

Can Lattice Models Predict the Density of States of Amorphous Organic Semiconductors?

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We extend existing lattice models of small-molecule amorphous semiconductors by accounting for changes in molecular polarizability upon charging or excitation. A compact expression of this contribution to the density of states is provided. Although the lattice model and the description based on a microscopic morphology both qualitatively predict an additional broadening, shift, and an exponential tail (traps) of the density of states, a quantitative agreement between the two cannot be achieved.

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Advancements in organic electronics, especially in improving efficiencies and lifetimes of organic light emitting diodes (OLEDs) [1] and solar cells [2] have been stimulated by the synthesis of new materials, optimization of their processing, and a deeper understanding of elementary processes in organic semiconductors. Computer simulations and modeling contributed substantially to this progress [3–6], in particular, lattice models with charges localized on point sites arranged on a regular grid have been successful in rationalizing the influence of finite carrier concentration [7,8], explicit Coulomb interactions [9], the shape of the density of states (DOS) [10,11], site energy spatial correlations [12], and positional disorder [13] on charge and exciton transport dynamics in amorphous [14] materials.

The drawback of lattice models is that they must be parametrized on experimental data and thus do not provide a direct link to underlying chemical structures. Therefore, they cannot aid compound screening, which is becoming more and more important in view of the large number of organic compounds with semiconducting properties [15]. One can, in principle, simulate realistic atomistic morphologies and perform off-lattice Monte Carlo simulations with rates calculated using first principles [16,17]. This approach is, however, computationally demanding and is limited in accessible system sizes and simulation times [18,19].

It is therefore tempting to parametrize a lattice model based on calculated electronic properties of single molecules, i.e., to predict the DOS (or distribution of site energies [20]) from charge distributions, polarizabilities, ionization potentials (IPs), van der Waals surfaces, etc. While the success of lattice models teaches us that this is possible qualitatively, the question is whether one can *quantitatively* account for a local environment of every molecule, without knowing the details of the (amorphous) material morphology?

To answer this question, we evaluate level shifts and the DOS broadening for one charge carrier, i.e., in a low charge

carrier concentration limit, by combining polarizable continuum and lattice models (mesoscopic approach), where we also incorporate the effect of the polarizability change on the carrier site. To then validate the predictions of these models, the DOS is computed using a microscopic approach, which is based on the explicit atomistic morphology, allowing to go beyond the multipole expansion, point-based molecular polarizability, and Gaussian uncorrelated positional disorder of lattice models. We first analyze the effect of bare Coulomb interactions by using atomic partial charges, then account for molecular polarizability by assigning polarizabilities to every atom, and finally incorporate the effect of the polarizability change upon charging. As a test system, we use a prototypical host-guest mixture [Figs. 1(a) and 1(b)] of the emission layer of a blue phosphorescent OLED.

To evaluate the free energy of a system with a charge localized on a specific molecule, we first split it on intramolecular and intermolecular contributions. The intramolecular part is given by the gas-phase electron affinity (EA) or IP for electrons and holes, respectively, and is relevant for multicomponent systems only. For the host-guest pair of interest, EAs are shown in Fig. 1(d) (gas) [21]. To partially account for the environment, one can use the polarizable continuum models (PCMs) [22], where a molecule is placed into a cavity (defined by its van der Waals surface) embedded in a homogeneous dielectric [23]. Since the individual nature of the environment is neglected, PCM leads only to a shift of the gas-phase levels. In our case host and guest have a similar stabilization of the gas-phase EAs, as shown in Fig. 1(d) (PCM).

To account for *individual* molecular environments, leading to the DOS broadening (energetic disorder), we employ lattice models. The lattice is constructed by placing randomly oriented molecules on grid points of a cubic lattice, where random orientations mimic an amorphous morphology. Molecular electrostatic potentials are then expanded in multipoles and the electrostatic contribution to the DOS is calculated by summing over interactions of these

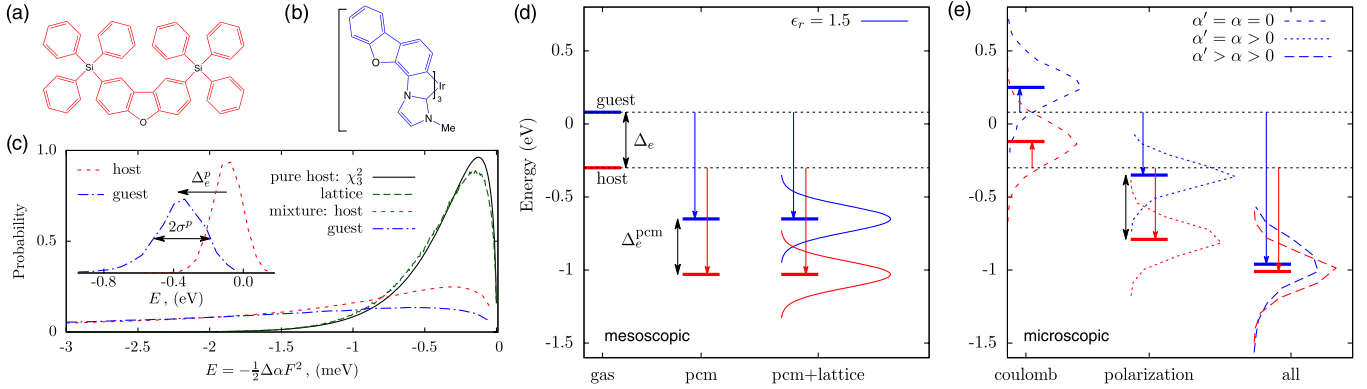


FIG. 1 (color online). Chemical structures of (a) host and (b) guest (emitter) of the OLED emission layer. (c) Histogram of the interaction energy between electric field \vec{F} of randomly oriented static dipoles with the induced dipole on a site with polarizability change $\Delta\alpha$ (see Table I) for a cubic lattice ($a = 1$ nm). Pure host: χ_3^2 is an analytical result, while numerical simulations are performed using 3375 lattice sites averaged over 600 realizations for the pure host and for the mixture with $c_g = 0.1$. Inset: microscopic evaluation of this energy based on a realistic morphology of 4000 molecules with $c_g = 0.1$, averaged over three molecular dynamics snapshots. (d), (e) The DOS for electrons localized on host (red) and guest (blue): gas-phase levels (gas) and their stabilization by PCM [24] (PCM) and broadening by a lattice model (PCM + lattice); microscopic model without polarization (Coulomb), with the same polarizabilities of the neutral and charged molecules (polarization), and polarizability change upon charging (all).

multipoles. This model leads to the spatially correlated on-site energies and is often referred to as a correlated disorder model [12,25]. To account for screening, each site is additionally assigned an isotropic polarizability. It reduces the broadening and leads to a shift of the DOS due to the stabilization of the charge. Both shift and broadening of the gas-phase levels can be evaluated within this model. Because the PCM provides a better estimate of the shift [26] in what follows we concentrate on the level broadening only.

In line with the central limit theorem, the contribution to the DOS due to interactions of multipole moments of a charged site (l') and the surrounding molecules (l) can, for physically relevant parameters, be approximated by a Gaussian distribution of variance $\sigma_{l'l}^2$, where

$$\sigma_{l'l} = \frac{\kappa_{l'l} \Delta q_{l'} q_l \sqrt{c}}{a^{l'+l+1} \epsilon_l^{\text{eff}}(\alpha)}, \quad l' = 0, 1, \dots, l = 1, 2, \dots \quad (1)$$

and $\Delta q_{l'}$ is the rotationally averaged change of the multipole moment of the carrier site upon charging, and q_l is the rotationally averaged moment of the surrounding neutral molecules, a is the lattice spacing, $\kappa_{l'l}$ is a constant of order one which accounts for the topology of the lattice [27,28], $\epsilon_l^{\text{eff}} \geq 1$ incorporates the effective screening parametrized as a function of the polarizability of the (surrounding) neutral molecules, α [29], and c accounts for a possible fractional filling of the lattice [32].

Using the *ab initio* molecular parameters introduced in Table I, filling factors of $c_{g(h)} = 0.1$ (0.9) for guest (host), and lattice spacing of $a = 1$ nm [34] we obtain $\sigma \sim [\sum_{m=g,h} \sigma_{01}^2(c_m, q_1^m)]^{1/2} = 0.09$ eV since the interaction between charge and dipole [33] leads to stronger broadening compared to the charge-quadrupole [28] or dipole-dipole

[30,35] interactions ($\sigma_{01} > \sigma_{02}$ and $\sigma_{01} > \sigma_{11}$). Note that the broadening is identical for host and guest, since $\Delta q_0 = e$ and both molecules are embedded in the same surrounding [36]. The host and guest DOS, based on the PCM levels and broadening given by Eq. (1), are shown in Fig. 1(d) (PCM + lattice).

We have so far recapitulated the results of various lattice models, estimated all static contributions to the DOS and taken into account the polarizability of the environment using the effective dielectric screening. An important contribution is, however, still missing, which is due to the interaction of electric fields of surrounding neutral molecules with the induced dipole moment of the *charged* site. Typically, the polarizability of a molecule would increase upon charging due to reduced binding of the unpaired electron, especially for anions [37].

To account for this effect on a lattice level, we assume that a point particle at $(0, 0, 0)$ has a polarizability tensor $\hat{\alpha}$ ($\hat{\alpha}'$) in a neutral (charged) state and is surrounded by randomly oriented static dipoles of strength d pinned to the lattice sites. For *one* randomly oriented dipole at $(0, 0, a)$, the components of the electric field at $(0, 0, 0)$ are uniformly distributed with zero means and variances

TABLE I. Single molecule parameters [24]. Quadrupole obtained from eigenvalues Q_k of the traceless tensor as $Q = (\frac{2}{3} \sum_k Q_k^2)^{1/2}$. Polarizability volume is defined as $\alpha = \frac{1}{3} \text{Tr} \hat{\alpha}$.

	Carrier site	Host	Guest	Neutral	Host	Guest	
Δq_0	$ q' - q (e)$	1	1	q_1	$d(\text{D})$	0.8	5.4
Δq_1	$ d' - d (\text{D})$	9.8	5.4	q_2	$Q(\text{D}\text{\AA})$	5.6	39.7
$\Delta \alpha$	$(\alpha' - \alpha)(\text{\AA}^3)$	119	219	α	$\alpha(\text{\AA}^3)$	91	107

$\langle f_{x,y}^2 \rangle = \frac{d^2}{3a^6}$, $\langle f_z^2 \rangle = \frac{4d^2}{3a^6}$. Summing over all dipoles on the lattice is then equivalent to a sum of *independent* uniform distributions. Hence, the central limit theorem implies that the components of the total field are (approximately) Gaussian-distributed with vanishing mean $\langle F_\gamma \rangle = 0$ and variance $\langle F_\gamma^2 \rangle = \sigma_{F_\gamma}^2 \approx (4 + 1 + 16/81 + 1/16 + \dots) \frac{d^2}{a^6} \approx 5.3 \frac{d^2}{a^6}$, where each term in the sum corresponds to a shell on a (cubic) lattice, and $\gamma = x, y, z$. The energy of the neutral (charged) site in this total field is $-\frac{1}{2} \vec{F} \hat{\alpha} \vec{F}$ ($-\frac{1}{2} \vec{F} \hat{\alpha}' \vec{F}$), leading to an energy shift of $-\frac{1}{2} \Delta \alpha F^2$ with $\Delta \alpha = \frac{1}{3} \text{Tr}(\hat{\alpha}' - \hat{\alpha})$, as the orientations of $\hat{\alpha}$ and \vec{F} are independent. If we neglect the correlations between the field components of the same dipole, then $F_{x,y,z}^2$ are independent normal random variables, and their sum is a χ_3^2 distributed variable

$$\chi_3^2(\xi) = \sqrt{\xi} \exp(-\xi/2), \quad \xi = F^2 / \sigma_{F_\gamma}^2. \quad (2)$$

It has a mean of $\langle \xi \rangle = 3$, variance $\sigma_\xi^2 = \langle \xi^2 \rangle - \langle \xi \rangle^2 = 6$, and an exponential tail at large ξ , which brings us to the main results of this section: the mean corresponds to a stabilization of the transport level by $\frac{3}{2} \Delta \alpha \sigma_{F_\gamma}^2$, the variance to its broadening by $\frac{\sqrt{6}}{2} |\Delta \alpha| \sigma_{F_\gamma}^2$, and the exponential tail results in low energy sites (traps).

The χ_3^2 distribution of a pure host, with the *ab initio* parameters taken from Table I, is shown in Fig. 1(c), where it is compared to a numerically evaluated (on a cubic lattice) DOS, which includes all correlations. The agreement is good, justifying the derivation. At the same time, Fig. 1(c) predicts that the polarizability change can be entirely neglected when calculating the DOS, as the absolute energy values involved are of the order of meV, both for the pure host and for host as well as guest in a host-guest mixture. Thus, the DOS shift and broadening are small within this simplified lattice-based approach, but will be shown to be large in a complete microscopic description of the DOS.

To verify the predictions of the lattice model, we now calculate the DOS using a realistic morphology obtained using atomistic molecular dynamics simulations. These simulations are performed using the GROMACS simulation package [38] in the NPT ensemble with the Berendsen barostat [39], Langevine thermostat, and a re-parametrized version of the optimized potentials for liquid simulations force field [40,41]. Amorphous systems of 3600 host and 400 guest molecules are equilibrated at 1000 K for 2 ns well above the glass transition temperature of the host, $T_g = 380$ K, followed first by quenching to 700 K and equilibration for 1 ns and then subsequent quenching to room temperature. The final length of the cubic box is $L = 15.96$ nm. The molecular charge distributions for charged and neutral states are approximated by fitting atomistic partial charges to reproduce the electrostatic potential of *ab initio* calculations in the gas phase [24].

Polarization interactions in the bulk are treated self-consistently using the Thole model [42] which we have parametrized on molecular polarizability tensors [43].

We first take into account bare Coulomb interactions, neglecting polarization contributions. The corresponding DOS, shown in Fig. 1(e) (Coulomb), is shifted with respect to the gas-phase values, both for host and guest. This shift is not predicted by lattice models which can be explained by a breakdown of the multipole expansion at small intermolecular separations (intercalating charge distributions) and local correlations in molecular orientations. The broadening of the levels is artificially strong because the screening is not taken into account.

We now include (partially) the effect of molecular polarizability by assigning the same polarizabilities to the atoms in charged and neutral molecules. The resulting DOS is shown in Fig. 1(e) (polarization). The screening of the charge reduces the broadening and the static shift and also leads to a strong stabilization similar to the PCM. This DOS agrees well (apart from the aforementioned static shift) with the one predicted by the PCM levels broadened by the lattice disorder [Fig. 1(d), PCM + lattice], as the charge-dipole interaction is well captured by the lattice model, and the contribution to the DOS due to the polarization change is small in the lattice model and is neglected at this stage of the microscopic description ($\alpha' = \alpha$).

Finally, we account for the polarizability change upon charging by scaling the atomic polarizabilities to reproduce the trace of the molecular polarizability tensor in charged states [44]. We first evaluate only the interaction of the field from the surrounding molecules with the resulting induced dipole on the carrier site [45], as this contribution can be directly compared to the lattice model presented in Fig. 1(c). The results are shown in the inset of Fig. 1(c) for both host and guest. One can see that the larger polarizability difference of the guest as compared to the host ($\Delta \alpha_g > \Delta \alpha_h$, see Table I) leads to a reduction of the energy difference between guest and host levels, Δ_e , by Δ_e^p . There is also an additional broadening of the DOS, σ^p , with a tail of low-lying states (especially for the guest). All three effects are in an excellent *qualitative* agreement with the lattice model, i.e., $\Delta_e^p = \frac{3}{2} (\Delta \alpha_g - \Delta \alpha_h) \sigma_{F_\gamma}^2$, and additional broadening is stronger for the guest than for the host because $\sigma_{h(g)}^p = \frac{\sqrt{6}}{2} |\Delta \alpha_{h(g)}| \sigma_{F_\gamma}^2$. The *quantitative* difference is, however, striking: the guest, for example, has a gas-phase level shift and broadening, $\langle E_g^p \rangle = -0.37$ eV, $\sigma_g^p = 0.15$ eV which are an order of magnitude larger than predicted by the lattice model.

This discrepancy can partially be attributed to two factors. First, a positional disorder, i.e., a standard deviation of lattice site displacements [13], σ_a , is not taken into account. Because the polarization-change contribution to the DOS scales as $1/a^6$, where a is the intermolecular distance, this additional broadening of the distribution of the electric field at a charged site has a strong effect on

the DOS, $\sim 6\sigma_a/a$. At the same time, charge-dipole contributions are proportional to $1/a^2$ and therefore are less sensitive to σ_a . As the positional disorder is an intrinsic property of the real morphology, it cannot be quantitatively predicted by lattice models and fitting to microscopic simulations or experimental data is unavoidable. Second, only the lowest moment (a second rank tensor) is used to account for molecular polarizability, while the description of an inhomogeneous distribution of the induced electrostatic potential requires higher order tensors [46]. In other words, the answer to the question posed in the title is “unlikely,” at least at this level of description of molecular polarizability.

We now briefly discuss the implications on the OLED functionality. The final DOS of the microscopic model, shown in Fig. 1(e) (all) [47], is substantially different from the one predicted by combining the PCM with a lattice model [Fig. 1(d), PCM + lattice]. The increased DOS width and the presence of trap states result in much lower electron mobility (one to two orders of magnitude) compared to predictions by lattice models. Moreover, the overlap of the host and guest DOS allows for electron transport also by the guest (neutral emitter), in contrast to the prediction of the PCM + lattice model where electrons are confined to the host only.

To summarize, we have shown that a different polarization-induced stabilization of a molecule in its charged and neutral (excited and ground) state can lead to shifts, broadening, and traps in the distribution of site energies. Thus, the polarizability change should be added to the set of molecular parameters essential for understanding transport in organic semiconductors. To quantitatively account for the effect of the change in polarizability in lattice models, accurate description of both molecular polarizabilities (beyond single-site tensors) and positional disorder is essential.

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