Temperature effects on the Davydov soliton

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As a possible mechanism for energy storage and transport in proteins, Davydov has proposed soliton formation and propagation. In this paper we investigate the stability of Davydov solitons at biological temperatures. From Davydov's original theory evolution equations are derived quantum mechanically without approximations, and their numerical solutions at different temperatures are presented. Our conclusion is that the Davydov soliton is stable at 310 K.

I. INTRODUCTION

Although in the science of bioenergetics considerable progress has been made in the past 20 years, the storage and transport of biological energy in protein structures is not yet well understood. An answer to this problem was suggested in 1973 by Davydov, who proposed that quantum units of peptide vibrational energy (in particular the amide-I or CO stretching vibration) might become "self-localized" through interactions with lattice phonons.[1,2] Following his original suggestion, many related studies have been published by Davydov and his colleagues[3] and by others[4] on this "Davydov soliton." Davydov's proposal should be considered in the context of two more general suggestions as to how to store and transport energy, which appeared at about the same time. The first of these was the "conformon" proposed by Green and Ji, on the basis of biochemical data, to explain energy transformation in the absence of a membrane.[5] The second was the "excimer" proposed by McClare on the basis of thermodynamic considerations.[6] The Davydov soliton is a specific biophysical mechanism that embodies essential features of both the conformon of Green and Ji[7] and the excimer of McClare.

Thermal stability of a Davydov soliton is an important consideration in deciding whether it could play a functional role in a living organism. Davydov has investigated the effect of temperature on soliton properties from a theoretical perspective.[8] His analytical results led him to conclude that the soliton size increases with increasing temperature, and its properties come even closer to those of a nonlocalized ("exciton") state. A similar conclusion emerges from the theoretical analysis of Alexander and Krumhansl.[9,10] Putting numbers into the formulas derived by Davydov,[8] one finds that his soliton should continue to function at physiological temperatures. Recent numerical studies, on the other hand, claim that the soliton would be completely destroyed by thermal effects far below 310 K.[11,12]

We see two possible explanations for the disagreement between Davydov and his critics: (i) The numerical studies[11,12] are essentially classical in the treatment of the coupling between the quantum system and the thermal bath and therefore neglect certain stabilizing quantum effects, and (ii) Davydov's theoretical analysis involves simplifying approximations which may lead to an erroneous conclusion. The first of these possibilities has been discussed in Refs. 13 and 14. Our aim in this paper is to consider the second possibility.

Our theoretical analysis follows closely that of Davydov.[8] Thus we start with his ansatz for the wave function, which allows for thermal occupation of the phonon states. With respect to this wave function the thermal average of the Hamiltonian operator is then calculated. Finally, the time evolution of parameters in the ansatz is determined from the thermally averaged Hamiltonian. The only difference between our development and that of Davydov is that we make no approximations (beyond that introduced by the original ansatz for the wave function), since we present our results in numerical rather than analytical form.

By its very nature Davydov's ansatz is an approximate wave function. This point has been discussed in considerable detail recently by Brown, Lindenberg, and West.[15–17] It is shown in Refs. 18 and 19, however, that Davydov's ansatz for the wave function at $T=0$ K, $|\psi\rangle$, is correct up to a time-dependent phase factor which would not be seen in the numerical plots of the probability of excitation ($|\psi|^2$) that are presented here. It is difficult to determine from Brown *et al.* the quantitative disagreement between Davydov's ansatz and the true wave function when $T\neq 0$ K. In any case, the point of this paper is to calculate the dynamical behavior of Davydov's ansatz without making any further approximations.

The paper is organized in the following manner. The theoretical analysis, described in Sec. II, leads to dynamical equations for the ansatz parameters which are appropriate for numerical study. In Sec. III we present numerical results from the study of the these equations. These results are discussed in Sec. IV. Some details of the numerical code are included in an appendix.

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II. THEORETICAL ANALYSIS

Following Davydov[2,3,8] we consider a one-dimensional molecular lattice with N sites. The Hamiltonian of that system will be

$$\hat{H}=\hat{H}_{\rm ex}+\hat{H}_{\rm ph}+\hat{H}_{\rm int} , \tag{2.1}$$

where $\hat{H}_{\rm ex}$ is the unperturbed exciton operator, $\hat{H}_{\rm ph}$ is the unperturbed phonon operator, and $\hat{H}_{\rm int}$ is an operator describing the interaction between the intramolecular excitations and the phonons. Thus,

$$\hat{H}_{\rm ex}=\sum_{n=1}^{N}[\varepsilon\hat{A}_n^{\dagger}\hat{A}_n-J(\hat{A}_n^{\dagger}\hat{A}_{n-1}+\hat{A}_n^{\dagger}\hat{A}_{n+1})] , \tag{2.2}$$

where ε is the intramolecular excitation energy (only one excited state is considered), $-J$ is the dipole-dipole interaction energy, and $\hat{A}_n^{\dagger}$ ($\hat{A}_n$) is the creation (annihilation) operator for the intramolecular excitations. Furthermore,

$$\hat{H}_{\rm ph}=\tfrac{1}{2}\kappa\sum_{n=1}^{N}(\hat{u}_n-\hat{u}_{n-1})^2+\frac{1}{2M}\sum_{n=1}^{N}\hat{P}_n^2 , \tag{2.3}$$

where κ is elasticity constant of the lattice, M is the mass of the molecules, and $\hat{u}_n$ is the displacement operator of site n from its equilibrium position. Finally, we consider a slightly more general expression for $\hat{H}_{\rm int}$ than that used by Davydov,[2,3,8] i.e.,

$$\hat{H}_{\rm int}=\chi^{+}\sum_{n=1}^{N}\hat{A}_n^{\dagger}\hat{A}_n(\hat{u}_{n+1}-\hat{u}_n)+\chi^{-}\sum_{n=1}^{N}\hat{A}_n^{\dagger}\hat{A}_n(\hat{u}_n-\hat{u}_{n-1}) , \tag{2.4}$$

where χ^{+} (χ^{-}) is an anharmonic parameter related to the coupling between the intramolecular excitation and the displacement of the following (previous) hydrogen bond in the chain. Substituting the expression of the displacement operator in terms of the phonon creation (annihilation) operators $\hat{b}_q^{\dagger}(\hat{b}_q)$ (Ref. 8) into Eqs. (2.3) and (2.4) we get

$$\hat{H}_{\rm ph}=\sum_q\hbar\Omega_q(\hat{b}_q^{\dagger}\hat{b}_q+\tfrac{1}{2}) , \tag{2.3'}$$

where $\hbar\Omega_q$ is the energy of a phonon with wave number q, $\Omega_q=2(\kappa/M)^{1/2}\,|\sin(qa/2)|$, a being the distance between the sites, and

$$\hat{H}_{\rm int}=\left[\frac{1}{N}\right]^{1/2}\sum_{n,q}F(q)\hat{A}_n^{\dagger}\hat{A}_n(\hat{b}_q+\hat{b}_{-q}^{\dagger})e^{iqna} , \tag{2.4'}$$

with

$$F(q)=\left[\frac{\hbar}{2M\Omega_q}\right]^{1/2}[(\chi^{+}-\chi^{-})(\cos qa-1)+i(\chi^{+}+\chi^{-})\sin qa] . \tag{2.5}$$

Davydov has suggested that the corresponding collective states of the lattice can be described by the ansatz wave function[8]

$$|\psi_\nu(t)\rangle=\sum_n\phi_n\hat{A}_n^{\dagger}|0\rangle\hat{U}_n|\nu\rangle , \tag{2.6}$$

where ϕ_n is the probability amplitude for an excitation in site n, $|\nu\rangle$ is the phonon wave function,

$$|\nu\rangle=\prod_q(\nu_q!)^{-1/2}(\hat{b}_q^{\dagger})^{\nu_q}|0\rangle , \tag{2.7}$$

and $\hat{U}_n(t)$ is a unitary operator of the displacements

$$\hat{U}_n(t)=\exp\left[\sum_q[\beta_{qn}^{*}(t)\hat{b}_q-\beta_{qn}(t)\hat{b}_q^{\dagger}]\right] . \tag{2.8}$$

The evolutions of $\phi_n(t)$ and $\beta_{qn}(t)$ are determined from dynamical equations derived from the thermally averaged Hamiltonian, H_T:[8]

$$H_T=\sum_\nu\rho_\nu H_{\nu\nu} , \tag{2.9}$$

where

$$H_{\nu\nu}=\langle\psi_\nu(t)|\hat{H}|\psi_\nu(t)\rangle \tag{2.10}$$

and

$$\rho_\nu=\frac{\langle\nu|\exp(-\hat{H}_{\rm ph}/kT)|\nu\rangle}{\sum_\nu\langle\nu|\exp(-H_{\rm ph}/kT)|\nu\rangle} , \tag{2.11}$$

k being Boltzmann's constant and T the absolute temperature. Inserting (2.6) and (2.11) into (2.9) and making use of the equalities,

$$\sum_{\nu_q}\exp(-\hbar\Omega_q\nu_q/kT)\langle\nu_q|\exp(\alpha^{*}\hat{b}_q)\exp(-\alpha\hat{b}_q^{\dagger})|\nu_q\rangle=(\bar{\nu}_q+1)\exp[-|\alpha|^2(\bar{\nu}_q+1)] , \tag{2.12a}$$

$$\bar{\nu}_q=[\exp(\hbar\Omega_q/kT)-1]^{-1} , \tag{2.12b}$$

$$\langle\nu|\hat{U}_n^{\dagger}(\hat{b}_q+\hat{b}_{-q})\hat{U}_n|\nu\rangle=-(\beta_{qn}+\beta_{-qn}^{*}) , \tag{2.12c}$$

$$\langle\nu|\hat{U}_n^{\dagger}\hat{b}_q^{\dagger}\hat{b}_q\hat{U}_n|\nu\rangle=(\nu_q+|\beta_{qn}|^2) , \tag{2.12d}$$

we get, after some tedious calculations, the following expression for H_T:

$$H_T=\sum_n\left[\varepsilon|\phi_n|^2-J(\phi_n^{*}\phi_{n-1}e^{W_{nn-1}}+\phi_n^{*}\phi_{n+1}e^{W_{nn+1}})-|\phi_n|^2\left[\frac{1}{N}\right]^{1/2}\sum_q F(q)e^{iqna}(\beta_{qn}+\beta_{-qn}^{*})+|\phi_n|^2\sum_q\hbar\Omega_q(\bar{\nu}_q+|\beta_{qn}|^2)\right]+\tfrac{1}{2}\sum_q\hbar\Omega_q . \tag{2.13}$$

In (2.13),

$$W_{nn\pm1}\equiv\sum_q[(\bar{\nu}_q+1)\beta_{qn}^{*}\beta_{qn\pm1}+\bar{\nu}_q\beta_{qn}\beta_{qn\pm1}^{*}-(\bar{\nu}_q+\tfrac{1}{2})(|\beta_{qn}|^2+|\beta_{qn\pm1}|^2)] . \tag{2.14}$$

This expression (2.13) for the thermally averaged Hamiltonian does not include any approximations. From it we derive dynamical equations for the parameters in the ansatz wave function (2.6):

$$i\hbar\frac{d\phi_n}{dt}=\frac{\partial H_T}{\partial\phi_n^*}=\varepsilon\phi_n-J(\phi_{n-1}e^{W_{nn-1}}+\phi_{n+1}e^{W_{nn+1}})-\phi_n\left[\frac{1}{N}\right]^{1/2}\sum_q[F(q)e^{iqna}(\beta_{qn}+\beta_{-qn}^*)]$$

$$+\phi_n\sum_q[\hbar\Omega_q(\bar{v}_q+|\beta_{qn}|^2)]\ , \tag{2.15a}$$

$$i\hbar\frac{d\beta_{qn}}{dt}=\frac{\partial H_T}{\partial\beta_{qn}^*}=-J\{\phi_n^*\phi_{n-1}e^{W_{nn-1}}[(\bar{v}_q+1)\beta_{qn-1}-(\bar{v}_q+cf12)\beta_{qn}]+\phi_{n+1}^*\phi_n e^{W_{n+1n}}[\bar{v}_q\beta_{qn+1}-(\bar{v}_q+\tfrac{1}{2})\beta_{qn}]$$

$$+\phi_n^*\phi_{n+1}e^{W_{nn+1}}[(\bar{v}_q+1)\beta_{qn+1}-(\bar{v}_q+\tfrac{1}{2})\beta_{qn}]+\phi_{n-1}^*\phi_n e^{W_{n-1n}}[\bar{v}_q\beta_{qn-1}-(\bar{v}_q+\tfrac{1}{2})\beta_{qn}]\}$$

$$-|\phi_n|^2\left[\frac{1}{N}\right]^{1/2}F^*(q)e^{-iqna}+|\phi_n|^2\hbar\Omega_q\beta_{qn}\ . \tag{2.15b}$$

It can easily be shown that Eq. (2.15a) conserves the norm, i.e.,

$$\frac{d}{dt}\left[\sum_{n=1}^{N}|\phi_n|^2\right]=0\ . \tag{2.16}$$

This property has been used as a test of the numerical results, which will be presented in Sec. III. The average displacement of the lattice at site n is calculated as

$$u_n(t)\equiv\langle\psi_v(t)|\hat{u}_n|\psi_v(t)\rangle^*$$

$$=-\sum_q\sum_m\left[\frac{\hbar}{2MN\Omega_q}\right]^{1/2}|\phi_m|^2e^{iqna}(\beta_{qm}+\beta_{-qm}^*)\ . \tag{2.17}$$

III. NUMERICAL RESULTS

In order to carry out a numerical integration of (2.15), it is necessary to select the parameters appearing in the original Hamiltonian operator (2.1). Since we are looking for the effects of raising the temperature from 0 to 310 K, the precise values of these parameters are not too important, but it is appropriate to use the same values as in previous numerical studies. They are listed in Table I. These values are close to those used in the numerical studies of Refs. 11 and 12. We do not list the intramolecular excitation energy ($\varepsilon\sim1660\ \text{cm}^{-1}$) because it is removed from the numerical calculations through a gauge transformation (see Appendix). The values of the anharmonic parameters χ^+ and χ^- and of the temperature T are indicated for specific numerical computations.

Davydov has considered $\chi^+=\chi^-$,[2,3,8] the case we shall present first (Sec. III A). However, as has already been discussed,[20] quantum-mechanical calculations show that χ^- is negligible when compared with χ^+. Thus, we shall also present results obtained when setting $\chi^-=0$ (asymmetric interaction Hamiltonian) (Sec. III B).

Two types of initial conditions are used,

$$\text{two sites}\begin{cases}|\phi_{24}(0)|^2=|\phi_{25}(0)|^2=0.5\ , & (3.1a)\\ |\beta_{qn}(0)|^2=0\ , & (3.1b)\end{cases}$$

$$\text{sech pulse}\begin{cases}|\phi_n(0)|^2=0.56\,\text{sech}^2[0.64(n-38)]\ , & (3.2a)\\ |\beta_{qn}(0)|^2=0\ . & (3.2b)\end{cases}$$

A. Davydov's interaction Hamiltonian ($\chi^+=\chi^-=\chi$)

Figure 1 shows the typical dynamical behavior in the molecular excitation observed in this case. Figure 1(a), where $\chi=0.17\times10^{-10}$ N, shows a case in which the initial excitation is completely *dispersed* after 10 psec; indeed, only dispersive waves form, which travel at about $\frac{1}{3}$ the maximum speed of sound in the chain $[(\kappa/M)^{1/2}a\sim3.7\times10^3\ \text{m/sec}]$ and are not accompanied by any molecular displacement. They are therefore excitons. Excitons are generated which travel in opposite directions in the chain and interfere with each other 10 psec afterwards. This interference is an artificial phenomenon due to the periodic boundary conditions (see Appendix). Figure 1(b), where $\chi=0.21\times10^{-10}$ N, shows another situation in which part of the initial excitation is *not* dispersed and remains pinned in the same bonds where it was initially located. Finally, in Fig. 1(c), where $\chi=0.23\times10^{-10}$ N, most of the initial excitation is not dispersed but remains localized where it was put

TABLE I. Physical parameters.

Name	Symbol	Value
Dipole interaction energy	J	7.8 cm^{-1}
Molecular mass	M	$114m_p$
Elasticity constant	κ	13 N/m

initially. We emphasize that whenever the term soliton has been used in the preceding and following discussions, we have checked that the pulse of molecular excitation is accompanied by corresponding distortion in the sound system. Explicit examples are shown below in Figs. 4 and 6. The continuous transition from *dispersion* [Fig. 1(a)] to a localized state [Fig. 1(c)] of the initial excitation is observed not only at biological temperatures, but also at lower temperatures, as summarized in Fig. 2. In this case, the consequence of increasing temperature is similar to that of increasing the nonlinearity. We see that as *temperature increases, the threshold for localization* of the initial excitation *decreases.* This is because the exponents $W_{nn\pm1}$ [Eq. (2.14)] are negative and increase in absolute value as temperature increases. Increasing the temperature thus produces a decrease in the effective dispersion, as was pointed out by Davydov.[8]

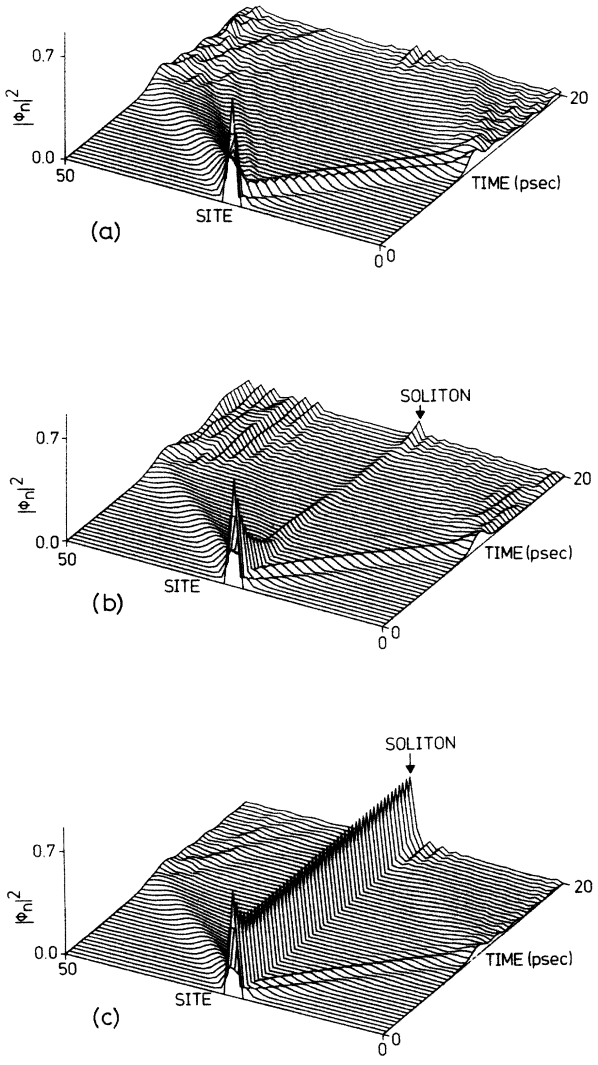

FIG. 1. Evolution of the probability of an excitation, $|\phi_n|^2$ in site n ($n=0,\ldots,50$). Temperature $T=310$ K. Initial condition: two sites [Eq. (3.1)]. (a) $\chi=0.17\times10^{-10}$ N, (b) $\chi=0.21\times10^{-10}$ N, and (c) $\chi=0.23\times10^{-10}$ N.

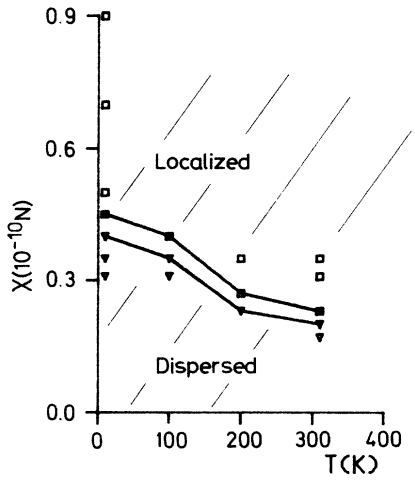

FIG. 2. Survey of the dynamics for the Davydov interaction Hamiltonian in the case of two initially excited sites. □, localized behavior; ∇, dispersed behavior.

B. Asymmetrical interaction Hamiltonian ($\chi^-=0$)

The dependence of the dynamical behavior on the remaining nonlinearity parameter χ^+ and temperature is given in Fig. 3. One distinction between the latter results and those shown in Fig. 2 is that the threshold of χ^+, below which there is dispersion, is not strongly dependent on the temperature. On the other hand, and as in Fig. 2, *the threshold of χ^+ for localization decreases* as temperature increases. The latter effect is explained by the decrease in effective dispersion, as was discussed above. However, the effective dispersion in Fig. 3 is now somewhat less dependent on the temperature than that of Fig. 2. Furthermore, the effective dispersion becomes less dependent on temperature as χ^+ decreases. A second, very important feature in Fig. 3 is that the tran-

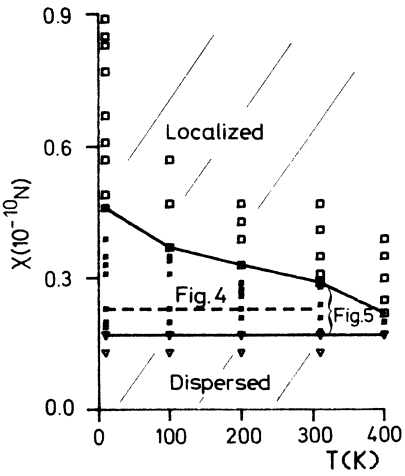

FIG. 3. Survey of the dynamics for the asymmetrical interaction Hamiltonian in the case of two initially excited sites. □, localized behavior; ■, propagating soliton; ∇, dispersed behavior. The dashed lines locate parameter values for Fig. 4. Parameter values for Fig. 5 are also indicated.

sition from dispersion to a localized state is not immediate; instead, there exists a window of χ^+ within which there is soliton propagation. The window decreases as the temperature increases and, at very high temperatures, the results correspond to those obtained for the Davydov interaction Hamiltonian. Figure 4 shows typical dynamical behaviors for a value of χ^+ fixed in the soliton propagation region, as temperature increases. It shows that, although part of the initial excitation is dispersed, the remaining part is built into a traveling soliton. As temperature increases, two main effects arise: (1) The amount of the initial excitation which is dispersed increases, and therefore the effective energy transported by the soliton decreases, and (2) the velocity of the soliton decreases. The molecular displacement accompanying the soliton at biological temperature, $T=310$ K, is shown in Fig. 4(e). Figure 5, on the other hand, shows typical dynamical behaviors, in the propagation region, for biological temperatures. Solitons form above $\chi^+ \sim 0.27\times 10^{-10}$ N, as shown in Fig. 5(a), and become more pronounced as χ^+ increases (with a consequent decrease of the amount of energy that is dispersed). Also, the velocity of the soliton decreases as χ^+ increases and, for $\chi^+ \gtrsim 0.28\times 10^{-10}$ N, there is no propagation, the energy is trapped and can hop around the initially excited bonds [see Fig. 5(d)]. Although Fig. 5 seems to indicate a poor energy efficiency of the soliton at biological temperatures, this efficiency depends strongly on the initial conditions. Figure 6, for example, shows a case where most of the initial excitation is deposited in a traveling soliton at 310 K.

IV. DISCUSSION

In the present paper we begin with the assumptions implied by Davydov's ansatz [Eq. (2.6)] and derive Eqs.

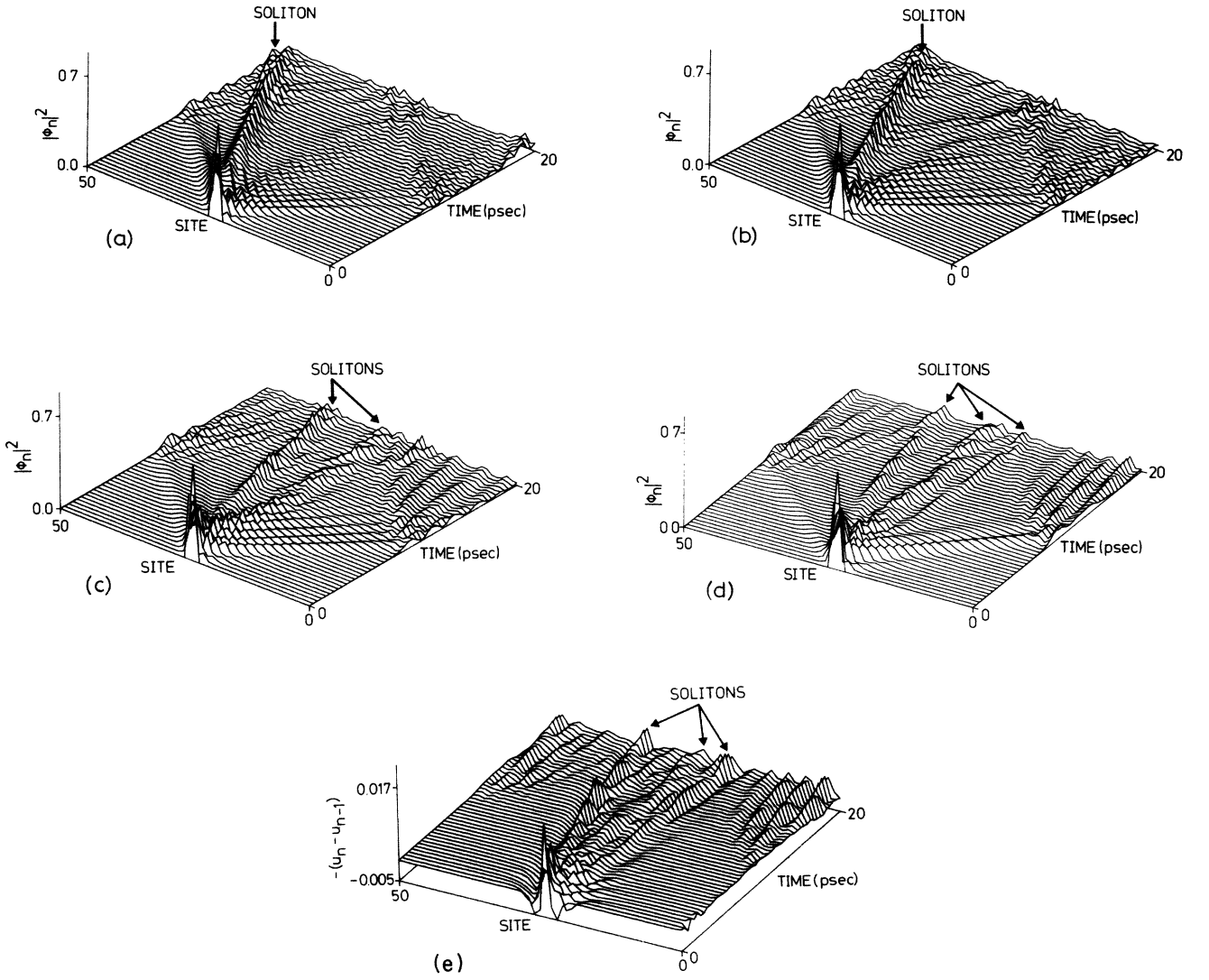

FIG. 4. Evolution of the probability of an excitation in site n, $|\phi_n|^2$ ($n=0,\ldots,50$). The nonlinearity parameter $\chi^+=0.23\times 10^{-10}$ N and the initial conditions are two sites [Eq. (3.1)]. (a) $T=10$ K; (b) $T=100$ K; (c) $T=200$ K; (d) $T=310$ K; and (e) the molecular displacement, $-(u_n-u_{n-1})$ in Å, for the conditions of (d).

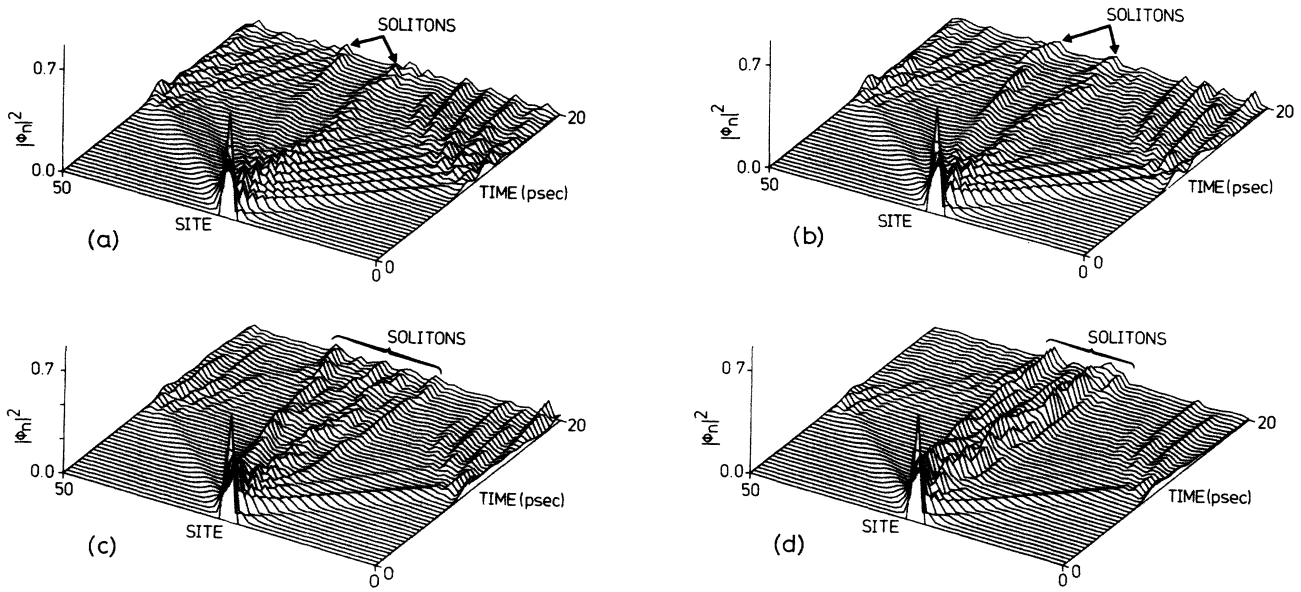

FIG. 5. Evolution of the probability of an excitation in site n, $|\phi_n|^2$ ($n=0,\ldots,50$). (a) $\chi^+=0.18\times10^{-10}$ N, (b) $\chi^+=0.21\times10^{-10}$ N, (c) $\chi^+=0.24\times10^{-10}$ N, and (d) $\chi^+=0.28\times10^{-10}$ N.

(2.15) without any further approximations. In this manner Davydov's approximations, criticized by a number of authors, are avoided. It is thus interesting to compare our results with Davydov's predictions.[8] A first observation is that, when temperature effects are included, the Davydov interaction Hamiltonian predicts results qualitatively different from the asymmetrical interaction Hamiltonian, and a proposed equivalence between the two by setting $\chi^+=\chi^-=\frac{1}{2}\chi$ (Ref. 21) is not valid. However, concentrating on the results obtained with the asymmetrical Hamiltonian, Davydov's predictions of the thermal effects on soliton propagation[8] are confirmed, i.e., an increase in the effective mass of the soliton, corresponding to a decrease in soliton velocity, as temperature increases, is observed in Fig. 4. Also, as temperature increases, see Fig. 4, the "soliton" becomes more "excitonlike." Because Davydov's approximate equations were not valid for soliton velocities around the sound velocity, Davydov could not predict whether the transition from the soliton to the exciton state would be continuous or discontinuous.[8] Our derivation is not limited in this way, and our conclusion is that the transition from a soliton to an exciton state is continuous. This happens both as χ decreases (Fig. 5) and as temperature increases (Fig. 4).

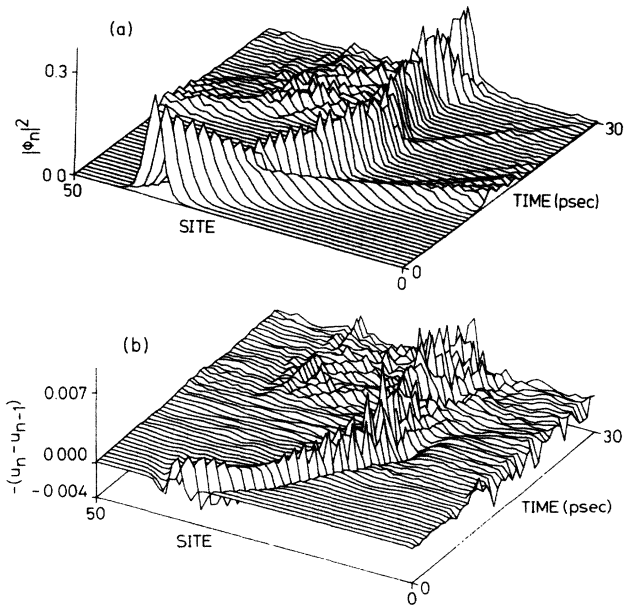

FIG. 6. (a) Evolution of the probability of an excitation $|\phi_n|^2$, and (b) the molecular displacement, $-(u_n-u_{n-1})$ in Å in site n ($n=0,\ldots,50$). Temperature $T=310$ K, the nonlinearity parameter $\chi^+=0.23\times10^{-10}$ N, and the initial condition is the sech pulse [Eq. (3.2)].

Figures 2 and 3 give a detailed picture of thermal effects. Both for Davydov's interaction Hamiltonian and the asymmetrical interaction Hamiltonian the threshold of the nonlinearity parameters above which there is soliton formation (either localized or traveling) is 0.17×10^{-10} N. Since theoretically determined values of χ^+ are $(0.265-0.364)\times10^{-10}$ N,[12,20] and an experimentally determined value is 0.62×10^{-10} N,[22] our basic conclusion is that an analysis based on Davydov's assumptions[8] does indeed imply that his soliton is robust at physiological temperatures (310 K).

ACKNOWLEDGMENTS

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APPENDIX: DETAILS OF THE NUMERICAL METHOD

The system to be integrated is

$$i\hbar\frac{d\phi_n}{\partial t}=-J(\phi_{n-1}e^{W_{nn-1}}+\phi_{n+1}e^{W_{nn+1}})-\phi_n\left[\frac{1}{N}\right]^{1/2}\sum_q F(q)e^{iqna}(\beta_{qn}+\beta^*_{-qn})+\phi_n\sum_q\bar{v}_q\,|\,\beta_{qn}\,|^2\,, \tag{A1}$$

$$\begin{aligned}i\hbar\frac{\partial\beta_{qn}}{dt}=&-J\{\phi^*_n\phi_{n-1}e^{W_{nn-1}}[(\bar{v}_q+1)\beta_{qn-1}-(\bar{v}_q+\tfrac{1}{2})\beta_{qn}]+\phi^*_{n+1}\phi_n e^{W_{n+1n}}[\bar{v}_q\beta_{qn+1}-(\bar{v}_q+\tfrac{1}{2})\beta_{qn}]\\&+\phi^*_n\phi_{n+1}e^{W_{nn+1}}[(\bar{v}_q+1)\beta_{qn+1}-(\bar{v}_q+\tfrac{1}{2})\beta_{qn}]+\phi^*_{n-1}\phi_n e^{W_{n-1n}}[\bar{v}_q\beta_{qn-1}-(\bar{v}_q+\tfrac{1}{2})\beta_{qn}]\}\\&-|\,\phi_n\,|^2\left[\frac{1}{N}\right]^{1/2}F^*(q)e^{-iqna}+|\,\phi_n\,|^2\hbar\Omega_q\beta_{qn}\,,\end{aligned} \tag{A2}$$

which is obtained from (2.15) after making the gauge transformation

$$\phi_n\rightarrow\phi_n\exp[i/\hbar(\varepsilon+\sum_q\hbar\Omega_q\bar{v}_q)t]\,.$$

We then set

$$\phi_n(t)=\phi^r_n(t)+i\phi^i_n(t)\,, \tag{A3}$$

$$\beta_{qn}(t)=\beta^r_{qn}(t)+i\beta^i_{qn}(t)\,, \tag{A4}$$

where $\phi^r_n(t)$, $\phi^i_n(t)$, $\beta^r_{qn}(t)$, and $\beta^i_{qn}(t)$ are real quantities. Substituting (A3) and (A4) into (A1) and (A2) we get a system of equations with real variables, which we integrated using International Mathematical and Statistical Library (IMSL) routine DVERK,[23] a Runge-Kutta-Verner fifth- and sixth-order method. The number N of sites was 51, and thus the number of equations in the real variables was 5304. Periodic boundary conditions were used, i.e.,

$$\phi_0(t)=\phi_{N+1}(t)\,, \tag{A5}$$

$$\beta_{q0}(t)=\beta_{qN+1}(t)\,. \tag{A6}$$

The code was tested by verifying that two properties of the system (A1), (A2) held throughout the integration, i.e., (1) the imaginary part of the average atomic displacement $\langle u_n(t)\rangle$,

$$\langle u_n(t)\rangle^{\rm im}=\sum_m|\,\phi_m\,|^2\sum_q\left[\frac{\hbar}{2MN\Omega_q}\right]^{1/2}[\beta^i_{qn}(t)-\beta^i_{-qn}(t)]=0\,, \tag{A7}$$

and (2)

$$\sum_n(\beta^r_{qn}A^r_{qn}+\beta^i_{qn}A^i_{qn})=0\,, \tag{A8}$$

where

$$\begin{aligned}A_{qn}=A^r_{qn}+iA^i_{qn}=&\phi^*_n\phi_{n-1}e^{W_{nn-1}}[(\bar{v}_q+1)\beta_{qn-1}-(\bar{v}_q+\tfrac{1}{2})\beta_{qn}]+\phi^*_{n+1}\phi_n e^{W_{n+1n}}[\bar{v}_q\beta_{qn+1}-(\bar{v}_q+\tfrac{1}{2})\beta_{qn}]\\&+\phi^*_n\phi_{n+1}e^{W_{nn+1}}[(\bar{v}_q+1)\beta_{qn+1}-(\bar{v}_q+\tfrac{1}{2})\beta_{qn}]+\phi^*_{n-1}\phi_n e^{W_{n-1n}}[\bar{v}_q\beta_{qn-1}-(\bar{v}_q+\tfrac{1}{2})\beta_{qn}]\,.\end{aligned} \tag{A9}$$

Equalities (A7) and (A8) were true with a very high precision.

Finally, the integration itself was tested by the conservation of the total probability of excitation [Eq. (2.16)], which was observed with a precision of, typically, 1%.

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