

Nature of the vibron self-trapped states in hydrogen-bonded macromolecular chains

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We study the influence of temperature and the values of basic energy parameters on the character of vibron self-trapped states in quasi-one-dimensional hydrogen-bonded molecular chains. Investigations have been carried out within the one-dimensional Holstein molecular crystal model employing the variational extension of the Lang-Firsov unitary transformation. It was found that, in the low-temperature regime, only partially dressed small-polaron states may exist. With the rise of temperature, the system enters the metastability region, where partially dressed (light and mobile) and fully dressed (heavy and practically immobile) small-polaron states may exist simultaneously.

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I. INTRODUCTION

The mechanism of a long-range intramolecular vibrational energy transfer in biological macromolecules such as DNA and α -helix has been studied extensively over the past three decades due to its great importance for the functioning of biological systems. However, despite all efforts, this problem has remained unresolved. An attractive explanation on the microscopic level was proposed in the mid-1970s by Davydov and co-workers [1]. The essence of their theory is the assumption that the energy released by the adenosine triphosphate (ATP) hydrolysis can be captured by the protein molecules and then transported along the polypeptide chain in a soliton form that arises due to the self-trapping (ST) of the amide-I (vibron or C=O stretching mode) quanta. The main argument in favor of such a concept has been a soliton's ability to maintain its shape and velocity for a long time and to transfer energy over large distances without dissipation. However, due to the lack of direct experimental evidence of the existence of solitons in these substances, Davydov's idea has long been considered just an interesting theoretical concept.

This situation changed at the beginning of the 1980s, when Careri and Scott suggested [2] that the appearance of the so-called unconventional amide-I band in absorption spectra of crystalline acetanilide (ACN) [3] might be explained in terms of Davydov's soliton theory. ACN is an organic molecular crystal containing quasi-one-dimensionally arranged hydrogen-bonded peptide groups. Its structure is similar to that of proteins [3]. For that reason, it is believed that it provides a good model for studying various phenomena, such as vibrational energy transfer in particular, in protein macromolecules. Accordingly, these experiments were considered to be direct proof that the soliton mechanism might have a key role in the energy transfer in proteins [2–5].

From the point of view of the general theory of ST phenomena [6], the soliton mechanism cannot explain the aforementioned experiments and transport processes in these media. In particular, the formation of stable solitonlike ST

states is possible provided that the energy parameters satisfy adiabatic and strong-coupling conditions, i.e., only if the quasi-particle (vibron) bandwidth and small-polaron binding energy highly exceed the maximal phonon energy. Unfortunately, the energy parameters of hydrogen-bonded chains correspond to nonadiabatic and weak-coupling limits [2–5], which makes soliton theory inapplicable. For these reasons, an alternative interpretation of Careri's experiments [7] and intramolecular vibrational energy transfer [8] in terms of small-polaron (SP) theories has been proposed.

The strength of vibron-phonon coupling in hydrogen-bonded macromolecules falls in the weak to intermediate limits, and conventional SP theories [9,10], which apply in the strong-coupling limit, cannot be the basis for the examination of vibron ST in these media. Consequently, a proper theoretical description of the vibron ST requires an approach that goes beyond the conventional strong-coupling SP theories.

In this paper, we examine the influence of temperature and the values of system parameters on the nature of ST states of vibron quanta in hydrogen-bonded macromolecules. We focus on the question of under which conditions their propagation attains coherent (bandlike) or incoherent (random jumps between neighboring sites) character. For that purpose, the degree of phonon-induced narrowing of vibron bands has been studied.

II. THEORETICAL ANALYSIS

In the early studies of vibrational transfer in hydrogen-bonded macromolecules, theoretical analysis was carried out within the idealized one-dimensional (1D) models involving vibron coupling with acoustic and optical phonons. Nevertheless, incoherent neutron scattering studies of ACN [11] indicate that the source of vibron ST in ACN is the coupling with optical phonons, exclusively. In addition, recent IR pump-probe experiments [12] seem to confirm the relevance of the vibron coupling with optical phonons for the proper understanding of IR absorption in ACN. For these reasons, most of the recent studies [13–15] on the subject have been based upon Holstein's 1D molecular crystal model. It describes the excess (quasi)particle, the vibron in the present case,

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interacting with nondispersive optical phonons in a 1D lattice. The model Hamiltonian reads [9]

$$H = \Delta \sum_n A_n^\dagger A_n - J \sum_{n,\delta=\pm 1} A_n^\dagger A_{n+\delta} + \sum_q \hbar\omega_q b_q^\dagger b_q + \frac{1}{\sqrt{N}} \sum_{q,n} F_q e^{iqnR_0} A_n^\dagger A_n (b_q + b_{-q}^\dagger). \quad (1)$$

Here A_n^\dagger (A_n) describes the presence (absence) of the vibron quanta on the n th lattice site, and Δ and J denote the vibron excitation energy and nearest-neighbor transfer integral, respectively. Operator b_q^\dagger (b_q) creates (annihilates) phonon quanta with the energy $\hbar\omega_q = \hbar\omega_0$, $F_q = F \equiv \text{const}$ denotes the vibron-phonon coupling parameter, while R_0 stands for the lattice constant. The intersite transfer integral in ACN for amide-I mode is about $J \approx 4 \text{ cm}^{-1}$ ($J \approx 0.496 \text{ meV}$), while the vibron-phonon coupling parameter attains $F \approx 25 \text{ cm}^{-1}$ ($F \approx 3.1 \text{ meV}$) [2–4,7,13,14]. Only two dimensionless parameters are needed for the comprehensive description of the SP properties: adiabatic parameter $B = 2J/\hbar\omega_0$ and coupling constant $S = E_B/\hbar\omega_0$. Here $E_B = F^2/\hbar\omega_0$ denotes the small polaron binding energy, i.e., the energy gain due to the formation of ST state in the transportless ($J = 0$) limit. Here they become $S = 0.25$ and $B = 0.16$, and the ST states, if any arise, would correspond to a partially dressed SP.

In order to examine under which conditions such excitations represent dynamically stable eigenstates of the system, we utilize a variational approach based on the modified Lang-Firsov transformation $U = \exp\{-\frac{1}{\sqrt{N}} \sum_{q,n} f_q e^{-iqnR_0} A_n^\dagger A_n (b_{-q} - b_q^\dagger)\}$ [7,10,16–22]. The transformed Hamiltonian ($\tilde{H} = U^\dagger H U$) describes the dressed vibron (i.e., SP) interacting with the new phonons in the lattice with the shifted equilibrium positions of molecular groups. To these new quasiparticles, i.e., a “dressed” vibron and new phonons, correspond the following transformed operators: $a_n = U^\dagger A_n U$ and $\tilde{b}_q = U^\dagger b_q U$. Quantities $f_q = f_{-q}^*$ are variational parameters that characterize the degree in which the vibron distorts the lattice and its feedback on the vibron, i.e., dressing. For the given set of system parameters and temperature, they should correspond to the minimum energy state, while the partially dressed SP would be the approximate eigenstates of the system. As a function of temperature, f_q 's represent mean-field quantities that can depend on the average properties of the system only. In this particular single-particle (vibron) case, temperature enters the transformed Hamiltonian only through the phonon fluctuations around the 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 an effective, mean-field Hamiltonian (H_0) in the following way: $\tilde{H} = H_0 + H_{\text{int}}$, where

$$H_0 = \sum_k E_{\text{SP}}(k) a_k^\dagger a_k + \sum_q \hbar\omega_0 \tilde{b}_q^\dagger \tilde{b}_q. \quad (2)$$

Apparently, interaction $H_{\text{int}} \equiv \tilde{H} - H_0$ represents the polaron-phonon interaction. Within the present approximation, it has been neglected implicitly assuming that it cannot affect the SP stability substantially. It is responsible for some

important phenomena, SP mobility in particular, and deserves a separate examination. Some possible consequences have been examined within the strong-coupling approximation in [23].

The vibron operators are taken in the Fourier representation for convenience: $a_k = \frac{1}{\sqrt{N}} \sum_n e^{iknR_0} a_n$,

$$E_{\text{SP}}(k) = \Delta - \frac{1}{N} \sum_q [(f_q + f_{-q}^*) F_q - \hbar\omega_0 |f_q|^2] - 2J e^{-W(T)} \cos(kR_0) \quad (3)$$

is the SP energy, while

$$W(T) = \frac{1}{N} \sum_q |f_q|^2 (2\bar{n} + 1) [1 - \cos(qR_0)] \quad (4)$$

denotes the vibron band-narrowing factor, which characterizes the degree of the reduction of the overlap integral or equivalently the enhancement of the polaron effective mass. For obvious reasons, it is sometimes called the “dressing fraction” or the “dressing parameter.” Finally, $\bar{n} = (e^{\hbar\omega_0/k_B T} - 1)^{-1}$ denotes the phonon average number.

Optimized variational parameters were found by the minimization of the system ground-state energy. Note that the ground-state vector of the effective Hamiltonian H_0 reads $|\Psi_{\text{GS}}\rangle = a_k^\dagger |0\rangle_v \otimes \prod_q |\bar{0}\rangle_q$ (where $\prod_q |\bar{0}\rangle_q$ is the phonon vacuum vector) so that the ground-state energy corresponds to the lowest level of SP energy, i.e., $E_{\text{GS}} = \langle \Psi_{\text{GS}} | H_0 | \Psi_{\text{GS}} \rangle \equiv E_{\text{SP}}(k)$. We must consider only the $k = 0$ case since it will be the polaron ground state. This is also the most relevant for the spectroscopy [13,24–26] due to the fact that the optical data of a quasiparticle (vibron) with a dispersion much smaller than its energy are in principle very similar to the data of a single impurity ion embedded in a host lattice. In particular, optical spectroscopy is restricted to the observation of excitations with momentum $k = 0$, and the selection rules are the same as for the case of a single impurity ion. Thus, imposing $\frac{\partial E_{\text{SP}}(k)}{\partial f_q} |_{k=0} = 0, \forall q$, we found

$$f_q = \frac{F}{\hbar\omega_0 + 2J e^{-W(T)} (2\bar{n} + 1) [1 - \cos(qR_0)]}. \quad (5)$$

Note that in this way, each single-particle energy level is minimized individually by this scheme, consequently the free energy is also minimized and the present ansatz is consistent with some other mean-field approaches based upon the Bogolyubov variational principle [16–18,20–22].

III. RESULTS AND DISCUSSION

Substituting the above expression for f_q into (3) and (4) and performing the summation over the phonon quasimomenta by virtue of the rule $\frac{1}{N} \sum_q \dots \rightarrow \frac{R_0}{2\pi} \int_{-\pi/R_0}^{\pi/R_0} \dots dq$, we obtain the self-consistent equations for the small-polaron ground-state energy and band-narrowing factor ($k = 0$):

$$\frac{E_{\text{GS}}^{\text{MLF}}}{\hbar\omega_0} = -S \frac{1 + 3B e^{-W(\tau)} \coth(1/2\tau)}{\{1 + 2B e^{-W(\tau)} \coth(1/2\tau)\}^{3/2}} - B e^{-W(\tau)}, \quad (6)$$

$$W(\tau) = S \frac{\coth(1/2\tau)}{\{1 + 2B e^{-W(\tau)} \coth(1/2\tau)\}^{3/2}},$$

where $\tau = \frac{k_B T}{\hbar\omega_0}$ is the normalized temperature.

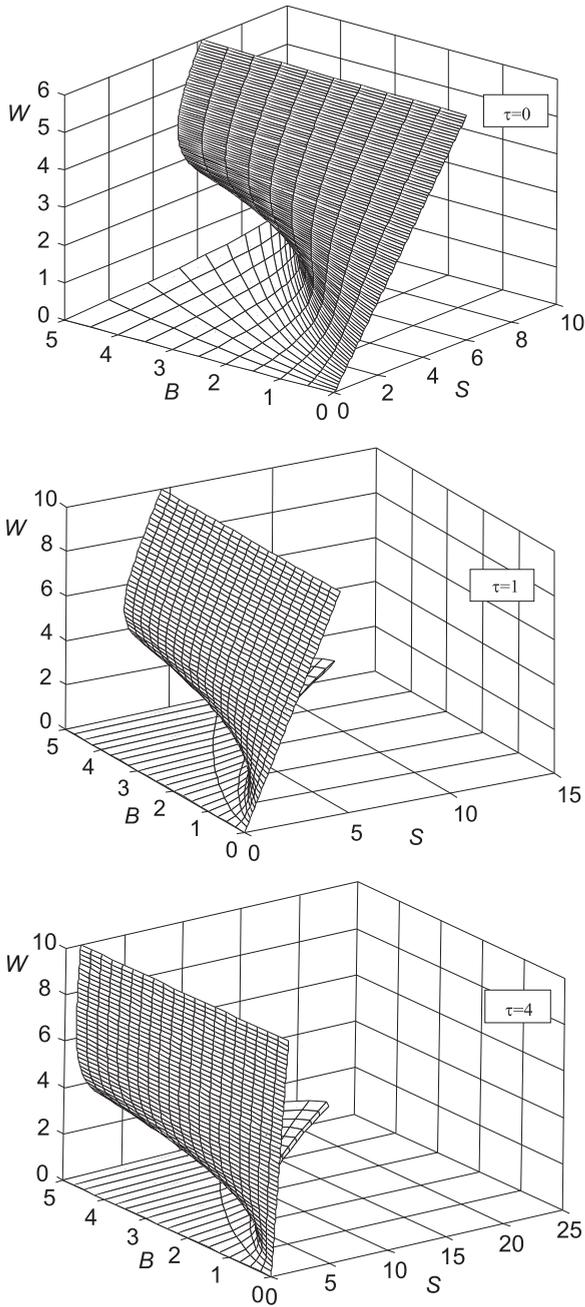


FIG. 1. The dependence of the vibron band-narrowing factor on system parameters S and B for three values of the normalized temperature.

These results are presented graphically in Figs. 1–3 for a few different values of normalized temperature.

Obviously, the dressing fraction displays a peculiar dependence on system parameters and temperature. In particular, for small B and in the low-temperature limit, W is the single-valued function of the coupling constant. With the rise of B over some critical value (different for each temperature) in system parameter space, there appears a region where, for each pair of S and B , the dressing fraction has three solutions. This indicates the possible appearance of three different types of SP states corresponding to each of these solutions.

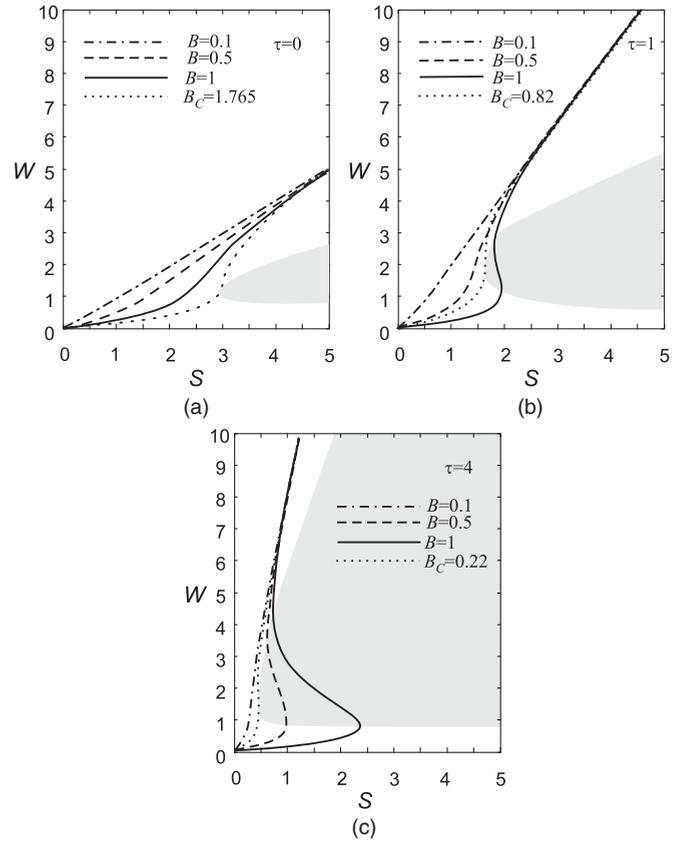


FIG. 2. The set of adiabatic curves for three values of the normalized temperature. The boundaries of the shadowed area correspond to the stability curve. The cross section of the stability curve and the adiabatic curve determines two points that have S coordinates: $S_L(B, \tau)$ and $S_U(B, \tau)$.

Much better insight into this interesting issue may be obtained by considering the functional dependence of the dressing fraction on the coupling constant, taking the adiabatic parameter and temperature as parameters. For that purpose, in Fig. 2 we have visualized the dependence of the dressing fraction on the coupling constant by the set of “adiabatic” curves $W = W(S)$, each corresponding to a particular fixed value of the adiabatic parameter B at three different temperatures τ . In such a way, each point on each adiabatic curve, for the given S , B , and τ , represents a particular solution of our self-consistent problem (6). Clearly, physically meaningful, i.e., stable, solutions are only those corresponding to the minima of the SP energy. Every point on each of these adiabatic curves is bijectively associated with the extremal value of the SP energy, whose dependence on the coupling constant is presented in Fig. 3. The points that correspond to the ground-state energy (i.e., to the minima of the SP energy) define the particular stable eigenstate of the system. The character of these eigenstates is determined by the magnitude of W , whose small and large values correspond to slightly dressed (practically free) or ST states, respectively.

As demonstrated in Figs. 2 and 3, there are two clearly distinguished areas in the system parameter space, where W and SP energy display qualitatively quite different behaviors. In fact, for each τ there exists the critical adiabatic parameter B_C ,

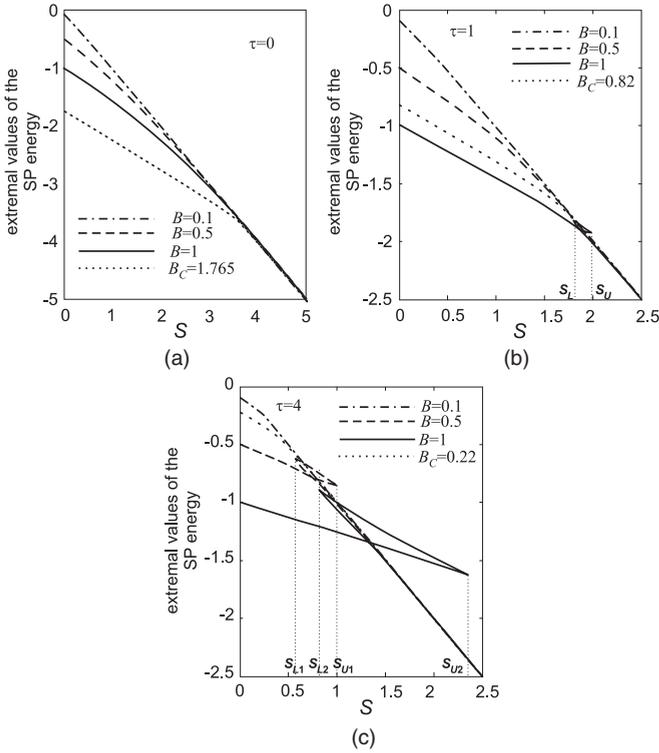


FIG. 3. The dependence of the extremal values of the SP energy (energy is presented in $\hbar\omega_0$ units) on S for several values of B and three values of the system temperature.

such that, for all $B < B_C$, the dressing fraction has only one solution for each coupling constant. In that case, the magnitude of $W(S)$ increases smoothly as a function of coupling constant (Fig. 2). At the same time (Fig. 3), the SP energy is in its minimal (ground) state, which decreases monotonically with the increasing coupling constant. This means that in this, say, nonadiabatic regime ($B \leq B_C$), all points on the “adiabatic” curves correspond to stable eigenstates: small-polaron band states with a gradual transition toward the self-trapped ones as the coupling constant increases.

This tendency persists until B overgrows that critical value when the functional dependence of the SP energy attains a characteristic looplike form with three branches [Figs. 3(b) and 3(c)]. Two lower branches correspond to the minima of SP energy and may be associated with (meta)stable SP eigenstates, while the remaining one corresponds to the energy maxima and has no physical significance. For $S < S_L(B, \tau)$ and $S > S_U(B, \tau)$, the dressing fraction is a single-valued function and attains small and large values, respectively. Consequently, only stable eigenstates, free and localized ones, appear in this region.

For the coupling constant from the interval $S_L(B, \tau) < S < S_U(B, \tau)$, two local minima and one local maximum in the SP energy emerge simultaneously [Figs. 3(b) and 3(c)]. At the same time, the dressing fraction becomes a three-valued function of the coupling constant so that the self-consistent equation (6) has three solutions, indicating the occurrence and possible coexistence of three different types of SP states. Clearly, only two of these solutions corresponding to the SP energy minima may have physical significance, while the third

one is irrelevant and corresponds to the absolutely unstable states. These states correspond to all the points in the S - W plane (Fig. 2) lying inside the shadowed area. Surrounding this area, there is a region wherein there are two relative minima of the SP energy and two metastable eigenstates appear. They are characterized by small and large values of the dressing fraction, respectively, which implies the possible coexistence of free and localized SP polaron states. In this metastability region, a transition between these states takes place. Regardless of where in this region a particular excitation undergoes a transition, the quantum state of excitation undergoes an abrupt change in character marked by a simultaneous discontinuous increase of both dressing parameters and a concomitant jump in the particle effective mass. This discontinuity is well known and arises as a consequence of the two-minima structure of the SP energy, which is sometimes even considered unphysical and the artefact of the particular theoretical approach used. Nevertheless, 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 ST transition and represents the general conclusion regardless of the particular theoretical method [4,27–31]. Moreover, recent theoretical investigations by Hamm and Tsironis [25] confirmed the two-minima structure of the energy of the Holstein model in the SP regime by means of the numerically exact diagonalization of the Holstein model in D dimensions. Their results indicate the coexistence of the free and ST polarons in a certain region of the parameter space regardless of the system dimensionality. It turns out that there exists an energy barrier separating the free and localized SP states, while the transition between them (small polaron crossover) was attributed to polaron tunneling. In addition, the infrared absorption data in oxides such as Pr_2NiO_4 [32] have been attributed to the simultaneous presence of large (mobile) and ST polarons.

Let us now briefly comment on the determination of particular values of the aforementioned critical parameters $S_L(B, \tau)$, $S_U(B, \tau)$, and B_C . For that purpose, it is useful to consider the adiabatic curves as a functional dependence of the coupling constant on the dressing fraction rather than vice versa. In this way, it is easy to notice that in the $B > B_C$ regime, two extrema (minimum and maximum) arise on each adiabatic curve. All these points lie on a single curve (“stability curve”), which is defined as the locus of the points where the first derivative of $S(W)$ vanishes: $\frac{\partial S}{\partial W} = 0$. An analytical function that represents the stability curve in the (S, W) plane has the following form: $S = \tanh(\frac{1}{2\tau})W(\frac{3W}{3W-2})^{3/2}$. The stability curves are represented in Fig. 2 by the boundaries of the shadowed areas. The crossing points of the stability curve and the particular adiabatic curve determine the critical values of the coupling constant, $S_L(B, \tau)$ and $S_U(B, \tau)$.

The value of the critical adiabatic parameter B_C corresponds to the adiabatic curve, which goes through the minimum of the stability curve. Thus, minimizing it with respect to W , we obtain $B_C = \frac{e^{5/3}}{3} \tanh(1/2\tau)$. From Figs. 2 and 3, one can notice that with an increase of the system temperature, the critical value of the adiabatic parameter B_C decreases, and at a normalized temperature $\tau = 4$ (which corresponds to room temperature for $\omega_0 \approx 50 \text{ cm}^{-1}$) it lies in the antiadiabatic region. In such a way, the rising temperature for a given set of system parameters may drive the system

toward the metastability region and the simultaneous existence of free and localized states. This is the consequence of the fact that temperature enters the dressing fraction only through the renormalization of the coupling constant and adiabatic parameter: $S(\tau) = S(2\bar{n} + 1)$ and $B(\tau) = B(2\bar{n} + 1)$ —see Eqs. (6). Thus, the rise in temperature increases the effective adiabatic parameter, which, in the final instance, may cause the aforementioned transition.

IV. CONCLUSIONS

On the basis of the results presented herein, it follows that in the hydrogen-bonded macromolecules, vibron self-trapping would result in the creation of partially dressed small-polaron band states. With the increase of temperature, a heavily dressed, practically localized small polaron may appear along with the band states. This coexistence of free and localized SP states has usually been considered to be an artifact of the particular theoretical method employed. However, in view of the study of Hamm and Tsironis [25], it follows that the results obtained here are consistent, at least on a qualitative level, with the exact numerics. Moreover, the present variational method is in close correspondence with their supplementary variational treatment of the problem by means of the Toyozawa ansatz [28]. To that end, we stress that the whole procedure that has been carried out here in a few separate steps may be unified by defining the trial state,

$$|\Psi_{\mathbf{k}}\rangle = U \sum_{\mathbf{n}} e^{i\mathbf{k}\cdot\mathbf{n}} \psi_n A_{\mathbf{n}}^{\dagger} |0\rangle_e \otimes \prod_q |\bar{0}\rangle_q,$$

where ψ_n is the vibron Wannier function, k represents the polaron momentum, while $|0\rangle$ and $|\bar{0}\rangle_q$ stand for the vibron and the phonon vacuum, respectively. By means of the identity $UA^{\dagger} \equiv UA^{\dagger}U^{\dagger}U$, the above trial state attains precisely the

form used in [25]:

$$|\Psi_{\mathbf{k}}\rangle = \sum_{\mathbf{n}} \psi_n e^{i\mathbf{k}\cdot\mathbf{n}} A_{\mathbf{n}}^{\dagger} |0\rangle_e \otimes |\beta_{\mathbf{n}}\rangle,$$

$$|\beta_{\mathbf{n}}\rangle = \exp \left\{ - \sum_{\mathbf{q}} \left[\left(\frac{1}{\sqrt{N}} f_{\mathbf{q}} e^{i\mathbf{q}\cdot\mathbf{n}R_0} \right) b_{\mathbf{q}}^{\dagger} - \text{H.c.} \right] \right\} \prod_q |\bar{0}\rangle_q.$$

The equivalence with our approach becomes apparent after the choice of the Wannier state as $\psi_n = \frac{1}{\sqrt{N}}$. This is justified in the present case (nonadiabatic weak-coupling limit) where the occurrence of the large polaron (soliton) cannot be expected. Otherwise, one must use the Wannier state in the general form to describe large-polaron solutions.

Note, however, that by means of such an approach, the analysis would be restricted to the zero-temperature case. Here we used a slightly more flexible method in order to discuss the temperature dependence of the character of SP states and to stress the importance of the residual polaron-phonon interaction. In the latter respect, our study represents the background for further investigations, especially for the understanding of the boundary between coherent and incoherent polaron motion. For that purpose, the present variational estimates represent just the first step, while further investigation will require an evaluation of the temperature-dependent mean lifetime of the localized states. This will be determined by the diagonal (without change of phonon number) and nondiagonal transition due to the residual interaction.

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