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Large-bandgap behavior in transport of electrons through individual DNA molecules caused by coupling with a two-level system

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We propose a model to interpret the large-bandgap behavior in transport of electrons through an individual DNA molecule where the tunneling electrons are coupled with two-level systems (TLS). The TLS can be regarded as the simplest way to describe vibrations and inelastic scattering in the molecules if the two levels represent the low-lying phonon states. The nonlinear current-voltage curves can be derived by the use of the transfer matrices in an equivalent single-particle multichannel network. At low temperatures, the gap of the conduction band is sensitive to the strength of the coupling between the TLS and the conduction electrons. It is shown that the large-bandgap behavior similar to that of semiconductors stems from the inelastic scattering by the TLS.

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I. INTRODUCTION

Owing to the advancement in nanotechnology, individual DNA molecules are expected to become promising candidates for molecular wires. However, the simple question on whether DNA is an electric conductor or not remains unsettled because of the complexity of the molecules. Recently, two outstanding investigations on the direct measurement of the transport of electrons through DNA molecules have been reported [1,2]. In particular, Porath *et al.* have shown that electron transport in the synthetic poly(G)-poly(C) DNA exhibits a large-bandgap behavior similar to a semiconductor. de Pablo *et al.* [3] carried out experimental measurements and calculations for DNA molecules in a random sequence of the base pairs, and clearly showed that the λ-DNA molecules have quite large resistance. Very recently, Li and Yan [4] have theoretically studied the tunneling of electrons through the synthetic poly(G)-poly(C) DNA by use of the Büttiker model, showing the existence of a voltage gap in the nonlinear current-voltage curves. A similar voltage gap has also been obtained in the calculated results of Hjort and Stafström [5], where a 2 V band gap is shown in the current-voltage curves at room temperature. At lower temperatures a smaller band gap (about 1 V) was observed in experiments, but no theoretical calculations were reported in the literature. The emergence of the voltage gap in the current-voltage curves seems to be a general phenomenon existing in a vast variety of materials, such as the fullerenes [6], the self-assembled monolayers [7], etc. This phenomenon is closely related to the inelastic electron-phonon scattering and the localization caused by the structural disorder in the stacks of molecules. One of the simplest models that can describe the vibrations and the inelastic scattering in the molecules is a two-level system (TLS) [8].

The aim of this paper is to present an analysis of the transport of electrons at low temperatures in a model of individual DNA molecules where the conduction electrons are strongly coupled with the TLS. In this analysis the transfer-matrix method based on an equivalent multichannel network (EMCN) and the Landauer formulas are adopted. In an EMCN the strong interaction between electrons and TLS can be treated more rigorously by using the combined states of electron and TLS as the basis wave functions. This avoids the poor approximation of the usual perturbation theory if the interaction is quite strong. It was successfully applied to the calculations of the electron transport through quantum dot where the electron-electron interaction is strong [9]. From the calculations the voltage gap of the current-voltage curves for low temperatures is derived and can be connected to the experimental data of Porath *et al.* in Ref. [2]. The large-bandgap behavior can be interpreted from the inelastic scattering of electrons by the TLS.

The paper is organized as follows. In Sec. II we describe the model and the basic formalism of the EMCN method; we present the calculated results in Sec. III; in the final section we give a brief summary and discussion.

II. THE MODEL AND THE BASIC FORMALISM

We consider a DNA molecule with a finite length where the electrons are coupled with an effective TLS. The Hamiltonian of the TLS can be written in terms of two local wave functions,

$$H_{TLS}=\Delta_0(|1\rangle\langle 1|-|2\rangle\langle 2|)+\Delta|2\rangle\langle 1|+\Delta^*|1\rangle\langle 2|, \quad (1)$$

where $|1\rangle$ and $|2\rangle$ denote the two states, Δ_0 describes the energy splitting between them, and Δ stands for the tunneling strength. This Hamiltonian can be diagonalized and expressed in terms of the eigenstates,

$$H_{TLS}=\sqrt{\Delta_0^2+|\Delta|^2}(|+\rangle\langle +|-|-\rangle\langle -|),$$

where

$$|\pm\rangle=\mu|1\rangle\pm\gamma|2\rangle,$$

$$\mu=\left(\frac{1+(1+|\Delta|^2/\Delta_0^2)^{1/2}}{2}\right)^{1/2},$$

$$\gamma=\left(\frac{1-(1+|\Delta|^2/\Delta_0^2)^{1/2}}{2}\right)^{1/2}.$$

The interaction between electrons and TLS is

$$H_{in}=g d^{\dagger}_{i,\sigma} d_{i,\sigma}(|1\rangle\langle 1|-|2\rangle\langle 2|), \tag{2}$$

where $d_{i,\sigma}$ is an annihilation operator of an electron in the ith level of the DNA molecule with spin σ, and g is the strength of the interaction. By using the diagonalized representation for the TLS, H_{in} can be rewritten as

$$\begin{aligned} H_{in}=g d^{\dagger}_{i,\sigma} d_{i,\sigma}[(\mu^2-\gamma^2)(|+\rangle\langle +|-|-\rangle\langle -|) \\ +2\mu\gamma|+\rangle\langle -|+2\mu^*\gamma^*|-\rangle\langle +|]. \end{aligned} \tag{3}$$

The sub-Hamiltonian of electrons includes (i) the motion in the leads,

$$H_0=t_0\sum_{|m|>1,\sigma}(c^{\dagger}_{m,\sigma}c_{m+1,\sigma}+\text{H.c.}), \tag{4}$$

with $c_{m,\sigma}$ annihilating an electron on the mth site of the leads and with spin σ, and t_0 being the hopping integral; (ii) the potential energy and the electron-electron interaction within the DNA molecule

$$H_M=\sum_{i,\sigma}(\xi_i+V_g)d^{\dagger}_{i,\sigma}d_{i,\sigma}+\frac{1}{2C}\left(e\sum_{i,\sigma}d^{\dagger}_{i,\sigma}d_{i,\sigma}\right)^2, \tag{5}$$

with ξ_i being the energy of the ith level, V_g being the potential tuned by a gate voltage, and C the effective capacity of the molecule; (iii) the tunneling between the molecule and the leads

$$H_T=\sum_{i,\sigma}(t^L c^{\dagger}_{-1,\sigma}d_{i,\sigma}+t^R c^{\dagger}_{1,\sigma}d_{i,\sigma}+\text{H.c.}), \tag{6}$$

with $t^{L(R)}$ being the tunneling strength to the left (right) lead. The total Hamiltonian of the system then reads

$$H=H_0+H_M+H_{TLS}+H_{in}+H_T. \tag{7}$$

Here we set the potential in the leads as the energy zero.

We suppose that there are M electrons occupying levels below the chemical potential in the molecule before and after tunneling. Including one tunneling electron under investigation, there are a total of $M+1$ electrons in relevant many-body states. To solve the Schrödinger equation we use the following many-body wave functions as the basis [9]:

$$\begin{aligned} \Phi^{(1)}_{m,\sigma,D}&=c^{\dagger}_{m\sigma}\left(\prod_{\{i\sigma'\}\in D}d^{\dagger}_{i\sigma'}\right)|F\rangle\otimes|+\rangle, \\ \Phi^{(1)}_{D^{(+)}}&=\left(\prod_{\{i\sigma'\}\in D^{(+)}}d^{\dagger}_{i\sigma'}\right)|F\rangle\otimes|+\rangle, \end{aligned} \tag{8}$$

$$\begin{aligned} \Phi^{(2)}_{m,\sigma,D}&=c^{\dagger}_{m\sigma}\left(\prod_{\{i\sigma'\}\in D}d^{\dagger}_{i\sigma'}\right)|F\rangle\otimes|-\rangle, \\ \Phi^{(2)}_{D^{(+)}}&=\left(\prod_{\{i\sigma'\}\in D^{(+)}}d^{\dagger}_{i\sigma'}\right)|F\rangle\otimes|-\rangle, \end{aligned} \tag{9}$$

where D and $D^{(+)}$ denote sets of M, $M+1$ states on the molecule, respectively, and $|F\rangle$ represents the Fermi sea in the leads. A wave function that describes the tunneling process of the system can be written as a linear combination of these basis functions,

$$\begin{aligned} \Psi=\sum_{m,\sigma}\sum_{D}p^{(1)}_{m,\sigma,D}\Phi^{(1)}_{m,\sigma,D}+\sum_{D^{(+)}}q^{(1)}_{D^{(+)}}\Phi^{(1)}_{D^{(+)}} \\ +\sum_{m,\sigma}\sum_{D}p^{(2)}_{m,\sigma,D}\Phi^{(2)}_{m,\sigma,D}+\sum_{D^{(+)}}q^{(2)}_{D^{(+)}}\Phi^{(2)}_{D^{(+)}}. \end{aligned} \tag{10}$$

By applying the Hamiltonian on Ψ, we obtain the following Schrödinger equations for coefficients $p^{(1)}_{m,\sigma,D}$, $p^{(2)}_{m,\sigma,D}$, $q^{(1)}_{D^{(+)}}$, and $q^{(2)}_{D^{(+)}}$:

$$\begin{aligned} (\chi_D\pm\sqrt{\Delta_0^2+\Delta^2})p^{(1,2)}_{m,\sigma,D}+t_0(p^{(1,2)}_{m+1,\sigma,D}+p^{(1,2)}_{m-1,\sigma,D}) \\ =Ep^{(1,2)}_{m,\sigma,D}\quad(|m|>1), \end{aligned} \tag{11}$$

$$\begin{aligned} (\chi_D\pm\sqrt{\triangle_0^2+\triangle^2})p^{(1,2)}_{-1,\sigma,D}+t_0p^{(1,2)}_{-2,\sigma,D}+\sum_i t^L q^{(1,2)}_{D^{(+)}(i,\sigma)} \\ =Ep^{(1,2)}_{-1,\sigma,D}, \end{aligned} \tag{12}$$

$$\begin{aligned} (\chi_D\pm\sqrt{\Delta_0^2+\Delta^2})p^{(1,2)}_{1,\sigma,D}+t_0p^{(1,2)}_{2,\sigma,D}+\sum_i t^R q^{(1,2)}_{D^{(+)}(i,\sigma)} \\ =Ep^{(1,2)}_{1,\sigma,D}, \end{aligned} \tag{13}$$

$$\begin{aligned} \chi_{D^{(+)}(i,\sigma)}q^{(1,2)}_{D^{(+)}(i,\sigma)}\pm(\sqrt{\triangle_0^2+\triangle^2}+g\mu^2-g\gamma^2)q^{(1,2)}_{D^{(+)}(i,\sigma)} \\ +2g\mu\gamma q^{(2,1)}_{D^{(+)}(i,\sigma)}+t^{L*}p^{(1,2)}_{-1,\sigma,D}+t^{R*}p^{(1,2)}_{1,\sigma,D} \\ =Eq^{(1,2)}_{D^{(+)}(i,\sigma)}, \end{aligned} \tag{14}$$

where E is the total energy of the $M+1$ electrons plus the TLS, $D^{(+)}(i,\sigma)$ is a set of the molecule states obtained from set D by adding state $\{i\sigma\}$, the sum for i is over all empty levels of the molecule, the upper sign in ± corresponds to the first index in the superscripts of coefficients p and q, and

$$\chi_D=\frac{e^2M^2}{2C}+MV_g+\sum_{i\in D}\xi_i, \tag{15}$$

$$\chi_{D^{(+)}(i,\sigma)}=\frac{e^2(M+1)^2}{2C}+(M+1)V_g+\sum_{j\in D^{(+)}(i,\sigma)}\xi_j. \tag{16}$$

In the following calculations we will include four levels with equal level spacing for the molecule. From the above equations the problem of the transmission of electrons through the system reduces to a single-particle picture of a multichannel network. In Fig. 1(a) we display the tunneling process in the case of even occupation of the molecule states. In Figs. 1(b) and 1(c) we show possible networks for a molecule with an odd number of electrons before and after tun-

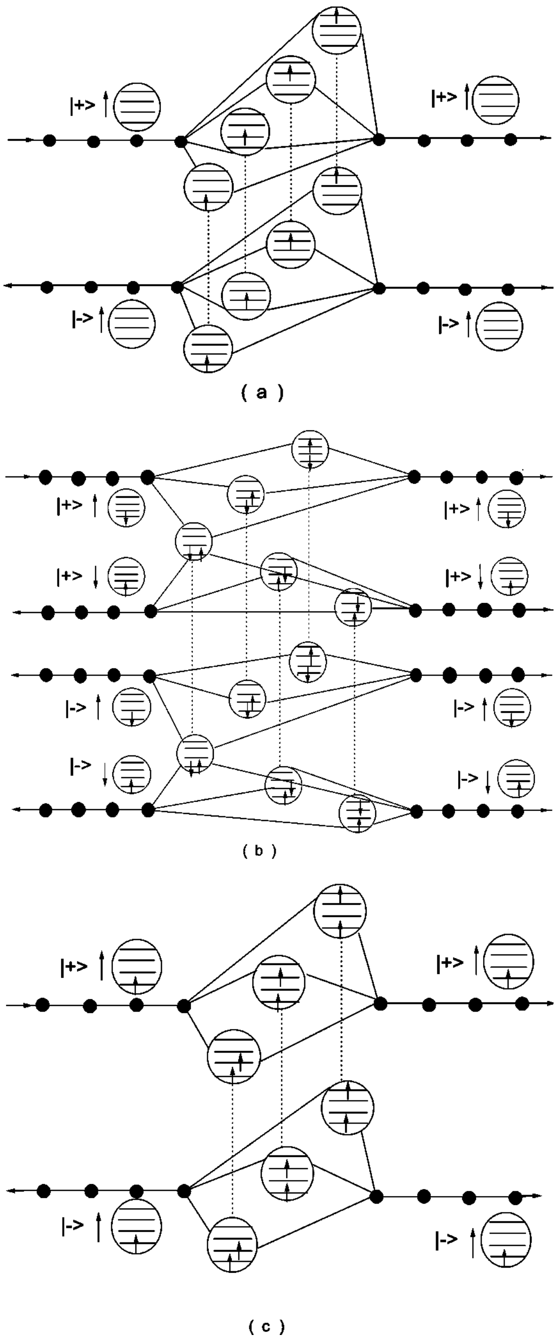

FIG. 1. Illustration of the equivalent single-particle networks for the electron tunneling through an individual DNA molecule. Four energy levels of the molecule are considered. In (a) there are no electrons in the molecule states, while in (b) and (c) the molecule states are occupied by an odd number of electrons.

neling. The states of the molecule are represented by the occupation status indicated in the circles. To maintain a steady current flow, the outgoing channels should have the same structure as that of the incoming channel. A spin-flip process in the tunneling can be seen from Fig. 1(b). There are also other possible networks which are not shown.

If a plane wave with spin σ and unit amplitude is incident from the left lead, meanwhile the TLS is in the jth state and the electrons in the molecule are in states of set D, the wave can be reflected (transmitted) into channels with spin σ' and TLS state j' in the left (right) lead, and the coefficients $p^{(1,2)}_{m,\sigma,D}$ can be written as

$$p^{(j')}_{m,\sigma,D} = e^{ik_L^{(j)}(m+1)}\delta_{j,j'}\delta_{\sigma,\sigma'} + r^{(j,j')}_{\sigma,\sigma',D}e^{-ik_L^{(j')}(m+1)} \quad \text{for } m<0, \tag{17}$$

$$p^{(j')}_{m,\sigma',D} = t^{(j,j')}_{\sigma,\sigma',D}e^{ik_R^{(j')}(m-1)} \quad \text{for } m>0, \tag{18}$$

where $r^{(j,j')}_{\sigma,\sigma',D}$ and $t^{(j,j')}_{\sigma,\sigma',D}$ are, respectively, the reflection and transmission amplitudes in the corresponding channel, and $k^{(j=1,2)}_{L,R}$ is the wave vector satisfying $\epsilon^{(1,2)} = 2t_0\cos k_L^{(1,2)}$ and $\epsilon^{(1,2)} = 2t_0\cos k_R^{(1,2)} - eV_b$ with $\epsilon^{(1,2)} = E - (\chi_D \pm \sqrt{\Delta_0^2 + |\Delta|^2})$ and V_b the bias voltage. It is worth noting that an incoming electron from the left with a specific energy can be reflected or transmitted into channels with different single-particle energy due to the inelastic scattering with the TLS. In this case the state of the TLS is changed in the process of tunneling. We can calculate the reflection and transmission amplitudes for all channels in a network by solving the above Schrödinger equations. By virtue of the current conservation, the current through the system can be obtained [10,11],

$$I(V_b) = \frac{2e^2}{h}\int_{-\infty}^{\infty} dE \sum_D \sum_{j,j'} \sum_{\sigma,\sigma'} [F_{j,j'}(E,eV_b,D,T) - F_{j,j'}(E,0,D,T)]F_D(T)|t^{(j,j')}_{\sigma,\sigma',D}|^2, \tag{19}$$

where

$$F_D(T) = \frac{1}{\mathcal{N}}\exp\left(-\frac{\chi_D}{k_BT}\right) \quad \text{with} \quad \mathcal{N} = \sum_{\{D\}} \exp\left(-\frac{\chi_D}{k_BT}\right) \tag{20}$$

is the thermal probability of the molecule state D, and

$$F_{j,j'}(E,eV_b,D,T) = \frac{F^{(j)}_{TLS}(T)F^{(j')}_{TLS}(T)}{1+\exp[(E-\chi_D-\epsilon_j)/k_BT]}, \tag{21}$$

with

$$F^{(j)}_{TLS}(T) = \frac{\exp(\epsilon_j/k_BT)}{\exp(\epsilon_1/k_BT)+\exp(\epsilon_2/k_BT)},$$

$$\epsilon_{1,2} = \pm\sqrt{\Delta_0^2+|\Delta|^2}.$$

By sweeping the gate voltage V_g, the occupation number of the molecule is sequentially changed, corresponding to a series of resonant conductance peaks. The spacing between peaks is mainly determined by the charging energy and the level spacing.

III. NUMERICAL RESULTS AND DISCUSSION

On the basis of the equations obtained in the preceding section, we carry out numerical calculations on the transport properties. Here, the system we consider is a 10.4-nm-long

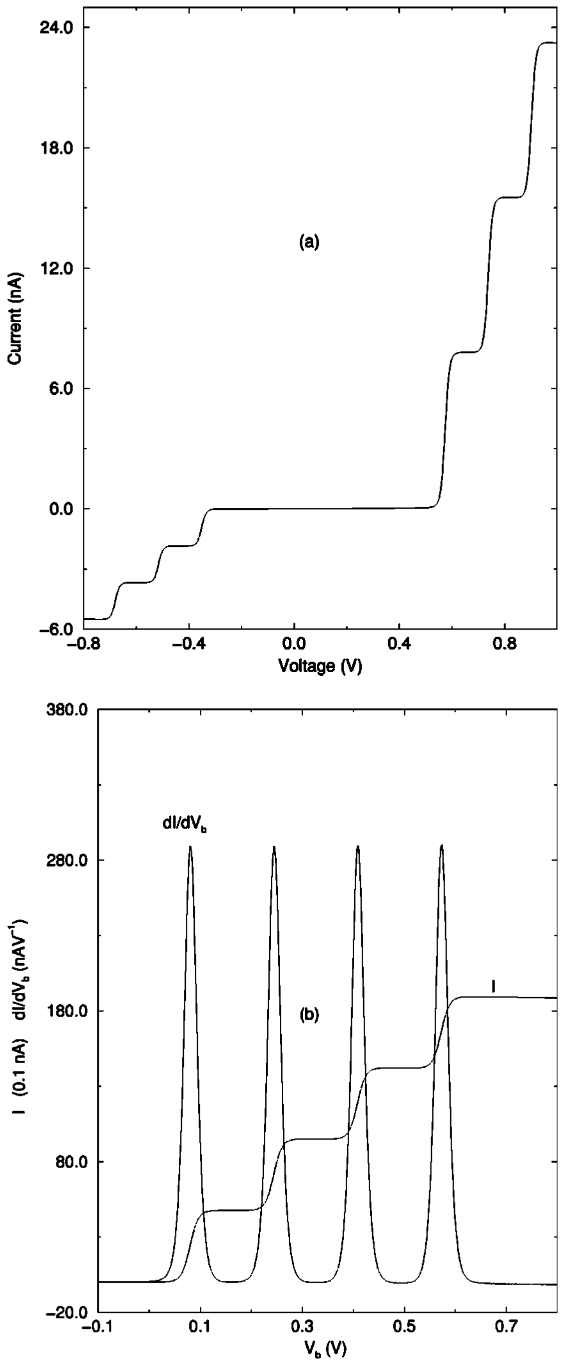

FIG. 2. The tunneling current I as a function of the bias voltage V_b in cases (a) with and (b) without electron-TLS interaction. In (b) the corresponding differential conductance is also shown.

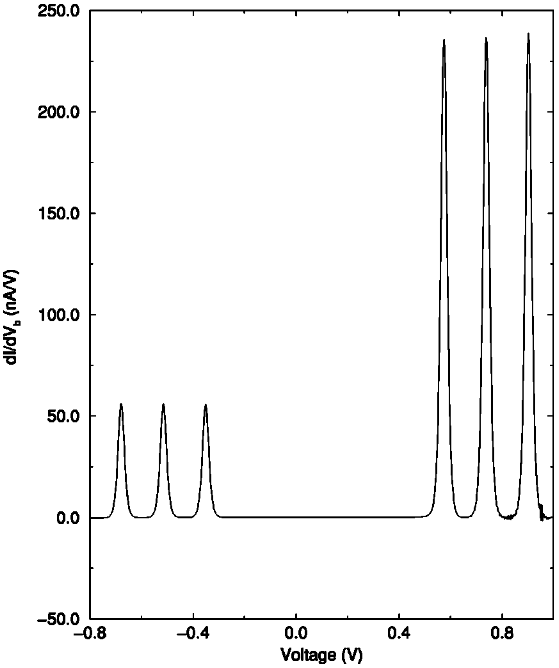

FIG. 3. The differential conductance dI/dV_b as a function of the bias voltage V_b in the case with electron-TLS interaction. The molecule states are empty, corresponding to the situation illustrated in Fig. 2(a).

(30 base pairs) poly(G)-poly(C) DNA oligomer connected to two semi-infinite linear chains, as measured in Ref. [2]. We also adopt the conduction band model of the DNA molecules suggested in Ref. [2]. The individual DNA molecule is sufficiently small so that its resonant levels are well separated in energy and the Coulomb interaction is large. The DNA molecules have critical structural disorder caused by the vibrations of the base atoms. Here we employ the TLS to mimic two low-lying states of a mode of the vibrations. To relate the model to the measured system, we take the hopping integral in the electrodes as $t_0=2$ eV, the energy-level spacing of the molecule as $\delta\xi_i=0.16$ eV, the first considered level at $\xi_1=0.0$, and the electron-electron interaction at the molecule as $e^2/2C=0.2$ eV. The molecule is coupled to the left (right) lead with a small tunneling matrix element

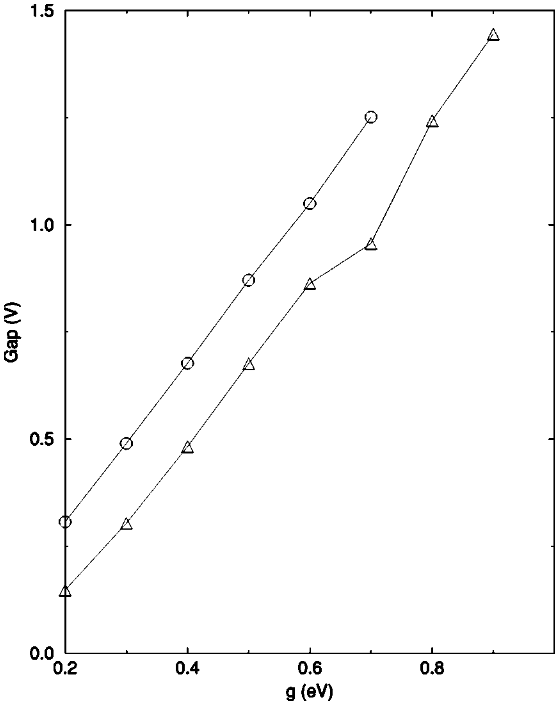

FIG. 4. The voltage gap as a function of the strength of the electron-TLS coupling for various values of the level spacing $\delta\xi$.

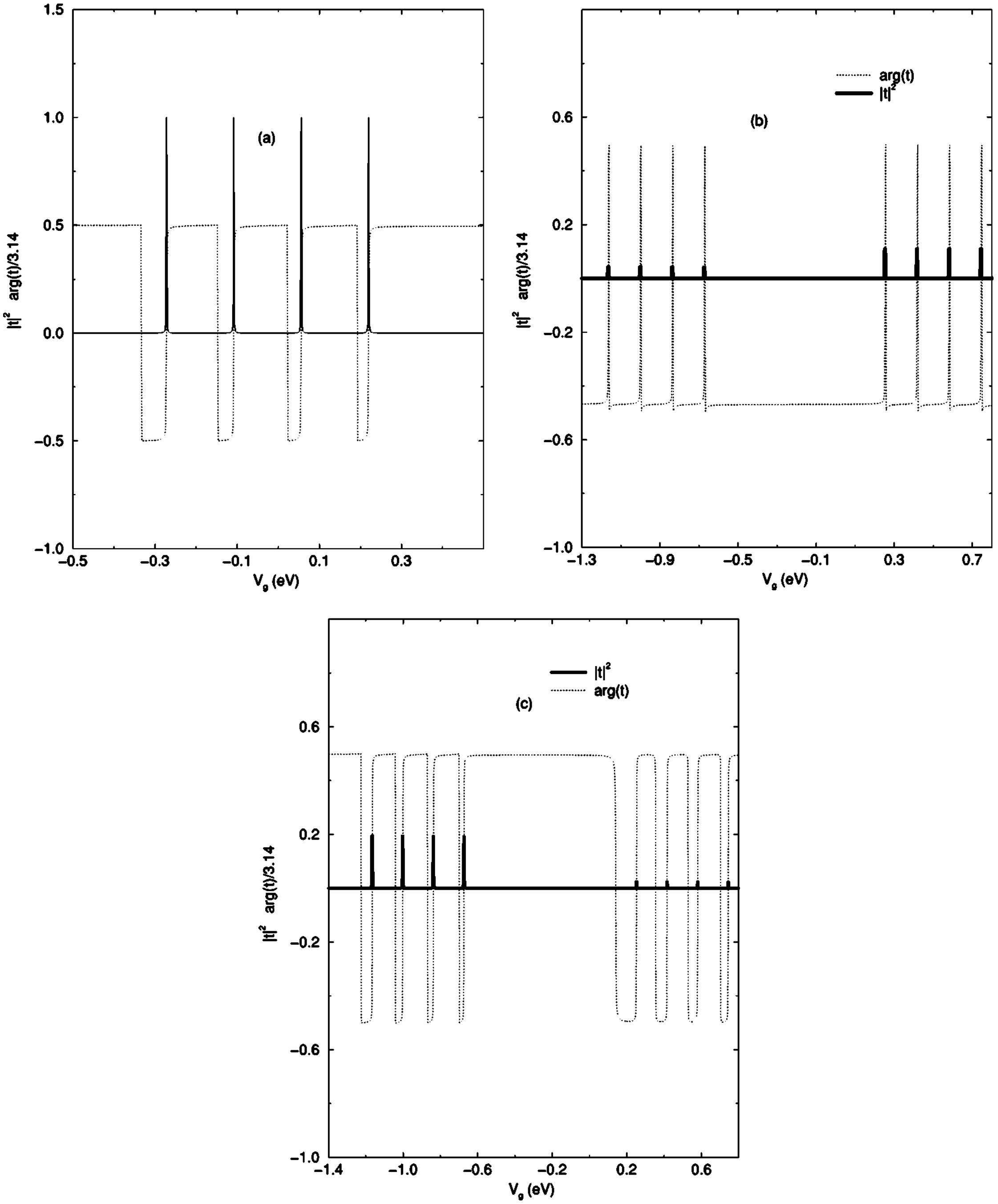

FIG. 5. The magnitude $|t|^2$ (solid line) and the phase $\arg(t)$ (dotted line) of the transmission amplitude as functions of the gate voltage for (a) the case without electron-TLS interaction, (b) the tunneling from the channel with $|+\rangle$ state to the channel with $|-\rangle$ state in the case with electron-TLS interaction, and (c) the tunneling from the channel with $|+\rangle$ state to the channel with $|+\rangle$ state in the case with electron-TLS interaction.

$t^{L(R)}=0.02$ eV. For the TLS, the energy splitting can be regarded as the excitation energy of the structure and can vary over a wide range. To be specific we take it to be $\Delta_0=0.08$ eV. In general, it is very difficult to estimate the transition strength Δ and the electron-TLS coupling g in disordered materials [12]. There exists an exponentially wide range of the relaxation rate for the structures, leading to various values of Δ. At the same time the quantity g depends on the microscopic structure of the TLS and its spatial position, which are also spread over a wide range for amorphous materials. For example, in a submicrometer silicon inversion layer the activation energies in a range 0.026 eV $\sim$0.28 eV were observed [13]. In this paper we take $\Delta=0.2$ eV and $g=0.6$ eV as typical values in the calculations, considering that the DNA molecules have critical structural disorder.

At gate voltage $V_g=-0.06$ eV ($V_g>-e^2/2C$), the considered states of the molecule are empty. Figure 2(a) shows the calculated *I-V* characteristics at a temperature $k_bT = 0.008$ eV. The obtained results are in quantitative agreement with the measured data. A voltage gap in the *I-V* curve is obviously seen. As a comparison, the calculated results for the case without the electron-TLS interaction $(g=0)$ are shown in Fig. 2(b). In this case the voltage gap vanishes. Thus it is evident that the voltage gap stems from the inelastic scattering of the TLS.

In Fig. 3 we plot the differential conductance as a function of the bias voltage. The peak structure can reflect the information about the energy spectrum of the DNA molecules, since the differential conductance is determined by the density of states resultant from the combined effect of the energy levels, the electron-electron interaction, and the electron-TLS interaction. The experimental data in Ref. [2] show the peak spacing in the range of $0.1 \sim 0.5$ eV and the peak width ~ 0.2 eV for relatively large bias voltages. The peak spacing shown in Fig. 3 is nearly equal to the sum of the Coulomb charging energy and the single-electron level spacing adopted in the calculations $(e^2/2C + \delta\xi_i)$. The charging energy is based on the geometrical self-capacitance of a 10.4-nm-long (30 base pairs) poly(G)-poly(C) DNA molecule.

From the experimental data of Ref. [2] it can be seen that the voltage gap is widened with increasing the temperature. The influence of the thermal vibrations in the DNA molecules on the transport of electrons should be enhanced with increasing the temperature. In this model this enhancement can be reflected by the increase of the coupling strength between the TLS and the conduction electrons. In Fig. 4 we plot the voltage gap as a function of the coupling strength g. It is evident that the voltage gap monotonically increases with increasing g.

In order to illustrate how the TLS affects the tunneling of electrons, in Figs. 5(a), 5(b), and 5(c) we plot the magnitude $(|t|^2)$ and the phase $[\arg(t)]$ of the transmission amplitude corresponding to the passageways of $g=0$, TLS state $|+\rangle$ and TLS state $|-\rangle$ as functions of the gate voltage V_g, respectively. As one can see, in the case without electron-TLS interaction $(g=0)$, the phase changes abruptly by π at resonant peaks for $g=0$ and varies consequently to its original value at other positions, reflecting the coherence of the phase of the quantum states in the resonant tunneling. If there is a coupling between the TLS and electron $(g \neq 0)$, a similar behavior of the phase is observed for the transmission with the same TLS state in the incoming and outgoing channels [Fig. 5(c)], but the transmission with different TLS states in these two channels shows a completely different behavior, where the peaks appear at almost the same positions in both the amplitude and phase curves [Fig. 5(b)]. This indicates the difference in the phase coherence between the elastic and inelastic tunneling.

IV. CONCLUSIONS

We have investigated the electrical transport through an individual DNA molecule. We consider a short molecule connected to two leads. In this case the levels in the molecule are well separated and the Coulomb interaction is large. We adopt a two-level system to describe the low-lying states of a mode of vibrations in the molecule. We suppose that the conduction electrons are strongly coupled with the TLS. We use the transfer-matrix method based on the EMCN method and the Landauer formulas to calculate the transport properties of electrons through the system. From the calculations, the voltage gap of the current-voltage curves for low temperatures is derived and can be connected to the experimental data in Ref. [2]. The large-bandgap behavior is related to the dephasing of the electron wave functions induced by the inelastic scattering of the TLS.

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