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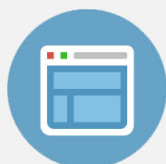
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# Quantitative description of interactions between linear organic chromophores

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To model intermolecular excitation transfer between organic chromophores in the framework of Förster theory, the interaction matrix element is needed for all relative orientations and separations of chromophores. Simulations of extended multi-chromophoric systems thus require a fast but reliable approximation scheme to calculate these dipole interactions. By means of a comparative study of the dipole approximation with quantum chemistry, we demonstrate that the usual line-dipole theory, while suitable for short molecules, breaks down for longer molecules with inter-molecular separations similar to or smaller than the length of the interacting chromophores; a limit that is typically found in conjugated polymer thin films. As a remedy, we propose an improved way of distributing the sub-dipole moments within a line which provides results in very good agreement with the quantum chemistry, and is still simple enough to be used in large scale simulations. © 2012 American Institute of Physics. [<http://dx.doi.org/10.1063/1.4768244>]

## I. INTRODUCTION

Quantifying the interactions between excitations in organic chromophores is key to optimizing the performance of organic solar cells, lasers and LEDs.<sup>1-4</sup> It has long been appreciated that the dominant inter-molecular interaction of excitations arises from a dipole (Förster) coupling.<sup>5-8</sup> Due to the complex morphology of the thin films used in such applications,<sup>9,10</sup> it is also crucial to be able to model this dipole coupling on the basis of a simple dipole-dipole interaction model rather than using an *ab initio* quantum chemical method for the whole sample.<sup>11,12</sup> With that in mind, it is interesting to ask what the range of validity is of such dipole-dipole models and how the dipole moments and intermolecular distances can be related to quantum chemistry calculations while retaining an accurate description of the interaction. The influence of the geometrical configurations of two molecules has been explored through quantum chemistry,<sup>13-16</sup> but to the best of our knowledge, the limits of the line-dipole model have never been explored in depth. This knowledge will enable future studies which explore the effect of morphology and phase aggregation on organic thin films as well as underpinning dynamical studies in relatively large systems, for example, using a quantum Monte Carlo approach,<sup>17-19</sup> or within the Ehrenfest approximation.<sup>20,21</sup>

In this paper, we examine the use and limits of transition dipole theory, both point- and line-dipole models, and compare the results with related sets of quantum chemistry calculations for interacting molecules. As a prototypical example of conjugated chromophores in use for various types of applications, we study the interaction between fluorene molecules.<sup>1,22</sup> Density-functional theory (DFT) and time-dependent DFT (TD-DFT) have been shown to provide an accurate description of isolated fluorenes.<sup>23,24</sup> In the present

study, we also show that it can be effectively used to calculate the transition dipole-dipole interaction energy between pairs of fluorene molecules. In Sec. III, we compare these results with simpler dipole-dipole interaction models where we analyze in detail the effect of the relative orientation of the two transition dipoles and their relative distance as well as changing the number of sub-dipoles within the line-dipole approach.<sup>15,16</sup> We demonstrate that the line-dipole model breaks down for long molecules at separations typical of organic thin films, whatever the number of sub-dipoles used is. In Sec. IV, we present an improved way of distributing the sub-dipole moments of the line-dipole that overcomes the limits of the usual line-dipole approximation, providing excellent agreement with the quantum chemistry benchmarks.

## II. METHODOLOGY

In the following, we investigate the interaction energy between two transition dipoles located on a pair of neighboring linear chromophores. This interaction energy is, for example, a crucial ingredient in the calculation of resonant energy transfer efficiency between the two molecules in a Förster-type transfer picture.<sup>5</sup> In bulk polymer systems, bimolecular interactions occur between molecules with all possible relative orientations. A direct way to calculate the interaction energy between transition dipoles in the two molecules would be to calculate the transition densities of the respective transition in each molecule and then to compute the Coulomb interaction between these two transition charge densities.<sup>11, 12, 14, 25-27</sup> This approach is accurate and intuitive but it is also computationally very expensive<sup>15</sup> and difficult to apply to a large number of different molecular orientations as may be needed for the microscopic modeling of truly extended

multi-chromophoric systems. For this purpose, it would be desirable to have a simpler phenomenological approach that still allows a sufficiently reliable prediction of inter-molecular interaction energies.

The simplest such model is obtained when the inter-molecular interaction is treated as the interaction between two point dipoles. The point dipoles then carry the total respective transition dipole of molecules A and B,  $\mu_A$  and  $\mu_B$ , and the relative distance is given by the center-to-center separation,  $d_{AB}$ , of the two molecules. The interaction energy is then

$$E_{\text{PD}} = \frac{\mu_A \cdot \mu_B}{|d_{AB}|^3} - 3 \frac{(\mu_A \cdot d_{AB})(\mu_B \cdot d_{AB})}{|d_{AB}|^5}. \quad (1)$$

While easy to evaluate, this approximation breaks down, and over-estimates the interactions,<sup>28</sup> when the separation of the molecules is of the order of their length or smaller. This limits the applicability of the point dipole approximation to dilute molecular systems, a limit that is typically not fulfilled, for example, in organic thin films. In a typical fluorene film,<sup>10</sup> the mass density is of the order of 1 g/cm<sup>3</sup>, which, assuming an isotropic distribution, implies an average intermolecular separation of 1.7 nm. This is significantly smaller than the ~6.8 nm length of the O8 chromophore so that such an isotropic morphology is over-simplified. If we assume that molecules are all lying parallel to the xy plane and arranged in parallel lines, sited on a square lattice, the square lattice spacing is 0.9 nm. Therefore, for such a system, we would not expect the point-dipole approximation to give accurate results. In what follows, we use the point-dipole model only as a reference at large inter-molecular separation.

A more accurate approximation has been applied to polythiophenes.<sup>15</sup> Each of the molecular transition dipoles  $\mu_A$  is replaced by  $N$  weaker sub-point-dipoles  $\mu_{A_i}$ , arranged along the backbone of the linear molecular chains. The inter-molecular interaction energy is then given by

$$E_{\text{LD}} = \sum_{i,j}^N \frac{\mu_{A_i} \cdot \mu_{B_j}}{|d_{A_i B_j}|^3} - 3 \frac{(\mu_{A_i} \cdot d_{A_i B_j})(\mu_{B_j} \cdot d_{A_i B_j})}{|d_{A_i B_j}|^5}. \quad (2)$$

For the lowest optical transition from the ground-state, the sub-dipole moments are modulated with a sinusoidal distribution.<sup>15</sup> Taking  $i = 1$  at one end of the molecule, to

$i = N$  at the other end, we then have

$$\mu_{A_i} = \frac{\sin\left(\frac{i\pi}{N}\right)}{\sum_j \sin\left(\frac{j\pi}{N}\right)} \mu_A, \quad (3)$$

with  $\sum_i^N \mu_{A_i} = \mu_A$  by construction. This approach has been successfully applied to estimate incoherent (Förster) transfer rates, for instance, in polythiophene solutions<sup>28</sup> or in supramolecular nanoassemblies.<sup>19</sup> The total length,  $L$ , of the interacting dipoles can be roughly estimated from the spatial extent of the chromophores studied. However, more accurately, it should be related to the actual spatial extent of the electronic transition induced. An example of the change in electronic density induced in a series of fluorene molecules upon photo-excitation from the  $S_0$  to the  $S_1$  electronic state is shown in Figure 1. For instance, the change in density in the octamer, O8, is extended over about six fluorene units which gives a rough estimate of the relevant total dipole length associated with this excitation. This estimate is in good agreement with the value extracted from more detailed quantum-chemistry calculations as discussed below.

In order to quantify the intermolecular interaction from first principles, we have performed TD-DFT calculations of the electronic excitations in a pair of two spatially close molecules. As a specific example, we study pairs of interacting fluorene oligomers. These molecules can, for example, serve as efficient emitters in a variety of devices, and they have been extensively studied in the recent past<sup>22</sup> such that their single-molecule properties are rather well understood. We have investigated in detail the interaction between short fluorene dimers, O2, and longer fluorene octamers, O8. Previous studies have shown that eight fluorene units roughly correspond to the observed conjugation length in fluorene oligomers<sup>23</sup> and with this should also represent typical properties of chromophores in polyfluorene chains reasonably well.

In the calculations, we place two identical oligomers close to each other (cf. Figure 2) and compute the lowest excitation energies from the electronic ground state. The mutual interaction of the two molecules leads to a splitting of the lowest transition energies compared to the transition energies obtained for each of the molecules independently. This splitting between the two lowest transitions can be identified as twice the inter-molecular interaction strength.<sup>15,29</sup> This condition

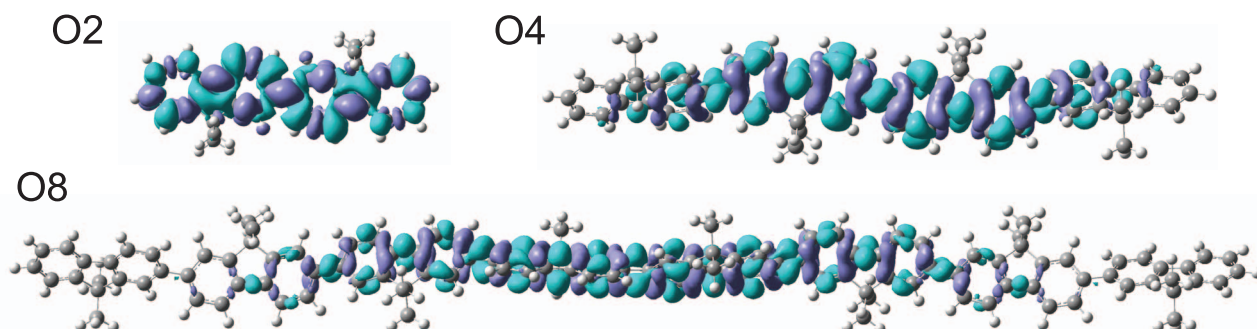


FIG. 1. The change of charge density upon photon absorption in the fluorene dimer, O2, quadramer, O4, and octamer, O8, respectively. Note that for O2 the absorption takes place over the whole molecule, whereas for O8 it takes place on about six fluorene units only.

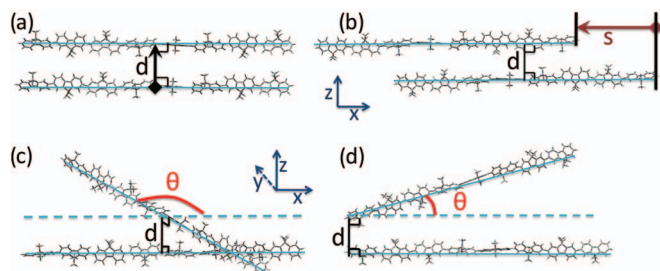


FIG. 2. Schematic of coupled fluorene octamers with different relative distances and orientations. In (a), the two molecules are parallel. (b) is same as (a), but with a translation of the molecular centers by  $s$  as indicated. In (c), both molecules lie in the  $xy$  plane, with their centers separated by a fixed distance  $d$ , and a variation in the angle of rotation  $\theta$  about the molecular centers. In (d), both molecules also lie in the  $xy$  plane and a variation in the angle of rotation about the end of the molecules,  $\theta$ , is indicated.

holds provided all other significantly bright transitions are far off resonance (on the energy scale of the interaction strength, which is the case here). In terms of coupled oscillators, the eigenvalues of the Hamiltonian matrix are  $E = E_{\text{single}} \pm E_{\text{int}}$ , where  $E_{\text{single}}$  is the oscillator energy (transition energy) of a single, isolated molecule and  $E_{\text{int}}$  the interaction energy between the two interacting oscillators (molecules).

To calculate the lowest optical transitions in single molecules and in the coupled molecular system, we use linear response TD-DFT with the B3LYP functional and 6-31G basis set, which have previously been shown to perform well for prediction of transition energies and oscillator strengths of oligofluorenes.<sup>23</sup> The molecular geometries have been optimized for each molecule in the electronic ground state separately, only the transition energies are calculated for the coupled system. The optimized geometries have finite dihedral angles between adjacent fluorene units (corresponding to the fluorene  $\alpha$ -phase) and the conformation is such that the sign of dihedral angles alternates while going along the chain. From the TD-DFT calculations for the coupled system, we extract the interaction energy as explained above from the splitting of the two lowest transitions. We then compare the results obtained from the full quantum-chemistry calculations, with the interaction energies obtained from the simplified dipole-dipole interaction models to assess their accuracy and applicability. The value used for the total transition dipole moment of each molecule is taken directly from the TD-DFT calculations for a single molecule. Values obtained are summarized in Table I. We obtain the length of the dipole,  $L$ , needed in the line-dipole model by fitting the calculated line-dipole interaction energy to the interaction calculated by quantum chemistry for parallel molecules (Figure 2(a)) at medium-range

TABLE I. Parameters for the three oligomers of different lengths as used in the dipole-dipole modeling. Details for the fluorene dimer, O2, and octamer, O8, are discussed in the text. Parameters for the quadramer, O4, are included for comparison.

	Physical length (nm)	Dipole length $L$ (nm)	Dipole moment $\mu$ (eÅ)
O2	1.7	1.5	1.97
O4	3.3	2.8	3.13
O8	6.8	5.7	4.66

separation ( $d$  between 1 and 2 nm for O2 and between 3 and 5 nm for O8). As expected, these values are slightly smaller than the overall length of the molecules and are also consistent with the spatial extent of the transition density shown in Figure 1.

In molecular systems of practical interest, bimolecular processes are (in a Förster-type picture) mediated by interaction matrix elements of the type discussed above. However, typically the interaction is between different molecular states (as in, e.g., exciton-exciton annihilation processes), or between absorption and emission dipoles of molecules (as in excitation transfer where one emission dipole and one absorption dipole contributes), or even between different molecular species. However, in the quantum-chemical approach discussed above, the interaction energy can only easily be identified in the symmetric case when both molecules are identical. This is why here all the calculations are performed for the absorption ( $S_0$ ) geometries of the two molecules. By comparing with this symmetric scenario, we will learn how a simple dipole-dipole model can be applied to accurately predict interaction energies between two line dipoles. After we have identified the limitations of these simpler models, they can then be reliably applied to more complicated scenarios of interest. In Sec. III, we will show that even the line-dipole approximation described above breaks down in some of the scenarios discussed such that it cannot safely be used to predict interaction energies in certain parameter ranges. To resolve this issue, we then propose an improved model which gives good agreement with the quantum-chemistry in all scenarios studied.

### III. RESULTS AND DISCUSSION

In the following, we analyze in detail the interaction energy between two identical fluorene oligomers. In Figure 2, the various different scenarios for the relative orientation of the two molecules we consider are defined. One molecule is fixed in space with the molecular backbone along the  $x$ -axis. The other molecule, whose position is being varied, always lies in the  $xy$  plane without loss of generality. These configurations are particularly relevant in the case of spin-coated films, where the molecules lie in parallel planes. The distance between the two molecules is  $d$ , and the angle between the two molecules, in the  $xy$  plane, is  $\theta$ , independent of the center of rotation. In Figures 2(a) and 2(b), we have  $\theta = 0$  whereas in cases (c) and (d)  $\theta \neq 0$ . In case (b), we shift the center of one molecule by the distance  $s$  on the  $x$ -axis. The rotation in case (c) is around the center of the molecule, whereas in case (d), it is around one end of the molecules. Below, we study two different molecular lengths in detail (fluorene dimer and octamer). We complement these two limiting cases of short and long molecules with additional modeling parameters for the intermediate case of a fluorene quadramer (cf. Figure 1 and Table I).

#### A. Short molecules: The O2 dimer

We first present results for a short molecule, O2, the oligomer made of two fluorene units where at all but the

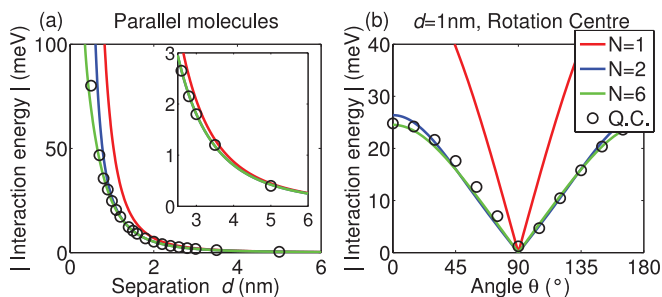


FIG. 3. The O2 interaction energies obtained by the point and line-dipole approximations are compared to the TD-DFT (Q.C.) results. The two line-dipoles lie in parallel planes with  $N$  sub-dipoles per line: (a) for parallel dipoles as a function of the separation,  $d$ , between the two line-dipoles [Fig. 2(a)] and (b) as function of  $\theta$  when  $d = 1$  nm (Fig. 2(c)). The inset (magnification of the graph (a) for  $2 \text{ nm} < d < 6 \text{ nm}$ ) shows the very good agreement of all the different approximation schemes for separations  $d > 2.5 \text{ nm}$ .

closest separations we expect the point dipole approximation to work reasonably well.

In Figure 3(a), the effect of varying the separation between the two parallel molecules [cf. Fig. 2(a)] on the interaction strength is shown. At separations  $d > 0.5 \text{ nm}$  a line-dipole with only two sub-dipoles is sufficient to obtain excellent agreement between the splittings calculated by quantum chemistry and the line-dipole interaction energy, with the average discrepancy being 2% in the case of six sub-dipoles. Fluorene molecules have a finite width of around  $0.25 \text{ nm}$  and cannot be closer than this. As expected, at large separations ( $d > 2 \text{ nm}$ ) even the point-dipole approximation is excellent.

In Figure 3(b), we show the interaction energy for two molecules lying in parallel planes separated by  $d = 1 \text{ nm}$ , with a rotation angle  $\theta$  around their centres, as described in Figure 2(c). At this relatively small separation, the line-dipole approximation works well at all angular orientations for line-dipoles made of at least two sub-dipoles (the average error is 3.3% in the case of six sub-dipoles). The point-dipole approximation,  $N = 1$ , is poor for all non-perpendicular angles. For perpendicular orientation ( $\theta = 90^\circ$ ), the interaction strength within the line- (and point-) dipole approximation is strictly zero. In the quantum chemistry calculations, it shows some very small residual interaction due to the finite width of the molecule (which is not taken into account in the simpler models).

The overall good performance of the line-dipole approximation demonstrated above clearly shows that it is quite safe to model interactions of neighboring fluorene dimers (even at small separations as in thin films) using a simple line-dipole approach. We now turn our attention to a more challenging case, molecules significantly longer than their separation.

## B. Long molecules: The O8 octamer

Figure 4 shows the interaction energy between two fluorene octamers, O8, aligned in a parallel configuration as depicted in Fig. 2(a). We note that the minimum separation for which it was possible to unambiguously extract the inter-

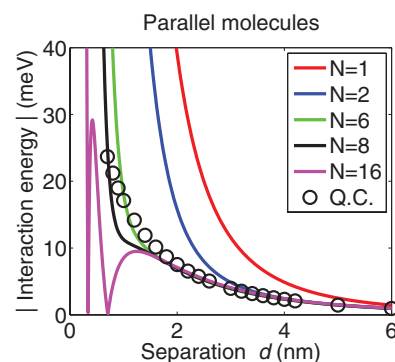


FIG. 4. The O8 interaction energy obtained by the point and line-dipole approximations are compared to the TD-DFT results. The two parallel line-dipoles lie in parallel planes with  $N$  sub-dipoles per line as a function of their separation,  $d$  [Fig. 2(a)].

molecular interaction energy from the quantum-chemistry calculations was  $\sim 0.8 \text{ nm}$ . For separations smaller than this, the structure of electronic transitions started to deviate significantly from a simple dipole-dipole interaction picture of the two molecules. This aspect might be worthwhile studying in more detail in future work. For the longer O8 molecules, the point-dipole approximation clearly breaks down at separations less than  $\sim 5 \text{ nm}$  (to be compared with the length of the chromophore dipole at  $5.7 \text{ nm}$ ). At separations larger than  $1 \text{ nm}$ , good agreement, having an average discrepancy of 5%, with the quantum chemistry is found when the line-dipole is made of six sub-dipoles. However, at smaller separations and when the number of sub-dipoles per line is at least 16, we observe a change of sign of the O8 interaction energy and correspondingly a very poor prediction of values for the interaction strength. (Note that in the figure we compare the absolute values of the interaction energy.) The origin of this sign change lies in the change in dominant character of the dipole interaction from repulsive to attractive and can be understood as follows. From Eq. (2), it is clear that two parallel dipoles [configured as in Fig. 2(a)] will experience a repulsive interaction ( $E_{LD} = \mu_A \cdot \mu_B / |d_{AB}|^3$ ), whereas two parallel dipoles arranged end on will experience an attractive interaction ( $E_{LD} = -2\mu_A \cdot \mu_B / |d_{AB}|^3$ ). Physically, this attraction arises from the dominant contribution of the two nearest ends of the dipoles which are oppositely charged. Considering now the line-dipole approximation as used in Figure 4, at small separations with many sub-dipoles, the unphysical switch to an attractive interaction arises from the large number of sub-dipole pairs which are aligned almost end on. Clearly, real molecules do not possess such a series of very small sub-dipoles such that modeling with very small sub-dipoles does not reflect the interactions between the molecules in a physically meaningful fashion. We find that this sign-change behavior limits the applicability of the usual line-dipole approximation as for small inter-molecular distance with increasing number of sub-dipoles convergence is not reached at the correct interaction strength.

In Figure 5, the separation,  $d$ , between the molecules is fixed at 1 or 2 nm, respectively, with a rotation of angle  $\theta$  either about the center or the end of the molecules. Seen from above, this results in a + - shaped or an L-shaped

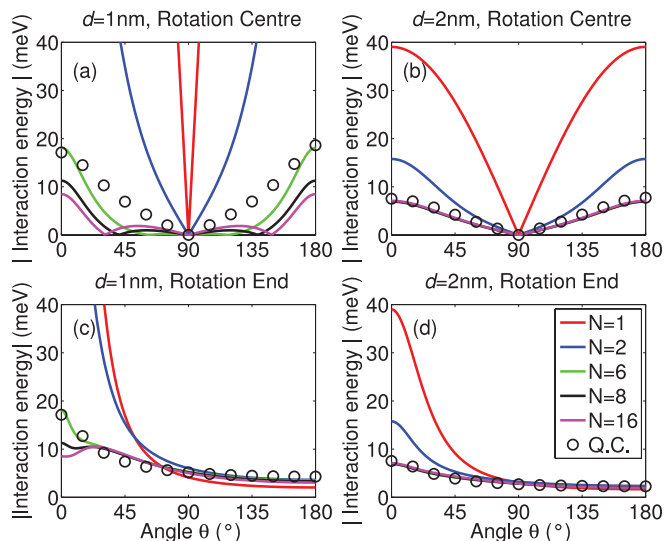


FIG. 5. Comparison of the O8 interaction energy obtained by the line-dipole approximation with the quantum chemistry results, for a range of number,  $N$ , of sub-dipoles per line-dipole, with the two line-dipoles lying in parallel planes, separated by either  $d = 1$  nm ((a) and (c)) or  $d = 2$  nm ((b) and (d)), and as a function of  $\theta$ , which denotes the angle of rotation around the center of the molecules ((a) and (b) [cf. Fig. 2(c)]) or around the end of the molecules ((c) and (d) [cf. Fig. 2(d)]).

configuration, respectively [cf. Figs. 2(c) and 2(d)]. We observe that when the separation between the molecules is large (2 nm), then the quantum chemistry and dipole-modeling agree well, as long as we use more than six sub-dipoles. This is also true for rotation around the end of the molecule. At smaller separation (1 nm), for line-dipoles made of about six sub-dipoles, the results agree qualitatively for both rotations, but not quantitatively for the rotation about the center. The latter represents the configuration for which the molecules are closest to each other, such that clearly the limit of the dipole-modeling is reached. In this case, all the dipole results are relatively far from the quantum chemistry results. At  $d = 1$  nm, it is clear that the line-dipole model starts losing its validity with worsening quantitative agreement for increasing number of sub-dipoles.

Finally, in Figure 6, the molecules are parallel ( $\theta = 0$ ), but the center of one molecule is shifted with respect to the center of the other molecule by a distance,  $s$ , along the molec-

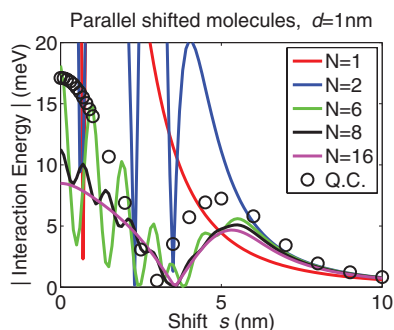


FIG. 6. Comparison of the O8 interaction energy obtained by the line-dipole approximation with the quantum chemistry results, for a range of number  $N$  of sub-dipoles per line-dipole, with the two parallel line-dipoles, separated by 1 nm, as function of the shift  $s$  between the two molecules (as in Fig. 2(b)).

ular length as sketched in Figure 2(b). The quantum chemistry results give a smooth trend for the interaction energies with a change in sign as the shift reaches about half the chromophore length at  $\sim 3$  nm. The reason again is that the molecules are getting almost aligned on the same line when the shift of the center becomes large enough. This is consistent with previous calculations presented for OP and OPV molecules, where the transition from H-aggregates to J-aggregates occurs when the shift becomes bigger than half the length of the chromophores.<sup>14</sup> The results for the dipole modeling are very different depending on the number of sub-dipoles used (they reach convergence at about 16 sub-dipoles). More importantly, however, for a smaller number of sub-dipoles, e.g., for 6 or 8 sub-dipoles, which gave good results for the scenarios studied in Figures 4 and 5, the predicted interaction energies undergo unphysical oscillations and changes in sign (again, the absolute value is plotted). With an average deviation from the quantum chemistry of 23% for six sub-dipoles, these results are in poor agreement with the quantum chemistry. The source of these oscillations is rooted in the discrete character of the line-dipole when the number of sub-dipoles is too small. As we shift one line made of discrete sub-dipoles, the interaction between the sub-dipoles of the two lines varies considerably. For instance, if two sub-dipoles, aligned in the same direction, are on top of each other, the interaction between them will be repulsive. However, if we shift one of these two sub-dipoles by half of the length of the sub-dipoles, the dominant interaction will become much smaller, before increasing again as we shift again by half the length of the sub-dipoles. These oscillations disappear when the lines are made of many sub-dipoles, because the line of sub-dipoles is continuous again. This mechanism is illustrated in Figure 7.

In the O8 molecules, the excitation is localized on approximately six fluorene units, as shown in the transition density plot of Figure 1. The results obtained so far for O2 and O8 indicate that the optimal number of sub-dipoles to use for the usual line-dipole approximation is roughly the number of active monomer units (apart from the scenario studied in Figure 6). Nevertheless, the interaction energies calculated with this line-dipole do not always give results in good agreement with the quantum chemistry and can sometimes cause unphysical artifacts, as in Figure 6. For the results in Figure 6, this can partly be fixed by introducing more and more sub-dipoles. On the other hand, however, the number of

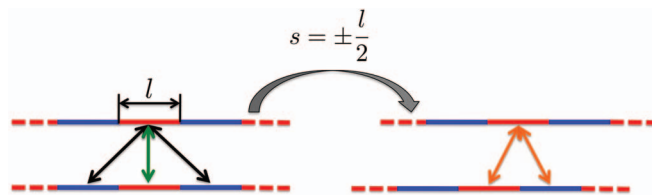


FIG. 7. Illustration of the origin of the oscillations in the interaction of Figure 6. With no shift (left), the strongest interaction between sub-dipoles is given by the green arrow.  $l$  is the length of the sub-dipoles. If we shift one molecule by  $l/2$  (right), then the interaction between the sub-dipoles is strongly reduced as the strongest one is now given by the orange arrows. If we shift again the molecule by a half of the length of the sub-dipoles, we are back to the situation with strong interactions (left) (neglecting end effects).

sub-dipoles needed in Figure 6 does not agree with the number of sub-dipoles giving good results and physical meaningful behavior in Figures 4 and 5. Unfortunately, this dilemma cannot be fixed for the system parameters studied here at distance of  $\sim 2$  nm or below. This severely limits the applicability of the usual line-dipole approximation to situations of great interest, e.g., thin films made from polyfluorene or other materials where extended chromophores are densely packed. In Sec. IV, we propose an improvement of the usual line-dipole approximation that resolves this issue.

#### IV. AN IMPROVED LINE-DIPOLE APPROXIMATION

Above we have demonstrated that the line-dipole approximation in its usual form<sup>15,28</sup> does not always give physically meaningful results for extended chromophores at separations smaller than their length, as is typically the case in thin films. In this section, we develop a slightly different formulation of the line-dipole approximation designed to resolve these issues. We then show that this new approximation scheme can safely be applied to calculate interaction energies also in molecular systems with extended chromophores that are densely packed.

Instructed by the structure of the density changes upon photoexcitation as shown in Fig. 1, we modify the line-dipole approximation, Eqs. (2) and (3), such that we introduce additional nodes to the distribution of sub-dipoles along the backbone of the molecule, Eq. (3). The new formulation for the distribution of sub-dipoles then reads

$$\mu_{A_i} = \frac{|\sin\left(\frac{iP\pi}{N}\right)|}{\sum_j |\sin\left(\frac{jP\pi}{N}\right)|} \mu_A, \quad (4)$$

where  $P$  is the number of antinodes of the distribution function. In the following, we demonstrate that this new approach more accurately represents the nature of the transitions as unphysical behavior even at small inter-molecular distances can completely be avoided if applied correctly.

For the example of a fluorene octamer O8, in Figure 8(a), we identify about five microscopic dipoles per fluorene unit (the figure shows a magnification of the centre of the fluorene

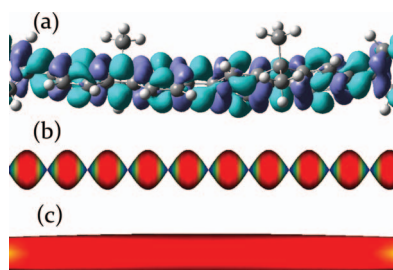


FIG. 8. (a) Magnification of the two central fluorene units in O8 of the transition density plot (Fig. 1). (b) Corresponding part of the sub-dipole distribution of the associated line-dipole representation with the improved model ( $P = 30$ ). The red parts have a high dipole moment, the blue parts a low one. The sub-dipole bumps mimic the distribution of pairs of negative and positive charges on the molecule. (c) Corresponding part of the sub-dipole distribution of the associated line-dipole representation with the usual model.

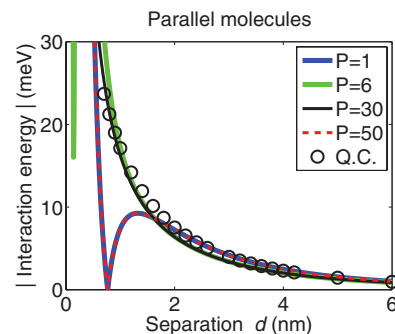


FIG. 9. Results for O8, in the case of Fig. 2(a) (parallel molecules), for a series of number of antinodes  $P$  in the distribution of sub-dipoles. The line-dipoles are made of  $N = 50$  sub-dipoles each, therefore,  $P = 1$  corresponds to the usual line-dipole approximation.

octamer in Figure 1). Guided by this observation, with the excitation being extended over about six fluorene units in O8, we would expect that inclusion of about 30 antinodes in the dipole distribution of the line-dipole approximately reflects the nature of this transition. A part of such a line-dipole is illustrated in Figure 8(b): roughly each pair of negative and positive charges in space is associated with a maximum of the sub-dipole distribution. To highlight the difference in construction, this is compared with the usual line-dipole approximation in Figure 8(c), where there is just a continuum of sub-dipoles representing about the same total dipole moment. The results discussed in the following clearly show that the microscopic physics of the actual charge distribution is mimicked more accurately by our new line-dipole approach. In the following, we chose to include  $N = 50$  sub-dipoles and vary the number of antinodes  $P$  in the distribution function to study its influence on the results.

Figure 9 shows the results for varying separation,  $d$ , in the parallel molecule case, as studied before in Figure 2(a). We notice, as expected, that the cases  $P = 1$  and  $P = 50$  approximately correspond to the case of the usual line-dipole approximation. The results for  $P = 6$  and  $P = 30$  are essentially identical, and we do not find the unphysical change of sign at  $d \approx 0.8$  nm any more (in the case of  $\theta = 0$ ). This indicates that the results are quite insensitive to the exact number of nodes included. These results are now only 2.6% away on average from the quantum chemistry results, in good agreement over the full range of values of  $d$  studied, including those small values of  $d$  where the usual line-dipole approximation failed—the largest error is now only 6%, compared to more than 80% previously. In Figure 10, results are presented for the rotation around the centre ((a) and (b)) and the end ((c) and (d)) of the molecules [cf. Figs. 2(c) and 2(d)], respectively, for the case where the molecules are separated by  $d = 1$  nm ((a) and (c)) and  $d = 2$  nm ((b) and (d)). The results for  $P = 6$  and  $P = 30$  show much better agreement with the quantum chemistry than any of the energies obtained previously with the usual line-dipole approximation. Good agreement is reached for all angles, with a maximum error of 15%. Figure 11 displays the result for a shift  $s$  between the two parallel molecules [cf. Figure 2(b)]. The unphysical oscillations observed previously when the number of sub-dipoles was too



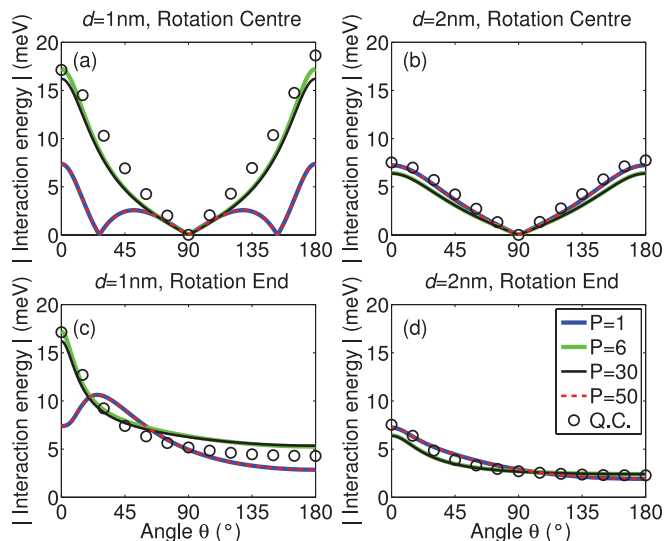


FIG. 10. Results for O8, in the case of Fig. 2(c) and case of Fig. 2(d) (rotation around the centre ((a) and (b)) or around the end ((c) and (d)), for a set of different numbers of antinodes  $P$  in the distribution of sub-dipoles. Here, either  $d = 1$  nm ((a) and (c)) or  $d = 2$  nm ((b) and (d)). The line-dipoles are made of  $N = 50$  sub-dipoles each, therefore,  $P = 1$  corresponds to the usual line-dipole approximation.

small are eliminated (cf. Fig. 6), and the results for  $P = 6$  and  $P = 30$  are now in good agreement with the quantum chemistry, with the average error being now only about 12%.

The results shown in Figures 9–11 clearly demonstrate the strength of our new formulation of a line-dipole approximation. In particular, we show that it can be applied to scenarios where the usual line-dipole approximation led to quantitatively poor results or even unphysical behavior, namely, those cases where the inter-molecular distance is significantly smaller than the spatial extension of each of the interacting chromophores. This case is particularly interesting as it is typically realized in molecular thin films. Apart from this small-distance case, our approach can equally well be applied to larger intermolecular separations and smaller molecules (such as O4) where we have checked that it also produces accurate results.

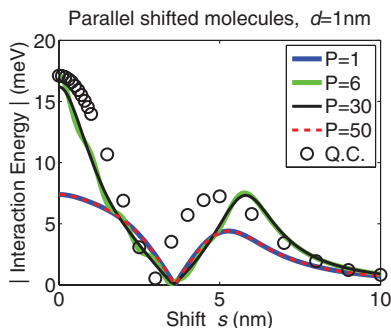


FIG. 11. Results for O8, in the case of Fig. 2(b) (parallel molecules with a shift  $s$  of one molecule along the  $x$ -axis) for a series of number of antinodes  $P$  in the distribution of sub-dipoles. The line-dipoles are made of  $N = 50$  sub-dipoles each, therefore,  $P = 1$  corresponds to the usual line-dipole approximation.

## V. CONCLUSIONS AND OUTLOOK

In the first part of this work, we have shown that for short molecules, like the fluorene dimer studied, the line-dipole model provides a very accurate approximation to the inter-molecular interaction energy. With a line-dipole made of two sub-dipoles only, the calculated interaction energy is in excellent agreement with the quantum chemistry calculations for the full range of separations studied, ranging from typical distances relevant to both dilute solutions and thin films. We demonstrated in the second part that the usual line-dipole model breaks down for longer molecules, where the inter-molecular separation is similar to or smaller than the molecular length. In certain parameter ranges which are very relevant to the description of molecular thin films, we have found unphysical behavior of the interaction strength calculated such that the usual line-dipole approximation cannot be safely applied to these scenarios. In the last part, we presented a new formulation of the line-dipole approximation which enables us to overcome these limitations. This new formulation of the interaction of transition dipoles includes nodes in the distribution of sub-dipole moments in addition to the simple line-dipole approximation. Results obtained are then in excellent quantitative agreement with the TD-DFT calculations for all spatial separations and relative orientations considered.

The applicability of our new approach to scenarios where also static dipoles contribute to the inter-molecular interaction, could be the subject of future studies.

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