

Charge transfer in DNA

- Role of structural fluctuations

Dissertation submitted by **Parag Ghosh**

Date: 15.10.2001

Introduction

The question whether or not DNA is able to conduct electrical charges has been addressed as early as 1960. But in spite of several attempts to understand the mechanism of charge transfer through DNA molecules in the past, the issue remained debatable. In the last decade, fluorescence quenching measurements on DNA strands doped with donor and acceptor molecules, drew more attention to the subject. But the major breakthrough came in the year 2000, from direct measurement of electrical transport through 10.4 nm-long DNA molecules by Porath et al [2]. Their results suggested a large-bandgap semiconducting behavior and a transport mechanism that were mediated by the molecular energy bands of DNA.

Motivation

The interest in the issue is not only from biological considerations but with the advent of molecular electronics DNA seems to be a promising candidate in the application of functional nano-electronic devices. There has been evidence that photo-induced radical cations can travel large distances (about 10 base pairs) along DNA molecules in aqueous solution. This project DNA as flexible, molecular-sized wires in aqueous solutions. The observed non-linear current-voltage characteristics suggest that DNA molecules be good molecular semiconductors.

Aim: This essay discusses the mechanism of charge transport induced by

structural fluctuations in the DNA [1]. It attempts to explain the two step decay process observed by Barton and Zewail using femtosecond spectroscopy.

DNA has the special double-helix structure with overlapping π orbitals in adjacent base pairs. Tunneling along overlapping π orbitals give us a possible mechanism for charge transfer along the DNA molecule. What Barton and Zewail [3] obtained from their femtosecond spectroscopy measurement was an unusual two-step decay process with characteristic time scales of 5 and 75 ps respectively. Ab-initio molecular-orbital calculations on the other hand yields a charge transfer rate that is much larger compared to what have been obtained by Barton and Zewail [3]. This indicates that coherent tunneling between the π orbital is not the correct description of what we are dealing with.

One of the alternative transport mechanisms that have been proposed suggests that the electron waves are fully localized at subsequent base pairs and the incoherent electron hopping is actually phonon mediated. This description indeed reduces the transfer rate to a typical intra-molecular vibrational frequency (ps^{-1}) but would still be inadequate to explain the second step of decay.

The idea discussed here is as follows: The results of thermal fluctuations are large structural disorders which interferes with the π orbital overlap. This changes the tunneling frequency and leads to long relaxation times. A model Hamiltonian has been proposed to treat charge transfer along a single strand of the DNA molecule under conditions of large structural fluctuations [1].

The model is simplified to include only two collective modes: The first mode is an angular variable $q(t)$, which is the relative rotation angle between the two bases. This angle couples with the corresponding angle between the next base pairs through the tunneling matrix element. The second collective mode is the displacement variable $y(t)$ that represents the displacement of the bases from their equilibrium value. This variable couples most effectively with the onsite energy of the radical. There is a thermal reservoir in the model that provides the energy required for the hopping of charges along the chain. The energy flow between the thermal reservoir and the charges is

connected mediated by the coupling between the displacement variable and the onsite energies. Treating the variables $q(t)$ and $y(t)$ as classical harmonic variables one can write down the corresponding Langevin equations. If we neglect mode coupling between adjacent base-pairs, then the Hamiltonian for single particle charge transfer can be written as:

$$\begin{aligned}
H = \sum_i \tau(\theta_{i,i+1})(c_{i+1}^\dagger c_i + c_i^\dagger c_{i+1}) + \epsilon_i c_i^\dagger c_i + \frac{1}{2} I_i (\dot{\theta}_{i,i+1}^2 + \Omega_{\theta,i}^2 \theta_{i,i+1}^2) \\
+ \sum_i \left\{ \frac{1}{2} M_i (\dot{y}_i^2 + \Omega_{y,i}^2 (y_i + y_{0,i} c_i^\dagger c_i)^2) \right\} + H_{bath}(\{\theta, y\})
\end{aligned} \tag{1}$$

In eq.(1), τ is the tunnel matrix element, ϵ_i is the onsite energy, I is the reduced moment of inertia for the relative rotation of the two adjacent bases, Ω_θ is the oscillator frequency of the rotation mode, while M and Ω_y are the reduced mass and natural frequency of the displacement mode. The operator c_i annihilates a charge at the i^{th} site while c_{i+1}^\dagger creates a charge at the $(i+1)^{th}$ site. So the first term denotes the hopping from site i to $i+1$ and vice versa. The second term is the self energy while the third term denotes the rotational energy of the bases. The distance $y_{0,i}$ is the change in the equilibrium value of the y variable of the i^{th} base when the particle localizes at that site, while $M\Omega^2 y_0^2$ is the deformation energy.

Taking certain limits of the above Hamiltonian transforms it to the more well known forms obtained from studies of one-dimensional charge transport. For uniform ϵ_i and for fixed θ , H is the Hamiltonian for tight-binding polaron. For fixed θ and y and random ϵ_i , H is the Hamiltonian for Anderson Localization in one dimension. For the case of DNA, it is assumed that the site-to-site differences in the onsite energy ϵ_i is of the order of 0.1eV based on sequence dependent ionization potential. It is through the random onsite energy that the sequence specificity is taken into account.

As can be seen easily the above Hamiltonian can not be diagonalized exactly. So we take recourse to certain approximations. First we assume, that the transfer integral $\tau(\theta)$ to be small compared to the thermal energy $k_B T$ for θ near a special value θ^* . Secondly, the characteristic interaction energy between the charged radical and the onsite structural variable y is assumed

to be large compared to $k_B T$ and of the order of ϵ . This limit is called the strong coupling limit and the hopping that takes place in this limit is dominated by incoherent hopping.

Now let us now consider hopping from site A to site B. It can be shown that in the high temperature, strong coupling limit described above, the onsite probability decays exponentially with a rate:

$$\Gamma(\theta) \approx \frac{\tau(\theta)^2}{\hbar} \left[\frac{\pi}{E_r k_B T} \right]^{1/2} \exp(-E_f/k_B T) \quad (2)$$

where E_r is defined as the difference of the onsite energies. Since we want that the less likely states to have low charge transfer rates, so we assume that $\tau(\theta)$ is appreciable only when θ is close to a special value θ^* .

Lets assume that at time $t = 0$ an ensemble of particles is prepared at site A. Now if the $\theta(0)$ variable obeys Boltzmann distribution then the equation for probability density of the particles to be on site A, yields two decay rates depending on the energy of the oscillator:

(1) *Early stage decay:* The fraction of the oscillators which have energy more than $(1/2)I(\Omega_\theta \theta^*)^2$ will be removed from the oscillator within a time of order $\max\{\tau_\theta, \Omega_\theta^{-1}\}$.

(2) *Late stage decay:* After the high energy oscillators have been removed from the distribution, further decay requires diffusion along the oscillator scale from energies lower than $(1/2)I(\Omega_\theta \theta^*)^2$. It is found that the rate for late stage decay is equal to the rate for the early stage multiplied by the thermal probability that θ exceeds θ^* . Hence one can conclude that the second stage decay rate strongly increases with temperature and is consistent with the result obtained by Barton and Zewail [3] if the thermal probability of θ^* is of the order of 10^2 .

Conclusion: So when we take the high temperature strong coupling limit, the model does predict the behaviour predicted by Barton and Zewail in certain ranges of the thermal probability. Also the fact that charge transfer rate strongly increases with temperature is consistent with experimental observations.

There are several limitations to the model we have considered. Not only have we considered the strong coupling limit to solve the Hamiltonian, we are also limited to considering the next nearest neighbor hopping process. The third approximation used is that there is no mode coupling between different pairs of adjacent bases. The model fails to take into account the charge transfer from one strand of the molecule to the other.

A better description of the mechanism discussed here would be to consider the transfer process as a repeated sequence of reversible oxidation-reduction reactions. The site-to-site hopping of charges can be viewed as a chemical reaction dominated by a transition state where the collective variables assume special values θ^* and y^* .

References

- [1] Bruinsma R., Gruner G., D'Orsogna M.R., Rudnick J., Preprint cond-mat/**0005200**
- [2] Porath D., Bezryadin A., de Vries S., Dekker C., *Nature* **403** (2000) 635,
- [3] Wan C., Fiebig T., Kelley S.O., Treadway C., Barton J., Zewail A.H., *Proc. Natl. Acad. Sci. (USA)* **96** (1996) 6014
- [4] Li X., Yan Y., Preprint cond-mat/**0107015**