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The properties of the collective excitation in the organic protein molecular system

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Abstract. The properties of the collective excitation and the motion of solitons originates in the inner local fluctuation and deformation of the structure of molecules in the organism, and protein has been discussed utilizing an analysis of inner excitation in the molecule and the sound oscillation caused by neighbouring correlation effects between molecules by considering the anomalous correlation interaction in this system. These new results show that the Davydov theory is only an approximate theory.

1. Introduction

Recently, different excitations of the collective types of solitons, e.g. the Davydov soliton, and their motion in quasi-periodic molecular systems consisting of weakly interacting identical molecules (groups of atoms) and α-helical protein molecular chains was studied using the Davydov theory by Davydov and co-workers [1–6], Scott and co-workers [7–10] and Pang [11–13], Careri *et al* [14], Takeno [15] and Wang *et al* [16] for example. This is a very important and intriguing problem. It is used to explain many biological phenomena, e.g. the contraction mechanism of animal muscles, at the molecular level. However, how correct is this model? What problems does it have? What are the limitations of the theory? These questions have not been discussed systematically yet. In this paper, the theory is studied by a new method in the following two sections.

2. Collective excitation and soliton motion in organic protein molecules

It is known that the Davydov soliton arises because of the local fluctuation and deformation of structure in the molecular system by means of the resonance interaction between these molecular groups or the dipole–dipole interaction due to a change in inner energy or applied excitation of light and electromagnetic field, etc. In this case, the inner excitation caused by motion of the excess electrons in the molecule and the sound oscillation of the molecules caused through the neighbouring correlation effect between

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molecules occurred. To analyse the features for these models of motion, we may use the following Hamiltonian in the organic molecular system [17]:

$$H = H_s + H_p + H_{int}. \tag{1}$$

H_s is the Hamiltonian of the sound oscillation caused by the localized deformation in this molecular system. It is of the form

$$H_s = \tfrac{1}{2}M\sum_i \dot{R}_i^2 + \tfrac{1}{2}\beta\sum_i (R_i - R_{i-1})^2 \qquad \left(\dot{R}_i = \frac{dR_i}{dt}\right) \tag{2}$$

where R_i is the displacement of the ith molecule from its equilibrium position. β is 'the elasticity coefficient' of this molecular chain. Meanwhile, we assume that each cell has only a molecule with mass M here.

H_p is the Hamiltonian of the inner excitation of the molecule by using Fröhlich's model of a small polaron. It is of the form

$$H_p = \sum_i \frac{P_i}{2\mu} + \tfrac{1}{2}\sum_i \mu\omega_0^2 r_i^2 - \tfrac{1}{2}\sum_i \mu\omega_1^2 r_i r_{i+1} \tag{3}$$

where μ is the mass of the polarized particle generated by inner excitation in the molecule. ω_0^2 and ω_1^2 are the diagonal and non-diagonal elements of the dynamical matrix. ω_0 is the Einstein frequency. $\frac{1}{2}\mu\omega_1^2 r_i r_{i+1}$ is the dispersion part of the longitudinal phonon caused by the neighbouring interaction between molecules in molecular vibration. r_i and $p_i = \mu\dot{r}_i$ are the normal coordinates of the ith oscillator in the molecule and its canonically conjugate momentum, respectively. This interaction between the oscillators and molecular lattice surely exist because of the local fluctuation and deformation of structure in this system. We take the Hamiltonian of this interaction to be of the form

$$H_{int} = \tfrac{1}{2}\sum_i \mu\chi_1(R_{i+1} - R_{i-1})r_i^2 + \sum_i \mu\chi_2(R_{i+1} - R_i)r_i r_{i+1} \tag{4}$$

where $2\chi_1 = \partial\omega_0^2/\partial R_i$ and $2\chi_2 = \partial\omega_1^2/\partial R_i$ are the change in the vibrating energy of molecular lattice and the coupling interaction between neighbouring molecules by unit extension.

Adopting the canonical second quantized method,

$$r_i = (2\mu\omega_0/\hbar)^{-1/2}(b_i + b_i^+) \qquad p_i = [(\hbar/2)\mu\omega_0]^{1/2}(-j)(b_i - b_i^+) \qquad (j = \sqrt{-1}) \tag{5}$$

where b_i is the excitation operator of a molecule of number i.

Substituting equation (5) into equations (3) and (4), we then have

$$H_p = \sum_i \hbar\omega_0(b_i^+ b_i + \tfrac{1}{2}) - \tfrac{1}{2}\sum_i \frac{\hbar\omega_1^2}{2\omega_0}(b_i^+ b_{i+1} + b_{i+1}^+ b_i + b_i^+ b_{i+1}^+ + b_i b_{i+1}) \tag{6}$$

$$H_{int} = \frac{\hbar}{4\omega_0}\sum_i \chi_1(R_{i+1} - R_{i-1})(b_i^+ b_i + b_i b_i^+ + b_i^+ b_i^+ + b_i b_i)$$

$$+ \frac{\hbar}{2\omega_0}\sum_i \chi_2(R_{i+1} - R_i)(b_i^+ b_{i+1} + b_{i+1}^+ b_i + b_i^+ b_{i+1}^+ + b_i b_{i+1}). \tag{7}$$

The equation of motion of operator b_i in the Heisenberg representation may be found from equations (1), (6) and (7) to be of the form

$$\begin{aligned} j\hbar\dot{b}_f(t) = [b_f(t), H] &= \hbar\omega_0 b_f(t) - (\hbar\omega_1^2/4\omega_0)(b_{f+1} + b_{f+1}^+) \\ &- (\hbar\omega_1^2/4\omega_0)(b_{f-1} + b_{f-1}^+) + (\hbar/2\omega_0)\chi_1(R_{f+1} - R_{f-1})(b_f + b_f^+) \\ &+ (\hbar/2\omega_0)\chi_2[(R_{f+1} - R_f)(b_{f+1} + b_{f+1}^+) + (R_f - R_{f-1})(b_{f-1} + b_{f-1}^+)]. \end{aligned} \tag{8}$$

Now we may assume that the trial collective exciting wavefunction of this system according to the properties of structure and change in state of the organic molecular system is of the form

$$|\psi(t)\rangle = \lambda^{-1}\left(1 + \sum_i \alpha_i b_i^+\right)|0\rangle \tag{9}$$

where λ is a factor of the normalization. Writing $\langle\psi|b_f|\psi\rangle = \alpha_f/|\lambda|^2$ and $\varphi_f = \alpha_f/\lambda$, from equations (8) and (9) we can obtain the following non-linear equation of motion:

$$\begin{aligned} j\hbar\dot{\varphi}_f &= \hbar\omega_0\varphi_f - (\hbar\omega_1^2/4\omega_0)(\varphi_{f-1} + \varphi_{f+1}^*) - (\hbar\omega_1^2/4\omega_0)(\varphi_{f-1} + \varphi_{f-1}^*) \\ &+ (\hbar\chi_1/2\omega_0)(R_{f+1} - R_{f-1})(\varphi_f + \varphi_f^*) \\ &+ (\hbar/2\omega_0)\chi_2[(R_{f+1} - R_f)(\varphi_{f+1} + \varphi_{f+1}^*) + (R_f - R_{f-1})(\varphi_{f-1} + \varphi_{f-1}^*)]. \end{aligned} \tag{10}$$

We adopt classical methods such as that in [17] for the part of the deformation in equation (1), and, applying equation (9), we then have

$$\begin{aligned} \langle\psi|H_{\text{int}}|\psi\rangle &= \frac{\hbar}{4\omega_o}\sum_i \chi_1(R_{i+1} - R_i)|\varphi_i|^2 + \frac{\hbar}{4\omega_0}\sum_i \chi_1(R_{i+1} - R_{i-1})|\varphi_i|^2 \\ &+ \frac{\hbar}{2\omega_0}\sum_i \chi_2(R_{i+1} - R_i)\varphi_i^*\varphi_{i+1} + \frac{\hbar}{2\omega_0}\sum_i \chi_2(R_i - R_{i-1})\varphi_i\varphi_{i-1}^*. \end{aligned} \tag{11}$$

The equation of motion for the molecular lattice vibration from the Hamilton equation and equations (1), (2) and (11) may be obtained as follows:

$$\begin{aligned} M\ddot{R}_f = -(\delta/\delta R_f)\langle\psi|H|\psi\rangle &= \beta(R_{f+1} + R_{f-1} - 2R_f) \\ &+ (\hbar/2\omega_0)\chi_1(|\varphi_{f+1}|^2 - |\varphi_{f-1}|^2) \\ &- (\hbar/2\omega_0)\chi_2[\varphi_f^*(\varphi_{f-1} - \varphi_{f+1}) + \varphi_f(\varphi_{f-1}^* - \varphi_{f+1}^*)]. \end{aligned} \tag{12}$$

Equations (10) and (12) are two complete equations describing the local intramolecular excitation accompanied by the deformation of structure. Obviously, it is different from that of Davydov and co-workers [1–6]. The reason is the existence of the anomalous correlation terms $b_i^+b_i^+ + b_ib_i$ and $b_i^+b_{i+1}^+ + b_ib_{i+1}$ in equation (1). However, if we neglect these terms or let $\varphi_f^* = 0$, then they can degenegate into the original Davydov equations. This shows that our theory has generality. The Davydov theory is only a special case of our theory. However, it is very difficult to find the solutions of equations (10) and (12).

Considering the symmetry of equation (10) and its conjugate equation satisfied by φ_f^*, we may make a transformation

$$\varphi_f^{\pm} = \varphi_f \pm \varphi_f^*. \tag{13}$$

From equations (10) and (13) we can obtain

$$-\ddot{\varphi}_f = \omega_0^2\varphi_f - (\omega_1^2/2)(\varphi_{f+1} - \varphi_{f-1}) + \chi_1(R_{f+1} - R_{f-1})\varphi_f + \chi_2[(R_{f+1} - R_f)\varphi_{f+1} + (R_f - R_{f-1})\varphi_{f-1}]. \tag{14}$$

When the inner excitation of the molecule and the sound vibration of the molecular lattice are small, we may adopt the continual approximate method. In the one-dimensional case, it may be represented in the following form:

$$\varphi_{f\pm1} \simeq \varphi_f \pm a(\partial\varphi_f/\partial x) + (1/2!)a^2(\partial^2\varphi_f/\partial x^2) \pm (1/3!)a^3(\partial^3\varphi_f/\partial x^3) + \ldots$$

$$R_{f\pm1} \simeq R_f \pm a(\partial R_f/\partial x) + (1/2!)a^2(\partial^2 R_f/\partial x^2) \pm (1/3!)a^3(\partial^3 R_f/\partial x^3) + \ldots \tag{15}$$

$$R_f \to R(x,t) \qquad \varphi_f \to \varphi(x,t).$$

Applying equation (15), and from equations (12) and (14), we can obtain

$$-\partial^2\varphi/\partial t^2 \simeq (\omega_0^2 - \omega_1^2)\varphi - \tfrac{1}{2}\omega_1^2a^2(\partial^2\varphi/\partial x^2) + 2\chi_1a(\partial R/\partial x)\varphi + 2\chi_2a(\partial R/\partial x)\varphi + \chi_2a^2(\partial^2 R/\partial x^2)\varphi + \chi_2a^3(\partial R/\partial x)(\partial^2\varphi/\partial x^2) + \ldots \tag{16}$$

$$M(\partial^2 R/\partial t^2) \approx \beta a^2(\partial^2 R/\partial x^2) + (\hbar a/\omega_0)(\chi_1 + \chi_2)(\partial/\partial x)|\varphi|^2. \tag{17}$$

Now let us assume that $V_{aq} = a\sqrt{\beta/M}$ determined as the velocity of the longitudinal sound wave in this molecular chain. The solutions of this set of equations corresponding to the excitation movement along the molecular chain with a velocity $V < V_{aq}$ may be looked for in the form

$$\rho(x,t) = -\partial R/\partial x = \rho(x - vt) \qquad \varphi(x,t) = \varphi(x - vt). \tag{18}$$

Equation (17) thus yields

$$-\partial R/\partial x = +\rho = [\hbar(\chi_1 + \chi_2)a/M(V_{aq}^2 - V^2)\omega_0]|\varphi|^2 + d \tag{19}$$

where d is a non-determinate constant determined by boundary conditions.

Substituting equation (19) into equation (16) yields the following equation:

$$\partial^2\varphi/\partial t^2 - A(\partial^2\varphi/\partial x^2) + B\varphi - C|\varphi|^2\varphi = E^1|\varphi|^2(\partial\varphi/\partial x) + F|\varphi|^2(\partial^2\varphi/\partial x^2) \tag{20}$$

where

$$A = \tfrac{1}{2}\omega_1^2a^2 \qquad B = (\omega_0^2 - \omega_1^2) + 2d(\chi_1 + \chi_2)a \qquad C = 2\hbar a^2(\chi_1 + \chi_2)^2/\omega_0M(V_{aq}^2 - V^2)$$

$$E^1 = \chi_1a^3\hbar(\chi_1 + \chi_2)/M\omega_0(V_{aq}^2 - V^2) \qquad F = \hbar a^4(\chi_1 + \chi_2)\chi_2/M\omega_0(V_{aq}^2 - V^2). \tag{21}$$

Because $\chi_2 \ll \chi_1$, $|a| \ll 1$ in the general case we may approximate up to order a^2 only, to neglect the terms $E^1|\varphi|^2(\partial\varphi/\partial x)$ and $F|\varphi|^2(\partial^2\varphi/\partial x^2)$; then equation (20) becomes

$$\partial^2\varphi/\partial t^2 - A(\partial^2\varphi/\partial x^2) + B\varphi - C|\varphi|^2\varphi = 0. \tag{22}$$

Now let us assume that the solution of equation (22) is of the form [18]

$$\varphi = f(\zeta)\exp[i\theta(x, t)] \tag{23}$$

(where $\theta = Kx - \omega t$ and $\zeta = x - Vt$). k, ω and V are some non-determinate constants. Substituting equation (23) into equation (22) yields

$$\tfrac{1}{2}(V^2 - A)(df/d\zeta)^2 + \tfrac{1}{2}(B + K^2 - \omega^2)f^2 - (c/4)f^4 = g.$$

We know that the non-determinate integration constant $g = 0$ from the nature of the boundary condition of φ. Thus we have

$$(df/d\zeta)^2 - \alpha f^2 + \gamma f^4 = 0$$

where $\alpha = (B + K^2 - \omega^2)/(A - V^2)$ and $\gamma = C/4(A - V^2)$. If $A > V^2$, then its solution is of the form

$$f(\zeta) = \sqrt{2\alpha/\gamma}\,\mathrm{sech}[\sqrt{\alpha}(\zeta - \zeta_0)] = \sqrt{2\alpha/\gamma}\,\mathrm{sech}\{\sqrt{\alpha}[x - x_0 - V(t - t_0)]\}. \tag{24}$$

So

$$\varphi = \sqrt{4(B + K^2 - \omega^2)/C}\,\mathrm{sech}\{\sqrt{(B + K^2 - \omega^2)/(A - V^2)}\times [x - x_0 - V(t - t_0)]\exp[i(Kx - \omega t)]. \tag{25}$$

This is a non-topological soliton solution which is consistent with the type of solution used in [1–13] $|\varphi(n, t)|^2$ is shown in figure 1. However, our equation (20) or (22) is different from those in [1–13]. This is very important.

From equations (19) and (25), we may obtain

$$\rho = -dR/dX = [\hbar(\chi_1 + \chi_2)a/M\omega_0(V_{aq}^2 - V^2)]|\varphi|^2 + d$$
$$= [4\hbar a(\chi_1 + \chi_2)(B + K^2 - \omega^2)/M\omega_0^2 C(V_{aq}^2 - V^2)]\times \mathrm{sech}^2\{\sqrt{(B + K^2 - \omega^2)/(A - V^2)}\,[x - x_0 - V(t - t_0)]\} + d. \tag{26}$$

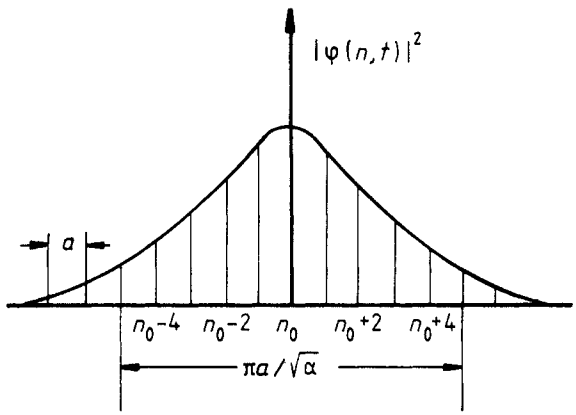

Figure 1. The probability of the distribution $|\varphi(n, t)|^2$ of internal excitation and change in relative distance of molecules.

Now let us find the energy of this soliton. The effective Hamiltonian H' contributing the energy of this soliton to the total Hamiltonian H is of the following form in the trial wavefunction equation (9):

$$H^1 = E_0 + T + U + \sum_i (\varepsilon - D) b_i^+ b_i - J \sum_i (b_i^+ b_{i+1} - b_i b_{i+1})$$
$$+ \sum_i \chi(R_{i+1} - R_{i-1}) b_i^+ b_i + \sum_i \chi^1(R_{i+1} - R_i)(b_i^+ b_{i+1} + b_i b_{i+1}^+) \qquad (27)$$

where

$$E_0 = \tfrac{1}{2} N\hbar\omega_0 + \frac{\hbar}{4\omega_0} \sum_i \chi_1(R_{i+1} - R_{i-1}) \qquad \varepsilon - D = \hbar\omega_0$$
$$J = \frac{\hbar\omega_1^2}{2\omega_0} \qquad \chi = \frac{\hbar\chi_1}{2\omega_0} \qquad \chi^1 = \frac{\hbar\chi^2}{2\omega_0}$$
$$S^2 = \frac{V^2}{V_{aq}^2} = \frac{MV^2}{\beta a^2}. \qquad (28)$$

Thus

$$\langle\psi|H^1|\psi\rangle = E_0 + T + V + \varepsilon - D - J \sum_i \varphi_i(\varphi_{i+1} + \varphi_{i-1}) + \textstyle\sum_i \chi(R_{i+1} - R_{i-1})|\varphi_i|^2$$
$$+ \sum_i \chi^1(R_{i+1} - R_i)(\varphi_i^* \varphi_{i+1} + \varphi_i \varphi_{i-1}^*). \qquad (29)$$

If we write equation (25) in the following form:

$$\varphi = \sqrt{1/2L_s}\,\mathrm{sech}[L_s^{-1}(X - Vt)] \exp[\mathrm{i}(KX - \omega t)]$$

in the continual approximation method, then we can obtain the soliton energy as follows:

$$E = \langle\psi|H^1|\psi\rangle = E_o + \varepsilon - 2J + 2(\chi + \chi^1)/\beta(1 - S^2)$$
$$+ J(K^2 + 1/3L_s^2) - [4(\chi + \chi^1)^2/\omega(1 - s^2)]\,(1/3L_s)$$
$$+ [2(\chi + \chi^1)^2(1 + s^2)/\omega(1 - s^2)]\,(1/3L_s). \qquad (30)$$

At all finite values of the energy equation (30) the soliton velocity is less than the velocity of the longitudinal sound in a molecular chain. In soft chains (small β) and in the cases when internal excitations are strongly bound to molecular displacements the effective soliton mass is very large. So, even at a small velocity of travel the kinetic soliton energy may be very high. In the presence of soliton excitation, the molecular chain is locally deformed. Since the mass of molecules is large, deformation is preserved during radiation. After radiation the local deformation energy dissipates into that of molecular vibrations. The radiation maximum corresponds to the frequency $\nu = (E - G)/h$, where $G = (\chi + \chi^1)^4/3\beta^2 J$ is the Stokes shift. This result can explain many biological phenomena, e.g. biological radiation of energy, which is well known.

We may completely apply the above theory to the structure properties of α-helical protein, where ω_0 is the eigenfrequency of the amide-I vibration, and r_i, μ and $\frac{1}{2}\mu\omega_1$ are the normal coordinates of the amide-I vibration of the ith peptide group (ith amide-I oscillator), its effective mass and a dipole–dipole interaction force constant between the

ith and $(i+1)$th amide-I oscillators, respectively. R_i, M and β are the longitudinal displacement of the ith peptide group, the mass of a peptide group plus residue and the force constant of hydrogen bonding, respectively. Thus correspondingly the distribution of excitations and the change in distance between peptide groups in each of the three chains ($j = 1, 2, 3$) are characterized, respectively, by the functions $\varphi_j(X, t)$ and $\rho_j(X, t)$ satisfying the set of equations

$$[\partial^2/\partial t^2 - \tfrac{1}{2}\omega_1^2 a^2(\partial^2/\partial x^2) + (\omega_0^2 - \omega_1^2) - 2a(\chi_1 + \chi_2)\rho_j]\varphi_{j-1}(x, t) = L[\varphi_{j+1}(x, t) + \varphi_{j-1}(x, t)] \tag{31}$$

$$[M(\partial^2/\partial t^2) - \beta a^2(\partial^2/\partial x^2)]\rho_j(x, t) = -[(\chi_1 + \chi_2)/\omega_0](\partial/\partial x)|\varphi_j(x, t)|^2 \qquad (\rho_j = -\partial R_j/\partial x \qquad j = 1, 2, 3) \tag{32}$$

where $J = \hbar\omega_1^2/2\omega_0$ is the resonance interaction energy of neighbouring peptide groups situated along each chain, and L is the resonance interaction energy between the nearest neighbouring peptide groups of different chains.

Applying our method [11–13], we can obtain from equations (31) and (32)

$$(\partial^2/\partial t^2)\varphi_j - A(\partial^2/\partial x^2)\varphi_j + B\varphi_j - C|\varphi_j|^2\varphi_j = L(\varphi_{j+1} - \varphi_{j-1}) \qquad (j = 1, 2, 3). \tag{33}$$

Just as in Scott's [7] method, we study only the case with no bending of the α-helix. This assumption is equivalent to requiring that

$$\rho_1 = \rho_2 = \rho_3 = \tfrac{1}{3}(|\varphi_1|^2 + |\varphi_2|^2 + |\varphi_3|^2)[\hbar(\chi_1 + \chi_2)a/M(V_{aq}^2 - V^2)\omega_0] + d. \tag{34}$$

Therefore equation (33) can be written in vector form as

$$\boldsymbol{\varphi}_{tt} - A\boldsymbol{\varphi}_{xx} - (C/3)(\boldsymbol{\varphi}^* \cdot \boldsymbol{\varphi})\boldsymbol{\varphi} = -\mathbf{Z}\boldsymbol{\varphi} \tag{35}$$

where

$$\boldsymbol{\varphi} = (\varphi_1, \varphi_2, \varphi_3)^t \qquad \mathbf{Z} = \begin{pmatrix} B & L & L \\ L & B & L \\ L & L & B \end{pmatrix}$$

$$\varphi_{tt} = \partial^2\varphi/\partial t^2 \qquad \varphi_{xx} = \partial^2\varphi/\partial x^2. \tag{36}$$

From the results obtained by Scott [7, 8] and Pang [11–13], we may assume that its solution is of the form

$$\boldsymbol{\varphi} = \boldsymbol{\Phi}\exp(-\mathrm{j}\omega t) \tag{37}$$

where

$$\bar{\boldsymbol{\phi}}_s = \begin{pmatrix} 1 \\ 1 \\ 1 \end{pmatrix} \phi \qquad \bar{\boldsymbol{\phi}}_{u1} = \begin{pmatrix} 1 \\ \exp(2\pi\mathrm{j}/3) \\ \exp(-2\pi\mathrm{j}/3) \end{pmatrix} \phi \qquad \bar{\boldsymbol{\phi}}_{u2} = \begin{pmatrix} 1 \\ \exp(-2\pi\mathrm{j}/3) \\ \exp(2\pi\mathrm{j}/3) \end{pmatrix} \phi.$$

Substituting equation (37) into equation (35), through a complicated operation, may yield

$$\phi_{tt} - A\phi_{xx} - C^1|\phi|^2\phi + l\phi = 0 \tag{38}$$

where $l = \det[\mathbf{Z} + \omega^2 I]$ and $C' = C/3$.

Thus equation (38) and its solution are similar to equations (22) and (24), respectively, only where $\alpha = (l + K^2 - \omega^2)/(A - V^2)$ and $r = C'/4(A - V^2)$.

3. Analyses and discussion of the results

At present, a very important problem is to determine the correct degree for our theory and method mentioned above. We shall discuss this in the following.

Our theoretical results approach the experimental results. Without losing the essential features of the problem, we use here a highly idealized model of the α-helix by confining ourselves to considering a single chain of peptide groups. Meanwhile, we confine ourselves to the case $V \ll V_{aq}$ as well as $V < V_g$ and, assuming the non-harmonicity of the amide-I vibration to be negligibly small, we present the following form of a one-soliton solution for α-helical proteins [17, 19]:

$$\varphi = \varphi_0 \operatorname{sech}[\varphi_0(3Q^2/\mu C_1^2(K)\beta)^{1/2}(na - vt)] \exp[-j(\omega t - Kna)] \tag{39}$$

where the dispersion relation is of the form

$$\omega = [\omega^0(K)^2 - (3Q^2/\beta\mu)\varphi_0^2]^{1/2} \qquad K = \omega V/C_1^2(K)$$

$$Q = (2\mu\omega_0/\hbar)(\chi + \chi') \simeq (2\mu\omega_0/\hbar)\chi. \tag{40}$$

Now we consider the binding energy of the solitons. For this purpose, we first assume that the squared amplitude φ_0^2 for this soliton is measured in units of the mean square displacement r_0^2 of the molecular lattice-free oscillator, i.e. $\varphi_0^2 = r_0^2 Y$. Then we may obtain the binding energy $E_B(k)$ of this soliton to be in the form

$$E_B(K) = E^0(k) - [E^0(k)^2 - 12E_0 Y\chi^2/\beta]^{1/2} \tag{41}$$

where $E_0 = \hbar\omega_0$, $E^0(k) = \hbar\omega^0(k)$. In the above equations, Y is a dimensionless quantity yet to be estimated. For the above vibrons in α-helical proteins and also those in most molecular crystals, the width ω_w^2 of the vibron squared-frequency band $\omega_w^2 = [\omega^0(k)]^2 - [\omega^0(0)]^2$ is much too small compared with ω_0^2. Then equation (41) may be always reduced approximately to $E_B(k) \simeq (6\chi^2/\beta)Y$. The dimensionless factor Y can be estimated from the stability conditions of the soliton squared-frequency band that $[\omega_1(k)]^2$ as a whole should be separated from the vibron squared-frequency band $[\omega^0(k)]^2$. From the formulae and conditions mentioned above, we can obtain

$$\tfrac{1}{4}(J\beta/\chi^2) \leqslant Y \leqslant \tfrac{3}{4}(J\beta/\chi^2).$$

To estimate Y and the binding energy of the soliton, we again adopt the numerical values of J, χ and β used in [7–10] as follows:

$$J = 7.8\ \text{cm}^{-1} \qquad \beta = 1.3 \times 10^4\ \text{erg cm}^{-2} \qquad \chi = 4 \times 10^{-6}\ \text{erg cm}^{-1}. \tag{42}$$

Then the binding energy of the vibron solitons is about $12\ \text{cm}^{-1} < E_B < 36\ \text{cm}^{-1}$ for the moderate value of $0.7 < Y < 1.96$.

Now we again consider the Davydov theory. Its Hamiltonian is of the form

$$H^{D} = H_s^{D} + \sum_i \hbar\omega_0 b_i^+ b_i - J\sum_i (b_i^+ b_{i+1} + b_{i+1}^+ b_i) + \chi \sum_i (R_{i+1} - R_{i-1}) b_i^+ b_i \tag{43}$$

where H_s^D is still given by equation (2). If we still adopt here the Davydov wavefunction

$$|\psi_D\rangle = \sum_i \alpha_i b_i^+ |0\rangle \tag{44}$$

and apply the method mentioned above, we can obtain a corresponding equation of motion as follows:

$$i\hbar(\partial\varphi^D/\partial t) + (1/2m_D)(\partial^2\varphi^D/\partial x^2) - \omega_D\varphi^D + g_D|\varphi^D|^2\varphi^D = 0. \tag{45}$$

Then a one-soliton solution can be obtained as follows:

$$\varphi^D(x,t) = \varphi_0^D \operatorname{sech}[\beta(m_D g_D)^{1/2}(x - Vt)] \exp[-i(\omega t - Kx)] \qquad (V \ll V_{aq}) \tag{46}$$

where

$$\varphi_0^D = a(m_D g_D)^{1/2}/2 \qquad \omega = \omega_D + K^2/2m_D - g_D^2/16J \qquad \omega_D = \omega_0 - 2J$$
$$\varepsilon - D = \omega_0 \qquad m_D = 1/2Ja^2 \qquad g_D = 4\chi^2/\beta(1 - s^2) \qquad K = m_D V \qquad \hbar = 1. \tag{47}$$

Here V is a parameter identified as the soliton velocity. Thus the soliton binding energy for the Davydov theory is obtained as follows

$$E_B^D = g_D^2/16J = \chi^4/\beta^2 J \approx 1.13\ \text{cm}^{-1}.$$

It is clear that the soliton binding energy for Davydov theory is much too small compared with the result obtained from our theory.

Until now, there has been no experimental evidence for the existence of a soliton in α-helical proteins, *in vivo* or *in vitro*. However, evidence for solitons of a similar character does exist for acetanilide $(CH_3CONHC_6H_5)_x$ (ACN) which is an organic solid having a structure somewhat similar to the α-helical proteins. In ACN, two close chains of hydrogen-bonded amide-I groups run through the crystal. It is an interesting system because nearly planar amide groups display bond distances which are close to those found in polypeptides. Careri *et al* [9, 14] have shown that a band in the infrared spectrum that is red shifted by about 15 cm^{-1} from the amide-I maximum at 1665 cm^{-1} may arise from the amide-I solitons originally suggested by Davydov. We should point out here that the frequency shift of 15 cm^{-1}, which can be considered as the binding energy of the solitons, lies in the range 12–36 cm^{-1} of the binding energy obtained above, although the numerical values of the J, χ and β given in equation (42) may be somewhat different from those for ACN, but deviates greatly from the value in the Davydov theory.

Also the Davydov theory gives the width E_w of the energy band of amide-I vibration excitations as follows: $E_w = 4J = 31.2\ cm^{-1}$. It is seen that, with such a small binding energy, almost all the soliton energy band merges into the amide-I energy band. In the meantime, the binding energies of Davydov solitons take a unique value since their amplitude is automatically given, whereas for vibron solitons the soliton amplitude is an arbitrary parameter and therefore the soliton binding energy increases as the soliton amplitude increases. So the properties of the soliton and its binding energy that we obtained are different from those of the Davydov theory. This and the numerical results

mentioned above support the advantages and correctness of our theory over the Davydov theory in comparison with experimental data.

Our soliton solution and corresponding results mentioned above are obtained from equation (21) or (33) with neglect of the small terms $E^1|\varphi|^2(\partial\varphi/\partial X)$ and $F|\varphi|^2(\partial^2\varphi/\partial x^2)$. We now study this problem further and compare our results with the experimental data to show the validity of this method. For this purpose, we introduce the maximal exciton group velocity in the linear case for this system; it is of the form $V_g = (1/\sqrt{2})\omega_1 a$. We shall use mostly the data for α-helical protein, since it is the case most cited in the literature [7–10, 14], i.e. $V_{aq} = a\sqrt{\beta/M}$, $\sqrt{M/\beta} \simeq 0.99 \times 10^{-13}\,s^{-1}$, $V \simeq 0.3733 + 0.0189\,m\,s^{-1}$, $a = 5 \times 10^{-10}\,m$, $\omega_1 \simeq 10^{12}\,s^{-1}$; thus, $V_g \approx 10^3\,m\,s^{-1}$ and we have $s = V/V_{aq} \ll 1$, $0.1 \leqslant \omega_1/(\beta/M)^{1/2} \leqslant 1$. The data for the velocity V_{aq} of sound vary greatly. Davydov and co-workers use the value $V_{aq} \simeq 100\,m\,s^{-1}$. For this value, the condition, $V_g \gg V_{aq}$ is satisfied. On the other hand, other workers [7–10, 20] quote other values and we calculate the value in the range $5 \times 10^3\,m\,s^{-1} \leqslant V_{aq} \leqslant 10^4\,m\,s^{-1}$. If these values of V_{aq} are relevant, the conditions, $V_g \gg V$, $V_{aq} \gg V$ and $0.1 \leqslant V_g/V_{aq} = \omega_1/(\beta/M)^{1/2} \leqslant 1$ are obviously satisfied, but the Davydov result is also not fulfilled. These results also show that our theory is correct, and that the Davydov theory is an approximate theory.

However, if the Davydov theory is valid, i.e. we adopt $V_{aq} \simeq 100\,m\,s^{-1}$ or $V_{aq} > V$, then we should consider further the terms $E^1|\varphi|^2(\partial\varphi/\partial x)$ and $F|\varphi|^2(\partial^2\varphi/\partial x^2)$. In this case, we shall solve equation (20). It is very complicated. We may estimate that its solution certainly deviates from the Davydov soliton solution.

Meanwhile, in this case, we shall also adopt the following equations:

$$M\ddot{R} \simeq \beta a^2(\partial^2 R/\partial x^2) + (\hbar a/\omega_0)(\chi_1 + \chi_2)(\partial/\partial x)|\varphi|^2 + (\hbar/6\omega_0)(\chi_1 + \chi_2)a^3(\partial^3|\varphi|^2/\partial x^3) - (\partial^2\varphi/\partial t^2) \tag{48}$$

$$= B\varphi - A(\partial^2\varphi/\partial x^2) - C|\varphi|^2\varphi - E^1|\varphi|^2(\partial\varphi/\partial x) - F|\varphi|^2(\partial^2\varphi/\partial x^2) - N^1\varphi(\partial^2|\varphi|^2/\partial x^2) - O(\partial^3|\varphi|^2/\partial x^3) - K(\partial^2\varphi/\partial x^2)(\partial^2|\varphi|^2/\partial x^2) \tag{49}$$

instead of equations (17) and (20), where

$$N^1 = 2a^4\hbar(\chi_1 + \chi_2)^2/6\omega_0(V_{aq}^2 - V^2)M \qquad O = \hbar a^5\chi_2(\chi_1 + \chi_2)/6M\omega_0(V_{aq}^2 - V^2)$$

$$K = \hbar a^6(\chi_1 + \chi_2)\chi_2/6M\omega_0(V_{aq}^2 - V^2).$$

Apparently equations (49) and (20), which are very complicated have not been solved at present. We can find only the approximate solutions by means of the perturbation method. Therefore, the collective excitations for the organism and α-helical protein pose a very complicated problem.

Now, a very important problem is the reasons that led to such a difference between the above results of our theory and results of the Davydov theory. Thus, what is needed is a clear comparison of the two theories. From a comparison between the Davydov theory and our theory the reasons are as follows. First of all, the Hamiltonian and the equations of motion describing the system and the properties of motion of the quasi-particles are different. In our theory there are the anomalous correlation terms $b_i^+ b_i^+ + b_i b_i$ and $b_i^+ b_{i+1}^+ + b_i b_{i+1}$. On the contrary, the Davydov theory has no correlation terms. Secondly, a crucial point seems to be the *ansatz* equation (9) which we believe may be the fundamental difference between our work and Davydov's work. We know that the Davydov wavefunction is given by equation (44); it is an eigenstate of the number operator $N = \Sigma_i b_i^+ b_i$. This describes the state of a single (collective) exciton, i.e. the Davydov wavefunction is restricted to the subspace of a single (collective)

excitation, $N = 1$. Therefore, in the Davydov theory a soliton is exactly one exciton (spread out over several sites) plus the resulting acoustic deformation. However, our wavefunction (equation (9)) is not an eigenstate of the number operator, $N = \Sigma_i b_i b_i$; it belongs to a large space with $N = 0, 1$. It represents rather a superposition of a state with no exciton and a state with one exciton. Let it be represented as

$$|\psi\rangle \geqslant \lambda^{-1} \exp\left(\sum_i \alpha_i b_i^+\right) |0\rangle.$$

Obviously, this is a coherent state, i.e. it is a superposition of the state of different quanta, the phases of which are the same. So, it is this superposition which leads to the anomalous correlation effect. Therefore, it is precisely a collective excitation wavefunction which can represent exactly the collective excitation in the organic protein system. In our theory the soliton contains less than one exciton, this state being a coherent superposition of zero plus one 'inner excitation'. Thus the differences between our theory and the Davydov theory lead to the distinctive features of the two theories mentioned above.

Yet, in our theory, if we let $\varphi^* = 0$, or if the anomalous correlation terms are neglected and our wavefunction is reduced to the Davydov wavefunction by subtracting the constant λ^{-1}, then the equations of motion can also degenerate to the original Davydov equations. This shows that our theory has generality, and the Davydov theory is a special case of our theory. However, from the results of a study by the present author [21, 22] and Haken [23], we know that the state of any organic protein or creature is one of orderly self-organization. In this state the particles are in co-operative motion. Therefore, to adapt the coherent wavefunction (equation (9)), which was used here and described the collective excitation, the collective motion and the coherent feature of the particles, is pertinent to organic proteins. So the above results obtained by our theory are better and more justifiable. For example, the results for the soliton energy indicate that our theory is preferable compared with the Davydov solution.

Lastly we should mention that Kapor and Stojanovic [24] conclude that the application of the continual approximate method in the particular case of the α-helical proteins in some data is not well justified (based on the Davydov theory). We think that this conclusion is not correct because our theory and the results mentioned above do not agree with this conclusion. The continual approximate method is still a very good method for α-helical proteins. Kapor and Stojanovic show only that the Davydov theory is an approximate theory.

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