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Solitons in models of an α-helix: influence of symmetry

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Abstract. Solitons in an α-helix are studied within the framework of a modified Davydov model which takes into account third-order axis symmetry. It is shown that antisymmetric solitons with one vanishing amplitude do not satisfy this demand. This result is confirmed by perturbational calculation for the static solitons.

1. Introduction

The problem of solitons in an α-helix has been extensively treated (Davydov 1982a, b, 1985, Scott 1982a, b). (We are aware that there are many other papers, which neglect the structure of the α-helix and treat it as a simple molecular chain and we shall not quote them.) The reason for the great interest is the idea that the soliton mechanism might offer an explanation for important biological processes related to the energy transfer in proteins. Our aim here is to show that some of the often-quoted results are in fact not compatible with the symmetry of the system.

The organization of the paper is as follows: in section 2 we describe in detail the model of the α-helix that is the subject of our study and in section 3 we outline the common treatment, emphasizing some more important physical properties. Section 4 is dedicated to a different approach which enables one to exploit the symmetry of the problem, and the essential results of this section are confirmed in the subsequent section by perturbational calculation. In the concluding section, we summarize our results and indicate the differences with respect to the results of other workers.

2. Davydov's model of the α-helix

The very complicated structure of α-proteins requires some simplifications. Following Davydov (1982a, b, 1985), we shall study only the excitations of peptide groups (PGs), the so-called amide-I excitations.

We know that PGs are distributed along the α-helix in such a way as to form three chains ('spines') while the PGs within the chain are connected by hydrogen bonds. We shall treat these three chains as one-dimensional structures distributed in the space in such a way that the nearest neighbours to each PG lie on different chains. PGs are distributed to form the helix and the most simple idea is that of a third-order screw axis, although from the crystallographic point of view the situation is more complicated.

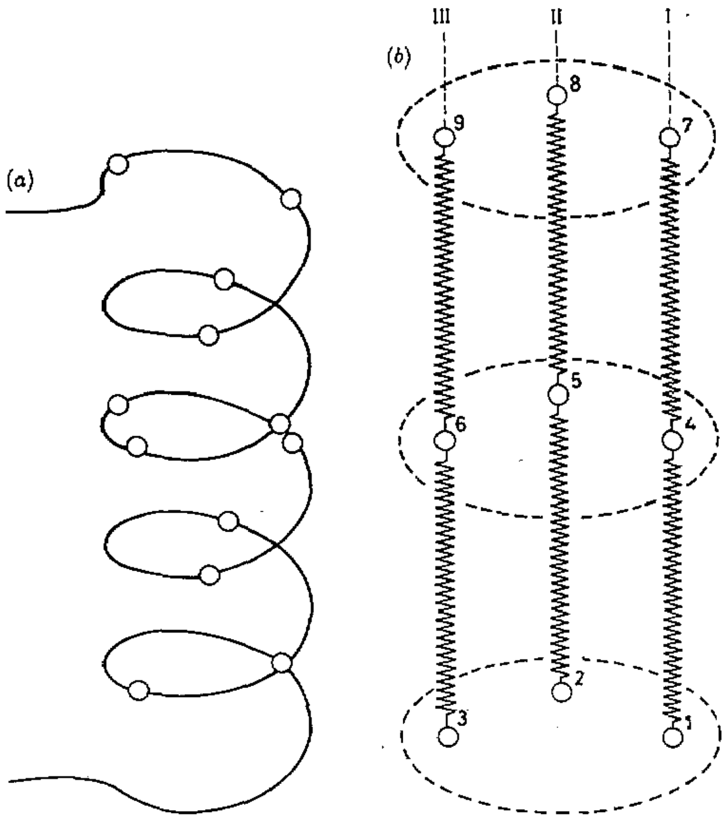

Figure 1. Structures of (a) the α-helix and (b) the simplified model with disks.

Davydov's model supposes that three nearest neighbours are distributed at equal distances on the horizontal planes orthogonal to helix axis, and such combinations are repeated with the period d_0. Scott (1982b) describes this structure in the following way: it 'does not represent a true helical structure but rather 'disks' connected by three "springs"'. We shall only study this model (figure 1) at the moment without the modifications introduced later.

The next step is to describe the excitations. We accept the usual two-level scheme which implies that only the first excited state is important. In that case the creation and annihilation of excitations (vibrons) are described by Pauli operators but, in the spirit of the usual approach, we shall suppose that they satisfy the boson relations

$$[\hat{B}_{n\alpha}, \hat{B}^{+}_{m\beta}] = \delta_{n,m}\delta_{\alpha,\beta} \qquad [\hat{B}_{n\alpha}, \hat{B}_{m\beta}] = 0. \tag{2.1}$$

Here n denotes the site along the axis of the helix which describes the position of the 'disk', and $\alpha = 1, 2, 3$ denotes the chains (spines). $\hat{B}^{+}$ are creation operators and $\hat{B}$ annihilation operators.

We shall suppose that the lattice is not rigid; so interaction with phonons exists. The other possibility of helix torsion will be neglected here. The complete Hamiltonian of the system can be written as

$$\hat{H} = \hat{H}_{v} + \hat{H}_{ph} + \hat{H}_{v-ph} \tag{2.2}$$

where

$$\hat{H}_{v} = \hat{H}_{v}^{(d)} + \hat{H}_{v}^{(nd)} \tag{2.3}$$

$$\hat{H}_{v}^{(d)} = \Delta \sum_{n\alpha} \hat{B}_{n\alpha}^{+}\hat{B}_{n\alpha} - J\sum_{n\alpha} \hat{B}_{n\alpha}^{+}(\hat{B}_{n+1\alpha} + \hat{B}_{n-1\alpha}) \tag{2.4}$$

$$\hat{H}_{v}^{(nd)} = L\sum_{n\alpha} (\hat{B}_{n\alpha}^{+}\hat{B}_{n\alpha+1} + \hat{B}_{n\alpha+1}^{+}\hat{B}_{n\alpha}). \tag{2.5}$$

The summation over n includes the whole chain with periodic boundary conditions included, while α takes the values 1, 2 and 3, which corresponds to the three-sublattice system. Δ is the excitation energy of the single PG and J is the resonant energy between the nearest neighbours within the same chain. L describes the interaction between the nearest neighbours within the same cell but belonging to different chains. The fact that L takes the same values for all three interactions reflects, partly, the helicoidal symmetry.

The more important symmetry property of the model proposed is contained in the fact that the correct developed form of the summation over α in (2.5) can be obtained only by the substitution $4 \rightarrow 1$. This means that the Hamiltonian (2.3) has to be invariant with respect to the transformation:

$$\alpha \rightarrow \alpha + 3\nu \qquad \nu = 0, \pm 1, \pm 2 \tag{2.6}$$

having the direct consequence that

$$\hat{B}_{n\alpha} = \hat{B}_{n\alpha+3\nu} \qquad \nu = 0, \pm 1, \pm 2, \ldots. \tag{2.7}$$

The symmetry property quoted follows from the indistinguishability of PGs belonging to the same sublattice I, II and III (see figure 1(*b*)). Because of this, the permutation of two PGs belonging to the same sublattice cannot change the physical properties of the system. The PGs belonging to different sublattices are indistinguishable also, but their permutation disturbs the initial assumption about a three-sublattice system and, consequently, is not allowed in the framework of the model proposed.

The consequences of the symmetry condition (2.7) will be discussed later. Here we continue with the explanations concerning the Hamiltonian (2.2).

The system of phonons is described by the Hamiltonian

$$\hat{H}_{ph} = \tfrac{1}{2}\sum_{n\alpha}\left(\frac{1}{M}\hat{p}_{n\alpha}^{2} + Q(\hat{u}_{n\alpha} - \hat{u}_{n-1\alpha})^{2}\right). \tag{2.8}$$

$u_{n\alpha}$ and $p_{n\alpha}$ are the displacement and momentum operators of PG on the nth site in the αth chain. M is the mass of the PG and Q is the force constant.

Finally, the coupling between vibrons and phonons will be described here by both 'strong' and 'weak' coupling, as can be seen from the introduction of two coupling constants χ_1 and χ_2:

$$\hat{H}_{v-ph} = \chi_1 \sum_{n\alpha} \hat{B}_{n\alpha}^{+}\hat{B}_{n\alpha}(\hat{u}_{n+1\alpha} - \hat{u}_{n-1\alpha}) + \chi_2 \sum_{n\alpha} (\hat{B}_{n\alpha}^{+}\hat{B}_{n-1\alpha} + \hat{B}_{n-1\alpha}^{+}\hat{B}_{n\alpha})(\hat{u}_{n\alpha} - \hat{u}_{n-1\alpha}). \tag{2.9}$$

Before starting the calculation, let us comment on our approach. The general idea is that the best results are obtained in the variational approach (Škrinjar *et al* 1988, Zhang *et al* 1988, and there are two possible choices of trial function, both first introduced by Davydov. We shall use current notation (Brown *et al* 1986).

The D_2 *ansatz* denotes the trial function which is the direct product of single-particle vibron wavefunctions and a phonon coherent state. The D_1 *ansatz* is more complicated and cannot be factorized in a simple manner. It has an important advantage with respect to the D_2 *ansatz*, namely that it manages to reproduce all the well known, exactly soluble limiting cases. Recently, another approach using a certain very suitable class of D_1 states was also proposed (Brown and Ivič 1989, 1990).

We have decided to accept the D_2 *ansatz* approach in this paper, for several reasons. First of all, the calculations for the α-helix are already rather complicated. We are interested in the influence of symmetry and we do not want to introduce additional complications which would prevent us from separating symmetry effects from the effects of a more complicated *ansatz*. We would like to compare our results with previous calculations and numerical simulations which were all performed using the D_2 *ansatz*. For all these reasons, we shall not discuss the numerous references presenting various calculations for the single chain and only combining them with α-helix parameters at the end of the calculation.

3. Standard approach

We shall review here Davydov's standard approach which will be applied consistently. Our initial point is the Hamiltonian given by (2.2). Once again, we stress the cyclic property of the summation over α, given by (2.7).

The trial function will be taken in the usual D_2 *ansatz* form:

$$|\Psi(t)\rangle = \sum_{n\alpha} a_{n\alpha}(t) \exp[\hat{S}(t)]\, \hat{B}^{+}_{n\alpha}\, |0\rangle. \tag{3.1}$$

Here $|0\rangle$ denotes the direct product of the vibron and phonon ground states. The operator $\hat{S}(t)$ has the anti-Hermitian property

$$\hat{S}(t) = -\frac{\mathrm{i}}{\hbar}\sum_{n\alpha} [\gamma_{n\alpha}(t)\hat{p}_{n\alpha} - \pi_{n\alpha}(t)\hat{u}_{n\alpha}] \tag{3.2}$$

where $\gamma_{n\alpha}(t)$ and $\pi_{n\alpha}(t)$ are real functions. The action of $\exp[\hat{S}(t)]$ on $|0\rangle_{\mathrm{ph}}$ gives a coherent phonon state. The normalization condition for $|\Psi(t)\rangle$ turns into

$$\sum_{n\alpha} |a_{n\alpha}(t)|^2 = 1. \tag{3.3}$$

Further details of the procedure are well known in the theory of solitons and therefore it will be discussed very briefly.

The equation

$$\mathrm{i}\hbar(\partial a_{n\alpha}/\partial t) = (\partial/\partial a^{*}_{n\alpha})\langle\psi(t)|\hat{H}|\psi(t)\rangle \tag{3.4}$$

has to be combined with the equations of motion for operators $\hat{u}_{n\alpha}$ and $\hat{p}_{n\alpha}$, averaged over states $|\psi(t)\rangle$. The continuum approximation

$$\Phi_{n\pm 1\alpha}(t) \xrightarrow{\sim} \Phi_\alpha(x) \pm d_0(\partial\Phi_\alpha/\partial x) + \tfrac{1}{2}d_0^2(\partial^2\Phi_\alpha/\partial x^2) \tag{3.5}$$

where Φ stands for a and γ and d_0 is the lattice constant, applied to the expressions obtained leads to the equation

$$\mathrm{i}\hbar(\partial a_\alpha/\partial t) = (C + \Delta - 2J)a_\alpha - d_0^2(\partial^2 a_\alpha/\partial x^2) + L(a_{\alpha+1} + a_{\alpha-1}) - G|a_\alpha|^2 a_\alpha = 0 \tag{3.6}$$

where

$$C = \frac{1}{2d_0}\sum_\alpha \int_{-\infty}^{+\infty} \mathrm{d}x \left[M\left(\frac{\partial \gamma_\alpha}{\partial t}\right)^2 + Qd_0^2\left(\frac{\partial \gamma_\alpha}{\partial x}\right)^2\right]$$

$$\partial^2\gamma_\alpha/\partial t^2 - V_0^2\partial^2\gamma_\alpha/\partial x^2 = [(2\chi/M)/(\partial/\partial x)]\,|a_\alpha|^2$$

$$\chi = d_0(\chi_1+\chi_2) \qquad v_k = 2d_0^2 Jk/\hbar \tag{3.7}$$

$$V_0^2 = d_0^2 Q/M \qquad s = v_k/V_0 \qquad G = 4\chi^2/MV_0^2(1-s^2).$$

The normalizing condition (3.3) becomes

$$\sum_\alpha \int_{-\infty}^{+\infty} \mathrm{d}x\,|a_\alpha(x,t)|^2 = d_0 \tag{3.8}$$

while the symmetry condition (2.7) becomes

$$a_\alpha(x,t) = a_{\alpha+3\nu}(x,t). \tag{3.9}$$

These equations in fact already presume certain particular solutions, because they are derived for the case of very particular dependence on time and space variable:

$$\gamma_\alpha(x,t) \Rightarrow \gamma_\alpha(\xi) \qquad \xi = x - v_k t \tag{3.10}$$

$$|a_\alpha(x,t)|^2 = |a_\alpha|^2(\xi). \tag{3.11}$$

We shall now look for the solution of (3.10) in the form

$$a_\alpha(x,t) = A_\alpha f(\xi)\exp(\mathrm{i}kx - \mathrm{i}\omega t). \tag{3.12}$$

A_α is the complex amplitude (this is a generalization with respect to standard treatment) characteristic for given α, while $f(\xi)$ is the real function independent on α. k was introduced through velocity v_k (3.7) and $E = \hbar\omega$ is the soliton energy.

Introducing (3.12) into (3.6) and using (3.7) to eliminate first derivatives $\mathrm{d}f/\mathrm{d}\xi$, we obtain

$$d_0^2 JA_\alpha(\mathrm{d}^2 f/\mathrm{d}\xi^2) = (E_0 - E)A_\alpha f + L(A_{\alpha+1} + A_{\alpha-1})f - G|A_\alpha|^2 A_\alpha f^3 \tag{3.13}$$

where

$$E_0 = C + \Delta - 2J + d_0^2 Jk^2. \tag{3.14}$$

Let us look for the solution of (3.13) in the form

$$f(\xi) = (d_0 M/2)^{1/2}[1/\cosh(\mu\xi)] \tag{3.15}$$

where μ is an undetermined parameter, independent of α since f is also independent of α. Substitution of (3.15) into (3.13) leads to the set of equations

$$A_{\alpha+1} + A_{\alpha-1} + YA_\alpha = 0 \qquad \alpha = 1,2,3,4 \rightarrow 1, 0 \rightarrow 3 \tag{3.16}$$

with

$$Y = (E_0 - E - d_0^2 J\mu^2)/L \tag{3.17}$$

and

$$[(G/4d_0J)\,|A_\alpha|^2 - \mu]A_\alpha = 0. \tag{3.18}$$

The normalizing condition becomes

$$|A_1|^2 + |A_2|^2 + |A_3|^2 = 1. \tag{3.19}$$

The fact that μ is α independent implies, according to (3.18), that $|A_\alpha|^2$ are α independent, too. This condition restricts very severely the family of possible solutions of (3.16). When this is taken into account, together with the symmetry condition (3.9) and definition of the amplitude f (3.12), only solutions of the type

$$A_\alpha = A\exp[\mathrm{i}p(2\pi/3)\alpha] \qquad p = 0, \pm 1, \pm 2 \qquad A \neq 0 \tag{3.20}$$

have a physical meaning.

The homogeneous system (3.16) has non-trivial solutions for $Y_1 = -2$ and $Y_2 = Y_3 = 1$. It can be easily shown that, for $Y = -2$, there exists only one set of A-values satisfying (3.19):

$$(A_1)_1 = (A_2)_1 = (A_3)_1 = 1/\sqrt{3}. \tag{3.21}$$

The corresponding soliton energy is

$$E_1 = \Delta - 2J + \hbar^2 v_k^2/4d_0^2J + 2L - [\chi^4/9J(Mv_0^2)^2][1 - \tfrac{8}{9}(1+s^2)/(1-s^2)][1/(1-s^2)^2]. \tag{3.22}$$

For $Y = 1$, the system (3.16) reduces to $A_1 + A_2 + A_3 = 0$. The only possible solution satisfying (3.19) is

$$(A_1)_2 = \exp(\mathrm{i}2\pi/3)/\sqrt{3} \qquad (A_2)_2 = \exp(-\mathrm{i}2\pi/3)/\sqrt{3} \qquad (A_3)_2 = 1/\sqrt{3} \tag{3.23}$$

with the energy

$$E_2 = \Delta - 2J + \hbar^2 v_k^2/4d_0^2J - L - [\chi^4/9J(Mv_0^2)^2][1 - \tfrac{8}{9}(1+s^2)/(1-s^2)] \times [1/(1-s^2)^2]. \tag{3.24}$$

On the other hand, there exists another solution with A-values which are α independent:

$$A_1 = -A_2 = 1/\sqrt{2} \qquad A_3 = 0$$

but which does not satisfy the symmetry condition (3.19). This solution proposed by Davydov (1982a) is usually called the antisymmetric soliton. In the spirit of the present discussion, we treat this solution as purely mathematical, satisfying (3.16)–(3.19), but not satisfying the essential physical symmetry condition (3.19).

4. Influence of symmetry

In this section we wish to show that one can reproduce most of the results from the previous section in a stricter manner, but using the conditions of third-order symmetry. This condition imposes a severe restriction on the results.

Let us start from equation (3.6) for $a_\alpha(x, t)$:

$$i\hbar(\partial a_\alpha/\partial t) = (C + \Delta - 2J)a_\alpha - d_0^2 J(\partial^2 a_\alpha/\partial x^2) + L(a_{\alpha+1} + a_{\alpha-1}) - G|a_\alpha|^2 a_\alpha = 0 \tag{4.1}$$

where we have used the definition of G (3.7).

We shall now try to solve this equation demanding an overall dependence on α in the following way:

$$a_\alpha(x, t) = f_\alpha(\xi)\exp(ikx - i\omega t) \qquad \xi = x - v_k t. \tag{4.2}$$

v_k is defined by (3.7). The normalizing condition (3.8) now becomes

$$\int_{-\infty}^{\infty} dx\,|f_\alpha|^2 = d_0. \tag{4.3}$$

Note that here f_α is a complex function. The substitution of (4.2) into (4.1) gives

$$d^2 f_\alpha/d\xi = \theta f_\alpha - 2\Omega|f_\alpha|^2 f_\alpha + (L/d_0^2 J)(f_{\alpha+1} + f_{\alpha-1}) \tag{4.4}$$

$$\theta = [(C + \Delta - 2J + d_0^2 Jk)^2 - E]/d_0^2 J \tag{4.5a}$$

$$\Omega = G/2Jd_0^2. \tag{4.5b}$$

The condition of third-order symmetry demands that f_α must be a periodic function of α with period equal to 3. We shall look for the solutions in the form

$$f_\alpha^{(p)}(\xi) = F(\xi)\exp[i(2p\pi/3)\alpha] \qquad p = 0, \pm1, \pm2, \ldots \tag{4.6}$$

where $F(\xi)$ is the real function. For any p, one has

$$f_{\alpha+1}^{(p)}(\xi) + f_{\alpha-1}^{(p)}(\xi) = 2C_p f_\alpha^{(p)}(\xi) \qquad C_p = \cos[p(2\pi/3)]. \tag{4.7}$$

It is important to note that, for $p = 0, \pm1, \pm2, \ldots, C_p$ can take only two values ±1 ($p = 0, \pm3, \pm6, \ldots$) and $-\frac{1}{2}$ ($p = \pm1, \pm2, \pm4, \pm5, \ldots$). If we define

$$\theta_p = \theta + (2L/d_0^2 J)C_p \tag{4.8}$$

equation (4.4) turns into

$$d^2F/d\xi^2 = \theta_p F - 2\Omega F^3 \tag{4.9}$$

while the normalizing condition (4.3) becomes

$$\int_{-\infty}^{+\infty} d\xi|F(\xi)|^2 = \frac{d_0}{3}. \tag{4.10}$$

Using standard procedures, one obtains the following energies corresponding to normalized solutions of (4.9):

$$E^{(p)} = E_0 + 2LC_p - G^2/144J \qquad (C_p = +1; -\tfrac{1}{2}). \tag{4.11}$$

It can be easily confirmed that we obtain not only the same energies as in the previous section but also the same amplitudes, following from (4.6).

5. Perturbational calculation

We wish to demonstrate in this section a different approach based on the perturbation calculation. The idea is that one can diagonalize a certain part of the Hamiltonian (2.2)–(2.5) and then look for the energies of the system in terms of new 'hybrid' excitations.

Let us first look at the vibron part $\hat{H}_v$ of the Hamiltonian (2.3) only. We shall perform the following unitary transformation:

$$\hat{B}_{n\alpha} = \sum_{\beta} \Omega_{\alpha\beta} \hat{b}_{n\beta} \tag{5.1}$$

where $\Omega_{\alpha\beta}$ are the elements of the unitary matrix Ω chosen in such a way to diagonalize $\hat{H}_v$ in the momentum space. The explicit form is

$$\Omega_{\alpha\beta} = (1/\sqrt{3}) \exp(\mathrm{i}\varphi_{\alpha\beta}) \tag{5.2}$$

$$\begin{aligned} &\varphi_{11} = \varphi_{12} = \varphi_{13} = \varphi_{21} = \varphi_{31} = 0 \\ &\varphi_{22} = \varphi_{33} = -\varphi_{23} = -\varphi_{32} = 2\pi/3. \end{aligned} \tag{5.3}$$

(One should note that the columns of this matrix are the amplitudes obtained by Scott (1982a, b) in his analysis of the coupled non-linear Schrödinger equation.)

The expression $\hat{H}_v$ will be given in direct space, because it is easier to derive the continuum limit in this way:

$$\hat{H}_v = \sum_n \sum_\beta \Delta_\beta \hat{b}^+_{n\beta} \hat{b}_{n\beta} - J \sum_n \sum_\beta \hat{b}^+_{n\beta} (\hat{b}_{n+1\beta} + \hat{b}_{n-1\beta}) \tag{5.4a}$$

$$\Delta_1 = \Delta + 2L \qquad \Delta_2 = \Delta_3 = \Delta - L. \tag{5.4b}$$

Substituting (5.1) into (2.4) and (2.5) we note that, in $\hat{H}_{\text{v-ph}}$, one can separate terms with equal indices and simplify the expressions by using the properties of the matrix $\mathbf{\Omega}$. The final expression for the Hamiltonian can be written in the form

$$\hat{H} = \hat{H}^{(0)} + \hat{H}^{(1)}_{\text{int}} + \hat{H}^{(2)}_{\text{int}} \tag{5.5a}$$

$$\hat{H}^{(0)} = \sum_\beta \hat{H}^{(0)}_\beta \tag{5.5b}$$

$$\begin{aligned} \hat{H}^{(0)}_\beta = \tfrac{1}{2} \sum_n \frac{1}{M} \hat{p}^2_{n\beta} + Q(\hat{u}_{n\beta} - \hat{u}_{n-1\beta})^2 + \sum_n \Delta_\beta \hat{b}^+_{n\beta} \hat{b}_{n\beta} - J \sum_n \hat{b}^+_{n\beta} (\hat{b}_{n+1\beta} + \hat{b}_{n-1\beta}) \\ + \tfrac{1}{3}\chi_1 \sum_n \hat{b}^+_{n\beta} \hat{b}_{n\beta} (\hat{u}_{n+1\beta} - \hat{u}_{n-1\beta}) + \tfrac{1}{3}\chi_2 \sum_n \hat{b}^+_{n\beta} \hat{b}_{n+1\beta} (u_{n+1\beta} - u_{n\beta}) \\ + (\hat{b}^+_{n\beta} \hat{b}_{n-1\beta} (\hat{u}_{n\beta} - \hat{u}_{n-1\beta}) \end{aligned} \tag{5.6}$$

$$\begin{aligned} \hat{H}^{(1)}_{\text{int}} = \tfrac{1}{3}\chi_1 \sum_n \sum_{\alpha,\beta} \hat{b}^+_{n\beta} \hat{b}_{n\beta} (\hat{u}_{n+1\alpha} - \hat{u}_{n-1\alpha}) + \tfrac{1}{3}\chi_2 \sum_n \sum_{\substack{\alpha,\beta \\ \alpha\neq\beta}} \hat{b}^+_{n\beta} \hat{b}_{n-1\beta} (\hat{u}_{n\alpha} - \hat{u}_{n-1\alpha}) \\ + \hat{b}^+_{n\beta} \hat{b}_{n+1\beta} (\hat{u}_{n+1\alpha} - \hat{u}_{n\alpha}) \end{aligned} \tag{5.7}$$

$$\begin{aligned} \hat{H}^{(2)}_{\text{int}} = \tfrac{1}{3}\chi_1 \sum_n \sum_{\substack{\alpha,\beta\beta' \\ \beta\neq\beta'}} \exp[\mathrm{i}(\varphi_{\alpha\beta'} - \varphi_{\alpha\beta})]\, \hat{b}^+_{n\beta} \hat{b}_{n\beta'} (\hat{u}_{n+1\alpha} - \hat{u}_{n-1\alpha}) + \tfrac{1}{3}\chi_2 \sum_n \sum_{\substack{\alpha,\beta\beta' \\ \beta\neq\beta'}} \\ \times \exp[\mathrm{i}(\varphi_{\alpha\beta'} - \varphi_{\alpha\beta})] (\hat{b}^+_{n\beta} \hat{b}_{n-1\beta'} + \hat{b}^+_{n-1\beta} \hat{b}_{n\beta'}) (\hat{u}_{n\alpha} - \hat{u}_{n-1\alpha}). \end{aligned} \tag{5.8}$$

We shall now study the excitations belonging to $\hat{H}_\beta^{(0)}$ for a particular β. Let us construct the single-particle vibron trial function

$$\varphi_\beta^{(0)}|(t)\rangle = \sum_n a_{n\beta}(t)\hat{b}_{n\beta}^+|0\rangle \tag{5.9}$$

which is normalized, so that

$$\sum_n |a_{n\beta}|^2 = 1. \tag{5.10}$$

We can write the Schrödinger equation for $|\varphi_\beta^{(0)}\rangle$ with the Hamiltonian $\hat{H}_\beta^{(0)}$ and project it onto the direction $\langle 0|\hat{b}_{n\beta}$. After that, we average the result with the coherent phonon state

$$|p_\beta\rangle = \exp[\hat{S}_\beta(t)]\,|0\rangle_{\rm ph} \tag{5.11}$$

with

$$\hat{S}_\beta(t) = -\frac{\mathrm{i}}{\hbar}\sum_n (\gamma_{n\beta}\hat{p}_{n\beta} - \pi_{n\beta}\hat{u}_{n\beta}). \tag{5.12}$$

The results are similar to those obtained in section 3; so we shall quote only the final results obtained after the continuum transition.

The zero-order energy is given by

$$E_\beta^{(0)}(k) = \Delta_\beta + Jd_0^2k^2 - \tfrac{1}{81}[\chi^4/J(Mv_0^2)^2(1-s^2)^2][1 - \tfrac{2}{3}(1+s^2)/(1-s^2)] \tag{5.13}$$

and the corresponding wavefunction is

$$|\varphi_\beta^{(0)}(t)\rangle = \frac{\sqrt{\Omega}}{2}\int \mathrm{d}x\,\frac{1}{\cosh[(d_0\Omega/2)(x - v_k t)]}\exp(\mathrm{i}kx - \mathrm{i}\omega_\beta t)\,\hat{b}_\beta^+(x)\,|0\rangle_{\rm v}$$

$$|0\rangle_{\rm v} = |0\rangle_1\,|0\rangle_2\,|0\rangle_2 \tag{5.14}$$

$$\Omega = \tfrac{2}{3}\chi^2/d_0^2JMV_0^2(1-s^2).$$

It should be noted that, except for ω_β and $\hat{b}_\beta$, nothing else depends on β in the expression for $|\varphi_\beta^{(0)}(t)\rangle$.

At this stage we face another problem: $|\varphi_\beta^{(0)}(t)\rangle$ is not a stationary state. This opens up many problems and, in order to simplify our calculations, we shall discuss only the case of the stationary soliton $v_k = 0$. In this case, one can write

$$|\varphi_\beta^{(0)}(t)\rangle\,\exp(-\mathrm{i}\omega_\beta t)\,|\varphi^{(0)}\rangle \tag{5.15a}$$

$$|\varphi_\beta^{(0)}\rangle = \frac{\sqrt{\Omega}}{2}\int_{-\infty}^{\infty}\mathrm{d}x\,\frac{\hat{b}_\beta^+(x)}{\cosh[(d_0\Omega/2)x]}\,|0\rangle_{\rm v}. \tag{5.15b}$$

Now we can study the perturbing terms (5.7) and (5.8). We average them over

$$|p\rangle = \prod_\beta |p\rangle_\beta. \tag{5.16}$$

After the continuum transition we obtain

$$\bar{H}_{\rm int}^{(1)} = \langle p|\hat{H}_{\rm int}^{(1)}|p\rangle = \tfrac{1}{3}\chi\frac{1}{d_0}\int_{-\infty}^{\infty}\mathrm{d}x\sum_{\substack{\alpha\beta\\ \alpha\neq\beta}}\hat{b}_\beta^+(x)\hat{b}_\beta(x)2\frac{\partial\gamma}{\partial x}. \tag{5.17}$$

We have neglected here terms of the order $d_0^2b_\beta^+(x)(d^2/dx^2)b_\beta(x)$ whose contribution is much smaller. Here, we use the expression $\partial\gamma/\partial x$ because one can show by direct calculation that γ_α is α independent. The above expression simplifies to

$$\bar{H}^{(1)}_{\rm int} = -d_0^3 J\Omega^2 \sum_\beta \int_{-\infty}^{\infty} {\rm d}x \frac{1}{\cosh^2[(d_0\Omega/2)x]} \hat{b}^+_\beta(x)\hat{b}_\beta(x). \tag{5.18}$$

The same procedure for $\bar{H}^{(2)}_{\rm int}$ leads to vanishing results owing to the unitary of the matrix $\mathbf{\Omega}$; so the final expression for the Hamiltonian of the interaction is

$$H_{\rm int} = \bar{H}^{(1)}_{\rm int} = -\frac{4}{81}\frac{1}{d_0 J}\frac{\chi^4}{(Mv_0^2)^2(1-s^2)^2}\sum_\beta \int_{-\infty}^{\infty} {\rm d}x \frac{1}{\cosh^2[(d_0\Omega/2)x]} \hat{b}^+_\beta(x)\hat{b}_\beta(x). \tag{5.19}$$

Let us look for the matrix elements of $H_{\rm int}$ (5.19) between the functions $|\varphi^{(0)}_\beta\rangle$. Since $|\varphi^{(0)}_\beta\rangle$ (5.15) is diagonal in $\hat{b}^+_\beta\hat{b}_\beta$ and so is $H_{\rm int}$ (5.19), it is obvious that $V_{\alpha\beta} = 0$ for $\alpha \neq \beta$:

$$V_{\beta\beta} = V = \langle\varphi^{(0)}_\beta|H_{\rm int}|\varphi^{(0)}_\beta\rangle = -\frac{1}{d_0^3}\frac{2\chi^6}{(Mv_0^2)^3J^2g^3}\int_{-\infty}^{\infty} {\rm d}x\,{\rm d}x'\,{\rm d}x''$$
$$\times \frac{1}{\cosh^2[(d_0\Omega/2)x]\cosh[(d_0\Omega/2)x']\cosh[(d_0\Omega/2)x'']}$$
$$\times \langle 0|\hat{b}_\beta(x'')\left(\sum_\alpha \hat{b}^+_\alpha(x)\hat{b}_\alpha(x)\right)\hat{b}^+_\beta(x')|0\rangle_{\rm v} = -\frac{4}{243}\frac{\chi^4}{J(Mv_0^2)^2}. \tag{5.20}$$

We note the following: in the first-order perturbation theory, there is no splitting of the degenerate level $E_2(0) = E_3(0)$. Also, there are no higher-order contributions; so, within the framework of accepted model, this is an exact result. The energy is

$$\begin{aligned} &E_\beta(0) = \Delta_\beta - \tfrac{1}{27} - \chi^4/(Mv_0^2)^2 J \qquad (\beta = 1,2,3)\\ &\Delta_1 = \Delta + 2L \qquad \Delta_2 = \Delta_3 = \Delta - L. \end{aligned} \tag{5.21}$$

We can formulate our result in the following way: using a perturbation calculation, we have reproduced the result in the previous section, showing that there is no energy solution which would correspond to solitons with one vanishing amplitude.

6. Discussion

We wish to summarize here our main results: the most important information in the standard approach lies in equations (3.16)–(3.18). Let us repeat the fact that (3.18) allows only three possible types of the solutions: case (*a*) is solutions where all three amplitudes have equal moduli; case (*b*) is solutions with one vanishing amplitude and two having equal moduli; case (*c*) is a solution with two vanishing amplitudes.

Case (*c*) is not consistent with the system (3.16) because the vanishing of any two amplitudes leads definitely to the vanishing of the third amplitude, too. This implies that numerical simulation using this type of initial condition and giving non-vanishing results cannot be trusted, since our result is quite general.

We have further shown that case (*b*), describing so-called 'asymmetric solitons', is not compatible with third-order symmetry which is implicitly assumed in Davydov's model of the α-helix. So we treat it as a purely mathematical artefact. It is important to note that our solutions refer only to the given model and that our aim was just to study Davydov's model of the α-helix, which still does not say much about the real α-helix, or even improved models.

Scott (1982a, b) uses a different approach for numerical studies. He defines a modifed Davydov Hamiltonian which models more realistic couplings of the form

$$i\dot{A}_{n1} = L(A_{n2} + A_{n-13}) + \dots .$$

This is a more realistic model which takes into account helicoidal symmetry but is rather complicated to use for calculation; so it was the basis only for numerical calculations whose purpose was to study the threshold coupling.

We think that analytical calculations with this modified Hamiltonian, or some of its versions would lead to important information concerning excitations in real α-proteins.

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