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PHENOMENA IN RESONANT TUNNELING THROUGH DEGENERATED ENERGY STATES WITH ELECTRON CORRELATION

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We introduce a general analysis method, which allows us to simulate the operation of high-performance molecular nano-devices and to design the expected function of a wide range of devices in nano-scale size. The method is based on the use of a resonant tunneling phenomenon, admitting strong electron correlation in a quantum dot with degenerated states. Three examples of the application of this method are given: Coulomb repulsion, uncorrelated resonant tunneling, and electron-phonon interaction. It is shown that there is a good agreement with experimental data in all three cases.

Keywords: Nano device; resonant tunneling; quantum dot; molecular electronics.

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1. Introduction

A single-molecule electronic device is one of the ultimate goals for realizing next-generation devices for the forthcoming high-speed information society. Potential applications in this field have motivated investigations in molecular nano-electronics for various materials.[1–13] It was predicted[14] that molecular-based computer chips could be created and used by 2005. For various reasons, however, this has not been realized so far. Therefore it is essential to study the novel electronic properties of molecular devices originating from their structural characteristics. The structure of molecular electronics is characterized by two features: a number of weakly transparent potential barriers and low dimensionality. A small distance between barriers causes the formation of quantum dots (QDs) or quantum wells (QWs). These are quasi one-dimensional objects responsible for creating important properties for applications. These properties and their physical behavior are already known.[15] The problem arises when QDs are characterized by degenerated energy states. When these states are occupied by electrons, they split in the case of even

slight interaction. The splitting can give rise to a strong electron correlation in the QD. The issue is to identify the physical processes in the QD using current-voltage (I-V) dependence. Nevertheless, a simple method is essential for describing the resonant tunneling with regards to the strong electron correlation in the QD. We propose a rather simple way to calculate the I-V characteristics of a one-dimensional two-barrier tunneling system, considering the features of the energy spectrum in the QD and possible electron correlation. The tunneling process is essentially a quantum-mechanical phenomenon if the splitting is accounted for. Therefore, we have used a strongly quantum-mechanical description of these phenomena, which is the approach used for the case of two-barriers structures,[16,17] rather than quasi-classical approximations.

2. Methods

A schematic drawing of a typical two-barrier nano-device is shown in Fig. 1(a). The diagram of its potential energy is represented in Fig. 1(b). The I-V characteristics

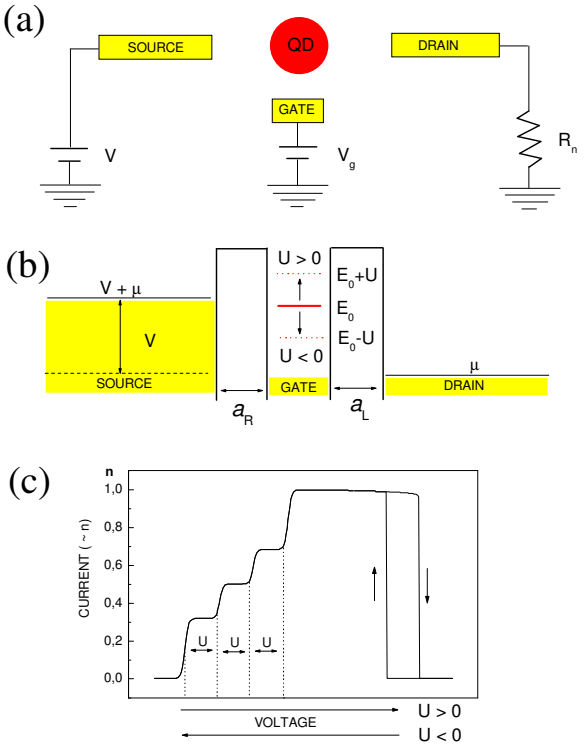

Fig. 1. (a) Schematic drawing of a nano-transistor. (b) The energy level diagram of the nano-device showing resonant tunneling phenomena through degenerated energy states with electron correlation U. (c) Theoretical prediction of current-voltage (I-V) curves. I-V characteristics depend on the sign of U. Applied voltage for positive (negative) U affects the right (left) direction of the shift in I-V curves in (c).

in the case of the splitting of degenerated energy levels in the QD are shown in Fig. 1(c). Depending on the sign of the interaction energy between the tunneling electrons ($U > 0$ or $U < 0$), the split energy levels shift correspondingly up or down. In Fig. 1(c) this circumstance is shown by the change in direction of the applied voltage. Stepped characteristics in an *I-V* curve originate from the splitting of energy levels. Change of gate voltage V_g results in a shift of energy levels of the QD with regards to the chemical potential of the electrodes, which is observed in the shift of the *I-V* curve along the horizontal axis.

At the low transparency barriers and low voltage V, the direct current J_{cd} is described by the equation

$$J_{cd} = \frac{e}{\hbar} \int G \cdot (f_L - f_R) \cdot \rho \cdot dE \,,$$

where e is the elementary charge, $\hbar$ is Planck's constant, conductance G is expressed by $\Gamma_L\Gamma_R/(\Gamma_L + \Gamma_R)$ with the rates of electron transmission through the left (right) barriers $\Gamma_L(\Gamma_R)$,[16,17] $f_L(f_R)$ is the electron distribution function in the source (the drain), and ρ is the density of state of a QD. Γ_L, Γ_R are exponential dependent on barriers widths, and Γ_L, Γ_R, f_L, f_R and ρ depend on energy (E) and voltage (V). Correlation effects of electrons in a QD can be taken into account by means of ρ. There is a harmless assumption in the case of low transparent barriers. The density of state ρ is defined by the energy structure of a QD

$$\rho = \sum_{m=1}^{N-1} C_{2N-1}^{m} (1-n)^{2N-m-1} n^m \delta(E - E_m) \,, \quad C_N^m = \frac{N!}{m!(N-1-m)!} \,. \tag{1}$$

Where n is the occupation rate of electrons defined by

$$0 \le n = \sum_{m=0}^{2N-1} C_{2N}^{m} g(E_m) n^{2N-m-1} n^m \le 1 \,, \quad g(E_m) = \frac{\Gamma_L f_L + \Gamma_R f_R}{\Gamma_L + \Gamma_R} \,, \tag{2}$$

N is a degree of degeneration, and E_m are energies of new split states $E_m = E_0 + mU$ ($m = 0, 1, \ldots, 2N-1$). In the correlated electron system, ρ depends on the number of injected electrons in the QD, and must be calculated for each case. Because the mean free path of electrons is larger than the size of the QD for the devices discussed in this work, a voltage drop in the QD, owing mainly to Ohm's law ($V = RI$), can be negligible. Therefore, we can assume that the voltage drop takes place in barriers and is proportional to the width of the barrier. The skewed conductance gap occurs in *I-V* characteristics due to asymmetric barriers. We will demonstrate this approach in three different cases, namely, the Coulomb interaction ($U > 0$), the failing interaction between electrons ($U = 0$), and the strong electron-deformation interaction ($U < 0$).

3. Results and Discussion

Figures 2(a) and 2(b) respectively show a schematic of the structure of a C_{60} nano-transistor and an idealized energy diagram of the device as reported by Park *et al.*[2]

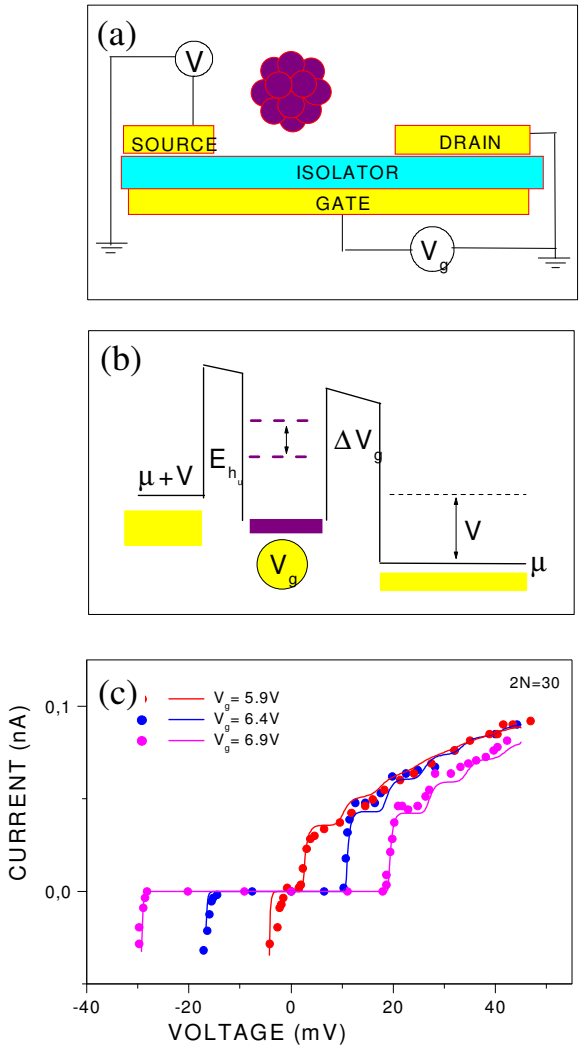

Fig. 2. An example of experimental data and theoretical fitting for the case of Coulomb interaction ($U > 0$). (a) Schematic drawing of C_{60} nano-transistor in (2). (b) An idealized energy level diagram of a C_{60}-transistor according to Ref. 2. (c) Current-voltage (I-V) curves in C_{60}-transistor. Three series of experimental data in I-V characteristics taken at different gate voltages ($V_g = 5.9$, 6.4, 6.9 V)[2] are shown by filled circles. Solid lines represent the theoretical results. The discussed phenomenon corresponds to the left part of Fig. 1(c).

In the case of $U > 0$, the I-V characteristic has step-like plateaus at low voltage and transparent barriers.[16,18] In our description, the plateau width is proportional to the value of Coulomb repulsion U (in the case of equivalent barriers the plateau width is equal to $2U$). The number of steps is equal to the degree of degeneracy of the energy levels in a QD. The threshold voltage value is determined by the energy difference between the energy level of a QD and the Fermi level at the

contacts without the application of a gate voltage. Using the gate voltage (V_g), it is possible to shift energy levels in the QD as shown in Fig. 2(b). The series of filled circles in Fig. 2(c) represent I-V characteristics for different gate voltages.[2] The device exhibits strongly suppressed conductance near zero bias voltage, followed by step-like current jumps at the highest voltages. The voltage width of the zero-conductance region (conductance gap) can be changed by changing V_g. The highest occupied molecular orbital (HOMO) of the C_{60} is the fifth-degenerated state h_u, and it is completely occupied by ten electrons. The numerical result is obtained in this scenario when the energy of the level h_u is equal to the Fermi energy of metal electrodes with $V_g = V_c$. Here, V_c is the gate voltage for the case that the conductance gap is equal to zero. For $V_g > V_c$, the level h_u becomes higher than the Fermi level. In this case, the C_{60} molecule eliminates electrons and obtains a positive charge. Thus, holes contributing to the resonant tunneling will occupy the states in the QD under the applied voltage V. The Coulomb interaction between them can split the h_u state. Our theory is in good agreement with the experimental results reported by Park *et al.*,[2] when the experimental conditions shown below are assumed. (1) Heating of the device during the process of electron resonant tunneling takes place. Although the experiments were performed at $T = 1.5$ K, the heating of the electrodes causes the increase in local electron temperature T^* of the device according to the equation $T^* = T + r_0 J^2$, where J is a current and r_0 is a resistance of the device. The fitting is possible when $T^* = 8$ K. (2) The device has asymmetric potential barriers with $a_L/a_R = 1.5$, and a_L/a_R decreases with increasing V. This means that the displacement of C_{60} is towards the left barrier, opposite to the electron motion. This assumption is consistent with positive charged states of C_{60}. (3) Theory and experiment are in better agreement when $2N > 20$. The fitting results in Fig. 2(c) represent the calculation with $2N = 30$, which means that the QD is a cluster consisting of C_{60}-molecules. It is worth noting that the change of V_g by 0.5 V leads to a change in the shift of energy level by 5 meV due to the screening effect of the cluster.

Resonant tunneling can be realized in a QD that is reasonably wide, and under the condition of weak electron-phonon and electron-electron interactions ($U = 0$). For example, a long molecular chain which contains a few injected electrons can be the QD in this situation. This case is perfectly suited to the experiment in Ref. 3 where the measurements of electrical transport through individual double-stranded poly(G)-poly(C) DNA molecules connected to two metal nano-electrodes have been measured (Fig. 3). The DNA molecule (30 base pairs, double stranded poly(G)-poly(C)) is 10.4 nm in length, and the nano-electrodes are separated by 8 nm. The voltage dependence of the differential conductance exhibits a peak structure, which suggests that the charge carrier transport is mediated by the molecular energy bands of DNA. According to Ref. 3, the current is essentially zero up to a threshold voltage, showing that this system behaves like an insulator at low bias. Above the threshold voltage, the current rises sharply, which makes it apparent that DNA

can transport charge carriers. Relatively large currents ($\sim 10^{12}$ electrons s^{-1}) can be attributed to the long DNA molecule of 10 nm. The transport mechanism is electron transport rather than electron transfer (the latter describes a one-step tunneling process). Therefore, we can suppose that there is a mechanism for energy band formation. To calculate the I-V curve, we have designed energy bands of DNA molecules as molecular conduction bands,

$$E_m = \sum_J \left\{ E_{0j} + \Delta E_{0j} \cos\left(\frac{2\pi m}{N}\right) \right\}. \tag{3}$$

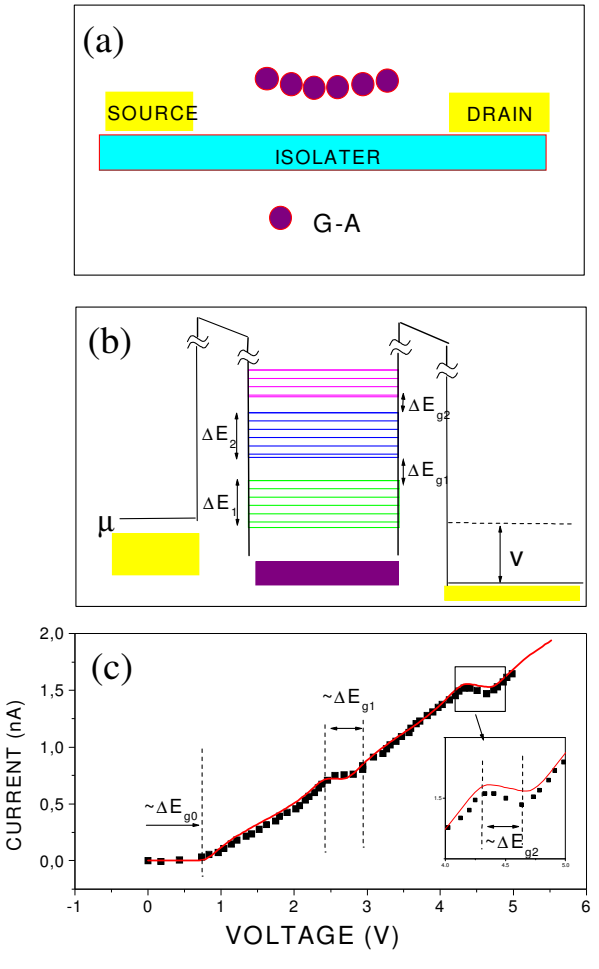

Fig. 3. An example of experimental data and theoretical fitting for the case of the failing interaction between electrons ($U = 0$). (a) Schematic drawing of DNA-transistor in Ref. 3. (b) An idealized energy level diagram of DNA-oligomers in a transistor according to Ref. 3. (c) Current-voltage (I-V) curves in DNA-transistor. Experimental data in Ref. 3 are marked by circles. Solid line represents the theoretical results.

The results of our calculation and some data from Ref. 3 are shown in Fig. 3(c). The calculation was made for the case of three electron bands ($\Delta E_1 = 0.26$ eV, $\Delta E_2 = 0.215$ eV, $\Delta E_3 = 0.3$ eV). The occupation numbers $n_m = g(E_m)$ are independent of each other. Bands are separated by band-gaps ($\Delta E_{g0} = 0.5$ eV, $\Delta E_{g1} = 0.25$ eV, $\Delta E_{g2} = 0.34$ eV). The inset in Fig. 3(c) shows the I-V curve for the bias when the Fermi level crosses the band-gap. The decrease in current in this voltage interval originates from the decrease in transparency of the left barrier with increasing voltage. The skewness of the barriers was found to be $a_L/a_R = 1.5$ for the best fitting.

The strong attractive interaction ($U < 0$) can occur in the QD with the strong electron-deformation (phonon) interaction. In general, such a situation is possible in the case of electron interaction through a phonon field. For example, bisolitons[19] or bipolarons[20] with degenerated electronic states are good candidates. Here, we focus on a device consisting of redox-active rotaxanes [Fig. 4(a)].[4] As shown by circles in Fig. 4(c), the current increased sharply with decreasing voltage when the device was initially probed with a reducing (negative) voltage. The switch was irreversibly opened by applying an oxidizing voltage of +0.7 V or more. Once a switch is opened, its states can be read by applying a negative voltage: the current remains around zero. It is well-known that the rotaxane and related materials have a great potential for molecular level switches by mechanical movement of a component of the molecule. Actually, this kind of behaviors are observed in solution[5–8] and in the form of Langmuir–Blodgett (LB) film.[9–12] A clear memory effect due to the molecular kinetics in those reports, however, was observed in the condition of molecules in the solution or under the external pressure. On the other hand, LB film of rotaxane in Ref. 4 was confined to a solid-state device in which molecular kinetics hardly occurs. Therefore, it is worthwhile examining the properties of this device by analysis without taking into account the electromechanical effect. Negative-U Hubbard model is one of the most powerful approaches for quantitative analysis. The attractive interaction can be considered as negative Coulomb interaction: degenerated states can be described as $E_m = E_0 - m|U|$. Energy levels at -4.05 eV and -4.14 eV are sufficiently close and can be considered as double-degenerate states [Fig. 4(b)]. When the difference ($\Delta E \approx 0.2$ eV) between these levels and the Fermi energy ($E_f = -4.26$ eV) is greater than U but smaller than $2U$, the tunnel system becomes bistable.[4] On the other hand, when this difference is smaller than U, the system will be occupied by electrons. We obtain $U = 0.15$ eV by fitting the theoretical model to the experiment in Ref. 4. The bistability state discussed here can only be realized under the condition of strong asymmetry transparencies of barriers. Under this condition, the direction of electron motion is essential for the operation. When the voltage is negative, the electrons are accumulated in rotaxane. Electrons are extracted from oxidized rotaxane under positive voltage (electrons move from low- to high-transparency barriers). This phenomena comes from electron dynamics in the coherent state of rotaxane.

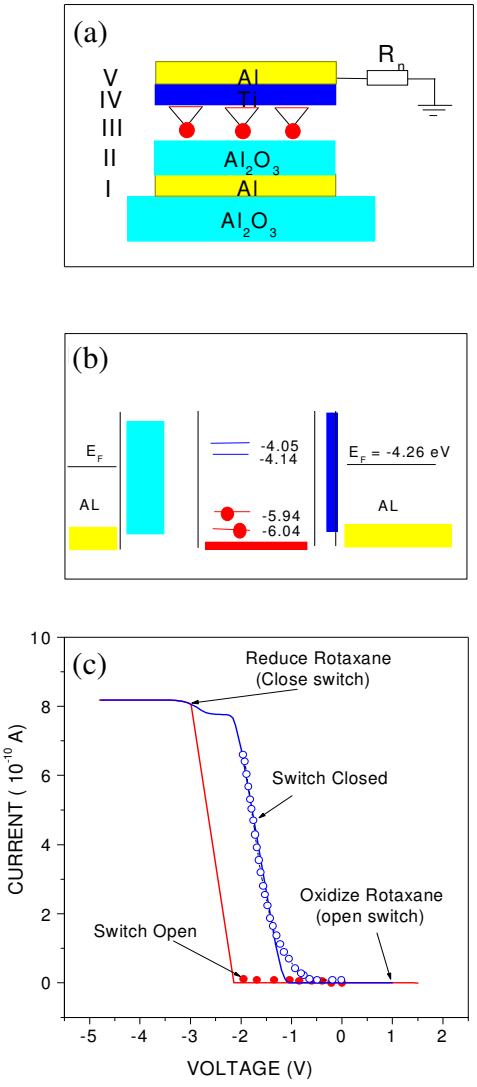

Fig. 4. An example of experimental data and theoretical fitting for the case of the strong electron-deformation interaction ($U < 0$). (a) Schematic cross-section of a single junction device with R(1) rotaxane in Ref. 4. The device consists of a monolayer of molecules sandwiched between two perpendicularly oriented aluminium electrodes. (b) Expected energy level diagram of the device for $V = 0$. Right (left) side of the diagram correspond to upper (lower) side of the device in (a). The Fermi levels (E_f) of Al electrodes are shown at both ends of the diagram. Discrete molecular redox energy levels (R(1) rotaxane) between barriers are shown. The oxidation (occupation by electrons) states are presented as filled circles. (c) Current-voltage (I-V) curves in the device. Experimental data in Ref. 4 are marked by circles. Solid line represents the theoretical results. Initially, the molecular switch is "closed". The status of the device is probed by applying a negative voltage to the bottom (I) electrode (red circles and solid line). The switch is "opened" by oxidising the molecules at a voltage greater than +0.7 V in experiment and approximately +1 V in theory. Finally, the open switch is interrogated again at negative bias (blue circles and solid line). The discussed phenomenon corresponds to the right part of Fig. 1(c).

4. Conclusion

In summary, we propose the method based on the use of the resonant tunneling phenomenon, admitting strong electron correlation in a quantum dot with degenerated states for the analysis of molecular devices. This method allows us to make both qualitative and quantitative comparisons between experimental and theoretical behaviour with a small number of fitting parameters. This is especially valuable in the absence of information relative to the nanosystem parameters. This method has an advantage in that it sufficiently represents the conditions for simulating correlation effects in a tunneling current and can be applied in future for simulating the operation of newly designed high-performance, single-molecule devices.

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