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Charge-transfer excitations on a linear chain

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One– and two–electron-hole-pair excitations are calculated for a finite chain by means of a generalized Bethe ansatz. It is shown that the static Coulomb interaction between correlated pairs reduces the respective bandwidth as compared to the single-pair excitation. The influence of single-particle overlap is discussed.

I. INTRODUCTION

Recent progress in material science allows us to design semiconductor heterostructures on a nanometer length scale. While this is being achieved with high precision along one dimension (layered materials), the extension to two and, in particular, to three dimensions is still in its infancy.[1–4]

Structuring in all three spatial dimensions amounts to introducing a type of custom-made "quasimolecular" bulk material: Just like "natural" molecular crystals, these artificial ones will be characterized by a kind of decoupling of the "molecular" units (in the following, called "cells") from one another, leading to the well-known hierarchy of strong intracell versus weak intercell interactions. However, the cells of the artificial material tend to be larger in linear scale by more than one order of magnitude, implying 10^4-10^8 atoms per cell with their corresponding number of electrons. Comparing with the few atoms per cell of the more conventional molecular crystals, such a system might properly be considered "mesoscopic." Nevertheless, realizing corresponding excitation conditions and low temperature, the dynamics will be controlled locally by only a few electronic states around the Fermi level. Thus, with respect to these special conditions, the mesoscopic cell may well act even as a rather simple functional unit, a module.

In the following we will restrict ourselves to three relevant states per cell: The local ground state $|1\rangle$, the metastable state $|2\rangle$, and the transient state $|3\rangle$ (see Fig. 1). The centers of charge of state $|1\rangle$ and $|2\rangle$, respectively, are assumed to be separated by distance R. One such cell without inversion symmetry can be regarded as a minimal model for an optically controlled bistable quantum system (a switch). As this switching process is accompanied by charge transfer, the Coulomb interaction between adjacent cells could be exploited for the realization of a quantum control system capable of information processing.[5–7] The challenge of such systems—investigated up to now in the form of theoretical feasibility studies—consists in the quest for microscopic (or quantum) control as opposed to macroscopic control realized, e.g., in conventional optics or thermodynamics.

Despite the mesoscopic scale of the individual cell, the bulk material is supposed to be periodic (length of periodicity d) so that Bloch's theorem applies: The true eigenstates should be delocalized. On the other hand, the modular nature of information representation rests upon localized eigenstates. Discrete localized states are, furthermore, prerequisites for optical control in frequency space: broad bands tend to render "microscopic" control impossible. Though this could be achieved to any degree by means of appropriate "spacer" material between the active cells, the interaction between the cells required for information processing (in the form of a cellular automaton[7]) severely interferes with this localization condition.

It is the purpose of this contribution to investigate the interplay between intercell interaction and the resulting excitation spectra. It will be shown that these interactions are not only responsible for the broadening of states but that under certain conditions they may even reduce the appropriate bandwidths: due to small coherence length the dynamics of narrow-band excitations does, indeed, call for a local description (hopping transport).

II. MODEL

We consider N three-level systems (cells) on a linear chain with periodic boundary conditions (see Fig. 1). It is assumed that in the ground state each cell has an electron in level 1. A different cell geometry but also with respect

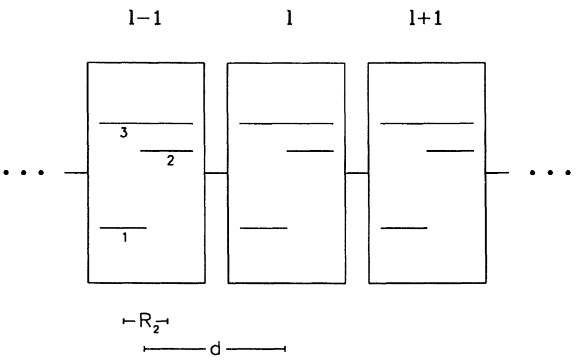

FIG. 1. Three-level systems with charge transfer on a linear chain; d is the intercell distance, R_2 the intracell charge-transfer distance as defined in Eq. (1).

to charge-transfer excitations has been considered by Petelenz.[8]

The excitation-induced charge transfer within a cell is

$$R_j=\langle j|\hat{x}|j\rangle-\langle 1|\hat{x}|1\rangle\ , \quad j=2,3\ . \tag{1}$$

R_j may be called the intracell electron-hole distance introducing a dipole moment $R_j|e|$ (e is the electron charge) with respect to the ground-state charge distribution. We assume, for simplicity, $R_3=R_2/2$.

Exciting a cell, which means creating an electron-hole pair (only one pair per cell shall be possible), thus leads to a dipole moment (charge-transfer exciton) because of the different localization of the respective one-particle wave functions.[5] Coupling the cell via dipole-dipole interaction, in addition to single-particle overlap, we expect optical nonlinearities and bound pair states.

Assuming that the distance d between two cell centers is much greater than R_2 ($d \gg R_2$), we get a hierarchy in the interaction energies, and the total Hamiltonian can be separated as follows:

$$\hat{H}_{\text{total}}=\hat{H}_{\text{intra}}+\hat{H}_{\text{inter}}=\sum_{l=1}^{N}\hat{H}_l+\tfrac{1}{2}\sum_{\substack{l,l'=1\\(l\neq l')}}^{N}\hat{H}_{l,l'}\ . \tag{2}$$

The interaction term within a cell, $\hat{H}_{\text{intra}}$, will be of no interest here, as it leads only to a local energy shift. The Hamiltonian for the interaction between two cells reads in the nearest-neighbor approximation ($l'=l\pm1$; electron, e; hole, d)

$$\hat{H}_{l,l'}=\hat{H}^{Ub}_{l,l'}+\hat{H}^{dd}_{l,l'}+\hat{H}^{ee}_{l,l'}+\hat{H}^{ed}_{l,l'}\ . \tag{3}$$

In this case spin effects are neglected and only processes conserving the energy and the number of particles are considered. The screening due to the material environment will be included by means of a phenomenological dielectric constant ϵ in the Coulomb law.

$\hat{H}^{Ub}$ describes the one-particle interaction, resulting from the wave-function overlap of two equal states but in different cells:

$$\hat{H}^{Ub}_{ll'}=\sum_{i=2,3}U^e_i\hat{a}^{\dagger}_{l,i}\hat{a}_{l',i}+U^d\hat{d}^{\dagger}_{l}\hat{d}_{l'}\ . \tag{4}$$

$\hat{H}^{ee}$, $\hat{H}^{dd}$, and $\hat{H}^{ed}$, finally, refer to the two-particle Coulomb interaction between two electrons, two holes, and one electron and one hole, respectively:

$$\begin{aligned}
\hat{H}^{dd}_{l,l'}&=W^{dd}\hat{d}^{\dagger}_{l}\hat{d}^{\dagger}_{l'}\hat{d}_{l'}\hat{d}_{l}\ ,\\
\hat{H}^{ee}_{l,l'}&=\sum_{i,j=2,3}W^{ee}_{ij}\hat{a}^{\dagger}_{l,i}\hat{a}^{\dagger}_{l',j}\hat{a}_{l',j}\hat{a}_{l,i}\\
&\quad+\sum_{\substack{i,j=2,3\\(i\neq j)}}F^{ee}_{ij}\hat{a}^{\dagger}_{l,i}\hat{a}^{\dagger}_{l',j}\hat{a}_{l',i}\hat{a}_{l,j}\ ,\\
\hat{H}^{ed}_{l,l'}&=\sum_{i=2,3}F^{ed}_i\hat{a}^{\dagger}_{l',i}\hat{a}_{l,i}\hat{d}^{\dagger}_{l'}\hat{d}_{l}\\
&\quad-\sum_{i=2,3}\hat{a}^{\dagger}_{l,i}\hat{a}_{l,i}\hat{d}^{\dagger}_{l'}\hat{d}_{l'}\times\begin{cases}W^{ed}_i\ , & l<l'\\ W^{de}_i\ , & l>l'\ .\end{cases}
\end{aligned} \tag{5}$$

As there is but one local hole state, its index 1 will be omitted. The indices $i,j=2,3$ denote the electronic energy levels in each cell, $\hat{a}^{\dagger},\hat{d}^{\dagger}$ are the Fermi operators for electron and hole creation, respectively. U^e_i, U^d, W^{dd}, W^{ee}_{ij}, W^{ed}_i, W^{de}_i, F^{ee}_{ij}, and F^{ed}_i are the respective interaction matrix elements in the nearest-neighbor approximation.

It is convenient to distinguish between the static (W^{dd}, W^{ee}_{ij}, W^{ed}_i, W^{de}_i) and the dynamic (F^{ee}_{ij},F^{ed}_i) Coulomb interaction. The latter can be seen in analogy to the so-called Förster interaction in molecular physics[8] by which the excitation of a molecule is able to travel along the chain.

We have to distinguish between W^{ed} and W^{de} because, in general, the distances between electron-hole and hole-electron of neighboring cells are different, $R^{ed}_j\equiv d-R_j$, while $R^{de}_j\equiv d+R_j$ (see Fig. 1). The ratio between the static and the dynamic Coulomb interactions in our model can be varied, as far as the dipole moment within the cells can be adjusted.

A macroscopic realization of such a hierarchical structure model appears possible either based on semiconductor material or with organic macromolecules.[1,5] Structuring a semiconductor material (quantum dot) on nanometer scale seems to be more promising in the near future due to the large amount of technological knowhow of the microelectronics of today. These complex molecular systems offer a wealth of possibilities, but usually suffer from incomplete characterization.[9,10]

III. ANALOGY TO SPIN-$\frac{1}{2}$ SYSTEMS

For a preliminary investigation we reduce our Hamiltonian, Eq. (2), to a two-level chain ($i,j=2$) and neglect the overlap term $\hat{H}^{Ub}$. The interaction matrix elements are defined as before but without the indices (i,j); elements F^{ee}_{ij} do not occur in this case.

We introduce exciton-creation and -annihilation operators,[11] obeying for small particle numbers a Bose commutation relation,

$$\hat{B}^{+}_{l}:=\hat{a}^{\dagger}_{l}\hat{d}^{\dagger}_{l}\ ,\quad \hat{B}^{-}_{l}:=\hat{d}_{l}\hat{a}_{l}\ ,$$

to get from Eq. (2) the exciton Hamiltonian

$$\begin{aligned}
\hat{H}_{\text{Exc}}&=\sum_{l=1}^{N}F^{ed}\hat{B}^{+}_{l+1}\hat{B}^{-}_{l}-\sum_{l=1}^{N}(W^{dd}+W^{ee})\hat{B}^{+}_{l}\hat{B}^{-}_{l}\\
&\quad+\sum_{l=1}^{N}(W^{dd}+W^{ee}-W^{ed}-W^{de})\hat{B}^{+}_{l+1}\hat{B}^{-}_{l+1}\hat{B}^{+}_{l}\hat{B}^{-}_{l}\ .
\end{aligned} \tag{6}$$

For comparison we take the anisotropic spin Hamiltonian (short-range Heisenberg exchange interaction) for N atoms of spin $\frac{1}{2}$ on a linear chain with periodical boundary conditions in an external magnetic field H_0 in the z direction to be[12]

$$\begin{aligned}
\hat{H}_{\text{Magn}}&=2J\sum_{l=1}^{N}[\hat{S}^{z}_{l}\hat{S}^{z}_{l+1}+(1-\alpha)(\hat{S}^{x}_{l}\hat{S}^{x}_{l+1}+\hat{S}^{y}_{l}\hat{S}^{y}_{l+1})]\\
&\quad-\mu_B gH_0\sum_{l=1}^{N}\hat{S}^{z}_{l}\ ,
\end{aligned} \tag{7}$$

where $\hat{S}_{N+1}=\hat{S}_1$. J is the exchange integral ($J<0$, ferromagnetic case; $J > 0$, antiferromagnetic case), μ_B is the Bohr magneton, g is the g factor. For the anisotropy parameter $\alpha = 0$ we have the isotropic Heisenberg interaction, and for $\alpha = 1$ we have the pure Ising interaction.

We now transform to creation and annihilation operators $\hat{S}^+, \hat{S}^-$, defined as

$$\hat{S}_l^{\pm} := \hat{S}_l^x \pm i\hat{S}_l^y ,$$

which obey Bose commutation relations, but with the restriction that it is not possible to have two or more spins at the same place (hard-core bosons[13]):

$$\begin{aligned}\hat{H}_{\text{Magn}} = 2J \sum_{l=1}^{N} \left(\tfrac{1}{4} - \hat{S}_l^+ \hat{S}_l^- + \hat{S}_l^+ \hat{S}_l^- \hat{S}_{l+1}^+ \hat{S}_{l+1}^-\right) \\ + J(1-\alpha) \sum_{l=1}^{N} \hat{S}_l^+ \hat{S}_{l+1}^- \\ - \mu_B g H_0 \sum_{l=1}^{N} \left(\hat{S}_l^+ \hat{S}_l^- - \tfrac{1}{2}\right) .\end{aligned} \tag{8}$$

Comparison with the exciton Hamiltonian, Eq. (6), implies the identification

$$\begin{aligned} J &= \tfrac{1}{2}(W^{dd} + W^{ee} - W^{de} - W^{ed}) , \\ \alpha &= 1 - \frac{F^{ed}}{W^{dd} + W^{ee} - W^{ed} - W^{de}} , \\ \mu_B g H_0 &= W^{ed} + W^{de} . \end{aligned} \tag{9}$$

The constant terms in Eq. (8) can be ignored.

From the definition of α with $0 \le \alpha \le 1$, we deduce the condition

$$0 \le F^{ed}/(W^{ee} + W^{dd} - W^{ed} - W^{de}) \le 1$$

for the parameters of the excitonic system to have the same results, especially with respect to the bound states, as in the magnetic case. For the general case of three-level systems we restrict ourselves in the following to $F_i^{ed} < 0$, and $W_i^{ed} + W_j^{de} - W_{ij}^{ee} - W^{dd} > 0$.

In analogy to the calculation for the spin-$\frac{1}{2}$ chain based on the Bethe ansatz,[14,12] we obtain, observing Eqs. (9), the exact energy eigenvalues of the linear two-level chain for an n-electron-hole-pair excitation in the nearest-neighbor approximation ($n \le N$):

$$\begin{aligned} E_n^{\text{Exc}}(k_1, k_2, \ldots, k_n) = n(W^{ed} + W^{de} - W^{ee} - W^{dd}) \\ + F^{ed} \sum_{i=1}^{n} \cos k_i . \end{aligned} \tag{10}$$

Here and in the following k will be given in units of d^{-1}. We see that the width of the energy band in the **k** space is determined by the matrix element of the Förster interaction while the static Coulomb interaction introduces only an energy shift. The wave vectors k_i will be complex, in general, to cover all possible states: For k_i real, we have uncorrelated excitons (continuum states), for k_i imaginary we get bound states (compare the so-called magnon bound states[12]) with lower energy. Those states can be interpreted here as states of neighboring electron-hole pairs, for which the Coulomb interaction leads to an energy lowering.

IV. ANALYTICAL RESULTS FOR PURE COULOMB INTERACTION

In this section we want to study the dispersion relation of three-level systems on a linear chain in the case of pure Coulomb interaction, still neglecting the overlap term in Eq. (3). This assumption allows us to restrict ourselves to intracell pair excitations. Taking the time-independent Schrödinger equation with the total Hamiltonian, Eq. (2), and $|n\rangle$ to be the wave function of n electron-hole excitations:

$$\hat{H}_{\text{total}} |n\rangle = E|n\rangle , \tag{11}$$

the eigenstates can be written as a coherent superposition (one exciton is at cell l, the electron being in the local state j, another exciton is at l', the electron in $j', \ldots$):

$$|n\rangle = \sum_{\substack{l,l',\ldots=1 \\ (l \ne l')}}^{N} \sum_{j,j',\ldots=2}^{3} c_{ljl'j'\ldots} (\hat{a}_{l,j}^\dagger \hat{d}_l^\dagger)(\hat{a}_{l',j'}^\dagger \hat{d}_{l'}^\dagger) \cdots |0\rangle , \tag{12}$$

where $|0\rangle$ is the vacuum state. Equation (11) is then reduced to an algebraic system of equations for the coefficients $c_{ljl'j'\ldots}$ (secular equation).

A. One-pair excitation

For the one–electron-hole-pair excitation in a periodic structure we get with

$$c_{lj} = c_0 e^{iKl} \tag{13}$$

the following dispersion relation:

$$E_{K,j} = F_j^{ed} \cos K , \tag{14}$$

where the band index $j = 2, 3$ denotes the local electron levels. For periodic boundary conditions, $c_{lj} = c_{l+Nj}$, we require $k_e + k_d \equiv K = 2\pi n/N$, with $n = 0, \pm 1, \pm 2, \ldots$.

B. Two-pair excitation

With the convention

$$1 \le n < n' \le N$$

to avoid double counting in Eq. (12), the secular equation is now

$$\begin{aligned}(E + \delta_{n'-n,1} D_{ij}) c_{nn'ij} = F_i^{ed}(c_{n+1n'ij} + c_{n-1n'ij}) \\ + F_j^{ed}(c_{nn'+1ij} + c_{nn'-1ij}) ,\end{aligned} \tag{15}$$

$$\begin{aligned}(E + \delta_{n'-n,1} D_{ji}) c_{nn'ji} = F_j^{ed}(c_{n+1n'ji} + c_{n-1n'ji}) \\ + F_i^{ed}(c_{nn'+1ji} + c_{nn'-1ji}) ,\end{aligned} \tag{16}$$

where D_{ij} is defined as

$$D_{ij} := W_i^{ed} + W_j^{de} - W_{ij}^{ee} - W^{dd} - F_{ij}^{ee}(1 - \delta_{i,j}) . \tag{17}$$

The boundary conditions

$$c_{0nij} = c_{nNji} \quad \text{and} \quad c_{nN+1ij} = c_{1nji} , \tag{18}$$

couple Eq. (15) with (16).

Taking Bloch's theorem for the eigenvectors of a system with translation symmetry, the coefficients $c_{nn'ij}$ satisfy the following expression [with respect to Eq. (18)]:

$$c_{n+an'+aij}=e^{ika}c_{nn'ij} \ . \tag{19}$$

The wave number k is constrained by the periodic boundary condition

$$c_{n+Nn'+Nij}=c_{nn'ij} \tag{20}$$

to $k=(2\pi/N)m$, $m=0,\pm 1,\pm 2,\ldots$ (N values).

To simplify notation, we introduce the effective Förster matrix element $F_0(k)$ and the wave number $k_0(k)$ by

$$\tfrac{1}{2}(F_j^{ed}+F_i^{ed}e^{ik})=:F_0e^{i(k/2-k_0)} \ , \tag{21}$$

where

$$k_0(k)=\frac{k}{2}-\arctan\frac{\sin k}{F_j^{ed}/F_i^{ed}+\cos k} \ , \tag{22}$$

$$F_0(k)=\tfrac{1}{2}(F_j^{ed^2}+F_i^{ed^2}+2F_i^{ed}F_j^{ed}\cos k)^{1/2} \ . \tag{23}$$

Let us first consider the case of two identical electron-hole pairs, which means $i=j$ (as for a two-level system). Equations (15) and (16) can then be reduced to

$$(E+\delta_{n'-n,1}D)c_{nn'}=F^{ed}(c_{n+1n'}+c_{n-1n'}+c_{nn'+1}+c_{nn'-1}) \ , \tag{24}$$

which is solved by a Bethe ansatz

$$c_{nn'}=e^{ik/2(n+n')}(B_1e^{-\kappa(n'-n)}+B_2e^{\kappa(n'-n)}) \ . \tag{25}$$

The energy calculated with Eq. (25) then reads [compare with Eq. (10)]

$$E_{k\kappa}=F^{ed}(\cos(k/2+i\kappa)+\cos(k/2-i\kappa)) \ . \tag{26}$$

In analogy to this special case we now make a generalized Bethe ansatz to solve the eigenvalue problem Eqs. (15), (16), with (18) for $i\neq j$:

$$c_{nn'ij}=e^{ik/2(n+n')}e^{-i(k_0+\pi)(n'-n)}(B_1e^{-\kappa(n'-n)}+B_2e^{\kappa(n'-n)}) \ , \tag{27}$$

$$c_{nn'ji}=e^{i\phi}e^{ik/2(n+n')}e^{+i(k_0+\pi)(n'-n)}(B_1e^{-\kappa(n'-n)}+B_2e^{\kappa(n'-n)}) \ . \tag{28}$$

With the expressions (27) and (28) introduced into Eq. (18) we find

$$\frac{B_1}{B_2}=e^{\kappa N}(-1)^{m'} \tag{29}$$

and

$$\phi=[k/2-k_0(k)+\pi]N+\pi m' \ . \tag{30}$$

If this ansatz is put into Eq. (15) for $n'\neq n+1$ (i.e., without the D_{ij} term), we find for the eigenvalues

$$E_{k\kappa}=-2F_0(k)\cos i\kappa \ . \tag{31}$$

Requiring that this result holds also for $n'=n+1$ gives the constraint

$$\frac{B_1}{B_2}=\frac{F_0(k)-D_{ij}e^{\kappa}}{-F_0(k)+D_{ij}e^{-\kappa}} \ . \tag{32}$$

Solving Eqs. (32) and (29) numerically for fixed m' and k, we, finally, get the relative wave vector κ.

In general, m' is arbitrary, which means $(-1)^{m'}=\pm 1$ in Eq. (29). In the case of two-level systems m' has to be $m'=kN/2\pi$ and thus leads to only half the number of eigenstates possible in the three-level chain. This means that for the (2,2)- and the (3,3)-two-pair bands we have $\frac{1}{2}N(N-1)$ states, while for the (2,3) band we have $N(N-1)$ states.

C. Results

For a finite chain of $N=11$ cells the one- and two-pair excitations are shown in Fig. 2(a) for static Coulomb interaction $D_{ij}=0$ and in Fig. 2(b) for $D_{22}=D_{23}=D_{33}=5$, the interaction matrix elements being $F_2^{ed}=-1$, $F_3^{ed}=-5$. Here and in the following all energies are given in units of $|F_2^{ed}|$. The position of the energy bands is arbitrary because of neglecting the respective excitation energies within the cell [see Eq. (2)]. The width of the single-pair energy band (j) is determined by the respective Förster matrix element F_j^{ed}: $\Delta_{(j)}=2|F_j^{ed}|$.

For the spectrum of the two-pair excitations (ij), we have to distinguish two cases with respect to the parameter D_{ij}, where D_{ij} stands essentially for the static Coulomb interaction [see Eq. (17)], the electron of one exciton being in the state i, the electron of the other in the state j ($i,j=2,3$):

For $D_{ij}=0$, we have only continuum bands of width $\Delta_{(ij)}=2|F_i^{ed}+F_j^{ed}|$, corresponding to uncorrelated electron-hole pairs. They belong to imaginary solutions of Eqs. (29) and (32) for the wave vector κ.

For $D_{ij}>0$, an energetically lower energy subband separates from the continuum, which can be interpreted as being due to correlated adjacent electron-hole pairs; this case corresponds to real κ's.

The energy shift with respect to the continuum is controlled by D_{ij}. This result can be interpreted as a nonlinearity, because creating a further exciton from a one-pair excitation we have the possibility of ending up either in a bound or in the continuum state, and for each case we need a different transition energy.

The width of the subband is calculated to be $\Delta_{(ij)}=[(F_i^{ed})^2+(F_j^{ed})^2]/D_{ij}$. It is interesting to note that, compared to the respective single-pair bands, $\Delta_{(ij)}$ is compressed by a factor $[(F_i^{ed})^2+(F_j^{ed})^2]/D_{ij}F_{i\,(j)}^{ed}$: For example, $\Delta_{(2,2)}$ is smaller than $\Delta_{(2)}$ by a factor $2F_2^{ed}/D_{22}$.

According to the quantum dot model, proposed and described in more detail in Ref. 7, we estimate the parameters as follows:

$$E_{23},E_{13}\approx 1\text{ eV} \ , \quad E_{12}\approx 10\text{ meV} \ ,$$

$$|F^{ed}|\leq 10^{-4}\text{ meV} \ , \quad |F^{ee}|\approx 10^{-6}\text{ meV} \ ,$$

$$U^e\approx U^d\approx |F^{ed}| \ .$$

For $R_2\approx 10$ nm, $d\approx 50$ nm, D_{ij} is dominated by the static contributions and typically amounts to $D_{ij}\approx 10^{-1}$ meV.

To appreciate the relevance of these compressed bandwidths, let us consider a single excitation, characterized by the dispersion relation $E(k)$, in thermal equilibrium, with a heat bath at temperature $T>0$. For a one-dimensional system (length of periodicity L) its density matrix is

$$\rho(k,k')=\frac{\lambda_{dB}}{L}e^{-E(k)/k_BT}\ , \tag{33}$$

from which we obtain for periodic boundary conditions

$$\rho(z,z')=\frac{1}{L}\sum_k e^{ik(z-z')}\rho(k,k')\ , \tag{34}$$

where $\lambda_{dB}=(2\pi\hbar^2/m^*k_BT)^{1/2}$ is the thermal de Broglie length,

$$\frac{1}{m^*}=\frac{1}{\hbar^2}\frac{d^2E(k)}{dk^2}\bigg|_{k=0}$$

is the effective mass, and a parabolic dispersion relation $E(k)=\hbar^2k^2/2m^*$ (infinite bandwidth) has been assumed.

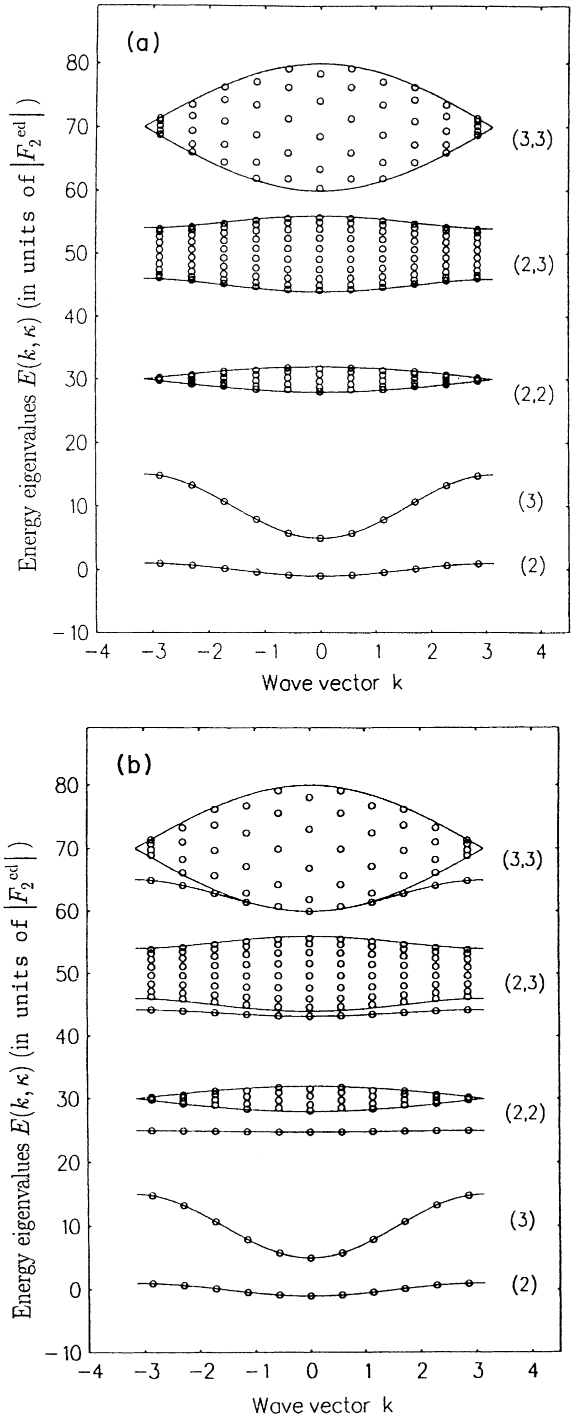

FIG. 2. Spectrum of the one-pair (j) and two-pair (i,j) excitations ($i,j=2,3$) for $F_2^{ed}=-1$, $F_3^{ed}=-5$, and $N=11$ cells. All energies are given in units of $|F_2^{ed}|$; absolute positions of bands are arbitrary, the lines drawn correspond to $N\rightarrow\infty$; (a) $D_{22}=D_{23}=D_{33}=0$; (b) $D_{22}=D_{23}=D_{33}=5$.

As is well known, see Ref. 15, for $L\gg\lambda_{dB}$ one finds

$$\rho(z,z')=\frac{1}{L}e^{-(z-z')^2\pi/\lambda_{dB}^2}\ , \tag{35}$$

i.e., a coherence length

$$l_c=\lambda_{dB}/\sqrt{\pi}\ . \tag{36}$$

An intuitive interpretation of l_c is obtained by noting that wave-type behavior (e.g., interference) is observable on length scales $l<l_c$, particlelike behavior on a length scale $l>l_c$. This result still holds approximately, for a bandwidth $\Delta\gg k_BT$.

On the other hand, for a small bandwidth $\Delta\ll k_BT$ and the dispersion relation $E(k)=\Delta\sin(kd)$, we find, instead,

$$l_c\approx d/\ln(k_BT/\Delta)\ll d\ . \tag{37}$$

Applying these considerations to the two-pair excitation, $\Delta_{(ij)}<k_BT\ll D_{ij}$, we conclude that the Coulomb interaction D_{ij} strongly reduces the coherence length. As $l_c\ll d$, where d is the cell length, the dynamics of the excitation is described as an incoherent particlelike hopping

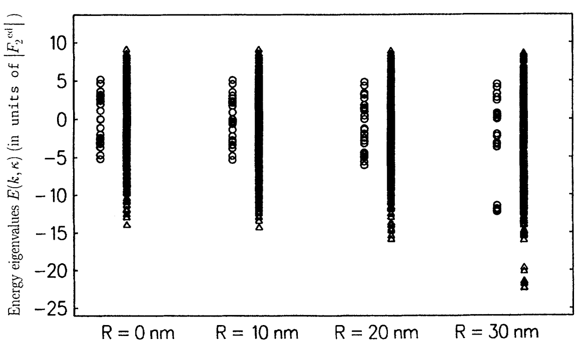

FIG. 3. Two-pair energies (2,3) as a function of the cell dipole moment $R|e|$ for $F_2^{ed}=-1$, $F_3^{ed}=-5$, and $N=6$ cells. All energies are given in units of $|F_2^{ed}|$, $R=R_2$; ○, $U=0$ (zero overlap); △, $U=3$.

process (with a hopping time $\tau=\hbar/\Delta$) rather than as a coherent wave: the hopping time for correlated pairs is significantly reduced.

V. TWO-PAIR STATES: INFLUENCE OF OVERLAP

In order to calculate the eigenstates of the total Hamiltonian (2), we have to take into account the complete state space:

$$|n\rangle = \sum_{\substack{l,m,\ldots=1\\ l',m',\ldots=1}}^{N} \sum_{j,j',\ldots=2}^{3} c_{ll'jmm'j'}\ldots(\hat{a}^{\dagger}_{l,j}\hat{d}^{\dagger}_{l'}) \times(\hat{a}^{\dagger}_{m,j'}\hat{d}^{\dagger}_{m'})\cdots|0\rangle \; . \tag{38}$$

Again we solve the secular equation in the case of two-pair excitations, but now numerically because the Bethe ansatz does not work any more.

Based on the notation introduced before, the secular equation is now

$$\begin{aligned}2\epsilon c_{nn'imm'j} = {} & U_i^e(c_{n+1n'imm'j}+c_{n-1n'imm'j})+U_j^e(c_{nn'im+1m'j}+c_{nn'im-1m'j})\\ & +U^d(c_{nn'+1imm'j}+c_{nn'-1imm'j}+c_{nn'imm'+1j}+c_{nn'imm'-1j})\\ & +c_{nn'imm'j}[\delta_{n,m-1}W^{ee}+\delta_{n',m'-1}W^{dd}-W_i^{ed}(\delta_{n,m'-1}+\delta_{n,n'-1})\\ & \qquad -W_j^{ed}\delta_{m,m'-1}-W_j^{de}(\delta_{n',m-1}+\delta_{m',m-1})-W_i^{de}\delta_{n',n-1}]\\ & +\delta_{n,n'}\delta_{m,m'}[F_i^{ed}(c_{n+1n'+1imm'j}+c_{n-1n'-1imm'j})+F_j^{ed}(c_{nn'im+1m'+1j}+c_{nn'im-1m'-1j})] \; ,\end{aligned} \tag{39}$$

with the boundary conditions to be satisfied:

$$\begin{aligned} & c_{nn'iN+1m'j}=c_{1n'jnm'i} \; ,\\ & c_{0n'imm'j}=c_{mn'jNm'i} \; ,\\ & c_{nn'imN+1j}=c_{n1imn'j} \; ,\\ & c_{n0imm'j}=c_{nm'imNj} \; . \end{aligned} \tag{40}$$

Equations (39) and (40) have been solved numerically by matrix diagonalization for a finite system of $N=6$ cells. The resulting discrete energy eigenvalues are shown in Fig. 3, where the parameters are taken to be $W^{ee}=W^{dd}=5$, $F_2^{ed}=-1$, $F_3^{ed}=-5$, with $U^e_{2(3)}=U^d\equiv U=0$ and $U=3$, respectively, and increasing dipole moment $R|e|$ ($W_i^{de}=W^{dd}/[(d+R_i)/d]$, $W_i^{ed}=W^{dd}/[(d-R_i)/d]$, see Fig. 1). We see that if R is large enough we will get a separate, energetically lowered bound-state subband even in the case of finite overlap.

VI. SUMMARY

The true eigenstates of the three-level system with charge transfer on a periodic linear chain should be delocalized Bloch states. However, the intercell interaction (static and Förster-Coulomb interaction) leads to a separate energy band in the two-pair-excitation spectrum, which splits off the continuum band caused by the Förster term. This lowered energy subband is due to charge-transfer excitons, correlated by the static Coulomb interaction. The width of this band, Δ, is compressed as compared to the respective single-pair band. Therefore the corresponding thermal state is characterized by a reduction of the coherence length l_c, and the local picture required for the information-processing system[7] tends, indeed, to be valid, on a time scale small compared with the hopping time, $\tau=\hbar/\Delta$. Exciting the system, which means creating a further electron-hole pair, causes the excitation energy to depend on the distribution of existing charge-transfer excitons, thus giving rise to optical nonlinearity. These results remain valid even in the presence of single-particle overlap.

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[1] *Molecular Electronic Devices*, edited by F. L. Carter, R. E. Siatkowski, and H. Wohltjen (North-Holland, Amsterdam, 1988).

[2] T. J. Thorton, Phys. Rev. Lett. **56**, 1181 (1986).

[3] W. Hansen, Phys. Rev. Lett. **62**, 2168 (1989).

[4] Ch. Sikorski and U. Merkt, Phys. Rev. Lett. **62**, 2164 (1989).

[5] G. Mahler and K. Obermayer, in *Computational Systems—Natural and Artificial, Proceedings of the International Symposium on Synergetics, Schloss Elmau, Bayern, 1987,* edited by H. Haken (Springer, Berlin, 1987).

[6] K. Obermayer, G. Mahler, and H. Haken, Phys. Rev. Lett. **58**, 1792 (1987).

[7] W. Teich and G. Mahler, Phys. Scr. **40**, 688 (1989).

[8] P. Petelenz, Chem. Phys. **133**, 199 (1989); **119**, 25 (1988).

[9] B. E. Robertson and J. J. Stezowski, Acta Crystallogr. Sec. B **34**, 3005 (1978).

[10] H. Sixl, Phys. Bl. **40**, 35 (1984).

[11] H. Haken, *Quantenfeldtheorie des Festkörpers* (Teubner, Stuttgart, 1973).

[12] R. Orbach, Phys. Rev. **112**, 309 (1958).

[13] N. Trivedi, Phys. Rev. B **41**, 4552 (1990).

[14] A. Sommerfeld and H. Bethe, *Handbuch der Physik* (Springer-Verlag, Berlin, 1933), Vol. 24, Pt. 2, pp. 598-607.

[15] See, e.g., E. Joos and H. D. Zeh, Z. Phys. B **59**, 223 (1985).