Convergence Issues in *Ab-Initio* Transport Calculation through Oxide Barriers and Molecules

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Abstract

We use *ab-initio* simulations to calculate tunneling currents through atomic scale structures. Two issues affecting the outcome of the calculations have been investigated: (1) the description of the wavefunction tails set by the choice of basis set and (2) the interaction between the structure and the electrodes. We selected two systems for investigation: $Si/SiO_2/Si$ MOS device and Au/benzene-1,4-dithiol/Au. Transport was calculated using non-perturbative scattering theory [1] operating on a Hamiltonian generated by the local orbital SIESTA code [2]. On issue (1) we show that the exponential leakage current decay with barrier thickness of ~1decade/2 Å measured on $Si/SiO_2/Si$ [3] can only be reproduced in SIESTA using at least a single-ζ plus polarization (SZP) basis set. On issue (2) we show that the number of electrode atomic layers affected by the molecular structure is large and that underestimating that number may result in a considerable overestimation of the tunneling current.

Keywords: nanotechnology, electron transport, scattering theory, density functional theory, molecular electronics.

1 Introduction

Ab-initio calculations of transport through nanometer scale structures, such as individual atoms or molecules [4,5], and ultra-thin oxide barriers [6] (both referred here as "devices"), directly link atomic structure and chemistry, which are difficult to probe, to transport properties, which are easier to access experimentally. However, in order to deliver results that are qualitatively and quantitatively meaningful, such calculations face three major challenges: (1) the band gap problem [7] inherited from density functional theory (DFT), which is the most used approach for self-consistent band structure calculations of solid state systems; (2) a proper description of the wavefunction tails of the tunneling states; (3) the interaction between the device and the electrodes. Issue (1) is hard to resolve and has been the source of much investigation for many years. It impacts band offsets in semiconductor/oxide systems and the Fermi level-LUMO separation in metal/molecule systems, which in turn affect the leakage current exponentially. Therefore, until a computationally affordable solution to this problem is found, tunneling current calculations based on DFT do not have the quantitative predictive power. On the other hand, DFT-based transport calculations have been very useful in providing insights and capturing the qualitative behavior of transport phenomena [4-6]. In this work we address issues (2), which in general has a qualitative effect on the tunneling current, and (3), which has a more quantitative character. We chose to simulate the model systems $Si/SiO_2/Si$ MOS device and Au/benzene-1,4-dithiol/Au since they are significant, the former for existing CMOS technology, and the latter for being an important benchmark system in molecular electronics (see for example [5]).

2 Theory

In the limit of low temperature the total tunneling current through a barrier is given by [1]:

$$I = \frac{2e}{h}\int_{\mu_l}^{\mu_r} dE\, T(E) \tag{3}$$

where the transmission function $T(E)$ in the absence of inelastic scattering is given by

$$T(E) = 4\pi^2 \sum_{lr} |T_{lr}(E)|^2 \delta(E - E_l)\delta(E - E_r) \tag{4}$$

where $T_{lr}(E)$ is the transmission matrix element between states in the left and in the right electrodes (see discussion below) and a multiplicative factor of two has been included to account for spin degeneracy. In first order perturbation theory, the transmission matrix element T_{lr} reduces to the matrix element of the scattering potential. Here T_{lr} are the matrix elements of the Lippmann-Schwinger scattering operator $\hat{T}$, which is accurate to all orders [1].

It has been demonstrated [1] that Eq. (4) can be written as

$$T(E) = Tr[\hat{\Gamma}_r \hat{G} \hat{\Gamma}_l \hat{G}] \tag{5}$$

where the indices l, r stand for left and right portions of the modeled system (the leads). The operator $\hat{\Gamma}$ is the non-Hermitian part of the Hamiltonian of the coupled system, and describes the level broadening due to the coupling of

the device with the electrode [1]. The retarded Green's function $\hat{G}$ is given by the usual expression,

$$\hat{G} = \frac{I}{E - \hat{H}_d^0 - \hat{\Sigma}_l - \hat{\Sigma}_r + i\eta} \quad (6)$$

where E is the energy, $\hat{H}_d^0$ is the Hamiltonian operator of the isolated device (the finite system considered in the DFT calculation), and η is a small real parameter. By choosing a plus sign in front of η we limit our analysis to waves outgoing from the scattering region (retarded Green's function). The operators $\hat{\Sigma}_i$ (i = l, r) are the so-called self-energies and originate from the coupling between the device and the two semi-infinite leads [4].

In the presence of an applied external bias V, the transmission function *T(E)* depends on *V*, namely *T(E)* is written as *T(E,V)*. In this work we adopt the rigid band approximation

$$T(E,V) = T(E + \eta V) \quad (7)$$

so that the current can be written as

$$I = \int_{E_f - \eta V}^{E_f + (1-\eta)V} T(E)dE \quad (8)$$

where η is the voltage division factor. η is taken as 0.5 following Datta *et al.* [4].

We previously applied this theory to a MOS capacitor and found excellent agreement between the calculated leakage current through a quasi-amorphous SiO_2 layer and experiment [6]. We also considered the problem of resonant tunneling and used a model system consisting of a single Al atom bridging two Al metallic leads to show that indeed this theory naturally captures tunneling resonance at the atomic level [1]. Finally we have used the same approach to study the impact of defects on the leakage current through monoclinic HfO_2 [8].

In the present study two model systems were investigated: Si/(β-quartz)SiO_2/Si and Au/benzene-1,4-dithiol/Au with the Si and Au lattices in the [001] and [111] directions, respectively. All calculations were performed using the local-density approximation [9,10] (LDA) within density-functional theory (DFT) [11,12] as implemented in the local orbital SIESTA code [2]. The electronic ground state was determined self-consistently using the preconditioned conjugate gradient method [13] through the solution of the Kohn-Sham equations, and the ionic positions were optimized to minimize the Hellmann-Feynman forces [14]. Norm-conserving non-local pseudopotentials of the Troullier-Martins type [15] were used to describe all the elements considered. In order to obtain qualitative convergence within a factor of two or so from k-point converged results, 12 and 24 k-points in the plane orthogonal to the electron current propagation were used for the cases of Si/SiO_2/Si and Au/benzene-1,4-dithiol/Au, respectively. Such simplification is justifiable due to the exponential character of the leakage current, the uncertainty in experimental barrier thickness, and the well-known limitation of DFT to correctly predict band gaps [7].

3 Results

The short-range nature of the SIESTA basis set enables a rather convenient partition of the Hamiltonian into two leads and "device". We include several atomic layers of the lead's materials as a buffer into the "device" sub-Hamiltonian. Also, the atomic layers of the leads are divided into slabs to ensure a "tight-binding" like block-tridiagonal matrices describing both semi-infinite leads. Figure 1 shows the tunneling current *versus* applied bias for different numbers of atomic layers in the electrode's slabs and the device buffer for the Si/SiO_2/Si system, where the stoichiometric and total SiO_2 barrier thickness are 12.9 Å and 20.9 Å, respectively. Single-ζ (SZ) basis set and two Si atoms per Si plane (1x1) were used. The figure label contains two numbers per *IxV* curve: the left one corresponds to the number of Si bulk-like atomic layers along the [001] direction used to generate semi-infinite electrodes [1], while the right one corresponds to the number of Si atomic layers surrounding the SiO_2 barrier. Based on the cutoff radius of the localized orbitals used and the lattice constant of Si, we find that orbital overlaps only take place within four layers of Si. This result is nicely confirmed by

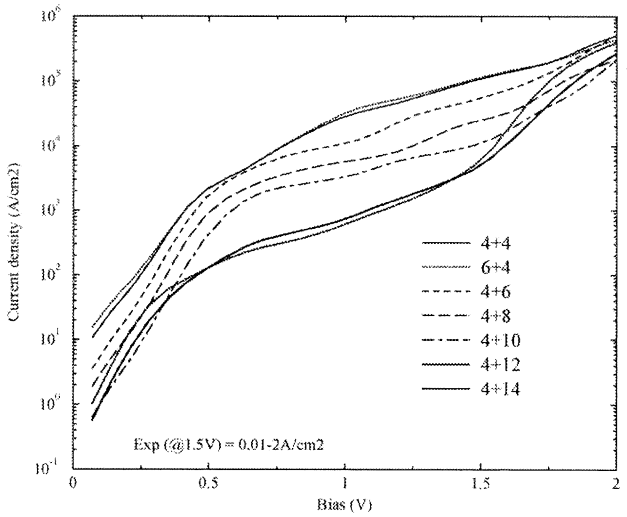

Figure 1: Current density through Si/SiO_2/Si. The first number in the label indicates the number of Si layers used to create the semi-infinite leads, while the second indicates the number of Si layers at each side of the SiO_2 barrier.

the fact that using four or six layers of Si to create the semi-infinite leads does not change the calculated current (curves

labeled as 4+4 and 6+4 in Fig. 1). However, the same argument does not apply to the number of Si layers surrounding the barrier, since the tunneling current only converges for 16 Si layers at each side of the barrier. The explanation for this rather unexpected result is that, because Si has such a small band gap and as a result states spread over a considerable distance, indirect overlap of orbitals (through off-diagonal terms in the Hamiltonian) plays a crucial role.

The same argument applies to the case of dithiol between two gold contacts, as shown in Fig. 2. These calculations were performed using an SZ basis set and four atoms per layer of gold (2x2). In this case, again we see a good agreement between conductances calculated using four or six layers of gold to build the semi-infinite leads, and a decrease of the conductance as the number of gold layers surrounding the dithiol molecule is increased. Notice that in this case, 18 layers of gold in each side of the molecule were not enough to reach convergence, even though convergence seems to be close. Since gold has no band gap, its states are delocalized and therefore indirect overlap of orbitals is even stronger than in the Si case. The shapes of the conductance curves shown in Fig. 2 are not in very good agreement with previous calculations on a similar system [5]. We have attributed that to the limited basis set (SZ) used to generate Fig. 2. The issue is currently being investigated.

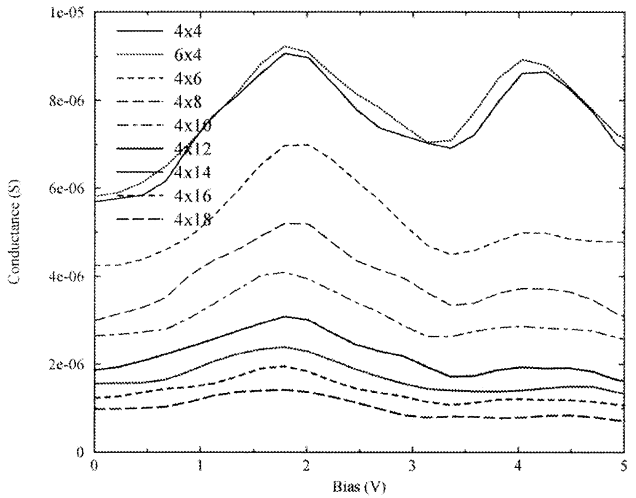

Figure 2: Conductance of the Au/dithiol/Au system for different combinations of numbers of Au layers in the leads and surrounding the molecule, as described in Fig. 1.

The measured tunneling current across an amorphous SiO_2 barrier of approximately the same thickness as the one considered above and biased at 1.5 V is in the range of 0.01-20 A/cm^2 for barriers of 1 and 2 nm thickness, respectively [3]. Comparing the experimental value with the results shown in Fig. 1, it is clear that the calculated tunneling currents are in most cases severely overestimated. One possible explanation for the disagreement is the DFT underestimation of the Si/SiO_2 conduction band (CB) offset. In fact, the offset obtained directly from the band alignment (using the calculated and not experimental band gaps) is only 1.2 eV for the SZ basis set, much less than the measured value of 3.5 eV. Figure 3 compares the tunneling current for different basis sets and indicates the CB offset obtained with each of them. In general we observe the expected trend that the higher the band offset, the smaller the current. Indeed, for the most complete basis sets available in the SIESTA code, single and double-ζ plus polarization (SZP/DZP) the current is in the range of 1-10 A/cm^2, in reasonable agreement with the experimental data.

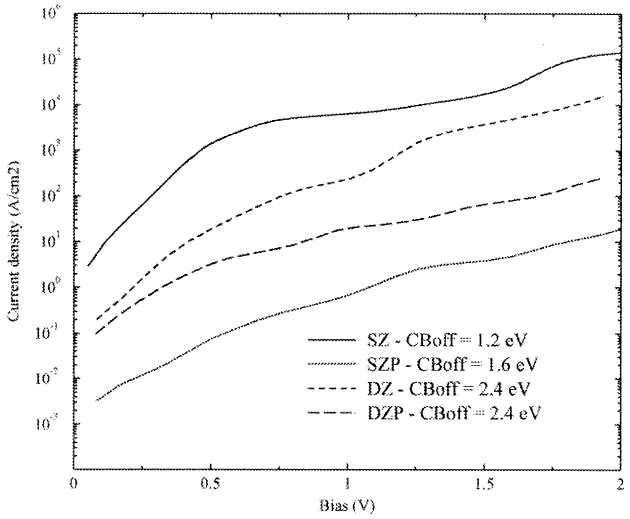

Figure 3: Current density through $Si/SiO_2/Si$ obtained with different basis sets. The conduction band offsets calculated for each basis is indicated.

Some of the results in Fig. 3, however, are unexpected. For example, even though the CB offsets obtained with DZ and DZP are the same, the tunneling current is higher in the DZ case than in the DZP case. Also, the CB offset obtained with SZP is smaller than both DZ and DZP but its current is the lowest. These facts indicate that CB offsets alone cannot explain all the data. Tunneling currents are strongly dependent on the tails of wavefunctions that penetrate the barrier. So it is natural to expect that the quality of the basis sets description of those tails has an impact on the calculated current. Instead of directly investigating the tails described by each basis set to determine which basis performs better (a difficult task since we do not have a standard to compare with), we calculated the slope of the tunneling current as a function of barrier thickness and compared it with experimental data. Figure 4 shows the tunneling current as a function of barrier thickness for each basis set. The slope of the corresponding experimental curve is 1 decade/2 Å. Notice that the slopes of all bases are approximately the same for thin barriers, however they differ considerably as the barriers becomes thicker. This is expected, since the tunneling current is very sensitive to the magnitude of the wavefunction tails under the barrier, which depend on the basis choice. While the slopes for SZ and DZ are much smaller than the measured value, indicating that the

wavefunction tails are too big, those obtained with SZP and DZP are in very good agreement with experiment, given the approximate nature of the model structure used in the calculations. Tomfohr and Sankey came to a similar conclusion analyzing the complex band structure of β-cristobalite [16].

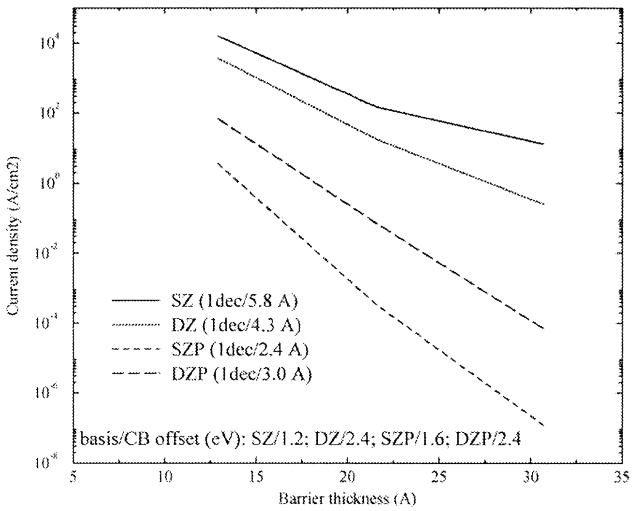

Figure 4: Dependence of the tunneling current through $Si/SiO_2/Si$ on the thickness of the SiO_2 barrier. The label indicates the slopes of the curves calculated by fitting straight lines. The measured slope is 1 decade/2 Å. [3].

Conclusion

We investigated two aspects of *ab-initio* tunneling current calculation: the impact of the number of lead-like atomic layers surrounding the device and the choice of basis set on the tunneling current. We found that the smaller the band gap the larger is the number of layers necessary to obtain a converged current. In the case of silicon, that number is 12 while in the case of gold it is larger than 18. We also found that, even though an accurate CB offset is necessary for quantitative estimation of tunneling current, a proper description of wavefunction tails under the barrier via an appropriate choice of basis set is also necessary. For the $Si/SiO_2/Si$ system we conclude that SZP and DZP basis sets are complete enough for predicting correct trends.

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