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To cite this article: D. evizovi *et al* 2016 *J. Phys.: Conf. Ser.* **670** 012018

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# Vibron properties in quasi 1D molecular structures: the case of two parallel unshifted macromolecuar chains

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**Abstract.** We study the hopping mechanism of the vibron excitation transport in the system of two parallel unshifted 1D macromolecuar chains in the framework of non-adiabatic polaron theory. We suppose that the vibron interaction with thermal oscillations of the macromolecuar structural elements will result in vibron self-trapping and the formation of the partial dressed vibron state. We also suppose that quasiparticle motion takes place via a sequence of random sitejumps, in each of which the quasiparticle can migrate either to the first neighbor site of the macromolecuar chain. With use of the modified Holstein polaron model, we calculate the vibron effective mass in dependence of the basic system parameters and temperature. Special attention is paid to the influence of interchain coupling on vibron dressing. We find that for certain values of the system parameters the quasiparticle mass abruptly changes.

## 1. Introduction

The interest for the application of organic macromolecules (e.g., protein macromolecules, DNA, polymers, and other biological macromolecuar structures) in construction of nanostructures, such as nanoparticles, nanocrystals, nanowires, and molecular circuits becomes again actual. Its ability in the field of the miniaturization of microelectronic and optoelectronic devices and, at the same time, its self-assembly capabilities makes them as a very promising materials in microelectronic and optoelectronic technology [1, 2, 3]. Efficient application of such materials requires the knowledge of mechanisms that rule the charge and energy migration along the macromolecuar spine at such distances which are comparable to the dimension of the macromolecuar. Similarly, the processes of energy and charge transport in biological macromolecules that operate inside living cells are not sufficiently elucidated. Unfortunately, formulation of a theoretical model based on the principle of quantum mechanics that might explain such processes on a satisfactory manner is not finished yet. At the present it is believed that the universal source of energy for many physical processes that take place in living cells is the process of the hydrolysis of adenosine triphosphate, ATP. The energy quanta that emerge in this process is large enough for the excitation of the intramolecuar oscillation (IMO) mode (vibron excitation) of the CO group (Amide I quanta) which is a part of the peptide bond of all protein macromolecules. But the lifetime of Amide I quanta is approximately 1 picosecond, which is too short to explain the process of long-distance energy transport through



the MC spine. The inability of a consistent explanation of the above mentioned problems led to a crisis in bioenergetics in the seventies of the last century.

One of the earliest quantum mechanical-based models of the charge and energy transfer in protein molecules was developed by Davydov and his coworkers [4, 5]. This model is founded on the assumption that an external excitation might be captured by MC due to the interaction with thermal oscillations of the MC structure elements. Such a self-trapped (ST) excitation becomes dressed by the phonon cloud and, according to Davydov, it can move in a soliton form through the macromolecular chain. The assumption of the soliton existence might explain the long lifetime of the formed quasiparticle.

However, it turned out that the soliton model can successfully describe the process of ST of the charge carriers and its transport through the macromolecule. As regards the intramolecular vibrational excitations, the Davydov model is inapplicable because the basic energy parameters of the protein macromolecules do not satisfy basic conditions for the soliton formation [6, 7, 8, 9, 10]. After some delay in further progress, in the late eighties it was proposed a new model based on the assumption that in the process of vibron excitation ST might arise a non-adiabatic (small) polaron (SP), rather than a soliton [8]. The new approach to the problem of ST of IMO was originated from the attempt to explain the origin of the anomalous peak in the IR absorption spectra of crystalline acetanilide (ACN).

The non-adiabatic (small) polaron theory is founded on the assumption that the interaction between quasiparticle and phonon subsystem is strong. Unfortunately, the values of system parameters that manage the process of a vibron ST do not belong to the vibron-phonon strong coupling region, but rather correspond to the weak or intermediate coupling strength [10]. This uncertainty stems mostly from the fact that the vibron-phonon coupling strength cannot be directly measured in experiment, but it is estimated according to pre-accepted theoretical model (i.e., it is the model dependent quantity). For that reason, it was necessary to go beyond the standard small polaron theory and to develop a model that will overcome its limitations. One of ways to overcome this problem is to apply the method of the partially dressed vibron quasiparticle. This method was developed in order to intermediate between the exciton-phonon strong coupling and weak coupling interactions. The method of the partially dressed quasiparticle is commonly used in complicated numerical calculations, which does not allow one to have a clear insight into the essence of the problem of quasiparticle dressing. Any analytical model, which will provide “insight” into the heart of physical processes that take place in the quasiparticle self-trapping or quasiparticle migration in the crystal lattice, requires the introduction of various approximations, which however should not neglect the basic processes in the system under consideration. In general, the model of the partially dressed vibron quasiparticle gave satisfactory results, but certain details still did not agree with the experimental results [9]. These details concern especially the problem of the temperature dependence of the anomalous peak position of Amide I quanta in IR absorption spectra of ACN. But all studies devoted to this problem were made under the assumption that ACN can be regarded as a truly 1D system [8, 13, 14, 15, 16, 17], neglecting the interaction among chains, which can affect the SP properties.

The mechanism of IMO migration in the ACN (and other macromolecular structures that are built by two macromolecular chains, like DNA) becomes very important in order to understand the processes of bio-information transmission in the living cells. According to the Holstein MC model, there are two basic mechanisms of polaron motion: a band mechanism, which is dominant at low temperatures, and polaron migration thorough the crystal by the series of successive jumps from one to its neighbor structure element. The latter mechanism dominates at intermediate and high temperatures, including the temperature at which living cells function. In both mechanisms, a key role has the probability of quasiparticle transition from one to some other structure element of a crystal structure. In this paper, the hopping mechanism of vibron exciton transport in the system which consists of two parallel macromolecular chain is investigated in the framework of partially dressed vibron states. It is taken into account the coupling between the chains. Among the typical

examples of such a structure we can specify the ACN macromolecule in which its two polypeptide chains are embedded and form a two-chain structure (Fig. 1). We calculate the dependence of the dressing parameter on the system parameters and temperature. Special attention is paid to the vibron properties at room temperatures and for the system parameter values that belong to moderately non-adiabatic and intermediate coupling regions.



**Figure 1.** The real structure of the part of crystalline acetanilide macromolecular chains is shown in the left, whereas its schematic structure is demonstrated in the right. The possible vibron hopping transitions are shown by the arrows.

## 2. Theoretical model

In order to investigate single-vibron properties in the system consisting of two parallel macromolecular chains, we modify the Holstein molecular crystal model [6] and adopt several assumptions: a vibron quasiparticle becomes self-trapped and forms a dressed quasiparticle due to the vibron-phonon interaction with optic phonon modes only; a vibron excited on the particular MC can interact only with phonons that belong to the same MC; a vibron can migrate along the macromolecule spine from the  $n$ -th to  $(n \pm 1)$ -th structural element. The Hamiltonian of the system of two parallel and untagged from each other MCs (see right Fig. 1) is defined as

$$\begin{aligned}
 H = & E_0 \sum_{n,j=1,2} A_{j,n}^\dagger A_{j,n} - J \sum_{n,j=1,2} A_{j,n}^\dagger (A_{j,n-1} + A_{j,n+1}) + L \sum_n (A_{1,n}^\dagger A_{2,n} + A_{2,n}^\dagger A_{1,n}) \\
 & + \sum_{q,j=1,2} \hbar\omega_0 B_{j,q}^\dagger B_{j,q} + \frac{1}{\sqrt{N}} \sum_{n,q,j=1,2} F_q e^{iqnR_0} A_{j,n}^\dagger A_{j,n} (B_{j,q} + B_{j,-q}^\dagger), \quad (1)
 \end{aligned}$$

where  $E_0$  is the vibron excitation energy in a particular structural element of two  $N$ -site MCs,  $A_{j,n}^\dagger$  ( $A_{j,n}$ ) are the vibron quasiparticle creation (annihilation) operators in the  $n$ -th site of the  $j$ -th MC,  $J$  and  $L$  stand for the energies of the dipole-dipole interaction of neighboring structure elements that belongs to the same chain and to different chains, respectively. The operators  $B_{j,q}^\dagger$  ( $B_{j,q}$ ) in Eq. (1) are the creation (annihilation) operators of phonon quanta with frequency  $\omega_q = \omega_0$  of the wave number  $q$  which belong to the  $j$ -th chain. The vibron-phonon coupling parameter is defined as  $F_q = F = \chi_{hb} \sqrt{\hbar/2M\omega_0}$  ( $\chi_{hb}$  is the coupling constant and  $M$  is a mass of the molecular group).  $R_0$  is a distance between two neighboring structure elements placed in the same MC. The transition to the polaron picture can be realized by the (modified) Lang-Firsov unitary transformation [9, 11, 18] with the operator  $U = U_1 \cdot U_2$ , where  $U_j = \exp\{-\sum_n \sigma_{j,n} A_{j,n}^\dagger A_{j,n}\}$  and  $\sigma_{j,n} = \frac{1}{\sqrt{N}} \sum_q f_{q,j} e^{-iqnR_0} (B_{j,q} - B_{j,-q}^\dagger)$ . In the standard theory of Lang and Firsov,  $f_{q,j}$  are the vibron-phonon coupling parameters. Such an approach corresponds to the standard non-adiabatic polaron (fully dressed vibron quasiparticle). In the case of partially dressed vibron quasiparticles, these parameters can be referred as a set of variational parameters, or they can contain one or more variational parameters. According to [12], we use the variational approach with only one single variational parameter  $\delta \in [0, 1]$  introduced as follows  $f_{q,j} = \delta \cdot F_q^* / \hbar\omega_0$ . The influence of the thermal fluctuations on the vibron properties are accounted by the averaging of the transformed

Hamiltonian over the phonon subsystem [11, 18, 19, 20]. At this manner, we find for the dressed vibron Hamiltonian

$$H_{vib} = \sum_{k,j=1,2} E(k) a_{j,k}^\dagger a_{j,k} + \lambda_0 \sum_k \left( a_{1,k}^\dagger a_{2,k} + a_{2,k}^\dagger a_{1,k} \right). \quad (2)$$

Here  $a_{j,k}^\dagger$  ( $a_{j,k}$ ) denote the creation (annihilation) operators of the dressed vibrons,  $\tau = k_B T / \hbar \omega_0$  is the normalized temperature,  $\lambda_0 = L \exp\{-\delta^2 S \coth(1/2\tau)\}$ , and

$$E(k) = E_0 + \delta(\delta - 2)E_b - 2J e^{-\delta^2 S \coth(1/2\tau)} \cos(kR_0) \quad (3)$$

is the polaron band energy,  $E_b = F^2 / \hbar \omega_0$  is the small polaron binding energy, and  $S = E_b / \hbar \omega_0$  is the coupling constant. The diagonalization of the Hamiltonian (2) can be done by means of the unitary transformation  $\alpha_{\pm,k} = (a_{1,k} \pm a_{2,k}) / \sqrt{2}$ . As the result, the vibron Hamiltonian takes the following form

$$H_{vib} = \sum_k \left[ E_+(k) \alpha_{+,k}^\dagger \alpha_{+,k} + E_-(k) \alpha_{-,k}^\dagger \alpha_{-,k} \right], \quad (4)$$

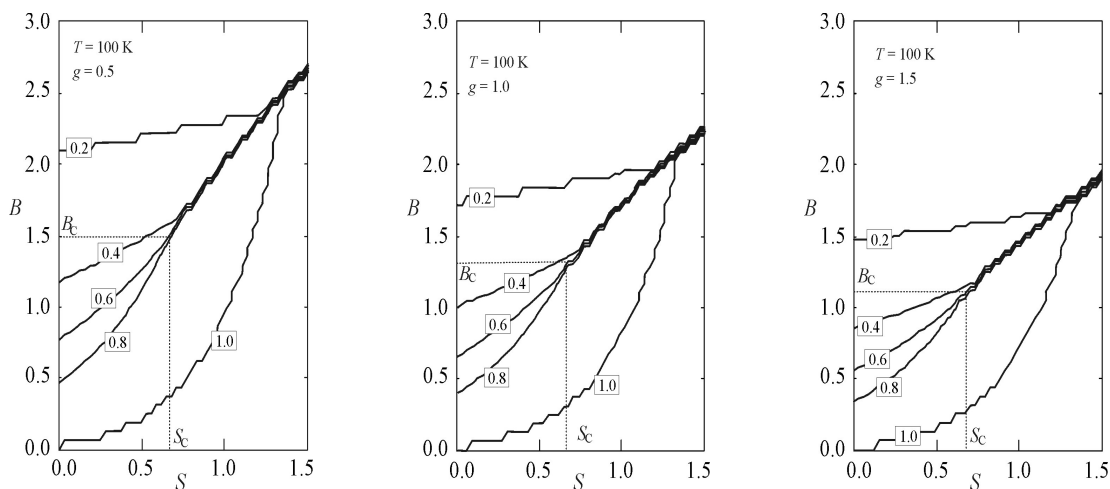
when the polaron band splits into two subbands:

$$E_{\pm}(k) = E_0 + \delta(\delta - 2)E_b - 2J e^{-\delta^2 S \coth(1/2\tau)} \cos(kR_0) \pm \lambda_0. \quad (5)$$

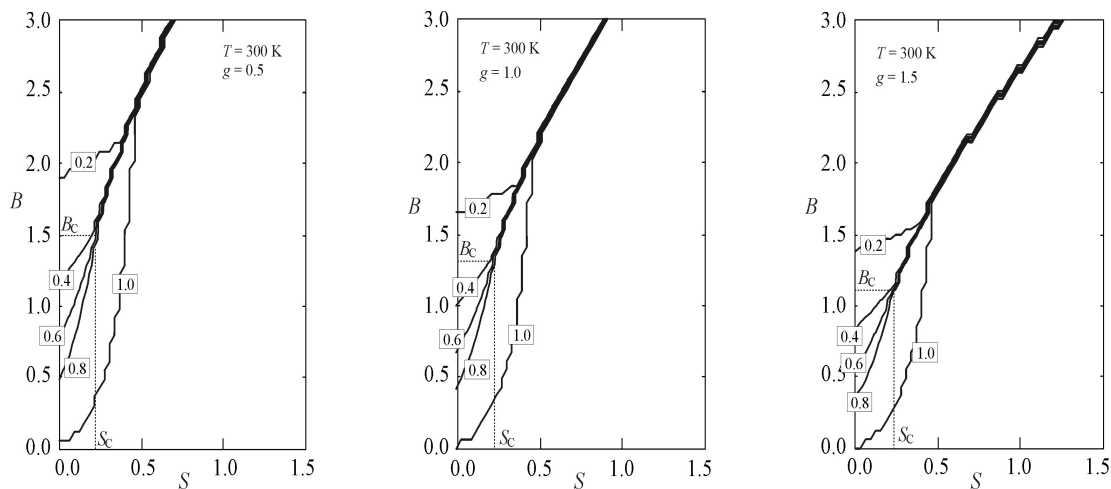
The optimal state of the system is determined by the minimum of the free energy of the whole system. Therefore, the value of the variational parameter should be found from the conditions  $\partial F_B / \partial \delta = 0$  and  $\partial^2 F_B / \partial \delta^2 > 0$ , where  $F_B$  is the upper bound of the system free energy determined by the Bogoliubov theorem [11, 19].

### 3. Obtained results and discussion

To study the vibron properties in the system of the molecular structure composed of two unstaggered single MCs, we have considered the dependence of the dressing parameter on coupling constant  $S$ , adiabatic parameter  $B = 2J / \hbar \omega_0$ , and interchain coupling parameter  $g = J / L$ . Obtained results are presented by the set of iso-lines  $\delta = \{0.2, 0.4, 0.6, 0.8, 1.0\}$  of the function  $\delta(S, B)$  in the low temperature limit ( $T = 100$  K) in Fig. 2 and at room temperature ( $T = 300$  K)



**Figure 2.** The dependence of the variational parameter  $\delta$  on the system parameters  $S$ ,  $B$ ,  $g$  at  $T = 100$  K.



**Figure 3.** The same as in Fig. 2 at  $T = 300$  K.

in Fig. 3.

In these figures one can see that for small values of parameters  $B$  and  $S$ , variational parameter  $\delta$  has a relatively high value, which is close to 1. With increasing of  $S$  (and for the fixed small value of  $B$ ) the variational parameter smoothly increases and reaches its maximum value. Consequently, in the strongly non-adiabatic regime the vibron quasiparticle is fully dressed by the phonon cloud and its properties are quite similar to the standard small polaron quasiparticle [6, 8, 18]. On the other hand, with increasing of  $B$  and for the fixed (small) value of  $S$ , the variational parameter smoothly decreases, and for the moderately adiabatic regime it becomes small (for example, when  $g = 0.5$  and  $B \approx 2.5$ , the variational parameter becomes  $\delta \approx 0.1$ ). Consequently, for the fixed small value of  $S$ , the nature of vibron quasiparticle moves toward undressed, practically free vibron state, when the adiabatic parameter increases. Such behavior is fully consistent with the standard polaron theory in the weak coupling, adiabatic limit.

However, there is a region in  $(S, B)$ -plane where the dressing parameter abruptly changes its value: for the sufficiently high value of  $B = B_c$  with increasing of  $S$ , the dressing parameter at first slowly increases, and for  $S = S_c$  it suffers an abrupt change to a value which is close to 1. Then its value again slowly decreases with a further increase of  $B$ . Such points  $(S_c, B_c)$  in the parameter space, where  $\delta$  suffers a discontinuous change, define so called the “critical area” of parameter space. Since the variational parameter measures the degree of vibron dressing, such a sudden change of the value of  $\delta$  indicates an abrupt change of the degree of vibron dressing, i.e., a sudden change of its nature.

It is worth noting that the strength of interchain coupling has no significant influence on  $S_c$ , but the increase of  $g$  may significantly reduce the value of  $B_c$ . On the other hand, the increase of temperature significantly decreases the minimum value of  $S_c$ , which lies in the weak coupling area at room temperature, while the minimum value of  $B_c$  remains practically unchanged.

Obtained results may play an important role in explaining the process of IMO self-trapping in biological macromolecules which are composed of two macromolecular chains, such as DNA and ACN. System parameter values of these structures belong to the non-adiabatic and to weak or moderately strong vibron-phonon interaction. Our analysis indicates that for such structures at room temperatures and for high interchain coupling the vibron quasiparticle must suffer a sharp change in its nature with a slight change in the value of system parameters and (or) temperature. This change of the properties of vibrational energy carriers may be easily verified by the study of temperature dependence of the maxima in the infrared absorption spectrum of these molecules.

## Acknowledgments

The work was supported by the Serbian Ministry of Education and Science under Contracts Nos. III-45010, III-45005, and by the Project within the Cooperation Agreement between the JINR, Dubna, Russian Federation and Ministry of Education and Science of Republic of Serbia. The work of A. R. was partially supported by the grant of Leading Scientific Schools of the Russian Federation under Project No. 88.2014.2. A. Ch. is grateful to the Votruba-Blokhintsev Program (JINR, Dubna) for the support of participation in the ISQS-23.

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