

## Exciton Solitons in One-Dimensional Molecular Crystals

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Exciton solitons in one-dimensional molecular crystals arising from interactions with lattice vibrations are studied by taking kinematical interactions of excitons into account. The nonlinear Schrödinger equation follows from a nonlinear Klein-Gordon-type equation by the use of rotating-wave approximation.

One of the most typical real systems in solid state or chemical physics that exhibit solitons may be considered as polymers due to their essentially one-dimensional (1d) nature. It is therefore not surprised to witness a number of recent studies on solitons in such diverse area as polyacetylene,<sup>1)</sup> certain organic 1d conductors,<sup>2)</sup> poly vinylidene fluorides,<sup>3)</sup>  $\alpha$ -helical proteins,<sup>4)</sup> DNA<sup>5)</sup> and so on. Of these, solitons in  $\alpha$ -helics have received particular attention due to their implication to energy transport in biological substances.<sup>4),6)</sup> Prior to these studies, Fröhlich discussed on phenomenological level the importance on biological activity of nonlinear coupling of polarization waves with elastic fields.<sup>7)</sup>

It is the purpose of this paper to give a brief report of a microscopic theory of exciton or polarization-wave solitons in model 1d molecular crystals the existence of which is made possible by nonlinear coupling with lattice field. A remark is given on the Davydov theory<sup>4)</sup> in this connection, in which a naive form of exciton model is employed. This is only an approximate and truncated form for an exact model exciton Hamiltonian having the form of the Ising-like model.<sup>8),9)</sup> The present theory starts with the exact model and preserves the kinematical interaction of excitons<sup>8),9)</sup> in its exact form. For a normal excited state in which the exciton density is very small, the theory gives a pair of a classical form of wave equations for

molecular transition dipole moments and for phonons nonlinearly coupled with each other. A situation here is somewhat analogous to the case in nonlinear optics in the sense that we finally arrive at the nonlinear Schrödinger (NLS) equation from a nonlinear Klein-Gordon-type equation by the use of a kind of rotating-wave approximation, whereas its appearance for the exciton amplitude governed by the quantal Schrödinger equation in the Davydov theory<sup>4)</sup> is almost self-evident.

We consider a model 1d molecular crystal with one molecule per unit cell, where the overlapping of molecular wave functions on neighbouring molecules is negligible. Let  $H_0(n)$  be the Hamiltonian for the free  $n$ th molecule. The electron part  $H_{el}$  of the Hamiltonian of the system can then be described in terms of molecular operators  $\sigma_{n\lambda\lambda'} = |\lambda_n\rangle\langle\lambda_n'|$  with  $\sum_\lambda \sigma_{n\lambda\lambda} = 1$  and  $\sigma_{n\lambda\lambda'}\sigma_{n\lambda''\lambda'''} = \sigma_{n\lambda\lambda'''}\delta(\lambda', \lambda'')$ ,<sup>10)</sup> where  $|\lambda_n\rangle$  is an eigenstate of  $H_0(n)$ . As an analytically tractable model, we employ a two-level approximation to pick up only two states, the ground state  $\lambda = 0$  and a relevant excited state  $\lambda = f$ , among many molecular eigenstates. The quantities  $\sigma_n^x = (\sigma_{nf0} + \sigma_{n0f})/2$ ,  $\sigma_n^y = (\sigma_{nf0} - \sigma_{n0f})/2i$  and  $\sigma_n^z = (\sigma_{nff} - \sigma_{n00})/2$  are then identified as the Pauli operators, in terms of which  $H_{el}$  can be written rigorously in the form of the Ising-like Hamiltonian<sup>9)</sup>

$$H_{el} = \sum_n \{ \epsilon_0 + \sum_m D(|x_m - x_n|) \} \sigma_n^z$$

$$\begin{aligned}
 & -2\sum_{nm} J(|x_m - x_n|) \sigma_n^x \sigma_m^x \\
 & + (1/2) \sum_{nm} I(|x_n - x_m|) \sigma_n^z \sigma_m^z. \quad (1)
 \end{aligned}$$

Here  $x_n$  and  $\epsilon_0$  are an instantaneous position of the  $n$ th molecule and the energy separation between the ground state and the excited state of the free molecule, respectively. The quantities  $D(|x_m - x_n|)$ ,  $J(|x_m - x_n|) > 0$  and  $I(|x_m - x_n|) > 0$  are the shift of  $\epsilon_0$  due to the presence of other molecules, the dipole-dipole interaction energy and the dynamical exciton-exciton interaction energy, respectively. It is assumed from the outset that the molecular transition dipole moment is oriented in such a way that the dipole-dipole interaction is attractive. Throughout this paper, we assume the exciton density to be very small, thereby neglecting the last term in Eq. (1). The model exciton Hamiltonian used by Davydov corresponds here to replacing  $\sigma_{nf0}$  and  $\sigma_{naf}$  by Boson creation and annihilation operators,  $a_n^+$  and  $a_n$ , and to discarding the term  $\sum_{nm} J(|x_m - x_n|) (a_n^+ a_m^+ + a_n a_m)$  at the same time. The Pauli or spin operators, when taken as the deviation from the Bose operators, give rise to the so-called kinematical interactions.<sup>11)</sup> Let

$$u_n = x_n - X_n \equiv x_n - na \quad (2)$$

be a displacement of the  $n$ th molecule from its equilibrium position  $X_n$ , where  $a$  is the lattice constant. The lattice or phonon part  $H_{ph}$  of the Hamiltonian is written as

$$\begin{aligned}
 H_{ph} &= (1/2M) \sum_n p_n^2 \\
 &+ (1/2) \sum_{nl} K(l) (u_{n+l} - u_n)^2, \\
 p_n &= M \dot{u}_n, \quad (3)
 \end{aligned}$$

where  $M$  and  $K(l)$  are the molecular mass and the force constant which exists for the  $n$  and  $m = n + l$  molecules, respectively. The quantities  $D(|x_m - x_n|)$  and  $J(|x_m - x_n|)$  are expanded to first order about the equilibrium position

$$D(|x_m - x_n|) = 2 \sum_{l>0} D(l) |l|$$

$$+ \sum_{l>0} D'(l) (u_{n+l} - u_{n-l}), \quad (4)$$

$$\begin{aligned}
 \sum_m J(|x_m - x_n|) \sigma_m^x &= \sum_l J(l) \sigma_{n+l}^x \\
 &+ \sum_{l>0} J'(l) \{ (u_{n+l} - u_n) \sigma_{n+l}^x \\
 &+ (u_n - u_{n-l}) \sigma_{n-l}^x \}. \quad (4')
 \end{aligned}$$

Using Eqs. (4) and (4') and omitting terms quadratic with respect to the  $u$ 's, we obtain equations of motion for  $\sigma_n^x$  corresponding to the transition dipole moment of the  $n$  molecule and for  $u_n^*$

$$\begin{aligned}
 \dot{\sigma}_n^x + \epsilon^2 \sigma_n^x + 4\epsilon \sigma_n^z \sum_l J(l) \sigma_{n+l}^x \\
 + 2\epsilon \sum_{l>0} D'(l) (u_{n+l} - u_{n-l}) \sigma_n^x \\
 + 4\epsilon \sigma_n^z \sum_{l>0} J'(l) \{ (u_{n+l} - u_n) \sigma_{n+l}^x \\
 + (u_n - u_{n-l}) \sigma_{n-l}^x \} \\
 + 4 \sum_{l>0} D'(l) (u_{n+l} - u_{n-l}) \sigma_n^z \\
 \times \sum_{l'} J(l') \sigma_{n+l'}^x \\
 + (1/M) \sum_{l>0} D'(l) (p_{n+l} - p_{n-l}) \sigma_n^y = 0, \quad (5)
 \end{aligned}$$

$$\begin{aligned}
 \ddot{u}_n - (1/M) \sum_{l>0} K(l) (u_{n+l} + u_{n-l} - 2u_n) \\
 - (1/M) \sum_{l>0} D'(l) (\sigma_{n+l}^z - \sigma_{n-l}^z) \\
 + (4/M) \sum_{l>0} J'(l) (\sigma_{n+l}^x - \sigma_{n-l}^x) \sigma = 0, \quad (6)
 \end{aligned}$$

where

$$\epsilon = \epsilon_0 + 2 \sum_{l>0} D(l) |l|$$

with

$$\sum_l J(l) |l| \equiv J > \epsilon/2. \quad (7)$$

Since the exciton density is very small, we employ the lowest order approximation to  $\sigma_n^z$ :

$$\begin{aligned}
 \sigma_n^z &= -(1/2) \quad \text{with} \quad \sigma_n^y = -\dot{\sigma}_n^x / \epsilon \\
 &\quad \text{for Eq. (5),} \quad (8)
 \end{aligned}$$

$$\begin{aligned}
 \sigma_{n+l}^z - \sigma_{n-l}^z &= (1/2) \{ (\sigma_{n+l}^x)^2 + (1/\epsilon^2) (\dot{\sigma}_{n+l}^x)^2 \\
 &- (\sigma_{n-l}^x)^2 - (1/\epsilon^2) (\dot{\sigma}_{n-l}^x)^2 \} \\
 &\quad \text{for Eq. (6).} \quad (9)
 \end{aligned}$$

\*) We use units with  $\hbar = 1$ .

Equations (5) and (6) are then closed by themselves.

We employ a continuum approximation

$$\begin{aligned} \sigma_n^x &\equiv (1/2)\rho_n \rightarrow (1/2)\rho(x, t), \\ u_n &\rightarrow u(x, t), \\ \sum_l \exp(ikla)J(|la|) &= J(1 - \gamma a^2 k^2), \\ \gamma &= \text{const} > 0 \end{aligned} \tag{10}$$

to reduce Eqs. (5) and (6) to

$$\begin{aligned} \frac{\partial^2 \rho}{\partial x^2} - \frac{1}{c_1^2} \frac{\partial^2 \rho}{\partial t^2} - A\rho - A'\rho w + \lambda_D w \frac{\partial^2 \rho}{\partial x^2} \\ + \frac{\lambda_D}{2\gamma a^2 \epsilon J} \frac{\partial w}{\partial t} \frac{\partial \rho}{\partial t} = 0, \\ \frac{\partial^2 w}{\partial x^2} - \frac{1}{c_2^2} \frac{\partial^2 w}{\partial t^2} + \frac{\partial^2}{\partial x^2} \left\{ A''\rho^2 \right. \\ \left. + A''' \frac{1}{\epsilon^2} \left( \frac{\partial \rho}{\partial t} \right)^2 \right\} = 0, \quad w \equiv \partial u / \partial x, \end{aligned} \tag{11}$$

where  $A, A', A'', A''', c_1, c_2, \lambda_D, \lambda_J$  are given by

$$\begin{aligned} A &= (\epsilon - 2J) / 2\gamma a^2 J, \\ A' &= \{2(\epsilon - J)\lambda_D - \epsilon\lambda_J\} / 2\gamma a^2 J, \\ A'' &= \epsilon(\lambda_D - \lambda_J) / 4Mc_2^2, \quad A''' = \epsilon\lambda_D / 4Mc_2^2, \\ c_1 &= (2\gamma a^2 \epsilon J)^{1/2}, \\ c_2 &= [\sum_l K(|la|)l^2 a^2 / M]^{1/2}, \\ \lambda_D &= 2 \sum_{l>0} D'(|la|)la / \epsilon \ll 1, \\ \lambda_J &= 4 \sum_{l>0} J'(|la|)la / \epsilon \ll 1 \end{aligned}$$

with

$$\epsilon > 2J, \quad \lambda_D > \lambda_J. \tag{13}$$

The last two terms in Eq. (11) can be neglected as compared with the first four ones. Phonon-free excitons are quasi-particles described by Eq. (11) for  $A' = \lambda_D = 0$  having the form of the Klein-Gordon equation. Solutions to this equation and the mass  $m$  of the quasi-particles are given by

$$\rho = \exp[i(kx - \omega t)]$$

with

$$\omega = (\epsilon^2 - 2\epsilon J + c_1^2 k^2)^{1/2} \equiv (\omega_0^2 + c_1^2 k^2)^{1/2}, \tag{14}$$

$$m = \omega_0 / c_1^2 = (\epsilon^2 - 2\epsilon J)^{1/2} / 2\gamma a^2 \epsilon J. \tag{15}$$

Equation (14) is identical to the results obtained by Agranovich and by Hopfield using the Bogoliubov transformation.<sup>12)</sup> We put

$$w = w(x - vt), \quad v = \text{const} < c_2 \tag{16}$$

in Eq. (12) to get

$$\begin{aligned} w &= -\frac{\epsilon(\lambda_D - \lambda_J)}{4M(c_2^2 - v^2)} \rho^2 \\ &\quad - \frac{\epsilon\lambda_D}{4M(c_2^2 - v^2)} \frac{1}{\epsilon^2} \left( \frac{\partial \rho}{\partial t} \right)^2 \\ &\equiv -D\rho^2 - D' \frac{1}{\epsilon^2} \left( \frac{\partial \rho}{\partial t} \right)^2. \end{aligned} \tag{17}$$

Both of two integral constants herein appeared have been set equal to zero. Inserting this back into Eq. (11) with the last two terms omitted, we obtain a nonlinear Klein-Gordon-type equation

$$\begin{aligned} \frac{\partial^2 \rho}{\partial x^2} - \frac{1}{c_1^2} \frac{\partial^2 \rho}{\partial t^2} - A\rho + B\rho^3 \\ + B' \frac{1}{\epsilon^2} \left( \frac{\partial \rho}{\partial t} \right)^2 = 0, \end{aligned} \tag{18}$$

where

$$\begin{aligned} B &= \frac{\epsilon(\lambda_D - \lambda_J)\{2(\epsilon - J)\lambda_D - \epsilon\lambda_J\}}{8M\gamma a^2 J(c_2^2 - v^2)}, \\ B' &= \{\lambda_D / (\lambda_D - \lambda_J)\} B. \end{aligned} \tag{19}$$

We put

$$\rho = \rho_+ \exp(-i\omega_0 t) + \rho_- \exp(i\omega_0 t) \tag{20}$$

in Eq. (18) and employ a kind of rotating-wave approximation to neglect terms containing the factors  $\exp(\pm i3\omega_0 t)$ . Equation (18) then reduces to the NLS equation

$$i \frac{\partial \rho_+}{\partial t} = -\frac{1}{2m} \frac{\partial^2 \rho_+}{\partial x^2} - g|\rho_+|^2 \rho_+ \quad \text{and c. c.}, \tag{21}$$

where

$$\begin{aligned} g &= \frac{\epsilon^2 [2(\epsilon - J)\lambda_D - \epsilon\lambda_J] \{4 - (2J/\epsilon)\lambda_D - 3\lambda_J\}}{8M(c_2^2 - v^2)(\epsilon^2 - 2\epsilon J)^{1/2}} \\ &> 0. \end{aligned} \tag{22}$$

Here we have also omitted the factors  $(1/c_1^2)$

$\times (\partial^2 \rho_{\pm} / \partial t^2)$ ,  $(B' / \varepsilon^2)(\partial \rho_{\pm} / \partial t)^2 \rho_{\pm}$ ,  $(2B' \omega_0 / \varepsilon^2) \times (\partial \rho_{\pm} / \partial t) \rho_{\pm}^2$ ,  $(2B' / \varepsilon^2)(\partial \rho_{+} / \partial t)(\partial \rho_{-} / \partial t) \rho_{\pm}$ , since all of these are much too small as compared with  $(2\omega_0 / c_1^2)(\partial \rho_{\pm} / \partial t)$ . In the limiting case  $\varepsilon \gg 2J$ , Eq. (21) so obtained reduces to the NLS equation in the Davydov theory except the factor  $C\rho_{\pm}$  ( $C = \text{const}$ ) appearing therein. As is well known,<sup>13</sup> there exist two independent parameters to the one-soliton solutions to the NLS equation. In the present case, however, only one of them is taken to be arbitrary due to the relation  $w(x - vt) = -D\rho^2 - D'(1/\varepsilon^2)(\partial \rho / \partial t)^2$ . The one-soliton solutions to Eq. (21) are then given by

$$\rho_{+} = \alpha \operatorname{sech}[\alpha(mg)^{1/2}(x - vt)] \times \exp[i(k_1 x - \omega_1 t)], \quad (23)$$

where

$$k_1 = mv, \quad \omega_1 = (m/2)v^2 - (\alpha^2/2)g. \quad (24)$$

Since  $\rho_{+}$  satisfies the inequality  $|\rho_{\pm}| \leq 1$  by definition, a parameter  $\alpha$  must satisfy the relation  $\alpha \leq 1$ . It is seen from Eqs. (20) and (23) that the energy  $\mathcal{Q}$  of soliton is given by

$$\mathcal{Q} = \omega_0 - (\alpha^2/2)g + (m/2)v^2 = \omega_0 - (\alpha^2/2)g + (k_1^2/2m). \quad (25)$$

This is to be compared with the energy  $\omega = \omega_0 + (k^2/2m)$  of exciton which exists for Eq. (14) for  $\omega_0 \gg c_1 k$ . It is seen that the soliton energy  $\mathcal{Q}$  is much smaller than the exciton energy  $\omega$  due to the factor  $(\alpha^2/2)g$  and to the relation  $k_1 \ll k$  (cf.,  $v < c_2$ ). This ensures the stability of the exciton solitons once these are formed. An optimum procedure of choosing  $\alpha$  would be to put  $\alpha = 1$ . A more detailed discussion on the properties of exciton solitons and a generalization of the present theory to helical polymers will be given else-

where.

In summary, we have put the Davydov theory of exciton solitons in 1d molecular crystals in a more rigorous basis by showing that inclusion of many-body effects inherent in Frenkel-exciton problems also leads to the NLS equation. The result so obtained appears to be non-trivial in the sense that it results from a nonlinear Klein-Gordon type equation by using a rotating-wave approximation, a situation which is rather analogous to the case in nonlinear optics.

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**Note added in proof:** Although Eq. (21) reduces to the NLS equation in the Davydov theory (D) in the limit  $J/\varepsilon \rightarrow 0$ , one-soliton solution (23) with  $\alpha = 1$  is different from that in D, since  $\alpha$  in D satisfies the relation  $\alpha = a(mg)^{1/2}/2 = (g/J)^{1/2}/2$  due to the normalization condition for the exciton probability density. The binding energy  $\omega_B = g/2$  of solitons with respect to excitons here is therefore different from the corresponding one,  $\omega_B = g^2/8J$ , in D.