

## Quantum-mechanical derivation of the equations of motion for Davydov solitons

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The equations of the Davydov model, which describe energy propagation along linear-chain molecules by a soliton mechanism, have heretofore been derived by a combination of quantum-mechanical and classical techniques. We give here a derivation which is completely based on quantum mechanics.

In the mid-1970s Davydov and Kisluska<sup>1</sup> suggested that energy transport in quasi-one-dimensional molecular chains could occur by a soliton mechanism. The fundamental physical idea is that a coupling between intramolecular vibrations and molecular displacements could lead to a self-trapped state which transports energy along the chain. This concept has been elaborated in subsequent papers by Davydov<sup>2</sup> and by Scott and co-workers.<sup>3</sup> The Hamiltonian used by these authors is the same as that used for the polaron problem (the Fröhlich Hamiltonian for electron-phonon interactions) with some changes in the meaning of the symbols. From this Davydov has derived equations which have self-trapped or soliton solutions. His derivation begins from an ansatz for the system's time-dependent quantum-mechanical state vector, with time-dependent parameters. Using that state vector he derives an expression for the expectation value of the Hamiltonian operator. He then uses that expression as

the classical Hamiltonian function and obtains equations of motion for time-dependent parameters from the classical Hamilton's equations. This use of a mixture of classical and quantum concepts has recently been criticized by Brown and co-workers.<sup>4</sup>

Our purpose in this Brief Report is to present a derivation of the Davydov equations which employs only quantum-mechanical techniques. This derivation is free from some of the objections made in Ref. 4. We emphasize that this paper deals only with the derivation of the Davydov equations; their physical content has previously been shown to have some limitations.<sup>5</sup> In view of the recent interest in obtaining better descriptions of this problem,<sup>6</sup> we feel that it is important to have a systematic derivation based on fundamental quantum-mechanical principles.

Davydov's Hamiltonian is<sup>1,2</sup>

$$H = \sum_n [E_0 B_n^\dagger B_n - J(B_{n+1}^\dagger B_n + B_n^\dagger B_{n+1})] + \sum_n \left( \frac{p_n^2}{2m} + \frac{1}{2} w(u_{n+1} - u_n)^2 \right) + \chi \sum_n (u_{n+1} - u_{n-1}) B_n^\dagger B_n = H_v + H_p + H_{int}. \quad (1)$$

Here,  $B_n^\dagger$  and  $B_n$  are boson creation and annihilation operators, respectively, for quanta of intramolecular vibrations with energy  $E_0$  at site  $n$ ;  $u_n$  and  $p_n$  are the molecular displacement and momentum operators, respectively, for the molecule at site  $n$ ;  $m$  and  $w$  are the molecular mass and intermolecular force constant; and  $J$  is the intersite transfer energy produced by dipole-dipole interactions. The nonlinear coupling constant  $\chi$  arises from modulation of the on-site energy by the molecular displacements. The vibrational part  $H_v$ , the phonon part  $H_p$ , and the interaction part  $H_{int}$  are defined to be the individual terms in (1).

The phonon part of the Hamiltonian can be cast into familiar form in terms of phonon creation and annihilation operators by the use of the standard transformation

$$u_n = \sum_q \left( \frac{\hbar}{2Nm\omega_q} \right)^{1/2} e^{iqnl} (a_{-q}^\dagger + a_q), \quad (2a)$$

$$p_n = \sum_q \left( \frac{m\hbar\omega_q}{2N} \right)^{1/2} e^{iqnl} i(a_{-q}^\dagger - a_q). \quad (2b)$$

In these formulas  $l$  is the lattice spacing (the distance be-

tween peptide groups), and

$$\omega_q = 2(w/m)^{1/2} |\sin(ql/2)| \quad (3)$$

is the dispersion relation for  $H_p$ .

To understand the dynamics arising from the Hamiltonian (1), Davydov<sup>1,2</sup> makes the ansatz for the state vector

$$|\psi(t)\rangle = \sum_n a_n(t) B_n^\dagger \exp \left[ -\frac{i}{\hbar} \sum_j [\beta_j(t) p_j - \pi_j(t) u_j] \right] |0\rangle, \quad (4)$$

where  $|0\rangle$  is the ground-state vector (i.e., it is annihilated both by  $B_n$  and by the phonon operators  $a_q$ ). Assuming that the time evolution of this state vector is approximately the same as that of the (unknown) exact state vector, one can then understand the system behavior by finding the time evolution of the three sets of unknown functions  $a_n(t)$ ,  $\beta_n(t)$ , and  $\pi_n(t)$ .

Normalization of this state vector requires

$$\langle \psi(t) | \psi(t) \rangle = \sum_n |a_n(t)|^2 = 1. \quad (5)$$

The form of the state vector restricts the system to have only a single amide-I quantum present,

$$\langle \psi(t) | \sum_m B_m^\dagger B_m | \psi(t) \rangle = 1, \quad (6)$$

and  $|a_n(t)|^2$  is the probability that the single quantum is on the  $n$ th site. The interpretation of  $\beta_n(t)$  and  $\pi_n(t)$  is obtained as follows. Davydov<sup>2</sup> points out that the part of  $|\psi(t)\rangle$  depending on the displacement and momentum operators is a coherent state of the normal mode creation and annihilation operators. A coherent state for the mode with wave vector  $q$  is<sup>7</sup>

$$|\alpha_q\rangle = \exp(\alpha_q a_q^\dagger - \alpha_q^* a_q) |0\rangle. \quad (7)$$

To see that (4) is a coherent state of all the normal modes, we use (2) to show that

$$-\frac{i}{\hbar} \sum_n (\beta_n p_n - \pi_n u_n) = \sum_q (\alpha_q a_q^\dagger - \alpha_q^* a_q), \quad (8)$$

where

$$\alpha_q = \left[ \frac{m\omega_q}{2\hbar} \right]^{1/2} \beta_q + i \left[ \frac{1}{2m\hbar\omega_q} \right]^{1/2} \pi_q. \quad (9)$$

(Here  $\beta_q$  is the spatial Fourier transform of  $\beta_n$ ,

$$\beta_q = \frac{1}{\sqrt{N}} \sum_n e^{-iqn} \beta_n, \quad (10)$$

and similarly for  $\pi_q$ .) We substitute (8) into (4) and get a factor of the form (7) for every normal mode. With the property

$$\langle \alpha_q | a_q | \alpha_q \rangle = \alpha_q, \quad (11)$$

and also using (2), (9), and (10), we straightforwardly obtain

$$\langle \psi(t) | u_n | \psi(t) \rangle = \beta_n(t), \quad (12a)$$

$$\langle \psi(t) | p_n | \psi(t) \rangle = \pi_n(t). \quad (12b)$$

The Davydov equations are typically derived by first ob-

taining a formula for the average value of the energy  $\langle \psi(t) | H | \psi(t) \rangle$  in terms of  $a_n$ ,  $\beta_n$ ,  $\pi_n$ , and then using that result in Hamilton's equations of classical mechanics after identifying conjugate coordinates and momenta. Here we give an alternative derivation which avoids any reference to the expectation value of the Hamiltonian and to Hamilton's equations.

The basic assumption is that  $|\psi(t)\rangle$  is a solution of the time-dependent Schrödinger equation

$$i\hbar \frac{\partial}{\partial t} |\psi(t)\rangle = H |\psi(t)\rangle. \quad (13)$$

Since (12) identifies  $\beta_n(t)$  and  $\pi_n(t)$  as expectation values, standard quantum-mechanical procedure gives

$$\dot{\beta}_n(t) = \frac{1}{i\hbar} \langle \psi(t) | [u_n, H] | \psi(t) \rangle, \quad (14a)$$

$$\dot{\pi}_n(t) = \frac{1}{i\hbar} \langle \psi(t) | [p_n, H] | \psi(t) \rangle. \quad (14b)$$

The commutators are

$$[u_n, H] = i\hbar p_n/m, \quad (15a)$$

$$[p_n, H] = i\hbar w(u_{n+1} - 2u_n + u_{n-1}) + i\hbar \chi(B_{n+1}^\dagger B_{n+1} - B_{n-1}^\dagger B_{n-1}). \quad (15b)$$

Using (11), (13), (14), and

$$\langle \psi(t) | B_{n\pm 1}^\dagger B_{n\pm 1} | \psi(t) \rangle = |a_{n\pm 1}(t)|^2, \quad (16)$$

we get one of Davydov's equations

$$m\ddot{\beta}_n = w(\beta_{n+1} - 2\beta_n + \beta_{n-1}) + \chi(|a_{n+1}|^2 - |a_{n-1}|^2). \quad (17)$$

Next we derive the equation for  $a_n(t)$ . First we introduce a notation for the two parts of the state vector in (4):

$$|\psi(t)\rangle = |a\rangle |\beta, \pi\rangle \quad (18)$$

[for economy of notation the site and time dependence of  $a_n(t)$ ,  $\beta_n(t)$ , and  $\pi_n(t)$  are left implicit]. We substitute  $|\psi(t)\rangle$  into (13). The left-hand side is

$$i\hbar \frac{\partial}{\partial t} |\psi(t)\rangle = \sum_n i\hbar \dot{a}_n B_n^\dagger |0\rangle |\beta, \pi\rangle + |a\rangle \left\{ \sum_n [\dot{\beta}_n p_n - \dot{\pi}_n u_n + \frac{1}{2} (\beta_n \dot{\pi}_n - \dot{\beta}_n \pi_n)] \right\} |\beta, \pi\rangle. \quad (19)$$

(See Appendix A for details about obtaining the last term.) The right-hand side is  $[H_p$  is defined in (1)]

$$H |\psi(t)\rangle = \sum_n [E_0 a_n - J(a_{n+1} + a_{n-1})] B_n^\dagger |0\rangle |\beta, \pi\rangle + |a\rangle H_p |\beta, \pi\rangle + \chi \sum_n a_n B_n^\dagger |0\rangle (u_{n+1} - u_{n-1}) |\beta, \pi\rangle. \quad (20)$$

Next we equate (19) and (20), form the inner product with  $\langle \beta, \pi |$ , use (12), and equate the coefficients of  $B_n^\dagger |0\rangle$  on the two sides of the equation. The result is

$$i\hbar \dot{a}_n = \left( E_0 + W(t) - \frac{1}{2} \sum_m (\dot{\beta}_m \pi_m - \beta_m \dot{\pi}_m) + \chi(\beta_{n+1} - \beta_{n-1}) \right) a_n - J(a_{n+1} + a_{n-1}), \quad (21)$$

where  $W(t)$  is the expectation value of the phonon energy

$$W(t) = \langle \psi(t) | H_p | \psi(t) \rangle. \quad (22)$$

In Appendix B we show that

$$W(t) = \sum_n \left[ \frac{1}{2m} \pi_n^2 + \frac{1}{2} w(\beta_{n+1} - \beta_n)^2 \right] + \sum_q \frac{1}{2} \hbar \omega_q. \quad (23)$$

Thus the total phonon energy includes the zero-point energy in addition to the part expressed in terms of the position and momentum expectation values.

We also show in Appendix B that the other term appearing in (21) is

$$\frac{1}{2} \sum_m (\dot{\beta}_m \pi_m - \beta_m \dot{\pi}_m) = \sum_m \left[ \frac{1}{2m} \pi_m^2 + \frac{1}{2} w (\beta_{m+1} - \beta_m)^2 \right] - \frac{1}{2} \chi \sum_m (|a_{m+1}|^2 - |a_{m-1}|^2) \beta_m. \quad (24)$$

When this is combined with  $W(t)$ , it cancels all but the zero-point energy  $W_0 = \sum_q \hbar \omega_q / 2$ , so (21) becomes

$$i \hbar \dot{a}_n = \left[ E_0 + W_0 - \frac{1}{2} \chi \sum_m (|a_{m+1}|^2 - |a_{m-1}|^2) \beta_m + \chi (\beta_{n+1} - \beta_{n-1}) \right] a_n - J (a_{n+1} + a_{n-1}). \quad (25)$$

Equation (25) contains a set of terms which are independent of the site index  $n$ ,

$$\gamma(t) = E_0 + W_0 - \frac{1}{2} \chi \sum_m (|a_{m+1}|^2 - |a_{m-1}|^2) \beta_m. \quad (26)$$

If a phase change is performed on the amplitudes  $a_n$ ,

$$a_n(t) \rightarrow a_n(t) \exp \left[ -i \int \gamma(t') dt' / \hbar \right], \quad (27)$$

then the equation for the redefined  $a_n$ 's is

$$i \hbar \dot{a}_n = \chi (\beta_{n+1} - \beta_{n-1}) a_n - J (a_{n+1} + a_{n-1}). \quad (28)$$

Davydov<sup>1,2</sup> obtains for  $a_n(t)$  the equation

$$i \hbar \dot{a}_n = [E_0 + W_D(t) + \chi (\beta_{n+1} - \beta_{n-1})] a_n - J (a_{n+1} + a_{n-1}), \quad (29)$$

where  $W_D$  is given by (23), except that the zero-point energy is missing. A phase transformation similar to (27) removes the site-independent terms from (29), and (28) is again the result.

Equations (17) and (28) are the Davydov equations. They have been obtained here completely by quantum-

mechanical manipulations. We note that Eq. (25) derived by this method and (29) obtained by use of the classical Hamiltonian equations differ by a time-dependent global phase factor. As pointed out in Sec. IV of Ref. 4(b), this means that the two equations make different predictions for physically measurable quantities, e.g., optical spectra.

## APPENDIX A

To derive the equation of motion for  $a_n(t)$ , we need to differentiate

$$B(t) = e^{A(t)}, \quad (A1)$$

where  $A(t)$  is the exponent in (4).  $A(t)$  is not proportional to  $t$ , and operators  $A(t)$  at different times do not commute, and so the derivative is neither  $A(t)B(t)$  nor  $B(t)A(t)$ . We start from the definition of derivative,

$$B(t + \Delta t) - B(t) = e^{[A(t + \Delta t) - A(t)] + A(t)} - e^{A(t)}. \quad (A2)$$

Using the position-momentum commutation rule, we find the commutator of the two operators in (A2) is

$$[A(t + \Delta t) - A(t), A(t)] = (i/\hbar) \sum_n [\beta_n(t) \pi_n(t + \Delta t) - \beta_n(t + \Delta t) \pi_n(t)]. \quad (A3)$$

This is a  $c$  number and commutes with both  $A(t + \Delta t) - A(t)$  and  $A(t)$ , so we can use the formula

$$e^{C+D} = e^{-[C,D]/2} e^C e^D, \quad (A4)$$

which is valid for two operators which commute with their commutator. Equation (A2) becomes

$$B(t + \Delta t) - B(t) = (e^{-[A(t + \Delta t) - A(t), A(t)]/2} e^{A(t + \Delta t) - A(t)} - 1) e^{A(t)}. \quad (A5)$$

We now expand the quantities in the parentheses to lowest order in  $\Delta t$ :

$$B(t + \Delta t) - B(t) = \left[ -\Delta t \frac{1}{2} \frac{i}{\hbar} \sum_n [\beta_n(t) \dot{\pi}_n(t) - \dot{\beta}_n(t) \pi_n(t)] - \Delta t \frac{i}{\hbar} \sum_n [\dot{\beta}_n(t) p_n - \dot{\pi}_n(t) u_n] + \dots \right] e^{A(t)}; \quad (A6)$$

the omitted terms are proportional to higher powers of  $\Delta t$ . Dividing by  $\Delta t$  and taking the limit  $\Delta t \rightarrow 0$  gives the result

$$\frac{d}{dt} \exp \left[ - (i/\hbar) \sum_n [\beta_n(t) p_n - \pi_n(t) u_n] \right] = \left[ \frac{1}{2} \frac{i}{\hbar} \sum_n [\beta_n(t) \dot{\pi}_n(t) - \dot{\beta}_n(t) \pi_n(t)] - \frac{i}{\hbar} \sum_n [\dot{\beta}_n(t) p_n - \dot{\pi}_n(t) u_n] \right] \exp \left[ - (i/\hbar) \sum_n [\beta_n(t) p_n - \pi_n(t) u_n] \right]. \quad (A7)$$

## APPENDIX B

The expectation value of the phonon energy is [Eq. (22)]

$$W = \langle \beta, \pi | H_p | \beta, \pi \rangle = \langle \beta, \pi | \sum_q \hbar \omega_q (a_q^\dagger a_q + \frac{1}{2}) | \beta, \pi \rangle . \quad (\text{B1})$$

Since  $|\beta, \pi\rangle$  is a coherent state [(6)–(8)],

$$\langle \alpha_q | a_q^\dagger a_q | \alpha_q \rangle = |\alpha_q|^2 . \quad (\text{B2})$$

Using (9), we get

$$|\alpha_q|^2 = \frac{1}{\hbar} \left[ \frac{1}{2} m \omega_q |\beta_q|^2 + \frac{1}{2m\omega_q} |\pi_q|^2 \right] + \frac{i}{2\hbar} (\pi_q \beta_{-q} - \beta_q \pi_{-q}) . \quad (\text{B3})$$

The last term (which is real) is an odd function of  $q$  and sums to zero. The result for  $W$  is then

$$W = \sum_q \left[ \frac{1}{2m} |\pi_q|^2 + \frac{1}{2} m \omega_q^2 |\beta_q|^2 + \frac{1}{2} \hbar \omega_q \right] . \quad (\text{B4})$$

If the Fourier transform relations in (10) and the definition of the frequency in (3) are substituted here, then the first two terms can be written as the sums in real space given in (23).

The other term in (21) can be rewritten using the equations of motion for  $\dot{\beta}_m$  and  $\dot{\pi}_m$ , Eq. (17):

$$\frac{1}{2} \sum_m [\dot{\beta}_m \pi_m - \beta_m \dot{\pi}_m] = \frac{1}{2} \sum_m \left[ \frac{\pi_m}{m} \pi_m - \beta_m [w(\beta_{m+1} - 2\beta_m + \beta_{m-1}) + \chi(|a_{m+1}|^2 - |a_{m-1}|^2)] \right] . \quad (\text{B5})$$

Simplifying this and using the transformation

$$\sum_m (\beta_{m+1} - 2\beta_m + \beta_{m-1}) \beta_m = - \sum_m (\beta_{m+1} - \beta_m)^2 , \quad (\text{B6})$$

gives the result in (24).

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