

Hole Mobility in (GC)_n Polynucleotides

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Abstract. The method based on self consistent solution of quantum-mechanical system with temperature fluctuations described by Langevine equations is developed to calculate the charge carrier mobility in a (GC)_n polynucleotide chain. The value obtained is used to explain conductance measurements of DNA molecules.

Keywords: DNA, mobility, Kubo formula, hole transfer rate.

Recent measurements have demonstrated with certainty that a charge can migrate in DNA over a long distance [1–4]. Interest in DNA charge transfer has been spurred by its relevance to potential applications in molecular electronics [5,6]. Of special concern is the problem of the mobility of charge carriers in DNA in the context of possible use of DNA-wires in nanoelectronics [7]. The authors of [8] have conducted direct measurements of the conductivity of single guanine-cytosine (GC)_n polynucleotide strand in aqueous solution.

The aim of this sketch is to compare experimental and calculated values for Poly(GC)/Poly(CG) duplex DNA (Fig.1). By now it has been determined reliably enough that in guanine-cytosine polynucleotides, a charge is transferred as a result of a hole migration over guanine bases, predominantly along one strand [9–11].

In modeling the process of transfer we consider the nucleotide sequence as a system of sites in which each site corresponds to a base pair. The Hamiltonian H of charge transfer along the chain of sites has the form [12]:

$$\begin{aligned} H &= H_e + T_K + U_P, \\ H_e &= \sum_i \alpha_i a_i^+ a_i + \sum_{i,j} v_{i,j} a_i^+ a_j, \quad \alpha_i = \alpha_i^0 + \alpha_i' u_i, \\ T_K &= v \sum_i M_i \dot{u}_i^2 / 2, \quad U_P = \sum_i K_i u_i^2 / 2, \end{aligned} \quad (1)$$

where H_e is Hamiltonian of a hole, a_i^+, a_i are operators of the creation and annihilation of a hole at the i -th site, α_i is the energy of a hole at the i -th site, $v_{i,j}$ are matrix elements of the transition from the i -th site to the j -th one. T_K is the kinetic energy of the sites, M_i is the mass of the i -th site, u_i is the displacement of the i -th site from its equilibrium position, U_P is the potential energy of the sites, K_i are elasticity coefficients. It is assumed that the energy of a hole at the sites is the linear function of the site displacements u_i from their equilibrium positions, α_i' is a constant of a hole interaction with the site displacements, $i = 1, \dots, N$, N is the number of sites in the chain. We choose the wave function of a hole $|\Psi\rangle$ in the form

$$|\Psi\rangle = \sum_{n=1}^N b_n |n\rangle, \quad (2)$$

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where b_n is an amplitude of the probability of hole occurrence at the n -th site, and derive from Hamiltonian (1) in the neighbouring approximation the following motion equations:

$$i \hbar \frac{d b_n}{d t} = (\alpha_n + \alpha'_n u_n) b_n + v_{n,n+1} b_{n+1} + v_{n-1,n} b_{n-1}, \quad (3)$$

$$M_n \frac{d^2 u_n}{d t^2} = -K_n u_n - \gamma_n \frac{d u_n}{d t} - \alpha'_n |b_n|^2 + A_n(t). \quad (4)$$

Equations (3) are Schroedinger equations for the probability amplitudes. To take into account the processes of dissipation, classical motion equations (4) are modified in such a way as to add the term $-\gamma_n \dot{u}_n$, γ_n being the friction coefficient, and random force $A_n(t)$ with the following statistical characteristics:

$$\langle A_n(t) \rangle = 0, \quad \langle A_n(t) A_m(t+t') \rangle = 2k_B T \gamma_n \delta(t'),$$

where T [K] is the temperature. So the site motion is described by the Langevine equation.

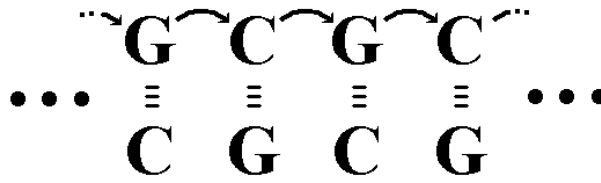


Figure 1. Hole transfer on single strand

In modeling the motion of a hole in sequences of Fig.1 we will consider hole migration over guanine bases along one DNA strand (Fig.1). To calculate the hole mobility we have chosen the following parameter values. According to [13], the values of matrix elements along the chain are $v_{GC} = 0,11$ eV, $v_{CG} = 0,042$ eV (5'-3' direction). As is shown in [14], matrix elements calculated in [13] yield good agreement with experimental data on relevant rates of charge transfer in DNA. The values $\alpha' = 0,13$ eV/Å, $\Omega = \sqrt{K_n/M_n} = 10^{12}$ sec⁻¹, $\gamma' = \gamma_n/M_n = 6 \cdot 10^{11}$ sec⁻¹ have been chosen the same as in the calculations of the mobility in homogeneous Poly(G)/Poly(C) nucleotide helix [15]¹. Notice that our parameter values are close to those calculated by quantum-mechanical methods in [16] $\alpha'_G = 0,2349$ eV/Å.

For numerical integration of the dimensionless Cauchy system corresponding to (3,4) we used the scheme of [17]. In the calculations, the normalizing condition was fulfilled with calculation accuracy $|\sum |b_n|^2 - 1| < 0,0001$. The initial conditions for the displacements and site velocities were taken from the equilibrium distribution at the prescribed temperature. At the initial moment, the charge was assumed to be localized in the middle of the chain consisting of 499 sites (at the 250-th site).

We calculated 500 realizations at the prescribed temperature $T = 300$ K. The coefficients $b_n(t)$ thus found were used to calculate the root-mean-square displacement of a hole $X^2(t) = \langle \Psi(t) | n^2 a^2 | \Psi(t) \rangle = \sum_n |b_n(t)|^2 n^2 a^2$, where a is the distance between neighboring sites, $a \approx 3,4$ Å. The mobility was calculated by the Kubo formula [15,18]

$$\mu = \frac{e}{2T} \lim_{\varepsilon \rightarrow 0} \varepsilon^2 \int_0^\infty \langle X^2(t) \rangle \exp(-\varepsilon t) dt, \quad (5)$$

where e is the electron charge, $\langle X^2(t) \rangle$ means averaging over an assembly (in our case over 500 realizations). We get from (5) the following value of the mobility: $\mu \approx 0,11$ cm²/(V·sec)

¹ In [15] erroneous value of $\alpha' = 0,00013$ eV/Å is given

This mobility value is comparable with the experimental one presented in [8]. According to Fig.1 in [8], on the linear part of the current versus voltage curve, the voltage $U = 0,4\text{V}$, applied to a 8-base pairs chain (the chain length being $27,2\text{\AA}$ and the electric field intensity $E = 1,5 \cdot 10^6\text{V/cm}$) corresponds to the current $I = 50\text{nA}$ (or $I \approx 3,1 \cdot 10^{11}$ charge per sec).

With our mobility value $\mu = 0,11\text{ cm}^2/\text{V}\cdot\text{sec}$ the rate of the charge drift along the chain $v = \mu E$ will be $v \approx 2 \cdot 10^5\text{ cm/sec}$, which will make $\approx 6 \cdot 10^{11}$ charge per sec. Thus our mobility value yields the current close to the experimental one in the order of magnitude.

Let us compare our mobility value with that derivable from the results of direct measurements of the hole transfer rate in oligonucleotides [19]. In [19] the time τ required for a hole to drift from G to duplet GG, separated by one AT pair (a hole hops over adenine) is found to be $\tau = 2 \cdot 10^{-8}\text{ sec}$. The time of transition between guanines separated by cytosine would be expected to be of the same order of magnitude if the charge travels along one chain. The mobility μ_R of a hole hopping over guanine bases can be assessed with the use of τ and the mean distance L between neighboring guanines as:

$$\mu_R \approx e L^2 / 2 k_B T \tau.$$

For DNA, $L = 6,8\text{\AA}$ and at room temperature the mobility will approximately be $\mu \sim 10^{-5}\text{ cm}^2/\text{V}\cdot\text{sec}$. The values of μ_R coinciding with the cited ones in the order of magnitude were also obtained in [20,21], where the maximum limit of the mobility was found not to exceed $10^{-3} \div 10^{-2}\text{ cm}^2/\text{V}\cdot\text{sec}$. In our opinion, these differences in the mobility assessments are due to the fact that in [19] they measured the charge transfer associated with relaxation of the ambient medium which is a slow process. Thus, in liquids, the time in which polaron state is formed, is of the order of microseconds. For this reason, the value of μ_R can serve as an estimation of the polaron mobility in polynucleotide helix in a solution. Our assessment of μ suggests insignificant influence of the solvent polarization on the hole mobility.

The question of the nature of charge carriers in DNA is still open and requires further experimental and theoretical investigations. In conclusion it may be said that the use of our method for mobility calculation predicts fast growth of the mobility with decreasing temperature [22], suggesting prospectivity of the use of polynucleotide chains as molecular wires.

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REFERENCES

1. Murphy C.J., Arkin M.R., Jenkins Y., Ghatlia N.D., Bossman S., Turro N.J., Barton J.K. 1993. *Science*. **262**. 1025.
2. Fink H.W., Schoenenberger C. 1999. *Nature*. **398**. 407-410.
3. Porath D., Bezryadin A., de Vries S., Dekker C. 2000. *Nature*. **403**. 635-638.
4. Henderson P.T., Jones D., Hampikian G., Kan Y., Schuster G.B. 1999. *PNAS*. **96**. 8353-8358.
5. Ratner M.A., Jortner J. 1997. *Molecular electronics*. Blackwell: Oxford.
6. Ventra D., Zwolak M. 2004. In: *Encyclopedia of Nanoscience and Nanotechnology*. Ed. Nalwa H.S. Stevenson Ranch, CA: American Scientific Publishers.
7. Dekker C., Ratner M.A. 2001. *Phys. World*. **14**. 29.
8. Xu B., Zhang P., Li X., Tao N. 2004. *Nanoletters*. **4**. 1105.
9. Meggers E., Michel-Beyerle M.E., Giese B.J. 1998. *J. Am. Chem. Soc.* **120**. 12950.
10. Giese B., Wessely S., Spormann M., Lindemann U., Meggers E. Michel-Beyerle, M.E. 1999. *Angew. Chem. Int. Ed.* **38**. 996.
11. Giese B. 2002. *Curr. Opin. Chem. Biol.* **6**. 612.
12. Fialko N.S., Lakhno V.D. 2000. *Phys. Lett. A*. **278**. 108-111.
13. Voityuk A.A., Rösch N., Bixon M., Jortner J. 2000. *J. Phys. Chem.* **104**. 9740-9745.
14. Lakhno V.D., Sultanov V.B., Pettitt B.M. 2004. *Chem. Phys. Lett.* **400**. 47-53.

15. Lakhno V.D., Fialko N.S. 2003. *JETP Letters* **78**. 336-338.
16. Starikov E.B. 2005. *Phil. Mag.* **85**. 3435.
17. Greenside H.S., Helfand E. 1981. *The Bell System Tech. J.* **60**. 1927.
18. Dure J., Schroder T.D. 2000. *Rev.Mod.Phys.* **72**. 873.
19. Lewis F.D., Lin X., Lin J., Miller S.E., Hayes R.T., Wasielewski M.R. 2000. *Nature*. **406**, 51-53.
20. Basko D.M., Conwell E.M. 2002. *Phys. Rev. Lett.* **88**. 098102.
21. Conwell E.M., Basko D.M. 2003. *Synth. Met.* **137**. 1381.
22. Lakhno V.D., Fialko N.S. 2004. *Pis'ma v ZhETF.* **79**. 575-578.

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