# First-Principles Transversal DNA Conductance Deconstructed

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ABSTRACT First-principles calculation of the transverse conductance across DNA fragments placed between gold nanoelectrodes reveals that such conductance describes electron tunneling that depends critically on geometrical rather than electronic-structure properties. By factoring the first-principles result into two simple and approximately independent tunneling factors, we show that the conductances of the A, C, G, and T fragments differ only because of their sizes: the larger is the DNA base, the smaller its distance to the electrode, and the larger its conductance. Because the geometrical factors are difficult to control in an experiment, the direct-current measurements across DNA with gold contact electrodes may not be a convenient approach to DNA sequencing.

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Electrical conductance of DNA molecules has attracted a lot of attention in recent years (1–6). This is due to the potential for using DNA (modified or unmodified) to construct molecular electronic devices, and for sequencing DNA by means of conductivity measurements (7). There are strong motivations for first-principles quantum transport calculations of molecular junctions, including junctions containing DNA molecules. Although experimental conditions on the nanoscale are often difficult to control, theoretically there is no ambiguity of the structure of the material under study. It is also generally believed that the energies and characteristics of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) decide the conductance characteristics of a molecular circuit. For example, the broadening of the HOMO and LUMO states were used to interpret some of the tunneling experiments (8). The importance of the electronic structure is accentuated in some of the recent molecular electronics calculations, which deduced transport properties entirely from the (complex) band structure calculations (9–11) using periodic boundary conditions.

A recent theoretical study indicates that it is possible to distinguish different nucleotides by measuring the transverse DNA conductances (6). This study raises the hope that differences in the electronic structure between the different DNA fragments can provide a means for DNA sequencing using direct-current (DC) conductance measurements. The result implies that the difference in the electronic structure of the nucleotides leads to large differences in conductivity. However, the electronic structure of the system that ''feeds'' the electronic transport calculation was obtained from a parameterized tight-binding Hamiltonian. Thus, questions remain for the cause of the orders of magnitude difference in the conductances of the nucleotides.

In this Letter, we present first-principles calculation of the conductance across DNA fragments and then use a simple model to connect the results with the pertinent physical factors such as the geometric and electronic properties of the molecules. We show that in the tunneling regime, the HOMO and the LUMO play little role in determining the conductance. Instead, the first-principles result can be easily explained by an expression derived from simple geometric considerations. The distinguishability of A, C, G, and T fragments in conductance is mainly correlated to the geometric dimensions of these fragments. When a DNA strand is pulled through metal leads, it is unlikely that all fragments line up in one direction to make the best contact with the leads. Our result shows that the DC measurement of the tunneling current may not be able to distinguish nucleotides in a reproducible way, unless there is an effective control of the critical factor in the conduction, i.e., the DNA-electrode mutual geometry.

There are two dominant charge transport modes in large molecules (12). At distances below 2 nm, coherent quantum transport is the primary mechanism. At larger distances, incoherent hopping or diffusion becomes dominant. In our study, the size of the gap between the two electrodes is kept fixed at 1.5 nm. Therefore we consider only the quantum transport effect. Instead of placing an entire single strand DNA chain between two electrodes, for the expedience of the calculation we use a portion of the ssDNA that contains only one base and a sugar-phosphate group, as shown in the inset of Fig. 1 for the fragment containing the adenine base. To ensure charge neutrality, the DNA fragments are modified in our model so that two oxygen atoms of the phosphate groups were saturated with hydrogen; the carbon 3′ of the sugar group was saturated with hydrogen as well.

The electronic structure of the open system, which is composed of lead-molecule-lead, is computed following the procedure given in Zhang et al. (13). The generalized


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tight-binding approach (13,14) in conjunction with the Green's function method was used to open the quantum system and connect it to the boundary conditions at infinity, computing $T$ in terms of the well known Caroli's formula (17). The transmission probabilities through A, G, C, and T fragments placed between gold nanowires are calculated as functions of the rotation of the DNA bases about the sugar-base axis. Detailed electronic structure will be presented elsewhere. Here we summarize the results relevant to electron transport. There are not large changes in the molecular orbital levels in any of the molecules as a function of the angle $\theta$, in contrast to the strong, almost exponential dependence of the conductance with this angle. The extended molecules containing electrode-molecule-electrode array have orbitals whose energies are close to the Fermi energy. But these orbitals are entirely confined within the electrode region. The evanescent tails of these electrode orbitals inside the molecule have nearly identical exponents of decay, ~1.02/Å. This value is similar to the longitudinal complex band calculation for polyA and polyT molecules (11).

To understand the first-principles results, we factor the calculated conductance using two geometric variables, the rotation angle $\theta$, and the thickness $d$ of the vacuum gap between the top electrode and the nearest atom of the molecule. We factor the conductance into the form, $g = F(\theta)e^{-k_0 d}$, where $k_0$ is the (density) decay wave vector in vacuum. The precise form for $F(\theta)$ depends on the geometric parameters of the DNA base. In deriving $F(\theta)$, we assume that the DNA base has effective dimensions $l_1 \times l_2 \times a$. The first parameter $l_1$ is the linear dimension of the DNA base along the direction of the electrodes and is deduced from the difference in the height of the DNA fragment at $\theta = 0°$ and at $\theta = 90°$. The second parameter, $l_2$, is an effective linear dimension of the base along the direction perpendicular to both $l_1$ and the $\theta$-rotation axis and is fitted from the $\theta$-dependence of the conductance. The effective cross section of the base is $al_2$ at $\theta = 0°$ and $al_1$ at $\theta = 90°$. Note that $l_1$ varies between different fragments, but $l_2$ is assumed to be the same for all fragments. The electron can tunnel through multiple paths, which we assume are coherent. The wave function amplitude for tunneling along a path is exp $\{ -[k_0 x \cos\theta + k_1(l_1 - x)]/2\}$, where $x$ takes a value between 0 and $l_1$ and the phase of the wave function is neglected (equivalent to an assumption that the wave vectors are imaginary along all paths, including those inside the molecule). The effective cross section for each path is $a \sin\theta dx$. Integrating the amplitudes over $x$, we find the following expression for $F(\theta)$:

$$F(\theta) = g_0\left[1 + \frac{2\sin\theta(e^{(k_1 - k_0\cos\theta)l_1/2} - 1)}{(k_1 - k_0\cos\theta)l_2}\right], \qquad (1)$$

where $g_0$ is a constant independent of $\theta$ but may be different for each type of DNA fragment, and $k_1$ is the (density) decay wave vector inside the molecule. An overall factor of $al_2$ exp($-k_1 l_1$) has been absorbed into $g_0$. Some of the parameters in Eq. 2 can be determined directly from the geometry. The values of $l_1$ are 1.6, 0.89, 2.7, and 0.8 Å for A, C, G, and T fragments, respectively. As discussed earlier, $k_1$ is nearly constant for all configurations, and is ~1.02/Å. The rest of the parameters are obtained after fitting Eq. 2 to the first-principles calculations.

To check whether factorization of $g$ is valid, we first examine the dependence of the conductance on $d$. In Fig. 1, we plot the normalized conductance, with the $\theta$-dependence removed in the form $g/F(\theta)$, as a function of $d$. Fitting this plot to the exponential yields $k_0 = 2.5$/Å, corresponding to a barrier height of 5.7 eV for an electron effective mass of $1m_e$. This is in good agreement with the surface work function of gold around 5.5 eV. Not surprisingly, different scaling factors are needed for each type of fragment to fit all data on a single curve, reflecting $g_0$ dependence on $l_1$ and $l_2$. The fitted parameters are $l_2 = 2$Å, and the values of $g_0$ are $2.8 \times 10^{-5}$, $2.2 \times 10^{-4}$, $3.4 \times 10^{-5}$, and $4.5 \times 10^{-4}$, in units of quantum conductance $e^2/h$, for A, C, G, and T fragments, respectively. The deviations of the first-principles results from the simple exponential are not random. They are oscillations due to quantum interference effect that is neglected in Eq. 1, and will be discussed below. For the case of the T fragment at $\theta > 60°$, the conductance drops sharply to nearly zero, possibly due to antiresonance. These data points are not included when fitting to the exponential. The cause of much higher conductance of the G fragment at small angles is clear from Fig. 1. It is due to the much smaller gap between the molecule and the electrode, which is the result of the larger size of the G fragment.

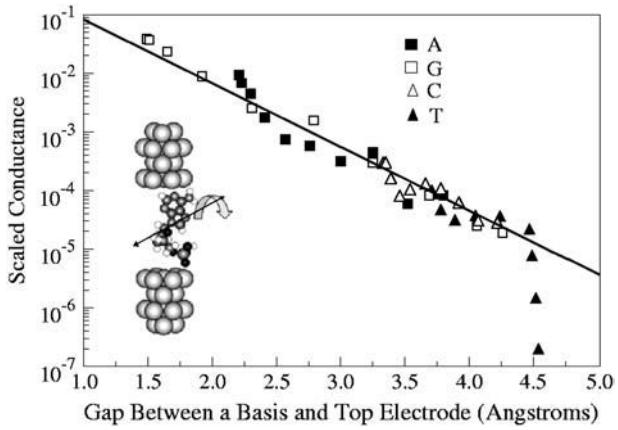


**FIGURE 1 Normalized conductance, $g/F(\theta)$, as a function of the distance between the top electrode and the nearest atom of the DNA. The solid line is the exponential exp($-k_0 d$) with $k_0 = 2.5$/Å. Inset shows the configuration of gold electrodes and a fragment containing the adenine base. The distance between the gold leads is 1.5 nm. Two unit cells of each gold lead are shown.**

Next we scale out the exponential factor, exp($-k_0 d$), from the conductance and examine the angular dependent factor, $F(\theta)$. In Fig. 2, we plot $F(\theta)$ for all of the DNA fragments and

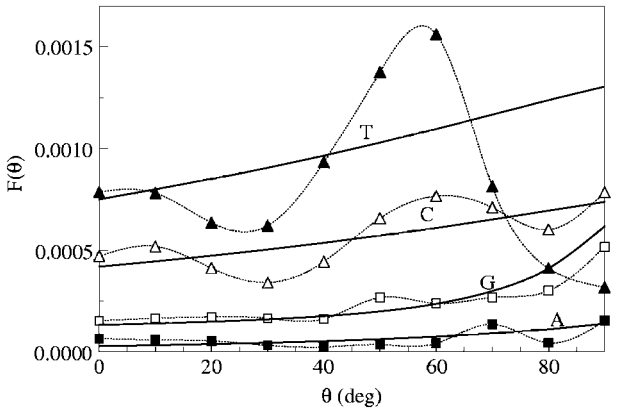


**FIGURE 2 Angular dependence of the conductance. The data for G, C, and T fragments are shifted by 0.0001, 0.0002, and 0.0003, respectively, for visibility. Solid lines are from Eq. 1.**

compare with Eq. 1. Although Eq. 1 captures the trend of the angular dependence pretty well, we see here that there are additional large oscillations in the first-principles results. These oscillations arise from the interference effect, neglected during derivation of Eq. 1, between different tunneling paths. If the complex wave vector inside the molecule has a nonzero real part, a summation of the wave function amplitudes over different tunneling paths yields a nonzero phase in the second term of Eq. 1. This can produce an oscillatory cross term in the conductance. A similar effect was predicted in Fe/MgO/Fe tunnel junctions (16).

There has been experimental evidence (17) that poor reproducibility of such geometric factors can be fatal to measurements of the DC conductance, except when strong bonds with the electrodes are formed on both ends of the molecule, a situation not desired for DNA sequencing techniques. Therefore, proposed approaches using DC measurements for DNA sequencing need to be reconsidered. This work also raises the more general question of how electronic structure is connected to the conductance of a molecule. Our work contradicts the common belief that the HOMO-LUMO gap is the determining factor of tunneling conductance, and that the conductance can be evaluated from the smeared tails of the HOMO or the LUMO due to the coupling with the electrodes. Rather, in the absence of resonance, the overwhelming factor is simply the geometric size and orientation. This factor also conveniently explains the apparent disagreement with Zwolak and Di Ventra (6), in which the A-type nucleotide was shown to have the largest conductance. Noting that due to the geometric conformation used in that work, the A has the largest size instead of the G fragment in this work. Thus in both cases the largest molecule has the largest conductance.

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## REFERENCES and FOOTNOTES

1. de Pablo, P. J., F. Moreno-Herrero, J. Colchero, J. Gomez Herrero, P. Herrero, A. M. Baro, P. Ordejon, J. M. Soler, and E. Artacho. 2000. Absence of dc-conductivity in λ-DNA. *Phys. Rev. Lett.* 85:4992–4995.
2. Porath, D., A. Bezryadin, S. de Vries, and C. Dekker. 2000. Direct measurement of electrical transport through DNA molecules. *Nature*. 403:635–638.
3. Fink, H.-W., and C. Schönenberger. 1999. Electrical conduction through DNA molecules. *Nature*. 398:407–410.
4. Xu, B., P. Zhang, X. Li, and N. Tao. 2004. Direct conductance measurement of single DNA molecules in aqueous solution. *Nano Lett*. 4: 1105–1108.
5. Stephan Roche. 2003. Sequence dependent DNA-mediated conduction. *Phys. Rev. Lett*. 91:108101.
6. Zwolak, M., and M. Di Ventra. 2005. Electronic signature of DNA nucleotides via transverse transport. *Nano Lett*. 5:421–424.
7. Church, George M. 2006. Genomes for all. *Sci. Am*. 294:47–54.
8. Langlais, V. J., R. R. Schlittler, H. Tang, A. Gourdon, C. Joachim, and J. K. Gimzewski. 1999. Spatially resolved tunneling along a molecular wire. *Phys. Rev. Lett*. 83:2809–2812.
9. Tomfohr, J. K., and O. F. Sankey. 2002. Complex band structure, decay lengths, and Fermi level alignment in simple molecular electronic systems. *Phys. Rev. B*. 65:245105.
10. Pomorski, P., C. Roland, and H. Guo. 2004. Quantum transport through short semiconducting nanotubes: A complex band structure analysis. *Phys. Rev. B*. 70:115408.
11. Wang, H., James P. Lewis, and Otto F. Sankey. 2004. Band-gap tunneling states in DNA. *Phys. Rev. Lett*. 93:016401.
12. Berlin, Y. A., A. L. Burin, and M. A. Ratner. 2002. Elementary steps for charge transport in DNA: thermal activation vs. tunneling. *Chem. Phys*. 275:61–74.
13. Zhang, X.-G., P. S. Krstić, and W. H. Butler. 2003. Generalized tight-binding approach for molecular electronics modeling. *Int. J. Quantum Chem*. 95:394–403.
14. Krstić, P. S., X.-G. Zhang, and W. H. Butler. 2002. Generalized conductance formula for the multiband tight-binding model. *Phys. Rev. B*. 66:205319.
15. Caroli, C., R. Combescot, P. Nozieres, and D. Saint-James. 1971. Direct calculation of the tunneling current. *J. Phys. C: Solid St. Phys*. 4:916–929.
16. Butler, W. H., X.-G. Zhang, T. C. Schulthess, and J. M. MacLaren. 2001. Spin-dependent tunneling conductance of Fe|MgO|Fe sandwiches. *Phys. Rev. B*. 63:054416.
17. Cui, X. D., A. Primak, X. Zarate, J. Tomfohr, O. F. Sankey, A. L. Moore, T. A. Moore, D. Gust, G. Harris, and S. M. Lindsay. 2001. Reproducible measurement of single-molecule conductivity. *Science*. 294:571–574.