The vibron dressing in α-helicoidal macromolecular chains*

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We present a study of the physical properties of the vibrational excitation in α-helicoidal macromolecular chains, caused by the interaction with acoustical and optical phonon modes. The influence of the temperature and the basic system parameters on the vibron dressing have been analyzed by employing the simple mean-field approach based on the variational extension of the Lang–Firsov unitary transformation. The applied approach predicts a region in system parameter space where one has an abrupt transition from a partially dressed (light and mobile) to a fully dressed (immobile) vibron state. We found that the boundary of this region depends on system temperature and the type of bond among structural elements in the macromolecular chain.

Keywords: vibron, small-polaron, α-helix, partial dressing

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1. Introduction

It is believed that the hydrolysis of adenosine triphosphate (ATP) is the universal mechanism providing energy for diverse biological processes such as photochemical reactions, cross–membrane ion transfer and signal transduction, muscle contraction, cellular mobility, and transport, to mention just a few.[1] All these processes involve protein molecules as mediators of the long distance energy transfer. However, it is not yet clearly understood how this energy can be transported along the polypeptide chain at long distances without being dissipated or dispersed.

An early explanation of this problem, based on the quantum mechanical model, was proposed in the mid-seventies by Davydov and collaborators.[2–4] The essence of their theory is the assumption that the energy released by ATP hydrolysis can be captured by the protein molecules where it excites the high-frequency amide-I vibrational mode (C=O stretching quanta or vibrons) of a peptide group. Due to the dipole–dipole coupling this energy delocalizes between the adjacent peptide groups giving rise to vibron band states. Such collective excitations may coherently propagate along the polypeptide chain participating in such a way in the energy transfer. Nevertheless, as shown by Davydov and collaborators,[1–4] their lifetime is too short, which rules out the long range energy transfer via a band-like mechanism. Instead, they suggested that the energy losses of the vibron may be prevented by its (self-)trapping in the potential well created by the induced local distortion of the molecular crystals. So the created complex entity, i.e. the vibron surrounded by local lattice distortion, may propagate in a soliton form along the chain with minimal energy losses preserving its shape and velocity for a long time.

According to the general theory of self-trapping (ST) phenomena,[5,6] the character of ST states is determined by the mutual ratio of the values of three basic energy parameters of the system. These parameters are the exciton (electron, vibron, etc.) bandwidth $2|J|$ and characteristic phonon energy $\hbar\omega_{\mathrm{C}}$ (determined by the phonon cut-off frequency ω_{C}) characterizing respectively, the time scale of motion in excitation and lattice subsystems. The third parameter is lattice deformation energy E_{B}, which measures the strength of vibron–phonon interaction.[5–10] Two limiting cases could be considered as being well understood: the large- and small-polaron limits.[5–10] The first one is reached when the excitation bandwidth and lattice deformation energy both highly exceed the characteristic phonon energy, i.e. in the adiabatic strong coupling regime. In that case, phonons are slow with respect to the excitation dynamics and form, essentially classical, large radius quasi-static potential wells in which that excitation (vibron) is trapped. Contrary, in the non-adiabatic limit, when the characteristic phonon energy is larger than the vibron bandwidth, the quantum nature of the phonons plays a crucial role, and small polaron (SP) formation takes place. They are characterized by a short-range lattice distortion that follows polaron motion instantaneously.

The vibron bandwidth in hydrogen-bonded macromolecules such as polypeptide chains is about 0.001 eV, while the phonon cut-off frequencies are typically about 10^{13} Hz.[11–13] As a consequence, basic assumptions for the soliton formation are not fulfilled.[14] For that reason, it has been suggested by some authors that vibron self-trapping in hydrogen-bonded macromolecular chains might result in the formation of a small-polaron, rather than a soliton.[14–19] The

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applicability of such a concept is restricted to the strong coupling and non-adiabatic limit which imposes certain doubts on the whole SP concept since only the non-adiabatic condition is satisfied, while the problem of the strength of vibron–phonon coupling in these structures is still under debate.

Usually, studies devoted to the vibron excitation problem in macromolecular chains involve the value of the strength of vibron–phonon coupling constant extracted from an indirect comparison between experimental and theoretical results.[16] According to these estimations, the value of this constant in hydrogen bonded macromolecular chains ranges between 30 pN and 60 pN.[16,20] However, there are such estimations of that parameter, performed by the *ab initio* calculations for the formamide dimmer, which suggest that its value is significantly lower.[21–23] This fact has become the motivation for some authors to define criteria to discriminate between the weak and the strong vibron–phonon coupling limits.[11,24] According to Ref. [24], the strength of the vibron–phonon coupling in a lattice of H-bonded peptide units at room temperatures belongs to the strong coupling limit, but uncertainty of the value of the coupling constant may lead to completely different conclusions. So, this problem is still unresolved and requires further research. Additionally, some recent numeric[25] and theoretical[26] studies of the ST phenomena in hydrogen-bonded macromolecular chains indicate that the character of ST states can be qualitatively very different depending on the values of system parameters, temperature and, therefore, its proper theoretical description requires an approach that goes beyond the conventional strong-coupling SP theories. Especially useful in that sense is the concept of partial dressing, which is applied in a quite wide part of system parameter space. It relies on modified Lang–Firsov (MLF) unitary transformation. Such an approach is in close correspondence with the supplementary variational treatment of the problem by means of the Toyozawa ansatz.[27]

In this paper we study the character of vibron states in α-helicoidal macromolecular chains. We supposed that a vibron interacts with acoustic and optical phonon modes. The problem of the vibron interaction with optical phonon modes has been intensively considered in many publications in the framework of the Holstein model,[11,28,29] especially after the indications that in ACN the vibron interaction with optical phonon modes plays a crucial role for the vibron small-polaron formation.[30,31] On the other side, the problem of the vibron interaction with acoustical phonon modes usually has not been considered. In our opinion, this problem, should not be disregarded since acoustical phonon modes have quite lower energies in comparison with the optical ones, and consequently, can be easily excited in the whole temperature range.

Our study is performed within the $D = 1$ dimensional model resembling the real α-helix structure. We assumed that, due to the dipole–dipole interaction, the vibron excitation could be delocalized either from some structural element to its first-neighbor ones (from the n-th to the $(n\pm1)$-th structural element), or from some structural element to its non-neighboring (from the n-th to the $m \neq (n, n\pm1)$-th) structural elements. This light generalization of a simple one-dimensional model enables treatment of the vibron delocalization along the direction defined by the covalent bonds in α-helix (corresponding to the vibron delocalization between the first neighboring structural elements), while the vibron delocalization along the hydrogen bonds in an α-helix macromolecule corresponds to vibron delocalization between each third neighboring structural element in the present model. We restrict our attention to the single-vibron case.

Our particular interest is to establish conditions when a vibron moves in a coherent (via band states) or incoherent (diffusive motion by means of the random hops between neighboring peptide groups) fashion along such a structure. Special attention will be paid to the examination of the phenomenon known as small polaron crossover, which may occur for certain values of system parameters and in the certain temperature range. This feature is connected with known ambiguities in SP parameters, effective mass, for example, arising as a consequence of the sudden jump in the magnitude of the degree of phonon dressing.

2. Model Hamiltonian

The system under the consideration consists of single vibron excited on the n-th structural element of the macromolecule, whose physical properties are affected by the thermal vibrations of the macromolecular chain. We suppose that vibron excitation can move along the chain from the n-th to the $(n\pm1)$-th structural element, either from the n-th to the $(n\pm3)$-th structural element. The first possibility corresponds to vibron delocalization along the covalent bonds, while the second possibility corresponds to vibron delocalization along the hydrogen bonds in a three-dimensional (3D) α-helix structure. Due to the fact that the energy of the dipole–dipole interaction between second-neighboring peptide groups is smaller than the energy of the dipole–dipole interaction between the first-neighboring ones,[12] the vibron delocalization from the n-th to the $(n\pm2)$-th structural element is not considered. The corresponding Hamiltonian of the vibration excitation and phonon subsystem can be written in the following form[8]

$$H = \Delta\sum_n A_n^\dagger A_n - \sum_n J_g A_n^\dagger (A_{n+g} + A_{n-g}) + \sum_q \hbar\omega_q B_q^\dagger B_q + \frac{1}{\sqrt{N}}\sum_q\sum_n F_q \mathrm{e}^{\mathrm{i}qnh} A_n^\dagger A_n (B_q + B_{-q}^\dagger). \quad (1)$$

In the above Hamiltonian the quantity Δ is the vibron excitation energy, $A_n^\dagger$ (A_n) describes the presence (absence) of the vibron quanta on the structural element, which is positioned on the n-th lattice site, $B_q^\dagger$ (B_q) creates (annihilates) phonon quanta, and ω_q is the phonon frequency. The inter-site overlap integral J_g characterizes the vibron transfer between macromolecular chain structural elements: $g = 1$ in the case of the

vibron transfer along the covalent bonds, and $g = 3$ in the case of the vibron transfer along the hydrogen bond. Delocalization along the covalent and hydrogen bonds will be examined separately, and therefore the summation over the index g was not included in Eq. (1). This refers to two practically independent models describing the vibron delocalization along particular bonds. In such a way, the mutual influence of the vibron delocalization along covalent bonds on vibron delocalization along hydrogen bonds (and *vice versa*) has been disregarded. Widely accepted datum for values of the hopping constant J_3 is $J_3 = J_{\rm hb} = 7.8\ {\rm cm}^{-1}$, while for the hopping constant between different spines of hydrogen-bonded peptide units is $J_1 = J_{\rm cov} = -12.4\ {\rm cm}^{-1}$.[11–13] The parameter h is a distance between two neighboring structural elements along the axis of the macromolecular chain. Finally, $F_q = F^*_{-q}$ is the vibron–phonon coupling parameter, which is a function of the coupling constants χ_g. The coupling constant accounts for the modulation of the vibron frequency placed on the n-th structural element due to the external motion of the $(n+g)$-th structural element. The value of the coupling constant that determines the vibron–phonon coupling in the direction defined by hydrogen bonds ($\chi_{\rm hb}$) in α-helix structure is known.[16,20] However, the influence of the motion of the $(n\pm1)$-th and the $(n\pm2)$-th structural elements on the amide-I vibration on the n-th structural element is still unknown. According to some authors,[32] numerical values of these parameters satisfy the following conditions: $\chi_{\rm hb} > \chi_1 \gg \chi_2$. In this paper we assume that $\chi_1 = 0$, $\chi_2 = 0$, and $\chi_3 = \chi_{\rm hb}$. Consequently, in the case of the vibron interacting with acoustic phonon modes, F_q becomes as, $F_q = 2{\rm i}\chi_{\rm hb}\sqrt{\hbar/(2M\omega_q)}\sin(3qh)$,[16,17] while in the case of the vibron interacting with optical phonon modes this parameter becomes: $F_q = \chi_{\rm hb}\sqrt{\hbar/(2M\omega_q)}$. Phonon dispersion law is determined by the geometric structure of the macromolecular chain, mass of the structural elements from which the chain is built, as well as the values of the elasticity coefficients that characterize the stiffness of the covalent and hydrogen bonds in the chain. Due to the fact that in the case of an α-helix secondary structure three intermolecular interactions is the minimal number of bonds required to have a stabilized structure,[33] we assumed that each structural element is connected with its first-neighbors, second-neighbors, and third-neighbors. The elasticity coefficient K_1 of the covalent bonds, that connects nearest-neighbor peptide units, varies between 45 N/m and 75 N/m,[34] while the elasticity coefficient K_3 of the hydrogen bonds ranges from 13 N/m to 20 N/m.[11,18,32,34] In contrast to the analysis carried out in Ref. [32] we take into account the non-zero value of the elasticity coefficient K_2 of the second-neighbor bonds which presence can significantly affect on the nature of the phonon spectra. We vary this value from interval $K_2 \in [\min K_2, \max K_2]$, where $\min K_2 \ll K_3$ and $K_1 > \max K_2 \gg K_3$. Consequently, the dispersion law for acoustic phonon modes have the following form

$$\omega_q^2 = \frac{4K_1}{M}\sin^2\Big(\frac{qh}{2}\Big) + \frac{4K_2}{M}\sin^2\Big(qh\Big) + \frac{4K_3}{M}\sin^2\Big(\frac{3qh}{2}\Big).$$

In the optical phonon case, we used the dispersioneless approximation: $\omega_q = \omega_{\rm C}$, where the phonon cut-off frequency is $\omega_{\rm C} = 2\sqrt{(K_1 + 4K_2 + 9K_3)/M}$.[35] Here, M is the mass of the peptide unit. For the mass parameter we adopted the following numerical value: $M = 5.7\times10^{-25}$ kg.[11]

In order to examine under which conditions dressed vibron excitations represent dynamically stable eigenstates of the system, we cross to the small-polaron picture using an MLF unitary transformation operator[26]

$$U = \exp\Big\{-\frac{1}{\sqrt{N}}\sum_q\sum_n f_q\,{\rm e}^{-{\rm i}qnh}A_n^\dagger A_n(B_{-q} - B_q^\dagger)\Big\}$$

and we rewrite Eq. (1) in terms of new operators $a_n = UA_nU^\dagger$ ($a_n^\dagger = UA_n^\dagger U^\dagger$) and $b_q = UB_qU^\dagger$ ($b_q^\dagger = UB_q^\dagger U^\dagger$), representing the dressed vibrons and new phonons in the lattice with shifted equilibrium positions of molecular groups.

Here $f_q = \delta F_q^*/(\hbar\omega_q)$, $0 < \delta < 1$ is the variational parameter, which characterizes the degree in which the vibron distorts the lattice and the lattice feedback on the vibron, i.e. vibron dressing.

In the next stage, we apply a simple mean-field approach, which enables explicit accounting for the influence of thermal fluctuations on SP properties and, in particular, the degree of dressing. In the present case, the temperature enters our model Hamiltonian implicitly through phonon fluctuations around its new equilibrium positions. Thus, the explicit temperature dependence may be introduced here by the appropriate averaging of the transformed Hamiltonian over the phonon subsystem. In particular, we define (in wave number representation) an effective mean-field Hamiltonian H_0 as follows:

$$H = H_0 + H_{\rm int}, \tag{2}$$

where $H_0 = H_v + H_{\rm ph}$, $H_v = \langle H - H_{\rm ph}\rangle_{\rm ph}$, and $H_{\rm int} = H - H_{\rm ph} - \langle H - H_{\rm ph}\rangle_{\rm ph}$. The symbol $\langle\ \rangle_{\rm ph}$ denotes the average over the new phonon ensemble, which is in thermal equilibrium state at temperature T. In such a way we obtain

$$H_0 = \sum_k E^g_{\rm SP}(k)a_k^\dagger a_k + \sum_q \hbar\omega_q b_q^\dagger b_q, \tag{3}$$

$$\begin{aligned} H_{\rm int} = {} & \frac{1}{\sqrt{N}}\sum_q\sum_k (F_q^* - \hbar\omega_q f_q)a_k^\dagger a_{k+q}(b_{-q} + b_q^\dagger) \\ & - \sum_{k_1}\sum_{k_2} J_g a_{k_1}^\dagger a_{k_2}\Big\{{\rm e}^{{\rm i}k_2gh}\big[T_{k_1,k_2}(g) - {\rm e}^{-W_g(T)}\delta_{k_1,k_2}\big] \\ & + {\rm e}^{-{\rm i}k_2gh}\big[T_{k_1,k_2}(-g) - {\rm e}^{-W_g(T)}\delta_{k_1,k_2}\big]\Big\}, \end{aligned} \tag{4}$$

where $a_k = (1/\sqrt{N})\sum_n {\rm e}^{{\rm i}knh}a_n$, and operators $T_{k_1,k_2}(\pm g)$ look as

$$T_{k_1,k_2}(\pm g) = \frac{1}{N}\sum_n {\rm e}^{{\rm i}(k_2-k_1)nh}\theta^\dagger_{n\pm g}\theta_n,$$

where

$$\theta_n = \exp\Big\{\frac{1}{\sqrt{N}}\sum_q f_q\,{\rm e}^{{\rm i}qnh}(b_q - b_{-q}^\dagger)\Big\}, \tag{5}$$

while mean values of $T_{k_1,k_2}(\pm g)$ over phonon subsystem are calculated as follows:

$$\begin{aligned}\left\langle T_{k_1,k_2}(\pm g)\right\rangle_{\rm ph} &= \frac{1}{\sqrt{N}}\sum_n \mathrm{e}^{\mathrm{i}(k_2-k_1)nh}\left\langle \theta^{\dagger}_{n\pm g}\theta_n\right\rangle_{\rm ph}\\ &= \mathrm{e}^{-W_g(T)}\delta_{k_1,k_2}. \end{aligned} \tag{6}$$

The variational energy of the small-polaron band state is given by the following formula

$$\begin{aligned}E^g_{\rm SP}(k) &= \Delta - \frac{1}{N}\sum_q \left\{(f_q + f^*_{-q})F_q - \hbar\omega_q|f_q|^2\right\}\\ &\quad - 2J_g\,\mathrm{e}^{-W_g(T)}\cos(gkh)\end{aligned} \tag{7}$$

with quantity

$$W_g(T) = \frac{1}{N}\sum_q |f_q|^2(2\bar{\nu}_q+1)(1-\cos(gqh)) \tag{8}$$

denoting the vibron-band narrowing factors, which characterizes the degree of the reduction of the corresponding overlap integrals or equivalently the enhancement of the polaron effective mass. For obvious reasons, they are sometimes called the dressing fractions or the dressing parameters. Lastly, $\bar{\nu}_q = 1/(\mathrm{e}^{\hbar\omega_q/k_{\rm B}T}-1)$ denotes the phonon average number.

Partially dressed vibron states represent dynamically stable eigenstates of the system provided that variational parameter corresponds to the minimum of the system free energy. Thus, we search for its optimized value minimizing the system free energy, $\mathscr{F} = -k_{\rm B}T\ln\mathrm{Tr}\{\mathrm{e}^{-H/k_{\rm B}T}\}$. According to the Bogoliubov variational theorem (which states that the function

$$\mathscr{F}_{\rm B} = -k_{\rm B}T\ln\mathrm{Tr}\{\mathrm{e}^{-H_0/k_{\rm B}T}\} + \langle H_{\rm int}\rangle_{H_0}$$

determines the upper bound of the system free energy: $\mathscr{F} \le \mathscr{F}_{\rm B}$), the procedure of the minimization of the $\mathscr{F}$ can be replaced by the procedure of the minimization of the $\mathscr{F}_{\rm B}$. In the above expression, $\langle H_{\rm int}\rangle_{H_0}$ denotes the mean value of the interaction polaron–phonon term, over non-interacting polaron–phonon system H_0.

Using vector basis

$$\left\{|\psi(k,\{n_q\})\rangle = a^{\dagger}_k|0\rangle_{\rm vib}\otimes\prod_q\frac{(b^{\dagger}_q)^{n_q}}{\sqrt{n_q!}}|0\rangle_{\rm ph}|,\forall k,\forall n_q\right\},$$

one can obtain the following form of $\mathscr{F}_{\rm B}$

$$\mathscr{F}^g_{\rm B} = -k_{\rm B}T\ln\sum_k \mathrm{e}^{-E^g_{\rm SP}(k)/k_{\rm B}T} - k_{\rm B}T\sum_q \ln\frac{1}{1-\mathrm{e}^{-\hbar\omega_q/k_{\rm B}T}}. \tag{9}$$

It is useful to have in mind that only the first term of $\mathscr{F}^g_{\rm B}$ depends on variational parameter δ.

3. Results and discussion

In order to analyze the character of the dressed vibron states in macromolecular chains, we examine the degree of the vibron–polaron dressing (i.e. its effective mass) and the vibron–polaron ground state energy. Note, the ground-state vector of the effective Hamiltonian H_0 reads

$$|\psi_{\rm GS}\rangle = a^{\dagger}_{k_0}|0\rangle_{\rm vib}\otimes\prod_q|0\rangle_q,$$

where $\prod_q|0\rangle_q$ is the phonon vacuum vector and $k_0 = \pi/3h$ ($g=3$), or $k_0 = 0$ ($g=1$). This case is also the most relevant for the spectroscopy since vibron bandwidths in these media are very narrow and its dispersion in all practical examination of optical spectra can be neglected.[7,11,25,36,37] As a consequence the ground-state energy corresponds to the lowest level of SP energy, i.e.

$$E^g_{\rm GS} = \langle\psi_{\rm GS}|H_0|\psi_{\rm GS}\rangle = E^g_{\rm SP}(k_0).$$

Further calculations are done in terms of two independent dimensionless parameters: adiabatic parameter $B = 2|J|/(\hbar\omega_{\rm B})$ determining the character of the lattice deformation engaged in the polaron formation and coupling constant $S = E_{\rm B}/(\hbar\omega_{\rm B})$ (where $E_{\rm B} = (1/N)\sum_q\{|F_q|^2/(\hbar\omega_q)\}$ is the lattice deformation energy), which determines the polaron spatial size and the degree of dressing. This parameter, which was originally introduced by Holstein[8,9] has special importance in the strong-coupling non-adiabatic regime ($S \gg 1$ and $B \ll 1$) where it characterizes the SP narrowing of a quasiparticle band which decreases exponentially as e^{-S}.

The expressions for the dressing fractions and normalized ground state energy are calculated for the vibron which delocalizes along the covalent bonds, and for the vibron which delocalizes along the hydrogen bonds. We take into account the vibron which interacts with acoustical and optical phonon modes separately. The variational parameter δ is calculated by the minimization of the Bogoliubov upper bound of the system free energy: $\partial\mathscr{F}_{\rm B}/(\partial\delta) = 0$ and $\partial^2\mathscr{F}_{\rm B}/(\partial\delta^2) > 0$.

A normalized ground state energy (normalized on the characteristic phonon energy and measured from the vibron excitation energy level: $\mathscr{E}^g_{\rm GS} = (E^g_{\rm GS} - \Delta)/(\hbar\omega_{\rm C})$ takes the value,

$$\mathscr{E}^g_{\rm GS}(\tau) = -S(2-\delta)\delta - B\,\mathrm{e}^{-W_g(\tau)}. \tag{10}$$

The first term in Eq. (10) corresponds to quasiparticle binding energy, while the second one corresponds to the width of the quasiparticle energy band. In the weak coupling limit or for intermediate coupling strength, there exists quasiparticle energy band of certain width. Consequently, in that case the quasiparticle is delocalized (it can move along the chain in a coherent band-like fashion). On the other side, in the strong coupling limit (i.e. for the full dressed vibron case when $\delta = 1$) the energy band is quite narrow, and consequently $\mathscr{E}_{\rm GS}$ is proportional to quasiparticle binding energy.[10,14] In that case the quasiparticle is almost localized on the particular macromolecular structural element (i.e. on the particular peptide unit), and it can move by random jumps between neighboring peptide units. The functional dependence of normalized ground state energy on coupling constant becomes $\mathscr{E}_{\rm GS}(S) \cong -S$. These simple conclusions may be very useful in analyzing the obtained results and explaining the nature of the dressed vibron states.

The expression for vibron dressing fraction, in the case of

the vibron which delocalizes along the covalent bond reads

$$W(\tau) = \delta^2 S \frac{I_W(\tau)}{I_{Eb}}, \tag{11}$$

when the vibron interacts with acoustical phonon modes, while the quantity

$$W(\tau) = \delta^2 S \coth\left(\frac{1}{2\tau}\right) \tag{12}$$

is vibron dressing fraction when vibron interacts with optical phonon modes. In Eq. (11) integrals

$$I_W(\tau) = \frac{1}{\pi}\int_0^\pi \frac{1}{\bar{\omega}_x^3}\coth\left(\frac{\bar{\omega}_x}{2\tau}\right)\sin^2 3x(1-\cos x)\,\mathrm{d}x$$

and

$$I_{Eb} = \frac{1}{\pi}\int_0^\pi \frac{\sin^2 3x}{\bar{\omega}_x^2}\,\mathrm{d}x$$

are obtained by the virtue of the standard rule,

$$\frac{1}{N}\sum_q \ldots \to \frac{h}{2\pi}\int_{-\pi/h}^{\pi/h} \ldots \mathrm{d}q.$$

In the case when the vibron delocalizes along the hydrogen bonds, the vibron dressing fraction becomes

$$W(\tau) = \delta^2 S \frac{\bar{I}_W(\tau)}{I_{Eb}}, \tag{13}$$

when the vibron interacts with acoustical phonon modes, and in the case when the vibron interacts with optical phonon modes it takes the form

$$W(\tau) = \delta^2 S \coth\left(\frac{1}{2\tau}\right). \tag{14}$$

The integral in Eq. (13) is

$$\bar{I}_W(\tau) = \frac{1}{\pi}\int_0^\pi \frac{1}{\bar{\omega}_x^3}\coth\left(\frac{\bar{\omega}_x}{2\tau}\right)\sin^2 3x(1-\cos 3x)\,\mathrm{d}x.$$

The system normalized temperature is $\tau = k_\mathrm{B}T/(\hbar\omega_\mathrm{C})$, $\bar{\omega}_x = \omega_x/(\omega_\mathrm{C})$ and $x = qh$.

The obtained results are illustrated in Figs. 1–6. In Figs. 1–4, the dressing fractions and ground state energy are presented by the set of 'adiabatic' curves $W(S)$ and $\mathscr{E}_\mathrm{GS}(S)$ (each curve corresponds to a particular fixed value of the adiabatic parameter B) for various values of B, system temperature T, for both types of the bonds between peptide units, and for both cases of the vibron–phonon interaction (interaction with acoustical and optical phonon modes). The adiabatic curves $\mathscr{E}_\mathrm{EG}(S)$ obtained by the standard LF theory are presented by the thin curves, while the ones obtained by the variational approach are represented by the thick curves.

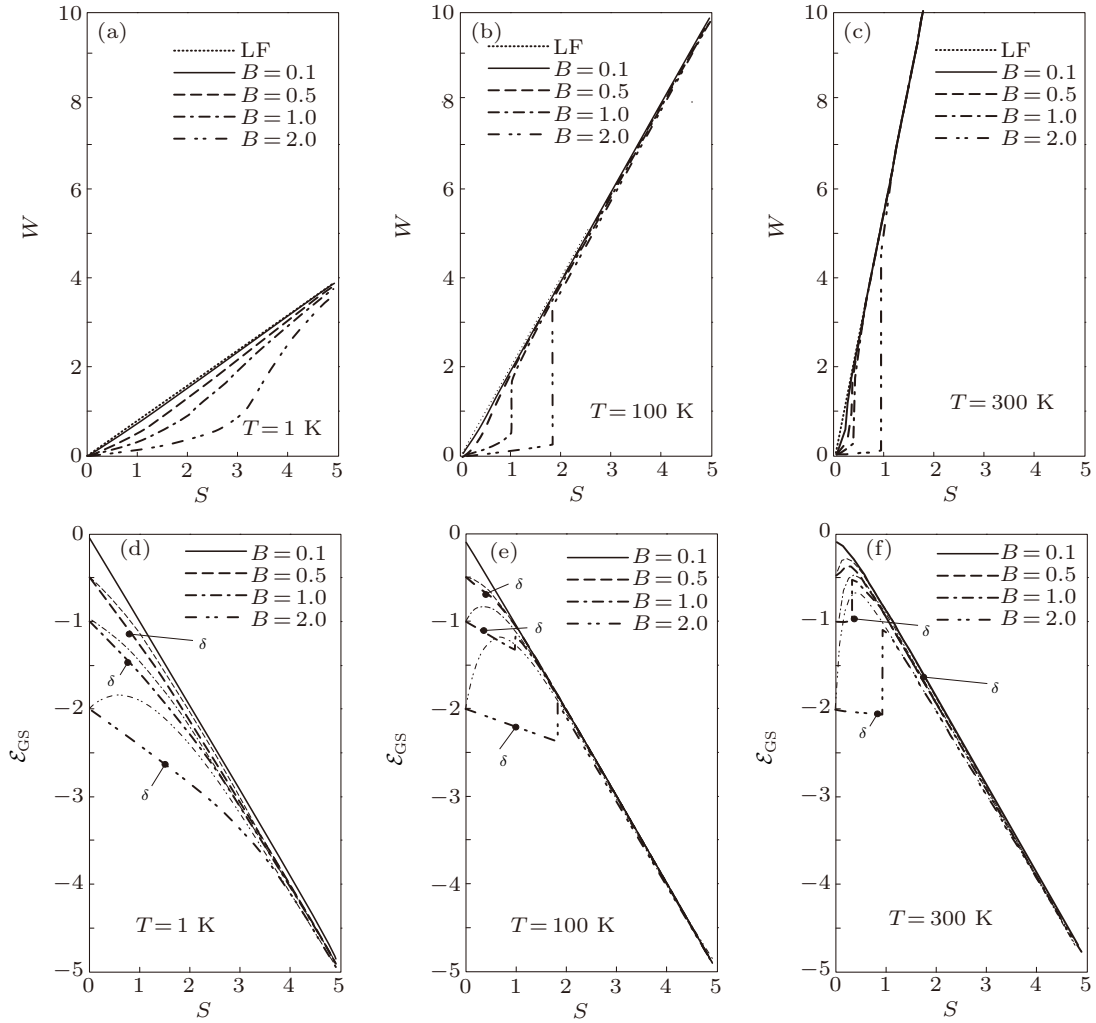


Fig. 1. Dependence of the vibron dressing fraction W (first row), and the vibron ground state energy $\mathscr{E}_\mathrm{GS}$ (second row), on the coupling constant S, for various B and T. The case of the vibron which moves along the covalent bonds and interacts with acoustical phonon modes.

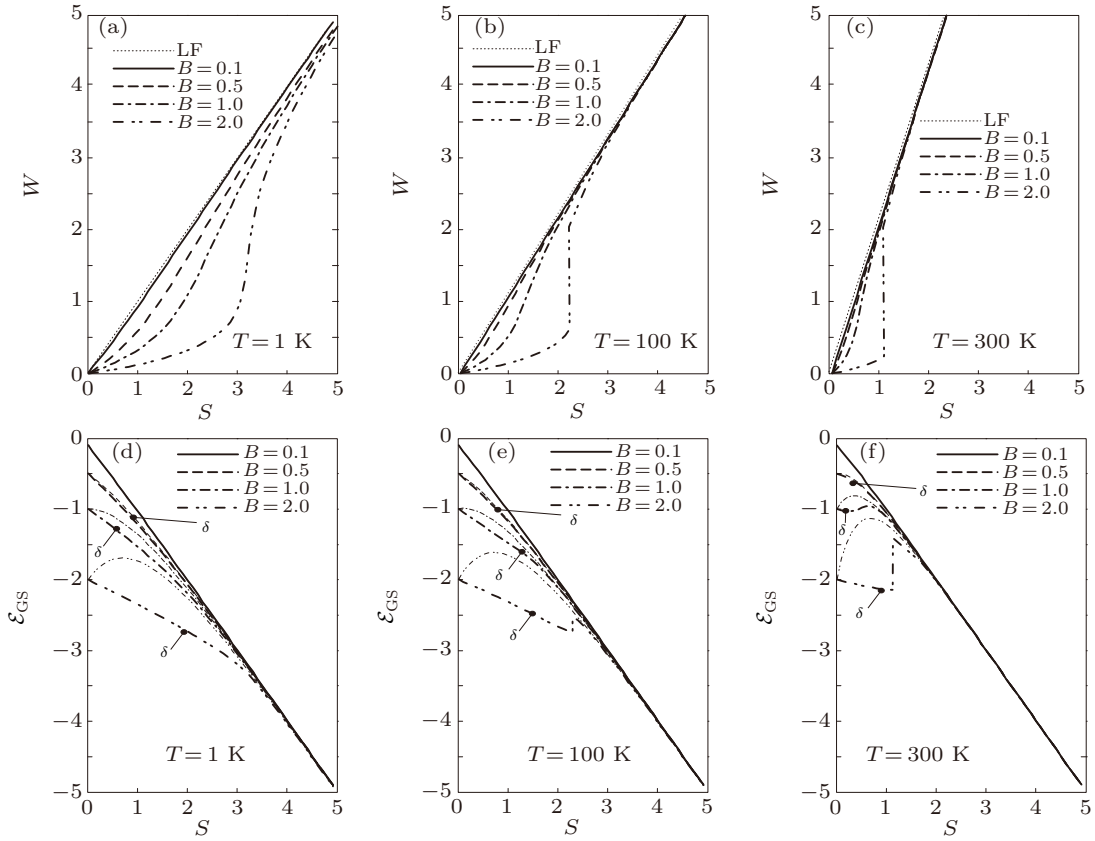


Fig. 2. Dependence of the vibron dressing fraction W (first row), and the vibron ground state energy $\mathscr{E}_{\rm GS}$ (second row), on the coupling constant S, for various B and T. The case of the vibron which moves along the covalent bonds and interacts with optical phonon modes.

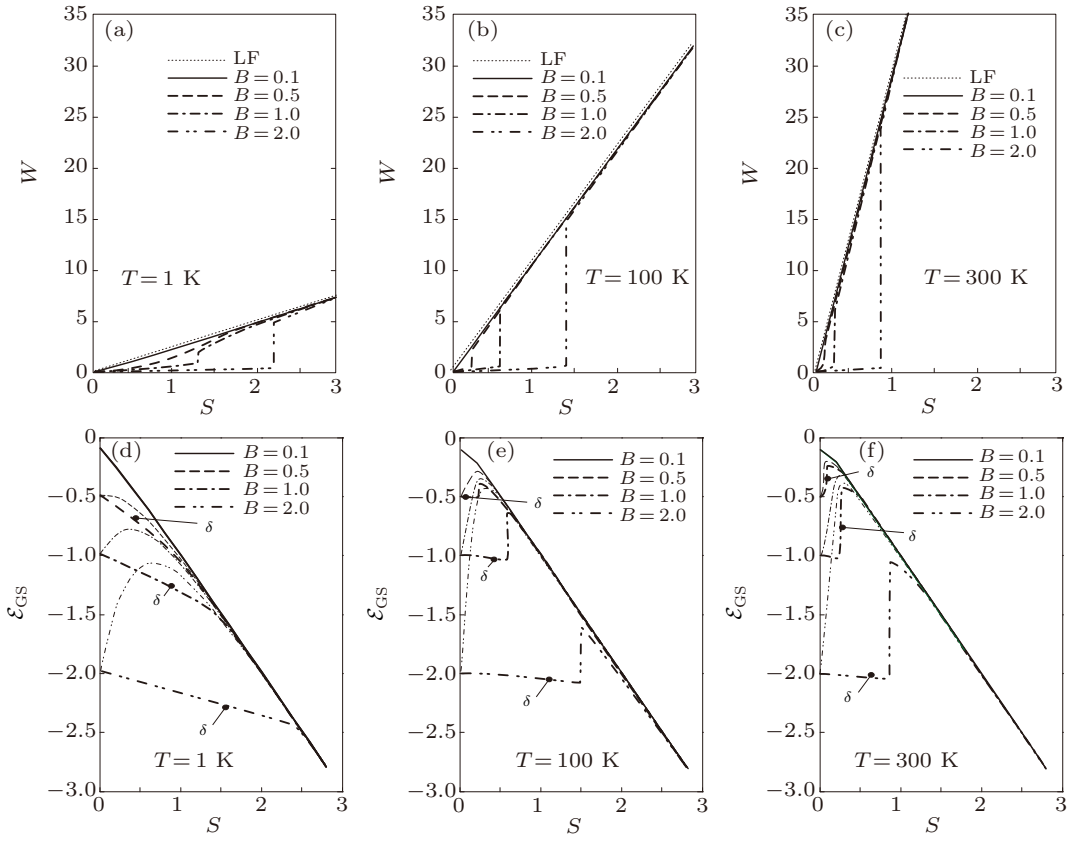


Fig. 3. Dependence of the vibron dressing fraction W (first row), and the vibron ground state energy $\mathscr{E}_{\rm GS}$ (second row), on the coupling constant S, for various B and T. The case of the vibron which moves along the hydrogen bonds and interact with acoustical phonon modes.

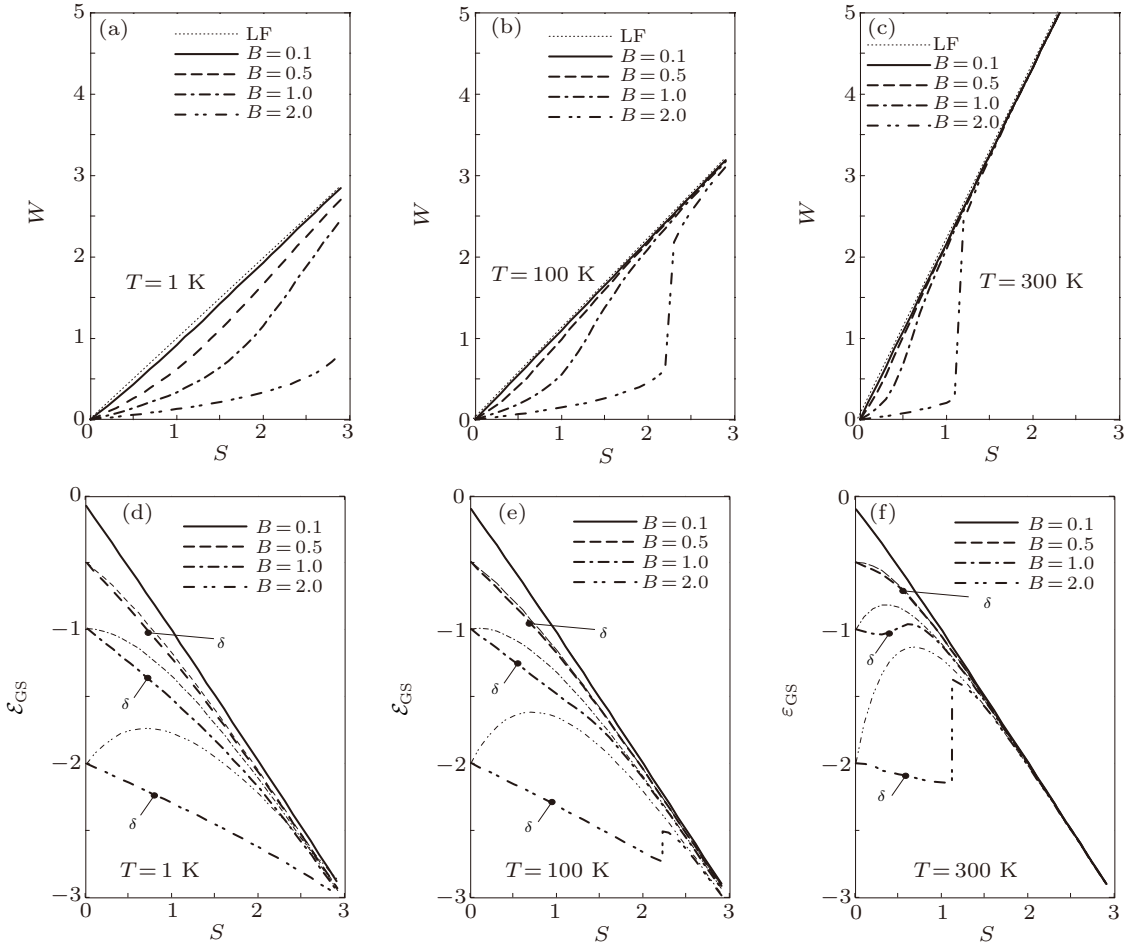


Fig. 4. Dependence of the vibron dressing fraction W (first row), and the vibron ground state energy $\mathscr{E}_{\rm GS}$ (second row), on the coupling constant S, for various B and T. The case of the vibron which moves along the hydrogen bonds and interacts with optical phonon modes.

It should be noted that from the above presented results in the strong coupling limit and for all values of B and T the obtained values of both quantities are qualitatively very similar with ones derived by the usage of standard SP approach (i.e. with results obtained by using of the Lang–Firsov unitary transformation). This similarity increases with the decreasing of B. For those values of the system parameters both approaches predict heavy dressed vibron states. In addition, with the growth of the system temperature and for a fixed value of B, the values of the parameter S for which our approach and standard SP theory yield similar results moves towards lower values. These observations seem to be unsurprising, because of the framework of the standard small-polaron approach, the growth of the system temperature has practically the same effect as the growth of the coupling constant. This point appears by the consequence of the fact that the SP dressing fraction (and consequently quasiparticle effective mass) increases as temperature grows, but it also increases with the increases of coupling constant value.[38]

On the other hand, for small and medium values of S our results significantly differ from those predicted by standard LF theory. In contrast to the standard SP theory, in that limit our approach predicts slightly dressed or partially dressed vibron states (instead of characteristic parabolic shape, the adiabatic curves $\mathscr{E}_{\rm GS}(S)$ has linear dependence of coupling constant). For a fixed value of system temperature and S this difference increases with increasing B. Similarly, for fixed S and B the difference increases with increasing of T. All these conclusions are fulfilled for both types of intermolecular forces between peptide units, and for both cases of the vibron–phonon interactions.

As is demonstrated in Figs. 1–4 there are two clearly distinguished areas in the system parameter space, where $W(S)$ and $\mathscr{E}_{\rm GS}(S)$ display qualitatively different behaviors. In fact, for each T, the type of the vibron–phonon interaction, and the bond type there exists a critical adiabatic parameter $B_{\rm C}$, such that, for all $B < B_{\rm C}$, dressing fraction $W(S)$ and ground state energy $\mathscr{E}_{\rm GS}(S)$ changes smoothly as a function of coupling constant S. In that case function $W(S)$ monotonically increases, while $\mathscr{E}_{\rm GS}(S)$ for small values of S slightly decreases, and after some value of S it becomes very close to the linear decreasing function. Thus, for $B < B_{\rm C}$ the vibron states for small values of S correspond to small-polaron band states with gradual transition towards the self-trapped ones as the cou-

pling constant increases.

But when B reaches some critical value B_C, adiabatic curves $W(S)$ have an infinity derivative at a point with abscissa S_C. In the same time, ground state energy $\mathscr{E}_{GS}(S)$ ceases to be smooth at the point with the same abscissa. The point in the system parameter space, with coordinates (S_C, B_C) determines the 'critical point'. By further increasing the value of B ($B > B_C$, i.e. for supercritical values of B), adiabatic curves are smooth up to a supercritical value of S, where they suffer from an abrupt change. The main characteristic of the system in this region of parameter space is the spontaneous abrupt transition between the low dressed and high dressed states, which takes place through the discontinuous change in the magnitude of SP parameters, effective mass, and ground state energy, in particular. As one can remark, with increasing of adiabatic parameter B, the S_C moves to larger values. But, as system temperature T increases, the S_C moves to lower values (for fixed value of B). One can also remark that these observations are stronger expressed for a vibron which delocalizes along the hydrogen bonds, especially in the case of vibron interaction with acoustic phonon modes.

The existence of the critical and supercritical points is a consequence of the appearance of multiple local extremes of the function $\mathscr{F}_B(\delta)$. In fact, in the case of supercritical values of B, and for small values of S, the function $\mathscr{F}_B(\delta)$ increases with respect to δ. With the increasing of S one local minimum firstly appears at a point at which the abscissa is $\delta \approx 0$. With further increasing of S, there appear two additional local extremes: one local maximum and one local minimum (the new minimum appears at the point with abscissa $\delta \approx 1$). For smaller values of S, the minimum that corresponds to the lower value of δ is deeper, and consequently, for these values of S and B the vibron is lightly dressed (a small value of δ implies a small value of the dressing fraction). When S reaches S_C, both local minima have equal depths. This means there exist two vibron states (light dressed vibron state and heavy dressed vibron state), they both correspond to the same minimal value of $\mathscr{F}_B$. With further increasing of S the deeper minimum of $\mathscr{F}_B$ becomes the minimum that corresponds to the heavy dressed vibron state ($\delta \approx 1$). This model predicts a similar vibron nature for both types of intermolecular chains, and for both types of vibron–phonon interactions.

The above-mentioned discontinuities are well known and have sometimes been considered as being unphysical and an artifact of the variational methods mostly used in particular calculations. Nevertheless, in spite of all doubts the rapid increase of the polaron effective mass with the coupling constant in the adiabatic regime ($B \gg 1$) is the main characteristic of the so-called SP crossover and represents the general conclusion regardless of the particular theoretical method used in Refs. [14], [27], [39]–[43]. The same qualitative and precise behavior has been undoubtedly confirmed recently by means of the numerically exact diagonalization[44] of the Holstein model where discontinuous transition from free electron to immobile small polaron $m_{eff} = \infty$ has been predicted. (The notion of phase transition has been used in Ref. [44] to emphasize its abrupt character). Moreover, the possible coexistence of free and localized states have been recently pointed out by Hamm and Tsironis[25] who had investigated the dimensionality effects on large to small polaron crossover in Holstein's model. The emergence of an energy barrier separating the two types of solutions has been predicted irrespectively of the system dimensionality. This barrier is responsible for the double-peak structure of the wave function and its appearance has been interpreted as a clear signature of the coexistence of free (large) and localized (small) polaron solutions in a certain parameter range, which is in qualitative agreement with our results. Finally, it is interesting that there exists the close analogy between abrupt change from delocalized to localized vibron state in macromolecular chains and thermally activated positronium state transitions in alkali halide crystals. It is known that the ground state of positronium in such structures is delocalized (Bloch-type), but there exists an additional metastable state which is localized and it can be achieved by increasing the system temperature. The localization of the positronium was investigated experimentally,[45–47] and theoretically,[48,49] and it can be explained by the thermally activated transition from ground state to excited metastable state.

As mentioned above, the critical values of coupling constant S_C and adiabatic parameter B_C depend on the nature of the intermolecular bonds, phonon nature, as well as the system temperature. This dependence is represented in Figs. 5 and 6 by dashed lines. Supercritical values of S and B are presented for several values of T by sets of isothermal curves (full lines).

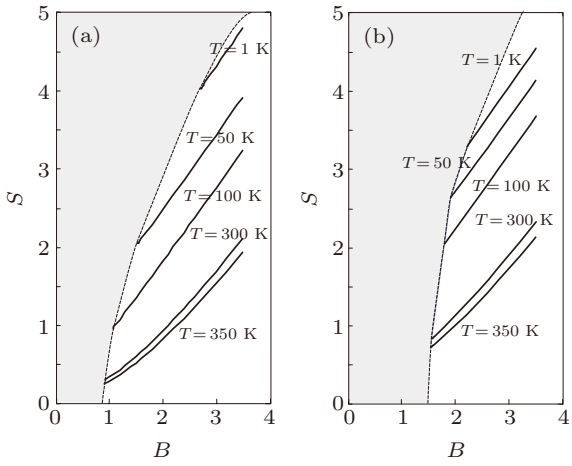


Fig. 5. The dependence on the boundary values of the system parameters (S, B) on temperature in the case of vibron delocalization along the covalent bonds: (a) vibron interacting with acoustical phonon modes; (b) vibron interacts with optical phonon modes.

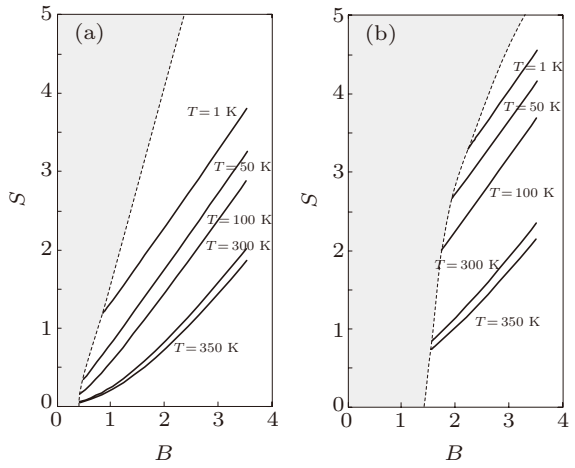


Fig. 6. The dependence on the boundary values of the system parameters (S,B) on temperature in the case of vibron delocalization along the hydrogen bonds: (a) vibron interacting with acoustical phonon modes; (b) vibron interacts with optical phonon modes.

The dashed line divides the system parameter space into two areas: for the system parameter values that belong to the left area the curves $W(S)$ and $\mathscr{E}_{\rm GS}(S)$ are smooth, and for larger values of S they are very close to the ones predicted by the standard LF approach. Here, the presented model predicts a significant difference with standard LF approach only for medium values of S, where the obtained adiabatic curves have a characteristic shape. The points that lie at the right side of the dashed line are supercritical points, where $W(S)$ and $\mathscr{E}_{\rm GS}(S)$ have an abrupt change.

The critical values of system parameters are shifted to lower values, with increasing of the system temperature. As an example, in the case of the vibron which delocalizes along the covalent bond and interacts with acoustical phonon modes, these values belong to the adiabatic and strong coupling region. They enter the non-adiabatic region approximately at $T = 145$ K (at room temperature $T = 300$ K, we obtain $B_{\rm C} = 0.92$ and $S_{\rm C} = 0.303$. These values of the system parameters belong to the non-adiabatic region of intermediate interaction. In the case when a vibron interacts with optical phonon modes, $B_{\rm C}$ belongs to the adiabatic region for the whole temperature range (at $T = 300$ K, we obtain $B_{\rm C} = 1.55$ and $S_{\rm C} = 0.819$). However, in the case of vibron delocalization along the hydrogen bonds, and interaction with acoustical phonon modes, $B_{\rm C}$ belongs to the non-adiabatic region for all values of the system temperatures (at $T = 1$ K we obtain $B_{\rm C} = 0.82$ and $S_{\rm C} = 1.179$), and at room temperatures it enters deeply into the non-adiabatic region (at $T = 300$ K we obtain $B_{\rm C} = 0.39$ and $S_{\rm C} = 0.056$). In the case of vibron interaction with optical phonon modes, the obtained results are very similar to the ones obtained for vibron delocalization along the covalent bonds and its interaction with optical phonon modes.

4. Conclusions

Summarizing, the presented model of the α-helicoidal macromolecular chain predicts that vibron self-trapping would result in the creation of partially dressed small-polaron band states. With the increase of temperature, heavy dressed, practically localized small-polaron states may appear instead of the band states, irrespective on the nature of the bonds between two structural units. The values of the critical parameters for which the vibron nature changes are dependent on the system temperature and nature of the bonds. It is noticeable that values of the $B_{\rm C}$ decrease with the increase of the system temperature.

In the case of an α-helix structure our system model predicts the following. When a vibron interacts with optical phonon modes, the critical value of the adiabatic parameter belongs to the adiabatic region for all values of system temperature, as well as for both intermolecular bond types. In that case the critical value of coupling constant $S_{\rm C}$ belongs to the strong coupling limit at low temperatures, and reaches an intermediate coupling strength approximately at room temperature.

When the vibron interacts with acoustical phonon modes, $B_{\rm C}$ enters the non-adiabatic region at $T = 145$ K in the case of vibron delocalization along the covalent bonds. However, in the case of vibron delocalization along the hydrogen bonds, $B_{\rm C}$ belongs to non-adiabatic region for all values of system temperature.

Due to the fact that the values of the system parameters for the alpha-helix macromolecules belong to the non-adiabatic and weak to intermediate coupling limit, it seems that at room temperature only a heavy dressed vibron may appear in such systems, which moves along the covalent bonds, but for a vibron which moves along the hydrogen bonds weakly dressed vibron states may appear.

The obtained results are similar to the results obtained in the study of the electron–polaron effective mass around the Γ point of the Brillouin zone.[42,43] Additionally, according to the study by Hamm and Tsironis,[25] it follows that the results obtained here are consistent, at least on a qualitative level, with the exact numeric ones.

In the latter respect, our study represents the background for investigations of the polaron properties in the three-dimensional structure of α-helicoidal proteins as well as the boundary between coherent and incoherent polaron motion. According to some authors,[32,33] the phonon spectra in α-helicoidal structures exhibit two acoustical phonon branches and one optical phonon branch. The first ones in the long-wavelength limit are essentially polarized along the axis of the direction defined by the axis of the helix (longitudinal vibration mode) and torsional mode. The second branch refers

to a radial motion of the helix structural elements (breathing mode). Due to the fact that the vibron–phonon coupling parameter for the three-dimensional problem depends on the projection of the phonon polarization vector on the direction of the vibron motion, it is necessary to investigate the vibron interaction with all three phonon modes in an appropriate manner. In addition, we stress that further studies will require the inclusion of the mutual influence of both dressing fractions and an evaluation of the temperature-dependent mean lifetime of the localized states.

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