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Environment and structure influence on DNA conduction

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Results for transmission through the poly$\{G\}$ DNA molecule are presented. We show that (i) periodically arranged sodium counterions in close proximity to dry DNA give rise to a conduction channel, and aperiodicity in the counterion sequence can lead to a significant reduction in conduction, (ii) modification of the rise of *B*-DNA induces a change in the width of the transmission window, and (iii) specifically designed sequences are predicted to show intrinsic resonant tunneling behavior.

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The growing interest in DNA for nanotechnology and molecular devices stems from the ability of controlled growth of nucleotide sequences and its surprising conducting properties. Recent transport measurements on DNA strands lying between metallic electrodes have produced contradictory results. Fink and Schönenberger[1] observed metallic behavior in λ-DNA using an electron projection microscope setup, Kasumov *et al.*[2] observed superconducting behavior, Porath *et al.*[3] observed semiconducting behavior with a well-defined poly$\{G\}$-poly$\{C\}$ DNA molecule, and de Pablo *et al.*[4] observed insulating behavior using a scanning force microscope based setup. Biochemists have established a link between oxidative damage of DNA due to hole transport and the occurrence of genetic mutations. It has also been shown that oxidative damage is sequence dependent.[5] Experiments[6,7] and modeling[8,9] have shown that both short-range coherent tunneling transport and long-range incoherent/hopping transport[8–10] are mechanisms for hole transport.

Charge transport in DNA is a complex phenomenon because the environment of the DNA plays a significant role in determining the energy levels of nucleotides and the structure.[11] The transformation of DNA structure has been correlated to the *p*H of the buffer. In this Rapid Communication, we model some aspects of structure and environment that influence charge transport in dry DNA.

I. MODEL AND METHOD

The system modeled is a single-strand *B*-DNA molecule, which has ten bases per turn with a distance of 3.38 Å between consecutive bases. We considered two cases. In case *A*, only the nucleic acids are included with an H atom termination of the base. For two bases there are six degrees of freedom, which lead to a very large number of possible conformations. We calculate the change in transmission probability through an infinite poly$\{G\}$ DNA molecule due to change in two of these degrees of freedom: *rise* (the distance between bases) and *twist* (angle between consecutive bases). The coordinates of the molecule are generated by applying the translations and rotations given in Ref. 12 to a single nucleotide. In case *B*, the sugar phosphate backbone and nucleic acids are explicitly included with the structure taken from Ref. 12. Hydration shells are absent in our model, and fluctuations in DNA conformation do not exist, as in the case of dry DNA. We consider a straightforward *B*-DNA model because the structure of DNA lying on a substrate is not well understood.[13] In the calculations involving the effect of the counterions (cations) of the phosphate group on charge transport, the backbone and counterions are both considered. The location of the counterions are determined by the energy minimization[14] of a one-phosphate two-sugar model of the DNA backbone.

The transmission through the molecule is computed using a Green's-function framework.[15] A block tridiagonal matrix representation of the Hamiltonian, with interaction only between nearest-neighbor bases is included to compute the transmission.[16] In constructing the block-tridiagonal Hamiltonian for the extended system, we follow the work of Gazdy *et al.*,[17] which is based on the Hamiltonian obtained from calculations on dimers or trimers. Such a calculation has been carried out in the context of the DNA by Ye and Jiang.[18] Our calculations on dimers, along the DNA chain to obtain the Hamiltonian/Fock matrix[18] are performed using the B3LYP exchange-correlation functional[19,20] in density-functional calculations using GAUSSIAN98.[14] The basis set used here corresponds to 6-21G. More diffuse or complete basis sets affect our results little.

The transmission through the molecule is computed using the following expression:[15] $T(E)=\mathrm{tr}(\Gamma_L G^r \Gamma_R G^a)$. In this equation, $G^{r(a)}$ represents the retarded (advanced) Green's function and $\Gamma_{L(R)}$ the coupling between the left (right) lead and the device. G^r is the solution of the following equation: $(ES-H-\Sigma_L^r-\Sigma_R^r)G^r=\mathbb{1}$, where E represents the energy of the electron, H the Hamiltonian, S the overlap matrix, and $\Sigma_{L(R)}^r$ the self-energy. In the framework of the nearest-neighbor approximation, $\Sigma_{L(R)}^r$ and $\Gamma_{L(R)}$ are given by $\Sigma_{L(R)}^r=H_{\mathrm{DNA}\text{-}L(R)}g_{L(R)}^r H_{L(R)\text{-}\mathrm{DNA}}$ and $\Gamma_{L(R)}=-2\mathrm{Im}(\Sigma_{L(R)}^r)$, where $g_{L(R)}^r$ is the retarded surface Green's function of the left (right) lead, $H_{\mathrm{DNA}\text{-}L(R)}$ represents the coupling between the DNA and the left (right) contact, $H_{L(R)\text{-}\mathrm{DNA}}=H_{\mathrm{DNA}\text{-}L(R)}^{\dagger}$, and $\mathrm{Im}[x]$ represents the imaginary part of x.

II. RESULTS

The highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of a nucleotide primarily lie on the bases. Hence it is believed that transport in native DNA occurs primarily along the base pairs, and the backbone does not play a role apart from pro-

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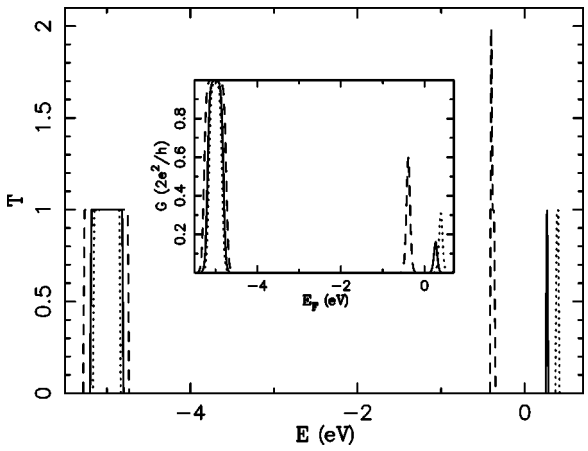


FIG. 1. Transmission vs energy for different distances between consecutive bases of a poly{G} DNA molecule without backbone. The solid line corresponds to a rise of 3.38 Å, the dashed line to 3.1 Å, and the dotted one to 3.5 Å. The inset corresponds to the linear response conductance at $T=298$ K.

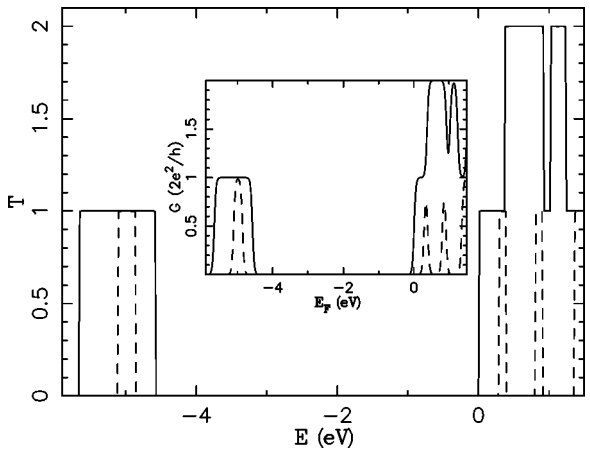


FIG. 2. Transmission vs energy for different twist angles between consecutive bases of a poly{G} DNA molecule without backbone. Solid line, $\Omega=0°$, dashed line: $\Omega=30°$. The inset corresponds to the linear-response conductance at $T=298$ K.

viding mechanical stability to the structure.[21] Figure 1 corresponds to the variation of transmission when the rise of a *B*-DNA is decreased (model *A*). When this distance is decreased from the regular value of 3.38 Å, the main effect is a broadening of the conduction channels. Physically, the broadening occurs due to an increase in the hybridization between the π orbitals of guanine. An increase of the rise (distance between consecutive bases) causes a shift and sharpening of the channel, because the hybridization between the π orbitals of neighboring bases is now diminished. Energetically, the decrease of the distance between nearest-neighbor bases by 0.28 Å produces an increase in the total energy of only 0.14 eV for a two-base system. Thus, even if this conformation is energetically higher, it may be encountered in specific conditions. Also, it may be possible to perform experiments where DNA lying between contacts can be stretched as in recent experiments with carbon nanotubes.[22] Broadening of the HOMO transmission window is also seen when the twist angle is decreased from its regular value of 36° (Fig. 2), as recently found by Di Felice *et al.* in Ref. 23. In the absence of strain, the width of the HOMO transmission channel is 370 meV (Fig. 1), which corresponds to an average nearest-neighbor hopping strength between bases of nearly 90 meV. Changing the twist angle from 36° to 30° and 0° changes the width of the HOMO transmission channel to 270 meV and 1.07 eV, respectively (Fig. 2).

We now consider the effect of counterions using a DNA strand with the backbone included (model *B*). One parameter that is not well characterized in most of the transport experiments on DNA is its close environment. It is only very recently that a combined theoretical and experimental study has pointed out the possible implications of the backbone with its close environment in hole transport.[24] Indeed, a DNA molecule in a saline solution is surrounded by a cloud of ionic species due to the presence of a negative charge mainly located on one of the oxygens of the phosphate group. Measurements of current by physicists involves dry DNA. In dry DNA, where are the cations and hydration shells located? Is a hydration shell necessary or can it be avoided all together? These questions are difficult to answer at this initial stage of the field. The answer will probably come from an interplay of high-resolution scanning tunneling microscope/atomic force microscope measurements and modeling, which is well beyond the scope of our work. Our model study here makes simple assumptions about the location of the cations without a hydration shell, to first understand what happens in this idealistic limit. As is shown below, even this ideal limit is interesting. We find that the cations have two main influences on conduction:

(a) Transport could occur via a channel composed of cations. The results do not depend significantly on the distance of the cation from the phosphate group as long as it is between 2.3 and 2.8 Å (distance to the nearest oxygen), and the cations are placed uniformly along the back bone.

(b) Cations affect the on-site potential of the bases, and hence alter conductance through the bases substantially. Specifically, nonuniformity in cation type could lead to a reduction in conductance through the bases. We have presented results for the decrease in transmission when a single cation is replaced or removed.

We discuss (a) and (b) now. We compare the influence of hydrogen, hydronium, and sodium counterions on the transmission of electrons through a poly{G} strand. The charge transfer from the counterion to the phosphate group is found using Mulliken population analysis to be 0.42, 0.80, and 0.60 for the cases of H, H_3O, and, Na respectively. In the case of H and H_3O, we find that the HOMO and LUMO channels are still on the base and so conduction would occur primarily through the base. In the calculations with Na, we find that a conduction channel occurs in the HOMO-LUMO gap (of the structure without the sodium). This channel is due to an empty band and corresponds to the LUMO of the structure with Na. Figure 3 shows the plot of transmission versus energy with Na counter-ions. The local density of states at the Sodium atom (not shown) further proves that this channel (located at -2.6 eV) is due to the sodium atoms. That is, the phosphate group acts as a template for a helical wire consist-

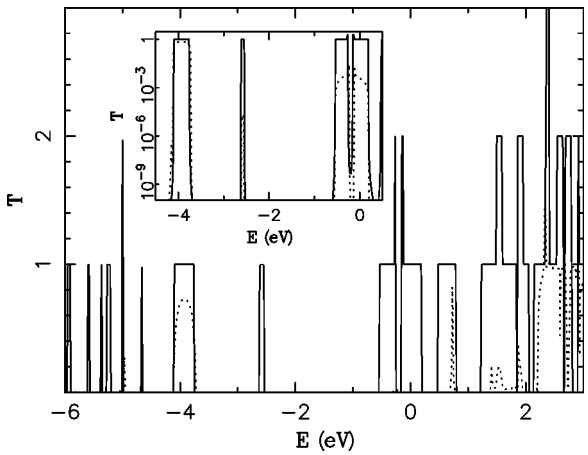


FIG. 3. Transmission vs energy for a poly$\{G\}$ *B*-DNA surrounded by periodically placed Na ions (solid line), and when a local ion mismatch is created by replacing one Na by a H_3O (dashed line).

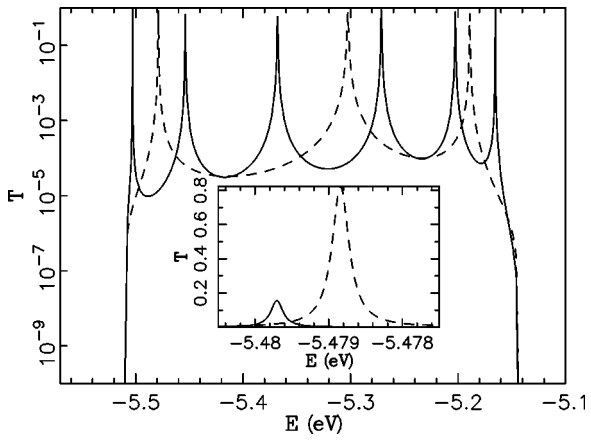


FIG. 4. Transmission vs energy for poly$\{G\}TGGGT$poly$\{G\}$ (dashed) and poly$\{G\}TGGGGGGT$poly$\{G\}$ (solid) double-barrier resonant tunneling structures. Inset: Symmetrical poly$\{G\}TGGGT$poly$\{G\}$ (dashed) and asymmetrical poly$\{G\}TTGGGT$poly$\{G\}$ (solid) sequences.

ing of sodium atoms, conduction through which gives rise to this channel. We have also verified that the transmission obtained by replacing the combined system of phosphate group, sugar, and base by OH at the location of the phosphate groups leads to the occurrence of these conduction channels due to the sodium wire. The above results indicate that depending on the location of the Fermi energy, the counterions of the phosphate group could play a role in determining the conductance. We also find that potassium and lithium also show the above feature of creating a channel in the HOMO-LUMO gap of the structure without these atoms.

We now present results for the influence of more than one ionic species in the backbone. Experimentally, we expect variation in both the type and location of the counterions in dry DNA. We consider a system with a chain of sodium counterions, where a single sodium atom is replaced by H_3O. The main effect of the H_3O counterion is to shift the HOMO and LUMO of the base closest to it, relative to other bases with a sodium counter-ion. The transmission probability through such a system is shown in Fig. 3 (dashed line). The decrease in transmission over relevant energy ranges near the HOMO and LUMO is significant. As a result, we expect the conductance of a DNA strand with fluctuation in the type of counterions to be significantly altered compared to a strand with uniformly placed counter-ions. We also find that the shift in the energy levels due to H_3O (with respect to sodium) is around 150 meV, which is comparable to the hybridization energy between nearest neighbor guanines. Thus, a random sequence of counterions along the backbone would eventually tend to localize the electron wave function along the bases.[25]

The principle of complementarity between bases and the ability to design arbitrary sequences has generated interest in DNA based electronics. Inspired by this, we have studied the possibility of intrinsic resonant tunneling in DNA strands. The underlying structure in resonant tunneling is a quantum well connected to the continuum by two barriers. Motivated by the fact that guanine has a lower ionization energy than thymine, we consider the following two strands, which are seemingly symmetric, poly$\{G\}TGGGGGGT$poly$\{G\}$ and poly$\{G\}TGGGT$poly$\{G\}$. We expect the thymines to comprise a barrier and the guanines in between to form a quantum well. Three and six clear transmission resonances due to hybridization of the guanines are seen in Fig. 4. The transmission probability through a system with symmetric barriers should peak at unity. Interestingly, the barriers created by the thymines have a small asymmetry, because the overlap Hamiltonians between G and T in $\{5'GT3'\}$ and $\{5'TG3'\}$ are not the same (these structures are not geometrically identical due to rotation of bases along the DNA helix). However, as the asymmetry is mild, the transmission is close to unity. Next, we consider a poly$\{G\}TTGGGT$poly$\{G\}$ strand, which has a much larger asymmetry in the barriers created by the thymines. Here, we find that while the location of the transmission resonances has not changed significantly, the peak values are smaller than 0.2 (inset of Fig. 4). It is noted that such resonant tunneling behavior may be observable in an experiment where the Fermi energy through the DNA is modified by applying a gate voltage, or in experiments looking at current as a function of the applied bias between the source and drain terminals.

We now briefly discuss two aspects that have been ignored in the previous discussion—the location of the Fermi level and electrostatics. Reliably computing the Fermi level of molecules connected to electrodes has proved to be a challenging problem, because charge transfer between the macroscopic contacts and the molecules should be precisely determined. For a large molecule such as DNA, it might be best to use values that can be inferred from experiments. A recent interesting experiment[26] finds that the Fermi energy in poly$\{G\}$-poly$\{C\}$ and poly$\{A\}$-poly$\{T\}$ molecules lie closer to the HOMO (p-doped) and LUMO (n-doped) channels, respectively. Experiments that involve an electrostatically coupled gate electrode have a significant advantage, because the Fermi energy can be tuned from the HOMO band to the LUMO band in a controlled manner.[27]

Our assumption of neglecting self-consistency for long strands is strictly not correct, as the potential profile will be determined by long-range charge transfer. In our calculations, charge transfer is accurately accounted for only in the Fock matrix of the subsystem. We have verified that expanding the subsystem from two to three bases does not significantly affect our results. Also, self-consistent calculations to determine the fraction of voltage drop across the DNA and contacts are important in understanding the mechanism of current flow at finite voltage biases but is beyond the scope of this Rapid Communication.

In conclusion, we numerically study the transmission properties of dry poly$\{G\}$ DNA. Change of the distance (rise) and angle (twist) between the bases from its regular value for B-DNA leads to a shift and change in width of the transmission window. Some ionic species such as sodium could create improved conduction channels. More importantly, we have shown that the variation of ionic species in the backbone can cause a significant reduction in transmission through the bases. Finally, we explore the possibility of resonant tunneling in engineered DNA structures and find that it may be possible to observe intrinsic resonant tunneling in a system composed of guanine and thymine.

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