

## Exciton energy disorder in polar amorphous organic thin films: Monte Carlo calculations

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We report on Monte Carlo calculations of the exciton energy level disorder in polar amorphous organic solids arising from electrostatic interactions between polarizable molecular charge distributions. In contrast to previous reports in which the discrete molecular polarizabilities are modeled as a dielectric continuum having dielectric constant  $\epsilon$ , our calculations take account of the molecular-scale polarization inhomogeneity. We demonstrate that exciton energy level disorder is only weakly dependent on  $\epsilon$ . For a range of  $\epsilon$  typical of organic solids, we report an empirical expression for the energy level disorder, and show that conventional dielectric continuum models are not consistent with the observed results. Results of our calculations are shown to be consistent with experimental measurements of exciton energy disorder in aluminum tris-(8-hydroxyquinoline).

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Over the last 20 years a wide variety of organic optoelectronic devices have been developed, including light emitting devices,<sup>1,2</sup> solar cells,<sup>3</sup> and photodetectors.<sup>3</sup> The operating performance of these structures is primarily governed by the behavior of bound electron-hole pairs known as excitons, which highlight the study of exciton physics of amorphous organic thin films as both technologically and scientifically significant. The physical disorder in amorphous organic solids generates disorder in exciton state energies, and the distribution of these energies, also known as the density of states (DOS), affects bulk absorption/emission spectra and exciton diffusion in amorphous organic solids (see, e.g., Refs. 4–7). For this reason, the calculation of the exciton DOS is of critical importance to the understanding of the optoelectronic behavior of organic solids.

In previous reports of exciton DOS calculations, the focus has been on nonpolar materials in which van der Waals or Lennard-Jones interactions (known collectively as “dispersion” interactions) are assumed to dominate (e.g., Ref. 8). In polar amorphous organic solids, however, the energy disorder is dominated by interactions between randomly oriented static dipoles, and this type of DOS has received comparatively little attention in the literature. To our knowledge the only significant treatment is due to Kador,<sup>4</sup> who reports approximate results assuming nonpolarizable molecules (i.e., a dielectric constant,  $\epsilon$ , of 1) based on an analytic approach known as the “statistical” method.<sup>9</sup> There are no reports of Monte Carlo DOS calculations (in which interactions between a discrete lattice of molecular sites are explicitly evaluated) applicable to general polar amorphous organic solids, and consequently the approximate results reported by Kador lack independent verification.<sup>10</sup> More importantly, there are no reports, using either statistical or Monte Carlo (MC) methods, of the impact of molecular polarization on the energy disorder, and thus it is not clear from existing literature to what extent  $\epsilon$  alters the excitonic DOS. Such calculations can enhance our understanding of the material factors controlling organic optoelectronic device performance and can also demonstrate the impact of polarization on local fields and interaction energies in organic solids.

In this Rapid Communication we report on Monte Carlo calculations of exciton energy disorder applicable to polar amorphous organic materials in which the molecular charge distributions are explicitly polarizable.<sup>11</sup> For nonpolarizable molecules, we find that the results reported by Kador are consistent with our calculations in the “Gaussian” limit. For polarizable molecules with polarizabilities typical of organic solids having  $\epsilon$  between 2 and 4, the exciton energy disorder is only weakly affected by molecular polarization, and we report an empirical expression for this dependence. Finally, we compare our results with the predictions of standard dielectric continuum models (DCMs), in which the individual molecular polarizabilities are replaced by a continuous dielectric, and find that such DCMs inadequately describe our MC results.

In obtaining the exciton DOS, we calculate the total electrostatic interaction energy,  $E^{int}$ , of a particular molecular system before and after introducing an exciton on one molecule in the system. The energy required to form this exciton state within the system is then given by the sum of the change in the total electrostatic interaction energy,  $\Delta E^{int}$ , and the change in the internal electronic energy,  $\Delta E_0$ , of the excited molecule. Assuming the molecules in the system are all of the same type,  $\Delta E_0$  is a constant for every molecule, and the shape of the DOS is entirely determined by the distribution of  $\Delta E^{int}$  values. To calculate  $\Delta E^{int}$ , we use conventional methods to model polar molecular charge distributions: each molecule is described by a point dipole moment,  $\mu$ , and to simulate molecular polarization, the total dipole moment includes an induced dipole moment of  $\alpha \vec{F}$  where  $\alpha$  is the molecular polarizability (assumed for simplicity to be isotropic) and  $\vec{F}$  is the local field at the site of the molecule. (In this calculation we assume electrostatic interactions between excitons are negligible, as appropriate for exciton densities at most typical device conditions.) Thus here the sole impact of introducing the exciton state is to change the static dipole moment of the excited molecule.

For a system of  $N$  molecules,  $E^{int}$  is given by

$$E^{int} = - \sum_{i=1, j>i}^N \vec{p}_i \cdot \frac{3(\vec{p}_j \cdot \hat{r}_{ij})\hat{r}_{ij} - \vec{p}_j}{r_{ij}^3} + \sum_{i=1}^N \frac{\alpha_i F_i^2}{2}, \quad (1)$$

where  $\vec{F}_i$ ,  $\alpha_i$ ,  $\vec{p}_i$ , and  $\vec{r}_i$  are, respectively, local field, polarizability, total dipole moment, and position of the  $i$ th molecule,  $\vec{r}_{ij} \equiv \vec{r}_i - \vec{r}_j$ , and  $\hat{r}_{ij}$  denotes the unit vector parallel to  $\vec{r}_{ij}$ .<sup>12</sup> Values of  $\vec{p}_i$  are obtained by summing the static dipole moment,  $\vec{\mu}_i$ , and the induced dipole moment,  $\alpha_i \vec{F}_i$ , of each molecule, i.e.,  $\vec{p}_i = \vec{\mu}_i + \alpha_i \vec{F}_i$ . The  $\vec{F}_i$  are obtained by summing the contribution to the local field at each molecule from each of the surrounding molecules:

$$\vec{F}_i = \sum_{j \neq i}^N \frac{3(\vec{p}_j \cdot \hat{r}_{ij})\hat{r}_{ij} - \vec{p}_j}{r_{ij}^3}. \quad (2)$$

The expressions governing the  $\vec{p}_i$  and  $\vec{F}_i$  form a system of  $2N$  coupled linear vector equations in  $2N$  vector unknowns. The value of  $\Delta E^{int}$  is then given by  $E_f^{int} - E_i^{int}$ , where  $E_f^{int}$  and  $E_i^{int}$  are the total interaction energies in the excited final and ground initial states, respectively.

In the limit of  $\alpha_i \rightarrow 0$ , the calculation is simplified. In this “static” case, the  $\vec{F}_i$  are trivially obtained by replacing the  $\vec{p}_i$  with  $\vec{\mu}_i$ . Furthermore, since the interactions between the inactive molecules remain unchanged by the presence of the exciton, they can be dropped from the calculation of  $\Delta E^{int}$ , so that

$$\Delta E^{int} = - \sum_{i \neq A}^N \Delta \vec{\mu}_A \cdot \frac{3(\vec{\mu}_i \cdot \hat{r}_{Ai})\hat{r}_{Ai} - \vec{\mu}_i}{r_{Ai}^3}, \quad (3)$$

where the index  $A$  denotes the “active” molecule undergoing excitation and  $\Delta \vec{\mu}_A$  is the change in dipole moment of the active molecule as a result of the formation of the exciton state. This is the type of DOS treated by Kador.<sup>4</sup> In his development, Kador<sup>4</sup> assumes that the exciton is surrounded by a spherical cavity of radius  $D_{min}$ , which sets the minimum interaction distance for the calculation.<sup>13</sup> Kador solved for the DOS under two different limiting conditions, which he found yielded differently shaped distributions. In the limit that the average intersite spacing between the surrounding dipoles,  $D_{site}$ , is much less than,  $D_{min}$ , then the DOS is a Gaussian with zero mean:

$$g(E) = \frac{1}{\sigma\sqrt{2\pi}} e^{-E^2/2\sigma^2}, \quad (4)$$

where  $\sigma$  is the standard deviation of the distribution, given by<sup>4</sup>

$$\sigma(\text{eV}) = 1.475 \frac{1}{[D_{site}(\text{\AA})]^3} \left[ \frac{D_{site}}{D_{min}} \right]^{3/2} \mu(D) \Delta \mu(D) \quad (5)$$

with the nonstandard units of each term specified in parentheses. In contrast, in the limit that  $D_{site} \gg D_{min}$ , the DOS is nearly Lorentzian with zero mean. As in this Rapid Communication we examine single component solids (which comprise the bulk of the layers employed in existing organic electronic devices), the size of each molecule is the same, and therefore  $D_{site} \approx D_{min}$ , a condition that is inconsistent

with both limits. Nevertheless, we show below that the Gaussian limit can be used in the  $D_{site} \approx D_{min}$  case.

Our Monte Carlo (MC) calculations for the  $\alpha_i=0$  (i.e.,  $\epsilon=1$ ) case use cubic lattices of  $L \times L \times L$  sites with lattice constant  $D_{site}$  in which each site has a randomly oriented static dipole moment of magnitude  $\mu$ . Periodic boundary conditions are employed to simulate an infinite lattice, and only interactions between sites separated by a distance less than or equal to  $R_{int}$  are included in the calculation, with the restriction that  $R_{int} < LD_{site}/2$  to avoid double counting of interactions between the same pairs of sites. We investigate the impact of  $L$  and  $R_{int}$  on the calculation, and find that the results are insensitive to further increases in  $L$  and  $R_{int}$  for  $L \geq 10$ , and  $R_{int} \geq 4.9D_{site}$ . For  $L$  and  $R_{int}$  satisfying this restriction, we find that within the uncertainty of the calculation the DOS is Gaussian and  $\sigma$  is equal to the value predicted by Kador<sup>4</sup> with  $D_{site} = D_{min}$ .

To perform calculations with nonzero  $\alpha_i$ , we employ the procedures described in Ref. 14 for self-consistently solving for the  $\vec{F}_i$  and  $\vec{p}_i$ . Due to the computational difficulty of the problem, we find that only DOS calculations with relatively small  $L$  are practical, and we employ values of  $L$  and  $R_{int}$  just above the minimum values required to eliminate lattice size errors. For the static case above, this implies  $L \geq 10$ , and  $R_{int} \geq 4.9D_{site}$ . To determine if larger lattices are required for the polarizable case we evaluate the impact of lattice size on the calculation of the polarization energy associated with introducing a dipole on a single site in a lattice with  $\mu=0$  and nonzero  $\alpha$ . We find that for  $L=14$  and  $R_{int}=6.9D_{site}$ , the polarization energy is within 0.2% of the fully converged energy, obtained for  $L=30$  and  $R_{int}=14.9D_{site}$ .<sup>15</sup> Since the dipole-dipole interactions are the sole source of exciton energy disorder in the lattices employed in this study, we conclude that  $L=14$  and  $R_{int}=6.9D_{site}$  are adequate for analyzing the impact of polarization on the exciton DOS, and use these values in the following.

We performed DOS calculations for the  $\alpha_i \neq 0$  case over a range of  $\alpha$ ,  $\mu$ , and  $\Delta \vec{\mu}$  values. Furthermore, in the following we use the Clausius-Mossotti equation to relate  $\alpha$  and  $\epsilon$ :

$$\alpha = \frac{\epsilon - 1}{\epsilon + 2} \frac{3}{4\pi} V_m, \quad (6)$$

where  $V_m$  is the molecular volume (here given by  $D_{site}^3$  in units of  $\text{cm}^3$ ). All of the reported results are averaged over ten different randomly generated lattices. To reflect the typical range of molecular dipole moments, molecular densities, and dielectric constants encountered in polar amorphous organic materials, we computed the DOS for  $\mu \in \{1, 2, 6\}$  D,  $\Delta \mu \in \{1, 2, 6\}$  D, and  $D_{site} \in \{0.5, 1.0, 2.0\}$  nm for  $\epsilon \in \{1, 2, 3, 4\}$ . To describe the impact of polarization on the exciton energy disorder we calculate the ratio  $\Phi(\epsilon) \equiv \sigma(\epsilon)/\sigma(\epsilon=1)$ , which gives the scaling of  $\sigma$  as a function of  $\epsilon$  relative to the  $\epsilon=1$  value.

In all cases the DOS is Gaussian to within the statistical uncertainty of the calculation. We also find that for each set of  $\mu$  and  $D_{site}$ ,  $\Phi(\epsilon)$  is the same to within the statistical uncertainty of the calculation, indicating that the scaling of  $\sigma$  with  $\epsilon$  is independent of  $\mu$ ,  $\Delta \vec{\mu}$ , and  $D_{site}$  for this range of

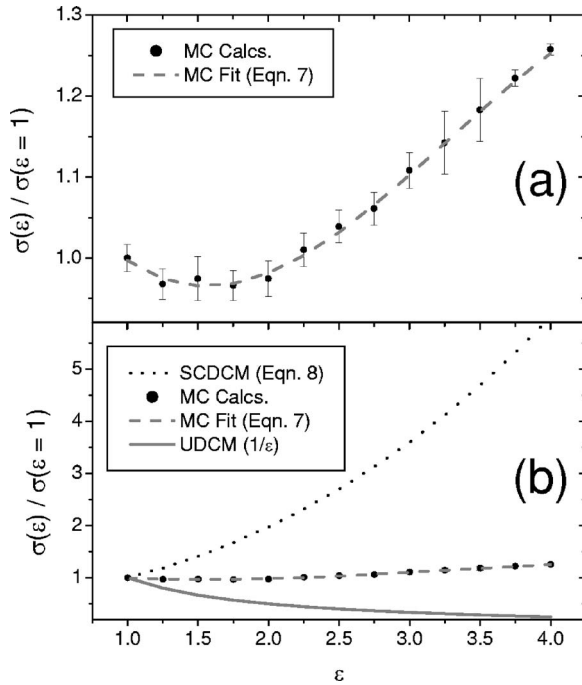


FIG. 1. Evolution of exciton energy disorder as a function of dielectric constant  $\epsilon$ , in terms of  $\Phi(\epsilon) = \sigma(\epsilon) / \sigma(\epsilon=1)$ , where  $\sigma$  is the standard deviation of the charge carrier density of states. In (a) are shown plots of  $\Phi(\epsilon)$  as derived from the Monte Carlo (MC) calculations (symbols) described in the text and the polynomial fit described in the text (dashed gray line). In (b) are added plots of  $\Phi(\epsilon)$  based on the UDCM (solid gray line) and the SCDCM (dashed black line). Note that both axes are unitless.

molecular parameters.<sup>16</sup> For  $\mu=2D$  and  $D_{site}=1.0$  nm, we performed calculations of  $\Phi(\epsilon)$  (see Fig. 1) at additional values of  $\epsilon$  between 1 and 4, which are fit by the polynomial:  $\Phi(\epsilon) = 1.26 - 0.416\epsilon + 0.175\epsilon^2 - 0.0178\epsilon^3$ .

These results show that nonzero  $\alpha$  only weakly impacts exciton energy disorder in organic solids with typical  $\epsilon$ . In calculations of charge carrier energy disorder, it has been conventional to employ a DCM in which the molecular polarizabilities are replaced by a continuous dielectric medium filling all space (see, e.g., Refs. 17–19), a model referred to here as the uniform DCM (UDCM). Applying the UDCM to the exciton case gives  $\Phi(\epsilon) = 1/\epsilon$ , due to dielectric screening which scales the strength of *all* electrostatic interaction energies by  $1/\epsilon$ . The plots in Fig. 1 show that the UDCM fails to even qualitatively reflect the observed evolution in the energy disorder with  $\epsilon$ .<sup>20</sup>

We also consider a more sophisticated DCM derived from early work by Onsager,<sup>21</sup> in which one places the molecular charge distribution in a spherical cavity surrounded by a dielectric continuum. In this case, the static dipole of a molecule polarizes a surrounding medium producing a reaction field that induces an additional dipole on that molecule. The reaction field is parallel to the static dipole and enhances the strength of the original dipole by the factor  $(\epsilon+2)(2\epsilon+1)/9\epsilon$ .<sup>21</sup> Furthermore, the field due to the molecular dipole as experienced in the surrounding dielectric medium is not scaled by a factor of  $1/\epsilon$ , as in the case of an individual charge, but rather is scaled by a factor of  $3\epsilon/(2\epsilon+1)$  (see,

e.g., Ref. 22). It is challenging to apply this “spherical cavity” DCM (SCDCM) self-consistently to the calculation of the interaction energies between an exciton and a collection of surrounding dipoles. However, an approximate calculation is possible if one neglects: (1) the internal polarization energy; and (2) the influence of induced dipoles on each other. In this case, the static molecular dipoles are scaled by  $(\epsilon+2)(2\epsilon+1)/9\epsilon$  (from above), and the local field at each dipole due to the surrounding dipoles is scaled by  $\epsilon(\epsilon+2)/(2\epsilon+1)$ . The scaling of the local field combines the factor  $3\epsilon/(2\epsilon+1)$  that describes the field due to each molecular dipole outside of its spherical cavity (as noted above), with the Lorentz local field correction,  $(\epsilon+2)/3$ , which gives the local field inside a virtual spherical cavity (see, e.g., Ref. 22).<sup>23</sup> This yields

$$\Phi_{SCDCA}(\epsilon) = \frac{\epsilon(\epsilon+2)}{(2\epsilon+1)} \left[ \frac{(\epsilon+2)(2\epsilon+1)}{9\epsilon} \right]^2, \quad (7)$$

which is plotted in Fig. 1, indicating that the SCDCM significantly overestimates the enhancement of the exciton energy disorder with increasing  $\epsilon$ . We therefore find that both the UDCM and SCDCM fail to describe the dependence of the exciton energy disorder on  $\epsilon$ .

One shortcoming of the UDCM and SCDCM is their assumption that a continuous dielectric medium fills the space between nearest neighbor sites, even though in a real system such sites (representing individual molecular charge distributions) are separated by vacuum. From our calculations we find that a majority of the total interaction energy between an exciton and the surrounding dipoles is due to the nearest neighbor interactions, and thus errors in the treatment of nearest neighbor interactions in the UDCM and SCDCM (and indeed, in conventional DCMs in general) should have a significant impact on their accuracy.

We can compare the results of the UDCM, SCDCM, and our MC calculations with an experimental value of  $\sigma = 0.039$  eV obtained for the archetypical amorphous organic electronic material aluminum tris-(8-hydroxyquinoline) (AlQ3) using time-resolved fluorescence measurements.<sup>7</sup> The AlQ3 parameters needed for the three models are collected from literature: Ellipsometry measurements of thermally deposited AlQ3 thin films yield  $n=1.70$ , which corresponds to  $\epsilon=n^2=2.89$ .<sup>7</sup> Average AlQ3-to-AlQ3 molecular site spacing was measured to be  $D_{site}=0.87$  nm.<sup>7</sup> From *ab initio* calculations of AlQ3 electronic structure  $\mu=5.3D$  (Ref. 24) and  $\Delta\mu=3.4D$  (Ref. 25). Inserting these values into Eq. (5) with  $D_{min}=D_{site}$ , and then applying the scaling factors for each model, we obtain  $\sigma_{UDCM}=0.014$  eV,  $\sigma_{SCDCM}=0.121$  eV, and  $\sigma_{MC}=0.042$  eV. Even if we allow for considerable (e.g.,  $\pm 30\%$  in both values) uncertainty in the *ab initio* dipole values, the MC calculation is still in the best agreement with the experimentally observed exciton energy disorder in AlQ3.

In this Rapid Communication we present MC calculations of the exciton energy level disorder in polar amorphous organic solids arising from electrostatic interactions between polarizable molecular charge distributions. Our MC calculations for static charge distributions (i.e.,  $\epsilon=1$ ) are in agree-

ment with the analytic treatment previously reported by Kador<sup>4</sup> for the Gaussian limit, providing independent verification of the statistical method for this calculation. For polarizable charge distributions, we find that the exciton energy disorder, as represented by  $\sigma$ , has a weak dependence on  $\epsilon$ , in contrast to conventional dielectric continuum models. We also demonstrate that our calculations are in agreement with the experimentally observed energy disorder in AIQ3. Since all organic solids are subject to substantial polarization (yielding  $\epsilon$  typically between 2 and 4), a general calculation of the exciton energy disorder in solids containing polariz-

able molecules represents an important step forward in the treatment of excitonic DOS calculations, particularly in light of the critical significance of the excitonic DOS in organic optoelectronic materials. This work also illustrates the impact (or surprising lack thereof) of polarization on the strength of the local fields present in polar organic solids.

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<sup>9</sup>The “statistical” method was first applied to exciton DOS calculations arising from dispersion relations (see, e.g., Refs. [4](#), [8](#), [26](#), and [27](#)), and was then adapted by Kador to the nonpolarizable dipole case.

<sup>10</sup>The Monte Carlo method, however, *has* been applied to the DOS arising from dispersion interactions, as in Ref. [27](#).

<sup>11</sup>These calculations represent an extension of a recent report (Ref. [14](#)) on the impact of polarization on charge carrier energy disorder in polar amorphous organic solids.

<sup>12</sup>Note that the  $\frac{1}{2}\alpha_i F_i^2$  term represents the internal polarization energy. For a review of interaction energies between polarizable charge distributions see, e.g., Ref. [22](#).

<sup>13</sup>Kador (Ref. [4](#)) also assumes for mathematical simplicity that the surrounding static dipoles are not randomly distributed but rather aligned radially relative to the exciton.

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<sup>15</sup>The convergence denotes the point at which further increases in  $L$  and  $R_{int}$  have no impact on the results to within the calculation uncertainty of 0.05%.

<sup>16</sup>We also performed calculations for different  $\Delta\hat{\mu}$ , but find that the direction of  $\Delta\mu$  impacts only the mean energy of the DOS, and not  $\sigma$ .

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<sup>20</sup>Our recent calculations of charge carrier energy disorder using the same MC techniques (Ref. [14](#)) also demonstrate that the UDCM is inadequate, but the deviations observed here for excitons are even greater than those observed for charge carriers.

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