Calculation of the Lifetime of a Davydov Soliton at Finite Temperature

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(Received 11 October 1988)

The standard Davydov Hamiltonian can be partially diagonalized using a method due to Eremko, Gaididei, and Vakhnenko. The complete Hamiltonian in this partially diagonalized form, however, includes a term omitted by these authors. Using this term in a first-order perturbation-theory calculation results in an estimate of the lifetime of a Davydov soliton at finite temperatures. The lifetime at 300 K is on the order of 10^{-12} s for parameters appropriate for the α-helical protein molecule. This is too short to be useful in biological processes.

PACS numbers: 87.15.By, 03.65.−w

In the 1970s Davydov proposed a soliton model for energy transport in biological molecules.[1-3] Following his original suggestion, the concept of the "Davydov soliton" has been utilized in many studies, including work by Davydov and his colleagues as well as a number of other investigators. In particular, the Davydov soliton has been put forward as the solution to the "crisis in bioenergetics" described by Green[4] and as a mechanism useful in the description of a variety of biological phenomena.[5,6] Numerical studies by Scott and co-workers[7,8] supported the appearance of Davydov solitons in α-helix protein molecules.

Considerable controversy has arisen in recent years over whether the lifetime of the Davydov soliton at nonzero temperature is sufficiently long for it to be biologically useful. This problem has been explored by a number of researchers using numerical simulations. Some have questioned the stability of Davydov solitons at temperatures of biological interest,[9,10] while others maintain that the Davydov soliton is stable at 300 K.[11,12] However, these investigations were based on the semiclassical Davydov treatment generalized for finite temperature.

In the research reported in this Letter, we have taken a different approach, exploring a quantum mechanical aspect of the Davydov model, namely, that an analytic perturbation-theoretic calculation of the lifetime can be made if the Hamiltonian is partially diagonalized using the method of Eremko, Gaididei, and Vakhnenko.[13] Our result is that the standard Davydov soliton has too short a lifetime at nonzero temperatures to be useful in biological processes.

In the Davydov model, the system is a one-dimensional chain of N identical sites described by the Hamiltonian

$$H=\sum_n[\epsilon_0 B_n^\dagger B_n - J(B_n^\dagger B_{n+1}+B_{n+1}^\dagger B_n)]+\tfrac{1}{2}\sum_n[p_n^2/m+w(u_n-u_{n-1})^2]+\chi\sum_n(u_{n+1}-u_{n-1})B_n^\dagger B_n\,, \tag{1}$$

where $B_n^\dagger$ and B_n are the creation and annihilation operators of an intramolecular excitation energy ϵ_0 on the nth site, and u_n and p_n are the displacement and momentum operators of the nth molecule.

By considering state vectors which are the product of a normalized one-exciton state and a coherent phonon state,

$$|\psi(t)\rangle=\sum_n \alpha(n,t)B_n^\dagger|0\rangle_{\text{ex}}\left[\exp\left(-\frac{1}{\sqrt{N}}\sum_q[f_q(t)a_q^\dagger+f_q^*(t)a_q]\right)\right]|0\rangle_{\text{ph}}\,. \tag{2}$$

Davydov obtained, using semiclassical approximations, nonlinear equations for the functions $\alpha(n,t)$ and $f_q(t)$ with soliton solutions of the form

$$\alpha(n,t)=\left(\frac{\mu}{2}\right)^{1/2}\operatorname{sech}[\mu(n-vt)]\exp\left[\frac{i}{\hbar}\left(\frac{\hbar^2 vn}{2J}-E_{\text{sol}}(v)t\right)\right], \tag{3}$$

$$f_q(t)=\frac{i\pi\chi}{w\mu(1-s^2)}\left(\frac{m}{2\hbar\omega_q}\right)^{1/2}\frac{\omega_q+qv}{\sinh(\pi qR/2\mu)}e^{iqvt}\equiv f_q e^{iqvt} \tag{4}$$

in the continuum limit. Here $a_q^\dagger$ and a_q are the phonon creation and annihilation operators, $v=\nu R$ is the soliton velocity, $s=v/v_a$ is the ratio of the soliton speed to the speed of sound in the chain,

$$E_{\text{sol}}(v)=\epsilon_0-2J+\frac{\hbar^2 v^2}{4J}-\frac{1}{3}\mu^2 J,\quad \mu=\frac{\chi^2}{(1-s^2)wJ},\quad v_a=R(w/m)^{1/2},\quad \omega_q=2(w/m)^{1/2}|\sin(qR/2)|\,.$$

In order to carry out the partial diagonalization, the Hamiltonian is first replaced by

$$\tilde{H}=H-\sum_k \hbar k v(a_k^\dagger a_k-B_k^\dagger-B_k)\,, \tag{5}$$

where

$$B_k^\dagger = \frac{1}{\sqrt{N}} \sum_n e^{iknR} B_n^\dagger .$$

Thus the analysis is made in the reference frame moving with the soliton at velocity v. New phonons can be defined by

$$b_q^\dagger = a_q^\dagger - \frac{1}{\sqrt{N}} f_q^*, \quad b_q = a_q - \frac{1}{\sqrt{N}} f_q . \tag{6}$$

The coherent phonon state (lattice distortion) then becomes the vacuum state of the new phonons:

$$|\tilde{0}\rangle_{\mathrm{ph}} = \exp\left[-\frac{1}{\sqrt{N}} \sum_q (f_q a_q^\dagger + f_q^* a_q) \right] |0\rangle_{\mathrm{ph}} , \tag{7}$$

where $b_q |\tilde{0}\rangle_{\mathrm{ph}} = 0$.

The partial diagonalization is achieved by the following transformation:

$$A_\lambda^\dagger = \sum_n a_\lambda(n) B_n^\dagger , \tag{8}$$

with

$$a_k(n) = \frac{1}{\sqrt{N}} \frac{\mu \tanh(\mu n) - ikR}{\mu - ikR} \exp\left[i \left(\frac{\hbar v}{2J} + kR \right) n \right] \tag{9}$$

and

$$a_s(n) = \left(\frac{\mu}{2} \right)^{1/2} \mathrm{sech}(\mu n) \exp\left[i \frac{\hbar v n}{2J} \right] . \tag{10}$$

Here $A_s^\dagger$ an excitation which is localized at the lattice distortion, while $A_k^\dagger$ creates an unbound excitation with wave vector k.

It is straightforward to calculate that

$$\tilde{H} = E_s A_s^\dagger A_s + \sum_k E_k A_k^\dagger A_k + \sum_q \hbar(\omega_q - qv) b_q^\dagger b_q + \tfrac{2}{3}\mu^2 J + \frac{1}{\sqrt{N}} \sum_q \hbar(\omega_q - qv)(1 - A_s^\dagger A_s)(B_q^\dagger f_q + f_q^* b_q)$$
$$+ \frac{1}{\sqrt{N}} \sum_{q,k} X(k,q) A_{k+q}^\dagger A_k (b_{-q}^\dagger + b_q) + \frac{1}{N} \sum_{q,k} \bar{X}(k,q)(A_s^\dagger A_{-k} + A_k^\dagger A_s)(b_{-q}^\dagger + b_q) , \tag{11}$$

where

$$E_s = \epsilon_0 - 2J - \hbar^2 v^2/4J - \mu^2 J, \quad E_k = \epsilon_0 - 2J - \hbar^2 v^2/4J + (kR)^2 J , \tag{12}$$

$$X(k,q) = i\chi \left(\frac{2\hbar}{m\omega_q} \right)^{1/2} \sin(qR) \left\{ 1 - \frac{i\mu q R}{[\mu - i(k+q)R][\mu - ikR]} \right\} , \tag{13}$$

$$\bar{X}(k,q) = \frac{2i\pi\chi}{\sqrt{2\mu}} \left(\frac{1}{2m\omega_q} \right)^{1/2} \sin(qR) \left[\frac{iqR}{\mu + ikR} \right] \mathrm{sech}\left[\frac{\pi R}{2\mu}(q-k) \right] . \tag{14}$$

In the paper by Eremko, Gaididei, and Vekhnenko[13] the last term of $\tilde{H}$, containing $(A_s^\dagger A_{-k} + A_k^\dagger A_s)(b_{-q}^\dagger + b_q)$, is omitted. If this term is omitted, the Davydov soliton state $A_s^\dagger |0\rangle_{\mathrm{ex}} |\tilde{0}\rangle_{\mathrm{ph}}$ is an exact eigenstate of $\tilde{H}$ with energy $E_s + \frac{2}{3}\mu^2 J$. It is this term, however, that yields a lifetime in first-order perturbation theory.

For the perturbation calculation, consider $\tilde{H} = \tilde{H}_0 + V$, where

$$V = \frac{1}{N} \sum_{q,k} \bar{X}(k,q)(A_s^\dagger A_{-k} + A_k^\dagger A_s)(b_{-q}^\dagger + b_q) + \frac{1}{\sqrt{N}} \sum_{q,k} X(k,q) A_{k+q}^\dagger A_k (b_{-q}^\dagger + b_q) . \tag{15}$$

In the calculation, the initial states are of the form

$$|i\rangle = \prod_q \frac{(b_q^\dagger)^{\tilde{n}_q}}{(\tilde{n}_q!)^{1/2}} A_s^\dagger |0\rangle_{\mathrm{ex}} |\tilde{0}\rangle_{\mathrm{ph}} \tag{16}$$

and the final states are of the form

$$|fk\rangle = \prod_q \frac{(a_q^\dagger)^{n_q}}{(n_q!)^{1/2}} A_k^\dagger |0\rangle_{\mathrm{ex}} |0\rangle_{\mathrm{ph}} . \tag{17}$$

Note that the initial state is expressed in terms of the "new" phonons, while the final state is expressed in terms of the ordinary phonons.

In the case of interest, the initial phonon distribution will be taken to be a thermal average, so that we consider the transition probability for a transition from a state consisting of a single Davydov soliton together with a thermal distribution of new phonons to a final state without the soliton:

$$W = \frac{1}{\hbar^2} \int_0^t dt' \int_0^t dt'' \left\{ \sum_{fk'} \sum_i P_i^{(\mathrm{ph})} \langle i | \exp\left[\frac{i\tilde{H}_0 t''}{\hbar} \right] V \exp\left[\frac{-i\tilde{H}_0 t''}{\hbar} \right] |fk'\rangle\langle fk'| \exp\left[\frac{i\tilde{H}_0 t'}{\hbar} \right] V \exp\left[\frac{-i\tilde{H}_0 t'}{\hbar} \right] |i\rangle \right\} . \tag{18}$$

Using the explicit form for V and the fact that the sum over states $|fk'\rangle$ contains a complete set of phonons for each value of k' one can rewrite W as

$$W=\frac{1}{\hbar^2}\frac{4\pi^2\chi^2}{2\mu N^2}\sum_k\sum_{k'}\sum_{k''}\left[\frac{\hbar}{2m\omega_k}\right]^{1/2}\left[\frac{\hbar}{2m\omega_{k''}}\right]^{1/2}\frac{(kR)(k''R)\sin(kR)\sin(k''R)}{\mu^2+(k'R)^2}\operatorname{sech}\left[\frac{\pi R}{2\mu}(k-k')\right]\operatorname{sech}\left[\frac{\pi R}{2\mu}(k''-k')\right]$$
$$\times\int_0^t dt'\int_0^t dt''\left\{\exp\left[\frac{-i}{\hbar}\left[\frac{J\mu^2}{3}+J(k'R)^2\right](t'-t'')\right]\right.$$
$$\times\left\langle\left\langle\exp\left[i\sum_q(\omega_q-qv)b_q^\dagger b_q(t'-t'')\right](b_k^\dagger+b_{-k})\right.\right.$$
$$\left.\left.\left.\times\exp\left[-i\sum_q(\omega_q-qv)a_q^\dagger a_q(t'-t'')\right](b_{-k''}^\dagger+b_{k''})\right\rangle\right\rangle\right\}, \quad (19)$$

where

$$\langle\langle\theta\rangle\rangle=\mathrm{Tr}\left\{\exp\left[-\beta\sum_q(\omega_q-qv)b_q^\dagger b_q\right]\theta\right\}\Big/\mathrm{Tr}\left\{\exp\left[-\beta\sum_q(\omega_q-qv)b_q^\dagger b_q\right]\right\}$$

is the thermal average.

To estimate a lifetime for the soliton, we are interested in the long-time behavior of dW/dt. By straightforward calculation this is seen to be

$$\lim_{t\to\infty}\frac{dW}{dt}=\frac{1}{\hbar^2}\left[\frac{4\pi^2\chi^2}{2\mu N^2}\right]\sum_k\sum_{k'}\sum_{k''}\left[\frac{\hbar}{2m\omega_k}\right]^{1/2}\left[\frac{\hbar}{2m\omega_{k''}}\right]^{1/2}\frac{(kR)(k''R)\sin(kR)\sin(k''R)}{\mu^2+(k'R)^2}\operatorname{sech}\left[\frac{\pi R}{2\mu}(k-k')\right]$$
$$\times\operatorname{sech}\left[\frac{\pi R}{2\mu}(k''-k')\right]2\,\mathrm{Re}\left\{\int_0^\infty dt\exp\left[-\frac{i}{\hbar}\left[\frac{J\mu^2}{3}+J(k'R)^2\right]t\right]\right.$$
$$\times\left\langle\left\langle\exp\left[i\sum_q(\omega_q-qv)b_q^\dagger b_q t\right](b_k^\dagger+b_{-k})\right.\right.$$
$$\left.\left.\left.\times\exp\left[-i\sum_q(\omega_q-qv)a_q^\dagger a_q t\right](b_{-k''}^\dagger+b_{k'})\right\rangle\right\rangle\right\}. \quad (20)$$

In order to evaluate this expression, it is necessary to calculate the thermal average,

$$U(k,k'')=\left\langle\left\langle\exp\left[i\sum_q(\omega_q-qv)b_q^\dagger b_q t\right](b_k^\dagger+b_{-k})\exp\left[-i\sum_q(\omega_q-qv)a_q^\dagger a_q t\right](b_{-k''}^\dagger+b_{k''})\right\rangle\right\rangle. \quad (21)$$

Since the energy of the soliton state is less than that of the localized exciton in the undeformed lattice, the part of $U(k,k'')$ corresponding to the absorption of a phonon makes the major contribution to the sum in (20) at the temperature and parameter values of interest. Furthermore, the off-diagonal terms of $U(k,k'')$ are negligible unless $|k|$ and $|k''|$ are of the order of $2\mu/\pi R$ or less. Since small wave vectors do not significantly contribute to the sum when $\pi^2/2\mu\gg1$, we may replace $U(k,k'')$ by $I_1(k,k'')\delta_{kk''}$ in (20), where

$$I_1(k,k)=\exp[i(\omega_k-kv)t]\left\langle\left\langle b_k^\dagger\exp\left[i\sum_q(\omega_q-qv)b_q^\dagger b_q t\right]\exp\left[-i\sum_q(\omega_q-qv)a_q^\dagger a_q t\right]b_k\right\rangle\right\rangle. \quad (22)$$

$I_1(k,k)$ can be evaluated exactly as

$$I_1(k,k)=\frac{\exp[i(\omega_k-kv)t+g(t)+\zeta(t)]}{\exp[\beta\hbar(\omega_k-kv)]-1}, \quad (23)$$

where

$$g(t)=\frac{1}{N}\sum_q|f_q|^2\{\exp[-i(\omega_q-qv)t]-1\}, \quad (24)$$

$$\zeta(t)=-\frac{4}{N}\sum_q\frac{|f_q|^2\sin^2[\frac{1}{2}(\omega_q-qv)t]}{\exp[\beta\hbar(\omega_q-qv)]-1}. \quad (25)$$

For soliton velocity $v=0$,

$$g(t)\simeq-g_0\int_0^\infty\frac{y}{\sinh^2 y}\{[1-\cos(\omega_a ty)]+i\sin(\omega_a ty)\}dy, \quad (26)$$

where

$$g_0=\frac{2\chi^2}{\pi\hbar w}\left[\frac{m}{w}\right]^{1/2}, \quad \omega_a=\frac{2\mu}{\pi}\left[\frac{w}{m}\right]^{1/2}.$$

For $t>0.002/\omega_a$, $g(t)$ is well approximated by

$$g(t)\simeq-g_0[\ln(\tfrac{1}{2}\omega_a t)+1.577+\tfrac{1}{2}i\pi]. \quad (27)$$

$\zeta(t)$ can be easily evaluated for $v=0$ and temperature $T>T_0$, where $T_0=\hbar\omega_a/k_B$:

$$\zeta(t)\simeq\frac{-4g_0}{\omega_a}\left[\frac{T}{T_0}\right]\int_0^\infty d\omega\frac{\sin^2[\frac{1}{2}\omega t]}{\sinh^2(\omega/\omega_a)}$$
$$=2g_0\left[\frac{T}{T_0}\right][1-\tfrac{1}{2}\pi\omega_a t\coth(\tfrac{1}{2}\pi\omega_a t)]. \quad (28)$$

We note that $\lim_{t\to\infty}\zeta(t) = -\gamma t$, where $\gamma = \pi g_0/\beta\hbar = \pi g_0 k_B T/\hbar$. If we write $\Delta(k,k') = \frac{1}{3}J\mu^2 + (k'R)^2 J - \hbar\omega_k$,

$$\lim_{t\to\infty}\frac{dW}{dt} = \frac{1}{\hbar^2}\left(\frac{\chi^2}{2\mu}\right)\left(\frac{2\pi}{N}\right)^2 \sum_{k,k'}\left(\frac{\hbar}{2m\omega_k}\right)\frac{(kR)^2\sin^2(kR)\operatorname{sech}^2[(\pi R/2\mu)(k-k')]}{\mu^2+(k'R)^2} \times 2\,\mathrm{Re}\left\{\int_0^\infty dt\,\frac{\exp(-i\Delta t/\hbar)\exp[g(t)+\zeta(t)]}{\exp[\beta\hbar\omega_k]-1}\right\}. \tag{29}$$

Using $\zeta(t) \simeq -\gamma t$ and $g(t) = -g_0[\ln(\frac{1}{2}\omega_a t) + 1.577 + \frac{1}{2}i\pi]$ the integral can be evaluated[14]:

$$\begin{aligned}
\mathrm{Re}\int_0^\infty dt\,\exp\left(\frac{i\Delta t}{\hbar}\right)\exp[g(t)+\zeta(t)]
&= (2.42\omega_a)^{-g_0}\Gamma(1-g_0)\left[\gamma^2+\left(\frac{\Delta}{\hbar}\right)^2\right]^{-(1-g_0)/2} \\
&\quad\times\left\{\cos\left(\frac{g_0\pi}{2}\right)\cos\left[(1-g_0)\tan^{-1}\left(\frac{\Delta}{\gamma\hbar}\right)\right] - \sin\left(\frac{g_0\pi}{2}\right)\sin\left[(1-g_0)\tan^{-1}\left(\frac{\Delta}{\gamma\hbar}\right)\right]\right\} \\
&\simeq \left(\frac{\omega_a}{\gamma}\right)^{-g_0}\frac{\gamma}{\gamma^2+(\Delta/\hbar)^2}, \quad \text{for } g_0 \ll 1\,.
\end{aligned} \tag{30}$$

The small-g_0 approximation is appropriate, since $g_0 \simeq 0.06$ for typical values of the physical constants used to describe the α-helical protein molecule.

Hence, for $g_0 \ll 1$, $T \gg T_0$, and $v=0$, we find

$$\lim_{t\to\infty}\frac{dW}{dt} = \frac{1}{\hbar^2}\frac{\chi^2}{\mu}\left(\frac{2\pi}{N}\right)^2 \sum_{k,k'}\left(\frac{\hbar}{2m\omega_k}\right)\frac{(kR)^2\sin^2(kR)\operatorname{sech}^2[(\pi R/2\mu)(k-k')]}{[\mu^2+(k'R)^2][\exp(\beta\hbar\omega_k - 1]} \times\left(\frac{\omega_a}{\gamma}\right)^{-g_0}\frac{\gamma}{\gamma^2+[J\mu^2/3\hbar + J(k'R)^2/\hbar - \omega_k]^2}. \tag{31}$$

This expression can be calculated numerically using generally accepted values for the physical constants. In the literature there is wide agreement on the following values[8-11]:

$J = 1.55\times10^{-22}$ J, $m = (1.17\text{–}1.91)\times10^{-25}$ kg, $w = 13\text{–}19.5$ N/m, $\chi = (2.0\text{–}6.2)\times10^{-11}$ N.

Using values in these ranges yields values for $\lim_{t\to\infty} dW/dt$ between $5.3\times10^{11}\ \mathrm{s}^{-1}$ and $2.9\times10^{12}\ \mathrm{s}^{-1}$ with corresponding lifetimes between 3.4×10^{-13} s and 1.9×10^{-12} s. In this amount of time a Davydov soliton, traveling at half the speed of sound in the chain, would travel fewer than ten lattice spacings. Thus the lifetime of the Davydov soliton at 300 K appears to be at least 2 orders of magnitude too small to allow this soliton to be biologically useful.

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