Abstract—We developed and implemented a first-principles based theory of the Landauer ballistic conductance, to determine the transport properties of nanosstructures and molecular-electronics devices. Our approach starts from a quantum-mechanical description of the electronic structure of the system under consideration, performed at the density-functional theory level and using finite-temperature molecular dynamics simulations to obtain an ensemble of the most likely microscopic configurations. The extended Bloch states are then converted into maximally-localized Wannier functions to allow us to construct the Green’s function of the conductor, from which we obtain the density of states (confirming the reliability of our microscopic calculations) and the Landauer conductance. A first application is presented to the case of carbon nanotubes.

Index Terms—Nanotubes and nanostructures, Landauer conductance, first-principles, Wannier functions.

I. INTRODUCTION

The physical and chemical behavior of engineered systems at the nanometer scale challenges both experimental and theoretical characterization. At these scales “your intuition fools you”, as Gerd Binnig puts it (he is the co-inventor of the most celebrated nanoscale probe, the scanning tunneling microscopy). First-principles simulation techniques are very natural tools to probe the properties of matter at such small scales, since they derive macroscopic properties from a detailed and fundamental quantum mechanical description of all the electrons interacting with the atomic nuclei. In doing so, they combine their fundamental quantum-mechanical predictive power with atomic resolution in length and time. We plan to use extensively these techniques in order to develop a microscopic understanding of transport properties of nanosized object (carbon nanotubes), and to provide testing and guidance for their design and functionalization toward target applications. Three fundamental steps are needed to determine the transport characteristics of a nanostructure:

- Structural Stability: Extensive first-principles molecular dynamics simulations are used to determine the ground-state structure and other low-energy configurations, to study their dependence on temperature, and in general to span as efficiently as possible the phase space of the system. As an example, finite-temperature simulations can be used to efficiently determine which are the most favorable adsorption sites for a molecule impinging on a carbon nanotube, or to follow the evolution of the contact between an organic compound and the metal substrate onto which it has been deposited.
- Electronic structure The first-principles molecular dynamics algorithm evolves “on-the-fly” the electronic structure of the system, in both the occupied and the conduction subspace. Since we are studying extended or semi-infinite systems (the leads), and due to the use of periodic boundary conditions, the orbitals are in their Bloch extended form. The Bloch representation is not useful to calculate the conductance (see below), but using the Marzari-Vanderbilt maximally-localized Wannier functions approach [1] [2] we can determine the optimal unitary rotations at every point in the Brillouin zone that transform the extended orbitals into localized Wannier functions, preserving the same identical Hilbert space (i.e. we are performing a unitary transformation on the orbitals that localizes them as much as possible).
- Quantum conductance The Landauer conductance is then calculated from the Green’s functions of the conductor and its coupling to the leads (via the self-energies). Namely, the conductance \( G \) of the full system is given by \( G = 2e^2/h Tr(\Gamma_L G_C \Gamma_R G_C) \), where \( G_C \) is the Green’s function of the conductor, and \( \Gamma_{L,R} \) are the coupling functions that describe the interaction between the conductor and the leads. These can be calculated from the retarded and advanced self-energies, using the formalism of principal layers and the surface Green’s function matching theory briefly outlined below, and exploiting the decomposition into localized orbitals obtained from the maximally-localized representation (see Refs. [3] and [4]). The Green’s function is also obtained straightforwardly in a localized orbital scheme from the Hamiltonian and overlap matrices.

II. STRUCTURAL STABILITY: AB-INITIO MOLECULAR DYNAMICS

We have shown [5] that the consistent approach to evolve the Kohn-Sham energy as an explicit functional of the orbitals \( \{ \psi_i \} \), whenever partially occupied or unoccupied states are introduced, requires the introduction of a matrix \( F_{ij} \) that takes into account the additional degrees of freedom: occupation numbers for the orbitals, and the unitary rotations that transform the orbitals into each other. This is due to the fact that direct methods (e.g. Car-Parrinello or conjugate-gradients
minimizations) evolve only the Hilbert space “perpendicular” to the subspace spanned by the orbitals introduced in the calculation. Whenever this latter “parallel” subspace loses invariance for unitary transformations (the canonical and very useful exception being that of a system with a gap, whenever solely the occupied bands are considered), it becomes necessary to introduce an additional evolution for the unitary rotations \( \{ U_{ij} \} \) and the occupations number \( \{ f_i \} \), via a matrix

\[
F_{ij} = \sum_k U_{ik}^\dagger f_k U_{kj}
\]

that connects the states that are evolved with the Car-Parrinello or conjugate-gradients minimization to the instantaneous (and non-selfconsistent, in general) eigenstates of the Hamiltonian. Thus, the charge density and the total free energy (assuming, for sake of generality, the presence of a finite electronic temperature) are written in the form of traces

\[
\rho(r) = \sum_{ij} F_{ij} \langle \psi_j | \psi_i \rangle
\]

\[
A = \sum_{ij} F_{ij} \langle \psi_j | \tilde{T} + \tilde{V}_{\text{ext}} | \psi_i \rangle + E_{\text{Hxc}}[\rho] - TS[\{ F_{ij} \}]
\]

that makes them covariant for any unitary transformation of the orbitals. A set of second-order molecular dynamics equations for all the degrees of freedom involved can be postulated

\[
\mu_e \dot{\psi}_i = -H \psi_i + \sum_j |\psi_j \rangle \Lambda_{ji}
\]

\[
\mu_U \dot{U}_{ji} = -f_j \sum_l U_{jl} (H_{li} + \mu_e K_{li}) + \sum_l \lambda_{jl} U_{li}
\]

\[
\ddot{\xi} = -\frac{1}{2} f_i^\prime \xi_i^2 + \frac{1}{\mu_\xi} (h_i - \epsilon_F - \xi_i)
\]

and shown to conserve rigorously a generalized constant of motion

\[
H = \mu_U Tr(\tilde{U}^\dagger \tilde{U}) - \frac{1}{2} \mu_\xi \sum_i f_i \dot{\xi}_i^2 + \mu_e Tr(KF) + \sum_{ij} F_{ij} \langle \psi_j | \tilde{T} + \tilde{V}_{\text{ext}} | \psi_i \rangle + E_{\text{Hxc}}[\rho] - TS[\{ F_{ij} \}]
\]

\[
- Tr[\langle \psi_j | \psi_j \rangle - 1) \Lambda F] - Tr[ (U^\dagger U - 1) \lambda] + \epsilon_F [ Tr F - N]
\]

(3)

III. ELECTRONIC STRUCTURE: MAXIMALLY-LOCALIZED WANNIER FUNCTIONS

A. Methodology

Electronic structure calculations are often carried out using periodic boundary conditions; this is the most natural choice to study perfect crystals and to minimize finite size-effects in the study of several non-periodic systems (e.g., surfaces, impurities, or the lead-conductor-lead geometries considered here). The one-particle effective Hamiltonian \( \tilde{H} \) then commutes with the lattice-translation operator \( \tilde{T}_R \), allowing one to choose as common eigenstates the Bloch orbitals \( | \psi_{nk} \rangle \):

\[
[ \tilde{H}, \tilde{T}_R ] = 0 \Rightarrow \psi_{nk}(r) = e^{i\phi_n(k)} u_{nk}(r) e^{ik \cdot r}
\]

where \( u_{nk}(r) \) has the periodicity of the Hamiltonian. There is an arbitrary phase \( \phi_n(k) \), periodic in reciprocal space, that is not assigned by the Schrödinger equation and that we have written out explicitly. We obtain a (non-unique) Wannier
representation using any unitary transformation of the form
\[ \langle n\mathbf{k} | \mathbf{R} n \rangle = e^{i\varphi_n(\mathbf{k}) - i\mathbf{k} \cdot \mathbf{R}} \]
\[ | \mathbf{R} n \rangle = \frac{V}{(2\pi)^3} \int_{BZ} | \psi_{nk} \rangle e^{i\varphi_n(\mathbf{k}) - i\mathbf{k} \cdot \mathbf{R}} d\mathbf{k} . \tag{6} \]

Here \( V \) is the real-space primitive cell volume. It is easily shown that the \( | \mathbf{R} n \rangle \) form an orthonormal set, and that two Wannier functions \( | \mathbf{R} n \rangle \) and \( | \mathbf{R} m \rangle \) transform into each other with a translation of a lattice vector \( \mathbf{R} - \mathbf{R}' \). The arbitrariness that is present in \( \varphi_n(\mathbf{k}) \) or \( \phi_n(\mathbf{k}) \) propagates to the resulting Wannier functions, making the Wannier representation non-unique. Since the electronic energy functional in an insulator is also invariant with respect to a unitary transformation of its \( n \) occupied Bloch orbitals, there is additional freedom associated with the choice of a full unitary matrix (and not just a diagonal one) transforming the orbitals between themselves at every wavevector \( \mathbf{k} \). Thus, the most general operation that transforms the Bloch orbitals into Wannier functions is given by
\[ | \mathbf{R} n \rangle = \frac{V}{(2\pi)^3} \int_{BZ} \sum_m U_m^{(k)} | \psi_{mk} \rangle e^{-i\mathbf{k} \cdot \mathbf{R}} d\mathbf{k} . \tag{7} \]

The Wannier functions \( w_n(\mathbf{r} - \mathbf{R}) = | \mathbf{R} n \rangle \), for non-pathological choices of phases, are “localized”: for a \( \mathbf{R} \), far away from \( \mathbf{R} \), \( w_n(\mathbf{r} - \mathbf{R}) \) is a combination of terms like \( \int_{BZ} u_{mk}(0) e^{i\mathbf{k} \cdot (\mathbf{R} - \mathbf{R}')} d\mathbf{k} \), which are small due to the rapidly varying character of the exponential factor [6].

B. Maximally-localized Wannier functions

Several heuristic approaches have been developed that construct reasonable sets of Wannier functions, reducing the arbitrariness in the \( U_m^{(k)} \) with symmetry considerations and analyticity requirements [7], or explicitly employing projection techniques on the occupied subspace spanned by the Bloch orbitals [8]. At variance with those approaches, we introduced a well-defined localization criterion, choosing the functional
\[ \Omega = \sum_n [(\mathbf{r}^2)_n - \bar{\mathbf{r}}^2_n] \tag{8} \]
as the measure of the spread of the Wannier functions. The sum runs over the \( n \) functions \( | 0n \rangle \); \( \langle \mathbf{r}^2 \rangle_n \) and \( \bar{\mathbf{r}}_n = (\langle \mathbf{r} \rangle)_n \) are the expectation values \( (0n | \mathbf{r}^2 | 0n \rangle \) and \( (0n | \mathbf{r} | 0n \rangle \). Given a set of Bloch orbitals \( | \psi_{mk} \rangle \), the goal is to find the choice of \( U_m^{(k)} \) in (7) that minimizes the values of the localization functional (8). We are able to express the gradient \( G = \frac{d\Omega}{dm} \) of the localization functional with respect to an infinitesimal unitary rotation of our set of Bloch orbitals
\[ | \mathbf{u}_{nk} \rangle \rightarrow | \mathbf{u}_{nk} \rangle + \sum_m dW_m^{(k)} | \mathbf{u}_{mk} \rangle , \tag{9} \]
where \( dW \) an infinitesimal unitary matrix \( dW^\dagger = -dW \) such that
\[ U_m^{(k)} = \delta_{mn} + dW_m^{(k)} . \tag{10} \]

This provides an equation of motion for the evolution of the \( U_m^{(k)} \), and of the \( | \mathbf{R} n \rangle \) derived in (7), toward the minimum of \( \Omega \); small finite steps in the direction opposite to the gradient decrease the value of \( \Omega \), until a minimum is reached.

1) Real-space representation: There are several interesting consequences stemming from the choice of (8) as the localization functional, that we briefly summarize here. Adding and subtracting the off-diagonal components \[ \Omega = \sum_n \sum_{m \neq 0n} | \langle \mathbf{R} m | | 0n \rangle |^2 , \tag{11} \]
we obtain the decomposition \( \Omega = \Omega_I + \Omega_D + \Omega_{OD} \), where \( \Omega_I \), \( \Omega_D \) and \( \Omega_{OD} \) are respectively
\[ \Omega_I = \sum_n \left[ (\mathbf{r}^2)_n - \sum_{Rm \neq 0n} | \langle \mathbf{R} m | | 0n \rangle |^2 \right] , \tag{11} \]
\[ \Omega_D = \sum_n \sum_{R \neq 0} | \langle \mathbf{R} n | | 0n \rangle |^2 , \tag{12} \]
\[ \Omega_{OD} = \sum_{m \neq n} \sum_{R} | \langle \mathbf{R} m | | 0n \rangle |^2 . \tag{13} \]

It can be shown that all terms are positive-definite (in particular \( \Omega_I \), see Ref. [1]); more importantly, \( \Omega_I \) is also gauge-invariant, i.e., it is invariant under any arbitrary unitary transformation (7) of the Bloch orbitals. The minimization procedure thus corresponds to the minimization of \( \Omega = \Omega_D + \Omega_{OD} \). At the minimum, the elements \( | \langle \mathbf{R} m | | 0n \rangle |^2 \) are as small as possible, realizing the best compromise in the simultaneous diagonalization, within the space of the Bloch bands considered, of the three position operators \( x, y \) and \( z \) (which do not in general commute when projected within this space).

2) Reciprocal-space representation: As shown by Blount[6], matrix elements of the position operator between Wannier functions take the form
\[ \langle \mathbf{R} n | \mathbf{r} | 0m \rangle = i | \frac{V}{(2\pi)^3} \int d\mathbf{k} e^{i\mathbf{k} \cdot \mathbf{R}} \langle \mathbf{u}_{nk} | \nabla_\mathbf{k} | \mathbf{u}_{mk} \rangle = i \tag{14} \]
\[ \langle \mathbf{R} n | \mathbf{r}^2 | 0m \rangle = - | \frac{V}{(2\pi)^3} \int d\mathbf{k} e^{i\mathbf{k} \cdot \mathbf{R}} \langle \mathbf{u}_{nk} | \nabla_\mathbf{k}^2 | \mathbf{u}_{mk} \rangle , \tag{15} \]

These expressions provide the needed connection with our underlying Bloch formalism, since they allow us to express the localization functional \( \Omega \) in terms of the matrix elements of \( \nabla_\mathbf{k} \) and \( \nabla_\mathbf{k}^2 \). We thus determine the Bloch orbitals \( | \mathbf{u}_{mk} \rangle \) on a regular mesh of \( \mathbf{k} \)-points, and use finite differences to evaluate the above derivatives. For any given \( \mathbf{k} \)-point in a regular cubical mesh (sc, fcc, bcc), we have a star \( \mathbf{b} \) of \( Z \) \( \mathbf{k} \)-points that are first-neighbors; their weights in the evaluation of derivatives are \( w_b = 3/Zb^2 \). We define \( M_{mn}^{(k,b)} = \langle \mathbf{u}_{mk} | \mathbf{u}_{nk} + \mathbf{b} \rangle \) as the matrix elements between Bloch orbitals at neighboring \( \mathbf{k} \)-points. The \( M_{mn}^{(k,b)} \) are a central quantity in our formalism, since we can then express all the contributions to the localization functional using the connection made by Blount, together with our finite-difference evaluations of the gradients. After some algebra we obtain[1]
\[ \Omega_I = \frac{1}{N} \sum_{k,b} w_b \left( N_{\text{bands}} - \sum_{m} | M_{mn}^{(k,b)} |^2 \right) , \tag{16} \]
\[ \Omega_{OD} = \frac{1}{N} \sum_{k,b} w_b \sum_{m \neq n} | M_{mn}^{(k,b)} |^2 , \tag{17} \]
O is dependent on the ionic positions through the $\beta^I_n$, which are projector functions localized within the core regions:

$$\beta^I_n(r) = \beta_n(r - R_I) .$$  

(23)

$\beta_n$ depends on the atomic species and is an angular momentum eigenfunction in the angular variables times a radial function which vanishes outside the core region. The indexes $n$ and $m$ run over the total number of such functions for each atom $I$; usually two reference energies, and therefore two radial functions, are required for each included angular momentum channel (for each atom). Another quantity in Eq. 22 is $q^I_{nm} = \int d\mathbf{r} Q^I_{nm}(r)$, where $Q^I_{nm}(r)$ is a charge-restoring augmentation function restricted within the core regions. $Q^I_{nm}(r)$ is dependent on the ionic positions, while $q^I_{nm}$ only depends on the atomic species at $I$:

$$Q^I_{nm}(r) = Q_{nm}(r - R_I) .$$  

(24)

$\beta^I_n$, $Q^I_{nm}$ and all other pseudopotential parameters are calculated in an atomic reference system.

In this ultrasoft pseudopotential scheme, the operator $|\mathbf{r}\rangle\langle\mathbf{r}|$ is replaced by

$$K(r) = |\mathbf{r}\rangle\langle\mathbf{r}| + \sum_{nm,I} Q^I_{nm}(r)|\beta^I_n\rangle\langle\beta^I_m| .$$  

(25)

and the total electron density becomes

$$n(r) = \sum_i \langle \phi_i | K(r) | \phi_i \rangle$$

(26)

$$= \sum_i |\phi_i(r)|^2 + \sum_{nm,I} Q^I_{nm}(r) \langle \phi_i | \beta^I_n \rangle \langle \beta^I_m | \phi_i \rangle .$$

The first term in Eq. (27) is the smooth pseudo-charge from the pseudo-wavefunctions; the $Q^I_{nm}(r)$ in the second term are the augmented charges within the core regions.

For isolated systems and insulating crystals, it is appropriate to use only the wavefunctions at the $\Gamma$-point of BZ to construct maximally-localized Wannier functions - provided the unit cell is large enough. We define the overlap matrices

$$M^I_{ij} = \langle w_i | e^{-iG_I \cdot \mathbf{r}} | w_j \rangle ,$$  

(27)

where $G_I$ are the reciprocal lattice vectors of the unit cell, and $w_i$ the $\Gamma$ point wavefunctions), a functional $S$ can be constructed:

$$S = \sum_{i=1}^N \sum_{l=1}^{N_G} W_i |M^I_{ii}|^2$$  

(28)

($N$ is the number of bands, $N_G$ is the number of the $G_I$ vectors required to preserve the natural symmetry, and $W_l$ is the weight corresponding to the specific vector $G_l$). This quantity is closely related to the spread of the Wannier functions, which measures their delocalization:

$$\Omega = \left( \frac{L}{2\pi} \right)^2 \sum_{i=1}^N \sum_{l=1}^{N_G} W_i \left[ (\omega_i | (G_I \cdot \mathbf{r})^2 | \omega_i) - (\omega_i | G_I \cdot \mathbf{r} | \omega_i)^2 \right]$$

$$= \left( \frac{L}{2\pi} \right)^2 \sum_{i=1}^N \sum_{l=1}^{N_G} W_l \left( 1 - |(\omega_i | e^{-iG_I \cdot \mathbf{r}} | \omega_i)^2 \right) + O(L^{-2})$$

$$= \left( \frac{L}{2\pi} \right)^2 \left( \sum_{i=1}^N \sum_{l=1}^{N_G} W_l - S \right) + O(L^{-2}) ,$$  

(29)
where $L$ is the supercell dimension. Instead of minimizing the spread we can maximize the functional $S$; the Wannier function center of the $i$-th occupied band $r_i$ is then computed using:

$$
\mathbf{r}_i = -\left(\frac{L}{2\pi}\right)^2 \sum_l W_l \mathbf{G}_l Im \ln M_{ii}^l.
$$

(30)

Within the ultrasoft pseudopotential approach, only the construction of the overlap matrices are different:

$$
M_{ij}^l = \langle \phi_i | K (\mathbf{r}) e^{-i \mathbf{G}_l \cdot \mathbf{r}} | \phi_j \rangle = \langle \phi_i (\mathbf{r}) | e^{-i \mathbf{G}_l \cdot \mathbf{r}} | \phi_j (\mathbf{r}) \rangle + \sum_{nm,l} \int Q_{mn}^l (\mathbf{r}) e^{-i \mathbf{G}_l \cdot \mathbf{r}} d\mathbf{r} \langle \phi_i | \beta_l^I | \phi_j \rangle.
$$

(31)

This equation reduces to Eq. 27 when $K (\mathbf{r}) = | r \rangle \langle r |$ and $w_i = \phi_i$ in the case of norm-conserving pseudopotential. With the new overlap matrices, the procedure of maximizing $S$ remains identically valid, and can be used in the same way to obtain maximally-localized Wannier functions and their centers and spreads.

IV. ELECTRON TRANSMISSION AND GREEN’S FUNCTION

We consider a system composed of a conductor $C$ connected to two semi-infinite leads, $R$ and $L$. The conductance through a region of interacting electrons is related to the scattering properties of the region itself via the Landauer formula [9]:

$$
C = \frac{2e^2}{h} T,
$$

(32)

where $T$ is the transmission function and $C$ is the conductance. $T$ is the probability that an electron injected at one end of the conductor will transmit to the other end. This transmission function can be expressed in terms of the Green’s functions of the conductors and the coupling of the conductor to the leads [10], [11]:

$$
T = Tr (\Gamma_L G_C^r \Gamma_R G_C^a),
$$

(33)

where $G_C^{r,a}$ 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. To compute the Green’s function of the conductor we start from the equation for the Green’s function of the whole system:

$$
(\epsilon - H) G = I
$$

(34)

where $\epsilon = E + i\eta$ with $\eta$ arbitrarily small and $I$ is the identity matrix. In the hypothesis that the Hamiltonian of the system can be expressed in a discrete real-space matrix representation, the previous equation corresponds to the inversion of an infinite matrix for the open system, consisting of the conductor and the semi-infinite leads. The above Green’s function can be partitioned into sub-matrices that correspond to the individual subsystems:

$$
\begin{pmatrix}
G_L & G_{LC} & G_{LCR} \\
G_{CL} & G_C & G_{CR} \\
G_{LRC} & G_{RC} & G_R
\end{pmatrix}
$$

(35)

where the matrix $\epsilon - H_{LC}$ represents the finite isolated conductor, $(\epsilon - H_{(R,L)})$ represent the infinite leads, and $h_{CR}$ and $h_{LC}$ are the coupling matrices that will be non-zero only for adjacent points in the conductor and the leads, respectively. From this equation it is straightforward to obtain an explicit expression for $G_C$ [10]:

$$
G_C = (\epsilon - H - \Sigma_L - \Sigma_R)^{-1}
$$

(36)

where we define $\Sigma_L = h_{LC}^H g_L h_{LC}$ and $\Sigma_R = h_{RC}^H g_R h_{RC}$ as the self-energy terms due to the semi-infinite leads and $g_{(L,R)} = (\epsilon - H_{(L,R)})^{-1}$ are the leads’ Green’s functions. The self-energy terms can be viewed as effective Hamiltonians that arise from the coupling of the conductor with the leads. Once the Green’s functions are known, the coupling functions $\Gamma_{(L,R)}$ can be easily obtained as [10]:

$$
\Gamma_{(L,R)} = i [\Sigma^a_{(L,R)} - \Sigma^a_{\{L,R\}}]
$$

(37)

where the advanced self-energy $\Sigma^a_{\{L,R\}}$ is the Hermitian conjugate of the retarded self-energy $\Sigma^a_{(L,R)}$. The core of the problem lies in the calculation of the Green’s functions of the semi-infinite leads. In what follows we will present an efficient approach to compute the self-energy terms in the general case of an arbitrary localized-orbital Hamiltonian.

A. Transmission through a bulk system

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 [12]. This corresponds to transforming the original system into a linear chain of principal layers. Within this approach, the matrix elements of Eq. (34) between layer orbitals will yield a set of equations for the Green’s functions:

$$
\begin{align*}
(\epsilon - H_{00}) G_{00} &= I + H_{01} G_{10} \\
(\epsilon - H_{00}) G_{10} &= H_{11}^g G_{00} + H_{01} G_{20} \\
&\vdots \\
(\epsilon - H_{00}) G_{n0} &= H_{11}^g G_{n-1,0} + H_{01} G_{n+1,0}
\end{align*}
$$

(38)

where $H_{nm}$ and $G_{nm}$ are the matrix elements of the Hamiltonian and the Green’s function between the layer orbitals, and we assume that in a bulk system $H_{00} = H_{11} = \ldots$ and $H_{01} = H_{12} = \ldots$. Following Lopez-Sancho et al. [13], 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 $T$, defined such that $G_{10} = TG_{00}$ and $G_{00} = TG_{10}$. The transfer matrix can be easily computed from the Hamiltonian matrix elements via an iterative procedure, as outlined in Ref. [13]. In particular $T$ and $T$ can be written as

$$
\begin{align*}
T &= t_0 + t_0 t_1 + t_0 t_1 t_2 + \ldots + t_0 t_1 t_2 \ldots t_n \\
T &= t_0 + t_0 t_1 + t_0 t_1 t_2 + \ldots + t_0 t_1 t_2 \ldots t_n
\end{align*}
$$
where \( t_i \) and \( \tilde{t}_i \) are defined via the recursion formulas:
\[
\begin{align*}
  t_i &= (I - t_{i-1} \tilde{t}_{i-1} - \tilde{t}_{i-1} t_{i-1})^{-1} t_{i-1}^2, \\
  \tilde{t}_i &= (I - t_{i-1} \tilde{t}_{i-1} - \tilde{t}_{i-1} t_{i-1})^{-1} \tilde{t}_{i-1}^2,
\end{align*}
\]
and
\[
\begin{align*}
  t_0 &= (\epsilon - H_{00})^{-1} H_{01}^\dagger, \\
  \tilde{t}_0 &= (\epsilon - H_{00})^{-1} H_{01}.
\end{align*}
\]
The process is repeated until \( t_n, \tilde{t}_n \leq \delta \) with \( \delta \) arbitrarily small. With this proviso, we can write the bulk Green’s function as:
\[
G(E) = (\epsilon - H_{00} - H_{01} T - H_{01}^\dagger T^{-1})^{-1}. \tag{39}
\]
If we compare the previous expression with Eq. (IV), in the hypothesis of leads and conductors being of the same material (bulk conductivity), we can identify the present bulk system, or rather one of its principal layers, with the conductor \( C \), so that \( H_{00} \equiv H_C, H_{01} \equiv h_{CR} \) and \( H_{01}^\dagger \equiv h_{LC}^\dagger \). In particular, by comparing with Eq. 36, we obtain the expression of the self-energies of the conductor-leads system:
\[
\Sigma_L = H_{01} T, \quad \Sigma_R = H_{01} T. \tag{40}
\]
The coupling functions are then obtained from the sole knowledge of the transfer matrices and the coupling Hamiltonian matrix elements: \( \Gamma_L = -\text{Im}(H_{01}^\dagger T^{-1}) \) and \( \Gamma_R = -\text{Im}(H_{01} T^{-1}) \). The knowledge of the bulk Green’s function \( G \) gives also direct informations on the electronic spectrum via the spectral density of bulk electronic states: \( N(E) = -(1/\pi) \text{Im}(\text{Tr}G(E)) \).

V. APPLICATION: (8,0) CARBON NANOTUBE

The overall formalism has been validated for the case of a (8,0) carbon nanotube. In particular we have calculated the band-structure using a standard, public domain pseudopotential code (upper panel of Fig. 3), using a unit cell with 32 atoms, and k-point sampling along the z direction (4 points). The same system has been studied using a supercell approach, with 128 atoms in the unit cell, and \( \Gamma \) sampling. In this latter case, the ultrasoft maximally-localized Wannier functions have been determined, and the matrix elements of the Hamiltonian have been calculated in real space. This in turn allows to determine the density of states, via the trace of the Green’s function. Excellent agreement is found between the two approaches, as highlighted by the correspondence in the peaks of the density of states with the flattening of the nanotube subbands. The transmission function is also shown in the lower panel of Fig. 3.

VI. CONCLUSION

In conclusion, we have developed a consistent formalism to investigate the ballistic conductance of nanostructures, using a combination of 1) large scale molecular dynamics simulations able to evolve simultaneously the occupied and unoccupied manifold; 2) the use of the Marzari-Vanderbilt localization procedure, to transform the extended Bloch orbitals into maximally-localized Wannier functions 3) leading to the construction in real space of the Green’s function and the Landauer ballistic conductance, thanks to a natural decomposition of the systems into principal layers. While still at its early stages, the procedure is general, robust, and very efficient, and shows great promise to investigate fully from first-principles the transport properties of molecular electronics devices.

ACKNOWLEDGMENT

The authors would like to thank David Vanderbilt, with which the maximally-localized Wannier function formalism has been developed and extended – together with Ivo Souza – to the case of metallic systems, and Roberto Car and Yudong Wu, for the ensemble-DFT Car-Parrinello simulations.

REFERENCES