the exponential nature of the localization in the
three–dimensional multiband case \cite{61}. Important evolutions there have been also in the algorithms used to generate MLWFs, including for example the ultrasoft pseudopotential formalism \cite{62,63}. Recent developments have extended their application in the construction of simplified Hamiltonians for multi–scale approaches, introducing purposely designed disentanglement procedures \cite{64,65}. In particular, these methodological developments found successful application in calculating transport in nanosized structures \cite{46,66,67}.

**Codes**

All the systems studied in this thesis are analyzed from an electronic and transport point of view, within the theoretical scheme above illustrated. We perform the electronic structure calculations using the DFT plane wave implementation included in the PWscf package, employing ultrasoft pseudopotentials \cite{68}. All the transport calculations are performed using WanT code which is publicly distributed within GPL licensing: The code computes the Landauer transport in terms of quantum conductance using Green’s functions on the MLWFs localized basis set \cite{69}. An original work in this thesis is my contribution to the development of the new online release of the code.

**Scheme of the thesis**

In this thesis several practical aspects entering the design of molecular devices have been thoroughly examined, using appropriate simulation tools. When the available state–of–the–art methodologies of analysis were not sufficient to reliably and feasibly solve complex problems, we have developed and set the theoretical and computational tools themselves: In particular I contributed to the inclusion of ultrasoft pseudopotentials into the Wannier functions calculation and to the extension to parallel \(k\)–points and non-Lorentzian smearing in the calculation of transport.

A thorough understanding of the fundamental electronic properties of the systems of interest is obtained by means of plane wave pseudopotential calculations within density functional theory. The DFT method and the plane wave calculation scheme for periodic systems is described in Chapter 1.

For all the electronic structure calculations, in order to make them more computationally affordable for the complex systems of interest, we employ ultrasoft pseudopotentials which allow to use a lower kinetic energy cut–off (so a smaller number of plane waves than normconserving ones) when representing the wavefunctions and the electron density. A methodological development (and the consequent numerical implementation in the WanT code) has been required to include ultrasoft pseudopotentials into the MLWFs calculation. The construction of MLWFs from projector–augmented waves or ultrasoft pseudopotentials is illustrated in Chapter 2 together with the
general Wannier function formalism and the polarization calculation scheme via Wannier functions and Berry phase.

When dealing with transport in nanostructures, one needs to address an open and non periodic system, on the other hand the description should contain the atomistic characterization of the conductor. The method that we use to investigate transport in realistic nanosized systems is illustrated in Chapter 3. To accurately treat the transport in truly three–dimensional systems, we introduced the parallel $k$–points technique, by imposing periodic boundary conditions on the plane perpendicular to the transport direction. Different smearing functions, which enters when dealing with $k$–points summations, have been consistently included in the Green’s functions expression. In Chapter 3 this technique is explained.

In order to fully characterize basic hybrid nanocontacts, a reliable description of the real nature of surfaces and a thorough understanding of functionalization mechanisms and effects on the electronic structure are needed. In Chapter 4 a first–principles investigation of chemisorption of unsaturated carboxylic acids on a silicon surface is presented as an example of application, where the chemical surface–molecule bond is accurately studied. In Sec.4.2 a prototype structure constituted of an organic(di–hydroxybiphenyl) monolayer between two silicon surfaces, where we calculate the transport in terms of quantum conductance and current, is studied in details, using the above illustrated WaN:T method.

An aspect of the electronic structure which is interesting to understand important physical properties of materials is the polarization: When dealing with a material having bulk spontaneous polarization, the surfaces can present a surface dipole or, even when they are non polar, an in–plane polarization. These properties strongly affect functionalization and growth processes, because the polarization highly influences surface relaxation and interactions with adatoms and molecules. In Chapter 5 we analyze the polarity effects induced by the surface formation and we quantitatively compare the surface components to the bulk spontaneous polarization in (1100) and (1120) 2H-SiC surfaces. The theoretical approach is based on the calculation of Wannier centers and, equivalently, on the evaluation of the Berry phase in the case of SiC bulk polytypes, as already proposed in the literature by Resta and King–Smith and Vanderbilt [49][50][51] (and extensively illustrated in Chapter 2). A second example of materials showing spontaneous bulk polarization is given, considering SiC/AlN interfaces: it is important to understand the transport properties of such heterostructures in view of possible applications in optoelectronics. A perspective of this work is to calculate the transport troughtwo different interfaces, the one in a polar direction the other in a non–polar one. The scheme of the systems is sketched in Chapter 5.
Bibliography


Introduction


Chapter 1

Electronic structure within Density Functional Theory

In this chapter we briefly introduce the density functional theory (DFT) \cite{1,2,3}. In solid state physics a reliable method to study structural and electronic properties of real materials is required: The theoretical approach here presented is one of the most commonly used in standard first principles calculations. Inorganic solids, both metals and semiconductors, are modelled as infinite periodic structures and they are as bigger (and more computationally demanding) systems as lower is their translational symmetry. The main objective of DFT is to replace the many-body electronic wavefunction with the electronic density as the basic quantity, in order to simplify the problem. A plane wave implementation of the DFT \cite{4} is, in particular, the computational tool that we use for all electronic structure calculations in this thesis and it constitutes the starting point of the theoretical method that we use (and contribute to develop) for transport properties calculations. In this chapter we will discuss an overview of the DFT theoretical ingredients and of its plane wave implementation.

1.1 Density functional theory

A solid state problem is a many-body problem, where electron–ion, electron–electron and ion–ion interactions has to be considered: The macroscopic physical quantities which we are dealing with depend on the set of all ionic and electronic coordinates. If we are dealing with $N$ ions and $n$ electrons we have to take into account $3(N + n)$ degrees of freedom: Considering the Born–Oppenheimer approximation \cite{5}, we are able to reduce the problem to two decoupled problems with $3N$ and $3n$ degrees of freedom respectively. One of the main advantage of using DFT is the replacement of the many-body electronic wavefunction with the electronic density as the basic quantity to be calculated. This is based on the Hohenberg–Kohn
What really makes this method appealing is the possibility of mapping the original interacting problem in an auxiliary non interacting one: We can calculate the exact density of the interacting system solving the Kohn–Sham equations for the non interacting one \[7\]. Up to this point the approach is exact: The first approximation will be introduced in calculating the exchange–correlation energy term of the Hamiltonian of the system.

The Born–Oppenheimer approximation

The formulation of the many–body problem is based on the determination of macroscopic physical properties (knowing the chemical species that are involved), through the solution of the eigenvalues problem for the Hamiltonian of the system. The Hamiltonian depends on all the nuclear and electronic coordinates. Considering \(n\) electrons and \(N\) ions, the eigenvalues problem has \(3(n + N)\) degree of freedom: The eigenstates represent the stationary states, while the eigenvalues are the corresponding energies.

\[
H(r, R, p, P)|\Psi\rangle = E|\Psi\rangle, \tag{1.1}
\]

where \(r, R\) are the position operators and \(p, P\) are the momentum operators of electrons and ions respectively

\[
\begin{align*}
r &= (r_1, \ldots, r_i, \ldots, r_n) \\
R &= (R_1, \ldots, R_I, \ldots, R_N) \\
p &= (p_1, \ldots, p_i, \ldots, p_n) \\
P &= (P_1, \ldots, P_I, \ldots, P_N).
\end{align*}
\]

The Hamiltonian contains kinetic and interaction terms for electrons and ions

\[
H(r, R, p, P) = T_{ion} + T_{el} + V_{ion,ion} + V_{ion,el} + V_{el,el}, \tag{1.2}
\]

where

\[
\begin{align*}
T_{ion} &= \sum_I \frac{P_I^2}{2M_I} \\
T_{el} &= \sum_i \frac{P_i^2}{2m} \\
V_{ion,ion} &= \frac{1}{2} \sum_I \sum_{J \neq I} \frac{Z_I Z_J e^2}{|R_I - R_J|} \\
V_{ion,el} &= -\sum_I \sum_i \frac{Z_I e^2}{|R_I - r_i|} \\
V_{el,el} &= \frac{1}{2} \sum_i \sum_{j \neq i} \frac{e^2}{|r_i - r_j|}.
\end{align*}
\]
1.1 Density functional theory

The solution of the problem will be in terms of eigenstates (eigenfunctions), depending on $3(n + N)$ coordinates

$$
\langle r_1, \ldots, r_n, R_1, \ldots, R_N | \Psi \rangle = \Psi(r_1, \ldots, r_n, R_1, \ldots, R_N). \quad (1.3)
$$

Real systems are constituted of a huge number of electrons and ions, so that the high complexity makes the solution of the problem unfeasible. The adiabatic Born–Oppenheimer approximation [5] allows to treat separately the electrons and the ions. This approximation is based on the observation that the masses of ions are much bigger than those of electrons: The typical ratio is

$$
\frac{m}{M_I} \simeq 10^{-3} \div 10^{-5} \quad (1.4)
$$

and it is considered zero, which is equivalent to neglect the ions kinetic contribution $T_{\text{ion}}$ in the total Hamiltonian. The meaning of this simplification is that the ions can be considered at rest during the motion of the electrons in a solid: The time scale for the electrons dynamics is much smaller than that of ions. While studying the electrons, the ionic degrees of freedom can be considered fixed and the total wavefunction can be written as the product of two functions, the one describing the ions and the other one the electrons (depending parametrically on the ionic coordinates)

$$
\Psi(r, R) = \Phi(R)\psi_R(r). \quad (1.5)
$$

The ionic wave function $\Phi(R)$ is the solution of the Schrödinger equation

$$
\left(-\sum_I \frac{\hbar^2}{2M_I} \frac{\partial^2}{\partial R_I^2} + E(R)\right) \Phi(R) = \epsilon \Phi(R). \quad (1.6)
$$

$E(R)$ is the so called Born–Oppenheimer potential energy surface, which is the ground state energy of the system when the ions are fixed in the position $R$ and can be calculated from the electronic Schrödinger equation

$$
\left(-\sum_i \frac{\hbar^2}{2m} \frac{\partial^2}{\partial r_i^2} + \frac{e^2}{2} \sum_{i\neq j} \frac{1}{|r_i - r_j|} - \sum_{iI} \frac{Z_I e^2}{|r_i - R_I|} + \frac{e^2}{2} \sum_{I\neq J} \frac{Z_I Z_J}{|R_I - R_J|}\right) \psi_{\alpha}^\alpha_R(r) = E_{\alpha}^\alpha(R)\psi_{\alpha}^\alpha_R(r), \quad (1.7)
$$

where $Z_I$ is the charge of the $I^{th}$ nucleus, $e$ and $m$ are the electronic charge and mass and $\alpha$ is an index for the electronic states. The equations (1.6) and (1.7) are written considering the factorization (1.5) and neglecting the non adiabatic terms coming from the ionic kinetic operator acting on the electronic part of the wavefunctions. The neglected terms are sufficiently small, of the order of $m/M_I$. Now, under the Born–Oppenheimer condition,
the problem to be solved is an eigenvalue problem parametrically depending on the ionic coordinates:

\[ H_{BO} |\psi_R \rangle = E_R |\psi_R \rangle. \] (1.8)

In this way it becomes possible to decouple the ionic and electronic degrees of freedom, solving two different problems of \(3N\) and \(3n\) dimensions respectively, instead of a more complex one of \(3(N + n)\) dimensions. Moreover the ionic coordinates can also be treated within a classical approach (e.g. classical molecular dynamics) \[8, 9\]. The electronic problem, however, remains a many-body problem and it is still extremely challenging. One of the most common methods to tackle the problem is based on the density functional theory (DFT).

**The Hohenberg–Kohn theorem**

The formal basis of DFT is the so-called Hohenberg–Kohn theorem \[6\]. The first Hohenberg–Kohn theorem states that "the ground state density \(n(r)\) of a bound system of interacting electrons in some external potential \(V(r)\) determines this potential uniquely" \[1\]. This means that the ground state expectation value of any physical observable of a many-electrons system is a unique functional of the ground state electron density. This theorem allows to treat the many-body problem using the electronic density as the basic quantity to be calculated instead of the far more complicated wavefunction, which is one of the main advantages of the DFT \[2\]. The second Hohenberg–Kohn theorem establishes the variational character of the total energy with respect to the density and the definition of a universal functional \(F[n(r)]\) (i.e. it is the same functional for all Coulomb systems) which has a minimum, the ground state energy, corresponding to the ground state density. \(N\) electrons within an external potential \(V_{\text{ext}}(r)\) are subjected to the Hamiltonian

\[ H = T + V_{\text{el,el}} + \sum_{i=1}^{N} V_{\text{ext}}(r_i) \] (1.9)

and the total energy can be expressed as

\[ E[n(r)] = F[n(r)] + \int V_{\text{ext}}(r)n(r) \, dr, \] (1.10)

where \(F[n(r)]\) is the universal functional containing the kinetic energy and the mutual Coulomb interaction among electrons. The total energy functional can be minimized with respect to the density within the constraint that the total particle number is conserved (it is the set of the \(N\)-representable densities):

\[ \int n(r) \, dr = N. \] (1.11)
1.1 Density functional theory

This minimization directly gives the ground state density from which, on the basis of the first Hohenberg–Kohn theorem, all the ground state physical quantities of the system can be derived. The functional \( F[n(r)] \) does not depend on the specific system nor on the number of electrons nor on the external potential: It is uniquely defined, but it is not known and a further development is needed.

The Kohn–Sham equations

The development introduced by Kohn and Sham \[7\] permits to calculate the exact density of the interacting system solving a problem for non-interacting particles subjected to a different potential. This can be done mapping the original interacting system into an auxiliary non-interacting one having the same electronic density. The main point is to determine the expression of the universal functional \( F[n(r)] \): In the case of the fictitious non-interacting system the Hohenberg–Kohn theorem remains valid and \( F[n(r)] \) corresponds to the kinetic energy of non-interacting electrons

\[
F[n(r)] = T_0[n(r)].
\] (1.12)

For the exact interacting system Kohn and Sham propose to split the functional into three parts

\[
F[n(r)] = T_0[n(r)] + E_H[n(r)] + E_{XC}[n(r)],
\] (1.13)

where

\[
E_H[n(r)] = \frac{e^2}{2} \int \frac{n(r)n(r')}{|r-r'|} drdr'
\]

is the Hartree energy which express the classical Coulomb interactions among electrons, while \( E_{XC}[n(r)] \) is the so called exchange–correlation energy which is not known \textit{a priori}. The \( E_{XC}[n(r)] \) term includes all the terms not explicitly expressed of the universal functional. We introduce the effective Kohn–Sham potential:

\[
V_{KS}(r) = V_{ext}(r) + e^2 \int \frac{n(r')}{|r-r'|} dr' + v_{XC}(r),
\] (1.14)

where

\[
v_{XC}(r) = \frac{\delta E_{XC}[n]}{\delta n(r)} + c.
\] (1.15)

Then the expression of the total energy functional for the non interacting system becomes

\[
E_0[n(r)] = T_0[n(r)] + \int V_{KS}(r)n(r)dr - \mu' \left( \int n(r)dr - N \right).
\] (1.16)
The same electron density which minimizes this total energy, also minimizes
the energy functional of the interacting system

$$
E_0[n(r)] = T_0[n(r)] + \frac{e^2}{2} \int \frac{n(r)n(r')}{|r - r'|} dr dr' + E_{XC}[n(r)] +
+ \int V_{ext}(r)n(r)dr - \mu \left( \int n(r)dr - N \right).
$$  (1.17)

The resulting effective Hamiltonian describes a non interacting system sub-
jected to the effective potential $V_{KS}$ where all the interactions among the
particles of the real system are included. The charge density can be given
in terms of the one particle wavefunction as

$$
n(r) = \sum_i f_i |\psi_i(r)|^2,
$$  (1.18)

where $i$ is the index of the single particle state and $f_i$ is the occupation
factor. The kinetic energy for the non interacting system is then written as

$$
T_0[n(r)] = -\sum_i f_i \int \psi_i^*(r) \frac{\hbar^2 \nabla^2}{2m} \psi_i(r) dr.
$$  (1.19)

Minimizing the total energy functional (1.16), with the constraint of conserva-
tion of the number of electrons, a set of Schrödinger–like equations, called
Kohn–Sham equations, is obtained:

$$
H_{KS}\psi_i(r) = \left[ -\frac{\hbar^2 \nabla^2}{2m} + V_{KS}(r) \right] \psi_i(r) = \epsilon_i \psi_i(r).
$$  (1.20)

It should be noticed that the wavefunctions used in the previous expressions
(1.19), (1.20) have no physical meaning: they represents the electronic
orbitals of the fictitious interacting system, while only being the density
calculated in (1.18) a meaningful quantity, the exact density of the real
interacting system.

The equation (1.20) is an eigenvalue equation for a non linear operator
$H_{KS}[n]$ which requires an iterative solution [1,2,4]. Starting from an initial
guess for the density, $V_{KS}$ is constructed. The eigenvalues of $H_{KS}$ and the
corresponding density are then calculated and the procedure is iteratively
repeated until the convergence on the density is achieved. This procedure
is called self–consistency.

It is worth underlining that the ground state density of the interact-
ring system calculated using this approach is in principle exact. However
the numerical solutions of real problems requires an approximation for the
exchange–correlation potential and functional. The accuracy and reliability
of the calculations depends on how $E_{XC}$ and $v_{XC}$ are described.
1.1 Density functional theory

Exchange–correlation functionals: LDA and GGA

The explicit expression of the exchange–correlation term is not known, so that an approximation is needed to make the DFT a practical tool for \textit{ab initio} calculations. The simplest approximation for the exchange–correlation term is the so called local density approximation (LDA) \cite{7,1,10,11,12}. It is based on the assumption that the exchange–correlation energy of the real system locally behaves as that of an homogeneous electron gas with the same density. The $E_{XC}$ term depends only on the local density of the system

$$E_{XC}^{LDA}[n] = \int \epsilon_{XC}^{hom}(n(r))n(r) dr,$$

where $\epsilon_{XC}^{hom}$ is the exchange–correlation energy density of the homogeneous electron gas. The exchange–correlation potential can be derived as

$$v_{XC}^{LDA}(r) = \frac{\delta E_{XC}^{LDA}[n]}{\delta n(r)} = \frac{d\epsilon_{XC}^{hom}(n)n}{dn} |_{n=n(r)}.$$ (1.22)

This approximation works well for systems having a smooth density (e.g. nearly–free–electron–like metals or intrinsic semiconductors), but it gives satisfactory results also for non homogeneous systems like atoms and molecules where the density varies quite abruptly, even if they are best treated by other many–body techniques (such as many–body perturbation theory or configuration–interaction expansions) \cite{4,3,13}. The main advantage of this approximation is that it well represents, in comparison with experiments, the structural and vibrational properties of systems: geometries are accurate (with an error $\sim 1\%$) and vibrational frequencies are exact to within 10–20\%. However this approach has the drawback of overestimating bonding energies of about 1\text{eV} (or 20\% relatively), but in some s–d bonded systems the error can be twice or three times as large \cite{14}. As a consequence LDA predicts shorter equilibrium bonds: lengths and angles are calculated with small errors for covalent, metallic and ionic systems (with an error of about 0.1 Å on the distances), while more important errors rise when dealing with weakly bonded systems (hydrogen or Van Der Waals bonds) \cite{3,13}.

In order to overcome the problems rising when using LDA, the generalized gradient approximation (GGA) was introduced \cite{10,15,16,17}. Within this approach the exchange–correlation energy is a functional not only of the density, but also of its local spatial variation

$$E_{XC}^{GGA}[n] = \int \epsilon_{XC}^{GGA}(n(r), |\nabla n(r)|)n(r) dr.$$ (1.23)

Several expression have been proposed for the GGA exchange–correlation energy density $\epsilon_{XC}^{GGA}$ \cite{18,19,20,21,16,17}. The exchange–correlation potential
in this case is written as
\[
v_{XC}^{GGA}(r) = \frac{\delta E_{XC}^{GGA}[n]}{\delta n(r)} = \left\{ \frac{\partial (E_{XC}^{GGA}[n])}{\partial n} - \nabla_r \left[ \frac{\partial (E_{XC}^{GGA}[n])}{\partial |\nabla n|} \right] \right\}_{|n=n(r)}.
\]

(1.24)

GGA approximation represents an improvement with respect to the LDA resulting in a higher dishomogeneity of the density. The errors in the calculated covalent binding energies and bond lengths are in this case reduced of a factor two \([13, 22, 23, 24, 25, 26]\), while for what concerns the Van Der Waals bonds GGA only slightly improves the approximation. The lattice parameters are also calculated in a closer agreement with the experimental data \([23]\). GGA corrects the LDA results and in general overestimates the lengths, underestimating the bonding energies \([27]\). It is well known that the Kohn–Sham gap (which has not a true physical meaning) is systematically underestimated (up to 50%) with respect to the real gap of semiconducting or insulating materials, both using LDA and GGA \([4]\): In these cases a correction (like e.g. GW \([28]\)) is necessary.

1.2 Periodic systems: the Bloch theorem

When dealing with real bulk materials the atoms are considered fixed in the equilibrium positions and the simulated structure is infinite periodically repeated. We consider the external potential \(V\) acting on the electrons which has the translational invariance:

\[
V(r + R) = V(r),
\]

(1.25)

where \(R\) is a direct lattice vector. The direct lattice \([29, 30]\) is determined by three linearly independent vectors \(a_i\):

\[
R = n_1a_1 + n_2a_2 + n_3a_3.
\]

(1.26)

In this way the unitary cell is defined, which is the periodically repeated unit of volume

\[
\Omega = |a_1 \cdot a_2 \times a_3|.
\]

(1.27)

We can also define an associated reciprocal lattice, whose vectors are written as

\[
G = m_1b_1 + m_2b_2 + m_3b_3,
\]

(1.28)

where \(b_i\) are three linearly independent vectors satisfying the relation

\[
b_i \cdot a_j = 2\pi \delta_{ij} \quad i, j = 1, 2, 3.
\]

(1.29)

The Bloch theorem states that in a periodic crystal the electronic single–particle wavefunction can be expressed in the form

\[
\psi_{nk}(r) = e^{ikr}u_{nk}(r),
\]

(1.30)
where \( \mathbf{k} \) is a reciprocal space vector, \( n \) is the band index distinguishing among states with the same \( \mathbf{k} \) and \( u_{nk}(\mathbf{r}) \) is a function having the same periodicity of the direct lattice:

\[
u_{nk}(\mathbf{r} + \mathbf{R}) = u_{nk}(\mathbf{r}). \tag{1.31}\]

The Hamiltonian of the system commutes with all the translation operators \( T_{\mathbf{R}} \) corresponding to the direct lattice vectors

\[
[H, T_{\mathbf{R}}] = 0 \quad \forall \mathbf{R}, \tag{1.32}\]

so that it is block diagonal on the basis set of the eigenvectors of those operators, i.e. the wavefunctions in the form (1.30). The \( \mathbf{k} \) vectors are defined within the first Brillouin zone (BZ), which is the volume of reciprocal space closest to the origin (\( \Gamma \)) of the lattice.

When we study a real bulk material we are considering an infinite system described by an infinite set of direct lattice vectors which are numerically impossible to handle: to this aim the Born–Von Karman periodic boundary conditions are introduced. On the basis of these conditions we can write the following relation for the wavefunction:

\[
\psi(\mathbf{r} + N_i \mathbf{a}_i) = \psi(\mathbf{r}) \quad i = 1, 2, 3, \tag{1.33}\]

where \( N_i \) are integer numbers. The real physical system is recovered at the thermodynamic limit \( N \to \infty \). In this way the \( \mathbf{k} \)-vectors result discretized and the quantities that should be integrated over the BZ are calculated as finite sums over \( \mathbf{k} \). Several special points integration techniques exist which permit to perform the reciprocal space integration over the BZ using a smaller number of \( \mathbf{k} \) vectors [31, 32]. For semiconducting or insulating materials the special points technique gives satisfactory results, while for metals a very accurate sampling of the region close to the Fermi level is required, which implies the use of a large number of \( \mathbf{k} \) vectors. In order to reduce the required number of \( \mathbf{k} \) points, keeping a good convergence, a finite smearing is introduced in the numerical integrations [4]. Increasing the number of the \( \mathbf{k} \) points and reducing the broadening of the smearing the convergence can be improved. Different expressions for the smearing function are used in standard electronic structure calculations: Gaussian, Lorentzian, Fermi–Dirac distribution, cold smearing, Methfessel–Paxton [33, 34].

### 1.3 The plane wave pseudopotential method

In order to more easily handle the Kohn–Sham problem, the wavefunctions and all the operators involved in the equations can be expanded on a basis set: The plane waves are employed in this thesis and are one of the most
commonly used basis set in \textit{ab initio} calculations \cite{3,5,8}. Using plane waves has the advantage of giving good results simply controlling the accuracy through a cut off parameter. Moreover fast Fourier transforms (FFT) can be employed, making the calculations computationally affordable. The Bloch electronic wavefunction in this representation takes the form:

\[
\psi_{nk}(r) = \frac{1}{(N\Omega)^{1/2}} \sum_{G} e^{i(k+G) \cdot r} c_{n}(k + G),
\]  

(1.34)

where \(\Omega\) is the volume of the unit cell, \(G\) are the reciprocal lattice vectors and the \(c_{n}(k + G)\) coefficients are normalized according to

\[
\sum_{G} |c_{n}(k + G)|^2 = 1.
\]  

(1.35)

Using plane waves, the FFT algorithm allows to easily go back and forth from reciprocal to direct space. The expression of the Kohn–Sham equations in reciprocal space is

\[
\sum_{G'} \left[ \frac{\hbar^2}{2m} |k + G|^2 + v_{H}(G - G') + v_{XC}(G - G') + v_{\text{ext}}(G, G') \right] c_{n}(k + G') = \epsilon_{nk} c_{n}(k + G)
\]  

(1.36)

In this representation the Hamiltonian is block diagonal in \(k\), so that the diagonalization can be separately performed on each block. The ground state charge density is calculated from a finite number of low–energy states. Starting from this density the new potential is derived and reintroduced into the Kohn–Sham equation for the subsequent step of self–consistency.

The plane wave expansion is exact in the limit of infinite number of \(G\). It is necessary to fix a cut–off criterion: only plane waves with kinetic energy obeying

\[
\frac{\hbar^2}{2m} |k + G|^2 \leq E_{\text{cut}},
\]  

(1.37)

where \(E_{\text{cut}}\) is the cut–off energy, are kept. When using plane waves, \(E_{\text{cut}}\) is the only parameter controlling the accuracy of the calculation, in contrast to localized basis set.

In order to accurately treat the core electrons localized around the nuclei a huge number of plane waves would be required, which would be computationally unaffordable. To overcome this difficulty the pseudopotential technique is introduced \cite{36,37,38}. This approach is justified by the fact that most chemical and physical properties of crystals are ruled by the valence electrons and that the core electrons do not participate in the chemical bonding but remain closely localized. These electrons are thus reasonably assumed to be frozen and keeping the same distribution in the crystal as in isolated
1.3 The plane wave pseudopotential method

Figure 1.1: All–electron and pseudo potentials and wavefunctions. The Coulomb potential \((Z/r)\) and the all–electron wavefunction are drawn with solid lines while the pseudo potential and wavefunction with dashed lines. All–electron and pseudo quantities are identical outside the cut–off radius \(r_c\).

atoms. In practice the ionic core potential is replaced by a pseudopotential which mimics the effects of the core on the valence electrons without explicitly including the core electrons. The use of the pseudopotential leads to a nodeless valence wavefunction which would have otherwise a strong nodal character (being orthogonal to the core states): This allows to reduce the number of plane waves required to represent it. The true all–electron potential is replaced by the pseudopotential within a sphere with radius \(r_c\) around the nucleus, where a nodeless pseudowavefunction \(\psi_{\text{pseudo}}\) is defined, outside which the full potential and the exact all-electron wavefunction \(\psi_V\) are identical. In Figure 1.1 are compared the all–electron and pseudo potentials and wavefunctions. In general the pseudopotential approach must satisfy the constraint that the all–electron and the pseudo wavefunctions have the same norm inside the sphere (norm conservation) to guarantee that both the wavefunctions reproduce the same electronic density outside the sphere. The construction of a pseudopotential starts from an all–electron \textit{ab initio} calculation on isolated atoms, then the innermost electrons are considered frozen in the ground–state atomic configuration, while for the external valence electrons a pseudowavefunction is built smooth and nodeless inside the core region conserving the total valence charge and matching the all–electron wavefunction outside the core radius \(r_c\).
The pseudopotential to be included within the Kohn–Sham Hamiltonian is a non local angular–momentum dependent operator splittable in a local and a non local part:

$$V(r, r') = V_{\text{loc}}(r) \delta(r - r') + \sum_{l=0}^{l_{\text{max}}} V_{\text{NL},l}(r) \delta(r - r') P_l(\hat r, \hat r'),$$

(1.38)

where $P_l$ is the projector operator onto the $l^{th}$ angular momentum subspace and the $V(r, r')$ is local with respect to the radial component $r$, while is non local with respect to the angular one (semilocal form). From a computational point of view, it is very convenient to express the pseudopotential in a fully non local and separable form: That proposed by Kleinman and Bylander is \[38\]

$$V(r, r') = V_{\text{loc}}(r) \delta(r - r') + \sum_{l=0}^{l_{\text{max}}} \sum_{m=-l}^{l} \frac{\beta_{lm}(r) \beta_{lm}^*(r')}{\langle \phi_{lm} | V_{\text{NL},l} | \phi_{ml} \rangle},$$

(1.39)

where

$$\beta_{lm}(r) = V_{\text{NL},l}(r) \phi_{lm}(r).$$

(1.40)

$\phi_{lm}(r)$ are atomic reference states. An important property of the pseudopotentials is the transferability: A good pseudopotential should be able to reproduce results with the same accuracy independently of the local chemical environment surrounding the atom. To the aim of computational feasibility the pseudopotential softness is also an important feature: The number of plane waves required to expand the pseudowavefunction should be as small as possible. For both this properties the critical parameter is the cut–off radius $R_{\text{cut}}$: Low cut–offs give good transferability, while high cut–offs make the pseudopotentials softer; An equilibrium between the two requirements has to be established.

A further development of the pseudopotential technique has been the introduction by Vanderbilt \[39\] of the ultrasoft pseudopotentials. This is particularly useful when dealing with elements with nodeless valence states (2p, 3d valence electrons) whose representation requires a large number of plane waves. Using the ultrasoft pseudopotentials the norm–conserving constraint is relaxed allowing for lower cutoff energies. A generalization of the expression (1.39) is given:

$$V(r, r') = V_{\text{loc}}(r, r') + V_{\text{NL}}(r, r')$$

(1.41)

$$V_{\text{NL}}(r, r') = \sum_{ij} D_{ij}^{(0)} \beta_i(r) \beta_j^*(r'),$$

(1.42)

where $D_{ij}^{(0)}$ are the coefficients computed in an atomic calculation and $i,j$ are multiple indices: $i \rightarrow nlm$. Within this approach the electronic density
1.3 The plane wave pseudopotential method

is written as

$$n(r) = 2\sum_{n=1}^{N/2} f_n \left[ |\psi_n(r)|^2 + \sum_I \sum_{ij} Q_{ij}^I (r - R_I) \langle \beta_I^j | \psi_n \rangle \langle \beta_I^j | \psi_n \rangle \right]. \quad (1.43)$$

The additional term in the density expression is called augmentation term and $I$ is the atomic index. The orthonormality of the eigenstates is recovered by introducing an overlap operator (depending on the ionic positions): The generalized orthonormality constraint becomes

$$\langle \psi_n | S | \psi_m \rangle = \delta_{nm} \quad (1.44)$$

where

$$S(rr') = \delta(r - r') + \sum_I \sum_{ij} q_{ij}^I (r - R_I) \beta_j^I (r' - R_I) \quad (1.45)$$

is the overlap operator and

$$q_{ij}^I = \int Q_{ij}^I (r) dr. \quad (1.46)$$

The generalized Kohn–Sham equations are written as

$$H_{KS} \psi_n(r) = \left[ -\frac{\hbar^2 \nabla^2}{2m} + V_{KS} \right] \psi_n(r) = \epsilon_n \int S(r'r') \psi_n(r') dr', \quad (1.47)$$

with

$$V_{KS} = V_{loc} + V_{NL} + V_{HXC}. \quad (1.48)$$

$V_{HXC}$ includes the Hartree and the exchange–correlation terms and $V_{NL}$ is the non local potential where the $D_{ij}^{(0)I}$ coefficients are substituted by the screened coefficients

$$D_{ij}^{I} = D_{ij}^{(0)I} + \int Q_{ij}^I (r) V_{eff}(r) dr, \quad (1.49)$$

where $V_{eff} = V_{loc} + V_{HXC}$.

The price to pay using the ultrasoft pseudopotentials is an additional complication in the Fourier representation of the Kohn–Sham equation, however this approach is extremely successful in treating large–scale electronic structure problems where reducing the computational cost becomes crucial.

Bibliography


1.3 The plane wave pseudopotential method


Chapter 2

Wannier Functions

The electronic structure of a periodic system is usually described in terms of extended Bloch orbitals, simultaneous eigenstates of the periodic Hamiltonian and of the direct lattice translations (see Chap. 1). An alternative representation in terms of localized orbitals has been introduced by Gregory Wannier in 1937 [1]. The connection between the Bloch and the Wannier representation is realized via a unitary transformation of the Bloch eigenfunctions, carrying a large degree of arbitrariness. Wannier functions (WFs) are thus non-uniquely defined and, among the possible sets, the maximally localized one [2] can be extracted.

Especially when maximally localized [1,2], WFs constitute a useful analysis tool. They have been extensively used in electronic structure calculations: WFs constitutes an orthonormal, complete and finite basis set. Moreover, being localized, they provide an insightful description of the chemical bond, whose investigation is of crucial importance in nanosized contacts.

In this chapter we describe the procedure introduced in 1997 by Marzari and Vanderbilt [2] to find the optimally localized set of WFs. We then illustrate a methodological development, including the plane augmented wave (PAW) and ultrasoft pseudopotential (USPP) formalism into the Wannier functions calculation. Finally, we consider the employment of WFs as analysis tool in the calculation of polarization properties of crystalline solids.

2.1 Maximally localized Wannier functions

A localization algorithm has been developed by Marzari and Vanderbilt [2] to obtain a set of maximally localized Wannier functions (MLWFs) from the delocalized Bloch orbitals.

In fact Wannier functions are non-uniquely defined, the arbitrariness in their definition coming from the phase present in the starting Bloch functions. A disentanglement procedure, more recently introduced [3], allows to extract a maximally connected manifold of any chosen dimension from a
given energy window, extending the original algorithm to the case of systems without gaps (e.g., metals) and overcoming the limitation to isolated groups of bands.

### Wannier functions for isolated groups of bands

The Bloch orbitals \( \psi_{nk}(r) \) of the examined system are labeled via their band \( n \) and \( k \) vector quantum numbers, as illustrated in Chap. 1:

\[
\psi_{nk}(r) = e^{ik \cdot r} u_{nk}(r). \tag{2.1}
\]

The representation in terms of Wannier functions (WFs), \( |R_n\rangle \), can be derived through a unitary transformation of the Bloch orbitals. Considering a single band, the transformation from Bloch to Wannier functions and the inverse are given by

\[
|R_n\rangle = \frac{V}{(2\pi)^3} \int_{BZ} dk e^{i\phi_n(k)} e^{-i k \cdot R} |\psi_{nk}\rangle, \tag{2.2}
\]

\[
|\psi_{nk}\rangle = \sum_R e^{+i k \cdot R} |R_n\rangle, \tag{2.3}
\]

where \( V \) is the volume of the primitive cell and the integration is performed over the Brillouin zone (BZ). It is easy to show that WFs form an orthonormal set and that the arbitrariness due to the phase \( \phi_n(k) \) present in the Bloch functions remains, making the resulting WFs set non-unique.

A Bloch band is said to be isolated if it is not degenerate with any other band in the Brillouin zone. By analogy, a group of bands is said to form an isolated group if they present degeneracies among themselves, but are isolated from all other bands. Taking into account an isolated group of \( N \) Bloch orbitals instead of a single band, there is additional freedom linked to the choice of a full unitary matrix: The most general WF expression becomes

\[
|R_n\rangle = \frac{V}{(2\pi)^3} \int_{BZ} dk \sum_{m=1}^N e^{-i k \cdot R} U_{mn}^{(k)} |\psi_{mk}\rangle, \tag{2.4}
\]

where \( U_{mn}^{(k)} \) is a generic set of unitary matrices of dimension \( N \) which is non-uniquely defined. The \( U_{mn}^{(k)} \) introduce additional degrees of freedom in the problem. The aim of Marzari and Vanderbilt is to pick out, among the equivalent WFs sets, that which is maximally localized.

### Spread functional

In order to give a measurement of the localization of the Wannier functions, Marzari and Vanderbilt [2] defined a spread functional:

\[
\Omega = \sum_n [(r^2)_n - \bar{r}_n^2], \tag{2.5}
\]
where

\[ \langle r^2 \rangle_n = \langle 0n| r^2 |0n \rangle, \tag{2.6} \]
\[ \bar{r}_n^2 = \langle 0n| r |0n \rangle. \tag{2.7} \]

This functional can be minimized with respect to the unitary transformation \( U_{mn}^{(k)} \), thus leading to the set of MLWFs. We can express the gradient \( \frac{d\Omega}{dW} \) of this functional with respect to an infinitesimal unitary rotation of the Bloch orbitals

\[ |u_{nk} \rangle \rightarrow |u_{nk} \rangle + \sum_{m} dW_{mn}^{(k)} |u_{mn} \rangle, \tag{2.8} \]

where \( dW \) is an infinitesimal antiunitary matrix \( dW^\dagger = -dW \), such that

\[ U_{mn}^{(k)} = \delta_{mn} + dW_{mn}^{(k)}. \tag{2.9} \]

The unitary matrices evolve following this equation until the minimum of \( \Omega \) is reached: e.g. in the steepest–descent approach small finite steps, in the direction opposite to the gradient, cause the reduction of \( \Omega \) until the minimization is completed. The unitary matrices are then used to construct the maximally localized Wannier functions.

It could be easily demonstrated that the spread functional can be decomposed into three contributions: Invariant, diagonal and off–diagonal terms respectively:

\[ \Omega = \Omega_I + \tilde{\Omega} = \Omega_I + \Omega_D + \Omega_{OD}, \tag{2.10} \]

where \( \Omega_I, \tilde{\Omega}, \Omega_D \) and \( \Omega_{OD} \) are

\[ \Omega_I = \sum_n \left[ \langle 0n| r^2 |0n \rangle - \sum_{Rm} |\langle Rm| r |0n \rangle|^2 \right] \tag{2.11} \]
\[ \tilde{\Omega} = \sum_n \sum_{Rm \neq 0_n} |\langle Rm| r |0n \rangle|^2 \tag{2.12} \]
\[ \Omega_D = \sum_n \sum_{R \neq 0} |\langle Rn| r |0n \rangle|^2 \tag{2.13} \]
\[ \Omega_{OD} = \sum_{m \neq n} \sum_{R} |\langle Rm| r |0n \rangle|^2. \tag{2.14} \]

It can be shown that all these quantities are positive definite (Ref. 2) and \( \Omega_I \) is gauge–invariant, i.e. it is invariant with respect to the choice of the unitary transformation \( U_{mn}^{(k)} \). The minimization procedure is thus applied to the \( \Omega = \Omega_D + \Omega_{OD} \) contribution only. When reaching the minimum, the terms \(|\langle Rm| r |0n \rangle|^2\) realize the best compromise in the simultaneous localization of the three components corresponding to the \( x, y \) and \( z \) directions.
Considering the expression of the Bloch functions (2.1), the matrix elements of the position operator between Wannier functions take the form

$$\langle R_n | r | 0m \rangle = \frac{i V}{(2\pi)^3} \int_{BZ} dk e^{i k \cdot R} \langle u_{nk} | \nabla_k | u_{mk} \rangle$$

(2.15)

and

$$\langle R_n | r^2 | 0m \rangle = -\frac{V}{(2\pi)^3} \int_{BZ} dk e^{i k \cdot R} \langle u_{nk} | \nabla_k^2 | u_{mk} \rangle.$$  

(2.16)

Deriving the expression for $\Omega$, $\Omega_I$ and $\tilde{\Omega}$ in terms of a discretized $k$–space mesh, we make the substitution

$$\frac{V}{(2\pi)^3} \int dk \rightarrow \frac{1}{N} \sum_k,$$

(2.17)

where $N$ is the number of real–space cells in the system or, equivalently, the number of $k$–points in the Brillouin zone. Assuming the BZ discretized into a regular mesh, if $f(k)$ is a smooth function of $k$, a finite–difference expression for its gradient can be written as

$$\nabla f(k) = \sum_b w_b [f(k + b) - f(k)],$$

(2.18)

where $b$ is the vector connecting a $k$–point to one of its nearest neighbors, $w_b$ is an appropriate weight associated with each shell $|b| = b$. The following condition has to be satisfied

$$\sum_b w_b a_\beta = \delta_{a\beta}.$$  

(2.19)

We can moreover define

$$|\nabla f(k)|^2 = \sum_b w_b [f(k + b) - f(k)]^2.$$  

(2.20)

Using these finite–difference expressions for $\nabla_k$ and $\nabla_k^2$, the matrix elements between Bloch orbitals at nearest neighbor $k$–points entering equations (2.15) and (2.16) can be calculated starting from the matrix elements

$$M_{m,n}^{k,b} = \langle u_{mk} | u_{n,k+b} \rangle = \langle \psi_{mk} | e^{-ib \cdot r} | \psi_{n,k+b} \rangle.$$  

(2.21)

On the basis of this definition, the terms of the spread functional can be derived as

$$\tilde{r}_n = -\frac{1}{N} \sum_{k,b} w_b \text{Im} \ln M_{mn}^{k,b}$$

(2.22)

and

$$\langle r^2 \rangle_n = \frac{1}{N} \sum_{k,b} w_b \left[ \left( 1 - |M_{mn}^{k,b}|^2 \right) + \left( \text{Im} \ln M_{mn}^{k,b} \right)^2 \right].$$  

(2.23)
2.1 Maximally localized Wannier functions

For further details on the complete derivation of these expressions we refer to ref. [2]. The terms of the spread functional $\Omega$ thus are written as:

$$\Omega_I = \frac{1}{N} \sum_{k,b} w_b \left( N_{\text{bands}} - \sum_{mn} |M_{mn}^{(k,b)}|^2 \right),$$ (2.24)

$$\Omega_{OD} = \frac{1}{N} \sum_{k,b} w_b \sum_{m \neq n} |M_{mn}^{(k,b)}|^2,$$ (2.25)

$$\Omega_D = \frac{1}{N} \sum_{k,b} w_b \sum_{n} \left( -\text{Im} \ln M_{nn}^{(k,b)} - b \cdot \bar{r}_n \right)^2.$$ (2.26)

The localization procedure is applied, calculating the change in the spread functional pieces due to an infinitesimal unitary transformation of the Bloch orbitals as a function of $M_{mn}^{(k,b)}$: The $U_{mn}^{(k,b)}$ (and consequently the $M_{mn}^{(k,b)}$) are then iteratively updated until the minimum of $\Omega$ is reached.

**Localization procedure**

We consider an infinitesimal gauge transformation $U_{mn}^{(k,b)} = \delta_{mn} + dW_{mn}^{(k,b)}$, where $dW$ is an infinitesimal antihermitean matrix, so that $|u_{nk} \rangle \rightarrow \sum_m dW_{mn}^{(k,b)} |u_{mk} \rangle$. The convention

$$\left( \frac{d\Omega}{dW} \right)_{nm} = \frac{d\Omega}{dW_{mn}}$$ (2.27)

will be used. We introduce the superoperators $A$ and $S$ defined as $A[B] = (B - B^\dagger)/2$ and $S[B] = (B + B^\dagger)/2i$. Considering

$$q_{mn}^{(k,b)} = \text{Im} \ln M_{mn}^{(k,b)} + b \cdot \bar{r}_n,$$ (2.28)

$$R_{mn}^{(k,b)} = M_{mn}^{(k,b)} M_{mn}^{(k,b)*},$$ (2.29)

$$\tilde{R}_{mn}^{(k,b)} = \frac{M_{mn}^{(k,b)}}{M_{nn}^{(k,b)}},$$ (2.30)

$$T_{mn}^{(k,b)} = \frac{q_{mn}^{(k,b)}}{M_{nn}^{(k,b)}},$$ (2.31)

we get the explicit expression for the gradient of the spread functional (see [2] for the details):

$$G^{(k)} = \frac{d\Omega}{dW^{(k)}} = 4 \sum_b w_b (A[R^{(k,b)}] - S[T^{(k,b)}]).$$ (2.32)

The condition which should be satisfied to minimize the spread is that the above expression vanishes.

Several minimization algorithms exist and the more efficient strategy is chosen depending on the treated problem. Since we have the expression of
46 Wannier Functions

the spread Ω and of its gradient \( G^{(k)} \), we can use, for example, the stepepest–
descent or the conjugate–gradient schemes, the latter especially useful when
dealing with large systems or very fine \( k \)-points meshes. Focusing on the
steepest–descent algorithm, small updates of the unitary matrices are made
as:

\[
dW^{(k)} = \epsilon G^{(k)},
\]

(2.33)

where \( \epsilon \) is a positive infinitesimal. To the first order in \( \epsilon \), we have

\[
d\Omega = \sum_k tr[G^{(k)}dW^{(k)}] = -\epsilon \sum_k ||G^k||^2.
\]

(2.34)

The advantage of using this approach resides in the fact that the convergence
path to the minimum requires only the updating of the unitary matrices and
not of the wavefunctions.

A reference set of Bloch orbitals is chosen, then the overlap matrix ele-
ments are calculated as

\[
M^{(0)}_{mn}(k,b) = \langle u^{(0)}_m(k) | u^{(0)}_n, k+b \rangle.
\]

(2.35)

The \( |u_{nk}\rangle \) (and consequently the Wannier functions) are then represented
as

\[
|u_{nk}\rangle = \sum_m U^{(k)}_{mn} |u^{(0)}_m\rangle.
\]

(2.36)

\( U^{(k)}_{mn} \) is initialized to \( \delta_{mn} \), then at each step of the steepest–descent procedure
\( \Delta W \) is calculated for a small step in the direction opposite to the gradient
and the unitary matrices are updated following

\[
U^{(k)} \rightarrow U^{(k)} \exp[\Delta W^{(k)}],
\]

(2.37)

then a new set of \( M \) matrices is computed

\[
M^{(k,b)} = U^{(k)+} M^{(0)}(k,b) U^{(k+b)}.
\]

(2.38)

The procedure is repeated until convergence is obtained. To start the min-
imization procedure, it is necessary to choose an initial guess for the \( U^{(k)} \):
This is done by projecting the Bloch states onto localized states which re-
semble to the required Wannier functions.

**Entangled bands and disentanglement procedure**

In many cases of interest the considered group of bands is not isolated from
other bands: This is the case when dealing with metals or with the empty
bands of insulators. In this situation solving the localization problem be-
comes more complex: It is first necessary to introduce a procedure which allows to separate the selected group of bands from the whole electronic
structure.
2.1 Maximally localized Wannier functions

The $\Omega_I$ part of the spread functional $\Omega$ (2.5) can be interpreted as a measure of the $k$–space dispersion of the band–projector operator. Based on this, Souza et al. [3] proposed the so–called disentanglement procedure to solve the problem of entangled bands. This procedure is in two steps: The first one is the minimization of the gauge–invariant spread $\Omega_I$. An energy window which includes $N$ bands of interest is taken. For each $k$–point, $N_k$ bands fall in the energy window, with $N_k \geq N$. In this way an $N_k$–dimensional Hilbert space $\mathcal{F}(k)$, spanned by the states $\psi_n$ in the window, is defined. If $N_k > N$, an $N$–dimensional subspace $\mathcal{S}(k) \subseteq \mathcal{F}(k)$ has to be found that minimizes the spread component $\Omega_I$ as a functional of $\mathcal{S}(k)$. The second step of this method consists in minimizing the term $\tilde{\Omega}$ using the algorithm of Marzari and Vanderbilt [2] within the subspaces $\mathcal{S}(k)$ optimized in the first step.

Referring to equations (2.11), (2.15) and (2.16) it is evident that $\Omega_I$ is small if the term $|\langle u_{n_k} | u_{m,k+b} \rangle|^2$ is large. This condition corresponds to self–consistently choose, at each $k$–point, the subspace $\mathcal{S}(k)$ that has minimum ”spillage” or mismatch with the neighbor subspaces. The expression for $\Omega_I$ that we use is

$$\Omega_I = \frac{1}{N_{kp}} \sum_{k,b} w_b T_{k,b}, \quad (2.39)$$

with

$$T_{k,b} = N - \sum_{mn} |M_{mn}^{(k,b)}|^2 = \text{Tr}[\hat{P}_k \hat{Q}_{k+b}], \quad (2.40)$$

where $\hat{P}_k = \sum_n |u_{n_k}\rangle\langle u_{n_k}|$ is the projector onto $\mathcal{S}(k)$, $\hat{Q}_k = 1 - \hat{P}_k$ and $N$ is the number of WFs. $T_{k,b}$ is the so–called ”spillage” between the subspaces $\mathcal{S}(k)$ and $\mathcal{S}(k+b)$, that measures the mismatch between them, which has to be minimized to find the best working subspace.

This problem has to be solved self–consistently spanning the whole Brillouin zone. The stationary condition to be satisfied is $d\Omega_I(u_{n_k}) = 0$, with the orthonormality constraint, which is equivalent to solve an eigenvalues problem:

$$\sum_{b} w_b \hat{P}_{k+b} |u_{n_k}\rangle = \lambda_{n_k} |u_{n_k}\rangle. \quad (2.41)$$

For each $k$–point, we set $N$ orthonormal states $u_{n_k}^{(i)}$ (at the $i$–th iteration step) defining a subspace $\mathcal{S}^{(i)}(k) \subseteq \mathcal{F}(k)$ such that the mismatch with the neighboring subspaces $\mathcal{S}^{(i-1)}(k+b)$ is minimal. At each iteration step the following set of equation has to be solved:

$$\sum_{b} w_b \hat{P}_{k+b}^{(i-1)} |u_{n_k}^{(i)}\rangle = \lambda_{n_k}^{(i)} |u_{n_k}^{(i)}\rangle. \quad (2.42)$$

The convergence is achieved when at all $k$–points $\mathcal{S}^{(i)}(k) = \mathcal{S}^{(i-1)}(k)$. To start the iterative procedure an initial guess for the subspaces $\mathcal{S}(k)$ should
be fixed. A set of \( N \) localized orbitals are chosen as starting WFs which are then projected onto the \( N_k \) Bloch states inside the energy window, exactly as we proceed for the minimization of \( \tilde{\Omega} \) illustrated above.

After the completion of the first step, the optimal \( N \)-dimensional subspace \( S(k) \) for each \( k \)-point is determined: Then the minimization of the \( \Omega \) component of the spread is performed following Marzari and Vanderbilt \cite{Marzari2012} recipe. The final aim of the procedure is to globally minimize \( \Omega \) to obtain the best localization of the WFs: \( \Omega_I \), even if gauge–invariant, depends on the choice of the \( N \)-dimensional subspaces, where the term \( \tilde{\Omega} \) will be subsequently minimized. The two–step method is in principle different from minimizing the total spread \( \Omega \), but very similar results are expected in practice.

### 2.2 MLWF from PAW or ultrasoft pseudopotentials

A development and improvement in maximally localized Wannier functions implementation has been introduced, constructing them from projector–augmented plane waves (PAW) or ultrasoft pseudopotentials (USPP). MLWFs has been originally implemented within a norm–conserving pseudopotential (NCPP) framework \cite{Marzari1997}, but the norm conservation is a very strong constraint which may require a large number of plane waves (PW) to represent the wavefunctions. Some chemical species (like e.g. first–row elements and especially transition metals) are difficult to be treated, implying a strong computational effort.

Within the USPP framework proposed by Vanderbilt \cite{Vanderbilt1990} the norm conservation constraint is relaxed so that the required kinetic energy cut–off is drastically reduced. The price to pay is the increase of the complexity of the formalism: An augmentation term has to be added to the calculation of the matrix elements of interest. In parallel, Blöchl has developed the more general PAW method \cite{Blochl1994} which includes both pseudopotentials and augmented bases. USPP can be regarded as a special case of the PAW framework, introducing further approximations.

We extend the original Marzari–Vanderbilt \cite{Marzari2012} localization procedure to the PAW (or USPP) case. In this way we are able to derive MLWFs starting from Bloch states calculated through USPP techniques.

The PAW formalism is based on the definition of two sets of wavelets, the one with all–electron (AE) functions, the other with smoother functions easily representable in plane waves: The two sets are mapped one into each other. In order to solve the quantum problem in the soft pseudostates representation it is necessary to augment the Hamiltonian of the system: Additional terms are introduced in the calculation of the physical quantities of interest, which have exactly the same role as that of the pseudopotentials.
in standard PW calculations. Considering the USPP, the advantage of the ultrasoftness consists in the increase of their portability and in the reduction of the cut–off energy required for PW calculations (see Chapter 1). While the PAW method is in principle an exact AE (frozen–core) approach, the USPP method adopts a further approximation, representing the requirement of pseudizing the augmentation densities.

When treating the MLWFs, the augmentation terms are included in the calculation of overlap matrix elements $M_{mn}^{(k,b)}$ (see section 2.1). The idea of calculating MLWFs within USPP has already been proposed in the literature \cite{6,7,8}: in \cite{6} Vanderbilt and King–Smith extend the calculation of the spontaneous polarization through the Berry phase to the USPP procedure. Bernasconi and Madden \cite{7} derive the formalism for MLWFs with USPP for $\Gamma$–sampled supercells. Following them, Thygesen and co–workers \cite{9} have recently derived an expression for overlap matrices within USPP for periodic systems, again considering a $\Gamma$–only supercell. Our treatment is in terms of the PAW theory and overcomes the previous ones, because it is also valid in the case of a uniform $k$–points mesh defined on the Brillouin zone (BZ). This allows us to calculate MLWFs for periodic systems, like e.g. crystals, surfaces and interfaces, describing the full BZ and not only for molecular, finite or amorphous systems.

The details of the formalism are reported in the paper that follows, where the results on some test problems (electronic structure of fcc copper, dipole moments of Watson–Crick DNA base pairs and spontaneous polarization of wurtzite AlN) demonstrates how the USPP formalism works with respect to the standard NCPP one.
Maximally localized Wannier functions from PAW or ultrasoft pseudopotentials

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Abstract. We report a theoretical scheme that enables the calculation of maximally localized Wannier functions in the formalism of projector-augmented-waves (PAW) which also includes the ultrasoft-pseudopotential (USPP) approach. We give a description of the basic underlying formalism and explicitly write all the required matrix elements from the common ingredients of the PAW/USPP theory. We report an implementation of the method in a form suitable to accept the input electronic structure from USPP plane-wave DFT simulations. We apply the method to the calculation of Wannier functions, dipole moments and spontaneous polarizations in a range of test cases. Comparison with norm-conserving pseudopotentials is reported as a benchmark.

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1. Introduction

Wannier functions (WFs) can be obtained by a unitary transformation of the extended wavefunctions of a periodic system [1, 2]. So far, the effective circulation/application of WFs in electronic structure calculations was hindered by their intrinsic non-uniqueness [1, 2]. The related degrees of freedom can be chosen, e.g., making use of the symmetry properties of the system, as proposed by [3] and lately by [4, 5]. In 1997 Marzari and Vanderbilt proposed a further approach [6, 7] to exploit the non-uniqueness: the proposed methodology allows one to extract, from a selected manifold of bands, the set of WFs with the maximum spatial localization, i.e. the maximally localized Wannier functions (MLWFs). On one hand, MLWFs are attractive because they constitute a complete and orthonormal basis set with real-space localization. On the other hand, with respect to other numerical real-space bases, they carry also the physical information of the starting Bloch functions. Indeed, MLWFs may yield the chemical view of molecular bond orbitals, and they can be exploited for the computation of the spontaneous polarization in periodic systems [8, 9, 10], becoming very popular to tackle these issues in advanced materials [11, 12, 13]. In addition, MLWFs have most recently been proposed to calculate the transport properties of nano-size conductors connected to external electrodes [14, 15, 16, 17, 18].

The calculation of MLWFs was originally implemented [6] for a projection from Bloch orbitals expanded on a plane-wave basis set in Density Functional Theory (DFT) calculations, within the norm-conserving pseudopotential (NCPP) framework.
Norm-conserving pseudopotentials [19, 20], that allow to neglect core electrons in the evaluation of physical observables, are usually characterized by a high transferability of an element to a variety of chemical environments. However, the norm conservation in the core region is a strong constraint, that affects the computational effort of the DFT calculations. As a consequence, some chemical species, such as first-row elements (e.g. C, N, O, F) and especially transition metals (e.g. Mn, Fe, Co, Ni, Cu) and rare earths (e.g. La, Gd, Yb), do require an extremely high number of basis functions (e.g. plane waves), in order to be described with a satisfactory accuracy. Unfortunately, the typical systems of interest in nanoscience and specifically in molecular electronics contain atoms of those critical species.

A first attempt to solve this problem within the pseudopotential framework is the use of ultrasoft pseudopotentials (USPPs) [21]. The norm conservation constraint is relaxed, allowing for a drastic reduction of the plane-waves kinetic-energy cutoff. The price of this reduction is an increase of the complexity of the formalism; further augmentation terms [21] must be added for the computation of relevant matrix elements, in order to correct the wrong normalization of the wavefunctions. In parallel, the theory of projector-augmented waves (PAW) [22] offers an alternative more general framework including both pseudopotentials and augmented bases (like e.g. LAPW). Indeed, it has been demonstrated [22, 23, 24] that the USPP procedure may be mapped into the PAW theory and we refer the reader to the original papers for further details.

We therefore extended the original Marzari-Vanderbilt [6] approach for MLWFs to the PAW scheme. This allows us on one hand to extend this technique to a larger electronic-structure community, and on the other hand to compute MLWFs from USPP Bloch functions as a direct application of the general theory.

The paper is organized as follows: in section 2 we first write down the salient quantities that enter the computation of the WFs, then we show the formal equivalence between PAW and USPP theories and express the MLWFs within such theories in a general framework; in Section 3 we report the results of the application of our method to several test cases, that explore both the chemical bonding and the electrical polarization in the pertinent cases; finally we draw our conclusions in section 4.

2. Formalism

2.1. Maximally localized Wannier functions

In this section we give a brief introduction to the theory of maximally localized Wannier functions. A more detailed description can be found in the original papers [6, 7]. In the case of an isolated band, Wannier functions can be defined [1, 2] as a combination of the Bloch orbitals $|\psi_k\rangle$ corresponding to different $k$-points as follows:

$$|w_R\rangle = \frac{V}{(2\pi)^3} \int_{BZ} dk \ e^{-ik\cdot R} e^{i\phi_k} |\psi_k\rangle \quad (1)$$

where $e^{i\phi_k}$ is a $k$-dependent phase factor. This definition has been generalized [6] to a group of bands leading to the expression:

$$|w_{R,m}\rangle = \frac{V}{(2\pi)^3} \int_{BZ} dk \ e^{-ik\cdot R} \sum_n U_{nm}^k |\psi_{kn}\rangle \quad (2)$$

Here the extra degrees of freedom related to the phases of the Bloch eigenstates are collected in the unitary matrix $U^k$. In the one-band case it has been demonstrated...
that a suitable choice of the phases $e^{i\phi_k}$ leads to WFs which are real and exponentially
decaying in a real space representation [2]. In the many-band case [25] this theorem
does not hold anymore but the arbitrariness in the unitary (gauge) transformation $U^k$
can be exploited. Following Marzari and Vanderbilt [6] we define a spread functional
$\Omega$, which gives a measure of the degree of localization of the WF set. It reads:

$$\Omega \left[ \{ U^k \} \right] = \sum_n \left[ \langle \hat{r}^2 \rangle_n - \langle \hat{r} \rangle_n^2 \right], \quad (3)$$

where $\langle \cdot \rangle_n$ is the expectation value of a given operator on the $n$-th WF calculated
using the $U^k$ gauge transformation. It is therefore possible to define the maximally
localized Wannier functions (MLWFs) as the WFs resulting from (2) by means of the
unitary transformation $\{ U^k \}$ that minimizes the spread functional. The $\{ U^k \}$ matrices
can be computed by the direct application of standard minimization algorithms (e.g.
steepest-descent or conjugate-gradient approach) on the functional $\Omega \left[ \{ U^k \} \right]$. The
related details have been fully discussed elsewhere [6].

According to the formal analysis of the $\langle \hat{r} \rangle_n$ and $\langle \hat{r}^2 \rangle_n$ terms given by Blount [26,
6], it is possible to demonstrate that the dependence of $\Omega$ on the gauge transformation
is determined only by the so-called overlap integrals $M_{m,n}^{k,k'}$:

$$M_{m,n}^{k,k'} = \langle \psi_{k,m} | e^{-ib\cdot \hat{r}} \psi_{k+b,n} \rangle$$

$$= \int_{\text{Crystal}} dr \ u_{k,m}^* (r) u_{k+b,n} (r), \quad (4)$$

$u_{k,m} (r)$ being the periodic part of the Bloch states $\psi_{k,m} (r) = e^{i\mathbf{k} \cdot r} u_{k,m} (r)$. Here we
deal with a regularly discretized mesh of $\mathbf{k}$-points, where the $\mathbf{b}$-vectors connect nearest-
neighbour $\mathbf{k}$-points. The detailed form of the position expectation values and of the
spread functional (including its gradient wrt to $U^k$) in terms of the overlap integrals
is reported in Appendix A. Since the representation of Bloch eigenstates enters only
the calculation of the $M_{m,n}^{k,k'}$ integrals, these quantities are the main objects to deal
with when using a USPP or PAW formalism. The detailed treatment is reported in
section 2.3.

2.2. PAW and ultra-soft pseudopotentials

The PAW formalism has been introduced by Blöchl [27, 28, 22] and it has also been demonstrated [24] that the Vanderbilt ultra-soft pseudopotential (USPP)
theory [21, 29, 30, 23, 31] can be obtained within the PAW approach with some
further approximations.

Blöchl’s starting point is to partition the volume of the system by setting spherical
regions (atomic spheres) around each atom. In each sphere two complete sets of
wavelets [32] ({$|\phi_i^{ae} \rangle$} and {$|\phi_i^{ps} \rangle$}) localized in the sphere are defined. While the
former, when truncated, is intended to work with all-electron (AE) functions, the latter
should be smoother and easily representable in plane waves. It is therefore possible
to introduce a well defined linear operator mapping one-to-one AE-like functions into
smoother pseudo (PS) functions and vice versa:

$$|\psi^{ae} \rangle = \hat{T} |\psi^{ps} \rangle,$$ 

where

$$\hat{T} = \mathbb{I} + \sum_{l,i} (|\phi_i^{ae} \rangle - |\phi_i^{ps} \rangle) (\beta_l |).$$ 

(6)
The index $I$ runs over different atoms (e.g. different atomic spheres), while $\langle \beta_{I_i} \rangle$ are the projectors [33] related to the pseudo wavelets $|\phi_{I_i}^{ps}\rangle$. The $\hat{T}$ operator acts on the pseudized functions to reconstruct [23] the AE ones.

Matrix elements and expectation values of a generic operator $\hat{A}$ on the physical AE states can be written as:

$$A_{mn} = \langle \psi^m_n | \hat{A} | \psi^m_n \rangle = \langle \psi^m_n | \hat{T} \hat{T}^\dagger \hat{A} | \psi^m_n \rangle.$$ \hfill (7)

One of the main results of [22] is the explicit expression for $\hat{A}^{ps}$, which we report here for the case of local and semilocal operators:

$$\hat{A}^{ps} = \hat{A} + \hat{A}^{aug},$$ \hfill (8)

$$\hat{A}^{aug} = \sum_{I,ij} (\phi_{I_i}^{r} | \hat{A} | \phi_{I_j}^{r}) - (\phi_{I_i}^{r} | \hat{A} | \phi_{I_j}^{r}) \langle \beta_{I_i} \rangle \langle \beta_{I_j} \rangle.$$ The second term $(\hat{A}^{aug})$ in the rhs of (8) takes into account the corrections due to the use of the pseudo functions instead of the AE ones, and from here on it will be called augmentation term. At this point it is useful to define the quantities $Q_{I_j}^r(r)$ and $q_{ij}^f$ (augmentation densities and charges respectively) as:

$$Q_{I_j}^r(r) = \phi_{I_j}^{r} \ast (r) \phi_{I_j}^{r} \ast (r) - \phi_{I_j}^{r} \ast (r) \phi_{I_j}^{r} \ast (r),$$ \hfill (9)

$$q_{ij}^f = \int dr Q_{I_j}^r(r).$$ \hfill (10)

Within these definitions, (8) for local operators $A(r)$ can be recast in a more convenient form:

$$\hat{A}^{aug} = \sum_{I,ij} \left[ \int dr Q_{I_j}^r(r) A(r) \right] \langle \beta_{I_i} \rangle \langle \beta_{I_j} \rangle.$$ \hfill (11)

Setting $\hat{A}$ to the identity in (8,11), scalar products are given by $\langle \psi^m_n | \hat{S} | \psi^m_n \rangle$ where the number operator [34] $\hat{S}$ (that characterizes also the USPP formalism) is given by:

$$\hat{S} = \hat{T}^\dagger \hat{T} = \mathbb{1} + \sum_{I,ij} \langle \beta_{I_i} \rangle q_{ij}^f \langle \beta_{I_j} \rangle.$$ \hfill (12)

In the same way, by setting $A(r') = e \delta(r' - r)$ we obtain an expression for the density:

$$n(r) = n^{ps}(r) + n^{aug}(r),$$ \hfill (13)

$$n^{aug}(r) = \frac{2e}{N_k} \sum_{mk} \sum_{I,ij} \langle \psi^m_{k,m} | \beta_{I_i} \rangle Q_{I_j}^r(\beta_{I_j} | \psi^m_{k,m} \rangle,$$

where $n^{ps}(r)$ is the density contribution of the pseudo wavefunctions. Since we are able to express all the quantities of interest in terms of the soft pseudo-states, the quantum problem can be solved directly in this representation. In order to do this, it is necessary to augment the Hamiltonian operator: the procedure leads to additional terms which have exactly the same role as that of the pseudopotentials in standard PW calculations. The inclusion of augmented elements will affect therefore also the procedure for MLWF calculation (see below).

Moving to the USPP framework, the generalization introduced by Vanderbilt [21] is twofold. (i) More than one projector per angular momentum channel can be taken into account: the inclusion of multiple projectors per channel enlarges the energy range [27, 21] over which logarithmic derivatives are comparable with the full potential case, thus increasing the overall portability of the pseudopotential. (ii) By
Maximally localized Wannier functions from PAW or ultrasoft pseudopotentials

relaxing the norm-conservation constraint of the pseudo reference-states, the pseudo wavefunctions are smoothened; thus, the required cutoff energy for PW representation can be drastically lowered. The fact that properties (i) and (ii) are verified for the PAW wavelets \( \phi_i \) establishes the connection between the PAW and USPP methods. In fact, (i) is naturally valid for the wavelets \( \phi_i^{ae} \), because these form a basis set, and therefore have in principle an infinite number of states for each angular momentum channel. (ii) is valid as well, and the possibility of non norm-conservation in passing from \( |\phi_i^{ae}\rangle \) to \( |\phi_i^{ps}\rangle \) is accounted by non-zero \( q_{ij}^l \) terms in (9,10). Consequently, the PAW theory for wavefunction reconstruction can be basically adopted also in the case of USPP [28, 24].

While the PAW method is in principle an exact AE (frozen-core) approach [35], the USPP method adopts a further approximation [24, 36] represented by the requirement of pseudizing the augmentation densities \( Q_{ij}^l(r) \) [(9)]. Since these terms contain the AE reference states, they are not simply writable on a PW basis: the USPP pseudization is done to make them suitable for a PW representation. This also means that the total density from (13) would be PW representable within such an approach. Even though the augmentation densities are pseudized, they must capture some features of the physical AE density. Consequently, their PW cutoff energy may be larger than the one associated to the pseudo wavefunction density \( |n^{ps}(r)\rangle \) in (13).

2.3. Maximally localized Wannier functions within PAW/USPP

As mentioned in Sec. 2.1, Bloch wavefunctions enter the calculation of MLWF’s only through the overlap matrix elements \( M_{kn}^{kb} \), defined in (4). Therefore, the reconstruction of these integrals from the knowledge of pseudo wavefunctions completely solves the problem of computing MLWF’s within a PAW/USPP formalism. Once overlap matrices have been calculated, we do not longer distinguish whether the parent Bloch wavefunctions were pseudized or not.

Being the overlaps \( M_{kn}^{kb} \) (4) the matrix elements of the local operator \( e^{-ib \cdot r} \), we built up the corresponding augmentation setting \( A(\mathbf{r}) = e^{-ib \cdot r} \) in (11). Exploiting the translational symmetry of the crystal, overlaps can be written as:

\[
M_{kn}^{kb} = \langle u_{k,m}^{ps} | u_{k+b,n}^{ps} \rangle + \sum_{I,j} Q_{ij}^l(b) \langle \psi_{k,m}^{ps} | \beta_{Ij}^{k+b} | \psi_{k+b,n}^{ps} \rangle ,
\]

where we have defined

\[
Q_{ij}^l(b) = \int d\mathbf{r} Q_{ij}^l(\mathbf{r}) e^{-ib \cdot \mathbf{r}},
\]

\[
\beta_{Ij}^{k}(\mathbf{r}) = \frac{1}{\sqrt{N_k}} \sum_{\mathbf{R}} e^{i\mathbf{k} \cdot \mathbf{R}} \beta_{Ij}(\mathbf{r} - \mathbf{R}).
\]

Summation over ions \( I \) in (14) is done in a single unit cell. Details about the calculation of these quantities are reported in Appendix B. We stress that the scalar product of \( |u^{ps}\rangle \) functions cannot be simply augmented by the \( \hat{S} \) (12) operator as those involving \( |\psi^{ps}\rangle \)’s. In order to work with the periodic part \( |u^{ps}\rangle \) of the Bloch functions, first we have to reconstruct the AE Bloch states by means of \( \hat{T} \) and then we can obtain the required \( |u_{k,m}^{ps}\rangle \) states by applying the local operator \( e^{-i\mathbf{k} \cdot \mathbf{r}} \). Since this last operator does not commute with \( \hat{T} \), we are not allowed to directly work on \( |u^{ps}\rangle \) with the reconstruction operator. In the first scalar product of (14) the number operator \( \hat{S} = \hat{T}^{\dagger} \hat{T} \) has been therefore substituted by the augmented operator \( \hat{M} = \hat{T}^{\dagger} e^{-ib \cdot r} \hat{T} \).
We thus need to introduce the Fourier transform of the augmentation densities $Q_{ij}^{0}(b)$ instead of the augmentation charges $q_{ij}^{0}$. We also note that in the thermodynamic limit the $k$-point grid becomes a continuum, so that $b \to 0$. This limit leads to identical $\hat{S}$ and $\hat{M}$ operators. Therefore, within discrete $k$-meshes the use of $\hat{S}$ instead of $\hat{M}$ is an approximation expected to give the best performance in the limit of a large number of $k$-points. We will refer to this approximation as the thermodynamic limit approximation (TLA). We will comment more on its numerical aspects in Sec. 3.

The problem of calculating Wannier functions within USPP has also been faced elsewhere in the literature [37, 38, 39]. In a first attempt, Vanderbilt and King-Smith [37] extended the calculation of the spontaneous polarization through the Berry phase [9, 10, 8] to the USPP procedure. Since the Berry phase [10] is directly related to overlap integrals, an expression for its calculation is reported in (23) of [37]. This expression adopts the $\hat{S}$ number operator instead of $\hat{M}$. Therefore, the result does not completely agree with the one presented here (14), but it can be read as an approximating formula having the right thermodynamic limit in view of the above discussion. Bernasconi and Madden [38, 39] derived instead the formalism for MLWFs with USPP in a simplified approach [40] valid only in the case of $\Gamma$-sampled supercells. Although the basic ingredients (e.g. overlaps) are the same, our treatment is valid for generic periodic systems, and recovers the $\Gamma$-only calculation as a special case. Furthermore, the proof given in [38] cannot be straightforwardly extended to the more general PAW case. The authors generalized the augmentation operator for the density (13) to the case of the density matrix and then derived the augmentation for the $e^{-iG \cdot r}$ operator. Here instead the $G_i$ are the generators of the reciprocal lattice. We note that the result by Bernasconi and Madden is coherent with our treatment, while the first one by Vanderbilt and King-Smith [37] is not. Following Bernasconi and Madden, Thygesen and coworkers [41] recently derived an expression for overlap matrices within USPP for periodic systems, considering a $\Gamma$-only supercell containing the whole crystal.

Closing this section we wish to underline that matrix elements of the form $\langle \psi_{k,m} | e^{-i(q+G) \cdot r} | \psi_{k'q,n} \rangle$ enter also other physical problems. A particularly appealing case is the calculation of one-particle Green function in the GW approximation [42, 43]. Current implementations [44, 45, 46] of the method experience DFT wavefunctions mainly through the above defined matrix elements (evaluation of the polarizability), while no direct access to the density is required. The extension of GW calculations to the case of PAW [47, 48] or USPP is therefore feasible along the same lines we presented here for Wannier functions. We note, however, that the numerical cost is extremely higher due to the larger number of overlaps to be computed.

2.4. Numerical details

In this section we would like to describe some issues related to the numerical performance of the method. We implemented this formalism in the freely-available WannT code [49], for the calculation of electronic and transport properties with WFs. We also took advantage of the complete integration of the WannT code with the PWscf package [50], which explicitly treats the DFT problem using USPPs. From here on we focus on the USPP formalism, even though a large part of the discussion is still valid also in the PAW case. The most important advantage of using the USPP construction for Wannier functions is the scaling of the original DFT calculations, which has been described elsewhere [30]. However, this scaling has also an effect on
the actual computation of WFs and we analyze this aspect in detail.

As we described above, almost the whole amount of changes induced by the USPP description (relative to NCPP) in the calculation of MLWFs is related to the implementation of (14). Details on how to compute $|\beta_{ik}\rangle$ and $Q_{ij}(b)$ are reported in Appendix B. Since no reference to the charge is made, only the very smooth wavefunction grid is used throughout the calculation. While a linear scaling with the number of plane waves is exploited in the first term (pseudo overlaps) of (14), scalar products between projectors and pseudo states in the second term (augmentation overlaps) are the price to pay for introducing USPPs. When we consider that the number of $\beta$-projectors $N_\beta$ is of the same order of the number of bands $N_b$ (but usually larger by a factor between one and two) we see that both pseudo and augmentation overlap terms have the same scaling, namely $N_b^2 \times N_k \times N_{PW}$. However, the pseudo overlaps turn out to have a larger prefactor [51] and represent the leading term. Usually, USPPs allow for a reduction of the PW cutoff by a factor of 2 to 3 for first-row elements up to 5 or even more for atoms with $d$- or $f$-states. This leads to a reduction of the PW number $N_{PW}$ by a factor of around 3 to 10 or more. Even if the scaling wrt $N_{PW}$ is linear, it more than compensates the effort for augmenting overlaps and makes the introduction of USPPs numerically advantageous. Our experience shows that USPPs avoid the creation of bottlenecks in the computation of overlaps and make the WF localization the leading part of the calculation.

Finally, we note that in order to give a guess for the iterative minimizations involved in the MLWF method, it is sometimes required to compute the projections of Bloch states onto some starting localized functions [6, 7]. The augmentation of scalar products is performed as usual accounting for the $\hat{S}$ number operator 12. Projections on the $\beta$-functions are required as well, but they have already been computed and it turned out that scaling is linear wrt the PW number as before. Therefore, no implications on the above discussion arise.

3. Applications

In this Section we apply the above described formalism to some test cases, ranging from periodic crystals to isolated molecules. Precisely, we study $fcc$ Copper bulk, wurtzite AlN, and Watson-Crick DNA base pairs. We address a number of physical properties connected to Wannier functions: interpolation of the electronic structure, calculation of dipole moments and spontaneous polarization, analysis of the chemical bonding. All the calculations are performed with both norm-conserving and ultra-soft pseudopotentials. The numerical implications in using the USPP-TLA approach for the augmentation of overlaps are also discussed. We choose very simple systems for which MLWFs can be computed also with NCPPs and USPPs are not required. This choices allow us to test directly the USPP accuracy against the standard accuracy of the NCPP framework, for which bibliographic record exists.

3.1. Copper bulk

We compute MLWFs for $fcc$-Copper, which has already been used as a test case in the literature [7, 39, 41] of WFs. We adopt a $6 \times 6 \times 6$ mesh of $k$-points to sample the Brillouin zone and compute six WFs corresponding to the lowest $s-d$ manyfold. In the disentanglement procedure [7] (used to get the optimal subspace for WF localization) we freeze the Bloch eigenstates below the Fermi energy ($\text{frozen states}$): this means
that the subspace is constructed by these selected states plus a mixture of the states above the Fermi level. We note that no symmetry constraint is imposed a priori on the WF set: Therefore the computed functions do not have in principle a well-defined symmetry. We note that different approaches dealing with symmetry-based WFs for the current class of systems can be found in the literature [4, 5].

We adopt a kinetic energy cutoff for wavefunctions of 120 Ry (25 Ry) when using NCPP (USPP) and of 480 Ry (200 Ry) for the density. In figure 1 we superimpose the band structure directly computed from a USPP-DFT calculation and that obtained from Wannier function interpolation [6, 7, 14] on the adopted 8x8x8 uniform k-point grid. These two sets of bands are almost superimposed below the Fermi energy and some slight differences arise only at higher energies. This is expected due to the choice of the energy window for the frozen states [52]: while the eigenvalues for the k-points in the adopted regular mesh are the same as those from the DFT calculation by construction, it is not trivial that the band structure along a generic Brillouin zone line is well reproduced. This is indeed the case here, being a signature of proper localization of the computed WFs. The band structure interpolation obtained from NCPP is essentially the same as the one in figure 1 and it is not reported. Some small discrepancies between NCPP and USPP interpolated bands are also present in the starting DFT calculations and are not of our interest in this context.

In table 1 we report a more detailed description of quantities related to WFs (spreads, real-space decay of the Hamiltonian matrix elements) in order to compare the NCPP and USPP approaches. A measure of the Hamiltonian decay is defined as:

$$d(R) = \left( \frac{1}{N_R} \sum_{mn} |H_{mn}(R)|^2 \right)^{1/2},$$

where we defined $H_{mn}(R) = \langle w_{0,m} | H | w_{R,n} \rangle$. These quantities are significant as a signature of the localization of the WFs used to compute the matrix elements (the more localized the WFs, the more rapidly the $H$ matrix elements decay in space).
Table 1. fcc-Copper: WF spreads (Bohr$^2$) and real-space decay of the Hamiltonian matrix elements (eV) for NCPP, USPP and USPP in the thermodynamic limit approximation (USPP-TLA). $\Omega$ is the total spread, $\Omega_I$, $\Omega_D$ and $\Omega_{OD}$ are the invariant, diagonal and off-diagonal terms, according to (A.3). $d(R)$ is a measure of the spatial decay of the Hamiltonian on the WF basis, as described in (17). $\tau$ is the (0.5 0.5 0.0) direct lattice vector.

<table>
<thead>
<tr>
<th></th>
<th>NCPP</th>
<th>USPP</th>
<th>USPP-TLA</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Omega$</td>
<td>22.434</td>
<td>23.010</td>
<td>18.886</td>
</tr>
<tr>
<td>$\Omega_I$</td>
<td>14.767</td>
<td>15.629</td>
<td>11.303</td>
</tr>
<tr>
<td>$\Omega_{D+OD}$</td>
<td>7.667</td>
<td>7.381</td>
<td>7.583</td>
</tr>
<tr>
<td>$d(\tau)$</td>
<td>0.4876</td>
<td>0.4795</td>
<td>0.4779</td>
</tr>
<tr>
<td>$d(2\tau)$</td>
<td>0.0493</td>
<td>0.0473</td>
<td>0.0476</td>
</tr>
<tr>
<td>$d(3\tau)$</td>
<td>0.0203</td>
<td>0.0207</td>
<td>0.0205</td>
</tr>
</tbody>
</table>

Figure 2. fcc-Copper: charge distribution for WFs computed using USPP. (a) interstitial WF, $\Omega_a = 11.28$ Bohr$^2$; (b–d) $d$-character WFs, $\Omega_b = 1.86$ Bohr$^2$, $\Omega_c = 2.70$ Bohr$^2$, $\Omega_d = 1.54$ Bohr$^2$. The two additional $d$-like WFs not reported here are strictly similar to (b) and (c) by virtue of symmetry relations.

USPP results appear to be in very good agreement with those related to NCPP, most of the differences being reasonably due to the pseudopotential generation and not to the WF computation. The average number of iterations to converge the disentanglement and the localization procedures are almost the same, as well as the singular spread values for each of the WFs. Figure 2 reports the spatial distribution of WFs from USPP calculations. As in previous works [7, 41], we find one interstitial $s$-like WF with the largest spread [figure 2(a)], and five more localized $d$-like WFs [figure 2(b–d)], correctly reproducing the physical $s-d$ picture of Copper.

As a last remark for the case of Copper, we analyze the effect of neglecting the $e^{-i b \cdot r}$ term in (14), i.e. the USPP thermodynamic limit approximation (USPP-TLA). The theoretical background has already been discussed in Sec. 2.3, here we focus on the numerical aspects. In table 1 the third column reports the results of the calculation performed within this approximation: it is evident that the numerical values of the USPP-TLA spreads deviate from the NCPP ones much more than the USPP do.
Maximally localized Wannier functions from PAW or ultrasoft pseudopotentials

Table 2. DNA bases: Dipole moments $|p|$ (Debye) for isolated nucleobases (G, C, A, T) and for Watson-Crick base pairs (G-C, A-T). Present work results for both USPP and NCPP approaches are compared with previous quantum chemistry HF/6-31G** calculations [66] and experimental data.

<table>
<thead>
<tr>
<th></th>
<th>USPP</th>
<th>NCPP</th>
<th>HF/6-31G**</th>
<th>Exp.</th>
</tr>
</thead>
<tbody>
<tr>
<td>G</td>
<td>7.1</td>
<td>7.2</td>
<td>7.1</td>
<td>7.1a</td>
</tr>
<tr>
<td>C</td>
<td>6.7</td>
<td>6.9</td>
<td>7.1</td>
<td>7.0b</td>
</tr>
<tr>
<td>A</td>
<td>2.3</td>
<td>2.3</td>
<td>2.5</td>
<td>2.5a</td>
</tr>
<tr>
<td>T</td>
<td>4.2</td>
<td>4.4</td>
<td>4.6</td>
<td>4.1c</td>
</tr>
<tr>
<td>G-C</td>
<td>4.9</td>
<td>4.9</td>
<td>6.5</td>
<td></td>
</tr>
<tr>
<td>A-T</td>
<td>1.7</td>
<td>1.8</td>
<td>2.0</td>
<td></td>
</tr>
</tbody>
</table>

*aDeVoe and Tinoco (Ref. [67])
*bWeber and Craven (Ref. [68])
*cKulakowski et al. (Ref. [69])

the contrary, the interpolated band structure and the real-space decay Hamiltonian matrix elements are definitely well-suited and comparable with those obtained in the full USPP treatment. Since the TLA is known to become exact in the thermodynamic limit, we expect it to work better when increasing the dimension of the $k$-point mesh. We checked the behavior of the approximation with respect to different meshes but no convergence could be reached for grids ranging from $4 \times 4 \times 4$ to $10 \times 10 \times 10$ $k$-points.

3.2. Isolated molecules: DNA bases and base pairs

Maximally localized Wannier functions [53] have been widely used to characterize the electrostatic properties of several molecular systems ranging from e.g. water [54, 55, 56] and small molecules [57, 58, 59, 60] to large biomolecules, such as proteins [61], nucleic acids [62, 63], enzymes [64] and ionic channels [65]. In fact, the Wannier transformation allows one to partition the charge density into localized distributions of charges sitting on the so-called Wannier centers $\langle \hat{r} \rangle_n$ [8, 9]. In the case of isolated molecular systems, the dipole moment is a well defined quantity given by

\[ p = p_{\text{ion}} + p_{\text{el}} \]

\[ p_{\text{ion}} = + e \sum_I Z_I R_I, \]

\[ p_{\text{el}} = - 2e \sum_n \langle \hat{r} \rangle_n, \]

where $p_{\text{ion}}$ and $p_{\text{el}}$ are the ionic and electronic component respectively; $e$ is the electron charge; the $I$ summation is over the ionic sites $R_I$ and $Z_I$ is the valence charge of the $I^{th}$ atom, as defined by the corresponding pseudopotential; the $n$ summation is over the doubly occupied valence states.

As a key test, we calculated the dipole moments of the four isolated DNA bases: Guanine (G), Cytosine (C), Adenine (A) and Thymine (T), and of the two Watson-Crick base pairs G-C and A-T, whose structures are reported in figure 3(a).

We simulated each system in a large $(22 \times 22 \times 22) \text{Å}^3$ supercell, which allows us to avoid spurious interactions among neighbor replicas. For isolated systems, the uniform $k$-point grid reduces to the case of $\Gamma$-point only, and the connecting vectors
Maximally localized Wannier functions from PAW or ultrasoft pseudopotentials

Figure 3. (Color online) DNA bases: (a) Chemical scheme of the four DNA bases (G, C, A, T) assembled in the two Watson-Crick base pairs (GC and AT). (b) Isosurface plots of selected MLWFs for the GC base pair, representing a single C-C bond (SB), a double N=C bond (DB) and two oxygen lone pairs (LP). Dashed lines represent hydrogen bonds that bind the base pairs.

\( \mathbf{b}_4 \) correspond to the generators of the reciprocal lattice vectors. We expanded the electronic wavefunctions (charge density) up to a kinetic energy cutoff of 25 (200) and 80 (320) Ry, using USPP and NCPP respectively.

We first optimized the atomic structure of the two base pairs G-C and A-T until forces on all atoms were lower than 0.03 eV/Å, using ultra-soft pseudopotentials. Then, keeping atoms fixed in the relaxed geometry, we calculated the electronic structure and the corresponding MLWFs for both the single bases and the base pairs. We maintained the same geometries also for the corresponding NCPP calculations. In this case we have checked that forces on single atoms never exceeded the value of 0.05 eV/Å.

Our results for both sets of calculations are reported in Table 2. We note a very good internal agreement between the USPP and NCPP cases, as well as in comparison with previous quantum chemistry HF/6-31G** calculations [66] and experimental results. As a benchmark, we have also computed the dipole of guanine from the plane-wave charge density, obtaining a difference of 0.04 (0.08) Debye for USPP (NCPP) wrt the value computed by means of WFs and reported in Tab. 2. These small deviations measure the precision of the results based on WFs, and we checked it can be controlled, i.e. made smaller and smaller, by increasing the simulation cell. The total spread \( \Omega \)
and its components $\Omega_I$, $\Omega_{OD}$ (not shown) are also very similar in the two set of calculations, while the diagonal term $\Omega_D$ is, by definition [6], identically zero for isolated systems.

Finally, we can take advantage from the calculated Wannier functions to further investigate the electronic distribution and the bonding pattern in the molecules [70]. For example, as shown in figure 3(b) for the case of the G-C base pair, we are able to characterize different kinds of bonds. The SB Wannier function represents a single $\sigma$ bond: It is centered in the middle point of the C-C bond. The two DB WFs describe instead a double N=C bond: This bond is partially polarized with a slight charge accumulation near the nitrogen atom. Finally, the LP WFs represents two electron lone pairs localized around the oxygen atom of the guanine molecule. Note also that the distribution of single/double bonds correctly reflects the theoretical one reported in figure 3(a). Let us remark here that our benchmark to assess the success of the newly developed USPP-WF methodology is its relative performance with respect to the NCPP-WF (already established) framework, namely the comparison between columns 2 and 3 in table 2.

3.3. AlN Wurtzite

Here we move to the calculation of polarization in periodic systems. See the review by Resta [8] for a more detailed description. We focus on the case of aluminum nitride and compute the spontaneous polarization $P_{SP}$ of the wurtzite phase. This is a particularly appealing test-case since a large debate exists in the literature and many results are present [71, 72, 73, 74, 75, 12, 76]. Moreover, Nitrogen may be more easily described (in terms of PW kinetic-energy cutoff) with USPPs than with NCPPs, allowing for an advantageous application of the current formalism. Following [12, 77] we evaluate the polarization (electronic and ionic contributions) for the wurtzite (WZ) phase taking the zinc-blend (ZB) structure as a reference. Our calculations adopt the GGA-PBE parameterization for the exchange-correlation functional, and uses cutoff energies of 60 Ry (25 Ry) for NCPP (USPP) for wavefunctions and 240 Ry (200 Ry) for the density. We relax both the cell dimensions and the atomic positions of the WZ phase. The ZB reference is assumed to have ideal atomic positions and the cell is taken to have the same volume (but not the shape) of the one computed for the WZ polytype (six bilayers are included in the cell). These structural calculations have been performed using USPP and the obtained (lattice and ionic) parameters have been used also in the NCPP simulations. Using a $16 \times 16 \times 4$ Monkhorst-Pack [78] mesh of $k$-points we obtained the $a$ and $c/a$ parameters of the hexagonal lattice as $a=3.1144$ Å and $c/a=1.6109$ (for the standard WZ cell including two bilayers, $c/a=4.8326$ for the actual cell we adopted). The resulting ZB cell has the ideal parameter $c/a=4.899$ while $a=3.1002$ Å.

In table 3 we report the comparison of USPP and NCPP results in our calculations as well as other results from the literature. We estimate the numerical accuracy of the calculation to be of the order of 0.005 C/m². The values of spontaneous polarization computed using NCPPs are almost identical to those obtained with USPPs ($P_{SP} = -0.080$ C/m²). The USPP-TLA behaves very accurately in this case and no difference can be found with respect to the full USPP calculation. Our results are also in nice agreement with the USPP-TLA calculation by Bernardini et al. [12], who used a Berry-phase formalism [9] and found a value of $P_{SP} = -0.090$ C/m². We thus conclude that the USPP-TLA approximation performs well for the computation of
AlN: electronic spontaneous polarization [C/m²] of wurtzite structure. The presented results (NCPP, USPP and USPP-TLA) are compared to the literature. As a reference we also report the invariant (Ω₀) and the total spread (Ω) [Bohr²] given by the WF calculations for wurtzite. Results from [12] are obtained using GGA and LDA (in parentheses) respectively.

<table>
<thead>
<tr>
<th>PSP</th>
<th>NCPP</th>
<th>USPP</th>
<th>USPP-TLA</th>
</tr>
</thead>
<tbody>
<tr>
<td>this work</td>
<td>-0.081</td>
<td>-0.080</td>
<td>-0.080</td>
</tr>
<tr>
<td>Ref. [12]</td>
<td>Ref. [75]</td>
<td>-0.120 (0.999)</td>
<td></td>
</tr>
<tr>
<td>Ω</td>
<td>80.895</td>
<td>80.756</td>
<td>80.271</td>
</tr>
<tr>
<td>Ω₀</td>
<td>67.683</td>
<td>67.857</td>
<td>67.282</td>
</tr>
</tbody>
</table>

the spontaneous polarization in nitrides, relative to a pure USPP treatment without the thermodynamic limit approximation.

These results for the PSP in AlN wurtzite are also in agreement with indirect experimental evidences as reported in [74, 73, 76]. While some earlier experimental fits [79, 80] claim for much lower values of PSP (ranging from -0.040 to -0.060 C/m²), later [76, 81] works explain this discrepancy as due the neglecting of bowing effects (non-linearity) of the PSP with respect to the composition of the alloy AlₓGa₁₋ₓN employed in the measurements.

4. Conclusions

In this paper we presented an approach to calculate maximally localized Wannier functions in the general framework of the PAW theory. This formalism then recovers the USPP framework as a special case. The main advantage using PAW/USPP over NCPP is the well known reduction of the computational effort in the evaluation of the electronic wavefunctions at the DFT level. This leads to a consequent reduction of computational load also in the calculation of MLWFs. Furthermore, the reformulation within the PAW scheme allows us to interface the computation of MLWFs to other popular approaches for the electronic structure calculation. Finally, our method is formulated in the case of a uniform k-point mesh for the sampling of the Brillouin zone (BZ), which includes (but is more general than) a previous attempt based on Γ-only calculations. This allows us to treat periodic solid-state systems (such as crystals, surfaces and interfaces), which require a full description of the BZ, as well as molecular, finite or amorphous systems which are well described with the Γ-only representation.

As a first illustration of the capability of this methodology, we presented the calculation of the MLWFs for a few selected test cases, easily referable to well established theoretical and experimental results. For each selected system we also compared the results for both USPP and NCPP calculations, underlying a very good agreement between the two cases.

The reduction of the computational cost resulting from USPP calculations opens the way to the exploitation of the MLWFS as a powerful tool to analyze the electronic structure of larger and more realistic nanoscale systems, in particular for transport in nano-junctions [14, 15].
Acknowledgments

We acknowledge discussions with Giovanni Bussi, Marco Buongiorno Nardelli and Elisa Molinari for the treatment of USPP. Funding was provided by the EC through TMR network “Exciting”, by INFN through “Commissione Calcolo Parallelo”, by the Italian MIUR through PRIN 2004, and by the regional laboratory of EM “Nanofaber”. Part of the figures has been realized using the XCrySDen package [82].

Appendix A. Main formulas for maximally localized Wannier functions

For sake of completeness we report here the main relations [6] entering the expression (3) for the spread functional Ω[U] and its first derivative wrt the unitary transformation U (2). These are all the quantities involved in the minimization procedure for the calculation of maximally localized Wannier functions. The expectation values of the position operator are:

\[ \langle r \rangle_n = -\frac{1}{N} \sum_{k,b} w_b \text{Im} \ln M_{kn}^{k,b}, \]

\[ \langle r^2 \rangle_n = \frac{1}{N} \sum_{k,b} w_b \left\{ \left[ 1 - |M_{nn}^{k,b}|^2 \right] + \left[ \text{Im} \ln M_{nn}^{k,b} \right]^2 \right\}, \]

where b vectors connect nearest-neighbor k-points and \( w_b \) are their weights according to Appendix B of [6].

To make the Ω dependence on the overlap explicit, the spread functional can be divided into three terms, the invariant (I), the diagonal (D) and the off-diagonal (OD) components [6]:

\[ \Omega[U] = \Omega_I + \Omega_D[U] + \Omega_{OD}[U], \]

whose definitions are, respectively:

\[ \Omega_I = \frac{1}{N} \sum_{k,b} w_b \left( N_w - \sum_{m} |M_{nn}^{k,b}|^2 \right), \]

\[ \Omega_D = \frac{1}{N} \sum_{k,b} w_b \sum_{n} \left( \text{Im} \ln M_{nn}^{k,b} + b \cdot r_n \right)^2, \]

\[ \Omega_{OD} = \frac{1}{N} \sum_{k,b} w_b \sum_{m \neq n} |M_{mn}^{k,b}|^2. \]

Appendix B. Detailed expressions for the calculation of \( |\beta_i^k\rangle \) and \( Q_{ij}(b) \)

We report the explicit expression for the calculation of the reciprocal space representation of the PAW/USPP projectors and the Fourier transform of the augmentation densities:

\[ Q_{ij}^I(b) = \int \text{d}r e^{-ib \cdot r} Q_{ij}^I(r - \tau_I). \]

Here we made explicit the dependence of \( Q_{ij}^I(b) \) on the atomic position \( \tau_I \). These tasks are also required in the evaluation e.g. of the density in reciprocal space and are therefore performed in standard plane-waves DFT codes. The index \( i, j \) in
Maximally localized Wannier functions from PAW or ultrasoft pseudopotentials

β(r) and Q_{ij}(r) stand for radial and angular numbers, e.g. n_i,l_i,m_i. Projectors and augmentation densities are explicitly written as a product of a radial part times (real) spherical harmonics:

\begin{align}
\beta_i(r) &= R_{n_i}(r) Y_l^{m_i}(\hat{r}) \\
Q_{ij}(r) &= g_{n_i,n_j} Y_l^{m_i}(\hat{r}) Y_l^{m_j}(\hat{r}).
\end{align}

First we focus on the expression for β projectors. Functions of the form \( f(r) = R(r) Y_L^m(\hat{r}) \) have a known semi-analytical Fourier transform which is given by:

\[ f(k) = 4\pi (-i)^l Y_l^m(\hat{k}) \int_0^\infty r^2 R(r) J_l(kr) dr \]

where \( J_l(x) \) is the spherical Bessel function of order \( l \). The problem for β projectors is therefore directly solved once we add the structure factors accounting for the actual positions of the ion:

\[ \beta^k_{ij}(G) = 4\pi (-i)^l e^{-i(k+G)\tau} Y_l^{m_i}(G) \int_0^\infty r^2 R_{n_i}(r) J_l(br) dr. \]

Moving to the case of the augmentation densities, we note that the product of two spherical harmonics can be expressed as a linear combination of single spherical harmonics using Clebsch-Gordan coefficients:

\[ Y_{l_i}^{m_i}(\hat{r}) Y_{l_j}^{m_j}(\hat{r}) = \sum_{L=|l_i-l_j|}^{l_i+l_j} \sum_{M=-L}^{L} C_{l_i,l_j,m_i,m_j}^{L,M} Y_L^M(\hat{r}). \]

This allows to follow the same strategy as before also for (B.3). Putting (B.6-B.4) together, the final expression for \( Q_{ij}(b) \) reads:

\[ Q_{ij}^L(b) = 4\pi e^{-ib\tau} \sum_{L} \sum_{M} C_{l_i,l_j,m_i,m_j}^{L,M} (-i)^L \times \]

\[ \times Y_L^M(\hat{b}) \int_0^\infty r^2 g_{n_i,n_j} J_L(br) dr. \]

where \( M, L \) indexes run as in (B.6).

References

Maximally localized Wannier functions from PAW or ultrasoft pseudopotentials

[32] Wavelets have defined angular momentum (e.g. their angular parts are spherical harmonics), but are not supposed to be atomic eigenstates or even to be orthogonal.
[33] Since the pseudo wavelets are not orthogonal their projectors are not simply the associated bra’s of the given ket’s.
[34] Number operator $\hat{\mathbf{n}}$ is also known as overlap operator. We here adopt the former notation in order to avoid confusion with the overlap integrals defined in (4).
[35] PAW are presented here in an all-electron frozen-core fashion but a full all-electron implementation is also compatible with the theory [22].
[36] Other differences between PAW and USPP approaches arise in the form of the effective (pseudo)-potential acting of the pseudo-wavefunctions. See e.g. [22] for a more detailed discussion.
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[38] Bernasconi L and Madden P A 2001 J. Mol. Struct. 544 49-60
[42] Hedin L 1965 Phys. Rev. 139(3A) A796–A824
[51] This fact comes first due to the presence of the sum over b-vectors (giving a prefactor from 3 to 6) and secondly because the coupling of different k-points for pseudo overlaps makes wavefunction managing more cumbersome.
[52] Frozen states in the disentangle procedure are described in details in [7].
[53] For isolated systems, which can be view as the limiting case of periodic systems in the Γ-only sampling of the BZ, MLWFs match the well-known localization criteria proposed by Boys in Boys S F 1960 Rev. Mod. Phys. 32(2) 296–299, giving raise to Boys orbitals. See e.g. [40, 39] for more details.
Maximally localized Wannier functions from PA W or ultrasoft pseudopotentials

[69] Foster J and Boys S 1960 Rev. Mod. Phys. 32(2) 300–302
2.3 Polarization of crystalline solids: Wannier functions and Berry phases

Polarization properties of materials, like e.g. piezoelectricity, pyroelectricity or spontaneous bulk polarization, are of wide interest and have been thoroughly investigated in the last decade \[10,11,12,13,14,15\]. When considering spontaneous bulk polarization, it is difficult to give an experimental measure and at the same time a good theoretical description \[11\]. While this is a bulk property, it is complicated to be treated excluding the influence of the boundary conditions or surface effects present in experiments and calculations. Bulk polarization is experimentally accessible only in non equilibrium condition: The observable that can be measured is the difference \(\Delta \mathbf{P}\) between two states of the same material, usually via hysteresis cycles \[10,15\].

The bulk spontaneous polarization is often defined as a dipole per unit volume:

\[
P = \frac{1}{V} \left[ e \sum_{I} Z_I \mathbf{r}_I + \int d\mathbf{r} \rho(\mathbf{r}) \right],
\]

where \(V\) is a sample volume, \(I\) indicates the ionic sites, \(e Z_I\) is the \(I\)-th ionic charge and \(\rho(\mathbf{r})\) is the electronic charge density. If we consider a periodic solid, with the unit cell as the sample volume, this quantity is ill defined, because it depends on how the cell is defined: This is clearly underlined by Resta in Ref. \[10\].

It is thus necessary to find an alternative expression based on the definition of a variation in polarization \(\Delta \mathbf{P}\), linked to the electronic wavefunction and not simply to the charge: The relevant quantity is in fact the phase which is present in the wavefunction \[10\]. The total bulk spontaneous polarization can be written as the sum of an ionic and an electronic contribution

\[
\mathbf{P} = \mathbf{P}_{\text{ion}} + \mathbf{P}_e;
\]

The ionic contribution is straightforwardly calculated as

\[
\mathbf{P}_{\text{ion}} = \frac{e}{\Omega} \sum_{j=1}^{N} Z_j \mathbf{u}_j,
\]

where \(\Omega\) is the volume of the unit cell, \(N\) is the number of atoms in the unit cell and \(Z_j\) and \(\mathbf{u}_j\) are the atomic numbers and position vectors. It should be noticed that \(\mathbf{P}_{\text{ion}}\) is well defined modulo \(e \mathbf{R}/\Omega\), because atomic positions shifted of a lattice vector \(\mathbf{R}\) are equivalent. The electronic term is the most complicated one: a treatment based on calculating a variation in electronic polarization has been proposed by Resta \[16\]. Considering an adiabatic transformation of the Hamiltonian (in particular of the Kohn–Sham potential) of the system, the consequent change in the electronic polarization is
\[ \frac{\partial P_e}{\partial \lambda} = -ife\frac{\hbar}{N\Omega m_e} \sum_k \sum_{n=1}^{M} \sum_{m=M+1}^{\infty} \frac{\langle \psi^{(\lambda)}_{nk} | P | \psi^{(\lambda)}_{nk} \rangle \langle \psi^{(\lambda)}_{nk} | \partial V_{KS} / \partial \lambda | \psi^{(\lambda)}_{nk} \rangle}{(e_{nk}^{(\lambda)} - e_{nk}^{(\lambda)})^2} + c.c., \]  

(2.46)

where \( m_e \) and \( e \) are the electronic mass and charge, \( N \) is the number of unit cells of volume \( \Omega \), \( f \) is the occupation number (in spin degenerate systems \( f = 2 \) for the valence), \( M \) is the number of occupied bands and \( V_{KS} \) is the Kohn–Sham potential. Here we have parametrized the change in the Hamiltonian with \( \lambda \) which takes the values 0 and 1 at the initial and final state of the adiabatic transformation. Following this expression, the change in polarization due to a finite adiabatic transformation is given by

\[ \Delta P_e = \int_0^1 d\lambda \frac{\partial P_e}{\partial \lambda}. \]

(2.47)

It could be written

\[ P_e = \frac{1}{\Omega} \int_\Omega d\mathbf{r} \rho_e(\mathbf{r}), \]

(2.48)

but this is a bulk quantity ill defined, as we mentioned before. Explicitly writing the matrix elements in equation (2.46) and considering only the valence bands, we have

\[ \Delta P_\alpha = -ife \frac{\hbar}{(2\pi)^3} \sum_{n=1}^{M} \int_{BZ} dk \int_0^1 d\lambda \left[ \langle \partial u^{(\lambda)}_{nk}/\partial k_\alpha | \partial u^{(\lambda)}_{nk}/\partial \lambda \rangle - \langle \partial u^{(\lambda)}_{nk}/\partial \lambda | \partial u^{(\lambda)}_{nk}/\partial k_\alpha \rangle \right], \]

(2.49)

for what concerns the \( \alpha \)-th component, then

\[ \Delta P_\alpha = -ife \frac{\hbar}{(2\pi)^3} \sum_{n=1}^{M} \int_{BZ} dk \left\{ \left[ \langle u^{(\lambda)}_{nk} | \partial/\partial k_\alpha | u^{(\lambda)}_{nk} \rangle \right]_0 - \int_0^1 \frac{\partial}{\partial k_\alpha} \langle u^{(\lambda)}_{nk} | \partial/\partial \lambda | u^{(\lambda)}_{nk} \rangle d\lambda \right\}. \]

(2.50)

If we are working in a gauge where the electronic wavefunction is periodic in reciprocal space \( \psi^{(\lambda)}_{nk}(\mathbf{r}) = \psi^{(\lambda)}_{nk+\mathbf{G}}(\mathbf{r}) \), the second term in curly brackets vanishes:

\[ \Delta P_e = -ife \frac{\hbar}{(2\pi)^3} \sum_{n=1}^{M} \int_{BZ} dk \left[ \langle u^{(\lambda)}_{nk} | \nabla_k | u^{(\lambda)}_{nk} \rangle \right]_0 \]

(2.51)

Considering a close loop \( V_{KS}^{(0)} = V_{KS}^{(1)} \), the transformation recasts the system at the state (1) into the initial state (0), and the corresponding variation of \( P_e \) is

\[ \Delta P_{e,loop} = \oint d\lambda \frac{\partial P_e}{\partial \lambda} = -feR/\Omega, \]

(2.52)

where \( \mathbf{R} \) is a lattice vector. Since the \( \Delta \mathbf{P} \) generated by an adiabatic transformation depends only on the initial and final states, the calculated variation...
of the electronic polarization is defined modulo $\frac{f_e R}{11}$. Thus, in general, the change in electronic polarization (defined modulo $\frac{f_e R}{11}$) is

$$\Delta P_e = \int_0^1 d\lambda \frac{\partial P_e}{\partial \lambda} = P_e(1) - P_e(0),$$

(2.53)

where $P_e(\lambda)$ is given in terms of cell-periodic functions $u_{nk}^{(\lambda)}$:

$$P_e(\lambda) = -i f_e \frac{M}{(2\pi)^3} \sum_{n=1}^{M} \int_{BZ} d\mathbf{k} \langle u_{nk}^{(\lambda)} | \nabla_{\mathbf{k}} | u_{nk}^{(\lambda)} \rangle,$$

(2.54)

which comes from equation (2.51). For further details of the formulation we refer to the original paper by King-Smith and Vanderbilt [17].

It should be noted that the integral entering equation (2.54) represents the Berry phase [18, 10]. In fact the overlap matrix elements of the lattice periodic Bloch function can be expressed as

$$S_{mn}^{(\lambda)}(\mathbf{k}, \mathbf{k}') = \langle u_{mk}^{(\lambda)} | u_{nk}^{(\lambda)} \rangle.$$  

(2.55)

The Berry phase is defined, modulo $2\pi$, as

$$\phi^{(\lambda)}(\mathbf{k}, \mathbf{k}') = \text{Im} \{ \ln[\det S^{(\lambda)}(\mathbf{k}, \mathbf{k}')] \}.$$  

(2.56)

It measures the phase difference between the Kohn–Sham orbitals at $\mathbf{k}$ and $\mathbf{k}'$, once the Bloch phase is removed. An infinitesimal variation in this phase can be written as

$$d\phi^{(\lambda)} = \nabla_{\mathbf{k}'} \phi^{(\lambda)}(\mathbf{k}, \mathbf{k}') |_{\mathbf{k}'=\mathbf{k}} d\mathbf{k}$$

(2.57)

and the definition of geometric Berry phase on a continuous path $C$ is

$$\gamma^{(\lambda)}(C) = -\int_C d\phi^{(\lambda)}.$$  

(2.58)

Moving to a quadridimensional notation, where the new coordinates system $\xi$ is fixed so that $H(\xi) = H^{(\lambda)}(\mathbf{k})$, we define the Berry curvature as

$$\chi(\xi) = i \sum_{n=1}^{M} \langle u_n(\xi) | \nabla_\xi | u_n(\xi) \rangle.$$  

(2.59)

The Berry phase that we use to calculate the spontaneous polarization is obtained integrating the curvature on a close path:

$$\gamma(C) = -\oint_C d\phi = \oint_C d\xi \chi(\xi).$$  

(2.60)

Finally the definition of the variation in electronic polarization based on the Berry phase becomes

$$\Delta P_e = -\frac{f_e}{(2\pi)^3} \int_{BZ} d\mathbf{k} \left[ -\nabla_{\mathbf{k}'} \phi^{(1)}(\mathbf{k}, \mathbf{k}') + \nabla_{\mathbf{k}'} \phi^{(0)}(\mathbf{k}, \mathbf{k}') \right] |_{\mathbf{k}'=\mathbf{k}}.$$  

(2.61)
Considering the definition of Wannier functions presented in section (2.1), equation (2.54) can be rewritten in terms of Wannier centers of the occupied bands:

\[ P_e(\lambda) = \frac{e}{\Omega} \sum_{n=1}^{M} \int_{\Omega} d\mathbf{r} |R_n^{(\lambda)}(\mathbf{r})|^2 = -\frac{e}{\Omega} \sum_{n=1}^{M} \mathbf{r}_n^{(\lambda)}, \quad (2.62) \]

where \( \mathbf{r}_n = \langle \mathbf{R}_n | \mathbf{r} | \mathbf{R}_n \rangle \). Also in this case the arbitrary phase entering \( u_{nk} \) leads to the definition of \( P_e(\lambda) \) modulo \( \frac{e}{\Omega} \mathbf{R}_n \). Equations (2.54) and (2.62) are two alternative and equivalent definitions of electronic polarization of a crystalline solid.

Polarization properties of materials are especially important when dealing with surfaces and interfaces: They strongly influence functionalization and growth processes, dramatically affecting the surface reconstruction, where the in–plane polarization component also plays a crucial role. With the aim of understanding this phenomena, it can be useful to distinguish between the bulk and surface contributions to the spontaneous polarization.

Once we have defined the bulk polarization, the following property of \( P \) should be satisfied:

\[ \sigma = \mathbf{P} \cdot \hat{n}, \quad (2.63) \]

where \( \sigma \) is the ”bound charge” accumulated at a surface of orientation \( \hat{n} \) when the surface is insulating [19]. This relation has been exploited by Posternak and co–workers [11] to calculate the interface charge at a wurtzite–zincblende BeO interface, using a supercell technique to calculate the wurtzite bulk polarization.

Vanderbilt and King–Smith demonstrates the so–called ”surface theorem”: They show in Ref. [19] the validity of the relation (2.63) supposing the bulk polarization defined as (2.54) or (2.62). The demonstration of this suggests that the polarization in terms of Berry phase or Wannier centers is a physical reasonable definition. In an analogous way they introduce in the same paper the ”interface theorem”, corresponding to the case of an interface between crystalline solids epitaxially aligned. Considering the charge concentration at the interface, one could generalize (2.63) to

\[ \sigma_{int} = (\mathbf{P}_2 - \mathbf{P}_1) \cdot \hat{n}. \quad (2.64) \]

However the presence of this charge causes the rise of an electric field, considered instead null when defining the spontaneous polarization. Thus we have to reconsider the formulation, taking into account the presence of an external surface charge density \( \sigma_{ext} \) which has the effect of making the total field vanish, producing an external field opposed to that originating from \( \sigma_{int} \):

\[ \sigma_{ext} = -(\mathbf{P}_2 - \mathbf{P}_1) \cdot \hat{n}. \quad (2.65) \]
It is worth noticing that $\sigma_{\text{ext}}$ is again defined modulo $e/A_{\text{int}}$. Also in this case Vanderbilt and King-Smith demonstrate that the relation between the charge accumulated at the interface and the polarization defined as $\text{(2.54)}$ or $\text{(2.62)}$ holds. Calculating the difference in the zero-field polarization between two similar materials using the Berry phase or the Wannier centers has thus physical significance.

A further development in the analysis of the polarization properties of insulating and semiconducting materials can be done, considering the in-plane polarization of surfaces, decoupling the bulk and surface contributions to the polarization. We give an example of that procedure, calculating the properties of two different non-polar SiC surfaces described in the paper \cite{20} included in Chapter 5 based on the specification of a minimal volume in which the local polarization can be defined. A similar approach has been used by Wu et al. \cite{21} to calculate a layer–by–layer polarization of a perovskite interface structure.

Bibliography


Chapter 3

Transport with maximally localized Wannier functions: the WANT method

When dealing with nanosized systems, a fully quantum approach for the calculations of physical properties is necessary. Also for electronic transport the semiclassical description based on the Boltzmann theory breaks down and the behavior of conductors is no longer Ohmic. The electrons flow through an atomic sized contact ballistically and the resistance becomes independent from its length. A good framework to describe this phenomenon is the Landauer formalism [1,2,3].

In this chapter we introduce the method that we use to calculate electronic transport in nanoscaled systems [4,5]. The method is based on the Landauer formalism, which relates transport to the scattering properties of the studied structure, combined with an accurate description of the electronic structure provided by density functional theory (see Chap. 1). Our calculation scheme (as implemented in the WANT code [6]) uses a real-space Green’s function approach, expanding the Hamiltonian of the system into the maximally localized Wannier functions basis set that we have thoroughly described in Chap. 2.

3.1 Transport in nanostructures: the Landauer formalism

A macroscopic conductor is said to show Ohmic behavior if:

\[ C = \sigma \frac{W}{L} \]  

(3.1)

where \( C \) is the conductance, \( W \) is the section, \( L \) the length of the considered conductor and \( \sigma \) is the material-dependent conductivity. When the conduc-
Transport with maximally localized Wannier functions: the \( \text{WanT} \) method

Figure 3.1: System calculation scheme: conductor \( C \) connected to two semi-infinite leads \( L \) and \( R \).

In order to classify the transport regime of the studied system, three critical length scales are introduced, to be compared with the characteristic length \( L \) of the system \([1,2]\). The Fermi wavelength is the wavelength of the conducting electrons carrying current with energies close to the Fermi level: 
\[ \lambda_F = \frac{2\pi}{k_F}, \]
where \( k_F \) is the Fermi wavenumber. In metals \( \lambda_F \) is typically of the order of few Å, while in semiconductor it can be several nanometers.

The phase coherent length is the distance covered by a conduction electron before losing its phase:
\[ l_\phi = v_F\tau_\phi, \]
where \( v_F \) is the Fermi velocity. \( \tau_\phi \) is the phase coherence time: the time during which the phase of an electron is completely lost because of the interactions with dynamic scatterers, such as phonons, magnetic impurities and other conduction electrons. The mean free path is the distance covered by a conduction electron before losing its initial momentum through elastic or inelastic scattering events with static or dynamic scatterers respectively:
\[ l_m = v_F\tau_m, \]
where \( v_F \) is the Fermi velocity and \( \tau_m \) is the momentum relaxation time. Static scatterers are e.g. lattice defects, boundaries or impurities which do not destroy the electron phase. If \( L > l_m \), the transport is diffusive and if \( L > l_\phi \) is incoherent: This is the case of macroscopic Ohmic conductors, where the transport is both diffusive and incoherent \((L \gg l_m, l_\phi, \lambda_F)\). If \( L < l_\phi \) the transport regime is called coherent and in the case of \( L < l_m \) is ballistic. This is a case where the Landauer formalism well describes the transport phenomena: The energy is not dissipated and there are not scattering events in the conductor region and the conductance becomes independent of the conductor length. The nanojunctions investigated in this thesis correspond to a coherent elastic transport regime:
\[ \lambda_F \approx l_m < L < l_\phi. \]

The Landauer approach is based on a scheme where the studied system is divided into three parts: The conductor \((C)\) region, where the electrons travel, attached to two reservoirs (or leads) left \((L)\) and right \((R)\). This scheme is represented in Fig. 3.1. The conductance \( C \) is defined as the current \( I \) flowing through the conductor divided by the potential difference \( V \) between the two leads:
\[ C = \frac{I}{V}. \]
3.1 Transport in nanostructures: the Landauer formalism

Within the Landauer formulation, considering a one dimensional system, the current is supposed to flow through a region containing scatterers, where the incoming wave is partly reflected and partly transmitted from the right to the left lead. Thus the current turns out to be closely related to the scattering properties of the system and can be expressed as:

\[ I(V) = \int_{-\infty}^{+\infty} T(E, V)[f(E - \mu_L) - f(E - \mu_R)] \, dE, \quad (3.3) \]

where \( T(E, V) \) is the transmission function (or transmittance) of the scattering region, \( \mu_L \) and \( \mu_R \) are the chemical potentials of the leads L and R respectively (with \( eV = \mu_L - \mu_R \)) and \( f \) is the Fermi distribution function of the charge at the two leads, depending on the temperature of the reservoirs. This approach, whose formal details can be found in the original paper by Landauer [3] or in Refs. [1, 2], relates the conduction to the transmission efficiency through the scattering barrier. When dealing with ballistic transport, the only contributions are given by the scattering at the interfaces between conductor and leads.

In the limit of small bias and low temperatures the conductance takes the explicit form

\[ C = \frac{2e^2}{h} T(E_F), \quad (3.4) \]

where \( E_F \) is the Fermi energy.

In the case of ballistic transport in nanostructures the conductance results quantized, being \( G_0 = \frac{2e^2}{h} \) the quantum of conductance, and shows a characteristic step-like behavior: The number of the steps depends on how many channels are open (see Figure 3.2). The nanocontacts studied in this thesis are in a coherent transport regime: The resistance is due not only to the interfaces, but also to the elastic scattering of the electrons on the potential change in the conductor volume. The conductance thus results quantized but no longer step-like, because channels are not completely open or closed: The initial momentum of the electrons can be lost, but without loss of energy or phase.

In a multiterminal case the Büttiker formula [7,8] extends the original two-terminal Landauer formulation:

\[ T_{\alpha\beta,mn} = |t_{\alpha\beta,mn}|^2, \quad (3.5) \]

where \( t_{\alpha\beta,mn} \) describes the transmission probability from the channel \( m \) of the lead \( \alpha \) to the channel \( n \) of the lead \( \beta \). In the following we describe the calculation method based on the Landauer formalism, using Green’s functions on the maximally localized Wannier functions basis set, implemented in WantT code.
Transport with maximally localized Wannier functions: the WanT method

Figure 3.2: Step-like behavior of the conductance as a function of the bias, due to the quantization of the channels in a ballistic conductor [2].

3.2 Landauer formalism using Green’s functions

Considering a system composed of a conductor, $C$, connected to two semi-infinite leads, $R$ and $L$, as sketched in Figure 3.1, a fundamental result in the theory of electronic transport is the Landauer formula [3], introduced in section 3.1. In principle, we can compute the transmission function for a coherent conductor, starting from the knowledge of the scattering matrix, $S$. In principle, the scattering matrix can be uniquely computed from the solution of the Schrödinger equation and would suffice to describe the transport processes we are interested in this work. However, it is a general result of scattering theory that the elements of the $S$-matrix can be expressed in terms of the Green’s function of the conductor [1, 9, 10] which, in practice, can be sometimes simpler to compute.

Let us consider a physical system represented by a single-particle Hamiltonian $H$. The Green’s functions of the system can be defined as:

$$(\omega \pm i\eta - H) G(\omega) = I$$

where $I$ is the identity operator and $i\eta > 0$ is an infinitesimal imaginary part added to the energy to incorporate the boundary conditions into the equation. The solution with $+$ sign is the retarded Green’s function $G^r$, while the solution with $-$ sign is called advanced Green’s function $G^a$.

In the following we are going to restrict the discussion to discrete systems that we can describe by ordinary matrix algebra. More precisely, we are going to work with matrices representing a physical system in the basis of localized electronic orbitals. It includes in particular the tight-binding model. For a discrete media, the Green’s function defined in Eq. (3.6) is then
the inverse of the \((\omega - H)\) matrix. To simplify the notation, we drop the exponents \(\{a, r\}\) referring to advanced and retarded functions and include the \(\pm i\eta\) factor in \(\omega\). For an open system, consisting of a conductor and two semi-infinite leads (see Fig. 3.1), the above Hamiltonian and Green’s function can be partitioned into sub-matrices that correspond to the individual subsystems:

\[
\begin{pmatrix}
g_L & g_{LC} & g_{LCR} 
g_{CL} & g_C & g_{CR} 
g_{LRC} & g_{RC} & g_R
\end{pmatrix} = \begin{pmatrix}
\omega - h_L & -h_{LC} & 0 
-h_{LC}^\dagger & \omega - H_C & -h_{CR} 
0 & -h_{CR}^\dagger & \omega - h_R
\end{pmatrix}^{-1},
\]

(3.7)

where the matrix \((\omega - H_C)\) represents the finite “isolated” conductor (with no coupling elements to the leads), \((\omega - h_{\{R,L\}})\) represent the semi-infinite leads, and \(h_{CR}\) and \(h_{LC}\) are the coupling matrices between the conductor and the leads. As a convention, we use lower case letters for (semi-)infinite matrices and upper case for finite dimension matrices. In Eq. (3.7) we have made the assumption that there is no direct interaction between the left and right leads. From this equation it is straightforward to obtain an explicit expression for \(G_C\):

\[
G_C(\omega) = [\omega - H_C - \Sigma_L(\omega) - \Sigma_R(\omega)]^{-1}
\]

(3.8)

where the finite dimension matrices

\[
\Sigma_L(\omega) = h_{LC}^\dagger(\omega - h_L)^{-1}h_{LC}, \quad \Sigma_R(\omega) = h_{RC}^\dagger(\omega - h_R)^{-1}h_{RC}^\dagger
\]

(3.9)

are defined as the self-energies due to the semi-infinite leads. These terms can be viewed as effective Hamiltonians that arise from the coupling of the conductor with the leads. The coupling functions \(\Gamma_{\{L,R\}}(\omega)\) can then be obtained as \[1\]:

\[
\Gamma_{\{L,R\}} = i \left[ \Sigma_{\{L,R\}}^a(\omega) - \Sigma_{\{L,R\}}(\omega) \right],
\]

(3.10)

where the advanced self-energy \(\Sigma_{\{L,R\}}^a\) is the Hermitian conjugate of the retarded self-energy \(\Sigma_{\{L,R\}}\). The core of the problem lies in the calculation of the self-energies of the semi-infinite leads. It is well known that any solid (or surface) can be viewed as an infinite (semi-infinite in the case of surfaces) stack of principal layers with nearest-neighbor interactions \[11\]. This corresponds to transforming the original system into a linear chain of principal layers. For a lead-conductor-lead system, the conductor can be considered as one principal layer sandwiched between two semi-infinite stacks of principal layers.

The transmission function can then be expressed in terms of the Green’s functions of the conductor and the couplings of the conductor to the leads in a simple manner using the Fisher and Lee formula \[9\]:

\[
T(\omega) = \text{Tr} [\Gamma_L G_C^r \Gamma_R G_C^a].
\]

(3.11)
Figure 3.3: Schematic definitions for Hamiltonian block matrices used in transport calculations.

Here $G^{\{r,a\}}$ are the retarded and advanced Green's functions of the conductor, and $\Gamma^{\{L,R\}}$ are functions that describe the coupling of the conductor to the leads.

The WanT method

The calculation method described above has been implemented in WanT, which is an open-source, GNU General Public License suite of codes that provides an integrated approach for the study of coherent electronic transport in low-dimensional, extended nanostructures. The core methodology combines the state-of-the-art density functional theory (DFT), plane-waves, pseudopotential calculations, described in Chap. 1, with the Green's functions method based on the Landauer formalism to calculate quantum conductance. The essential connection between the two, and a crucial step in the calculation, is the use of the maximally-localized Wannier function representation (see Chap. 2) to introduce naturally the ground-state electronic structure into the lattice Green's function approach. Moreover, the knowledge of Wannier functions allows for a direct link between the electronic transport properties of the device with the nature of the chemical bonds, providing insight into the mechanisms that govern electron flow at the nanoscale. The scheme at the base of the WanT method was originally described in Ref. [4]. The extension to PAW and ultrasoft pseudopotentials can be found in Ref. [12], also reported in Chap. 2.

Calculations of the quantum conductance are based on a recently developed efficient method for evaluating quantum transport in extended systems [5][13][14]. This method is applicable to any Hamiltonian that can be expanded within a localized-orbital basis and can be used as a general theoretical scheme for the computation and analysis of the electrical properties of nanostructures.
3.2 Landauer formalism using Green’s functions

Transmission through a bulk system.

When using Eqs. (3.10) and (3.11), the core of the problem lies in the calculation of the self-energies of the semi-infinite leads. It is well known that any solid (or surface) can be viewed as an infinite (semi-infinite in the case of surfaces) stack of principal layers with nearest-neighbor interactions [11]. This corresponds to transforming the original system into a linear chain of principal layers. For a lead-conductor-lead system, the conductor can be considered as one principal layer sandwiched between two semi-infinite stacks of principal layers.

Within the principal layer approach, the matrix elements of Eq. (3.6) between layer orbitals yield a series of matrix equations for the Green’s functions:

\[
(\omega - H_{00}) G_{00} = I + H_{01} G_{10} \quad (3.12)
\]
\[
(\omega - H_{00}) G_{10} = H_{01}^\dagger G_{00} + H_{01} G_{20}
\]
\[
\vdots
\]
\[
(\omega - H_{00}) G_{n0} = H_{01}^\dagger G_{n-1,0} + H_{01} G_{n+1,0}
\]

where the finite dimension matrices \( H_{nm} \) and \( G_{nm} \) are formed by the matrix elements of the Hamiltonian and Green’s function between the layer orbitals. We assume that in a bulk system \( H_{00} = H_{11} = \ldots \) and \( H_{01} = H_{12} = \ldots \). Following Refs. [15, 16], this chain can be transformed in order to express the Green’s function of an individual layer in terms of the Green’s function of the preceding (or following) one. This is done via the introduction of the transfer matrices \( T \) and \( \tilde{T} \), defined such that \( G_{10} = TG_{00} \) and \( G_{00} = \tilde{T} G_{10} \).

Using these definitions, we can write the bulk Green’s function as [17]:

\[
G(\omega) = (\omega - H_{00} - H_{01} T - H_{01}^\dagger \tilde{T})^{-1}. \quad (3.13)
\]

The transfer matrix can be easily computed from the Hamiltonian matrix elements via an iterative procedure, as outlined in [15, 16]. In particular \( T \) and \( \tilde{T} \) can be written as:

\[
T = t_0 + \tilde{t}_0 t_1 + \tilde{t}_0 \tilde{t}_1 t_2 + \ldots + \tilde{t}_0 \tilde{t}_1 \tilde{t}_2 \cdots t_n, \quad (3.14)
\]
\[
\tilde{T} = \tilde{t}_0 + t_0 \tilde{t}_1 + t_0 t_1 \tilde{t}_2 + \ldots + t_0 t_1 t_2 \cdots \tilde{t}_n,
\]

where \( t_i \) and \( \tilde{t}_i \) are defined via the recursion formulas:

\[
t_i = (I - t_{i-1} \tilde{t}_{i-1} - \tilde{t}_{i-1} t_{i-1})^{-1} t_{i-1}^2, \quad (3.15)
\]
\[
\tilde{t}_i = (I - t_{i-1} \tilde{t}_{i-1} - \tilde{t}_{i-1} t_{i-1})^{-1} \tilde{t}_{i-1}^2,
\]

and

\[
t_0 = (\omega - H_{00})^{-1} H_{01}^\dagger, \quad (3.16)
\]
\[
\tilde{t}_0 = (\omega - H_{00})^{-1} H_{01}.
\]
The process is repeated until $t_n, \tilde{t}_n \leq \delta$ with $\delta$ arbitrarily small.

If we compare Eq. (3.13) with Eq. (3.8), in the hypothesis of leads and conductors being of the same material, we can identify one principal layer of the bulk system with the conductor $C$, so that $H_{00} \equiv H_C$. In particular, by comparing with Eq. (3.8), we obtain the expression of the self-energies of the conductor-leads system:

$$\Sigma_L = H_{01}^T, \quad \Sigma_R = H_{01}T. \quad (3.17)$$

The coupling functions are then obtained [5] from the sole knowledge of the transfer matrices and the coupling Hamiltonian matrix elements: $\Gamma_L = -\text{Im}(H_{01}^T)$ and $\Gamma_R = -\text{Im}(H_{01}T)$.

**Transmission through a left lead-conductor-right lead (LCR) system.**

The procedure outlined above can also be applied to the case of electron transmission through one or more interfaces, between different media. For the calculation of conductances in realistic experimental geometry, the method can be expanded to the general configuration of a Left-lead-Conductor-Right-lead (LCR) systems — as displayed in Fig. 3.1. To study this case we make use of the Surface Green’s Function Matching (SGFM) theory, pioneered by [17].

We have to compute the Green’s function $G_I$, where the subscript $I$ refers to the interface region composed of two principal layers — one in each media — (L, C, R in our case). Using the SGFM method, $G_I$ is calculated from the bulk Green’s function of the isolated systems, and the coupling between the two principal layers at the two sides of the interface. Via the calculation of the transmitted and reflected amplitudes of an elementary excitation that propagates from one medium to another, it can be shown that the interface Green’s function obeys the following secular equation [17]:

$$G_{LCR} = \begin{pmatrix} G_L & G_{LC} & G_{LR} \\ G_{CL} & G_C & G_{CR} \\ G_{RL} & G_{RC} & G_R \end{pmatrix} = \begin{pmatrix} \omega - H_{00}^L - (H_{01}^L)^T \\ -H_{CL} & \omega - H_C \\ 0 & -H_{00}^R - H_{01}^R T \end{pmatrix}^{-1} \quad (3.18)$$

where $H_{nm}^{(L,R)}$ are the block matrices of the Hamiltonian between the layer orbitals in the left and right leads respectively, and $T_{(L,R)}$ and $T_{(L,R)}$ are the appropriate transfer matrices. The latter are easily computed from the Hamiltonian matrix elements via the iterative procedure already described in the bulk case. Correspondingly, $H_{LC}$ and $H_{CR}$ are the coupling matrices.
3.2 Landauer formalism using Green’s functions

between the conductor and the leads principal layers in contact with the conductor. A scheme of the system, where the meaning of the Hamiltonian blocks is underlined, is reported in Fig. 3.3. It is straightforward to obtain in the form of Eq. (3.8), \( G_C = (\omega - H_C - \Sigma_L - \Sigma_R)^{-1} \), where \( \Sigma_L \) and \( \Sigma_R \) are the self-energy terms due to the semi-infinite leads, and identify \([5]\):

\[
\begin{align*}
\Sigma_L(\omega) &= H_L^\dagger [\omega - H_{00}^L - (H_{01}^L)^\dagger T_L]^{-1} H_{LC}, \\
\Sigma_R(\omega) &= H_{CR} [\omega - H_{00}^R - H_{01}^RT_R]^{-1} H_{CR}^\dagger.
\end{align*}
\tag{3.19}
\]

The transmission function in the LCR geometry can then be derived from Eqs. (3.11) and (3.10). The knowledge of the conductor’s Green’s function \( G_C \) gives also direct information on the electronic spectrum of the system via the spectral density of states:

\[
N(\omega) = -\frac{1}{\pi} \text{Im} \text{Tr} G_C(\omega).
\tag{3.20}
\]

Once we have derived the transmission function as described above [Eq. (3.11)], we can calculate the current flowing through the system in the zero–temperature and small bias limit:

\[
I(V) = \int_{-\infty}^{+\infty} T(E)[f(E - \mu_L) - f(E - \mu_R)] dE,
\tag{3.21}
\]

where \( T \) is independent of the bias.

**Real space hamiltonians**

In order to calculate the conductance according to the above prescriptions, we need in input the matrix elements of the Hamiltonian calculated on a localized basis: in our case, it is the minimal basis of the maximally-localized WFs introduced in Chap. 2. Assuming a BZ sampling fine enough to eliminate the interaction with the WF periodic images, we can simply compute the WF Hamiltonians \( H_{ij}(R) = \langle \emptyset | H | R | j \rangle \), from the unitary rotations \( U^{(k)} \) obtained in the localization procedure.

In the Bloch representation we have by definition \( H_{mn}(k) = \epsilon_{mk} \delta_{m,n} \). Moving to the Wannier basis, first we have:

\[
H^{(\text{rot})}(k) = U^{(k)\dagger} H(k) U^{(k)}.
\tag{3.22}
\]

Next we Fourier transform \( H^{(\text{rot})}(k) \) into the corresponding set of Bravais lattice vectors \( \{R\} \):

\[
H_{ij}(R) = \frac{1}{N_{kp}} \sum_k e^{-ik\cdot R} H_{ij}^{(\text{rot})}(k).
\tag{3.23}
\]
Truly three-dimensional systems

Up to this point, we have assumed a one-dimensional chain of principal layers; the extension to a truly three-dimensional case is straightforward using Bloch functions in the directions perpendicular to the transport axis. The introduction of the principal layer concept implies that along the direction of the layer expansion the system is described by an infinite set of $k_\perp$, while $k_\parallel$ are still good quantum numbers for the problem. The above procedure effectively reduces the three-dimensional system to a set of non-interacting linear-chains, one for each $k_\parallel$. We can then use the usual $k$-point summation techniques to evaluate the quantum conductance:

$$T(\omega) = \sum_{k_\parallel} w_{k_\parallel} T_{k_\parallel}(\omega)$$

(3.24)

where $w_{k_\parallel}$ are the relative weights of the different $k_\parallel$ in the irreducible wedge of the surface Brillouin zone [18].

3.3 The smearing issue in Green’s functions

When summing over the $k_\parallel$, we have to introduce a smearing, as is usually done in electronic structure calculation to numerically perform integrations over the Brillouin zone (see Chap. 1) [19,20,21].

In the case of Eq. (3.24) we have a discretized mesh only on the plane perpendicular to the transport axis. However, along the transport direction too, an effective smearing is introduced: The leads self-energies employed in the calculation of the Green’s function are non-Hermitian operators, which cause the broadening of the energy levels. The smearing is thus treated in an anisotropic way over the plane and along the transport axis. On the extended surface, to have the same accuracy as along the transport direction, a very large number of $k_\parallel$-points should be used, of the order of $1/\delta$, where $\delta$ indicates the broadening measure.

In order to reduce the required number of $k_\parallel$-points, we have considered the smearing issue from the very beginning, focusing on how it enters into the Green’s function calculation. To do this, a methodological development, then the implementation of new features in the WanT code, have been necessary, where I have given my personal contribution.

Different smearing types

The smearing functions most commonly used in electronic structure calculations have been considered: Lorentzian, Gaussian, Methfessel–Paxton [20].
3.3 The smearing issue in Green’s functions

Figure 3.4: Different smearing functions: Lorentzian, Gaussian, Methfessel–Paxton, Marzari–Vanderbilt. All the curves are calculated with the same broadening ($\delta = 0.1\text{eV}$) and are normalized to 1.

and Marzari–Vanderbilt cold smearing \cite{21} respectively:

\begin{align*}
  f_L(x) &= \frac{1}{\pi} \frac{1}{x^2 + 1}, \\
  f_G(x) &= \frac{1}{\sqrt{\pi}} e^{-x^2}, \\
  f_{MP}^{(1)}(x) &= \frac{1}{\sqrt{\pi}} \left( \frac{3}{2} - x^2 \right) e^{-x^2}, \\
  f_{MV}(x) &= \frac{1}{\sqrt{\pi}} e^{-(x - \frac{1}{\sqrt{2}})^2 (2 - \sqrt{2}x)}.
\end{align*}

Eq. (3.27) is only the first order of the expression of Methfessel–Paxton smearing function: It can be expanded to further orders according to Ref. \cite{20}. In Fig. 3.4 the curves representing the different smearing forms are compared, with the same broadening $\delta$ and all equally normalized. Looking at the shape of the different functions, it is easy to notice that, with respect to the Lorentzian one, the other curves are narrower and they have much shorter tails: This means that they introduce less spurious interaction effects when used in $k$–points summations. They are thus better candidates to be employed in calculations; in fact we can use a larger broadening, keeping the same accuracy with a smaller number of $k_{\parallel}$–points.
Smearing in Green’s functions

The different smearing types are introduced in the Green’s functions, starting from the spectral representation:

\[ G_{nk}(\omega) = \int d\epsilon \frac{A_{nk}(\epsilon)}{\omega - \epsilon + i0^+}, \]  
\[ A_{nk}(\omega) = -\frac{1}{\pi} \text{Im}[G_{nk}(\omega)]. \]

\( A_{nk}(\omega) \) is the spectral function, labeled via the two quantum numbers \( n \) and \( k \). The smeared spectral function can be written as

\[ A_{nk}^S(\omega) = \frac{1}{\delta} f \left( \frac{\omega - \epsilon_{nk}}{\delta} \right), \]

where \( f \) can take one of the forms proposed above [Eqs. (3.25)–(3.28)] and \( \delta \) is the broadening parameter.

We can thus give a general expression of the smeared Green’s function, which depends both on the smearing function shape \( f \) and on the broadening value \( \delta \):

\[ G^S(\omega) = F^S(\omega - H), \]

where \( S = \{\delta, f\} \). Remembering the standard expression of the Green’s function, the introduction of a smearing can be interpreted as an effective self–energy term:

\[ G^S(\omega) = \frac{1}{\omega - H - \Sigma^S(\omega)}, \]

\( \Sigma^S(\omega) \) is a non–Hermitean operator, in general dynamic.

We can easily verify that including in the \( G^S \) a Lorentzian smearing, we re–obtain the well known standard expression for the Green’s function as a pole with finite \( \delta \):

\[ G^S(\omega) = F^S(\omega - H) = (\omega - H + i\delta)^{-1}. \]

In this case the effective smearing self–energy is simply \( \Sigma^S = -i\delta \), which is anti–Hermitean, static and short ranged.

Smearing in transport

Including the smearing self–energy into the Green’s functions calculation in a Left–lead–Conductor–Right–lead (LCR) system like that shown in Figure 3.1 we have

\[ \omega - H^S(\omega) = \omega - H - \Sigma^S(\omega), \]
Figure 3.5: Monoatomic gold chain: density of states and transmittance. The calculations have been performed with Lorentzian and Gaussian smearing with $\delta = 0.05\text{eV}$. The reference curves are calculated with $\delta = 0.001\text{eV}$.

and equation \((3.7)\) becomes

\[
\begin{pmatrix}
g_L & g_{LC} & g_{LCR} \\
g_{CL} & G_C & g_{CR} \\
g_{RCL} & g_{RC} & g_R
\end{pmatrix}
= 
\begin{pmatrix}
\omega - h_L - \Sigma_L^S & \omega - h_{LC} - \Sigma_{LC}^S & 0 \\
- h_{CL} - \Sigma_{CL}^S & \omega - h_C - \Sigma_C^S & - h_{CR} - \Sigma_{CR}^S \\
0 & - h_{RC} - \Sigma_{RC}^S & \omega - h_R - \Sigma_R^S
\end{pmatrix}^{-1}.
\] \(3.36\)

The conductor Green’s function is still expressed as \((3.8)\), where the leads self–energy terms include the chosen smearing type.

Some tests have been performed to check the reliability of our implementation. In Figure 3.5 is reported the example of transport in a monoatomic gold chain calculated using Lorentzian and Gaussian smearing. Here we do not have parallel $k$–points and the system is truly one–dimensional. We thus expect the well known Van Hove singularities in the spectral density of states, calculated according to \((3.20)\). If we compare the obtained results to a reference curve calculated with a very small broadening, we see that, using the same $\delta$, the Gaussian smearing is better behaved than the Lorentzian one, in the sense that it is in a better agreement with the reference data. Similar considerations can be done for the conductance, whose step–like behavior is better reproduced by using the Gaussian smearing.

A second test here reported is the calculation of the bulk conductance in
Figure 3.6: Silicon bulk transport: density of states and conductance. The calculations have been performed with Gaussian smearing with $\delta = 0.05eV$. Increasing the number of $k_\parallel$-points the convergence to the reference shaded curve (resulting from an accurate PW calculation) is improved. In the lowest panel: comparison between Gaussian and Lorentzian smearing on a 16 x 8 $k_\parallel$-points mesh, with $\delta = 0.05eV$. 
3.3 The smearing issue in Green’s functions

silicon. In Figure 3.6, we notice that the use of a converged $k_\parallel$-points mesh is necessary to obtain the correct features of this truly three-dimensional system. Using a Lorentzian smearing with the same $\delta$, the calculated behavior of the density of states is incorrect, in particular the band gap results closed.

It is worth remembering that the use of a good smearing function allows to obtain an accurate convergence with a reduced number of $k_\parallel$-points. This is the reason for which it is so crucial to have a reliable implementation of the different smearing types when using the Green’s function approach to calculate the transport properties in truly three-dimensional systems. It is thus possible to choose the most convenient smearing function, to find a good balance between accuracy and computational cost.

Bibliography


Transport with maximally localized Wannier functions: the \textsc{WanT} method


Chapter 4

Applications I: Hybrid silicon–organic interfaces

The adsorption of molecules on semiconductor substrates has recently been the subject of intensive investigation, both because of the intrinsic physical and chemical properties of the hybrid interfaces and for the prospective applications in the emerging field of the nanotechnology [1, 2, 3, 4, 5, 6, 7]. Specific complex molecules are considered good candidates as basic building blocks for molecular electronics and nanomechanical devices [6]. The study of molecule/substrate interfaces, both with metals and semiconductors, is fundamental to realize good conductor/lead contacts [8, 9]. In general, molecular ordering on a surface is controlled by a delicate balance between intermolecular forces and molecule–substrate interactions [3, 10, 11, 12]. In the pursuit of studying these topics, the first point to be solved is the characterization of the adsorption mechanism of a single molecule on the selected surface: Several studies have indicated that surfaces do not always behave as static templates upon molecular adsorption, but they interact with molecules in a wide range of possible scenarios (chemisorption, physisorption, weak coupling etc.), depending on the specific choice of the pristine subsystems [1, 13]. Furthermore, increasing the adsorbate dosage, the surface may rearrange dramatically to accommodate different molecular species, as well as it may drive the formation of supramolecular adlayer with specific spatial arrangement.

Most of the studies in the literature deal with silicon surfaces, for its straightforward technological use, based on the thorough theoretical and experimental knowledge of this material, acquired during years. Moreover, functionalization of silicon substrates allows for stable covalently bonded surfaces [2, 14, 15, 16]. Among the silicon surfaces, the H:Si(100) and the H:Si(111) are often used by the experimentalists, for their easy production with atomic flatness: Several examples are given in the literature of functionalization of these surfaces with organic (both aliphatic and aro-
matic) molecules as a possible route for designing new nanodevices.

In this chapter we characterize two molecule/silicon interfaces from a microscopic point of view by means of fully first-principles calculations, based on the plane-wave pseudopotential density functional theory approach, described in Chap. 1 and using maximally localized Wannier functions (see Chap. 2). For both systems, we deeply characterize the electronic structure of the interface and the adsorption mechanism and, in the case of the symmetrically bonded interface presented in Sec. 4.2, we directly calculate the quantum transport properties of the molecules in the lead/conductor/lead model device, using the WANT method illustrated in Chap. 3.

4.1 First-principles investigation of silicon surfaces: chemisorption of unsaturated carboxylic acids

Semiconductor surfaces functionalization through organics is seen as a feasible way to control and modify the materials properties, in order to exploit new functionalities given by organic assembling or adsorption of special molecules on surfaces. For some applications such as subsequent layering or specific sensing functionalities, an active outer surface is required which can be made using carboxylic terminated molecules. We theoretically study the chemisorption of \( \text{CH}≡\text{C-CH}_2\text{-COOH} \) molecules on the H:Si(100) surface, analyzing different configurations of the molecules on the surface, all realized by chemical bonding through the alkyne tail. We find several stable chemisorbed structures: a single Si-C and a double Si-C-Si bridges and a third possible anchorage Si-C-C-Si.

For the three proposed systems, we thoroughly analyze the electronic structure, in terms of directional average electrostatic potential, Löwdin charges, total and projected density of states (DOS and PDOS), charge density and relevant electronic states. All the calculations are performed within the density functional theory plane wave framework, using ultrasoft pseudopotentials in a supercell approach. The single–bonded configuration results very stable, but the most stable one is the Si-C-Si (with a not so relevant difference in binding energy).

Among the anchorage addressed in this work, the Si-C-Si one is unfavored: However it is structurally very interesting because characterized by drastic changes in the surface geometry. We thus focus a deeper analysis on this ”defected” structure. The prominent surface defects are two: a dangling bond localized at a subsurface Si atom and a shared proton between two surface Si atoms (as found for the metastable illuminated porous Si surface or as a stable center in amorphous silicon).
4.1 First–principles investigation of silicon surfaces: chemisorption of unsaturated carboxylic acids

Since the structural defect would be a plausible trap for carriers for this strongly disrupted surface, we also consider the same system in the case of a doped substrate. We select boron, since it is widely used for p-type doping in Si device fabrication [20].

From a peak just above the Si valence top in the DOS of the intrinsic Si-C-Si system, it results evident that hole and electron traps are introduced in the energy gap region. Considering the same configuration with doped substrate, the defect peak is merged into the acceptor band and spread closer to the valence band. We also perform an analysis of Löwdin charges, confirming that the Si-C-Si configuration deeply affects the electronic structure of the interface.

As a further investigation step of the electronic structure of the defected configuration, we compute the maximally localized Wannier functions (MLWF), starting from the Bloch states as described in Chap. 2. MLFWs provide a meaningful picture of the nature of chemical bonds: We compare a typical Si-Si bulk bond and a Si-H surface bond with the distribution of charge (showing the isosurfaces of charge density) close to the atoms involved in the defected structure. The concentration of charge confirms the presence of the dangling bond on a subsurface Si atom and the picture of the shared proton with charge localized on the H atom belonging to the Si-H-Si complex. This last analysis has been possible, exploiting the localization properties of MLWFs: they contain the information about the chemical bond coming from the Bloch states, but they are localized and allow to clearly visualize the distribution of charge.

To have further details of the calculations and results we refer the reader to the paper that follows.
First-principles investigation of functionalization-defects on silicon surfaces

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Abstract

We present a theoretical study of chemisorption of CH≡C–CH$_2$–COOH molecules on the H:Si(100) surface. We perform simulations for different chemisorbed configurations, attained by reactions through the alkyne tail. We use the periodic slab approximation for the extended surface, within ab initio density functional theory, and analyse results from several different approaches. We conclude that structures composed of single Si–C bridges are very stable, while a previously proposed structure, with a double Si–C–Si bridge, should be metastable on the flat surface, and introduce electron and hole traps in the Si band gap.

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Keywords: Density functional theory; Silicon (100) surface; Organic molecules; Chemisorption; Surface functionalization

Surface functionalization through organics [1–9] is becoming the standard route to provide new functionalities to semiconductors, be it for devising new dielectric interface layers, or in view of novel hybrid (bio)molecular devices. In particular, for subsequent layering or specific sensing functionalities it is interesting to obtain an active outer-surface, as can be offered by carboxylic terminated molecules [6,8]. On the other hand, Si-based technology makes this material the ideal candidate for exploiting new opportunities offered by organic assembling, and indeed the absorption of special molecules on Si surfaces is beginning to be studied in detail. However, still little is known about the electronic properties induced by the organic/inorganic interface, and the presence of electronic states in the gap are of major relevance to the operation of devices [10,11]. In this sense, working with pre-hydrogenated Si surfaces may help as they should be intrinsically gap-level free, and also more resilient to oxidation than clean surfaces.

Both Si–O–C and Si–C anchorages can be formed between organic molecules and Si substrates [12,13,14,2,15–20,7,21,9], and in particular for bifunctional molecules there is intrinsic competition between anchorage mechanisms. We focus here on the electronic properties of Si–C bonded $\alpha$-carboxylic-$\alpha$-alkynes on di-hydride terminated Si(100) surfaces, that at once would start from a well known, technologically relevant Si substrate [22], and might offer at the outer surface the reactive carboxylic head. Furthermore, the reaction of a $\alpha$-alkyne with H:Si substrates can follow several paths, producing different bonding configurations at the interface, and thus different electronic properties: the presence of the alkenyl-type chain (Si–CH=CH–R), that characterizes the singly Si–C bonded systems, can induce the formation of a second Si–C bond per interacting alkyne through opening of the residual double bond. One of the resulting configurations is reached by the bonding of the second C-atom to a neighbor Si surface atom, Si–C–C–Si, while a second possibility involves bonding of the same first C-atom of the chain to two surface Si...
atoms, Si–C–Si. Reaction of \( \omega \)-alkynes on this H:Si(100) surface has already been studied experimentally [23,18,9,21], however, since the Si(100) is not a normal cleavage surface, the initial H:Si(100) surface configuration may be strongly dependent on preparation procedure [24,25], and analysis of experimental results has to be very careful. Indeed the actual structure of the interface layer was not univocally recognized from experiments, also due to the reconstruction- and technique-dependence of alkyne hydrosilation. While the authors of Ref. [23] find almost complete suppression of double C–C bonds, recent studies in Ref. [9] reach the opposite conclusion.

Concerning theoretical studies of these specific systems, previous cluster model results [23,9] pointed to the greater stability of the Si–C–Si configuration, but did not address the resulting electronic structure. We here report theoretical results for the three carbon-bonded configurations, obtained by means of accurate ab initio supercell-based calculations. We found that the most stable configuration is Si–C–C–Si bonded, while the Si–C–Si configuration is metastable, although still exothermic [26]. We investigate the resulting structures in terms of directional averages of the electrostatic potential, group charges, densities of states (DOS), Wannier and Bloch states. In particular we will show that the Si–C–Si configuration introduces hole and electron traps in the energy gap, thus we also investigate the same interface in the case of a p-doped substrate, similar to most actual experimental conditions [6].

1. Methodology

We adopt ab initio density-functional theory (DFT), implemented with periodic boundary conditions and a plane-wave basis set. This scheme allows one to take into account the extended nature of the surface electronic states, which can critically affect both reaction mechanism and surface structure. We focus here on the H:Si(100)1 × 1 reconstruction [27] of the hydrogenated surface, characterized by dihydride terminations for the surface Si atoms. The intrinsic H:Si(100) 1 × 1-reconstructed surface is simulated using a supercell with four Si atoms per layer (two 1 × 1 unit cells), six Si layers, H-saturation (dihydride) on both sides, and with a vacuum layer of 15 Å. The cell dimensions are 10.933 × 5.466 × 27.332 Å\(^3\). For the functionalized surfaces one slab side is reacted with the target molecule, reproducing the 0.5 ML coverage regime [28]. We simulate p-doping by introducing a boron substitutional impurity, so that we still have a neutral cell, and investigate the effect of doping on both electronic and structural properties. The simulation cell for the doped system contains 11 Si layers, and a vacuum layer of 22 Å; the B atom is substitutional in the seventh layer from the reacted surface. The first nine Si layers are free to relax, and the last two layers are kept fixed.

All initial configurations, used as input for ab initio DFT structural relaxations, were obtained through empirical molecular mechanics simulations using the well-estab-

lished PCFF parametrization [29]. All DFT calculations are performed with the PWSCF code [30], using “ultrasoft” pseudopotentials [31] and the PW91 [32] generalized gradient approximation for the exchange and correlation functional. The wave functions (density) cutoff is 25 (200) Ry, with 16 irreducible Monkhorst–Pack special k-points [33] in the first Brillouin zone. The systems are relaxed until the forces on all free atoms vanish within 0.005 eV/Å.

2. Results

Several chemisorption schemes for the CH≡C–CH\(_2\)–COOH molecule at the H:Si(100)1 × 1 surface (see Fig. 1) are possible: in Fig. 2, the stable alkyne-tail reacted configurations are summarized, indicated as Si–C, Si–C–C–Si and Si–C–Si, together with the corresponding binding energies for the intrinsic substrate. As indicated, we find that the single-bonded configuration is already very stable, and may explain the results found by Cerofolini and coworkers [9]: although 0.36 eV more can be gained by a second bond in the Si–C–C–Si configuration, the difference is not so relevant and we recall that there may be barriers for the rearrangement. On the other hand, the configuration with bonding of a single C-atom to two surface Si-atoms is definitely unfavored, by \( \approx 0.8 \) eV, with respect to the singly bonded configuration. The analysis of this configuration,
the focus of this paper, would thus seem superfluous were it not for some specific characteristics that warrant the probable occurrence of similar centers in more disordered situations. Indeed, as we argue below, the results of Refs. [28,21] would seem to indicate that, in a “softer” environment, the structure could have a relevant presence.

The Si–C–Si system focused here is characterized by drastic changes in the geometrical structure: the energetic consequences of such surface deformations could not be gauged within a cluster approach [23,21], since it does not properly take into account fields of the periodic surface. We note that the two Si–C bonds are much shorter than the regular Si–Si bond, and generally induce a rearrangement of the surrounding atoms. As a consequence, we see two prominent surface defects: a dangling bond localized at a subsurface Si atom, SiDB, and a shared proton structure (see Fig. 3).

In Fig. 3, we also illustrate the shared proton Si$^0$–H–Si$^0$ structure. These two Si surface atoms would have been each di-hydrogen saturated, however in the final structure the bond-breaking causes the abstraction, without a relevant energy barrier, of the closest surface H atom to saturate the second dangling bond, that would otherwise arise, at the carbon-bonded atom (Si$_1$ in the figure). The resulting surface structure of a shared proton Si$^0$–H–Si$^0$ thus mini-

mizes the number of dangling bonds and consequently stabilizes the system. The H atom is found in the midpoint between Si$^0$ and Si$^0$, as found for the metastable illuminated porous-Si surface [38], and as a stable center in amorphous Si [39]. Since such a strongly disrupted surface defect would be a plausible trap for carriers, as we discuss below, we considered also the same system, in the case of a doped substrate. We selected boron, since it is widely used for p-type doping in Si device fabrication [40]. We find that the presence of a B atom deep inside the substrate does not substantially modify the geometrical structure at the interface: a slightly weaker sharpening of the SiDB center and a non-perfectly-symmetrical position of the shared proton are the main differences induced on the surface by the different electronic structures.

### 2.1. Electronic properties

The Si–C bonded interfaces are investigated in terms of average electrostatic potentials, Löwdin charges, total and projected density of states (DOS and PDOS, respectively), charge density and relevant electronic states. We first analyse the overall behavior of the electrostatic potential investigating its average decay along the $z$ direction. Fig. 4 represents the macroscopic average of the electrostatic potential (the sum of the Hartree and external potentials) for the hybrid systems and for the unreacted H:Si surfaces [41]. The trend of $V_{\text{macro}}$ at the outside of the surface (the last Si layer is marked by a dashed line in Fig. 4) shows the differences in charge distribution of the hybrid systems with respect to the clean H:Si surface. A well-defined step is observed in the Si–C–Si potential outside the slab, pointing to the presence of an additional layer at interface. The two carbon atoms closest to the surface, indeed, are in

---

1 The experimental average extent of this defect ($\geq 3 \, \text{Å}$) in a-Si:H measured on Ref. [34] is consistent with our computational estimate, see Fig. 3.

2 The average potential $V_{\text{macro}}$ has been calculated by integrating over the plane of the surface and then performing a second running average in the (100) direction with a period equal to the bilayer distance.
this configuration in the same plane and form a well-defined layer parallel to the Si substrate. More spatially extended interface regions are found for the Si–C and Si–C–Si configurations: in particular for the Si–C–Si bonded system the potential tail spreads up and reaches an extent of more \( \approx 6.8 \text{ Å} \), indicating the presence of a very reactive area. We also remark that, of the three configurations, the Si–C–Si is the only one to introduce a perturbation of the averaged potential inside the slab (see Fig. 4), confirming the strong surface structure deformation, and signaling the presence of defects and roughness.

A microscopic description of these perturbations can more easily be obtained through the analysis of Löwdin charges of interface atoms. The doubly Si–C bonded interfaces are characterized by a high electron density on the C atoms closest to the surface (see Fig. 5); these results are in accord with X-ray reflectivity data \([28]\) which indeed points to the presence of a strongly negative interface charge. The excess electrons on the C atoms are partly compensated by charges on the bonded Si atoms, that are slightly more positive, by \( \approx 0.2e \), than the usual surface Si for this surface. We find an excess charge of \( \approx 1.20e \) for the Si–C–Si system around the SiDB center, signaling the presence of a charged dangling bond. On the other hand, it is interesting to note that the positive charge on the Si’ and Si’’ atoms results perfectly symmetrical, as compatible with the shared proton character. In the case of the doped system, Löwdin charges attest a quite identical charge distribution at the interface, according to the surface character of the defect levels. Summarizing results up to now, we can see that the Si–C–Si configuration deeply affects the geometrical and electronic structure of the interface. Arriving now at the discussion of the effect on the band-edge electronic structure, we plot in Fig. 6 the DOS of the Si–C–Si intrinsic and doped systems, in the energy region down to the bottom of the valence band of Si (molecular semi-core levels are also seen deeper in energy \([20]\), but are not relevant to the discussion here). The origin of the energy scale corresponds to the valence band top of the clean hydrogenated surface. We aligned the hydrogenated and functionalized surfaces in the intrinsic case through the H peak of the unreacted surface. We see clearly, in the case of the intrinsic substrate shown in Fig. 6(a), that hole and electron traps are introduced in the energy gap region: the peak just above the Si valence band top corresponds to a fully occupied level, while the state at the conduction band edge is unoccupied. For the doped substrate the DOS is shown in Fig. 6(b), and the Fermi energy of the system crosses the highest occupied state peak, since we have in this case a semi-occupied level. We observe that for this strong doping, the defect peak is merged into the acceptor band and spreads closer to the valence band. For both the intrinsic and the doped structure we also calculated the DOS projection on relevant atoms, shown also in the same figure. Focusing on the peak at the valence band top, we find that it is in practice almost completely due to the SiDB atom (dashed line in Fig. 6), with a tail of few eV below. It will thus also be an efficient hole trap, as seen in Fig. 6(b). The shared-proton structure, on the other hand, is mostly responsible for the feature at the conduction band edge, as seen from the PDOS on the Si’ atom; it will act as an electron trap, and is unaffected by p-doping.

As a last illustration of the electronic structure in the Si–C–Si configuration, we computed the maximally localized Wannier functions \([42]\) (MLWFs), with the localization algorithm proposed by Marzari and Vanderbilt \([42]\), using the recently developed WANT code \([43]\). MLWFs are the solid state equivalent of localized molecular states and provide a meaningful picture of the nature of chemical bonds \([44]\). The electronic states are represented in an orthonormal real-space localized basis set, as an alternative to Bloch orbitals which are intrinsically delocalized, and also to the usual combinations of numerical non-orthogonal localized basis sets. In Fig. 7, we show the isosurfaces of charge density, i.e. the square modulus of the corresponding WF, for four of the WF that represent the electronic structure of the system. For example, we plot the WF isosurfaces localized on a typical Si–Si bulk bond (WF3) and on a Si–H surface bond (WF4) far from the defected interface. We now focus our attention on the two defects

![Fig. 5. Löwdin charges for the Si–C–C–Si (a) and Si–C–Si (b) configurations, in the undoped situation.](image-url)
involving the Si dangling bond and the shared proton in the Si–H–Si bond. The strong concentration of charge in the neighborhood of the SiDB defect clearly shows the presence of a charged dangling orbital on the Si atom where we would expect to find the broken bond (WF1). Moreover, the symmetric charge distribution (WF2) localized on the H atom belonging to the Si′–H–Si″ complex confirms the picture of the shared proton associated to the sp² defect. The analysis of one-electron Bloch orbitals, and in particular of the gap states corresponding to WF2, shows that the hole trap strongly contributes to WF1, while the electron trap is mainly localized on the Si′–H–Si″ bonds and provides the antibonding state corresponding to WF2.

3. Summary and conclusions

In summary, we addressed the energetically stable configurations for chemisorption, through the alkyne tail, of the bi-functional CH≡C–CH₂–COOH molecule on the hydrogenated Si surface. The geometric and electronic properties of the hybrid systems are investigated and compared, with special emphasis on the defect-like structures arising in the Si–C–Si configuration. In this case, the strong distortions provoke charge concentration at the surface defects, with the introduction of hole and electron traps. We conclude that the configuration Si–C–Si is the most stable on the perfectly flat surface; at the same time, we find that the configuration Si–C–Si, definitely metastable on the flat surface, produces and is probably favored by a porous or defected substrate.

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[26] A more extended study of reactions of these bi-functional 3-carboxylate molecules on the H:Si(100) surface is presented on C.S. Cucinotta, A. Ruini, E. Molinari, M.J. Caldas, submitted for publication.
4.2 *Ab initio* electron transport through hybrid silicon–organic interfaces

The design of hybrid organic–inorganic interfaces is viewed as a key idea for the production of new nano–bio devices in molecular electronics [25,26,27,28,29]. By functionalizing semiconducting rather than metallic substrates, more stable covalently bonded interfaces can be obtained. In particular the organic functionalization of silicon [26,27,30,31,32] can take advantage of the well–established Si technology and of the thorough experimental and theoretical knowledge, achieved in the last years, about self–assembling and wet–chemistry processes.

The electronic properties of extended two–dimensional monolayers on silicon have been extensively analyzed [2,14,16,33], while few are the fully first–principles studies of electronic transport in such structures, even in the case of single molecule junctions [31].

We construct an ideal system, consisting of an organic monolayer of π–conjugated biphenyl molecules, symmetrically bonded to Si leads, through two different covalent bridges, Si-O-C and Si-S-C [34,35,36]. We show that transport properties depend not only on the characteristics of the chosen molecule, but also on the molecule–surface bonding. The functionalized surface is the H:Si(111).

The description of the properties of the interface is done within a fully *ab initio* DFT approach (see Chap. 1) and the coherent transport is investigated according to the WanT method presented in Chap. 3, following the Landauer formalism and using maximally localized Wannier functions as a basis set. The transmittance and the current of the system are calculated in a zero temperature, low bias regime, taking into account the 2D periodicity in the plane perpendicular to the transport direction. We use the original technique illustrated in Chap. 3 using Gaussian smearing instead of the standard low–decaying Lorentzian one.

From the analysis of the electronic structure of the hybrid interface it results that the bandgap is not affected by the functionalization. However a peak is present close to the valence band edge, clearly originating from the molecular HOMO, which should be used for selective hole transfer. While for the Si-S-C interface the molecular peak is very clearly defined, in the Si-O-C case we observe a broadening typical of stronger molecule–surface interaction. It is also evident from the band structure analysis, in comparison with the projected band structure of silicon bulk, where we notice a strong coupling between molecule and silicon close to Γ, while the coupling is weaker close to the Brillouin zone edge.

Analyzing the transport results in presence of heavy substrate doping ($10^{20}$ cm$^{-3}$), we clearly see that the O–bridge has better characteristics for hole transport, compared to the S–bridge. This is due to the electronic struc-
ture close to the valence band top and underlines the optimal hybridization between silicon and oxygen. We also compare the oxygen–bonded surface with a second Si-O-C configuration with the molecules rings slightly rotated with respect to the first one: The transport across the molecular segment results very little influenced by the surrounding monolayer.

To get a deeper insight into the transport mechanism, we consider the quantum conductance of the Si-O-C heavily doped surface and, focusing on a fixed energy level close to the valence top, we report the $k_\parallel$-resolved transmittance: Just few $k_\parallel$-points close to $\Gamma$ give a significant transmittance contribution, confirming that the coupling between molecules and substrate is strong just in the area next to $\Gamma$, as observed from the band structure.

The main results are reported in details in the included paper, where we underline the importance of the molecule–surface bonding for the transport mechanism through the described hybrid interface.
We theoretically investigate the electronic and transport properties of a prototype hybrid device, constituted of two semi-infinite silicon bulk leads and a conductor region composed of an organic conjugated monolayer, covalently bonded to the substrate by thiol- and hydroxy-bridges. We address the electronic structure of the system in the density functional theory framework and directly evaluate the electron transport across the interfaces within the Landauer approach in terms of quantum conductance and I–V characteristics. We explicitly analyse the effects of bonding molecule–substrate on the transport, and identify oxygen as the preferred termination for hole transfer. We find that this interface, under proper substrate doping conditions, has remarkable transport properties, that may be profitably exploited for the design of efficient silicon-based molecular electronics.
promises smooth electronic coupling [14]. Our results indeed point to much higher efficiency of hole transport across the Si-O-C compared to the Si-S-C interface, and to the possibility of controlling transport characteristics by doping the Si substrate.

We consider the Si(111) surface with maximum coverage – one biphenyl molecule for every two surface silicon atoms – and the remaining Si sites passivated with H atoms. In Fig. 1(a,b) we show the interface structure for the O-bridge and the optimized orientation of the molecules on the surface. The description of the properties of the interface is provided by a fully ab initio DFT approach, starting with the calculation of the ground state electronic structure, and proceeding with the investigation of the coherent electronic transport within the Landauer formalism. For the electronic structure we employ the plane-waves implementation included in the PWSCF [18] package with the PW91-GGA exchange-correlation functional. All the details of our DFT calculations are given in note 19. To compute transport properties [20] we adopt the WANt method [21, 22] using maximally localized Wannier functions [23] extended to the case of ultrasoft pseudopotentials [24]. This procedure allows for a homogeneous treatment of conductor (molecule) and leads.

Within the Landauer approach, the leading resistance term is due to the interface contact. [25] The quantum conductance is obtained as the transmittance value at the Fermi energy \( G = T(E_F) \), while the I-V characteristic curve (linear regime at zero temperature) is obtained by a direct integration of \( T(E) \):

\[
I(V) = \int_{-\infty}^{+\infty} T(E)[f(E - \mu_L) - f(E - \mu_R)]dE, \tag{1}
\]

where \( f \) is the Fermi distribution function, \( \mu_{L,R} \) are the chemical potentials of the (left, right) leads, \( \mu_L - \mu_R = e \cdot V \) is the applied bias and we assume, as justified by the perfect conjugation of the organic segment, that the potential drops occur abruptly and symmetrically at the covalent bridges. Taking into account the 2D periodicity of the system in the \( xy \) plane (Fig. 1) we write the energy-dependent transmittance as:

\[
T(E) = \sum_{k_1} w_{k_1} T_{k_1}(E), \tag{2}
\]

where \( T_{k_1}(E) \) is the one-dimensional \( k_\parallel \) contribution to the total transmittance and \( w_{k_1} \) is the correspondent weight. We note that this 2D character is not usually included, since the majority of calculations up to now are restricted to \( \Gamma \)-point evaluations of \( T(E) \). Our \( k_1 \)-point summation [26] demanded for an original technique [27] substituting the standard slow-decay Lorentzian smearing, typically used in Green’s function approaches, with a Gaussian smearing which ensures faster, more physical decay.

![Figure 2](image)

FIG. 2: (Color online) Interface total DOS (black thin line), molecule-projected DOS (blue or green thick line) and bulk Si DOS (grey shaded area) for the Si-S-C (a) and Si-O-C systems (b), respectively. The valence band maxima are aligned to zero.

We start the analysis by the results for the electronic structure of the two interface systems: we plot in Fig. 2(a,b) the density of states (DOS) of the complete system, its projection (pDOS) on the molecule, as well as the Si bulk DOS, for the Si-S-C and Si-O-C interfaces, respectively. As expected the surface functionalization does not affect the bandgap with respect to the hydrogenated surface and no molecular state appears within the gap. The peak close to the valence band edge clearly originates from the molecular HOMO in both cases, as visible from the pDOS projections on the molecule. Here we already note the difference between the two bridges, in that for the Si-S-C interface the molecular peak (at \( \sim 0.4 \, \text{eV} \), marked H in the figure) is very clearly defined, while for the Si-O-C interface we see a broadening characteristic of stronger molecule-surface interaction, with contributions from the molecular orbitals reaching up to the VBM. A more detailed analysis is provided for this last system in Fig. 3, where we show the projected-bulk band-structure (PBBs) for Si together with the band structure for the interface. We see a strong coupling between molecule and silicon close to \( \Gamma \), while the coupling is weaker close to the Brillouin zone (BZ) edge, where the states remain localized on the molecule. The dispersion of the molecule-related bands, larger along the \( \Gamma - X \) direction (0.60 eV) than along \( \Gamma - Y \) (0.28 eV), is due to inter-molecular interactions: this reflects the fact that along \( \hat{x} \) the phenyl rings are almost cofacial with a stronger \( \pi - \pi \) coupling. The delocalization across the interface of the top-valence state at \( \Gamma \) is made evident in the plot of the corresponding state [Fig. 3(b)], while at \( X \) the state is mostly localized.
on the molecule [Fig. 3(c)]. In the case of the Si-S-C bonding, the peak H is also related to the states close to the X-point, and is also completely localized on the molecule (with contributions from the S orbitals) but we find no state, at energies close to the valence band top, delocalized over both molecular HOMO and Si surface states.

We turn now to the current across the organic layer [from Eq. (1)] for which we need to set the position of the Fermi level, determined here by the dopant concentration as in the case of simple semiconductors (there are no trap or gap levels in this perfectly saturated model). We choose three typical p-dopant concentrations for silicon, $10^{20}$, $10^{18}$ and $10^{16}$ cm$^{-3}$, and follow the standard model [28] in associating Fermi levels at the VBM, and at 0.1, 0.2 eV above the VBM respectively (at a temperature of 300 K). We look first at the heavy-doping limit, and compare in Fig. 4(a) results for the two bridges, where we clearly see the O-bridge presents superior characteristics for hole transport compared to the S-bridge. This is due to the electronic structure close to VBM, and highlights the optimal hybridization between silicon and oxygen, not easily obtainable with other group VI element. We show also in the same plot results for a slightly different geometry for the O-bonded system, in which the molecules are placed in a more effective $\pi$-stacking in the x-direction. In that case we see a larger dispersion of the molecular bands, however no strong effect is seen in the transport characteristics; as we discuss below, this indicates that transport across the molecular segment is very little influenced by the surrounding monolayer.

We continue our analysis, now just for the O-bridge system: The I–V curves for the different dopant concentrations, are reported in Fig. 4(b). The current at the interface shows a non-ohmic behavior, with a threshold bias tightly related to the position of the Fermi level. In order to better understand the transport mechanism at the microscopic level, the transmittance (per molecule) curve at the heavy doping limit is also shown and compared with the Si bulk transmittance for the energies close to the top of the valence band [see Fig. 4(c)]. Our values for transmittance and current are of the same order of magnitude of other results for similar systems, from both experiments [29, 30] and calculations [8]. In particular we compare our results with those of Lu et al. [8], where they consider a single molecule ($\pi$-conjugated) between the two silicon leads; We obtain a current with similar characteristics and of the same order of magnitude (slightly higher, however this can probably be traced to the optimal coupling of the Si-O-C bridge). This confirms that the intermolecular interactions are not so important for the transport in this case, and that there is no significant difference in the current-per-molecule using SAMs or a single molecule as active element. Now, this is due...
in this particular case (hole transport, Si substrate and phenylene-based molecules) to the fact that the coupling between molecules and substrate is strong just in the area next to Γ, as shown by the analysis of band-crossings and anti-crossings in the PBBS [see Fig. 3(a)]. We can confirm that also from the detailed description of the transmittance: focusing on the energy level indicated by $E_1$ we analyzed the $k_{\parallel}$-resolved transmittance [31]. We see [Fig. 4(d)] that just few $k_{\parallel}$-points close to Γ give a significant transmittance contribution at this energy (to capture contributions from a larger BZ area we should have to sample energies further down the valence band).

Summarizing, our approach allows us to treat the impact of lateral intermolecular coupling on the transport, which is an issue of general importance; however we find that for the specific cases treated here this is not the main parameter to be tested, and that the behavior per molecule in the compact monolayer is very similar to that of the isolated molecule. Our main finding concerns the importance of the bonding molecule-surface. We compared two very similar elements with regard to hybridization mechanisms, S and O, and also of particular relevance in the field of molecular electronics, since the thiol and hydroxyl groups are often adopted as active terminations. Our results show that in bonding to Si, the O-terminations should be preferred due to the superior electronic and transport properties for hole transfer.

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[19] The DFT simulations employ an orthorhombic cell of 3.839 × 6.649 × 29.227 Å3 including a slab formed of 12 layers, with two Si atoms per layer. We use ultrasoft pseudopotentials with kinetic-energy cut-off of 25 Ry (200 Ry) for the wavefunctions (charge density). The summations over the Brillouin zone are performed with a 16×8 k-point mesh in the xy-plane [Fig. 1(a)]. To fix the simulation geometry, we perform a classical force-field relaxation of the single molecule/Si interface (monolayer). Then we check the commensurability of the second surface on top of the monolayer and we make a second force-field relaxation of the entire structure. Starting from this configuration we relax the system quantistically, until forces acting on atoms are less than 0.03 eV/A, checking that the atomic positions do not drastically change.
[26] The transmittance is calculated performing the summation over the Brillouin zone with a 32×6 $k_{\parallel}$-points mesh, using a gaussian smearing of 0.1 eV.
[27] B. Bonferroni et al., to be published.
[31] We performed the transport calculation using a larger $k_{\parallel}$-point mesh (40×20), in order to obtain a better definition of the transmittance map.
Bibliography


4.2 Ab initio electron transport through hybrid silicon–organic interfaces


Chapter 5

Applications II: Semiconductor surfaces and interfaces

Semiconductor surfaces and interfaces are at the base of the development and design of new generation electronics and optoelectronics devices. The specific properties connected to the two–dimensional character of such systems can be exploited where new features with respect to the bulk are required.

Particular interest resides in wide band gap semiconductor, whose heterostructures find application in optoelectronics and high–power, high–frequency microelectronics [1, 2]. Among this, group III nitride, such as AlN or GaN, are largely used, e. g. in the blue lasers fabrication [3, 4, 5].

For the production of heterostructures, it is crucial to find proper substrates on which to grow nitrides, with a sufficiently small lattice mismatch: In fact a large mismatch gives rise to defects, which reduce the electrical and optical efficiency of devices. In these cases a suitable candidate for substrate is SiC, which is in turn a wide band gap semiconductor and presents a 1% lattice mismatch with AlN and 3% with GaN [3, 4, 7, 8, 9]. Moreover SiC is a particularly interesting material in itself, because it shows different crystal structures, both cubic (3C) and hexagonal (2H, 4H, 6H) polytypes [10, 11, 12]. Exploiting this characteristic 4H/3C or 6H/3C SiC heterostructures have been proposed [13, 14, 15, 16], where there is no lattice mismatch, but band offset and variation in spontaneous polarization, exactly as in the case of layered systems constituted of different chemical materials.

All these materials, having hexagonal wurtzite structure, show spontaneous bulk polarization [17, 18, 12, 16] which is responsible, when different solids are interfaced, for charge accumulation at the interface and for rising electrostatic fields in the structure [19, 20].

An accurate analysis of the structural and electronic properties of these
semiconductor surfaces and interfaces is thus important, when they are involved in heterostructures, but also individually considered.

In this chapter, we present an analysis of polarization effects in two different SiC surfaces: the (1100) and the (1120) ones. In section 5.2 we introduce a work in progress on two different SiC/AlN interfaces whose electron transport properties we are calculating.

5.1 Polarization properties of (1100) and (1120) SiC surfaces from first principles

The spontaneous polarization in solid has attracted large interest in the last years, because it is responsible for physical properties, such as ferroelectricity or pyroelectricity, exploitable in technological applications. Polarization properties are experimentally accessible, but the direct calculation of $P$ is impractical [21], as we already mentioned in Chap. 2. The approach proposed by Resta [22] and King-Smith and Vanderbilt [23], that we have described in Chap. 2, based on the calculation of the Berry phase or equivalently of the Wannier functions, has been extensively used in the last decade [24, 19, 17, 25, 26, 27, 28, 29, 30]. Here the method is applied to the investigation of polarization for two SiC surfaces compared to the bulk case.

Despite the investigation of bulk systems properties, very few studies are dedicated to surfaces or low dimensional cases [31,32,33,34]. When dealing with surfaces, polarization effects have high impact in adsorption experiments since they strongly affect functionalization and growth processes, influencing surface reconstruction [35,36]. Moreover they are important for thin film technology: The polarization behavior of few layers of materials may largely differ from the bulk one.

Here we investigate two non–polar surfaces, focusing on the polarity effects induced by the surface formation, compared to the bulk spontaneous polarization. Non–polar surfaces are called those for which the projection of the bulk polarization along the normal to the surface is zero. We choose as a prototypical material SiC, because it has different polytypes with different polarization properties [11,37].

First we investigate the polarization in the bulk 2H, 4H and 6H wurtzite structures (in order of decreasing hexagonality) [11,10,38], by means of the two different implementation based on Berry phase and Wannier functions: We thus revise the methodology and we show that spontaneous polarization decreases linearly from 2H to 6H, as a function of the number of bond inversion along the stacking direction (6H is the polytype closest to the 3C cubic geometry). Within our bulk calculations we fix as a reference structure the zincblende 3C polytype, whose spontaneous polarization is zero, based on symmetry considerations [39]. In fact, as explained in Chapter 2 only
a difference in polarization $\Delta P$ is a well-defined quantity and not $P$ as an absolute value, so that a reference is necessary.

Choosing the 2H wurtzite, we analyze the (1100) and (1120) non-polar surfaces: This is the simplest and computationally less demanding polytype, but the other ones can be analogously treated. We study the structural and electronic properties of the two surfaces, in terms of band structure and considering the charge density transfer among the atoms on the surface, within the density functional theory, plane wave framework, using ultrasoft pseudopotentials.

After having analyzed the electronic structure, we calculate the in-plane polarization of the surfaces, using Wannier functions. The evaluation of the in-plane contribution, usually neglected, is one of the most relevant achievements of the work reported in the paper that follows: It can dramatically affect the interaction of the material with an environment, especially important e.g. in functionalization or adsorption processes [36]. It is expressed as a dipole moment per unit area: In our calculations we exploit the localized character of the Wannier functions set that allows us to treat the system as an ensemble of classical point charges.

It is useful to distinguish between bulk and surface polarization effects, to understand how the formation of the surface influences the distribution of the charge and the consequent interaction with the environment. To do this, it is necessary to define a minimal volume such that the local polarization can be defined on the same ground of the bulk, reproducing the bulk in the limit of infinite slab thickness. We follow the extrapolation scheme proposed by Fiorentini and Methfessel [40], while another possible partition of the simulation supercell is given by Wu and coworkers [41]. We choose the former because it allows for a direct comparison with bulk values.

The choice of an appropriate reference volume to calculate the in-plane and perpendicular surface polarization is crucial to obtain a physical picture consistent with the bulk polarization properties of the material. In the case of SiC (1120) and (1100) non-polar surfaces, the charge transfer effects are strong enough to cause a large surface perpendicular polarization and to deeply modify the in-plane component along the bulk polar direction, for the first film layers. This demonstrates that the commonly called non-polar surfaces may present remarkable polarity effects which can influence the adsorption and interaction mechanisms.

Further details about the calculation methodology and results can be found in the following reported paper.
Polarization properties of (1\bar{1}00) and (11\bar{2}0) SiC surfaces from first principles.

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We report on first principles density functional calculations of non-polar low index surfaces of hexagonal silicon carbide. We provide an accurate analysis of the macroscopic bulk spontaneous polarization as a function of the hexagonality of the compound, and we describe in details the electronic and structural properties of the relaxed surfaces. We revise the methodology to achieve a detailed description of the surface polarization effects. Our results on low-index surfaces reveal a strong in-plane polar contribution, opposing the spontaneous polarization field present in hexagonal polytypes. This in-plane surface polarization component has not been considered before, although it is of significant impact in adsorption experiments, affecting functionalization and growth processes, as well as the electronic properties of confined, low-dimensional systems.

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I. INTRODUCTION

The spontaneous polarization in solids has been intensively investigated, since it is responsible for intrinsic physical properties of matter (e.g. ferroelectricity, pyroelectricity, high-k dielectric behavior, etc), that may be profitably exploited in technological applications. However, despite its intuitive meaning, the theoretical description from an atomistic point of view is a challenging problem. The spontaneous polarization of a material is experimentally accessible but its direct calculation is impractical. In 1993 Resta and King-Smith and Vanderbilt proposed a theoretical approach based on the evaluation of the Berry Phase (BP) or equivalently of the centers of Wannier Functions (WFs). On the basis of this approach, the polarization properties (spontaneous polarization, Born charges, piezoelectric tensor, ferroelectric properties, etc) of several bulk materials - such as metal oxides (BeO, ZnO), III-V nitrides (GaN, AlN, InN), perovskites (BaTiO$_3$, PbTiO$_3$, KNBO$_3$), ionic compounds (LiF, LiCl, NaCl) - have been routinely calculated.

Despite the wide investigation of bulk system properties, very few reports are dedicated to surfaces or low-dimensional cases. Polarization effects may highly influence the characteristics of surfaces, being responsible for surface relaxation and affecting the interaction with adatoms and molecules, and consequently of impact on the functionalization and growth processes. Moreover, they are also relevant for thin film technology, since the polarization behavior of a few layers of material may largely differ from the bulk ones.

It is a common custom to refer to the surfaces for which the projection of the spontaneous bulk polarization vector along the normal to the surface is zero as non-polar ones. However, further electrostatic effects may arise at the surface due to the presence of dangling bonds. The rearrangement of the bonding at surfaces leads to a charge displacement, that may deeply modify the polarization properties of the surface with respect to the bulk.

In this paper we investigate the polarization properties of a class of non-polar semiconductor surfaces, along directions both parallel and perpendicular to the surface. In particular, we focus on the polarity effects induced by the surface formation with quantitative comparison to the bulk spontaneous polarization. In this frame, we highlight benefits and limits of the different techniques, and propose a methodology to evaluate the local dipole moment. We selected silicon carbide as a prototype material to study bulk and surface spontaneous polarization, because of the different polytypes existing in nature which exhibit different polarization properties. Polytypes only differ for the stacking sequence of the basic tetrahedral units and are characterized by a partial charge transfer (from silicon to carbon atoms) imparting some ion-ici to the bond. Amongst the various polytypes, the most common and studied are the cubic and the hexagonal ones, which can be further distinguished by the number of bilayers representing the minimum repeating unit along the stacking direction. Both the zincblende and hexagonal systems are non centrosymmetric, and can thus sustain the piezoelectric effect; furthermore, the hexagonal structures exhibit a unique rotation axis (the
polar 6-fold axis) and are thus compatible with the conditions for pyroelectricity.\textsuperscript{19}

First, we evaluated the bulk spontaneous polarization of selected SiC polytypes of decreasing hexagonal-ity (2H, 4H, 6H, the latter one being closer to the cubic system)\textsuperscript{21-23} by using two different numerical implementations based on both the BP and WFs. This allowed us to test the method, comparing our results with previously reported values,\textsuperscript{28,29} and to obtain surface and bulk quantities with comparable computational accuracy. Then, we studied the \((1\times1)\) relaxed (1100) and (1120) surfaces of 2H-SiC. We analyzed the structural and electronic properties of these surfaces as well as their polarization behaviors, using the WFs approach. The formation of buckled Si-C bonds associated with the creation of the surface is responsible for a net dipole along the direction normal to the surface. More remarkably, we observed a large change in the in-plane component of polarization, opposing the bulk spontaneous polarization. This variation is consistent with the direction of the local electric field along the surface Si-C bond.

The evaluation of the in-plane contribution, usually neglected in standard calculations, constitutes one of the most relevant achievements of the present work: indeed, the strong change in polarization at the surface can dramatically affect the interaction of a material with the environment and in particular it may be of significant impact in adsorption experiments.\textsuperscript{18} For example in the case of non-covalent functionalization of surfaces with organic molecules, the components of the dipoles both parallel and perpendicular to the surface influence the packing and the geometry of the self assembly. Growth processes performed employing polar molecules (precursors) will as well interact with surface dipoles.

The paper is organized as follows: Section II describes the theoretical basis of the method as well as the computational details adopted in this work. The main results for the SiC polytypes and surfaces are presented in Sections III A and III B respectively; conclusions are reported in Section IV.

## II. METHOD

### A. Theory

The complete description of the theoretical method to address the spontaneous polarization has been extensively reported elsewhere\textsuperscript{4,4}: here we briefly describe the most relevant features of the scheme employed in this work.

The spontaneous polarization \(\Delta P\) of a bulk system has been evaluated as the difference between the structure in study and a reference structure, having null polarization by symmetry.\textsuperscript{19,20} One of the prerequisites of this approach is that the two structures have to be connected by an adiabatic transformation, described by a parameter \((\lambda)\), during which the system must remain an insulator. \(\Delta P\) can be decomposed into an ionic and an electronic component, as: \(\Delta P = \Delta P_{\text{ion}} + \Delta P_{\text{el}}\). Labeling \((0)\) and \((1)\) the reference and the final configurations over the adiabatic transformation \((\lambda)\), the ionic component is trivially given by:

\[
\Delta P_{\text{ion}} = \frac{+e}{\Omega} \sum_I Z_I (\tau_I^{(1)} - \tau_I^{(0)})
\]

where \(e\) is the electron charge and \(\Omega\) is the cell volume; the \(I\) summation runs over the ionic sites \(\tau_I^{(\lambda)}\) and \(Z_I\) is the valence charge of the \(I^{th}\) atom.

The electronic component \(\Delta P_{\text{el}}\) may be evaluated in terms of the variation of the BP of the electronic Bloch functions, along the transformation \((\lambda)\):

\[
P_{\text{el}}^{(\lambda)} = -\frac{2ei}{(2\pi)^3} \sum_n \int_{BZ} d^3k \langle u_{kn}^{(\lambda)} | \nabla_k | u_{kn}^{(\lambda)} \rangle,
\]

where \(u_{kn}\) is the periodic part of the double occupied Bloch states and the sum over \(n\) is taken on occupied bands.\textsuperscript{30}

Following the formulation provided by Blount,\textsuperscript{31} we write the expectation value of the position operator \(\hat{r}\) on the WF \(\{u_{kn}^{(\lambda)}\}\) basis set as:

\[
\langle \hat{r} \rangle_{n}^{(\lambda)} = \langle u_{kn}^{(\lambda)} | \hat{r} | u_{kn}^{(\lambda)} \rangle = i\frac{\Omega}{(2\pi)^3} \int_{BZ} d^3k \langle u_{kn}^{(\lambda)} | \nabla_k | u_{kn}^{(\lambda)} \rangle.
\]

Thus Eq. (2) may be expressed in terms of the centers of charge \(\langle \hat{r} \rangle_{n}^{(\lambda)}\) of the WFs of the occupied bands:

\[
P_{\text{el}}^{(\lambda)} = -\frac{2e}{\Omega} \sum_n \langle \hat{r} \rangle_{n}^{(\lambda)}.
\]

Despite the formal equivalence of the two implementations (BP and WF), the Wannier centers provide an intuitive correspondence with the concept of electron localization that is used in the classical definition of the macroscopic polarization.\textsuperscript{32}

We remind that for a bulk system the spontaneous polarization is a multivalued quantity (measured in C/m\(^2\)), defined modulo \(\pi\), where \(\pi\) is a vector of the three dimensional direct lattice. The case of surfaces is different since the quantities of interest are generally defined with respect to the surface unit area. Therefore, to quantify the polarization properties of surfaces we will adopt the use of an in-plane polarization as the dipole moment per unit area (measured in C/m). We note that while the BP approach can be used to calculate the total polarization for a slab in the supercell approach, where a (fictitious) periodicity is always maintained, whenever the periodicity is broken, the local contribution of the polarization, or the projections along e.g. interface planes, are in general ill defined.

In this work, we propose a unified scheme for the calculation of the polarization effects in surfaces and interfaces. We exploit the localization properties of the WF
set, that allow us to treat the system as an ensemble of classical point charges. Furthermore, noting that the surfaces are periodic in two directions but non periodic in the third one, we show how to calculate separately the in-plane (periodic) and perpendicular (non-periodic) contributions of the polarization. The proposed procedure provides a physical picture which is consistent with the polarization properties of the corresponding bulk. This approach is indeed the natural extension of the method described above for the bulk system: The polarization stems from the neutralization of localized charges associated to the ions and to the WF included in the simulation supercell.

In the study of surfaces, to assign a surface property one needs to define a region where significant changes from the bulk occur to the same property in the presence of a surface: this definition is thus associated with a decaying length, as the distance from surface, where this deviation is observable. In particular, in order to analyze the polarization effect, while moving from the bulk towards the surface, it is useful to define a minimal volume, in such a way that the local (in-plane, or two-dimensional) polarization can be defined on the same ground of the bulk.

In a recent paper, Wu et al., proposed a definition of the polarization for an interface structure as the sum of dipoles, calculated in subunits obtained partitioning the simulation supercell in the direction perpendicular to the layers. In the specific case of perovskite materials, such as BaTiO$_3$ or SrTiO$_3$, the Wannier centers are naturally localized in atomic layers. This allows one to have a layer-by-layer decomposition of the polarization in the slab. In other words, such localization leads to the definition of the in-plane polarization over a building block (one single atomic layer) smaller than the natural unit cell of the corresponding bulk phase (two layers). Although formally correct, this localization method does not allow a direct comparison with bulk values.

Alternatively to a pure WFs approach, we propose a novel procedure to define the polarization for finite systems, in such a way to reproduce the bulk value, in the limit of infinite slab thickness. In order to define the in-plane (periodic) quantities and decouple the bulk and surface contribution to polarization, we make use of the extrapolation scheme originally proposed for the surface energy by Fiorentini and Methfessel. On the other hand, the perpendicular contribution (non-periodic) to the surface polarization can be described by macroscopically averaging the electrostatic potential (local ionic term + Hartree potential) over suitable intervals in the slab, following the technique proposed by Baldereschi, Baroni and Resta.

The combination of the two approaches allows us to define the minimal cell over which we can evaluate the polarization of the system.

The extrapolation method consists in evaluating the surface polarization for slabs $p_{\text{slab}}$ of increasing thickness. The total supercell polarization is the sum of $n$ bulk units, not yet specified, plus the surface contribution $p_{\text{surf}}$ (or two times $p_{\text{surf}}$ for symmetric slabs):

$$p_{\text{slab}} = 2p_{\text{surf}} + np_{\text{bulk}}.$$  \hspace{1cm} (5)

The fitting from Eq (5) depends on how many units $n$ constitute the bulk part of the slab, i.e. it depends on how the slab is partitioned on surface and bulk contributions and on the size of each bulk unit. This subdivision alters the reciprocal weight of surface and bulk contributions. The proper setting of the spacer $n$ allows one to recover the value of the bulk spontaneous polarization. The smallest volume that realizes the condition for the fit in Eq. (5) fulfills the request of minimal meaningful unit to compare bulk and surface properties.

The perpendicular contribution of the total surface dipole $p_s$ can be also estimated via the ionization potential ($I_p$). This quantity is directly accessible to experiments, and it is obtained with respect to the vacuum level of the slab calculation, from the macroscopic average of the electrostatic potential. The average is performed by integration over a length $L$, which should be chosen so that $L = nc$, where $c$ is a typical length of the system, related to the bulk periodicity in the z direction. The minimal volume is thus defined when the extrapolation (for the parallel component) and the macroscopic average (for the $z$ component) provide the same slab subdivision in $n$ units. In principle, such a unit may be smaller than the unit cell. This happens every time the periodicity of the macroscopic average of the potential is higher than the periodicity of the underlying lattice.

The polarization effects on the surface should be related to the projection of the bulk polarization vector along the direction normal to the surface. However the details of our results highlight a more complex scenario: the surface effects may deeply modify the polarization properties of the infinite periodic structure, with no direct correlation to the bulk value.

### B. Computational details

We performed ab initio density functional theory (DFT) calculations, in the planewaves pseudopotential framework, as implemented in the PWscf package. We used ultrasoft pseudopotentials and the PBE approximation to the exchange-correlation functional. A kinetic energy cutoff of 30 Ry (300 Ry) for the wavefunctions (charge density) was found to give converged bulk properties.

Bulk calculations were performed in a $C_{3v}$ supercell (24 atoms) that contains replicas of the full stacking sequence along the $z$ direction, to maintain comparable computational accuracy for all the polytypes. The SiC surfaces were instead represented by slabs with two and four atoms per layer for the (1100) and (1120) surfaces respectively. We checked the effects of the slab thickness by varying the number of layers from 10 to 16 in the case of (1100) and from 8 to 12 in the case of (1120) surface. For both surfaces a thick space of vacuum ($\sim 10$ Å) is
included in the direction perpendicular to the surface, in order to avoid spurious interactions among adjacent replicas.

The integration on the Brillouin zone was performed by using a k-point grid of \((10 \times 10 \times 4)\) for bulk calculations and \((6 \times 6 \times 1)\) for \((1100)\) and \((1120)\) surfaces.\(^{40}\) Both bulk and surface systems were fully relaxed (no fixed atom position) until the forces varied less than 0.03 eV/Å. We note that the spontaneous polarization is a slow converging quantity with respect to Brillouin zone sampling, much more sensitive than standard quantities evaluated in DFT calculations, such as the total energy, the charge density, etc.

We evaluated the polarization using the BP approach included in the PWSCF package\(^{37}\) as well as the WFs approach as implemented in the WANT\(^{41,42}\) code. We note that no layer-by-layer decomposition is possible when using the BP approach, as mentioned above. The WFs and the corresponding centers [Eq. (3)] are calculated following the maximum localization procedure proposed by Marzari and Vanderbilt\(^{43}\) and successively extended to the ultrasoft pseudopotential case.\(^{44}\)

Every bulk polarization calculation requires a reference structure, since only changes in polarization are defined. The simplest reference structure when dealing with hexagonal compounds is the zincblende (3C) due to the previous first-principle calculations. For further comparison with the surface calculations, we also evaluated the bulk polarization for the 2H and 3C polytypes both in a hexagonal and orthorhombic structures, we also evaluated the bulk polarization for the 3C polytypes both in a hexagonal and orthorhombic equation of state. The lattice parameters has been optimized using Murnaghan procedure proposed

### III. RESULTS AND DISCUSSION

#### A. Bulk SiC polytypes

We studied the variation of the spontaneous polarization as a function of the hexagonality, namely while passing from the 2H (the most hexagonal) to the 4H and 6H polytypes.\(^{21,22,26,27}\)

For each structure we relaxed both the lattice parameters and the atomic positions in the cell. The equilibrium data (Table I) show the typical behavior of PBE calculations, with lattice parameters overestimated of roughly 1% with respect to experiment.\(^{21}\) and in good agreement with previous first-principle calculations.\(^{22}\)

We evaluated the polarization of the three SiC polytypes using both the BP and the WFs approaches. In both cases, the components of the spontaneous polarization result to be zero by symmetry in the plane orthogonal to the stacking direction. The results for the component of the polarization in the stacking direction are summarized in Table II.

For all the polytypes we found similar results, using both BP and WFs approaches. Both sets of values are in very good agreement with the published theoretical\(^{28}\) and the experimental\(^{29}\) results. We also note that the spontaneous polarization decreases linearly from 2H to 6H, as a function of the number of bond inversions along the stacking direction, approaching as a limiting case the

| TABLE I: Computed and experimental structural parameters for different hexagonal (H) and cubic (C) bulk SiC polytypes. The lattice parameters has been optimized using Murnaghan equation of state. |
|-----------------|-----------------|-----------------|-----------------|-----------------|
|                | This work       | Theory\(^a\)    | Exp.\(^b\)      | Exp.\(^c\)      |
| 2H a(Å)        | 3.096           | 3.105           | 3.076           |
| 2H c(Å)        | 5.080           | 5.113           | 5.048           |
| 2H c/a         | 1.641           | 1.647           | 1.640           |
| 4H a(Å)        | 3.094           | 3.108           | 3.073           |
| 4H c(Å)        | 10.142          | 10.186          | 10.053          |
| 4H c/a         | 3.278           | 3.277           | 3.268           |
| 6H a(Å)        | 3.094           | 3.062           | 3.081           |
| 6H c(Å)        | 15.206          | 15.014          | 15.117          |
| 6H c/a         | 4.915           | 4.903           | 4.907           |
| 3C a(Å)        | 4.384           | 4.402           | 4.360           |

\(a\) Ref. \[22\]
\(b\) Ref. \[21\]
\(c\) Ref. \[27\]
\(d\) Ref. \[45\]

| TABLE II: Spontaneous polarization along the stacking direction calculated both with BP and WFs approaches. Experimental and other theoretical values are also reported for comparison. All the values are expressed in C/m². The values for the 3C polytypes both in a hexagonal and orthorhombic cell are reported as a reference. |
|-----------------|-----------------|-----------------|-----------------|-----------------|
|                | BP              | WFs             | Theory\(^a\)    | Exp.\(^b\)      |
| 2H             | -0.046          | -0.048          | -0.043          |
| 4H             | -0.021          | -0.023          | -0.018          | -0.01           |
| 6H             | -0.015          | -0.015          | -0.009          |
| 3C             | 0.0001          | 0.0001          |
| 3C\(^d\)       | 0.0010          | 0.0013          |

\(a\)Ref. \[28\]
\(b\)Ref. \[29\]
\(c\)2H in orthorhombic cell with z along a non polar direction ([1100] or [1120])
\(d\)3C in orthorhombic cell
3C structure (Fig. 1).

B. Low-index non-polar SiC surfaces

The main goal of this work is to understand any possible relation between the intrinsic spontaneous polarization and the charge transfer occurring upon surface formation at the so-called non-polar surfaces. For crystal lattices that present a bulk spontaneous polarization, the term non-polar surface indicates a plane containing the polarization axis. It is known that surface effects can cancel the spontaneous polarization even at polar surfaces, via reconstruction, adatoms, or vacancy formation. It is desirable to understand and quantify the polarization close to the surface, in view of selected applications such as adsorption, ultra-thin films or nanodevices, where surface properties play the major role.

We considered two low-index SiC surfaces, namely the (1100) and (1120) surfaces. For these surfaces, the (1×1) periodicity is stable, although different preparation conditions may give rise to reconstructions. For the sake of simplicity, we focused on the (1×1) clean relaxed surfaces, thus avoiding possible effects arising from surface reconstruction.

As shown in Fig. 2, both surfaces would be referred to as non-polar, since they present the stacking direction ([0001], the polar direction in the bulk) parallel to the surface plane. These surfaces constitute the simplest example to address the problem of surface dipole formation, stemming from two decoupled terms, the bulk and the surface, respectively. The study of the polar SiC(0001) surface constitutes a much more complicated case. The surface undergoes a strong reconstruction, which includes the presence of Si adatoms to stabilize the structure. Moreover, both the ideal and the reconstructed (0001) surfaces result to be metallic in DFT calculations, invalidating the goal of the work, which requires an insulating system.

In the following, we will focus on the wurtzite (2H), polytype. Even though 2H is not easily accessible from the experimental point of view (but see Ref. [27]), this constitutes a template for developing a general method to evaluate surface polarization effects. The case of the other polytypes would be straightforward, although computationally more demanding.

1. SiC(1100) surface

We simulated the SiC(1100) surface in a repeated slab geometry. For this surface, two terminations are possible, usually labeled Type I and Type II (shuffle and glide plane respectively), as displayed in Fig. 3. The analysis of the two terminations shows that Type II truncation gives rise to a metallic surface which is energetically less favorable than Type I. For these reasons we focus on Type I surfaces.

The polar [0001] axis lies along the y-direction [Fig. 3(b)], while the z-axis is perpendicular to the surface. In order to reduce rounding errors, we chose the most symmetric slab: this leads to an even number of layers. While we found that a 12-layer slab gives converged structural and electronic properties, a 16-layer slab is required to get converged surface polarization val-
FIG. 3: (color online) Side (a) and top (b) view of the relaxed (1¯100) surface. The hexagonal stacking direction is the [0001] direction. The larger spheres (yellow) indicate silicon atoms, while the smaller ones (gray) stand for carbon atoms. The possible terminations are indicated as Type I and Type II. The rectangular zone sketched in (b) identifies the surface unit cell used in the simulations.

TABLE III: Details of the relaxed non-polar (1¯100) surface in comparison with published data: tilt angle ω of the surface bond, bond length BL (in Å and % of the corresponding bulk value) of the surface bonds, surface energy per surface unit area σ, displacements along the perpendicular direction for surface atoms (d⊥Si and d⊥C) and ionization potentialIp.

<table>
<thead>
<tr>
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<th>This Work</th>
<th>LDAa</th>
<th>SCC-DFTBb</th>
</tr>
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<tbody>
<tr>
<td>ω (deg)</td>
<td>5.2</td>
<td>3.8</td>
<td>2.4</td>
</tr>
<tr>
<td>BL (Å)</td>
<td>1.74 (-8.9%)</td>
<td>1.71(-9.0%)</td>
<td>1.73 (-8.2%)</td>
</tr>
<tr>
<td>d⊥Si (Å)</td>
<td>-0.26</td>
<td>-0.28</td>
<td>-0.02</td>
</tr>
<tr>
<td>d⊥C (Å)</td>
<td>-0.10</td>
<td>-0.17</td>
<td>-0.01</td>
</tr>
<tr>
<td>σ (eV/Å²)</td>
<td>0.15</td>
<td>0.19</td>
<td></td>
</tr>
<tr>
<td>Ip (eV)</td>
<td>5.60</td>
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aRef. [51]  

bRef. [48]

The surface relaxation mainly involves the outer Si and C layer. The Si-C surface bonds are tilted of ∼5.2°, with the silicon atom relaxing inward by 0.26 Å. These findings are in good agreement with previous results. The surface energies are calculated using the linear extrapolation approach at increasing slab thickness. We obtained a value of 0.15 eV/Å², in agreement with other theoretical results obtained for similar SiC surfaces. The surface projected bulk band structure is shown in Fig. 4(a); continuous lines identify the surface states.

Two surface states in the band gap are present, one occupied, and the other empty, in agreement with e.g. Ref. 51. The isocontour plot for the highest occupied molecular orbital (HOMO) [Fig. 4(b)] shows that the charge density is mainly localized on the surface Si-C bond, with charge transfer from Si to C, which strengthens the surface bond. This behavior is consistent with the observed relaxation mechanism where the “depleted” Si moves inside the surface, leaving C as outermost atom.

To understand the surface effect on the polarization behavior while moving from the surface to bulk, we need to define the minimal unit on which the surface polarization can be calculated. From Fig. 3 we see that the periodic units for this slab is formed of four layers. The
application of the procedure proposed in Sec. II A yields a different result. Indeed, two layers are already sufficient to reproduce the polarization of the bulk system. Such a cell constitutes the minimal unit over which we will evaluate the surface polarization.

A unit-by-unit analysis shows that after four layers the surface polarization converges to the bulk values, as shown in Fig. 5. Here we see that the creation of a surface strongly modifies the polarization. Adding up all the contributions of the different units, we evaluate the surface effect as the deviation from the bulk value: the results are summarized in Table IV. The component of the surface polarization normal to the surface (the positive direction is oriented outwards) is \( p_z = 0.35 \times 10^{-10} \text{ C/m} \), to be compared to a bulk term which is zero.

The large charge transfer that occurs along the surface bond is responsible also for a large in-plane dipole component. Analyzing the position of the Wannier centers on the surface, we notice that they are no more in the tetrahedral configuration typical of the bulk structure; indeed two of them lie along the surface Si-C bonds, with a total displacement from the bulk position of roughly \( -0.7 \text{Å} \). Since each Wannier center carries a \( -2e \) electric charge, this corresponds to a contribution to the surface polarization \( y \)-component equal to \( 1.4 \times 10^{-10} \text{ C/m} \), to be compared with the bulk spontaneous polarization \( -0.12 \times 10^{-10} \text{ C/m} \). The main contribution to surface polarization along the stacking direction \( (y) \) comes from the first unit \( 1.48 \times 10^{-10} \text{ C/m} \), while the units beneath contribute with smaller amounts: their electrons are localized along the Si-C bonds although in a slightly distorted tetrahedral coordination. The \( x \)-component remains zero as in the bulk. Table IV shows the total excess of the surface polarization with respect to the bulk value, \( i.e. \) the sum of the contributions of each unit, as previously discussed. This in-plane component along the stacking direction results to be the strongest contribution to the surface dipole, being about one order of magnitude larger than the spontaneous polarization; furthermore, it contributes with opposite sign, thus it tends to cancel the bulk contribution.

The surface effects on polarization strongly depend on the difference in electronegativity between silicon and carbon atoms, \( i.e. \) on the ionicity of the bond, which is responsible for the displacement of WF centers. Large ionicity does not allow electrons to move much from bulk positions, while a smaller one allows bigger displacements. Similar ongoing studies on ZnO surfaces\(^{53}\) show indeed that surface polarization contributions are lower than those for SiC.

2. SiC(1120) surface

In the case of the (1120) surface, the two surfaces of the slab are equivalent for any choice of the number of layers, as shown in Fig. 6(a). Here, nine SiC layers are sufficient to reach the convergence in structural parameters. However, to obtain converged surface polarization values, we increased the thickness of the slab up to twelve layers. The unit cell in this surface contains two Si-C bonds, as shown in Fig. 6(b). The structural characteristics of the relaxed surface are reported in Table V.

As for the (1100) surface, the relaxation mainly involves the outermost layers, with the outermost Si-C bonds tilted by 5.9° and contracted by -7.9%.

The band-structure of Fig. 7 shows the presence of four states, two fully occupied and two empty, two by two almost degenerate in energy, localized on the surface. This is related to the presence of the two surface Si-C bonds, with two surface states each. Similarly to what happens at the (1100) surface, these states correspond to large charge transfer along the surface bonds. In this case one layer is enough to correctly describe the polarization properties of the system.

Since both the geometrical and electronic properties of the Si-C bonds are close to those of the (1100) surface,
FIG. 6: (color online) Side (a) and top (b) view of the relaxed (11\textbar{2}0) surface. The hexagonal stacking direction is the [0001] direction. The rectangular zone sketched in (b) identifies the surface unit cell used in the simulations. In the picture a (2\times2) replica of the unit cell is shown. Color code as in Fig. 3.

TABLE V: Structural properties of the relaxed non-polar (11\textbar{2}0) surface versus published data: tilt angle $\omega$ of the surface bond, bond-length BL (in Å and % of the corresponding bulk value) of the surface bonds, surface energy per surface unit area $\sigma$, displacements along the perpendicular direction for surface atoms ($d_{\perp Si}$ and $d_{\perp C}$) and ionization potential $I_p$.

<table>
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<th>This Work</th>
<th>SCC-DFTB$^a$</th>
</tr>
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<tbody>
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<td>$\omega$ (deg)</td>
<td>5.9</td>
<td>5</td>
</tr>
<tr>
<td>BL (Å)</td>
<td>1.76(-7.9%)</td>
<td>1.76(-6.7%)</td>
</tr>
<tr>
<td>$d_{\perp Si}$ (Å)</td>
<td>-0.22</td>
<td>-0.15</td>
</tr>
<tr>
<td>$d_{\perp C}$ (Å)</td>
<td>-0.04</td>
<td>0.02</td>
</tr>
<tr>
<td>$\sigma$ (eV/Å$^2$)</td>
<td>0.16</td>
<td>0.20</td>
</tr>
<tr>
<td>$I_p$ (eV)</td>
<td>5.65</td>
<td></td>
</tr>
</tbody>
</table>

$^a$Ref. [48]

it would be reasonable to expect also similar results for the surface polarization. Indeed a layer-by-layer analysis (Fig. 5) reveals that it is possible to recover the bulk-like configuration after only four layers. At the outermost layer, we observe the rise of a surface polarization component perpendicular to the surface as well as a large modification of the [0001] component, $1.51 \times 10^{-10}$ C/m (see Fig. 5). Table IV reports the total excess of the surface polarization with respect to the bulk value, i.e. the sum of the contributions of each layer shown in Fig. 5.

The (11\textbar{2}0) surface shows a smaller surface polarization with respect to (11\textbar{0}0), which may be ascribed to a smaller charge transfer, due to different surface truncation. This is consistent also with the smaller bond contraction of the surface Si-C bonds: a smaller amount of charge along the bond results in a weaker, and so longer, bond.

As a consistency check, we apply the extrapolation technique of Sec. II A to evaluate the in-plane component of the dipole moment via BP calculations of the total polarization in slabs with different thickness: the results are in perfect agreement with the previous data, giving a y dipole component of $1.45 \times 10^{-10}$ C/m. Furthermore, the component of the local dipole perpendicular to the surface as estimated by means of the ionization potential technique (see Sec. II A) gives $p_z=0.50 \times 10^{-10}$ C/m, for both surfaces, slightly larger than the WF result.

IV. CONCLUSIONS

In this paper we have calculated the polarization field in different SiC structures (bulk and surfaces), by means of different approaches. We first studied the bulk spontaneous polarization, to provide a trend as a function of the hexagonality of the structure, for comparison with surfaces. Our results, obtained by means of both BP and WFs, indicate that polarization effects are highly sensitive to the details of the calculation: accurate results can be achieved improving the k-point sampling beyond that typically exploited for structural and electronic investigations.

We proposed an unified scheme to calculate the surface polarization, based on the evaluation of the WF and the average potential profiles: the choice of a proper reference volume over which calculating the in-plane and perpendicular components of the polarization leads to a physical picture that is consistent with the bulk polarization properties of the material. The internal consistency of the proposed method is not fortuitous. Keeping in mind that the spontaneous polarization is a macroscopic
property of matter, from one hand, the introduction of WFs centers allows us to reduce the problem of a semi-infinite surface to a finite and neutral system of localized charges. On the other hand, the average procedure moves from the atomistic details of the crystalline structure giving a macroscopic picture of the system.

In the case of SiC (1120) and (1100) non-polar surfaces we demonstrated that the charge transfer that arises upon truncation of a bulk structure is strong enough to create a large surface polarization along the direction normal to the surface, and to deeply modify the surface polarization component along the bulk polar direction for the first film layers. We therefore showed that the commonly called non-polar surfaces may present remarkable polarity effects. On the other hand, the surface polarization can be considered as a local contribution in thicker slabs, since it approaches the bulk values inside the slabs, within a few atomic layers from the surface.

Finally, we remark that the presence of non-vanishing in-plane polarization components in the case of non polar surfaces is fundamental for the understanding of adsorption and interaction mechanisms of ad-atoms and small molecules at surfaces and to eventually rationalize interface formation. The decaying behavior of the in-plane surface polarization components, which counterbalances and even cancels the one derived from the spontaneous polarization field, poses a question on the size extension of polarization and pyroelectric effects, which may be relevant for nanodevices.

V. ACKNOWLEDGMENTS

We are indebted to Alfonso Baldereschi and Raffaele Resta, for invaluable help and illuminating discussions; we also thank M. Clelia Righi who shared with us results of her work prior to publication. Computational resources were provided by CNR-INFN through “Commissione Calcolo Parallelo”. This work was supported in part by MIUR through FIRB LATEMAR and by the regional laboratory of EM “Nanofaber”.

30 The Berry’s phase (modulo 2π) is defined as φ(x, k′) = Im det [ln |det S(x, k′)] = Im ln |det S(x, k′)|, where Smn(x, k) = (ukm/wk)n is the overlap matrix of lattice periodic Bloch function w(x).
41 WA NT code by A. Calzolari, A. Ferretti, C. Cavazzoni, N. Marzari and M. Buongiorno Nardelli, http://www.wannier-transport.org, see also Ref. 42.
5.2 Perspectives: electronic transport properties of SiC/AlN interfaces

Considering the semiconductor heterostructures mentioned above, it is an interesting issue to study transport properties in such interfaces. In fact they are used for the production of lasers and optoelectronic devices, where the charge injection process is involved. Understanding transport properties through the interface is important to predict the charge injection mechanism, which strongly influences the efficiency of the designed device and depends on the charge mobility into the system.

We consider two interfaces with different orientations along the (0001) and (1120) directions, which are respectively polar and non polar in the bulk of both the considered materials. These interfaces have been thoroughly characterized from a theoretical and experimental point of view \cite{3,4,12,7,6,8}: electronic properties typical of semiconductor heterostructures, such as band offsets or polarization fields have been investigated and measured.

We are interested in a comparison between the transport properties of the two systems, to see how the transport can result influenced by the polarization effects which are also responsible for reconstruction, connected to charge accumulation at the interface and macroscopic electric field rising in the structure. In fact the discontinuity of the spontaneous bulk polarization of SiC and AlN originates the $2\times2$ reconstruction of the (0001) structure, with interdiffusion of atoms at the interface, while the (1120) results unreconstructed.

We have calculated the electronic properties of the two relaxed heterostructures by means of the DFT plane wave technique described in Chap.\ref{chap:1}, finding good agreement with that already described in the literature \cite{3,4,8,7}. This is the preliminary step to the transport calculations along the direction perpendicular to the interface which we are currently performing. The SiC/AlN interfaces are chemically covalently bonded, so that we would expect to find strong dispersion in the band structure: A fully three–dimensional transport treatment, including the parallel $k$–points discretization on the interface, is thus necessary to give a correct description of the system. To do this we will exploit the developed method illustrated in Chap.\ref{chap:3}.

We mimic the layered structure, applying periodic boundary conditions: For the (0001) we use an hexagonal $2\times2$ simulation unit cell with twelve layers of SiC and twelve layers of AlN, allowing the reconstruction with interdiffusion, while for the (1120) an orthorombic cell with ten layers of SiC and ten layers of AlN is used. The two analyzed structures are sketched in Figs. 5.1 and 5.2.
5.2 Perspectives: electronic transport properties of SiC/AlN interfaces

Figure 5.1: SiC/AlN polar interface in the (0001) direction: side (a) and top (b) view. In the zoom A the reconstruction with interdiffusion of Al atoms at the interface can be clearly seen.

Figure 5.2: SiC/AlN non polar (1120) interface: side (a) and top (b) view. The interface is unreconstructed, formed through Si-N and Al-C covalent bonds (zoom A).
Bibliography


5.2 Perspectives: electronic transport properties of SiC/AlN interfaces


Conclusions

The main goal of this thesis was the accurate theoretical analysis of electronic and transport properties of nanostructured semiconductor–based surfaces and interfaces. This has been done using an *ab initio* real space description of the systems.

Several aspects have been considered which influence hybrid semiconductor interfaces transport properties: This has led to the structural and electronic characterization in terms of chemical bonding, band structure, density of states, polarization effects. Moreover we have addressed the most commonly measured transport characteristics in the nanosized junctions, quantum conductance and I–V curve.

To calculate all these properties we have used appropriate theoretical and computational tools: starting from the density functional theory in a plane wave pseudopotential implementation for the electronic structure; moving to the real space basis of maximally localized Wannier functions (MLWFs) for local properties, like chemical bonding and polarization; up to the Landauer formalism based on the Green’s functions technique for conductance and current calculations. MLWFs have also been used as the basis set for Landauer transport calculations.

When the available tools were not sufficient or needed developments, we have provided the necessary improvements, as in the case of the inclusion of the ultrasoft pseudopotentials formalism in the Wannier functions calculation or the extension to the parallel *k*-points technique for calculating transport in fully three–dimensional systems. We have illustrated in details all these developments, which have been implemented in the WanT code.

Examples of calculations of the properties of interest in hybrid organic–silicon interfaces and in compound semiconductor surfaces and heterointerfaces have been reported. In the case of functionalized silicon surfaces, we found that the molecule–surface bonding is crucial for determining the transport properties in terms of quantum conductance and current through an interface. In fact it strongly influence the conductor/lead coupling, while the lateral coupling among the molecules is less important. Considering biphenyl molecules on H:Si(111), the Si-O bonding has superior electronic and transport characteristics for holes transfer, with respect to the Si-S anchorage.
Several aspects of the interfaces influence transport, among them the polarization effects. We studied them in SiC surfaces and we demonstrated that the truncation of a bulk having spontaneous polarization lead to the formation of surfaces presenting remarkable polarity effects (in plane polarization components) even when they are commonly called non polar. Thus we would expect to find interesting transport properties in interfaces coming from solids with spontaneous bulk polarization.

To proceed with this work, we plan to complete the characterization of these systems, calculating the conductance and I–V curve in the SiC/AlN interfaces described in Chapter 5 and in other systems, good candidates for applications in nanoelectronics or optoelectronics, using the properly optimized and developed tools.
Full list of publications


