Resonant tunnelling device at the molecular scale. A simple exactly solvable model

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Abstract
We present a simple exactly solvable model, based on an Anderson–Newns–Grimley type Hamiltonian, for a three-terminal device at molecular level. This device contains two nanowires as source and drain, a scanning tunnelling microscopy (STM) tip as gate and an active atom or molecule between the STM tip and the two nanowires. We show that an amplification effect of the tunnelling current between the source and the drain is obtained by changing the gate voltage and the distance between the gate and the active molecule.

Scanning tunnelling microscopy (STM) and atomic force microscopy (AFM) routinely image surfaces with atomic scale details. STM and AFM may also be used to locally modify the surfaces and to manipulate individual atoms and molecules with atomic scale precision [1]. The first quantum device built with STM is the atomic switch, realized by Eigler *et al* [2]. This device operates by reversible transfer of a Xe atom between the Ni(110) surface and the STM tip, under a small bias pulse. Experimental and theoretical studies lead to the realization of a voltage amplifier employing a single molecule as an active element [3].

Recent theoretical studies reported transistor-like behaviour of three-terminal geometries in various molecule-based devices [4–6]. Fully quantum mechanical calculations of various molecules attached to two electrodes and a capacitive gate showed that for a fixed small source–drain bias, the gate voltage could lead to an amplification of the current by orders of magnitude. Another mechanism leading to current amplification can be the mechanical deformation of the molecule, as demonstrated experimentally and theoretically in the case of two-terminal molecular devices [7]. In this paper we study theoretically a three-terminal quantum device at molecular level using a simple one-electron Green function approach. This device include two nanowires, an STM tip and an active molecule trapped between the STM tip and the two nanowires.

We consider two nanoelectrodes deposited on a dielectric surface separated by a very small gap. These two nanoelectrodes can be obtained by sectioning a nanowire or a nanotube
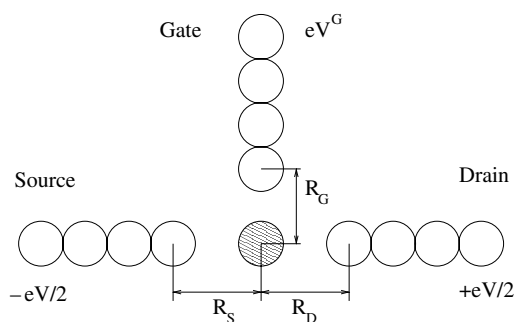
Figure 1. A schematic model of the three-terminal device. V is the bias voltage between source and drain, V^G is the gate voltage and R_S, R_G, R_D are the source–molecule, gate–molecule and drain–molecule distances respectively.

with the AFM or the STM tip. An atom or molecule fixed in a controlled way on an STM tip is brought into the gap between the two electrodes so that a chemical bond is realized between the molecule and the two nanoelectrodes. The present status of the planar technology and the use of STM/AFM technique seems to make possible the realization of the proposed structure [8]. Even if this is a delicate experimental problem, we appreciate that such a device is feasible and we use a theoretical model for this device to study its characteristics.

By analogy to the micro-electronic transistor, we refer to the left and right nanometric electrode as source (S) and drain (D) respectively, while the STM tip will be the gate (G). We schematically represent this nanometric device using three atomic chains (gate perpendicular to the source and drain, see figure 1).

First we consider the polarization of this device which allows the flow of the electrons from the source through the molecule to the drain. This implies that the source is negatively polarized and the drain has a positive polarization. A separate voltage source V^G is coupled to the gate through an ideal capacitor (with infinite resistance—to avoid a tunnelling current between the gate and the drain).

We suppose that the molecule has an electronic resonance near the Fermi level of the source and drain. This electronic resonance is derived from a localized energy level of the molecule, coupled with three continuum energy bands (of the source, drain and gate). This coupling can be treated as a simultaneous chemisorption problem in the Anderson–Newns–Grimley formalism [9]. A resonant tunnelling problem through a localized level coupled with two electrodes is a well known phenomenon [10].

The following Hamiltonian describes our system of the molecule and the three nanoelectrodes:

$$H = H_0 + V \tag{1}$$

$$H_0 = \epsilon_0 a_0^+ a_0 + \sum_{k_S} \epsilon_{k_S} a_{k_S}^+ a_{k_S} + \sum_{k_G} \epsilon_{k_G} a_{k_G}^+ a_{k_G} + \sum_{k_D} \epsilon_{k_D} a_{k_D}^+ a_{k_D} \tag{2}$$

$$V = \sum_{k_S} (V_{0k_S} a_0^+ a_{k_S} + hc) + \sum_{k_G} (V_{0k_G} a_0^+ a_{k_G} + hc) + \sum_{k_D} (V_{0k_D} a_0^+ a_{k_D} + hc) \tag{3}$$

where ϵ_0 is the resonant level of the active molecule and ϵ_{k_S}, ϵ_{k_G}, ϵ_{k_D} label the energy of the one-particle eigenstates of the source (S), gate (G) and drain (D) respectively. V_{0k_S}, V_{0k_G}, V_{0k_D} are the matrix elements for the electron transfer between the source and the molecule, the gate and the molecule and the drain and the molecule respectively.

To compute the resonant tunnelling current between the source and drain we need the following transition matrix elements:

$$\mathcal{T}(k_D, k_S) = \langle k_D | T | k_S \rangle \tag{4}$$

where

$$T = V + VGV \tag{5}$$

with

$$G = \frac{1}{E - H_0 + i\eta}. \tag{6}$$

The calculation of this matrix elements is similar as in [8],

$$\mathcal{T}(k_D, k_S) = \frac{V_{0k_D} V_{0k_S}}{E - \epsilon_0 - \Delta_S(E) - \Delta_G(E) - \Delta_D(E) - i(\Gamma_S(E) + \Gamma_G(E) + \Gamma_D(E))}, \tag{7}$$

with $E = \epsilon_{k_S} = \epsilon_{k_D}$ being imposed by energy conservation and where Δ is the shift of the resonant level due to the change of the chemical interaction between the molecule and the electrodes and due to the mechanical deformation of the molecule,

$$\Delta_{S,G,D}(E) = P \sum_{k'_{S,G,D}} V_{0k'_{S,G,D}} \frac{1}{E - \epsilon_{k'_{S,G,D}}} V_{k'_{S,G,D}0}, \tag{8}$$

and Γ is its width (which is inversely proportional to the lifetime of the resonant level):

$$\Gamma_{S,G,D}(E) = \pi \sum_{k'_{S,G,D}} V_{0k'_{S,G,D}} \delta(E - \epsilon_{k'_{S,G,D}}) V_{k'_{S,G,D}0}. \tag{9}$$

Taking into account the shifts of the energy levels after the application of the bias voltage between the source and drain V and the gate voltage V^G, the expression for the tunnelling current is

$$J = \int_{\epsilon_F - \frac{eV}{2}}^{\epsilon_F + \frac{eV}{2}} dE \, \Gamma_S\left(E + \frac{eV}{2}\right) \Gamma_D\left(E - \frac{eV}{2}\right) \bigg| E - \epsilon_0 - \Delta_S\left(E + \frac{eV}{2}\right) - \Delta_G(E - eV^G)$$
$$- \Delta_D\left(E - \frac{eV}{2}\right) - i\left(\Gamma_S\left(E + \frac{eV}{2}\right) + \Gamma_G(E - eV^G) + \Gamma_D\left(E - \frac{eV}{2}\right)\right) \bigg|^{-2} \tag{10}$$

where ϵ_F is the position of the source, drain and gate Fermi level $\epsilon_F^S = \epsilon_F^G = \epsilon_F^D$ in the absence of any applied voltage.

The energy level of the molecule ϵ_0 depends on V^G through the electric field of the STM tip. We suppose that the shift of ϵ_0 when V^G is varied is given by this simple relation:

$$\epsilon_0 = \epsilon_M - eV^G \tag{11}$$

where ϵ_M is the resonant level of the molecule in the absence of the STM electric field.

In the following calculations we choose a hydrogen atom to represent the molecule placed between a tungsten STM tip (gate) and two nanowires. For the description of the source, drain and gate we use the tight-binding approximation in which the functions $\Gamma_{S,G,D}(E)$ are proportional to the local density of states (LDOS) on the atom closest to the molecule of the source, drain or gate:

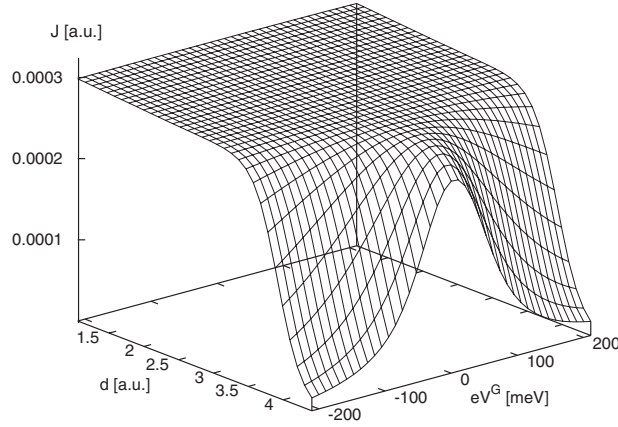$$\Gamma_{S,G,D}(E) = 2\pi |\beta_{S,G,D}|^2 \rho_{S,G,D}^0(E) \tag{12}$$

Figure 2. The tunnelling current dependence on the distances $d = R_S = R_G = R_D$ and on the gate voltage V^G.

where $\beta_{S,G,D}$ is the hopping integral between the molecule and its nearest neighbour atom of the source, drain or gate. Using three semi-infinite atomic chains to represent the source, gate and drain, the expression for the LDOS reads [12]

$$\rho^0_{S,G,D}(E) = \frac{1}{2\pi} \frac{\sqrt{4\alpha^2_{S,G,D} - E^2}}{\alpha^2_{S,G,D}} \tag{13}$$

where $\alpha_{S,G,D}$ is the hopping integral between two neighbour atoms of the source, gate or drain. The functions $\Delta_{S,G,D}(E)$ are then obtained from $\Gamma_{S,G,D}(E)$ through a Hilbert transform. We also performed the same calculations with simple rectangular shape densities but the results were not very dependent on this change.

All the parameters entering the hopping integrals are taken from [11]. The distances involved in our calculations might appear too small compared with the distances involved in real STM experiments. However, if we consider bigger active molecules—and larger distances—the results should reveal the same qualitative behaviour as in the present study, provided that the density of states of the molecule has one single peak close to the Fermi level of the electrodes [4]. In the present calculations we describe the resonant state of the isolated molecule using a discrete level ϵ_M. A finite width of the resonant level of the molecule (which could be due to the intrinsic properties of the isolated molecule but also to the electric field of the STM tip) can be taken into account through an appropriate imaginary part of ϵ_M. We checked the effects of such a finite width and we found that a realistic broadening of the resonant level of the isolated molecule can be neglected in a first approximation.

Figure 2 shows a tridimensional plot of the tunnelling current dependence for different values of the distance $d = R_S = R_G = R_D$ (see figure 1), and the applied gate voltage V^G. ($eV = 75$ meV, $\epsilon_F - \epsilon_M = 0$.) As expected the tunnelling current decreases when this distance increases. This is due to the fact that the projection of the density of states of the STM tip and nanowires on the molecule decreases exponentially with the distance. At the same time the current does not change significantly when the distance d is reduced to around 2 au, even if the projected electronic density of states of the STM tip on the molecule increases, the broadening and shift of the resonant level becomes appreciable enough in order to give rise to a saturation of the resonant current. For a fixed distance d, the tunnelling current depends on the gate voltage V^G since by modifying V^G one can change the position of the resonant level relative
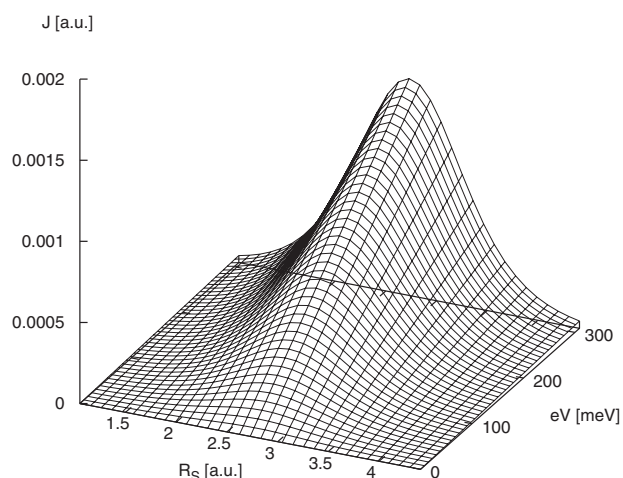
Figure 3. The tunnelling current dependence on the source–molecule distance R_S and on the applied bias voltage V.

to the Fermi level of the nanowires and the STM tip: $\epsilon_F - \epsilon_0 = eV^G$. This level can be situated above or below the Fermi level depending on the gate voltage V^G. In these cases, if V^G is too positive or too negative, the tunnelling is possible only on the tail of the Lorentzian shape of the resonant level and the tunnelling current is not so high. The maximum of the current is obtained when the resonant level coincides with the midpoint between the source and drain Fermi levels in the presence of the applied bias voltage V. Since we chose a symmetric voltage drop across the junction, this is happening when $\epsilon_0 = \epsilon_F$ or $V^G = 0$.

Figure 3 presents the resonant tunnelling current as a function of the bias voltage and the distance R_S between one nanowire (left) and the molecule (the distance between the molecule and the other nanowire (right) and between the molecule and the STM tip is kept constant, $R_G = R_D = 3$ au; $V^G = 0$). It is very interesting to note that by changing the distance between one nanowire and the molecule the resonant tunnelling current shows a maximum somewhere in between 2.5 au (which corresponds to the equilibrium distance of an H atom adsorbed on a tungsten surface) and 3 au (here we note that the position of the maximum increases with $R_G = R_D$ and does not change appreciably with V^G). By lowering R_S, the projected electronic density of states of the left nanowire on the molecule grows. At the same time there is a considerable increase of the broadening and shift of the resonant level (due to the change of chemical interaction between molecule and source and to the mechanical deformation of the molecule). This last effect is dominant, which explains the decrease of the resonant tunnelling current for low separation between the left nanowire and the molecule.

In figure 4 we plot the variation of the tunnelling current as a function of the applied bias voltage V between the source and drain, and the distance R_G between molecule and STM tip ($V^G = 0$, $R_S = R_D = 3$ au). This plot shows an amplification effect of the tunnelling current by changing the distance between the molecule and the gate. Increasing R_G over 2.5 au a strong increase in the source–drain current is observed and for $R_G = 4$ au a saturation value occurs in the tunnelling current. This saturation is determined by the level of the tunnelling current in the absence of the gate. The decrease of the tunnelling current for low tip–molecule separation is due to the change of chemical interaction between the molecule and the STM tip and to the mechanical deformation of the molecule, which leads to the increase of the broadening and shift of the resonant level.
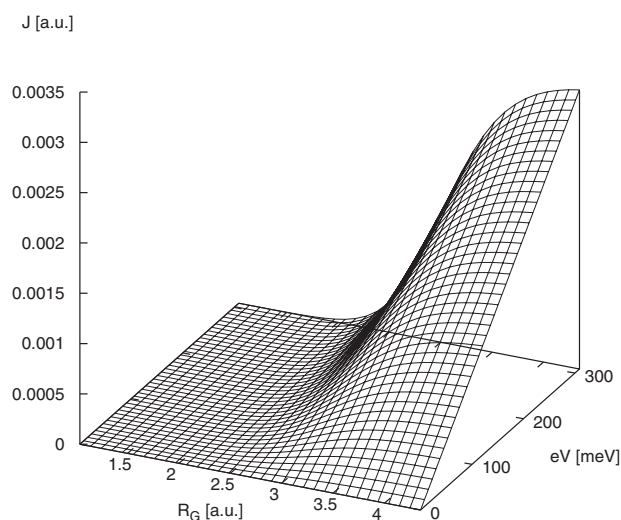
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Figure 4. The tunnelling current dependence on the gate–molecule distance R_G and on the applied bias voltage V.

It is worth noting that the decrease of the source–drain current for low molecule–gate separation in figure 4 is more pronounced than the one seen in figure 3 for low molecule–source separation. This is due to the fact that the source–drain current does not depend directly on the projected density of states of the gate on the molecule (only indirectly, through the broadening of the resonant level—see the denominator of the integrand on the rhs of equation (10)) while it does depend (linearly) on the projected density of states of the source on the molecule (see equations (10) and (12)). For the same reason the tunnelling current stabilizes for large molecule–gate separation while it decreases exponentially for large molecule–source separation.

By comparing figure 2 with 4, one can see that in both cases we have an amplification effect of the tunnelling current between source and drain.

- In figure 2 the amplification effect is due to the linear dependence of the shift of the resonant level on V^G (see equation (11)). Because ϵ_0 appears in the denominator of the expression for the tunnelling current (see equation (10)), the amplification effect is non-linear in V^G, following the shape of a Lorentzian.
- In figure 4 the amplification effect is due to the dependence of the broadening and shift of the resonant level on the distance R^G. This dependence is exponential since the hopping parameter β_G depends exponentially on R_G. As a consequence, the amplification effect is also exponential in R_G (as long as the molecule–gate separation allows a considerable overlap between the wavefunctions of the STM tip and the molecule), and more pronounced than the one in figure 2.

In conclusion we have studied the transport properties of a three-terminal device at molecular level. An amplification of the tunnelling current between source and drain is obtained through the variation of the gate voltage and the distance between the gate and the active molecule. The amplification effect obtained through the variation of the gate–molecule distance is much more effective than the one obtained through the variation of the gate voltage. These kinds of calculation are important in the design and realization of the future generation of electronic devices at the molecular level.

Acknowledgments

References

[1] Eigler D M and Schweizer E K 1990 *Nature* **344** 524
[2] Eigler D M, Lutz C P and Rudge W E 1991 *Nature* **352** 600
[3] Joachim C, Gimzewski J K and Aviram A 2000 *Nature* **408** 541
[4] Di Ventra M, Pantelides S T and Lang N D 1997 *Appl. Phys. Lett.* **76** 3448
[5] Taylor J, Guo H and Wang J 2001 *Phys. Rev.* B **63** 121104(R)
[6] Emberly E G and Kirczenow G 2000 *Phys. Rev.* B **62** 10 451
[7] Joachim C, Gimzewski J K, Schlittler R R and Chavy C 1995 *Phys. Rev. Lett.* **74** 2102
[8] Spataru C and Budau P 1997 *J. Phys.: Condens. Matter* **9** 8333
[9] Anderson P W 1961 *Phys. Rev.* **124** 41
    Grimley T B 1967 *Phil. Trans. R. Soc.* **90** 751
    Newns D M 1969 *Phys. Rev.* **178** 1123
[10] Wingreen N S, Jacobson K W and Wilkins J W 1989 *Phys. Rev.* B **40** 11 834
[11] Forni A, Desjonqueres M C, Spanjard D and Tantardini G F 1992 *Surf. Sci.* **274** 161
[12] Desjonqueres M C and Spanjard D 1993 *Concepts in Surface Physics (Springer Surface Science Series)* (Berlin: Springer)