Ab initio quantum transport calculations using plane waves

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Abstract

We present an *ab initio* method to calculate elastic quantum transport at the nanoscale. The method is based on a combination of density functional theory using plane wave nonlocal pseudopotentials and the use of auxiliary periodic boundary conditions to obtain the scattering states. The method can be applied to any applied bias voltage and the charge density and potential profile can either be calculated self-consistently, or using an approximated self-consistent field (SCF) approach. Based on the scattering states one can straightforwardly calculate the transmission coefficients and the corresponding electronic current. The overall scheme allows us to obtain accurate and numerically stable solutions for the elastic transport, with a computational time similar to that of a ground state calculation. This method is particularly suitable for calculations of tunneling currents through vacuum, where some of the nonequilibrium Greens function (NEGF) approaches based on atomic basis sets might have difficulty to deal with. Several examples are provided using this method from electron tunneling, to molecular electronics, to electronic devices: i) On a Au nanojunction, the tunneling current dependence on the electrode-electrode distance is investigated. ii) The tunneling through field emission resonances (FERs) is studied via an accurate description of the surface vacuum states. iii) Based on quantum transport calculations, we have designed a molecular conformational switch, which can turn on and off a molecular junction by applying a perpendicular electric field. iv) Finally, we have used the method to simulate tunnel field-effect transistors (TFETs) based on two-dimensional transition-metal dichalcogenides (TMDCs), where we have studied the performance and scaling limits of such nanodevices and proposed atomic doping to enhance the transistor performance.

Keywords: Simulation of quantum transport, Density functional theory, Scattering states, Plane waves, Tunneling regime

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1. Introduction

The field of electronic transport through nanometer-scale systems, such as molecular junctions or atomic wires, has been an extremely active area during the last decades. Although a great number of advancements have been made both from the fundamental and the application point of view,[1–5] there is still much to learn before nanoelectronics and, in particular, molecular electronics can replace the silicon based technology. The effect that the development of a post-silicon era might have on our daily lives, together with the existence of a number of extremely interesting scientific and technological open questions, indicates a bright future of this field.[3, 4]

The experimental investigation of electron transport across nanosystems was launched with the advent of the scanning tunneling microscope (STM),[6] which enables the measurement of current across a single molecule under the application of an external bias voltage. A few years later, break-junction

techniques emerged as alternative ways to measure the transport across molecular bridges.[7, 8] All these techniques have proven to be extremely powerful and, consequently, are still the prime tools for the measurement of transport properties across nanosystems. Recent experimental advances include the demonstration of various interesting effects, such as conductance switching, rectification, and interference effects.[9–15]

Along with the huge amount of experimental activity, an equally major effort has been devoted to the development of computational methods appropriate for the theoretical investigation of electron transport at nanoscale. Due to the difficulty of experimentally probing the detailed atomic structures of the nanosystem, theoretical modeling plays a key role in the understanding and interpretation of experimental observations.[1, 5] After the first semiempirical studies,[16–18] *ab initio* simulations based on first-principles have been extensively developed. In particular, given the high sensitivity of conductance to atomic-structure details, density functional theory (DFT) has become an essential tool in transport calculations. [19–31] The most commonly employed method combines the nonequilibrium Green's function (NEGF) with a DFT electronic structure.[22, 23, 25–29]. Such NEGF methods are usually based on localized basis set where the Green's function can be expressed as a matrix. Wannier functions generated from

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either plane wave basis set [32] or real space grid method [33] have also been used to construct the Green's function.

An alternative route is to explicitly solve the scattering states. A scattering state can be defined as a wave function satisfying the Schrödinger's equation at a given energy E , but also satisfying some special open boundary conditions. This approach can be realized by using the transfer-matrix method [19, 34] with some simplified Hamiltonian (either finite difference method in z -direction or tight-binding method) or the Lippmann-Schwinger equation,[21, 35] where the scattering state is solved in a linear equation with the help of a simplified jellium electrode. Similarly, in the work of Ref. 31, the scattering state is solved by a linear equation, converting the original open boundary condition problem into a linear equation problem. In all these methods, especially under *ab initio* calculations, the low order finite difference method in real space is used for the Hamiltonian, which can lead to some inaccuracy. Furthermore, the linear equation can often have a dimension which equals to the number of real space grid points of the problem. That can make the calculation extremely expensive.

In the method reviewed under this article,[30, 36] a different approach is used to solve the scattering state. This new approach allows the use of techniques already existing in a conventional *ab initio* DFT code (e.g., a plane wave nonlocal pseudopotential code), which was developed over the past two decades to accelerate the *ab initio* ground state calculations. These techniques include the real and reciprocal space representation of the Hamiltonian; the use of FFT to calculate the application of the Hamiltonian to a wave function; and the iterative conjugate gradient method to calculate the eigen states. In a way, under these techniques, one never needs to explicitly solve either the eigen state problem, or the linear equation problems with a dimension equal to the number of real space grid points or G -space plane wave basis components. One caveat however is that, in order to use such techniques, one has to keep the periodic boundary conditions. This is solved by using an auxiliary periodic boundary condition, together with a linear combination scheme to satisfy the open boundary conditions. Another major advantage of this approach is that, it keeps the conventional plane wave nonlocal pseudopotential Hamiltonian, without the need to approximate it using low order finite difference methods in real space grid.

It should be emphasized that, in principle, DFT methods cannot rigorously handle nanojunctions, open systems that are infinite, nonperiodic and out of equilibrium, because DFT describes systems in their ground state. Besides, for almost any practical DFT calculation, one needs to consider some reasonable approximation for the xc functional. Nevertheless, this approach has been proven to be valid and helpful to describe a vast number of transport experiments, although sometime corrections (e.g., from GW calculations [37]) might be necessary to fix the level alignment between the conduction molecule and the electrode. Thus, despite being one of the best choices currently available for quantum transport calculations, DFT should be treated as a practical method rather than a rigorously exact theory. On the other hand, although various many-body techniques have been proposed and applied with success in the in-

terpretation of experimental observations,[37–40] their use for the study of large systems is usually beyond computational limits. All in all, in many cases DFT is still the most suitable theoretical tool to study transport properties at the nanoscale.[41]

However, there are important issues regarding the numerical solutions of the transport problem under the usual DFT formalism. This is of key relevance, as many of the current DFT transport calculations are focused on the resolution of the experimental and theoretical differences, especially for the amplitude of the transport currents. Within this scenario, the choice of basis set might be of utmost importance. As mentioned above, most of the NEGF-DFT-based quantum transport calculations are performed using atomic centered localized basis sets.[22, 23, 28, 29] The use of this type of basis set enables the treatment of relatively large systems, particularly if a limited number of localized basis functions are used - e.g., the tight-binding basis set. On the other hand, the variational incompleteness of the atomic basis set can be a serious drawback when dealing with transport problems in tunneling regime. For example, the tunneling current crossing a vacuum gap cannot be described adequately by the conventional atomic basis set due to the lack of flexibility to describe the tunneling wave functions in the vacuum region. Similarly, in a STM image simulation the use of atomic basis sets often leads to the prediction of shorter tip to substrate distances than in the experiments, again due to the lack of flexibility to describe the wave function. In some cases, these problems can be overcome by introducing ghost orbitals, but their locations and orbital types are not unique.[42]

The most widely used basis set in material science simulation is the plane wave basis set. This basis set is considered to be more flexible and variational than a localized basis set, especially when pseudopotentials are used. Thus, numerically more accurate results can be expected from plane wave transport calculations. There are recent approaches which generate the localized Wannier functions as the localized basis starting from the plane wave basis set for NEGF-DFT calculation. But approximations need to be made to truncate the number of Wannier functions and the interactions between Wannier functions.[32] Another alternative route within plane wave based DFT is given by the novel quantum kinetic approach introduced in Ref. 43. In this approach, a time-dependent Hamiltonian is used to describe an external circular electric field within a periodic boundary condition, and a quantum mechanical Liouville master equation is solved including the electron-phonon interaction.

Here, we will focus on the elastic quantum transport calculations based on Refs. 30 and 36. We will show that, this method allows one to obtain numerically accurate and stable solutions, with a computational time similar to that of a standard ground-state calculations. Moreover, as the plane wave basis set is variational enough to describe the wave function in the vacuum region, this quantum transport calculation method is expected to be well suited to describe the tunneling problem. We have applied this method to various transport problems, both in contact and tunneling regime, as well as for nanodevice simulations.

The article is organized as follows: in Section 2 we present the details of our computational scheme, focusing in the calcu-

lation of the scattering states; Section 3 presents a short review of the existent applications of the method; we close with some general conclusions in Section 4.

2. Methodology

Due to their high conductivity and stability, the most common systems in transport experiments are composed of organic molecules connected to metallic electrodes. For this reason, we have chosen the model system in Fig. 1 to introduce our plane-wave based transport method. Nevertheless, this method is general and can be applied to any atomic-scale and molecular device connected by two electrodes.

The current flowing through such a two-terminal nanojunction can be calculated using the Landauer formula

$$I = \frac{2e}{h} \int_{\mu_L}^{\mu_R} \sum_n T_n(E) dE, \quad (1)$$

where μ_L and μ_R are the left and right electrode Fermi energies, assuming that the current flows from right to left, and $T_n(E)$ is the transmission coefficient for the n th right hand electrode band with energy E .

Figure 1: Model system used for the calculations, which consists of a di-thiol-benzene (DBT) molecule connected by two Cu wires. Ω_L and Ω_R (visualized in blue for clarity) represent the left and right primitive unit cells, respectively.

The transmission coefficient can be calculated solving the following Schrödinger equation for the scattering states

$$H\psi_{sc}(r) = E\psi_{sc}(r). \quad (2)$$

$H = \left[-\frac{1}{2}\nabla^2 + V(r) + V_{nonloc}\right]$ is the single particle Hamiltonian and includes the nonlocal potential V_{nonloc} . Here, we have considered a Kleinman-Bylander type projector-based nonlocal pseudopotential, i.e., $V_{nonloc} = \sum_l |\varphi_l\rangle\langle\varphi_l|$, where $|\varphi_l\rangle$ are the projector states of the nonlocal pseudopotential. This is needed to provide distinct s, p, d pseudopotentials.

The scattering states $\psi_{sc}(r)$ must fulfill the boundary conditions of the problem given by

$$\psi_{sc}(r) = \begin{cases} \phi_m^{R*}(r) + \sum_{n \neq m} B_n^R \phi_n^R(r), & \text{if } z \rightarrow \infty, \\ \sum_n A_n^L \phi_n^{L*}(r), & \text{if } z \rightarrow -\infty, \end{cases} \quad (3)$$

where z is chosen as the direction of current propagation, and periodic boundary conditions are assumed in the xy directions. $\phi_n^{L(R)}(r)$ [$\phi_n^{L(R)*}(r)$] represent the left-going [right going] running wave states in the left(L) and right(R) electrodes, respectively,

and $\phi_m^{R*}(r)$ is an incoming running wave from the right electrode with energy E . If $E_n^{R(L)}(k_n^{R(L)})$ represent the right and left electrode band structures, the summation in Eq. (3) stands for all bands n and $k_n^{R(L)}$ which satisfy $E_n^{R(L)}(k_n^{R(L)}) = E$. Equation 3 thus describes an incoming running wave $\phi_m^{R*}(r)$ from the right electrode band m which is scattered back through outgoing running waves $B_n^R \phi_n^R(r)$ at the right electrode, and transmitted into the left going running waves $A_n^L \phi_n^{L*}(r)$ at the left electrode. The transmission coefficient [$T_m(E)$] for channel m associated with this scattering process can be calculated as

$$T_m(E) = \left(\sum_n |A_n^L|^2 \left[dE_n^L(k)/dk \right] \Big|_{k=k_m^L} \right) / \left[dE_m^R(k)/dk \right] \Big|_{k=k_m^R}. \quad (4)$$

Similarly, the reflection coefficient for channel m is

$$R_m(E) = \left(\sum_n |B_n^R|^2 \left[dE_n^R(k)/dk \right] \Big|_{k=k_m^R} \right) / \left[dE_m^R(k)/dk \right] \Big|_{k=k_m^R}, \quad (5)$$

where, due to current conservation, $T_m(E) + R_m(E) = 1$.

Hence, the main ingredient in our transport approach is the scattering state ψ_{sc} , from which the transmission and reflection coefficients can be calculated straightforwardly. In the following, the method employed in this work to obtain ψ_{sc} is briefly described.

2.1. Scattering states

In order to solve Eq. (2), we impose auxiliary periodic boundary conditions at the boundary B of the system, so that our open boundary problem is transformed into a conventional closed boundary problem. Under these conditions we can solve the following linear equation:

$$(H - E)\psi_l(r) = W_l(r), \quad (6)$$

where $W_l(r)$ represent some perturbation functions that are nonzero only near the boundaries B of the system. Here, we have chosen the Γ point Bloch states of the electrode [$u_{l,\Gamma}(r)$] multiplied by a Gaussian envelope function near the boundary as the perturbation functions $W_l(r)$ (for z within the last unit cell of the right electrode near the boundary B as shown in Fig. 1, and zero elsewhere). This is advantageous because these Bloch states provide the proper symmetries for the possible scattering states, and the scattering states are likely to have strong coupling with $u_{l,\Gamma}(r)$. Strictly speaking, the final scattering states should be independent of the exact choice of $W_l(r)$ as long as the $W_l(r)$ include all the proper symmetries to induce all the needed ψ_l . For a given choice of $W_l(r)$ functions, the solutions of Eq. (6) [$\psi_l(r)$] are obtained using the conjugate gradient method and are denoted as system states. Notably, the $\psi_l(r)$ states are defined over the whole space, but satisfy the Schrödinger's of Eq. (2) only in the region between left (Ω_L) and right (Ω_R) electrode primary cells (see Fig. 1), i.e. in the region where $W_l(r)$ are zero.

Furthermore, as far enough from the molecular region the system potential will change to the potential of the electrode, at

Ω_L and Ω_R each system state ψ_l with energy E can be decomposed using the electrode wave functions as follows:

$$\psi_l(r) = \begin{cases} \sum_{n=1}^{N_R} A_n^R(l) \phi_n^{R*}(r) + B_n^R(l) \phi_n^R(r) & \text{if } z \in \Omega_R \\ \sum_{n=1}^{N_L} A_n^L(l) \phi_n^{L*}(r) + B_n^L(l) \phi_n^L(r) & \text{if } z \in \Omega_L, \end{cases} \quad (7)$$

where $\phi_n^{R(L)}$ are the running wave electrode states as in Eq. (3), and $N_{R(L)}$ denote the number of running wave states involved on the right(left) primary cells for a given energy E . As illustration, Fig. 2 shows the band structure alignment between the right and left electrodes for a 4 V bias voltage. For a given energy E , the electrode states involved in the decomposition are those represented by small black dots on the dashed line.

Finally, in the extended region consisting of the molecule and the short electrodes (see Fig. 1), we will linearly combine the $\psi_l(r)$ system states to generate the scattering states of Eq. (2) as follows:

$$\psi_{sc} = \sum_{l=1}^M C_l \psi_l(r). \quad (8)$$

Remarkably, since all the $\psi_l(r)$ satisfy Eq. (6) with the same energy E , this ψ_{sc} satisfies the Schrödinger equation [Eq. (2)] in the region where W_l are zero, i.e. in the central region and in the left and right primary cells. Thus, to make ψ_{sc} of Eq. (8) one of the scattering states, the coefficients $\{C_l\}$ must be chosen so

that the boundary condition of Eq. (3) is satisfied at Ω_L and Ω_R . If this is satisfied exactly, we have then solved the scattering state exactly.

Figure 2: Cu(100) electrode employed for the Cu-DBT-Cu junction of Fig. 1. The band alignment between the left electrode band structure and the right electrode band structure. The voltage bias is 4 V. The numbers in the right electrode band structure are the band index. The small black dots on the line E are the k_n^L and k_n^R points satisfying $E_n^L(k_n^L) = E$ and $E_n^R(k_n^R) = E$, respectively. Figure taken from Ref. 30.

With this aim, we apply the following procedure. First, the electrode-state based decomposition of the system states [Eq. (7)] is introduced in the linear combination of Eq. (8). This yields the following equation for ψ_{sc} at Ω_R and Ω_L :

$$\psi_{sc}(r) = \begin{cases} \sum_{n=1}^{N_R} \left[\left(\sum_{l=1}^M A_n^R(l) C_l \right) \phi_n^{R*}(r) + \left(\sum_{l=1}^M B_n^R(l) C_l \right) \phi_n^R(r) \right] & \text{if } z \in \Omega_R \\ \sum_{n=1}^{N_L} \left[\left(\sum_{l=1}^M A_n^L(l) C_l \right) \phi_n^{L*}(r) + \left(\sum_{l=1}^M B_n^L(l) C_l \right) \phi_n^L(r) \right] & \text{if } z \in \Omega_L. \end{cases} \quad (9)$$

Then, comparing this equation with the boundary equation of Eq. (3), we obtain the following $N_R + N_L$ linear equations for a scattering state based on a ϕ_m^{R*} incoming wave:

$$\sum_{l=1}^M A_n^R(l) C_l = \delta_{n,m} \quad \text{for } n = 1, N_R \quad (10)$$

$$\sum_{l=1}^M B_n^L(l) C_l = 0 \quad \text{for } n = 1, N_L \quad (11)$$

$$(12)$$

These linear equations for $\{C_l\}$ can be solved easily, as described in detail in Refs. 30 and 36. From the solution of these equations one can then construct the scattering states using Eq. (8).

As mentioned above, such scattering states are only correct in the extended region of Fig. 1. Outside the extended region the scattering states should be extended from Ω_L and Ω_R following the propagations of the nonzero electrode running waves into

negative and positive infinities, respectively. Then, the exact scattering state over the whole space is obtained by matching the scattering state in the central region with extended solutions in the right and left electrodes. In the following discussion, we will call such obtained scattering state the “extended scattering state” and the ψ_{sc} as constructed from Eq. (8) the “as-constructed scattering state”. Note that the as-constructed scattering state is only correct within the region $[\Omega_L, \Omega_R]$.

This transport calculation method is general and can be applied to any Hamiltonian. In particular, we use a plane wave nonlocal pseudopotential Hamiltonian and, as a result, we are able to calculate scattering states for an open boundary problem using plane waves. However, to make the description exact, the system state decomposition of Eq. (7) should contain not only the electrode running wave states, but also the electrode evanescent states for a given energy E . For this purpose, we have designed a procedure to calculate the complex band structure of the electrode.

Figure 3: Calculation scheme for the scattering states.

2.2. Complex band structure

The conventional band structure contains Bloch-like states with real $\mathbf{k}$ vectors, i.e. running states. However, whenever the translational symmetry of the crystal structure is broken states with complex $\mathbf{k}$ will be involved in the electron wave function. This is the case for the transport through atomic scale or molecular devices under consideration here. The complex band structure (CBS) is an extension of the conventional bandstructure to include evanescent states, i.e. those states for which the Bloch vector $\mathbf{k}$ has an imaginary component while the eigen energy is real. Such states are known to be important in the simulation of scattering states and, consequently, of transport properties.[36, 44]

A conventional band structure is obtained by solving the Hamiltonian for a fixed real $\mathbf{k}$ vector, which yields the well-known $E(\mathbf{k})$ bandstructure. For the complex band structure, the most common calculation methods are based on a 'reverted' procedure: an input real energy E is provided, and the complex $\mathbf{k}$ is solved for this given energy E . This inverted approach

has been extensively used over the years.[20, 24, 45–47] Unfortunately, these inverse techniques can only be used with local pseudopotentials, as they do not work for nonlocal pseudopotentials.

In Refs. [36] and [48] we introduced an alternative 'direct' method to calculate the complex band structure for a general Hamiltonian (more specifically, here for the plane wave pseudopotential method). In this approach, a complex $\mathbf{k}$ is chosen as the input, and the unit cell Hamiltonian under this $\mathbf{k}$ is diagonalized to obtain the energy E . The challenge then is to find those complex $\mathbf{k}$ which yield the real E . For typical electrodes used in quantum transport calculations, we have designed a practical procedure to search for the imaginary $\mathbf{k}$ which give real eigen energies. For the generalized complex bands in the middle of the Brillouine zone, a two band anticrossing model is used to aid the search of the complex $\mathbf{k}$ which yields real energy E . This results in a systematic and inexpensive way of calculating evanescent states in an exact manner.[36, 48]

Now, if we include the evanescent states in the electrode-state decomposition of the system states ψ_l , Eq. (7) turns into

$$\psi_l(r) = \begin{cases} \left[\sum_{n=1}^{N_R} A_n^R(l) \phi_n^{R*}(r) + B_n^R(l) \phi_n^R(r) \right] + \left[\sum_{ne=1}^{M_R} C_{ne}^R(l) \phi_{ne}^{R,\kappa}(r) + D_{ne}^R(l) \phi_{ne}^{R,-\kappa}(r) \right] & \text{if } z \in \Omega_R \\ \left[\sum_{n=1}^{N_L} A_n^L(l) \phi_n^{L*}(r) + B_n^L(l) \phi_n^L(r) \right] + \left[\sum_{ne=1}^{M_L} C_{ne}^L(l) \phi_{ne}^{L,\kappa}(r) + D_{ne}^L(l) \phi_{ne}^{L,-\kappa}(r) \right] & \text{if } z \in \Omega_L. \end{cases} \quad (13)$$

While $\phi_n^{R(L)}$ are the running wave electrode states as in Eq. (7), the $\phi_{ne}^{R,\kappa}, \phi_{ne}^{L,-\kappa}$ are right-electrode, left-electrode evanescent states decaying from the boundary B, respectively, and $\phi_{ne}^{R,-\kappa}, \phi_{ne}^{L,\kappa}$ are right-electrode, left-electrode evanescent states decaying from the central molecule, respectively. $N_{R(L)}$ and $M_{R(L)}$ denote the number of running and evanescent states involved on the right(left) primary cells for a given energy E. Then, incorporating this new decomposition equation into Eq. (8) and taking into account the boundary conditions of Eq. (3), we obtain a new set of linear equations for the coefficients C_l . [36] Using these newly calculated C_l coefficients, the exact scattering states including both running and evanescent states are obtained.

The need of incorporating evanescent states in the scattering state calculation is clear from the analysis in Ref. 36, where a comparison between the scattering states and the corresponding transmission coefficients for the model system in Fig. 1, as obtained with and without evanescent states is reported. Fig. 4 shows the scattering state of Cu-DBT-Cu for a running wave of energy $E = 0.283$ eV coming from the right electrode, and a very small applied bias voltage (0.1 V). The upper panel shows the scattering states obtained using only running waves, where the dashed line is the as-constructed scattering state and the solid line represents the electrode-state decomposition of the as-constructed scattering state inside Ω_L and Ω_R and extended outwards. In the middle panel we depict the solution achieved using all electrode states, both running and evanescent. Clearly, if no evanescent states are taken into account, the decomposition of the scattering state on the left electrode is very bad (upper panel), whereas if evanescent states are included, the decomposition is very good at both Ω_L and Ω_R (middle panel). This is clear by looking at the extended scattering states obtained by these two procedures (bottom panel). If only running-wave electrode states are included, the extended state is discontinued at Ω_L , giving rise to an incorrect scattering state and, ultimately, to incorrect transport properties.

Having mentioned above the importance of the evanescent states for accurately decomposing the system states within Ω_L and Ω_R into electrode states, in practice, due to the complexity of calculating the evanescent states for an electrode, we found that it is often more convenient to approximate the evanescent states following the procedure described in Ref. [30]. In Ref. 30, the evanescent states were approximated by band structure valley Bloch states (ϕ_{max}), i.e., bottom of band or top of band running wave states. Notice that these are just normal running wave states, except that they carry no current since $dE_n(k)/dk|_{k=k_e} = 0$. Thus the evanescent states can be approximated by $\phi_{max} e^{\pm k_z z}$. However, we are only concerned with such evanescent states for the system state decomposition within Ω_L and Ω_R (Equation 7) and, because only the evanescent states with small k will have large amplitudes within Ω_L and Ω_R , we can further drop $e^{\pm k_z z}$ and use ϕ_{max} to represent the evanescent states. This procedure is found to be appropriate if the Ω_L and Ω_R are away from the central region, and if a proper decomposing procedure is used, which ensures that, after the linear combination of Eq. (8), the evanescent state components in the scattering state are minimum. Thus, in many of the practical

Figure 4: Cu-DBT-Cu junction (see Fig. 1). Scattering states for an incoming running wave with $E = 0.238$ eV and $n = 5$ band index, and an applied bias voltage $V = 0.1$ V. Upper and middle panels show the results obtained using only running states and all electrode states, respectively. Dashed lines represent the as-constructed scattering states; solid lines the electrode decompositions extended to negative and positive infinities. Lower panel shows the corresponding extended scattering states (dashed-dotted: including only running states, solid: including running and evanescent states). Figure adapted from Ref. 36.

calculations, we do not precalculate the electrode evanescent states. This makes the whole procedure much simpler.

We should also emphasize that, in order to properly account for the evanescent states, a special cutoff method is introduced in our calculations. As in typical plane wave calculations, an energy cutoff E_{cut} is used to select the plane waves $\mathbf{G}$ entering the representation of Bloch states. However, if the conventional way ($\frac{1}{2}|\mathbf{G}|^2 < E_{cut}$) is used to select the plane wave basis, the representation of the decaying evanescent states is not correct, simply because the given plane wave basis set cannot describe the ever-decaying evanescent state.[36] In order to describe such evanescent state, more plane waves are needed in the z direction. This is important to describe any scattering states which might have decayed beyond a few order of magnitudes when it crosses the molecule (or a barrier). In order to overcome this problem, we have used a cylindrical plane wave selection rule: the plane wave basis vectors will lie inside a cylinder $\frac{1}{2}|\mathbf{G}_\perp|^2 < E_{cut}$, and no cutoff is associated with G_z . Using this cylindrical cutoff method, the evanescent states are well described over the entire system and, hence, we have employed this cutoff both for the complex band structure and for the system state calculation of Eq. (13).

Regarding the computational cost of our calculations, it is worth mentioning that the use of a cylindrical cutoff method implies that, for a given E_{cut} , our number of plane waves is roughly twice that of the conventional calculations performed with the spherical cutoff method. In particular, the most time consuming step is calculating the system states, where the extended region made up of the central region and the short electrodes are included. Depending on the problem, this extended region can contain from a few dozens to a few hundred atoms. Nevertheless, if a few hundred CPUs are used for the large system runs, each system state takes only a few minutes to calculate. Therefore, in most of the cases the computational time of the

transport calculations using our method is similar to that of a ground state calculation.

2.3. Self-consistency

Under zero or small applied bias voltages, the transport problem can be studied considering a non-self-consistent treatment of the system potential. For example, in Refs. 30 and 36, we first obtain the Kohn-Sham single particle potential of the system from a self-consistent local-density approximation (LDA) calculation at zero bias. Then, to simulate the application of a finite bias V to the system, a sine-like potential $[V/2 \sin(\pi z/L')]$ is added in the central region (L' is the length of the central region in the transport direction). This central potential is matched to the potential on the left and right electrodes shifted by $\mp V/2$, respectively, thus yielding a non-self-consistent potential defined over the entire space. We found that our result does not depend sensitively on the exact form of this added potential as long as it is a smooth function.

On the contrary, for problems with a large bias voltage a self-consistent treatment of the potential is crucial. For this reason, we introduced an iterative approach to obtain self-consistently charge density and potential.[49] The first step is to obtain the electron charge density from the occupied wave functions. In the case of open systems, as the model system considered here (Fig. 1), it is traditional to separate the charge density into two contributions: the contribution from scattering states that connect right and left electrodes crossing the molecular region, and the contribution coming from bound states that might exist inside the molecular region. As shown in Ref. [49], under appropriate assumptions, the total charge density of the system can be expressed as

$$\rho(\mathbf{r}) = \rho_h(\mathbf{r}) + \rho_{sc}(\mathbf{r}), \quad (14)$$

where

$$\rho_h(\mathbf{r}) = 2 \sum_{E_h < E_L} f_L(E_h) |\psi_h^{E_h}(\mathbf{r})|^2 \quad (15)$$

and

$$\rho_{sc}(\mathbf{r}) = 2 \int_{E_L}^{E_R} (f_R(E) - f_L(E)) \sum_k |\psi_{sc,R}^{E,k}(\mathbf{r})|^2 D_k^R(E) dE. \quad (16)$$

The charge density $\rho_h(\mathbf{r})$ is just the ground state charge density of the Hamiltonian H occupied by the Fermi energy E_F^L , which is obtained by occupying the eigen states ψ_h of H calculated by the conventional conjugate gradient method. In $\rho_{sc}(\mathbf{r})$, $\psi_{sc,R}^{E,k}(\mathbf{r})$ represents a scattering state incoming from the right with energy E and wave vector k in the direction of propagation, and $D_k^R(E)$ is defined as the density of states of the right electrode at wave vector k and energy E ,

$$D_k^R(E) = \left(\frac{a}{2\pi} \right) \frac{\partial k}{\partial E} \Big|_E, \quad (17)$$

where a is the unit cell length of the electrode in the direction of current propagation (z).

Following Eq. (14), the charge density in the central region is first calculated. In the next step, the potential of the system is

obtained from the charge density. The potential of the system contains three terms: $V(r) = V_H(r) + \mu_{xc}(\rho(r)) + V_{ion}(r)$. The first term is the Hartree potential caused by the charge density $\rho(r)$, the second term is the exchange and correlation potential under the density functional formalism, while the third term is a fixed bare ionic potential. The Hartree potential $V_H(r)$ can be obtained by solving the Poisson equation. While the Poisson equation needs to be solved only in the central region of Fig. 1, we can solve it within a bigger supercell. In particular, here we use a supercell of the extended region of Fig. 1. Beyond the central region of Fig. 1, the stand alone electrode charge density is used to connect with the central region charge density calculated from Eq. (14).

Here, we use Fourier transform (FFT) to solve the Poisson equation, which can then be expressed as

$$\nabla^2 \phi_H(\mathbf{r}) = -4\pi[\rho(\mathbf{r}) - \rho_0]. \quad (18)$$

$\phi_H(\mathbf{r})$ is the Hartree potential and $\rho_0 = Q_0/\Omega$, Q_0 being the total nuclear charge in the supercell and Ω the supercell volume. In a charge neutral case this will make the net charge of Eq. (18) to be zero, and consequently the FFT method can be used directly. However, in a transport calculation there is no guarantee that the total charge of $\rho(\mathbf{r})$ will equal Q_0 . Fortunately, we only need to solve Eq. (18) correctly within the central region of Fig. 1. Hence, we have added a delta planar charge density $\Delta Q \delta(z - z_0)$ at the right hand side of Eq. (18) (z_0 is the position of the dashed line shown in Fig. 1 at the left side of the extended region box).[31] This $\Delta Q \delta(z - z_0)$ is used to cancel out the extra charge of $\rho(\mathbf{r}) - \rho_0$. After this delta charge density is added, the FFT can be used to solve the ϕ_H for the whole supercell. However, since the $\Delta Q \delta(z - z_0)$ is outside the central region, the ϕ_H still satisfies the original Eq. (18) in the central region without the extra charge, which is what is needed for our transport problem. Note, one can add a simple linear term to $\phi_H(r)$ without affecting its satisfaction of the original Poisson equation of Eq. (18), thus we have a general solution for V_H as: $V_H(r) = \phi_H(r) + Ez + v_0$ and $V(r) = \phi_H(r) + Ez + v_0 + \mu_{xc}(\rho(r)) + V_{ion}(r)$. This formula is used for the potential within the central region, while the two parameters E and v_0 are obtained by requiring that $V(r)$ matches the electrode potentials at the left and right hand sides of the central region.

Now, from this newly calculated system potential, we can in turn obtain a new charge density following Eq. (14). This procedure is repeated iteratively until self-consistency is achieved. For that purpose, we implemented in our method an algorithm based on the Pulay-Kerker potential mixing approach, which is a widely used potential mixing approach in conventional (equilibrium) ground state plane wave DFT calculations.[50–52] It should be emphasized that the use of a complete basis set as the one employed in our approach makes the convergence of the charge density an even more challenging task. Nevertheless, our self-consistent procedure shows good convergence properties, and although the speed of convergence is slower for larger bias, a well-converged system potential is usually obtained before approximately 20 iterations. This should be considered as

very fast, as it is not uncommon that the self-consistent iterations take hundreds of steps to converge in some of the transport codes.[31] Hence, our self-consistent approach can be used to obtain fast, accurate and stable numerical solutions of the nonequilibrium problem.

As an illustration, in Fig. 5 we have represented the total transmission coefficient for the model system (Au-DBT-Au) as a function of the energy and for different applied bias voltages. Non-self-consistent results are also depicted for comparison. For small bias voltages, non-SC and SC results give very similar results, but as the bias increases SC results start to deviate from non-SC ones. For $V = 2$ V for example, non-SC transmission shows a large peak at around -1.8 eV which is not present in the SC transmission spectrum. These results clearly demonstrate that a full self-consistent treatment is pivotal for finite bias problems.

Figure 5: Cu-DBT-Cu junction (see Fig. 1). Total transmission coefficients calculated non-self-consistently (dashed lines) and self-consistently (solid lines), measured with respect to the Fermi energy of the left electrode. Vertical dashed lines mark the energy range involved for different applied bias voltages. Figure adapted from Ref. 49.

We have to mention that, there are some uncertainties in carrying out the charge density selfconsistent calculations under nonequilibrium. If large transmission exists for a scattering state, that will lead to extra electrode charge in the left electrode and depletion of the electrode charge in the right electrode, as compared to their neutral electrode solutions. This is not realistic. In reality, this problem disappears after inelastic scattering converts the scattering states in the electrode into their equilibrium states under their respective Fermi energies. Since we do not consider such inelastic processes within the electrode, the charge neutrality problem has to be enforced within the procedure, and only a finite region near the central transport system is included in the selfconsistent calculations.[49]

We have also developed an alternative method for selfconsistent charge density calculations. This method is suitable for systems where the transmission current is small, and there are no localized states of the central transport region within the left and right electrode Fermi energy window. Within the new approach, we first calculate the self-consistent potential of the

central part. This is done by employing a modified central region surrounded by vacuum on left and right sides, as displayed in Fig. 6. The effect of the applied bias is taken into account by redefining the occupation of the central system in the following way

$$\rho_C(\mathbf{r}) = \sum_i \left\{ |\psi_i(\mathbf{r})|^2 W_L(\mathbf{r}) f(\epsilon_i - \mu_L) + |\psi_i(\mathbf{r})|^2 W_R(\mathbf{r}) f(\epsilon_i - \mu_R) \right\}, \quad (19)$$

where $\mu_{L(R)}$ are the left and right Fermi energies given by $E_F \pm V/2$, respectively, and $f(\epsilon_i - \mu_{L(R)})$ are the corresponding Fermi-Dirac distributions. $W_{L(R)}(\mathbf{r})$ are some auxiliary mask functions, and $W_R = 1 - W_L$. [53]

Figure 6: Model system used for transport calculations in tunneling regime. a) Full model system, equivalent to Fig. 1. b) Modified central region used for the self-consistent calculation of the potential in tunneling problems. Figure taken from Ref. 53.

This procedure works well for tunneling cases, where the charge density at the barrier region is very small. In such cases, the $W_L(\mathbf{r})$ is one at the left electrode, then drops abruptly in the barrier region (at the point of maximum potential, or said minimum charge density) to zero, and it remains to be zero at the right electrode. Ref. 54 shows that the charge density obtained in that way is almost indistinguishable to the charge density obtained by occupying the scattering states as described above (Equation 14).

Once the self-consistent potential for the central region is obtained following the new occupation procedure, it is matched to left and right electrode potentials. From the resulting full system potential, the scattering states are calculated following the approach described above.[30, 36] In this way, the scattering states of the full system under bias voltage are achieved in a SC manner. This approach has been used to get the charge density and potential profile for the Cu-vacuum-Cu system,[53] and it can also be used for other tunneling problems like the tunneling field effect transistors.

2.4. Plane-wave basis set

As already pointed out, the use of plane waves poses an important advantage in comparison with more commonly used localized atomic orbitals (LAO): it provides a very accurate description of the scattering wave function in the vacuum region, making this method highly appropriate for the investigation of

transport properties in the tunneling regime. This has been verified in Ref. 57, by comparing transport calculations obtained with our plane wave method and with a NEGF-DFT transport approach with atomic orbitals.[58] In particular, the transmission coefficient at the Fermi level for a broken linear Au chain has been calculated as a function of the electrode separation. As seen in Fig. 7, plane waves (solid lines) and atomic orbitals (dashed lines) give the same result in contact regime. However, as the vacuum gap increases the results start to deviate, and well into the tunneling regime, the atomic orbitals are not able to nicely reproduce the exponential decay of the transmission. This problem can be overcome by introducing ghost-atoms, i.e. floating orbitals that do not have electrons nor pseudopotential associated. Making use of ghost atoms, the transmission obtained with atomic orbitals (dashed-dotted line) can be made to have exponential decay and it agrees with the plane wave calculation result. However, we found that the NEGF results depend strongly on the location and number of ghost atoms, and are difficult to converge. This result calls into question the reliability of LAO based transport calculations in tunneling regime.

Figure 7: Linear Au chain (inset). Total transmission at the Fermi level as a function of the vacuum gap width obtained using plane waves (solid line), atomic orbitals (dashed line) and atomic orbitals with ghost atoms (dashed-dotted line). Figure taken from Ref. 57.

Nonetheless, it should also be pointed out that in the case of systems involving a large number of atoms, transport calculations using plane waves can be significantly more expensive than those based on localized atomic orbitals. Therefore, the choice of using a plane wave or a localized atomic basis set will depend on the system under investigation and on the size of the vacuum region between the electrodes.

3. Review of applications

3.1. Electron tunneling across nanojunctions

In the last years, the low-conductance or tunneling regime of nanojunctions has been thoroughly studied with the scanning tunneling microscope (STM). In particular, an experimental quantity that can be extracted from STM experiments and

which may be very useful to understand the mechanism of electron tunneling is the apparent barrier height.[59, 60] This quantity is obtained by measuring the variation of the tunneling current (I) as a function of the distance between both sides of the junction, i.e. between the tip and the apex (Δz). Although many experimental results of apparent barrier heights have been reported,[61–66] there are not many studies on the effect of the detailed atomic structure of the junction on the apparent barrier height, mainly due to the difficulty of experimentally investigating the tip atomic structure. Equally, the coupling between the electronic states in the electrode and the electronic states and modes in the vacuum, as well as the way the atomic structure of the electrode tip affects such coupling is not well understood. The investigation of all these tunneling regimes constitutes an excellent example for the application of our plane wave based transport calculation method, which has been shown to provide an adequate description of transport properties in that regime.

According to a one-dimensional description of the tunneling barrier,[67, 68] the apparent barrier height for constant bias, can be expressed as the rate of change of the logarithm of the current with the tip-apex distance,[60] as follows

$$\Phi = 0.952 \left(\frac{d \ln I}{d \Delta z} \right)^2, \quad (20)$$

with Φ in eV, Δz in Å, and arbitrary units for I .

In the low-bias regime only the states at the Fermi level take part, so according to Eq. (1) the current is proportional to the total transmission coefficient at the Fermi level given by

$$T(E_F) = \sum_m T_m(E_F), \quad (21)$$

where the summation $\sum_m$ stands for all band m that cross the real band structure of the electrode at the Fermi level. It then follows from Eq. (20) that the apparent barrier height in the low-bias limit can be extracted from the slope of the logarithm of $T(E_F)$ with the electrode separation or vacuum gap width. Therefore, the calculation of the apparent barrier height is performed by first calculating the scattering states at the Fermi level for different electrode separations in the tunneling regime. From the scattering states the transmission coefficients for different channels and electrode separations are obtained, and finally the apparent barrier height is extracted following Eq. (20).

To exemplify this, the tunneling properties of the model Au junctions in Fig. 8 (upper row) were studied in Ref. 57. System 1 consists of two facing 4x4-Au(001) surfaces, periodic in the (x, y) plane perpendicular to the direction of propagation (z). System 2 or system 3 are constructed by placing a single Au adatom or a 5-atom pyramidal bases on each 4x4-Au(001) surface, respectively. By investigating these junctions we were able to determine the influence of the detailed atomic structure of the junction on the tunneling regime properties.

In first place, the electronic structure of the 4x4-Au(001) electrode must be analyzed carefully. Fig. 9 shows the band structure obtained with the s -only pseudopotential, where k_z represents the wavevector in the direction of propagation (z).

With respect to $K_{\parallel}$, the wavevector in the direction perpendicular to the current propagation, we consider the Γ -point only approximation. As represented by circles in Fig. 9, four bands cross the Fermi level: the $n = 1$ band is non-degenerated, the other 3 bands are 4-times degenerated. Thus, the total transmission at the Fermi level is the sum of the contributions from these 4 different channels, originated by 13 different incoming electrode states. The degeneracy of the bands can be understood in terms of the K_{xy} of the fcc unit cell, which are all folded into the $K_{\parallel} = 0$ of the electrode supercell. Using the reciprocal lattice vectors, K_{xy} can be expressed as $K_{xy} = \frac{2\pi}{4a}(n_x, n_y)$ where n_x and n_y are integer numbers and represent the components of the wavevector in the x and y directions, respectively, and a is the Au lattice constant. The non-degenerated band would correspond to the $(n_x, n_y) = (0, 0)$ case, and the $\{2, 3, 4, 5\}$, $\{6, 7, 8, 9\}$, $\{10, 11, 12, 13\}$ bands would correspond to (n_x, n_y) equal to $(\pm 1, 0)$, $(0, \pm 1)$; $(\pm 1, \pm 1)$; and $(\pm 2, 0)$, $(0, \pm 2)$ cases, respectively.

Figure 9: Real band structure of the 4x4-Au(001) electrode. Figure taken from Ref. 57.

The transmission coefficients at the Fermi level for systems 1, 2 and 3 were calculated as a function of the vacuum-gap width using our plane wave based method. The contribution from each channel was calculated separately, in order to extract information about the properties of each of the tunneling states involved. Fitting the transmission curves, which showed a perfect exponential decay, we extracted the apparent barrier heights for each channel as well as for the entire system. The results, as summarized in Table 1, allowed us to conclude that in the case of flat surfaces (system 1), the 4 channels exhibit different barriers, whereas for corrugated surfaces (systems 2 and 3) all channels have the same barrier height.

The origin of this different apparent barrier height for different junctions and different shapes was elucidated by taking into account the following: in the vacuum region the barrier height in the tunneling direction (z direction) is determined by the potential height and the (x, y) direction kinetic energies in the middle plane between the left and right sides of the junction. Accordingly, the sum of the kinetic energy and the potential height of the system should give the barrier height of that specific channel. This is indeed confirmed by the results

reported in Ref. 57 and reproduced in Table 1, which provides the kinetic energy (K) and the sum of the kinetic energy and the potential ($K + V$) as obtained for the three systems under consideration. Clearly, there is a close agreement between the $K + V$ and Φ , the apparent barrier height (Φ) obtained by fitting the corresponding transmission curves. These results also show that the corrugated junctions (system 2 and 3) yield very similar kinetic energy for different channels, whereas in the flat junction (system 1) different channels have very distinct K values. This allows to conclude that in corrugated systems different electrode states couple to different vacuum states compare to the flat surface case. Equally, this explains why in system 2 and 3 different channels have similar barrier heights, whereas in the flat junction each channel has a very different barrier height.

State index	$K(\text{eV})$	$K + V(\text{eV})$	$\Phi(\text{eV})$
System 1			
1	6.31×10^{-5}	5.80	5.72
2,3,4,5	1.07	6.87	6.80
6,7,8,9	2.15	7.95	7.87
10,11,12,13	4.3	10.10	10.00
System 2			
1	0.83	6.63	6.71
2,3,4,5	0.95	6.75	6.68
6,7,8,9	0.96	6.76	6.69
10,11,12,13	1.02	6.82	6.50
System 3			
1	0.95	6.75	6.79
2,3,4,5	0.93	6.73	6.77
6,7,8,9	0.93	6.73	6.75
10,11,12,13	0.86	6.66	6.71

Table 1: (x, y) kinetic energy (K), $(K + V)$ and barrier height (Φ). The barrier heights obtained from the fitted total transmission curve are 6.4, 6.7 and 6.8 eV for systems 1, 2 and 3, respectively. Table taken from Ref. 57.

Interestingly, our plane wave method also offers a nice way to visualize the scattering states and the coupling of the electrode states to vacuum states. For example, $\ln |\psi_{sc}(x, y, z)|^2$ for the $(n_x, n_y) = (0, 0)$ scattering state is plotted in Fig. 8. One interesting feature is that in the flat surface (system 1), the $(0, 0)$ electrode state is coupled with a flat vacuum state. As a result, the (x, y) kinetic energy in the midplane is expected to be almost zero, as confirmed by the results reported in Table 1. On the other hand, for the corrugated cases, the original flat front $(0, 0)$ electrode state is coupled with a concave wavefront, spherical like state. This is most predominant for system 3, which has a pyramid shape. As shown in Table 1, such a spherical vacuum wavefunction has a large (x, y) direction kinetic energy, which raises the apparent barrier height. It is thus interesting to note that each corrugated atom at the surface of the electrode can behave like an antenna which emits spherical electron waves.

3.2. Field-emission resonances

Using our plane wave transport calculation method, we have also investigated field emission resonances (FERs) on Cu(100). When the scanning tunneling microscope (STM) is operated in

Figure 8: Au nanojunctions. a), b) and c): model systems used for the calculations. d), e) and f): 2D plots of $\ln|\psi_{sc}(x, y, z)|^2$ for the $(n_x, n_y) = (0, 0)$ scattering state on the XZ plane for Y in the middle of the gap, as obtained for systems 1, 2 and 3, respectively. Figure adapted from Ref. 57.

the field-emission regime, i.e. at bias voltages larger than the tip work function, image-potential states are Stark-shifted and become field-emission resonances. FERs are located near the surface and decay into the vacuum, so that their accurate simulation requires a faithful description of vacuum states. This type of simulations is thus not possible with the popular transport methods based on atom-centered localized basis sets, and the use of plane waves becomes essential.

Experimentally, FERs can be detected using scanning tunneling spectroscopy (STS) in constant-current mode, i.e. using $z - V$ spectroscopy. Within this operation mode, the feedback loop is left on and, thus, the tunneling current I is kept constant while scanning the bias voltage V . This way, the derivative of I with respect to V , $\partial_V I(V)$, as well as the varying tip-sample separation, $z(V)$, are acquired simultaneously. Under these experimental conditions, every time a new FER is available for tunneling a jump in $z(V)$ and a peak in $\partial_V I(V)$ are observed.[69, 70]

Theoretically, FERs are commonly interpreted based on simple one-dimensional (1D) models for the description of the surface potential.[71–75] However, these 1D model potentials pose many drawbacks that can be avoided by using an atomic-scale description of the effective potential. Motivated by this clear lack of an appropriate tool to investigate FERs, for which a renewed interest has emerged over the last years,[74, 76–87] we developed a DFT-based procedure that treats the finite bias nonequilibrium problem in tunneling regime and solves the potential of the tip-sample self-consistently. Besides, the well-known limitation of DFT to describe the asymptotic behavior of the image potential towards vacuum has been overcome by applying a matching procedure to enforce the correct imagelike potential tail within our DFT-based self-consistent approach. The inclusion of the image-potential, together with the self-consistent treatment of the finite voltage drop across the system, enables the quantitative analysis of FERs.[53]

With the aim of demonstrating the potential of our method,

we studied the FERs in a well-established system, the Cu(100) surface. On this surface, a projected band gap exists around $\bar{\Gamma}$ point, which together with the tip-field effect gives rise to FERs.[74, 82, 85, 88, 89] The model set up used in this work consisted of two facing (3×3) -Cu(100) surfaces resembling a flat STM tip in front of a Cu(100) sample. For this system, the influence of the electric field, fixed by the applied voltage (V_b) and surface-tip distance (z_{vac}) has been investigated.

In particular, we have tested the adequacy of our procedure for the SC calculation of the system potential under applied bias voltage, as well as the effect of the image potential. As shown in Table 2, the energies of the FERs do not exhibit a remarkable influence of the self-consistent calculation. However, the small differences between SC and non-SC potentials can be important regarding confinement of image states with high quantum number. This is illustrated in Fig. 10, where we have represented the wave functions of the first three FER states at $\bar{\Gamma}$ for ($z_{vac} = 16.8 \text{ \AA}$, $V_b = 8.4 \text{ V}$) as obtained non self-consistently and self-consistently.[90] We observe that the effect of self-consistency on the confinement of FER wave functions is more prominent for states with quantum numbers $n > 1$.

We have also studied the effect of the image potential based on the comparison of the SC potentials as obtained with and without taking into account the imagelike behavior of the potential on the vacuum side. As shown in Table 2, in terms of the eigen energies of FERs, the image potential is crucial for $n = 1$ state, but its effects on the higher quantum number states are negligible. On the contrary, the effect of the image potential on the wave function of FERs is stronger for states with high quantum number, as confirmed by the FER states given in Fig. 10. All in all, we conclude that both ingredients, the SC treatment of the nonequilibrium problem and the introduction of the image potential, should be included for a proper description of FERs.

It should be noted as well that since our FER simulation tool

Figure 10: FERs on Cu(100). (a) Atomistic illustration of the two-facing (3x3)-Cu(100) surfaces used in the calculations. (b) First three FER states of left Cu(100) surface for ($z_{vac} = 16.8\text{\AA}$, $V_b = 8.4\text{V}$), as obtained non-self-consistently without image potential (blue, dashed line), self-consistently without image potential (red, dash-dotted line) and self-consistently including image potential (black, solid line). The gray area represents Cu(100) metallic region. Figure taken from Ref. 57.

	E [non-SC]	E [SC]	E [SC + V_{im}]
$n = 1$	6.16	6.02	4.81
$n = 2$	8.05	7.96	7.51
$n = 3$	9.76	9.79	9.73
$n = 4$	10.36	10.49	10.50

Table 2: Energy values in eV of the first four FERs of Cu(100) corresponding to the ($z_{vac} = 16.8\text{\AA}$, $V_b = 8.4\text{V}$) set point, as obtained non self-consistently (non-SC), or self-consistently with (SC + V_{im}) and without (SC) image potential. These energy values are measured with respect to the Fermi level of the left electrode. Table taken from Ref. 53.

incorporates a full three-dimensional treatment of the surface potential, it can be very useful for the investigation of the effect of the tip geometry on the FERs. As an example, we have examined how the FERs of Cu(100) change when a sharp tip is employed. In particular, in Ref. 53 we have considered a pyramidal tip made of four basal atoms and one apex atom. We find that when a sharp tip is employed FERs are shifted downwards in energy. With respect to the FER states, the first FER ($n=1$) is found to be independent of the atomic structure of the tip, whereas higher FER states are clearly affected by the tip. All these tip effects might be crucial for a correct interpretation of FERs detected by STS. In this sense, our method provides an ideal tool for the simulation of FERs aimed at the understanding of experimental STS observations.

3.3. Molecular switch

Molecular electronic switches are recognized as strong candidates to succeed the silicon based technology and, as a result,

they have been intensively studied in the last few years.[10, 91–100] Among all the different types of switches proposed and tested in the literature, we have focused our interest on a three-terminal transistor design where the current between source and drain electrodes is controlled by the gate potential. The switching behaviour of such a transistor can be realized, for example, via a molecular conformation change. In this case, the gate induced electric field gives rise to a modification in the conformation of the molecule and, consequently, to an alteration in the current across the channel.[101]

The methodology described in the previous section has been applied to the study of such a conformational switch. With this aim, we designed an actual molecule made of two benzene rings with a methyl group and a fluorine atom on each ring, as depicted in Fig. 11(a). The two sulfur atoms, on left and right sides, connect the molecule to the electrodes. The F atoms induce a dipole moment at each ring, so that under the influence of an electric field the molecule will rotate along its c -axis (the axis connecting both S atoms). The calculation of the ground state total energy as a function of both the torsion angle of the molecule [defined in Fig. 11(a)] and the applied electric field yields the following results: i) at zero electric field the torsion angle is 103° and the energy valley is rather flat near the valley bottom; ii) under large electric field the ground state of the system corresponds to a torsion angle of 45° , which can be understood taking into account the steric effects that dominate at small torsion angles.

Figure 11: Molecular switch (a) The atomic structure of the $SH - C_6H_2F(CH_3) - C_6H_3(CH_2)F - SH$ molecule. The C_1 , C_2 , C_3 and C_4 are the atoms defining the torsion angle. (b) Schematic plot of the three terminal transistor, the current between the source and the drain is controlled by the gate potential. Figure adapted from Ref. 48.

Next, the molecule is connected to two bulk Au(111) electrodes, as shown in the schematic plot of the three terminal transistor in Fig. 11(b). Using this set up, the electron quantum transport across the molecule is calculated at different torsion-angle conformations and at zero source-drain bias. With this knowledge, and making use of the Boltzmann conformation

Figure 12: Molecular switch in Fig. 11. The conductance as a function of the applied gate electric field at temperature 300K, 77K, and 3K. $G_0 = 2e/h = 77\mu S$. Figure taken from Ref. 48.

distribution to account for the influence of the temperature, we obtained the averaged conductance as a function of the applied electric field at different temperatures. The main results reported in Ref. 102 are summarized in Fig. 12. At room temperature, $G_{ave} = 1.33 \times 10^{-2} G_0$ for $E=0$, and $G_{ave} = 5.10 \times 10^{-2} G_0$ for $E=0.0225$ a.u. Thus the switch-on ratio is 4. At liquid nitrogen temperature of 77K, $G_{ave} = 6.95 \times 10^{-3} G_0$ for $E=0$, and $G_{ave} = 5.16 \times 10^{-2} G_0$ for $E=0.0225$ a.u., so that the switch-on ratio increases to 7. Decreasing the temperature further does not increase the switch-on ratio too much mainly because at $E=0$ the ground state conformation is not at $\theta = 90$. Thus, even without thermal fluctuation, there will be some leaking current. However, such leaking current can be reduced at low temperature by applying a small electric field ($E=0.0022$ a.u.), which shifts the minimum energy conformation to $\theta = 90$. The switch-on ratio between this small electric field point and the $E=0.0225$ a.u. point is 27, which is still not very large. The reason is that at $E=0.0022$ a.u. the current is not completely shut off, due to the extreme flatness at the bottom of the molecule energy curve (presented in Ref. 102), and to the corresponding thermal fluctuations of the molecular conformation.

Finally, in order to estimate the actual switching capability of this molecule, we considered the double gate electrode geometry with two parallel plate electrodes along the c-axis of the molecule represented in Fig. 11(b). Based on this set up we calculated the transconductance, i.e., the change in current as a function of the applied gate potential ($\partial \ln(I)/\partial V_g$). The maximum transconductance values we obtained are 0.09, 0.23, and 1.79 V⁻¹ for 300, 77, and 3 K temperatures, respectively. It is worth pointing out that these values are an order of magnitude smaller than the maximum theoretical limit reported before for general models,[103] and 10-1000 times smaller than the theoretical limit (e/kT) of the electrostatic transistor, where kT represents the thermal energy. These results highlight the difficulties and challenges of using molecular conformation change as the mechanism for three-terminal transistors. It also highlights the needs for performing *ab initio* simulations in order to obtain realistic predictions of the switching capabilities of such

nanodevices.

3.4. Two-Dimensional Tunnel Transistors

Aggressive scaling of the metal-oxide-semiconductor field-effect transistor (MOSFET) following Moore's law requires fundamental innovations not only in device structures, but also in device materials as well as operational mechanisms. One of the most important features of a MOSFET's current-voltage characteristics is the so-called subthreshold-swing (SS) which is defined as $SS = \partial V_g / \partial \log_{10}(I_d)$, i.e., the increment of the gate voltage V_g needed to raise the drain current I_d by one order of magnitude. The smaller the SS, the faster the transistor can be switched on, hence the better performance of the integrated circuits. However, there is a fundamental limit of the MOSFET operation. In subthreshold region of a MOSFET, the current is controlled by the thermal-excited carriers above the potential barrier of the channel. As a result, the subthreshold-swing of the traditional MOSFET cannot be smaller than a theoretical limit called Boltzmann limit $SS = \ln(10)kT/e$. To achieve ideal device performance in nanometer region, one has to search for novel materials or even change to new transistors with different operational mechanisms.

Layered Molybdenum Disulfide (MoS_2) and its related transition-metal dichalcogenides (TMDCs) have been discovered with several interesting electrical, mechanical, and optical properties, and have been receiving great attention as potential new channel materials.[104–108] Besides their potential in regular MOSFETs, another opportunity is to use layered TMDCs in band-to-band tunneling (BTBT) or tunnel field-effect (TFET) transistors, which offer abrupt switch beyond the Boltzmann limit ($SS=60$ mV/dec at room temperature).[109] Questions remain for how good the performance of TFETs based on layered TMDCs is and how small the devices can be scaled to. Due to the ultimate thickness of the 2D crystal based devices, atomic details of the structure will have significant influence on the device physics and performance. Atomic designs from first principles and fully *ab initio* simulations thus become indispensable for device engineering.

The plane wave quantum transport calculations as described in the previous section have been applied to the study of the 2D tunnel transistors based on mono-layer MoS_2 . The mono-layer MoS_2 based double-gate TFET is schematically shown in Fig. 13, where the electrons from valence band of the source region can tunnel through the band gap barrier of the channel region and reach the drain region. The gate voltage V_g is applied to modulate the thickness of the band gap barrier, so as to switch on/off the device. We have considered three cases of physical gate length $L_g = 4.41, 6.30$ and 12.6 nm, and 2.0 nm thick HfO_2 is assumed for gate dielectric. To better evaluate the device performance in an ideal case, we assumed no source or drain underlap. The electrostatic potential $\phi(r)$ is first solved from the Poisson equation of the whole device system including the HfO_2 layer under a continuous model with standard boundary conditions (Dirichlet boundary conditions for source/drain and gate contacts). Then, the atomistic scattering states $\psi_{sc}(r)$ are calculated using the plane-wave based quantum transport method with the MoS_2 alone. Note that we did not perform

Figure 13: Double-gate TFET. (a) Schematic view of the simulated double-gate TFET based on mono-layer MoS₂. (b) Band profile of the TFET with 6.30 nm physical gate length, as well as the band structure of left and right electrodes.

self-consistent calculations for the external electrostatic potential, i.e. the potential induced by the gate and source/drain. The reason is that, being the tunneling current very small, the effect of the self-consistent external potential is expected to be also very small. This means that the potential profile is mostly dominated by the gate and source/drain contacts via the Poisson equation.

The resulted current characteristics $I_d - V_g$ are presented in Fig. 14. In the above mentioned ideal cases with ultra-thin high-k gate dielectric ($t_{HfO_2} = 2.0$ nm) and perfect source(drain)-channel alignment (no underlap), excellent switch performance is found. The ON-state tunneling currents at $V_g = V_d = 0.5$ V are calculated to be around $600 \mu A/\mu m$, which outperforms most reported TFETs based on regular bulk semiconductors.[110] This higher performance lies in the better gate control of the atomic thin layer, which results in abrupt interband tunneling junction, hence larger tunneling current. The ON/OFF ratios in the work window of 0.5 V are found to be 3.2×10^3 , 3.8×10^4 and 4.5×10^5 for the three physical gate lengths, respectively. Subthreshold-swing beyond the classical Boltzmann limit is found even in the 6.30 nm physical gate length case. This indicates that sub-10 nm physical gate length scaling can be achieved in mono-layer MoS₂ TFETs in ideal cases. The degraded SS in sub-10 nm physical gate length cases is a result of the source-to-drain direct tunneling due to the thin tunneling barrier, rather than the interband tunneling leakage at the channel-drain interface in small band gap semiconductor (such as InAs) based TFETs, where drain underlap must be used for leakage suppression.

To further enhance the TFET performance (by increasing the turn-on tunneling current), we have investigated the atomic design of the mono-layer TMDC tunneling diode by introducing

Figure 14: Double-gate TFET. Transfer characteristics ($I_d - V_g$) of three TFETs based on mono-layer MoS₂ with physical gate length $L_g = 4.41, 6.30$ and 12.6 nm.

Figure 15: MoS₂ tunnel diode. Band structure, potential profile and band-to-band tunneling of the diode. Figure taken from Ref. 55.

transition-metal, and S vacancies.[55] The band structure as well as the potential profile of the mono-layer MoS₂ tunneling diode are shown in Fig. 15, where the Mo and S vacancies are introduced in the center of the diode. First-principle calculations show that both types of vacancies can introduce band gap states which could possibly bridge the band-to-band tunneling (as shown in Fig. 15). However, since the band edge states of TMDCs are mainly located on the central transition-metal layer,[55] one expects major effects from the transition-metal vacancy, not the chalcogenide vacancy, which is confirmed by our direct calculations.

The BTBT current of mono-layer MoS₂ tunneling diode with and without vacancies are shown in Fig. 16. Note that the bias voltage $V_b = 0$ is defined as when the conduction band of the left electrode and the valence band of the right electrode are just about to overlap. As can be seen from the comparison, by introducing the transition-metal vacancy, the ON-state BTBT current is increased by a factor of 10 (similar results are found

Figure 16: MoS₂ tunnel diode. Comparison of the band-to-band tunneling currents before and after introducing transition-metal and dichalcogenide vacancies. Results taken from Ref. 55.

for other TMDCs [55]). Also note that, if the chalcogenide vacancy is introduced, there is almost no effect on the BTBT current. By examining the partial density of states (PDOS) projected onto transition-metal, we found that it is the transition-metal vacancy induced middle of the band-gap states which reduce the effective length of the tunneling transition region, and enhance the ON-state tunneling current. Further more, the gap states existing only in the transition region will not affect the steep subthreshold-swing (SS) in TFET. This is because when the device is switched off, there is no overlap between conduction band of left electrode and valence band of right electrode, so no carriers can be transported. This finding provides physical guidance for TFET engineering based on atomic defect designs.

4. Conclusions

In this article, we have reviewed a methodology which we have developed over the past decade to perform *ab initio* calculations of electron transport across nanoscale systems. The method is based on the solution of the scattering states using a plane wave basis set and nonlocal pseudopotential. A special auxiliary boundary condition is introduced to solve for the "system states" at a given energy E , and these "system states" are linearly combined to obtain the scattering states satisfying the scattering state open boundary conditions. This approach can be applied to any bias voltage, and the density and potential of the system can be calculated self-consistently.

We have reviewed the problems studied using this method. Firstly, taking Au nanojunctions as a model system, the suitability of our method to investigate electron tunneling has been demonstrated. The tunneling regime has been further explored by the simulation of the transmission through field emission resonances, yielding results which can be compared directly with the STS experimental measurements. For molecular electronics, we have designed a molecule switch, which can be turned on or off by a perpendicular electric field. The *ab initio* calculations established the practical limits of such a molecular

switch. Finally, we have studied the performance and scaling limits of the tunneling field-effect transistors based on monolayer transition-metal dichalcogenides, and proposed atomic defect designs to further enhance the transistor performance.

All in all, we have shown that our plane-wave-based transport method provides a good practical and accurate approach to study elastic quantum transport for a variety of problems. It is particularly useful to study quantum tunneling through vacuum or other barriers where the localized atomic orbital based method might face a difficulty to describe the electronic wave functions. Besides that, it can be used to study any quantum transport problem, e.g., through transmission from defect states within a semiconductor barrier. We expect it to find broad applications in the future.

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