Contact-dependent effects and tunneling currents in DNA molecules

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(Received 16 November 2004; published 31 March 2005)

We report on theoretical results about contact-dependent effects and tunneling currents through DNA molecules. A tetranucleotide PolyGACT chain, connected in between metallic contacts, is studied as a generic case, and compared to other periodic sequences such as PolyAT or PolyGC. Remarkable resonance conditions are analytically derived, indicating that a strong coupling does not always result in a larger conductance. This result is properly illustrated by considering intrinsic features of bias-dependent tunneling currents in the coherent regime.

DOI: 10.1103/PhysRevB.71.113106 PACS number(s): 72.80.Le, 72.20.Ee, 87.14.Gg

In recent years, many experimental measurements have directly probed the electrical current as a function of the applied potential across DNA molecules.[1–5] These experiments are performed in a variety of conditions where important factors, including the substrate surface, contacts to the electrodes, counterions, and DNA structure are not kept constant.[3] This state of affairs considerably makes difficult a proper comparison among different experimental reports, which range from completely insulating to semiconducting, and even superconducting, behaviors.[2] In turn, such scatter makes it difficult to set the basis for a meaningful theoretical approach to the *intrinsic* DNA electrical transport properties.

To this end, the role of contacts deserves particular attention. In many measurements, contact with metal electrodes was achieved by laying down the molecules directly on the electrodes. In this case, it is rather difficult to prove that the DNA molecule is in direct contact with the electrodes. Even so, the weak physical *adhesion* between DNA and metal may produce an insulating contact. Recent transport experiments have shown that deliberate *chemical bonding* between DNA and metal electrodes is a prerequisite for achieving reproducible conductivity results.[3–5]

Generally, any current measured through a DNA molecule results from the carrier injection onto the stack of bases, combined with the intrinsic conduction along the DNA sequence. At low voltage, the main contribution to the resistance comes from the metal-DNA junction potential mismatch (barrier), whereas for high enough voltage, new conduction channels are provided by the molecular states. The $I(V)$ characteristics are thus somehow inferred from the energy difference between the metallic work function and the lowest ionization energy levels of the DNA (in case of hole transport).[6] Besides, charge transfer in DNA has been proven to be mainly conveyed by intrastrand π–π coupling,[7] through sequential incoherent hopping or coherent tunneling (superexchange).[7] The latter mechanism might be expected to dominate the conduction in the very low-temperature regime. Despite great experimental efforts,[8,9] few theoretical works have so far precisely addressed the nature of measured currents and its relation with device characteristics.

In this work, we present a theoretical study on coherent charge tunneling in DNA molecules connected in between metallic contacts. An effective tight-binding Hamiltonian is constructed from *ab initio* parameters, and an analytical expression of the transmission coefficient is derived. The role played by the DNA-metal interface in determining the overall transport and $I(V)$ characteristics is also addressed. In this way, we determine the limits for large turn-on currents (in the nA regime), that result from the resonance (alignment) between the DNA molecular levels and the bias-modulated Fermi levels of contacts.

As a suitable representative example, the properties of a periodic polyGACT tetranucleotide chain, connected to metallic leads at both ends, will be considered. Many details on the geometry and chemical bonding nature of the DNA-lead interface are poorly known currently. In our model the coupling between the metal orbitals and the DNA energy levels at the interface will be described in terms of an effective parameter. Thus, the lead-DNA global system will be described by means of the tight-binding Hamiltonian $\mathcal{H}$ as

$$\sum_{j=1}^{N} (\varepsilon_j c_j^\dagger c_j - t c_j^\dagger c_{j+1} + \text{h.c.}) - \tau(c_0^\dagger c_1 + c_{N+1}^\dagger c_N + \text{h.c.}) + \sum_{k,l=0,N+1}^{\mp\infty} (\varepsilon_m c_{k,l}^\dagger c_{k,l} - t_m c_{k,l}^\dagger c_{k+1,l+1} + \text{h.c.}),$$

where c_j ($c_j^\dagger$) is the creation (annihilation) operator for a charge at jth site in the chain. The first term describes the intrastrand hole propagation through the DNA chain, where $\varepsilon_A = 8.24$ eV, $\varepsilon_T = 9.14$ eV, $\varepsilon_C = 8.87$ eV, $\varepsilon_G = 7.75$ eV are the nucleotides on-site energies, t is the hopping term between adjacent nucleotides, and N is the number of nucleotides in the chain.[6,10] The second term describes the DNA-metal coupling, where τ measures the coupling strength, whereas the third term gives the energetics of the metallic leads, with $\varepsilon_m = 5.36$ eV (related to the platinum metallic work function[6]), while t_m is the hopping term. First-principles calculations have reported values ranging from $t = 0.01$ to $t = 0.4$ eV.[11] Following previous works, properly accounting for experimental *I-V* curves, we will take $t = 0.4$.[12] By considering nearest-neighbors interactions the first term of $\mathcal{H}$ can be cast in terms of the unimodular matrices

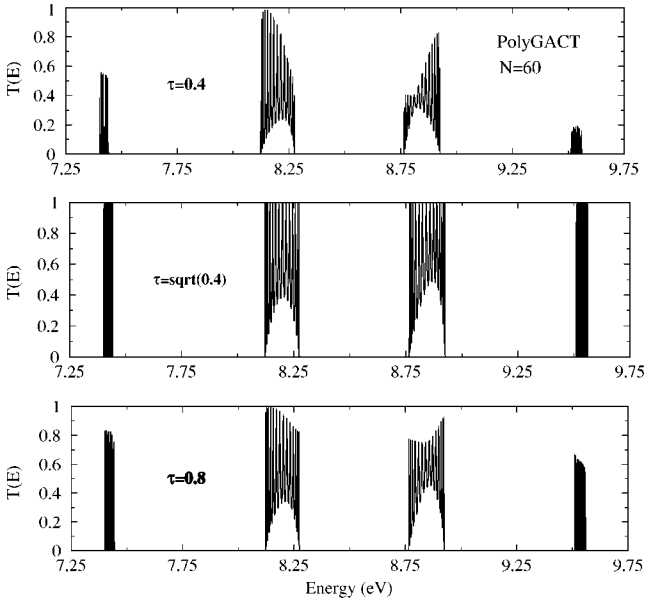

FIG. 1. Transmission coefficient curve for a polyGACT chain with $N=60$, $t_m=1.0$ eV, $t=0.4$ eV, and $\tau=0.4$ eV (top panel); $\tau=\sqrt{0.4}$ eV (central panel); and $\tau=0.8$ eV (bottom panel).

$$Q_i \equiv \begin{pmatrix} 2x_i & -1 \\ 1 & 0 \end{pmatrix}, \tag{1}$$

where $x_i=(E-\varepsilon_i)/2t$ with $i=\{\mathrm{G},\mathrm{A},\mathrm{C},\mathrm{T}\}$. The dispersion relation is given by $2\cos(qN)=\mathrm{Tr}[M(E,N)]$, where the DNA transfer matrix is $M\equiv(Q_TQ_CQ_AQ_G)^n=$

$$\begin{pmatrix} U_n - JU_{n-1} & -2DU_{n-1} \\ 2FU_{n-1} & JU_{n-1}-U_{n-2} \end{pmatrix},$$

where $n=N/4$, $J\equiv 1-4x_Cx_A$, $D\equiv 4x_Tx_Cx_A-x_T-x_A$, $F\equiv 4x_Cx_Ax_G-x_C-x_G$, and $U_n(u)\equiv\sin((n+1)\theta)/\sin\theta$, with $u\equiv\cos\theta=8x_Gx_Ax_Cx_T-2(x_A+x_T)(x_G+x_C)+1$, are Chebyshev polynomials of the second kind, satisfying $U_{n+1}-2uU_n+U_{n-1}=0$. From the expression $(U_n-U_{n-2})/2=T_n\equiv\cos(n\theta)$, we finally obtain the dispersion relation

$$4t^4\sin^2(2q)-t^2(2E-\varepsilon_T-\varepsilon_A)(2E-\varepsilon_C-\varepsilon_G)+\prod_i(E-\varepsilon_i) = 0, \tag{2}$$

so that the relevant energy spectrum of a polyGACT chain (see Fig. 1) is composed of two relatively wide bands ($W_A=0.15$ eV and $W_C=0.16$ eV), respectively, centered at 8.198 and 8.844 eV, plus two narrower bands ($W_G=0.04$ eV and $W_T=0.05$ eV) centered at 7.422 and 9.535 eV. These allowed bands are separated by the relatively broad gaps $\Delta_{GA}=0.830$ eV, $\Delta_{AC}=0.488$ eV, and $\Delta_{CT}=0.583$ eV. Note that Eq. (2) is invariant under cyclic permutations of the nucleotide on-site energies. Thus, the obtained energy spectrum is representative of a broad class of tetranucleotide-based DNA chains. To compute the transmission coefficient at zero bias, the chain is connected to two semi-infinite electrodes so that the global transfer matrix can be expressed as $\tilde{M}=RP^{n-2}L$, where

$$L = Q_TQ_CQ_A\begin{pmatrix} 2x_G & -\mu \\ 1 & 0 \end{pmatrix}\begin{pmatrix} 2\eta\mu^{-1}\cos k & -\eta\mu^{-1} \\ 1 & 0 \end{pmatrix},$$

$$R = \begin{pmatrix} 2\cos k & -\mu\eta^{-1} \\ 1 & 0 \end{pmatrix}\begin{pmatrix} 2x_T\mu^{-1} & -\mu^{-1} \\ 1 & 0 \end{pmatrix}Q_CQ_AQ_G,$$

with $\mu=\tau/t$, $\eta=t_m/t$, and

$$P^{n-2} = \begin{pmatrix} BU_{n-3}-U_{n-4} & -2DU_{n-3} \\ 2FU_{n-3} & U_{n-2}-BU_{n-3} \end{pmatrix},$$

where $B=2u-J$ satisfies the relationship $B^2-4DF=2uB-1$. The contact matrices L and R explicitly take into account the symmetry breaking due to the presence of the hopping integral τ connecting the G (T) nucleotide at the left (right) metallic leads, respectively. After some algebra, the matrix elements of $\tilde{M}(N,E)$ are expressed as $\tilde{M}_{11}(N,E)=4\beta_n^+\cos^2 k-4(D+F)U_{n-1}\cos k+\beta_n^-$, $\tilde{M}_{12}(N,E)=2FU_{n-1}-2\beta_n^+\cos k$, $\tilde{M}_{21}(N,E)=-2DU_{n-1}+2\beta_n^+\cos k$ and $\tilde{M}_{22}(N,E)=-\beta_n^+$, where $\beta_n^+\equiv\eta\mu^{-2}\alpha_{n-2}^+$, $\beta_n^-\equiv\eta^{-1}\mu^2\alpha_n^-$, and $\alpha_n^\pm\equiv BU_{n\pm1}-U_n$. It is readily checked that $\det[\tilde{M}(N,E)]=U_{n-1}^2-U_nU_{n-2}=1$, so that the metal-contact-DNA transfer matrix belongs to the $SL(2,R)$ group. The transmission coefficient $T_N(E)$ is then given by the expression[14]

$$\frac{1}{1+\gamma^2-4DFU_{n-1}^2+[(D+F)U_{n-1}-\gamma\cos k]^2\csc^2 k}, \tag{3}$$

where $\gamma\equiv(\beta_n^++\beta_n^-)/2$. In Fig. 1 we show the transmission patterns for a system with $t_m=1.0$ eV and $t=0.4$ eV for several values of the DNA-metal coupling. We can readily see the narrow G and T bands at the edges, as well as the relatively broader A and C bands at the central regions of the energy spectrum. We have checked that by decreasing t these bands progressively stretch, eventually collapsing into the series $\{\varepsilon_i\}$ describing the energy levels of a set of isolated nucleotides. By inspecting the top and bottom panels we realize that the transmission peaks do not reach in general the full transmission condition. This transmission degradation is a direct consequence of *contact effects*. In fact, by taking $U_{n-1}(u)=0$ in Eq. (3), one gets

$$T^*(E_p)=\left(1+\gamma_0^2\frac{4\eta^2t^2}{4\eta^2t^2-(E_p-\varepsilon_m)^2}\right)^{-1}, \tag{4}$$

where $\gamma_0=(\eta^2-\mu^4)/2\mu^2\eta$, and the integer p labels the different peaks in the $T_N(E)$ curve. By imposing the extreme conditions $\partial T^*/\partial\eta=0$ and $\partial T^*/\partial\mu=0$ to Eq. (4), we get $\gamma_0=0\Rightarrow\eta=\mu^2$. Thus, full transmission ($T^*=1$) requires $\gamma_0=0$. Otherwise, T^* depends on η, t, and ε_m values. Depending on their adopted values quite small transmission peaks can be obtained at certain E_p energies, as shown in Fig. 1 (top and bottom panels). This result properly illustrates the influence of the contacts on electrical transport. This extreme sensitivity is due to interference effects between the DNA molecular bands and the electronic structure of the leads at the metal-DNA interface, and indicates that the *optimal* system configuration for efficient charge transfer is determined by the resonance condition $\gamma_0=0$, i.e.,

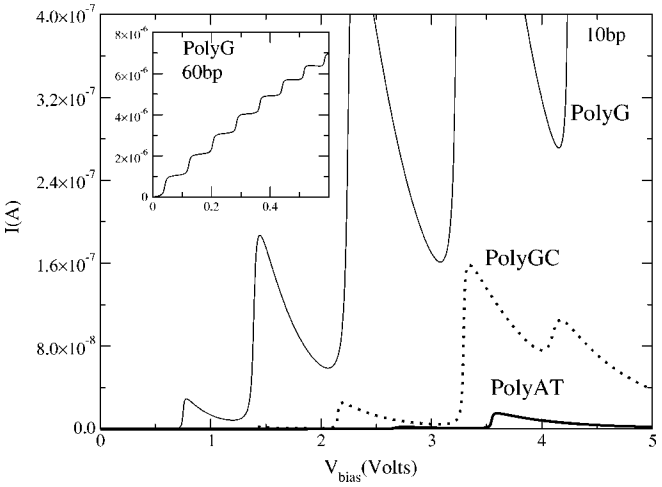

FIG. 2. Main frame: Tunneling currents for several $N=10$ sequences (PolyG, PolyAT, and polyGC) with parameters $t_m=1.0$ eV, $t=1$ eV, $\tau=1$ eV, and $\varepsilon_m=5.36$ eV. Inset: Tunneling current through a $N=60$ PolyG sequence with $t_m=1.0$ eV, $t=1$ eV, $\tau=1$ eV, $\varepsilon_m=\varepsilon_G$.

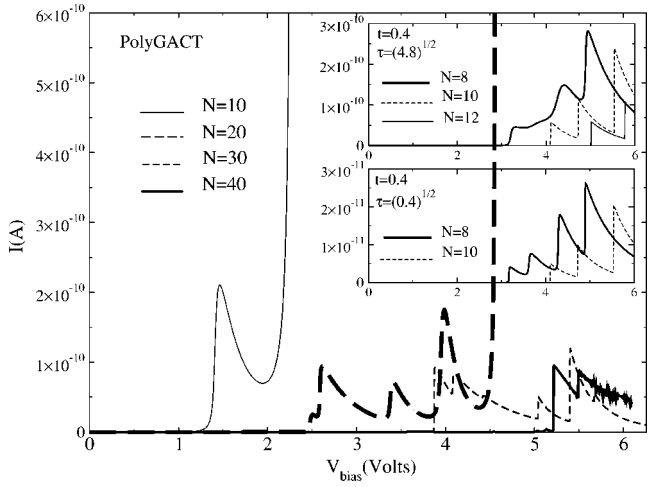

FIG. 3. Main frame: Tunneling currents for several periodic PolyGACT-based sequences with parameters $t_m=12.0$ eV, $t=1$ eV, $\tau=1$ eV, and $\varepsilon_m=5.36$ eV. Inset: Tunneling currents for PolyGACT sequences with $N=8$ (GACTGACT), $N=10$, and $N=12$, with parameters $t=0.4$ eV, and $\tau=\sqrt{0.4}$ eV (bottom inset) or $\tau=\sqrt{4.8}$ eV (top inset).

$\tau=\sqrt{t*t_m}$. A complete set of such resonant states is shown in the central panel of Fig. 1.

In order to further substantiate that a stronger coupling does not always result in a larger conductance[16] due to resonance effects, we shall consider the current density through our system. The bias voltage dependence of the contact energies is given by $E_L(k)=\varepsilon_m+V_{bias}+2t_m\cos k$ and $E_R(k)=\varepsilon_m+2t_m\cos k$, at the left ($L$) and right ($R$) leads, respectively. Inside the DNA, a linear potential drop is assumed. In the coherent regime, the electrical current $I(V_{bias})$ is computed by using a standard Landauer-Büttiker-like approach[15] as

$$\frac{2e}{h}\int_{-\infty}^{+\infty} T_N(E,V_{bias})[f_L(E-\mu_1)-f_R(E-\mu_2)]dE,$$

where the charges propagate from left to right. Here, μ_1 and μ_2 stand for the electrochemical potentials in the two contacts (that will remain at equilibrium), $f(E)$ is the Fermi-Dirac distribution, and $T_N(E,V_{bias})$ is the bias-dependent transmission coefficient, which will be numerically evaluated. In what follows, we restrict to the coherent tunneling regime at zero temperature. Accordingly,

$$I(V_{bias})=\frac{2e}{h}\int_{E_F}^{E_F+eV_{bias}} T_N(E,V_{bias})dE.$$

To extract the main features of tunneling currents in DNA chains, let us first compare the behavior of a PolyG chain with that corresponding to PolyAT and PolyGC sequences under the resonance condition given by the coupling parameters choice $t=\tau=t_m=1$ (Fig. 2). In this case, if the potential barrier between the metallic contacts and the DNA is set to zero, a staircase increase of $I(V_{bias})$ is found (Fig. 2 inset), in agreement with prior calculations.[13] In contrast, as soon as a potential barrier between the DNA and the metals is introduced, great changes are observed in the $I(V)$ curves, which now exhibit typical *negative differential resistance*. Such a phenomenon is a tunneling-related effect that has been observed in silicon-based heterostructures,[17] as well as in small molecules.[18] The comparison of a pure G based with PolyGC and PolyAT periodic chains is striking. The current density through a $N=10$ PolyAT is several orders of magnitude lower that the one corresponding to PolyGC or PolyG of the same length, hence illustrating the influence of the considered DNA sequence in charge transport. The voltage threshold at a given current scale is also very sensitive to the presence of guanine, and can differ by several volts. Such results are easily understood as the result of both deeper and larger tunneling barriers, related to the presence of bases with higher ionization potentials.

Let us now analyze the effect of the interface potential mismatch, on charge injection and turn-on currents. In Fig. 3, the characteristics of $I(V)$ curves are shown for PolyGACT sequences of increasing length. First, the potential barrier is set to 2.39 eV (the energy difference between platinum Fermi level and HOMO state of guanine), while the coupling parameter is set to $t_m=12$ eV, to ensure a large bandwidth. In the main frame we take $t=\tau=1$ eV. Compared to the case of chemically simpler DNA chains (Fig. 2), the current density in polyGACT chains is reduced by about three orders of magnitude. By increasing the DNA length from $N=10$ to $N=40$, the voltage threshold [determining an apparent $I(V)$ gap] is upscaled, while turn-on currents are progressively degraded (Fig. 3 main frame). By further taking the coupling parameters closer to *ab initio* estimates (that is $t=0.4$ eV, while $\tau=\sqrt{0.4}$ eV), the overall current intensity is further reduced by typically one order of magnitude, leading to currents in the pA range (Fig. 3 bottom inset), with a larger voltage threshold. Conversely, in the resonance setup given by $\tau=\sqrt{4.8}$ eV, the current intensity is enhanced by an order of magnitude (Fig. 3 top inset). This result provides additional evidence on the importance of contact effects on

turn-on currents characteristics. For this last set of parameters, PolyGACT sequences with $N=20$ exhibit currents in the fA range, defining the limit for the coherent tunneling regime.

We have also compared PolyG and PolyGACT sequences of the same length. Typically, in the situation where turn-on currents through a PolyG sequence with eight guanine are in the range of the nA, currents flowing through the GACT-based sequence will be two orders of magnitude lower, for similar voltage drop (not shown here) and Hamiltonian parameters. This demonstrates the importance of DNA sequence in the possible fluctuations of apparent gap and relative $I(V)$ intensities. Interestingly, similar differences between simple periodic sequences are found in experimental data[8,9] where the DNA sequences are about 20-nm long.

In conclusion, we have provided a theoretical background on the possible use of a particular contact design aimed to improve the electronic performance of DNA-based devices. Our study also clearly points out that coherent charge transport can hardly sustain nA currents over distances much larger than typically 20 nm (that is, $N=60$). Other transport mechanisms, such as sequential hopping, should be included in the theoretical analysis to assess the possibility of large turn-on currents for even much larger scales.[8,9] More elaborate *ab initio* descriptions of the electronic structure of the DNA are also required for a better consideration of substrate effects or interaction with an ionic chemical surrounding,[19] as well as Schottky-like effects between the DNA and the metallic leads.[20]

This work was partly supported by UCM through Project No. PR3/04-12450, the Ministerio de Educación y Ciencia through Project No. FIS2004-00067, the Consejería de Educación de la CAM and European Union FEDER through Project No. GR/MAT/0768/2004.

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