Lifetime of the Davydov soliton

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Quantum and thermal effects on the lifetime of the Davydov soliton are studied. Results of a quantum-mechanical perturbation treatment of the lifetime are presented for a wide range of parameter values. We derive a simple condition on the parameter values that must be satisfied for the soliton to be a viable mechanism for localized energy transport in the Davydov model for the α-helix region of protein. Our conclusion is that the Davydov soliton as originally proposed is not a likely candidate for this mechanism, but that a single soliton with a very large excitation number could provide the mechanism.

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I. INTRODUCTION

There continues to be considerable interest and controversy in the literature [1] concerning the Davydov soliton mechanism for energy localization and transport in the α-helix region of protein [2]. This mechanism, first proposed by Davydov and Kislukha [3] in the early 1970s, involves the self-trapping of vibrational excitons into envelope solitons by their interaction with acoustic phonons. The central question of the controversy is whether this soliton, or localized quantum state, has a lifetime that is sufficiently long to play an important role in the energy transfer along the polypeptide chains of the protein structure.

Quantum and thermal effects are expected to cause this state to decay into delocalized states. In order to investigate these effects quantitatively, it is necessary to make assumptions for (i) the quantum-mechanical model Hamiltonian and the parameter values, (ii) the particular form of the Davydov soliton state, and (iii) the interaction with the heat bath at finite temperatures. Estimates of the average lifetime of the Davydov soliton will obviously depend on these assumptions. Nevertheless, some progress toward the resolution of the lifetime controversy should be possible if estimates are obtained from credible calculations, i.e., calculations that are fully consistent with quantum mechanics. The many numerical studies [4–7] that have been based on essentially classical equations of evolution are clearly subject to the criticism that they are likely to yield unreliable estimates for the stability of this localized quantum state since the dynamics is not being determined by the Schrödinger equation [8].

In previous publications [9,10] we have presented the details of a straight-forward quantum-mechanical perturbation calculation of the average lifetime for the Davydov soliton having the form of a simple product of an exciton state and a coherent phonon state. The calculation treated the continuum approximation to the standard one-dimensional model described by the Fröhlich Hamiltonian. An initial thermal equilibrium phonon distribution relative to the lattice distortion described by the coherent state was assumed. There was no explicit interaction with the thermal bath. For the parameter values considered, the lifetimes at physiological temperatures were found to be much too short for the soliton to be a possible mechanism for energy transfer. This result does not completely rule out the Davydov mechanism since it depends on the specific assumptions made for the form of the soliton state, the parameter values, and the initial phonon distribution. However, we believe that this calculation can make a major contribution toward resolving the lifetime controversy since, to our knowledge, it is the only direct calculation for this dynamical problem that is not based on some classical or semiclassical approximation.

The main purposes of this paper are as follows. (i) First, we present results based on our calculation for a large range of parameter values. Our previously published results were for the so-called "widely accepted" parameter values. It is now clear to us that there is considerable uncertainty in attempting to assign realistic values because the model is highly oversimplified, there is little experimental information, and different *ab initio* calculations have produced very different estimates for some of the parameters [1]. Thus it is important to investigate how the average lifetime of this particular Davydov soliton depends on the parameter values. (ii) Second, we critique some of the work by others where quantum concepts were either incompletely or incorrectly applied. (iii) Third, we present a speculative proposal for a possible generalization of the Davydov soliton that could work.

The plan of this paper is as follows. In Sec. II we review our previous analytical results for the decay rate of the Davydov soliton. We also introduce the dimensionless parameters that will be used in presenting the numerical results. The numerical results are given in Sec. III. These include (i) the soliton lifetime as a function of temperature for three sets of parameters that have been suggested as realistic, and (ii) the soliton lifetime for a very large range of parameter values. Also we present a simple inequality among the parameters that would have to be satisfied at physiological temperatures for this soliton to be able to play an important role in energy transport. Section IV is devoted to comparisons with other studies. In this section we also point out several errors that have contributed to the stability controversy. In Sec. V we propose a generalization of the Davydov soliton that is not ruled out by our results. Conclusions are presented in Sec. VI.

II. LIFETIME CALCULATION

The standard model that underlies the Davydov soliton mechanism is described by a Fröhlich-type Hamiltonian for a one-dimensional chain of molecular units on a finite lattice of N sites with periodic boundary conditions. Thus for our calculation of the lifetime we used the Hamiltonian

$$H = H_{\rm ex} + H_{\rm ph} + H_{\rm int} \ , \tag{1}$$

where

$$H_{\rm ex} = \sum_n [\varepsilon_0 B_n^\dagger B_n - J(B_n^\dagger B_{n+1} + B_{n+1}^\dagger B_n)] \ , \tag{2}$$

$$H_{\rm ph} = \frac{1}{2}\sum_n [p_n^2/m + w(u_{n+1}-u_n)^2] \ , \tag{3}$$

$$H_{\rm int} = \chi \sum_n (u_{n+1}-u_{n-1}) B_n^\dagger B_n \ . \tag{4}$$

Here $B_n^\dagger$ and B_n are boson creation and annihilation operators for the vibrational excitation at the nth site associated with the amide-I oscillator having $\varepsilon_0 \approx 0.205$ eV. The parameter J describes a nearest-neighbor hopping. Thus $H_{\rm ex}$ describes boson-type Frenkel excitons. $H_{\rm ph}$ describes a harmonic lattice in terms of the coordinates and momenta of the molecular units, and can be rewritten in terms of the acoustic phonons as

$$H_{\rm ph} = \sum_q \hbar\omega_q (a_q^\dagger a_q + \tfrac{1}{2}) \ , \tag{5}$$

with

$$\omega_q = 2(v_a/R)|\sin qR/2| \ , \tag{6}$$

where R is the lattice constant and the speed of sound $v_a = R\sqrt{w/m}$. The term $H_{\rm int}$ provides a linear coupling between the exciton and the lattice.

In the simplest Davydov theory one assumes that the state

$$|D(t)\rangle = \sum_n \alpha(n,t) B_n^\dagger |0\rangle_{\rm ex} |\beta(t)\rangle \tag{7}$$

with

$$|\beta(t)\rangle = \exp\left[\sum_q [\beta_q(t) a_q^\dagger - \beta_q^*(t) a_q]\right] |0\rangle_{\rm ph} \tag{8}$$

adequately approximates a solution of the time-dependent Schrödinger equation if the complex coefficients $\alpha(n,t)$ and $\beta_q(t)$ are solutions to the essentially classical equations

$$i\hbar\frac{\partial}{\partial t}\alpha(n,t) = \frac{\partial}{\partial \alpha^*(n,t)}\langle D(t)|H|D(t)\rangle \ , \tag{9}$$

$$i\hbar\frac{\partial}{\partial t}\beta_q(t) = \frac{\partial}{\partial \beta_q^*(t)}\langle D(t)|H|D(t)\rangle \ . \tag{10}$$

These equations can be reduced to a nonlinear Schrödinger equation for $\alpha(n,t)$ that, in the continuum limit, has the envelope soliton solution

$$\alpha(n,t) = \sqrt{\mu/2}\,\mathrm{sech}[\mu(n - vt/R)] \times \exp\left[\frac{i}{\hbar}\left[\frac{\hbar^2 vn}{2JR} - E_{\rm sol} t\right]\right] \ , \tag{11}$$

$$\beta_q(t) = \frac{i\pi\chi}{w\mu(1-v^2/v_a^2)}(m/2N\hbar\omega_q)^{1/2}(\omega_q + qv) \times \mathrm{csch}(\pi qR/2\mu) e^{iqvt} \ , \tag{12}$$

with

$$\mu = \frac{\chi^2}{Jw(1-v^2/v_a^2)}, \quad E_{\rm sol} = \varepsilon_0 - 2J + \frac{\hbar^2 v^2}{4JR^2} - J\mu^2/3 \ . \tag{13}$$

Thus this treatment yields a localized coherent structure with size of order R/μ that propagates with a velocity v and can transfer energy $E_{\rm sol} \approx \varepsilon_0$. However, since this essentially classical treatment of the dynamics does not give an exact solution of the Schrödinger equation, an initial soliton state of the form of Eq. (7) with $\alpha(n,0)$ and $\beta_q(0)$ corresponding to the soliton solution is expected to evolve into a less localized state. Furthermore, at finite temperatures where there are phonons present in addition to the coherent state, this decay should be enhanced. Our calculation gives a quantitative estimate of this decay rate.

Davydov has argued qualitatively that such a soliton state should be stable enough for it to propagate the length of a typical protein structure without significant distortion [11]. He observes the following. (i) Unlike bare excitons that are scattered by the interactions with the phonons, this soliton state describes a quasiparticle consisting of the exciton plus lattice deformation and hence it already includes interactions with the acoustic phonons. (ii) The soliton state will not spread like an ordinary wave packet. (iii) The energy of the soliton state is below the bottom of the bare exciton band, the energy difference being $J\mu^2/3$ for small velocity of propagation. Hence energy must be added to have a transition from the soliton state to a bare exciton state. (iv) Destruction of the soliton requires the removal of the lattice distortion. The transition probability to a lattice state with no distortion is proportional to a Frank-Condon factor that is negligibly small for a long chain. While these observations are certainly true, the full quantitative effect must be calculated to determine the stability of the Davydov soliton state. Our calculation addresses all these points rather explicitly.

Since we are interested in investigating the case where there is initially a soliton moving with a velocity v on the chain, we consider the Hamiltonian in the rest frame of the soliton, $H' = H - vP$, where P is the total momentum. First we rewrite this Hamiltonian using new basis states that were first introduced by Eremko, Gaididei, and Vakhnenko [12]. For the excitonic system, the basis states are the eigenstates determined by

$$\left[-JR^2\frac{\partial^2}{\partial x^2}+i\hbar v\frac{\partial}{\partial x}+\varepsilon_0-2J[1+\mu^2\mathrm{sech}^2(\mu x/R)]\right]\times\Phi_\alpha(x)=E_\alpha\Phi_\alpha(x) \ . \quad (14)$$

There is just one bound state,

$$\Phi_s(x)=\sqrt{\mu/2R}\ \mathrm{sech}(\mu x/R)\exp(i\hbar v x/2JR^2) \ , \quad (15)$$

with

$$E_s=\varepsilon_0-2J-\hbar^2v^2/4JR^2-J\mu^2 \ , \quad (16)$$

which is just the excitonic part of the Davydov soliton state, and continuum states

$$\Phi_k(x)=\frac{1}{\sqrt{L}}\frac{kR+i\mu\tanh(\mu x/R)}{[\mu^2+(kR)^2]^{1/2}}\times\exp(ikR+i\hbar v x/2JR^2) \quad (17)$$

with

$$E_k=\varepsilon_0-2J-\hbar^2v^2/4JR^2+J(kR)^2 \ . \quad (18)$$

For the phonon system, one introduces new phonon operators

$$b_q=a_q-f_q/\sqrt{N} \quad (19)$$

with

$$f_q=\frac{i\pi\chi}{w\mu(1-v^2/v_a^2)}\left[\frac{m}{2\hbar\omega_q}\right]^{1/2}(\omega_q+qv)\times\mathrm{csch}(\pi qR/2\mu) \ , \quad (20)$$

such that the coherent-state part of the Davydov soliton state is the vacuum state for the new phonon operators. In this representation

$$H'=H_0+V_1+V_2 \ , \quad (21)$$

where

$$H_0=W+E_sA_s^\dagger A_s+\sum_k E_kA_k^\dagger A_k+\sum_q\hbar(\omega_q-qv)b_q^\dagger b_q+\frac{1}{\sqrt{N}}\sum_q\hbar(\omega_q-qv)(f_qb_q^\dagger+f_q^*b_q)(1-A_s^\dagger A_s) \ , \quad (22)$$

$$V_1=\frac{1}{\sqrt{N}}\sum_{k,k',q}X_1(k,k',q)(b_{-q}^\dagger+b_q)A_{k'}^\dagger A_k \ , \quad (23)$$

$$V_2=\frac{1}{\sqrt{N}}\sum_{k,q}X_2(k,q)(b_{-q}^\dagger+b_q)(A_k^\dagger A_s-A_s^\dagger A_k) \quad (24)$$

with

$$X_1(k,k',q)=F(q)\int_{-L/2}^{L/2}dx\ e^{iqx}\Phi_{k'}^*(x)\Phi_k(x) \ , \quad (25)$$

$$X_2(k,q)=F(q)\int_{-L/2}^{L/2}dx\ e^{iqx}\Phi_k^*(x)\Phi_s(x) \ , \quad (26)$$

where

$$F(q)=i\chi\left[\frac{2\hbar}{m\omega_q}\right]^{1/2}\sin qR \ . \quad (27)$$

The operators $A_s^\dagger$ and $A_k^\dagger$ are the creation operators for the states $\Phi_s(x)$ and $\Phi_k(x)$, respectively. For the single-exciton subspace the eigenstates of H_0 are

$$|s,\{n_q\}\rangle=A_s^\dagger|0\rangle_{\mathrm{ex}}\prod_q\frac{(b_q^\dagger)^{n_q}}{\sqrt{n_q!}}|\tilde{0}\rangle_{\mathrm{ph}} \quad (28)$$

and

$$|k,\{n_q\}\rangle=A_k^\dagger|0\rangle_{\mathrm{ex}}\prod_q\frac{(a_q^\dagger)^{n_q}}{\sqrt{n_q!}}|0\rangle_{\mathrm{ph}} \ , \quad (29)$$

with corresponding energies

$$E_{s,\{n_q\}}=W+E_s+\sum_q\hbar(\omega_q-qv)n_q \quad (30)$$

and

$$E_{k,\{n_q\}}=E_k+\sum_q\hbar(\omega_q-qv)n_q \ . \quad (31)$$

Here

$$|\tilde{0}\rangle_{\mathrm{ph}}=\exp\left[\frac{1}{\sqrt{N}}\sum_q(f_qa_q^+-f_q^*a_q)\right]|0\rangle_{\mathrm{ph}} \quad (32)$$

is the coherent phonon state satisfying $b_q|\tilde{0}\rangle_{\mathrm{ph}}=0$. The quantity W is given by

$$W=\frac{1}{N}\sum_q\hbar(\omega_q-qv)|f_q|^2=\tfrac{2}{3}J\mu^2 \ . \quad (33)$$

Clearly in the subspace where $\sum_n B_n^\dagger B_n=A_s^\dagger A_s+\sum_k A_k^\dagger A_k=1$, H_0 describes the relevant quasiparticles of the Davydov theory: a Davydov soliton together with phonons relative to the distorted lattice and delocalized excitations belonging to an excitonlike band with phonons relative to a uniform lattice. The bottom of the band is at the energy $J\mu^2/3$ relative to the soliton, and the topological stability associated with removing the lattice distortion is included.

We use first-order perturbation theory in (V_1+V_2) to estimate the decay rate of the soliton. The transitions from the soliton to delocalized excitations are produced by the V_2 term, which can be satisfactorily treated by perturbation theory since the coefficient $X_2(k,q)$ as defined by Eq. (26) is proportional to an integral over the product of the localized state and a delocalized state, and therefore is of order $1/\sqrt{N}$. The V_1 term in the Hamiltonian is an interaction between the delocalized excitations and the phonons. As a result the delocalized excitations and phonons will have their energies shifted and will have finite lifetimes; however, these effects are ignored in our calculation since they are of second order in V_1. The estimate of the soliton lifetime would be improved by treating V_1 to all orders, but that would make the calculation intractable. In Sec. IV we give a qualitative discussion of how our results would be modified if the energy shifts and lifetime effects were included.

The average transition rate Γ from the soliton state in first-order perturbation theory is given by

$$\Gamma=\lim_{t\to\infty}\frac{1}{\hbar^2}\frac{d}{dt}\sum_i P_i\sum_k\sum_{\{n_q'\}}\left|\int_0^t dt'\langle k,\{n_q'\}|V_2(t')|s,\{n_q\}_i\rangle\right|^2 , \tag{34}$$

where

$$V_2(t)=e^{iH_0t/\hbar}V_2e^{-iH_0t/\hbar} . \tag{35}$$

The sum over i indicates a sum over initial sets of occupation numbers for phonons relative to the distorted lattice with probability distribution P_i, which is taken to be the thermal equilibrium distribution for temperature T. The evaluation of Γ is nontrivial but straightforward. The details have been previously presented [9,10]. For $\mu \ll \pi^2/2$, the result is

$$\Gamma=\frac{2\pi^2\chi^2}{\hbar m\mu}\sum_{k,q}\frac{\sin qR}{\omega_q}(qR)^2\operatorname{sech}^2[\pi(k-q)R/2\mu]\times\operatorname{Re}\int_0^\infty dt\left[\left[\frac{\exp[i(\omega_q-qv)t]}{\exp[\hbar(\omega_q-qv)/k_BT]-1}+\frac{\exp[-i(\omega_q-qv)t]}{1-\exp[-\hbar(\omega_q-qv)/k_BT]}\right]\times\exp\{-i[J(kR)^2+J\mu^2/3]t/\hbar+g(t)+b(t)\}\right] , \tag{36}$$

where

$$g(t)=-\frac{1}{N}\sum_q|f_q|^2\{1-\exp[-i(\omega_q-qv)t]\} , \tag{37}$$

$$b(t)=-\frac{4}{N}\sum_q\frac{|f_q|^2\sin^2[\frac{1}{2}(\omega_q-qv)t]}{\exp[\hbar(\omega_q-qv)/k_BT]-1} . \tag{38}$$

The average soliton lifetime τ is defined as $1/\Gamma$. The characteristic unit of time for the model is $\tau_0=R/v_a$, which is the time to move one lattice space when moving at the sound speed for the chain. A useful energy scale is the Debye energy $k_B\Theta=\hbar\pi v_a/R$. For $v=0$, τ/τ_0 is determined by the dimensionless parameters $\mu=\chi^2/Jw$, $J/k_B\Theta$, and T/Θ. Since one is interested in the case where $v \ll v_a$, the results presented in Sec. III are for $v=0$ and are in terms of these parameters.

III. NUMERICAL RESULTS

In previous publications [9,10] we concluded that the lifetime of the Davydov soliton at 300 K was at least two orders of magnitude too small for the soliton mechanism to work. Although we indicated that our estimate for the lifetime was not very sensitive to the parameter values used, the results presented were for parameter values near the so-called widely accepted values $J=1.55\times10^{-22}$ J, $w=13$ N/m, $\chi=62\times10^{-12}$ N, and $m=1.9\times10^{-25}$ kg. It has been argued that these are not the most realistic values to use for the evaluation of the lifetime expression [1]. One suggestion is that H_{int} of Eq. (4) should be replaced by the so-called asymmetrical form

$$H_{\text{int}}'=\chi\sum_n(u_{n+1}-u_n)B_n^\dagger B_n . \tag{39}$$

In the continuum approximation H_{int}' is identical to H_{int} with χ replaced by $\chi/2$. Hence μ is changed to $\mu/4$. Also, the real protein structure consists of three chains or "channels," which suggests that the w and m parameters in the simple single-chain model should be replaced by $3w$ and $3m$, respectively. This does not change Θ or τ_0, but further reduces μ by a factor of 3.

Figure 1 shows the lifetime as a function of temperature for the three sets of parameter values: the widely accepted values, the asymmetrical interaction correction, and the asymmetrical case with the three channel parameters. Since one assumes that $v \ll v_a$, the soliton will not travel the length of the chain unless τ/τ_0 is large com-

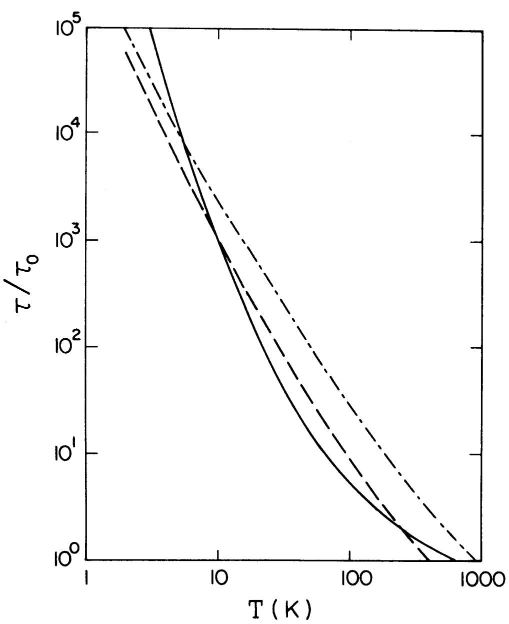

FIG. 1. Soliton lifetime τ relative to τ_0, time to travel one lattice space at the sound speed, as a function of the temperature T for the widely accepted parameter values with symmetrical (solid curve), asymmetrical (dashed curve), and asymmetrical interaction with correction for three channels (dot-dashed curve).

pared with L/R, where L is the typical length of the protein chain. Hence for $L/R \approx 100$, $\tau/\tau_0 > 500$ is a reasonable criterion for the soliton to be a possible mechanism for energy transfer in protein. The lifetimes in Fig. 1 at 300 K are two orders of magnitude too small and differences between the three parameter sets are insignificant on the scale of $\tau/\tau_0 \approx 500$. As the temperature decreases, the lifetimes increase rapidly, and at sufficiently low temperatures τ becomes large compared with $\hbar/k_B T$. This suggests soliton quasiparticles at low temperatures. Comparisons with the thermal equilibrium results of Monte Carlo calculations will be made in Sec. IV.

We have also evaluated Eq. (36) for a very wide range of parameter values. A summary of our results for the lifetime of the soliton state is given in Figs. 2 and 3 for $\mu=2$ and 0.2, respectively. Since the distance between points where $|\Phi(x)|^2$ is equal to half its maximum is approximately $1.8R/\mu$, the soliton size for $\mu=2$ is of the order of one lattice spacing and therefore represents about the limit for using the continuum approximation. The soliton size for $\mu=0.2$ is of the order of ten lattice spacings, which is approaching the opposite limit where the excitation is not well localized. Hence these values span the usual range of interest. The calculated values of τ/τ_0 are plotted as functions of $JT/k_B\Theta^2$ for several values of T/Θ. As a point of reference, note that these parameters have the values $T/\Theta=1.5$, $JT/k_B\Theta^2=8.4\times10^{-2}$ at 300 K, and $\mu=1.9$ or 0.16 depending on whether the widely accepted or the "asymmetrical three-channel" parameter values are assumed. Although there could be considerable uncertainty in assigning realistic values, it would seem to be safe to assume that $1<T/\Theta<5$ at 300 K and $J/k_B\Theta \ll 1$. Consequently it is clear from the results shown in Figs. 2 and 3 that the only possibility to satisfy the criterion $\tau/\tau_0>500$ at physiological temperatures is at small μ and small $JT/k_B\Theta^2$.

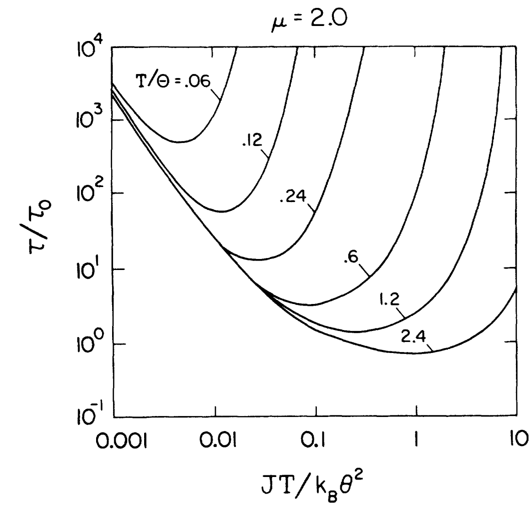

FIG. 2. Soliton lifetime τ relative to τ_0 as a function of $JT/k_B\Theta^2$ for several values of T/Θ for the case of $\mu=2$, where soliton size is of the order of a single lattice spacing.

In order to understand the general features of the curves in Figs. 2 and 3, it is useful to approximate the integral in Eq. (36). We show in Appendix A that

$$\frac{1}{\pi\hbar}\mathrm{Re}\int_0^\infty dt\,\exp\{-i[J(kR)^2+J\mu^2/3\mp\hbar\omega_q]t/\hbar+g(t)+b(t)\}\simeq(4\pi\Delta^2)^{-1/2}\exp\{-[J(kR)^2+J\mu^2\mp\hbar\omega_q]^2/4\Delta^2\}\ , \quad (40)$$

with

$$\Delta^2=2J\mu^2k_BT/3\ , \quad (41)$$

when $T/\Theta>1$ and $\pi^4JT/k_B\Theta^2\gg1$. This integral is the generalization of the usual δ function for energy conservation in zero-temperature perturbation theory. Although the limits $T/\Theta>1$ and $\pi^4JT/k_B\Theta^2\gg1$ are not well satisfied for the entire range of parameters in Figs. 2 and 3, this Gaussian expression yields results that are in good agreement with the plotted results, which were obtained from the direct numerical evaluation of Eq. (36). It is clear from this Gaussian expression that the lifetime will be large if $J/k_B\Theta$ is either so large or so small that the Gaussian is very small for k and q between $-\pi/R$ and $+\pi/R$, i.e., in the Brillouin zone. The temperature dependence of the lifetime of the soliton is mainly due to the temperature dependence of the width of the Gaussian, which decreases with decreasing temperature. Using the approximation of Eq. (40) with Eq. (36), it is straightforward to show that

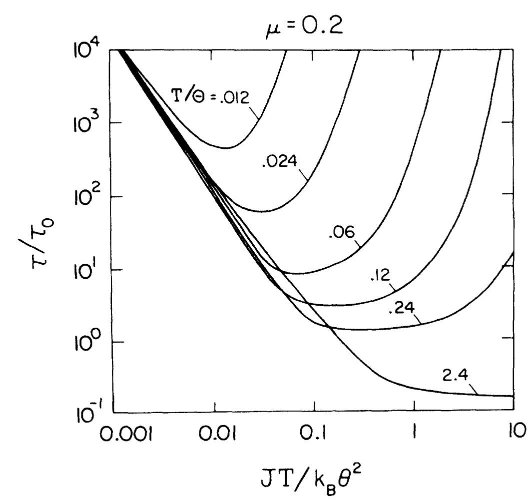

FIG. 3. Soliton lifetime τ relative to τ_0 as a function of $JT/k_B\Theta^2$ for several values of T/Θ for the case of $\mu=0.2$, where soliton size is of the order of ten lattice spacings.

$$\tau/\tau_0 \approx 9/[2\pi^6(JT/k_B\Theta^2)^2\mu]$$

in the limit of small $J/k_B\Theta$ and μ. This simple functional form is clearly seen in the numerical results presented. Hence our perturbation calculation yields the following simple condition on the parameters

$$(JT/k_B\Theta^2)^2\mu \le 9\times 10^{-3}/\pi^6 \approx 10^{-5} \quad (42)$$

that needs to be satisfied for this Davydov soliton to be a possible mechanism for energy transfer in protein, i.e., $\tau/\tau_0 \ge 500$. For the asymmetrical three channel values $(JT/k_B\Theta^2)^2\mu = 1.1\times 10^{-3}$. Although it seems unlikely that Eq. (42) can be satisfied since it would require parameter values that are very different from those previously assumed, there clearly needs to be more confidence in the values before a definite conclusion can be made concerning the Davydov mechanism with this form of the soliton.

IV. COMPARISONS

As noted in Sec. II, our calculation of the soliton lifetime does not include effects associated with the V_1 term of the Hamiltonian. While H_0 describes the relevant excitations of the Davydov treatment, the main effect of V_1 is to modify the spectrum of the delocalized excitations in the weak-coupling limit ($J\mu/k_B\Theta \ll 1$). The energies of these excitations will be shifted and also broadened to reflect a finite lifetime. For small μ one can show that in the subspace where $N_s = A_s^\dagger A_s = 0$ the operator $H_0 + V_1$ is essentially the Fröhlich Hamiltonian

$$(H_0+V_1)_{N_s=0} = \sum_k E_k A_k^\dagger A_k + \sum_q \hbar(\omega_q - qv)a_q^\dagger a_q \times \frac{1}{\sqrt{N}} \sum_{k,q} F(q)(a_q + a_{-q}^\dagger)A_{k+q}^\dagger A_k + O\left[\frac{1}{N}\right] . \quad (43)$$

Therefore, we can estimate the energy shift from weak-coupling polaron theory, which shows that the bottom of the excitation band is shifted downward by an amount of order $J\mu$. The calculation of Venzl and Fisher [13] found $3.541J\mu$ for this binding energy. Since the binding energy of the Davydov soliton is $J\mu^2/3$, there are delocalized states at energies below the soliton state energy for the values of μ that are of interest. This fact invalidates one of the qualitative arguments of Davydov for the soliton stability that we noted in Sec. II. In general, if H_0+V_1 were used instead of H_0 as the zero-order Hamiltonian in the perturbation calculation, one would expect shorter soliton lifetimes.

In order to make a crude estimate of the effect of including V_1, one can replace in our calculation of the soliton lifetime the energy E_k of the delocalized excitation by $E_k + \delta E - i\hbar\Gamma$, where $\delta E \approx -J\mu$ corrects for the energy shift and Γ describes the decay rate or damping of the excitation. For $T > \Theta \gg J/k_B$ one can estimate $\hbar\Gamma$ to be of order $J\mu T/\Theta$. At higher temperatures there will be very little effect on the calculated lifetimes provided $T > \Theta \gg J/k_B$. This can be seen in terms of the integral of Eq. (40), which describes the smeared energy conservation. Our criterion, Eq. (42), should remain valid at physiological temperatures, since it corresponds to the limit where the phonon energy dominates in Eq. (40). However, at low temperatures where energy conservation is more strictly obeyed, the existence of delocalized states below the soliton state will permit the soliton to decay by the process where there is spontaneous emission of a phonon. Hence our results in Sec. III clearly overestimate the soliton lifetime at very low temperatures.

Next we wish to consider our perturbation results in comparison with some claims that have been made in the literature. Bolterauer [14] has argued that the soliton lifetime at zero temperature can be calculated from the uncertainty of energy with the lifetime being given by $\hbar/\Delta E$, where

$$\Delta E^2 = \langle s|H^2|s\rangle - \langle s|H|s\rangle^2 , \quad (44)$$

with $|s\rangle$ denoting the Davydov soliton state. Using our representation, it is easy to show that

$$\Delta E^2 = \langle s|V_2^2|s\rangle = -\frac{1}{N}\sum_{k,q} X_2(k,q)X_2(-k,-q) , \quad (45)$$

where $X_2(k,q)$ is given by Eq. (26). The numerical evaluation of this expression with the widely accepted parameter values yields a value for ΔE of 2.6×10^{-22} J (Bolterauer reported 3.2×10^{-22} J). Thus based on $\hbar/\Delta E$, one obtains a lifetime at $T=0$ K of 4×10^{-13} sec, which is essentially the same as our perturbation result for $T=300$ K. Since the soliton lifetime increases rapidly with decreasing temperature in our perturbation treatment, the Bolterauer estimate is inconsistent with our results. However, this is not unexpected since the uncertainty in the energy as defined by Eq. (44) does not give a correct estimate for the lifetime of the soliton state. The relationship between lifetime and energy uncertainty as measured by the square root of the variance assumes a Gaussian or near-Gaussian distribution for the superposition of energy states in the quantum state. The soliton state is not an ordinary wave packet, since the phonons are described by a coherent state. We show by simple example in Appendix B that this definition of the uncertainty in energy yields an estimate for the lifetime that is qualitatively wrong for the Davydov soliton where the phonon part is a coherent state. Thus the very short "quantum lifetime" calculated by Bolterauer is essentially unrelated to the actual lifetime of the Davydov soliton.

At the opposite extreme is the claim by Scott [15] that there is a stabilizing quantum effect that will cause the soliton state to have an infinite lifetime in the limit of an infinite chain ($N\to\infty$). The essential idea, as noted in (iv) of the arguments of Davydov in Sec. II, is that the decay of the Davydov soliton requires the removal of the lattice distortion that is described by the coherent state $|\tilde{0}\rangle_{\rm ph}$, defined by Eq. (32). Scott argued that the transition probability to any undistorted state should be proportional to the Franck-Condon factor

$$|_{\rm ph}\langle 0|\tilde{0}\rangle_{\rm ph}|^2=\exp\left[-\frac{1}{N}\sum_q |f_q|^2\right], \quad (46)$$

where here as in all our phonon sums the $q=0$ term is excluded. Scott carefully evaluated this factor for a finite chain with free ends and found that it could be so small as to effectively forbid the decay of the soliton. For our calculation where periodic boundary conditions were used, it is sufficient to note that since $|f_q|^2$ diverges as q^{-1} as q goes to zero, the Franck-Condon factor vanishes for N infinite. The implication would seem to be that the decay rate for the Davydov soliton should be determined by this Franck-Condon factor and therefore would be zero in the limit of a long chain.

Our results obviously give a finite decay rate. It is also clear that our calculation takes into account the removal of the distortion in the lattice. As can be seen from Eq. (29), the delocalized states are in terms of the phonon vacuum $|0\rangle_{\rm ph}$, not the coherent state $|\tilde{0}\rangle_{\rm ph}$. Inspection of Eq. (36) shows that instead of the Franck-Condon factor there is a somewhat similar term, $\exp[g(t)]$ at $T=0$ or $\exp[g(t)+b(t)]$ at a finite temperature. From the definitions of $g(t)$ and $b(t)$ in Eqs. (37) and (38) it is clear that the large-N limit yields integrals where the functions integrated are regular at $q=0$.

The argument for the Franck-Condon factor made by Scott involves a hodgepodge of the Davydov classical dynamics and quantum dynamics. It has relevance as a criticism of the numerical treatments that use the dynamics described by the Davydov equations; however, since it completely ignores the transitions caused by the V_2 term in our notation, it has essentially no relevance to an actual quantum-mechanical calculation of the lifetime of the Davydov soliton.

There have been many numerical simulations [4–7] of the soliton dynamics based on the equations of motion derived by Davydov for the soliton state of the form used in our calculation, the so-called $|D_2\rangle$ state, as well as a more general soliton state $|D_1\rangle$, which is a linear combination of the products of an exciton state and a coherent phonon state. The simulations based on the $|D_2\rangle$ state generally agree that the stability of the soliton decreases with increasing temperature and that the soliton is not sufficiently stable at physiological temperatures if the widely accepted parameter values are used; although results are clearly sensitive to the initial and boundary conditions used and the method of generalizing to finite temperature. Under certain conditions on the parameter values, stable solitons are found at 300 K, but these results are not in agreement with our quantum-mechanical perturbation results. Since the dynamical equations used in the simulations are not equivalent to the Schrödinger equation and there seems to be no way to characterize the difference with the true dynamics, it is our view that these numerical simulations have only added confusion to the question of the stability of the Davydov soliton.

The simulations [7] based on the $|D_1\rangle$ state with the thermal treatment of Davydov [16], where the equations of motion are derived from a thermally averaged Hamiltonian, yield the surprising result that the stability of the soliton can be enhanced with increasing temperature. Thus these treatments predict stable-type $|D_1\rangle$ solitons at physiological temperatures. However, the Davydov procedure where one constructs an equation of motion for an average dynamical state from an average Hamiltonian, corresponding to the Hamiltonian averaged over a thermal distribution of phonons, is inconsistent with standard concepts of quantum-statistical mechanics where a density matrix must be used to describe the system. Consequently this treatment for the $|D_1\rangle$ state is subject to even more criticisms than the corresponding treatment for the $|D_2\rangle$ state. Unfortunately our quantum-mechanical calculation cannot be easily generalized to the linear combination of product states.

There exists no exact numerical treatment for the dynamics of the Davydov model with which to compare our perturbation treatment in a quantitative manner. However, for the thermal equilibrium properties there are quantum Monte Carlo simulations [17]. In these simulations correlations characteristic of solitonlike quasiparticles are only seen at low temperatures ($T \lesssim 10$ K) for the widely accepted parameter values. For the Davydov soliton to contribute to equilibrium correlations at temperature T, its lifetime should satisfy

$$h/\tau \ll \delta E_{\rm ex} \le k_B T , \quad (47)$$

where $\delta E_{\rm ex}=\langle D_2|H|D_2\rangle - E$ (ground state) is the excitation energy of the soliton, which is of order $J\mu$ as previously noted. If this is satisfied, the Davydov soliton is a well-defined quasiparticle that contributes to the thermal equilibrium properties. Our perturbation results for the lifetime show that this condition is not satisfied at higher temperatures, and therefore we are consistent at a qualitative level with the Monte Carlo results. Since the lifetime increases rapidly with decreasing temperature the condition could be satisfied at lower temperatures. However, since the Davydov soliton has a finite excitation energy $J\mu/k_B \approx 10$ K, its contribution would become negligible as the temperature goes to zero. In contrast, the Monte Carlo simulations show that the correlation of the excitation site with the lattice deformation, which is similar to the correlation in the Davydov soliton state, improves as the temperature goes to zero. As noted by the authors, this is consistent with the picture where the lowest states belong to a band corresponding to a superposition of soliton states satisfying Bloch's theorem. Consequently there is no real evidence for the existence of the Davydov soliton as a persistent localized entity in the thermal equilibrium results at low temperatures, although these results do not in any way contradict our result that the lifetime can be sufficiently long at low temperatures for the Davydov soliton to be a well-defined quasiparticle.

V. LARGE EXCITATION NUMBER

In a previous paper [10] we generalized our perturbation treatment to the case of a single soliton with an excitation number greater than 1, i.e., $\sum_j B_j^\dagger B_j = n$. To rewrite the Hamiltonian we used basis states corresponding to a generalization of Eqs. (14)–(18), where μ is replaced by $n\mu$. In the subspace of an excitation number equal to n, the eigenstates of the generalized H_0 have the simple form

$$|n-m;k_1\cdots k_m;\{n_q\}\rangle = \frac{1}{\sqrt{(n-m)!}}(A_s^\dagger)^{n-m}A_{k_1}^\dagger\cdots A_{k_m}^\dagger|0\rangle_{\text{ex}} \times\prod_q \frac{(c_q^\dagger)^{n_q}}{\sqrt{n_q!}}|\tilde{0}\rangle_{\text{ph}}^{(n-m)} , \quad (48)$$

where $b_q = c_q - (m/n\sqrt{N})f_q$ and $c_q|\tilde{0}\rangle_{\text{ph}}^{(n-m)}=0$. Here f_q is given by Eq. (20) with $\operatorname{csch}(\pi qR/2\mu)$ replaced by $\operatorname{csch}(\pi qR/2n\mu)$. The corresponding unperturbed energies are

$$E_{n-m;k_1\cdots k_m;\{n_1\}} = [1-(m/n)^2]W+(n-m)E_s + \sum_{i=1}^{m} E_{k_i} + \sum_q \hbar(\omega_q - qv)n_q , \quad (49)$$

with $W=2n^3J\mu^2/3$. In this formalism the Davydov soliton with excitation number n is the n-particle state

$$|n\rangle = \frac{1}{\sqrt{n!}}(A_s^\dagger)^n|0\rangle_{\text{ex}}|\tilde{0}\rangle_{\text{ph}}^{(n)} , \quad (50)$$

which is the ground state of H_0 with energy

$$E_n = W + nE_s = (\varepsilon_0 - 2J - \hbar^2 v^2/4JR^2)n - J\mu^2 n^3/3 , \quad (51)$$

as given by Eq. (49).

In first-order perturbation theory the term V_2 causes transitions that partially delocalize the state, i.e., transitions from n to $n-1$ for the occupation number of the localized state. From Eq. (49) the binding energy of the n state relative to the $n-1$ states is

$$E_{n-1,k} - E_n = (n^2 - 2n/3)J\mu^2 + J(kR)^2 . \quad (52)$$

The calculation of the soliton lifetime defined as the inverse of the transition rate from the soliton state to the $n-1$ states is a straightforward generalization of the $n=1$ case, provided $n\mu$ is not so large as to cause the continuum approximation to fail. The generalization of the condition given in Eq. (42) for a sufficiently stable soliton is

$$(JT/k_B\Theta^2)^2\mu/n \le 10^{-5} . \quad (53)$$

The $1/n$ factor makes this condition only slightly easier to satisfy. It is not applicable for large n. Apart from the continuum approximation, the analysis that yields this condition requires that the binding energy of Eq. (52) be small compared with the Debye energy, which sets the scale for the energy of the phonon absorbed or emitted in the transition. Consequently the Davydov soliton as originally proposed with $n=1$ or 2 is not a likely candidate for localized energy transport in protein.

The viewpoint that n should be a small number is based on the fact that ε_0, the quantum of the amide-I oscillator, is approximately one half the free energy released in the hydrolysis of adenosine triphosphate to adenosine diphosphate (ATP to ADP). Since $\varepsilon_0 \ll J$, this energy release would be about right to excite a single $n=2$ soliton. However, Eq. (51) allows for another possibility, namely a soliton with a very large excitation number $n \approx (3\varepsilon_0/J)^{1/2}/\mu$ such that the nonlinear term in the expression for the soliton energy approximately cancels the linear term. This possibility fully exploits the Bose character of the vibrational exciton and the nonlinearity resulting from the coupling with the lattice. Furthermore, it is clear that this large-n soliton would be stable at physiological temperatures since by Eq. (52) it would have a binding energy of order ε_0, which is large compared with the Debye energy and k_BT at 300 K. Thus even with the thermal smearing, transitions are suppressed by the large energy difference between initial and final states that cannot be compensated by the energy of the phonon absorbed. Instead of k_BT/J or T/Θ being the relevant parameter, k_BT/ε_0 determines the decay rate. Consequently it seems that this large-n soliton could provide a realistic mechanism for localized energy transport in protein. The resulting picture is very compelling for biological applications since the soliton is a quasiclassical entity for large-n values.

VI. DISCUSSION

Our calculations show quite clearly that the $|D_2\rangle$ Davydov soliton with $n=1$ or 2 is not a likely candidate for a mechanism for localized energy transport in protein. Parameter values would have to be vastly different from those previously assumed for the soliton to be sufficiently stable, i.e., satisfy Eq. (42) or its generalization, Eq. (53). Since our calculation is a straightforward application of quantum-mechanical perturbation theory, we have complete confidence in this conclusion. As argued in Sec. IV, the lifetime estimates should only be reduced by effects that are neglected in this lowest-order perturbation treatment. Also, we showed in Sec. IV that results in the literature that are inconsistent with our results are clearly unreliable for specific reasons.

Our proposal in Sec. V, that a single soliton with a very large excitation number could provide a mechanism for localized energy transport, is admittedly based on qualitative arguments. Clearly the continuum approximation should not be used since $\mu n \approx (3\varepsilon_0/J)^{1/2} \approx 25$, therefore the term "soliton" may not be appropriate for this entity. However, the Bose character of the exciton plus the coupling with the lattice will allow a stable large-n entity with an energy of the order of the relevant biological energy. A quantitative study of this entity will require going beyond the continuum approximation. Also, it is very probable that anharmonic terms that are neglected in the simple Davydov model must be taken into account to obtain a reasonable description of the physics of a molecular chain with a localized large-n excitation. These generalizations are currently under investigation.

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APPENDIX A

The approximation Eq. (40) for the time integral in Eq. (36) follows from an analysis of the functions $g(t)$ and $b(t)$. For the soliton velocity set equal to zero and the phonon frequency ω_q approximated by $\sqrt{w/m}\,|q|R$, $g(t)$ can be exactly evaluated in terms of the digamma function and its derivative.

$$g(t)=-(2J\mu/k_B\Theta)[ix\psi'(1+ix)+\psi(1+ix)-\psi(1)] , \tag{A1}$$

where $x=\mu k_B\Theta t/\pi^2 h$. Also, $b(t)$ can be approximated for $T/\Theta>1$ as follows:

$$b(t)\simeq-(\pi^2 JT/k_B\Theta^2)(\pi x\coth\pi x-1) . \tag{A2}$$

For $x<1$, both g and b have power-series expansions. To lowest order as $x\to 0$,

$$g(t)\simeq-(2J\mu/k_B\Theta)[i\pi^2 x/6+3\zeta(3)x^2] , \tag{A3}$$

$$b(t)\simeq-(\pi^2 JT/3k_B\Theta^2)x^2 . \tag{A4}$$

As $x\to\infty$, the leading terms in the asymptotic formulas are

$$g(t)\simeq-(2J\mu/k_B\Theta)(i\pi/2+\ln x+1+\gamma) , \tag{A5}$$

$$b(t)\simeq-(\pi^3 JT/k_B\Theta^2)x . \tag{A6}$$

Except at low temperatures, the x-dependent term in the real part of $g(t)$ is small compared with $b(t)$ for parameter values of interest and can be neglected. Approximating $g(t)$ and $b(t)$ by Eqs. (A3) and (A4), one obtains the Gaussian expression of Eq. (40) for the integral. The Eqs. (A5) and (A6) would instead yield a Lorentzian expression. If $\pi^4 JT/k_B\Theta^2\gg 1$, the integral is determined by the small x dependence and therefore the Gaussian expression is a good approximation in that limit.

APPENDIX B

In order to demonstrate that the uncertainty in energy as defined by Bolterauer does not give a correct estimate for the lifetime of the Davydov soliton, we consider the very simple dynamics associated with the free phonon Hamiltonian $H_{\rm ph}$ given in Eq. (5). Let the phonon system be initially in the coherent state given by Eq. (32), which is the phonon part of the Davydov soliton state. The probability $P(t)$ that the phonon system is in the same state at time t is given by

$$P(t)=|{}_{\rm ph}\langle\tilde{0}|e^{-iH_{\rm ph}t/\hbar}|\tilde{0}\rangle_{\rm ph}|^2 . \tag{B1}$$

$P(t)$ provides the quantitative measure of the decay of this coherent state. For this simple Hamiltonian the exact evaluation of this expression is trivial. The result is

$$P(t)=\left|\exp\left[-\frac{1}{N}\sum_q|f_q|^2(1-e^{-i\omega_q t})\right]\right|^2 =e^{g(t)+g^*(t)} , \tag{B2}$$

where this is the same $g(t)$ that was previously defined in Eq. (37). Using the asymptotic formula of Eq. (A5), one sees that

$$P(t)\underset{t\to\infty}{\sim}(e^{1+\gamma}\mu k_B\Theta t/\pi^2\hbar)^{-4J\mu/k_B\Theta} . \tag{B3}$$

Hence the coherent state decays only as a power of t. For small $J\mu/k_B\Theta$ this gives essentially an infinite lifetime.

One can easily calculate ΔE defined by

$$\Delta E^2={}_{\rm ph}\langle\tilde{0}|H_{\rm ph}^2|\tilde{0}\rangle_{\rm ph}-{}_{\rm ph}\langle\tilde{0}|H_{\rm ph}|\tilde{0}\rangle_{\rm ph}^2 . \tag{B4}$$

The result is

$$\Delta E^2=\frac{1}{N}\sum_q(\hbar\omega_q)^2|f_q|^2 , \tag{B5}$$

which for small μ is approximately $0.15k_B\Theta J\mu^3$. If the energy-time uncertainty relation were applicable, this would yield a lifetime that is orders of magnitude shorter than that implied by Eq. (B3). This procedure is only valid when the quantum state consists of a superposition of energy eigenstates where the probability distribution is Gaussian or near Gaussian. This is not the case with our coherent phonon state, where higher-order cumulants are of the same order as the variance that is used for the ΔE^2 calculation.

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