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Frenkel exciton model of ultrafast excited state dynamics in AT DNA double helices

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Abstract

Recent ultrafast experiments have implicated intrachain base-stacking rather than base-pairing as the crucial factor in determining the fate and transport of photoexcited species in DNA chains. An important issue that has emerged concerns whether or not a Frenkel excitons is sufficient one needs charge-transfer states to fully account for the dynamics. Here we present an $SU(2) \otimes SU(2)$ lattice model which incorporates both intrachain and interchain electronic interactions to study the quantum mechanical evolution of an initial excitonic state placed on either the adenosine or thymidine side of a model B DNA poly(dA).poly(dT) duplex. Our calculations indicate that over several hundred femtoseconds, the adenosine exciton remains a cohesive excitonic wave packet on the adenosine side of the chain where as the thymidine exciton rapidly decomposes into mobile electron/hole pairs along the thymidine side of the chain. In both cases, the very little transfer to the other chain is seen over the time-scale of our calculations. We attribute the difference in these dynamics to the roughly 4:1 ratio of hole versus electron mobility along the thymidine chain. We also show that this difference is robust even when structural fluctuations are introduced in the form of static off-diagonal disorder.

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Keywords: DNA; Molecular biophysics; Excited states; Lattice theory; Quantum chromodynamics

1. Introduction

For all life-forms on Earth with the exception of certain viruses, genetic information is carried within the cellular nucleus via strands of strands of deoxyribonucleic acid (DNA). The genetic information itself is encoded in the specific sequence of the nucleic acid bases: adenine (A), thymine (T), guanine (G), and cytidine (C). DNA is also a strong absorber of ultraviolet light leaving it highly susceptible to photomutagenic damage with the primary photoproducts being bipyrimidine dimers linking neighboring T bases. For all organisms, this susceptibility is compensated for in part through enzymatic repair actions that remove damaged segments along one strand using the complementary strand as a template for replacement. Such repair mechanisms are quite costly energetically. Remarkably, however, DNA is intrinsically photochemically stable as single bases are able to rapidly convert photoexcitation energy into thermal energy on a picosecond time scale through non-radiative electronic processes. What remains poorly understood is the role that base-pairing and base-stacking plays in the transport and migration of the initial excitation along the double helix. Clearly, such factors are important since the UV absorption of DNA largely represents the weighted sum of the absorption spectra of it constituent bases whereas the distribution of lesions formed as the result of photoexcitation are generally not uniformly distributed along the chain itself and depend strongly upon sequence, suggesting some degree of coupling between bases [1].

Given the importance of DNA in biological system and its emerging role as a scaffold and conduit for electronic transport in molecular electronic devices [2], DNA in its many forms is a well-studied and well-characterized system. What remains poorly understood, however, is the role that base-pairing and base-stacking plays in the transport and migration of the initial excitation along the double helix [3,1]. Such factors are

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Recent work by various groups has underscored the different roles that base-stacking and base-pairing play in mediating the fate of an electronic excitation in DNA [1,3]. Over 40 years ago, Lowdin discussed proton tunneling between bases as a excited state deactivation mechanism in DNA [4] and evidence of this was recently reported by Schultz et al. [5]. In contrast, however, ultrafast fluorescence of double helix poly(dA).poly(dT) oligomers by Crespo-Hernandez et al. [3] and by Markovitsi et al. [1] give compelling evidence that base-stacking rather than base-pairing largely determines the fate of an excited state in DNA chains composed of A and T bases with long-lived intrastrand states forming when ever A is stacked with itself or with T. However, there is considerable debate regarding whether or not the dynamics can be explained via purely Frenkel exciton models [6–8] or whether charge-transfer states play an intermediate role [9].

Here we report on a series of quantum dynamical calculations that explore the fate of a localized exciton placed on either the A side or T side of the B DNA duplex poly(dA)$_{10}$.poly(dT)$_{10}$. Our theoretical model is based upon a $SU(2)\otimes SU(2)$ lattice model we recently introduced [10] that consists of localized hopping interactions for electrons and holes between adjacent base pairs along each strand (t_{aj}) as well as cross-strand terms linking paired bases (h_i) and "diagonal" terms which account for the π-stacking interaction between base j on one chain and base $j\pm1$ on the other chain ($r_i^{\pm}$) in which r_j^- denotes coupling in the 5′-5′ direction and r_i^+ coupling in the 3′-3′ direction. Fig. 1 shows the three-dimensional structure of poly(dA)$_{10}$.poly(dT)$_{10}$ and the topology of the equivalent lattice model. We also consider here the role of geometric or structural fluctuations in the electronic dynamics.

2. Theoretical model

Taking each link as Fig. 1 as a specific electron, hole, or excitonic, hopping term, we arrive at the following single particle Hamiltonian,

$$h_1 = \sum_j \epsilon_j \hat{\psi}_j^\dagger \hat{\psi}_j + t_j(\hat{\psi}_{j+1}^\dagger \hat{\psi}_j + \hat{\psi}_j^\dagger \hat{\psi}_{j+1}) + h_j \bar{\psi}_j \hat{\psi}_j + \hat{\psi}_{j+1}^\dagger (r_j^+ \hat{\gamma}_+ + r_j^- \hat{\gamma}_-)\hat{\psi}_j + \hat{\psi}_j^\dagger (r_j^+ \hat{\gamma}_+ + r_j^- \hat{\gamma}_-)\hat{\psi}_{j+1} \quad (1)$$

where $\hat{\psi}_j^\dagger$ and $\hat{\psi}_j$ are $SU(2)$ spinors that act on the ground-state to create and remove an electron (or hole) on the jth adenosine or thymidine base along the chain. The $\hat{\gamma}$ operators are the 2×2 Pauli spin matrices with $\bar{\psi}_j = \hat{\gamma}_1 \hat{\psi}_j^\dagger$ and $\hat{\gamma}_+ + \hat{\gamma}_- = \hat{\gamma}_1$ providing the mixing between the two chains. As discussed in Ref. [10], we used the highest occupied and lowest unoccupied (π and π^*) orbitals localized on each base as a orthonormal basis. For the single particle terms (representing electron and hole transfer between bases), we use values reported by Mehrez and Anantram as determined by computing the Coulomb integrals between HOMO and LUMO levels on adjacent base pairs with in a double-strand B DNA sequence using density functional theory (B3LYP/6-31G) [11] taking the geometries of each base from the B-DNA structure. When $r_j^+ = r_j^-$, Eq. (2) is identical to the Hamiltonian used by Creutz and Horvgath [12] to describe chiral symmetry in quantum chromodynamics in which the terms proportional to r are introduced to make the "doublers" at $q\propto\pi$ heavier than the states at $q\propto0$.

Taking the chain to homogeneous and infinite in extent, one can easily determine the energy spectrum of the valence and conduction bands by diagonal-izing

$$\hat{h}_1 = \begin{pmatrix} \epsilon_a + 2t_a\cos(q) & h + r^+e^{-iq} + r^-e^{+iq} \\ h + r^+e^{+iq} + r^-e^{-iq} & \epsilon_b + 2t_b\cos(q) \end{pmatrix} \quad (2)$$

where $\epsilon_{a,b}$, and $t_{a,b}$ are the valence band or conduction band site energies and intra-strand hopping integrals. When $r_j^+ = r_j^-$, Eq. (2) is identical to the Hamiltonian used by Creutz and Horvgath [12] to describe chiral symmetry in quantum chromodynamics in which the terms proportional to r are introduced to make the "doublers" at $q\propto\pi$ heavier than the states at $q\propto0$. In particular, we note that when $t = h/2r$, the band closes at $q = \pm\pi$ but has a gap at $q = 0$.

The single particle parameters are taken from Mehrez and Anantram as determined by computing the Coulomb integrals between HOMO and LUMO levels on adjacent base pairs with in a double-strand B DNA sequence using density functional

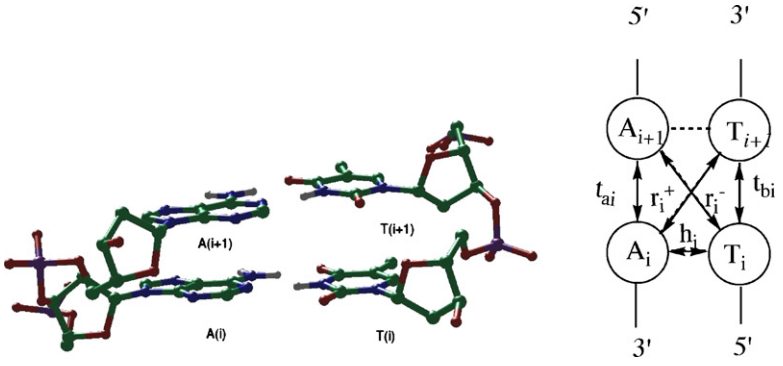

Fig. 1. Three-dimensional structure of stacked A–T base pairs along with the corresponding lattice model.