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Hole Mobility in DNA: Effects of Static and Dynamic Structural Fluctuations

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KEYWORDS:

ab initio calculations • charge carrier mobility • charge transfer • DNA damage

Charge migration in DNA is a subject of intense current study^[1–13] partially motivated by various potential applications ranging from functional nanoscale electronic devices^[14–16] to long-range detection of DNA damage.^[17, 18] A key structural element, which makes DNA an interesting medium for long-range charge transfer, is the array of stacked base pairs in the interior of the double helix with a stacking distance of ~ 3.4 Å. The overlapping π -orbitals of the nucleobases provide a pathway for motion of charge carriers generated on the stack. This “ π -pathway” resembles the columnar stacking of macrocyclic cores in mesomorphic discotic materials such as triphenylenes or phthalocyanines, which are known to have similar stacking distances (3.5 ± 0.1 Å) as found in DNA.^[19–21] The analogy becomes fairly close if one strand in the B-form duplex contains only guanine (G) bases while the other strand contains only cytosine (C) bases. Since G bases have a lower ionization potential than C bases,^[22] holes will predominantly move in such poly(G)–poly(C) oligomers along the G strand. An important factor governing charge transport in π -stacked systems is the electronic coupling between neighbouring sites.^[23] For triphenylenes this electronic coupling was calculated to be ~ 0.04 eV,^[24] which is similar to the values calculated for the coupling between nucleobases in DNA.^[25]

Based on the above common features, one might expect that charge migration in DNA and in discotic materials is equally efficient. Verification of this assumption is rather difficult due to the use of different methodologies used to quantify the efficiency of charge transport in both types of systems. In discotic materials the efficiency of charge transport along the π -stack is usually characterized in terms of the charge carrier mobility. Values for the intracolumnar mobility in discotic materials as high as ~ 0.2 cm² V^{−1} s^{−1} have been reported.^[19–21]

By contrast, it has not yet been possible to measure the mobility of charge carriers along the stack of base pairs in DNA

directly. Therefore, other quantities have been exploited for indirect characterization of the efficiency of charge transport. These include the rates of charge-transfer processes between covalently attached donors and acceptors^[13, 26, 27] and the analysis of the time-independent yields of products formed by reaction with water at different distances from the position where the charge was generated site selectively.^[3, 4, 28] There have also been reports describing direct measurements of the electrical conductivity of DNA molecules, however, since the number of charges contributing to the measured conductivity is unknown in these experiments, the mobility of the charges could not be derived.^[29–34] Experimental DC or high-frequency photoconductivity studies with known quantum yield for charge carrier generation would provide valuable information on the charge carrier mobility.

The structure of DNA dissolved in water, the condition in which most experiments have been performed, is highly disordered with dynamic fluctuations occurring on pico- and nanosecond time scales.^[35, 36] These fluctuations are expected to have a rather large effect on the ability of DNA to transport charges, since the electronic coupling between neighbouring bases depends critically on the mutual orientation (twist angle and stacking distance) of the bases.^[37, 38] Such an effect of dynamic fluctuations on the efficiency of charge transport has also been observed for discotic materials; in the liquid crystalline mesophase, where the structural fluctuations are considerable, the mobility of charge carriers is usually found to be much lower than in the rigid crystalline phase.^[19] The effects of dynamic structural fluctuations on charge transport in DNA have only been discussed qualitatively so far.

In this Communication we give a theoretical estimation of the mobility of positive charges (holes) on poly(G)–poly(C) DNA duplexes. Particular attention is paid to the effects of static and dynamic structural fluctuations.

The model used here is an extension of our previous work in which holes are described by the tight-binding Hamiltonian, Equation (1),^[8, 39, 40] with c_k^+ and c_k being the creation and annihilation operators for a positive charge on the k -th G base with a site energy ε_k .

$$H = \sum_{k=1}^N \varepsilon_k c_k^+ c_k - \sum_{k=1}^{N-1} b(R_{k+1,k}(t), \varphi_{k+1,k}(t)) (c_k^+ c_{k+1} + c_{k+1}^+ c_k) \quad (1)$$

The motion of holes is coupled to structural fluctuations of the poly(G)–poly(C) duplex via the dependence of electronic coupling for hole transfer, b , on the distance between neighboring bases R and on their mutual orientation φ . This motion was simulated numerically using the time-dependent self-consistent field (TDSCF) approach.^[41, 42] Note that the TDSCF method should be used with some care. It is known that this method yields exact results only for noninteracting degrees of freedom. If the couplings are weak, as in the cases with significant separation in effective masses or frequencies of individual modes, the TDSCF approximation also works very well. However, for hole motion coupled with dynamic disorder the coupling can be strong. In this situation the TDSCF approach remains accurate only for short times and can yield unreliable results for times that exceed the timescale of the base pair motion (~ 1 ps) by more

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than an order of magnitude.^[41, 42] Such timescales are not considered in the work here. The wavefunction of the charge was taken as a time-dependent linear combination of the HOMO orbitals on G bases. Initially, a hole was assumed to be localized on a single G base in the middle of the poly(G)–poly(C) chain. Propagation of the wave function in time yields the mean-squared displacement of charges moving along stacked G bases. In the simulations the total number of base pairs in the chain, N , was large enough to avoid chain end effects.

Two types of dynamic structural fluctuations were considered: twisting of the base pairs around the equilibrium twist angle $\varphi_{\text{eq}} = 36^\circ$ and vibrations of base pairs around the equilibrium distance $R_{\text{eq}} = 3.4 \text{ \AA}$ in the direction of the double helix axis. Both dynamic modes were described classically as two sets of coupled harmonic oscillators with vibrational and rotational force constants denoted by K and F , respectively. The mass and the moment of inertia around the twisting axis were derived from the geometry of a GC base pair and found to be $4.8 \times 10^5 \text{ au}$ and $1.7 \times 10^7 \text{ au}$, respectively. The initial angular velocities of G bases, the interbase distances, and twisting angles were sampled from the Boltzmann distribution. The simulated results described below were obtained for 293 K by averaging over 1000 realizations of the initial conditions, which was found to be sufficient for numerical convergence. Note that, apart from the fluctuations considered here, there are additional types of deviations from the regular B-DNA structure that can affect the charge transfer integral.^[38] In this work we have selected the two degrees of freedom that are expected to be most influential on the ability of DNA to transport charges. Future work should of course include the additional degrees of freedom.

The calculations require a detailed knowledge of the electronic coupling as a function of the inter-base distance and the twist angle, since these dependencies are responsible for the effect of structural fluctuations on hole transport. This information was obtained from DFT calculations using the Amsterdam Density Functional (ADF) program^[43] with the Becke–Perdew exchange–correlation functional and a triple zeta basis set including polarization functions. Geometries for stacked guanine bases at different twist angle were generated using the SCHNARP program.^[44]

The ADF program offers the unique possibility to analyze the wavefunction in terms of so-called fragment orbitals. This means that the orbitals of the stacked DNA bases (for example, a guanine dimer) can be expressed in terms of the orbitals of the stacked fragments (that is, the individual bases). The electronic coupling b between the HOMO orbitals of the guanine bases is related to the energies of the HOMO and the HOMO-1 in the dimer and the normalized orbital coefficients in terms of the fragment orbitals by Equation (2).

$$b = (E_+ - E_-)c_A c_B \quad (2)$$

In this expression E_+ and E_- are the energies of the antibonding and bonding combinations of the fragment orbitals, and c_A and c_B are the orbital coefficients of the HOMOs of the individual guanine nucleobases in the antibonding orbital.

Equation (2) is the exact solution for the charge transfer integral in the case of a two-state problem but can be applied to obtain an approximate value for the effective transfer integral in cases where the dimer orbitals (HOMO and HOMO-1) predominantly consist of the HOMOs in the separate bases.^[45] In our case the HOMO and HOMO-1 of the dimer were indeed found to consist mainly of contributions from the HOMO orbitals of the individual G bases, which justifies the use of Equation (2). This procedure, using the fragment orbital coefficients, simplifies the evaluation of the electronic coupling for asymmetric dimers as compared to the procedure used in recent work of Voityuk et al.,^[25] where an electric field was used to bring both bases in resonance.

The dependence of b on the twist angle φ is shown in Figure 1. At zero twist the coupling has its maximum value of 0.26 eV. The coupling goes through a minimum at 22° and

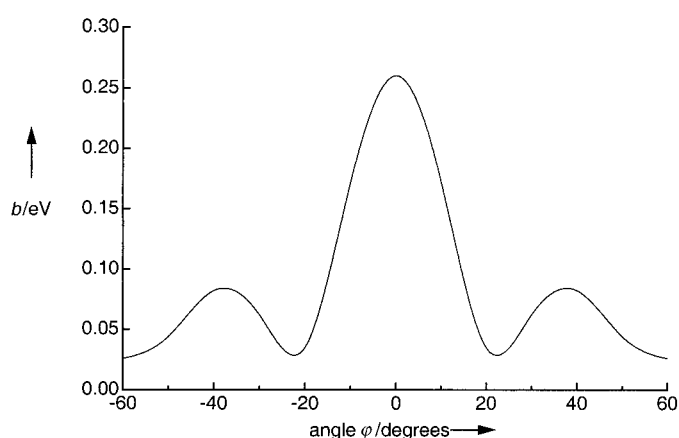


Figure 1. Electronic coupling b for hole transfer between guanine bases at different twist angles φ .

exhibits a local maximum close to the equilibrium angle $\varphi_{\text{eq}} = 36^\circ$. The b value at 36° (0.083 eV) agrees closely with the result obtained by Voityuk et al. (0.084 eV) from Hartree–Fock calculations. Ladik et al. have performed bandstructure calculations on regular (poly(G)–poly(C)) DNA structures and found for the valence band a bandwidth of 0.282 eV which corresponds to a transfer integral of 0.07 eV^[46] which is also in good agreement with our value in the equilibrium geometry for B-DNA. Near the equilibrium distance the electronic coupling b decreases with the inter-base distance R , following the exponential dependence $b = b_0 \exp(-\alpha R)$ with $\alpha = 1.7 \text{ \AA}^{-1}$.

The effect of twisting on the motion of holes was examined by performing simulations with $K = 0.85 \text{ eV \AA}^{-2}$ (see ref. [47]) and different values of the rotational force constant F . As follows from the results presented in Figure 2, the mean-squared displacement of moving holes $\langle x^2(t) \rangle$ increases linearly with time t for all F values used in the calculations. Such behavior is typical for normal diffusive transport with a time-independent diffusion coefficient $D = \langle x^2(t) \rangle / (2t)$. This makes it possible to obtain the intrastack hole mobility μ from the Einstein relation, $\mu = eD/kT$, where e is the elementary charge, T is the temperature, and k is the Boltzmann constant.

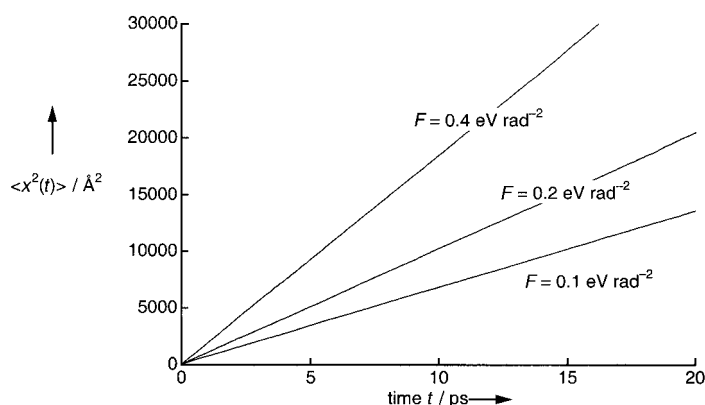


Figure 2. Mean-squared displacement of a hole for different values of the rotational force constant F .

The data summarized in the first four lines of Table 1 demonstrate that μ increases with F , approaching the limiting value of $22 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$ as $F \rightarrow \infty$, namely when the twist motion is "frozen" and $\varphi = \varphi_{\text{eq}} = 36^\circ$. In other words, stiffness of the base pair configuration inside the stack enhances the intrastack mobility. This tendency is consistent with the calculated angular

$F [\text{eV rad}^{-2}]$	$\sigma [\text{eV}]$	$\mu [\text{cm}^2 \text{V}^{-1} \text{s}^{-1}]$
0.1	0.0	1.3
0.2	0.0	2.0
0.4	0.0	3.7
∞	0.0	22.0
0.2	0.1	0.2
0.2	0.2	0.04

dependence of electronic coupling (see Figure 1). Indeed, DFT calculations show that the coupling is most efficient near 36° , thus providing the highest intrastack hole mobility. However, this optimal orientation of G bases can exist only if F is infinitely large; otherwise thermally induced twisting motion will vary the stack geometry away from that most favorable for hole transport. Then the mobility of charge carriers will be controlled by the dependence of the electronic coupling on the twist angle. Thermal twisting motion may involve G bases with twist angles deviating from 36° by about $\sim 30^\circ$ for $F = 0.2 \text{ eV rad}^{-2}$. Simple probabilistic analysis shows that such deviations are more likely as F decreases. Therefore the mobility should decrease for less stiff stacks, in agreement with the results of our simulations.

So far we have considered poly(G)–poly(C) duplexes as dynamically disordered systems with identical site energies ε_k along the stack of base pairs. The values of ε_k were taken to be equal to the ionization potential of G bases. In reality, however, site energies can deviate from this value by 0.1–0.2 eV. Such deviations can be caused by inherent disorder in the surrounding water and by the inhomogeneous distribution of counterions along the DNA duplex.^[5] Energetic disorder can also be of an intramolecular nature. It was shown recently that the nature of neighbouring bases can cause site energies to fluctuate consid-

erably.^[48] Both types of disorder can cause changes of site energies of at least the same order of magnitude as b , and should therefore not be neglected.

To include static energy disorder in the simulations, the site energies were sampled from a Gaussian distribution with the root-mean-square deviation σ . The time-dependence of $\langle x^2(t) \rangle$ was computed for a given value of σ as described above. Similar to the case of dynamic fluctuations associated with twisting of G bases, the mobility of holes was derived from the slope of the calculated dependence $\langle x^2(t) \rangle$ versus time (see Figure 3) using

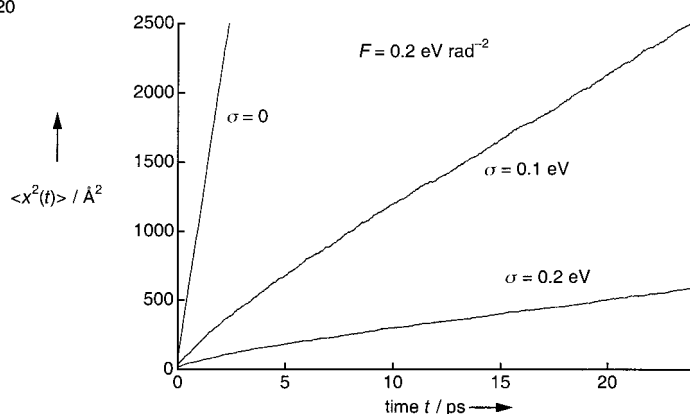


Figure 3. Effect of Gaussian site-energy disorder on the mean-squared displacement of a hole for a fixed rotational force $F = 0.2 \text{ eV rad}^{-2}$.

the Einstein relation. Based on the results obtained (two lower lines in Table 1), we infer that a spread in site energies comparable with the average electronic coupling strongly reduces the hole mobility. For instance, the value $\mu = 0.2 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$ estimated for the poly(G)–poly(C) duplex with $F = 0.2 \text{ eV rad}^{-2}$ and $\sigma = 0.1 \text{ eV}$ turns out to be less than the mobility for the analogous system without static energy disorder ($\sigma = 0$) by one order of magnitude. An increase of the disorder to $\sigma = 0.2 \text{ eV}$ decrease the mobility by another factor of five ($\mu = 0.04 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$).

In conclusion, the mobility of holes in ideally ordered poly(G)–poly(C) duplexes can be of the order of $10 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$. Twisting of base pairs and disorder in the site energies reduce the value of this transport coefficient significantly. For realistic rotational force constants and static energy disorder, we predict a hole mobility $0.1 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$. This is comparable to the values found experimentally for discotic materials. For DNA duplexes with base pair sequences containing all types of nucleobases we expect the mobility to be much lower since the static disorder introduced by differences in ionization potentials is much higher than the largest degree of static disorder considered here. Indeed, the calculations of the hopping conductivity by Ladik and co-workers for random sequences of DNA show that rather low mobilities are obtained for such sequences.^[49, 50]

We thank A. A. Voityuk for helpful comments via electronic mail. The Priority Program for Materials (PPM) research of the Netherlands Organization for Scientific Research (NWO) is acknowledged

for financial support. The High Performance Applied Computing Centre (HPAC) of the Delft University of Technology is acknowledged for granting access to supercomputing facilities.

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Received: January 16, 2002 [Z362]

A Cylindrical Polymer: A Stack of Discotic Triphenylene Within Comblike Polymethacrylate

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KEYWORDS:

fluorescence · polymers · self-assembly

Polymers of triphenylene derivatives have excellent photophysical and electronic properties and have thus received much attention due to their applications in large-area light-emitting devices (LEDs) and molecular energy guides,^[1, 2] and because of their relation to biological energy transduction in natural photosynthesis.^[3] Their interesting properties arise due to their ordered structures. For example, a series of 2,3,6,7,10,11-hexakis(*n*-alkoxy)triphenylenes display columnar liquid-crystalline phases which consist of microdomains. In each microdomain, the columns are hexagonally packed and the distance between two neighboring columns is about 20.2–24.3 Å, depending on the flexible alkyl chain length; the intramolecular distance inside the column is 3.6 Å.^[2, 4] In the columnar liquid-crystalline state of hexapentyl oxytriphenylene, the charge carrier mobilities exceed that of commercially available polymers by three order of magnitude.^[5] The fluorescence spectra of hexa-*n*-hexoxytriphenylene (C6HET) in 1,2-dichloroethane and in the crystalline phase with $\lambda_{\text{ex}} = 280$ nm exhibit the same maximum, at 385 ± 2 nm, but, in the columnar mesophase, the spectrum is slightly shifted to 393 ± 2 nm.^[6]

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