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Effects of quantum lattice fluctuations on multiquanta Davydov-like solitons in a molecular chain

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Abstract. The dressing effect due to the quantum nature of phonons may cause the creation of bound states of several vibrons in the molecular chain. The possibility of creating soliton states of this type is discussed for the simple Fröhlich one-dimensional model. The regions of the system parameter space where different mechanisms dominate the behaviour of such entities are characterized.

1. Introduction

Long-distance charge (electron–proton, etc) and intramolecular vibrational energy (amide-I or C–O stretching mode quanta vibrons) transfer through the polypeptide chains of an α-helix molecule plays an important role in a number of phenomena in biological systems including photochemical reactions, photosynthesis and metabolism [1–8]. Therefore the explanation of transport mechanisms in an α-helix molecule is of great importance to understanding these phenomena on a microscopic level. A potential solution was proposed by Davydov and co-workers [2, 4, 6, 7] who introduced the soliton model as a basic theoretical framework for the description of the role of an α-helix molecule in transfer processes. The main idea of the Davydov theory (DT) is that the exciton (we use this term here to denote electron, vibron, proton, etc) may be trapped by the local distortion of the host lattice and then resonantly transferred along the chain in the soliton form. Such entities are usually called Davydov solitons (DSs) [8]. However, in the numerous studies on the Davydov model the use of this term is not unique and, in order to avoid any confusion which may arise because of the arbitrariness in its use, we emphasize that DSs are used by us to denote stable large-radius particle-like solutions of the set of equations for exciton and lattice (phonon) variables.

In its simplest version, the Davydov model for a molecular chain is specified by the following Fröhlich-like Hamiltonian:

$$H = \Delta \sum_n A_n^+ A_n - J \sum_n A_n^+ \left(A_{n+1} + A_{n-1}\right) + \frac{1}{\sqrt{N}} \sum_{q,n} F_q \exp\left(\mathrm{i}qnR_0\right) A_n^+ A_n \left(b_q + b_{-q}^+\right) + \sum_q \hbar\omega_q b_q^+ b_q \tag{1}$$

where A_n^+ (A_n) describes the presence (absence) of the excitation with the energy Δ on nth molecular group, b_q^+ (b_q) creates (annihilates) phonon quanta with frequency

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ω_q, while F_q denotes the exciton–phonon coupling parameter. It is given by $F_q = 2i\chi(\hbar/2M\omega_q)^{1/2}\ \sin(qR_0)$ in the case of coupling with acoustic phonons with frequency $\omega_q = \omega_B\ \sin|qR_0/2|$, $\omega_B = 2(\kappa/M)^{1/2}$ denotes maximal phonon frequency, κ is the spring constant, M denotes the mass of the molecular group, R_0 denotes the lattice constant, and finally J and χ represent the intersite dipole–dipole transfer integral and coupling strength, respectively. In particular calculations we shall use $\omega_q \simeq c_0|q|$ where $c_0 = R_0\sqrt{\kappa/m}$ denotes the sound velocity. In the case of coupling with dispersionless optical modes we have $\omega_q = \omega_0 \equiv$ constant and $F = \chi(\hbar/2M\omega_0)^{1/2}$; the meaning of the symbols is as before. Obviously this corresponds to the well known Holstein molecular crystal model [9].

The only connection of this simplified model with realistic biological systems are the values of the parameters appearing in (1). Consequently, its relevance for the description of transport phenomena in a particular biological context is of limited validity. This especially concerns its applicability at physiological ($T \sim 300$ K) temperatures. For that reason, different thermalization schemes were utilized in order to simulate soliton dynamics and to estimate the lifetime of the soliton at finite temperatures [10–18]. The results are rather different, and sometimes mutually quite opposite. Thus, while some workers find that thermal fluctuations destabilize the soliton, causing its finite lifetime to be too short to be relevant in realistic conditions [10, 11, 17, 18], others find that thermal effects even support soliton creation and its stability [13, 16].

The origin of these discrepancies lies, in part, in unjustified application of different approximate approaches without precise understanding of their domain of applicability. Namely, as known from the general theory of self-trapping (ST) phenomena [19–21], to which this problem obviously belongs, the choice of the theoretical tool, and the physical picture following from it, depend strongly on the mutual ratio of three basic parameters determining the energy spectrum of the system: the width $2J$ of the exciton band, the maximal phonon energy $\hbar\omega_B$ and the small polaron binding energy $E_B = (1/N)\sum_q(|F_q|^2/\hbar\omega_q)$. It is useful to define the so-called adiabaticity parameter $B \simeq 2J/\hbar\omega_B$ and coupling constant $S \simeq E_B/\hbar\omega_B$ in order to discuss different extreme limits [22–24].

Thus, in the adiabatic limit ($B \gg 1$), lattice distortion with high inertia fails to follow the exciton motion and it forms an essentially static potential well where that particle may be trapped. Depending on the value of coupling constant, the spatial extent of an entity created in this way, the polaron, may vary from being concentrated around one site only ($S \gg 1$), i.e. an adiabatic small polaron, to be spread over a large number of lattice sites ($S < 1$), i.e. a large adiabatic polaron or soliton in one-dimensional media. Under these conditions ($B \gg 1$) the phonon subsystem behaves in a classical way and a theoretical description is possible on the basis of the time-dependent version of the Pekar [21, 25] semiclassical variational method: the Davydov D_2 *ansatz* [22–24].

For that reason the thermalization procedures of Lomdahl and Kerr [10, 11], consisting of a numerical analysis of the Davydov set of equations perturbed by phenomenological random forces simulating the influence of thermal bath, and that of Cottingham and Schweitzer [17] and Schweitzer [18] involving direct perturbational evaluation of soliton lifetime on the basis of a microscopic model, could be applied in the adiabatic limit only. In both cases examination was caried out within the framework of the D_2 *ansatz*. Unfortunately the common set of parameters used in the studies of vibron transfer in an α-helix molecule [4, 5, 10, 18, 19] ($J = 1.55 \times 10^{-22}$ J, $\hbar\omega_B =$(18–21) $\times 10^{-22}$ J and $\chi =$ (35–62) pN) and explanation of the optical spectra of acetanilide (ACN) ($J \simeq 4$ cm^{-1} or 7.9×10^{-23} J and $\hbar\omega_B \simeq 57$ cm^{-1} or 1.13×10^{-21} J [26, 27]) clearly correspond to the non-adiabatic limit ($B \simeq 0.14$–0.17) where quantum lattice fluctuations play the essential role so that the

application of the D_2 *ansatz* is inconsistent. Recent detailed analysis in a series of papers of Brown and co-workers [22, 23] and our group [24] indicates that the single-vibron polaron states in an α-helix and ACN, if any exist, should correspond to the vibron analogue of Holstein's small polaron (non-adiabatic small polaron) [9] rather than a soliton. In this way these results confirm the ideas of Alexander [26] and Alexander and Krumhansl [27] who used the Holstein small-polaron theory in the explanation of optical spectra of ACN and other related molecules.

Note that we do not criticize these methods but rather point to their domain of applicability. Thus, if one uses different sets of parameters, e.g. in the case of an extra electron transfer along an α-helix [3] or conducting polymers [28] where the adiabaticity condition is satisfied, these methods may be utilized; yet one should expect results quite different from those in the original papers.

The system properties and the character of polaron states in the non-adiabatic limit are dominated by the quantum nature of phonons. In this case the 'dressing' effect occurs and the exciton is surrounded by the cloud of virtual phonons engaged in the creation of short-ranged lattice distortion which follows its motion instantaneously [9, 19, 20]. As a result, an increase in the exciton effective mass and a decrease in the effective transfer matrix element J arises. Furthermore, in many particle systems, 'dressing' causes the effective attractive interaction between the different particles which may lead to the creation of their bound state: an exciton or more precisely a vibron drop [29–35]. These solutions may attain a soliton form [36] depending on the values of the system parameters S and B. This effect has not been examined so far, within the DT, and it will be the subject of this paper, where we shall analyse the conditions for the existence of solitons representing the bound state of the large number of vibron quanta. In what follows, we shall call such quantities multivibron solitons. Special attention will be devoted to the study of the character of these states. In particular, we wish to determine whether they arise as a consequence of the ST of more vibrons in the common potential well created by the lattice distortion or on account of the induced vibron–vibron interaction. Finally, we shall specify the conditions favouring a particular mechanism.

For that purpose we shall apply the variational method well known from the small-polaron theories [37–40] based upon the application of unitary transformation technique developed by Lang and Firsov [37]. Note that the so-called D_1 *ansatz* [22–24], which may be considered as a generalization of the variational methods of Emin [39] and Toyozawa [40], is inapplicable for that purpose since it successfully describes the effects of small-polaron narrowing of the exciton bandwidth but fails to include the effects of dynamical exciton–exciton (vibron–vibron) interaction.

The importance of this examination follows from the fact that in some recent studies it was proposed that ST of the bound state of two or more vibron quanta is more relevant in real biological systems [11, 14, 15].

2. Model Hamiltonian of the system and soliton solution

In order to examine the influence of quantum fluctuations on the multivibron soliton, and especially to find the conditions for their existence, we shall consider the system described by the Hamiltonian (1) but populated with $\mathcal{N}$ vibrons: $\sum_n A_n^+ A_n = \mathcal{N}$, and in the first instance we rewrite (1) in terms of new, i.e polaron, operators $B_n = U^+ A_n U$ describing the 'dressed' particle (polaron), consisting of the original particle surrounded by the phonon cloud and $a_q = U^+ b_q U$ representing new phonons in the chain with shifted equilibrium

positions of the molecular groups. U is the unitary operator given by

$$U = \exp\left(\frac{1}{\sqrt{N}}\sum_{n,q} f_q \ \exp\left(-\mathrm{i}qnR_0\right)\ A_n^+ A_n\left(b_{-q} - b_q^+\right)\right) \qquad f_q = f_{-q}^* \tag{2}$$

defining the so-called incomplete Lang–Firsov transformation. Here f_q denotes the variational parameter or, more precisely, the set of them—one for each q, whose value defines the degree of dressing and the strength of the induced phonon-mediated vibron–vibron interaction. It should be determined by the minimization of the ground-state (GS) energy of the system. However, the variational procedure is rather complicated since it demands the optimization of a function (GS energy) of the large number of parameters and, even with the use of sophisticated numerical methods, one can hardly obtain a comprehensive physical picture in the whole parameter space of the system. Yet, it can be greatly simplified by introducing the assumption of equal dressing fractions for all modes [22–24, 39]: $f_q = -\delta F_q^*/\hbar\omega_q$, where δ is the new variational parameter measuring the relative extent of the induced lattice distortion. In this way the whole set of variational parameters is replaced by a single parameter. At first sight it looks like a very strong assumption; however, according to some previous results [22–24, 39–42], concerning the single polaron and related problems, we know that this method gives qualitatively the same results as q-dependent methods with slightly higher estimates for the GS energy. Within this approximation, the model Hamiltonian (1) is given in terms of new operators as follows:

$$\begin{aligned} H = {} & \left[\Delta - \delta(2-\delta)E_B\right]\sum_n B_n^+ B_n - J\sum_n\Big(B_n^+ B_{n+1}\Theta_n^+\Theta_{n+1} + \ \mathrm{HC}\Big) \\ & + \frac{1-\delta}{\sqrt{N}}\sum_{q,n} F_q \ \exp\left(\mathrm{i}qnR_0\right)\ B_n^+ B_n\left(a_q + a_{-q}^+\right) \\ & + \sum_q \hbar\omega_q a_q^+ a_q - \delta(2-\delta)E_B\Bigg[\tfrac{1}{2}\sum_n B_n^{+2} B_n^2 \\ & + \tfrac{1}{4}\sum_n\Big(B_n^+ B_{n+1}^+ B_{n+1} B_n + B_n^+ B_{n-1}^+ B_{n-1} B_n\Big)\Bigg]. \end{aligned} \tag{3}$$

Here

$$\Theta_n = \exp\left(\frac{\delta}{\sqrt{N}}\sum_q \frac{f_q^*}{\hbar\omega_q}\ \exp\left(-\mathrm{i}qnR_0\right)\ \left(a_q - a_{-q}^+\right)\right).$$

Written in this form, our model Hamiltonian contains an additional term, the last in the above equation, describing an effective vibron–vibron interaction. In this way it gives us the possibility of examining the role of dynamical effects in the soliton formation. However, this advantage is offset by the appearance of the additional vibron–phonon interaction, highly non-linear in phonon operators, which greatly complicates further analysis. Thus, in order to deal with the difficulties arising from this term, we shall proceed in a typical mean-field manner [22–24, 43] which was successfully utilized previously in the examination of the problem of the exciton dynamics in the case of strong coupling with lattice vibrations, when the polaronic effect ('dressing') could affect exciton properties significantly. In what follows, we shall avoid the details of the calculational procedure which can be found in a number of papers (see, e.g. [43] and references therein) and let us point out just that the main step consists in substituting the above Hamiltonian by the effective Hamiltonian in which the transfer integral J is replaced by its mean-field value:

$$J_{eff} = J\left\langle\Theta_n^+\Theta_{n\pm1}\right\rangle_{ph} = J\ \exp\left[-\delta^2 S(T)\right].$$

Here

$$S(T) = \frac{2}{N}\sum_q \frac{|F_q|^2}{(\hbar\omega_q)^2}\ \sin^2\left(\frac{qR_0}{2}\right)\left(2\bar{\nu_q}+1\right)$$

($\bar{\nu_q}$ is the equilibrium phonon distribution) denotes the temperature-dependent coupling constant introduced in [22, 23]. It approaches the previously defined form at $T = 0$: $S(0) = (8/3\pi)(E_B/\hbar\omega_B)$. The explicit form of the effective Hamiltonian will be formulated in analogy with the application of the Bogolyubov theorem for a single exciton in [43]. Adding and subtracting the term $H' = J\sum_n (B_n^+ B_{n+1}\langle\Theta_n^+\Theta_{n+1}\rangle + \text{HC})$ to the Hamiltonian (3) we see that it can be represented as a sum of two terms: $H = H_{eff} + H_{int}$ where:

$$\begin{aligned} H_{eff} = {} & \left[\Delta - \delta(2-\delta)E_B\right]\sum_n B_n^+ B_n - J_{eff}\sum_n B_n^+\left(B_{n+1}+B_{n-1}\right) \\ & + \frac{1-\delta}{\sqrt{N}}\sum_{q,n} F_q\ \exp\left(\mathrm{i}qnR_0\right)\ B_n^+ B_n\left(a_q + a_{-q}^+\right) \\ & + \sum_q \hbar\omega_q a_q^+ a_q - \delta(2-\delta)E_B\left[\tfrac{1}{2}\sum_n B_n^{+2}B_n^2\right. \\ & \left. + \tfrac{1}{4}\sum_n\left(B_n^+ B_{n+1}^+ B_{n+1}B_n + B_n^+ B_{n-1}^+ B_{n-1}B_n\right)\right] \end{aligned} \tag{4}$$

and

$$H_{int} = J\sum_n\left\{B_n^+ B_{n+1}\left[\left\langle\Theta_n^+\Theta_{n+1}\right\rangle - \Theta_n^+\Theta_{n+1}\right] + \text{HC}\right\}. \tag{5}$$

In the spirit of the mean-field method we shall base our further analysis upon the effective Hamiltonian (4) assuming the smallness of the interaction term. The validity of this assumption will be analysed subsequently.

The main advantage of the Hamiltonian (4) with respect to the original Hamiltonian is that it includes the effective dynamical inter-vibron interaction. Now it describes the system of the 'dressed' vibrons (vibron polarons) interacting mutually with each other and with lattice vibrations. In this way it could be the basis for examination of the whole scale of the many-particle effects in a multivibron system such as the creation of two-vibron, three-vibron or multivibron bound states. In the present context, however, we are only examining the possibility of the soliton (i.e. multivibron soliton) creation. Obviously two competing mechanisms could give rise to soliton formation: vibron–phonon and vibron–vibron interaction. Which prevails depends on the value of δ, whose determination is our primary task. In this context the value of δ will also determine the nature of phonon behaviour characteristic for the particular mechanism. Namely, according to the previous results [22–24] concerning the single-vibron transfer, the ST mechanism prevails if the phonons, engaged in the formation of the lattice distortion, behave as the classical field while the vibron–vibron interaction dominates soliton formation when their quantum nature prevails.

In order to find the multiquanta soliton solution we shall apply a slightly modified standard Davydov D_2 *ansatz* which is based upon the following trial state of the system:

$$|\Psi(t)\rangle = |\beta(t)\rangle \otimes |\alpha(t)\rangle \qquad |\beta(t)\rangle = \prod_n |\beta_n(t)\rangle \qquad |\alpha(t)\rangle = \prod_q |\alpha_q(t)\rangle \tag{6}$$

where $|\beta_n(t)\rangle$ and $|\alpha_q(t)\rangle$ are coherent states of the polaron operator B_n and the phonon operator a_q, respectively. The trial state (6) is normalized to unity: $\langle\Psi|\Psi\rangle = 1$. If the number of 'dressed' vibrons in the system is $\mathcal{N}$, the following relation holds:

$\mathcal{N} = \langle\Psi|\sum_n B_n^+ B_n|\Psi\rangle = \sum_n |\beta_n|^2$. It is easy to prove, using the time-dependent variational principle [22, 23], that coherent amplitudes $\beta_n(t)$ and $\alpha_q(t)$ satisfy the following set of Hamiltonian equations:

$$\mathrm{i}\hbar\dot{\beta}_n(t) = \frac{\partial\mathcal{H}_{eff}}{\partial\beta_n^*} \qquad \mathrm{i}\hbar\dot{\alpha}_q(t) = \frac{\partial\mathcal{H}_{eff}}{\partial\alpha_q^*} \tag{7}$$

where $\mathcal{H}_{eff} = \langle\Psi|H_{eff}|\Psi\rangle$ corresponds to the classical Hamiltonian function.

The proposed *ansatz* is flexible enough to describe soliton properties in the whole parameter space of the system (S–B plane); so we have the possibility, by calculating the dependence of the dressing fraction δ on the system parameters, to determine whether the classical or quantum nature of lattice vibrations dominates the system properties, and the soliton character in particular. To see how the value of δ is related to the nature of the phonons involved in the creation of lattice distortion, let us find the expectation value of the lattice displacement operator $\hat{u}_n$, expressed in terms of new phonon operators, in the trial state (6). We easily find that

$$u_n = \langle\Psi|\hat{u}_n|\Psi\rangle = \frac{1}{\sqrt{N}}\sum_q\left(\frac{\hbar}{2M\omega_q}\right)^{1/2}\left(\alpha_q + \alpha_{-q}^*\right)\,\exp\left(\mathrm{i}qnR_0\right)$$
$$+ \frac{2}{\sqrt{N}}\sum_{q,m} f_q\left(\frac{\hbar}{2M\omega_q}\right)^{1/2}\,\exp\left[\mathrm{i}q(n-m)R_0\right]|\beta_m|^2. \tag{8}$$

We see that lattice distortion consists of two competing contributions. The first, measured by the magnitude of the coherent phonon amplitudes $-\alpha_q$, defines the slow or classical part of lattice distortion while the remaining contribution arises from the quantum corrections. Going over to continuum approximation and solving the equation of motion (7) for phonon amplitudes, following the standard proceedure [4–8, 22–24] we find in the continuum approximation that

$$\alpha_q(t) = -\frac{(1-\delta)F_q^*}{\hbar(\omega_q - qv)}\int_{-\infty}^{+\infty}\,\exp(-\mathrm{i}qx)\;|\beta(x-vt)|^2\frac{\mathrm{d}x}{R_0}. \tag{9}$$

According to (8) and (9) it follows that δ is limited to the range $0 < \delta < 1$. Thus when δ vanishes, only the α_q contribution to u_n survives and therefore the phonon subsystem behaves in a classical way and the soliton solution, if any exist, corresponds to the $\mathcal{N}$ vibrons trapped in the common potential well. Such solitons were examined by Lomdahl and Kerr [11] who, in their numerical simulations, found that increasing the number of quanta to $\mathcal{N} = 6$ leads to the enhanced stability of solitons even at physiological temperatures. If, however, $\delta \to 1$, $\alpha_q \to 0$ and the quantum nature of phonons prevails so that a soliton may be created on account of the effective vibron–vibron interaction, approximately $E_B\sum_n B_n^{+2}B_n^2$ only. Exact eigenstates of such system are known on the basis of the Bethe *ansatz*, and, if the number of particles in the cluster is large enough, these solutions attain a soliton form [36]. This condition, namely a large value of the vibron population, is also the condition for the applicability of the above-proposed factorization of the vibron part of trial state which is equivalent to the application of the Hartree approximation. Clearly, according to [31–33], $\mathcal{N}$ cannot be too large because its increase would shrink the soliton width and the applicability of the continuum approximation breaks down.

Eliminating the phonon coherent amplitudes from the equation of motion for vibrons by virtue of equation (9) and going over to continuum, we obtain

$$\mathrm{i}\hbar\dot{\beta}(x,t) = \left[\Delta - \delta(2-\delta)E_B - 2J_{eff}\right]\beta(x,t) - J_{eff}R_0^2\beta_{xx}(x,t)$$

$$- 2E_B\left[\frac{(1-\delta)^2}{1-v^2/c^2} + \delta(2-\delta)\right]|\beta(x,t)|^2\beta(x,t). \tag{10}$$

Dispersion of non-linear terms was neglected; so we have dropped the terms $\propto R_0^2(|\beta(x,t)|^2)_{xx}\beta(x,t)$. Equation (10) possesses a soliton solution subject to the normalization condition $\mathcal{N} = \int(\mathrm{d}x/R_0)|\beta(x,t)|^2$:

$$\beta(x,t) = \exp[\mathrm{i}(kx-\omega t)]\,\mathcal{N}\left(\frac{\mu}{2}\right)^{1/2}\operatorname{sech}\left(\frac{\mu\mathcal{N}}{R_0}(x-x_0-vt)\right). \tag{11}$$

Here the soliton quasi-momentum k and the so-called soliton parameter μ, which is related to soliton width as $\Delta l \approx R_0/\mathcal{N}\mu$, are given as

$$k = \frac{m^*v}{\hbar} \equiv \frac{\hbar v}{2J_{eff}R_0^2} \qquad \mu = \frac{E_B}{2J_{eff}}\left[\frac{(1-\delta)^2}{1-v^2/c^2} + \delta(2-\delta)\right] \tag{12}$$

while ω is found from the following expression:

$$\hbar\omega = \Delta - \delta(2-\delta)E_B - 2J_{eff} + \frac{m^*v^2}{2} - \frac{\mathcal{N}^2{E_B}^2}{4J_{eff}}\left[\frac{(1-\delta)^2}{1-v^2/c^2} + \delta(2-\delta)\right]^2. \tag{13}$$

Finally substituting (12) into the explicit expression for $\mathcal{H}_{eff}$, we obtain the system energy and the soliton effective mass:

$$E = \mathcal{N}\big[\Delta - \delta(2-\delta)E_B - 2J_{eff}\big] + \frac{m_s v^2}{2} - \left[\frac{(1-\delta)^2}{1-v^2/c^2} + \delta(2-\delta)\right]^2\frac{E_B^2\mathcal{N}^3}{12J_{eff}} \tag{14}$$

$$m_s = \mathcal{N}m^*\left[1 + \frac{4{E_B}^2(1-\delta)^2\mathcal{N}^2R_0^2}{3c^2\hbar^2}\right]. \tag{15}$$

Clearly, almost all soliton features and the nature of the mechanism leading to its formation are determined by the value of δ. Therefore one must determine the dependence of δ on the system parameters in order to classify the soliton states and to define the conditions for their existence. This is the subject of the next section.

3. Optimization of the dressing parameter and the character of the soliton

The results of the preceding paragraph were obtained for a fixed but arbitrary value of δ with the only restriction $0 < \delta < 1$, and various values of δ could be used to obtain different types of soliton solution.

For the given set of the system parameters, however, the choice of δ is not arbitrary and there should exist an optimal value of δ corresponding to the minimum-energy state. For this optimized value of δ, the above time-dependent solution (11) describes the evolution near this minimal-energy state [22]. We shall find those optimized values of δ by minimizing the GS energy of the system which follows from (14) in the static ($v = 0$) limit:

$$E_{GS} = \mathcal{N}\big\{\Delta - \delta(2-\delta)E_B - 2J\ \exp\big[-\delta^2S(T)\big]\big\} - \frac{E_B^2\mathcal{N}^3\ \exp[\delta^2S(T)]}{12J}. \tag{16}$$

Stable (minimum-energy) eigenstates of the system correspond to those values of δ which are the solutions of equation $\partial E_{GS}/\partial\delta = 0$ subject to the condition $\partial^2E_{GS}/\partial\delta^2 > 0$. The stationarity condition ($\partial E_{GS}/\partial\delta = 0$) can be solved as the quadratic equation for $B(T)\ \exp[-\delta^2S(T)]$, where $B(T) = (2JE_B)S(T) = (8/3\pi)(2J/\hbar\omega_B)S(T)/S(0)$ denotes

the temperature-dependent adiabaticity parameter. In this way we obtain the self-consistent equation for the dressing parameter:

$$\delta = \left[1 + \frac{2B(T)\ \exp[-\delta^2 S(T)]}{1+K}\right]^{-1} \qquad K = \sqrt{1 + \frac{2\mathcal{N}^2 S(T)^2 \delta^2}{3(1-\delta)^2}}. \tag{17}$$

It is written in the form which we found the most convenient for the numerical procedure [24].

In order to define physically meaningful solutions of δ we simply insert the above-obtained result for $B(T)\ \exp[-\delta^2 S(T)]$ into $\partial^2 E_{GS}/\partial\delta^2 > 0$. In this way we have eliminated the adiabaticity parameter, and the stability condition is given as follows:

$$S(T) < \frac{\sqrt{3}}{2\mathcal{N}} \frac{1-\delta}{\delta} \left[\sqrt{1 + \frac{2\mathcal{N}^2}{3\delta^2(1-\delta)^4}} - 1\right]^{1/2}. \tag{18}$$

Soliton solutions are restricted by another condition $\mathcal{N}\mu < 1$ which determines the applicability of the continuum approximation. Combining it with equation (17), we obtain the condition for the applicability of the continuum approximation:

$$S(T) < \frac{6}{5\mathcal{N}} \frac{1-\delta}{\delta}. \tag{19}$$

Strictly speaking, applicability of the continuum approximation demands that $\mathcal{N}\mu \ll 1$. However, we have adopted here the less restrictive criterion, which is common in the continuum polaron model [20, 41], where the extent of the polaron approximately equal to the lattice constant R_0 has been used as the boundary separating a large polaron (soliton) from a small polaron (see also the second reference of [40]). From that condition one can find the values of the physical parameters of the system where the transition from large polaron to small polaron occurs. In the present context the analogous condition, i.e. $\Delta l/R_0 \simeq 1$, should be understood as the boundary where the soliton collapses into the extremely localized $\mathcal{N}$-vibron bound state.

Thus, in order to classify stable eigenstates of the system, to analyse the possibility of soliton formation and finally to determine their character and which mechanism dominates their creation, one should find the values of δ for the particular values of $S(T)$ and $B(T)$ by solving equation (17). This can be done only numerically and our results are visualized in figures 1–3 where we have plotted, for a few fixed vibron populations ($\mathcal{N} = 5$, 10 and 100, respectively), the set of adiabatic curves; the curves $S(T) = S(\delta, B(T))$ each corresponding to a particular $B(T)$. The values of $B(T)$ are chosen to span the whole range of adiabaticity varying from non-adiabatic ($B(T) \ll 1$) to the adiabatic ($B(T) \gg 1$) limit. In this way, the interpretation of our result is quite simplified with respect to the case when one chooses to plot $\delta = \delta(S(T), B(T))$ which looks like a natural choice. Using equations (18) and (19), one may define the stability line ($S(T)$ equals the right-hand side (RHS) of (18)) and continuum boundary ($S(T)$ equals the RHS of (19)). The stability line separates the stable from the unstable solutions and according to (18) the physically meaningful region of the $S(T)$–δ plane corresponds to those points lying below the stability lines (solid lines in figures 1–3) while soliton solutions correspond to those points lying below the continuum boundary (broken (long dashes) curves in figures 1–3).

Looking at these adiabatic curves as a functional dependence of the dressing parameter on coupling constant and adiabaticity, we see that, as long as $B(T)$ is less than some critical value, these lie below the stability line and therefore include only minima in the GS energy. When $B(T)$ exceeds this critical value, each adiabatic curve intersects the stability line at one point. Consequently each adiabatic curve for each $S(T)$ which is higher than the

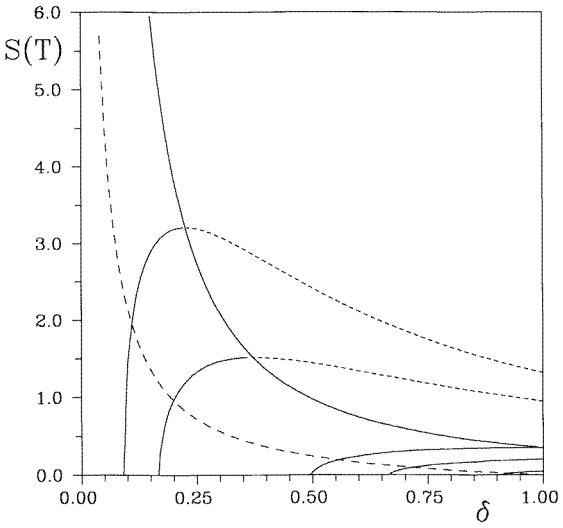

Figure 1. Adiabatic curves $S = S(\delta)$ ($\mathcal{N} = 5$) for a few chosen values of adiabaticity parameter B where these curves from left to right, correspond to $B(T) = 10$, 5, $B_C \simeq 1.014$, 0.5 and 0.1 respectively: ——, so-called *stability line*; — — —, *continuum boundary*; - - - -, part of each adiabatic curve for $B(T)) > B_C$ corresponding to the unstable region.

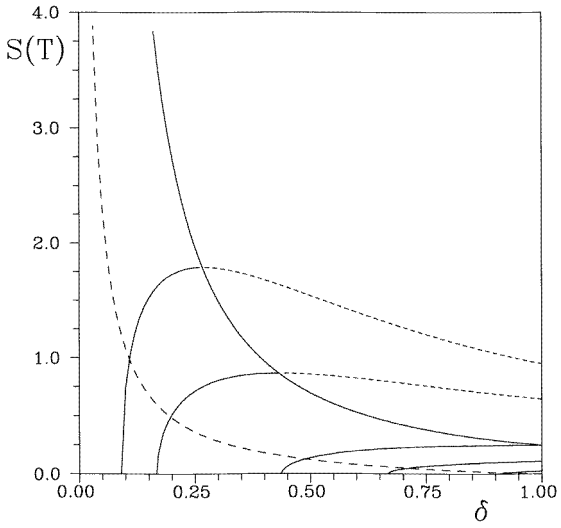

Figure 2. Adiabatic curves for $\mathcal{N} = 10$ and the same set of adiabatic parameters ($B_C \simeq 1.294$).

critical value has two solutions for δ corresponding to GS extrema. Clearly, owing to the stability condition (18), only the lower solution defines the stable eigenstate of the system. The critical adiabaticity parameter corresponds to that adiabatic curve which has a single common point with the stability line. Obviously it falls onto $\delta = 1$. Thus, taking the limit $\delta \to 1$ in the expression for stability line, we find that $S_C = \sqrt[4]{6}/(2\sqrt{\mathcal{N}})$. In a similar way by setting $\delta \to 1$ in the self-consistent equation for δ and substituting $S(T) = S_C$ we obtain

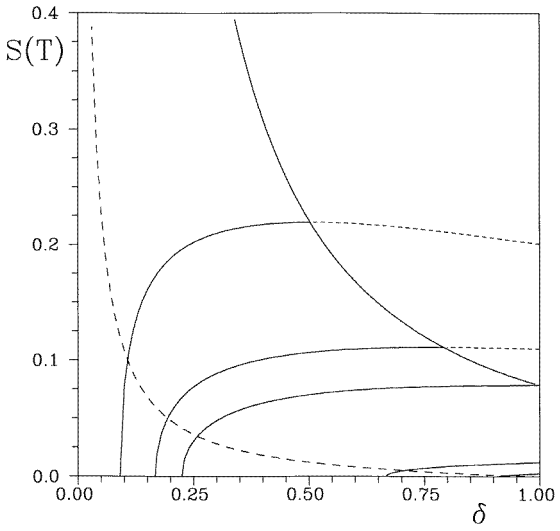

Figure 3. The same set of adiabatic curves for $\mathcal{N} = 100$ ($B_C \simeq 3.455$).

the critical adiabaticity as follows: $B_C = (\sqrt{\mathcal{N}}/2\sqrt[4]{6})\ \exp(\sqrt[4]{6}/2\sqrt{\mathcal{N}})$.

Concerning the validity of the soliton picture we see from figures 1–3 that, since the continuum boundary always lies below the stability line, the condition for the applicability of the continuum approximation is also the condition for soliton existence. To find the range of coupling constants in which the soliton may exist for a particular adiabaticity, one must find the crossing points of each adiabatic curve with the continuum boundary. So we find that $\delta_0 \approx 1/(1+\frac{5}{6}B(T))$ which separates those values of δ corresponding to soliton solutions from those which define a second type of solution, namely an intrinsic self-localized mode (ISM). Inserting δ_0 into the continuum boundary we find the simple condition

$$S(T) < \frac{B(T)}{\mathcal{N}}. \tag{20}$$

Thus the soliton may exist for each adiabaticity if $\delta < \delta_0$ and if (20) holds. When S exceeds this value, the soliton collapses into an extremely narrow vibron complex.

This indicates that in the multivibron system interacting with the lattice, we can expect two types of solution: the soliton solution if condition (20) is satisfied and the extremely localized $\mathcal{N}$-vibron cluster in the opposite case. These solutions, the ISMs, were examined by Takeno and co-workers [44–47] and Zhu and Kobayashi [47] who found that they may arise in systems of strongly interacting phonons [44], magnons [45, 46] and excitons [47]. However, because of the application of the continuum soliton solution (11) in our variational treatment, i.e. optimization of the dressing parameter, our results and conclusions concern solitons exclusively and, for the investigation of the properties of the second type of solution, one must take into account the discreteness of the lattice.

The character of the soliton and the mechanism which dominates its formation are determined by the value of δ. As one can see from figures 1–3 in the extreme adiabatic limit $\delta \approx [1/(1+B(T)] \to 0$, the semiclassical nature of the phonon prevails and the soliton arises as a result of ST of $\mathcal{N}$ vibrons in a common potential well. In the intermediate range of adiabaticity, but still higher than B_C, both mechanisms give rise to soliton formation but still ST is dominant. Lowering of the adiabaticity disturbs this balance to the benefit of

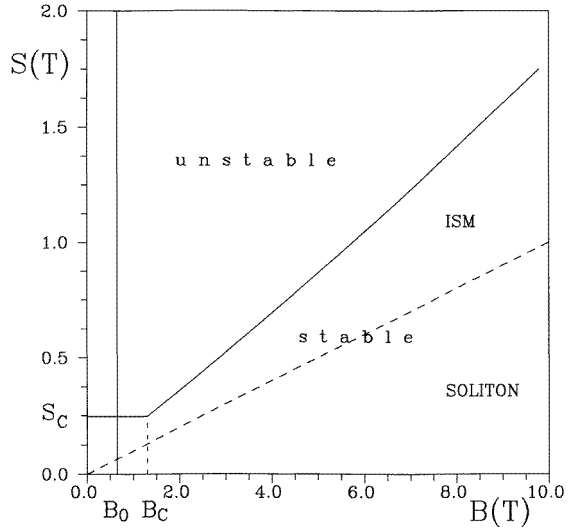

Figure 4. Phase diagram of system for $\mathcal{N} = 10$: - - - - boundary between the regions in parameter space (S–B plane) corresponding to stable (lower) and unstable states: — — —, continuum boundary in the S–B plane separating the soliton region from the region in which ISM prevails. The vertical line $B_0 = 0.65$ defines the domain of applicability of the present 'partial dressing' approach. If system parameters correspond to $B \leqslant B_0$, one must take $\delta = 1$.

the vibron–vibron interaction. In the non-adiabatic limit the soliton can exist in the weak-coupling limit, but the ST mechanism could play a certain role in soliton formation in the extremely weak case only if B is not too small. Increasing the coupling constant, even by a very small amount, rapidly turns δ to unity, and soliton formation is almost exclusively influenced by the effective vibron–vibron interaction.

On the basis of these results, one may construct, for a particular $\mathcal{N}$, the phase diagram of the system and in this way determine in which part of the parameter space of the system a particular type of solution would be expected. In figure 4 we have plotted the phase diagram of the system for $\mathcal{N} = 10$. From the crossing points of each adiabatic curve with the stability line we may determine the physically meaningful region in the parameter space, i.e. those points in the $S(T)$–$B(T)$ plane corresponding to the minimum-energy eigenstates of the system. It lies below the broken line in figure 4. Soliton solutions correspond to those points for which condition (20) is satisfied, i.e. below the line $S(T) = B(T)/\mathcal{N}$. For the values of $S(T)$ and $B(T)$ lying between these two lines, only ISMs can exist.

Clearly the variational character of our partial dressing method imposes certain restrictions on the domain of applicability of our results. Thus, in order to determine the degree to which our results are reliable for understanding the soliton properties in a realistic biological context, we must compare them with those obtained by other methods. To our best knowledge, multi-exciton (vibron) soliton states, arising on account of the exciton (vibron)–phonon interaction, have been examined in only a few papers [29–35]. So Weidlich and Heudorfer [30], Kislukha [33] and finally Lomdahl and Kerr in the context of DT [11] investigated such solitons using semiclassical analysis, which corresponds to our choice $\delta = 0$, while Nakamura [32] and one of the present authors with co-workers [35] utilized unitary transformation techniques with the choice $\delta = 1$ (full dressing approximation). The superiority of the present approach corresponds to that part of the parameter space where

it predicts lower estimates for the GS energy of the system. Substituting $\delta = 0$ in (16) and $\delta = 1/(1 + B)$, which is a good approximation for δ in the range where the soliton existence condition (20) is satisfied, we estimate that $E_{GS}(\delta) - E_{GS}(\delta = 0) \approx -(2S/B)E_B$, which ensures better applicability of the partial dressing method with respect to the strict semiclassical analysis in almost the whole parameter space of the system. Note that in the limit of infinite adiabaticity ($B \to \infty$) the difference between these two methods disappears, the result which was to be expected. Repeating this procedure for $\delta = 1$ and $\delta \approx 1/(1+B)$ we found that $E_{GS}(\delta) - E_{GS}(1) < 0$ if $B(T) > B_0$ ($B_0 = 0.65$). This means that, when the adiabaticity lies below this value (i.e. $B(T) < 0.65$), one must take $\delta = 1$ while for the rest our results are unaffected.

Let us now estimate how the variations in the vibron number and the temperature could modify the above conclusions. As follows from figures 1–3 the dependences of δ on adiabaticity and coupling constant are qualitatively the same for all values of $\mathcal{N}$; however, increasing $\mathcal{N}$ significantly reduces the allowed range of the coupling constant in which (for given $B(T)$) the soliton may exist. This could be seen especially from the above-mentioned condition for soliton existence ($S(T) < B(T)/\mathcal{N}$). Concerning the thermal effects we note that, within this mean-field method, these could be manifested only through the temperature dependence of the coupling constant and the adiabaticity which increase on increase in temperature. At $T = 0$ they are $S(0) = (3\pi/8)(E_B/\hbar\omega_B)$ and $B(0) = (3\pi/8)(2J/\hbar\omega_B)$ while at high temperatures they can be approximated as $S(\infty) \approx 3\pi(k_BT/\hbar\omega_B)S(0)$ and $B(\infty) = 3\pi(k_BT/\hbar\omega_B)B(0)$. In order to understand how temperature affects the results of the preceeding discussion, let us assume that we initially examine the system at zero temperature. Furthermore let us suppose that the condition for soliton existence (20) is satisfied; i.e $S(0) < B(0)/\mathcal{N}$. Multiplying both sides of this inequality by $3\pi(k_BT/\hbar\omega_B)$ we see that this condition is satisfied also for $T \neq 0$, so that the soliton survives even at finite temperatures. The character of these states, however, could be modified owing to the increase in adiabaticity parameter on a rise in temperature. Consequently, an increase in the temperature drives the system towards the adiabatic limit; so it follows that the temperature favours the ST mechanism of soliton formation.

4. Concluding remarks

Finally before using our results in order to examine the possibility of the $\mathcal{N}$-vibron soliton existence in an α-helix, let us estimate the contribution of the remaining interaction term (H_{int}) which has been neglected so far. Strictly following the mean-field procedure as proposed for example in [48], this term could be approximated as

$$H_{int} = \frac{\delta}{\sqrt{N}} J_{eff} \sum_{n,q} \frac{F_q}{\hbar\omega_B} \left[1 - \exp\left(\mathrm{i}qR_0\right)\right] \exp\left(\mathrm{i}qnR_0\right) B_n^+ B_{n+1} \left(a_q^+ - a_{-q}\right) + \text{HC.} \quad (21)$$

Corrections arising from this term are negligible in the adiabatic limit owing to the smallness of δ since, in the final instance, it causes changes in the soliton parameters and GS energy of the order of $1/B$ and $1/B^2$.

In the non-adiabatic limit we must put $\delta = 1$ while (21) should be considered as a small perturbation since it is of the order of $\sqrt{S}$ ($F_q/\hbar\omega_B \sim \sqrt{S}$) which in the soliton region is small. Under these conditions, the 'new' phonons do not participate in soliton creation and (21) represents the interaction of the soliton, which is the fundamental excitation of H_{eff} for $\delta = 1$, with phonons which now play the role of the thermal bath.

Finally we may summarize the results of the preceding sections.

(1) Vibron (exciton)–phonon interaction may lead to soliton formation on account of two mechanisms:

(*a*) ST in which $\mathcal{N}$ vibrons (excitons) are captured in the common potential well created by the large-radius static lattice distortion and which is fully equivalent to the formation of a single large polaron and arises in the adiabatic limit only where the semiclassical approximation for a phonon field is valid;

(*b*) as a result of the effective vibron–vibron interaction which prevails in the non-adiabatic limit.

(2) The condition for the existence of solitons irrespective of the mechanism which induces their creation is given by $S(T) < B(T)/\mathcal{N}$. When $S(T) > B(T)/\mathcal{N}$, the continuum approximation is no longer valid and our approach fails to describe the properties of these extremely localized states properly. Thus we satisfied ourselves just with pointing out that, if (20) does not hold in our system, the so-called intrinsic self-localized vibrons analogous to recently discovered intrinsic localized excitations such as phonons, magnons and Frenkel excitons [44–47] should arise.

(3) The rise in temperature does not affect the soliton existence condition but may change its character, driving the system towards the adiabatic (semiclassical) limit.

Using the set of parameters which is usually quoted as representative for an α-helix and related molecules (ACN, for example) we found that $B(0) \simeq 0.14$–0.16, $E_B = (10^{-23}$–$10^{-22})$ J and $S \simeq 0.01$–0.1. Clearly these values correspond to the non-adiabatic and weak-coupling limit; so, if $\mathcal{N}$ is not too large, a soliton may be formed. In this way our results in a certain sense support the ideas of Lomdahl and Kerr [11] that a multiquantum soliton is more relevant in realistic biological conditions than the originally proposed soliton. However, the properties of these solitons which arise on account of induced vibron–vibron interaction are quite different from those originally proposed. At 300 K, $k_BT/\hbar\omega_B \simeq 1.95$–$2.27$, resulting in $B \simeq 0.28$–0.32 which still belongs to the non-adiabatic limit and therefore does not change the character of the soliton.

In concluding this paper we must stress that our results only point to the possibility that such solitons may be relevant as a transport mechanism in biological systems. However, the extrapolation of these ideas to real systems should be taken with certain reserves. Namely our results were obtained within the framework of the (over)simplified model where the only connections with realistic biological systems are the values of the physical parameters of system. Furthermore we focused on the examination of the equilibrium properties of solitons, neglecting the dynamics. Therefore one of the next steps would be the examination of soliton dynamics under the influence of a thermal bath whose coupling with a soliton is defined by H_{int} (equation (21)). Its influence should be manifested through the small changes in soliton parameters which now become a function of time. According to some previous analyses of related problems [49], we can assume that this interaction will lead to diffusive motion of the soliton and in the final instance it will result in the finite lifetime of the soliton. The examination of these effects is of particular interest and will be done separately.

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