Quantum confinement and superradiance of one-dimensional self-trapped Frenkel excitons

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Received 21 January 1999

Abstract

It is known that in one-dimensional (1D) molecular crystals with finite length \(2L \ll \lambda\) (\(\lambda\) is the optical wavelength) an overwhelming part of the total oscillator strength is concentrated in the lowest excitonic state and it is equal to \(F_1 \approx 0.85 f_0 (2L/a)\), where \(f_0\) is the oscillator strength of a monomer and \(a\) is the lattice constant. This leads to the superradiance from the lowest excitonic state and its domination in the absorption spectrum of the crystal. We show that self-trapping of excitons destroys this simple picture so that it takes place only for short chains with length \(2L\) small compared to the length \(2l_0\) of self-trapping. For long enough chains the value of \(F_1\) does not increase with growth of \(L\), as it occurs in linear case, but tends to the saturation limit \(F_1 \approx 5f_0 (l_0/a)\). The oscillator strength of the next bright state also tends to the same limit with growth of \(L\), but it takes place only at the length \(L > 9l_0\), and analogous relations are true for the following bright states. Contrary to the case of infinite chain, where only one self-trapped state exists, in the chains of finite length several self-trapped states can arise, number of which depends on the length of the chain. We consider also the influence of quantum confinement and self-trapping on the superradiance of 1D molecular crystals. © 1999 Elsevier Science B.V. All rights reserved.

1. Introduction

In spite of the fact that the theory of excitons in molecular crystals has been developing for many years, it still attracts much attention and remains very topical. Nowadays, this interest is connected with permanently arising number of organic crystals available for investigations of their optical and electrical properties, and also with development of new methods of fabrication of very thin crystalline films and even organic superlattices on different types of substrates. In the most well studied molecular crystals, such as anthracene, tetracene and other crystals of aromatic series, the intermolecular distances are quite large in all directions and, hence, the overlap of the wave functions of neighboring molecules is very small. In such crystals the deviation from electroneutrality of the molecules in the lowest energy excitations is negligibly small. Frenkel excitons and a weak exciton–phonon interaction are the most typical just in this type of crystals. On the other hand, there are crystals (which are called quasi-one-dimensional) in which the distances between molecules in one direction is much smaller than in the others. As an example of such a crystal we can mention the 3,4,9,10-perylenetetracarboxilic dianhydride (PTCDA), a prototypical material for current studies of electroluminescence in molecular and polymeric systems. PTCDA is an organic molecular crystal and excellent hole conductor [1]. During last years the
intensive investigations are performed with the aim to determine the nature of its lowest energy electronic states [2]. Analogous examples can be found among molecular aggregates and polymers. In the analysis of the lowest electronic excitations in quasi-one-dimensional crystals, it is natural to take into account not only Frenkel excitons, but also as another alternative the one-dimensional Wannier-Mott excitons (i.e., the excitons of large radius). Investigations of optical phenomena, such as absorption, fluorescence and, for example, electroabsorption, are the major tools for establishing the nature of lowest energy states. In particular, the optical properties of nanostructures, where the characteristic features of quantum confinement can appear, are especially interesting. Just the study of quantum confinement permits one in many cases to shed light on the real structure of the lowest energy electronic excitations. In semiconductor crystals the characteristic length, which determines the properties of the quantum confinement phenomenon, is the Bohr radius $a_B = \frac{\hbar^2}{\epsilon M}$ ($M$ is the exciton mass, $\epsilon$ the dielectric constant of the crystal). As a rule, this radius is equal to 30–100 Å and even more. The very thin crystalline films of high quality with the width 50–100 Å can be fabricated by the molecular beam epitaxy method, and therefore in these semiconductor crystals the quantum confinement is studied very well and widely used in investigations of different electrical and optical (linear and nonlinear) properties of quantum wells and superlattices [3]. In organic crystals with one-dimensional Wannier-Mott excitons we can expect that the quantum confinement effects appear also at the crystal length of the order of magnitude of Bohr radius of the exciton. A natural question arises about possibility of quantum confinement in those molecular crystals where the electroneutrality of molecules is not violated and the Wannier-Mott excitons do not appear. The present paper is devoted to consideration of this problem. We shall show here that even in molecular crystals in which the lowest electronic excitations are the Frenkel excitons, i.e. where the Bohr radius is of order of the molecular size, the quantum confinement is possible, if, for example, one takes into account the electron–phonon interaction and the possibility of self-trapping of excitons. It is clear that in this case a new characteristic length, a size of the self-trapped state, appears, whence the phenomenon of quantum confinement becomes possible, if this length is of order of magnitude of the film thickness (or the molecular chain length).

If the exciton–phonon interaction is weak, i.e. the line width of exciton optical transition is much smaller than the exciton band width, then at small film thickness we shall get the usual space quantization of exciton states inside the band. It will be demonstrated below for a simplest and well-known example of 1D molecular chain. For ideal linear chains of finite length without exciton–phonon interaction and in approximation of nearest neighbors interaction (this model is often used for analysis of spectra of J-aggregates, see, e.g., [4]), the energy of exciton states is equal to

$$E_j = E_0 - 2 J \cos \left( \frac{\pi j}{N + 1} \right),$$

where $N$ is the number of molecules in the chain, $J$ the matrix element of transferring the excitation to the neighboring site, $j = 1, \ldots, N$ enumerates the states, and $E_0$ is the energy of molecular excitation including the gas-condensed matter shift. In what follows we neglect the variation of this quantity at the ends of the chain. The exciton band (1) extends from $E = E_0 - 2 J$ to $E = E_0 + 2 J$, and is symmetric around $E = E_0$. For $J > 0$, the $j = 1$ state lies at the bottom of the band (direct band edge), whereas for $J < 0$ this state is located at the top of the band. For large $N \gg 1$ we have

$$E_j \equiv E_0 - 2 J \cos \left( \frac{\pi j a}{2 L} \right),$$

where $a$ is the 1D lattice constant and $2L$ denoted the length of the chain. At the bottom of the band (i.e. for small $j$ and supposing $J > 0$) the expansion of this expression defines an effective mass of the exciton:

$$M = \frac{\hbar^2}{2 J a^2}.$$
It can be shown [4,5] that only eigenstates with \( j \) odd have nonzero oscillator strength, \( F_j \propto |\mu_j|^2 \),

\[
\mu_j^2 = \frac{2\mu_{\text{mon}}^2}{N+1} \cot^2\left(\frac{\pi j}{2(N+1)}\right), \quad j = \text{odd},
\]

\[
\mu_j^2 = 0, \quad j = \text{even},
\]

where \( \mu_j \) is the transition dipole moment to the state \( j \), \( \mu_{\text{mon}} \) the dipole moment of a monomer. Elementary analysis of these expressions shows that the state \( j = 1 \) contains an overwhelming part of the total oscillator strength up to 81\% for \( N \gg 1 \), what is expressed by the formula

\[
F_{j=1} = \frac{8}{\pi^2} N f_0,
\]

where \( f_0 \) is the oscillator strength of a monomer. This leads to superradiant emission with radiative lifetime \( \tau = \tau_0 / N \), where \( \tau_0 \) is the radiative lifetime of a monomer, and to domination of this state in the absorption spectrum (for the first time the superradiance from \( J \)-aggregates was observed in Ref. [6]).

The oscillator strengths of higher states drop off as \( 1/j^2 \) for \( j \ll N \). The exciton–phonon interaction leads to widening of lines corresponding to the states with different \( j \). In the really observed absorption spectra these transition usually overlap with each other. Such an overlap, however, does not shift considerably the position of the maximum of the absorption line. Therefore we can accept with sufficient accuracy that the maximum of the absorption line corresponds to the transition to the state \( j = 1 \). It follows from Eq. (1) that for \( N \gg 1 \) the frequency corresponding to the maximum of the absorption band has to vary with \( N \) according to the law

\[
\Delta \propto \frac{1}{N^2}.
\]

We neglect here the influence of disorder. In this approximation the shift occurs in the direction of higher frequencies (blue shift) for \( J > 0 \) and in the direction of lower frequencies (red shift) for \( J < 0 \).

Now let us turn to the discussion of the systems with exciton–phonon interaction. As is known, in this case the self-trapping of excitons becomes possible. Two limiting cases can be distinguished in this phenomenon (see, e.g. [7]). The first limiting case, which was firstly discussed by Peierls [8] and Frenkel [9], corresponds to the excitons with a narrow exciton band \( J \ll \hbar \omega_0 \), \( \omega_0 \) being the characteristic frequency of phonons strongly interacting with excitons. In this case the exciton is the slow subsystem and the lattice deformation around the exciton is able to follow its position. As it was metaphorically described by Frenkel, the exciton, when traveling in the lattice, “drags with itself the entire load of atomic displacement”. The spectra of excitonic absorption in this limiting case of “heavy” excitons are analogous to the absorption spectrum of impurities in solid solution, and just for this case the dependence of the maximum of the spectrum on the film’s width (or on the number of molecules in the 1D chain) was considered in Ref. [10]. In this case the frequency shift obeys the relation

\[
\Delta \propto \frac{1}{N}.
\]

This shift in framework of the theory [10] was caused by the fact that the gas-condensed matter shift for molecules near the boundaries can differ from that in the bulk. In fact, this result is more general and takes place when frequencies of molecules at surfaces (or of end molecules in the chains) are changed due to mechanisms of various nature different from discussed in Ref. [10] (e.g., if there is charge transfer in the ground or excited states of molecules at the surfaces).

In this paper we shall consider another limiting case which corresponds to the excitonic bands being much wider than the typical energy of phonons, \( J \gg \hbar \omega_0 \) (the case of “light” excitons [7]). Such a limiting case takes place, as is known, for many \( J \)-aggregates and also, probably, for PTCDA crystal which according to estimates [11] has the band width equal to \( \approx 0.5 \) eV. For the first time this model was applied to excitons by Rashba [12]. Just for this case of light excitons and weak exciton–phonon coupling one can expect a large size of the self-trapped excitonic states and quantum confinement becomes the most interesting. In what follows we consider the phenomenon of quantum confinement in the model of 1D molecular crystal. This model is often used for analysis of optical properties of \( J \)-aggregates. These properties have been investigated for a long time, but recently this interest has risen considerably in connection with new experimental results on the superradiance of excitonic states and its temperature de-
The basic feature of the self-trapping phenomenon is that the exciton creates a static lattice deformation and then becomes self-trapped in the potential well that results from this deformation. Therefore it is natural to define the displacement $q_k$ as a sum of two terms,

$$q_k = d_k + \tilde{q}_k,$$

where the variables $d_k$ refer to the static potential well deformation ($d_k = d'_k$, $d_k = d'_k$) and $\tilde{q}_k$ to small vibrations around this displaced field. On substituting Eqs. (9), (11) into (8), we obtain the exciton–phonon Hamiltonian in terms of new variables

$$H = -\frac{\hbar^2}{2M} \frac{\partial^2}{\partial x^2} + \frac{\hbar \omega_0}{2} \sum_k \left( p_k p_{-k} + \tilde{q}_k \tilde{q}_{-k} - 1 \right)$$

$$+ \hbar \omega_0 \sum_k d_k^2 + \frac{\hbar \omega_0}{2} \sum_k d_k \tilde{q}_k$$

$$+ \frac{\gamma}{\sqrt{N}} \sum_k \exp(ikx)(d_k + \tilde{q}_{-k}).$$

(12)

In obtaining Eq. (12) we have used Eq. (10) and the fact that $d_k$ is an even function of wave vector $k$. The displacements $d_k$ caused by the existence of the exciton with wave function $\psi(x)$ can be estimated by means of the variational principle. We average the Hamiltonian (12) over trial function $\psi(x)\phi_0$, where $\phi_0$ is the phonon ground state function, to obtain the functional

$$H[\psi, d_k] = -\frac{\hbar^2}{2M} \int \psi^*(x) \frac{\partial^2 \psi(x)}{\partial x^2} \, dx$$

$$+ \hbar \omega_0 \int d_k^2 + \frac{\gamma}{\sqrt{N}} \int \sum_k d_k \exp(ikx)$$

$$\times \psi^*(x) \psi(x) \, dx,$$

(13)

where the usual normalization condition

$$\int \psi^*(x) \psi(x) \, dx = 1$$

(14)

was used. The first term in Eq. (13) corresponds to the kinetic energy of the exciton which after integration by parts and with taking into account vanishing of $\psi(x)$ at the boundaries of the system becomes

$$E_{\text{kin}} = \frac{\hbar^2}{2M} \int |\psi|^2 \, dx.$$

(15)
where $\psi = \partial \psi / \partial x$. The other terms in the right-hand side of Eq. (13) represent the deformation energy of the lattice. We determine the displacements $d_i$ by minimizing $H[\psi, d_i]$ with respect to the set $\{d_i\}$. Then the condition
\[
\frac{\partial H[\psi, d_i]}{\partial d_i} = 0
\]
gives
\[
d_k = -\frac{\gamma}{2\hbar \omega_0 \sqrt{N}} \int \exp(i k x) \psi^* (x) \psi(x) \, \mathrm{d} x.
\]  
(16)

Substitution of Eq. (16) into (13) yields
\[
H[\psi] = \int \left[ \frac{\hbar^2}{2 M} |\psi_i|^2 \, \mathrm{d} x - \frac{\gamma^2}{4 \hbar \omega_0 N} \times \int \sum_k \exp[i k (x + x')] \psi^* (x) \psi^* (x') \psi(x') \, \mathrm{d} x \, \mathrm{d} x'. \right.
\]
(17)

In the lattice site representation we have
\[
\sum_k \exp[i k (x + x')] = N \delta(x + x').
\]

Taking into account the rule $\sum_x \to \int \mathrm{d} x / a$ of transition from summation over lattice sites to integration over the coordinate along the chain and also that $\psi^* (x)$ and $\psi(x)$ have the same parity with respect to inversion transformation $x \to -x$, we finally arrive at the Hamiltonian
\[
H[\psi] = \int \left[ \frac{\hbar^2}{2 M} |\psi_i|^2 - g |\psi|^4 \right] \, \mathrm{d} x.
\]  
(18)

where
\[
g = \frac{\gamma^2 a}{4 \hbar \omega_0}
\]  
(19)
is an effective nonlinear coupling constant and
\[
E_0 = g \int |\psi(x)|^4 \, \mathrm{d} x
\]  
(20)
is the deformation energy of the lattice. In case of interaction of exciton with acoustical phonons we obtain the same Hamiltonian with different definition of the effective coupling constant $g$.

The equation for the exciton wave function $\psi(x)$ is obtained by minimizing the Hamiltonian (18) with respect to $\psi(x)$. We introduce a Lagrange multiplier $E$ in order to maintain the normalization condition
\[
\int |\psi(x)|^2 \, \mathrm{d} x = 1
\]  
(14) and get the nonlinear Schrödinger (NLS) equation
\[
- \frac{\hbar^2}{2 M} \frac{\mathrm{d}^2 \psi}{\mathrm{d} x^2} - 2 g |\psi|^2 \psi = E \psi.
\]  
(21)
The nonlinear Schrödinger equation for exciton (what is equivalent to the polaron case) for the first time was obtained in Ref. [16].

The time dependent wave-function $\psi(t, x)$ obeys the Schrödinger equation which can be written in the Hamiltonian form
\[
\frac{\hbar}{i} \frac{\partial \psi}{\partial t} = \frac{\delta H}{\delta \psi^*}.
\]  
(22)

where $\delta / \delta \psi^*$ is the variational derivative. Then the stationary states have the wave functions in the form
\[
\psi(t, x) = \exp(-iEt/\hbar) \psi(x),
\]  
(23)

and $\psi(x)$ satisfies Eq. (21). In an infinite 1D system Eq. (21) has the well-known solution [12,17]
\[
\psi(x) = \sqrt{\frac{Mg}{2 \cosh(Mgx/\hbar^2)}}
\]  
(24)

with
\[
E = -Mg^2/2 \hbar^2.
\]  
(25)

This solution is normalized according to the condition (14). As is clear from the solution (24), the characteristic length of localization is equal to
\[
l_0 = \hbar^2/Mg,
\]  
(26)

and can be large for light exciton and small $g$.

Now let us turn to the study of properties of the self-trapped states in finite nanostructures. An important feature of the exciton theory in nanostructures is the condition of vanishing of the wave function at the boundaries of the structure. In the case under consideration of the layer of the width $2L$ with plain boundaries (or 1D chain of the length $2L$) this condition can be written in the form
\[
\psi(L) = \psi(-L) = 0,
\]  
(27)

where $\psi(x)$ depends only on the coordinate $x$ perpendicular to the boundaries (or along the chain),

Note that in the paper [18] Rashba imposed the periodicity condition on the wave function and investigated the threshold behavior of the self-trapping phenomenon as a function of the coupling constant. The wave function which he used did not vanish at $x = \pm L$ (in fact, it could be expressed in terms of elliptic ‘dn’ function instead of our ‘cn’ or ‘sn’ functions; see below) and only the ground one-exciton state was studied.
and the points \( x = \pm L \) correspond to the boundaries positions. By analogy with usual linear Schrödinger equation, the wave functions can be constructed from the periodic solution of the NLS equation. The necessary particular periodic solution was found long ago [19–21] and can also be obtained by proper specifications from the general solution [22]. In accordance with the symmetry of the system with respect to inversion \( x \to -x \), the eigenfunctions must be even or odd functions of \( x \) and, correspondingly, have the form

\[
\psi(x,t) = A \exp \left[ -i \left( \frac{\hbar q^2}{2M} - gA^2 \right) t \right] \times \left\{ \frac{\text{cn}}{\text{sn}} \right\} \left[ \sqrt{q^2 + \frac{2MA^2g}{\hbar^2}} - x, m \right].
\]

(28)

where \( \text{cn}(u,m) \) and \( \text{sn}(u,m) \) are the Jacoby elliptic functions [23] with the parameter

\[
m = \frac{gA^2}{\hbar^2q^2/2M + gA^2}.
\]

(29)

The amplitude \( A \) and the “wave number” \( q \) are determined by the boundary condition (27),

\[
\sqrt{q^2 + \frac{2MA^2g}{\hbar^2}} - L = jK(m),
\]

(30)

and the normalization condition (14),

\[
\int_{-L}^{L} |\psi|^2 \, dx = \frac{2\hbar k^2}{q^2 + \frac{2MA^2g}{\hbar^2}} \times \frac{E(m) - (1 - m)K(m)}{m} = 1,
\]

(31)

where \( K(m) \) and \( E(m) \) are the complete elliptic integrals of the first and the second kind, respectively, and \( j \) is equal to \((1,3,5,\ldots)\) for even states and \((2,4,6\ldots)\) for odd states. The Eqs. (29)–(31) permit one to express the length \( L \) and the energy

\[
E = \frac{\hbar^2q^2}{2M} - gA^2
\]

(32)
as functions of the parameter \( m \). Simple calculation yields

\[
L(m) = l_0j^2K(m) \left[ E(m) - (1 - m)K(m) \right],
\]

(33)

\[
E(m) = \frac{E_s}{j^2} \left[ \frac{1 - 2m}{E(m) - (1 - m)K(m)} \right],
\]

(34)

where the localization length \( l_0 \) is given by Eq. (26) and \( E_s \) is the absolute value of the self-trapped state energy in the infinite chain (see (25))

\[
E_s = \frac{Mg^2}{2\hbar^2} = \frac{\hbar^2}{2Ml_0^2}.
\]

(35)

The formulas (33) and (34) give the dependence of the \( j \)-th exciton energy level \( E_j \) on the chain length \( 2L \) in a parametric form.

In the limit of strong quantum confinement for \( j \)-th level, \( L \ll j^2l_0 \) (i.e., \( m \ll 1 \)), this dependence can be expressed explicitly. The series expansions of \( L(m) \) and \( E(m) \) in powers of the small parameter \( m \) have the forms

\[
L(m) \equiv \frac{l_0j^2\pi^2}{8} m(1 + \frac{m}{2})
\]

\[
E(m) \equiv \frac{16E_s}{j^2\pi^2m^2}(1 - \frac{m}{2})
\]

Elimination of \( m \) from these expressions gives the \( j \)-th energy level of the exciton as a function of \( L \):

\[
E_j(L) \equiv \frac{\hbar^2}{2M} \left( \frac{j\pi}{2L} \right)^2 - \frac{3g}{2L} \quad L \ll j^2l_0,
\]

(36)

where two terms of series expansion in powers of the small parameter \((L/j^2l_0)\) are taken into account. The first term in (36) represents the usual energy levels of a quantum particle with mass \( M \) moving inside the potential well of width \( 2L \). The second term describes the correction to this energy due to the self-trapping interaction.

In the opposite limit \( L \gg j^2l_0 \) we obtain in a similar way

\[
E_j \equiv -\frac{E_s}{j^2}, \quad L \gg j^2l_0,
\]

(37)

and in this limit the energy levels with \( j \) satisfying the above inequality do not depend on \( L \). All these states beginning from the state \( j = 1 \) have negative energy and thus are self-trapped. It is clear that the number of these states depends on \( L \). The dependence of the first lowest three levels of the exciton on the length \( L \) is shown in Fig. 1. From this figure
and above formulas we conclude that for a given $L$ the quantum confinement influences considerably the levels with $j \lesssim \sqrt{L/l_0}$, while the other levels with $j \gg \sqrt{L/l_0}$ remain actually the same as those of a free exciton in a linear chain.

It is important to note that one exciton spectrum in the finite 1D system of length $2L$ differs drastically from the spectrum of the infinite 1D system with self-trapping interaction. In the infinite chain the spectrum consists of a continuous spectrum of freely moving particle and of single discrete level corresponding to the self-trapped state of the exciton. In the finite chain all spectrum is discrete and the number of self-trapped states with $E_0$ depends on $L$. In the limit $L \to \infty$ the lowest level $j = 1$ goes to the self-trapped state described by the formulas (23)–(25) with the wave function vanishing at infinity. Other states (37) ($j \neq 1$) do not correspond to eigenfunctions vanishing at infinity and therefore they exist only in finite systems.

### 3. Oscillator strengths and superradiance of excitons from a finite molecular chain

Now let us turn to the analysis of the oscillator strengths of transitions to the self-trapped excitonic states. The matrix element of a dipole moment transition consists of two factors. The first one is determined by the excitonic wave function and can be calculated with the use of the results of the preceding section (see below). The second factor is determined by the overlap of the lattice vibrational wave functions of the crystal in the ground and excited states. In the expression for the oscillator strength it results in the so called Franck-Condon factor. This factor depends crucially on the properties of vibrations with which the excitonic transition under consideration interacts most intensively. In many organic crystals, as, e.g., in $J$-aggregates of pseudoisocyanine (PIC), it is supposed [13] that the lowest electronic transitions interact most intensively with the lattice optical vibrations with the frequencies of the order of magnitude $100–300$ cm$^{-1}$. The dispersion of such vibrations is usually small ($\sim 10$ cm$^{-1}$). If this dispersion is neglected, then the above mentioned Franck-Condon factor is equal to (see, e.g. [12])

$$\exp\left(-\frac{E_g}{\hbar \omega_0}\right),$$

where $E_g$ is the deformation energy of the crystal (see (20)). If the energy $E_g \ll \hbar \omega_0$, this factor is very close to unity. Therefore in this case (the case of weak exciton–phonon coupling) we can concentrate our attention on the calculation of the part of the matrix element which is determined by the excitonic wave function.
The coupling of the radiation field of wave vector \( \mathbf{k} \) to the eigenstate \( j \) is determined by the value of the sum of the monomer dipole moments \( \mu_{\text{mon}} \) multiplied by the amplitudes \( \psi(n) \) that the exciton is situated at the site \( n \), and the phase factor \( \exp(i \mathbf{k} \cdot \mathbf{r}_n) \), \( \mathbf{r}_n \) being the radius-vector of the site \( n \).

\[
\sum_{n=1}^{N} \mu_{\text{mon}} \psi(n) \exp(i \mathbf{k} \cdot \mathbf{r}_n).
\]

We consider aggregates with the length \( 2L \) small compared to an optical wavelength \(|\mathbf{k}|L \ll 1\), so the transition dipole moment of the aggregate in the continuous approximation is equal to

\[
\mu_j = \frac{\mu_{\text{mon}}}{a} \int_{-L}^{L} \psi_j(x) \, dx,
\]

(39)

where \( a \) is the lattice constant. The oscillator strength of the aggregate, which determines the one-photon absorption and the radiative lifetime of the \( j \)-th state is then proportional to \( \mu_j^2 \), and it can be easily calculated with the use of already known eigenfunctions (28).

The integral in (39) vanishes for odd eigenfunctions \( \psi(x) \), so that only the states with \( j = 1, 3, 5 \ldots \) contribute to the radiative transitions. Substitution of the "cn" wave function (28) into (39) leads to the table integral (see formula 16.24.2 in Ref. [23]) and after simple calculation yields

\[
\int_{-L}^{L} \psi_j(x) \, dx = (-1)^{j-1} \frac{2 A}{\sqrt{q^2 + 2 Mq^2 / \hbar^2}} \times \frac{\arcsin \sqrt{m}}{\sqrt{m}} , \quad j = 1, 3, 5, \ldots
\]

(40)

where \( A, q, \) and \( m \) are related with each other by the Eqs. (29)–(31). Taking them into account, we obtain the oscillator strength of the chain as a function of the parameter \( m \):

\[
F_j = f_0 \frac{2 \ell_0}{a} \arcsin \sqrt{m}, \quad j = 1, 3, 5, \ldots
\]

(41)

where \( m \) depends on the length \( L \) and the number of the state \( j \) according to Eq. (33).

The formulas obtained permit us to make the analysis of some features of the superradiance from such 1D molecular crystals as, e.g., \( J \)-aggregates, as a function of their length and exciton–phonon interaction constant. As is clear from the above formulas, the oscillator strengths of radiation are determined by the ratio of the chain’s length \( L \) to the localization length \( \ell_0 \). At given \( L \) there are states \( j \) satisfying the inequality \( L \ll j^2 \ell_0 \) (\( j \) odd). For these states the corresponding values of the parameter \( m \) are much less than unity and according to Eq. (33) are equal to

\[
m = \frac{8}{\pi^2} \frac{1}{\ell_0 j^2},
\]

(42)

so the corresponding limit of Eq. (41) takes the form

\[
F_j \equiv f_0 \frac{8}{\pi^2} \frac{2 L}{a} \frac{1}{j^2}.
\]

(43)

If \( L \ll \ell_0 \), the formula (43) holds for all odd \( j = 1, 3, 5, \ldots \). But if \( 9 \ell_0 > L > \ell_0 \), then this formula is valid only for \( j = 3, 5, \ldots \). Of course, \( F_j = 0 \) for all dark states \( j = 2, 4, 6, \ldots \). Let us return to the limit of strong confinement when \( L \ll \ell_0 \) and hence Eq. (43) is valid for all \( j \). In this limit we reproduce from (43) the Eq. (5) for the state \( j = 1 \). Summation of (43) over all odd values of \( j \) gives an obvious sum rule

\[
\sum_{j=1}^{\infty} F_{2j-1} = f_0 \frac{2L}{a} = f_0 N.
\]

(44)

Note, that this sum rule takes place for any values of \( L \), even if the condition of strong confinement is not satisfied for all states.

Let us consider this case in more detail. We assume that \( L \gg j^2 \ell_0 \) (\( j \) odd). Then there are a few states with values of \( j \) satisfying this inequality. For these states \( m \approx 1 \), and for corresponding value of \( F_j \) we obtain

\[
F_j \equiv f_0 \left( \frac{\pi}{2} \right)^2 \frac{2 \ell_0}{a}.
\]

(45)

which already does not depend on \( L \), i.e. there is saturation of the oscillator strength. It is remarkable that all these states (with \( j \ll (L/\ell_0) \)) have equal oscillator strengths what contrasts drastically to the theory without self-trapping. The dependence of the
Fig. 2. The dependence of oscillator strengths $F_j$ (in units $f_0 l_0/a$) for $j = 1, 3, 5$ on the length $L$ (measured in units $l_0$).

oscillator strength $F_j$ on $L/l_0$ for levels $j = 1, 3, 5$ is shown in Fig. 2.

4. Discussion

As we see from Fig. 2, for all energy levels with odd $j = 1, 3, 5 \ldots$ the oscillator strengths tend to the same saturation limit but this limit is achieved at different lengths of the chain. This feature of the self-trapping can play an important role in discussion of the radiative properties of molecular nanostructures, for example, of $J$-aggregates. Indeed, if $L$ is greater than $l_0$, the oscillator strength of the lowest energy state $j = 1$ reduces considerably compared to the case of system without self-trapping. In this case only about $(\pi/2)^2(2l_0/a)$ molecules radiate coherently. Using the common terminology, we can say that the coherence length is equal to $(\pi/2)^2l_0$ and does not depend on the length of the chain. This effect appears due to self-trapping and is not connected with scattering of excitons by phonons or lattice defects.

Let us make now some estimations. For example, at $l_0/a \sim 10$ the oscillator strength, and hence the radiation width of the state, is about 50 times as large as the value for a monomer and this leads to the lifetime 50 times as small as the lifetime of the excited state in a monomer. For the state $j = 1$ such a decrease of the radiative lifetime takes place for the chain length $2L \geq 2l_0$. At this $L$ the oscillator strength $F_j$ for states $j = 3, 5, \ldots$ is much less than the value of $F_1$. Therefore in this case only the lowest energy exciton state ($j = 1$) has a considerable oscillator strength and therefore this situation is similar to that for linear (without self-trapping) chain with the same length. However, with increase of the length $L$ up to the values in the interval $9l_0 < L < 25l_0$ the oscillator strength $F_1$ does not change, whereas $F_{3} \rightarrow F_1$ and for $j = 5, 7, \ldots$ we have $F_j \ll F_1$. Thus, already for this chain length the relationship between oscillator strengths of the two low energy levels differs considerably from that for linear case. We can say that now the states with small oscillator strengths are shifted to the region $j \geq 5$, for longer chains to $j \geq 7$, and so on.

Note also that in the theory under consideration the main characteristic parameters are $l_0/a$ and $L/l_0$, and the relationship between radiative excitonic lifetime and position of its energy levels arises very naturally. For example, let the exciton–phonon coupling constant be such that $l_0/a \approx 10$. Then, according to Fig. 2, at length $L \approx 1.3l_0$ we have $F_1 \approx 20f_0$, so the radiative lifetime of this state is $\tau_1 \approx \tau_0/20$. On the other hand, according to Fig. 1 at the same value of $L$ the energy of the lowest level is equal to $E_1 \approx -E_r = -\hbar^2/(2Ml_0^2)$, or with account of (2) $E_1 \approx -J(a/l_0)^2$. Thus, if as in Ref. [13] we take the value $J = 600 \text{ cm}^{-1}$, then at $l_0/a \approx 10$ and $L \equiv$
we obtain $E_0 \equiv -6 \text{ cm}^{-1}$. The next state with $j = 2$ is dark and from Fig. 1 we find that at $L \equiv 1.3l_0$ its energy is equal to $2E_0$. Thus the gap between bright (lowest energy $j = 1$ state) and the nearest dark state ($j = 2$) is equal to $\equiv 3E_0 \equiv 20 \text{ K}$. Here we have to mention that, strictly speaking, the energy of self-consistent state is equal to the mean value of the Hamiltonian $H$ (see (18)) rather than to the exciton energy $E$ as we considered above. This circumstance has to be taken into account in considerations of such problems as population of different states under influence of slow perturbations where the role of small energy phonons is important. However, in our estimation this fact leads to only very small corrections. Therefore, from this estimation it follows that at temperature $T < 20 \text{ K}$ the radiative lifetime will be equal to $\tau \equiv \tau_1$ and does not depend on temperature $T$. Only at higher temperature $T > 20 \text{ K}$, when an occupation of the first dark state begins, we can expect that the radiative lifetime will start to arise going gradually to the radiative lifetime of a monomer. Recently, the new data on the temperature dependence of radiative lifetime of $J$-aggregates at low temperature were discussed in the literature (see [13]). As follows from our illustrative estimates, even in the case of weak exciton–phonon interaction (i.e. when $E_j \ll \hbar \omega_0$), the effects of quantum confinement and self-trapping should be taken into account in the discussion of this interesting phenomenon. More thorough treatment of temperature effects and of influence of disorder on the superradiance require considerable numerical calculations and will be discussed elsewhere.

Acknowledgements

We acknowledge partial support from Grant 97–1074 of Russian Ministry of Science and Technology and Grant 99–03–32178 of Russian Foundation of Basic Researches.

References