

## Towards a Parameter-Free Characterization of Charge Transfer via Hopping: The Case of tris(8-Hydroxyquinolato) Aluminum

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By using calculations based on density functional theory, we investigate the physical factors determining the elemental charge transfer in  $\text{Alq}_3$ , taken as a prototype of molecular systems in condensed phase. The effect of the environment on the hopping of the charge carrier is evaluated self-consistently in a model in which an  $\text{Alq}_3$  dimer is embedded in an ensemble of permanent and polarizable dipoles, including orientational disorder and the presence of impurities. The results indicate that the origin of the activation barrier is mainly extrinsic and that the local orientation of the dipole moments plays a major role. The influence of nonadiabaticity is also studied and found to be more important for a hole than for an electron.

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New concepts for electronic and optical devices are increasingly arising from the development of molecular superstructures, organic electronics, or bioinspired nanostructures (see, e.g., [1–3]). Their successful application will ultimately depend on the ability to solve several practical problems, but also on the level of understanding of the microscopic processes that underlie their functioning. For example, any technology based on organic electronics has long been facing the challenge of increasing the mobility of either electrons or holes. However, even where experimental data leave little doubt about the primary nature of charge transport and show that it can be described as hopping from one molecular unit to the neighboring one rather than as band conductivity, several questions still remain unanswered. The typical output of experimental measurements is the carrier mobility as a function of temperature and of the applied electric field, which often exhibits a behavior of Poole-Frenkel type. However, this information is not sufficient to infer whether the polaron model provides an adequate description of the underlying physics or disorder sources must be invoked to account for it, or whether the origin for activation is intrinsic or extrinsic to the particular system. Charge transfer, on the other hand, is one of the most fundamental processes in nature and still one that state-of-the-art calculations have difficulty to treat quantitatively [4].

In this Letter we make a step forward in the characterization of charge transfer via hopping within a simple scheme that is based on density functional theory (DFT) with gradient-corrected exchange-correlation (xc) functionals and properly takes care of the necessary corrections to the energetics. The specific system we have chosen is tris(8-hydroxyquinolato) aluminum ( $\text{Alq}_3$ ), a compound commonly used both as an emission and an electron-transport layer in organic light-emitting diodes (OLEDs) [2,5]. Despite intense experimental investigation,  $\text{Alq}_3$  is no exception to the generic case: so far no consensus has been achieved on the predominant mechanism, the electron

mobility is determined only within 1 order of magnitude [6–9], and the hole mobility is known to be lower by 2 orders of magnitude [6–8] but the reason for this is also not understood. Taking our calculated value of the activation energy for the transfer of an electron (or a hole) in an isolated  $\text{Alq}_3$  dimer within the adiabatic approximation as reference, we calculate the changes induced by the environment by embedding it (embedded-dimer model) in an ensemble of polarizable dipoles representing the rest of the molecular units, both in an ordered state as in crystalline  $\text{Alq}_3$  and in partially disordered states as in an amorphous phase. The influence of the environment is found to be of utmost importance and to strongly depend on the static molecular dipole moments via their relative orientations. The activation barrier in  $\text{Alq}_3$  is shown to result primarily from extrinsic factors that tend to localize the elemental charge on one monomer. This is true for both the electron and the hole. However, as expected, the calculated barriers tend to be higher for hole transfer than for that of an electron. Moreover, we consider the effect of the non-adiabatic coupling between electronic and nuclear degrees of freedom on the charge displacement in the framework of a DFT-based approach that was recently developed and tested on simple molecules [10]. Nonadiabaticity is found to be non-negligible at room temperature, and more relevant for the hole than for the electron.

The basic computational framework is the one adopted in our previous studies of structural, vibrational, and other electronic properties of  $\text{Alq}_3$  [11,12]. This uses the Becke [13] and Lee-Yang-Parr [14] approximations for the exchange and correlation functionals (BLYP) including spin polarization, norm-conserving pseudopotentials for the description of the core-valence interaction, and plane waves for the expansion of the valence electron wave functions, with a 70 Ry cutoff. Our studies, in particular, revealed some characteristics of the  $\text{Alq}_3$  molecule that are of interest here. Of its two structural isomers, called meridional and facial, the former was predicted to be thermo-

dynamically more stable by a few kcal/mol: this indicated that the hindering factor to crystallization could be related to the coexistence of the two isomers in the material, which under normal conditions is amorphous. Both isomers were found to possess relatively high dipole moments, and a relatively small value ( $\sim 0.1$  eV) was calculated for the reorganization energy associated with the addition of either an electron or a hole, and especially so in the case of the electron. The facial isomer was, however, predicted to have a substantially higher dipole moment ( $\sim 7$  D vs  $\sim 4$  D) as well as a greater tendency to trap electrons than the meridional one. Moreover, the calculated valence and conduction bands of the crystalline phase of the meridional  $\text{Alq}_3$  [15] exhibited dispersion on the order of the small polaron energy, thus indicating that the band picture was inadequate for the description of either electron or hole transport.

Therefore as a basic model of the coupled donor-acceptor ( $D$ - $A$ ) system, we consider here a dimer of meridional isomers at a distance of  $8.81$  Å between the Al atoms and with the relative orientation they have in the crystal. In an adiabatic picture, the physical quantity that directly accounts for the greater or weaker tendency of a charged particle to “hop” from one monomer to the next is the energy difference  $\Delta E_a$  between the “symmetric” state (transition state “ $t$ ”), where the charge  $q$  is equally distributed between them, and the “asymmetric” state, where the charge is fully localized on one molecule (“ $m$ ”):

$$\Delta E_a = E_t - E_m(q=0) - E_m(q=\pm 1) - E_{\text{int}} - E_{\text{corr}}. \quad (1)$$

Here  $E_m(q=0)$  and  $E_m(q=\pm 1)$  refer to the individual monomers, neutral and charged, respectively,  $E_{\text{int}}$  is their interaction energy calculated as the sum of the charge-permanent dipole and charge-induced dipole interaction terms, and the correction term  $E_{\text{corr}}$  is the binding energy of the two neutral monomers, which we take as estimate of their interaction incorrectly included in  $E_t$  and thus to be subtracted. Indeed, splitting the individual energy terms as in Eq. (1) is necessary to avoid the problems inherent to our DFT scheme for which the ground state of the dimer corresponds to a delocalized charge distribution.

$\Delta E_a$  was computed both for the system *in vacuo* and for the system embedded in an ordered ensemble of polarizable dipoles (188 within a sphere of  $30$  Å radius) that are located at the lattice positions of the crystalline phase [16] and have permanent dipole moments equal to that of the meridional isomer ( $3.8$  D). In the self-consistent procedure, relaxation of both electronic and geometric variables was considered for the dimer. As can be seen from Table I, the results were consistent with a barrierless process for both the electron and the hole. However, the antagonist effect of the environment, namely, of the reorganization of the medium associated with the redistribution of the charge density in the dimer, is strong and quantitatively very important in both cases. Moreover, the response of the

TABLE I. Activation energies  $\Delta E_a$  (eV) from Eq. (1) for charge transfer between two  $\text{Alq}_3$  molecules *in vacuo* and embedded in a sphere of polarizable dipoles with permanent dipole moments (see text).

Environment	Electron	Hole
<i>In vacuo</i>	$-0.30$	$-0.42$
Embedded	$-0.12$	$-0.03$

medium, ordered as in the crystalline phase, tends to oppose the transfer of a positive charge more than that of a negative charge. To gain better insight into the underlying mechanisms, we have repeated the calculations for a fictitious ensemble of polarizable dipoles with no permanent moment, and obtained a much weaker effect, namely  $-0.297$  and  $-0.380$  eV for the negative and positive charge, respectively. Therefore in both cases the response of the environment is dominated by the molecular static dipole moments. It would be tempting to interpret the results in Table I also as a decomposition of the charge-transfer barrier into the reorganization energy of an inner shell (our dimer) and that of an outer shell, in analogy with Marcus theory; however, this is not possible given the interdependency of these two processes, which is inherent to our self-consistent procedure.

The stable phase of the  $\text{Alq}_3$  material in the actual devices is amorphous. In our embedded-dimer scheme, we can study the influence of orientational disorder on the charge transfer by considering a more elaborate model for the dipole distribution and by taking the case of crystalline order as reference. Within a sphere of  $10$  Å around the center of the line joining the two Al atoms (which contains the four molecules of the first shell of neighbors of the central dimer), the dipoles were left unchanged, whereas outside this sphere different distributions were considered: *the orientations* of half of the dipoles were randomized while the magnitudes of the permanent dipoles were fixed. Regarding the latter, either all were kept equal to that of the meridional isomer or one of them (at different locations) was replaced with the value pertaining to the facial isomer, thus allowing for the presence of this minority species as an impurity (with the relative population chosen to be consistent with their energy difference [11]). Consistently, the polarizability tensor was also calculated in our DFT scheme. DFT-based molecular dynamics (Car-Parrinello [17]) simulations, in which the orientation of the external dipoles evolves due to the addition of the induced dipole moments, showed that the onset of disorder drives stabilization of the asymmetric state for the dimer and thus charge localization, be it negative or positive, on one of the monomers. Indeed, as shown in Fig. 1, in contrast to the case of order, the dipole moment of the central dimer does not change sign during the simulation. By selecting this quantity as reaction coordinate, the mean force coincides with the average electric field needed to induce a certain dipole moment. Thus the

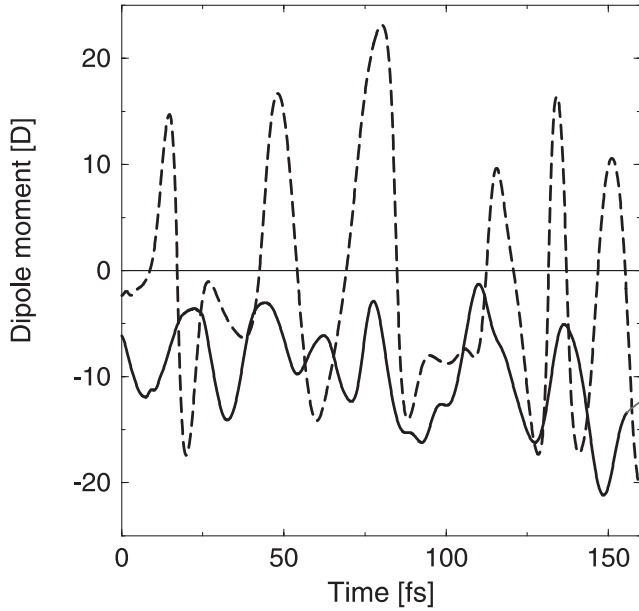


FIG. 1. Variation of the central-dimer dipole moment over the simulation time. The dimer is embedded in an ordered (dashed) or partially disordered (solid) dipole array.

free energy  $\Delta F_a$  for the activation of the charge transfer from one monomer to the other was obtained from thermodynamic integration over the Car-Parrinello trajectories corresponding to five different values of an applied homogeneous electric field for each charge state (electron or hole). In each case the overall length of the trajectories used for the thermodynamic integrations was 1.25 ps, namely, sufficiently long compared to the typical oscillation of 25 fs (see Fig. 1) [18]. While in the case of order such calculations would yield  $\Delta F_a = 0$ , consistent with the estimate made above, in all other cases  $\Delta F_a$  was found to be in the range of 0.15–0.25 eV. We have also verified that a facial isomer included in the ordered array of the meridional isomers tends to increase  $\Delta F_a$  by  $\sim 0.05$  eV. This effect is preserved in the presence of orientational disorder.

To investigate to what extent our conclusions might be affected by approximations intrinsic to our theoretical scheme, we have performed further calculations for the dimer *in vacuo*. One included a correction to the self-interaction (SIC) error via a scaled Coulomb term in the xc functional as introduced in Ref. [19] and the other adopted the hybrid Becke three-parameter Lee-Yang-Parr hybrid functional (B3LYP) [20] xc functional that partially corrects for the same error and also partially accounts for the nonlocality of the exchange. The former resulted in charge distributions which were indistinguishable from those obtained in the BLYP scheme for both anion and cation dimers and in energy differences varying only within few meV. The drastic weakening of the self-interaction error compared to small radicals [19] can be ascribed to the large size of the molecules under study. However, it is also true that all SIC implementations suffer

from empiricism, being dependent on the choice of a few *ad hoc* parameters. This has motivated us further to the B3LYP study, which was highly computationally demanding [21,22]. The B3LYP functional tends to localize the electron and hole densities slightly but still predicts vanishing activation both for the electron and the hole transfer ( $\Delta E_a = 0.005$  eV and  $-0.02$  eV, respectively), thus confirming our conclusions on the origin of the activation energy.

The charge-transfer processes we have so far analyzed in the Alq<sub>3</sub> dimer take place on the Born-Oppenheimer potential energy surface. Nonadiabaticity has a direct influence on the rate of charge transfer via the preexponential factor [23]. So far, no discussion of such effects has been reported in connection with a system like Alq<sub>3</sub>. We obtain an estimate of their role by comparing the period of the lowest excitation between adiabatic electronic states and that of the nonadiabatic transition, which is obtained from the reciprocal of the coupling matrix element

$$\langle o | \frac{d}{dt} | u \rangle = \langle o | \nabla_{\mathbf{R}} | u \rangle \cdot \dot{\mathbf{R}}. \quad (2)$$

Here  $\langle o | \nabla_{\mathbf{R}} | u \rangle$  is the nonadiabatic coupling vector between nuclear motion and an electronic excitation and is the critical physical quantity to be calculated. In the Kohn-Sham representation of a many-electron system, the coupling vector can be expressed as

$$\langle o | \nabla_{\mathbf{R}} | u \rangle = \frac{\langle o | \nabla_{\mathbf{R}} \hat{H}_{\text{KS}}[n(r)](\mathbf{R}) | u \rangle}{\epsilon_u - \epsilon_o}, \quad (3)$$

where  $H_{\text{KS}}[n(r)]$  is the Kohn-Sham Hamiltonian and  $\epsilon_o$  and  $\epsilon_u$  are the corresponding eigenvalues. We follow the formulation introduced in Ref. [10], in which the Hamiltonian is taken at the density  $n(r)$  of the Slater transition state in the symmetric configuration of the dimer that we consider isolated.

For the negatively charged dimer, the lowest excitation energy of the unpaired electron  $\delta\epsilon$  is 0.05 eV, which corresponds to a period of  $\sim 80$  fs. For the positively charged dimer  $\delta\epsilon = 0.0025$  eV, which corresponds to a period of  $\sim 1600$  fs. A schematic illustration of the vectors coupling these excitations to the nuclear motion is given in Figs. 2(a) and 2(b). In both cases, the components on the two different monomers are in antiphase, which suggests their involvement in the transfer process. Also, their values are larger than in the case of the hole. The characteristic time of the nonadiabatic transition [see Eq. (2)] was calculated from 1000 randomly sampled velocity distributions of a canonical ensemble at room temperature. This turns out to be  $\sim 6$  fs for the negatively charged dimer and much shorter, namely, only 0.5 fs, for the positively charged dimer, which is consistent with the stronger coupling. Therefore, we consider this finding as an indication that at room temperature nonadiabatic effects cannot be neglected and tend to reduce the mobility of the hole more strongly than that of the electron.

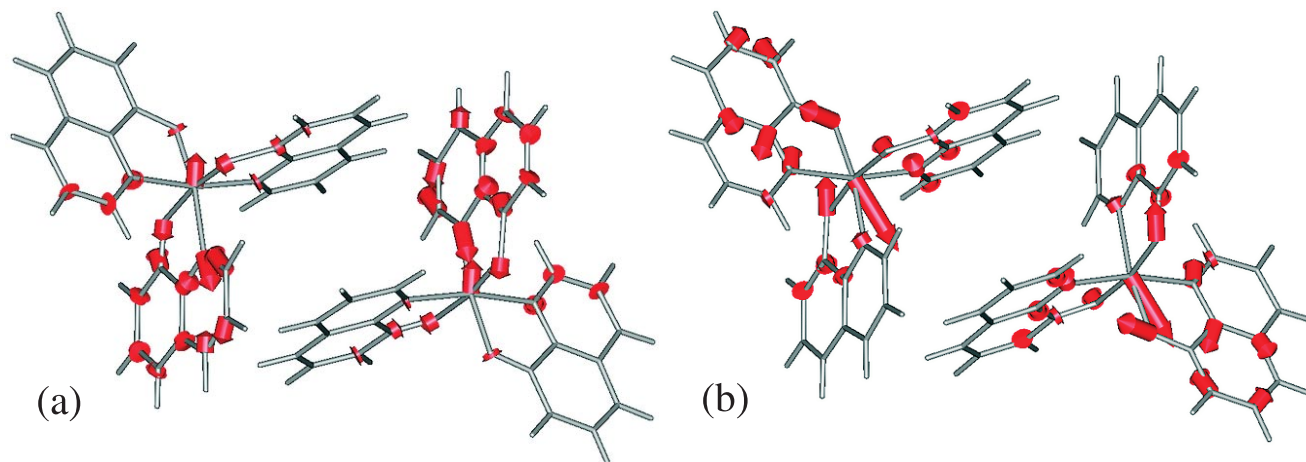


FIG. 2 (color). Nonadiabatic coupling vector (arrows) between the ground state and the lowest excited state of a (a) negatively and (b) positively charged Alq<sub>3</sub> dimer. Note that the length scales of the two coupling vectors differ.

In a simple scheme that takes into account only the properties of the monomer, the difference between the electron and hole mobilities was associated with the difference in the reorganization energy associated with the addition of a charge carrier [11]. The embedded-dimer scheme, on the other hand, shows that the antagonist role of the environment to charge transfer is important, and that it differs in the two cases. Further differences are expected owing to the different weight of nonadiabatic effects on the preexponential factor in the reaction rate expression.

In conclusion, the calculations presented here have provided new insights into the fundamental physics governing the charge transfer in Alq<sub>3</sub> and analogous materials. In particular, our results imply that the activation energy for charge transfer in Alq<sub>3</sub> must be mainly of extrinsic origin, and is bound to be strongly dependent on the specific sample, namely, on the degree of inhomogeneity and the state of disorder. Indeed this finding accounts for the fact that experiments have failed to provide a consistent quantitative account of the activation barriers, but resulted in a widely scattered set of data.

Being based on a simple but well-defined and parameter-free approach, the calculations presented here can easily be extended to many other systems. What we have learned in the case of Alq<sub>3</sub> is very general. By showing that the static molecular dipole moment plays a crucial role, this Letter emphasizes the peculiarity of charge transfer in condensed phases of molecular systems compared with that in a uniform dielectric medium, and challenges the validity of traditional semiclassical mean-field approaches that neglect the contribution of permanent dipoles compared with the global effect of polarizability. This result could also provide new hints for the selection of the components of molecular electronics that exploits their permanent dipoles (both magnitude and arrangement) for the optimization of the carrier mobility.

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