Numerical study of absorption spectra of Frenkel excitons in two-dimensional disordered lattices with long-range dipole–dipole interaction

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Abstract

We consider two-dimensional arrays of two-level molecules whose excited states are described by Frenkel excitons. Local dipole moments are assumed to be perpendicular to the system plane so that intersite interaction depends only on the distance between far neighbors. We consider Gaussian randomness in the molecular positions and numerically determine the optical absorption line shape of finite random lattices with different degrees of disorder. Results are compared to those obtained within the framework of the nearest-neighbor approximation. © 1999 Published by Elsevier Science B.V. All rights reserved.

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1. Introduction

The concept of Frenkel exciton has been successfully applied in the study of optical properties of one-dimensional (1D) molecular J-aggregates of cyanine dyes (see Refs. [1,2] and references therein). Optical properties of two-dimensional (2D) systems comprised of cyanine dyes were also interpreted in terms of 2D Frenkel excitons [3–6]. Theoretical approaches often consider the nearest-neighbor (NN) approximation but it has been found that coupling to far neighbors originates remarkable effects on 1D Frenkel exciton states [4,7–10]. Simple geometrical considerations suggest that even stronger effects should be expected in 2D systems, as we will show below. To this end, we will focus on 2D arrays of two-level molecules whose excited states are described by Frenkel excitons. We assume that disorder arises from randomness in the positions of molecules and keep the long-range dipole–dipole terms as well.

2. One-exciton absorption spectra

Let us consider a 2D array of $\mathcal{N} = N \times N$ optically active molecules whose positions are r_n around a regular 2D square lattice with spacing

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unity. Each molecule has two levels, the transition energy between them we set to zero for all the molecules of the array. The effective Frenkel Hamiltonian describing this system can be then written as follows:

$$\mathcal{H} = \sum_{m \neq n} J_{nm} \, a_n^\dagger \, a_m, \qquad (1)$$

where $a_n^\dagger$ and a_n represent creation and annihilation operators of excitons at site $\boldsymbol{n}$ and J_{nm} stands for the dipolar coupling between two different molecules located at $\boldsymbol{r}_n$ and $\boldsymbol{r}_m$.

We assume that dipoles are equal and perpendicular to the plane of the 2D regular lattice so that the intersite interaction is found to be of the form $J_{nm} = J/|\boldsymbol{r}_n - \boldsymbol{r}_m|^3$, where $J > 0$ is the coupling between NN centers in the regular lattice. At $J < 0$, the state coupled to the light lies at the top of the one-exciton band (similar to that one gets for H-aggregates). The exciton–phonon coupling is neglected in this paper.

Now we consider an optical process in which an exciton is created after a very short pulse excitation. We restrict ourselves to those systems whose typical size is much smaller than the optical wavelength. To evaluate the optical absorption line shape, $I(E)$, as a function of the energy we must consider the total dipole moment operator $\mathcal{D} = \sum_n (a_n^\dagger + a_n)$, where the dipole moment of each molecule is taken to be unity [11]. The line shape is then given by

$$I(E) = \frac{1}{\mathcal{N}} \sum_k |\langle k|\mathcal{D}|\mathrm{vac}\rangle|^2 \frac{\alpha}{\pi} \frac{1}{\alpha^2 + (E - E_k)^2}, \qquad (2)$$

where $|\mathrm{vac}\rangle$ is the exciton vacuum. The sum runs over all the $\mathcal{N}$ eigenstates $|k\rangle$ of the Hamiltonian (1), E_k denotes their corresponding eigenvalues and the Lorentzian function accounts for finite instrumental resolution or any other source of homogeneous broadening. Replacing the Lorentzian function by $(1/\pi)\mathrm{Re}\int_0^\infty \mathrm{d}t \exp[-\alpha t + i(E - E_k)t]$ we arrive at

$$I(E) = \frac{1}{\pi \mathcal{N}} \mathrm{Re} \left[\int_0^\infty \mathrm{d}t \, e^{-\alpha t + iEt} \sum_n G_n(t) \right]. \qquad (3)$$

Here, we have introduced the Green's function $G_n(t)$ according to Ref. [11]. This function obeys the

equation of motion

$$i \frac{\mathrm{d}}{\mathrm{d}t} G_n(t) = \sum_{m \neq n} J_{nm} G_m(t). \qquad (4)$$

Initial conditions read $G_n(0) = 1$ and free-end boundary conditions are used. The microscopic equation of motion is a 2D discrete Schrödinger-like equation on a lattice and standard numerical techniques may be applied to obtain the solution. Once the equation of motion is solved, the line shape is found from Eq. (3).

3. Periodic lattice

In this section we discuss the case of a periodic lattice where molecules are placed over regular lattice points. Thus $\boldsymbol{r}_n = \boldsymbol{n}$, with $\boldsymbol{n} = (n_x, n_y)$, n_x and n_y being integers. The microscopic equation of motion (4) can be solved by means of the Fourier transform

$$G_n(t) = \sum_{k \in \mathrm{BZ}} e^{ik \cdot n} G_k(t), \qquad (5)$$

where BZ refers to the first Brillouin zone, that is, $\boldsymbol{k} = (2\pi/N)(k_x, k_y)$ with $-N/2 < k_x, k_y \leq N/2$. The calculation is straightforward and yields

$$G_n(t) = \exp(-iE_{k=0}\, t), \qquad (6)$$

where the exciton dispersion relation is given by

$$E_k = J \sum_{n \neq 0} \frac{1}{|\boldsymbol{n}|^3} e^{ik \cdot n}. \qquad (7)$$

After inserting Eq. (6) in Eq. (3) the one-exciton absorption spectrum is found to consist of a single line centered at the energy $E_{k=0} = J\mathscr{F}$ where $\mathscr{F} = \sum_n |\boldsymbol{n}|^{-3} \simeq 9.03$. As it was found in Ref. [12], at $|\boldsymbol{k}| \ll 1$ Eq. (7) reduces to

$$E_k \simeq 9.03J - 2\pi J|\boldsymbol{k}|. \qquad (8)$$

Therefore, the exact exciton energy E_k scales linearly as $\boldsymbol{k}$, namely as N^{-1}, close to the top of the exciton band. This behavior is rather different than that obtained in the NN approximation, which yields the parabolic spectrum $E_k \simeq 4J - J\boldsymbol{k}^2$.

4. Disordered lattice

We assume that molecular positions are Gaussian distributed around regular lattice sites with probability distribution

$$P(\xi_n) = \frac{1}{2\pi\sigma^2} \exp\left(-\frac{\xi_n^2}{2\sigma^2}\right), \qquad (9)$$

where $\xi_n = r_n - n$ and $n = (n_x, n_y)$ with $0 \leq n_x$, $n_y \leq N$ being integers.

4.1. Effective medium approximation

For a small degree of disorder, the effective medium approximation (EMA) consists simply of making the average over the realizations of disorder directly in Eq. (4) and replacing $\langle \sum_m |r_n - r_m|^{-3} G_m(t) \rangle$ by $\langle \sum_m |r_n - r_m|^{-3} \rangle \langle G_m(t) \rangle$. Then one obtains the following equation of motion for the averaged Green function

$$i\frac{d}{dt}\langle G(t)\rangle = J\langle G(t)\rangle \sum_m \left\langle \frac{1}{|r_n - r_m|^3} \right\rangle. \qquad (10)$$

Expanding $|r_n - r_m|^{-3}$ in the Taylor series up to ξ^4 we obtain the shift of the optical absorption line

$$E(\sigma) - E(\sigma = 0) \simeq J(45.81\sigma^2 + 497.60\sigma^4), \qquad (11)$$

for a 2D dipolar exciton.

5. Numerical results

We have numerically solved (4) for finite lattices using the fourth-order Runge–Kutta method for the cases of ordered and disordered lattices. The calculations have been carried out choosing $J = 1$ and $\alpha = 0.15$. The maximum integration time was 50 in these units and the number of time steps was 4000.

Fig. 1 shows the absorption spectra for ordered lattices of different sizes, indicated on each plot, up to 100×100. The main absorption line is blue-shifted on increasing the lattice size and its position progressively approaches 9.03, as expected. The energy shift between the main line of the infinite lattice and the main line of the $N \times N$ lattice scales as $\sim N^{-1}$, as predicted in Eq. (8). In addition, we
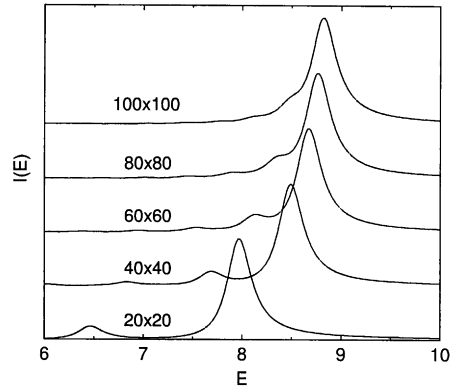

Fig. 1. Absorption spectra in arbitrary units for finite ordered 2D lattices of different sizes.
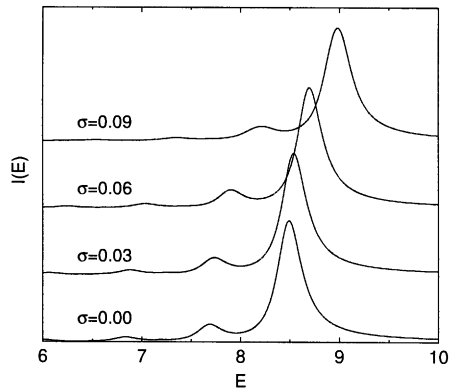

Fig. 2. Absorption spectra in arbitrary units for 40×40 disordered lattices.

observe the occurrence of well-defined and equidistant satellite lines in the low-energy region of the spectra, which we relate to the transitions to the lower exciton states having oscillator strengths smaller than the main transition (to the top band state), similar to what occurs for a finite linear chain (see, for instance, Ref. [7]).

Fig. 2 shows the absorption spectra of 40×40 disordered lattices (obtained by averaging over 10 realizations of the disorder) for different values of σ, when dipole–dipole interaction between different sites is taken into account. Notice that within the range $\sigma \leq 0.09$, both the main line and satellites are present in the absorption spectra, blue-shifting
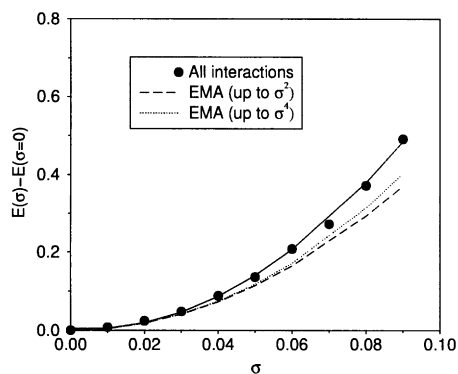
Fig. 3. Shift in energy of the main absorption line versus σ when dipole–dipole interaction between different sites is taken into account. Solid line is the result of quadratic fit.

upon increasing σ, however, without noticible changes of their relative positions. Besides, the peak broadening are determined by the artificial width α and not by disorder. All the peculiarities found unambigiously mean that the system we are dealing with correspond rather to the perturbative limit of disorder, unlike it occurs in a 1D exciton system under similar conditions [4,7].

Fig. 3 compares the shift of the main line obtained numerically with the EMA prediction given in Eq. (11). We see that EMA works very well for $\sigma \leq 0.03$ but underestimates the value of the shift for stronger disorder. This is to be expected since we assumed that σ was small to arrive at Eq. (11).

6. Summary

We have found that long-range dipolar coupling has noticeable effects on the one-exciton absorption spectra of 2D lattices. Periodic lattices manifest a single-absorption line whereas finite lattices also present satellite lines in the low-energy region (for positive intersite coupling) originating of the finite size effect. These satellite lines are equally spaced due to the linear behavior of the exciton eigenenergy spectrum near the top of the band. This is to be compared to the parabolic behavior

obtained in ordered lattices within the NN approximation. The main peak is blue-shifted approximately two-times more as compared to that arising in the NN approximation. Introducing a Gaussian positional disorder yields a blue shift of both the main peak of the exciton absorption spectrum and satellite lines without noticeable changes of their relative positions (within the range of standard deviation of positions $\sigma \leq 0.09$). The shift obeys a polynomial biquadratic law with respect to σ and reasonably well fits that determined numerically.

Acknowledgements

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