Effect of dipole moment on current-voltage characteristics of single molecules

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Abstract—**We perform empirical calculations of the tunneling current through various small organic molecules sandwiched between gold electrodes by using the Wenzel-Kramers-Brillouin (WKB) approximation. The barrier to tunneling is taken to be the work function of gold and calculated from a first principles electronic structure code. The current-voltage characteristics of these molecules are compared in the context of existing first principles and experimental results. In this model the surface dipole moment, induced by the adsorbed molecule, can have a significant effect on the current and hence dipole moments may be an important property for prediction of the conductance characteristics of a molecule.**

Keywords- Molecular electronics, single molecule conductance, electron transport, **ab-initio** *transport calculations, surface dipole moment.*

I.   INTRODUCTION

Studies of electron tunneling between two electrodes with adsorbed bridging molecules are attracting considerable attention due to the possible application of this configuration in the fabrication of an electronic device with components consisting of molecules [1]. The response of such a system to an applied bias between the electrodes depends on the geometric and electronic structure of the molecule, the coupling between the molecule and electrodes and the potential profile across the molecule.

The most prolific experimental technique used to probe the current-voltage characteristics of electrode-molecule-electrode systems is scanning tunneling microscopy (STM) [2-10]. An STM tip acting as top electrode is lowered onto a self-assembled monolayer of the molecule under study, which is attached to the bottom electrode. Thiolate molecules on gold surfaces are the most commonly studied system [11]. These scanning probe techniques suffer from large uncertainties associated with the nature of the coupling between the STM tip and molecule. Break junction experiments attempt to improve on this by creating a junction in which assembled molecules are chemically bound to both electrodes [12-14].

Ab-initio theoretical studies of the current-voltage characteristics that take into account a full quantum-mechanical description of the electrode- molecule -electrode-system under an applied bias [15, 16] typically overestimate the experimental conductance of individual molecules [2, 3, 13, 17] by two orders of magnitude. The contact geometries assumed in these *ab-initio* calculations are idealised and studies have been done to measure the actual effect that geometry variation has on the results [18-23]. While the uncertain experimental geometries could account for the large discrepancies between theory and experiment, other possible problems with the application of the most commonly used *ab-initio* technique, Density Functional Theory (DFT) [24, 25], to the transport problem have been pointed out by various authors [26-29].

To obtain a qualitative understanding of the transport in these systems it may be useful to simply describe the tunneling due to a barrier occurring in the gap between the top and bottom electrodes. The presence of a molecule will then affect the barrier shape and height. In this paper we investigate tunneling between two Au(111) electrodes in the presence of representative aromatic dithiols. We use the potential from an *ab-initio* electronic description of the gold slab with adsorbed molecule to obtain the barrier height for an electron to escape from the slab. We describe how this is related to the work function of gold and the surface induced dipole moment. The WKB approximation is then used to calculate corresponding current-voltage characteristics and this is compared with *ab-initio* I(V) data.

II.   METHOD

The optimum adsorption geometry and corresponding electronic structure of the molecules on an Au(111) slab was calculated with the SIESTA [30, 31] software package. Atom-centered basis functions are used for the valence electrons with a double zeta plus polarization orbital for each atom. The orbitals are strictly localized with the localization defined by an energy parameter, being the excitation energy due to the confinement. This parameter is set to 5 mRy. Core electrons are modeled with norm-conserving pseudo-potentials constructed according to the scheme of Troullier and Martins [32]. The exchange and correlation energy is calculated with the generalised gradient approximation with parametrisation due to Perdew, Burke and Ernzerhof [33]. Conjugate gradient optimisations and surface scans are performed to find the minimum interaction energy of the molecules on an Au(111) surface approximated by 4 layers of 3x3 Au atoms repeated periodically in the plane parallel to the slab.

The electronic structure of the optimum geometry is used to calculate the potential outside the slab and the bulk and slab Fermi energies. The surface dipole moment is calculated by integrating the charge from the middle of the slab outward to a position beyond the molecule.

We model tunneling through the gap with the WKB approximation for the transmission function $T(E)$ between electrodes

$$T(E,V,d) = e^{-\frac{2\sqrt{2}}{\hbar}\int_0^d \sqrt{m(U(x)-E)}dx} \qquad (1)$$

where m is the electron mass, d is the width of the barrier and $U(x)$ is the potential function across the barrier. The current is then found from the Landauer formalism as

$$i(V,d) = \frac{2e}{h}\int_{-\infty}^{\infty} T(E,V,d)\rho_1(E-eV)\rho_2(E) \\ \times \left[f(E) - f(E-eV) \right] dE \qquad (2)$$

where ρ_1 and ρ_2 are the local densities of states of the top and bottom electrodes, $f(E)$ and $f(E-eV)$ are the Fermi-Dirac distribution functions for the two electrodes, and $V = V_{top} - V_{bottom}$ is the bias applied between the electrodes with the convention that the top electrode is grounded. The contact conductance is taken to be the quantum of conductance, $2e/h \approx 77 \ \mu S$ [34]. We use the zero temperature approximation and assume a constant density of states to find the simplified relation

$$i(V,d) = \frac{2e}{h}\int_0^{eV} e^{-\frac{2\sqrt{2}}{\hbar}\int_0^d \sqrt{m(U(x)-E}dx} \, dE \qquad (3)$$

We use a trapezoidal barrier with barrier height ϕ modified by a sinusoidal function which approximately accounts for image charging [35]

$$U(x) = eV\left(1 - \frac{x}{d}\right) + \phi\left[\sin\left(\frac{\pi x}{d}\right)\right]^{\alpha} \qquad (4)$$

with the dimensionless parameter $\alpha = 0.2$ that controls barrier shape.

The barrier height is calculated using two methods: (A), the Fermi level of bulk gold modified by the energy required to move an electron through the induced surface dipole in the presence of the adsorbed molecule

$$\phi_1 = -E_{F,bulk} + W_{\mu} \qquad (5)$$

This energy, W_{μ}, is calculated from the dipole moment per unit area, P_{σ}, by a simple parallel plate approximation,

$$W_{\mu} = \frac{eP_{\sigma}}{\varepsilon_0} \qquad (6)$$

where ε_0 is the permittivity of vacuum. The dipole moment is extracted from the SIESTA DFT calculations as described above. In method (B), the difference in potential energy between the vacuum and the Fermi level of the surface including the effect of the adsorbed molecule is calculated directly in SIESTA. This quantity is well approximated by the difference in energy between the Fermi energy and potential calculated a large distance from the slab surface. In our case we take the potential in the middle of the gap between periodically repeating slabs.

$$\phi_2 = V_{vac} - E_{F,surface} \qquad (7)$$

The barrier width d is the distance between the two electrodes, taken as 9 Å – this is roughly the length of all three molecules.

The DFT transport calculations are performed with the TRANSIESTA-C package [36]. The electronic structure is calculated according to the SIESTA method although we use a relaxed set of parameters which is sufficient for qualitative information. The transport is calculated using the non-equilibrium Green's functions method (NEGF). The device region is modeled as the molecule plus two layers of Au(111) on either side and is coupled to semi-infinite bulk electrode regions on the left and right. Including three Au(111) layers on either side of the molecule made no difference to the result of a test case.

III. RESULTS AND DISCUSSION

The analysis is carried out for the adsorbed molecules 1,4-dimethanethiol (XYL), ethynylbenzene (EB) and 1-ethynyl-4-nitrobenzene (ENB) shown in Fig. 1.

The bulk Fermi level is calculated as $E_{F,bulk} = 3.01$ eV. Table 1 lists the barrier heights calculated according to equations (5) and (7) for the bare gold slab as well as with each adsorbed molecule. Clearly the two methods result in the same trend for the barrier height for the different molecules and bare slab. Adsorption of XYL and EB reduce the surface dipole moment and hence the barrier height whereas ENB increases the dipole moment and hence barrier height. The parallel plate approximation (equation (5)) seems to overestimate the effect of the dipole moment on the work function (barrier height).
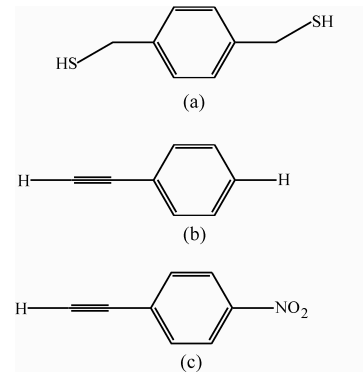

Figure 1. The molecules used in the investigation (a) 1,4-dimethanthiol (XYL), (b) ethynylbenzene (EB) and (c) 1-ethynyl-4-nitrobenzene (ENB).

TABLE I. SURFACE DIPOLE MOMENT PER UNIT AREA P_σ, ENERGY REQUIRED TO MOVE EN ELECTRON THROUGH THE DIPOLE W_μ, AND BARRIER HEIGHTS CALCULATED ACCORDING TO EQUATION (5) ϕ_1, AND EQUATION (7) ϕ_2 FOR THE MOLECULES IN FIG. 1.

Molecule	P_σ $(10^{-2}\ e/a_0)$	W_μ (eV)	ϕ_1 (eV)	ϕ_2 (eV)
Au(111)	-1.14	3.90	6.91	4.57
XYL	-0.97	3.31	6.32	4.42
EB	-0.78	2.66	5.67	4.27
ENB	-1.60	5.47	8.48	5.09

Fig. 2 shows the corresponding current-voltage characteristics for both methods of calculating the barrier height. Although the absolute values are not of particular significance, we note that they are closer to recent state of the art experimental data than typical *ab-initio* calculations. Akkerman et. al. [37] recently obtained reliable measurements of the current through large-area molecular junctions and the current normalised to a single decanethiol molecule amounts to ~ 0.01 pA. In contrast DFT calculations result in currents several orders of magnitude higher. Fig. 3 shows our DFT+NEGF results for the XYL, 1,4-diethynylbezene (DEB) and ENB molecules.

While conclusive experimental proof of differences in conductance between distinct molecules is rare, the conventional wisdom is that conductance is increased by small HOMO-LUMO gaps and a high level of conjugation of the molecules' orbitals. However recent STM break junction experiments by Tao *et. al.* [2, 3] that probe the conductance of aromatic- and alkane-dithiols do not support this. In fact they find a higher conductance for the alkane chains with more localized orbitals [22].
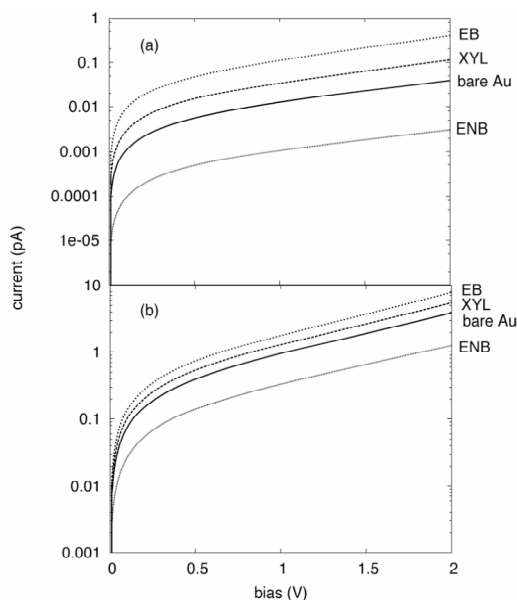

Figure 2. Current-voltage characteristics of the Au(111)-molecule-Au(111) system for the three molecules as well as an empty vacuum gap calculated from (a) equation (5) and (b) equation (6).
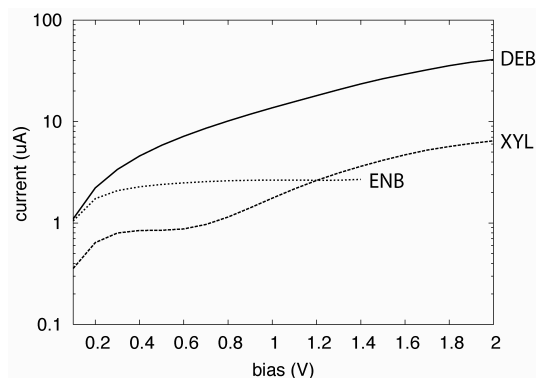

Figure 3. Current-voltage characteristics of 1,4-diethynylbenzene (DEB), 1,4-dimethanethiol (XYL) and 1-ethynyl-4-nitrobenzene adsorbed between Au(111) electrodes. Calculations were done using standard DFT+NEGF calculations.

The dipole moment of a molecule is therefore potentially an important property with regards to its conductance and current-voltage response. While more complicated mechanisms are clearly present, comparison of the *ab-initio* results of Fig. 3 with the tunneling barrier model results of Fig. 2 shows that this could be the case for the molecules studied here.

CONCLUSIONS

We have calculated the tunneling current through different molecules adsorbed between gold slabs using the WKB approximation where the barrier to tunneling is taken to be the work function of gold. We used two methods to calculate the work function. Although they result in different values, the trend is the same: the dipole moment of the gold surface with/without adsorbed molecules affects the work function. Therefore depending on the direction of the dipole of the adsorbed molecule, it can either enhance or impede the tunneling process. Thus the dipole moment may be a very important property when interpreting experiments that probe the conductivity of molecules.

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