Band-Gap Tunneling States in DNA

Hao Wang,[1] James P. Lewis,[1] and Otto F. Sankey[2]

[1]*Department of Physics and Astronomy, Brigham Young University, Provo, Utah 84602-4658, USA*
[2]*Department of Physics and Astronomy, Arizona State University, Tempe, Arizona 85287-1504, USA*
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An important issue regarding DNA electrical conductivity is the electron (hole) transfer rate. Experiments have found that this transfer rate involves quantum mechanical tunneling for short distances and thermally activated hopping over large distances. The electron (or hole) tunneling probability through a molecule depends on the length of molecule L, as $e^{-\beta(E)L}$, where the tunneling $\beta(E)$ factor is strongly energy dependent. We have calculated $\beta(E)$ in DNA for poly(dA)-poly(dT) and poly(dG)-poly(dC) for the first time using a complex band structure approach. Although the DNA band gap is not exceptionally large, we find that the very large β value near midgap makes DNA a poor tunneling conductor. The tunneling decay in DNA is more rapid than many other organic molecules, including those with a far wider gap.

DNA, which is the blueprint of life, is being considered as a molecular wire in a new generation of electronic devices and computers. However, its electronic properties are elusive and remain controversial. Reference [1] has an excellent review. Despite the current debate, the subject is far from new. Soon after Watson and Crick discovered the double-helix structure of DNA [2], Eley and Spivey were the first to suggest that DNA could serve as an electronic conductor [3]. The notion of a molecular wire is thought to apply to the DNA double helix because of its π-electron (the π-way) system of bases stacked upon each other. More recently, Barton and colleagues [4] measured the fluorescence of an excited molecule and found that it no longer emitted light when attached to DNA. Their results suggested that this "fluorescence quenching" was due to the charge on the excited donor molecule leaking along the length of the DNA to a nearby acceptor molecule.

Other extensive experimental and theoretical work over the past decade has led to substantial clarification of charge-transfer mechanisms in DNA [4–17]. The dominant mechanisms appear to be both short-range quantum mechanical tunneling and long-range thermally activated hopping. Guanine has the highest occupied molecular orbital (HOMO) level of the four bases, and can act as a trap for holes. Experiments on repeats of this base are used to investigate long-range hopping, and models have been developed to clarify the long-range hopping data in G repeats [13]. Charge transport in DNA is also made more complex because of the influences of the local environment, such as counterions, thermal vibrations, contact resistance, and sequence variability, which are difficult to control [18–22]. Whether DNA is a good conductor or not remains somewhat unsettled and the crucial quantitative information about its electronic structure is still missing.

In this work, we investigate the tunneling decay $\beta(E)$ factor of DNA, which is obtained from the complex band structure method [23,24]. The transmission probability of a charge is proportional to $e^{-\beta(E)L}$, where L is the tunneling distance. Our analysis here is for periodic poly(dA)-poly(dT) and poly(dG)-poly(dC) double-helix (model) DNA molecules. The complex band structure is calculated using an *ab initio* tight-binding method, call FIRE-BALL, which is based on density-functional theory (DFT) with a nonlocal pseudopotential scheme [25]. This method has already been used with success in a variety of inorganic systems and biomolecules [24–26]. In this work, we use Becke exchange [27] with Lee-Yang-Parr (LYP) correlation [28]. We choose a minimal basis set for H, C, N, and P. A double numerical basis is used for O because oxygen atoms on the phosphate groups require additional flexibility to yield correct polarization. We have performed comparison calculations using the SIESTA package [29], with equivalent basis sets as used in FIREBALL, which produced very similar results (not presented here).

The complex band structure of a periodic system is the conventional band structure extended to complex Bloch k vectors. In a "conventional" band structure calculation, one inputs a k vector for a propagating state using Bloch's theorem, and solves the Schrödinger equation for eigenvalues of energy E. In contrast, the complex band structure inputs the energy E, and the output is the k vector (now complex) that produces this energy. A generalization of Bloch's theorem is used that allows the wave function to decay or increase as one move from periodic cell to cell. References [23,24] give the mathematical details. The Bloch k vectors with an imaginary part describe spatially decaying wave functions and arise in, for example, the analysis of impurity and surface states [30,31]. They also represent the quantum tunneling states which are vehicles of electron (hole) transport through a barrier such as a thin oxide layer or a molecule [32]. Analogous to a simple square barrier, for complex Bloch k states the tunneling probability will be approximately $e^{-\beta L}$, where $\beta = 2\,\mathrm{Im}(k)$, and β is a function of

energy. Reviewing previous reports regarding DNA conductivity, much of the experimental work has focused on current-voltage characteristics [1]. These experiments are likely sensitive to a number of variables not directly related to the molecule (e.g., the nature of the contacts or the chemical environment). A key advantage of the complex band structure approach is that it takes the contacts (electrodes) and other environmental variables out of the system. The complex band structure tells us about conduction characteristics which are solely intrinsic to the molecule.

For a helical system such as DNA, Bloch's theorem refers to a pair of symmetry operations—one of translation followed by one of rotation (by 36°). This is a modification of the usual Bloch's theorem (translation only). There is no need to develop a special electronic structure code to handle this. We simply use the conventional periodic code for a unit cell of ten base pairs (one complete turn) which has translational symmetry and does not require the rotational symmetry operator to solve for the self-consistent charge and Hamiltonian matrix. Smaller Hamiltonian and overlap submatrices which treat a single base pair with translation and rotation are retrieved from the Hamiltonian and overlap matrices of the model DNA system. From these smaller submatrices, translation and rotation operators are used to generate the complex band structure for a helical system.

The input geometries of periodic poly(dA)-poly(dT) and poly(dG)-poly(dC) double-helix DNA molecules were created from the Arnott B-DNA [33] fiber model. Each base pair is rotated by 36° and translated by 3.38 Å; ten base pairs complete one full pitch of the double helix. Periodicity is enforced in our calculations. Hydrogen atoms are attached near the phosphate groups to preserve charge neutrality. Water molecules are not included as we are interested solely in the tunneling properties of the model DNA molecule. The band structure (for both complex and real k) of the poly(dA)-poly(dT) and the poly(dG)-poly(dC) periodic DNA molecules are presented by Figs. 1(a) and 1(b), respectively. The right panels show regions where the k vector is entirely real, representing the conventional band structure. The left panels show $\beta(E)$ which is twice the imaginary part of $k(E)$ for all energies E.

We first discuss the conventional band structures for poly(dA)-poly(dT) and poly(dG)-poly(dC) periodic DNA molecules. From the right panel of Fig. 1(a), we see that the poly(dA)-poly(dT) periodic double-helix DNA molecule is semiconducting with a band gap of 2.7 eV and the valance band edge occurs at $k = \pi/a$. A similar semiconducting behavior is found in poly(dG)-poly(dC) which has a smaller band gap of 2.0 eV [see right panel of Fig. 1(b)]. This finding agrees with experiment and previous calculations; however, DFT is well known to generally underestimate band gaps. In the gate-voltage dependent transport measurements, Yoo et al. [34] find that both poly(dA)-poly(dT) and poly(dG)-poly(dC)
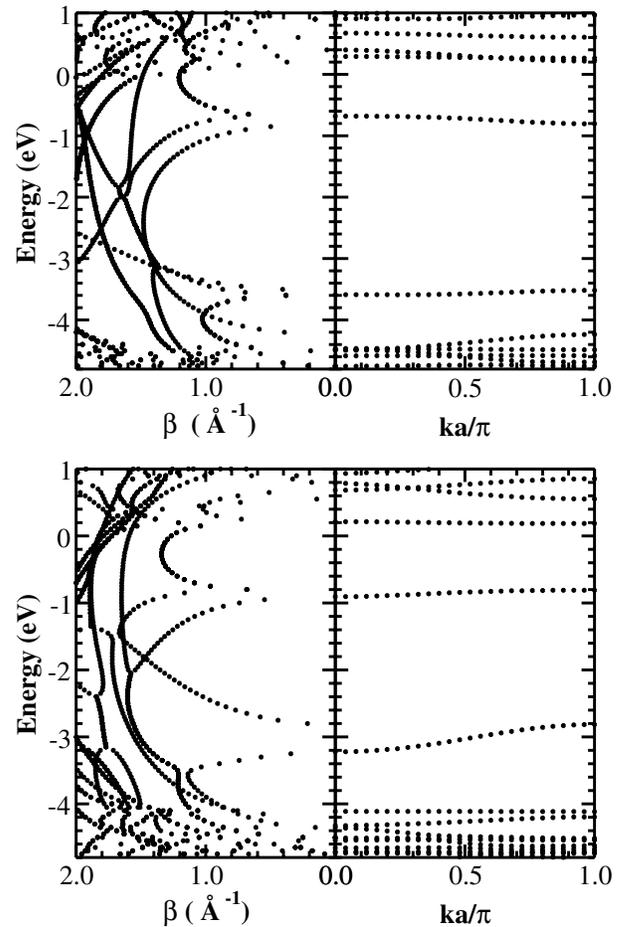
FIG. 1. The complex band structure for (a) the poly(dA)-poly(dT) and (b) the poly(dG)-poly(dC) periodic DNA double helix molecules. The right panel shows the conventional band structure $E(k)$, for real k vectors along the DNA strand, while the left panel shows the complex band structure $k(E)$, where only the imaginary part of k, $\beta(E)$, is shown.

DNA molecules are semiconducting. Our band gap of 2.0 eV for poly(dG)-poly(dC) agrees with the 2.0 eV gap reported in experiments of Porath et al. [35], and with the 2.1 eV theoretical gap obtained by Maragakis et al. [21] using a tight-binding DFT approach.

Within the band gap, there are no propagating states, but rather only exponential tunneling states. The amount of tunneling is controlled by the $\beta(E)$ curve. Within the fundamental band gap between the valence and conduction bands, there are several $\beta(E)$ curves. Since the tunneling probability decays similar to $e^{-\beta L}$ (L is the distance along the length of molecule), the states with large β values do not play a significant role in conduction. In particular, we need only to consider the smallest β states, described by the semielliptical-like curve in the band-gap energy region. This branch produces the most penetrating state and overwhelmingly dominates tunneling. The curve $\beta(E)$ reaches a maximum value near midgap. This maximum is called the branch point which is approximately where the wave function changes from valence-band character (bonding) to conduction-band

character (antibonding). For the purpose of definiteness, we identify the branch point as being that point where the β value reaches a maximum, and $dE/d\beta \rightarrow \infty$. An analysis of the left panels of Figs. 1(a) and 1(b) finds the branch point β value of $\beta_{bp} = 1.5$ Å^{-1} for both poly(dA)-poly(dT) and poly(dG)-poly(dC) periodic DNA double helices. The tunneling probability for an electron passing through one base pair ($L = 3.38$ Å) of the DNA molecule is therefore about $e^{-\beta L} = e^{-1.5 \times 3.38} \approx 6 \times 10^{-3}$.

In molecular electronics, metallic contacts are made at two ends of the molecule and electronic current is expected to be carried by electrons tunneling from the metal with energies in the band-gap region. The branch point plays an important role in the analysis of band-gap tunneling states and the electron transport properties. The branch point energy E_{bp} is an estimate for the lineup of the metal Fermi level (E_F) with the molecular levels and $\beta_{bp} = \beta(E_{bp})$ provides the tunneling decay rate. We now use this information to obtain a simple estimate of the conductance of a molecule. According to Landauer theory [36], when E_F crosses a propagating molecular state (such as the HOMO, i.e., the "valence band" of the molecule) in the real k region of the complex band structure, the low-voltage conductance of the molecule will be approximately equal to the quantum of conductance, $G_0 \approx 77$ μS. However, E_F will lie in the band gap and the conductance g will be reduced from its value of G_0 by the approximate factor $e^{-\beta_{bp}L}$, where β_{bp} is the β value of the most penetrating gap state at the Fermi level E_F and L is the length of the molecule. Using these approximations, the estimated conductance is given by $g \approx G_0 e^{-\beta_{bp}L}$.

Let us consider electron tunneling through three-base pairs ($L \approx 10$ Å); then the estimated conductance is $g(\text{DNA}) \approx G_0 e^{-\beta_{bp}L} = G_0 e^{-(1.5 \times 10)} = 2.4 \times 10^{-5}$ μS and the corresponding resistance is $R(\text{DNA}) \approx 4.2$ GΩ. We can compare this to a "typical" organic molecule wired in a molecular electronics experiment. Specifically, consider (i) alkenes, $(\text{CH})_n$, a zigzag conjugated chain with alternating single and double bonds between carbon atoms, and (ii) alkanes, $(\text{CH}_2)_n$, a zigzag chain of single sp^3 bonds between carbon atoms. The estimated conductance for an alkene chain ($\beta = 0.27$ Å^{-1} with a narrow band gap of 1.9 eV) [24] of length $L \approx 10$ Å gives $g(\text{alkane}) \approx 5.2$ μS. Similarly, for an alkane chain of the same length ($\beta = 0.79$ Å^{-1} with a very wide band gap near 10 eV) [24] it gives $g(\text{alkane}) \approx 2.9 \times 10^{-2}$ μS. This comparison emphasizes just how poor DNA is as a conductor through conventional band-gap tunneling.

Experiment and theory on DNA have reported [4–17] β values ranging from greater than 1.4 Å^{-1} to less than 0.1 Å^{-1} and there is no general agreement about the magnitude of β in duplex DNA. As has been demonstrated [15], the almost distance independent charge-transfer rate corresponding to small β value can be con-

tributed to incoherent hopping motion of the charge along the helix, while when a coherent tunneling mechanism is active $\beta > 1$. The large β value that we find at the branch point is in qualitative agreement with experimental data and calculations of others which yield $\beta \approx 1.2$–1.6 Å^{-1} [10,12,16,17]. The electronic transport properties of DNA are affected strongly by the lineup of the metal Fermi level with molecular levels since the transfer rate $\beta(E)$ is energy dependent.

To investigate the charge distribution in DNA for states near the fundamental band gap, we calculate the density of states (DOS) and projected DOS onto each base in the DNA molecules. The result for the poly(dA)-poly(dT) periodic molecule is plotted in Fig. 2. The total DOS is plotted in the upper panel, while the projected DOS onto adenine bases, thymine bases, and phosphate groups are illustrated by the lower panel. Figure 3 presents the result of the poly(dG)-poly(dC) periodic DNA molecule, where again the total DOS is plotted in the upper panel, while the projected DOS onto the guanine bases, cytosine bases, and phosphate groups are illustrated by the lower panel. Figure 2 shows that the charge density of the HOMO state resides on adenine bases while the charge density of the lowest unoccupied molecular orbital (LUMO) resides on thymine bases. For poly(dG)-poly(dC) (see Fig. 3), we see that the charge density of the HOMO state resides on guanine bases while the charge density of the LUMO state resides on cytosine bases. These findings are in agreement with the results reported by de Pablo *et al.* [20] and Maragakis *et al.* [21]. The HOMO and LUMO states lie primarily on the bases. Hence, it is believed that transport in native DNA occurs primarily along the base pairs, and the backbone plays a secondary role.

In summary, the complex band structure of poly(dA)-poly(dT) and poly(dG)-poly(dC) has been evaluated
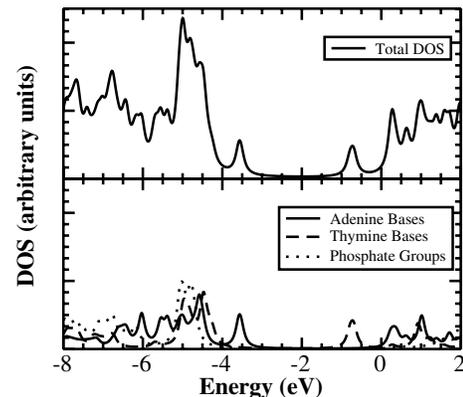
FIG. 2. The density of states (DOS) and the projected densities of states onto each type of base in poly(dA)-poly(dT) periodic DNA double helix molecules. Here, the top panel shows the DOS in the DNA molecule, while the projected DOS onto adenine bases, thymine bases, and phosphate groups are plotted in the lower panel.
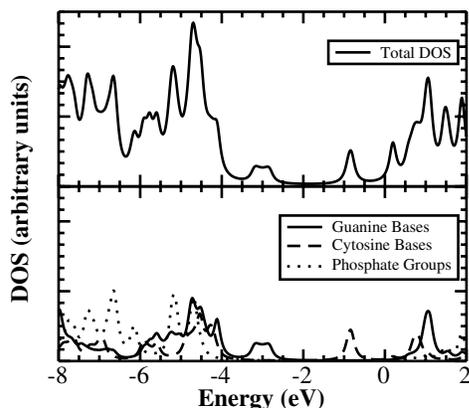
FIG. 3. The density of states (DOS) and the projected densities of states onto each type of base in poly(dG)-poly(dC) periodic DNA double helix molecules. Here, the upper panel shows the density of states in the DNA molecule, while the projected DOS onto guanine bases, cytosine bases, and phosphate groups are plotted in the lower panel.

to obtain the energy dependence of the tunneling decay constant $\beta(E)$ in DNA. The electronic structure calculations show that periodic DNA molecules have semiconductorlike band gaps. The theory reported here results in the first *ab initio* quantum mechanical calculations of the band-gap tunneling states in DNA, and find a minimum electron transfer rate for electron energies near midgap with a decay constant of $\beta = 1.5 \text{ Å}^{-1}$. Compared with other organic molecules, we find that DNA is a poor tunneling semiconductor. Based on our calculations, we conclude that periodic DNA double-helix molecules do not generally exhibit good "molecular wire" characteristics.

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