Exciton bound states and solitons in the deformable molecular chain

M J Škrinjar, D V Kapor and S Stojanović

Institute of Physics, Faculty of Sciences, University of Novi Sad, 21000 Novi Sad, Yugoslavia

Abstract. The Hamiltonian of a molecular chain, describing the interaction of excitons (Pauli quasi-particles) with acoustic phonons, after a suitable unitary transformation is diagonalised using the Bethe *ansatz*. The spectrum of the collective excitations at $T = 0$, including strings of excitons, is calculated and compared with the energies of classical solitons. Relevant experiments are discussed.

1. Introduction

The theory of Davydov solitons—non-linear excitations in molecular chains—has attracted much attention in the last 15 years (see, e.g., Davydov 1985), because there are some indications that similar excitations may exist in living tissues, e.g. nerve pulses. Much experimental work (Carreri *et al* 1984a, b, 1988) and numerical research (Scott 1982, MacNeil and Scott 1984, Kerr and Lomdahl 1987) has been done, but there is no definite proof yet. For this reason, the work on this subject continues, in order to obtain more realistic models whose predictions might be closely related to the experimental results.

One particular aspect of the present models has not received the necessary attention: the whole theory is based on the so-called Fröhlich (1952, 1954) Hamiltonian where molecular excitations are treated as bosons, which they are not. In fact their nature is neither bosonic nor fermionic and, although this fact is well known and well respected in the theory of excitons in molecular crystals (Agranovich and Galanin 1982), in the soliton theory there have been only a few attempts (to our knowledge) to treat these excitations properly (Kruglov 1983, Takeno 1983).

In this paper, we wish to present a theory which takes into account the proper nature of these excitations. Section 2 is devoted to the formulation of an effective Hamiltonian and in § 3 we use the pseudo-spin representation for exciton operators in order to exploit the analogy with magnetic systems and to use the results of Bethe *ansatz* calculations. Multi-exciton bound states are compared with classical solitons in § 4. The results are discussed and compared with relevant experimental data, in the concluding section, § 5, together with a review of open questions.

2. Effective Hamiltonian of the system

We shall study the simple molecular chain with one molecule per site and the molecular separation (lattice constant) will be denoted by a. We shall suppose that the first excited level is well separated from the other levels, so that they can be all neglected. In this way, we are dealing with a simple two-level scheme: a molecule at site n can be either in its ground state or in the excited state separated from the ground state by the energy Δ. The dipole–dipole interaction of nearest neighbours is described by the resonant energy I.

The system of excitons is then described by the Hamiltonian

$$\hat{H}_{ex} = \Delta \sum_n \hat{P}_n^+ \hat{P}_n - I \sum_n (\hat{P}_n^+ \hat{P}_{n+1} + \hat{P}_{n+1}^+ \hat{P}_n). \tag{2.1}$$

$\hat{P}_n$ are so-called Pauli operators, creating an exciton at the site n. They satisfy the following commutation relations:

$$[\hat{P}_n, \hat{P}_m] = [\hat{P}_n^+, \hat{P}_m^+] = 0 \qquad \hat{P}_n^2 = \hat{P}_n^{+2} = 0$$
$$[\hat{P}_n, \hat{P}_m^+] = \delta_{n,m}(1 - 2\hat{P}_n^+ \hat{P}_n). \tag{2.2}$$

The system is not rigid; so we must include lattice vibrations in the calculation. We shall take into account only the longitudinal branch of acoustical phonons since the coupling of excitons with this branch is the most important effect. For this reason, we accept the following form of the phonon Hamiltonian:

$$\hat{H}_{ph} = \sum_q \hbar\omega_q \hat{b}_q^+ \hat{b}_q. \tag{2.3}$$

$\hat{b}_q^+$ creates the phonon with the wavevector q. The phonon dispersion law is

$$\omega_q^2 = 4\omega_0^2 \sin(qa/2) \qquad \omega_0^2 = v_0^2/a^2 \tag{2.4}$$

where v_0 is the velocity of sound.

We shall study here the case of strong (local) exciton–phonon coupling of the form

$$\hat{H}_{int} = \sum_{n,q} \chi(q) \exp(iqna) \hat{P}_n^+ \hat{P}_n (\hat{b}_{-q}^+ + \hat{b}_q). \tag{2.5a}$$

The coefficient $\chi(q)$ is given by the expression (Davydov 1985)

$$\chi(q) = 2i\chi(\hbar/2MN\omega_q)^{1/2} \sin(qa) \tag{2.5b}$$

where M is the mass of the molecule and χ is the exciton–phonon coupling constant.

The total Hamiltonian of the system is the sum of these three terms:

$$\hat{H} = \hat{H}_{ex} + \hat{H}_{ph} + \hat{H}_{int}. \tag{2.6}$$

The general treatment of this Hamiltonian is not possible; so we shall try a different approach. We are going to perform a unitary transformation which will help us to

'decouple' excitons and phonons, in the sense that will be explained later. We introduce the equivalent Hamiltonian

$$\hat{H}_{eq} = \exp(i\hat{s})\,\hat{H}\exp(-i\hat{s}) \tag{2.7}$$

by the unitary transformation with the Hermitian operator $\hat{s}$:

$$\hat{s} = \sum_{q,m} F(q)\hat{P}_m^+\hat{P}_m(\hat{b}_q - \hat{b}_q^+)\exp(iqma). \tag{2.8}$$

Choosing $F(q)$ in the form

$$F(q) = -i\chi(q)/\hbar\omega_q \tag{2.9}$$

we obtain

$$\hat{H}_{eq} = \left(\Delta - \frac{\chi}{M\omega_0^2}\right)\sum_n \hat{P}_n^+\hat{P}_n - I\sum_n (\hat{T}_n\hat{P}_n^+\hat{P}_{n+1} + \text{HC})$$

$$+ \sum_q \hbar\omega_q\hat{b}_q^+\hat{b}_q - \frac{\chi^2}{M\omega_0^2}\sum_n \hat{P}_n^+\hat{P}_n\hat{P}_{n+1}^+\hat{P}_{n+1} \tag{2.10}$$

where the operator $\hat{T}_n$ is defined by

$$\hat{T}_n = \exp\left(\sum_q \gamma(q)(\hat{b}_q - \hat{b}_q^+)\exp(iqna)\right) \tag{2.11}$$

and the coefficient $\gamma(q)$ is

$$\gamma(q) = \chi(q)[\exp(iqa) - 1]/\hbar\omega_q. \tag{2.12}$$

We shall study the system at $T \simeq 0$, by averaging $\hat{H}_{eq}$ over the phonon vacuum. In this way, the influence of the phonons is introduced through coefficients and an effective exciton–exciton coupling; so we obtain

$$\hat{H}_{eff} = {}_{ph}\langle 0|\hat{H}_{eq}|0\rangle_{ph} = \left(\Delta - \frac{\chi^2}{M\omega_0^2}\right)\sum_n \hat{P}_n^+\hat{P}_n$$

$$- \tfrac{1}{2}J\sum_n (\hat{P}_n^+\hat{P}_{n+1} + \hat{P}_{n+1}^+\hat{P}_n) - \frac{\chi^2}{M\omega_0^2}\sum_n \hat{P}_n^+\hat{P}_n\hat{P}_{n+1}^+\hat{P}_{n+1} \tag{2.13}$$

where the renormalised resonant interaction becomes

$$J = 2I_{ph}\langle 0|\hat{T}_n|0\rangle_{ph}. \tag{2.14}$$

The Hamiltonian (2.13) will be the starting point of further calculation. (It is important to note that renormalisation due to the coupling with phonons leads to a Hamiltonian whose form is similar to the BCS Hamiltonian.)

We wish to stress already here the differences between our results up to now and those from the usual treatment (Davydov 1985), which describes excitons in terms of Bose operators. First of all, such a substitution means that more than one excitation is allowed on one site, which is a physically incorrect picture. Practically, the result of the transformation (2.7) performed with Bose operators B instead of Pauli operators P would introduce an extra term in H_{eff} (equation (2.13)) of the form $(B_n^+B_n)^2$. This term describes the scattering on the delta potential and has certain important consequences (Kapor *et al* 1989).

3. Analogy with magnetic systems

An extensive literature exists concerning the magnetic systems with spin $\frac{1}{2}$, and we wish to exploit these results. It can be done rather easily, if one remembers that any two-level system can be represented by operators of spin $\frac{1}{2}$, which are then entitled pseudo-spins. If we use the fact that $\hat{P}_n^+ \hat{P}_n = 0$ for the ground state, we can write the following equations (which treat spins as dimensionless variables):

$$\hat{S}_n^- = \hat{P}_n^+ \qquad \hat{S}_n^+ = \hat{P}_n \qquad \hat{S}_n^z = \tfrac{1}{2} - \hat{P}_n^+ \hat{P}_n \tag{3.1}$$

where the ground state of the system corresponds to the configuration of all pseudo-spins 'pointing up', i.e. $\langle S^z \rangle = \frac{1}{2}N$.

Using this representation, H_{eff} (equation (2.13)) takes the form common for the Heisenberg ferromagnetic chain with 'easy-plane' or 'easy-axis' anisotropy:

$$H_{\mathrm{eff}} = \varepsilon_0 \sum_n (\tfrac{1}{2} - \hat{S}_n^z) - J \sum_n [\hat{S}_n^x \hat{S}_{n+1}^x + \hat{S}_n^y \hat{S}_{n+1}^y + g(\hat{S}_n^z \hat{S}_{n+1}^z - \tfrac{1}{4})] \tag{3.2}$$

where

$$\varepsilon_{0'} = \Delta - 2\chi^2/M\omega_0^2 \qquad g = \chi^2/M\omega_0^2 J. \tag{3.3}$$

(One should note that the term analogous to the external field is always present $\Delta \neq 0$; so the ground state is always that defined above, irrespective of the ratio $J_z/J = g$.)

Now we can use the results based on the Bethe *ansatz* obtained by Johnson and Bonner (1980) and Hodgson and Parkinson (1984) to analyse the spectrum of the renormalised exciton system. We obtain the energy of m bound excitons with the momentum p: for $g > 1$, $g = \cosh \alpha$,

$$\varepsilon_m(p_\nu) = m\varepsilon_0 + J \sinh \alpha[\cosh(m\alpha) - \cos p_\nu]/\sinh(m\alpha) \tag{3.4}$$

and, for $g < 1$, $g = \cos \theta$, $0 < \theta < \pi/2$,

$$\varepsilon_m(p_\nu) = m\varepsilon_0 + J \sin \theta \, [\cos(m\theta) - \cos p_\nu]/\sin(m\theta) \tag{3.5}$$

where $m = 1, 2, \ldots$ and $p_\nu(\pi/N)\nu$, $\nu = 0, \pm 1, \pm 2, \ldots$ ($\hbar = 1$, $a = 1$).

Let us briefly discuss some of the consequences of these expressions. For $m = 1$, the energy ε_1 of an exciton (renormalised owing to exciton–phonon interaction) is 'red shifted' from the energy $\varepsilon_{\mathrm{ex}}$ of an unperturbed exciton:

$$\varepsilon_1 = \Delta - J \cos p - \chi^2/M\omega_0^2 \tag{3.6a}$$

$$\varepsilon_{\mathrm{ex}} = \Delta - 2I \cos p. \tag{3.6b}$$

Since $J \simeq 2I$, we obtain an estimate

$$\varepsilon_1 - \varepsilon_{\mathrm{ex}} \simeq -\chi^2/M\omega_0^2. \tag{3.6c}$$

We shall also quote here the expression for the energy of the bi-exciton ($m = 2$) and show that it represents a stable bound state of two excitons, i.e. that the following is valid:

$$\varepsilon_2(p) \leqslant \varepsilon_1(p_1) + \varepsilon_2(p_2) \tag{3.7}$$

if the total momentum of the system is the same in both cases:

$$p = p_1 + p_2.$$

Using (2.4) or (2.5), we have

$$\varepsilon_2(p) = 2\varepsilon_0 + (J/g)[g^2 - \cos^2(p/2)]. \tag{3.8}$$

The condition of bi-exciton stability is

$$\Delta\varepsilon = \varepsilon_2(p) - \min[\varepsilon_1(p_1) + \varepsilon_2(p_2)] < 0 \tag{3.9}$$

where the second term on the right-hand side represents the bottom of the two-exciton continuum. A simple calculation leads to the result

$$\Delta\varepsilon = -(J/g)[1 - \cos(p/2)]^2 < 0 \tag{3.10}$$

for $g \lesssim 1$; so in both cases the bi-exciton is the stable excitation.

The last relation implies that bound states are formed in the system of excitons for any $g > 0$ (attractive interaction), meaning that a threshold coupling need not exist. It is important to stress that this last conclusion is valid only in the case when excitons are treated as paulions, which are equivalent to fermions in one spatial dimension (Agranovich and Galanin 1982) (see also the Jordan–Wigner transformation, for example, in the textbook by Mattis (1988)).

In this sense, the creation of bound states for any small finite attractive interaction can be considered as analogous to Cooper pairing in the system of electrons.

In the next section we shall analyse the classical soliton excitations of the equivalent Hamiltonian and indicate the connection between solitons and bound exciton states.

4. Solitons in a molecular chain

Using the definition of spin coherent states (SCS) for $S = \frac{1}{2}$ (Radcliffe 1971, Perelomov 1985)

$$|\alpha\rangle = \prod_n |\alpha_n\rangle \qquad |\alpha_n\rangle = \frac{1}{\sqrt{1 + |\alpha_n|^2}} \exp(-\alpha_n \hat{S}_n^-)|0\rangle_{\mathrm{ex}} \tag{4.1a}$$

with the parametrisation

$$\alpha_n = \tan(\theta_n/2) \exp(i\phi_n) \tag{4.1b}$$

we can define the classical spins as the average values of spin operators over SCS:

$$\begin{aligned}
S_n^{\pm} &= \langle\alpha|\hat{S}_n^{\pm}|\alpha\rangle = \tfrac{1}{2}\sin\theta_n \exp(\pm i\phi_n) \\
S_n^z &= \langle\alpha|\hat{S}_n^z|\alpha\rangle = \tfrac{1}{2}\cos\theta_n.
\end{aligned} \tag{4.2a}$$

One should have in mind that the 'magnetic' part of the calculation is performed for $\hbar = 1$, but it does not influence the proper dimensionality of the results, owing to the dimensionless relation (3.1). Using the procedure introduced by Klauder (1960) and

Mead and Papanicolaou (1983), we can also define the Lagrangian of the system described by the equivalent Hamiltonian (3.2):

$$L = \langle \alpha | i\hbar(\overleftrightarrow{\partial}/\partial t) | \alpha \rangle - \langle \alpha | \hat{H} | \alpha \rangle = L_t - \mathcal{H} \tag{4.3}$$

where

$$L_t = \frac{\hbar}{2} \sum_n (1 - \cos \theta_n) \dot{\phi}_n \tag{4.4a}$$

and

$$\mathcal{H} = \varepsilon_0 \sum_n (\tfrac{1}{2} - \cos \theta_n) - \frac{J}{4} \sum_n \Big(\sin \theta_n \sin \theta_{n+1} \cos(\phi_{n+1} - \phi_n)$$

$$+ \frac{g}{4} (\cos \theta_n \cos \theta_{n+1} - 1) \Big). \tag{4.4b}$$

The equations of motion for the conjugated variables $(\phi_n, \tfrac{1}{2} \cos \theta_n)$ are simply classical Lagrangian (or Hamiltonian) equations. Since there exists complete analogy with the classical anisotropic Heisenberg chain (Tjon and Wright 1977, Kapor *et al* 1986, Haldane 1982, Nakamura *et al* 1983), we shall not solve here the equations of motion for $\theta(x, t)$ and $\phi(x, t)$ in the continuum approximation (i.e. Landau–Lifshitz equations) but quote instead the well known single-soliton solutions in order to analyse the solitons in a molecular chain. For simplicity, we shall study only the isotropic chain ($g = 1$), but most of the conclusions are qualitatively valid for the anisotropic case, too. (We shall see later that the value $g \simeq 1$ is good approximation for the α-helix.)

The single-soliton solution with $M = \langle \alpha | \Sigma_n(\tfrac{1}{2} - \hat{S}_n^t) | \alpha \rangle$ excited molecules (M is the magnetisation of the ferromagnetic chain and corresponds to the number of rotated spins since $\hbar = 1$) and total momentum p, defined in the continuum approximation (Tjon and Wright 1977) by

$$p = \frac{\hbar}{2a} \int_{-\infty}^{\infty} (1 - \cos \theta) \frac{\partial \phi}{\partial x} \, dx \tag{4.5}$$

has the following form (Haldane 1982):

$$\cos[\theta(x, t)] = 1 - 2\varphi_0^2 / \cosh^2[(2/l_0)(x - vt)] \tag{4.6}$$

with the following characteristic properties: an amplitude of

$$\varphi_0^2 = \sin^2(pa/2\hbar) = \sin^2(ka/2) \tag{4.7a}$$

a dimension of

$$l_0 = (M/\varphi_0^2)a = [M/\sin^2(ka/2)]a \tag{4.7b}$$

and a velocity of

$$v = (Ja/M\hbar) \sin(ka). \tag{4.7c}$$

The soliton energy is obtained from (4.4b) by going over to the continuum and substituting (4.6), which for $g = 1$ leads to

$$E = M\varepsilon_0 + (J/M)[1 - \cos(pa/\hbar)]. \tag{4.8}$$

We see that the above expression for the soliton energy coincides with the energy of

m-bound excitons (3.4) and (3.5) for the case $g = 1$ and the same momentum p only if the number M is 'quantised', i.e. if we demand that it takes only the integer values (classical value of $M = (1/2a)\int(1 - \cos\theta)\,dx$ need not be an integer!):

$$M = m \qquad m = 1, 2, \ldots . \tag{4.9}$$

This last relation represents in fact the Bohr–Sommerfeld semi-classical quantisation (Nakamura *et al* 1983, Kapor *et al* 1986).

In order to obtain the complete analogy between the soliton energy and the energy of bound exciton states (3.4) and (3.5), we must also perform the 'box quantisation' of the momentum p (or k) (de Broglie quantisation) for a particle in the chain of the length $L = Na$:

$$k_{\nu'} = (\pi/Na)\nu \qquad \nu = 0, \pm 1, \ldots, \pm\tfrac{1}{2}N. \tag{4.10}$$

(This choice of ν defines the first Brillouin zone.)

Analysing equations (4.7a) and (4.7b) for soliton amplitude and dimension, we see that at the Brillouin zone boundary ($k = \pm\pi/a$), $l_0 = ma$ and $\varphi_0^2 = 1$, i.e. the classical soliton dimension coincides with the lattice constant a multiplied by the number of excited molecules (the number of rotated spins in the magnetic chain). At the Brillouin zone centre $k = 0$, we see that l_0 diverges and $\varphi_0^2 \to 0$, meaning that 'soliton' excitation becomes delocalised, turning into an unlocalised exciton state.

At this point it is important to note that in the standard Davydov treatment, one calculates the averages over the so-called $|D_2\rangle$ trial function which is the product of coherent phonon states and single-particle exciton states. The structure of the exciton part implies that no multi-exciton bound states can appear in such a calculation; so most of our results would be lost.

Finally, let us look for the average value of the relative phonon displacement $\hat{\rho}_n$ (defined by the phonon operators $\hat{b}_q$ and $\hat{b}_q^+$):

$$\hat{\rho}_n = -\frac{1}{a}(\hat{u}_{n+1} - \hat{u}_n)$$

$$= -\frac{1}{a}\sum_q \left(\frac{\hbar}{2MN\omega_q}\right)^{1/2} \exp(iqna)\,[\exp(iqa) - 1](\hat{b}_q + \hat{b}_{-q}^+). \tag{4.11}$$

Bearing in mind the unitary transformation (2.7) and the fact that the equivalent Hamiltonian was averaged over the phonon vacuum, we obtain

$$\langle\hat{\rho}_n\rangle = {}_{\mathrm{ph}}\langle 0|\langle\alpha|\exp(i\hat{s})\,\hat{\rho}_n\,\exp(-i\hat{s})|\alpha\rangle|0\rangle_{\mathrm{ph}}$$

$$= -\frac{1}{a}\sum_q \left(\frac{\hbar}{2MN\omega_q}\right)^{1/2} \exp(iqna)\,[\exp(iqa) - 1]_{\mathrm{ph}}\langle 0|\langle\alpha|\exp(i\hat{s})$$

$$\times (\hat{b}_q + \hat{b}_{-q}^+)\exp(-i\hat{s})|\alpha\rangle|0\rangle_{\mathrm{ph}}. \tag{4.12}$$

Using the definition of $\hat{s}$, we obtain

$$\exp(i\hat{s})\,\hat{b}_q\,\exp(-i\hat{s}) \equiv \hat{b}_q - i\sum_m F(q)\exp(-iqma)\,\hat{P}_m^+\hat{P}_m \tag{4.13}$$

leading to

$$\langle\hat{\rho}_n\rangle = -(4a\chi/Mv_0^2)[\langle\alpha|\hat{P}_n^+\hat{P}_n|\alpha\rangle + \langle\alpha|\hat{P}_{n+1}^+\hat{P}_{n+1}|\alpha\rangle]. \tag{4.14}$$

Since

$$\langle \alpha | \hat{P}_n^+ \hat{P}_n | \alpha \rangle = \langle \alpha | (\tfrac{1}{2} - \hat{S}_n^z) | \alpha \rangle = \tfrac{1}{2}(1 - \cos \theta_n)$$

using the solution (4.6) in the continuum approximation, we obtain ($\langle \hat{P}_{n+1}^+ \hat{P}_{n+1} \rangle \simeq \langle \hat{P}_n^+ \hat{P}_n \rangle$)

$$\rho(x, t) = -(4a\chi/Mv_0^2)\{1 - \cos[\theta(x, t)]\} = -(8a\chi/Mv_0^2)\{\varphi_0^2/\cosh^2[(2/l_0)(x - vt)]\}.$$

The phonon displacement can be calculated as

$$u(x, t) = -\int \rho(x', t)\, dx' \qquad (4.15)$$

leading to

$$u(x, t) = u_0 \tanh[(2/l_0)(x - vt)] \qquad (4.16a)$$

with

$$u_0 = (4a\chi/Mv_0^2)ma. \qquad (4.16b)$$

We can see that the phonon displacement accepts the form of a kink moving along the chain with the velocity v_0.

Let us conclude by noting that the phonon displacement $u(x, t)$ (or $\rho(x, t)$) in our approximation results as the consequence of the excitation of the molecule (owing to the interaction between excitons and lattice vibrations), which leads to the displacement of the molecule from the equilibrium position; if $\langle \hat{P}_n^+ \hat{P}_n \rangle = 0$, it follows from (4.12) and (4.13) that $_{\text{ph}}\langle 0 | \hat{u}_n | 0 \rangle_{\text{ph}} = 0$. One should not, however, forget that the energy given by equation (4.8) or (3.5), (3.6) represents the energy of the whole system, which was calculated by averaging the equivalent Hamiltonian over the phonon vacuum and coherent exciton-spin states, so that it cannot be 'separated' into an ('excitonic') soliton energy part and the phonon energy. In other words, the soliton is not a two-component entity in our approximation (contrary to Davydov's picture) but represents some 'effective' excitation of the total system, whose energy is given by (4.8).

5. Discussion of the results and conclusion

It is well known that Davydov (1985) was the first to propose solitons as possible collective excitations in biomolecular chains, the α-helix in proteins being the most prominent representative. Carreri *et al* (1984a, b) also considered Davydov-like solitons in order to explain the IR spectrum of acetanilide (ACN) crystals in which two close chains of H-bonded amide groups define quasi-one-dimensional system, which is certainly interesting from the biological viewpoint (Carreri 1973).

We are going to discuss our results with respect to the application to the case of the α-helix. (The experimental situation with ACN is more complicated; so this case will not be considered here.)

Numerical values for the parameters characterising the soliton (χ, I and the spring constant w, where $Mv_0^2 = wa^2$) for the α-helix are usually accepted as follows (Scott 1982):

$$\chi = (4 - 8) \times 10^{-11} \text{ N}$$

$$M = 2 \times 10^{-25} \text{ kg}$$

$$I = 7.8 \text{ cm}^{-1} = 1.4 \times 10^{-22} \text{ J}$$

$$w = 13 \text{ N m}^{-1}$$

$$\Delta = \varepsilon_{\text{I}} = 0.205 \text{ eV } (=1650 \text{ cm}^{-1}) = \text{energy of amide–I bond.}$$

This leads to the following estimate:

$$g = \chi^2/JM\omega_0^2 \simeq \chi^2/2Iw \simeq 0.6\text{–}2.$$

We see that the case where $g = 1$ studied in the previous sections fits the above data well.

Let us repeat that the important novelty of our approach with respect to Davydov's theory is the appearance of bound exciton states which can be (classically) described as solitons—we can call them multi-quantum solitons because they include several bound excitations. The two-quantum soliton (with approximate energy $\simeq 2\varepsilon_{\text{I}}$) might be especially important in biology, since it is nearly resonant with the energy released through the hydrolysis of adenosine triphosphate into adenosine diphosphate (about 0.43 eV) (Bolterauer and Henkel 1986). This theory needs further refinement concerning biologically relevant finite temperatures.

We would like also to comment finally on the previous work based on the treatment of excitons as paulions. Takeno (1983) uses the approximation $\langle S_n^z \rangle = 0$ at $T = 0$ K but, when a localised excitation exists in the system, this might not be the case; so there appear to be some doubts about the results. Kruglov (1984) on the other hand averages Heisenberg equations of motion for exciton operators and uses a decoupling procedure to arrive at a non-linear Schrödinger equation with an additional term. Unfortunately, he calculates only functions and no other parameters of the system; so it is difficult to compare his results with ours.

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