Comment on "Improvement of the Davydov theory of bioenergy transport in protein molecular systems"

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The validity of the recently proposed tentative improvement of the Davydov theory of intramolecular vibrational transfer is discussed. It is shown that it contains a few principal shortcomings and cannot be a sound ground for studies of the transport processes in molecular systems.

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In a recent paper [1] and in subsequent articles [2] Pang has suggested that Davydov soliton theory (DST) [3], with some modifications of the original model Hamiltonian and by virtue of the improved theoretical approach based upon a new trial state, may be improved and used in the explanation of energy transfer in molecular crystals such as acetanilide (ACN), α helix, etc. Unfortunately, as we shall demonstrate below, the "improved" theory suffers from the number of shortcomings, even more serious than the original one.

The modified model Hamiltonian is supplemented with the additional exciton-phonon coupling term added with the purpose of accounting for the effects of the modulation of the resonant dipole-dipole energy caused by the molecular displacements. It seems that the author is completely unaware that this interaction had been introduced long ago by Davydov and co-workers [4], "revived" by Scott [5], and consequently does not represent any new improvements. Moreover, within the continuum treatment of the problem, all these new coupling terms may be absorbed in the single one with the joint coupling constant: the sum of the individual ones. In such a way the original Davydov's model Hamiltonian

$$H = \Delta \sum_n B_n^\dagger B_n - J \sum_{n;l=\pm 1} B_n^\dagger B_{n+l} + \sum_q \hbar\, \omega_q a_q^\dagger a_q + \frac{1}{\sqrt{N}} \sum_q F_q e^{iqnR_0} B_n^\dagger B_n (a_q + a_{-q}^\dagger), \tag{1}$$

with precisely the same meaning of system parameters and operators could be used as a theoretical basis for the "improved" theory. Here, as usual, J denotes the intersite transfer integral, operator $B_n^\dagger(B_n)$ describes the presence (absence) of the excitation on nth lattice site; $a_q^\dagger(a_q)$ creates (annihilates) phonon quanta with the frequency ω_q. $\chi_1 = d\Delta/dR_o$ is the modulation of the on-site energy, $F_q = 2i\chi_1(\hbar/2M\omega_q)^{1/2} \sin qR_0$, denotes electron-phonon coupling parameter $\omega_q = \omega_B \sin |qR_0/2|$. Here $\omega_B = 2(\kappa/M)^{1/2}$ denotes the phonon bandwidth, κ is a spring constant, M is the mass of the molecular group and finally R_0 is lattice constant. Replacement of coupling parameter χ_1 by the effective one would be sufficient, within the continuum approximation, to include practically all effects coming from additional exciton-phonon couplings.

Pang's second improvement of DST consists in an alternative proposal of the vector of state of system that is, again, chosen as a total product of exciton and phonon wave functions $|\Psi(t)\rangle = |\Psi(t)\rangle_{ex} \otimes |\Phi(t)\rangle_{ph}$. The phonon-part of the vector of state is taken in precisely the same form as in DST; i.e., as a product of the single-mode phonon coherent states defined as an eigenstate of the phonon annihilation operator: i.e., $|\Phi\rangle = \Pi_q |\alpha_q\rangle$ where $a_q|\alpha_q\rangle = \alpha_q|\alpha_q\rangle$. The excitonic part, in contrast to the original Davydov's treatment, is taken in a form of the so-called quasicoherent state and reads

$$|\Psi(t)\rangle_{ex} = \frac{1}{\lambda}\left(1 + \sum_n \Psi_n(t) B_n^\dagger\right)|0\rangle_{ex} \otimes |\alpha(t)\rangle, \tag{2}$$

if the single exciton is excited in the system, and

$$|\Psi(t)\rangle_{ex} = \frac{1}{\lambda}\left(1 + \sum_n \Psi_n(t) B_n^\dagger + \frac{1}{2!}\left(\sum_n \Psi_n(t) B_n^\dagger\right)^2\right)|0\rangle_{ex} \tag{3}$$

for the two-particle case. λ is the normalization constant that cannot be determined within the present method so $\lambda = 1$ is usually taken.

Some doubts concerning the validity of that approach have been raised recently by Cruzeiro-Hansson [6] who pointed to some controversies in Pang's theory. Unfortunately, her criticism is based upon some qualitative arguments without any detailed calculations and analysis in support or against the Pang theory. In particular, since she admits that, in spite of the vague physical meaning of the proposed trial state, it may give a lower estimate for the ground state energy (GSE) of the system than DST, it remains unclear whether or not Pang's approach represents real improvement of the DST.

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It will be done here and for that purpose we shall calculate the GSE of the system employing both Davydov's ansatz (DA) and Pang's trial state. Comparison of the obtained results will clarify which approach is superior.

However, before that, let us point that the factorized ansatz, the basis of both methods, holds in the adiabatic limit $2J/\hbar\omega_B \gg 1$ when semiclassical treatment of phonon subsystem is justified [7]. At this stage we must underline that the main shortcoming of both approaches is their application to the problem of intramolecular energy transfer that does not involve parameter regimes where the semiclassical approximation holds. In that respect the term "superior" refers to the adiabatic limit only.

Before the explicit calculation of the system GS energy we must discuss some properties of Davydov's and Pang's trial states that were overlooked in [1,2]. The only difference in both approaches lies in the specific choice of exciton part. In particular, in the case of the single exciton self-trapping (ST), the basis of DA is the normalized wave function specified as

$$|\Psi(t)\rangle = \sum_n \Psi_n(t) B_n^\dagger |0\rangle_{ex} \otimes |\alpha(t)\rangle, \langle\Psi(t)|\Psi(t)\rangle = 1 \Rightarrow \sum_n |\Psi_n|^2 = 1. \tag{4}$$

For the soliton formation on the account of simultaneous ST of the two excitons, the following ansatz state has been proposed [8]

$$|\Psi(t)\rangle = \sum_{m,n} \Psi_{n,m} B_m^\dagger B_n^\dagger |0\rangle \otimes |\alpha\rangle, \quad \Psi_{m,n} = \Psi_{n,m},$$

$$\langle\Psi(t)|\Psi(t)\rangle = 1, \quad \Rightarrow \quad \sum_n |\Psi_{n,m}|^2 = \frac{1}{2}. \tag{5}$$

At this stage we must underline that the above-proposed trial functions [both (4) and (5)], contrary to the Pang's claim in [1,2], are the eigenstates of the exciton number operator. In the mentioned reference Pang stated that, for the two-exciton case, $\langle\Psi(t)|\Sigma_n B_n^\dagger B_n|\Psi(t)\rangle = 4$. This result stems from the *ad hoc* introduced normalization constraint $\Sigma_{m,n}|\Psi_{m,n}|^2 = 1$ that if accepted would impose $\langle\Psi(t)|\Psi(t)\rangle = 2$. If, however, one works with the properly normalized trial states (i.e., $\langle\Psi(t)|\Psi(t)\rangle = 1$) it follows that $\Sigma_{m,n}|\Psi_{m,n}|^2 = 1/2$, which implies $\langle\Psi(t)|\Sigma_n B_n^\dagger B_n|\Psi(t)\rangle = 2$. The main difference of the so-proposed trial states with respect to those specified by Eqs. (2) and (3) are that the latter ones are not normalized to unity. More precisely, instead of looking for normalization constraints on exciton amplitudes Ψ_n imposing $\langle\Psi|\Psi\rangle = 1$, Pang has postulated $\Sigma_n|\Psi_n|^2 = 1$, which, in accordance with Eqs. (2) and (3) yields,

$$\langle\Psi|\Psi\rangle = \begin{cases} 2 & \text{for state (2)} \\ \frac{5}{2} & \text{for state (3)}, \end{cases} \tag{6}$$

i.e., in both cases $\langle\Psi|\Psi\rangle \neq 1$.

So, let us for the moment discuss the problem of the normalization. It concerns the above *ad hoc* (postulated) introduced normalization condition $\Sigma_n|\Psi_n|^2 = 1$, which cannot be derived in accordance with the usual quantum-mechanical procedure, i.e., imposing the normalization of the vector of state: $\langle\Psi|\Psi\rangle = 1$. Namely, such demand for the trial state (2), would lead to $1 + \Sigma_n|\Psi_n|^2 = 1$ while the choice of trial state in the form (3) results in $1 = 1 + \Sigma_n|\Psi_n|^2 + \frac{1}{2}(\Sigma_n|\Psi_n|^2)^2$. Both of these equalities can be satisfied only for $\Sigma_n|\Psi_n|^2 = 0$.

Furthermore, another possibility of its determination on the basis of the calculation of the expectation value of operator of total exciton number leads to the paradox. Following the general quantum-mechanical rules, we have

$$\frac{\langle\Psi|\sum_n B_n^\dagger B_n|\Psi\rangle}{\langle\Psi|\Psi\rangle} \equiv \mathcal{N}. \tag{7}$$

This expression after the straightforward calculations involving the substitution of the explicit expressions for $\langle\Psi|\Psi\rangle$ and $\langle\Psi|\Sigma_n B_n^\dagger B_n|\Psi\rangle$ leads to a controversy. Let us combine

$$\langle\Psi|\Psi\rangle = \begin{cases} 1 + \sum_n |\Psi_n|^2 & \text{state (2)} \\ 1 + \sum_n |\Psi_n|^2 + \frac{1}{2}(\sum_n |\Psi_n|^2)^2 & \text{state (3)}, \end{cases} \tag{8}$$

and

$$\left\langle\Psi\middle|\sum_n B_n^\dagger B_n\middle|\Psi\right\rangle = \begin{cases} \sum_n |\Psi_n|^2 & \text{state (2)} \\ \sum_n |\Psi_n|^2 (1 + \sum_m |\Psi_m|^2) & \text{state (3)}. \end{cases} \tag{9}$$

By means of the above expressions we found for the trial state (2)

$$\sum_n |\Psi_n|^2 = \mathcal{N}\left(1 + \sum_n |\Psi_n|^2\right). \tag{10}$$

This relation can never be satisfied for physically meaningful values of $\mathcal{N}$. Namely, if one takes $\Sigma_n|\Psi_n|^2 = 1$ as done in [1,2] fulfilling of the above equation demands $\mathcal{N} = 1/2$. On the other hand if we try to calculate $\Sigma_n|\Psi_n|^2$ from the condition $\mathcal{N} = 1$ we arrive at paradox $\Sigma_n|\Psi_n|^2 = 1 + \Sigma_n|\Psi_n|^2$.

Choosing the trial state (3) we obtain

$$\sum_n |\Psi_n|^2 \left(1 + \sum_n |\Psi_n|^2\right) = \mathcal{N}\left[1 + \sum_n |\Psi_n|^2 + \frac{1}{2}\left(\sum_n |\Psi_n|^2\right)^2\right]. \tag{11}$$

Similarly imposing $\Sigma_n|\Psi_n|^2 = 1$ leads to $\mathcal{N} = 4/5$ while the attempt of evaluation of normalization condition from the last equation substituting $\mathcal{N} = 2$ leads to controversial result $\Sigma_n|\Psi_n|^2 = -2$.

The single formally meaningful result, i.e., the one that does not lead to the above-listed controversial results, can be obtained if, contrary to Pang's interpretation of the trial states, one imposes the condition $\mathcal{N} = 1$ to the trial function (3). In this case, one obtains $\Sigma_n|\Psi_n|^2 = \sqrt{2}$. At this stage, however, we must note that in spite of the formal consistency, this demand is physically meaningless since the vector of state in the form (3) represents a kind of two-particle ansatz and therefore the restriction of $\mathcal{N} = 1$ is meaningless.

The origin of these controversies lies in the fact that the trial states (2) and (3) are not the eigenstates of the exciton number operator but represent an unusual superposition of three states with zero, one, and two excitons present. Thus, in view of these arguments, description of the solitons in the systems with the fixed number of quasiparticles is meaningless. If, however, the exciton number is not conserved, trial states (2) and (3) could be applied but $\mathcal{N}$ should be left unspecified while the examination of the possible advantages of such an approach with respect to the alternative ones (coherent state ansatz, for example) demands separate analysis.

The above facts have significant consequences for the calculation of GSE and derivation of the equations of motion for exciton (Ψ_n) and phonon (α_q) variables. More precisely, in contrast to Davydov's approach where GSE follows simply after the substitution of the soliton solutions in $\langle\Psi|H|\Psi\rangle$ and after the explicit calculation of corresponding sums (integrals), in Pang's approach, due to the fact that $|\Psi\rangle$ is not normalized, GSE should be calculated by means of

$$E_{gs} = \frac{\langle\Psi|H|\Psi\rangle}{\langle\Psi|\Psi\rangle}. \tag{12}$$

Furthermore, while taking the expectation values of the phonon operators within DA corresponds simply to the substitution of a_q and $a_q^\dagger$ with α_q and α_q^*, in Pang's approach it becomes

$$\langle\Psi|a_q^\dagger|\Psi\rangle = \langle\Psi|\Psi\rangle\alpha_q^*, \quad \langle\Psi|a_q|\Psi\rangle = \langle\Psi|\Psi\rangle\alpha_q. \tag{13}$$

The above-mentioned facts have been overseen in deriving the equations of motion for phonon amplitudes and in calculating GSE. In particular, in deriving of the equation of motion for the lattice deformation field (see Eqs. (13)–(15) in [1]), incorrect expectation values for the lattice displacement field and momentum operators in trial states (2) and (3) were used. Correct expressions should be multiplied by $\langle\Psi|\Psi\rangle$, i.e., they would read $\langle\Psi(t)|u_n|\Psi(t)\rangle = \langle\Psi|\Psi\rangle\beta_n(t)$ and $\langle\Psi(t)|P_n|\Psi(t)\rangle = \langle\Psi|\Psi\rangle\pi_n(t)$. In such a way, the resulting equation of motion for the lattice displacement field and consequently the soliton equation that follows in the final step, are inconsistent with the initially introduced ansatz specified through the choice of trial states as (2) and (3). For that reason final results are not reliable and the estimation of the validity of Pang's theory with the respect to the DST demands consistent evaluation of evolution equations and calculation of GSE. Obtained results should be compared with the ones following on the basis of DA, as shown below. Let us start with the evaluation of the equations of motion for quasiparticle wave functions and coherent amplitudes. It may be done by means of the time-dependent variational principle (TDVP) that in the final step results in the following set of evolution equations:

$$i\hbar\,\dot{\Psi}_n = \frac{1}{\varepsilon}\frac{\partial\mathcal{H}}{\partial\Psi_n^*}, \quad i\hbar\,\dot{\alpha}_q = \frac{1}{\langle\Psi|\Psi\rangle}\frac{\partial\mathcal{H}}{\partial\alpha_q^*}. \tag{14}$$

Here parameter ε is specific for each particular choice of trial state and value of $\mathcal{N}$. In particular it attains unity at $\varepsilon=1$ for the both variant of one-particle states. For the two-particle trial state (3), together with the constraint $\mathcal{N}=1$, we have $\varepsilon=1$; $\varepsilon=2\sqrt{2}$ for the particular choice of two-particle amplitude in trial state (5) $\Psi_{m,n}=\Psi_m\Psi_n$. We made such choice for the sake of comparison with Pang's results.

TABLE I. Comparison of the system GS energies calculated within different proposals for trial state.

Trial state	G	μ	E_{GS}
One-particle DA	$2E_B$	$\frac{E_B}{J}$	$-\frac{E_B^2}{3J}$
One-particle Pang	$\frac{16E_B}{\sqrt{2}}$	$\frac{E_B}{2J}$	$-\frac{E_B^2}{24J}$
Two-particle DA	$4E_B$	$\frac{2E_B}{J}$	$-\frac{8E_B^2}{3J}$
Two-particle Pang	$\frac{16E_B}{5}$	$\frac{4E_B}{5J}$	$-\frac{64E_B^2}{375J}$

Further procedure is straightforward and standard so we shall skip the most of the calculation details. Thus, irrespective of the explicit choice trial state, in the final step we obtain the known nonlinear Schrödinger equation for exciton wave function, which in the continuum limit attains the familiar form

$$i\hbar\,\dot{\Psi} = (\Delta - 2J)\Psi - JR_0^2\Psi_{xx} - G|\Psi|^2\Psi. \tag{15}$$

Nonlinearity parameter G is proportional to the small-polaron binding energy

$$\left(E_B = \frac{1}{N}\sum_q \frac{|F_q|^2}{\hbar\,\omega_q} \equiv \frac{4\chi_1^2}{M\omega_B^2}\right)$$

and different for each of the above-discussed variants of the trial state.

Equation (15) possesses the well-known bell-shaped soliton solution

$$\Psi = \sqrt{\frac{\mu}{2\delta}}\frac{1}{\cosh\frac{\mu}{R_0}x}e^{-i\omega t}. \tag{16}$$

Here δ and μ, the so-called soliton parameters depend again on the choice of trial state and $\mathcal{N}$. More precisely, $\delta=\sqrt{2}$ for the above-postulated two-particle DA. For other choices, $\delta=1$.

We have calculated GSE employing each of the above-discussed trial states and our results are presented in Table I.

The choice of trial function (3) and $\mathcal{N}=1$ leads to the same value of GSE as the DA. Formally applying the procedure to all other cases, it is obvious that DA gives lower estimates of the exciton-phonon GSE in one- and two-particle cases. Thus the soliton solutions following on the basis of the original Davydov's proposal are comparably more stable than the ones that result from the unusual trial state proposed by Pang. Pang's belief that the so-proposed trial states yield lower values for GSE and, consequently, more stable soliton solutions is based upon the inconsistent calculations that arise, when it is overlooked that these new

states are not normalized. This oversight results in erroneous equations of motion for phonon variables that imply all subsequent results and, in the final instance, incorrect expressions for GSE are obtained.

The aim of this comment was to clarify the effect that is achieved by using improved Hamiltonian and so-called quasicoherent trial states proposed by Pang for the study of energy transfer in molecular chains. We have shown that the improper normalization leads to many inconsistencies and that even if one disregards the inherent controversies connected with the normalization of exciton amplitudes, Pang's theory—due to the fact that it predicts either equal or higher values of GSE—is still inferior with the respect to the DA. We have also indicated that there exist alternative approaches using complete coherent or multiquanta states proposed much earlier [9,10], which do not encounter such problems, but lead to the same results as the standard DA.

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