

## THE PROBLEM OF DNA CONDUCTIVITY

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The paper gives a review of experiments on a charge transfer in DNA and presents a discussion of various theoretical approaches to the interpretation of the transfer phenomenon. It is shown that an adequate mathematical description of the nonlinear dynamics of this transfer can be based on Holstein Hamiltonian. The main results obtained for this charge transfer with the help of Holstein Hamiltonian are presented. Special attention is given to conducting properties of homogeneous nucleotide chains. It is demonstrated that regular and homogeneous chains are promising candidates for the role of molecular wires in nanoelectronic devices.

Дан обзор экспериментов по переносу заряда в ДНК и их теоретическая интерпретация. Показано, что адекватное математическое описание нелинейной динамики такого переноса может быть основано на использовании гамильтониана Холстейна. Представлены основные результаты, касающиеся переноса заряда, вытекающие из гамильтониана Холстейна. Особое внимание уделено проводящим свойствам однородных нуклеотидных цепочек. Сделан вывод, что однородные и регулярные цепочки являются перспективными кандидатами на роль молекулярных проволок в наноэлектронных устройствах.

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### INTRODUCTION

Numerous experiments have revealed that the DNA conductivity can vary from the value typical of dielectrics and semiconductors to that peculiar to conductors and superconductors [1–8]. Recall that DNA consists of four types of nucleotides designated as *A* (adenine), *T* (thymine), *C* (cytosine), and *G* (guanine), which unite into complementary pairs in such a way that nucleotide *A* always pairs with *T*, and nucleotide *C* always pairs with *G*. These nucleotide pairs are arranged in a stack to form a DNA double helix. Nowadays long sequences with a prescribed set of nucleotide pairs can be synthesized artificially. Chains composed of uniform pairs which could serve as molecular wires in nanoelectronic devices are of great interest. In the majority of experiments on charge transfer in DNA, the charge is carried not by electrons, but by holes. If a nucleotide in a nucleotide chain be freed from one electron, the hole which would arise would have a potential energy  $U$  such that  $U_G < U_A < U_C < U_T$ .

Overlapping of electron  $\pi$  orbitals of neighboring pairs will lead to delocalization of the hole over the chain and its capture by nucleotides with lower oxidation potentials. Since, according to the above inequality, guanine has the lowest oxidation potential, the hole will

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travel over guanines, while all the other nucleotides will act as potential barriers. Since there is a strong dependence of the DNA conductivity on the type of a nucleotide sequence, in an effort to reveal some regularities in this dependence it may be profitable to consider the mechanisms of charge transfer in homogeneous and regular sequences [4, 8, 9]. As is shown in [10], charge transfer in such sequences can be described on the basis of Holstein model [11]. The aim of this work is to analyze temperature dependences of the charge mobility in regular chains with the use of the results obtained for Holstein Hamiltonian. We will deal with the cases of the band mechanism of charge transfer, and charge transfer by small-radius polarons (SRP) and large-radius polarons (LRP).

### 1. SMALL-RADIUS POLARONS

To model quantum dynamics of a particle in a chain of  $N$  nucleotide pairs we will proceed from Holstein Hamiltonian which was the first to consider the chain in which each site presents a biatomic molecule [10, 11]:

$$H = \nu \sum_n (a_n^+ a_{n-1} + a_n^+ a_{n+1}) + \alpha' \sum_n q_n a_n^+ a_n + \sum_n \hat{P}_n^2 / 2M + \sum_n K q_n^2 / 2, \quad (1)$$

where  $a_n^+$ ,  $a_n$  are operators of the birth and annihilation of a charge on the  $n$ th site;  $\alpha'$  is a constant of the charge interaction with the displacement  $q_n$  of the  $n$ th site from the equilibrium position;  $\hat{P}_n$  is an impulse canonically conjugated to the displacement  $q_n$ ,  $M$  is the effective mass of the site;  $K$  is an elastic constant;  $\nu$  is a matrix element of the charge transition from the  $n$ th site to the  $n + 1$  site.

According to [12], on condition that

$$t_p \gg \Delta t \gg t_0, \quad t_0 < \omega^{-1}, \quad \Delta t \gg \omega^{-1}, \quad (2)$$

$$\nu^2 \ll (E_a T)^{1/2} \hbar \omega, \quad (3)$$

where

$$t_p \sim \frac{\hbar}{\nu} \exp(1 + 2\bar{N})S, \quad t_0 \sim \frac{\hbar}{(E_a T)^{1/2}}, \quad \Delta t \sim \left( \frac{\hbar^2}{\nu^2 t_0} \right) \exp\left( \frac{E_a}{T} \right), \quad (4)$$

$\hbar = h/2\pi$ ,  $h$  is the Plank constant;  $T$  is temperature;  $\bar{N} = \exp(\omega/T - 1)^{-1}$ ,  $E_a = \alpha'^2 / 4M\omega^2$ ,  $\omega = (K/M)^{1/2}$ ,  $S = \alpha'^2 / (2M\omega^2 \hbar \omega)$ , a SRP arises in the chain under consideration. The dependence of the SRP energy  $E_k$  on the wave vector  $k$  is given by the expression

$$E_k = -2\nu \cos ka \cdot \exp\{-S(\dots, N_k, \dots)\} \quad (5)$$

$$S(\dots, N_k, \dots) = \sum_k (1 + 2N_k) \gamma_k / N$$

$$\gamma_k = \frac{\alpha'^2}{2M\omega_k^2 \hbar \omega_k} (1 - \cos ka),$$

where  $N_k$  is an average number of the population of phonons with vector  $k$ ;  $a$  is the distance between neighboring sites;  $N$  is the number of sites (nucleotide pairs) in the chain.

In inequalities (2), (3)  $t_p$  is the time of tunneling of SRPs between sites,  $\Delta t$  is the time interval between transitions,  $t_0$  is the time of a transition. Relations (5) describe narrowing of the initial band of a charged particle caused by formation of a SRP. In the case of dispersionless phonons we are dealing with (5), which yields the following expression for the SRP mass  $m_p$ :

$$m_p = \hbar^2/2\tilde{\nu}a^2, \quad \tilde{\nu} = \nu \exp(-S(1 + 2\bar{N})). \quad (6)$$

So, narrowing of the SRP band is determined by the exponential factor in (6) which leads to a large value of the SRP mass. The mobility of a SRP  $\mu$  in the case of dispersionless phonons was found by Holstein to be [11]

$$\mu = eD/T, \quad (7)$$

where:

$$D = \omega a^2 \frac{\nu^2}{\hbar^2 \omega^2} \left[ \frac{\pi}{\gamma \operatorname{csch}(\hbar\omega/2T)} \right]^{1/2} \exp \left[ -2\gamma \operatorname{th} \left( \frac{\hbar\omega}{4T} \right) \right] \quad (8)$$

for the case of  $T > T_t$ ,  $\gamma = \alpha'^2/2M\omega^3\hbar$ , where  $T_t$  corresponds to the temperature at which the lifetime of a SRP in the band state is comparable with the time of its transition to a neighboring site.

For the case of  $T < T_t$ , Holstein found that

$$D = 2\omega a^2 \left[ \frac{\gamma}{\pi} \operatorname{csch}(\hbar\omega/2T) \right]^{1/2} \exp \left[ -2\gamma \operatorname{csch} \left( \frac{\hbar\omega}{2T} \right) \right]. \quad (9)$$

In the case of SRP existence, in the case of high temperatures, (8) yields a classical expression for the mobility  $\mu_{cl}$ :

$$\mu_{cl} = \frac{ea^2\nu^2}{\hbar T} \left[ \frac{\pi}{4TE_a} \right]^{1/2} \exp \left( -\frac{E_a}{T} \right). \quad (10)$$

So, in the SRP case under consideration, the temperature dependence of the mobility looks as follows. At  $\theta/2 < T \leq \theta$ , where  $\theta$  is the Debye temperature (in the dispersionless case  $\theta = \hbar\omega$ ), a SRP makes hops activated by temperature and its mobility in this region grows with growing temperature. At  $T \leq \theta/2$ , the SRP motion has a band character, but the band width quickly increases with decreasing  $T$ , which leads to the increase of the SRP mobility. At very low  $T$ , the band width is independent of temperature and the temperature dependence is determined by SRP scattering over the band and dissipative processes concerned with the motion of a SRP over the chain. The temperature dependence of the mobility at  $T > \theta$  is determined by (10) and will be considered in general case in Sec.4.

## 2. LARGE-RADIUS POLARON

**A Weak Coupling LRP.** In the case of Hamiltonian (1) under consideration, a weak coupling LRP is formed on condition that [13]

$$\bar{\alpha}^{1/2} \ll \hbar\omega, \quad |\Delta E| < 4|\nu|, \quad (11)$$

where:

$$\bar{\alpha} = \frac{\alpha'^2\hbar}{2M\omega}, \quad \Delta E = \bar{\alpha}a\sqrt{\frac{m}{2\hbar^3\omega}}.$$

The quantity  $\Delta E$  stands for the polaron shift in the energy caused by the interaction with phonons.

In this case, in order to calculate the mobility, it is profitable to use the quasi-classical Bloch–Boltzmann theory based on the solution of the Boltzmann kinetic equation for the electron distribution function  $f_k$ :

$$\frac{df_k}{dt} = \frac{4\pi\bar{\alpha}}{\hbar} \frac{T}{\hbar\omega} \sum_{k',q} |\langle e^{ikx} | k' \rangle|^2 \delta(\varepsilon_k - \varepsilon_{k'}) (f_{k'} - f_k), \quad (12)$$

which is valid on condition that  $T/\hbar\omega > 1$ . The quantity  $\varepsilon_k = k^2/2m$  represents the band electron energy with the effective mass  $m = \hbar^2/2\nu a^2$ , and  $x = na$  is considered to be continuous in the continuum approximation.

Solution of equation (12) yields the mobility  $\mu$  equal to

$$\mu = 2\sqrt{\frac{2}{\pi}} \frac{e^2 \hbar^3 \omega}{a m^{3/2} T^{1/2} \bar{\alpha}} \quad (13)$$

(where  $e$  is the electron charge) and specifies its growth as  $\mu \sim T^{-1/2}$  with decreasing temperature.

At  $T < \hbar\omega$ , the chain conductivity has a nonohmic character and the equilibrium velocity of a particle  $v$  in the electric field of intensity  $E$  is determined by Cherenkov radiation [13]:

$$v = \sqrt{\frac{\hbar\omega}{m} + \sqrt{\left(\frac{\hbar\omega}{m}\right)^2 + \xi^2}}, \quad \xi = \frac{\hbar\omega}{m} \left(\frac{E_0}{E}\right), \quad E_0 = \frac{ma}{\pi\hbar\omega} \frac{\alpha'^2}{Me}. \quad (14)$$

From (14) follows that the charge velocity decreases as the electric field intensity grows which corresponds to a negative differential conductivity. In this case, the electron motion is unstable and has a character of Bloch oscillations.

**A Strong Coupling LRP.** In the case of strong coupling, on condition that

$$\bar{\alpha}^{1/2} \gg \hbar\omega, \quad |\Delta E| < 4|\nu| \quad (15)$$

at  $T = 0$ , a large radius polaron is formed. At temperatures considerably lower to that of the polaron decay, the polaron mobility depends on temperature only slightly and, according to [14], is equal to

$$\mu = 240ea^2\nu^3\omega^{10}M^5/\gamma_f\alpha'^8, \quad (16)$$

where  $\gamma_f$  is the friction coefficient in the semiclassical equations of the site motion (20). In expression (16), a strong dependence of the mobility on the parameters  $\omega$  and  $\alpha'$  is striking. Notice that, according to [14], the mobility in the strong coupling limit is contributed by both the dissipation over the chain and the Cherenkov radiation which is barrierless in the case under consideration.

At temperatures close to that of the strong coupling LRP decay and still higher the system dynamics becomes particularly complicated and any analytical expressions for the mobility are lacking. The results of numerical calculations for this case are given in Sec. 4.

### 3. GENERAL APPROACH TO CALCULATION OF THE MOBILITY AT HIGH TEMPERATURES

As was noted above, at temperatures higher than that of the polaron decay, any analytical expressions for  $\mu$  are lacking. Since the polaron decay takes place at  $T > \hbar\omega$ , in these conditions the site oscillations can be described by classical Langevin equations. We can pass on to such a semiclassical description of the system «a particle + phonons» under investigation, if we choose the wave function of the system  $|\Psi(t)\rangle$  as an expansion over coherent states

$$|\Psi(t)\rangle = \sum_n b_n(t) a_n^+ \exp \left\{ -\frac{i}{\hbar} \sum_j [\beta_j(t) \hat{P}_j - \pi_j(t) q_j] \right\} |0\rangle, \quad (17)$$

where  $|0\rangle$  is the vacuum wave function and the quantities  $\beta_j(t)$  and  $\pi_j(t)$  satisfy the relations

$$\langle \Psi(t) | q_n | \Psi(t) \rangle = \beta_n(t), \quad \langle \Psi(t) | \hat{P}_n | \Psi(t) \rangle = \pi_n(t). \quad (18)$$

Dynamical equations for the quantities  $b_n(t)$  and  $\beta_n(t)$  resulting from (1), (17), and (18) have the form

$$i\hbar \frac{db_n}{dt} = \alpha' \beta_n b_n + \nu(b_{n+1} + b_{n-1}), \quad (19)$$

$$M \frac{d^2 \beta_n}{dt^2} = -k\beta_n - \gamma_f \frac{d\beta_n}{dt} - \alpha' |b_n|^2 + A_n(t). \quad (20)$$

Equation (19) are a Schrödinger equation for the probability amplitudes  $b_n(t)$ . To take into account the dissipation processes, Eq. (20) involves the term  $\gamma_f d\beta_n/dt$  responsible for friction and the force  $A_n(t)$  with the following statistical properties:

$$\langle A_n(t) \rangle = 0, \quad \langle A_n(t) A_m(t+t') \rangle = 2T\gamma_f \delta_{nm} \delta(t'). \quad (21)$$

So, the site motion is described by Langevin equations.

With the use of (19), (20) a particle mobility can be calculated by Kubo formula

$$\mu = \frac{e}{2T} \lim_{\varepsilon \rightarrow 0} \varepsilon^2 \int_0^\infty \langle x^2(t) \rangle \exp(-\varepsilon t) dt, \quad (22)$$

where  $\langle x^2(t) \rangle$  is the mean square of the particle displacement  $x(t)$  along the chain with  $x^2(t)$  determined by the relation

$$x^2(t) = a^2 \sum_n n^2 |b_n(t)|^2. \quad (23)$$

This scheme for calculation of the mobility is computationally intensive, since it implies averaging over a large number of realizations given by a solution of dynamical Eqs. (19), (20). As applied to DNA, the results of such calculations are discussed in the following section.

#### 4. CALCULATION RESULTS

The results obtained can be used to study the temperature dependence of the hole mobility in regular nucleotide sequences. Since a nucleotide chain of any structure can be synthesized, one can deal with highly diversified types of the charge motion. For a homogeneous (PolyG/PolyC) sequence, the parameters, according to [10], take the following values:  $\nu = \nu_{GC} = 0.084$  eV,  $\alpha' = 0.13$  eV/Å,  $\omega = \sqrt{K/M} = 10^{12}$  s<sup>-1</sup>,  $\omega' = \gamma_f/M = 6 \cdot 10^{11}$  s<sup>-1</sup>. These parameter values correspond to a LRP. The mobility LRP of a strong coupling LRP calculated by formula (16) for these parameter values at  $T = 0$  will be  $\mu = 5.7 \cdot 10^{-2}$  cm<sup>2</sup>/V·s. In this case, the temperature dependence of the mobility at  $T > \hbar\omega$  ( $\hbar\omega \approx 7.7$  K) calculated by Kubo formula (22) takes the form [15]:  $\mu = \mu_0(T/T_0)^{-2,3}$ ,  $\mu_0 = 2.87$  cm<sup>2</sup>/V·s,  $T_0 = 300$  K. According to [16], the polaron decay temperature  $T_p$  in a (PolyG/PolyC) chain is  $T_p \approx 20$  K. Kubo formula for this temperature yields  $\mu \approx 1.5 \cdot 10^3$  cm<sup>2</sup>/V·s. Most likely, this is the maximum value of the mobility, which can have a hole in a homogeneous (PolyG/PolyC) chain, since at  $T < T_p$  a LRP with low mobility ( $\approx 5.7 \cdot 10^{-2}$  cm<sup>2</sup>/V·s) is formed. In a regular (PolyGA/PolyCT) chain with  $\nu_{GA} = 0.089$  eV,  $\nu_{AG} = 0.049$  eV,  $\nu_A = 0.45$  eV,  $\nu = \nu_{\text{eff}} = \nu_{GA}\nu_{AG}/\nu_A = 9.7 \cdot 10^{-3}$  eV  $\approx 10^{-2}$  eV inequalities (2), (3) are not fulfilled either even at very high temperatures ( $\sim 3600$  K). So, a hopping mechanism of a SRP is not realized in this case. In regular sequences of the form of (PolyGA<sub>1</sub>...A<sub>k-1</sub>/PolyCT<sub>1</sub>...T<sub>k-1</sub>) with  $k > 2$  this hopping transfer takes place. In particular, for chains with  $k = 3$  condition (3) leads to the requirement of  $T \gg 0.07$  K. As distinct from homogeneous chains, in regular chains the value of  $T_p$  is much larger.

In regular chains with  $k > 2$ , temperature dependences of the SRP hopping mobility, which are characterized by several orders of magnitude variation of the resistance in narrow temperature intervals (Sec. 1) take place.

These effects of salutatory growth or decrease of the particle mobility in a narrow temperature range can be used in nanotechnologies in constructing various nanopositioners, where they can serve as switches, heating controllers, nanoheat sensors, etc.

Notice that in the high-temperature range  $T > \hbar\omega$ , expression (10) for the mobility of a SRP in a (PolyG/PolyC) chain can be obtained immediately from the mobility expression [17]

$$\mu = \frac{eL^2K_t}{T}, \quad (24)$$

where  $K_t$  is the rate of charge transfer between neighboring guanine sites, which, according to [18], has the form

$$K_t = \frac{|V_{ba}|^2}{\hbar} \sqrt{\frac{\pi}{E_r T}} e^{E_r/4T}. \quad (25)$$

If in (24), (25) we put  $V_{ba} = \nu$ ,  $E_r = 4E_a$ ,  $L = a$ , where  $E_r$  is the medium reorganization energy,  $V_{ba}$  is the matrix element of the transition between neighboring guanines,  $L$  is the transfer distance, expression (24) changes to expression (10).

As was, however, shown above, the condition for the formation of a SRP is not fulfilled in the case of a regular (PolyG/PolyC) chain, while the applicability of Marcus theory may not be violated. In this situation the temperature dependence determined by (10) may have Holstein form at  $T \gg \hbar\omega$ , however, the absolute value of the mobility may be different from the Holstein one, since in this case instead of  $E_a$  (involved in (10)), expression (10)

will contain its effective value, which obeys the inequality  $E_{a,\text{eff}} < E_a$ . Thus, Holstein relation (10) determines minimum value of the mobility corresponding to complete relaxation of a charge on guanine sites. If so, exact value of the mobility must be calculated on the basis of the approach developed in Sec. 3.

For regular (PolyGA<sub>1</sub>...A<sub>k-1</sub> / PolyCT<sub>1</sub>...T<sub>k-1</sub>) chains with  $k > 2$ , the mobility values determined by (24), (25) and calculated by Kubo formula (22) must be close, since in this case the conditions for the formation of a SRP are fulfilled. Then, to compare the results, we should replace the quantity  $V_{ba}$  in (25) by its effective value  $V_{ba,\text{eff}}$  obtained in the superexchange theory:

$$V_{ba,\text{eff}} = \frac{V_{GA}V_{AG}}{\Delta E_{AG}} \left( \frac{V_{AA}}{\Delta E_{AG}} \right)^{k-2},$$

where  $\Delta E_{AG}$  is the difference between the energies of holes localized on guanine and adenine.

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