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Bethe splitting of exciton bands and solitons

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Abstract. The formation of solitons and bisolitons under the conditions of Bethe splitting of exciton bands is analysed by means of an equivalent Hamiltonian, which is correct up to terms linear in the ratio of exciton bandwidth and isolated molecule excitation energy. Several types of solitons appear in such a system and their properties are analysed, as well as the conditions for bisoliton formation and their properties. It is shown that two solitons of the same type can always form a bisoliton, while two solitons of different types can form a bisoliton only under certain conditions related to the ratios of their effective masses and their coupling constants. Special conditions are indicated when the binding energy of two solitons of different type can be higher than the binding energy of two solitons of the same type. These conditions present the basis for the stability analysis of bound soliton states.

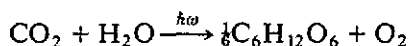
1. Introduction

The theory of solitons in molecular systems represents a very important field of physics today. In spite of very intensive research performed over the last few years, there still exists a 'gap'. Most of the work concerns the interaction of one type of exciton with phonons, or the influence of Davydov splitting of exciton bands on solitons (important owing to interest in α -helix structures). On the other hand, to the authors' knowledge, the effect of Bethe splitting of exciton bands in the study of solitons has not been treated previously. In this case, several different types of excitons can be excited in molecular crystals, depending on light-induced transitions in isolated molecules.

The first studies concerning Bethe splitting of exciton zones were given in Craig (1955), Craig and Hobbins (1955) and Agranovič (1959). The numerical calculations of some Bethe splitting consequences were carried out for a one-dimensional structure in Hoffmann (1963) and for an anthracene crystal in Agranovič (1968, pp 96–9). Experimental data concerning different types of isolated molecule excitations are quoted in Davydov (1979, pp 86, 88, 96 and 98, tables 5–8) for anthracene, naphthalene, naphthalene and benzole, respectively.

It is obvious that Bethe splitting takes place when optically active materials are illuminated by non-monochromatic light quanta, capable of inducing different molecular transitions. Consequently, this effect could be important in the explanation of some biophysical phenomena in plants illuminated by the sun. The most interesting of these phenomena are photosynthesis processes, which are induced by light quanta. A number of photosynthesis characteristics have not had, up to now, a satisfactory theoretical explanation.

So, for example, the reaction



requires about 5.12 eV energy (Davydov 1979, p 174), i.e. it can be realized by absorption of several light quanta. The transformation of electromagnetic energy into chemical energy requires a finite time, much longer than the excitonic lifetime, which is of the order of 10^{-8} s. So, it is plausible to assume that light quanta in plants previously transform into stable excitations, such as solitons or bisolitons, whose lifetimes are sufficiently long to realize the reaction.

The second example, which can be directly connected with Bethe splitting, is Emerson's amplifying of photosynthesis, which is observed when algae samples are illuminated by two kinds of photons with wavelengths of 650 and 700 nm (see Levinne 1969, p 58). This indicates that a lot of photosynthesis characteristics essentially depend upon the number as well as upon the kind of optical excitations, and that the study of these excitons can give a good ground for photosynthesis theory.

In order to extend this ground we shall study the types of soliton excitations in molecular chains where Bethe splitting of exciton bands occurs. A complete solution of the problem would lead to complicated equations that can be solved only numerically. In order to obtain at least qualitative results, we shall perform an approximate analysis based on the fact that the single-site excitation energy is much higher than the exciton bandwidth. The ratio of bandwidth to molecular excitation energy is the small parameters of our theory. An equivalent Hamiltonian linear in the small parameter will be formulated and we shall see that this Hamiltonian turns into a sum of independent terms. We shall study the solitons in such a system using the standard procedure (Davydov and Eremko 1977, Davydov *et al* 1978, Davydov 1980, Scott 1982).

The system described above allows for the existence of several types of excitons, so it is interesting to study the conditions under which the bound states of two solitons can be formed. It is obvious that a bisoliton can be formed by two solitons of the same kind or different kinds, which makes the problem more complicated.

The procedure of determining the approximate equivalent Hamiltonian will be described in section 2. Soliton states in the chain where several kinds of excitons exist will be studied in section 3, based on the equivalent Hamiltonian. In section 4, the conditions for the formation of bisolitons and their properties will be described.

2. Equivalent Hamiltonian of exciton-phonon system with the Bethe splitting of exciton bands included

Bethe splitting of exciton bands in molecular crystals occurs due to the fact that an isolated molecule can be excited by photons in several ways. This means that an electron from the ground state 0 can be excited into several states numerated as 1, 2—up to w . A different exciton wave corresponds to each of the excitations of the isolated molecule, and the appearance of several kinds of excitons is entitled Bethe splitting of exciton zones (Knox 1966). It is reasonable to assume that in such a situation, there can appear w kinds of solitons, too. We shall analyse this possibility here and determine the properties of the solitons that appear in crystals where the usual 'two-level approximation' of excitons is not valid, but a multilevel scheme for the isolated molecule must be accepted.

The Hamiltonian of the 'frozen' exciton system corresponding to w -level schemes of molecular excitations will be written in the form:

$$H_0 = \sum_{n\alpha} \Delta_\alpha B_{n\alpha}^+ B_{n\alpha} + \sum_{nm\alpha} D_{nm}^{\alpha\alpha} B_{n\alpha}^+ B_{m\alpha} - \sum_{nm\alpha} R_{nm}^{\alpha\alpha} B_{n\alpha}^+ B_{m\alpha} + \sum_{nm\alpha\alpha'} D_{nm}^{\alpha\alpha'} B_{n\alpha}^+ B_{m\alpha'} - \sum_{nm\alpha\alpha'} R_{nm}^{\alpha\alpha'} B_{n\alpha}^+ B_{m\alpha'} \quad \alpha' \neq \alpha. \quad (2.1)$$

Operators $B_{n\alpha}^+$ create excitations of type α on the molecule at site n . These operators are Bose operators, which implies that the Hamiltonian is treated in the harmonic approximation (Lalović *et al* 1969). Indices α and α' take the values

$$\alpha, \alpha' \in (1, 2, \dots, w). \quad (2.2)$$

The quantity Δ_α denotes the excitation energy of the isolated molecule, while D and R are dipole-dipole interaction matrix elements. A common situation for optical excitations is that Δ_α is two orders of magnitude larger than R and D and we shall suppose that this is the case. Coefficients in the Hamiltonian (2.2) satisfy the following symmetry relations:

$$\Delta_\alpha^* = \Delta_\alpha \quad D_{nm}^{\alpha\alpha*} = D_{nm}^{\alpha\alpha} \quad R_{mn}^{\alpha\alpha*} = R_{mn}^{\alpha\alpha} \quad D_{nm}^{\alpha'\alpha*} = D_{nm}^{\alpha\alpha'} \quad R_{mn}^{\alpha'\alpha*} = R_{mn}^{\alpha'\alpha}. \quad (2.3)$$

It is important to note that in the expression (2.1) we have separated explicitly the terms diagonal in types of molecular excitations (the first three terms in (2.1)) and non-diagonal terms.

The usual way of treating Bethe splitting is to put the Hamiltonian (2.1) in the following form:

$$H_0 = \sum_{nm\alpha\alpha'} (B_{n1}^+ \quad B_{n2}^+ \quad \dots \quad B_{nw}^+) \begin{pmatrix} M_{nm}^{11} & \dots & M_{nm}^{1w} \\ \vdots & & \vdots \\ M_{nm}^{w1} & \dots & M_{nm}^{ww} \end{pmatrix} \begin{pmatrix} B_{m1} \\ \vdots \\ B_{mw} \end{pmatrix} \quad (2.4)$$

where the matrix \mathbf{M} is given by

$$M_{nm}^{\alpha\alpha'} = \bar{\Delta}_\alpha \delta_{\alpha\alpha'} \delta_{nm} + D_{nm}^{\alpha\alpha'} - R_{nm}^{\alpha\alpha'} \quad \bar{\Delta}_\alpha = \Delta_\alpha + \sum_l D_l^{\alpha\alpha} \quad (2.5)$$

and the given bilinear form is diagonalized through some unitary transformation \mathbf{U} which must be of the same order as \mathbf{M} . This standard treatment leads in the general case to an algebraic equation of w th order. It is very difficult to obtain any particular conclusion in this approach except for the simplest case 2×2 .

We wish to obtain tractable results in our analysis, so we shall use an approximate method, consisting of the substitution of the Hamiltonian H_0 by an equivalent Hamiltonian that is diagonal in molecular excitation indices. This is an approximate procedure based on the existence of a small parameter R/Δ or D/Δ , which is of the order 0.01.

In order to arrive at soliton theory, one has to take into account also the Hamiltonian of the phonon subsystem as well as the Hamiltonian of the exciton-phonon interaction. For this reason, we are looking for an equivalent Hamiltonian of the total system of interacting excitons and phonons.

For vibrating sites, we have

$$n \rightarrow n + U_n \quad m \rightarrow m + U_m \quad H_0 \rightarrow H. \quad (2.6)$$

In the approximation linear in molecular displacements U_n , one can write

$$Z_{nm}^{\alpha\alpha'} \rightarrow \hat{Z}_{nm}^{\alpha\alpha'} = Z_{nm}^{\alpha\alpha'} + \frac{1}{N} \sum_k k Z_k^{\alpha\alpha'} (U_n - U_m) e^{ika(n-m)} \quad (2.7)$$

where Z stands for R and D , and Z_k are the Fourier transforms of Z_{nm} . So the Hamiltonian that includes excitons and their interaction with phonons has the form

$$H = \sum_{n\alpha} \Delta_\alpha B_{n\alpha}^+ B_{n\alpha} + \sum_{nm\alpha} \hat{D}_{nm}^{\alpha\alpha} B_{n\alpha}^+ B_{n\alpha} - \sum_{nm\alpha} \hat{R}_{nm}^{\alpha\alpha} B_{n\alpha}^+ B_{m\alpha} \\ + \sum_{nm\alpha\alpha'} \hat{D}_{nm}^{\alpha\alpha'} B_{n\alpha}^+ B_{n\alpha'} - \sum_{nm\alpha\alpha'} \hat{R}_{nm}^{\alpha\alpha'} B_{n\alpha}^+ B_{m\alpha'} \quad (2.8)$$

and operator coefficients satisfy symmetry conditions

$$\Delta_\alpha^* = \Delta_\alpha \quad (\hat{Z}_{nm}^{\alpha'\alpha})^+ = \hat{Z}_{nm}^{\alpha\alpha'} \quad \hat{Z}_{nm} \equiv (\hat{R}_{nm}, \hat{D}_{nm}). \quad (2.9)$$

This implies symmetry conditions for their Fourier transforms too:

$$Z_{-k}^{\alpha'\alpha} = Z_k^{\alpha\alpha'} \quad \hat{Z}_k \equiv (\hat{R}_k, \hat{D}_k). \quad (2.10)$$

The total Hamiltonian of the system can be written as

$$H_{\text{tot}} = H + H_p \quad (2.11)$$

where H is given by (2.8) and

$$H_p = \frac{1}{2} \sum_n [p_n^2/M + Q(U_n - U_{n-1})^2] \quad (2.12)$$

is the Hamiltonian of the phonon subsystem. Here M is the mass of the molecule, Q is the force constant and $p_n = M\dot{U}_n$ is the momentum of the molecule.

The transition from the Hamiltonian (2.11) to the equivalent Hamiltonian will be performed using the following unitary transformation:

$$H_{\text{eq}} = e^{-i\hat{\lambda}} \hat{H}_{\text{tot}} e^{i\hat{\lambda}} = \sum_{n=0}^{\infty} \frac{(-i)^n}{n!} [\hat{\lambda}, [\hat{\lambda}, \dots [\hat{\lambda}, \hat{H}_{\text{tot}}] \dots]] \\ = \hat{H}_{\text{tot}} - i[\hat{\lambda}, \hat{H}_{\text{tot}}] - \frac{1}{2}[\hat{\lambda}, [\hat{\lambda}, \hat{H}_{\text{tot}}]] \quad (2.13)$$

where the Hermitian operator $\hat{\lambda}$ is defined as

$$\hat{\lambda} = \sum_{fg\mu\nu} (\hat{X}_{fg}^{\mu\nu} B_{f\mu}^+ B_{g\nu} + \hat{Y}_{fg}^{\mu\nu} B_{f\mu}^+ B_{g\nu}) \quad \hat{X}^{\mu\mu} = \hat{Y}^{\mu\mu} = 0 \quad \mu, \nu \in (1, 2, \dots, w). \quad (2.14)$$

The operators \hat{X} and \hat{Y} satisfy the symmetry relations:

$$(\hat{X}_{fg}^{\mu\nu})^+ = \hat{X}_{fg}^{\nu\mu} \quad (\hat{Y}_{fg}^{\mu\nu})^+ = \hat{Y}_{fg}^{\nu\mu}. \quad (2.15)$$

The operators \hat{X} and \hat{Y} are chosen in such a way to make the term non-diagonal in excitation indices vanish from the equivalent Hamiltonian.

In the approximation linear in the small parameter $\eta = \phi/(\Delta_\alpha - \Delta_{\alpha'})$, $\alpha \neq \alpha'$, where ϕ means D , R or phonon energy, operators \hat{X} and \hat{Y} have the form

$$\hat{X}_{fg}^{\mu\nu} = i \hat{D}_{fg}^{\mu\nu}/(\Delta_\mu - \Delta_\nu) \quad \hat{Y}_{fg}^{\mu\nu} = -i \hat{R}_{fg}^{\mu\nu}/(\Delta_\mu - \Delta_\nu) \quad \mu \neq \nu \quad (2.16)$$

while the equivalent Hamiltonian in the nearest-neighbour approximation can be written as

$$\begin{aligned} H_{\text{eq}} = & \sum_{nm} \bar{\Delta}_\alpha B_{n\alpha}^+ B_{n\alpha} - \sum_{n\alpha} \bar{R}_\alpha (B_{n\alpha}^+ B_{n+1,\alpha} + B_{n\alpha}^+ B_{n-1,\alpha}) \\ & + \sum_{n\alpha} \bar{J}_{\alpha R} [B_{n\alpha}^+ B_{n+1,\alpha} (U_{n+1} - U_n) + B_{n\alpha}^+ B_{n-1,\alpha} (U_n - U_{n-1})] \\ & - \sum_{n\alpha} \bar{J}_{\alpha D} B_{n\alpha}^+ B_{n\alpha} (U_{n+1} - U_{n-1}) \\ & + \sum_{n\alpha} (\bar{g}_{RD}^{\alpha\alpha*} B_{n\alpha}^+ B_{n-1,\alpha} + \bar{g}_{RD}^{\alpha\alpha} B_{n-1,\alpha}^+ B_{n\alpha}) (U_{n+1} - U_n) \\ & + \sum_{n\alpha} (\bar{g}_{RD}^{\alpha\alpha*} B_{n\alpha}^+ B_{n+1,\alpha} + \bar{g}_{RD}^{\alpha\alpha} B_{n+1,\alpha}^+ B_{n\alpha}) (U_n - U_{n-1}) \\ & + \sum_n [(1/2M)p_n^2 + \frac{1}{2}Q(U_n - U_{n-1})^2] \end{aligned} \quad (2.17)$$

where

$$\begin{aligned} \bar{\Delta}_\alpha &= \Delta_\alpha + 2D^{\alpha\alpha} + 4 \sum_{\alpha'} \frac{|D^{\alpha\alpha'}|^2}{\Delta_\alpha - \Delta_{\alpha'}} & \bar{R}_\alpha &= R^{\alpha\alpha} + 4 \sum_{\alpha'} \frac{\text{Re}(R^{\alpha\alpha'} D^{\alpha\alpha'})}{\Delta_\alpha - \Delta_{\alpha'}} \\ \bar{J}_{\alpha R} &= J_R^{\alpha\alpha} + 2 \sum_{\alpha'} \frac{\text{Re}(R^{\alpha\alpha'} J_D^{\alpha\alpha'} + 2J_R^{\alpha\alpha'} D^{\alpha\alpha'})}{\Delta_\alpha - \Delta_{\alpha'}} \\ \bar{J}_{\alpha D} &= J_D^{\alpha\alpha} + 4 \sum_{\alpha'} \frac{\text{Re}(D^{\alpha\alpha'} J_D^{\alpha\alpha'})}{\Delta_\alpha - \Delta_{\alpha'}} & \bar{g}_{RD} &= \sum_{\alpha'} \frac{R^{\alpha\alpha'} J_D^{\alpha\alpha'}}{\Delta_\alpha - \Delta_{\alpha'}} \\ J_R^{\alpha\alpha'} &= N^{-1} \sum_k k R_k^{\alpha\alpha'} \sin(ak) & J_D^{\alpha\alpha'} &= N^{-1} \sum_k k D_k^{\alpha\alpha'} \sin(ak). \end{aligned} \quad (2.18)$$

One can see that the equivalent Hamiltonian (2.17) represents the sum of w independent Hamiltonians in terms of α indices, which simplifies the subsequent analysis. It is sufficient to study just one type of soliton (index μ) and the results are generally valid. There still exists a restriction. It is well known that solitons can form only from excitons with positive effective mass. According to (2.17) this condition becomes $\bar{R}_\mu > 0$. This means that the number of different wavepackets corresponds to the number of terms in (2.17) with $\bar{R}_\mu > 0$.

3. Solitons

We shall suppose that $\mu \bar{R}_\mu > 0$ for some μ , and using the standard approach study properties of the soliton of type μ .

The trial function is taken in the form

$$|\mu\rangle = \sum_f A_f^\mu(t) B_{f\mu}^\dagger |0e\rangle \quad \langle\mu, \mu\rangle = 1 \quad \sum_f |A_f^\mu(t)|^2 = 1. \quad (3.1)$$

We write down Schrödinger's equation, average it over coherent phonon states $|C_p\rangle$ and perform the continuum transition; we arrive at the equation

$$i\hbar \partial A^\mu(t)/\partial t = (C_\mu + \bar{\Delta}_\mu - 2\bar{R}_\mu)A^\mu - a^2 \bar{R}_\mu \partial^2 A^\mu(t)/\partial x^2 + 2\chi_\mu A^\mu \partial \beta/\partial x \quad (3.2)$$

$$\chi_\mu = a(\bar{J}_{\mu R} - \bar{J}_{\mu D} + g_{\mu B}^{\mu\mu} + g_{\mu D}^{\mu\mu*})$$

where

$$C_\mu = \frac{1}{2a} \int_{-x}^{+\infty} dx \left[M \left(\frac{\partial \beta}{\partial t} \right)^2 + Qa^2 \left(\frac{\partial \beta}{\partial x} \right)^2 \right]. \quad (3.3)$$

The combined equation of motion for phonon operators, averaged over states $\langle\mu|C_p\rangle$, in the continuum, has the form

$$\partial^2 \beta/\partial t^2 = v_0^2 \partial^2 \beta/\partial x^2 + (2\chi_\mu/M)\partial(A^{\mu*}A^\mu)/\partial x \quad (3.4)$$

$$v_0^2 = a^2 Q/\mu$$

and the normalizing condition becomes

$$\int_{-x}^{+\infty} dx |A^\mu(x, t)|^2 = a. \quad (3.5)$$

The procedure for solving the system of equations (3.2) and (3.4) is a standard one, so we shall only quote the final results. The energy of the solitons of μ type is given by

$$E_\mu(k) = \bar{\Delta}_\mu - 2\bar{R}_\mu + a^2 k^2 \bar{R}_\mu - \frac{\chi_\mu^4}{\bar{R}_\mu M^2 v_0^4 (1 - \varepsilon_{\mu k}^2)^2} \left(1 - \frac{2}{3} \frac{1 + \varepsilon_{\mu k}^2}{1 - \varepsilon_{\mu k}^2} \right) \quad (3.6)$$

where

$$\varepsilon_{\mu k} = v_{\mu k}/v_0 < 1 \quad v_{\mu k} = (2a^2 \bar{R}_\mu/\hbar)k. \quad (3.7)$$

The normalized amplitude has the form

$$A^\mu(x, t) = \frac{a\Omega_\mu^{1/2} \exp[ikx - iE_\mu(k)t/\hbar]}{2 \cosh[(a\Omega_\mu/2)\xi]} \quad (3.8)$$

where

$$\Omega_\mu = \Omega_\mu(k) = 2\chi_\mu^2/[a^2 \bar{R}_\mu M v_0^2 (1 - \varepsilon_{\mu k}^2)]. \quad (3.9)$$

It is important to note that, to each type of soliton μ , there corresponds another type of lattice deformation:

$$\frac{d\beta_\mu}{d\xi} = \frac{1}{2} \frac{a^2 \Omega_\mu \chi_\mu}{M v_0^2 (1 - \varepsilon_{\mu k}^2)} \frac{1}{\cosh^2[(a\Omega_\mu/2)\xi]} \quad (3.10)$$

with

$$\xi = x - v_{\mu k}t. \quad (3.11)$$

The number of different types of soliton corresponds to the number of coefficients $\bar{R}_\mu > 0$.

Using the general expression for the soliton energy of type μ (3.6), we can compare the general properties of the exciton of type μ and corresponding soliton.

The first three terms in (3.6) represent the energy of the exciton of type μ , which can be written in the form

$$E_{\mu}^{(\text{exc})}(k) = \tilde{\Delta}_{\mu} - 2\tilde{R}_{\mu} + \tilde{R}_{\mu}a^2k^2 = G_{\mu}^{(\text{exc})} + \frac{1}{2}m_{\mu}v_{\mu k}^2 \tag{3.12}$$

with effective mass of exciton of type μ

$$m_{\mu} = \hbar^2/(2a^2\tilde{R}_{\mu}) \tag{3.13}$$

and the energy needed for the excitation of the exciton of type μ

$$G_{\mu}^{(\text{exc})} = \tilde{\Delta}_{\mu} - \hbar^2/a^2m_{\mu}. \tag{3.14}$$

In order to study the corresponding soliton properties, the fourth term of the general formula (3.6) will be written in the approximation quadratic in parameter $\varepsilon_{\mu k}^2$. We can then write

$$E_{\mu}^{(\text{sol})}(k) = G_{\mu}^{(\text{sol})} + \frac{1}{2}m_{\mu}^{(\text{sol})}v_{\mu k}^2 \tag{3.15}$$

where

$$G_{\mu}^{(\text{sol})} = G_{\mu}^{(\text{exc})} - \delta G_{\mu} \quad \delta G_{\mu} = \frac{2}{3}a^2m_{\mu}\chi_{\mu}^4/\hbar^2M^2v_0^2 \tag{3.16}$$

and

$$m_{\mu}^{(\text{sol})} = m_{\mu}(1 + \frac{2}{3}a^2\chi_{\mu}^4/\hbar^2M^2v_0^2). \tag{3.17}$$

One can see that the soliton excitation energy is smaller than the excitation energy of the corresponding exciton. On the other hand, the μ -type soliton has larger effective mass, which can be understood, since it ‘drags’ the lattice deformation.

4. Bisolitons

We shall now study the general case when two solitons, one of type μ and the other of type ν , form a bisoliton. The general expressions allow one to study the case of two solitons of the same kind by setting $\nu \rightarrow \mu$.

The two-particle exciton wavefunction will be written in the symmetrized form

$$|\mu\nu\rangle = \sum_{fg} A_{fg}^{\mu\nu}(t)(B_{f\mu}^{\dagger}B_{g\nu}^{\dagger} + B_{f\nu}^{\dagger}B_{g\mu}^{\dagger})|0e\rangle \tag{4.1}$$

where the coefficient A satisfies the following symmetry relations

$$A_{fg}^{\mu\nu}(t) = A_{gf}^{\mu\nu}(t) \quad A_{fg}^{\mu\nu}(t) = A_{fg}^{\nu\mu}(t). \tag{4.2}$$

The normalizing condition $\langle\mu\nu|\mu\nu\rangle = 1$ turns into

$$\sum_{fg} |A_{fg}^{\mu\nu}(t)| = \frac{1}{4}. \tag{4.3}$$

Further on, we shall apply the procedure presented in Mirjanić *et al* (1984). Let us also mention that in the previous paper (Mašković *et al* 1986) we explained why it is not necessary to use boson forms of fourth order in bisoliton analysis. By using this

procedure, we arrive at the following set of equations for the determination of coefficients $A^{\mu\nu}$ and lattice deformation β :

$$i\hbar \frac{\partial A^{\mu\nu}}{\partial t} = (C_{\mu\nu} + \bar{\Delta}_\mu + \bar{\Delta}_\nu - 2\bar{R}_\mu - 2\bar{R}_\nu)A^{\mu\nu} - \frac{1}{2}a^2(\bar{R}_\mu + \bar{R}_\nu) \left(\frac{\partial^2 A^{\mu\nu}}{\partial x^2} + \frac{\partial^2 A^{\mu\nu}}{\partial y^2} \right) + (\chi_\mu + \chi_\nu)A^{\mu\nu} \left(\frac{\partial \beta}{\partial x} + \frac{\partial \beta}{\partial y} \right) \quad (4.4)$$

$$\frac{\partial^2 \beta}{\partial t^2} - v_0^2 \frac{\partial^2 \beta}{\partial z_j^2} = \frac{8(\chi_\mu + \chi_\nu)}{aM} \frac{\partial}{\partial z_j} \int_{-\infty}^{+\infty} dz_j |A^{\mu\nu}|^2 \quad j = 1, 2 \quad z_1 \equiv x \quad z_2 \equiv y. \quad (4.5)$$

The following notation was used:

$$\begin{aligned} x_\mu &= a(\bar{J}_{R\mu} - \bar{J}_{D\mu} + g_{RD}^{\mu\mu} + g_{RD}^{\mu\mu*}) \\ x_\nu &= a(\bar{J}_{R\nu} - \bar{J}_{D\nu} + g_{RD}^{\nu\nu} + g_{RD}^{\nu\nu*}) \end{aligned} \quad (4.6)$$

and

$$C_{\mu\nu} = \frac{1}{4a} \left\{ \int_{-\infty}^{+\infty} dx \left[M \left(\frac{\partial \beta}{\partial t} \right)^2 + Qa^2 \left(\frac{\partial \beta}{\partial x} \right)^2 \right] + \int_{-\infty}^{+\infty} dy \left[M \left(\frac{\partial \beta}{\partial t} \right)^2 + Qa^2 \left(\frac{\partial \beta}{\partial y} \right)^2 \right] \right\}. \quad (4.7)$$

The continuum version of the normalizing condition is

$$\int_{-\infty}^{+\infty} dx dy |A^{\mu\nu}(x, y; t)|^2 = a^2/4. \quad (4.8)$$

We shall look for the solution of the system (4.4)–(4.5) in the form

$$\begin{aligned} A^{\mu\nu}(x, y; t) &= f_\mu(\xi)f_\nu(\eta) \exp[ik(\rho_\mu x + \rho_\nu y) - i\omega t] \\ \xi &= x - v_\nu t \quad \eta = y - v_\eta t \quad f_\mu^* = f_\mu \quad f_\nu^* = f_\nu \\ \beta(x, t) &\rightarrow \beta(\xi) \quad \beta(y, t) \rightarrow \beta(\eta) \quad x \neq y \end{aligned} \quad (4.9)$$

where

$$\rho_s = m_s / \sum_s m_s \quad m_s = \hbar^2/2\bar{R}_s a^2 \quad s = (\mu, \nu). \quad (4.10)$$

Since m_μ and m_ν are effective masses of the excitons of types μ and ν respectively, it is obvious that the coordinate multiplying k in the expression for $A^{\mu\nu}$ represents the coordinate of the centre of mass of the excitons μ and ν .

Using (4.9), the system of equations (4.4)–(4.5) becomes the system of ordinary differential equations:

$$\begin{aligned} \frac{f_\mu''}{f_\mu} + \frac{f_\nu''}{f_\nu} &= \frac{C_{\mu\nu} + \bar{\Delta}_\mu + \bar{\Delta}_\nu - 2\bar{R}_\mu - 2\bar{R}_\nu + \frac{1}{2}a^2 k^2 (\bar{R}_\mu + \bar{R}_\nu)(\rho_\mu^2 + \rho_\nu^2) - E}{\frac{1}{2}a^2(\bar{R}_\mu + \bar{R}_\nu)} \\ &+ \frac{\chi_\mu + \chi_\nu}{\frac{1}{2}a^2(\bar{R}_\mu + \bar{R}_\nu)} \left(\frac{\partial \beta}{\partial \xi} + \frac{\partial \beta}{\partial \eta} \right) \quad E = \hbar\omega \end{aligned} \quad (4.11)$$

$$\frac{d\beta_s}{d\varphi_s} = -\frac{8(\chi_\mu + \chi_\nu)\mathfrak{D}_{s'}}{aM(v_0^2 - v_s^2)}f_s^2 \quad s' \neq s \tag{4.12}$$

$$\mathfrak{D}_s = \int_{-\infty}^{+\infty} dz f_s^2(z) \quad s, s' \equiv (\mu, \nu) \quad \varphi_\mu \equiv \xi \quad \varphi_\nu \equiv \eta$$

where

$$v_s = a^2\rho_s k \sum_s \bar{R}_s / \hbar \quad s \equiv (\mu, \nu). \tag{4.13}$$

Substituting (4.12) into (4.11), we arrive at the equation

$$f_\mu''/f_\mu + f_\nu''/f_\nu = \Theta_{\mu\nu}(k, E) - 2\bar{\Omega}_\mu(k)\mathfrak{D}_\nu f_1^2 - 2\bar{\Omega}_\nu(k)\mathfrak{D}_\mu f_2^2 \tag{4.14}$$

where

$$\Theta_{\mu\nu}(k, E) = \frac{C_{\mu\nu} + \bar{\Delta}_\mu + \bar{\Delta}_\nu - 2\bar{R}_\mu - 2\bar{R}_\nu + \frac{1}{2}(\bar{R}_\mu + \bar{R}_\nu)(\rho_\mu^2 + \rho_\nu^2)a^2k^2 - E}{\frac{1}{2}(\bar{R}_\mu + \bar{R}_\nu)a^2} \tag{4.15}$$

$$\bar{\Omega}_s(k) = \frac{4\left(\sum_s \chi_s\right)^2}{\frac{1}{2}a^3M(v_0^2 - v_s^2)\sum_s \bar{R}_s} \quad s \equiv (\mu, \nu). \tag{4.16}$$

Separation of the variables in (4.14) leads to

$$\begin{aligned} d^2f_s/d\varphi^2 &= (\Theta_{\mu\nu}/2 + \lambda)f_s - 2\bar{\Omega}_s\mathfrak{D}_{s'}f_s^3 = 0 \\ s, s' &\equiv (\mu, \nu) \quad s' \neq s \quad \varphi_\mu \equiv \xi \quad \varphi_\nu \equiv \eta \end{aligned} \tag{4.17}$$

where λ is the parameter arising from variable separation. It follows from (4.17) that

$$\begin{aligned} f_s(\varphi_s) &= \left(\frac{\Theta_{\mu\nu}/2 + \lambda}{\bar{\Omega}_s\mathfrak{D}_{s'}}\right)^{1/2} \frac{1}{\cosh[\varphi_s(\Theta_{\mu\nu}/2 + \lambda)^{1/2}]} \\ s, s' &\equiv (\mu, \nu) \quad s' \neq s \quad \varphi_\mu \equiv \xi \quad \varphi_\nu \equiv \eta. \end{aligned} \tag{4.18}$$

Introducing f_μ and f_ν into the expressions for \mathfrak{D}_μ and \mathfrak{D}_ν , we find

$$\lambda = (\Theta_{\mu\nu}/2)(\bar{\Omega}_\mu^2 - \bar{\Omega}_\nu^2)/(\bar{\Omega}_\mu^2 + \bar{\Omega}_\nu^2) \tag{4.19}$$

$$\mathfrak{D}_\mu\mathfrak{D}_\nu = 2[\Theta_{\mu\nu}/(\bar{\Omega}_\mu^2 + \bar{\Omega}_\nu^2)]^{1/2} \tag{4.20}$$

which gives

$$\begin{aligned} f_s(\varphi_s) &= \left(\frac{\Theta_{\mu\nu}\bar{\Omega}_s}{\mathfrak{D}_{s'}\sum_s \bar{\Omega}_s^2}\right) \frac{1}{\cosh\left[\varphi_s\bar{\Omega}_s\left(\Theta_{\mu\nu}/\sum_s \bar{\Omega}_s^2\right)^{1/2}\right]} \\ s, s' &\equiv (\mu, \nu) \quad s' \neq s \quad \varphi_\mu = \xi \quad \varphi_\nu = \eta \end{aligned} \tag{4.21}$$

while lattice deformations are given by

$$\frac{d\beta_s}{d\varphi_s} = - \frac{8\Theta_{\mu\nu}\tilde{\Omega}_s}{aM(v_0^2 - v_s^2) \sum_s \tilde{\Omega}_s^2} \frac{1}{\cosh^2 \left[\varphi_s \tilde{\Omega}_s \left(\Theta_{\mu\nu} / \sum_s \tilde{\Omega}_s^2 \right)^{1/2} \right]} \quad s \equiv (\mu, \nu). \quad (4.22)$$

Using the last two expressions, one can find the energy of lattice deformation:

$$c_{\mu\nu} = \frac{1}{3} \frac{(\chi_\mu + \chi_\nu)^4}{(\tilde{R}_\mu + \tilde{R}_\nu)M^2} \left(\frac{1}{(v_0^2 - v_\mu^2)^2} \frac{v_0^2 + v_\mu^2}{v_0^2 - v_\mu^2} + \frac{1}{(v_0^2 - v_\nu^2)^2} \frac{v_0^2 + v_\nu^2}{v_0^2 - v_\nu^2} \right). \quad (4.23)$$

Using the normalizing condition for the coefficients $A^{\mu\nu}$, we find the energy of the bisoliton of $\mu\nu$ type as

$$E_{\mu\nu}(k) = \tilde{\Delta}_\mu + \tilde{\Delta}_\nu - 2\tilde{R}_\mu - 2\tilde{R}_\nu + \frac{1}{2}(\tilde{R}_\mu + \tilde{R}_\nu)(\rho_\mu^2 + \rho_\nu^2)a^2k^2 - \frac{(\chi_\mu + \chi_\nu)^4}{2(\tilde{R}_\mu + \tilde{R}_\nu)M^2} \\ \times \left[\frac{1}{(v_0^2 - v_\mu^2)^2} \left(1 - \frac{2v_0^2 + v_\mu^2}{3v_0^2 - v_\mu^2} + \frac{1}{(v_0^2 - v_\nu^2)^2} \left(1 - \frac{2v_0^2 + v_\nu^2}{3v_0^2 - v_\nu^2} \right) \right) \right]. \quad (4.24)$$

Normalized bisoliton amplitudes are given by

$$A^{\mu\nu}(x, y, t) = \frac{a^3(\tilde{\Omega}_\mu\tilde{\Omega}_\nu)^{1/2}}{32} \frac{[ik(\rho_\mu x + \rho_\nu y) - iE_{\mu\nu}(k)t/\hbar]}{\cosh[(a^2\tilde{\Omega}_\mu/8)(x - v_\mu t)] \cosh[(a^2\tilde{\Omega}_\nu/8)(y - v_\nu t)]} \quad x \neq y. \quad (4.25)$$

In the case when a bisoliton is formed by two solitons of the same type ($\nu \rightarrow \mu$), we obtain the energy as

$$E_{\mu\mu}(k) = 2\tilde{\Delta}_\mu - 4\tilde{R}_\mu + \frac{1}{2}\tilde{R}_\mu a^2k^2 - \frac{8\chi_\mu^4}{\tilde{R}_\mu M^2 v_0^4 (1 - \varepsilon_{\mu k}^2)^2} \left(1 - \frac{2}{3} \frac{1 + \varepsilon_{\mu k}^2}{1 - \varepsilon_{\mu k}^2} \right) \quad (4.26)$$

and normalized amplitude as

$$A^{\mu\mu}(x, y, t) = \frac{a^3\Omega_\mu}{8\sqrt{2}} \frac{\exp[ik(x+y)/2 - iE_{\mu\mu}(k)t/\hbar]}{\cosh[(a^2\Omega_\mu/4)\xi] \cosh[(a^2\Omega_\mu/4)\eta]} \quad x \neq y. \quad (4.27)$$

The first four terms in the general expression for the bisoliton energy (4.24) represent the sum of excitations of excitons of type μ and ν , while the fifth term represents the kinetic energy of the centre of mass of the pair of excitons.

This excitonic part of the bisoliton energy can be written as

$$E_{\mu\nu}^{(2exc)} = G_{\mu\nu}^{(2exc)} + \frac{1}{2}M_{\mu\nu}^{(red)}v_{2exc}^2 \quad (4.28)$$

where

$$G_{\mu\nu}^{(2exc)} = \tilde{\Delta}_\mu + \tilde{\Delta}_\nu - \hbar^2/a^2 M_{\mu\nu}^{(red)} \quad (4.29)$$

is the excitation energy of the pair of excitons of type ν and μ and

$$M_{\mu\nu}^{(red)} = m_\mu m_\nu / (m_\mu + m_\nu) \quad (4.30)$$

is the reduced mass of the pair, while

$$v_{2exc}^2 = \frac{1}{2}\hbar^2 k^2 (m_\mu^2 + m_\nu^2) / m_\mu^2 m_\nu^2. \quad (4.31)$$

One should note that (4.31) can be obtained from the identity

$$\frac{1}{2}M_{\mu\nu}^{(\text{red})}v_{2\text{exc}}^2 \equiv \frac{1}{2}(\bar{R}_\mu + \bar{R}_\nu)(\rho_\mu^2 + \rho_\nu^2)a^2k^2. \tag{4.32}$$

In order to study corresponding properties of bisolitons, in the sixth term of general expression (4.24) we shall keep only the terms of order $\epsilon_{\mu\nu}^2$. In this way we obtain

$$E_{\mu\nu}^{(\text{bs})}(k) = G_{\mu\nu}^{(\text{bs})} + \frac{1}{2}m_{\mu\nu}^{(\text{bs})}v_{2\text{exc}}^2 \tag{4.33}$$

where the excitation energy of the bisoliton is given by

$$G_{\mu\nu}^{(\text{bs})} = G_{\mu\nu}^{(2\text{exc})} - \delta G_{\mu\nu} \tag{4.34}$$

with

$$\delta G_{\mu\nu} = \frac{2}{3}a^2M_{\mu\nu}^{(\text{red})}(\chi_\mu + \chi_\nu)^4/\hbar^2M^2v_0^4. \tag{4.35}$$

Bisoliton mass is given by

$$m_{\mu\nu}^{(\text{bs})} = M_{\mu\nu}^{(\text{red})}[1 + \frac{2}{3}a^2(\chi_\mu + \chi_\nu)^4/\hbar^2M^2v_0^4]. \tag{4.36}$$

It can be seen that the bisoliton excitation energy is less than the energy necessary for the excitation of a pair of excitons. On the other hand, the bisoliton mass is larger than the reduced mass of the pair of excitons.

In the case of pairing of two solitons of the same type, bisoliton quantities $\delta G_{\mu\nu}$ and $m_{\mu\nu}^{(\text{bs})}$ become

$$\delta G_{\mu\mu} = \frac{16}{3}a^2m_\mu\chi_\mu^4/\hbar^2M^2v_0^4 \tag{4.37}$$

and

$$m_{\mu\mu}^{(\text{bs})} = \frac{1}{2}m_\mu(1 + \frac{32}{3}a^2\chi_\mu^4/\hbar^2M^2v_0^4). \tag{4.38}$$

At the end of this analysis, we shall examine the conditions under which two solitons of type μ and ν can form bisolitons of $\mu\nu$ type. It is well known that the energy of a bound state formed by pairing of two free excitations must be lower than the sum of the energies of the free excitations. Physical interpretation of this condition is clear: two free particles must ‘invest’ a part of their energy in order to form a bound state. Following this, the binding energy of the bisoliton is given by

$$E_{\mu\nu}(k, q) = E_\mu^{(\text{sol})}(k/2 + q) + E_\nu^{(\text{sol})}(k - q/2) - E_{\mu\nu}^{(\text{bs})}(k) > 0. \tag{4.39}$$

The analysis of this condition is rather complicated, so it will be substituted by an approximate expression:

$$E_{\mu\nu}(0, 0) = G_\mu^{(\text{sol})} + G_\nu^{(\text{sol})} - G_{\mu\nu}^{(\text{bs})} > 0. \tag{4.40}$$

It is obvious that if (4.40) is fulfilled, bisolitons do form, but in a restricted range of wavevectors k and q .

The condition (4.40) can be written in the form:

$$F_{\mu\nu}(0, 0) = \frac{C_\mu}{(\bar{\varphi} + 1)\gamma^4}(-\bar{\varphi}^2 + 2\Gamma\bar{\varphi} - \gamma^4) > 0 \tag{4.41}$$

where

$$\begin{aligned} C_\mu &= \frac{2}{3}a^2m_\mu\chi_\mu^4/\hbar^2M^2v_0^4 > 0 & \bar{\varphi} &= m_\nu/m_\mu > 0 \\ \gamma &= \chi_\mu/\chi_\nu > 0 & \Gamma &= 2\gamma^3 + 3\gamma^2 + 2\gamma. \end{aligned} \tag{4.42}$$

The condition (4.41) is certainly satisfied for

$$\Gamma - (\Gamma - \gamma^4)^{1/2} < \bar{\varphi} < \Gamma + (\Gamma - \gamma^4)^{1/2} \tag{4.43}$$

implying that $\mu\nu$ -type bisolitons ($\mu \neq \nu$) can be formed only for certain ratios of masses m_μ and m_ν and exciton–phonon coupling constants χ_μ and χ_ν .

In the case of the bisoliton formed from two excitons of the same type ($\bar{\varphi} = 1$ and $\gamma = 1$), it follows from (4.41) that

$$F_{\mu\mu}(0, 0) = 6C_{\mu} > 0 \quad (4.44)$$

meaning that two solitons of the same type can always form a bisoliton.

One should also stress that the expression (4.41) for the binding energy has an extremal value with respect to mass ratio $\bar{\varphi}$, for the value

$$\bar{\varphi} = \gamma(\gamma + 2)$$

and the form of corresponding extremal function Γ is given as

$$\max F_{\mu\nu}(0, 0) = 4C_{\mu}(\gamma + 1)/\gamma^2 \quad \bar{\varphi} = \gamma(\gamma + 2). \quad (4.45)$$

Comparing the expressions for bonding energies of two solitons of the same and of different types, we can conclude that, under certain conditions, two solitons can be more strongly bonded. This happens for the mass ratio $m_{\nu}/m_{\mu} = (\chi_{\mu}/\chi_{\nu})(\chi_{\mu}/\chi_{\nu} + 2)$ and when the coupling constant ratio falls into the range

$$0 < \chi_{\mu}/\chi_{\nu} < (1 + \sqrt{7})/3. \quad (4.46)$$

5. Conclusions

The results of the analysis of properties of solitons and bisolitons in molecular chains with Bethe splitting of exciton bands can be summarized as follows:

(i) The Hamiltonian of the exciton system with Bethe zone splitting can be unitarily transformed into an equivalent Hamiltonian that is the sum of the Hamiltonian of each one corresponding to a single band. This equivalent Hamiltonian is an approximate one, and the error introduced is of the order of the square of the ratio of exciton bandwidth and isolated molecule excitation energy. The accuracy of that degree can be considered satisfactory in the case of an exciton system, because the above-mentioned ratio is of the order of 10^{-2} .

(ii) Soliton excitations in the system are analysed by means of the equivalent Hamiltonian. The number of soliton branches need not be equal to the number of exciton branches, because solitons are formed only by excitons with positive effective mass. In the case when a soliton is formed, comparison between exciton and soliton properties is made. The result indicates that the soliton is excited more easily, while its effective mass is higher than the exciton effective mass.

(iii) Analysis of the behaviour of bisolitons in the system has shown that bisolitons can be formed from solitons of same type as well as from solitons of different types. Bisolitons can be always formed from the solitons of the same type, while solitons of different types can form a bisoliton under particular conditions for the effective masses and coupling constants of excitons involved. For very particular conditions, this bisoliton can be bounded more strongly than the bisoliton formed by solitons of the same type.

Finally, we wish to stress once again that, owing to the limitations mentioned in (i), our results should be accepted as a qualitative description of the behaviour of solitons in a molecular chain with Bethe splitting of exciton bands.

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