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Davydov Solitons in Polypeptides [and Discussion]

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Davydov solitons in polypeptides

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The experimental evidence for self-trapping of amide-I (CO stretching) vibrational energy in crystalline acetanilide (a model protein) is reviewed and related to A. S. Davydov's theory of solitons as a mechanism for energy storage and transport in protein. Particular attention is paid to the construction of quantum states that contain N amide-I vibrational quanta. It is noted that the '$N=2$' state is almost exactly resonant with the free energy that is released upon hydrolysis of adenosine triphosphate.

1. Introduction

In living organisms a fundamental mechanism for the transfer of energy into functional proteins or enzymes is the hydrolysis of adenosine triphosphate (ATP) into adenosine diphosphate (ADP) according to the reaction

$$\mathrm{ATP}^{4-} + \mathrm{H_2O} \rightarrow \mathrm{ADP}^{3-} + \mathrm{HPO}_4^{2-} + \mathrm{H}^+. \tag{1.1}$$

Under normal physiological conditions about 10 kcal mol^{-1}† or 0.422 eV of free energy is released by this reaction (Fox 1982), which leads to several interesting questions: how is this free energy transferred into protein? How is it stored there? How does it move inside a protein? How is it transformed into useful work?

To answer questions of this sort a theory was proposed by Davydov & Kislukha (1973), which focused attention on the self-trapping of molecular vibrational energy in the amide-I (or CO stretch) vibration of the peptide unit (CONH), a basic structural element of all proteins. Roughly speaking, it was proposed that the localization of amide-I vibrational energy would alter the surrounding structure (primarily the hydrogen bonding) and that this local alteration would, in turn, lower the amide-I energy enough to prevent its dispersion.

At about the same time as the original paper by Davydov & Kislukha (1973), Careri (1973) published some unexpected spectral measurements in the amide-I region of crystalline acetanilide $(\mathrm{CH_3CONHC_6H_5})_x$ or ACN. As the temperature was lowered from room temperature, he observed an anomalous amide-I band (at 1650 cm^{-1}) growing up on the red side of the normal amide-I band (at 1665 cm^{-1}). This 1650 cm^{-1} band was called anomalous because it could not be explained with accepted concepts of molecular spectroscopy (for example, Fermi resonance, Davydov splitting, etc). At first Careri suspected some unusual one-dimensional phase transformation might provide an explanation, but no such evidence was found after several years of experimental work. Recently a self-trapping theory was proposed (Careri *et al.* 1983), which is closely related to that of Davydov and explains the salient experimental facts (Careri *et al.* 1984; Eilbeck *et al.* 1984).

The present situation, therefore, is that the 1650 cm^{-1} band in ACN seems to provide direct experimental evidence for a self-trapped state of molecular vibrational energy. The 'red shift'

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† 1 kcal = 4.184 kJ.

of 15 cm^{-1} from the normal band can be considered as the binding energy of a 'Davydov-like' soliton, and this interpretation leads to quantitative predictions of biological significance.

This paper is organized into three broad phases. The first is a review of Davydov soliton theory and the experimental observations in crystalline acetanilide. The second phase is a detailed comparison of various attempts to provide a quantum mechanical explanation for self-trapping of molecular vibrations. Finally, some questions of biological significance are briefly considered.

Before turning to the details let me interject a comment on the nature of research in biophysics and in biology. Biophysics, in my view, is different from biology. Biophysics attempts to make known the mechanisms that are possible in biological organisms and those that are not. Given this 'menu of possible mechanisms', it is the task of true biological research to make known what actually happens in an organism. This paper is primarily an exercise in biophysics.

2. DAVYDOV SOLITON THEORY

This section is intended to provide a brief summary of Davydov soliton theory for the convenience of the reader. Such a summary is helpful to appreciate the differences between the theory of self-trapping proposed for proteins and the theory proposed recently to explain experimental measurements on crystalline acetanilide. It is also necessary to see how the quantum theory developed by Davydov as a basis for self-trapping is related to other quantum analyses. Several detailed surveys of this work are available for further reference (Davydov 1979*a*, 1982*b*), and a somewhat more general analysis has recently been published by Takeno (1983).

Consider the α-helix structure of protein that is shown in figure 1. Careful inspection reveals three channels situated approximately in the longitudinal direction with the sequence

$$\text{---H–N–C=O---H–N–C=O---H–N–C=O---H–N–C=O---},$$

where the broken lines represent hydrogen bonds. One of these channels is indicated by hatching on figure 1. For a detailed analysis it is necessary to consider the interaction of all three channels, but one is sufficient to lay out the basic ideas.

A single channel is governed by the energy operator

$$\hat{H} = \hat{H}_{\mathrm{CO}} + \hat{H}_{\mathrm{ph}} + \hat{H}_{\mathrm{int}}. \tag{2.1}$$

(Throughout this paper the circumflex will be used to indicate an operator.) Taking the components of $\hat{H}$ in order, $\hat{H}_{\mathrm{CO}}$ is an energy operator for the CO stretch (amide-I) vibration including the effects of nearest-neighbour dipole–dipole interactions. Thus

$$\hat{H}_{\mathrm{CO}} = \sum_n [E_0 \hat{b}_n^\dagger \hat{b}_n - J(\hat{b}_{n+1}^\dagger \hat{b}_n + \hat{b}_n^\dagger \hat{b}_{n+1})], \tag{2.2}$$

where E_0 is the fundamental energy of the amide-I vibration, $-J$ is the nearest neighbour dipole–dipole interaction energy, and $\hat{b}_n^\dagger(\hat{b}_n)$ are boson creation (annihilation) operators for amide-I quanta on the *n*th molecule.

$\hat{H}_{\mathrm{ph}}$ is the energy operator for longitudinal (acoustic) sound waves. Thus

$$\hat{H}_{\mathrm{ph}} = \tfrac{1}{2} \sum_n [M^{-1}\hat{p}_n^2 + W(\hat{u}_n - \hat{u}_{n-1})^2], \tag{2.3}$$

where M is the mass of a molecule, W is the spring constant of a hydrogen bond, $\hat{p}_n$ is a longitudinal momentum operator for the nth molecule, and $\hat{u}_n$ is the corresponding longitudinal position operator.

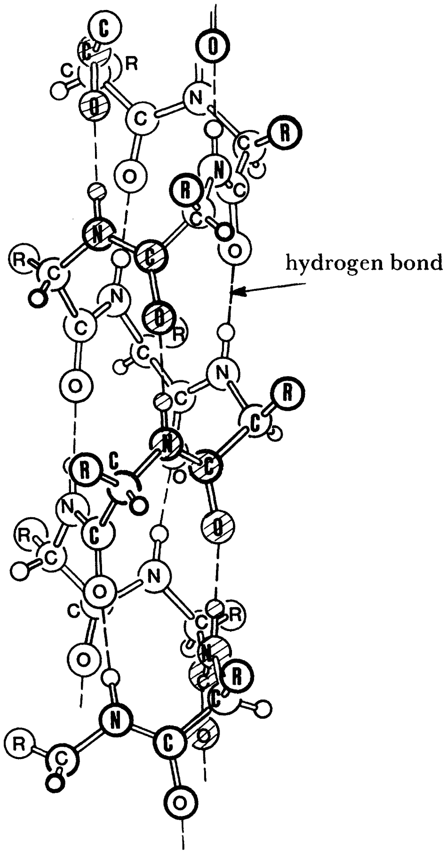

FIGURE 1. The atomic structure of α-helix in protein. One of the longitudinal, hydrogen-bonded, peptide channels is shown hatched.

Interaction between amide-I vibrations and longitudinal sound waves occurs through the interaction energy operator

$$\hat{H}_{\text{int}} = \chi_{\text{a}} \Sigma \, (\hat{u}_n - \hat{u}_{n-1}) \, \hat{b}_n^{\dagger} \, \hat{b}_n, \tag{2.4}$$

where χ_{a} is the derivative of amide-I vibrational energy with respect to the length (R) of the adjacent hydrogen bond. Thus

$$\chi_{\text{a}} \equiv \mathrm{d}E_0/\mathrm{d}R. \tag{2.5}$$

Values for the parameters in these equations are listed in table 1.

TABLE 1. PHYSICAL PARAMETERS FOR DAVYDOV'S HAMILTONIAN

parameter	value	unit	references
E_0	0.21	eV	Nevskaya & Chirgadze (1976)
J	7.8	cm^{-1}	Nevskaya & Chirgadze (1976)
M	114	m_{p}	Scott (1982, 1983)
W	13	N m^{-1}	Itoh & Shimanouchi (1972)
χ_{a}	6.2×10^{-11}	N	Careri *et al.* (1984)

It is interesting to observe that this is a biological problem for which all the physical parameters have been determined.

Davydov minimizes the average value of $\hat{H}$ with respect to the wavefunction

$$|\psi\rangle = \sum_n a_n(t) \exp[\hat{\sigma}(t)]\, \hat{b}_n^\dagger |0\rangle, \tag{2.6}$$

where

$$\hat{\sigma} \equiv -\frac{\mathrm{i}}{\hbar} \sum_n [\beta_n(t)\, \hat{p}_n - \pi_n(t)\, \hat{u}_n]. \tag{2.7}$$

A straightforward calculation shows that

$$\beta_n(t) = \langle\psi|\hat{u}_n|\psi\rangle \tag{2.8}$$

and

$$\pi_n(t) = \langle\psi|\hat{p}_n|\psi\rangle. \tag{2.9}$$

The wavefunction in (2.6) will be called *Davydov's ansatz* throughout this paper. One of the aims here is to study the range of validity of this ansatz.

Assuming that Davydov's ansatz approximates the true wavefunction, (2.8) and (2.9) show that β_n and π_n are the average values of the position and momentum operators respectively. Furthermore, a_n is the probability amplitude for finding a quantum of amide-I vibrational energy on the nth molecule. The normalization condition $\langle\psi|\psi\rangle = 1$ implies that

$$\sum_n |a_n|^2 = 1. \tag{2.10}$$

Thus Davydov's ansatz describes the dynamics of a single quantum of amide-I vibrational energy.

Minimization of $\langle\psi|\hat{H}|\psi\rangle$ with respect to a_n, β_n and π_n leads to the differential difference equations

$$\left(\mathrm{i}\hbar\frac{\mathrm{d}}{\mathrm{d}t} - E_0\right) a_n + J(a_{n+1} + a_{n-1}) - \chi_a(\beta_n - \beta_{n-1})\, a_n = 0, \tag{2.11a}$$

$$M\frac{\mathrm{d}^2\beta_n}{\mathrm{d}t^2} - W(\beta_{n+1} - 2\beta_n + \beta_{n-1}) = \chi_a[|a_{n+1}|^2 - |a_n|^2]. \tag{2.11b}$$

Extensive numerical and theoretical analysis of (2.11) yields the following results (Scott 1982, 1984; MacNeil & Scott 1984). (i) It is reasonable to expect soliton formation at the level of energy released by ATP hydrolosis (1.1), and (ii) such a soliton travels rather slowly with respect to the speed of longitudinal sound waves. This suggests neglecting the kinetic energy of longitudinal sound by assuming $\dot{\beta}_n = 0$, whereupon

$$\beta_n - \beta_{n-1} \approx -\chi_\mathrm{a} |a_n|^2 / W \tag{2.12}$$

and, in this 'adiabatic approximation', (2.11) becomes

$$\left(\mathrm{i}\hbar\frac{\mathrm{d}}{\mathrm{d}t} - E_0\right) a_n + J(a_{n+1} + a_{n-1}) + \gamma_\mathrm{a} |a_n|^2 a_n = 0, \tag{2.13}$$

where

$$\gamma_\mathrm{a} \equiv \chi_\mathrm{a}^2 / W. \tag{2.14}$$

Davydov has emphasized that a solitary wave solution of (2.11) cannot be created directly by absorption of a photon because of an unfavourable Franck–Condon factor. This is because the necessary intermolecular displacement in (2.11 *b*) cannot occur in a time that is short enough for photon absorption. The Franck–Condon factor will be discussed in detail in the following section.

3. Self-trapping in crystalline acetanilide

A unit cell of crystalline acetanilide (ACN) is shown in figure 2. Just as in the α-helix, careful inspection of figure 2 reveals channels situated in the *b*-direction with the sequence

$$\text{---H–N–C=O---H–N–C=O---H–N–C=O---H–N–C=O---.}$$

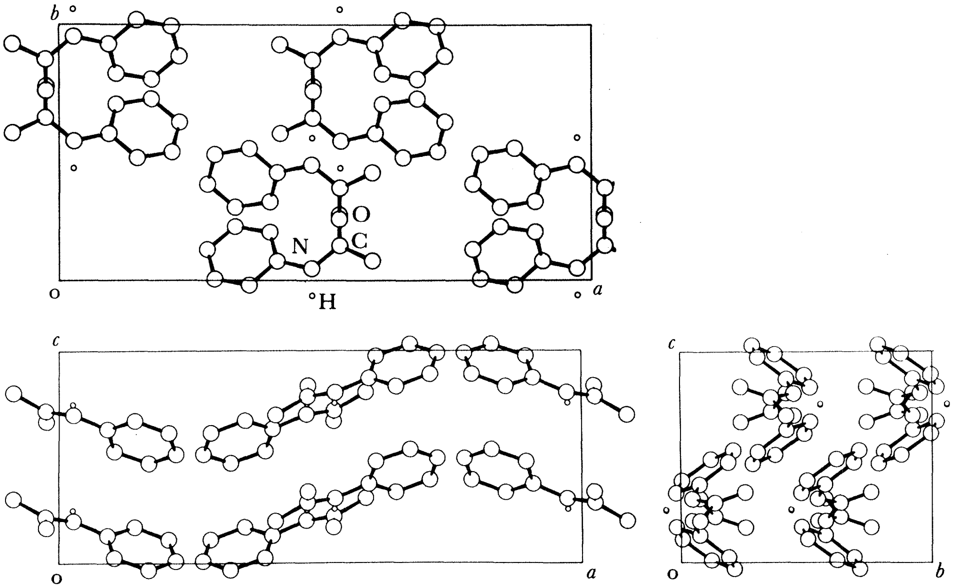

Figure 2. The unit cell of crystalline acetanilide.

Recent infrared absorption measurements on microcrystals of ACN are shown in figure 3. Attention here is focused on the band at 1650 cm^{-1}, which rises with decreasing temperature to become the dominant spectral feature below 100 K.

When this band was discovered, Careri (1973) suspected it to be caused by a subtle phase change along the *b*-direction of the crystal, but careful studies over a period of several years (Careri *et al.* 1984) failed to reveal any such evidence. The lack of a viable alternative eventually led to the suggestion that the 1650 cm^{-1} band might be caused by direct absorption of an infrared photon into a self-trapped state similar to that proposed by Davydov. The qualifier 'similar' is important because, as was noted above, the Franck–Condon factor is unfavourable for direct photon absorption by a self-trapped solution of (2.11).

The corresponding theory proceeds, as in the previous section, by defining the energy operator

$$\hat{H} = \hat{H}_{\text{CO}} + \hat{H}_{\text{ph}} + \hat{H}_{\text{int}}, \tag{3.1}$$

where $\hat{H}_{\text{CO}}$ is again given by (2.2), but with (Eilbeck *et al.* 1984)

$$J = 3.96\ \text{cm}^{-1}. \tag{3.2}$$

In the present analysis, however, self-trapping is assumed to be caused by interaction with an optical phonon rather than an acoustic phonon. Thus

$$\hat{H}_{\mathrm{ph}} = \tfrac{1}{2}\sum_n \,[m^{-1}\hat{p}_n^2 + w\hat{q}_n^2] \tag{3.3}$$

and

$$\hat{H}_{\mathrm{int}} = \chi_0 \sum_n \hat{q}_n\, \hat{b}_n^{\dagger}\, \hat{b}_n. \tag{3.4}$$

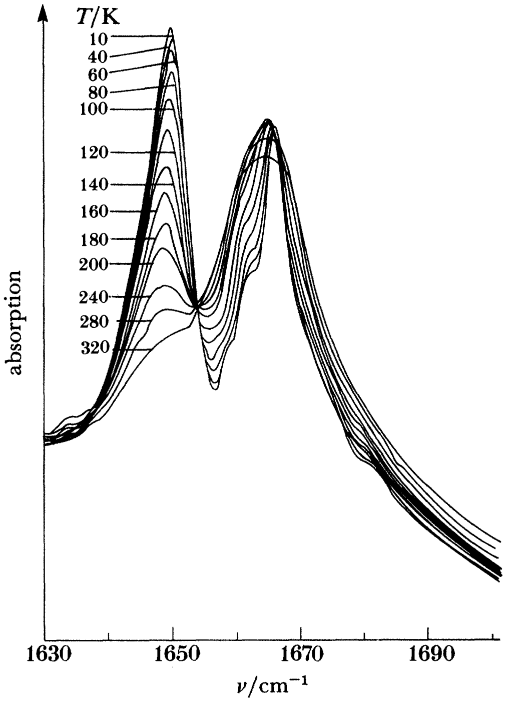

FIGURE 3. Infrared absorption spectra in the amide-I (CO stretching) region of crystalline acetanilide. (From Careri *et al.* 1984.)

Minimization of $\langle\psi|\hat{H}|\psi\rangle$ with respect to the parameters of the Davydov ansatz wave-function (2.6), where

$$\hat{\sigma} \equiv -\frac{\mathrm{i}}{\hbar}\sum_n \,[q_n(t)\,\hat{p}_n - p_n(t)\,\hat{q}_n] \tag{3.5}$$

leads to the dynamic equations

$$\left(\mathrm{i}\hbar\frac{\mathrm{d}}{\mathrm{d}t} - E_0\right)a_n + J(a_{n+1} + a_{n-1}) - \chi_0\, q_n\, a_n = 0, \tag{3.6a}$$

$$m\frac{\mathrm{d}^2 q_n}{\mathrm{d}t^2} - wq_n = \chi_0\,|a_n|^2. \tag{3.6b}$$

As before

$$q_n(t) = \langle\psi|\,\hat{q}_n\,|\psi\rangle. \tag{3.7}$$

The adiabatic approximation ($\dot{q}_n = 0$) reduces (3.6) to

$$\left(\mathrm{i}\hbar\frac{\mathrm{d}}{\mathrm{d}t} - E_0\right)a_n + J(a_{n+1} + a_{n-1}) + \gamma_0\,|a_n|^2\, a_n = 0, \tag{3.8}$$

where
$$\gamma_0 \equiv \chi_0^2/w. \tag{3.9}$$

A detailed numerical study of a system of equations similar to (3.8), but representing one hundred molecules of ACN in two coupled channels has recently been made by Eilbeck *et al.* (1984). This work shows that the red shift from the normal amide-I band at 1665 $\mathrm{cm^{-1}}$ to the 1650 $\mathrm{cm^{-1}}$ band is best fitted by choosing

$$\gamma_0 = 44.7\ \mathrm{cm^{-1}}. \tag{3.10}$$

We turn next to an estimate of the Franck–Condon factor for direct photon absorption by a self-trapped state of (3.6). Before absorption $|a_n|^2 = 0$, and after absorption $|a_n|^2 \neq 0$ over a localized region, such that (2.10) is satisfied. Thus the ground state wavefunction of (3.6*b*) must shift from

$$\Phi_0 = \left(\frac{w}{\pi\hbar\omega}\right)^{\frac{1}{2}} \exp\left(-q_n^2 \frac{w}{2\hbar\omega}\right) \tag{3.11}$$

before absorption to

$$\tilde{\Phi}_0 = \left(\frac{w}{\pi\hbar\omega}\right)^{\frac{1}{2}} \exp\left[-(q_n+\gamma_0|a_n|^2)^2 \frac{w}{2\hbar\omega}\right] \tag{3.12}$$

after absorption, where

$$\omega = (w/m)^{\frac{1}{2}} \tag{3.13}$$

is the frequency of the optical mode that is mediating the self-trapping. The transition probability for soliton absorption is therefore reduced by the Franck–Condon factor

$$\left(\int \Phi_0 \tilde{\Phi}_0 \,\mathrm{d}q_n\right)^2 \geqslant \exp(-\gamma_0/2\hbar\omega), \tag{3.14}$$

which is close to unity for

$$\gamma_0 \ll \hbar\omega. \tag{3.15}$$

The frequency (ω) of the optical mode can be determined from the temperature dependence of the 1650 $\mathrm{cm^{-1}}$ line in figure 3. Such temperature dependence is expected, because the probability of (3.6*b*) being in its ground state, and therefore able to participate in self-trapping, is $[1-\exp(-\hbar\omega/kT)]$. Thus as temperature is raised, the low temperature factor given in (3.14) should be reduced by the additional factor $[1-\exp(-\hbar\omega/kT)]^2$. A least-square fit to intensity data of figure 3 is obtained for $\hbar\omega = 131\ \mathrm{cm^{-1}}$. Together with (3.10) this implies that $\exp(-\gamma_0/2\hbar\omega) = 0.84$.

Further evidence tending to favour a self-trapping explanation for the 1650 $\mathrm{cm^{-1}}$ band is the recent observation of the overtone series shown in table 2 (Scott *et al.* 1985).

Table 2. Overtone series for the ACN soliton

N	$v(N)/\mathrm{cm^{-1}}$	energy/eV
1	1650	0.205
2	3250	0.403
3	4803	0.595
4	6304	0.782

Since the overtones $N \geqslant 2$ are in some sense self-trapped states involving more than one quantum of the amide-I vibration, it is interesting to consider self-trapped states that avoid the constraint of (2.10).

4. THE QUANTUM THEORY OF SELF-TRAPPING

In this section we approach the problem from a classical perspective (Takeno 1984). Starting with the classical amide-I coordinates, P_n and Q_n, for which the Hamiltonian is $\Sigma_n\,(P_n^2+Q_n^2)$, it is convenient to define the complex mode amplitudes

$$A_n \equiv \omega_0^{\frac{1}{2}}(P_n+\mathrm{i}Q_n). \tag{4.1}$$

In terms of these complex mode amplitudes (including dipole–dipole interactions)

$$H_{\mathrm{CO}} = \sum_n \left[\frac{E_0}{\hbar}|A_n|^2 - J(A^*_{n+1}A_n + A^*_n A_{n+1})\right], \tag{4.2}$$

where
$$\omega_0 = E_0/\hbar \tag{4.3}$$

is the classical oscillation frequency of an amide-I vibration. (From here on we will assume $\hbar = 1$ and measure energy and frequency in the same units.)

With a classical interaction energy

$$H_{\mathrm{int}} = \chi \sum_n q_n |A_n|^2, \tag{4.4}$$

where q_n is the coordinate of some low frequency phonon with adiabatic energy

$$H_{\mathrm{ph}} = \tfrac{1}{2}w \sum_n q_n^2, \tag{4.5}$$

one arrives at the total classical Hamiltonian

$$H = H_{\mathrm{CO}} + H_{\mathrm{ph}} + H_{\mathrm{int}}. \tag{4.6}$$

Minimizing (4.6) with respect to the q_n requires

$$q_n = -\frac{\chi}{w}|A_n|^2, \tag{4.7}$$

whereupon (4.6) can be reduced to

$$H = \sum_n \left[E_0|A_n|^2 - J(A^*_{n+1}A_n + A^*_n A_{n+1}) - \tfrac{1}{2}\gamma|A_n|^4\right], \tag{4.8}$$

where
$$\gamma \equiv \chi^2/w. \tag{4.9}$$

The corresponding dynamical equation for A_n is

$$\left(\mathrm{i}\frac{\mathrm{d}}{\mathrm{d}t} - E_0\right)A_n + J(A_{n+1}+A_{n-1}) + \gamma|A_n|^2 A_n = 0. \tag{4.10}$$

In addition to the *energy*, H, another constant of the motion along solutions of (4.10) is the *number*

$$N = \sum_n |A_n|^2. \tag{4.11}$$

Up to this point the discussion of the present section has been entirely classical. We now consider quantization in four special cases: (i) $J \ll \gamma$; (ii) $\gamma \ll J$; (iii) semiclassical quantization; and (iv) the Davydov ansatz. In each case it will be of particular interest to calculate an overtone series corresponding to that presented in table 2 for crystalline acetanilide.

(i) $J \ll \gamma$

In this case we neglect the dipole–dipole interaction terms in (4.8) and (4.10), and write the energy

$$H = \sum_n h_n, \tag{4.12}$$

where

$$h_n = E_0 |A_n|^2 - \tfrac{1}{2}\gamma |A_n|^4. \tag{4.13}$$

Under quantization, the terms in (4.12) become operators

$$h_n \rightarrow \hat{h}_n \tag{4.14}$$

through replacement of the complex mode amplitudes by creation and annihilation operators for bosons. Thus

$$A_n \rightarrow \hat{b}_n, \tag{4.15a}$$

$$A_n^* \rightarrow \hat{b}_n^\dagger. \tag{4.15b}$$

Since the ordering of these operators is not determined by (4.13), we take the averages

$$|A|^2 \rightarrow \tfrac{1}{2}(\hat{b}^\dagger\hat{b} + \hat{b}\hat{b}^\dagger), \tag{4.16}$$

$$|A|^4 \rightarrow \tfrac{1}{6}(\hat{b}^\dagger\hat{b}^\dagger\hat{b}\hat{b} + \hat{b}^\dagger\hat{b}\hat{b}^\dagger\hat{b} + \hat{b}^\dagger\hat{b}\hat{b}\hat{b}^\dagger + \hat{b}\hat{b}^\dagger\hat{b}\hat{b}^\dagger + \hat{b}\hat{b}\hat{b}^\dagger\hat{b}^\dagger + \hat{b}\hat{b}^\dagger\hat{b}^\dagger\hat{b}), \tag{4.17}$$

where the subscripts have been dropped for typographical convenience. Noting that $\hat{b}^\dagger$ and $\hat{b}$ have the properties $\hat{b}^\dagger |N\rangle = (N+1)^{\frac{1}{2}} |N+1\rangle$ and $\hat{b}|N\rangle = N^{\frac{1}{2}}|N-1\rangle$ (where $|N\rangle$ is an harmonic oscillator eigenstate), it is straightforward to show that

$$\hat{h} = (E_0 - \tfrac{1}{2}\gamma)(\hat{b}^\dagger\hat{b} + \tfrac{1}{2}) - \tfrac{1}{2}\gamma\hat{b}^\dagger\hat{b}\hat{b}^\dagger\hat{b}. \tag{4.18}$$

Thus

$$\hat{h}|N\rangle = E(N)|N\rangle, \tag{4.19}$$

where

$$E(N) = (E_0 - \tfrac{1}{2}\gamma)(N + \tfrac{1}{2}) - \tfrac{1}{2}\gamma N^2. \tag{4.20}$$

In summary, eigenvectors of the operators defined through (4.13), (4.14), (4.16) and (4.17) are identical to those of an harmonic oscillator, but the corresponding eigenvalues are given by (4.20).

The form of (4.20) is significant; it can be written as

$$E(N) = E^{\mathrm{C}} + E^{\mathrm{L}} + E^{\mathrm{NL}}, \tag{4.21}$$

where E^{C} is the ground state ($N = 0$) energy, $E^{\mathrm{L}} \propto N$ and

$$E^{\mathrm{NL}} = -\tfrac{1}{2}\gamma N^2. \tag{4.22}$$

This 'nonlinear' contribution is directly measured from the overtone series in table 2.

(ii) $\gamma \ll J$

In this case the classical equation (4.10) reduces to the nonlinear Schrödinger (n.l.S.) equation of soliton theory. To see how this goes, assume the repeat distance between molecules is d and replace the discrete variable n by a continuous variable, $x = n$, which measures distance in units of d. Then (4.10) takes the form

$$\left(\mathrm{i}\frac{\partial}{\partial t} - E_0 + 2J\right)A + J\frac{\partial^2 A}{\partial x^2} + \gamma|A|^2 A = 0. \tag{4.23}$$

28-2

Quantization of this equation was originally achieved by using the Bethe ansatz method, and recently it has been shown that such solutions can be efficiently constructed from a quantum version of inverse scattering theory (Sklyanin & Faddeev 1978; Thacker & Wilkinson 1979).

Under quantization, the functions, A and A^* are replaced by annihilation and creation operators for boson fields, $\hat{\phi}$ and $\hat{\phi}^\dagger$. At equal times these have the commutation relations

$$[\hat{\phi}(x), \hat{\phi}(y)] = [\hat{\phi}^\dagger(x), \hat{\phi}^\dagger(y)] = 0 \quad \text{and} \quad [\hat{\phi}(x), \hat{\phi}^\dagger(y)] = \delta(x-y).$$

In terms of the previous discussion, it is evident that $\hat{\phi}(x)$ is equivalent (under scaling) to $\hat{b}_n$ in the continuous limit $n = x$. In effecting this limit two procedures are customary: (i) neglect consideration of the ground state energy, which is unbounded in the limit, and (ii) 'normal order' all operator expressions, i.e. move all creation operators to the left.

Since $bb^\dagger = b^\dagger b + 1$, normal ordering of (4.18) and neglect of the ground state energy imply

$$\hat{h}_n = (E_0 - \gamma)\,\hat{b}_n^\dagger \hat{b}_n - \tfrac{1}{2}\gamma \hat{b}_n^\dagger \hat{b}_n^\dagger \hat{b}_n \hat{b}_n. \tag{4.24}$$

Thus to put (4.23) in standard form for quantum analysis, let

$$A = \varPhi \exp[-\mathrm{i}(E_0 - 2J - \gamma)\,t] \tag{4.25}$$

and scale time as $t \to t/J$. Then (4.23) becomes

$$\mathrm{i}\varPhi_t + \varPhi_{xx} + \gamma\,|\varPhi|^2\,\varPhi/J = 0, \tag{4.26}$$

where a subscript notation is used for the partial derivatives. Under quantization $\varPhi \to \hat{\phi}$ and (4.26) becomes the operator equation

$$\mathrm{i}\hat{\phi}_t + \hat{\phi}_{xx} + \gamma\hat{\phi}^\dagger\hat{\phi}\hat{\phi}/J = 0 \tag{4.27}$$

with energy operator

$$\hat{H} = \int \mathrm{d}x\, \hat{\phi}_x^\dagger \hat{\phi}_x - \frac{1}{2}\frac{\gamma}{J}\int \mathrm{d}x\, \hat{\phi}^\dagger \hat{\phi}^\dagger \hat{\phi}\hat{\phi}, \tag{4.28}$$

number operator

$$\hat{N} = \int \mathrm{d}x\, \hat{\phi}^\dagger\hat{\phi}, \tag{4.29}$$

and momentum operator

$$\hat{P} = -\mathrm{i}\int \mathrm{d}x\, \hat{\phi}^\dagger\hat{\phi}_x. \tag{4.30}$$

The quantum inverse scattering method provides exact wavefunctions, $|\psi\rangle$, that diagonalize $\hat{N}$, $\hat{P}$ and $\hat{H}$ as follows (Wadati 1985),

$$\hat{N}|\psi\rangle = N|\psi\rangle, \tag{4.31}$$

where

$$N = \text{integer} \geqslant 0, \tag{4.32}$$

$$\hat{P}|\psi\rangle = Np|\psi\rangle, \tag{4.33}$$

where p is a real number, and

$$\hat{H}|\psi\rangle = [Np^2 + \gamma^2\,(N - N^3)/48\,J^2]\,|\psi\rangle. \tag{4.34}$$

Furthermore, in the limit $\gamma/J \to 0$ (Thacker & Wilkinson 1979)

$$|\psi\rangle \to \int \mathrm{d}x\, \mathrm{e}^{\mathrm{i}px}\hat{\phi}^\dagger\,|0\rangle. \tag{4.35}$$

Equations (4.32) and (4.34) imply an overtone series

$$E(N) = E^{\mathrm{L}} + E^{\mathrm{NL}}, \tag{4.36}$$

where $E^{\mathrm{L}} \propto N$ and

$$E^{\mathrm{NL}} = -\gamma^2 N^3/48\, J^2. \tag{4.37}$$

(iii) *Semiclassical quantization*

In the parameter range $\gamma \approx J$, no exact quantization procedure is known to the present author. It is, however, possible to impose elementary quantum conditions on stationary solutions of (4.10). By writing such a solution in the form

$$A_n = \frac{J^{\frac{1}{2}}}{\gamma} \alpha_n \exp\left[-\mathrm{i}\left(\frac{E_0}{J} + \omega\right) t\right], \tag{4.38}$$

(4.10) reduces to the standard form

$$\omega \alpha_n + \alpha_{n+1} + \alpha_{n-1} + \alpha_n^3 = 0. \tag{4.39}$$

By using a 'shooting' method (Scott & MacNeil 1983) it is possible to find a family of numerical solutions for (4.39) with the following properties: (i) $\alpha_n = \alpha_{-n}$; (ii) for $n \geqslant 0$, $\alpha_n > \alpha_{n+1}$; and (iii) $\lim_{n\to\infty} \alpha_n = 0$. From such a solution the conserved quantities H and N defined in (4.8) and (4.11) are readily calculated as

$$N = \frac{J}{\gamma} \sum_n \alpha_n^2 \tag{4.40}$$

and

$$H(N) = \left(E_0 - J \frac{\sum_n \alpha_n \alpha_{n-1}}{\sum_n \alpha_n^2}\right) N - \tfrac{1}{2}\gamma N^2 \frac{\sum_n \alpha_n^4}{\left(\sum_n \alpha_n^2\right)^2}. \tag{4.41}$$

Semiclassical quantization (Percival 1977) is effected by noting that stationary solutions are of the form

$$A_n(t) = A_{n0} \exp\left[-\mathrm{i}\theta(t)\right],$$

where

$$\dot{\theta} = \mathrm{d}H(N)/\mathrm{d}N. \tag{4.42}$$

Thus N and θ are conjugate variables and the quantum condition

$$\oint N \mathrm{d}\theta = 2\pi\,(\text{integer}) \tag{4.43}$$

together with the definition of N (4.11) imply

$$N = \text{integer} \geqslant 0. \tag{4.44}$$

Equation (4.41) has the form

$$E(N) = E^{\mathrm{L}} + E^{\mathrm{NL}}, \tag{4.45}$$

where

$$E^{\mathrm{NL}} = -\tfrac{1}{2}\gamma N^2 \left(\sum_n \alpha_n^4\right) \Big/ \left(\sum_n \alpha_n^2\right)^2. \tag{4.46}$$

In the limit $J \ll \gamma, \alpha_n \ll \alpha_0$ for $|n| \geqslant 1$ so (4.46) evidently reduces to (4.22). In the limit $\gamma \ll J$, it is straightforward to show that (4.46) reduces to (4.37). Thus (4.46) is expected to provide an accurate calculation of E^{NL} over the entire parameter range and is sketched in figure 4.

It is now possible to consider how data from the overtone series for the 1650 cm^{-1} band in acetanilide compares with these calculations. From (3.2) and (3.10)

$$\gamma_0/J = 11.3. \tag{4.47}$$

Figure 4 shows that this lies in the range for which

$$E(N) = E_0 N - \tfrac{1}{2}\gamma N^2, \tag{4.48}$$

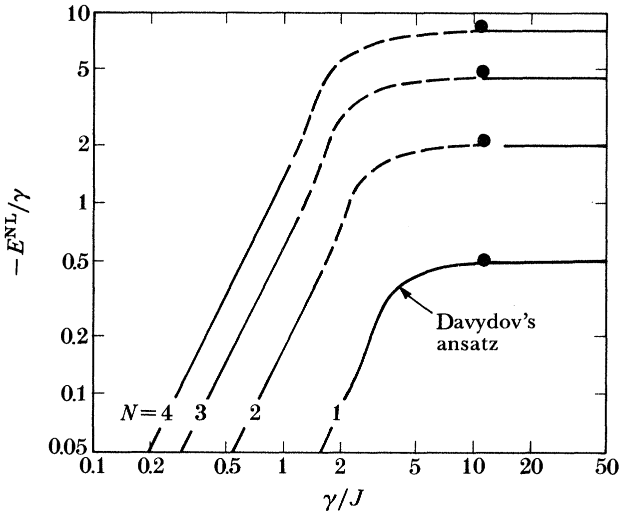

FIGURE 4. The nonlinear contribution to the energy level (E^{NL}) as a function of the ratio of anharmonicity to dispersion (γ/J). N is the number of amide-I quanta. Experimental points are from measurements of the overtone series in crystalline acetanilide (see table 3). Broken lines indicate parameter ranges for which the wavefunction is not known.

so the line at 1650 cm^{-1} implies that

$$E_0 = 1672.3\ \text{cm}^{-1}. \tag{4.49}$$

From the measured values of overtone frequency, $\nu(N)$ in table 2, the nonlinear contributions to the overtone spectrum can be calculated to be

$$E^{\text{NL}} = \nu(N) - NE_0. \tag{4.50}$$

In table 3 we compare these calculations with those computed from (4.48). The measured values of E^{NL} are indicated on figure 4.

TABLE 3. NONLINEAR TERMS IN ACN OVERTONE SERIES

N	$-E^{\text{NL}}/\text{cm}^{-1}$	$(-\frac{1}{2}N^2)/\text{cm}^{-1}$
1	22	22
2	95	89
3	214	201
4	385	357

(iv) *Davydov's ansatz*

We are now in a position to evaluate Davydov's analysis. In the context of an adiabatic approximation, the wavefunction introduced in (2.6) takes the form

$$|\psi\rangle = \sum_n a_n(t)\, \hat{b}_n^\dagger\, |0\rangle, \tag{4.51}$$

where the $a_n(t)$ are solutions of (2.13). This form of the Davydov ansatz has the following properties.

(i) In the limit $J \ll \gamma$, it reduces to the first eigenfunction, $|1\rangle$, in (4.19).

(ii) In the limit $\gamma \ll J$, it reduces to the asymptotic form of Bethe's ansatz in (4.35).

(iii) Between these two limits, Davydov's ansatz gives energies that agree with semiclassical calculations.

Thus one concludes that Davydov's ansatz is a useful approximation to the exact wavefunction over the entire parameter range $0 \leqslant \gamma/J < \infty$ with the constraint (2.10), which implies $N = 1$.

Biological significance of self-trapping

Measurements on crystalline acetanilide (ACN) confirm Davydov's theory of self-trapped states (solitons) in hydrogen-bonded polypeptide chains. Furthermore, table 2 shows that the '$N = 2$' state in ACN can absorb almost all (95%) of the free energy released in hydrolysis of ATP. It is reasonable to suppose that a corresponding state can form on the hydrogen-bonded polypeptide chains of α-helix (figure 1).

Over a decade ago McClare (1972*a*, *b*) argued that the free energy released in ATP hydrolysis should transfer resonantly into a protein to avoid thermal degradation. To store and transport this energy he proposed an 'excimer' state in protein, which would be closely related to the amide-A band of α-helix at 3240 cm^{-1} (McClare 1974). McClare's excimer is qualitatively similar to the 'conformon' of Green & Ji (1972) and the basic properties of both are provided by a Davydov soliton in the '$N = 2$' state (Davydov 1973, 1974, 1977, 1979*b*, 1982*a*). In the past such suggestions have been rejected or ignored by the biochemical community because a localized region of free energy within a protein was believed to be physically impossible. Since this view is no longer tenable, the early proposals of Davydov (1972), McClare (1972), and Green & Ji (1972) must be re-evaluated. A recent paper by Careri & Wyman (1984), suggesting a soliton mechanism for cyclic enzyme activity provides a first step in this direction.

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References

Careri, G. 1973 Search for cooperative phenomena in hydrogen-bonded amide structures. In *Cooperative phenomena* (ed. H. Haken & M. Wagner), pp. 391–394. Berlin, Heidelberg and New York: Springer-Verlag.

Careri, G., Buontempo, U., Carta, R., Gratton, E. & Scott, A. C. 1983 Infrared absorption in acetanilide by solitons. *Phys. Rev. Lett.* **51**, 304–307.

Careri, G., Buontempo, U., Galluzzi, F., Scott, A. C., Gratton, E. & Shyamsunder, E. 1984 Spectroscopic evidence for Davydov-like solitons in acetanilide. *Phys. Rev.* B **30**, 4689–4702.

Careri, G. & Wyman, J. 1984 Soliton assisted unidirectional circulation in a biochemical cycle. *Proc. natn. Acad. Sci. U.S.A.* **81**, 4386–4388.

Davydov, A. S. 1973 The theory of contraction of proteins under their excitation. *J. theor. Biol.* **38**, 559–569.

Davydov, A. S. 1974 Quantum theory of muscular contraction. *Biofizika* **19**, 670–676.

Davydov, A. S. 1977 Solitons and energy transfer along protein molecules. *J. theor. Biol.* **66**, 379–387.

Davydov, A. S. 1979*a* Solitons in molecular systems. *Physica Scr.* **20**, 387–394.

Davydov, A. S. 1979*b* Solitons, bioenergetics and the mechanism of muscle contraction. *Int. J. Quantum Chem.* **16**, 5–17.

Davydov, A. S. 1982*a* *Biology and quantum mechanics*. New York: Pergamon Press.

Davydov, A. S. 1982*b* Solitons in quasi-one-dimensional molecular structures. *Soviet Phys. Usp.* **25**, 898–918 (Transl. of *Usp. fiz. Nauk* **138**, 603–643.)

Davydov, A. S. & Kislukha, N. I. 1973 Solitary excitations in one-dimensional molecular chains. *Physica Status Solidi* B **59**, 465–470.

Eilbeck, J. C., Lomdahl, P. S. & Scott, A. C. 1984 Soliton structure in crystalline acetanilide. *Phys. Rev.* B **30**, 4703–4712.

Fox, R. F. 1982 *Biological energy transduction*, p. 216. New York: John Wiley & Sons.

Green, D. E. & Ji, S. 1972 The electromechanochemical model of mitochondrial structure and function. In *The molecular basis of electron transport*, pp. 1–43. New York and London: Academic Press.

Itoh, K. & Shimanouchi, T. 1972 Vibrational spectra of crystalline formamide. *J. molec. Spectrosc.* **42**, 86–99.

MacNeil, L. & Scott, A. C. 1984 Launching a Davydov soliton: II. Numerical studies. *Physica Scr.* **29**, 284–287.

McClare, C. W. F. 1972*a* A quantum mechanical muscle model. *Nature, Lond.* **240** (10), 88–90.

McClare, C. W. F. 1972*b* A 'molecular energy' muscle model. *J. theor. Biol.* **35**, 569–595.

McClare, C. W. F. 1974 Resonance in bioenergetics. *Ann. N.Y. Acad. Sci.* **227**, 74–97.

Nevskaya, N. A. & Chirgadze, Yu. N. 1976 Infrared spectra and resonance interactions of amide-I and II vibrations of α-helix. *Biopolymers* **15**, 637–648.

Percival, I. C. 1977 Semiclassical theory of bound states. *Adv. chem. Phys.* **36**, 1–61.

Scott, A. C. 1982 Dynamics of Davydov solitons. *Phys. Rev.* A **26**, 578–595.

Scott, A. C. 1983 Errata to Scott (1982). *Phys. Rev.* A **27**, 2767.

Scott, A. C. 1984 Launching a Davydov soliton. I. Soliton analysis. *Physica Scr.* **29**, 279–283.

Scott, A. C., Gratton, E., Shyamsunder, E. & Careri, G. 1985 The IR overtone spectrum of the vibrational soliton in crystalline acetanilide. (In the press.)

Scott, A. C. & MacNeil, L. 1983 Binding energy versus nonlinearity for a 'small' stationary soliton. *Phys. Lett.* A **98**, 87–88.

Sklyanin, E. K. & Faddeev, L. D. 1978 Quantum mechanical approach to completely integrable field theory models. *Soviet Phys. Dokl.* **23**, 902–904. (Transl. of *Dokl. Akad. Nauk SSSR* (*fiz.*) **243**, 1430–1433.)

Takeno, S. 1983 Exciton solitons in one-dimensional molecular crystals. *Prog. theor. Phys.* **69**, 1798–1801.

Takeno, S. 1984 Vibron solitons in one-dimensional molecular crystals. *Prog. theor. Phys.* **71**, 395–398.

Thacker, H. B. & Wilkinson, D. 1979 Inverse scattering transform as an operator method in field theory. *Phys. Rev.* D **19**, 3660–3665.

Wadati, M. 1985 Quantum inverse scattering method. (In the press.)

Discussion

M. TABOR (*Department of Applied Physics, Columbia University, New York, U.S.A.*). Is it clear that the energy trapping is due to nonlinear, soliton-like effects rather than transitions to other electronic states?

A. C. SCOTT. Yes, for crystalline acetanilide this is quite clear. Every effort has been made to find an explanation for the 1650 cm^{-1} line that does not involve nonlinear effects (see Careri *et al.* (1984)), but nobody has been successful.