Effects of quantum lattice fluctuations on vibron pairing in two-site systems

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The existence of a two-vibron (amide-I quanta) bound state has been examined within the framework of a two-site realization of the Davydov model. The parameter space of the system is divided into two regions where the nature of pairing and the character of bound states are determined by the quite different physical mechanisms. The validity of the semiclassical approximation was discussed. [S0163-1829(96)03726-5]

Understanding of the underlying physical mechanisms of the charge and energy transfer in biological macromolecules such as α-*helix* proteins, for example, is one of the most challenging problems in modern condensed-matter theory.[1] An interesting attempt, in that sense, was made by Davydov[2] who proposed the soliton model as a basic theoretical framework for the explanation of the role of an α-*helix* molecule in the long-distance charge (electron, proton, etc.) and intramolecular vibrational energy (amid-I quanta, vibron or CO-stretching mode) transfer. The basic idea of Davydov theory (DT) is that the energy losses of the particle through dissipation and dispersion may be prevented by its self-trapping (ST) in the induced local distortion of polypeptide chain and soliton formation. Over the last decade, various aspects of the DT concerning its relevance for the explanation of the transport processes in realistic biological systems became the subject of the numerous critical reexaminations.[3–5] Special attention was focused on two major points. The first one is the analysis of the soliton stability, its lifetime in particular, at biologically relevant temperatures.[3] The second one concerns the validity of the approximations involved in the choice of the wave functions used in a description of the soliton in the framework of the so-called Davydov ansatz (DA).[4] While the first problem still remains wide open,[5] we can safely accept the applicability of the DA in the adiabatic limit, i.e., when the (quasi-)particle bandwidth $(2J)$ highly exceeds maximal phonon energy $(\hbar\omega_B)$, so that a semiclassical description of the phonon subsystem is justified.[6,7]

Parallely with the analysis of the original Davydov proposal where ST of a single excitation has been considered, it was also suggested that the ST of the bound state of two or more amid-I quanta is more relevant in real biological systems.[8] The arguments in benefit of such an attitude are that the energy released in the adenosine triphosphate (ATP) hydrolysis is approximately twice the vibron energy and that the bisoliton energy (per particle) could be considerably lower then the energy of the single soliton which implies better stability of the former. Practically in all these studies, theoretical analysis has been founded upon the assumption about the classical nature of phonons. However the set of system parameters usually used in these studies correspond to the nonadiabatic limit where quantum fluctuations of lattice play an essential role[9] so that the semiclassical approximation is no longer valid. Namely the applicability of the semiclassical approximation assumes that the particle is fast as compared with lattice so that the induced lattice distortion cannot follow its motion. Under these conditions pairing may arise as a consequence of the trapping of both particles in the common potential well formed by the static, large radius, lattice distortion. Quite on the contrary, in the nonadiabatic limit the particle is surrounded (dressed) by the cloud of virtual phonons engaged in the creation of the short-ranged lattice distortion which follows particle motion instantaneously.[9] As a result, the enhancement of the particle's effective mass and decreasing of the effective tunneling energy (J) arises. In many-particle systems the ''dressing'' effect causes an effective attractive interaction between different particles which may also lead to the creation of the bound states of two or more particles. This possibility has been neglected so far and it will be examined in the present work. For that purpose we shall consider a simple system which consists of two vibrons tunneling between two impurity molecules embedded in an otherwise perfect lattice. Such a situation may be described by the two-site approximation of the original Davydov Hamiltonian, which, using the vibron number conservation condition $B_1^+B_1+B_2^+B_2=2$ after some trivial transformation, may be written in the symmetrical form

$$H=-J(B_1^+B_2+B_2^+B_1)+(B_1^+B_1-B_2^+B_2)\sum_q \lambda_q(a_q+a_{-q}^+) + \sum_q \hbar\omega_q a_q^+ a_q . \tag{1}$$

Here $\lambda_q=(F_q/2N^{1/2})(1-e^{iqR_0})$, while $F_q\equiv F=$ const and $\omega_q\equiv\omega_0=$ const in the case of interaction with dispersionless optical phonons, Holstein's molecular crystal model (MCM) and $F_q=2i\chi(\hbar/2M\omega_q)^{1/2}\sin(qR_0)$ in the case of an interaction with long-wavelength acoustical phonons with frequency $\omega_q=\omega_B\sin(qR_0/2)$, Davydov model. Here $\omega_B=2(\kappa/M)^{1/2}$ is the maximal phonon frequency, κ and M denote the elastic constant of the molecular chain and mass of the peptide group (PG), respectively, while R_0 denotes the lattice constant. In the context of the explanation of

amid-I quanta transfer the following set of parameters was usually used:[2–5] $J=1.55\times10^{-22}$ J, $\chi=62pN$, $M=1.9\times10^{-25}$ kg, $R_0=4.5\times10^{-10}$ m, while $\kappa\sim13$ N/m.

Our examination of such a simplified model is motivated by its recent application in the analysis of the thermal stability of Davydov solitons (DS) where it was found that the creation of the two-vibron bound state may lead to the enhanced stability of DS even at high temperatures.[10] However the validity of these predictions is not quite clear. Namely the above set of parameters corresponds to the nonadiabatic limit so that the applicability of the semiclassical approximation for phonons, without analysis of its validity, is questionable. Thus in order to understand the problem of a two-vibron bound-state formation and the stability of these entities, one should formulate the criteria determining the region of the parameter space of a system in which a particular type of phonon field behavior will dominate system properties, the nature of pairing especially. As well as in the case of the analysis of the single-particle ST, these criteria may be formulated in terms of two parameters only: $B=2J/\hbar\omega_B$, adiabaticity and coupling constant, $S=E_B/\hbar\omega_B$. Here $E_B=\Sigma_q(|\lambda_q|^2/\hbar\omega_q)$ denotes the so-called small-polaron binding energy.

In order to examine the bivibron formation due to the ''dressing'' mechanism we first rewrite the Hamiltonian (1) in terms of new operators: $C_n=U^+B_nU$ describing the dressed particle polaron, consisting of the original excitations accompanied by the phonon cloud and $b_q=U^+a_qU$ representing the new phonons with shifted equilibrium positions. U denotes the so-called incomplete Lang-Firsov unitary transformation operator widely used in the small-polaron theories[9] and the bipolaron model of superconductivity:[11]

$$U=\exp\left[(B_1^+B_1-B_2^+B_2)\sum_q f_q(a_q-a_{-q}^+)\right],$$

$$f_q=f_{-q}^*, \tag{2}$$

here f_q denotes variational parameter to be determined by minimizing the ground-state (GS) energy of the system. Averaging the so-obtained result over the new phonon vacuum we found an effective Hamiltonian describing the system of two interacting ''polarons:''

$$H=-Je^{-x}(C_1^+C_2+C_2^+C_1)-2\sigma(C_1^{+2}C_1^2+C_2^{+2}C_2^2). \tag{3}$$

In deriving this expression we have used the vibron number conservation condition in order to eliminate the ''mixed'' terms: $C_1^+C_1C_2^+C_2$. Here $\sigma=\Sigma_q[\lambda_q(f_q+f_{-q}^*)-\hbar\omega_q|f_q|^2]$ while $x=2\Sigma_q|f_q|^2$ is the so-called dressing parameter measuring the degree of the reduction of the effective tunneling term.

Writing down the eigenvalue problem of the effective Hamiltonian using the bivibron vector of state in the form $|\Psi\rangle=\Sigma_{n,m=1,2}\Psi_{n,m}C_n^+C_m^+|0\rangle_{\rm vib}$, $(\langle\Psi|\Psi\rangle=2\Sigma_{n,m}|\Psi_{n,m}|^2=1$, $(\Psi_{mn}=\Psi_{nm})$ we arrive at the homogeneous system of equations for bivibron amplitudes:

$$(E+4\sigma\delta_{n,m})\Psi_{nm}+J\sum_{l=\pm1}(\Psi_{n,m+l}+\Psi_{n+1,m})=0,$$

$$\Psi_{n,m}=0 \quad \text{for all } n,m\neq1,2. \tag{4}$$

This leads to the following result for the bivibron energy:

$$E_{\rm biv}^{\rm dress}=-2\sigma-2\sqrt{\sigma^2+J^2e^{-2x}}. \tag{5}$$

Repeating the same procedure using the single-particle vector of state we found the energy of the free vibron as follows: $E_f=-J$, or in units of E_B in terms of adiabaticity and coupling constant $\mathcal{E}_f=-B/2S$.

Now we should minimize the bivibron energy (5) with respect to the parameter f_q. However, the variational procedure may be greatly simplified by introducing the assumption of equal dressing for all phonon modes:[9] $f_q=\delta(\lambda^*/\hbar\omega_q)$, where $\delta(0<\delta<1)$ is the new variational parameter measuring the relative extent of the induced lattice distortion. This assumption, at first sight, looks like a very strong approximation since the whole set of variational parameters, one for each mode, is substituted by a single one. However, according to some previous results,[7,9] concerning the single polaron and some other related problems, one can see that it gives the same qualitative predictions as the q-dependent one, while the estimates of the GS energy are slightly higher. Thus for the present purpose we may utilize this simplified version. The problem is now reduced to minimizing the following expression:

$$\mathcal{E}=-\delta(2-\delta)-\sqrt{\delta^2(2-\delta)^2+\left(\frac{B}{2S}\right)^2e^{-4S\delta^2}}, \tag{6}$$

representing the bivibron energy per particle expressed in units of E_B ($\mathcal{E}=E_{\rm biv}^{\rm dress}/2E_B$). In such a way we obtain the self-consistent equation for δ:

$$\delta=\left[1-\frac{(1-\delta)(2-\delta)-(B^2/2S)e^{-4\delta^2S}}{\sqrt{\delta^2(2-\delta)^2+\left(\frac{B}{2S}\right)^2e^{-4\delta^2S}}}\right]^{-1}. \tag{7}$$

It can be solved numerically and our results are visualized in Fig. 1 where we have plotted the set of adiabates [curves $S=S(\delta,B)$] for a few chosen values of B spanning the whole range of adiabaticity. Each of these adiabates represents the set of points in the S,δ plane corresponding to the extrema of the GS energy. Clearly the physically meaningful region is the one where the stability condition holds ($\partial^2\mathcal{E}/\partial\delta^2>0$), i.e., below the stability line: $S=[8\delta^2(1-\delta)]^{-1}$. For representing our results in such a way instead of $\delta=\delta(S)$ we have some practical reasons and the most important one is that the points where the first two derivatives of $\mathcal{E}$ vanish correspond to the points on $S=S(\delta)$ lines where $\partial S/\partial\delta=0$. Thus the stability line passes through the stationary points of each adiabate. Looking at Fig. 1 as a graph of $\delta=\delta(S,B)$ one can see that as long as the adiabaticity parameter is less than some critical value, $B_c=\sqrt{(7/4)e^{3/2}}$ corresponding to the adiabate which is tangential to stability line in its minimum, these curves include only minima of the GS energy while δ shows continuous growth with the increase of the coupling strength (S). When B exceeds that critical value, δ becomes a multivalued function on S and in the certain region of the coupling constant, determined by the crossing points of stability line and particular adiabate, there appear, for each value of S, two values δ corresponding to the

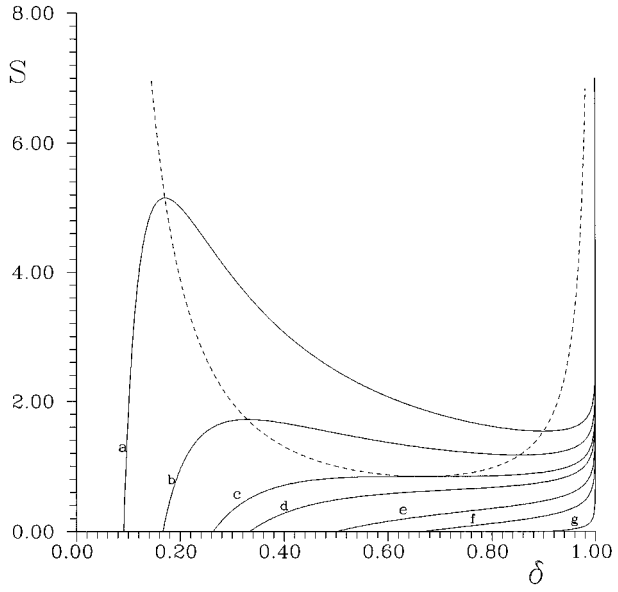

FIG. 1. Dressing fraction δ vs coupling constant (S) for a few chosen values of the adiabaticity parameter (B). Curves a, b, c, d, e, f, and g correspond to the following values of B: 10, 5; $B_c \simeq 2.8$, 2, 1, 0.5, and 0.1, respectively. The dotted line represents the so-called *stability line*: $S=[8\delta^2(1-\delta)]^{-1}$.

minima of GS energy. The first of these two solutions of δ falls onto a relatively small value, which is approximately $\delta \simeq 1/(1+B)$, and characterizes a quasifree partially dressed bivibron, while the second one falls onto $\delta \sim 1$. States characterized with $\delta \approx 1$, occurring on each adiabate either for $S \to \infty$ or when $B \ll 1$, define a highly dressed practically localized quasiparticle (bipolaron or bivibron) with very large effective mass. Comparing energies of these states with each other and with the energies of free ones ($\mathcal{E}_f=-B/2S$) we found that (i) in the nonadiabatic limit ($B \ll 1$) and for practically all nonvanishing values of the coupling constant, the bipolaron is energetically more favorable than the free vibrons; (ii) in the adiabatic case ($B \gg 1$) the energy per particle of the quasifree bipolaron [$\mathcal{E}_{\rm qf} \simeq -2/(B+1)-B/2S$] obviously is always lower than the energy of free states; (iii) the quasifree bipolaron is more superior than the localized ($\mathcal{E}_l \simeq -2-O[(B/2S)^2 e^{-4S}]$) states as far as $S<(B+1)/4$, while localization occurs in the opposite case.

As one can see the above analysis does not exclude the possibility of bipolaron formation on account of an effective vibron-vibron interaction even in the highly adiabatic limit, where, according to usually accepted premise of the theory of ST phenomena[6,7,9] one should expect applicability of the semiclassical concept. Thus in order to discuss the validity of the above conclusions and determine criteria where a particular mechanism of pairing would prevail we have to examine the possibility of bipolaron formation applying a semiclassical approximation. For that purpose we first average the model Hamiltonian (1) over the phonon coherent states: $|\alpha\rangle=\Pi_q|\alpha_q\rangle$ ($a_q|\alpha\rangle=\alpha_q|\alpha\rangle$). Then we solve the eigenvalue problem of a so-obtained effective semiclassical Hamiltonian using the analogous vector of state of the system as before substituting dressed vibron operators by the bare ones. Thus we again obtain the homogeneous set of equations for bivibron amplitudes:

$$[E+(-1)^n 2\eta\delta_{n,m}]\Psi_{n,m}+J\sum_{l=\pm 1}(\Psi_{n,m+l}+\Psi_{n+l,m})=0,$$

$$\Psi_{n,m}=0 \quad \text{if } n,m \neq 1,2, \tag{8}$$

where $\eta=\Sigma_q \lambda_q(\alpha_q+\alpha^*_{-q})$. This procedure is fully equivalent to Davidov's D_2 ansatz and two vibron bound states, if any arises, should be related to bisolitons. These entities are minimal energy configurations created by the capture of both vibrons in the common potential well formed by the static lattice distortion. They can be created only in the case when the coherent phonon amplitudes α_q, which measure the extent of the induced lattice distortion, are different from zero. From the condition that system (8) possesses nontrivial solutions, we find three solutions for E. Naturally only the lowest one, $E=-2\sqrt{\eta^2+J^2}$, is physically meaningful. Finally, minimizing the system energy $E_s=E+\Sigma_q \hbar\omega_q|\alpha_q|^2$ we obtain $\alpha_q=\gamma(\lambda^*_q/\hbar\omega_q)$ where $\gamma=0$ if $J/4E_B>1$ and $\gamma=2\sqrt{1-(J/4E_B)^2}$ if $J/4E_B<1$. The first solution ($\gamma=0$) corresponds to the undeformed lattice with two free vibrons with the energy (in units of E_B) per particle $\mathcal{E}_f=-B/2S$. The second one defines the bivibron with the energy per particle:

$$\mathcal{E}^{\rm class}_{\rm biv}=-2-\frac{1}{2}\left(\frac{B}{4S}\right)^2. \tag{9}$$

The corresponding bivibron amplitudes are given as follows: $\Psi_{11,22}=(1/\sqrt{8})(1\pm\gamma)$ and $\Psi_{12}=(1/\sqrt{8})\sqrt{1-\gamma^2}$. In terms of the adiabaticity parameter and coupling constant, the condition for the existence of such states $J<4E_B$ may be written as follows: $B<8S$. Using an analogous procedure with a single-particle wave function we find the energy of the single vibron trapped in its own potential well as $\mathcal{E}_v=-1-(B/4S)^2$. The condition for the formation of such states is $J/(2E_B)<1$. In order to analyze bivibron stability with respect to these states we found a bivibron binding energy which represents the difference between the energy (9) and single vibron energy:

$$\Delta\mathcal{E}=-1+\frac{1}{2}\left(\frac{B}{4S}\right)^2. \tag{10}$$

It is negative in practically the whole physically meaningful region (i.e., if $B<8S$). Thus under this condition, a system populated with two vibrons is always unstable with respect to the *semiclassical* bivibron formation.

We are now in a position to determine in which region of parameter space of a system (S-B plane) a particular method should give a more accurate description of the two-site two-vibron system. Owing to the variational character of both approaches the one which gives a lower estimate for the GS energy of the system is superior. Substituting the optimized values of δ into (6) one may calculate the GS energy of the dressed bivibron for the arbitrary value of S and B. Comparing the so-obtained result with the semiclassical bivibron energy we found, as well as in the single-polaron case,[12] a so-called semiclassical boundary, the solid line in Fig. 2, which divides the parameter space of the system into two regions with quite distinct physical properties. In the first one, corresponding to those points in the S-B plane lying above this line, system properties and the nature of pairing

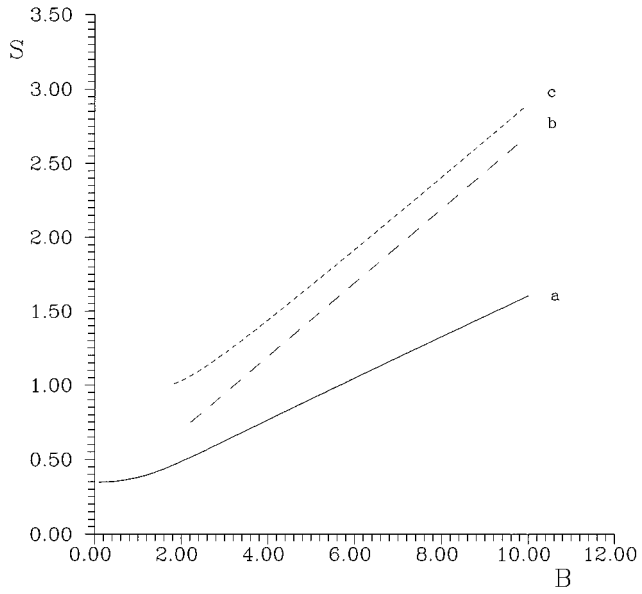

FIG. 2. The semiclassical boundaries in the S-B plane for the bivibron (a) and single-polaron cases. (b) Davydov model and (c) MCM.

are determined by the classical nature of phonons. In the opposite case, a semiclassical approximation is no more valid and pairing should be achieved through the effective vibron-vibron interaction. Since the above-quoted values of physical parameters for the α-helix fall into this region ($B \simeq 0.17$ and $S \simeq 0.04$) we conclude that, for this particular case, the bivibron will be formed, but such an entity cannot be related to the Davydov (bi)soliton since it arises as a consequence of a different mechanism. As compared with the single-polaron problem where the semiclassical boundary is determined by the lines (b) for the Davydov model and (c) for the MCM in Fig. 2 (see Ref. 12), in the present case the semiclassical approximation is valid in a quite larger region of the parameter space.

Our results in a certain sense question the main ideas of papers[10] since, within this model and for the usually used set of system parameters, we found that vibron pairing arises due to a quite different mechanism than originally proposed in Ref. 10. Therefore the stability of such entities, their transport properties in particular, should be quite different than those predicted on the basis of a semiclassical approximation. Furthermore, we must stress that the above analysis strictly concerns the problem of bivibron formation in two-site systems only and any generalization of these arguments to the problem of Davidov-like (bi)soliton formation in realistic biological systems is doubtful. Namely the above results show remarkable similarities with a single-particle ST in two-site systems which differ in many respects from the ST in extended systems[6,7,12] so that the condition for applicability of the semiclassical approximation is not simply an adiabatic condition ($B \gg 1$).[12,13]

The above choice of the simplified variational method imposes certain restrictions on a domain of validity of our results. However these restrictions concern the accuracy of that method to describe the dressed bivibron properly, behavior of its effective mass as a function of system parameters in particular, but cannot affect our conclusion against the applicability of the semiclassical approximation. It will hold even if one uses a more accurate variational procedure for the description of a dressed entity. Namely such an improved treatment would result with lower estimates of the GS energy for the particular values of S and B than the present one, in such a way enlarging the region of parameter space where the dressing mechanism is dominant.

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