

## Localization of exciton states in structurally disordered materials

A. Blumen, J. P. Lemaistre, and I. Mathlouthi

Citation: *The Journal of Chemical Physics* **81**, 4610 (1984); doi: 10.1063/1.447393

View online: <http://dx.doi.org/10.1063/1.447393>

View Table of Contents: <http://scitation.aip.org/content/aip/journal/jcp/81/10?ver=pdfcov>

Published by the [AIP Publishing](#)

---

### Articles you may be interested in

[Exciton localization in disordered poly\(3-hexylthiophene\)](#)

*J. Chem. Phys.* **133**, 044504 (2010); 10.1063/1.3459099

[Local exciton states at isoelectronic centers in superlattices](#)

*Low Temp. Phys.* **30**, 171 (2004); 10.1063/1.1645171

[Spatial structure of anomalously localized states in disordered conductors](#)

*J. Math. Phys.* **38**, 1888 (1997); 10.1063/1.531910

[Electronic structure of the disordered local moment state of facecentered cubic iron](#)

*J. Appl. Phys.* **61**, 3712 (1987); 10.1063/1.338669

[Effects of structural disorder on twoparticle exciton–phonon excitations in organic materials](#)

*J. Chem. Phys.* **77**, 2812 (1982); 10.1063/1.444171

---



# Localization of exciton states in structurally disordered materials

A. Blumen,<sup>a)</sup> J. P. Lemaistre, and I. Mathlouthi

Centre de Mécanique Ondulatoire Appliquée, 23, rue du Maroc, F-75019 Paris, France

(Received 16 July 1984; accepted 24 July 1984)

A comparative study of the influence of the structural disorder on the localization properties of exciton wave functions is presented. The localization behavior of exciton states is analyzed by means of the inverse participation ratio (IPR) and of related quantities. We have performed numerical, configurationally averaged calculations using short-ranged (exchange, octupolar) and long-ranged (dipolar) types of interactions and also including the diagonal disorder. We provide the density of states and the energy distribution of the IPR considering various trap concentrations and interactions which are typical for aromatic crystals like naphthalene.

## I. INTRODUCTION

In the last decades the problem of a transition between localized and delocalized quantum states in disordered systems has attracted considerable attention.<sup>1-3</sup> The question arises in many areas, ranging from electronic processes in noncrystalline materials<sup>4,5</sup> to energy transfer in matrix-isolated species and in mixed molecular crystals.<sup>6-8</sup>

In the classical Anderson-transition approach one focuses on the diagonal disorder which obtains when, on a periodic lattice, the site energies are stochastic variables. The off-diagonal disorder, when considered, is generally included by taking the coupling coefficients between nearest-neighbor sites to be independently distributed random variables. Only recent investigations have begun to unveil the important role of the *structural* inhomogeneities, and of their influence on the localization properties.<sup>8-13</sup> Structural disorder arises when active particles are randomly placed on an underlying lattice, thus creating random patterns. In this case, the off-diagonal terms are highly correlated, since the absence of an active particle from a site cuts off all interactions with that site. Furthermore, for a low occupancy of sites by particles (high disorder), restricting the interactions to nearest neighbors is not justified in general, since then longer-ranged, distance-dependent interactions become effective and should be accounted for.

The main parameters which determine the structural disorder are thus the concentration of particles and the range of the interparticle potential  $V(r)$ . In a former work,<sup>8</sup> in the following denoted by I, we have studied the localization of the eigenfunctions in a two-dimensional model for the triplet (exchange-dominated) excitonic states of naphthalene. In this work we extend our investigations to three-dimensional lattices and, in order to display the role of  $V(r)$ , we consider both exchange and also multipolar (dipolar and octupolar) interactions. Furthermore, we also perform calculations in which we include diagonal disorder. As will become obvious in the following, the off-diagonal structural disorder influences the localization properties in a very different way than the substitutional, uncorrelated, off-diagonal disorder. Thus, it is generally accepted that pure substitutional disorder

does not lead to localization<sup>3,9,14</sup>; on the other hand, the structural disorder localizes strongly (*vide infra* and Ref. 8). Also the joint effects of diagonal and structural disorder enhance the localization, whereas substitutional disorder acts rather delocalizing.<sup>9</sup>

As in I we focus on the properties of the *eigenfunctions* and do not address in this work the problem of the *transfer*. Note, however, that the existence of localized states does not exclude an efficient transfer between them, which is mediated by additional degrees of freedom, i.e., phonons, not considered here. As localization criterium for the eigenfunctions we use the inverse participation ratio (IPR)<sup>8-10,15</sup> and we establish numerically both the density of eigenstates and the distribution of IPR's as a function of energy. We found that the cumulative density of eigenstates  $\lambda(L)$  with a localization index (IPR) below a fixed value  $L$  is a particularly easy-to-view quantity; with its help the localization behavior and also the role of particle pairs (consisting of two, not necessarily nearest-neighbor particles) are readily displayed.

The paper is arranged as follows: In Sec. II we introduce the Hamiltonian and the interparticle interactions which will be considered. There we also define the IPR and its related quantities. Section III is devoted to the description of the numerical procedure and to the presentation and discussion of the numerical results.

## II. HAMILTONIAN AND EIGENSTATES

The starting point of our investigations is a regular lattice in which a fraction  $c$  of sites is occupied by active particles. Here we begin with a cubic arrangement of  $N$  sites. In a particular realization of the disordered system some  $M$  sites,  $M \simeq cN$ , are occupied. Note that  $M$  is a stochastic number, which depends on the realization. The total Hamiltonian for such a system of  $M$  interacting species is

$$H = \sum_i E_i |i\rangle \langle i| + \sum_{ij}' V(r_{ij}) |i\rangle \langle j|. \quad (1)$$

In Eq. (1) the summation runs over all the *occupied* lattice sites and  $r_{ij}$  are their mutual distances. As typical  $V(r_{ij})$  dependencies we have chosen both short-ranged (exchange and octupolar) as well as long-ranged (dipolar) interactions, namely

$$V(r) = V_0 \exp[-\alpha(r-1)] \quad (2a)$$

and

<sup>a)</sup> On leave from Lehrstuhl für Theoretische Chemie, Technische Universität München, D 8046 Garching, West Germany.

$$V(r) = V_0 r^{-s} \quad (s = 3 \text{ or } 7). \quad (2b)$$

Here  $r \equiv |\mathbf{r}|$  is expressed in lattice units and  $V_0$  is the interaction strength between nearest-neighbor particles. For simplicity we assume that the interactions are isotropic  $V(r) \equiv V(\mathbf{r})$ . The interactions of Eq. (2) occur often in molecular crystals, where Eq. (2a) is decisive in triplet energy transfer<sup>16</sup> and the Coulomb-type interactions, Eq. (2b) are common in the singlet case.<sup>17</sup>

In the absence of diagonal disorder  $E_i = E_0$ , and for simplicity we take  $E_0$  to be at the origin of the energy scale  $E_0 = 0$ . In the cases for which we include the diagonal disorder, we follow the Anderson-model's prescription<sup>1-3</sup> and take the  $E_i$  to be randomly and uniformly distributed in the interval  $[-W/2, +W/2]$  around the mean value  $E_0 = 0$ .

For a given configuration of interacting particles, the numerical procedure consists in the complete diagonalization of the Hamiltonian [Eq. (1)], thereby obtaining all eigenvalues  $E_k$  and eigenvectors  $|\Psi_k\rangle$ ,  $H|\Psi_k\rangle = E_k|\Psi_k\rangle$ . Here the index  $k$  denotes the different eigenstates, which in the local basis  $|i\rangle$  are

$$|\Psi_k\rangle = \sum_i C_i^k |i\rangle. \quad (3a)$$

The coefficients  $C_i^k$  fulfill the normalization requirement:

$$\sum_i |C_i^k|^2 = 1. \quad (3b)$$

The computed  $E_k$  values give the density of states (DOS). From the coefficients  $C_i^k$  we obtain readily the inverse participation ratio (IPR), defined through<sup>15</sup>

$$L_k \equiv \sum_i |C_i^k|^4. \quad (4)$$

The IPR is a commonly used localization criterium<sup>8-10,15</sup> which has the major advantage that it stresses the properties of the eigenfunctions of the Hamiltonian [Eq. (1)]. The name IPR derives from the fact that  $L_k$  is unity for a state localized on a single site only, and that  $L_k$  drops to  $1/n$  for a state evenly delocalized over  $n$  sites. From the evaluation of  $E_k$  we thus obtain, in addition to the DOS, the distribution of the IPR as a function of energy. Furthermore, we can also study the distribution of IPR's directly, by analyzing, as in I, the number of states  $n(L)dL$  whose  $L_k$  fulfill  $L < L_k \leq L + dL$ . An even more descriptive way of displaying this dependence is to consider  $\lambda(L)$  the cumulative density of eigenstates, whose IPR lie below  $L$ :

$$\lambda(L) = \int_0^L n(L') dL' / M. \quad (5)$$

In Sec. III we present examples for  $\lambda(L)$ .

### III. RESULTS AND DISCUSSION

In this section we evaluate numerically the IPR for several three-dimensional systems of randomly distributed particles. In view of the relevance for experimental systems<sup>6-8,16-19</sup> and for ready comparison to our two-dimensional analysis<sup>8</sup> we choose the interactions  $V(r)$  [Eq. (2)] to take values typical for aromatic crystals, such as naphthalene. For exchange interactions this specification is important, since the problem does not scale with distance<sup>10,17</sup>; for multipolar interactions and low concentrations  $c$  the prob-

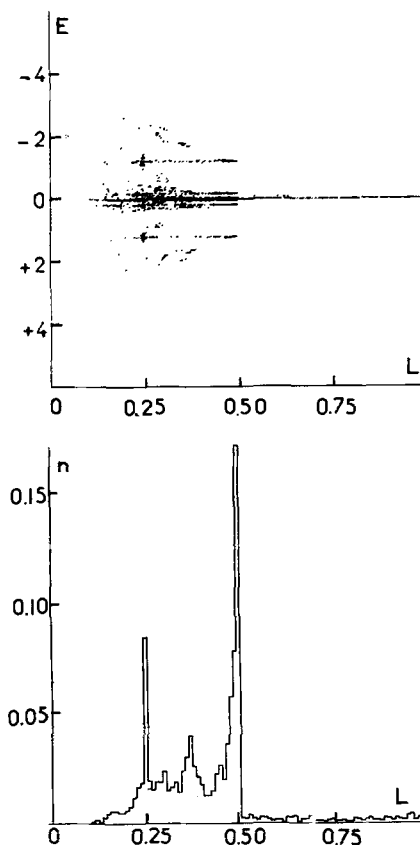


FIG. 1. The number density  $n$  of eigenstates (bottom) and their energy distribution (top) as a function of  $L$ . The particle concentration is  $c = 0.05$  and the interactions are exponential, Eq. (2a); the energy is expressed in units of  $V_0$ . Here we consider the off-diagonal disorder only. Displayed are the cumulative average results over 30 configurations.

lem scales,<sup>17</sup> so that the following results have a large range of validity. We take  $V_0 = 1.4 \text{ cm}^{-1}$  and  $\alpha = 4.6$  to describe the exchange (or superexchange) triplet interactions in naphthalene [Eq. (2a)]. A typical value for the nearest-neighbor singlet interactions is  $V_0 = 10 \text{ cm}^{-1}$  which has been used to scale the octupolar [Eq. (2b)] and the dipolar [Eq. (2c)] types of coupling.<sup>19</sup> The diagonal disorder, whenever introduced, has been expressed in units of  $V_0$  and we choose  $W/V_0 = 0.3$  for the three types of interactions involved. With the above values for nearest-neighbor interactions the value  $W/V_0 = 0.3$  corresponds to inhomogeneous linewidths of 0.42 and  $3 \text{ cm}^{-1}$ , consistent with the observed broadenings in phosphorescence and fluorescence spectra, respectively. We first evaluate the IPR by only considering the off-diagonal disorder; these results are then compared to those obtained by adding the diagonal disorder.

As a rule, we have taken the number of particles  $M$  to be around 100. For this we have fixed the finite lattice to be such that  $cN \approx 100$ . Evidently, the size of the system depends on  $c$ . By this procedure we differ from authors,<sup>10,20</sup> who diagonalize a *single* configuration of around 1000 particles: in order to exclude possible statistical fluctuations, we have settled for somewhat smaller systems, but we have performed all the calculations for 30 distinct configurations; the results for  $\lambda(L)$  are configurationally averaged.

In Fig. 1 we display the results of the diagonalization procedure. The calculation is based on 30 disordered distri-

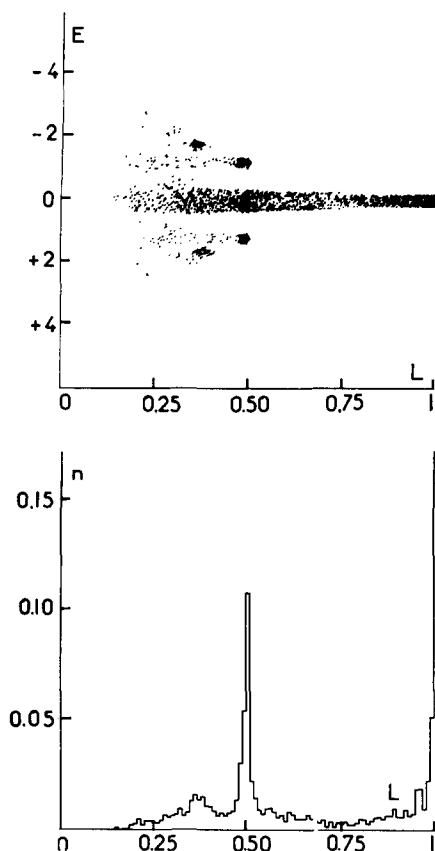


FIG. 2. Same as in Fig. 1 with a superimposed diagonal disorder.

butions of particles at the concentration  $c = 0.05$  on a cubic lattice. Here no diagonal disorder is involved and the interparticle interactions are of exchange-type. The upper part of the figure presents the distribution in energy of the localization indices  $L_k$ . As is evident, the projection on the energy axis of the  $L_k$  gives the density of states (DOS). We, however, concentrate here on the projection of the  $L$  axis, which is given as a histogram in the lower part of Fig. 1. Two features are remarkable: Firstly, there are practically no states with  $L_k < 0.1$  and very few states with  $0.1 < L_k < 0.2$ . Taking the somewhat arbitrary value  $1/5$  as boundary,<sup>10</sup> we may state that in our system most states are localized. Secondly, the figure shows a prominent peak around  $L_k = 0.5$ , which implies that in many cases two particles couple strongly with each other. From an analysis of the eigenfunctions (not presented here) we conclude that in many instances the particles of these pairs are *not* in a nearest-neighbor position.

The role of these pairs may be better visualized by also considering Fig. 2. The only difference between this figure and the previous one is the introduction of the diagonal disorder. On the energy axis the effect of the energetic disorder  $[-W/2, +W/2]$  is clearly visible in the broadening of the main DOS peak. Interestingly the diagonal disorder influences also the  $L_k$  histogram given in the lower part of Fig. 2. Now there are practically no states with  $L_k < 0.2$  and the peak at  $1.0$  gains in intensity at the detriment of the peak at  $0.5$ , the remaining states with  $L_k = 0.5$  being mainly the dimer states, i.e., pairs in nearest-neighbor position.

The diagonal disorder disrupts the perfect energetic resonance between all particles, which has a negative influence

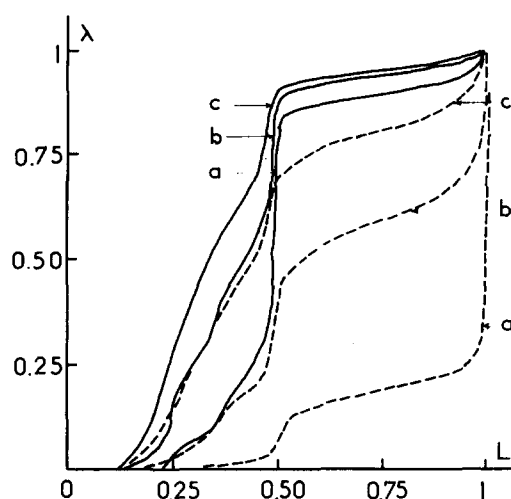


FIG. 3. Plot of  $\lambda(L)$  the relative number of eigenstates with a localization index less than  $L$  for exponential interactions at low concentrations;  $c = 0.01$  (a),  $c = 0.05$  (b),  $c = 0.1$  (c). These plots correspond to calculations performed in the absence (full lines) and in the presence (dotted lines) of diagonal disorder.

for the even delocalization on the pairs formed on distant sites. Note also that both the diagonal and the off-diagonal structural disorder favor the localization, and that their combined influence is cooperative. This contrasts with the findings for the off-diagonal substitutional disorder, which acts delocalizing.<sup>9,14</sup>

The histogram representations of Figs. 1 and 2 is very adequate for representing results for a given set of parameters:  $c$ ,  $W$ , and  $V(r)$ , and, as previously shown it also allows to perform configurational averages. However, this representation is less adequate in comparing data for different sets of parameters. For these we find it more convenient to plot the cumulative normalization distribution  $\lambda(L)$ , as given in Eq. (5). Mathematically, the two descriptions are equivalent, the density of localization indices (IPR) being the derivative of  $\lambda(L)$  with respect to  $L$ . As an example, we show in Fig. 3  $\lambda(L)$  for exponential interactions, for configurations in which  $c$  equals  $0.1$ ,  $0.05$ , and  $0.01$ . The figure allows us also to display the forms of  $\lambda(L)$  in the presence or absence of the diagonal disorder; the results are an average over 30 configurations. From Fig. 3 we infer that with increasing  $c$  the states become more and more delocalized. This finding is intuitively evident, since an increase in  $c$  corresponds to higher order; for  $c = 1.0$  the particle arrangement is perfectly ordered. We note however, that with a cutoff at  $L = 1/5$  we still view the states at  $c = 0.1$  to be localized. As in I, we find the tendency to delocalization to increase gradually with  $c$ . For all three values of  $c$  displayed, the inclusion of the diagonal disorder is dramatic and acts localizing. Comparing Fig. 3 to Fig. 2 of I, which gives the localization behavior for a two-dimensional system [the interaction  $V(r)$  is the same], we find that the states of the three-dimensional system are less localized than their counterparts in  $2D$ .

In Fig. 4 we compare the situation which arises when  $V(r)$ , the interaction type, changes. As concentration we have chosen  $c = 0.1$  and have plotted  $\lambda(L)$  for exchange, octupolar, and dipolar interactions, both in the presence and in the absence of diagonal disorder. We note that the exchange and

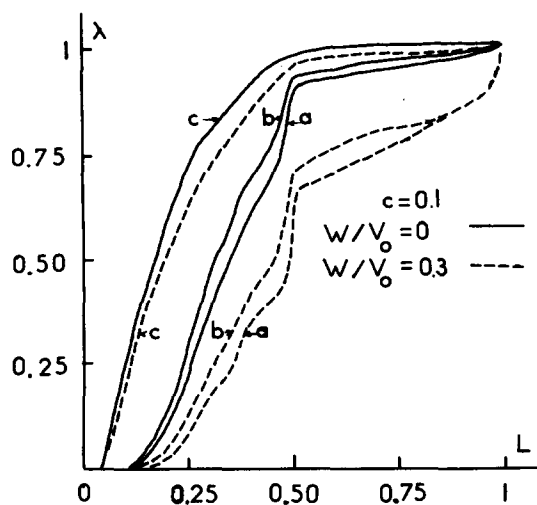


FIG. 4. Plot of  $\lambda(L)$  at the concentration  $c = 0.1$  for various types of interactions; exponential (a), octupolar (b), and dipolar (c). Full lines are for off-diagonal disorder only, while dotted lines account for both disorders.

octupolar interactions, both being short ranged, act similarly,<sup>17</sup> and for these most states are localized at  $c = 0.1$ . The octupolar interaction is intermediate between the exchange and the long-ranged dipolar interaction. Under the influence of the dipolar interactions the majority of the eigenstates have already at  $c = 0.1$  their IPR below 0.2. Another aspect worth mentioning is that the inclusion of the diagonal disorder is felt most strongly by states which are not very delocalized, whereas states delocalized over many sites are less influenced. Thus in Fig. 4 the shifts on  $\lambda(L)$  due to diagonal disorder are larger for the exchange and the octupolar than for the dipolar case.

In summary, we have presented a comparative study of the influence of the structural disorder on the localization properties of exciton wave functions, basic quantities in the

description of dynamical processes in disordered media. Here we have shown that direct numerical procedures are a very flexible means to analyze the properties of disordered systems under wide variations in the concentrations and interactions of the active particles.

## ACKNOWLEDGMENTS

The support of the Deutsche Forschungsgemeinschaft and of the Fonds der Chemischen Industrie is gratefully acknowledged.

- <sup>1</sup>P. W. Anderson, Phys. Rev. **109**, 1492 (1958).
- <sup>2</sup>D. J. Thouless, in *Ill-Condensed Matter*, edited by R. Balian, R. Maynard, and G. Toulouse (North-Holland, Amsterdam, 1979), p. 1.
- <sup>3</sup>*Anderson Localization*, edited by Y. Nagaoka and H. Fukuyama (Springer, Berlin, 1982).
- <sup>4</sup>N. F. Mott and E. A. Davis, *Electronic Processes in Non-Crystalline Materials*, 2nd ed. (Clarendon, Oxford, 1979).
- <sup>5</sup>E. N. Economou, *Green's Functions in Quantum Physics*, 2nd ed. (Springer, Berlin, 1983).
- <sup>6</sup>A. H. Francis and R. Kopelman, *Laser Spectroscopy of Solids*, edited by W. M. Yen and P. M. Selzer (Springer, Berlin, 1981), p. 241.
- <sup>7</sup>J. Klafter and J. Jortner, J. Chem. Phys. **71**, 2210 (1979).
- <sup>8</sup>J. P. Lemaistre and A. Blumen, Chem. Phys. Lett. **99**, 291 (1983).
- <sup>9</sup>F. Yonezawa, J. Non-Cryst. Solids **35/36**, 29 (1980).
- <sup>10</sup>W. Y. Ching and D. L. Huber, Phys. Rev. B **25**, 1096 (1982); **26**, 5596 (1982).
- <sup>11</sup>S. Stafström, R. Ricklund, and K. A. Chao, Phys. Rev. B **27**, 6158 (1983).
- <sup>12</sup>S. N. Evangelou, Phys. Rev. B **27**, 1397 (1983).
- <sup>13</sup>R. Raghavan, Phys. Rev. B **29**, 748 (1984).
- <sup>14</sup>P. D. Antoniou and E. N. Economou, Phys. Rev. B **16**, 3768 (1977).
- <sup>15</sup>P. Dean, Proc. Phys. Soc. London **73**, 413 (1959); Proc. Phys. Soc. London Ser. A **254**, 507 (1960); Rev. Mod. Phys. **44**, 127 (1972).
- <sup>16</sup>Ph. Pee, R. Brown, F. Dupuy, Ph. Kottis, and J. P. Lemaistre, Chem. Phys. **35**, 429 (1978).
- <sup>17</sup>A. Blumen and R. Silbey, J. Chem. Phys. **70**, 3707 (1979).
- <sup>18</sup>J. P. Lemaistre, A. Blumen, F. Dupuy, Ph. Pee, R. Brown, and Ph. Kottis, J. Phys. Chem. (to be published).
- <sup>19</sup>I. Mathlouthi, Thesis, Paris VI, 1984.
- <sup>20</sup>J. Canisius and J. L. van Hemmen, Phys. Rev. Lett. **46**, 1487 (1981).