# Variational approach to the Davydov soliton

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The soliton states suggested by Davydov as approximate solutions to the Schrödinger equation for one-dimensional systems are examined from the standpoint of the variational principle. We show that the correct equations of motion are, in general, different from those proposed by Davydov. In addition, we comment on the time evolution of these states.

## I. INTRODUCTION

In a classic study of energy transport in one-dimensional exciton systems with exciton-phonon coupling, Davydov[1–3] has proposed a soliton as a particularly efficient transport state. Experimentally, Scott and Careri *et al.*[4] have examined crystalline acetanilide and have discussed the results using Davydov's model. Alexander and Krumhansl[5] have also examined this system theoretically. In this paper, we concentrate on the theoretical situation, in particular, the derivation of the dynamical equations. We derive a new set of equations, different in some respects from Davydov's equations, and show that these repair some of the problems of the latter. Davydov's method is to guess a functional form for the trial wave function which has a number of parameters. By identifying these parameters as "momenta" conjugate to other "coordinates" in the problem, he is able to write the equations of motion for these parameters in the form of the classical Hamilton equations. This procedure has been criticized by Brown *et al.*[6,7] and shown to have flaws. In this paper, we examine this problem anew, and by using the variational principle of time-dependent quantum mechanics[8,9] we derive corrected equations of motion for the parameters in Davydov's trial wave functions.

The system consists of molecules on a one-dimensional lattice with nearest-neighbor separation $a$. The Hamiltonian for this system is

$$H=\sum_n \left[ \varepsilon a_n^\dagger a_n + J(a_{n+1}^\dagger a_n + a_n^\dagger a_{n+1}) + \frac{p_n^2}{2m} + \tfrac{1}{2}\kappa(u_{n+1}-u_n)^2 + \chi a_n^\dagger a_n (u_{n+1}-u_{n-1}) \right] \tag{1a}$$

or, more generally,

$$H=\sum_n [\varepsilon a_n^\dagger a_n + J(a_{n+1}^\dagger a_n + a_n^\dagger a_{n+1})] + \sum_q \hbar\omega_q b_q^\dagger b_q + \sum_{q,n} \chi_n^q \hbar\omega_q a_n^\dagger a_n (b_q^\dagger + b_{-q}) , \tag{1b}$$

where

$$\chi_n^q = e^{-iqna}\chi^q = (\chi_n^{-q})^* .$$

In these forms, $a_n^\dagger (a_n)$ create (destroy) an excitation on molecule $n$, $J$ is the resonant-energy-transfer matrix element between nearest-neighbor molecules, $p_n$ and $u_n$ are the momentum and displacement operators of the molecule at site $n$, $b_q^\dagger$ $(b_q)$ create (destroy) a quantum of vibrational (phonon) energy of wave vector $q$ with frequency $\omega_q$, $m$ is the mass of the molecule, $k$ the intermolecular constant, and finally $\chi(\chi_n^q)$ is the exciton-phonon coupling constant. The local [Eq. (1a)] and extended [Eq. (1b)] forms of $H$ are related by

$$u_n = \sum_q \left[ \frac{\hbar}{2Nm\omega_q} \right]^{1/2} e^{iqna}(b_{-q}^\dagger + b_q) , \tag{2a}$$

$$p_n = i\sum_q \left[ \frac{\hbar m\omega_q}{2N} \right]^{1/2} e^{iqna}(b_{-q}^\dagger - b_q) , \tag{2b}$$

$$\omega_q = \omega_D \sin\tfrac{1}{2}qa , \quad \omega_D = 2\sqrt{\kappa/m} \tag{2c}$$

$$\chi^q = -i\chi \left[ \frac{2\hbar}{mN\omega_q} \right]^{1/2} \frac{\sin qa}{\hbar\omega_q} . \tag{2d}$$

Davydov suggested two trial wave functions which we call, following Brown *et al.*,[7] $|D_1(t)\rangle$ and $|D_2(t)\rangle$ given by

$$|D_1(t)\rangle = \sum_n A_n(t) a_n^\dagger \exp\left[ \sum_q [\beta_{q,n}(t) b_q^\dagger - \beta_{q,n}^*(t) b_q] \right] |0\rangle \tag{3a}$$

and

$$|D_2(t)\rangle = \sum_n A_n(t) a_n^\dagger \exp\left[ -\frac{i}{\hbar} \sum_m [\gamma_m(t) p_m - \Pi_m(t) u_m] \right] |0\rangle . \tag{3b}$$

Note that the phonon part of $|D_2(t)\rangle$ is independent of the site of the excitation $n$, while the phonon part of $|D_1(t)\rangle$ depends on $n$. The next step in the Davydov's procedure is to identify $i\hbar A_n^*$ and $i\hbar\beta_{qn}^*$ as the momenta conjugate to $A_n$ and $\beta_{qn}$ for $|D_1\rangle$ and $i\hbar A_n^*$ and $\Pi_n$ as the momenta conjugate to $A_n$ and $\gamma_n$ in $|D_2\rangle$. Finally, by identifying the Hamiltonian function as the expectation value of $H$ over either $|D_1\rangle$ or $|D_2\rangle$, Davydov asserted that the evolution of the parameters is described by Hamilton's equations. This leads for $|D_1\rangle$ to

$$\begin{aligned} i\hbar\dot{A}_n &= \frac{\partial}{\partial A_n^*}\langle D_1|H|D_1\rangle \equiv \frac{\partial}{\partial A_n^*}\langle H\rangle_1 , \\ i\hbar\dot{A}_n^* &= -\frac{\partial}{\partial A_n}\langle H\rangle_1 , \\ i\hbar\dot{\beta}_{qn} &= \frac{\partial}{\partial\beta_{qn}^*}\langle H\rangle_1 , \\ i\hbar\dot{\beta}_{qn}^* &= -\frac{\partial}{\partial\beta_{qn}}\langle H\rangle_1 , \end{aligned} \tag{4a}$$

and for $|D_2\rangle$ to

$$\begin{aligned} i\hbar\dot{A}_n &= \frac{\partial}{\partial A_n^*}\langle H\rangle_2 , \\ i\hbar\dot{A}_n^* &= -\frac{\partial}{\partial A_n}\langle H\rangle_2 , \\ \dot{\gamma}_n &= \frac{\partial}{\partial\Pi_n}\langle H\rangle_2 , \\ \dot{\Pi}_n &= -\frac{\partial}{\partial\gamma_n}\langle H\rangle_2 . \end{aligned} \tag{4b}$$

From these starting points and making some further approximations, Davydov obtained his soliton solutions.[10]

Recently, Brown *et al.*[6,7] have shown that the two assumptions of this method [(i) the form of the state vector and (ii) the equations of motion] are not equivalent to the Schrödinger equation. In particular, these authors show that the time evolution of $|D_1\rangle$ or $|D_2\rangle$ found from Schrödinger's equation is different from that implied by (4a) and (4b). That is, these authors found that $|\Phi_i(t)\rangle = e^{-iHt/h}|D_i(0)\rangle$ is different from $|D_i(t)\rangle$.

In this article, we use the variational principle of quantum mechanics to derive new equations of motion for the parameters of the trial state vectors. By doing this we avoid the second of Davydov's assumptions while keeping the first. We will comment on the form of the trial states later in this article.

## II. VARIATIONAL PROCEDURE

The Schrödinger equation,

$$H|\psi\rangle = i\hbar\frac{\partial}{\partial t}|\psi\rangle , \tag{5}$$

can be derived from the principle of least action

$$\delta\int_{t_1}^{t_2}\left\langle\psi\left|i\hbar\frac{\partial}{\partial t}-\hat{H}\right|\psi\right\rangle dt = 0 , \tag{6}$$

if we allow $|\psi\rangle$ and $\langle\psi|$ to be varied independently with the requirement that the variations at the end points vanish (see Appendix A). This procedure is equivalent to the variational method described by Langhoff *et al.*[8] based on the Frenkel variational method.[9]

Since we are using the variational method, we must insert the condition that the trial state vector be normalized at all times, i.e.,

$$\langle\psi|\psi\rangle = 1 . \tag{7}$$

This condition for either $|D_1\rangle$ or $|D_2\rangle$ reduces to

$$\sum_n A_n^*(t)A_n(t) = 1 . \tag{8}$$

We therefore introduce a constraint into the variation, Eq. (6), which now becomes

$$\delta\int_{t_1}^{t_2}\left[\left\langle\psi\left|i\hbar\frac{\partial}{\partial t}-\hat{H}\right|\psi\right\rangle - \lambda\langle\psi|\psi\rangle\right]dt = 0 , \tag{9}$$

where the role of the Lagrange multiplier $\lambda$ is discussed below.

We may now derive equations of motion for the parameters $A_n$, $A_n^*$, $\beta_{qn}$, and $\beta_{qn}^*$ in $|D_1\rangle$ and $A_n$, $A_n^*$, $\gamma_n$, and $\Pi_n$ in $|D_2\rangle$ by substituting the form of these trial state vectors for $|\psi\rangle$ in Eq. (9) and performing the variations with respect to these assumed independent parameters. The equations which replace Eq. (4) are

$$\begin{aligned} \frac{\partial\langle H\rangle_1}{\partial A_n^*} &= i\hbar\frac{dA_n}{dt} + i\hbar A_n\sum_q\frac{1}{2}\left[\beta_{q,n}^*\frac{d\beta_{q,n}}{dt} - \beta_{q,n}\frac{d\beta_{q,n}^*}{dt}\right] - \lambda A_n , \\ \frac{\partial\langle H\rangle_1}{\partial A_n} &= -i\hbar\frac{dA_n^*}{dt} + i\hbar A_n^*\sum_q\frac{1}{2}\left[\beta_{q,n}^*\frac{d\beta_{q,n}}{dt} - \beta_{q,n}\frac{d\beta_{q,n}^*}{dt}\right] - \lambda A_n^* ; \\ \frac{\partial\langle H\rangle_1}{\partial\beta_{q,n}^*} &= i\hbar A_n A_n^*\frac{d\beta_{q,n}}{dt} + \tfrac{1}{2}i\hbar\beta_{q,n}\frac{d^*(A_n A_n)}{dt} , \\ \frac{\partial\langle H\rangle_1}{\partial\beta_{q,n}} &= -i\hbar A_n A_n^*\frac{d\beta_{q,n}^*}{dt} - \tfrac{1}{2}i\hbar\beta_{q,n}^*\frac{d}{dt}(A_n^* A_n) , \end{aligned} \tag{10a}$$

and

$$\begin{aligned} \frac{\partial\langle H\rangle_2}{\partial A_n^*} &= i\hbar\frac{dA_n}{dt} + \sum_m\frac{1}{2}\left[\Pi\frac{d\gamma_m}{dt} - \gamma_m\frac{d\Pi_m}{dt}\right]A_n - \lambda A_n , \\ \frac{\partial\langle H\rangle_2}{\partial A_n} &= -i\hbar\frac{dA_n^*}{dt} + \sum_m\frac{1}{2}\left[\Pi_m\frac{d\gamma_m}{dt} - \gamma_m\frac{d\Pi_m}{dt}\right]A_n^* - \lambda A_n^* , \\ \frac{\partial\langle H\rangle_2}{\partial\Pi_n} &= \frac{d\gamma_n}{dt} , \\ \frac{\partial\langle H\rangle_2}{\partial\gamma_n} &= -\frac{d\Pi_n}{dt} . \end{aligned} \tag{10b}$$

In these equations, we have defined the following:

$$\langle H\rangle_1=\langle D_1|H|D_1\rangle$$
$$=\sum_n \varepsilon_0 A_n^* A_n+\sum_q\sum_n A_n^* A_n \hbar\omega_q \beta_{q,n}^*\beta_{q,n}$$
$$+\sum_{q,n} A_n^* A_n \hbar\omega_q(\chi_n^q\beta_{q,n}^*+\chi_n^{q*}\beta_{q,n})$$
$$+\sum_n A_n^*(A_{n+1}\tilde{J}_n+A_{n-1}\tilde{\tilde{J}}_n)\;,$$

where $\tilde{J}_n$, $\tilde{\tilde{J}}_n$ are defined as

$$\tilde{J}_n=J\exp\sum_q(\beta_{q,n}^*\beta_{q,n+1}-\tfrac{1}{2}|\beta_{q,n}|^2-\tfrac{1}{2}|\beta_{q,n+1}|^2)\;,$$
$$\tilde{\tilde{J}}_n=J\exp\sum_q(\beta_{q,n}^*\beta_{q,n-1}-\tfrac{1}{2}|\beta_{q,n}|^2-\tfrac{1}{2}|\beta_{q,n-1}|^2)$$
$$=\tilde{J}_{n-1}^*\;,$$
$$\langle H\rangle_2=\langle D_2|H|D_2\rangle$$
$$=\sum_n A_n^*[(\varepsilon_0+W)A_n+J(A_{n+1}+A_{n-1})$$
$$+\chi A_n(\gamma_{n+1}-\gamma_{n-1})]\;,$$

where

$$W=\tfrac{1}{2}\sum_n\left[\frac{1}{m}\Pi_n^2+\kappa(\gamma_n-\gamma_{n-1})^2\right].$$

We emphasize that the above set of equations is consistent with quantum mechanics. Whether their solution, for the initial condition $|D_1(0)\rangle$ or $|D_2(0)\rangle$, agrees with the exactly propagated state depends absolutely on the proposed structure of the trial state vector.

If, for example, the trial state vector were given as a sum of a complete set of states of the Hilbert space of the Hamiltonian $H$, with arbitrary coefficients, the set of equations obtained with the present method (which would have the form of Hamilton's equations) and those obtained by using the Schrödinger equation and the orthogonality condition of the basis mentioned, would only differ by the inclusion of the Lagrange multiplier. This, in turn, implies a shift of the zero-point energy or an overall constant phase factor, which is of course irrelevant. For an arbitrary trial state this is not necessarily true: the role of $\lambda$ has to be assessed once the solution is obtained.

## III. COMPARISON TO EARLIER WORK

Comparing Eqs. (10) with Davydov's equations Eqs. (4), we see evident differences. Note that for $|D_2(t)\rangle$, Eqs. (10b) have been derived by Kerr and Lomdahl[11] also using quantum-mechanical principles by assuming the ansatz state to be the exact solution of the Schrödinger equation. They point out that the solutions of these and Davydov's equations differ only by a time-dependent phase factor, so that although the soliton solution would still be obtained, differences in some of their predictions compared to those of Davydov may occur.

We can examine the general validity of the form of $|D_1(t)\rangle$ and $|D_2(t)\rangle$ by looking at limiting cases. There are two limits in which the dynamics of the problem can be solved exactly: (a) $J=0$, general $\chi_n^q$, i.e., no exciton motion and (b) $\chi_n^q=0$, general $J$, i.e., no exciton-phonon interaction.

In the case $J=0$, Brown *et al.*[7] showed that Davydov's approach applied to either $|D_1\rangle$ or $|D_2\rangle$ failed to reproduce the exact dynamics. We now show that our approach, embodied in Eqs. (10) applied to $|D_1\rangle$ yields the exact dynamics in this case.

By setting $J=0$ in Eqs. (10a), we get

$$\varepsilon_0 A_n+\left[\sum_q\hbar\omega_q(\beta_{qn}^*\beta_{qn}+\chi_n^q\beta_{qn}^*+\chi_n^{q*}\beta_{qn})\right]A_n$$
$$=i\hbar\frac{d}{dt}A_n+i\hbar A_n\sum_q\tfrac{1}{2}(\beta_{qn}^*\dot{\beta}_{qn}-\beta_{qn}\dot{\beta}_{qn}^*)-\lambda A_n\;, \tag{11}$$

$$\hbar\omega_q A_n^* A_n(\beta_{qn}+\chi_n^q)=i\hbar A_n^* A_n\dot{\beta}_{qn}+\tfrac{1}{2}i\hbar\beta_{qn}\frac{d(A_n^* A_n)}{dt}\;. \tag{12}$$

By multiplying Eq. (11) by $A_n^*$ and then subtracting the result from its conjugate, it is easy to show that

$$\frac{d}{dt}(A_n^* A_n)=0,\quad \text{i.e.,}\quad A_n^*(t)A_n(t)=\text{const}\;, \tag{13}$$

so that Eq. (12) becomes

$$\hbar\omega_q A_n^* A_n(\beta_{qn}+\chi_n^q)=A_n^* A_n i\hbar\dot{\beta}_{qn}\;, \tag{14}$$

whose solution can be written down immediately:

$$\beta_{qn}(t)=e^{-i\omega_q t}\beta_{qn}(0)-\chi_n^q(1-e^{-i\omega_q t})\;. \tag{15}$$

By substituting Eq. (15) into Eq. (11), we obtain a linear differential equation for $A_n$,

$$\dot{A}_n=-i\left[\sum_q\omega_q|\chi^q|^2\cos\omega_q t\right]A_n$$
$$-A_n\frac{i}{2}\sum_q\omega_q[\beta_{qn}(0)\chi_n^{q*}e^{-i\omega_q t}+\beta_{qn}^*(0)\chi_n^q e^{i\omega_q t}]$$
$$+iA_n\sum_q\omega_q|\chi_n^q|^2-\frac{i(\varepsilon_0+\lambda)}{\hbar}A_n\;, \tag{16a}$$

whose solution is

$$A_n(t)=A_n(0)\exp\left\{-i\sum_q|\chi^q|^2\sin\omega_q t+i\left[\sum_q|\chi^q|^2\omega_q-\left[\frac{\varepsilon_0+\lambda}{\hbar}\right]\right]t\right.$$
$$\left.+\tfrac{1}{2}\sum_q[\beta_{qn}(0)\chi_n^{q*}(e^{-i\omega_q t}-1)-\beta_{qn}^*(0)\chi_n^q(e^{i\omega_q t}-1)]\right\}. \tag{16b}$$

In order to show that $|D_1(t)\rangle$ with Eqs. (15) and (16) is the solution to the Schrödinger equation with initial condition $|D_1(0)\rangle$, we only need to verify that their overlap equals unity for all times, i.e,

$$\langle D_1(t)|e^{-iHt/\hbar}|D_1(0)\rangle = 1 \; . \tag{17}$$

In Appendix B, we show that

$$e^{-iHt/\hbar}|D_1(0)\rangle = e^{i\lambda t/\hbar}|D_1(t)\rangle \; , \tag{18}$$

that is, they differ by a phase factor, so they represent the same physical state at all times.

The fact that Eq. (10a) yields the correct Schrödinger dynamics for the wave function in the limit $J=0$ contrasts sharply with the dynamics embodied in Eq. (4a), which as Brown *et al.*[6,7] have shown, yields incorrect results when applied to this limiting case. The reason for this discrepancy lies in the very different way the terms $A_n^* A_n$ (the probability of the excitation being on site $n$) appear in Eq. (4a) and Eq. (10a). We note that for the general case, $J\neq 0$, these terms are responsible in Davydov's equations for the interesting dynamics of the soliton.[10]

We now turn to the other limiting case mentioned above, that of no exciton-phonon interaction, $\chi_n^q = 0$. The initial wave function $|D_2(0)\rangle$ represents the direct product of a coherent phonon state and a general exciton state; therefore, it will retain its form under the time evolution of the Hamiltonian with $\chi_n^q=0$. That is,

$$\begin{aligned}|D_2(0)\rangle &= \sum_n A_n(0)a_n^\dagger|0\rangle_{\rm ex}\exp\left[\frac{-i}{\hbar}\sum_m[\gamma_m(0)p_m-\Pi_m(0)u_m]\right]|0\rangle_{\rm ph} \\ &= \sum_n A_n(0)a_n^\dagger|0\rangle_{\rm ex}\exp\left[+\sum_q[\beta_q(0)b_q^\dagger-\beta_q^*(0)b_q]\right]|0\rangle_{\rm ph} \; ,\end{aligned} \tag{19}$$

with

$$\beta_q = (2\hbar MN\omega_q)^{-1/2}\sum_m[M\omega_q\gamma_m(0)+i\Pi_m(0)]e^{-iqma} \; .$$

Note that the phonon state is independent of the exciton state for all $t$. The *exact* dynamics for $\chi_n^q=0$ is straightforward,

$$e^{-iHt}|D_2(0)\rangle = \sum_n\left[\sum_{m,k}\frac{1}{N}A_m(0)e^{ik(n-m)}e^{-i(\varepsilon+2J\cos k)t}\right]a_n^\dagger|0\rangle_{\rm ex}\exp\left[-\sum_q[\beta_q(0)e^{-i\omega_q t}b_q^\dagger-\beta_q^*(0)e^{i\omega_q t}b_q]\right]|0\rangle_{\rm ph} \; . \tag{20}$$

This agrees with the solutions to Eq. (10b) [as well as Eq. (4b)]; therefore, the variational approach (and Davydov's approach) yields the exact dynamics for this wave function.

When we turn to the dynamics of $|D_1\rangle$ in this limit (i.e., $J\neq 0$) we find that neither Davydov's approach nor the variational approach can yield the exact dynamics. This can be seen by examining the exact time-evolved state:

$$e^{-iHt}|D_1(0)\rangle = e^{-iHt}\sum_n A_n(0)a_n^\dagger\exp\left[\sum_q[\beta_{qn}(0)b_q^\dagger-\beta_{qn}^*(0)b_q]\right]|0\rangle \; . \tag{21}$$

[Note that $|D_1(0)\rangle$ cannot be factored into a simple direct product of an exciton state with a phonon state.] Thus

$$e^{-iHt}|D_1(0)\rangle = \sum_m a_m^\dagger\sum_n\left[\frac{1}{N}\sum_k e^{-ik(n-m)}e^{-i(\varepsilon+2J\cos k)t}\right]A_n(0)\exp\left[\sum_q[\beta_{qn}(0)e^{-i\omega_q t}b_q^\dagger-\beta_{qn}^*(0)e^{i\omega_q t}b_q]\right]|0\rangle \tag{22}$$

$$= \sum_m a_m^\dagger\sum_n I_{n-m}(t)A_n(0)\prod_q e^{-1/2|\beta_{qn}(0)|^2}\sum_{l=0}^{\infty}\frac{[\beta_{qn}(0)]^l}{l!}(b_q^\dagger)^l|0\rangle \; , \tag{23}$$

where we have expanded the exponential phonon operator and written

$$I_{n-m}(t) = \frac{1}{N}\sum_k e^{-ik(n-m)}e^{-i(\varepsilon+2J\cos k)t} \; . \tag{24}$$

If we compare this to the *assumed* form of $|D_1(t)\rangle$,

$$|D_1(t)\rangle = \sum_m A_m(t)a_m^\dagger\exp\left[\sum_q[\beta_{qm}(t)b_q^\dagger-\beta_{qm}^*(t)b_q]\right]|0\rangle \tag{25}$$

$$= \sum_m A_m(t)a_m^\dagger\prod_q e^{-1/2|\beta_{qm}(t)|^2}\sum_{l=0}^{\infty}\frac{[\beta_{qm}(t)]^l}{l!}(b_q^\dagger)^l|0\rangle \; , \tag{26}$$

we find that there is no way to make (23) and (25) equal (unless $J=0$, which is a trivial case) *unless* $\beta_{qm}$ *is independent of* $m$ in which case $|D_1(0)\rangle$ becomes identical to $|D_2(0)\rangle$.

Thus the exact dynamics of the problem for $\chi=0$, $J\neq 0$, cannot be represented by the Davydov $D_1$ ansatz for the wave function and neither Eq. (4a) nor Eq. (10a) can yield exact results. Another way of saying this is that if the wave function has the form $|D_1(0)\rangle$ at $t=0$, it does not retain this form for $t>0$ if $\chi=0$ and $J\neq 0$, and thus the $D_1$ ansatz fails.

## IV. CONCLUSIONS

There are two different components of Davydov's theory of soliton transport in one-dimensional coupled exciton phonon systems. The first is the form of the wave function (either $|D_1\rangle$ or $|D_2\rangle$); the second is the set of equations describing the time evolution of these wave functions. In the present paper, we have examined both of these components using a variational approach; we find the following.

(i) The equations of motion for the parameters in Davydov's trial wave functions are different from those suggested by Davydov.[1-3] In particular, the equations using $|D_1\rangle$ are much more complex than believed heretofore. Those for $|D_2\rangle$ are found to be as given by Kerr and Lomdahl.[11]

(ii) In the limit that $J=0$ (no exciton transport), the new equations of motion for the parameters in $|D_1\rangle$ are exact and lead to the correct state at all times, while the equation of motion suggested by Davydov yields incorrect results in this limit.

(iii) In the limit of no exciton-phonon interaction, the ansatz $|D_1\rangle$ for the wave function cannot yield the exact dynamics since this wave function does not retain its form under the exact time evolution. On the other hand, $|D_2\rangle$ can yield the exact dynamics, and both the variational and Davydov approaches to the dynamics yield this correct answer.

Thus, neither ansatz for the wave function ($|D_1\rangle$ or $|D_2\rangle$) can yield the exact dynamics in both limits discussed in this paper; however, either (or both) form may be useful in describing the dynamics away from these limit. We believe that the new equations of motion for the evolution of these wave functions, derived by a time-dependent variational method consistent with the principles of quantum mechanics, are more general than those derived by Davydov, and will be useful to describe the dynamics in this interesting system.

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## APPENDIX A

In this appendix we review how the time-dependent Schrödinger equation can be derived from the principle of least action in its Hamiltonian form, i.e., Eq. (6).

Let $\hat{H}$ be the Hamiltonian of the system

$$\hat{H}=\hat{T}+\hat{V}\ , \tag{A1}$$

where $\hat{T}$ is the kinetic energy operator and $\hat{V}$ the potential energy term. We consider only time- and/or velocity-independent interactions.

The Schrödinger equation is

$$\hat{H}|\psi\rangle=i\hbar\frac{\partial}{\partial t}|\psi\rangle\ , \tag{A2}$$

or in the position representation, with $\psi(x)=\langle x|\psi\rangle$ being the wave function

$$-\frac{\hbar^2}{2m}\nabla^2\psi(x)+V(x)\psi(x)=i\hbar\frac{\partial}{\partial t}\psi(x)\ . \tag{A3}$$

Now, by defining a Lagrangian density

$$\underline{L}(\psi(x),\dot{\psi}(x))=i\hbar\psi^*(x)\dot{\psi}(x)-(\hbar^2/2m)\nabla\psi^*(x)\cdot\nabla\psi(x)-V(x)\psi^*(x)\psi(x)\ , \tag{A4}$$

Eq. (A3) can be derived from the principle of least action[12] by considering $\psi(x)$ and $\dot{\psi}(x)$ as independent:

$$\delta\int_{t_1}^{t_2}dt\int dx\,\underline{L}(x)=0\ , \tag{A5}$$

with $\delta\psi=\delta\dot{\psi}=0$ at the end points.

Since we are interested in its Hamiltonian form, we first find the canonical conjugate momentum to $\psi(x)$:

$$\Pi(x)=\left[\frac{\delta}{\delta\dot{\psi}(x)}\right]\underline{L}=i\hbar\psi^*(x)\ , \tag{A6}$$

then, the Hamiltonian density is

$$\underline{H}(\psi(x),i\hbar\psi^*(x))=\underline{L}(x)-i\hbar\psi^*(x)\dot{\psi}(x) \tag{A7}$$

or

$$\underline{H}(x)=\left[\frac{1}{i\hbar}\right]\left[\Pi(x)\frac{\hbar 2}{2m}\nabla^2\psi(x)-\Pi(x)\hat{V}(x)\psi(x)\right]\ , \tag{A8}$$

where we have already performed an integration by parts on $x$.

Using Eq. (A8), the Schrödinger equation follows from the variational principle in the form

$$\delta\int_{t_1}^{t_2}dt\int dx\left[\underline{H}(x)-\Pi(x)\frac{\partial}{\partial t}\psi(x)\right]=0 \tag{A9}$$

by varying $\Pi(x)$, or $\psi^*(x)$, and $\psi(x)$ independently with the variations vanishing at the end points.

Now, by disposing of the $x$ representation, Eq. (A9) becomes

$$\delta\int_{t_1}^{t_2}dt\left\langle\psi\left|H-i\hbar\frac{\partial}{\partial t}\right|\psi\right\rangle=0\ . \tag{A10}$$

Hence from Eq. (A10) we can formally assume that, by varying $\langle\psi|$ and $|\psi\rangle$ independently, we obtain the Schrödinger equation, Eq. (A2).

## APPENDIX B

We show here that

$$|\Phi(t)\rangle \equiv e^{-iHt/\hbar}|D_1(0)\rangle = e^{i\lambda t/\hbar}|D_1(0)\rangle \tag{B1}$$

by using the fact that the Hamiltonian, given by Eq. (1b), can be diagonalized by the transformation

$$U = \exp\left[-\sum_{q,m}(\chi_m^q b_q^\dagger - \chi_m^{q*} b_q)a_m^\dagger a_m\right] . \tag{B2}$$

That is,

$$\tilde{H} = U^\dagger H U = \sum \varepsilon_0 a_n^\dagger a_n + \sum_q \hbar\omega_q b_q^\dagger b_q - \sum_{q,n} \hbar\omega_q |\chi_n^q|^2 a_n^\dagger a_n . \tag{B3}$$

We may therefore write

$$|\Phi(t)\rangle = UU^\dagger e^{-iHt/\hbar} UU^\dagger |D_1(0)\rangle = Ue^{-i\tilde{H}t/\hbar}U^\dagger|D_1(0)\rangle . \tag{B4}$$

Now, we note that

$$|D_1(0)\rangle = \sum_n A_n(0)a_n^\dagger \exp\left[\sum_q [\beta_{qn}(0)b_q^\dagger - \beta_{qn}^*(0)b_q]\right]|0\rangle$$

so that we may write

$$U^\dagger|D_1(0)\rangle = U^\dagger \sum_n A_n(0)a_n^\dagger UU^\dagger \exp\left[\sum_q [\beta_{qn}(0)b_q^\dagger - \beta_{qn}^*(0)b_q]\right]UU^\dagger|0\rangle . \tag{B5}$$

However,

$$U^\dagger a_n^\dagger U = a_n^\dagger \exp\left[\sum_q (\chi_n^q b_q^\dagger - \chi_n^{q*} b_q)\right] \tag{B6}$$

and

$$U^\dagger b_q^\dagger U = b_q^\dagger - \sum_m \chi_m^{q*} a_m^\dagger a_m . \tag{B7}$$

Noting that $U^\dagger|0\rangle = |0\rangle$ and $a_m^\dagger a_m|0\rangle = 0$, we find

$$U^\dagger|D_1(0)\rangle = \sum_n A_n(0)a_n^\dagger \exp\left[+\sum_q (\chi_n^q b_q^\dagger - \chi_n^{q*}b_q)\right]\exp\left[+\sum_q [\beta_{qn}(0)b_q^\dagger - \beta_{qn}^*(0)b_q]\right]|0\rangle . \tag{B8}$$

Returning to Eq. (B4) and noting that the evolution of $a_n^\dagger$, $b_q^\dagger$, and $b_q$ are simple under the Hamiltonian $\tilde{H}$, we may write

$$|\Phi(t)\rangle = U\sum_n A_n(0)a_n^\dagger e^{-i\Omega t}e^{+F_n(t)}e^{G_n(t)}|0\rangle , \tag{B9}$$

where

$$\Omega = \frac{\varepsilon_0}{\hbar} - \sum_q |\chi_n^q|^2\omega_q , \tag{B10}$$

$$F_n(t) = \sum_q (\chi_n^q b_q^\dagger e^{-i\omega_q t} - \chi_n^{q*} b_q e^{+i\omega_q t}) , \tag{B11}$$

and

$$G_n(t) = \sum_q [\beta_{qn}(0)b_q^\dagger e^{-i\omega_q t} - \beta_{qn}^*(0)b_q e^{+i\omega_q t}] . \tag{B12}$$

We may now insert $U^\dagger U = 1$ in front of $|0\rangle$ in Eq. (B9) to find (noting $U|0\rangle = |0\rangle$)

$$|\Phi(t)\rangle = U\sum_n A_n(0)a_n^\dagger e^{-i\Omega t}e^{+F_n(t)}e^{G_n(t)}U^\dagger|0\rangle \tag{B13}$$

$$= \sum_n A_n(0)a_n^\dagger e^{-F_n(0)}e^{-i\Omega t}e^{+F_n(t)}e^{G_n(t)}|0\rangle , \tag{B14}$$

using $a_m^\dagger a_m|0\rangle = 0$ again. We must now combine the exponentials $F_n(0)$, $F_n(t)$, and $G_n(t)$ which do not commute. However, since the commutator of any two is a $c$ number, we have

$$e^{-F_n(0)}e^{+F_n(t)}e^{G_n(t)} = \exp[-F_n(0)+F_n(t)+G_n(t)] \times \exp\{+\tfrac{1}{2}[F_n(t),G_n(t)] - \tfrac{1}{2}[F_n(0),F_n(t)] - \tfrac{1}{2}[F_n(0),G_n(t)]\} . \tag{B15}$$

Thus

$$e^{F_n(0)}e^{-F_n(t)}e^{G_n(t)} = \exp\sum_q \{[\beta_{qn}(0)e^{-i\omega_q t} + \chi_n^q(e^{-i\omega_q t}-1)]b_q^\dagger - [\beta_{qn}^* e^{+i\omega_q t} + \chi_n^{q*}(e^{i\omega_q t}-1)]b_q\}$$
$$\times \exp\left[\sum_q \{\tfrac{1}{2}[\chi_n^q\beta_{qn}^*(0)(1-e^{i\omega_q t}) - \chi_n^{q*}\beta_{qn}(0)(1-e^{-i\omega_q t})] - \tfrac{1}{2}|\chi_n^q|^2(e^{i\omega_q t}-e^{-i\omega_q t})\}\right] . \tag{B16}$$

By substituting (B16) into (B14) and comparing to Eqs. (3a), (16b), and (15), we find

$$|\Phi(t)\rangle = e^{i\lambda t/\hbar}|D_1(t)\rangle . \tag{B17}$$

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