Charge transport in the α-helix proteins

Journal of Physics: Conference Series **248** (2010) 012051 doi:10.1088/1742-6596/248/1/012051

Charge transport in the α-helix proteins

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Abstract. In this paper we investigate charge transport in the α- helix proteins. It is considered that charge carriers are partially dressed small polarons, that are formed by electron self-trapping in the weak coupling limit. Polaron properties are considered by applying mean-field theory based upon the modified Lang-Firsov transformation and the Bogolyubov theorem. The transport properties have been calculated on the basis of the Holstein MC model. The obtained results are compared with the results of previous models.

1. Introduction

In the late fifties of the 20th century, Albert Szent-Gyorgy referred to demand of employment of ideas and methods of quantum physics in the problem of biochemistry of cancer. He believed that the cancer was related to the changes of electron transport properties at the molecular scale. The first serious examination of charge and energy transport in protein macromolecules at the quantum level was proposed in mid seventies by Davydov and co–workers [1]. The essence of their theory is the assumption that an extra electron or energy quanta released in the hydrolysis of adenosine triphosphate can be captured by the protein molecules and then transported along the polypeptide chain in a soliton form. However, due to the lack of direct experimental evidence of soliton existence in these substances, Davydov's idea has been for a long time considered just an interesting theoretical concept.

The situation changed at the beginning of the eighties, when G. Careri and A. Scott suggested [2] that appearance of the so–called unconventional amide–I band, observed in a previous year experiment by Careri in crystalline acetanilide (ACN) [3], might be explained in terms of Davydov's soliton theory. However, according to the general theory of self–trapping (ST) phenomenon, the original Davydov's concept should be substantially modified, and as shown by Alexander and Krumhansl [4], the whole concept must be reinterpreted in terms of the small–polaron (SP) model. Because of the ACN hydrogen–bonded structure that is similar to the structure of the α–helix proteins, it is believed that it provides a good model for studing ST phenomena in protein macromolecules. It means that transport processes in hydrogen–bonded biological macromolecules could be investigated within the standard SP models based on the Lang–Firsov (LF) transformation. As a consequence, these concepts rely on the assumption of fully dressed excitations. However, the values of basic energy parameters in hydrogen–bonded macromolecular chains fall into nonadiabatic weak coupling regime [5]. It means that the true states of system should be partially dressed SP states rather than the fully dressed ones. This fact refers to the necessity of using some kind of partial dressing strategy, or variational approach [5, 6, 7]. Another indication that it is necessary to approve the classic SP model in order to apply it to hydrogen–bonded macromolecules is the fact that the position of the anomal amide–I

peak in IR spectra of ACN is temperature dependent. This fact cannot be explained within the scope of standard SP theories and the LF approach [7].

In this paper we offer a charge transport model in hydrogen–bonded biological macromolecules. It is based on the famous Holstein molecular crystal model (MCM) [8], and improved treatment of the ST, based on the modified Lang–Firsov (MLF) transformation and the Bogolyubov theorem [6, 9, 10, 11]. The results that our model predicts are compared with the results predicted by transport model based on the standard LF transformation.

2. Theoretical model

We base our further analysis on the results of the paper [7, 11] where, employing the nonadiabatic weak coupling approximation, we obtained the following expression for the optimal form of variational parameter:

$$f_q = \frac{F_q^*}{\hbar\omega_q + 2J\mathrm{e}^{-S(T)}(2\bar{n}_q + 1)(1 - \cos qR_0)}. \tag{1}$$

Its magnitude defines the degree of dressing and the character of ST states. In the above equation, $S(T) = \frac{1}{N}\sum_q |f_q|^2 (2\bar{n}_q + 1)(1 - \cos qR_0)$ is the electron band narrowing factor, J is the intersite transfer integral, ω_q is the phonon frequency, R_0 is the lattice constant, $F_q = F_{-q}^*$ is the electron–phonon coupling parameter, and $\bar{n}_q = 1/(\mathrm{e}^{\hbar\omega_q/k_BT} - 1)$ is the phonon average number. Incoherent neutron scattering studies of ACN [12] indicate that acoustic modes are not involved in vibron ST, and that the source of vibron ST in ACN is its coupling with optical phonons only. Additionally, recent pump–probe experiments seem to show that a unique phonon of frequency approximately equal to $\omega_0 \approx 50$ cm^{-1} is responsible for the self–trapping phenomenon [13]. In that case, the vibron (electron)–phonon coupling parameter is q–independent, and has the value $F \approx 25$ cm^{-1} [5, 14, 15]. Numerical values of the intersite transfer integral in ACN for amide–I mode is about $J \approx 5$ cm^{-1} [4, 5, 14, 15]. In the case of electron ST in proteins, this parameter ranges from ~ 1cm^{-1} to ~ 10cm^{-1} [16], depending on protein types, as well as on model based experimental estimations. In this paper we adopt numerical value that is characteristic of the vibron ST in ACN.

The character of the ST states is determined by relationships among the values of the basic energy parameters of the system: characteristic phonon energy $\hbar\omega_0$, quasiparticle energy bandwidth $2J$, and SP binding energy $E_b = \frac{1}{N}\sum_q \frac{|F_q|^2}{\hbar\omega_q}$. In particular, just two parameters characterize the ST in these media: adiabatic parameter $B = \frac{2J}{\hbar\omega_0}$ and the coupling constant $S = \frac{E_b}{\hbar\omega_0}$. In nonadiabatic limes (when $B << 1$) where quasiparticle and lattice deformation form new entity, we have "'dressed"' quasiparticle with new effective mass, and with reduced energy band. The above mentioned system parameter values that characterize ACN suggest that the vibron (electron) ST would result in the creation of the weakly dressed (S=0,25) nonadiabatic (B=0,16) small polaron.

In the next step we shall explore how the above result affects charge conductivity calculated within the conventional theories of SP transport [8, 10, 17, 18]. Conventional theories of SP transport predict substantially different character of SP motion in the low and high temperature regimes [8, 10, 18]. The first one is the coherent (band–like) SP motion appearing at low temperatures. The increase in temperature gradually destroys the polaron band and SP motion attains the character of random jumps between the neighbouring sites (incoherent, hopping motion).

Improving the Holstein results [8, 19, 20] using (Eq.1), in nondispersive phonon case we have the following relations for the hopping and band conductivities:

$$\frac{\sigma_{\text{hopping}}}{\sigma_0} = \frac{B^2}{4\tau}\sqrt{\frac{\pi\cosh\left(\frac{1}{2\tau}\right)}{S(\tau)}}\ \mathrm{e}^{-2S(\tau)\tanh\left(\frac{1}{4\tau}\right)\tanh\left(\frac{1}{2\tau}\right)} \tag{2}$$

$$\frac{\sigma_{\text{band}}}{\sigma_0} = \frac{1}{\tau}\sqrt{\frac{S(\tau)}{\pi\cosh\left(\frac{1}{2\tau}\right)}}\ \mathrm{e}^{-2\frac{S(\tau)}{\cosh\left(\frac{1}{2\tau}\right)}} \tag{3}$$

where $\sigma_0 = \frac{n_e e^2 R_0^2}{\hbar}$, n_e is the carrier concentration, $\tau = \frac{k_B T}{\hbar\omega_0}$ is normalized temperature, and the band narrowing factor has the form $S(\tau) = S\text{cotanh}\left(\frac{1}{2\tau}\right)\left\{1 + 2B\mathrm{e}^{-S(\tau)}\text{cotanh}\left(\frac{1}{2\tau}\right)\right\}^{-3/2}$

3. The obtained results

Figs. 1a and 1b graphically present the temperature dependence of the polaron band narrowing factor, for a few values of S and B.

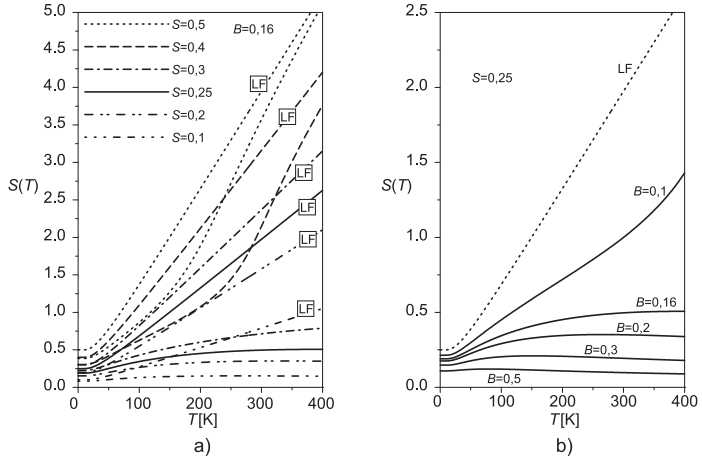

Figure 1. Temperature dependence of the SP band narrowing factor versus temperature for a few values of S and $B = \text{const}$. (Fig. 1a), and a few values of B and $S = \text{const}$. (Fig. 1b).

As it can be noticed, a variational approach based on MLF transformation predicts that the temperature dependence of $S(\tau)$ is quite different from $S(\tau)$ predicted by models based on the LF approach. The obtained values are significantly lower than the values predicted by standard SP theories, especially for the lower values of the coupling constant S (weak coupling limit) (Fig.1a), higher values of adiabatic constant B (Fig.1b) and at higher system temperature. For lower values of S there is a different temperature behaviour of $S(\tau)$, where, with increase of temperature after abrupt increasing of the band narrowing factor, a slow increase occurs. The obtained results suggest that the SP dressing in nonadiabatic weak coupling limit is lower than those predicted by the LF approach, and consequently SP must have lower values of effective mass (which is proportional to $\mathrm{e}^{S(\tau)}$), and higher mobility and electric conductivity. This prediction is confirmed by the results showed in Figs. 2a and 2b.

System parameter values that characterize ACN and hydrogen–bonded macromolecular chains imply that variational approach based on the MLF transformation can provide better description of SP in these systems [7, 11]. As a consequence, SP that may be formed in these structures are partially dressed, and have lower values of effective mass compared with the values that predict traditional SP theories. This fact implies that the SP mobility and electric

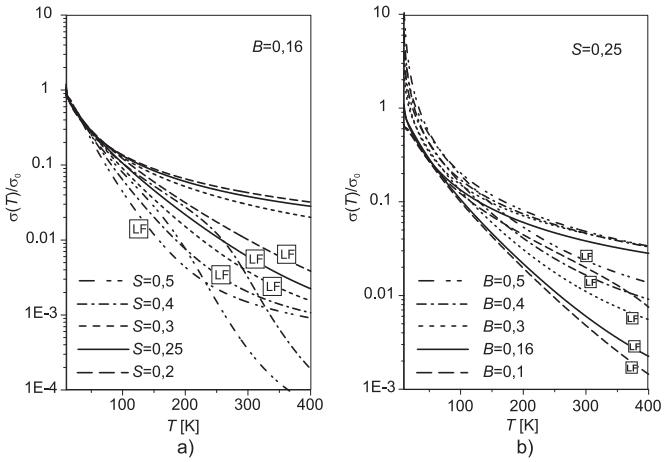

Figure 2. Temperature dependence of electric conductivity for a fixed value of B (Fig. 2a), and a fixed value of S (Fig. 2b).

conductance are greater than the values predicted by standard SP theories based on the LF approach, esspecially in the high temperature regime, and points to a possible significant role of self–trapping mechanism in charge and energy transport in biological macromolecules.

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