Influence of counter-ion-induced disorder in DNA conduction

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Disorder along a DNA strand due to nonuniformity associated with the counter ion type and location, and in rise and twist are investigated using density functional theory. We then model the conductance through a poly(G) DNA strand by including the influence of disorder. We show that the conductance drops by a few orders of magnitude between typical lengths of 10 and 100 nm. Such a decrease occurs with on-site potential disorder that is larger than 100 meV. © *2003 American Institute of Physics.* [DOI: 10.1063/1.1563811]

During the last few years, the possibility to use DNA in nanotechnology and as a nanodevice has been increasingly investigated. This interest stems from the ability of controlled growth of nucleotide sequences and DNAs surprising conducting properties. Transport measurements[1–7] have led to a broad range of conductances, opening a huge controversy on this issue. While Ref. 1 found a long (600 nm) rope of DNA strands to be metallic (resistance in the 2-MΩ range), Ref. 2 found a short strand (8 nm) to be semiconducting (resistance in the gigaohm range). Refs. 6 and 7 found both poly(G)–poly(C) and λ-DNA to be insulating over a length scale of 40 and 30 nm, respectively. In contrast to the above, Ref. 4 found DNA could be induced to superconduct. The physical mechanisms leading to the wide range of results is unclear. It is hoped that modeling of various factors controlling DNA conductance would eventually help in understanding the mechanisms. We expect DNA conductance to be very sensitive to the nature of the metal contacts, defects, conformational changes, and to the location of the Fermi energy, among other factors. In this letter, we study the role of counter ions in causing conductance reduction with increase in strand length of dry DNA. The main motivation for this work was Refs. 2 and 6, which show a superlinear increase in resistance with length of poly(G)–poly(C) (the experimental setups were different).

The distance between base pairs in B-DNA is approximately 3.4 Å and the hybridization energy (U) between the highest unoccupied molecular orbital (HOMO) levels of adjacent guanines of a poly(G) sequence is small (around 87 meV).[3,8,9] The corresponding HOMO band width (4 U) is a narrow 350 meV. Small changes in the environment of the base pairs or irregularities along the length of the poly(G) molecule are bound to exist in dry DNA. For example, upon drying, it is unlikely that the counter ions of the phosphate group will all be identical and periodically arranged. It is also conceivable that a counter ion could be missing from a phosphate group. Such nonidealities will lead to change in the energy eigenvalues (on-site potential) of base pairs along the strand. If this perturbation is small compared to U, then transport through poly(G) will be unaffected. The main idea of this letter is that the eigenvalues of base pairs are modified by values comparable to U because of irregularities. Then, electronic delocalization arising from the π stacking of the base pairs is broken over long distances, and the conductance of even a poly(G) molecule will significantly diminish with increase in length.

We investigate the influence of various structural irregularities, such as change in rise and twist, and ion mismatches on the eigenvalues of a dimer of guanines. The *ab initio* calculations are performed using Gaussian 98[10] in the density functional approximation with the B3LYP[11,12] exchange-correlation functional. The basis set used here corresponds to 6-21G. More diffuse or complete basis sets like the 6-31G(d) do not significantly affect our results. Each base pair is assumed to have only a single counter ion as discussed subsequently. We note that work on dry DNA that clarifies the number of counter ions around each base pair would be useful and could quantitatively change our results. We have compared the eigenvalues corresponding to the HOMO, lowest unoccupied molecular orbital (LUMO) and the average difference between all the eigenvalues of the system (Table I). Change of rise and twist (by 6°) do not lead to very large variations of the HOMO and LUMO eigenvalues. Variation in the counter ion characteristics affect the HOMO and LUMO eigenvalues more significantly. The HOMO eigen value changes by 100 and 50 meV in the cases where both H_3O^+ are replaced by Na^+ and K^+ Variations of the distance between the counter ion and the phosphate group also lead to variations of the order of 50 meV. A larger difference, nearly 500 and 1000 meV, in the HOMO and LUMO values is found between hydrogen (bonded to one oxygen of the phosphate) and H_3O^+ and Na^+ counter ions. We should note that the occurrence of a hydrogen bonded to the phosphate is rather unlikely. Overall, the change in eigenvalues in Table I makes our suggestion that irregularities along a poly(G) causes a reduction in conductance with length plausible.

The conductance is calculated using the Landauer–Buttiker approach.[13] The Hamiltonian for an extended system of base pairs is contructed by starting from the Hamiltonian of dimers, following the nearest-neighbor-approximation scheme of Refs. 14 and 15. The Hamiltonian of the dimers are calculated using Gaussian 98[10] and the transmission probability is calculated using the scheme in Ref. 16. A key ingredient to the calculation is the strength of the disorder potential. The disorder is introduced via a uniform change in the on-site potential of all atoms in a base

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TABLE I. Eigenvalue differences (for the HOMO and LUMO eigenvalues and also for the average differences between all the eigenvalues) between various dimers. Three kinds of system variations are presented: Mismatch of the counter ions (first seven rows), mismatch of the distance of the counterions with respect to the phosphate group (next two rows) and mismatch of the twist and rise of the dimer (next seven rows).

	$\Delta\epsilon_{\mathrm{HOMO}}$ (meV)	$\Delta\epsilon_{\mathrm{LUMO}}$ (meV)	$\overline{\Delta\epsilon}$ (meV)
Na^+ vs H_3O^+	93.4	136.4	125.9
K^+ vs H_3O^+	69.6	89.8	106.7
Na^+, Na^+ vs Na^+, H_3O^+	49.1	65.3	59.7
H_3O^+, H_3O^+ vs Na^+, H_3O^+	44.3	71.1	68.1
K^+ vs Na^+	23.8	46.6	58.6
H_- vs H_3O^+	552.8	1054.4	1161.1
H_- vs Na^+	646.2	1190.8	1285.5
Na^+ distance ($\Delta d=+0.1$ Å)	27.1	51.0	48.3
Na^+ distance ($\Delta d=-0.2$ Å)	63.1	119.4	114.6
Twist ($\Delta\Omega=\pm 2°$)	2.0	5.	32.0
Twist ($\Delta\Omega=-6°$)	0.9	19.5	115.6
Twist ($\Delta\Omega=+6°$)	16.9	10.4	73.1
Rise ($\Delta r=-0.1$ Å)	17.4	12.9	47.7
Rise ($\Delta r=+0.1$ Å)	14.6	11.1	43.9
Rise ($\Delta r=-0.2$ Å)	37.9	28.6	98.2
Rise ($\Delta r=+0.2$ Å)	26.6	20.8	81.5

pair by $\delta\epsilon_i$, where i corresponds to the base pair labeled i. Further, it is expected that for two adjacent nucleotides, there is some degree of correlation between the amplitude of disorder potential at neighboring base pairs. A correlation in the variation of the on-site potential of the base pairs is introduced using the following procedure. The disorder potential of the first nucleotide in the sequence is chosen randomly in the interval $\pm|\epsilon_M|$. The disorder of the second nucleotide is chosen randomly subject to the constraint that $\delta\epsilon_2$ cannot differ from ϵ_1 by more than $\epsilon_M/2$. This procedure is continued for the other base pairs. A typical potential profile is shown in Fig. 1. To justify the use of the smoothing procedure, we have compared the eigenvalues of dimers with two Na^+, two H_3O^+ and a Na^+ and H_3O^+ each. We find that the change in the HOMO level of the third case is in between the first two cases. Finally, in order to focus on the effect of disorder, the open boundaries correspond to disorder-free semi-infinite nanotube leads instead of realistic metal contacts.

For a DNA molecule trapped between two electrodes, the HOMO/LUMO are the most important in determining the conductance. Here, we investigate the conductance when the Fermi energy is close to the HOMO channel.[2] The system considered is a poly(G) without the backbone. This should be a good approximation because for regular B-DNA the HOMO is due to the bases and the backbone only plays a role in the structural stability. The conductance for a disorder-free poly(G) molecule is presented in Fig. 2. The HOMO channel is located at around -5.5 eV and has a width of approximately 350 meV. At zero bias, the maximum possible conductance with this molecule is around $2G_0$ (where $G_0 \simeq 1/12.9$ kΩ). The experimentally observed conductances have been orders of magnitude smaller. Various factors such as DNA–contact coupling, conformational changes of the DNA lying on the metal and on the substrate will play a role in determining the conductance. Also, mismatch in the work function of the metal and DNA will play a role in determining the conductance. For example, in a long strand of DNA, the band bending between DNA regions lying on the metal contact and over the substrate could be larger than the HOMO band width. Neglecting the aforementioned issues (especially the last item which is important for systems with a small energy band width), we focus on the role of disorder in affecting the linear response conductance. Based on the review of Ref. 17, it is expected that the conductance will decrease drastically for devices longer than the localization length. This is what we basically observe. The conductance (for a Fermi level of -5.55 eV, which corresponds to the maximum value of the conductance obtained without disorder) as a function of the length of the device for

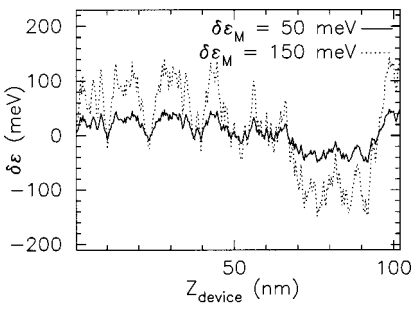


FIG. 1. Amplitude of the disorders as function of the length of the device. The solid line corresponds to a maximum amplitude of the disorder of 50 meV and the dashed line to 150 meV.

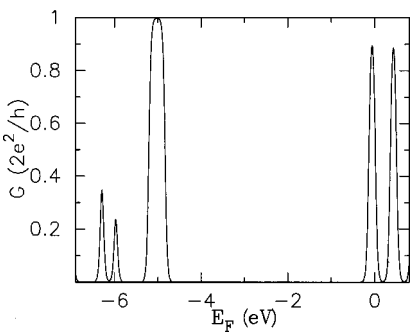


FIG. 2. Conductance versus fermi energy for an infinite poly(G) DNA molecule in a B conformation without disorders.

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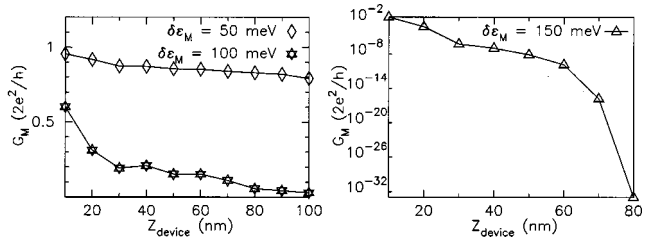


FIG. 3. Conductance (at $T=298$ K and a Fermi level of -5.55 eV) of a poly(G) B-DNA molecule as function of its length. The lines with diamonds, stars, and triangles correspond to cases in which the maximum amplitude of the disorder is 50, 100, and 150 meV respectively.

different value of the disorder strength ϵ_M (is shown in Fig. 3). The exponential decrease over the length scale shown is not observed for small disorders ($\epsilon_M \simeq 50$ meV), and the conductance remains of the order of unity for lengths up to 300 nm (not presented). However, for values of ϵ_M larger than 100 meV, the conductance tends to drop very rapidly with length over the length scale of 100 nm considered, due to the large mismatch of the on-site potential between the nucleotides. The plot shown for $\epsilon_M = 150$ meV is an example of this. Furthermore, considering that small disorders (smaller than 100 meV) do not lead to significant drop of the conductance over a length scale of 100 nm, it seems very unlikely that twist or rise mismatches (of the strength shown in Table I) can explain the phenomenon of very large resistances experimentally observed. Mismatch in the counter ions could lead to a large decrease in conductance with length but such an effect can only be verified if both short and long DNA strands are suspended between the metal contacts. A direct comparison to the experiments is difficult because while the DNA strand was suspended in Ref. 2, it was lying on a substrate in Ref. 6. In this letter, we did not model the DNA–substrate interaction and an experimental setup such as in Ref. 18, where a nanotube was suspended between metal contacts, may be able to verify our prediction.

In conclusion, we have shown that disorder induced by variation in the specifics (type and distance) of the counter ions along a DNA strand is likely to hinder the delocalization of the π orbitals even in a poly(G) molecule. We find that, while random changes in the twist and rise affect the eigenvalues of the guanines, a noncrystalline counter ion arrangement, can lead to significant changes in the eigenvalues of base pairs when compared to the hybridization energy between guanines in poly(G). We calculated the coherent conductance through a poly(G) molecule and find that the conductance of strands over a length scale of 100 nm is significantly affected when counter ions cause a change in the eigenvalues of guanines by more than about 100 meV. Modeling of the coupling of electrons to vibrational degrees of freedom, which will lead to realistic values of the residual conductance with disorder was beyond the scope of this work.

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