Phenomena in Resonant Tunneling Trough Degenerated Energy States with Electron Correlation

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Abstract

We introduce a general analysis method, which allows us to simulate the operation of high-performance moleculer 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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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 yet realized so far. Therefore it is essential to study 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 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 regard 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 an essentially 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.

A schematic drawing of a typical two-barrier nano-device is shown in figure 1(a). The diagram of its potential energy is represented in figure 1(b). The *I-V* characteristics in the case of the splitting of degenerated energy levels in QD are shown in figure 1(c). Depending on the sign of interaction energy between the tunneling electrons ($U > 0$ or $U < 0$) the split energy levels shift correspondingly up or down. In figure 1(c) this circumstance is shown by the change of the direction of applied voltage. Stepped characteristics in an *I-V* curve originates from the splitting of energy levels. Change of gate voltage V_g results in a shift of energy levels of the QD with regard to the chemical potential of the electrodes, which is observed in the shift of *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 left (right) barriers Γ_L (Γ_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 energy structure of a QD

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

Where n is the occupation rate of electrons defined by

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

N is a degree of degeneration, and E_m is energies of new split states $E_m=E_0+mU$ (m =0,1,…,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 QD for the devices discussed in this work, a voltage drop in the QD, mainly owing to Ohm's law (V=RI), can be negligible. Therefore, we can assume the voltage drop that 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).

Figure 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]. 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 contacts without application of gate voltage. Using the gate voltage (V_g), it is possible to shift energy levels in the QD as shown in figure 2(b). The series of filled circles in figure 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 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 positive charge. Thus, holes contributing the resonant tunneling will occupy the states in the

QD under the applied voltage V. The Coulomb interaction between them can split h_u state. Our theory is in good agreement with the experimental results reported by Park et al.[2], when the experimental conditions shown in 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 of local electron temperature T* in the device according to the equation $T^* = T + r_0 J^2$, where J is a current and r_0 is a resistance of 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 the displacement of C_{60} toward 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 a better agreement when $2N > 20$. The fitting results in figure 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 0.5V leads to a change in the shift of energy level by 5 meV due to the screening effect of 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 of this situation. This case is perfectly suited to the experiment in [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 (figure 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 reference [3], the current is essentially zero up to a threshold voltage, showing that this system behaves like an insulator at low bias. Above threshold voltage, the current rises sharply, which makes it apparent that DNA can transport the charge carriers. Relatively large currents (~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 formations. To calculate the *I-V* curve we have designed energy bands of DNA molecules as molecular conduction bands,

$$E_m = \sum_j \{E_{0j} + \Delta E_{0j} \cos(\frac{2\pi m}{N})\}.$$

The results of our calculation and some data from reference [3] are shown in figure 3(c). The calculation was made for the case of three electron bands (ΔE_1 = 0.26 eV, ΔE_2 = 0.215 eV, ΔE_3 = 0.3 eV). The occupation numbers $n_m = g(E_m)$ are independent from each other. Bands are separated by band-gaps (ΔE_{g0}=0.5 eV, ΔE_{g1}=0.25 eV, ΔE_{g2}=0.34 eV). The inset in figure 3(c) shows the *I-V* curve

for the bias when Fermi level crosses the band-gap. The decrease of current in this voltage interval originates from decrease in transparency of 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 (figure 4(a)) [4]. As shown by circles in figure 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 remained 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 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 reference [4] was confined to a solid-state device in which molecular kinetics hardly occurs. Therefore, it is worthwhile examining properties of this device

by analysis without taking account of an 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 (figure 4(b)). When the difference ($\Delta E \approx 0.2$ eV) between these levels and 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 reference [4]. The bistability state discussed here can be only realized under condition of strong asymmetry transparencies of barriers. Under this condition, a direction of electron motion is essential for the operation. When voltage is negative, the electrons are accumulated in rotaxane. Electrons are extracted from oxidize rotaxane under positive voltage (electrons move from low- to high-transparency barriers). This phenomena comes from an electron dynamics in the coherent state of rotaxane.

In summary, we propose the method based on the use of a resonant tunneling phenomenon, admitting strong electron correlation in a quantum dot with degenerated states for the analysis of molecular devices. The method allows us to make both a qualitative and a quantitative comparison 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 tunneling current and can be applied in the future for simulating the operation of newly designed high-performance, single-molecule devices.

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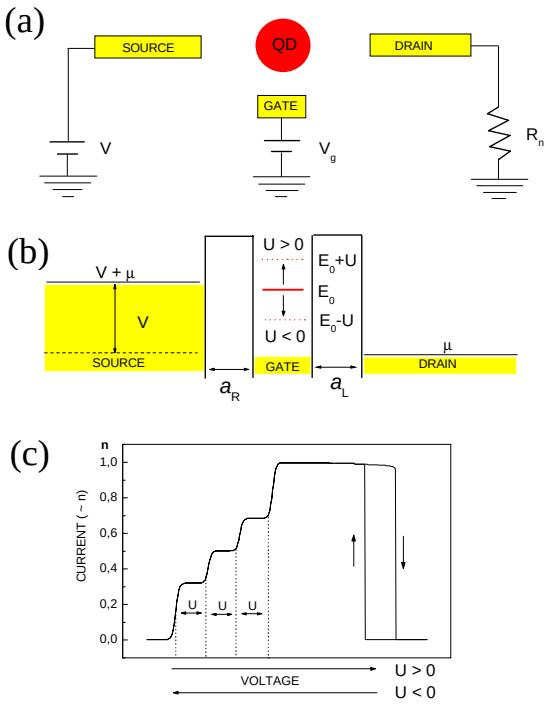

Figure 1. (a) Schematic drawing of a nano-transistor. (b) The energy level diagram of the nano-device showing resonant tunnelling phenomena through degenerated energy states with electron correlation *U*. (c) Theoretical prediction of current-voltage (*I-V*) curves. *I-V* characteristics depend on the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

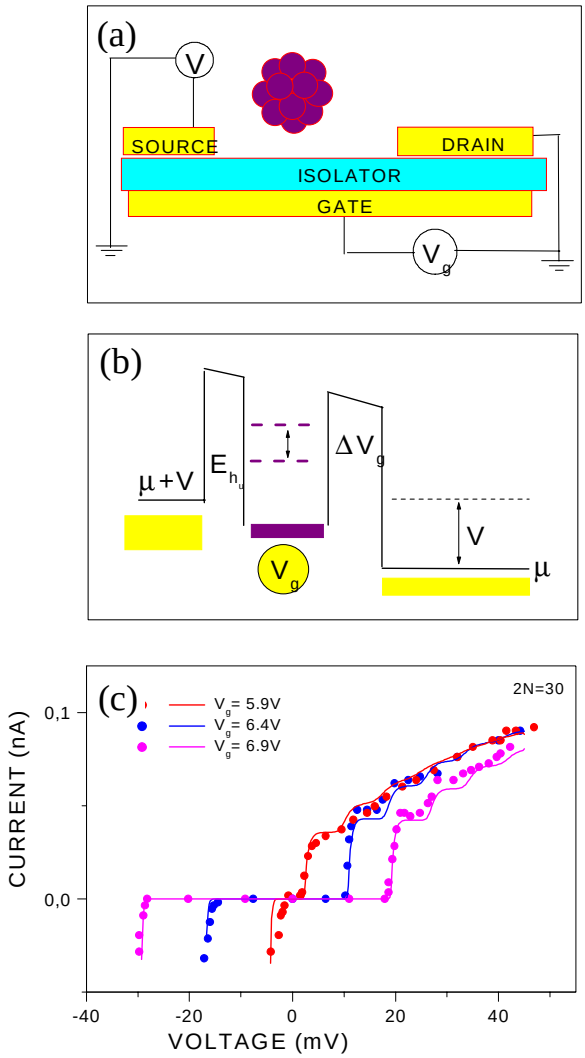

Figure 2. An example of experimental data and theoretical fitting for the case of Coulomb interaction ($U > 0$). (a) Schematic drawing of C_{60} nano-transistor in (2). (b) An idealized energy level diagram of a C_{60}-transistor according to reference [2]. (c) Current-voltage (I-V) curves in C_{60}-transistor. 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 figure 1(c).

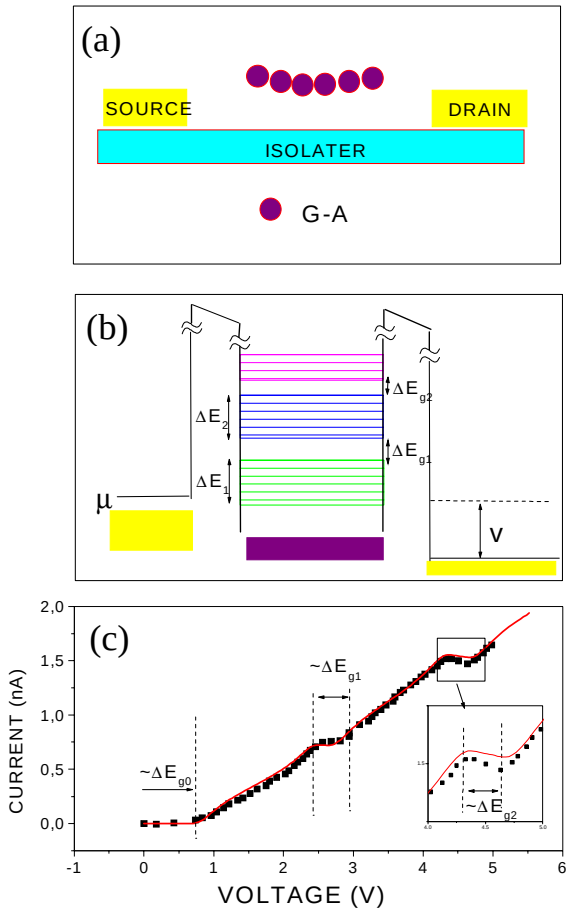

Figure 3. An example of experimental data and theoretical fitting for the case of the failing interaction between electrons ($U = 0$). (a) Schematic drawing of DNA-transistor in reference [3]. (b) An idealized energy level diagram of a DNA-oligomers in a transistor according to reference [3]. (c) Current-voltage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

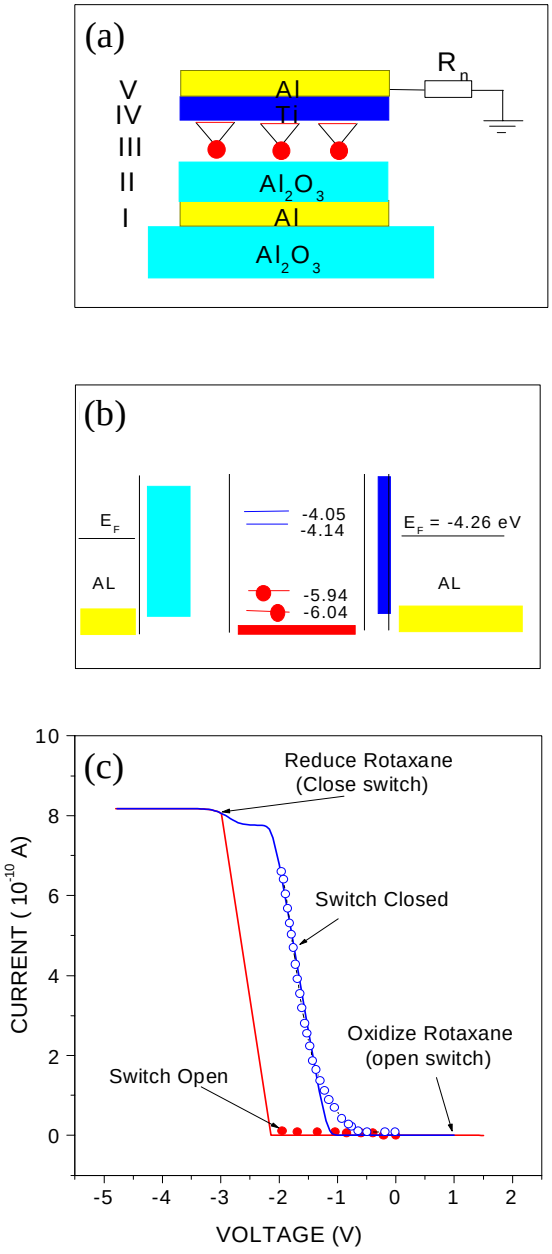

Figure 4. An example of experimental data and theoretical fitting for the case of the strong electron-deformation interaction ($U < 0$). (a) Schematic cross-section of a single junction device with R(1) rotaxane in reference [4]. The device consists of a monolayer of molecules sandwiched between two 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 reference [4] are marked by circles. Solid line represents the theoretical results. Initially, the molecular switch is “closed”. The status of 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 voltage greater than +0.7 V in experiment and approximately +1 V in the theory. Finally, the open switch is again interrogated at negative bias (blue circles and solid line). The discussed phenomenon corresponds to the right part of figure 1(c).