JETP Letters, Vol. 78, No. 5, 2003, pp. 336–338. Translated from Pis'ma v Zhurnal Éksperimental'noĭ i Teoreticheskoĭ Fiziki, Vol. 78, No. 5, 2003, pp. 786–788.

Hole Mobility in a Homogeneous Nucleotide Chain

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Received August 5, 2003

The conductivity of molecular DNA-based conductors has been calculated. Charge motion is described by quantum-mechanical equations, and macromolecular vibrations are described by classical equations of motion with dissipation and a source of temperature fluctuations. In a homogeneous sequence of G–C nucleotide pairs, the calculated hole mobility at $T = 300$ K equals ≈ 2 cm^2 V^{-1} s^{-1}. © *2003 MAIK "Nauka/Interperiodica".*

PACS numbers: 87.14.Gg; 81.07.Nb; 36.20.-r

In a number of experiments carried out in recent years, it has been found that the DNA molecule can conduct a charge [1–4]. Hence, this opens the possibility of using DNA as a molecular wire in nanoelectronics [5]. In this connection, it seems important to understand the magnitude of the mobility of charge carriers in the "DNA conductor" and to estimate the molecular chain length at which charge transport is efficient.

At present, no experimental data is available on the magnitude of electron and hole mobility in DNA. The reported experiments on charge transfer in DNA provide information on the relative transfer reaction rates rather than mobilities [2–4].

In this paper, we report the results of calculations of hole mobilities at room temperature in a synthetic DNA molecule composed of only guanine (G)–cytosine (C) nucleotide pairs. In such chains, a hole moves over guanine bases, which possess a lower oxidation potential than cytosine bases [6]. The regular arrangement of similar nucleotides in the chain under consideration allows us to estimate the maximum mobility value, which is a limiting one for irregular sequences. In modeling the transfer process, we consider nucleotide sequences as a system of sites in which each site corresponds to a pair of bases. The Hamiltonian H of charge transfer along a chain of sites has the form [7–9]

$$H = H_e + T_K + U_P, \tag{1}$$

$$H_e = \sum_i \alpha_i a_i^+ a_i + \sum_{i,j} \nu_{i,j}(a_i^+ a_j + a_j^+ a_i),$$

$$\alpha_i = \alpha_i^0 + \alpha_i' u_i,$$

$$T_K = \sum_i M_i \dot{u}_i^2/2, \quad U_P = \sum_i K_i u_i^2/2,$$

where H_e is the Hamiltonian of a hole, a_i^+ and a_i are the operators of hole creation and annihilation at the ith site, α_i is the energy of a hole at the ith site, $\nu_{i,j}$ are the matrix elements of the transition from the ith to the jth site, T_K is the kinetic energy of the sites, M_i is the mass of the ith site, u_i is the displacement of the ith site from its equilibrium position, U_P is the potential energy of the sites, K_i are elastic constants. We assume that the energy of a hole at the sites is a linear function of displacements of the sites u_i from their equilibrium positions, and α_i' is the hole–site displacement coupling constant; $i = 1, \ldots, N$; and N is the number of sites in the chain.

Choosing the hole wave function $|\Psi\rangle$ in the form

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

where b_n is the probability amplitude of finding a hole at the nth site, from Hamiltonian (1) in the nearest neighbor approximation, we obtain the following equations of motion [8, 9]:

$$i\hbar \frac{db_n}{dt} = (\alpha_n + \alpha_n' u_n) b_n + \nu_{n,n+1} b_{n+1} + \nu_{n-1,n} b_{n-1}, \tag{3}$$

$$M_n \frac{d^2 u_n}{dt^2} = -K_n u_n - \gamma_n \frac{du_n}{dt} - \alpha_n' |b_n|^2 + A_n(t). \tag{4}$$

Equations (3) are the Schrödinger equations for the probability amplitudes. To take into account dissipation processes in the classical equations of motion for site displacements (4), we added the term $-\gamma_n \dot{u}_n$, where γ_n is the friction coefficient, and the random force $A_n(t)$ with the following statistical properties:

$$\langle A_n(t) \rangle = 0,$$
$$\langle A_n(t) A_m(t + t') \rangle = 2k_B T \gamma_n \delta_{nm} \delta(t'), \tag{5}$$

where T [K] is temperature; that is the motion of the sites described by the Langevin equation.

When modeling the motion of holes in a GG…G sequence, we assumed the same values of the parameters as in [9]: $\alpha_n^0 = 0$, $\omega_n^2\tau^2 = 0.0001$, where $\omega_n^2 = K_n/M_n$, $\alpha_n' = 0.02\sqrt{M_n\hbar/\tau^3}$ (for $M_n = 10^{-21}$ g, respectively, $\alpha_n' \approx 1.3 \times 10^{-4}$ eV/Å), $\tau = 10^{-1}$ s. The matrix elements were taken from [10], $\nu_{n,n\pm1} = 0.084$ eV.

The scheme from [11] was used for the numerical integration of the Cauchy system reduced to a dimensionless form. In the calculations, the normalization condition was accurate to three significant figures: $\left|\sum |b_n|^2 - 1\right| < 0.001$. The initial conditions for the site displacements and velocities were taken according to the equilibrium distribution for the specified temperature; at the initial instant of time, the charge was considered to be localized at the middle of the chain consisting of 99 sites (at the 50th site). Various values of the friction coefficient $\omega_n' = \tau\gamma_n/M_n$ were considered. The results given below were obtained for $\omega_n' = 0.03$, $\omega_n' = 0.006$ (as in [9]), and $\omega_n' = 0.001$.

For each value, the calculation was performed for 1000 realizations at the specified temperature T = 300 K for a time of 2 ps.

The coefficients $b_n(t)$ found in this way were used for the calculation of the mean-square hole displacement $X^2(t)$

$$X^2(t) = \langle\Psi(t)|n^2a^2|\Psi(t)\rangle = \sum_n |b_n(t)|^2 n^2a^2, \quad (6)$$

where a is the distance between neighboring sites ($a \approx$ 3.4 Å).

The time dependence of the mean-square hole displacement (averaged over 1000 realizations) is shown in Fig. 1 for the case of $\omega_n' = 0.006$ on the interval of 2 ps. In the initial part of this interval (<0.02 ps), the ballistic regime of hole motion is observed, at which $X^2(t) \approx t^2$ (Fig. 2). After ~ 0.2 ps, the time dependence of the mean-square displacement can be considered linear. At $t \geq 2$ ps, the effects associated with the finiteness of the chain under consideration become notable.

For the homogeneous chain considered in this work, the hole mobility can be found by the Kubo equation [12]

$$\mu(\Omega) = -\frac{e\Omega^2a^2}{2k_BT}, \mathrm{Re}\left[\int_0^\infty \langle X^2(t)\rangle \exp(-i\Omega t)dt\right], \quad (7)$$

where e is the electron charge, Ω is the angular frequency of the alternating electric field, T is temperature (K). $\langle X^2\rangle$ designates ensemble averaging (in our case, over 1000 realizations). In the steady-state case, the following expression follows for the mobility from Eq. (7): $\mu = eD/k_BT$, where $D = \langle X^2(t)\rangle/2t$ is the diffusion coefficient determined by the slope of the straight line approximating the dependence $\langle X^2(t)\rangle$ in the interval [0.2, 2] ps (Fig. 1). At the selected values of parameters, the hole mobility equals $\mu \cong 2.4$ cm^2 V^{-1} s^{-1} for $\omega_n' = 0.001$, $\mu \cong 2.3$ cm^2 V^{-1} s^{-1} for $\omega_n' = 0.006$, and $\mu \cong 2$ cm^2 V^{-1} s^{-1} for $\omega_n' = 0.03$. Note that the hole mobility in a homogeneous G–C chain was found to be equal to $\mu \cong 10$ cm^2 V^{-1} s^{-1} in [13] (on the time interval of the same order). The higher mobility value is apparently associated with the fact that dissipation was not included in the model system considered in [13].

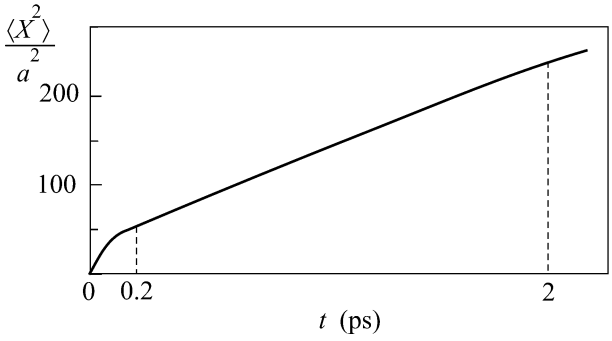

Fig. 1. Plot of the time dependence of the mean-square hole displacement on the interval of 2 ps.

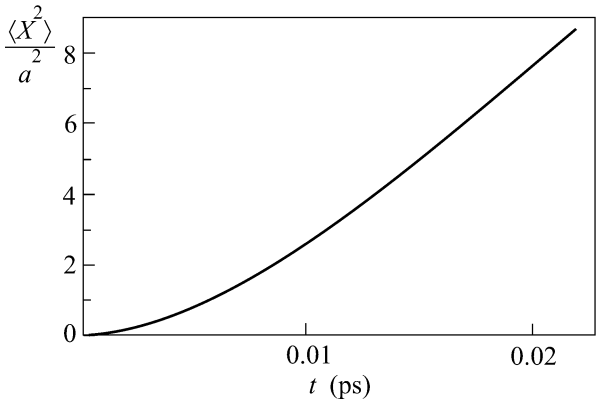

Fig. 2. Plot of the time dependence of $\langle X^2\rangle/a^2$ at small values of t.

Despite the not-too-high mobility value, the holes in DNA can be transferred for long distances, because the main mechanism of their capture in the process of transfer along the nucleotide sequence is the chemical reaction of a hole with water, whose rate is $K_{reac} \approx 10^6$ s^{-1} [14]. This leads to the following estimate for the distance at which a hole can be transferred before it is cap-

tured by water: $l = \sqrt{2D/K_{reac}}$. With the use of the results obtained, we find $l \approx 5 \times 10^4$ Å.

This work was supported by the Russian Foundation for Basic Research, project nos. 01-07-90317 and 03-04-49225.

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Translated by A. Bagatur'yants