Two Reasons Why the Davydov Soliton May Be Thermally Stable After All

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Davydov has proposed a mechanism for energy transfer in proteins, according to which the energy liberated in an enzymatic reaction can be stored and transported in the form of a soliton. In recent years a debate has been going on concerning the thermal stability of the Davydov soliton. Here it is shown, first, that the two-quantum state is visibly more stable than the one-quantum state, and, second, that the usual Langevin dynamics, whereby the thermal lifetime of the Davydov soliton is estimated, must be viewed as underestimating, possibly very strongly, the soliton lifetime.

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The problem of the mechanism of energy transfer in proteins is a long-standing problem [1]. A very well defined model was first proposed by Davydov and Kislukha [2]. In Davydov's model the energy liberated in the hydrolysis of Adenosinetriphosphate (ATP) leads to the creation of amide I vibrations in the hydrogen-bonded spines of protein α helices. The interaction of the amide I vibration with the hydrogen bonds leads to a nonlinear interaction and soliton states. This is at least the picture at low temperatures, which even fully quantum mechanical simulations confirm [3,4]. The Hamiltonian $\hat{H}$ is

$$\hat{H} = \hat{H}_{\mathrm{qp}} + \hat{H}_{\mathrm{ph}} + \hat{H}_{\mathrm{int}}, \tag{1}$$

where $\hat{H}_{\mathrm{qp}}$ is the quasiparticle Hamiltonian, associated with the amide I vibration, $\hat{H}_{\mathrm{ph}}$ is the phonon Hamiltonian, and $\hat{H}_{\mathrm{int}}$ is the interaction Hamiltonian. The quasiparticle Hamiltonian $\hat{H}_{\mathrm{qp}}$ is

$$\hat{H}_{\mathrm{qp}} = \sum_{n=1,N} [\epsilon \hat{a}_n^\dagger \hat{a}_n - J(\hat{a}_n^\dagger \hat{a}_{n-1} + \hat{a}_n^\dagger \hat{a}_{n+1})], \tag{2}$$

where ϵ is the amide I energy, $-J$ is the dipole-dipole interaction energy between neighboring sites, and $\hat{a}_n^\dagger$ ($\hat{a}_n$) is the creation (annihilation) operator for an amide I excitation in site n. The phonon Hamiltonian $\hat{H}_{\mathrm{ph}}$ is

$$\hat{H}_{\mathrm{ph}} = \sum_{n=1,N} \left[\frac{\hat{P}_n^2}{2M} + \frac{1}{2} \kappa (\hat{u}_n - \hat{u}_{n-1})^2 \right], \tag{3}$$

where $\hat{u}_n$ is the displacement operator for site n, $\hat{P}_n$ is the momentum operator of site n, M is the mass of each site, and κ is the elasticity constant of the lattice. Finally, the interaction Hamiltonian $\hat{H}_{\mathrm{int}}$ is

$$\hat{H}_{\mathrm{int}} = \sum_{n=1,N} [\chi^+ (\hat{u}_{n+1} - \hat{u}_n) \hat{a}_n^\dagger \hat{a}_n + \chi^- (\hat{u}_n - \hat{u}_{n-1}) \hat{a}_n^\dagger \hat{a}_n], \tag{4}$$

where χ^+ (χ^-) is an anharmonic parameter related to the coupling between the amide I excitation.

At higher temperatures, such as occur *in vivo,* the stability and lifetime of the soliton states is still an open question. A full review of the area can be found in [5], but, in short, there are two main issues. First, the exact wave function of the fully quantum Davydov model is not known. Different wave functions have been used to describe the states of the fully quantum mechanical system [6]. Although some of these wave functions lead to exact quantum states and exact quantum dynamics in the limit $J = 0$, they also share a problem with the original Davydov wave function, namely, that the degree of approximation involved when $J \neq 0$ is not known. The second issue is the lifetime of the Davydov soliton at biological temperatures. The first Langevin simulations, which implicitly assume that the lattice part of the Hamiltonian is classical, suggested that the soliton lifetime is only a few picoseconds, too short to be biologically relevant [7]. A thorough study in terms of parameter values, different types of disorder, different thermalization schemes, different wave functions, and different associated dynamics leads to a very complex picture [8]. On the other hand, fully quantum mechanical calculations, using perturbation theory, lead to subpicosecond lifetimes for the original Davydov solution [9]. The Davydov solution, however, is not a true wave function of the system, and thus this does not eliminate the possibility of other, true wave functions having longer lifetimes.

While the study of the thermal behavior of the fully quantum Davydov system is an extremely difficult problem, the approach implicit in the Langevin simulations that the lattice is classical presents much fewer mathematical and computational difficulties. Here only the latter case, designated as the semiclassical Davydov system, shall be studied. This means that the displacements and momenta of the lattice cease to be operators and are instead real variables. In contrast with the fully quantum mechanical system, the exact wave function of the semiclassical system is known [10,11] and exact minimum one-quantum states have been calculated [11]. Since the hydrolysis of ATP liberates enough energy to create two quanta of amide I vibration, here exact two-quantum states will be determined and their energies and stability compared with that of the one-quantum states. Also, the approximations involved in Langevin dynamics of mixed quantum and classical systems will be illustrated. This complements previous work by other authors [12,13]. It will be shown that exact thermal averages lead to more stable soliton solutions. Together with the greater stability of two-quantum states, these constitute two reasons why the Davydov soliton may be stable at biological temperatures.

Exact two-quantum states of the semiclassical Davydov system are

$$|\psi(t)\rangle = \sum_{n,m=1,N} \varphi_{n,m}(\{u_l\},\{p_l\},t)\hat{a}_n^{\dagger}\hat{a}_m^{\dagger}|0\rangle, \qquad (5)$$

where $\varphi_{n,m}$ is the probability amplitude matrix for an amide I excitation in sites n,m. Other authors have also considered two-quantum states, also in the semiclassical case [14], but their wave function is not exact. Indeed, they considered the following form [15]:

$$|\psi(t)\rangle = \left[\sum_{n=1,N} \varphi_n(\{u_l\},\{p_l\},t)\hat{a}_n^{\dagger}\right]^2 |0\rangle \qquad (6)$$

which is only equivalent to (5) if $\varphi_{n,m} = \varphi_n\varphi_m$, which is generally not the case. The dynamics of wave packets as described by (5) is found by integrating a system of the order of N^2 coupled differential equations, while (6) leads to a system of order N. Exact multiquanta states at finite temperatures have also been considered for the full quantum mechanical model [4]. Bound polaron states are found at low temperatures, which dissociate at higher temperatures. However, these studies describe the behavior at thermal equilibrium and cannot be used to make inferences about thermal lifetimes.

As for one-quantum states [11], exact minimum two-quantum states can be found by averaging the Hamiltonian (1)–(4) over the state (5) and minimizing the resulting functional with respect to the displacements u_l, the momenta p_l, and the probability amplitudes $\varphi_{n,m}$. In Fig. 1 the thermal stability of the minimum two-quantum state is compared with that of the minimum one-quantum state, both obtained for the values of the parameters used in [7], i.e., $J = 1.549 \times 10^{-22}$ J, $\kappa = 13$ N/m, $M = 1.907 \times 10^{-25}$ kg, and $\chi^+ = \chi^- = 62 \times 10^{-12}$ N. Inserting each state in the corresponding Langevin equation, with a target temperature of $T = 310$ K, the average state over the first 50 ps is calculated. The average state is defined by the average probability distribution for the excitation and by the average displacement difference versus site n. These are calculated by summing over the states at each time step, after having located, for each state, the maximum of the probability distribution and translated this maximum to the middle of the chain and performing exactly the same rotation with the displacement differences. The figure shows that the two-quantum state is visibly more stable that the one-quantum state. Although the period considered, of 50 ps, is an order of magnitude greater than the few picoseconds estimated for the soliton lifetime, in the original Langevin simulations [7], the difference in stability between the two states, as seen in Fig. 1, is, *per se*, too small for a conclusion that the exact two-quantum states of Davydov system are stable at biological temperatures. However, the next results show that traditional Langevin simulations, as have been performed here and in [14], lead to an underestimation of the soliton lifetimes. Indeed, it has been shown that the Nosé thermalization scheme [16], when applied to mixed quantum and classical systems, leads to a classical treatment of the quantum part of the system, as well [13]. I.e., while the exact thermal average, for one-quantum states, of a quantum variable $\hat{A}(\{u_n\}, \{\hat{a}_n\})$ is given by

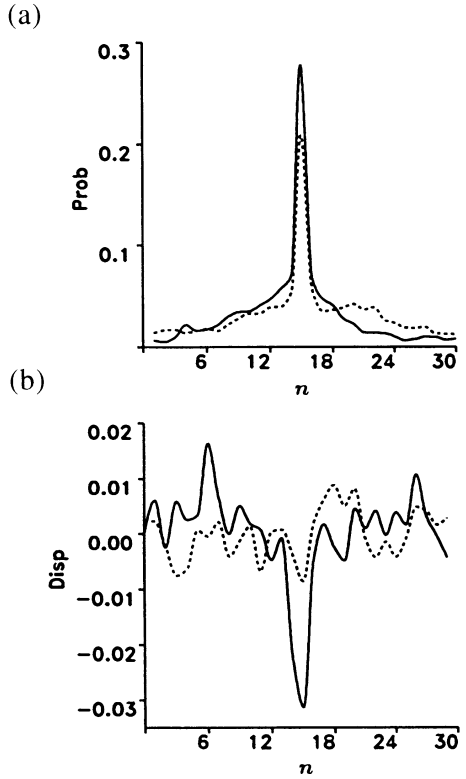

FIG. 1. Thermodynamic average state (see text) for the two-quantum state (solid line) and the one-quantum state (dashed line). (a) The average probability distribution of the excitation per site and (b) the average displacement difference per site $N = 30$.

$$\langle\langle\hat{A}\rangle\rangle = \frac{\int\{du_n\}\mathrm{Tr}[e^{-\beta\hat{H}}\hat{A}]}{\int\{du_n\}\mathrm{Tr}[e^{-\beta\hat{H}}]}, \qquad (7)$$

where $\langle\langle\cdots\rangle\rangle$ stands for thermal averaging, $\beta = 1/kT$, k being Boltzmann constant and T the absolute temperature; the Nosé thermalization scheme and Langevin simulations [12] lead to

$$\langle\langle\hat{A}\rangle\rangle = \frac{\int_{2N-\text{unit sphere}}\{d\varphi_n\}\int\{du_n\}e^{-\beta\langle\psi|\hat{H}|\psi\rangle}\langle\psi\,|A|\,\psi\rangle}{\int_{2N-\text{unit sphere}}\{d\varphi_n\}\int\{du_n\}e^{-\beta\langle\psi|\hat{H}|\psi\rangle}}. \qquad (8)$$

This has been shown numerically for Langevin simulations in [17] and misled the present author into the conclusion that Langevin simulations do reproduce the correct thermal behavior of the semiclassical Davydov system. On the contrary, comparison of the two types of averages shows the approximations involved in the traditional Langevin dynamics. Expressions (7) and (8) can be evaluated by Monte Carlo methods. However, calculating (7) means solving an eigenvalue problem in each successful Monte Carlo step which is extremely time consuming computationally, especially as the number of sites N is relatively large. Since the point is equally made for any number of sites, here the smallest number $N = 2$ is used. In this case (7) reduces to a one-dimensional integration which can easily be performed numerically [18].

As a measure of localization, the variable $\hat{p} = \hat{a}_1^\dagger \hat{a}_1 - \hat{a}_2^\dagger \hat{a}_2$ is chosen. This variable is 0 for delocalized states and 1 for completely localized states. The thermodynamic average is obtained by substituting $\hat{p}$ for $\hat{A}$ in expressions (7) and (8). As was shown previously, for a dimer, the thermal behavior of $\hat{p}$ is only dependent on the quantity $v = J\kappa/\chi^2$ and on β [18]. The exact thermodynamic average $\langle\langle p \rangle\rangle$ versus v and $\ln(\beta)$ is displayed in Fig. 2(a). As observed in [18], $\langle\langle p \rangle\rangle$ shows two possible effects of thermal agitation, for values of v, for which at low temperature the states tend to be delocalized. In this case, raising the temperature leads first to a strengthening of the localized states, which is eliminated by further increases in temperature. The overall result is a peak in the $\langle\langle p \rangle\rangle$ as the temperature increases. Figure 2(b) shows the corresponding thermodynamic average of $\hat{p}$ as obtained from expression (8) and, consequently, Langevin dynamics. At low temperatures, for which the minimum energy eigenstates are important, (8) is a relatively good approximation. On the other hand, as temperature increases, average (8) becomes increasingly incorrect. More specifically, the peak in localization versus temperature is very much attenuated and, moreover, the importance of localized states at finite temperatures is generally underestimated. For the values of the parameters J, χ, κ that have been used in previous Langevin simulations [7], $v \approx 0.52$ and $\ln\beta \approx -2.67$ and expression (8) gives $\langle\langle p \rangle\rangle \approx 0.06$, while the exact expression (7) leads to a value approximately 3 times larger.

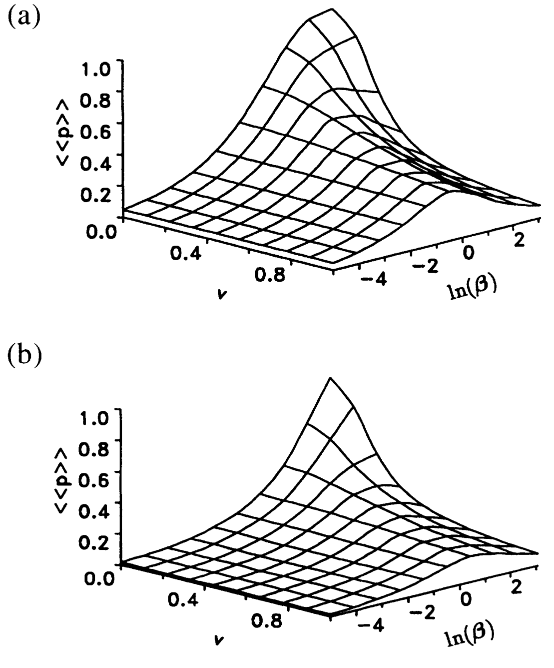

FIG. 2. Thermodynamic average localization $\langle\langle p \rangle\rangle$ (see text) versus v and $\ln(\beta)$ for (a) exact average and (b) Langevin average.

In Fig. 2 only an equilibrium measure of the localization is calculated and thus it cannot be used to estimate the lifetimes of the Davydov soliton. However, the results in this paper do call for a reinterpretation of the conclusions drawn, using the Langevin method. Indeed, Figs. 1 and 2 suggest Davydov solitons to be more stable than heretofore indicated by Langevin simulations of single amide I quanta. While precise estimates of the soliton lifetimes require the development of more correct ways of simulating thermal effects in a dynamical context in mixed quantum and classical systems [13], these results indicate that the Davydov soliton remains a possible candidate for a mechanism for energy transfer in biological systems. As stated above, the formalism used here assumes that the lattice is classical. Another important question to be addressed is the validity of this semiclassical approximation for the Davydov system, a subject that is currently under investigation.

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