

# SIMULATIONS OF THE TRANSPORT OF ELECTRONS THROUGH MOLECULAR AND ATOMIC NANODEVICES

*Peter Bokes<sup>1</sup>, Miroslava Zemanová Diešková<sup>1</sup>*

<sup>1</sup> INPE, Faculty of Electrical Engineering and Information Technology, Slovak University of  
Technology, Ilkovičova 3, 812 19 Bratislava, Slovakia

E-mail: Peter.Bokes@stuba.sk

Received 30 April 2012; accepted 5 May 2012.

## 1. Introduction

The inherent impossibility of experimental methods to give us a complete picture of molecular nanojunctions and atomic-sized nanodevices can be overcome by resorting to the simulations from first principles (*ab initio*). These simulations aim at complementing our understanding of the geometry, electronic and ultimately transport and optical properties of solids, of which nanojunctions are a special example. While the reference to the first principles indicates that these simulations employ only the fundamental constants - the mass of electron, its charge, the mass of atomic cores and the Planck constant, the immense numerical complexity of the many-electron quantum-mechanical problem forces us to use several approximations, some of which are controlled, some less so. In this contribution we give the overall framework and describe steps needed to perform first principles simulations of systems of interest in molecular electronics and atomic nanodevices, starting from the geometry considerations and finishing with the calculation of their conductance. The obtainable results and the approximations employed are discussed for two examples of systems studied recently by the authors: (1) the ultra-thin Al/AlO<sub>x</sub>/Al interfaces and (2) the dithioazobenzene molecule (DAB) bridging two gold electrodes. All the here presented results are obtained using the Quantum Espresso code [1].

## 2. Geometry of the model and ground state properties

Nanojunctions do not have a clearly defined size or number of atoms. The border between *the system* and *the electrodes* is blurred. The system must be described at the quantum-mechanical level to capture the chemical specificity of the nanojunction, whereas

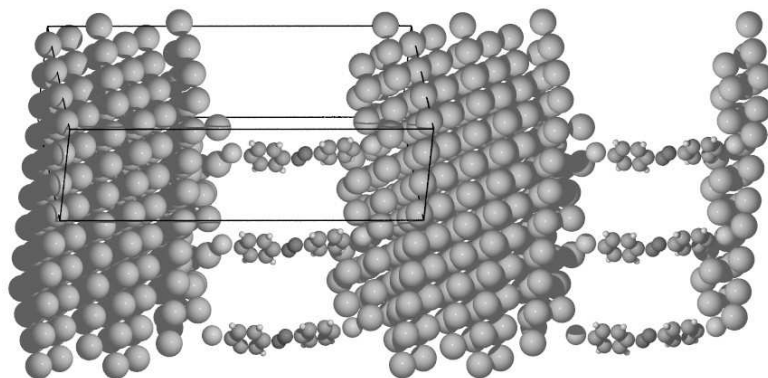


Fig. 1: The DAB nanojunction in a periodically repeated box (indicated by black lines)

the electrodes act mostly as a reservoir of electrons. The transition region can be estimated to be the larger of the two relevant length scales - the Debye screening length  $l_D$  and the Fermi wavelength  $l_F$ . Within the first principles simulation, specifically the ground state calculation, this is conveniently achieved by putting the system with sufficiently large portion of the electrode into a box with periodic boundary conditions (see Fig. 1). Within the box's coordinates we distinguish the direction in which the device is meant to carry electrical current, which we will assign as the  $z$  axis within this paper, and the two perpendicular directions. The periodicity of the box along the perpendicular directions is often desired, e.g. if we study interfaces, or its effect can be made negligibly small for monomolecular junctions by increasing the size of the box along this direction. Rather than being a problem, this periodicity improves the quality of the model by increasing the density of states in the electrode. On the other hand, the periodicity along the  $z$  axis is totally artificial and the size of the box along this directions must be tested (converged) against possible influence on the local electronic structure of the nanojunction.

The size of the periodic box, the type of atoms and their positions within the box define the many-electron Hamiltonian for the nanojunction. To find it's ground state density and energy, the density functional theory become the method of choice since the mid 80's [2]. This method circumvents the many-electron problem by an effective Kohn-Sham system of non-interacting electrons moving in an *effective self-consistent potential*. The Kohn-Sham electrons are guaranteed to give us the exact many-electron density  $n(\vec{r})$  and the total energy  $E_{\text{tot}}$ , even though the actual calculations need to use an approximative contribution to the effective potential - *the exchange-correlation potential*. The quality of the latter has been perfected in the last 20 years, particularly for *sp*-bonded elements. Perhaps the most successful and popular approximation for the exchange-correlation potential is the generalized gradient approximation (GGA). In the following we describe the performance of the GGA for several experimentally accessible physical quantities.

The total energy of electronic system depends parametrically on the positions of the atoms  $E_{\text{tot}}(\{\vec{R}_i\}_{i=1}^N)$ . Minimizing the total energy with respect to the atomic coordinates we find the geometrical arrangement of atoms with the smallest energy  $E_{\text{tot}}^0 = \min_{\{\vec{R}_i\}_{i=1}^N} E_{\text{tot}}(\{\vec{R}_i\}_{i=1}^N)$ , where the ground state geometry is given by the optimized coordinates of atomic centres  $\{\vec{R}_i^0\}_{i=1}^N$ . It has been demonstrated on a ensemble of molecules that the error of predicting the geometry using the GGA functional, i.e. the coordinates of atoms, is typically less than 1% [3]. Another quantity of interest is the *dissociation energy* given by the difference in the total energies of two atomic arrangements corresponding to two local minima (the reactants and products in chemical language), over-binding the difference typically by 0.3eV. In the context of molecular electronics, the difference in total energy between two local minima is important in identifying several possible stable geometrie. An example is the case of two isomers of the dithioazobenzene molecule (DAB) - the cis and the trans - shown in the Fig.2. The difference in their GGA total energy is  $\Delta E_{\text{tot}} = E_{\text{tot}}^{\text{trans}} - E_{\text{tot}}^{\text{cis}} = -5.15 \text{ eV}$ , which is much larger than the expected precision of the GGA method and hence this number is reliable. It shows that work needs to be done to transform the nanojunction with trans isomer to the nanojunction with cis isomer. It is interesting to note that the ideal cis and trans molecules in the vacuum differ only by  $\Delta E_{\text{tot}}^{\text{vac}} = E_{\text{tot}}^{\text{trans, vac}} - E_{\text{tot}}^{\text{cis, vac}} = -0.5 \text{ eV}$  [4], so that most of the work done corresponds to the rearrangement of the gold atoms on the surface of the electrodes. On the other hand, in our study of the Al/AlO<sub>x</sub>/Al interfaces we found two similar geometrical arrangements of the

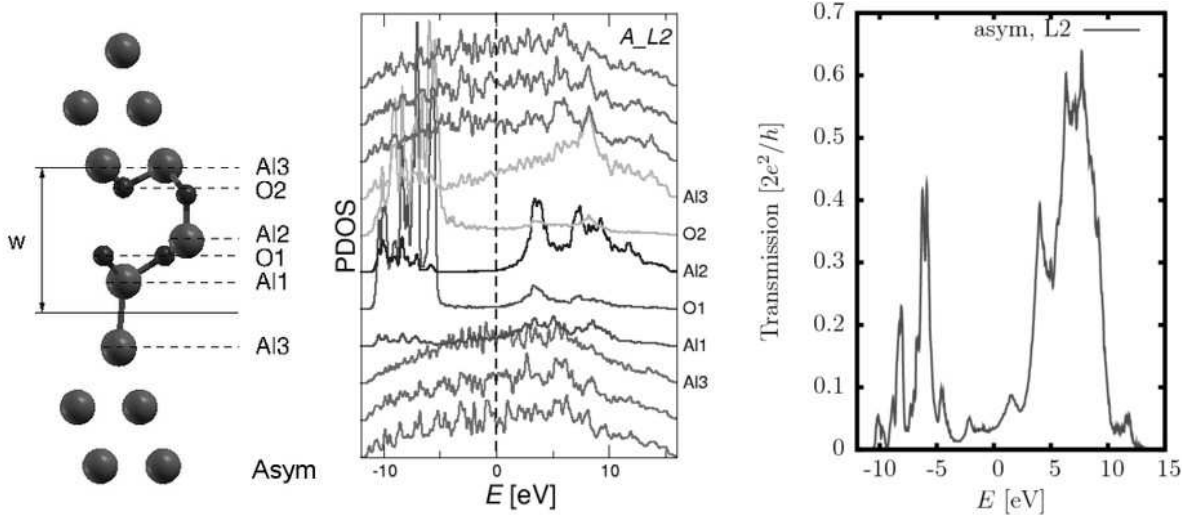


Fig. 3: The geometry, projected density of states and the transmission function of the asymmetric Al/AIO<sub>x</sub>/Al interface.

atoms in the oxide - the symmetric and the asymmetric structures, named after their symmetry properties with respect to the centre of the interface. In this case, the difference of their total energies  $\Delta E_{\text{tot}} = E_{\text{tot}}^{\text{asym}} - E_{\text{tot}}^{\text{sym}} = -0.07 \text{ eV}$  [5], which is much less than the precision of the GGA method so that the only conclusion in this case is that the two structures are equally good candidates for realisation in experiment. This is in agreement with the well known fact that the Al/AIO<sub>x</sub>/Al interfaces are disordered.

### 3. Response function, transmission and the conductance.

In contrast to the ground state properties, discussed in the previous section, transport properties reflect the character of low energy excitations in nanojunctions. These are accessible through a linear response functions like the nonlocal, frequency-dependent conductivity,

$$\vec{j}_{\omega}(\vec{r}) = \int d^3 r' \vec{\sigma}_{\omega}(\vec{r}, \vec{r}') \cdot \vec{E}_{\omega}(\vec{r}') \quad (1)$$

The conductivity is not a characteristics of the ground state, so that for its calculation one needs to use more general theory than the DFT, the time-dependent density functional theory [6], which similarly to the DFT in principle gives exact time-dependent density and hence the conductivity. In practice, not much is known about the *time-dependent exchange-correlation potential* and researches resort to the use of the so called *adiabatic approximation*, which means using the exchange-correlation potential of the ground state DFT. Under these circumstances it can be shown that the conductance of the nanojunction is [7]

$$G = \lim_{\omega \rightarrow 0} \int_{z < 0} d^3 r \int_{z' > 0} d^3 r' \vec{e}_3 \cdot \vec{\sigma}_{\omega}(\vec{r}, \vec{r}') \cdot \vec{e}_3 = \frac{2e^2}{h} T(E_F) \quad (2)$$

where  $T(E_F)$  is the *average transmission probability* for electrons at the Fermi energy to pass through a nanojunction in the  $z$  direction given by the unit vector  $\vec{e}_3$ , calculated for the ground state self-consistent Kohn-Sham potential. The calculation of the transmission probability can be done in several different ways. One of them is the matching technique, where the Bloch eigenstates of an ideal bulk electrode are continuously matched to the Bloch

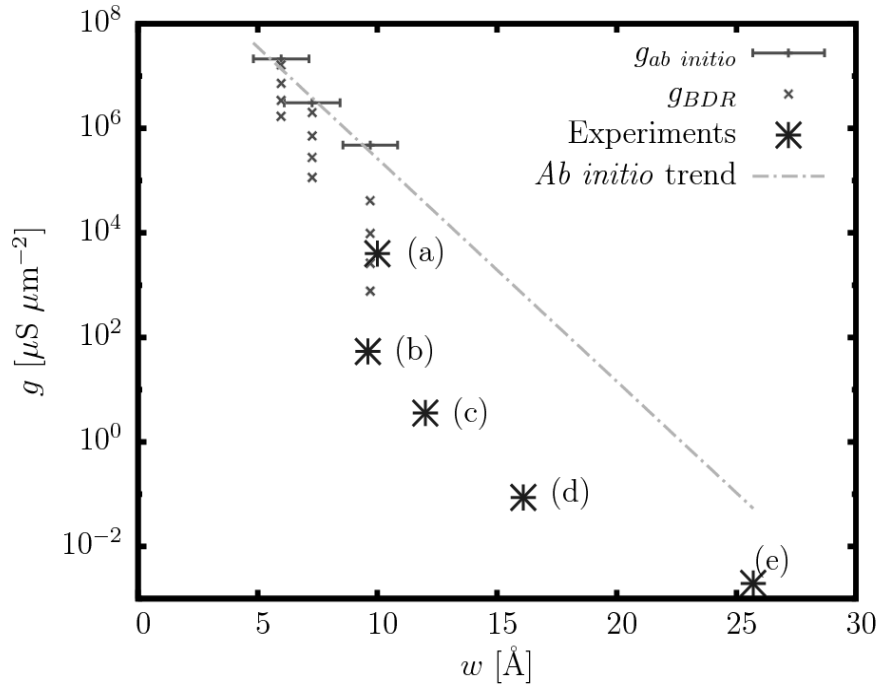


Fig. 4: The conductance per area Al/AIO<sub>x</sub>/Al interfaces versus the interface width. The BDR model assumes simple square barrier of a sequence of barrier heights  $\phi=2.0;2.5;3.0;3.5$  eV.

The experiments are (a) [13], (b) [14], (c) [15] (d) [16] (e) [17].

eigenstates of the periodic box described in the previous section [8], implemented in the Quantum Espresso code [1].

#### 4. Transmission function and projected density of states

Although the conductance is given by the average transmission at the Fermi energy only, one usually obtains the transmission for a whole interval of energies around the Fermi energy. Apart from having implications for temperature dependence of the conductance and the non-linear  $I$ - $V$  characteristics, the obtained position of the Fermi energy might not be perfect and it is then important to know how sensitive is the resulting conductance on the location of the Fermi energy. Typically, this *transmission function* is a collection of peaks and valleys (see Fig. 3, right). The peaks appear at energies corresponding to the positions of molecular orbitals and their widths indicate the strength of coupling between these orbitals and the Bloch states in the electrodes. The transmission function is, in the position of its peaks, similar to the more familiar *projected density of states* (PDOS), but here the height and width of the peaks does not indicate the orbital's coupling to the electrode. Still, since the calculation of PDOS is essentially part of the ground state DFT, and is easier to calculate than the transmission function, it is frequently used as a guide or first information on the conductive properties of the nanojunction. In particular, PDOS can be used to devise a simple barrier model for tunnelling, where the effective barrier height is the energetic distance from the Fermi energy to the nearest non-zero density of states in the molecule/oxide. This is demonstrated in Fig. 3. The barrier width  $w$  is obtained from the geometry of the system (left), the barrier height  $\phi$  is typically taken as the energy distance from the Fermi energy to the nearest non-zero density of states (about 3.5 eV in the PDOS, central graph, most easily seen on the atomic layer Al2 in the oxide region). Finally, the transmission function shown on the right, evaluated at the Fermi energy gives the conductance. The form of the

transmission function clearly reflects the character of the PDOS in the oxide region - the peaks in the transmission coincide with large values of the projected density of states.

## 5. Examples of transport simulation

The predictive power of the adiabatic approximation and its improvements are topics of active research in first principles simulation of quantum transport. One of the most important error of the adiabatic approximation is the underestimation of the energy of low energy excitations [9,10]. The underestimation of the energy of low energy excitation is a well known problem in the simulation of optical spectra [6]. It is frequently remedied by an artificial increase of the excitations band gap using a scissor operator, and this approach has been also used in transport problems with a moderate success, but a generally working method does not exist. Its typical example is the correction of the 'adiabatic' conductance of the benzenediamine molecule anchored to gold electrodes towards its experimental value, where the dynamical image charge induced in the metallic electrode (a correlation effect) has been accounted for by a shift of the unoccupied states [10].

This problem is also relevant for the Al/AIO<sub>x</sub>/Al interface. The band gap in a bulk corundum (Al<sub>2</sub>O<sub>3</sub>) is experimentally known to be about 9 eV, whereas the optical gap resulting from the adiabatic approximation is about 6 eV [11]. Hence, it is expected that the effective barrier height in the AlO<sub>x</sub>. However, the oxide that is found by geometry optimization on the Al (111) surface differs from the ideal corundum, and its calculated band gap is about close to the 'experimental' value 9 eV (Fig. 3). This opening of the gap is due to the presence of the metal induced gap states which shift the unoccupied orbitals up in energy. This effect of the metal on the oxide is similar to the *N+1* method in the optical gap calculation in the ground state DFT of insulators which gives much better results than the adiabatic approximation used for perfect insulating crystal [2]. Due to these reasons our estimate is that the correction to the barrier height should be no more than 1.5 eV. This correction has noticeable effect on the calculated conductance of these interfaces. In Fig. 4 we show the conductances (per micrometer squared of the interface), obtained from the first principle simulation using the adiabatic approximation ( $g_{ab\text{ initio}}$ ), conductances from simple trapezoid barrier ( $g_{BDR}$ ) for a sequence of barrier heights  $\phi=2.0; 2.5; 3.0; 3.5$  eV to demonstrate the importance of the error in the barrier width, and selected experimental results. The severe overestimation of the conductance is typical for most present *ab initio* simulations. However, increasing the band gap, or what it corresponds to, increasing the effective barrier height, the calculated conductances move towards the experimental values. We should stress, that the experimental interface widths do have a significant uncertainty, as they are typically obtained using assumptions about the dielectric permeability of effective mass of electrons. The figure suggests, that many of the experimental data underestimate the interface widths.

In spite of the uncertainties in the quantitative conductance prediction, a lot can be learned from these calculations. In our second example - the dithioazobenzene molecule (DAB) - it has been assumed that its two conformations, the cis and trans geometry, could be used as a nanomolecular switch for electrical current. In the past it has been shown experimentally as well as in a DFT calculations [4,12], that these two isomers do behave as an opto-mechanical switch so that its similar behaviour seems as an attractive possibility. Unfortunately, this has turned to be incorrect, as our preliminary results give very similar conductances for both geometries,  $G_{\text{trans}} = 0.211 e^2/h$  and  $G_{\text{cis}} = 0.178 e^2/h$  for the trans and cis configuration respectively, in contrast to the previous claims based on possibly oversimplified models of gold electrodes [12]. The conductance of the DAB nanojunctions

seems surprisingly rigid. This can be explained by relatively good coupling of the DAB molecule to the gold electrodes, demonstrated by the broad peak of the highest occupied molecular orbital on the molecule. The cis-trans transition causes only very mild changes in the position of this peak and the position of the Fermi energy. We have checked for several geometries obtained from previous DFT optimizations [4] and all exhibit essentially identical transmission characteristics and hence the conductances. It is very unlikely that this observed rigidity would depend on the approximations involved in the conductance calculations so that we expect that this behaviour for real molecular nanojunctions based on single DAB molecular switch. Publication of the details of these calculations is in preparation.

#### 4. Conclusions

In the conclusions, we have discussed the steps that are involved in performing a simulation of transport properties of nanojunctions from the first principles. We have explained the construction of the model using a periodic box and described the utilization of the ground state DFT for finding the atomic geometry of the nanojunction and the following transmission calculations. The obtainable quantities as well as potential problems related to the quality of the involved approximations were discussed.

#### Acknowledgement

The authors acknowledge Ivan Štich for discussions and encouragement to work on the DAB molecules. This work was partially supported by the Slovak Grant Agency for Science through Grant No. 2/0192/10 and ERDF OP R&D, Project "meta-QUTE" (26240120022).

#### References:

- [1] P. Giannozzi *et al.*: *J. Phys. Condens. Matter* **21**, 395502 (2009).
- [2] U. von Barth: *Phys. Scr.* **2004**, 9 (2004).
- [3] J. Perdew, S. Kurth: In: *A Primer in Density Functional Theory*, C. Fiolhais, F. Nogueira, and M. Marques (eds.), Springer-Verlag, New York (2003).
- [4] R. Turanský, M. Konôpka, N. L. Doltsinis, I. Štich, D. Marx: *Chem. Phys. Phys. Chem.*, **11**, 345 (2010).
- [5] M. Diešková, M. Konôpka, and P. Bokes: *Surf. Science* **601**, 4134 (2007).
- [6] G. Onida, L. Reining, and A. Rubio: *Rev. Mod. Phys.* **74**, 601 (2002).
- [7] P. Bokes and R. W. Godby: *Phys. Rev B* **69**, 245420 (2004).
- [8] A. Smogunov, A. Dal Corso, E. Tosatti: *Phys. Rev. B* **70**, 045417 (2004).
- [9] C. Toher, A. Filippetti, S. Sanvito, and Kieron Burke: *Phys. Rev. Lett.* **95**, 146402 (2005).
- [10] Su Ying Quek *et al.*: *Nano Letters* **7**, 3477 (2007).
- [11] K. Sankaran *et al.*: *Appl. Phys. Lett.* **97**, 212906 (2010).
- [12] C. Zhang *et al.*: *Phys. Rev. Lett.* **92**, 158301 (2004).
- [13] H. Jung *et al.*: *Phys. Rev B* **80**, 125413 (2009).
- [14] K. Gloos, P. J. Koppinen, and J. P. Pekola: *J. of Phys. Cond. Matt.* **15**, 1733 (2003).
- [15] T. Holmqvist *et al.*: *J. Vac. Sci. Technol. B* **26**, 28 (2008).
- [16] W. F. Brinkman, R. C. Dynes, and J. M. Rowell: *J. Appl. Phys.* **41**, 1915 (1970).
- [17] T. E. Hartman, and J. S. Chivian: *Phys. Rev.* **134**, A1094 (1964).