Alternative formulation of Davydov's theory of energy transport in biomolecular systems

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We consider the system of equations obtained by Davydov from the Fröhlich Hamiltonian through the use of a coherent-state Ansatz. We obtain equations of motion which, although entirely equivalent to the usual Davydov system, allow the dynamics to be analyzed in a more transparent way. In the continuum limit the exact equations reduce to the usual nonlinear Schrödinger equation. Initial states and the soliton formation process are discussed, and time and length scales governing soliton coherence properties are determined. In order to address the case of intermediate wavelengths, where the discreteness of the underlying lattice has significant consequences for soliton motion, we formulate a modified nonlinear Schrödinger equation which resolves a number of difficulties implicit in the usual nonlinear Schrödinger equation.

I. INTRODUCTION

In the mid 1970s Davydov and Kisluka[1] proposed a molecular soliton model for the description of energy transport processes in biological systems. Interest in a soliton channel of transport arises largely from the expectation that such a mechanism would reduce energy delocalization through dispersion and inhibit energy loss through dissipation, making it an attractive mechanism for bioenergetics.[2] The theory of molecular solitons[1-7] has received increasing attention since numerical simulations of the Davydov system of equations[8-12] have raised questions about the stability of solitons at biologically relevant temperatures.[10-12] Efforts directed at improving our understanding of soliton dynamics involve several distinct components: One component takes aim at understanding the distinctly quantum-mechanical aspects of energy transport.[12-20] Another's priority lies in determining the effect of thermal fluctuations on soliton stability.[10-12,20-22] Others are concerned with the problem of distinguishing between linear and nonlinear relaxed states,[14,16,21] the design and execution of pivotal experiments,[23,24] and the refinement or generalization of the Davydov model itself.[22]

Davydov's theory is a description of a single electronic or vibronic excitation (which we shall call an "exciton") propagating along a deformable molecular chain. The deformability of the molecular chain affects the dynamics of the mobile excitation through the dependence of exciton energies on the configuration of the chain. The theory is based on the Fröhlich Hamiltonian,[25] which for a particular choice of exciton-phonon coupling geometry can be written

$$H=\sum_n E a_n^\dagger a_n - J\sum_n (a_{n+1}^\dagger a_n + a_n^\dagger a_{n+1}) + \sum_n \left[\frac{\hat{P}_n^2}{2M}+\frac{w}{2}(\hat{Q}_n-\hat{Q}_{n-1})^2\right] + \chi\sum_n(\hat{Q}_{n+1}-\hat{Q}_{n-1})a_n^\dagger a_n , \tag{1.1}$$

where $a_n^\dagger$ and a_n are, respectively, the creation and annihilation operators of the exciton on the nth molecule, $\hat{Q}_n$ is the operator representing the longitudinal displacement of the nth molecule from its equilibrium position R_n, $\hat{P}_n$ is the momentum operator conjugate to $\hat{Q}_n$, M is the molecular mass, w is the stiffness coefficient, and χ is the force exerted by an exciton on the molecules immediately adjacent to it.

The Davydov Ansatz for the state vector of the exciton-phonon system (1.1) is given by[4-13,17,18,20,26]

$$|\Psi(t)\rangle \approx |\Psi_a(t)\rangle \equiv |\alpha(t)\rangle \otimes |\beta(t)\rangle , \tag{1.2a}$$

$$|\alpha(t)\rangle = \sum_n \alpha_n(t) a_n^\dagger |0\rangle , \tag{1.2b}$$

$$|\beta(t)\rangle = \exp\left[-\sum_q [\beta_q(t) b_q^\dagger - \beta_q^*(t) b_q]\right]|0\rangle = \exp\left[-\frac{i}{\hbar}\sum_n [Q_n(t)\hat{P}_n - P_n(t)\hat{Q}_n]\right]|0\rangle , \tag{1.2c}$$

where the β_q (b_q) are the normal coordinates (operators) corresponding to Q_n and P_n ($\hat{Q}_n$ and $\hat{P}_n$) and q is a wave vector.[18] With these definitions, the Ansatz state has the following properties:

$$\langle \Psi_a(t) | a_m^\dagger a_n | \Psi_a(t) \rangle = \alpha_m^*(t)\alpha_n(t) , \tag{1.3a}$$

$$\sum_n |\alpha_n(t)|^2 = 1 , \tag{1.3b}$$

$$\langle \Psi_a(t) | b_q | \Psi_a(t) \rangle = \beta_q(t) , \tag{1.3c}$$

$$\langle \Psi_a(t) | \hat{Q}_n | \Psi_a(t) \rangle = Q_n(t) , \tag{1.3d}$$

$$\langle \Psi_a(t) | \hat{P}_n | \Psi_a(t) \rangle = P_n(t) . \tag{1.3e}$$

One may apply various arguments to obtain the set of equations commonly referred to as the Davydov system. One common line of development uses the Ansatz state (1.2) to form the expectation value of the total energy, $H\{\alpha,\beta\} = \langle \Psi_a(t) | H | \Psi_a(t) \rangle$, which is then used as a Hamilton function to develop equations of motion for the wave-function parameters $\{\alpha(t),\beta(t)\}$ which are assumed to evolve as classical variables. The result of this argument is the Davydov system of equations

$$i\hbar\dot{\alpha}_n(t) = \{E + W(t) + \chi[Q_{n+1}(t) - Q_{n-1}(t)]\}\alpha_n(t) - J[\alpha_{n+1}(t) + \alpha_{n-1}(t)] \tag{1.4a}$$

$$M\ddot{Q}_n(t) = w[Q_{n+1}(t) + Q_{n-1}(t) - 2Q_n(t)] + \chi[\,|\alpha_{n+1}(t)|^2 - |\alpha_{n-1}(t)|^2\,] , \tag{1.4b}$$

$$W(t) = \sum_n \left[\frac{1}{2M} P_n^2(t) + \frac{w}{2}[Q_n(t) - Q_{n-1}(t)]^2 \right] . \tag{1.4c}$$

A recent alternative derivation of the Davydov system has been given by Kerr and Lomdahl.[13] This derivation avoids the invocation of Hamilton's equations and obtains the system (1.4) from the Ansatz (1.2) by strictly quantum-mechanical manipulations. The two methods result in Ansatz state vectors which differ by a time-dependent global phase; thus, while the two methods yield the same expectation values $\langle \Psi_a(t) | O | \Psi_a(t) \rangle$ they yield different correlation functions $\langle \Psi_a(t) | \Psi_a(t') \rangle$.

Subsequent approximations, including a long-wavelength approximation or continuum limit, lead to the nonlinear Schrödinger (NLS) equation

$$i\hbar \frac{\partial}{\partial t}\alpha(x,t) = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\alpha(x,t) + E(0)\alpha(x,t) - G_v |\alpha(x,t)|^2 \alpha(x,t) , \tag{1.5}$$

where $E(0) = E - 2J$ is the bottom of the bare exciton band with an associated effective mass m and G_v depends on both the soliton speed v and the speed of sound v_a,

$$G_v = \frac{4\chi^2 l}{w} \frac{v_a^2}{v_a^2 - v^2} . \tag{1.6}$$

The soliton solution of the nonlinear Schrödinger equation is given by

$$\alpha(x,t) = \left[\frac{\kappa}{2} \right]^{1/2} \frac{e^{-i(kx-\omega t)} e^{-i[E(0)/\hbar]t}}{\cosh[\kappa(x - vt)]} , \tag{1.7}$$

where

$$\hbar k \equiv -mv , \tag{1.8a}$$

$$\hbar\kappa \equiv \frac{mG_v}{2\hbar} , \tag{1.8b}$$

$$\hbar\omega \equiv \frac{mG_v^2}{8\hbar^2} - \tfrac{1}{2}mv^2 . \tag{1.8c}$$

[These expressions are those appropriate for the normalization convention $\int dx\, |\alpha(x,t)|^2 = 1$.]

We set aside numerous important questions surrounding the domain of validity of the Davydov system (1.4) (Refs. 17, 18, and 20–22) and focus on obtaining approximate evolution equations which afford an analysis of the dynamics embodied in the full Davydov system which is more penetrating than that allowed by the nonlinear Schrödinger equation (1.5) alone. In the following, therefore, the modifiers "exact" and "approximate" are understood to apply only to the reasoning which follows from the central assumption embodied in the Davydov Ansatz.

II. LATTICE EQUATIONS

Employing the Davydov Ansatz (1.2), one can easily obtain[13,18] the following sets of equations which are equivalent to (1.4):

$$i\hbar\dot{\alpha}_n(t) = E\alpha_n(t) - J[\alpha_{n+1}(t) + \alpha_{n-1}(t)] + \sum_q \chi_n^q \hbar\omega_q[\beta_q^*(t) + \beta_{-q}(t)]\alpha_n(t) , \tag{2.1a}$$

$$\dot{\beta}_q(t) = -\omega_q\beta_q(t) - i\omega_q \sum_m \chi_m^q |\alpha_m(t)|^2 , \tag{2.1b}$$

in which ω_q is the acoustic dispersion relation

$$\omega_q = \omega_B \sin\left[\frac{|ql|}{2} \right] = 2\left[\frac{w}{M} \right]^{1/2} \sin\left[\frac{|ql|}{2} \right] , \tag{2.2}$$

and χ_n^q is the dimensionless coupling function

$$\chi_n^q = \frac{-2i\chi \sin(ql)}{(2NM\hbar\omega_q^3)^{1/2}} e^{-iqR_n} . \tag{2.3}$$

R_n is the equilibrium position of the nth molecule and l is the lattice constant. Integrating (2.1b) we obtain the exact integral relation

$$\beta_q(t) = e^{-i\omega_q t}\beta_q(0) - i\int_0^t d\tau\, e^{-i\omega_q(t-\tau)} \sum_m \chi_m^q \omega_q |\alpha_m(\tau)|^2 . \tag{2.4}$$

[We note that while (2.1b) is not quantum-mechanically exact, (2.4) follows exactly from (2.1b).] Substituting (2.4) into Eq. (2.1a), we then obtain

$$i\hbar\dot{\alpha}_n(t)=E\alpha_n(t)-J[\alpha_{n+1}(t)+\alpha_{n-1}(t)]+f_n(t)\alpha_n(t)+\left[\int_0^t d\tau\sum_m \dot{K}_{nm}(t-\tau)\,|\alpha_m(\tau)|^2\right]\alpha_n(t)\ , \tag{2.5}$$

where $f_n(t)$, $K_{mn}(t)$ are defined by

$$f_n(t)=\sum_q \chi_n^q\hbar\omega_q[e^{i\omega_q t}\beta_q^*(0)+e^{-i\omega_q t}\beta_{-q}(0)]\ , \tag{2.6}$$

$$K_{mn}(t)=2\sum_q \chi_m^q\chi_n^{-q}\hbar\omega_q\cos(\omega_q t)\ . \tag{2.7}$$

For initial conditions representing the creation of a bare exciton in a lattice initially in thermal equilibrium, $f_n(t)$ and $K_{mn}(t)$ are related through a fluctuation dissipation relation which at high temperatures may be written[15,20,21]

$$\lim_{T\to\infty}\langle f_m(t)f_n(\tau)\rangle=k_B T K_{mn}(t-\tau)\ . \tag{2.8}$$

For an infinite linear chain, $K_{mn}(t)$ can be evaluated by changing the summation over the allowed wave vectors to an integration over a continuous Brillouin zone [see, e.g., Ref. 19] with the result that

$$K_{mn}(t)=\frac{\chi^2}{w}[J_{2(m-n+1)}(2\omega_B t)+2J_{2(m-n)}(2\omega_B t)+J_{2(m-n-1)}(2\omega_B t)]\ , \tag{2.9}$$

where $J_n(t)$ is the Bessel function of the first kind. Noting that

$$K_{mn}(0)=\frac{\chi^2}{w}(\delta_{m,n+1}+2\delta_{mn}+\delta_{m,n-1})\ , \tag{2.10}$$

(2.5) can be integrated by parts and (2.10) used to yield

$$i\hbar\dot{\alpha}_n(t)=E\alpha_n(t)-J[\alpha_{n+1}(t)+\alpha_{n-1}(t)]+f_n(t)\alpha_n(t)-\frac{\chi^2}{w}[\,|\alpha_{n+1}(t)|^2+2|\alpha_n(t)|^2+|\alpha_{n-1}(t)|^2]\alpha_n(t)+\sum_m[K_{nm}(t)\,|\alpha_m(0)|^2]\alpha_n(t)+\left[\int_0^t d\tau\sum_m K_{nm}(t-\tau)\frac{\partial}{\partial\tau}|\alpha_m(\tau)|^2\right]\alpha_n(t)\ . \tag{2.11}$$

Since no approximation has been made in obtaining (2.5) or (2.11) from the Ansatz (1.2), both (2.5) and (2.11) are equivalent to the Davydov system (1.4).

III. CONTINUUM EQUATIONS

In carrying out the strict continuum limit, certain combinations of parameters must be held constant as the lattice constant vanishes,

$$Jl^2=\frac{\hbar^2}{2m},\quad \chi l=\varepsilon,\quad wl=\zeta,\quad M/l=\eta\ ,\qquad v_a=\left[\frac{\zeta}{\eta}\right]^{1/2}, \tag{3.1}$$

in which m is the effective mass of the free exciton, ε is the energy change resulting from a molecular displacement of one lattice constant in the linearized exciton field, ζ is the tension, and η is the mass density. The energy $E(0)=E-2J$ is divergent in the strict continuum limit since the preservation of the effective mass leads to a divergent bandwidth. This causes no difficulties, however, since it introduces only a global phase precession which is irrelevant to transport. Since this energy represents the bottom of the free-exciton band $[E(k)|_{k=0}]$, its principal role is to determine the position of spectral features, and when retained for such purposes must be maintained at its proper microscopic value. Thus in passing to the continuum limit, we have

$$R_n\to x\ , \tag{3.2a}$$

$$\sum_n |\alpha_n(t)|^2=1\to\int dx\,|\alpha(x,t)|^2=1\ , \tag{3.2b}$$

$$\frac{O_{n+1}-O_n}{l}\to\frac{\partial}{\partial x}O(x)\ , \tag{3.2c}$$

$$K_{mn}(t)\to K(x,y,t)=\frac{2\varepsilon^2}{\zeta}[\delta(x-y+v_a t)+\delta(x-y-v_a t)]\ , \tag{3.2d}$$

which together allow the exact equations to be rewritten in the form

$$i\hbar\dot{\alpha}(x,t)=-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\alpha(x,t)+E(0)\alpha(x,t)-\frac{4\varepsilon^2}{\zeta}|\alpha(x,t)|^2\alpha(x,t)+f(x,t)\alpha(x,t)+\frac{2\varepsilon^2}{\zeta}[\,|\alpha(x+v_a t,0)|^2+|\alpha(x-v_a t,0)|^2]\alpha(x,t)+\frac{2\varepsilon^2}{\zeta}\int_0^t d\tau\left[\frac{\partial}{\partial\tau}|\alpha(y,\tau)|^2\Big|_{y=x+v_a(t-\tau)}+\frac{\partial}{\partial\tau}|\alpha(y,\tau)|^2\Big|_{y=x-v_a(t-\tau)}\right]\alpha(x,t)\ . \tag{3.3}$$

The presence of the space-time integration in (3.3) indicates the persistence of nontrivial fluctuation-dissipation properties even in the continuum limit.

If we look for nondissipative solutions by assuming $|\alpha(x,t)|^2=\rho(x-vt)$, then the partial derivative can be manipulated and the indicated integrations carried out explicitly. Subject to this condition we find

$$i\hbar\dot{\alpha}(x,t)=-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\alpha(x,t)+E(0)\alpha(x,t)+f(x,t)\alpha(x,t)+\frac{2\varepsilon^2}{\zeta}\left[\frac{v_a}{v_a+v}\rho(x+v_at)-\frac{2v_a^2}{v_a^2-v^2}\rho(x-vt)+\frac{v_a}{v_a-v}\rho(x-v_at)\right]\alpha(x,t)\ . \qquad (3.4)$$

The implications of this form are investigated in Sec. IV.

IV. INITIAL DATA AND TRANSIENTS

There are two classes of initial conditions which are of broad interest in soliton-supporting systems. The most obvious is the "preformed soliton" representing a situation in which an electronic wave packet is prepared together with the appropriate distortion of the medium required to maintain the coherent structure for an indefinite period. It is often the case, however, that the apparatus supplying the stimulus couples directly only to the electronic degrees of freedom, and so generates a "bare exciton," i.e., an electronic excitation initially uncorrelated with the medium. This distinction in initial data is manifest in Eqs. (3.3) and (3.4) through $f(x,t)$, since $f(x,t)$ is the only term dependent on the initial condition of the medium. We consider first the bare-exciton initial condition for a quiescent medium (zero temperature), for which $f(x,t)=0$.

A. The bare exciton

We can arrange Eq. (3.4) in the form of a Schrödinger equation with a time-dependent potential $U(x,t)$:

$$i\hbar\dot{\alpha}(x,t)=-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\alpha(x,t)+E(0)\alpha(x,t)+U(x,t)\alpha(x,t)\ , \qquad (4.1)$$

$$U(x,t)=\frac{2\varepsilon^2}{\zeta}\left[\frac{v_a}{v_a+v}\rho(x+v_at)-\frac{2v_a^2}{v_a^2-v^2}\rho(x-vt)+\frac{v_a}{v_a-v}\rho(x-v_at)\right], \qquad (4.2)$$

and depict the co-evolution of the soliton probability density $\rho(x-vt)$ and the potential $U(x,t)$ as shown in Fig. 1.

For a time $O\{\tau_D^\pm\}$, where

$$\tau_D^\pm=\frac{\lambda}{v_a\pm v}\ , \qquad (4.3)$$

following the preparation of an initially bare wave packet of width λ, the several contributions to $U(x,t)$ overlap. The overlap is such that the centroid of the would-be soliton is not exactly at the bottom of the potential well, but rather on the leading slope of the well. In other words, the excitation experiences a resistive force which must result in its deceleration. The dynamical consequences of this deceleration depend on the competition of the lattice dynamics occurring on the time scales $\tau_D^\pm$ and the response of the wave packet to the potential, which occurs on a time scale τ_U yet to be determined.

Up to numerical factors that we assume to be unimportant, we estimate the time τ_U as the time required for the excitation to reach the bottom of the potential well, which because of transient processes is displaced from the centroid of the wave packet. Since this time would be a quarter period of an oscillation in a stationary well, an estimate for this time is provided by the classical formula for the period of a bound oscillation,

$$\tau_U\approx\tfrac{1}{4}T=\tfrac{1}{4}\oint\frac{m\,dx}{\sqrt{2m[E-U(x)]}}\ . \qquad (4.4)$$

Using the parameters of the NLS soliton, we estimate $[E-U(x)]\approx\frac{1}{2}G_v\rho(0)$ and use (4.3) to eliminate λ with the result that

$$\tau_U\approx(\tau_D^+\tau_D^-)^{1/2}\left[\frac{G_v}{\hbar(v_a^2-v^2)^{1/2}}\right]^{-1}\ . \qquad (4.5)$$

Figure 2 compares the time scales $\tau_D^\pm$ and τ_U in several parameter regimes. When $G_0(\hbar v_a)\ll 1$, it is apparently possible for slow wave packets to be transformed into similar slow solitons since the inequality $\tau_D^-\ll\tau_U$ which holds in this case indicates that the soliton deformation is completed before the wave packet has sufficient opportunity to deviate significantly from its D'Alembert trajectory.

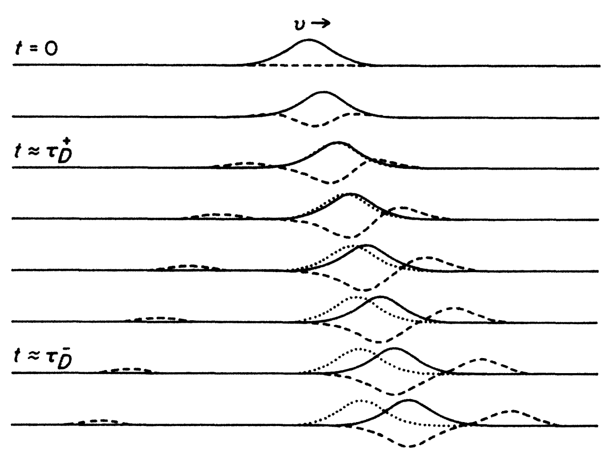

FIG. 1. Soliton formation. Solid lines (——), envelope of an initial wave packet, assumed to propagate as $\rho(x-vt)$; dashed lines (— — —), potential $U(x,t)$ in arbitrary units; dotted lines (· · ·), hypothetical response of a wave packet when $G_0/\hbar v_a>1$, based on the conclusions of Sec. IV A; the corresponding lattice response is not shown.

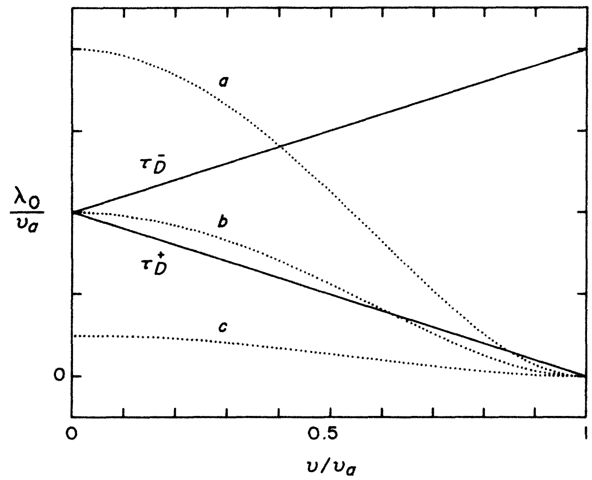

FIG. 2. Time scales for soliton formation. Solid lines (——), time scales for forward (τ_D^-) and backward (τ_D^+) propagating deformations to leave the excitation region; dotted lines (· · ·), time scales for wave packet response (τ_U). Curve a, $G_0/\hbar v_a < 1$; curve b, $G_0/\hbar v_a = 1$; curve c, $G_0/\hbar v_a > 1$.

On the other hand, when $G_0(\hbar v_a) \gg 1$, a qualitatively different behavior must follow. In this regime $\tau_U \ll \tau_D^+$, indicating that the wave packet responds to changes in the deformation potential as fast as these changes occur. Each differential change involves a differential reduction in group velocity. Though a decreasing velocity is inconsistent with the initial assumption that $|\alpha(x,t)|^2 = \rho(x-vt)$, one can imagine that such a deceleration may result in a transient cascade through solitonlike states with ever diminishing velocities, perhaps settling down to a final constant speed. We estimate the change in velocity Δv using (4.2) as follows:

$$\Delta v \approx \int_0^t dt' \left[\frac{-\nabla U(x,t')}{m} \right]_{x=vt'} , \tag{4.6}$$

where the force is evaluated at the centroid of the would-be soliton and m is the effective mass of the exciton. Using the parameters appropriate for the NLS soliton [see (1.5)–(1.8)], (4.6) becomes

$$\frac{\Delta v}{v} \approx \frac{G_v^2}{\hbar^2(v_a^2 - v^2)} . \tag{4.7}$$

The minimal condition for an initially bare state to decay into a soliton of nearly the same speed and shape as the initial wave packet can thus be given as

$$\frac{G_0^2}{\hbar^2 v_a^2} \ll 1 ; \tag{4.8}$$

"relativistic" soliton velocities (v^2/v_a^2 nonnegligible) impose stronger conditions. When $G_0/\hbar v_a > 1$, (4.7) indicates a velocity change greater than the initial speed, which cannot realistically occur. However, this breakdown of our estimates suggests that a bare exciton prepared in a medium for which $G_0/\hbar v_a \gg 1$ suffers dramatic changes in form in a time $O\{\tau_U\}$, perhaps breaking up or coming to rest. An excitation coming to rest in such a scenario would travel a distance

$$d \approx v\tau_U \approx \lambda \left[\frac{v}{v_a} \right] \left[\frac{G_v}{\hbar v_a} \right]^{-1} \tag{4.9}$$

before stopping, a distance which is less than the width of the initial wave packet.

A physical system for which the Davydov model has been thought to be appropriate is the hydrogen-bonded backbone of α-helix proteins. Using the system parameters $\chi \approx 0.62 \times 10^{-10}$ N, $M = 114 m_p$, $k = 13$ N/m, as given by Scott (m_p is the proton mass, see Ref. 26), we find

$$\frac{G_0}{\hbar v_a} \approx 1.36 . \tag{4.10}$$

In the absence of further evidence, and considering the coarseness of the approximations made in obtaining the above estimates, it would appear that little more could be said except that the α helix appears to lie in the transition region between the distinguishable behaviors discussed above. However, numerical simulations by Lomdahl and Kerr[10] have shown that for the α-helix parameters given above, excitations typically exist in fragmented self-trapped states which are pinned to the lattice. Moreover, a reduction of χ by only 20% was found to result in depinning. Depinning as observed in these simulations corresponds to

$$\frac{G_0}{\hbar v_a} \approx 0.87 . \tag{4.11}$$

Thus, the transition between pinned and unpinned relaxed states appears to be accurately marked by the condition

$$\frac{G_0}{\hbar v_a} = 1 \tag{4.12}$$

suggested by our approximate analysis.

The inequality (4.8) is essentially the same as the weak-coupling condition of polaron theory;[21] moreover, since τ_D^- is the minimum time required for a soliton to form from a bare initial state, τ_D^- is the natural generalization of the polaron formation time discussed by Brown *et al.*[19]

B. The preformed soliton

Using the normal-mode transformation relating $\{\beta_q\}$ to $\{P_n, Q_n\}$ (Ref. 18) and implementing the continuum limit as in (3.1) and (3.2), one can show that the "fluctuation" $f(x,t)$ can be expressed as

$$f(x,t) = \varepsilon \left[\frac{\partial Q_0(y)}{\partial y} + \frac{P_0(y)}{\eta v_a} \right]_{y=x+v_a t} + \varepsilon \left[\frac{\partial Q_0(y)}{\partial y} - \frac{P_0(y)}{\eta v_a} \right]_{y=x-v_a t} . \tag{4.13}$$

[Note that here $P_0(y)$ is a momentum *density*.] This shows that there is sufficient freedom in the choice of initial coordinates $\{Q_0(x),P_0(x)\}$ for $f(x,t)$ to reproduce arbitrary solutions of the continuum wave equation. In particular, it follows that for any solution of the nonlinear Schrödinger equation we can always find the suitable initial condition of the lattice so that

$$f(x,t)=-\frac{2\varepsilon^2}{\zeta}\left[\frac{v_a}{v_a+v}\rho(x+v_at)+\frac{v_a}{v_a-v}\rho(x-v_at)\right] . \quad (4.14)$$

In this case, the sound pulses which would otherwise interfere with soliton propagation may be cancelled exactly, with the consequence that any such solutions are also solutions of the continuum equations (3.3) (at zero temperature) and (3.4). We thus have a prescription for assembling coherent structures which are exact solutions of the Davydov system in the continuum limit:

(1) Choose any solution $\alpha(x,t)$ of the nonlinear Schrödinger equation such that $|\alpha(x,t)|^2=\rho(x-vt)$.

(2) Choose initial conditions for the medium

$$Q_0(x)=-\frac{G_v}{2\varepsilon}\int^x dy\,\rho(y) , \quad (4.15a)$$

$$P_0(x)=\eta v\frac{G_v}{2\varepsilon}\rho(x) . \quad (4.15b)$$

For the particular case of the NLS soliton (1.7), (4.15) yields

$$Q_0(x)=-\frac{G_v}{4\varepsilon}\tanh(\kappa x) , \quad (4.16a)$$

$$P_0(x)=\eta v\frac{G_v}{4\varepsilon}\kappa\,\mathrm{sech}^2(\kappa x) , \quad (4.16b)$$

as is well known.[6]

At finite temperatures, the "fluctuation" $f(x,t)$ is a superposition of the soliton or coherent potential just discussed and the thermal or incoherent potential arising from the random motion of the medium

$$f(x,t)=f^{\mathrm{sol}}(x,t)+f^{\mathrm{th}}(x,t) .$$

When describing the dynamics of a preformed soliton at finite temperatures, the coherent component $f^{\mathrm{sol}}(x,t)$ cancels transients as discussed above leaving the incoherent component $f^{\mathrm{th}}(x,t)$ as a persistent perturbation. A fluctuation-dissipation relation exists for this component.

The nonlinear potential $U(x,t)=-G_v\rho(x-vt)$ which remains uncancelled for a preformed soliton can be viewed as a result of feedback channeled through the lattice. The derivation of (3.4) shows that this lattice-mediated feedback is an amalgamation of two distinct components corresponding to the decomposition of the nonlinearity parameter G_v into its speed-independent (G_0) and speed-dependent (G_v-G_0) parts: The potential $-G_0\rho(x-vt)$ corresponding to the speed-independent part appears in the exact equations of motion (3.3) as a time-local self-interaction. The potential $-(G_v-G_0)\times\rho(x-vt)$ corresponding to the speed-dependent part represents an enhancement of the nonlinear potential due to the motion of the soliton and appears in the exact equations of motion (3.3) as a consequence of lattice memory.

The simplicity of the nonlinear Schrödinger equation obscures the fact that the nonlinear potential is partly dependent upon the existence of coherence over a region of space larger than the soliton width. Figure 3 shows schematically the space-time region which contributes the speed-dependent nonlinear potential. Coherence over this space-time region is necessary for lattice memory to contribute constructively and enhance soliton stability. The "shadow" cast by the soliton has a length

$$\Lambda=\lambda_0\frac{v}{v_a}\left[1+\frac{v}{v_a}\right] , \quad (4.17)$$

where λ_0 is the resting width of the soliton. Although this shadow is never more than twice the resting width of the soliton [the total width $(\lambda+\Lambda)$ is always between λ_0 and $2\lambda_0$], the ratio Λ/λ diverges as the soliton speed approaches the sound speed; that is, the spatial extent of the space-time region over which coherence is required may be much greater than the soliton width (see Fig. 4).

Since the shadow is a space-time region, it has a second dimension to which there corresponds a time scale

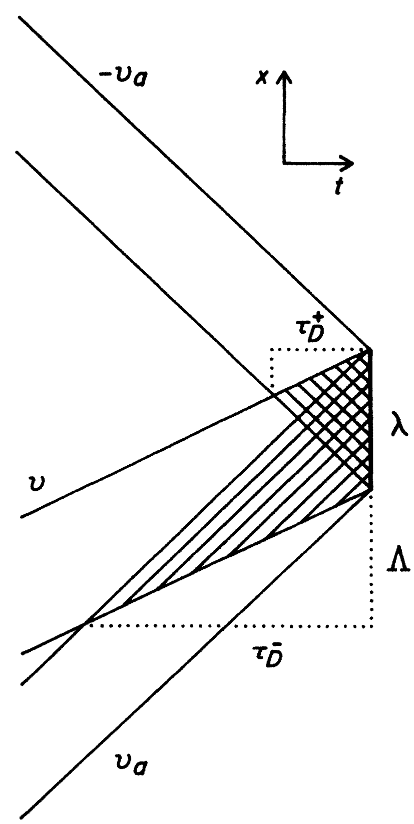

FIG. 3. Space-time region participating in the NLS nonlinearity; λ is the width of the NLS soliton, $\tau_D^{\pm}$ is defined in (4.3), Λ is defined in (4.17). Hatched regions are integrated to produce $(G_v-G_0)\rho(x-vt)$.

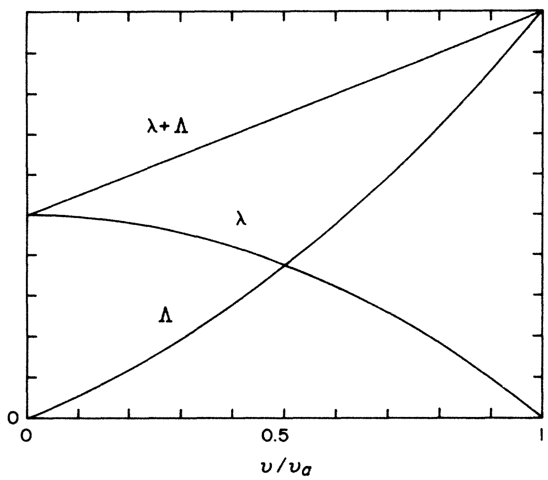

FIG. 4. Relative magnitudes of the NLS soliton width λ and the width Λ of the space-time shadow which contributes the speed dependence of the nonlinearity.

$(\Lambda+\lambda)/v_a$ over which coherence must persist. From (4.3) and (4.17), it is easy to see that this time scale is *precisely* τ_D^-, the soliton formation time. While it is perhaps not obvious why the soliton formation time should be a determinant of soliton coherence properties, it is easy to see from this point of view why τ_D^- should be the soliton formation time: Since the stabilization of the soliton requires a coherent space-time shadow of duration τ_D^-, a minimum time of τ_D^- is needed for the requisite coherence to develop from an initial state in which it is lacking.

V. QUASICONTINUA

The continuum limit and long-wavelength approximations become inappropriate when the microstructure of a host medium significantly influences the structure or dynamics of an excitation. At intermediate wavelengths some accommodation of the influence of microstructure can be made by retaining low-order corrections in a gradient expansion of the relevant quantities (see Appendix A). Such corrections may be implemented by replacing (3.2b) and (3.2c) with

$$|\alpha_{n+1}(t)|^2+2|\alpha_n(t)|^2+|\alpha_{n-1}(t)|^2 \rightarrow 4\left[1+\frac{l^2}{4}\frac{\partial^2}{\partial x^2}\right]|\alpha(x,t)|^2 \quad (5.1a)$$

and

$$K_{mn}(t)\rightarrow K(x,y,t)\approx\frac{2\chi^2 l}{w}\left[1+\frac{l^2}{4}\frac{\partial^2}{\partial x^2}\right] \times[\delta(x-y+v_a t)+\delta(x-y-v_a t)]\ , \quad (5.1b)$$

respectively.

Considering the case of preformed soliton, the results of Sec. IV show that using (5.1) we can obtain from (2.11) a *modified* nonlinear Schrödinger (MNLS) equation,

$$i\hbar\dot{\alpha}(x,t)=-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\alpha(x,t)+E(0)\alpha(x,t) -G_v\alpha(x,t)\left[1+\frac{l^2}{4}\frac{\partial^2}{\partial x^2}\right]|\alpha(x,t)|^2\ . \quad (5.2)$$

The derivatives in the last term in (5.2) cause a softening of the nonlinear potential in regions of high curvature. Retaining this term allows us to account for the discreteness of the underlying lattice in an approximate way while retaining the advantages of a continuum analysis.

As in the case of the original nonlinear Schrödinger equation, the validity of the modified nonlinear Schrödinger equation (5.2) is subject to the existence of nondissipative solutions. We seek solutions of the form

$$\alpha(x,t)=\phi(x-vt)e^{-i(kx-\omega t)}e^{-iE(0)/\hbar t}\ , \quad (5.3)$$

where $\phi(x-vt)$ is a smooth real function. The substitution of (5.3) into (5.2) shows the parameters k and v to be related through $\hbar k=-mv$, and allows the nonlinear equation for $\alpha(x,t)$ to be transformed into a nonlinear equation for the envelope function,

$$\frac{\partial^2\phi}{\partial x^2}-A\phi+B\phi^3+C\phi\frac{\partial^2\phi^2}{\partial x^2}=0\ , \quad (5.4)$$

wherein we have defined

$$A=\frac{Jl^2k^2+\hbar\omega}{Jl^2}=\frac{2m}{\hbar^2}(\tfrac{1}{2}mv^2+\hbar\omega)\ , \quad (5.5a)$$

$$B=\frac{4\chi^2}{wJl}\frac{v_a^2}{v_a^2-v^2}=\frac{2m}{\hbar^2}G_v\ , \quad (5.5b)$$

$$C=\frac{\chi^2 l}{wJ}\frac{v_a^2}{v_a^2-v^2}=\frac{2m}{\hbar^2}G_v\frac{l^2}{4}\ . \quad (5.5c)$$

The envelope equation (5.4) can be put into the form of a "Newton's Law,"

$$\frac{\partial^2\phi}{\partial x^2}=-\frac{\partial V(\phi)}{\partial\phi}\ , \quad (5.6)$$

wherein the "potential" $V(\phi)$ is given by

$$V(\phi)=\frac{1}{2}\left[\frac{-A\phi^2+\frac{1}{2}B\phi^4}{1+2C\phi^2}\right] \quad (5.7)$$

(see Appendix B). $V(\phi)$ has a nontrivial zero at $\phi=\phi_0\equiv\sqrt{2A/B}$ which allows $V(\phi)$ to be conveniently rescaled,

$$V(\phi)=\frac{D^2}{l^3}\left[\frac{G_v}{Ja}\right]^{-1}\left[\frac{-(\phi/\phi_0)^2+(\phi/\phi_0)^4}{1+D(\phi/\phi_0)^2}\right]\ , \quad (5.8)$$

where D is a dimensionless constant defined by $D=2C\phi_0^2$. The dependence of D on Hamiltonian parameters is difficult to determine in the general case [$\hbar\omega$ in (5.5a) is an implicit function of ϕ_0, so it is necessary to have some detailed knowledge of the dependence of ϕ_0 on the Hamiltonian parameters before D can be completely specified]; however, it is easy to show that for small and large D,

$$D \approx \left[\frac{G_v}{4Jl} \right]^2, \quad D \ll 1 \tag{5.9a}$$

$$D \approx \frac{1}{\pi} \frac{G_v}{Jl}, \quad D \gg 1 \ . \tag{5.9b}$$

For the purposes of illustration, we use the interpolation

$$D \approx \frac{G_v^2}{\pi G_v Jl + (4Jl)^2} \ . \tag{5.10}$$

The dependence of $V(\phi)$ on its parameters is shown in Fig. 5.

The soliton envelope is found by considering the infinite-period separatrix trajectory separating rotational and librational oscillations in the potential $V(\phi)$. The boundary conditions appropriate to the soliton solution are

$$\phi(+\infty) = \phi(-\infty) = 0, \quad \frac{\partial \phi(+\infty)}{\partial x} = \frac{\partial \phi(-\infty)}{\partial x} = 0 \ . \tag{5.11}$$

For the "initial conditions" ($x = -\infty$) given by Eq. (5.11), this solution can be viewed as the trajectory of a mass starting from the top of the central peak $V(\phi)$ with an infinitesimal displacement. There are nonlocalized solutions to Eq. (5.2) as well. These solutions correspond to trajectories for which the mass starts from a point above or below the top of the central peak in the double-well picture. These solutions include linear and nonlinear waves such as plane waves (uniform probability density) and cnoidal waves.

When $D = 0$, as in the strict continuum limit, $V(\phi)$ reduces to the quartic double-well potential whose solutions are well known[27,28] and whose separatrix trajectory yields the usual NLS soliton. The envelope $\phi(x)$ of the MNLS soliton can be found by inverting the equation

$$\frac{x - x_0}{l} = \frac{1}{\sqrt{D}} \int_1^{\phi/\phi_0} \frac{du}{u} \left[\frac{1 + Du^2}{1 - u^2} \right]^{1/2} \ . \tag{5.12}$$

The limits of small and large D are clearly of greatest interest. When $D \ll 1$, (5.12) gives the usual envelope function of the NLS soliton. On the other hand, when D is large, indicating that the role of discreteness is important, the envelope function of the MNLS soliton is given by

$$\phi(x) = \begin{cases} \left[\dfrac{2}{\pi l} \right]^{1/2} \cos \left[\dfrac{x - x_0}{l} \right], & |x - x_0| < \dfrac{\pi l}{2} \\ 0, \quad |x - x_0| > \dfrac{\pi l}{2} \end{cases} \tag{5.13}$$

(see Fig. 6).

Thus for soliton velocities approaching the sound speed, and in the $J \to 0$ limit, the solitons of the modified nonlinear Schrödinger equation resist collapse to physical dimensions smaller than a lattice constant. (Note $J \to 0$ implies $v \to 0$.) This self-limiting property of the MNLS solitons represents a significant improvement over the behavior of the usual NLS solitons, since in the high-D regime the latter collapse without limit, rendering the nonlinear Schrödinger equation a singular approximation. Moreover, the collapse of the NLS wave function is accompanied by a divergence of the binding energy of the NLS soliton in the $J \to 0$ limit. (Note that this divergence also appears in the continuum limit of the exact $J = 0$ po-

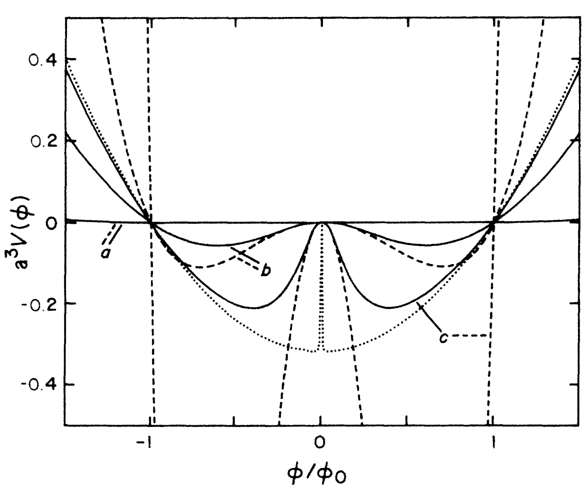

FIG. 5. "Newton's-law potential" for the modified nonlinear Schrödinger equation. Dashed lines (— — —), quartic potential implicit in the nonlinear Schrödinger equation; solid lines (——), modified potential (5.8) implicit in the modified nonlinear Schrödinger equation. Curve a, $G_v/Jl = 1 \to D = 0.05$; curve b, $G_v/Jl = 10 \to D \approx 2$; curve c, $G_v/Jl = 100 \to D \approx 30$. Dotted line ($\cdots$), modified potential representative of the high-D limit; $G_v/Jl = 10^6 \to D \approx 3.2 \times 10^5$.

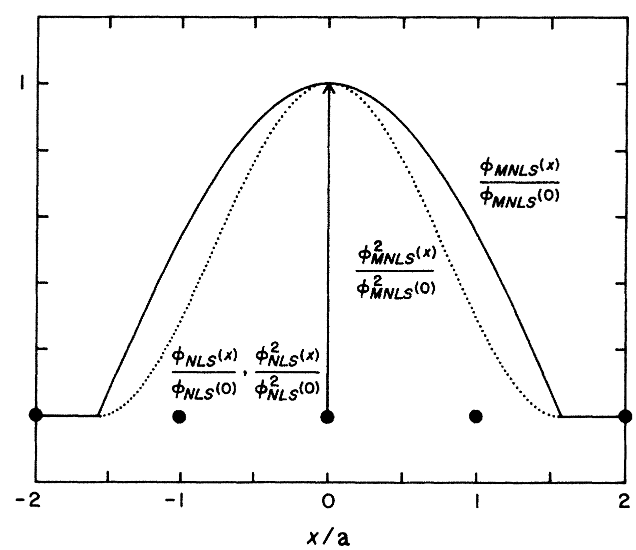

FIG. 6. Solid line (——), MNLS soliton envelope $\phi_{\rm MNLS}(x)/\phi_{\rm MNLS}(0)$ in the high-D limit; dotted line ($\cdots$), MNLS probability density $\phi^2_{\rm MNLS}(x)/\phi^2_{\rm MNLS}(0)$ in the high-D limit. The corresponding NLS functions are singular distributions of vanishing width. (●) indicate lattice sites.

laron treatment.[19]) This is to be contrasted with the binding energy of the MNLS solitons which is finite in the high-D regime.

VI. CONCLUSION

Starting from the Fröhlich Hamiltonian and the Davydov Ansatz for the state vector of an exciton-phonon system, we have eliminated phonon variables to obtain sets of equations which are equivalent to the Davydov system but different in form. By integrating phonon variables exactly we retain and are able to treat explicitly terms which are typically lost in passing from the Davydov system (1.4) to the nonlinear Schrödinger equation (1.5).

The different form taken by our equations clarifies the separate roles of initial conditions, lattice memory and coherent self-interaction. Also clarified, but not detailed in the present work, are the fluctuation-dissipation properties crucial for understanding the (in)stability of Davydov solitons at elevated temperatures.

The continuum limit leads to somewhat simplified equations; however, real simplification occurs only when soliton solutions are sought. Davydov's nonlinear Schrödinger equation is recovered under special conditions. We have considered separately the cases of a preformed soliton and a bare initial state for which the possibility of soliton formation was investigated. We conclude that although our continuum equations admit preformed soliton solutions for all values of the system parameters, the spontaneous formation of a propagating soliton from a bare initial state is unlikely in systems with strong exciton-phonon coupling (characterized by $G_v/\hbar v_a > 1$). More specifically, an initial wave packet with group velocity v can be expected to slow dramatically during the dressing process, perhaps becoming immobilized. Conclusions drawn from analytic estimates agree with results of independent numerical simulations of the Davydov system. The time and length scales involved are determined.

Practical use of the Davydov system of equations has proven to be problematic, in part due to the lack of a useful intermediate between the complete Davydov system and the nonlinear Schrödinger equation. In an effort to improve this situation, we have derived a *modified* nonlinear Schrödinger equation which admits soliton solutions and retains some of the effects originating in the discreteness of the underlying lattice. The principal result is that the MNLS solitons resist the collapse to physical dimensions smaller than a lattice constant which plagues the usual NLS solitons. Related divergences are suppressed. The general MNLS soliton envelope function is algebraically complicated, and so has been given here only in implicit form and in limits. The long-wavelength limit of the MNLS soliton is the usual NLS soliton.

ACKNOWLEDGMENT

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APPENDIX A

Using (2.2) and (2.3) in (2.7) yields

$$K_{mn}(t) \propto \sum_q \cos^2\left[\frac{ql}{2}\right] e^{-iq(R_m-R_n)}\cos(\omega_q t) \ . \tag{A1}$$

We make use of the fact that

$$K_{mn}(t) \propto \cosh^2\left[\frac{l}{2}\nabla_{R_m}\right] \sum_q e^{-iq(R_m-R_n)}\cos(\omega_q t) \ . \tag{A2}$$

Considering the infinite-chain limit, we make the single approximation

$$\cos(\omega_q t) \approx \cos(v_a\,|\,q\,|\,t) \tag{A3}$$

and identify $x \leftrightarrow R_m$, $y \leftrightarrow R_n$ with the result that

$$K(x,y,t) \approx \cosh^2\left[\frac{l}{2}\nabla_x\right] \tfrac{1}{2}[\delta(x-y+v_a t) + \delta(x-y-v_a t)] \ . \tag{A4}$$

Using this form of $K(x,y,t)$ in (2.11) leads to the envelope equation

$$\nabla^2\phi - A\phi + B\phi\cosh^2\left[\frac{l}{2}\nabla\right]\phi^2 = 0 \ . \tag{A5}$$

Equation (5.6) is a truncation of (A5) at second order in $(l/2)\nabla$.

The error involved in using the second-order truncation of the envelope equation (A5) may be estimated as follows: For a typical envelope of width λ, we have

$$\cosh^2(\tfrac{1}{2}l\nabla)\phi^2 \approx \cosh^2\left[\frac{l}{\lambda}\right]\phi^2 \equiv \Delta \quad \text{(untruncated)} \tag{A6}$$

$$[1+(\tfrac{1}{2}l\nabla)^2]\phi^2 \approx \left[1+\left[\frac{l}{\lambda}\right]^2\right]\phi^2 \equiv \Delta_{\text{MNLS}} \quad \text{(MNLS approximation)} \tag{A7}$$

$$1\phi^2 = 1\phi^2 \equiv \Delta_{\text{NLS}} \quad \text{(NLS approximation)} \ . \tag{A8}$$

Both the MNLS and NLS approximations are accurate for sufficiently long wavelengths; however, for wavelengths as short as $2l$ we find the MNLS to be a dramatic improvement over the NLS,

$$\frac{\Delta-\Delta_{\text{NLS}}}{\Delta} \approx 27\% \quad \text{for } \lambda = 2l \ . \tag{A9}$$

$$\frac{\Delta-\Delta_{\text{MNLS}}}{\Delta} \approx 1.6\% \quad \text{for } \lambda = 2l \ . \tag{A10}$$

One indicator of the fitness of a continuum treatment is the degree to which the discrete and continuum normalizations agree. Both the NLS and MNLS solitons are continuum normalized to unity [see (3.2b)]; however, in the high-D limit, we find

$$\sum_n l \mid \alpha(R_n,t) \mid^2 \rightarrow \infty \quad \text{for } \Delta_{\text{NLS}} , \tag{A11}$$

$$\sum_n l \mid \alpha(R_n,t) \mid^2 \rightarrow 1.0083 \quad \text{for } \Delta_{\text{MNLS}} . \tag{A12}$$

We note that the replacement of $l^2/4$ in (5.2) with l^2/π results in both the exact discrete normalization of the MNLS soliton in the high-D limit, and exact agreement of its binding energy with the polaron binding energy in the $J=0$ limit. While such a modification may prove useful for approximating high-D behavior, it does *not* constitute an exact recovery of the limiting behavior of either the Davydov model or the exact polaron model.

APPENDIX B

To solve Eq. (5.6), we note that

$$\frac{\partial^2\phi^2}{\partial x^2} = 2\left[\frac{\partial\phi}{\partial x}\right]\left[\frac{\partial\phi}{\partial x}\right] + 2\phi\frac{\partial^2\phi}{\partial x^2} . \tag{B1}$$

The change of variable $\partial\phi/\partial x \rightarrow v(\phi)$ and use of (B1) in (5.6) yields

$$v\frac{\partial v}{\partial\phi} - A\phi + B\phi^3 + 2C\phi v^2 + 2C\phi^2 v\frac{\partial v}{\partial\phi} = 0 . \tag{B2}$$

With the transformation $y(\phi)=v^2(\phi)$, we can obtain the equation

$$\frac{\partial}{\partial\phi}[(1+2C\phi^2)y] = -(-2A\phi+2B\phi^3) . \tag{B3}$$

Integrating the above equation with respect to ϕ gives

$$\frac{\text{const}}{1+2C\phi^2} = \frac{1}{2}\left[\frac{\partial\phi}{\partial x}\right]^2 + \frac{1}{2}\left[\frac{-A\phi^2+\frac{1}{2}B\phi^4}{1+2C\phi^2}\right] , \tag{B4}$$

which can be regarded as the energy relationship $E=T+V$. Under the boundary condition (5.11), we know that the integration constant is zero, so we obtain the effective potential given by Eq. (5.7).

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