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Abstract. Polaronic mechanism of charge transfer in DNA is considered on the basis of one-dimensional Su-Schrieffer-Heeger (SSH) model Hamiltonian. It is shown that usually used values of SSH model Hamiltonian parameters, especially transfer integral and electron-phonon coupling constant which are obtained in the framework of ab initio calculations, do not give reliable resolution of the problem of (large) polaron applicability for charge migration in DNA. Because of that, theoretical method is proposed which enables us to estimate explicitly electron-phonon coupling constant on the basis of transfer integral. The value of polaron width obtained for such determined parameters leads to the conclusion that coherent motion of large polaron represents dominant mechanism of charge transfer in DNA.

1. Introduction

Topic of charge transfer in DNA has been in the focus of researchers in various branches of science for a long time. It is the consequence of the fact that the results obtained by the inspection of this problem can be applied in physics, chemistry, biology, medicine, nanotechnology; for instance: damage, mutation and repair of DNA [1], nanoscale sensors for mutations or protein binding [2], nanotechnology aspects of single molecule conduction [3]. At the same time, there exist very conflicting and controversial experimental data concerning the conductivity in DNA. So, DNA was found to behave like metallic wire [4], semiconductor [5] and insulator [6]. The reasons for this are experimental complications in the measurements such as: chemical details of the environment, length and structure of DNA, impurity, temperature, water solution etc.

In order to interpret inconsistent experimental results, a number of charge transfer mechanisms have been proposed. During the past decade polaron motion was actively considered as a possible mechanism of charge transfer in DNA. This possibility was supported by the experimental findings [7, 8]. But, there is not yet clear answer on the question which kind of polarons (large polarons and coherent motion or small polarons and random hopping) is responsible for charge transport.

Our aim in this paper is to give a contribution in clarifying polaronic mechanism of charge migration in DNA.

2. SSH model Hamiltonian

DNA is too large and too complicated system for complete ab initio calculations. For that reason, model investigations have been performed. Here we base our calculations on Su-Schrieffer-Heeger (SSH) model [9].

Tight binding SSH model was firstly introduced to describe the properties of polarons in conducting polymer. Later, its modified form has been applied to DNA by the Conwell group [10, 11, 12].

DNA may be considered as a one dimensional chain composed of the stacked base pairs (A-T and G-C), which enables charge transfer by the $\pi-\pi$ electron interaction between the adjacent nuclei bases. From theoretical point of view, large polaron formation is expected if an extra electron (or hole) is added to one-dimensional chain.

In order to support polaron formation, Hamiltonian must contain the following essential ingredients:

1) electronic system that realizes the charge conduction;
2) electron-phonon coupling to allow the formation of lattice distortion;
3) an elastic restoring force that keeps distortion finite.

SSH Hamiltonian, which fulfils this request, in the usual form is given as:

$$H_{SSH} = \sum_n d_n B_n^+ B_n - t_o \sum_n \left(B_n^+ B_{n+1} + B_{n+1}^+ B_n \right) + \alpha \sum_n \left(u_{n+1} - u_n \right) \left(B_n^+ B_{n+1} + B_{n+1}^+ B_n \right) + \frac{\kappa}{2} \sum_n \left(u_{n+1} - u_n \right)^2 + \frac{1}{2M} \sum_n p_n^2 \,. \quad (1)$$

Here:

$B_n^+ \left(B_n \right)$ is the electron creation (annihilation) operator,

d_n denotes on-site energy,

u_n is the displacement of the n_{th} site from thermal equilibrium position (sites evenly spaced at distance equal to lattice constant $a \approx 3.4 \,\text{Å}$),

κ denotes elastic constant,

M is the mass of the entity at each site,

t_o denotes transfer integral in thermal equilibrium,

α is electron-phonon coupling constant.

The assumption which is inherent to this Hamiltonian is the linear dependence of transfer integral $t_{n,\,n+1}$ on separation between adjacent sites, namely

$$t_{n,\,n+1} = t_o - \alpha (u_{n+1} - u_n) \,. \quad (2)$$

Main and difficult problem in dealing with SSH Hamiltonian is the selection of its parameters, especially the transfer integral t_o and the electron-phonon coupling constant α. It is very

important to emphasize that their precise determination is necessary if we want to know the nature of polaron, character of its motion and mathematical tool for the theoretical description.

We note that the elastic constant κ is determined by the experimental value of speed of sound:

$$\kappa = 0.85 \frac{\mathrm{eV}}{\mathrm{\mathring{A}}^2}. \tag{3}$$

As for the transfer integral t_o, very diverse values may be found in the literature [10,13,14,15]. These values, which mainly depend on the kind of adjacent base pairs, are obtained by ab initio calculations.

According to the same type of calculation, the electron-phonon coupling constant is given as

$$\alpha \approx 2t_o \mathrm{\mathring{A}}^{-1}. \tag{4}$$

Significant remark to such obtained values for t_o and α is that ab initio calculations are very complicated and with doubtful precision.

3. Theoretical method for explicit estimation of electron-phonon coupling constant

In this paper, the theoretical method which enables one to calculate explicitly the value of α on the basis of the transfer integral t_o is developed. For the reason of simplicity, in the following we will consider periodic DNA. Such kinds of sequences can be engineered artificially and provide macromolecules that should display fast charge transfer properties. It this case we may use

$$d_n = 0. \tag{5}$$

We begin with the Hamiltonian:

$$H = -\sum_{n,m} t(u_n - u_m) B_n^+ B_m + \frac{1}{2M}\sum_n P_n^2 + \frac{1}{2}\sum_{n,m}\left(V_{n-m} - V_{n-m+u_n-u_m}\right). \tag{6}$$

The next step is to use Fourier transformations

$$t(u_n - u_m) = \frac{1}{\sqrt{N}}\sum_k t_k e^{ika(n-m)+ik(u_n-u_m)}, \tag{7}$$

$$V_{n-m} = \frac{1}{\sqrt{N}}\sum_k V_k e^{ika(n-m)} \tag{8}$$

and

$$V_{n-m+u_n-u_m} = \frac{1}{\sqrt{N}}\sum_k V_k e^{ika(n-m)+ik(u_n-u_m)}\,. \tag{9}$$

Now, in the approximation of the nearest neighbours and for small displacements u_{n+1} and u_n, the well known SSH Hamiltonian is obtained:

$$H_{SSH} = -t_o\sum_n\left(B_n^+B_{n+1}+B_{n+1}^+B_n\right)+\alpha\sum_n\left(u_{n+1}-u_n\right)\left(B_n^+B_{n+1}+B_{n+1}^+B_n\right)$$
$$+\frac{\kappa}{2}\sum_n\left(u_{n+1}-u_n\right)^2+\frac{1}{2M}\sum_n P_n^2\,, \tag{10}$$

where

$$t_o = \frac{1}{\sqrt{N}}\sum_k t_k\cos ka\,, \tag{11}$$

$$\alpha = \frac{1}{\sqrt{N}}\sum_k k\cdot t_k\sin ka\,, \tag{12}$$

$$\kappa = \frac{1}{\sqrt{N}}\sum_k k^2\cdot V_k\cos ka \tag{13}$$

and

$$t_k = \sum_l e^{ikal}t_l\,;\quad l=n-m\,. \tag{14}$$

Taking into account the nature of forces between stacked bases we calculate t_k. Finally, it follows:

$$\alpha = \frac{t_o}{a}\,. \tag{15}$$

4. Results

Starting point of our analysis is the above tight binding one-dimensional SSH Hamiltonian. Then, Fourrier transformation and quantisation of phonon degrees of freedom are performed. In such a way, we obtain

$$H = -t_o \sum_n \left(B_n^+ B_{n+1} + B_{n+1}^+ B_n \right) + \frac{1}{\sqrt{N}} \sum_{q,n} F_q e^{iqna} \left(B_n^+ B_{n+1} + B_{n+1}^+ B_n \right) \left(a_q + a_{-q}^+ \right) + \sum_q \hbar \omega_q a_q^+ a_q \,. \tag{16}$$

Here:

$$F_q = \alpha \sqrt{\frac{\hbar}{2MN\omega_q}} \left(e^{iqa} - 1 \right) \tag{17}$$

and

$$\omega_q = \omega_o \sin\left| \frac{qa}{2} \right|; \qquad \omega_o = 2\sqrt{\frac{\kappa}{M}} \,. \tag{18}$$

Polaron solution is used in the form:

$$|\psi\rangle = \sum_n \psi_n B_n^+ |0\rangle \times |\beta\rangle; \qquad |\beta\rangle = \prod_q |\beta_q\rangle; \qquad a_q |\beta_q\rangle = \beta_q |\beta_q\rangle, \tag{19}$$

where ψ_n represents an electron wave function (amplitude) and β_q is obtained by the optimization of the energy $\mathcal{H} = \langle \psi | H | \psi \rangle$.

From the equation of motion for ψ_n

$$i\hbar \dot{\psi}_n = \frac{\partial \mathcal{H}}{\partial \psi_n^*}, \tag{20}$$

in continuum approximation $\psi_n(t) \to \psi(x,t)$, the famous nonlinear Schrödinger equation (NSE) appears in the lowest order:

$$i\hbar \dot{\psi}(x,t) = -2t_o \psi - t_o a^2 \psi_{xx} - 8E_B |\psi|^2 \psi, \tag{21}$$

where indexes x in ψ denote double differentiation over x and the dot represents differentiation over time t. E_B is small-polaron binding energy:

$$E_B = \frac{1}{N} \sum_q \frac{|F_q|^2}{\hbar \omega_q} = \frac{\alpha^2}{2\kappa} \,. \tag{22}$$

The solution of NSE is well known "soliton-like" solution:

$$\psi(x,t) = \sqrt{\frac{\mu}{2}} \frac{e^{i(kx-\omega t)}}{\cosh\left[\frac{\mu}{a}(x-vt)\right]}. \tag{23}$$

For the purpose of this paper, it is enough to mention that the parameter μ has the meaning of inverse polaron width in unit of a. If we substitute the "soliton-like" solution (23) in NSE (21), it is easy to show that:

$$\mu = \frac{2E_B}{t_o} = \frac{\alpha^2}{\kappa t_o}. \tag{24}$$

Then, the polaron width l_p follows directly:

$$l_p = \frac{1}{\mu} a = \frac{t_o \kappa}{\alpha^2} a. \tag{25}$$

Polaron binding energy can be calculated from the expression:

$$E_{pb} = t_o a^2 \int \frac{dx}{a} |\psi_x|^2 - 4E_B \int \frac{dx}{a} |\psi|^4. \tag{26}$$

Finally,

$$E_{pb} = -\frac{1}{3}\mu^2 t_o = -\frac{1}{3}\frac{\alpha^4}{t_o \kappa^2}. \tag{27}$$

Polaron width and polaron binding energy are completely determined by the parameters of SSH Hamiltonian.

Now, we will compare the results for polaron width (25) and polaron binding energy (27) using ab initio value of α and the value obtained by our theoretical method.

If we take ab initio value $\alpha_{ai} = 2t_o \overset{\circ}{\mathrm{A}}^{-1}$, $\kappa = 0.85 \frac{\mathrm{eV}}{\overset{\circ}{\mathrm{A}}^2}$ and $t_o \in [0.1 - 0.3]\mathrm{eV}$ which represent usually used values of t_o in DNA, the obtained results are:

1) $t_o = 0.3\mathrm{eV}$, $\alpha_{ai} = 0.6 \frac{\mathrm{eV}}{\overset{\circ}{\mathrm{A}}}$; $l_p^{ai} \approx 0.71a$, $E_{pb}(\alpha_{ai}) \approx -0.2\mathrm{eV}$,

2) $t_o = 0.2\text{eV}$, $\alpha_{ai} = 0.4\frac{\text{eV}}{\text{Å}}$; $l_p^{ai} \approx 1.06a$, $E_{pb}(\alpha_{ai}) \approx -0.059\text{eV}$,

3) $t_o = 0.1\text{eV}$, $\alpha_{ai} = 0.2\frac{\text{eV}}{\text{Å}}$; $l_p^{ai} \approx 2.12a$, $E_{pb}(\alpha_{ai}) \approx -0.0073\text{eV}$.

As for the theoretical method given above, i.e. $\alpha_{TM} = \frac{t_o}{a}$, the following relations arise:

$$l_p^{TM} \approx 46.3 l_p^{ai}, \qquad E_{pb}(\alpha_{TM}) \approx 4.67 \cdot 10^{-4} E_{pb}(\alpha_{ai}). \tag{28}$$

For instance, if $t_o = 0.3\text{eV}$ and $\kappa = 0.85\frac{\text{eV}}{\text{Å}^2}$ then:

$$l_p^{TM} \approx 33a, \qquad E_{pb}(\alpha_{TM}) \approx -9.34 \cdot 10^{-5}\text{eV}. \tag{29}$$

It is easy to see that when the transfer integral t_o decreases the polaron width l_p^{TM} increases.

5. Discussion and conclusion

In this paper we consider polaron motion as a possible mechanism of charge transfer in DNA. In order to do this we use tight binding one-dimensional SSH model Hamiltonian. The main problem is the selection of its parameters, particularly the transfer integral t_o and electron-phonon coupling constant α. Precise determination of these parameters is very important for adequate description of the nature of polaron and character of its motion.

Ab initio calculations of the above parameters are not reliable enough. From the results obtained for polaron width in this case, it is hard to say that large polaron exists.

In order to understand better polaronic mechanism of charge transfer in DNA, theoretical method is suggested which makes possible to estimate explicitly the value of electron - phonon coupling constant α. On the basis of this value of α we calculate polaron length and polaron binding energy for periodic DNA. From the obtained results for polaron width we conclude that charge transfer in DNA may be achieved by means of coherent motion of large polaron.

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