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Bloch Oscillations in a Homogeneous Nucleotide Chain

V. D. Lakhno[1)], *N. S. Fialko*[1)]

+*Institute of Mathematical Problems of Biology RAS*
142290 Pushchino, Moscow Reg., Russia

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It is shown that at zero temperature, a hole placed in homogeneous synthetic nucleotide chain with applied electric field demonstrates Bloch oscillations. The oscillations of the hole placed initially on one of base pairs arise in response to disruption of the initial charge distribution caused by nucleotide vibrations. The finite temperature fluctuations result in degradation of coherent oscillations. The maximum permissible temperature for DNA "Bloch oscillator" occurrence is estimated.

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In recent years, experiments on the study of the charge migration in DNA placed in external electric field have become feasible [1 – 3]. Of special interest for future nanotechnology are the experiments with synthetic homogeneous nucleotide sequences [1]. The properties of electrons or holes in such nucleotide sequences should be similar to those of band charge carriers in crystals of the solid body.

As is known, in the case of the ideal periodical crystal structure, an electron places therein exhibits oscillations [4]. In semiconductors with superlattices this gives rise to such phenomena as radiation of electromagnetic waves (Bloch oscillator) [5], negative differential conductivity [6, 7], absolute negative conductivity [8], dynamical localization [9 – 13] and multiphoton absorption [14, 15].

One-dimensional and homogeneous "DNA-crystal" differs significantly from its solid analog, because oscillations of the nucleotide pairs play a great role there. Motion of the charge carriers in DNA is accompanied by considerable displacements of the nucleotide pairs from their equilibrium positions, that, in turn, affect the motion of the charge carriers.

Our purpose here is to report the results of charge transfer modeling: dynamical behavior of a hole in the DNA sequence of the form $(\mathbf{G}\text{-}\mathbf{C})_n$ (where **G** is guanine, **C** is cytosine) in electric field applied along the chain.

In such chain, a hole travels over guanine bases whose oxidation potentials are lower than that of cytosine [16]. Hamiltonian of the charge transfer along the chain of nucleotide sites has the form [17, 18]:

$$\begin{aligned} H &= H_h + T_K + U_P, \qquad (1)\\ H_h &= \sum_n \alpha_n\, a_n^+ a_n + \sum_{n,m} \nu_{n,m}(a_n^+ a_m + a_m^+ a_n),\\ \alpha_n &= \alpha_n^0 + {\alpha_n}' u_n + n\hbar\omega_B,\\ T_K &= \sum_n M_n\, \dot{u}_n^2/2, \quad U_P = \sum_n K_n\, u_n^2/2. \end{aligned}$$

Here H_h is the Hamiltonian of a hole; a_n^+, a_n are the operators of creation and annihilation of the hole at the nth site; α_n is the energy of a hole at the nth site. $\hbar\omega_B = eEa$, where E is the intensity of the electric field, e is the electron charge, a is the distance between neighboring bases. $\nu_{n,m}$ is the matrix element of the transition from the nth site to the mth one. T_K is the kinetic energy of the sites, U_P is the potential energy of the sites (M_n is the mass of the nth site, u_n is the displacement of the nth site from its equilibrium position; K_n is the elastic coefficient). α_n' is the hole – site displasement coupling constant. $n = 1, \ldots, N$, N is the number of sites in the chain.

We choose the wave function of a hole $|\Psi\rangle$ in the form:

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

where b_n is the amplitude of probability of the hole localization at the nth site, then derive from Hamiltonian (1) in the nearest-neighbor approximation the following motion equations [17, 18]:

$$i\hbar\frac{db_n}{dt} = \alpha_n b_n + \nu_{n,n+1} b_{n+1} + \nu_{n-1,n} b_{n-1}, \qquad (2)$$

$$M_n\frac{d^2u_n}{dt^2} = -K_n u_n - \gamma_n\frac{du_n}{dt} - \alpha_n' |b_n|^2. \qquad (3)$$

Eq. (2) are the Schrödinger equations for the probability amplitudes. To take into account the processes of dissipation, in the classical motion equations (3) we added

[1)]e-mail: lak@impb.psn.ru, fialka@impb.psn.ru the term $-\gamma_n \dot{u}_n$ (γ_n are the friction coefficients). System (2), (3) corresponds to the case of the zero temperature $T = 0$.

In the absence of the interaction between a hole and the displacements of the chain sites (at $\alpha'_n = 0$ for all n) equations (2) have the solution [19, 20]:

$$b_n(t) = \sum_{m=-\infty}^{\infty} b_m(0)(-i)^{n-m} e^{-i(n+m)\omega_B t/2} J_{n-m}\big(\xi(t)\big),$$
$$\xi(t) = \frac{4\nu}{\hbar\omega_B} \sin\left(\frac{\omega_B t}{2}\right), \tag{4}$$

where $\nu_{n,n\pm1} = \nu$ in the case of a homogeneous chain, J_n are the first kind Bessel functions. Solution (4) corresponds to Bloch oscillations of a hole with frequency ω_B and the position expectation value of the hole center mass value $x(t) = \sum |b_n|^2 na$. By the use of (4) it can be expressed as

$$x(t) = x(0) + \frac{2a\nu}{\hbar\omega_B}|S_0|\big(\cos\Theta_0 - \cos(\omega_B t + \Theta_0)\big),$$
$$S_0 = \sum_{m=-\infty}^{\infty} b^*_m(0) b_{m-1}(0) = |S_0| e^{i\Theta_0},$$
$$x(0) = a \sum_{m=-\infty}^{\infty} m|b_m(0)|^2. \tag{5}$$

Expression (5) exactly corresponds to the quasiclassical description of the charge migration in crystal lattice [4–15] if $b_m(0) \approx b_{m-1}(0)$, when $\Theta_0 = 0$ and $S_0 = 1$.

By (5), the amplitude of $x(t)$ oscillations is equal to zero if at the initial moment the charge was localized at just one site. In this case the density of the hole probability at each moment is distributed symmetrically about the initial position $x = 0$. Classically, a hole moves along the field and opposite it with acceleration identical in modulus and contrary in direction, deriving energy from the field when traveling along it and at the same time loosing energy when moving in the opposite direction.

In contrast to $x(t)$ the mean square value of hole position $X^2(t) = \sum |b_n|^2 n^2 a^2$ other than zero and is equal to:

$$X^2(t) = X^2(0) + \frac{a^2}{2}\left(\frac{4\nu}{\hbar\omega_B}\right)^2 \sin^2 \frac{\omega_B t}{2}, \tag{6}$$
$$X^2(0) = a^2 \sum_{m=-\infty}^{\infty} m^2 |b_m(0)|^2.$$

Thus, the motion of the charge density represents the coherent oscillations with Bloch period.

In modeling the motion of a hole in **GG** ... **G** sequence with account of the site displacements, we took the same parameter values as in [17]: $\alpha^0_n = 0$, $\omega^2\tau^2 = 0.0001$ (where $\omega^2_n = K_n/M_n$), $\omega'_n = \tau\gamma_n/M_n = 0.006$, $\kappa = (\alpha'_n)^2\tau/(\hbar K_n) = 4$; $\tau = 10^{-14}$ sec, $M_n = 10^{-21}$ g. Matrix elements were taken from [21]: $\nu_{n,n\pm1} = 0.084$ eV.

Corresponding to (1) dimensionless Cauchy system was numerical solved by the fourth order Runge-Kutta method. In the calculations, the normalizing condition was controlled; it fulfilled with accuracy $|\sum |b_n|^2 - 1| < 0.0001$. The initial conditions for the displacements and site velocities were taken to be zero. At the initial moment, charge was assumed to be localized in the middle of the chain consisting of 499 sites (at the 250 th site), i.e. we dealt with the case when in a rigid lattice with $\alpha'_n = 0$, oscillations of the mass center of a hole are lacking. The initial conditions under discussion are typical since in charge transfer experiments, a hole arises due to photoexcitation on one nucleotide pair [22–24]. We calculated the system with a number of electric field intensity values $\tilde{E} = eaE\tau/\hbar$.

Fig.1 shows the dependencies of $x(t)$ for some values of the electric field intensity which varies from the minimum at which the effects concerned with the finiteness of the chain do not manifest themselves $E_{\min} = 8\nu/eaN$ to the maximum $E_{\max} = 4\nu/ea$ which corresponds to Stark localization of the hole at one site. Thus, taking into account of interactions between the hole and the chain displacements u_n leads to arising of the hole oscillations, the period T of which is quite close to $T_B = 2\pi/\omega_B$ (Fig.2). Changes in the values of the friction coefficient γ and the constant α'_n influence the amplitude of the oscillations (vanishing at $\alpha'_n = 0$), but not their period. We relate this fact to violation of the initial charge distribution caused by displacements of sites from their equilibrium positions.

To explain physical mechanism of the studied effect let us consider an infinite nondeformable chain with $\alpha'_n = 0$. In this chain, a hole initially localized at the site with number $n = 0$, at the subsequent moments will produce symmetrical distributions of the charge density. The reason is that in this case the hole moves in antisymmetric potential α_n where it can transfer to the site n and to the site $-n$ with equal probability. If the interaction $\alpha'_n \neq 0$ takes place, symmetrical distribution of the charge density at the moment t=0 will cause (in view of equation (3)) at the next moment displacements u_n, which are like-sign and $u_n \approx u_{-n}$ So, the total potential energy α_n, associated with the external electric field and site displacements looses its symmetry. As a result, the probabilities of transitions along the electric field and in the opposite direction become different. This breaks the symmetry in the charge distribution and, con-

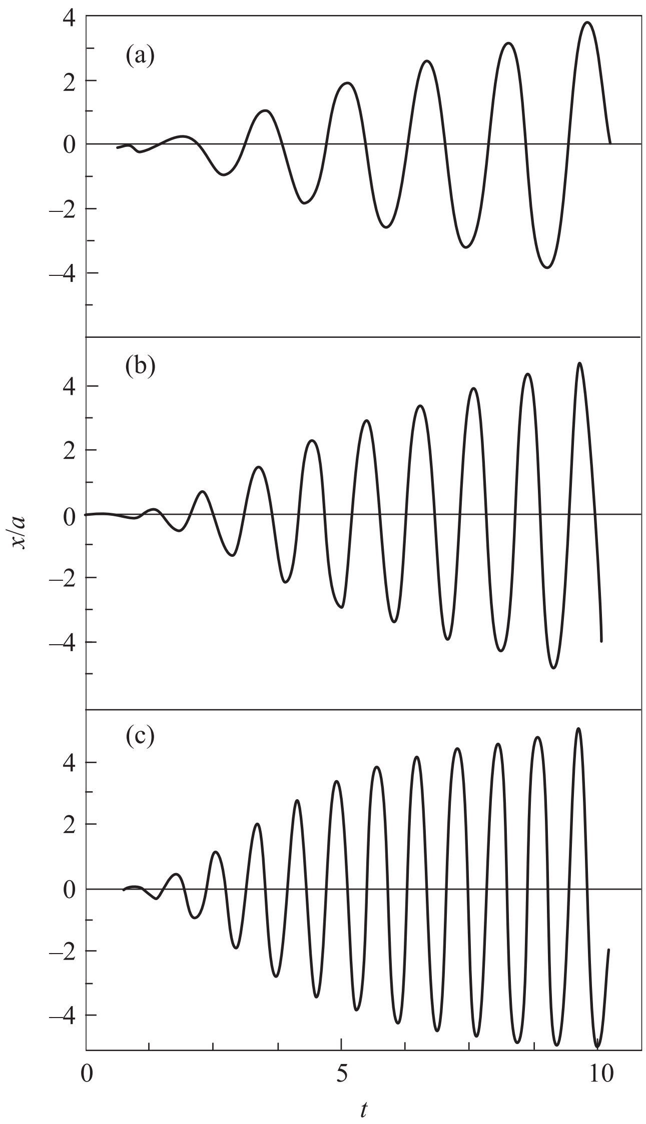

Fig.1. Graps of position expectation (normed to a), dependent on t (psec), for the next dimensionless values of the electric field intensity: (a) $\tilde{E} = 0.04$, (b) $\tilde{E} = 0.06$, and (c) $\tilde{E} = 0.08$

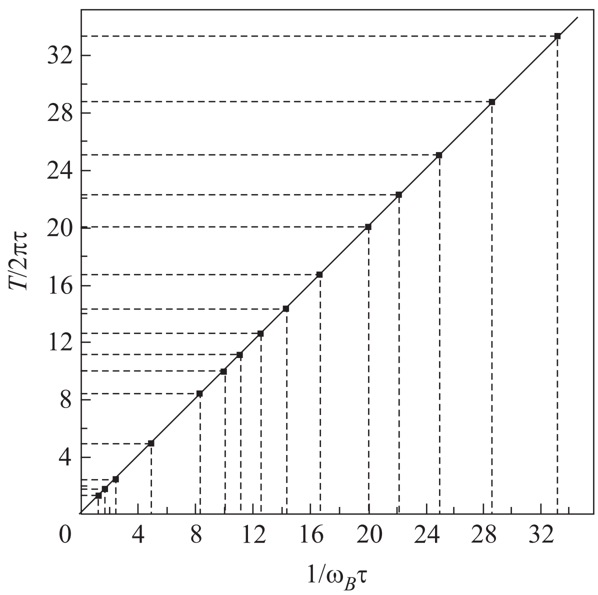

Fig.2. Continuous line determines the Bloch oscillation T_B dependence on the electric field intensity E ($T_B = 2\pi/\omega_B$, $w_B = eEa/\hbar$ is the Bloch frequency) at $\kappa = 0$ (accordingly, $\alpha'_n = 0$). The bold dotes show periods calculated at $\kappa = 4$ ($\alpha'_n \sim 1.3 \cdot 10^{-4}$ eV/Å)

sequently, causes nonzero displacement of the hole mass center $x(t)$. Classically, in this case (i.e. at $\alpha'_n \neq 0$) acceleration of the hole along the field is not equal in modulus to that opposite the field, and the energy which the hole derives from the field can radiate in the form of electromagnetic waves and oscillating quanta of the nucleotide chain. Note, that the mechanism we deal with is general and is realized at any parameter values, with only quantitative characteristics of the effect varying.

For the parameter values used, the value of the electric field intensity E lies in the range $E_{\min} \approx \approx 4 \cdot 10^4$ V/cm $< E < 10^7$ V/cm $\approx E_{\max}$. These values of the field correspond to the frequencies of the electromagnetic waves Ω_n multiple of the Bloch frequency: $\Omega_n = n\omega_B$, $n = 1, 2, \ldots$, with $\min \omega_B = 2 \cdot 10^{12}$ sec^{-1} and $\max \omega_B = 5 \cdot 10^{14}$ sec^{-1}. So, for really attainable electric field intensities, the radiation frequencies fall in the terahertz range.

Until the present time, no experiments have been carried out on the observation of microwave radiation in nucleotide sequences.

Bloch oscillations are observed at finite temperature on condition $\omega_B \tau > 1$, where τ is the time of the hole relaxation determined by dissipation on site oscillations. The value of τ can be estimated from the relation $\tau = \mu m^*/e$, where μ is the hole mobility, $m^* = \hbar^2/2\nu a^2$ is the effective mass of hole. For our parameter values the mass $m^* \approx 3.94 m_0$ (m_0 is the electron mass).

In computations of the temperature dependence of the mobility μ we used the method described in [25]. Classical equations for site motions obtained from (1) were modified so as to add the term $A_n(t)$ for taking into account the temperature fluctuations. So, the site motions follows the Langevin equations. The mobility was calculated by the Kubo formula

$$\mu = \frac{e}{2T} \lim_{\varepsilon \to 0} \varepsilon^2 \int_0^\infty \langle X^2(t) \rangle \exp(-\varepsilon t)\, dt \qquad (7)$$

where $\langle X^2(t) \rangle$ is an averaged square of the hole displacement along a chain of sites for the temperature range from 10 K to 350 K. For each given temperature averaging was performed over a large number of realizations, then the meansquare displacement of a hole was found, from which the mobility was calculated by (7). The best approximation of the results obtained is given by the function

$$\mu \approx \mu_0 \cdot (T/T_0)^{-2.3} \tag{8}$$

where $\mu_0 \approx 2.87\,\text{cm}^2/\text{V}\cdot\text{sec}$ (the improved value of [25]) is the mobility at $T = 300\,\text{K}$.

Increase in the hole mobility with decreasing temperature given by dependence (8) can be explained as follows. As a result of temperature fluctuations, at each moment of time a hole travels in a random potential field determined by random distribution of the hole energy on the sites α_i (1). Since in the one-dimensional case considered, in a random field there always exists a localized state, increase in the mobility will always occur with decreasing the amplitude of the random field. According to (1) this will take place as the contribution of $\alpha' u_i$ into the energy of a hole on i-th site decreases, i.e. the temperature falls.

With the use of the temperature dependence of the mobility (8) in the chain one can estimate the temperature T at which Bloch oscillations take place at the frequency of ω_B: $T < (\omega_B \tau_0)^{1/2.3} T_0$, $\tau_0 \sim 6.4 \cdot 10^{-15}$ sec being the relaxation time at $T_0 = 300\,\text{K}$, e.g. at $\min \omega_B = 2 \cdot 10^{12}\,\text{sec}^{-1}$ the expression for the temperature value at which Bloch oscillations can be observed is $T < 45\,\text{K}$.

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