Exciton solitons in molecular crystals

M. T. Primatarowa, K. T. Stoychev, and R. S. Kamburova
Institute of Solid State Physics, Bulgarian Academy of Sciences, 1784 Sofia, Bulgaria
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Envelope solitons formed of Frenkel electronic excitons in molecular crystals are investigated. Their dynamics is governed by a nonlinear Schrödinger equation which reflects the Pauli character of the excitations and takes account of the kinematical and the dynamical nonlinear exciton interactions. Analytical solutions are found in the semicontinuum limit corresponding to wide solitons and in the discrete limit corresponding to narrow solitons. The type of the solution and the regions of their validity depend on the carrier wave vector, the nonlinearities, and the density of the excitations. Numerical simulations of the solitons' dynamics are carried out.

I. INTRODUCTION

Solitons in molecular systems have been studied for over twenty years. In their early works[1,2] Davydov and Kislukha investigated pulses of coupled intramolecular and lattice vibrations in biopolymers and showed that they can propagate with a constant velocity and profile. The main nonlinear mechanism which balances the dispersion is the Frölich-type exciton-phonon interaction. In Refs. 1–5 a one-exciton approximation has been employed, corresponding to low exciton densities, where the difference between vibrational and electronic excitons is obscured, the latter being approximated by bosons. Brown *et al.*[6,7] gave an alternative (Hamilton) formulation of Davydov's theory and analyzed different trial state vectors. Weidlich and Heudorfer[8] and later Kruglov[9] and Takeno[3] developed the soliton theory for excitons with higher densities using many-exciton states and taking into account the Pauli character of the excitations. This results in an additional (kinematical) nonlinear exciton interaction, which, however, has been considered to play a minor role compared to the exciton-phonon interaction. The effects of the intramolecular anharmonicity have been taken into account in Refs. 10 and 11 and the soliton dynamics of more complicated models has been studied numerically in Refs. 12–16. The statistical mechanics of solitons has been developed in Refs. 17 and 18.

Solitons in exciton-photon (polariton) systems have been investigated in Refs. 19–27 in connection with the phenomenon known as self-induced transparency. The nonlinearities in these systems are associated with the exciton-exciton interactions, while the linear exciton-photon coupling yields the specific polariton dispersion. Due to it, however, the nonlinear polariton dynamics is in general quite different from that of the pure (mechanical) excitons. To our knowledge, the only attempt to investigate solitons in a one-component system of Frenkel excitons (with no other quasiparticles) has been made in Ref. 28 on the basis of a bosonization approach. The purpose of the present paper is to revise the theory of electronic exciton solitons in molecular crystals keeping the Pauli statistics and taking correct account of both the kinematical and the dynamical exciton-exciton interactions. Our treatment holds for arbitrary carrier wave vectors inside the Brillouin zone and it is not restricted to small exciton densities.

The outline of the paper is as follows. In Sec. II a system of nonlinear equations for the averaged exciton amplitudes is derived and analytical soliton solutions are obtained in the semicontinuum limit corresponding to wide solitons. The dependence of the solutions on the nonlinearities, the wave number, and the exciton density is analyzed. In Sec. III the full set of nonlinear lattice equations describing the dynamics of narrow solitons is solved analytically and numerically and discreteness-induced corrections to the soliton parameters are obtained. Section IV is devoted to a comparison between the present approach and the boson approximation which has often been used for the description of Pauli excitations. A rule for the separation of the contribution from nonphysical states in the equations of motion is formulated. Section V is a summary.

II. THE SEMICONTINUUM LIMIT

In this part we shall investigate nonlinear waves with slowly varying envelopes (compared to the lattice constant), formed of Frenkel electronic excitons in molecular crystals. We shall consider for simplicity structures with one molecule per unit cell and we shall employ the Heitler-London approximation, appropriate to excitons with narrow energy bands. In order to study the intrinsic nonlinear properties of the exciton system we shall neglect any vibrational modes of the crystal (either lattice or intramolecular) and we shall take into account only the ground state and lowest excited electronic state of the molecules. The Hamiltonian of the system can be cast in the following second-quantization form:[29,30,21,8]

$$H=\hbar\omega_0\sum_n P_n^\dagger P_n+\sum_{n,m} M_{nm}P_n^\dagger P_m+\sum_{n,m} J_{nm}P_n^\dagger P_m^\dagger P_n P_m , \tag{1}$$

where $\hbar\omega_0$ is the intramolecular excitation energy. $P_n^\dagger(P_n)$ are the Pauli creation (annihilation) operators of an electron-hole pair in the nth molecule,[29,30,21] which obey the relations

$$[P_n,P_m^\dagger]=(1-2N_n)\delta_{n,m}, \quad [P_n,P_m]=0,$$
$$P_n^2=(P_n^\dagger)^2=0, \quad N_n\equiv P_n^\dagger P_n , \tag{2}$$

which combine commutation on neighboring molecules with Fermi anticommutation relations on one and the same molecule and prohibit the localization of more than one excitation on a single molecule. The Hamiltonian (1) of the two-level exciton system is equivalent to that of a spin-1/2 anisotropic Heisenberg ferromagnet[30,21] in the presence of a magnetic field. The second term in(1) describes the dipole-dipole intermolecular interaction responsible for the exciton transfer from one molecule to another, where M_{nm} are the corresponding matrix elements. The last term $\sim J_{nm}$ describes the nonlinear dynamical interaction between excitations on neighboring molecules. It has a different form as compared to the intramolecular anharmonicity term in the case of vibrational excitations, where the two bosons can be localized on one and the same molecule. The direct dynamical exciton-exciton interaction has a quadrupole character and it is usually negative and much weaker than the dipole intermolecular interaction ($|J| \ll |M|$). The excitons, however, may interact also in an indirect way (exchanging other quasiparticles, like lattice phonons, for example), which may result in a considerable increase of the effective nonlinear exciton interaction or even a change of its sign.

The equation of motion for the operators P_n yields

$$i\hbar \frac{\partial}{\partial t} P_n = \hbar \omega_0 P_n + (1-2N_n) \sum_m M_{nm} P_m + 2P_n \sum_m J_{nm} N_m . \tag{3}$$

In comparison with the case of vibrational excitons, Eq. (3) contains an additional nonlinear term proportional to M_{nm} which describes the so-called kinematical exciton-exciton interaction. It has a statistical nature associated with the specific commutation relations (2) for the Pauli operators and corresponds to repulsion between excitons on neighboring molecules. An equation similar to (3) has been obtained for magnon solitons in ferromagnetic chains.[31]

Further on we shall consider for simplicity one-dimensional motion along a principal crystal axis and we shall take into account only nearest-neighbor interactions in this direction,

$$M_{nn+1} = M_{n+1n} = M, \quad J_{nn+1} = J_{n+1n} = J. \tag{4}$$

We shall average Eq. (3) using a normalized wave function of the form[9,22]

$$|\Psi(t)\rangle = \prod_n [u_n(t) + v_n(t) P_n^\dagger] |0\rangle, \quad |u_n|^2 + |v_n|^2 = 1, \tag{5}$$

where $|0\rangle$ is the ground-state wave function corresponding to the exciton and phonon vacuum, for which

$$P_n |0\rangle = 0.$$

The function (5) is of the form of a truncated coherent-state wave function where nonphysical states with more than one excitation on a single molecule have been excluded. It is the site analog of the BCS wave function in the theory of superconductivity (see, for example, Ref. 30), which has been successfully applied to describe coherent macroscopic states of the electron pairs. The soliton solutions which we obtain below also describe a coherent macroscopic state of a large number of intramolecular excitations (electron-hole pairs) moving through the crystal with a constant velocity and profile.

With the help of (2) and (5) the following decoupling relations can be established:[9]

$$\langle N_n P_m \rangle = \langle N_n \rangle \langle P_m \rangle,$$
$$\langle N_n \rangle = (1/2)(1 \mp \sqrt{1 - 4|\langle P_n \rangle|^2}). \tag{6}$$

The two signs in (6) correspond to different exciton densities. The upper sign holds for $0 \leq \langle N_n \rangle \leq 1/2$ and the lower sign for $1/2 \leq \langle N_n \rangle \leq 1$. Equation (6) reflects the Pauli character of the excitations and describes the deviations of the average local density from the squared modulus of the average amplitudes. In the small-density limit ($\langle N_n \rangle \ll 1$) Eq. (6) yields

$$\langle N_n \rangle \approx |\langle P_n \rangle|^2, \tag{7}$$

which is the usual decoupling relation when the average is taken over Glauber's coherent states.[32] As they involve states with arbitrary occupation numbers, they are applicable to vibrational excitons (bosons) and to low-density electronic excitons which can be approximated by bosons. For higher exciton densities a wave function of the type (5) should be used, which does not contain nonphysical states with occupation numbers $n > 1$. In the numerical calculations carried out in the next section we have checked that the average exciton number of large-amplitude solitons is conserved when described by (6) and not by (7).

As (6) shows, the average exciton density $\langle N_n \rangle$ can deviate dramatically from $|\langle P_n \rangle|^2$ and in the high-density limit ($\langle N_n \rangle \sim 1$, $|\langle P_n \rangle|^2 \ll 1$) is given by

$$\langle N_n \rangle \approx 1 - |\langle P_n \rangle|^2. \tag{8}$$

An inverse behavior of the density of excitations on the wave function associated with $\langle P_n \rangle$ is observed in this case.

Denoting

$$\langle P_n \rangle = \alpha_n(t) \tag{9}$$

and averaging Eq. (3) with the help of (5) and (6) gives

$$i\hbar \frac{\partial \alpha_n}{\partial t} = (\hbar \omega_0 + 2J)\alpha_n \pm M \sqrt{1 - 4|\alpha_n|^2} (\alpha_{n+1} + \alpha_{n-1}) \mp J(\sqrt{1 - 4|\alpha_{n+1}|^2} + \sqrt{1 - 4|\alpha_{n-1}|^2})\alpha_n. \tag{10}$$

The upper or lower signs correspond to $\langle N_n \rangle < 1/2$ or $\langle N_n \rangle > 1/2$, respectively. In the small- or high-density limits, when $|\langle P_n \rangle|^2 \ll 1$, Eq. (10) becomes

$$i\hbar \frac{\partial \alpha_n}{\partial t} = (\hbar \omega_0 + 2J \mp 2J)\alpha_n \pm M(\alpha_{n+1} + \alpha_{n-1})(1 - 2|\alpha_n|^2) \pm 2J(|\alpha_{n+1}|^2 + |\alpha_{n-1}|^2)\alpha_n . \tag{11}$$

In this section we shall seek solutions of Eq. (11) in the form of amplitude-modulated waves

$$\alpha_n(t) = e^{i(kn - \omega t)} \varphi_n(t), \tag{12}$$

where k and ω are the wave vector and the frequency of the carrier wave (the lattice constant equals unity) and the envelope $\varphi_n(t)$ is a real slowly varying function of the position and time. We shall employ the semidiscrete approach,[33,34] treating the phase factor exactly and using a continuum approximation for the envelope $\varphi_n(t)\rightarrow\varphi(x,t)$. Thus we obtain the following nonlinear Schrödinger equation:

$$i\hbar\frac{\partial\varphi}{\partial t}=(\epsilon_k+2J\mp2J-\hbar\omega)\varphi\mp i\frac{\partial\epsilon_k}{\partial k}\frac{\partial\varphi}{\partial x}\pm b_k\frac{\partial^2\varphi}{\partial x^2}$$
$$\pm4(J-b_k)\varphi^3, \tag{13}$$

where

$$\epsilon_k=\hbar\omega_0+2b_k, \quad b_k=M\cos k \tag{14}$$

is the energy of the noninteracting excitons.

The quantity $4(J-b_k)$ is the effective nonlinear interaction parameter, which is wave-vector dependent and contains contributions from both the dynamical ($\sim J$) and the kinematical ($\sim b_k$) exciton-exciton interaction. Note that (13) is the lowest-order equation which takes account of the Pauli character of electronic excitons. Higher-order corrections can be included in (13) from the square root and nearest-neighbor expansions in (10). The transition to high exciton densities changes the signs in front of the terms containing derivatives and the nonlinear terms and adds a quantity of $4J$ to the carrier frequency.

The solutions of Eq. (13) depend on the quantity $b_k/4(J-b_k)$. Positive values yield

$$\varphi(x,t)=\varphi_0\operatorname{sech}\frac{x-vt}{L}, \tag{15}$$

$$\hbar\omega=\epsilon_k+2J\mp2J+\frac{b_k}{L^2}, \quad \varphi_0^2=\frac{b_k}{2(J-b_k)L^2}, \tag{16}$$

while negative values

$$\varphi(x,t)=\varphi_1\tanh\frac{x-vt}{L}, \tag{17}$$

$$\hbar\omega=\epsilon_k+2J\mp2J+\frac{2b_k}{L^2}, \quad \varphi_1^2=-\frac{b_k}{2(J-b_k)L^2}. \tag{18}$$

$2L$ is the width of the nonlinear formation. Depending on the signs of J and b_k, the dynamical and kinematical interaction can have either additive or compensatory action, and soliton solutions exist in the continuum limit for arbitrary small (but finite) nonlinear parameters $4(J-b_k)$.

The velocity of both soliton solutions determined from Eq. (13) is

$$v=\mp\frac{2M}{\hbar}\sin k. \tag{19}$$

This coincides in magnitude with the group velocity of the noninteracting excitons and the two signs correspond to the low- and high-density limits.

It should be noted that, although the type of the solution for φ is one and the same for low and high exciton densities (the signs in front of the derivatives and the nonlinear terms change simultaneously), the quantity which has physical meaning is $\langle N_n\rangle$ and according to (6) it has an inverse behavior in these two limiting cases. Thus the bright soliton for $\langle N_n\rangle\ll1$ under the same interactions turns into a "gray" soliton in the case of $\langle N_n\rangle\sim1$ and vice versa (Fig. 1). The high-density solitons have a frequency shift of $4J$ and opposite velocities. The dynamics in this case can be reformulated in terms of the dynamics of "exciton vacancies" if we consider P_n as creation and $P_n^\dagger$ as annihilation operators for the vacancies, and $\langle P_nP_n^\dagger\rangle$ as their density. In what follows we shall focus on the small-density limit, keeping in mind that the transition to high densities is straightforward.

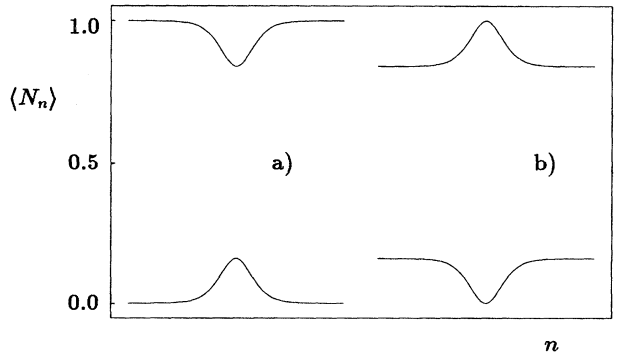

FIG. 1. Density profiles for low and high exciton concentrations. (a) sech solution; (b) tanh solution.

The energy of the dark soliton calculated from the Hamiltonian (1) in the continuum approximation with the solution (17) and (18) is

$$E=\left(\epsilon_k-\frac{b_k}{L^2}\frac{J}{J-b_k}+\frac{4b_k}{3LN}\frac{J+b_k}{J-b_k}\right)N_{\text{ex}}, \tag{20}$$

where N_{ex} is the number of the excitations and N is the number of the molecules in the chain. The energy of the bright soliton corresponding to the solution (15) and (16) is

$$E=\left(\epsilon_k+\frac{b_k}{3L^2}\frac{J+b_k}{J-b_k}\right)N_{\text{ex}}. \tag{21}$$

The factors $J/(J-b_k)$ and $(J+b_k)/(J-b_k)$ in (20) and (21) describe the contribution of the kinematical interaction to the soliton energy and in the case of vibrational excitons they are equal to unity.

When the dynamical interaction between the excitons is negligible ($J=0$), only dark-soliton solutions (17) are possible, with a constant width $L=1/\varphi_1\sqrt{2}$ for arbitrary values of the wave vector k. This result follows from the fact that the kinematical interaction is proportional to the dispersion coefficient b_k and this leads always to repulsion between the excitons and the formation of a region of deexcitation with a constant profile. Only the soliton velocity (19) and the energy (20) in this case depend on the wave vector.

The presence of a dynamical exciton-exciton interaction ($J\neq0$) leads to some specific spatial-dispersion effects in the exciton solitary waves. Two types of critical points and corresponding critical behavior can be observed (Fig. 2). The first one (k_d) is associated with the zero of the dispersion coefficient [$b(k_d)=0$], and the second (k_n) with the pos-

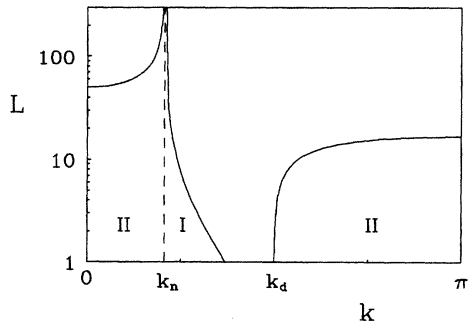

FIG. 2. Regions of existence and spatial width of the bright (I) and dark (II) soliton solutions for $N_{ex}=1$, $N=1000$, $M=-0.1$, and $J=-0.08$.

sible zero of the nonlinear coefficient $[J-b(k_n)=0]$. Within our model b_k changes sign at $k_d=\pi/2$ and depending on the signs of M and J a change from bright- to dark-soliton solution or vice versa takes place around k_d, accompanied by a critical behavior of the soliton parameters. In the vicinity of k_d the soliton width becomes very small ($L<1$) and the amplitude quite large and the slowly-varying-envelope solutions (15) and (17) may not be valid.

In the case of a strong dynamical exciton interaction ($|J|>|M|$), the nonlinear coefficient does not change sign and k_d is the only critical point. The bright- and dark-soliton solutions coexist in the two adjacent regions of the Brillouin zone on both sides of k_d.

For weaker dynamical interaction ($|J|<|M|$) the nonlinear coefficient vanishes at k_n $[J-b(k_n)=0]$ and this leads to a second change of the type of the solution. Depending on the signs of J and M, k_n can be situated to the left or to the right of k_d. The Brillouin zone in this case is divided into three regions with respect to the soliton solutions. A bright-soliton solution exists in the region between k_n and k_d, and dark-soliton solutions in the outside regions. Near k_n the soliton width becomes very large and the solution turns into a plane wave of noninteracting excitons. Similar wave-vector dependence of the soliton solution and parameters has been obtained in Ref. 34 for lattice solitons.

III. THE DISCRETE LIMIT

In this section we shall concentrate on the dynamics of narrow solitons, whose width is of the order of a few lattice constants. We shall abandon the continuum approximation for the envelope and solve the complete set of nonlinear equations (10) or (11). For small exciton densities ($\langle N_n\rangle\approx|\langle P_n\rangle|^2\ll 1$) and vanishing dynamical interaction ($J=0$), Eq. (11) is of a form which is known to be completely integrable.[35,36] For the parameters of Eq. (11) with $J=0$ we have found the following dark-soliton solution:

$$\alpha_n(t)=e^{i(kn-\omega t)}\varphi_n(t), \tag{22}$$

$$\varphi_n(t)=\varphi_1\tanh\frac{n-vt}{L}, \tag{23}$$

with

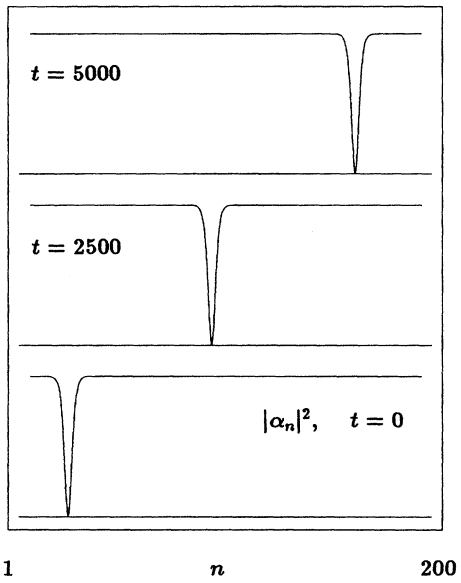

FIG. 3. Time evolution of a narrow dark soliton with $L=2.5$, $k=0.61$, $M=-0.1$, and $J=0$. (The energies are measured in $\hbar\omega_0$, the lengths in lattice constants, and the time in ω_0^{-1}.) The obtained velocity is $v=0.109$.

$$\hbar\omega=\hbar\omega_0+2b_k\operatorname{sech}^2\frac{1}{L},\quad \varphi_1=\frac{1}{\sqrt{2}}\tanh\frac{1}{L}, \tag{24}$$

and velocity

$$v=-\frac{2ML}{\hbar}\tanh\frac{1}{L}\sin k. \tag{25}$$

The above result shows that the system of low-density Frenkel excitons with only kinematical interaction possesses a stable dark-soliton solution even in the case of narrow solitons with $L\sim 1$. As in the case of wide exciton solitons, the amplitude and the width of the solution (23) are independent of the carrier wave vector. The difference between (23)–(25) and the wide-soliton solution (17)–(19) is in the hyperbolic functions of $1/L$ in the expressions for the amplitude, velocity, and carrier frequency. As it should be, the solution (23)–(25) of the discrete set of equations is more general and it turns into (17)–(19) for $L\gg 1$. According to (24) and (25) the narrow-soliton parameters may deviate considerably from those of wide solitons.

We have checked numerically the stability of the solution (23) and Fig. 3 shows the time evolution of a dark soliton with $L=2.5$. The amplitude and the velocity of the soliton coincide with the ones calculated from (24) and (25) and are smaller than these of wide solitons with the same carrier wave vector.

It is of physical interest to compare the above results with the case of narrow vibrational solitons with on-site repulsive nonlinear interaction described by the equation

$$i\hbar\frac{\partial\alpha_n}{\partial t}=\hbar\omega_0\alpha_n+M(\alpha_{n+1}+\alpha_{n-1})+4J|\alpha_n|^2\alpha_n. \tag{26}$$

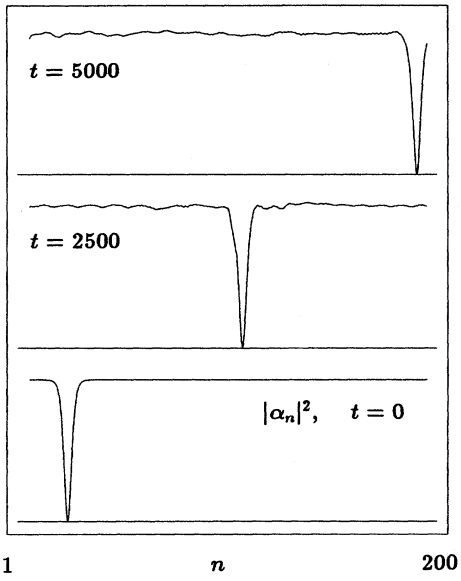

FIG. 4. Time evolution of a narrow vibrational dark soliton with $J=0.0818$ and $L=2.5$. $v=0.115$.

No exact soliton solutions of this equation are known.[36] The evolution of a dark vibrational soliton with the same parameters as in Fig. 3 and initial distribution governed by (23) and (24) is shown in Fig. 4. The background density is slightly perturbed and the dark soliton propagates faster, with a velocity which coincides with the group velocity of the noninteracting excitations and corresponds to wide solitons. Thus, in contrast to the case of electronic exciton solitons, there are no nonlinear corrections to the velocity of narrow vibrational solitons.

Equation (11) with nonvanishing dynamical interaction is not completely integrable and possesses no exact soliton solutions. Nevertheless, it supports quasistable soliton solutions for a wide range of values of the dynamical interaction as shown by our numerical simulation. Figures 5 and 6 illustrate the evolution of narrow solitons in the presence of an attractive dynamical interaction $J<0$. For small values of J [$|J|<|b_k|$, Fig. 5(a)] the dark-soliton solution is accompanied by a number of small-amplitude "gray" solitons. The initial amplitude in this case is approximated by

$$\varphi_1=\sqrt{\frac{-b_k}{2(J-b_k)}}\tanh\frac{1}{L}. \tag{27}$$

Larger values of $|J|$ lead to stronger perturbations of the dark soliton [Fig. 5(b)].

In the previous section we have seen that a strong attractive dynamical interaction ($|J|>|b_k|$) changes the sign of the nonlinear parameter $(J-b_k)$ and leads to a bright-soliton solution. This feature is preserved in the discrete limit too (Fig. 6), where the amplitude can be approximated by

$$\varphi_n(t)=\varphi_0\ \mathrm{sech}\frac{n-vt}{L},\quad \varphi_0=\sqrt{\frac{b_k}{2(J-b_k)}}\sinh\frac{1}{L}. \tag{28}$$

Figure 6 shows that a stable narrow bright soliton can exist in this case.

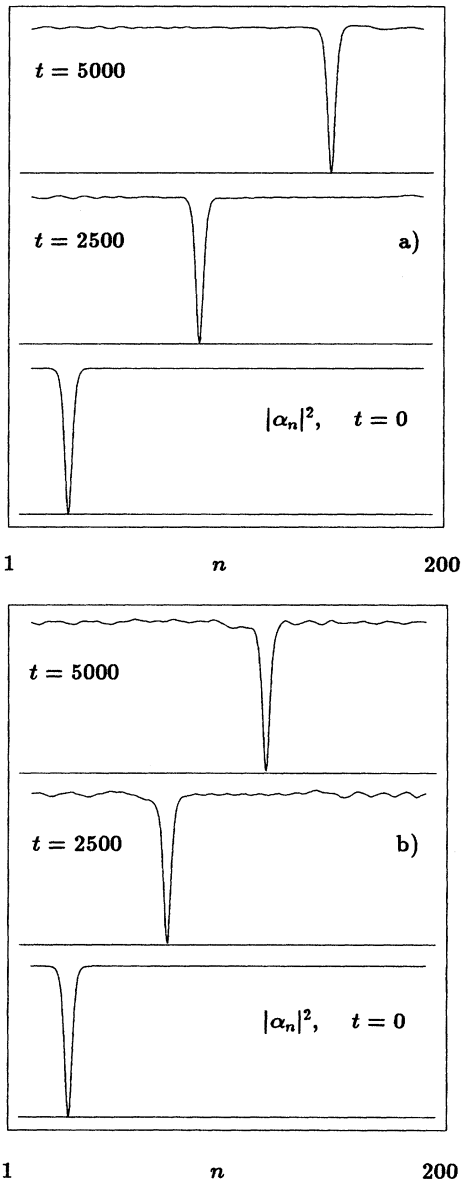

FIG. 5. Time evolution of a narrow dark soliton for weak attractive dynamical interaction. (a) $J=-0.025$, $v=0.106$. (b) $J=-0.0425$, $v=0.10$.

The dynamical interaction influences considerably the soliton velocity as shown in Fig. 7. The left and right branches correspond to bright- and dark-soliton solutions, respectively. In the intermediate region where $J\approx b_k$ no narrow-soliton solutions exist.

We have investigated also the influence of the exciton density on the soliton dynamics as described by (6). For narrow solitons with high amplitudes, the quantity $\Sigma\langle N_n\rangle$ is conserved with time while $\Sigma|\langle P_n\rangle|^2$ is not, and thus the former is the true integral of motion describing the total number of quasiparticles. The use of (6) instead of (7) and the resulting equation of motion (10) leads to noticeable perturbation of the soliton solution in the region $1.5<L<2$ when also $4|\alpha_n|^2\sim 1$. For $L<1.5$ the soliton solution is de-

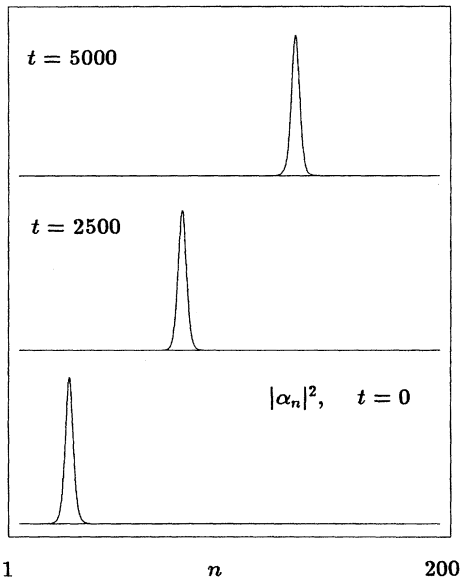

FIG. 6. Time evolution of a narrow bright soliton in the case of strong attractive dynamical interaction with $J=-0.15$, $v=0.103$.

stroyed. In this case the higher-order nonlinear terms introduced from the square-root expansion cannot be treated as small compared to $|\alpha_n|^2\alpha_n$.

IV. COMPARISON WITH THE BOSONIZATION APPROACH

A widely used approach for the investigation of the excited states of (1) is the expansion of the Pauli operators in terms of Bose operators based on the Holstein-Primakoff relations. This introduces additional nonlinear terms in the Hamiltonian, which have been assumed to describe the so-called kinematical exciton-exciton interaction. The ambiguities arising from such a transformation have been discussed in a number of works.[29,37–40] It has pointed out that the change to an infinite boson basis introduces uncontrolled errors in the evaluation of physical quantities in all cases when the number of excitations is greater than unity, known as "contributions from nonphysical states." To our knowledge, the problem of the separation of the contributions from the "physical" and the "nonphysical" states in the boson representation has remained open. In this section we make an attempt to solve this problem on the basis of the equations of motion, averaged over truncated coherent states with occupation numbers $n=0,1$.

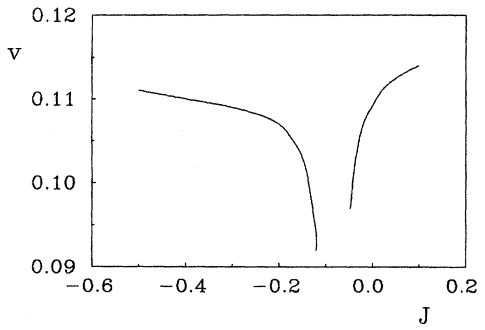

FIG. 7. Dependence of the soliton velocity on the dynamical interaction.

A similar bosonization procedure has been used in Ref. 28 for the investigation of pulses of Frenkel electronic excitons. There, the exciton Pauli operators have been approximately expressed in terms of Bose operators through the relations[29,39]

$$P_n=(1-B_n^\dagger B_n)B_n, \quad P_n^\dagger=B_n^\dagger(1-B_n^\dagger B_n). \tag{29}$$

Applied to the Hamiltonian (1) this gives

$$\begin{aligned} H=\hbar\omega_0\sum_n B_n^\dagger B_n+\sum_{n,m} M_{nm}B_n^\dagger B_m+\sum_{n,m} J_{nm}B_n^\dagger B_m^\dagger B_n B_m \\ -\hbar\omega_0\sum_n B_n^\dagger B_n^\dagger B_n B_n-\sum_{nm} M_{nm}(B_m^\dagger B_n^\dagger B_n B_n \\ +B_m^\dagger B_m^\dagger B_m B_n), \end{aligned} \tag{30}$$

where the last three terms have been identified in Ref. 28 as a kinematical interaction operator. It includes a diagonal term corresponding to a strong on-site *attraction* $(-\hbar\omega_0\Sigma B_n^\dagger B_n^\dagger B_n B_n)$ as well as nondiagonal terms associated with the intermolecular interaction. Although it has been argued[29,39] that the diagonal term can produce a low-level exciton bound state, it has the wrong sign and magnitude and its contribution to the soliton dynamics in the $\hbar\omega_0$ region should be negligible. It is important to note that it is practically impossible to separate the "physical" from the "nonphysical" terms in the Hamiltonian. It is tempting to consider states with boson occupation numbers $n>1$ as nonphysical; however, all kinematical terms in the Hamiltonian vanish when averaged over states with $n=0,1$. Their contribution to the energy is "hidden" in the wave function which is to be determined from the corresponding time-dependent nonlinear Schrödinger equation. The problem thus reduces to the correct evaluation of the kinematical-interaction terms in the equations of motion.

The equation of motion which follows from the Hamiltonian (30) is

$$\begin{aligned} i\hbar\frac{\partial}{\partial t}B_n=\hbar\omega_0 B_n+\sum_m M_{nm}(B_m-2B_n^\dagger B_n B_m) \\ +2B_n\sum_m J_{nm}B_m^\dagger B_m-\sum_m M_{nm}(B_m^\dagger B_n B_n \\ +B_m^\dagger B_m B_m)-2\hbar\omega_0 B_n^\dagger B_n B_n. \end{aligned} \tag{31}$$

Compared with the equation of motion for the Pauli operators (3) it contains three additional nonlinear kinematical-interaction terms (the last three). They all give nonvanishing contributions if averaged over Glauber's coherent states and as $\hbar\omega_0 \gg |M|$ the last one is dominant. In Ref. 28 only this large kinematical term has been kept in the equation of motion and a bright-soliton solution has been obtained near the center of the Brillouin zone, in contradiction with the assumption for negative exciton effective mass and the results obtained in the previous section (it is easy to see that the amplitude (16) in Ref. 28 is imaginary in this case and the

solution is extremely narrow $[4B/(C-2\omega_0)<1]$, which violates the continuum approximation). Even if the large kinematical term is dropped on physical grounds, the additional kinematical terms containing the combination B_nB_n and B_mB_m which have no counterpart in Eq. (3) will lead to modified results.

The correct contribution from the kinematical interaction in the boson representation can be evaluated if the equation of motion (31) is averaged with a wave function of the type (5) which does not contain states with occupation numbers $n>1$. All averaged "nonphysical" terms vanish in this case and the resulting equation is identical with the averaged equation of motion for the Pauli operators in the small-density limit.

V. CONCLUSION

We have investigated envelope solitons in a one-component system of Frenkel excitons. We have shown that the Pauli character of the excitations leads to repulsive nonlinear kinematical interaction between the excitons which is proportional to the dispersion coefficient and for small exciton densities yields dark-soliton solutions in the whole Brillouin zone. The presence of an attractive dynamical exciton interaction forms a region in the zone where bright-soliton solutions exist. For high exciton densities the inverse picture is observed.

Wide solitons are treated in the continuum-envelope limit where exact soliton solutions are obtained. The dependence of the solution on the carrier wave vector and the nonlinearities is analyzed. Narrow solitons are studied using the discrete set of nonlinear equations and an exact dark-soliton solution is found in the case of small exciton densities and vanishing dynamical interaction. The parameters of the solution involve nonlinear corrections which are different from these for wide solitons. As most important may be considered the nonlinear correction to the soliton's velocity.

Weak dynamical interaction and higher exciton densities are shown to produce small background perturbations of the dark soliton, while a strong attractive dynamical interaction changes the type of the solution into a bright-soliton one. The dynamical interaction influences the velocity of narrow solitons considerably. The dynamics of narrow vibrational solitons is studied for comparison and it is shown that there are no nonlinear corrections to the velocity in this case.

A critical analysis of the approach based on the bosonization of the Hamiltonian is carried out and a rule for the elimination of the nonphysical terms in the equations of motion is formulated.

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