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Nonlinear self-localized modes in a chain of two-level molecules

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Abstract. Exact and approximate nonlinear self-localized modes are shown to exist in a one-dimensional chain of interacting Frenkel excitons due to exciton–exciton static attraction. Two different modes are found and their frequencies are below the exciton frequency band. These results suggest a possible new mechanism for localization of the energy of the amide–I excitons through the exciton–exciton interaction in protein molecules.

Stationary intrinsic self-localized modes have been found to exist in pure nonlinear discrete systems. They appear in pure anharmonic lattices [1-4] and Heisenberg antiferromagnets [5, 6]. Recently Zhu and Kobayashi showed that intrinsic self-localized Frenkel excitons can exist in a linear chain of interacting Frenkel excitons [7]. This system has many applications. With the exception of J-aggregates [8], this system also describes the well known quantum spin system, the XXY model, in an external magnetic field. Furthermore, it also exactly describes the system of the amide–I vibrations in protein molecules [9]. Thus, a further investigation of this system is necessary. In [7], approximate nonlinear self-localized modes were found numerically. In the present paper, we will show analytically that this system has two kinds of new nonlinear self-localized modes.

Following [7], we consider a system of one-dimensional molecular chain composed of N two-level molecules, in which a Frenkel exciton accompanied by a static dipole moment $\boldsymbol{\mu}$ can propagate to a neighbouring molecule with a transfer matrix element $-J$. The Hamiltonian describing this system is

$$H = \hbar\omega_0 \sum_j s_j^z - \frac{1}{2} J \sum_{j,\delta} (s_j^+ s_{j+\delta}^- + s_j^- s_{j+\delta}^+) - J_z \sum_{j,\delta} (s_j^z + \tfrac{1}{2})(s_{j+\delta}^z + \tfrac{1}{2}) \tag{1}$$

where the operators $s_j^+ = s_j^x + \mathrm{i}s_j^y$ and $s_j^- = s_j^x - \mathrm{i}s_j^y$ indicate excitation and de-excitation, respectively, between two levels with an excitation energy $\hbar\omega_0$ at the jth site, δ runs over the nearest neighbours of j, and

$$[s_i^z, s_j^\pm] = \pm s_i^\pm \delta_{ij} \qquad [s_i^+, s_j^-] = 2 s_i^z \delta_{ij}\,. \tag{2}$$

In (1), the first term corresponds to the energy of the non-interacting molecules, the second term describes propagation of the excitation associated with the transfer matrix element $-J$

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and the last term comes from electrostatic interaction between two Frenkel excitons and the interaction energy is $-J_z$.

As a spin Hamiltonian, equation (1) describes the well known quantum spin system, the XXY model, in an external magnetic field $\hbar\omega_0$. Here we represent the spin operators by means of the Bose operators a and a^+ according to Dyson–Maleev transformation as follows:

$$s_j^+ = a_j^+(1 - a_j^+ a_j) \tag{3}$$

$$s_j^- = a_j \tag{4}$$

$$s_j^z = a_j^+ a_j - \tfrac{1}{2}\,. \tag{5}$$

The Bose operators a and a^+ satisfy the following commutation relations:

$$[a_j, a_j^+] = \delta_{ij} \qquad [a_i, a_j] = [a_i^+, a_j^+] = 0\,. \tag{6}$$

Substituting equations (3)–(5) in (1), we obtain

$$H = -\frac{1}{2}N\hbar\omega_0 + \hbar\omega_0 \sum_j a_j^+ a_j - \frac{1}{2}J \sum_{j,\delta}(a_j^+ a_{j+\delta} + a_j a_{j+\delta}^+) - J_z \sum_{j,\delta} a_j^+ a_j a_{j+\delta}^+ a_{j+\delta}$$
$$+\frac{1}{2}J \sum_{j,\delta}(a_j^+ a_j^+ a_j a_{j+\delta} + a_{j+\delta}^+ a_{j+\delta}^+ a_j a_{j+\delta}) \tag{7}$$

where N is the number of molecules in the chain. In (7), the first three terms are simply the exciton Hamiltonian in Davydov's model [10], which do not include the nonlinear terms and so cannot have self-localized modes. The Heisenberg equation of motion for the system described by (7) is

$$\mathrm{i}\hbar\dot{a}_j = \hbar\omega_0 a_j - J\sum_\delta a_{j+\delta} - 2J_z \sum_\delta a_{j+\delta}^+ a_{j+\delta} a_j + 2J\sum_\delta a_j^+ a_j a_{j+\delta} \tag{8}$$

where the dot denotes the derivative with respect to time.

We are concerned with soliton-like intrinsic nonlinear mode in the system induced by exciton–exciton interactions, for which many excitons are presumed to participate. A physically acceptable candidate for quantum states of such a particle-like entity may be coherent state. Therefore, we use Glauber's coherent states [12]:

$$|\{\alpha_j\}\rangle = \prod_j |\alpha_j\rangle$$

as the ansatz for the eigenstates of H. The coherent states satisfy the following equation:

$$a_j|\alpha_j\rangle = \alpha_j|\alpha_j\rangle \tag{9}$$

where α_j is a complex eigenvalue. In the coherent state representation, equation (8) becomes

$$\mathrm{i}\hbar\dot{\alpha}_j = \hbar\omega_0\alpha_j - J(\alpha_{j+1} + \alpha_{j-1}) - 2J_z(|\alpha_{j+1}|^2 + |\alpha_{j-1}|^2)\alpha_j + 2J|\alpha_j|^2(\alpha_{j+1} + \alpha_{j-1})\,. \tag{10}$$

In this paper, we will consider the stationary localized-mode solution to (10), so we set

$$\alpha_j = \xi_j \mathrm{e}^{-\mathrm{i}\omega t} \tag{11}$$

where ξ_j and ω are time-independent and real; equation (10) thus becomes

$$\omega_d\xi_j = -(1 - 2\xi_j^2)(\xi_{j+1} + \xi_{j-1}) - 2\gamma\xi_j(\xi_{j+1}^2 + \xi_{j-1}^2) \tag{12}$$

where

$$\omega_d = (\omega - \omega_0)/J \qquad \gamma = J_z/J\ .$$

When $\gamma = 0$, equation (12) is the well known stationary discrete nonlinear Schrodinger equation and it has kink solutions. We will show that equation (12) has both bright soliton and kink solutions.

(i) *Bright soliton solution*. It appears difficult to find exact analytical bright soliton solutions to (12). However, fairly good approximate analytical lattice-soliton solutions do exist, provided that

$$\xi_j(\xi_{j+1}^2 + \xi_{j-1}^2) = B\xi_j^2(\xi_{j+1} + \xi_{j-1}) \tag{13}$$

where B is a constant. The condition under which equation (13) holds and the constant B will be determined later. Then equation (12) can be rewritten as

$$\omega_d\xi_j = -[1 + 2(\gamma B - 1)\xi_j^2](\xi_{j+1} + \xi_{j-1})\ . \tag{14}$$

Equation (14) is the stationary discrete nonlinear Schrodinger equation. It can be shown [10] that (14) has the following soliton solution if $\gamma B > 1$:

$$\xi_j = [1/\sqrt{2(\gamma B - 1)}]\sinh(K)\,\mathrm{sech}[K(j - j_0)] \tag{15}$$

with

$$\omega_d = -2\cosh K) \tag{16}$$

where K and j_0 are constants. To ensure that (13) holds for the above solution, we find by substituting (15) in (13) that B is approximately a constant and that

$$B \approx 1/\cosh(K)$$

when $K \ll 1$. Thus $\gamma B > 1$ requires

$$1 < \cosh(K) < \gamma\ . \tag{17}$$

Furthermore, in order to take into account the finite-ladder structure of the spin operators [5, 11], the amplitude A of α_j must satisfy

$$A^2 = \sinh^2(K)/[2(\gamma B - 1)] = \cosh K)\sinh^2(K)/[2(\gamma - \cosh K))] < 1\ . \tag{18}$$

This equation gives

$$\cosh(K) = (2/3)^{\frac{1}{3}}(1 - A')/f(A') + f(A')/18^{\frac{1}{3}} \tag{19}$$

where $A' = 2A^2$ and

$$f(A') = [9\gamma A' + \sqrt{3}(-4 + 12A' - 12A'^2 + 4A'^3 + 27\gamma^2 A'^2)^{\frac{1}{2}}]^{\frac{1}{3}}\ . \tag{20}$$

Equations (17), (19) determine the possible range of the value of K when A is given.

In order for the stationary mode given by (15) to be stable, its frequency must be above (below) the top (bottom) of the exciton frequency band

$$\omega(k) = \omega_0 - 2J\cos(k) \tag{21}$$

where k is a wavevector of the exciton. It is easy to show that only the latter case is possible. From (16) we have

$$\omega = \omega_m + 2J[1 - \cosh(K)] \tag{22}$$

where $\omega_m = \omega_0 - 2J$ is the bottom of the exciton frequency band. It is clear that ω is always smaller than ω_m since K is not equal to zero.

For a given value of γ, the frequency, amplitude and profile of the self-localized mode described by (11) with (15), (16) are determined by K, while K is determined by (17), (18). For example, taking $A^2 = \frac{1}{2}$, from (19) we obtain

$$\cosh(K) = \gamma^{\frac{1}{3}} . \tag{23}$$

This also satisfies (17). Thus the frequency of the mode described by (11) is proportional to $\gamma^{1/3}$. Therefore this mode is different from that obtained in [7], where the frequency of the mode is proportional to γ when $A^2 = \frac{1}{2}$.

(ii) *Kink soliton solution*. It is easy to prove that equation (12) also has the following kink solution:

$$\xi_j = \pm A \tanh[K(j - j_0)] \tag{24}$$

with $\tanh(K) = 1$ and

$$\omega_d = -2\gamma A^2 . \tag{25}$$

This is an interesting kink-like solution. From (25) the frequency of this localized mode is

$$\omega = \omega_m + 2J(1 - \gamma A^2) . \tag{26}$$

This shows that ω is below the bottom of the exciton frequency band when $\gamma A^2 > 1$. The kink solution given by (24) is a population inversion state with all molecules being in the excitation state except one, since the probability of the jth molecule being in the excitation state is proportional to ξ_j^2. Thus, it is similar to a stationary dark soliton.

In conclusion, we have found two kinds of analytical nonlinear self-localized modes in one-dimensional molecular chain of interacting Frenkel excitons. Recently Agranovich and IIinski [13] have shown that strong static dipole–dipole repulsion of one-dimensional and two-dimensional charge-transfer excitons can induce, at sufficiently high exciton concentrations, an electron dielectric–metal phase transition. Mysyrowicz *et al* theoretically pointed out that the superfluid excitons can propagate as a bright soliton under the condition of their Bose condensation and successfully observed this effect in Cu_2O [14, 15]. We hope that our results will help in providing a better understanding of the nonlinear effects of excitons in low-dimensional molecular systems. Since the system handled in this paper can also be taken as a model for the system of the amide–I vibrations in protein molecules, our results suggest a possible new mechanism of the localization of the energy of the amide–I excitons through the exciton–exciton interaction.

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