Excitonic Strings in one dimensional organic compounds

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Abstract

Important questions concern the existence of excitonic strings in organic compounds and their signatures in the photophysics of these systems. A model in terms of Hard Core Bosons is proposed to study this problem in one dimension. Mainly the cases with two and three particles are studied for finite and infinite lattices, where analytical results are accessible. It is shown that if bi-excitonic states exist, three-excitonic and even, n-excitonic strings, at least in a certain range of parameters, will exist. Moreover, the behaviour of the transitions from one exciton to the biexciton is fully clarified. The results are in agreement with exact finite cluster diagonalizations of several model Hamiltonians.

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I. INTRODUCTION

Excitonic molecules - or biexcitons - are known and well studied since several decades in conventional semiconductors. Their formations due to the coupling of a pair of exciton and their photophysics properties have been well established both theoretically and experimentally \[1\]. The outstanding facts are related to the giant oscillator strength associated with the one exciton-biexciton transition; we may cite, for instance, the giant two photon absorption, shown theoretically by Hanamura \[2\] and observed first on CuCl by Gale and Mysyrowicz \[3\]. There, five or six orders of magnitude more than for typical two-photon interband transitions are observed.

In organic compounds, the interest for excitonic bound states - or excitonic complexes or last, to use a terminology coming from the Bethe Ansatz technique, excitonic strings - is rather new since the main studies started about five or six years ago. They concern three types of compounds: some organic Charge Transfer solids (CT), \(J\) or \(H\)-aggregates (\(J-HA\)) and Conjugated Polymers (CP).

The organic CT solids considered here, consist of planar aromatic Donor (D) and Acceptor (A) molecules alternately arranged along a one-dimensional stack. A large distance between molecules of the same stack (more than 3 Å) gives a rather small hopping integral compared to the characteristic Coulomb repulsion. Moreover, a very large distance between neighbouring chains ensures the quasi-one dimensionality of these systems. A prototype is given by the anthracene-PMDA (pyromellitic acid dianhydride); for this compound, by comparison between theoretical calculations on small clusters and experimental results of differential transmission spectroscopies, the existence of biexcitons - and even triexcitons - has been demonstrated recently \[4\]. This result stays, for the moment, the only clear evidence for excitonic strings in organic compounds.

\(J\) and \(H\)-aggregates are also, in many cases, one dimensional stacks of organic molecules. But, on the contrary to the previous class of compounds, they have no ionic character and the attractive exciton-exciton interaction is smaller. They are typical organic solids in
the sense that their low-lying excitations can be understood in terms of Frenkel excitons. These compounds are claimed to be the ideal ones to get biexcitons but, without convincing demonstration for the moment - possibly be due to a too small binding energy [5,6].

Conjugated polymers are very complex compounds. As far as we are concerned with low-lying excitations, we may consider them, at first approximation, as an one dimensional interacting electron gas, which strongly interacts with the lattice too [5]. Moreover, for a more realistic description, in many cases, three dimensional effects and inter- and intra-chain disorder should be considered. Because of these difficulties, despite a large amount of work, even the nature of the primary excitations remains subject of intense controversies [8]. Anyway, some Photoinduced Absorption (PA) experiments [1,10] and Two Photon Absorption (TPA) experiments [11,12] show some features which are possibly due to biexcitons.

Only a few theoretical investigations of excitonic strings in organic compounds have been done [4–12,13]. Most of them are based on exact diagonalizations of small clusters using different kinds of model Hamiltonians depending on the system under consideration [4–6,13]. From these results and based on physical reasoning, it has been argued that, when biexcitonic states exist, the intensity of the optical one exciton-biexciton transition may decrease when the binding energy of the biexciton increases; moreover, this intensity is shown to be less important than the one of the one exciton-two excitons (two free excitons) transitions and, even, is supposed to be independent of the system size for sufficiently large binding energies [5]. Therefore, if the tendencies observed on finite clusters remain the same for the infinite system, on the contrary to the situation observed in some inorganic semiconductors [2,3], it may be difficult to create biexcitons by TPA. A more appropriated experimental technique to observe excitonic strings would then be the Differential Transmission Spectroscopy used by the way in [6]. Throughout this manuscript, we often refer to these numerical works for comparisons, especially concerning the intensity of the transition from one exciton to biexciton states.

In this paper, we propose a model for studying excitonic complexes in organic compounds. Based on physical arguments, we think, this model is relevant for the three classes
of compounds enumerated above. For organic crystals, as the \( J \) and \( H \) aggregates, our model is equivalent, in the low energy sector, to an effective XXZ spin one-half Heisenberg model already used to study this problem \[5,14–16\]. For the CT solids and CP, some extensions are necessary because the proper excitons are not of Frenkel type. They are realized by introducing effective Hard Core Boson particles with a finite extension on a lattice, which mimics the exciton extension. Next, we propose an effective Hamiltonian in terms of these particles which captures the essential physical ingredients to describe excitonic strings in organic compounds. This model is considerably easier to study than the traditionally employed models and therefore some analytical investigations are possible. In this paper, we study the proposed model for two and three particles in a finite and infinite lattice. Our main interests concern the behaviours of the binding energies of the excitonic strings with the parameters of the model and of the one exciton-biexciton transition oscillator strengths; are they giant as in inorganic semiconductors or, on the contrary, small as suggested by exact diagonalizations on small clusters \[14,15\]? This question is crucial in order to clarify the role of hypothetical biexcitons - or even more extended excitonic strings - in the photophysics of organic compounds.

The paper is organized as follow. In section II, we introduce our Hard Core Boson Hamiltonian. In section III, IV and V, we study this Hamiltonian for one, two and three particles respectively.

II. MODEL

First, for each class of systems mentioned in this study, we emphasize the main characteristics which are important for our purpose.

\( J \) and \( H \) aggregates are typical Organic Crystals. The ground state of these systems is the tensorial product of the molecular ground states. The low-lying excitations are Frenkel-type excitons where the hole and the electron of a monoexcitation are located on the same molecular site \[14,16,19\]. We can draw a picture of these excitations in the following way:
if we represent symbolically the ground state of such a quasi-one dimensional system as ...
\[ \text{MMM...MMM...}, \]
where \( M \) stands for a Molecule in its ground state, the Frenkel excitons are the Bloch states of local configurations such as ...
\[ \text{MMM}^\pm \text{MMM...} \]
where the superscripts \(-\) and \(+\) are for the electron and the hole, respectively; \( M^\pm \) is then a monoexcited molecule.

Organic CT solids are stacks of Donor (D) and Acceptor (A) molecules. We already mentioned that they are, with a good approximation, quasi-one dimensional systems with a nearest-neighbour hopping term small compared to the Coulombic term. The strong coupling regime is then a good starting point to consider such systems. Moreover, if one consider only a short range Coulombic term, their ground state would be a Charge Density Wave depicted roughly by the unique configuration ...
\[ \text{DADADA...} \]
where D molecules get two electrons and A molecules none. The low-lying excitations would then be the excitons where an electron is transfered from a D to an A molecule; they would be Bloch states of excited configurations such as ...
\[ \text{DAD}^\pm A^{-1}DA... \]
more details could be found in ref [4]. We get a so-called Charge Transfer Exciton (CTE). For a more realistic Coulomb potential, the picture proposed above will remain reasonable, at first approximation.

Conjugated Polymers are quite different from the other systems just considered since, obviously, they are not molecular crystals. On the contrary, they are usually described as an one dimensional electron gas governed by the Pariser-Parr-Pople (PPP) Hamiltonian which includes both long range Coulomb interaction and, semi-classically, electron-phonon interaction [7]. Numerical studies of this Hamiltonian give, for a proper choice of parameters, excitonic states of small radius, typically a few monomeric units [12, 17]. On the other hand, the ground state may be analyzed in terms of basis sets completely localized on the monomers. Then, the ground state of finite clusters is shown to contain mainly intermonomer charge fluctuations of very short range - especially the nearest-neighbours ones [20]. According to these specificities, an effective model has been proposed very recently [21, 22]. Starting from the PPP Hamiltonian, this model reaches a kind of molecular-crystal description for the low-lying excitations in conjugated polymers. In this new approach the vacuum (or ground
state) is still not the simple molecular-type of ground state, proper to the Simpson related models \cite{23,24}, but a matrix-product like state composed by local configurations extended at most, over two monomers. Excitons are then composed mainly by local configurations where either the electron and the hole are localized on the same monomer or distant by only one monomer; the weight of the configurations where the electron and the hole are more separated decreases exponentially in the wave functions. Therefore, the radius of the exciton, $r$, defined as an average distance between the hole and the electron is rather small. If we assume $r = 1$, the following pictorial representation can be done: if we represent the ground state as $...MMMM...$, where $M$ is a Monomer, the excitons will be the Bloch states of such configurations ($...MMM^+M^-MM...$) $\pm$ ($...MMM^-M^+MM...$). Because of the electron-hole symmetry, the charge transfer of the electron on the right side and on the left side must be combined either symmetrically or antisymmetrically. In contrast to the two previous cases, excitons have here, a structure.

In conclusion, in these three cases, excitons are Bloch states of very localized excitations. The vacuum and the nature of these local excitations vary, of course, following the system under consideration: crystal molecular ground state and Frenkel excitons for $J$ and $H$ aggregates, CDW and CTE for CT solids and finally, matrix-product state and some kind of CTE but including the two possible arrangements of the charges, for CP. However, all these very localized excitations can be thought in terms of effective Hard Core Bosons (HCB) extended over a few bonds - with an extension of the order of the exciton’s radius. We adopt such a view in this work, and describe the dynamics of these excitations within the same model which we introduce now.

In this study, we consider only one dimensional lattices with $N$ sites, a site being a molecular-site in the case of molecular crystals \cite{1} and a monomer-site in the case of CP \cite{21,22}. As we already mentioned, this is a good approximation for a large class of compounds studied here. However, the generalization to higher dimensions should be possible and the subject of further studies.

Excitons are extended over $r$ sites, the radius of the excitons, which varies from zero to
a few units in the cases considered here. In this study, to mimic the excitons, we introduce HCB particles extended over one bond \((r = 1)\). This ‘minimal’ extension is adopted more by a pictorial preoccupation but, also, in accordance with the work developed in ref \[21,22\]. Indeed, at the thermodynamic limit where we will derive all the analytical formulae, this extension plays obviously no role, since it remains small compared to the system size. Moreover, for finite size cluster calculations, the qualitative behaviours shown in this paper could also be obtained by choosing \(r = 0\), \(r = 2\) or even other ‘small’ \(r\). The restriction to \(r = 1\) does not affect the conclusions but, if necessary, more (or less) extended particles could also be considered without any difficulties. Working with extended particles, instead of particles localized on a site, does not imply technical complications.

The Coulomb interaction between excitons must be included in order to describe excitonic strings. For that purpose, the relative position between the electron and the hole, the two elementary constituents of an exciton, becomes important. We introduce then two species of HCB extended over one bond:

- The so-called Right-bosons \((R)\) which mimic nearest neighbour electron-hole pairs with the electron on the right (see figure 1.a).
- The so-called Left-bosons \((L)\) which also mimic nearest neighbour electron-hole pairs but with the electron on the left (see figure 1.b).

The \(R\) and \(L\) particles obey the following Hamiltonian

\[
H = \omega_0 \sum_n (R_n^\dagger R_n^\dagger + L_n^\dagger L_n^\dagger) - J \sum_n (R_n^\dagger R_{n+1}^\dagger + h.c.) - J \sum_n (L_n^\dagger L_{n+1}^\dagger + h.c.) - \alpha \sum_n (R_n^\dagger L_n^\dagger + h.c.) - V \sum_n (\hat{N}_n^R - \hat{N}_n^L)(\hat{N}_{n+2}^R - \hat{N}_{n+2}^L)
\]  

\[(1)\]

\(R_n^\dagger\) and \(L_n^\dagger\) are the destruction (creation) operators of the \(R\) and \(L\) bosons at site \(n\), \(\hat{N}_n^R(L)\), the operators number of HCB \(R\) \((L)\) at site \(n\). \(\omega_0\) is the excitonic energy \((\omega_0 > 0)\). The \(J\) term is the hopping term of the HCB \((J > 0)\); it is directly related to the exciton band width given by \(4J\). \(\alpha\) is an effective term for virtual interactions which couple locally \(R\) and \(L\) bosons \((\alpha > 0)\). The \(R\) and \(L\) particles are effective representations of more complex
particles, invoking a more sophisticated level of description; these "high level" particles possess a structure which can be very complicated as it is the case for most of the CP. The interaction $\alpha$ reflects the existence of virtual processes exchanging the relative position of the electron and the hole of an exciton; this can be due, for instance, to kinetic terms. Indeed, by a second order process involving a n.n. hopping term, it is readily possible to exchange the relative position of the two building particles of an exciton. The last term of (1), $V (V > 0)$, is the interaction between excitons restricted to nearest-neighbours. We have to distinguish between two situations: for two excitons of the same species, $RR$ or $LL$, the nearest charges are of opposite sign so that the resulting interaction must be attractive; the situation is reversed for two excitons of opposite species, $RL$ or $LR$, where the resulting interaction is repulsive.

For structureless excitons, Frenkel or CT-excitons, the definition of two species of degenerate HCB makes no sense. To study strings of such excitons with the general Hamiltonian (1), it is sufficient to: (i) identify the $R$ and $L$ particles and (ii) to take the limit $\alpha = 0$. To be more precise, $R$ and $L$ particles may exist in the case of CT solids, but with a large energy difference which results, in our model, in a very small $\alpha$; therefore, it is a good approximation to simply neglect this term in this case.

In the following, we will study the Hamiltonian (1) for one, two and three particles, which are the cases of experimental interest.

III. ONE EXCITON STATES

Excitons appear as Bloch states of symmetric or antisymmetric combinations of $R$ and $L$ bosons, corresponding to two different symmetry classes

$$| \pm, k > = \frac{1}{\sqrt{2(N-1)}} \sum_n e^{i k n} (R_n^\dagger \pm L_n^\dagger) | 0 >$$

(2)

where $| 0 >$ is the state without any boson. The separation in energy between this two states is given by $2\alpha$, the (+) state being lower.
In the case of \( J(H) \) aggregates and CT solids, we identify \( R \) and \( L \) bosons and get only one excitonic state

\[
| -, k > = | 0 >, \quad | +, k > = | k > = \frac{1}{\sqrt{N - 1}} \sum_n e^{i k n} R_n^\dagger | 0 > \tag{3}
\]

In all cases, exciton states result in a very intense peak in the linear absorption spectrum for \( k = 0 \), while the electron-hole continuum is almost not visible. This very unusual feature, if we think about conventional semiconductors, is an important characteristic of these one dimensional compounds \[21,22,25\]. This is easily understandable since the radius of the exciton is very small and the ground state contains mainly short range charge fluctuations \[21,22\].

Now, we write down the elementary transition moments due to a localized HCB, \( \vec{m}_{cp} \), in the case of CP and \( \vec{m}_{oc} \), in the case of \( J(H) \) aggregates and CT solids (\( oc \) is for Organic Crystal); these quantities will serve in the following to express the transition moments between one exciton and two exciton states

\[
\vec{m}_{cp} = \frac{1}{\sqrt{2}} < 0 | e \vec{r} (R_n^\dagger + L_n^\dagger) | 0 > \tag{4}
\]

\[
\vec{m}_{oc} = < 0 | e \vec{r} R_n^\dagger | 0 >
\]

where \( e \) is the charge of the electron and \( \vec{r} \) the position operator.

The intensity of the ground state-one exciton transition at \( k = 0 \) is proportional to \( N | \vec{m}_{oc} |^2 \) or \( N | \vec{m}_{cp} |^2 \), depending on the system under consideration \[22\]. In the case of CP, only the excitonic state \( | +, 0 > \) is observable in linear absorption. However, the state \( | -, 0 > \) could become important, as it is the case in electroabsorption experiments for instance.

**IV. TWO EXCITON STATES**

The wave functions with two excitons are written as

\[
| \Psi_2 > = \sum_{n_1 < n_2 - 1} \Psi_{\sigma_1,\sigma_2}(n_1, n_2) | n_1, n_2 > \tag{5}
\]
where $\sigma_1$ and $\sigma_2$ are $R$ or $L$ bosons, $|n_1,n_2>$ the ket relative to the situation where the particle $\sigma_1$ is in $n_1$ and $\sigma_2$ in $n_2$ with $n_1 < n_2 - 1$, $\Psi_{\sigma_1\sigma_2}(n_1,n_2)$ is the corresponding amplitude.

As usual, we treat separately the movement of the center of mass and of the relative position of the two particles. Moreover, we have to specify the nature, $R$ or $L$, of the particles located on $n_1$ and $n_2$, it is then convenient to use matrix formalism. We write

$$|\Psi_2> = \sum_{n>1,n_1} e^{iQ(n_1+n_2)}[\varphi]_n |n_1,n_2>$$

with $n = n_2 - n_1$ ($n > 1$) and

$$[\varphi]_n = \begin{pmatrix} \varphi_{rr}(n) \\ \varphi_{rl}(n) \\ \varphi_{ll}(n) \\ \varphi_{lr}(n) \end{pmatrix}$$

where the small left (right) indices refer to the nature of the left (right) particle, $R$ or $L$ bosons.

We apply Periodic Boundary Conditions (PBC) to the wave functions which give the following constraints

$$\begin{cases} Q = \frac{2\pi}{N} , & j = 1,...,N \ (j \text{ an integer}) \\
[\varphi]_{-n+N} = [\varphi]_n \text{ where } n = n_2 - n_1 \end{cases}$$

Moreover, we work with Hard Core Bosons extended over one link so that we must preserve

$$[\varphi]_0 = [\varphi]_1 = [0]$$

where $[0]$ is the zeroth four component vector.

With the wave function (6), the eigenvalue equation is written

$$E[\varphi]_n = -2J \cos Q[I][[\varphi]_{n-1} + [\varphi]_{n+1}] - \alpha[\Sigma][\varphi]_n - \delta_{n,2}V[\Lambda][\varphi]_n$$
where \([I]\) is the 4 by 4 identity matrix, and

\[
\begin{bmatrix} 
\Sigma \\
\Lambda 
\end{bmatrix} =
\begin{bmatrix}
0 & 1 & 0 & 1 \\
1 & 0 & 1 & 0 \\
0 & 1 & 0 & 1 \\
1 & 0 & 1 & 0
\end{bmatrix},
\begin{bmatrix}
1 \\
-1 \\
1 \\
-1
\end{bmatrix}
\] (11)

With the equation (10), we have reached an impurity like problem where free particles, belonging to four different continuum, interact with impurities pinned at \(n = 2\). First, by applying a local unitary transformation, we solve (10) away from the impurities.

\[
\begin{bmatrix} \bar{\varphi} \end{bmatrix}_n = \begin{bmatrix} U \end{bmatrix} \begin{bmatrix} \varphi \end{bmatrix}_n
\]

\[
\begin{bmatrix}
\varphi_0(n) \\
\varphi_0(n) \\
\varphi_+(n) \\
\varphi_-(n)
\end{bmatrix} =
\begin{bmatrix}
\frac{1}{\sqrt{2}} & 0 & -\frac{1}{\sqrt{2}} & 0 \\
0 & \frac{1}{\sqrt{2}} & 0 & -\frac{1}{\sqrt{2}} \\
\frac{1}{2} & \frac{1}{2} & \frac{1}{2} & \frac{1}{2} \\
\frac{1}{2} & -\frac{1}{2} & \frac{1}{2} & -\frac{1}{2}
\end{bmatrix}
\begin{bmatrix}
\varphi_{rr}(n) \\
\varphi_{rl}(n) \\
\varphi_{ll}(n) \\
\varphi_{lr}(n)
\end{bmatrix}
\] (12)

We can now rewrite equation (11) in terms of \([\bar{\varphi}]_n\); we find

\[
E[\bar{\varphi}]_n = -2J \cos Q[I\{[\bar{\varphi}]_{n-1} + [\bar{\varphi}]_{n+1}\} - 2\alpha[\sigma_2][\bar{\varphi}]_n - \delta_{n,2}V\{[\sigma_1][\bar{\varphi}]_n + [\sigma_3][\bar{\varphi}]_n\}
\] (13)

where

\[
[\sigma_1] = 
\begin{bmatrix}
1 & 0 & 0 & 0 \\
-1 & 0 & 0 & 0 \\
0 & -1 & 0 & 0 \\
0 & 0 & 1 & 0
\end{bmatrix},
[\sigma_2] =
\begin{bmatrix}
0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 \\
0 & 0 & 1 & 0 \\
0 & 0 & 0 & 1
\end{bmatrix},
[\sigma_3] =
\begin{bmatrix}
0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 \\
0 & 0 & 1 & 0 \\
0 & 0 & 0 & 1
\end{bmatrix}
\] (14)

Without the impurity like states at \(n = 2\), there is no mixing between \(\varphi_0\), \(\varphi_0\), \(\varphi_+\) and \(\varphi_-\) components; with the scattering of particles at \(n = 2\), only the \(\varphi_+\) and \(\varphi_-\) components are mixed.
From equations (4) and (12), it is clear that only the $\varphi_+(n)$ and the $\varphi_-(n)$ components of $[\varphi]_n$ are relevant to study the optical responses of two exciton states. Since we are mainly interested in spectroscopic properties of biexcitons, we consider only these two components in the following. The $\varphi_0(n)$ and $\varphi_0(n)$ components have no physical meaning for structureless excitons, but could be important for CP; their characteristics could be calculated, following exactly the same way as the one presented here.

We write, following H. Bethe [26],

$$\varphi_+(n) = A_+ e^{\mu n} + B_+ e^{-\mu n} \quad \text{and} \quad \varphi_-(n) = A_- e^{\eta n} + B_- e^{-\eta n}$$

which give the following expressions for the energy where $J(Q) = 2J \cos Q$ and where we choose $2\omega_0$ as reference

$$E = -2\alpha - J(Q)(e^{\mu} + e^{-\mu}) \quad \text{and} \quad E = 2\alpha - J(Q)(e^{\eta} + e^{-\eta})$$

$A_+, A_-, B_+ \text{ and } B_-$, $\mu$ and $\eta$ are the constants to be determined. Note that, if in (15) $\mu$ and $\eta$ are purely imaginary numbers, we get free excitons. On the contrary, if they are purely real numbers, we get bound-states, the biexcitons.

The ansatz (15) gives obviously the exact solution of (13) without impurities ($V = 0$); with impurities, (15) must fulfill the following constraints in order to remain solution of (13)

$$J(Q)\varphi_+(1) - V\varphi_-(2) = 0$$
$$J(Q)\varphi_-(1) - V\varphi_+(2) = 0$$

Moreover, the PBC imply

$$A_+ = e^{-\mu N} B_+ \quad \text{and} \quad A_- = e^{-\eta N} B_-$$

In the following, we give the solutions of the above mentioned problem for different choices of parameters.
A. $\alpha = 0, V = 0$

In this trivial case, the two excitons are free; we get two degenerated continuum for $\varphi_+(n)$ and $\varphi_-(n)$ within the energy range $[-2J(Q), 2J(Q)]$. It is easy to show that a very intense linear absorption takes place for $Q = 0$ and $\mu = \eta = 0$ only; then the transition moment of the one exciton - two free exciton transition at the edge of the continuum behaves as

$$| \tilde{M}_{1\text{ exciton}-2\text{ free excitons}} |^2 \sim N | \tilde{m}_{cp/oc} |^2$$

(19)

plus corrections in $\frac{1}{N}$. For $\alpha \neq 0$ and/or $V \neq 0$, this strong absorption remains but slightly shifted toward the high energies.

This transition is similar to the ground state - one exciton transition; indeed, the excitation energies and the behaviour of the transition moments are the same in these two cases. This characteristic was already used in [4,5] to explain the lack of bleaching signal in PA experiments for Charge Transfer and Frenkel exciton systems.

B. $\alpha = 0, V \neq 0$

This case concerns CT solids and $J$ or $H$ aggregates for instance. Without the $\alpha$ term, our model is equivalent to a standard interacting Frenkel exciton Hamiltonian already studied numerically [5] and analytically [14–16]. Our results, obtained with a different technique, are in accordance with the conclusions reach by these various studies.

Since $V \neq 0$, bound states - or biexcitons - may exist; in this subsection we consider the biexcitonic states only and then $\mu$ and $\eta$ of equations (15) as real quantities.

When $\alpha = 0$, equations (16) imply that $\mu = \eta$. From equations (17) together with the PBC (18), we get at the thermodynamic limit, the following set of equations

$$B_- = \lambda B_+ e^\mu$$

$$\lambda^2 - e^{-2\mu} = 0$$

(20)

where $\lambda = \frac{J(Q)}{V}$.  

13
Additionally to the continuum, if $\lambda < 1$, i.e $V > J(Q) = 2J \cos Q$, we get with the second equation of (20) and equations (16), two bound states with energies given by the following simple expressions

$$E = -V - \frac{J^2(Q)}{V} \quad \text{and} \quad E = +V + \frac{J^2(Q)}{V}$$

(21)

By using a two-particle Green function approach [14], these equations have already been obtained for $Q = 0$ in [15] and for every $Q$ in [14,16] together with the biexciton condition $V > J(Q)$.

The first equation gives a bound state below the continuum of two free exciton states, this is the biexciton of interest for us; the second equation gives another bound state on top of the continuum. In the following, we consider only the first state and calculate its wave function and the transition moment associated with the one exciton-biexciton transition.

First, we write $A_\pm = e^{-\delta/2}$ and $B_\pm = e^{\delta/2}$. With the PBC (18) and equations (20), we get the expression for $\delta$

$$-\delta = N \ln \lambda$$

(22)

Then, with equations (13) and (20), we get

$$\varphi_\pm = N \cosh(-\ln \lambda|n - \frac{N}{2}|)$$

(23)

valid in the interval $1 < n < N - 1$. $\mathcal{N}$ is the normalization constant given by

$$\mathcal{N} = \left[\frac{1}{2}(N - 3) + \frac{1}{2\lambda^2(1 - \lambda^2)} \left(\frac{1}{\lambda^{N-4}} - \lambda^{N-2}\right)\right]^{-\frac{1}{2}}$$

(24)

The first equation of (20) shows that the wave function of the lowest bound state is a symmetric mixture of the $\varphi_+$ and $\varphi_-$ components resulting in configurations with two like particles $RR$ or $LL$. On the contrary, the highest bound state contains only configurations with two unlike particles $RL$ or $LR$. We recall that for this case $R$ and $L$ particles are identified so that the distinction between the case with $RR$ or $LL$ bosons and $RL$ or $LR$ bosons is then a way to treat the case of attractive and repulsive interaction between bosons.
at the same time. In case of attractive interaction (two bosons of same species), we get a bound state below the two exciton continuum; the situation is reversed in the case of repulsive interaction (two bosons of opposite species), where a bound state appears above the two exciton continuum \[4\].

For large systems, the transition moment of the one exciton-biexciton transition is non-zero only for \(Q = 0\) and \(k = 0\) \((Q,\) the center of mass of the biexciton, \(k,\) the exciton momentum\); its expression is then given with the help of the elementary transition moment \((4)\) by (more precisely, the square of the transition moment is shown here)

\[
|\vec{M}_{oc}|^2 = 2 |\vec{m}_{oc}|^2 \sum_n \varphi_+(n) \varphi_+(n)|^2 = 2 |\vec{m}_{oc}|^2 N^2 \left( \frac{1}{1-\lambda} \left( \frac{1}{\lambda^{N/2-2}} - \lambda^{N/2-1} \right) \right)^2
\]

Going to the thermodynamic limit, we found the simple result

\[
|\vec{M}_{oc}|^2 = 4 |\vec{m}_{oc}|^2 \frac{1+\lambda}{1-\lambda}
\]

which is exactly the result found in \([15,16]\) by using a two particle Green function approach.

We recall that the bound states (biexcitons) exist only if \(0 < \lambda < 1\) and that the biexciton binding energy increases when \(\lambda\) approaches 0. With this formula, the behaviour of the absorption from the one exciton to biexciton state appears very clearly. First let us consider its behavior when \(\lambda\) approaches 0 or 1, at the thermodynamic limit (equation \((26)\)): for \(\lambda \to 0\), the transition moment reaches saturation to \(4 |\vec{m}_{oc}|^2\) which is easily understandable since, in this case, the two excitons are strongly bounded together in two n.n. sites; for \(\lambda \to 1\), the transition moment diverges following the asymptotic behaviour in \(4 |\vec{m}_{oc}|^2 \frac{2}{1-\lambda}\). Next, we can make some conclusions by studying the equation \((25)\).

- At large and fixed \(N\), with decreasing \(\lambda\) (which means, with increasing the biexciton binding energy), the intensity of the transition decreases.

- At fixed \(\lambda\) and sufficiently large \(N\), \(\vec{M}_{oc}\) is almost independent of the system size. On the contrary, the intensity of the transition between one exciton and two free excitons increases linearly with the system size (cf. eq. \((19)\)). However, as expected, when \(\lambda\) approaches 1, \( |\vec{M}_{oc}|^2 \) recovers progressively a linear dependence in \(N\).
Both of these behaviours depict inverse mechanisms than the ones theoretically predicted for the ground state-one exciton transition [21,22], where the intensity of the excitonic peak is proportional to the size of the system and increases with the binding energy.

These behaviours are illustrated in figure 2 where the equation (25) is evaluated for $N = 100$. There, we see that the intensity of the one exciton-biexciton transition decreases dramatically when $\lambda$ decreases (which means, when the binding energy increases) reaching saturation for small $\lambda$. Then, this intensity is independent of $N$ which gives in PA and TPA spectroscopy an intensity proportional to $\sqrt{N}$ instead of $N$ for the transition to the continuum of two free excitons; this last behaviour can be seen by comparison with equation (26) evaluated at the large $N$ limit (dashed line). Consequently, at the thermodynamic limit, biexcitons may be observable by spectroscopy experiments, but with the need of very clean compounds, otherwise we may expect at first analyse, that the intense transition to two free excitons would not permit to detect possible biexcitons. Within our model, no two-photon giant resonance [2] can be expected for $J, H$ aggregates and organic Charge Transfer Solids. The very same conclusions were already pointed out in ref [3] from numerical calculations and in [14,15] from analytical studies.

C. $\alpha \neq 0, \nu \neq 0$

This case concerns CP. As in the previous subsection, we look for bound states only so that $\mu$ and $\eta$ are again assumed to be real quantities. The question we want to address more specifically here is how the $\alpha$ term will affect the binding energy, the wave function and the transition moment related to the biexcitons.

For $\alpha \neq 0$, from equations (17) and (18), we get at the thermodynamic limit the following set of equations

\[
B_- = \lambda e^{-\mu} e^{2\eta} B_+
\]

\[
\lambda^2 e^{\eta} - e^{-\mu} = 0
\]

(27)

From equations (16) and the second equation of (27), we get
\[ e^{-\mu} = \frac{\lambda^2}{1 - \lambda^2} \left( \beta + \sqrt{\beta^2 - (1 - \lambda^2)(1 - \frac{1}{\lambda^2})} \right) \]  

(28)

where \( \lambda = \frac{J(Q)}{\sqrt{\beta}} \) and \( \beta = \frac{\alpha}{J(Q)} \). This expression together with equations (16), gives the energy of the lowest biexciton.

The binding energy of the biexciton, \( E_b \), is then given by the following equation

\[ E_b(\alpha) = J(Q)((e^{-\mu} + e^\mu) - 2) \]  

(29)

The study of this expression shows that the biexciton binding energy decreases when \( \alpha \) increases (see figure 4). This behaviour is not surprising since the \( \alpha \) term mixed together \( R \) and \( L \) particles; by doing so, configurations with two unlike particles, \( RL \) or \( LR \), appear in the wave function which increase its energy and then reduce the binding energy with respect to the case for \( \alpha = 0 \). The critical value \( \alpha_c \) for which the binding energy becomes zero is given by the solution of the equation \( e^\mu + e^{-\mu} = 2 \),

\[ \beta_c = \frac{\alpha_c}{J(Q)} = \frac{1}{2} \left( 1 - \frac{(1 - \lambda^2)^2}{\lambda^2} \right) \]  

(30)

The critical value, \( \alpha_c \), increases when \( \lambda \) decreases, to diverge for \( \lambda = 0 \): for a very large binding energy, \( \alpha \) has no effect on the bound states anymore. Another interesting quantity along this critical line, is the critical value \( V_c \)

\[ \frac{1}{\lambda_c} = \frac{V_c}{J(Q)} = \frac{2}{\sqrt{4 + 2\beta} - \sqrt{2\beta}} \]  

(31)

From this equation, we can see without any surprise, than \( V_c \) - the critical value above which one gets biexcitonic states - continuously increases when \( \beta \) increases. The attraction between excitons must be stronger when the mixing between \( R \) and \( L \) bosons becomes more important.

We analyze now the wave function and the resulting transition moment associated with the one exciton-biexciton transition at \( Q = 0 \). We proceed as in the previous case; we write \( A_+ = a_+e^{-\delta_+} \), \( B_+ = a_+e^{\delta_+} \) and \( A_- = a_-e^{-\delta_-} \), \( B_- = a_-e^{\delta_-} \) and get with equations (18) and (27)
\[ \varphi_{\sigma_1\sigma_2} = \mathcal{N}_\alpha \left( \cosh(\mu[n - \frac{N}{2}]) + (-1)^{\delta_{\sigma_1\sigma_2}}e^{(\mu+\ln\lambda)(N-3)}\cosh([\mu + 2\ln\lambda][n - \frac{N}{2}]) \right) \quad (32) \]

where again \( 1 < n < N-2 \). \( \mathcal{N}_\alpha \) is the normalization constant which could be easily calculated if necessary. The first term of (32) comes from the \( \varphi_+ \) component, the second term from the \( \varphi_- \) component. For \( \alpha = 0 \), \( \mu = -\ln(\lambda) \) and the previous result is recovered. For \( \alpha \neq 0 \), the weight of the \( \varphi_- \) component decreases smoothly in the wave function. Consequently, the a priori unfavourable configurations \( RL \) or \( LR \) appear in the biexciton wave function, on the contrary to the previous case without the \( \alpha \) interaction.

The transition moment of the one exciton-biexciton transition at \( Q = 0 \) can be easily calculated with the expression of the wave function (32), but contains no new information compared to what was already pointed out for \( \alpha = 0 \). The results obtained in the previous subsection remain valid in this case. The only difference comes from the fact that the \( \varphi_- \) component is non active in linear absorption. Consequently, for the same binding energy, if we assume \( |m_{cp}| = |m_{oc}| \), the biexcitonic peak would be a bit more intense for \( J \) (\( H \)) aggregates or CT solids than for CP. For instance, for \( \alpha = 0 \), we get \( |M_{cp}|^2 = \frac{|M_{oc}|^2}{2} \); for \( \alpha \neq 0 \), the \( \varphi_+ \) becomes more important than the \( \varphi_- \) component in the wave function: the intensity of the one exciton-biexciton transition then increases.

Now, let us take reasonable parameters for Conjugated Polymers. Extracting from experimental data (we take roughly the binding energy of the \( 1B_u^+ \) exciton state observed in Polydiacetylene compounds), we get \( 4J = 0.5eV \) \[25\]. By calculating the Coulomb interaction between two HCB using the Mataga potential (for instance) \[7\] and for a reasonable lattice constant \( (a = 1.5\AA) \), we get \( V = 0.5eV \). The \( \alpha \) term may be evaluated from the energy difference between the \( 1B_u^+ \) exciton and the \( nA_g^- \) ”ionic” exciton. These states are represented here, in an effective way, by \( |+,0> \) and \( |-,0> \) respectively (see eq. 4). This quantity could be estimated, for instance, from exact resolutions of the PPP Hamiltonian for small clusters or, in a better way, from electroabsorption experiments. There, the state \( |+,0> \) shows a red-shift with no change of the spectral line and a quadratic dependence on the applied field. This quadratic Stark effect of the exciton can be reasonably well re-
produced with the state $|-,0>\text{ only, neglecting, in particular, the continuum effects}$ [25]. Within this assumption, it is then very easy to estimate $\alpha$. We take here a reasonable value, $\alpha = 0.2eV$. With this choice of parameters, we get a binding energy of $0.12eV$ for the biexcitons which is in accordance with experimental results [9,11]. By the way, it is easy within our model to get such a value for the binding energy for other values of $\alpha$ or/and $J$ by changing $V$, which is more flexible.

In figure 3, a calculation for a finite cluster of ten sites is shown. The parameters are $\Delta = 3.33$ and $\beta = 0.2$ which give a typical spectrum. BE is for the peak associated with the BiExciton and, FE, for the peak associated with the more intense two Free Exciton state (even if such concepts are not well defined for finite clusters). The BE peak is a bit smaller than the FE one, which is in accordance with the results of ref. [13] from exact calculations using the Extended Hubbard Hamiltonian, a short version of the PPP Hamiltonian. At the thermodynamics limit, only the FE peaks will survive, slightly shifted toward the low energies.

To conclude with the two particle case, we may summarize our main results. For $\alpha = 0$, biexcitons exist if $0 < \lambda < 1$; the transition moment of the one exciton-biexciton transition shows inverse behaviour compared to the ground-state-one exciton transition: it decreases when the biexciton binding energy increases and, for sufficiently large $N$, is independent of the system size. For $\alpha \neq 0$, the conclusions aforementioned remain valid at the condition that $\alpha < \alpha_c$ for $J$ and $V$ fixed. Above this critical value, biexcitons fall in the continuum. Finite size cluster calculations give qualitatively similar results as other calculations performed with more complicated Hamiltonians.

V. THREE (AND MORE) EXCITON STATES

For more than two particles, the question about the integrability of the Hamiltonian (1) becomes important. To answer this question, it is sufficient to analyze carefully the case with only two particles [27,28]. For that purpose, let us first rewrite the Hamiltonian (1) in
a more convenient way by introducing two new operators

\[ B_n^\dagger = \frac{1}{\sqrt{2}}(R_n^\dagger + L_n^\dagger) \]
\[ A_n^\dagger = \frac{1}{\sqrt{2}}(R_n^\dagger - L_n^\dagger) \]  (33)

Then, the Hamiltonian becomes diagonal in \( \alpha \)

\[ H = (\omega_0 - \alpha) \sum_n B_n^\dagger B_n + (\omega_0 + \alpha) \sum_n A_n^\dagger A_n - J \sum_n (B_n^\dagger B_{n+1} + h.c.) - J \sum_n (A_n^\dagger A_{n+1} + h.c.) - V \sum_n (A_n^\dagger B_n + B_n^\dagger A_n)(A_{n+2}^\dagger B_{n+2} + B_{n+2}^\dagger A_{n+2}) \]  (34)

To illustrate this new picture, note that the states with one exciton (2) are the Bloch functions of one \( B \) or one \( A \) particle.

Let us now consider the case with two like particles (\( BB \) or \( AA \)) located in \( n_1 \) and \( n_2 \) \((n_1 < n_2 - 1)\). Because the last term of (34) exchanges the color (\( B \) or \( A \)) of the two particles, the corresponding amplitude in the wave function is written as

\[ \Psi(n_1, n_2) = C(B, k_1; B, k_2)e^{ik_1 n_1 + ik_2 n_2} + C(B, k_2; B, k_1)e^{ik_2 n_1 + ik_1 n_2} + C(A, k_1'; A, k_2')e^{ik_1 n_1 + ik_2 n_2} + C(A, k_2'; A, k_1')e^{ik_2 n_1 + ik_1 n_2} \]  (35)

the constants \( C \) being complex numbers determined in the previous section by solving the Schrödinger equation.

The system is invariant by translation, hence the total momentum is conserved: \( k_1 + k_2 = k_1' + k_2' = Q \). We then write \( k_1 = Q - q, k_2 = Q + q \) and \( k_1' = Q - k, k_2' = Q + k \).

Now, let us do a scattering ’experiment’. Starting, for instance, with two \( B \) particles, after the scattering processes we get two \( A \) particles. The collision being elastic, the energy (16) must be conserved

\[ -2\alpha - J(Q)(e^q + e^{-q}) = 2\alpha - J(Q)(e^k + e^{-k}) \]  (36)

Depending on the \( \alpha \) value, we can make some conclusions.

• If \( \alpha \neq 0, q \neq k \) (see eq. 32 for instance). Hence, there is a change in the momenta during the scattering processes. In other words, diffractive processes are involved during the scattering which is sufficient to conclude that the model defined by (1) (or (34)) is non-integrable [27].
If $\alpha = 0$, $q = k$. There is no diffractive processes anymore; then, as we look for the lowest bound-states, we will see that the model (1) may be expressed, in that case, as an effective spin-1/2 XXZ Hamiltonian which is well known to be integrable [27–30].

Rigorously, to conclude about the integrability of this model in the general case, the study of the two particles $S$ matrix has to be done [28]. We will not attempt such study here.

In the following two subsections, we will study both cases, starting with the simplest one where $\alpha = 0$.

A. $\alpha = 0$

For $\alpha = 0$, by interacting with each other, particles do not exchange their color; the interaction is reduced to an exchange of momenta alone. In such case, it is better to consider the Hamiltonian (1) expressed in terms of $R$ and $L$ particles.

Since $R$ and $L$ particles are HCB, an $n$-electron configuration is subdivided into $n$ separated regions. Each particle stays in its own area of the chain; within optical terminology, only reflections are allowed. The Hamiltonian is studied independently for each configuration of color which corresponds to a configuration of pair-interactions, attractive or repulsive, depending on the nature of the neighbouring particles. In the general case, the problem is very complex. However, the interesting case for us is given by the configurations where all the particles have the same color. In this case, the model can be written in the form of a XXZ ferromagnetic Hamiltonian for spin-1/2 which has been solved exactly by using the Bethe-Ansatz [26,28–30].

First, our goal is to show the equivalence of our model (1) in the low energy sector and the XXZ model. For simplicity, we consider here particles without extension ($r = 0$). Of course, it is possible to work with our defined $R$ and $L$ particles, but the comparison with the XXZ model would then claimed some additional notations unnecessary for our purpose. By the way, in the second subsection of this section, we will show more formally the equivalence
between the two models working with the extended particles.

Second, since we consider the simplest case with \( n \)-particles like - for instance, the states with \( n \) \( R \) particles - the Hamiltonian of the system may be expressed in terms of spin-one-half operators: \( S^z_n = +\frac{1}{2} \) being for a site \( n \) without any particle and \( S^z_n = -\frac{1}{2} \), for a site occupied by a \( R \) particle (an exciton). The model becomes then equivalent to the spin-1/2 \( XXZ \) model with an 'attractive' anisotropic term \[ (37) \]

\[
H = 2\omega_0 \sum_n S^z_n - 2J \sum_n \frac{1}{2}(S^+_n S^-_{n+1} + S^-_n S^+_n) - V \sum_n (S^z_n - \frac{1}{2})(S^z_{n+1} - \frac{1}{2})
\]

The Ground state of (37) is the state with only up-spins, \(|GS⟩ = |...↑↑↑↑↑...⟩\). \( S^-_n \) creates a down-spin (a \( R \) particle or exciton) localized at site \( n \), \( S^-_n |GS⟩ = |...↑↑↑↓↑↑↑...⟩ \). We introduce here, as usual, the parameter of anisotropy \( \Delta = \frac{V}{2J} \) [28–30].

This model has been subject of intense studies since several decades, and many results are known about it [28–31]. Concerning the bound states, or more precisely, the so-called "string-states", their properties depend on the anisotropic parameter \( \Delta \). Within the "string hypothesis", the following results were found [28–31].

- If \( \Delta > 1 \), the bound states of \( n \)-spins, here \( n \)-excitons, exist without any restriction on \( n \) [28–31]. The energy of a \( n \)-excitonic string is then given by the following formula first appeared in [31]

\[
E^{(n)}_s = n\omega_0 - n V - J \sinh \gamma \frac{\cos Q - \cosh n\gamma}{\sinh n\gamma}
\]

with \( \cosh \gamma = \Delta \) and \( Q \) being the wave number of the \( n \)-string center of mass. For \( n = 2 \), the energy [31] is of course recovered.

- If \( 0 < \Delta < 1 \), the \( n \)-excitonic strings may exist but with a strong restriction on \( n \)

\[
(n - 1)\Theta < \pi
\]

with \( \cos \Theta = \Delta \), \( 0 < \Theta < \frac{\pi}{2} \). Moreover, these excitonic strings fall in the continuum spectrum.
We have seen in the previous section, that biexcitons exist if \( \Delta > 1 \). In this case, from the above conclusions about the XXZ-model, we can say that \( n \)-excitonic strings will also exist and that their binding energies will increase with \( n \) \((38)\); this result is in agreement with numerical studies on small clusters \([3]\). However, as we have shown in detail for the biexcitonic case, it is not easy to observe such states experimentally, since the particles are tightly bounded inside the complex, resulting in a lack of oscillator strength. For \( 0 < \Delta < 1 \), excitonic strings may still exist but with an energy falling in the continuum. In this limit, the excitons are less bounded and, therefore, it could be interesting to study the signatures of these states under the influence of an electric field. We leave this question to further work.

**B. \( \alpha \neq 0 \)**

For \( \alpha \neq 0 \), the interactions between particles involve both exchange of momenta and exchange of color. By a simple argument, showing the appearance of diffractive terms in the two particles scattering case, the non-integrability of the model \((34)\) has been shown. Therefore, to study \( n \)-excitonic strings with \( n > 2 \) one needs to do some approximations. In the following, we propose a trial wave function for the three particle case build from the Bethe Ansatz solution of the XXZ-Heisenberg model within the string hypothesis.

Let us consider the expression \((34)\) of our model expressed in terms of \( A \) and \( B \) particles. For the three particle case, eight configurations have to be distinguished depending on the color of the particles and on their relative positions; we denote these configurations as \( \sigma_1 \sigma_2 \sigma_3 \), where \( \sigma_i \) is for the color \((A \text{ or } B)\). These configurations are separated into two disconnected channels: on one hand, we have \( AAA, BBA, BAB \) and \( ABB \); on the other hand, \( BBB, AAB, ABA \) and \( BAA \). We consider only the latter channel which is the lowest in energy.

The wave function for the triexciton is expressed as a linear combination

\[
| \psi_T > = a_0 | \psi_0 > + a_l | \psi_l > + a_c | \psi_c > + a_r | \psi_r >
\]

(40)

where \( x = 0, r, c, l \) stands for the \( BBB, AAB, ABA \) and \( BAA \) states respectively \((r, c, l \text{ for...})\)
right, center and left refer to the position of the \( B \) particle in the three particles complex). \( a_x \) are the coefficients to determine. Every component \(|\Psi_x\rangle\) is assumed to have the Bethe ansatz structure

\[
|\Psi_x\rangle = \sum_{1 \leq n_1 < n_2 < n_3 \leq N-1} \psi_x(n_1, n_2, n_3) |n_1, n_2, n_3\rangle_x \tag{41}
\]

where, more precisely, the particles are again separated by one bond, at least, and with

\[
\psi_x(n_1, n_2, n_3) = \sum_{P \in S_3} e^{i \sum_{j=1,3} k_x^{P_j} n_j + \frac{i}{2} \sum_{i<j} \theta_x^{P_i P_j}} \tag{42}
\]

The \( k_x^P \) are the quasi-momenta and the \( \theta_{ij}^x \) the phase terms \[28–30\]. The summation runs over the 3! permutations of the indices. We apply periodic boundary conditions to the wave functions, \( \psi_x(n_2, n_3, n_1 + N) = \psi_x(n_1, n_2, n_3) \), and we get the well known equations \[26\]

\[
e^{ik_x^P N + i \sum \theta_x^{P_a P_j}} = 1 \tag{43}
\]

Since we are looking for excitonic complexes, we are interested in complex solutions of these equations. Following Ovchinnikov \[31\], we assume that the only relevant phase terms are \( \theta_{12}^x \) and \( \theta_{23}^x \), then

\[
\begin{align*}
N k_1^x &= 2\pi \lambda_1^x + \theta_{12}^x \\
N k_2^x &= 2\pi \lambda_2^x - \theta_{12}^x + \theta_{23}^x \\
N k_3^x &= 2\pi \lambda_3^x - \theta_{23}^x
\end{align*} \tag{44}
\]

where \( \lambda_i^x \) are integers between 0 and \( N - 1 \). It follows

\[
\begin{align*}
N \text{Im} k_1^x &= \text{Im} \theta_{12}^x \\
N \text{Im} k_2^x &= \text{Im}(\theta_{23}^x - \theta_{12}^x) => 2 \text{Im} \theta_{12}^x &= N(\text{Im} k_1^x - \text{Im} k_2^x) \tag{45} \\
N \text{Im} k_3^x &= -\text{Im} \theta_{23}^x \\
N \text{Im} k_2^x &= N(\text{Im} k_2^x - \text{Im} k_3^x)
\end{align*}
\]

Next, we assume \( \theta_{12}^x = \text{Im} \theta_{12}^x < 0 \) and \( \theta_{23}^x = \text{Im} \theta_{23}^x < 0 \) without loss of generality; then, at the thermodynamic limit, among the summation \[42\] only one term remains with an exponential accuracy in \( N \)

\[
\psi_x(n_1, n_2, n_3) = e^{ik_1^x n_1 + ik_2^x n_2 + ik_3^x n_3 + \theta_{12}^x + \theta_{23}^x} \tag{46}
\]
We may notice, that the used assumption about the phase terms \( \theta_{ij} \), is rigorously correct in the case without \( \alpha \).

The wave function (44) with the simplification (46), must satisfy the following constraints due to the \( V \) term, in order to be an eigenfunction of (34):

- for \( n_2 = n_1 + 2, (\forall n_3) \)
  \[
  a_0 J(\Psi_0(n_1 + 1, n_1 + 2, n_3)) - a_l V \Psi_t(n_1, n_1 + 2, n_3) = 0 \\
  a_l J(\Psi_t(n_1 + 1, n_1 + 2, n_3)) - a_0 V \Psi_0(n_1, n_1 + 2, n_3) = 0 \\
  a_c J(\Psi_c(n_1 + 1, n_1 + 2, n_3)) - a_r V \Psi_r(n_1, n_1 + 2, n_3) = 0 \\
  a_r J(\Psi_r(n_1 + 1, n_1 + 2, n_3)) - a_c V \Psi_c(n_1, n_1 + 2, n_3) = 0
  \]

(47)

- for \( n_3 = n_2 + 2, (\forall n_1) \)
  \[
  a_0 J(\Psi_0(n_1, n_2 + 1, n_2 + 2)) - a_r V \Psi_r(n_1, n_2, n_2 + 2) = 0 \\
  a_r J(\Psi_r(n_1, n_2 + 1, n_2 + 2)) - a_0 V \Psi_0(n_1, n_2, n_2 + 2) = 0 \\
  a_c J(\Psi_c(n_1, n_2 + 1, n_2 + 2)) - a_l V \Psi_l(n_1, n_2, n_2 + 2) = 0 \\
  a_l J(\Psi_l(n_1, n_2 + 1, n_2 + 2)) - a_c V \Psi_c(n_1, n_2, n_2 + 2) = 0
  \]

(48)

Moreover, by symmetry, we have \( k_i^e = k_i^l, \theta_{i,i+1}^e = \theta_{i,i+1}^l, \forall i \) and \( a_r = a_l \). Then, the previous set of equations together with the expression (44) gives

\[
\begin{align*}
J [e^{i(k_0^0 + k_0^0)} + 1] - V e^{i k_0^0} J e^{i k_0^0} = 0 \\
J [e^{i(k_0^0 + k_0^0)} + 1] - V e^{i k_0^0} J e^{i k_0^0} = 0 \\
J [e^{i(k_0^1 + k_0^1)} + 1] - V e^{i k_0^1} J e^{i k_0^1} = 0 \\
J [e^{i(k_0^0 + k_0^1)} + 1] - V e^{i k_0^0} J e^{i k_0^1} = 0
\end{align*}
\]

(49)

to which we add the momentum conservation law

\[
k_1^x + k_2^x + k_3^x = Q
\]

(50)

\( Q \) being the momentum associated with the motion of the center of mass of the excitonic complex. This system of equations is obviously non-soluble in the general case. Hence, we add an additional simplification to the trial wave function.
If \( \alpha = 0 \), \( k_i^x = k_i^0 \), and therefore \( a_x = \frac{1}{2}, \forall x \); it is easy to verify that the system (49) becomes equivalent, in that case, to the corresponding equations for the XXZ Heisenberg model [31] as we already pointed out in the previous subsection. Then the system (49) leads to the energy (38), for \( \Delta > 1 \). Within the string hypothesis, \( k_1^0 \) and \( k_3^0 \) are complex conjugate, \( k_2^0 \), a purely real quantity.

Enlightened by the exact results for \( \alpha = 0 \) [31], we assume for \( \alpha \neq 0 \)

\[
\begin{align*}
  k_1^l &= k_1^0 + \epsilon \\
  k_2^l &= k_2^0 \\
  k_3^l &= k_3^0 - \epsilon
\end{align*}
\]

(51)

where \( \epsilon \), a real number, is given by the following equation obtained from the energy conservation law

\[
-3\alpha - \sum_{i=1}^{3}(e^{ik_i^0} + e^{-ik_i^0}) = \alpha - \sum_{i=1}^{3}(e^{ik_i^l} + e^{-ik_i^l})
\]

(52)

The left-hand-side is the energy of the \( BBB \) component, the right-hand-side, the energy of the three other components.

With this assumption on the momenta \( k_i^x \), the solutions stay very close to the Bethe Ansatz form; the binding between the two bordered particles of the complex (with momenta \( k_1^x \) and \( k_3^x \)), ensures the cohesion of the three particle bound states. The set of equations composed by the two first equations of (49) and equations (50), (51) and (52) are then solved numerically.

It is important to realize that our approximation is variational. This important statement could be checked in the following way. One starts with the trial wave function given by (40) where the components \( |\Psi_x> \) are assumed to be of the form defined by the equations (41), (46) and (51) together with the restrictions (50) and (52). The coefficients \( a_x \) of (40), and their complex conjugates, are determined variationally by minimizing the functional

\[
\mathcal{F}(\{a_x, a_x^*\}) = <\Psi_T | H | \Psi_T> - E <\Psi_T | \Psi_T>
\]

(53)

where \(-E\) is the Lagrange parameter for the normalization constraint of the wave function. We get
\[
\frac{\partial F}{\partial a_0} = 0 \Rightarrow a_0 < \Psi_0 | H | \Psi_0 > + a_r < \Psi_0 | H | \Psi_r > + a_l < \Psi_0 | H | \Psi_l > = a_0 E < \Psi_0 | \Psi_0 >
\]  
(54)

and similar equations for all the other minimizations. At the end of the day, we obtain nothing else than the usual secular equations and one way to solve them, following A. Bethe [26], is to impose the constraints given by the sets of equations (47) and (48). Our procedure is then variational and the results found are an upper bound for the problem.

Typical results are shown in figure (4). The binding energy of the biexciton got in the previous section and the one of the triexciton, obtained with our variational calculation, are represented for \( Q = 0 \) and \( \Delta = 3.33 \) as a function of \( \beta = \frac{\alpha}{J} \). The triexciton binding energy is defined with respect to the continuum of one biexciton plus one free exciton which is the lowest in energy. The following remarks can be made. (i) The triexciton binding energy for \( \alpha = 0 \) is the exact one. (ii) The binding energy of the triexciton is larger than the one of the biexciton. (iii) A critical value of \( \alpha \) exists also for the triexciton; it is larger than \( \alpha_c (30) \) for the biexciton. It follows that triexcitons may exist without biexcitons (in the sense that \( E_b > 0 \)). We may suspect the same behaviour for the binding energy of \( n \)-string for any \( n \): the binding energy and the critical \( \alpha \) may be larger for a \( n \)-string than for a \( (n-1) \)-string in accordance with the results for the XXZ model. (iv) Since our result is variational, we get an upper bound for the triexciton binding energy so that our conclusions are qualitatively correct.

To illustrate the behaviour of the binding energy of a \( n \)-string at strong \( \alpha \), we study this limit perturbatively. For \( \alpha >> V \), the Hilbert space of (34) is naturally separated in two subspaces: the first, lower in energy, with configurations without \( A \) particles and, the second, higher in energy, with configurations with at least one \( A \) particle. The first one is associated with the projector \( P_0 \), the second one with the projector \( P_\eta \) \((P_0 + P_\eta = 1)\). The Hamiltonian may be written as

\[
H = P_0 HP_0 + P_\eta HP_\eta + P_0 HP_\eta + P_\eta HP_0
\]  
(55)
By a Schrieffer-Wolf type of canonical transformation \[32,33\], we want to derive an effective Hamiltonian \( \tilde{H} = P_0 H P_0 + P_\eta H P_\eta + \hat{W} \), with \( P_0 \tilde{H} P_0 = 0 \), \( \hat{W} \) being the effective term to be determined. The study of the \( n \)-excitonic strings will then be performed by diagonalizing the projection of this model into the space without \( A \) particle, \( H_{eff} = P_0 \tilde{H} P_0 \). Introducing the unitary transformation \( U = e^S \) (with \( S^\dagger = -S \)), and following the method described in detail in \[33\], we found the simple effective Hamiltonian valid in the strong coupling limit where \( \alpha >> V \), at second order in \( \frac{V}{\alpha} \)

\[
H_{eff} = (\omega_0 - \alpha) \sum_n B_n^d B_n - 2J \sum_n \frac{1}{2}(B_n^d B_{n+1} + h.c.) - \frac{V^2}{4\alpha} \sum_n B_n^d B_n B_{n+2}^d B_{n+2}
\] (56)

We have recovered, once again, the spin-1/2 XXZ Hamiltonian \[37\]. However, the anisotropic parameter is now given by \( \Delta = \frac{V^2}{8aJ} \), instead of \( \frac{V}{2J} \), and the interpretation of the spin operators is different: \( S_n^z = +\frac{1}{2} \) is still for a site without any particle but, \( S_n^z = -\frac{1}{2} \), is now for a site occupied by a \( B \) particle instead of a \( R \) particle.

In the effective model, the attractive interaction is reduced by the \( \alpha \) term and, for the strong limit \((\alpha >> V)\) where this derivation is valid, one reaches a XX-Heisenberg Hamiltonian which is well known to be equivalent to a spinless free fermion system \[34\]. Hence, in this limit, the excitonic strings do not exist which is consistent with the results of our variational calculation for \( \alpha > \alpha_c \). The states with free \( B \) particles are then preferred.

VI. CONCLUSION

In this paper, we propose a simplified model to describe excitonic strings in quasi-one dimensional organic compounds including organic Charge Transfer solids, \( J- \) and \( H \)-aggregates and Conjugated Polymers. For all these compounds, the excitonic states are characterized by small radius. Hence, our model starts with the definition of Hard Core Boson particles extended over one bond which describe, in an effective way, the excitons in one dimensional organic compounds.

There are two possibilities in one dimension to place the electron and the hole, the two elementary constituents of an exciton. Either the electron is on the right or on the left of the
hole; we introduce two kinds of HCB which illustrate these two situations: the Right-bosons and the Left-bosons.

The proposed model in terms of these effective particles contains four terms: the excitonic energy ($\omega_0$), which separate in energy the space with $n$ particles from the space with $n - 1$ particles; the kinetic energy of the HCB ($J$); the local interaction between the two species of bosons ($\alpha$), which illustrates the fact that there exist effective interactions which can exchange the relative position of the hole and the electron of an exciton; and last, the interaction between two excitons which are attractive between particles of the same species and repulsive between particles of opposite species (interaction of intensity $V$). The kinetic energy and the $\alpha$-interaction combined with the repulsive two body interaction act against the attractive two body interaction - they tend to delocalize the excitons on the contrary to the two particle attraction which tends to create bound states. The cases with two and three particles are mainly studied in this work. We summarize briefly our results considering the case where $Q$, the momentum of the center of mass of the excitonic complexes, is zero.

The case with two particles is solved exactly. For $\alpha = 0$, biexcitonic states exist if $\frac{V}{2J} > 1$. Then, the intensity of the transition from the one exciton state decreases dramatically with the increase of the binding energy, to saturate and become independent of the system size. This behaviour makes the biexcitonic state difficult to observe at the thermodynamic limit. For $\alpha \neq 0$, a critical value $\alpha_c$ is found, above which biexcitonic states do not exist. Otherwise, the behaviour of the oscillator strength remains qualitatively unchanged.

For $\alpha = 0$, the $n$ particle case can be solved in the low energy sector. Then, the model is equivalent to the spin one half XXZ Heisenberg model which is exactly solvable in one dimension. For $\frac{V}{2J} > 1$, it is well known that $n$-excitonic strings exist with a binding energy which increases with $n$ [28, 31]. For $\alpha \neq 0$, the model is non-integrable. The three particle case is then studied using a variational ansatz, which may be extended to a more general case with $n$ particles. Again, a 3-string is found with a binding energy larger than the one for the biexciton. We also found a critical value for $\alpha$, larger than the $\alpha_c$ valid for the 2-strings.

From numerical studies on small clusters [4], it has been argued that $n$-strings may exist
for any value of $n$ in organic compounds. Our work gives some confidence to this statement. Indeed, with our HCB Hamiltonian, if biexcitons exist, triexcitons will exist with a larger binding energy; moreover, if $\alpha = 0$, $n$-strings will also exist with binding energies which increase with $n$ and, we believe, from our present results, that it will also be the case for $\alpha \neq 0$.

The next important question concerning the $n$-string peaks in PA and TPA experiments, is fully clarified for the biexciton (the most important case) and confirms some conclusions of previous works [3,8,13,16]. The intensity of the transition from the one exciton to the biexciton decreases with the binding energy and, for sufficient binding energy, becomes independent of the system size. Hence, the PA intensity to the biexciton is proportional to $\sqrt{N}$ instead of $N$ for the two free exciton case. This property comes from the fact that the two excitons are tightly bounded within the complex, rendering the 2-string states difficult to observe for infinite systems (clean samples are needed) and more accessible experimentally for small oligomers [5,10].

In the case of Conjugated Polymers, we think some additional studies are needed going in two different directions. First, in the context of PA experiments, excitations extended over two molecules have been invoked [8,35]; extension of our work to two dimensions or, at least, for two coupled polymers would be suitable. Second, Conjugated Polymers are disordered systems with several possible sources of disorder which result, in practice, in the vague definition of the so-called conjugation length [8]. As we have already mentioned, since the transitions to biexcitons are much less intense than the ones involving two free excitons, we may expect at first analyse - and it was implicitly our point of view all along this manuscript - that a sufficient disorder will render the biexcitons not observable. However, some relatively recent results about the two interacting particle problem in a disordered medium [36] show very unexpected behaviours which may have dramatic consequences for our problem, and possibly in a way reverse to our intuition. In the light of the intriguing results of [36], the effects of disorder on transition moments should be clarified for a correct interpretation of PA and TPA results. We leave these considerations to further works.
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FIGURES

a) \[ n \quad n+1 \]

b) \[ n \quad n+1 \]

FIG. 1. Pictures for a) Right-bosons and b) Left-bosons. The arrows show the position of the electron, the hole being on the other side.

FIG. 2. Intensity of the one exciton-biexciton transition for N=100 (full line) and at the thermodynamic limit (dashed line) as a function of \( \lambda = \frac{2J}{V} (\alpha = 0, Q = 0) \)
FIG. 3. Normalized transition moment for the one exciton - 2 exciton transitions for a finite cluster (N=10), $\Delta = 3.33$ and $\beta = 0.2$. BE (Bound Excitons) is the biexcitonic peak; FE (Free Excitons) is the more intense peak due to two free excitons. At the thermodynamic limit, only FE will survive, slightly shifted toward the low energies.

FIG. 4. Negative of the binding energies for the bi- and tri-excitons for $\Delta = 3.33$ in function of $\beta = \frac{4}{J} (Q = 0)$