Brief Reports

Frenkel excitons in random systems with correlated Gaussian disorder

F. Domínguez-Adame

Departamento de Física de Materiales, Facultad de Físicas, Universidad Complutense, E-28040 Madrid, Spain

(Received 5 December 1994)

Optical-absorption spectra of Frenkel excitons in random one-dimensional systems are presented. Two models of inhomogeneous broadening, arising from a Gaussian distribution of on-site energies, are considered. In one case the on-site energies are uncorrelated variables whereas in the second model the on-site energies are pairwise correlated (dimers). We observe a red shift and a broadening of the absorption line on increasing the width of the Gaussian distribution. In the two cases we find that the shift is the same, within our numerical accuracy, whereas the broadening is larger when dimers are introduced. The increase of the width of the Gaussian distribution leads to larger differences between uncorrelated and correlated disordered models. We suggest that this higher broadening is due to stronger scattering effects from dimers.

I. INTRODUCTION

Recently, several researchers have shown that structural *correlated disorder* has profound effects in random systems and produces a variety of unexpected phenomena. It is by now well known that a band of delocalized electrons appears in tight-binding Hamiltonians with correlated diagonal and/or off-diagonal elements.[1-5] A more dramatic occurrence of electron delocalization arises in continuous models with dimer impurities as well as in disordered semiconductor superlattices with dimer quantum wells, where there exist infinitely many bands of delocalized states.[6-8] What is most important, delocalization by correlation is not restricted to electrons, as suggested by the occurrence of delocalized vibrations in classical random chains with paired disorder.[9,10] Furthermore, time-domain analysis of Frenkel excitons in systems with traps randomly placed in an otherwise perfect lattice shows that the coherent quantum transport is also affected by pairing of these traps, but trapping is less effective as compared to systems with the same fraction of unpaired traps.[11]

Roughly speaking, correlated disorder seems to retain some of those special features characterizing periodic systems; in other words, there exists a competition betweeen short-range correlation and long-range disorder leading, for instance, to delocalization of electrons and phonons or to the occurrence of a major contribution of the slowly decaying modes in exciton trapping processes, as mentioned above. However, in this paper we point out that this conjecture is not always valid. In particular, we consider optical absorption of Frenkel excitons in unpaired as well as in paired disordered models, focusing our attention on inhomogeneous broadening due to a Gaussian distribution of on-site energies in a one-dimensional lattice. We show that inhomogeneous broadening is enhanced when structural correlations arise since exciton scattering from dimers is stronger as compared to scattering from unpaired sites.

II. MODEL

We consider N optically active centers in a regular lattice with spacing unity. For our present purposes, we neglect all thermal degrees of freedom (electron-phonon coupling and local lattice distortions). Therefore, the effective Hamiltonian for the Frenkel-exciton problem can be written in the tight-binding form with nearest-neighbor interactions as follows (we use units such that $\hbar = 1$):

$$\mathcal{H} = \sum_k \epsilon_k a_k^\dagger a_k + T \sum_k (a_k^\dagger a_{k+1} + a_{k+1}^\dagger a_k), \quad (1)$$

where a_k and $a_k^\dagger$ are Bose operators creating or annihilating an electronic excitation of on-site energy ϵ_k. Here T is the nearest-neighbor coupling, which is assumed to be constant in the whole lattice. On-site energies are subject to diagonal disorder representing inhomogeneous broadening, for which a Gaussian distribution is the proper theoretical approximation. In what follows we consider two different models, namely uncorrelated and correlated disordered systems. This enables us to separate the effects merely due to optical absorption in one-dimension from those which manifest the peculiarities of the correlation between random parameters. The first model can be drawn from the distribution[12,13]

$$P(\epsilon_k, \bar{\epsilon}, \sigma) = \frac{1}{\sqrt{2\pi\sigma^2}} \exp\left[-\frac{(\epsilon_k - \bar{\epsilon})^2}{2\sigma^2}\right], \quad (2)$$

   <u>51</u>   12 801

with average $\bar{\epsilon}$ and width σ. It is important to stress that neighbor on-site energies are uncorrelated random variables. On the other side, to build up our correlated disordered model, we choose ϵ_{2k-1} according to the Gaussian distribution given in (2) and then take $\epsilon_{2k} = \epsilon_{2k-1}$. This step is repeated at every odd site of the lattice, hence leading to a set of paired correlated on-site energies (dimers).

Having presented our model we now describe the method we have used to calculate the absorption spectra. The line shape $I(E)$ of optical absorption in which a single exciton is created after pulse excitation in a lattice with N sites can be obtained as follows:[12]

$$I(E) = -\frac{2}{\pi N} \int_0^\infty dt \, e^{-\alpha t} \sin(Et) \, \text{Im} \left(\sum_k G_k(t) \right),$$
(3)

where the factor $\exp(-\alpha t)$ takes into account the broadening due to the Lorentzian instrumental resolution function of half-width α. Hence the resulting spectra are the convolution of the inhomogeneous broadening due to Gaussian disorder and the instrumental resolution function. The correlation functions $G_k(t)$ obey the equation of motion

$$i\frac{d}{dt}G_k(t) = \sum_j H_{kj}G_j(t),$$
(4)

with $H_{kj} = \epsilon_k \delta_{kj} + (1 - \delta_{kj})T$ with $j = k - 1, k, k + 1$, and initial condition $G_k(0) = 1$. Therefore, the computation of optical spectra reduces to solving the discrete Schrödinger-like equation (4) using standard numerical techniques.

III. NUMERICAL RESULTS AND DISCUSSIONS

We have solved the equation of motion (4) for chains of $N = 2\,000$ sites using an implicit integration scheme. In order to minimize end effects, spatial periodic boundary conditions are introduced. Energy will be measured in units of T whereas time will be expressed in units of T^{-1}. To make contact with experiments, we note that $|T|$ is proportional to the exciton bandwidth in the perfect lattice, so that energy and time scales can be deduced from experimental data. Since we are mainly interested in the comparison between uncorrelated and correlated disordered models rather than in the effects of the different parameters on the optical absorption process, we will fix the values of $\bar{\epsilon}$ and T focusing our attention on the width σ. In particular, we have set $\bar{\epsilon} = 4$ and $T = -1$ henceforth as representative values. The width of the instrumental resolution was $\alpha = 1/4$. The distribution width σ ranged from 0 up to 0.5.

In the absence of inhomogeneous broadening ($\sigma = 0$), the absorption line shape is a Lorentzian function centered at $E = \bar{\epsilon} + 2T$, which with our choice of parameters is $E = 2$. The full width at half maximum (FWHM) is 2α. For $\sigma \neq 0$ a broadening of this main line is observed accompanied by a shift of its position to lower energies on increasing σ, as shown in Fig. 1 for correlated as well as uncorrelated disorder. Unlike optical spectra
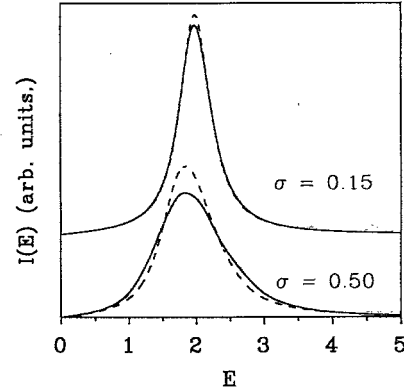

FIG. 1. Absorption spectra for one-dimensional random lattices with Gaussian distribution of correlated (solid lines) and uncorrelated (dashed lines) on-site energies with $\sigma = 0.15$ and $\sigma = 0.50$. Vertical scale is the same in all cases.

in random binary systems, where ϵ_k takes only two different unpaired[12] or paired[14] values, there are no signatures of satellites appearing in the high-energy region of the spectra, at least in the range of parameters we have considered. Only a long high-energy tail is observed on increasing σ.

From Fig. 1 several conclusions can be drawn. First, the shift to lower energies increases with increasing σ in both models. A similar shift is also found using the coherent potential approximation (CPA) but the CPA fails to predict its value correctly, bringing up a smaller shift than that observed in numerical simulations.[12] Second, this red shift is the same in both models for a given value of σ, within our numerical accuracy. Hence, we are led to the conclusion that the effects of correlation cannot be deduced from this shift. Third, and more important from an experimental viewpoint, there are substantial differences regarding the width of the optical spectra. In all cases we have studied we found that the FWHM is larger for correlated inhomogeneous broadening, and that the difference increases on increasing σ. This result is shown in Fig. 2, where it is seen that the FWHM is $2\alpha = 0.5$ close to $\sigma = 0$, as expected, but increases more
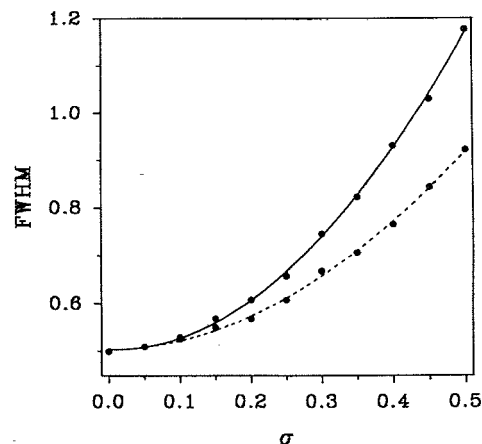

FIG. 2. Full width at half maximum (FWHM) as a function of σ for correlated (solid lines) and uncorrelated (dashed lines) disordered systems.

pronouncedly when correlation is present. This result is somewhat unexpected since it indicates that correlated Gaussian disorder disturbs exciton dynamics much more than uncorrelated disorder. This is to be compared with previous results on random systems with traps appearing as pairs in an otherwise perfect lattice, where pairing causes less disruption of Frenkel-exciton dynamics as compared to those systems without this constraint,[11] as mentioned in the Introduction. In particular, the depletion of the $q = 0$ exciton mode is slower when traps are paired. However, our present results suggest that in the case of inhomogeneous broadening the behavior is just the opposite, i.e., correlations create centers causing larger scattering effects on excitons. To validate or discard this suggestion we have evaluated the probability of finding an exciton in the $q = 0$ mode at time t after pulse excitation, obtained as follows:[15]

$$P(t) = \frac{1}{N^2} \left| \sum_k G_k(t) \right|^2 . \tag{5}$$

Figure 3 shows the results for $\sigma = 0.50$, although we have found similar behavior in all cases. From this figure we can see that $P(t)$ decays faster when correlations are present. Since in our system there is no trapping, the $q = 0$ mode is only depleted by disorder, thus indicating that scattering by dimers is more important than scattering by uncorrelated single sites. In this sense correlated systems are *more* disordered than uncorrelated ones, thus explaining the larger inhomogeneous broadening in the former systems.

Finally, let us comment that the CPA predicts a much smaller FWHM than that found by numerical integration in the case of inhomogeneous broadening in uncorrelated disordered lattices.[12] Therefore, the CPA failure is even more dramatic in the case of correlated disorder, strongly suggesting that future theoretical works should rely on different grounds. Probably, a *renormalization* of the lattice considering the dimer defect as a single entity, as much as in the line we have recently proposed in the case of trapping of classical excitons in correlated disordered systems,[16] could be a good starting theoretical scenario to fully account for optical spectra.
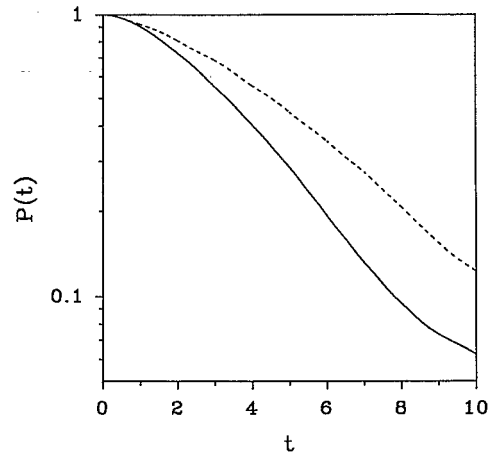

FIG. 3. Probability of finding an exciton in the $q = 0$ mode at time t for correlated (solid lines) and uncorrelated (dashed lines) disordered systems with $\sigma = 0.50$.

dom systems. Two different models have been considered; in both cases broadening arises from a Gaussian distribution of on-site energies. In uncorrelated disordered systems on-site energies are chosen according to the Gaussian distribution at every site, whereas in correlated disordered systems this selection is made only at odd sites and even sites take the value of the preceding site. Therefore, the correlation length is of the order of the lattice spacing. Our results show that the presence of structural correlations in random systems can be then readily determined from the analysis of the absorption spectra of these samples. By comparing the obtained spectra in both models we found an identical red shift of the absorption line while inhomogeneous broadening is more pronounced whenever correlations are present in the lattice. We have realized that the $q = 0$ mode is depleted faster in systems with correlated disorder, thus indicating stronger scattering effects from dimers. From a theoretical viewpoint, we have pointed out that CPA failures are even more noteworthy in the case of correlated disordered systems. Hence, the necessity of a new theoretical framework to deal with random systems with structural correlations becomes a very appealing task.

IV. CONCLUSIONS

In summary, we have studied the effects of inhomogeneous broadening on the absorption spectrum corresponding to the Frenkel-exciton Hamiltonian for ran-

[1] J. C. Flores, J. Phys. Condens. Matter **1**, 8471 (1989).

[2] D. H. Dunlap, H.-L. Wu, and P. Phillips, Phys. Rev. Lett. **65**, 88 (1990).

[3] H.-L. Wu and P. Phillips, Phys. Rev. Lett. **66**, 1366 (1991).

[4] P. Phillips and H.-L. Wu, Science **252**, 1805 (1991).

[5] J. C. Flores and M. Hilke, J. Phys. A **26**, L1255 (1993).

[6] A. Sánchez, E. Maciá, and F. Domínguez-Adame, Phys. Rev. B **49**, 147 (1994).

[7] E. Diez, A. Sánchez, and F. Domínguez-Adame, Phys. Rev. B **50**, 14 359 (1994).

[8] F. Domínguez-Adame, A. Sánchez, and E. Diez, Phys. Rev. B **50**, 17 736 (1994).

[9] F. Domínguez-Adame, E. Maciá, and A. Sánchez, Phys. Rev. B **48**, 6054 (1993).

[10] P. K. Datta and K. Kundu, J. Phys. Condens. Matter **6**, 4465 (1994).

[11] F. Domínguez-Adame, B. Méndez, A. Sánchez, and E. Maciá, Phys. Rev. B **49**, 3839 (1994).

[12] D. L. Huber and W. Y. Ching, Phys. Rev. B **39**, 8652 (1989).

[13] Th. Wagersreiter and H. F. Kauffmann, Phys. Rev. B **49**, 8655 (1994).

[14] F. Domínguez-Adame, E. Maciá, and A. Sánchez, Phys. Rev. B **50**, 6453 (1994).

[15] D. L. Huber and W. Y. Ching, Chem. Phys. **146**, 409 (1990).

[16] A. Sánchez, F. Domínguez-Adame, and E. Maciá, Phys. Rev. B **51**, 173 (1995).