

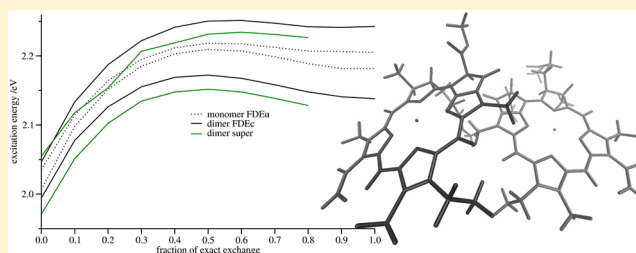
# Exciton Coupling Mechanisms Analyzed with Subsystem TDDFT: Direct vs Pseudo Exchange Effects

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**S** Supporting Information

**ABSTRACT:** The dominant effect in exciton coupling is usually the so-called Coulomb coupling contribution, that is the Coulomb interaction between transition densities of localized excitations. At short distances, Dexter-type exchange effects are discussed to play a role, which are not well described by (semi)local functionals in time-dependent density functional theory (TDDFT) calculations. Overall, a large effect of the percentage of exact exchange on the resulting exciton splittings is known. Subsystem TDDFT allows one to analyze the exciton coupling mechanism by distinguishing direct from indirect effects, that is, changes in the actual coupling mechanism from modifications in the underlying local excitations. Our analysis shows that the strong influence of exact exchange is not due to a direct Dexter-type (exchange) coupling, but rather to an increased Coulomb (or pseudo-exchange) coupling triggered by a change in transition densities. This is demonstrated in calculations for 2-pyridone and chlorophyll dimers. We finally propose a route to efficient calculations of excited states of large pigment aggregates with hybrid functionals, which so far has been out of reach for quantum chemical methods.



## 1. INTRODUCTION

Excitonic coupling, that is, the interaction of two excited states localized at different chromophores, is a common model used in the theoretical description of spectral properties and energy transfer processes in chromophore aggregates. Traditionally, Coulombic ("Förster")<sup>1</sup> and exchange ("Dexter")<sup>2</sup> coupling mechanisms are distinguished. Later extensions concerned the consideration of overlap, charge-transfer, and correlation contributions to the coupling, which are significant only at short distances (see, for instance, refs 3–7, and the overview given in refs 8–11). Some of these studies also indicated that the impact of the Dexter-type coupling is small in most cases, even if compared to other short-distance effects. However, density-functional theory (DFT)-based studies often report a strong dependence of exciton couplings on the percentage of exact exchange,<sup>12,13</sup> which could be regarded as a hint for increased Dexter-type contributions.

Among the methods used to calculate exciton couplings are perturbative approaches, which are based on the idea of interacting monomers. These approximations, which may break down at very small intermolecular distances, can be validated against supermolecular calculations (see also refs 14–16). The latter, however, do not directly allow one to identify the different coupling contributions mentioned above, and thus make it more difficult to actually distinguish different types of coupling mechanisms. How these different effects are considered in a supermolecular calculation depends on the theoretical method applied. In time-dependent density functional theory (TDDFT) studies employing nonhybrid

exchange–correlation kernels, Dexter-coupling is included in terms of matrix elements of an induced density-dependent exchange potential rather than "true" exchange-type two-electron integrals (called "direct" Dexter coupling in the following). Applying nonlocal hybrid functionals leads to (partial) inclusion of the this direct Dexter-coupling mechanism according to the fraction of exact exchange applied. The exchange–correlation contribution to the coupling in pure density functional approximations (DFA) is often much smaller than in corresponding hybrid DFA in the generalized Kohn–Sham (GKS) framework or configuration interaction singles (CIS) calculations (effectively corresponding to 100% exact exchange), c.f., for instance, refs 17, 18. This could suggest that the exchange part accounted for in a (semi-)local exchange–correlation approximation only covers a rather small part of the "exact exchange" or direct Dexter coupling. The observations reported on this issue are diverse: On one hand, direct Dexter-type terms can significantly change the exciton coupling at very small distances.<sup>19</sup> But on the other hand, it was shown for an ethene dimer with a distance of 4 Å that short-range effects are clearly dominated by other than direct Dexter-type terms.<sup>4,5</sup> It was also reported that the amount of the exact exchange can have a large effect on the exciton coupling in some cases,<sup>12,13</sup> while it appears to be less important in others.<sup>20</sup> The question thus arises whether the main effect of the increase in exact

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exchange in TDDFT-based calculations is due to a pseudo exchange effect rather than a direct Dexter-type coupling mechanism.

The change in calculated exciton splittings in supermolecular TDDFT calculations upon inclusion of exact exchange can be due to several factors, which are differences in (i) the ground state density, (ii) the local transition densities, (iii) the coupling mechanism (via inclusion of direct Dexter-type couplings), and (iv) the description of charge-transfer states. Point (iv) is related to the amount of exact exchange through the failure of standard TDDFT methods to describe long-range charge-transfer excitations.<sup>21–28</sup> For the calculation of exciton splittings, the resulting artificially low-lying charge-transfer states are disadvantageous, since they may mix with the valence excitations of interest and thus adulterate them.<sup>12,16</sup> One possibility is to “ignore” these excitations in a selective TDDFT scheme<sup>29</sup> but the problem can also (partially) be cured by introducing exact exchange,<sup>22,25,28,30</sup> that is generalizing the Kohn–Sham formalism to allow for nonlocal density functionals.<sup>31</sup> For a recent review, concerning the challenges and progress made in TDDFT including partitioning schemes, the reader is referred to ref 32. We would like to mention that some previous studies concluded that charge-transfer<sup>4–6,33</sup> and double-excitation<sup>7</sup> contributions to the exciton coupling are significant at short range. Moreover, it was suggested that the neglect of Dexter and charge-transfer contributions might lead to fortunate cancellation of errors in the exciton coupling parameters, as the first typically increases the exciton coupling parameters whereas the latter decreases them.<sup>34</sup>

Supermolecular TDDFT calculations do not allow for direct conclusions on the precise coupling mechanisms and their analysis can be complicated by the problems in describing charge-transfer states. Subsystem TDDFT,<sup>35</sup> which is based on work by Casida and Wesolowski,<sup>36</sup> forms an alternative approach to supersystem calculations and intermolecular perturbation theory. In this approach, the transition density of the coupled systems is constructed as a linear combination of local transition densities. Thus, it does not suffer from incorrectly placed charge-transfer states from one pigment to the other.<sup>37</sup> Moreover, it allows one to employ different approximations for the inter- and intrasubsystem part of the response matrix. The original implementation of coupled frozen density embedding (FDEC)<sup>35</sup> only supported nonhybrid exchange-correlation functionals. Recently, we extended this implementation to enable FDEC calculations within the Tamm–Dancoff approximation (TDA).<sup>38</sup> In this approach, hybrid functionals can easily be used within the subsystems, which enables us to employ exact exchange for the intra-subsystem part in FDEC calculations. It was shown that FDEC calculations with hybrid functionals solely applied within the subsystems and generalized-gradient approximation (GGA) for the nonadditive part yield good agreement of the electron densities to those of the supermolecular calculations with the same hybrid functional.<sup>39</sup> FDEC calculations of this kind only contain the indirect effect of the exact exchange due to the change in the ground-state and localized transition densities, but no direct Dexter-type exchange interaction. In this way, a comparison of the FDEC results to supermolecular hybrid-TDDFT calculations allows to draw conclusions on the impact of the direct Dexter-type coupling compared to the indirect effects of the exact exchange, which is not possible on the basis of supermolecular calculations alone. This also allows us to test and refine, in a qualitative sense, earlier recommendations for

exchange–correlation functionals suited for exciton coupling calculations. For a precise quantitative recommendation of the fraction of exact exchange to be used for this purpose, a more extensive benchmark study would be required, which is beyond the scope of this work. As will be shown in the following, it is much more important to include the exact exchange in the intrasubsystem part of the coupling calculations than in the actual intersubsystem part. This is an important observation as it allows one to restrict the expensive exact exchange integral calculations to within the subsystems and to maintain a linear scaling effort with the number of subsystems. This opens up the way for exciton-coupling calculations of effective hybrid-functional quality for very large system size. In this study, we provide qualitative evidence that the inclusion of exact exchange in the intrasubsystem part can be important to reproduce more accurate CC2 results, as similarly done for the supermolecular case in ref 12. We can thus make an important statement about the actual mechanism by which exact exchange affects the exciton couplings, a question which was not addressed in ref 12.

This article is organized as follows. After a brief outline of the theory and the computational details in Section 2, we present and discuss the results for a 2-pyridone dimer (Section 3.1) and a chlorophyll *a* dimer taken from the light-harvesting complex II of green plants (Section 3.2). In the first example, the focus is on the reproducibility of the distance dependent excitation energies and exciton splittings. Here we will also analyze the different impact of the charge-transfer problem in supermolecular and subsystem TDDFT calculations and how it is affected by the amount of exact exchange. In the second example, we investigate the dependence of the excitation energies, exciton splittings, and transition densities on the amount of exact exchange in more detail for a fixed structure, taken from a biological system. Finally, we will conclude from our results in Section 4.

## 2. THEORY AND COMPUTATIONAL DETAILS

At this point we will only briefly outline the FDEC-TDA working equations. For a more detailed discussion and a comparison to the complete FDEC-TDDFT scheme, we refer the reader to ref 38.

The supermolecular TDA equations read

$$\mathbf{Ax} = \omega \mathbf{x} \quad (1)$$

where  $\mathbf{A}$  is the response matrix,  $\mathbf{x}$  a solution vector, and  $\omega$  is the corresponding excitation energy.<sup>40,41</sup> After transformation to the basis of the local excitations, the FDEC-TDA working equation for two subsystems reads

$$\begin{pmatrix} \tilde{\mathbf{A}}^I & \tilde{\mathbf{C}}^{I/II} \\ \tilde{\mathbf{C}}^{II/I} & \tilde{\mathbf{A}}^{II} \end{pmatrix} \begin{pmatrix} \tilde{\mathbf{x}}^I \\ \tilde{\mathbf{x}}^{II} \end{pmatrix} = \omega \begin{pmatrix} \tilde{\mathbf{x}}^I \\ \tilde{\mathbf{x}}^{II} \end{pmatrix} \quad (2)$$

where,

$$\tilde{\mathbf{A}}_{\nu\mu}^I = \delta_{\nu\mu} \omega_{\nu}^I \quad (3)$$

$$\tilde{\mathbf{C}}_{\nu(I)\mu(II)}^{I/II} = \int d\mathbf{r}_1 \int d\mathbf{r}_2 \rho_{\nu(I)}^t(\mathbf{r}_1) f_{\text{Cxc}}^{I/II} \rho_{\mu(II)}^t(\mathbf{r}_2) \quad (4)$$

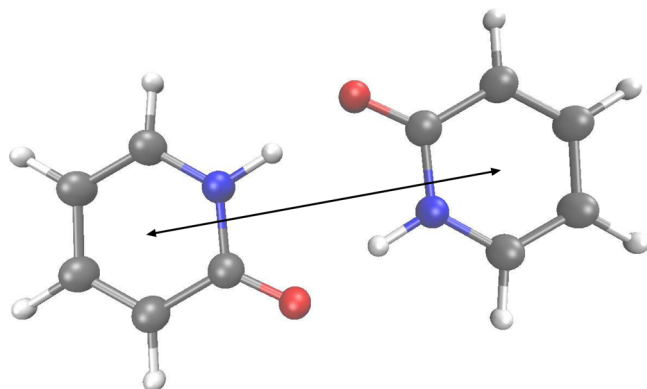
Here, the response matrix consists of diagonal intra- ( $\tilde{\mathbf{A}}^I$ ,  $\tilde{\mathbf{A}}^{II}$ )- and nondiagonal intersubsystem ( $\tilde{\mathbf{C}}^{I/II}$ ,  $\tilde{\mathbf{C}}^{II/I}$ ) blocks. In this formulation, matrix elements of the intersubsystem blocks,  $\tilde{\mathbf{C}}_{\nu(I)\mu(II)}^{I/II}$ , contain the transition density  $\rho_{\nu(I)}^t$  of one particular excitation  $\nu$  in subsystem *I* coupled to that of the excitation  $\mu$  in

subsystem  $II$  ( $\rho_{\mu(II)}^t$ ) by the coupling kernel  $f_{Cock}^{I/II}$ .<sup>35</sup> In contrast to the full FDEc-TDDFT, the intersubsystem matrix elements in FDEc-TDA can directly be interpreted as excitonic coupling constants between particular local excitations.<sup>38</sup>

All calculations were performed with a locally modified version of the Amsterdam Density Functional (ADF) program package.<sup>42</sup> Hereby, we employed the triple- $\zeta$  basis set with one set of polarization functions for all atoms (TZP) in combination with the Becke–Perdew functional (BP86)<sup>43,44</sup> for geometry optimizations and Becke's three parameter functional (B3LYP)<sup>45,46</sup> with varying amount of exact exchange for excited state calculations. For the nonadditive kinetic contribution of the embedding functional, we employed the so-called GGA97.<sup>47</sup> The calculations were performed with the ADF implementation of FDEu<sup>48,49</sup> and a modified version of the FDEc formalism reported in ref 35. The CC2 reference calculations were performed with the RICC2 module<sup>50</sup> of the TURBOMOLE program package<sup>51</sup> employing a triple- $\zeta$  basis set with polarization functions (TZVP) from the TURBOMOLE basis set library. Further details of the FDE calculations and the effect of the TDA are discussed in the Supporting Information (SI).

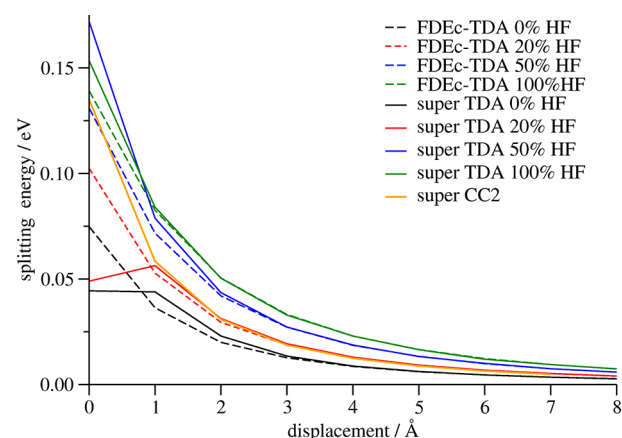
### 3. RESULTS

**3.1. 2-Pyridone Dimer.** For the 2-pyridone dimer it is known that the amount of exact exchange can have a quite drastic effect on the exciton splitting energies.<sup>12</sup> Thus, we have chosen this example as a first test case. Figure 1 shows its



**Figure 1.** Equilibrium ground state structure of the 2-pyridone dimer taken from ref 12. The arrow shows the center-to-center distance varied in the calculations. The figure was generated using VMD.<sup>62</sup>

ground state equilibrium structure reported in ref 12. The ring-centers in this structure lie 5.9 Å apart and the hydrogen bonds have a length of 1.7 Å. Starting from this structure, we increased the intermolecular distance in steps of 1 Å, as indicated in Figure 1. The resulting structures were, without further geometry optimization, used for supermolecular and FDEc-TDA calculations. The exciton splitting energies calculated for different amounts of exact exchange are shown in Figure 2. The exciton splittings increase with closer proximity and higher fraction of exact exchange, in line with the findings of ref 12. For displacements larger than 3 Å the exciton splittings from the FDE-TDA calculations closely resemble those of the supermolecular calculations with the same hybrid functional as employed in the intrasubsystem calculations. The deviations at smaller distances cannot clearly be correlated with the amount of exact exchange. In fact, the smallest deviation is found with



**Figure 2.** Exciton splitting energies in the 2-pyridone dimer as a function of the distance for FDEc-TDA and supermolecular TDA calculations with varying amount of exact exchange (HF) in a B3LYP-type functional with TZP basis set. As a reference, also CC2/TZVP results are shown.

100% exact exchange. This finding shows that the contribution of direct Dexter coupling is negligible in that case.

Deviations between the supermolecular and FDEc calculations at short distances might indicate that terms neglected in the FDEc scheme, for instance, charge transfer and direct Dexter-type contributions, are important. This interpretation is in agreement with conclusions drawn also for other systems before.<sup>4–6</sup> An alternative explanation could be the well-known failure of TDDFT methods in describing charge-transfer excitations. This interpretation is supported by the non-systematic behavior upon increasing the amount of exact exchange: The charge-transfer excitations are strongly shifted by the amount of exact exchange and so is their interaction with the exciton states. Thus, it is desirable to estimate the impact of these effects on the deviations, and thereby judge which approach yields a more physically consistent picture. Therefore, we analyze the interpigment interactions in supermolecular calculations with delocalized orbitals in the following. We will first discuss the transition densities from supermolecular and subsystem TDA in a simplified four-orbital picture. In this minimal model, we only consider two frontier orbitals  $\phi$  and  $\phi'$  for each monomer in a symmetric dimer of chromophores A and B. Due to the symmetry, the corresponding orbital energies are identical in both chromophores. In TDDFT and TDA, the transition density  $\rho^t$  is obtained as a linear combination of all possible products of one occupied and one virtual orbital. In TDA, the expansion coefficients are the elements of the solution vector, whereas in TDDFT these elements of the solution vectors need to be multiplied with the square root of the corresponding orbital energy differences. In the FDEc case, no interchromophore transitions are included, so that the transition density in the four-orbital case reads

$$\rho^t = c_A \phi_A \phi'_A + c_B \phi_B \phi'_B \quad (5)$$

In the minimal model, we assume that the supermolecular orbitals are (symmetric/antisymmetric) delocalized linear combinations of the localized pigments' highest occupied molecular orbitals (HOMOs,  $\phi_A$ ,  $\phi_B$ ) and lowest unoccupied molecular orbitals (LUMOs,  $\phi'_A$ ,  $\phi'_B$ ). At larger distances, this assumption breaks down (see below). The resulting transition density for a single excitation

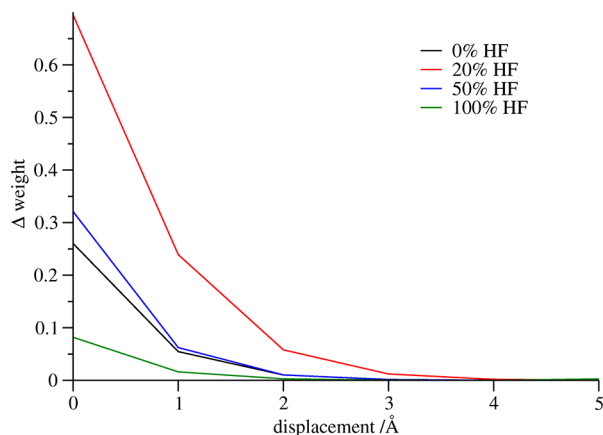


$$\begin{aligned} \rho^t = & c_1(\phi_A + \phi_B)(\phi'_A + \phi'_B) + c_2(\phi_A - \phi_B)(\phi'_A + \phi'_B) \\ & + c_3(\phi_A + \phi_B)(\phi'_A - \phi'_B) + c_4(\phi_A - \phi_B)(\phi'_A - \phi'_B) \end{aligned} \quad (6)$$

is only free of interchromophore contributions (i.e.,  $\phi_A\phi'_B$  and  $\phi_B\phi'_A$ ) if  $c_1 = c_4 \wedge c_2 = c_3$ , which will be termed “ideal, neutral picture” in the following. The supermolecular transition density is then equal to that of FDEC if  $c_A = c_1 + c_2$  and  $c_B = c_1 - c_2$ . Please note that in case of nonorthogonality of  $\phi_A$  and  $\phi_B$  or  $\phi'_A$  and  $\phi'_B$  the coefficients  $c_n$  contain overlap contributions.

Thus, for the TDA calculations, the absolute differences between the weights of the relevant orbital transitions, which are the squared contributions to the transition densities, can give useful information on the contribution of charge-transfer-type transitions between the chromophores to the dimer excitation. However, it should be noted that more elaborate analysis tools based on the one-electron transition density have been reported.<sup>52,53</sup> If the deviations from this picture are too large, a clear assignment of the excitations to the exciton states is ambiguous or even impossible. The latter situation occurred in the supermolecular TDDFT calculations with 20% exact exchange at the two shortest distances (see the SI).

The absolute differences between the main contributions of the dominating pair of orbital transitions ( $\Delta w$ ) to the lower excitation (either  $|(\text{HOMO}-1 \rightarrow \text{LUMO}) - (\text{HOMO} \rightarrow \text{LUMO} + 1)|$  or  $|(\text{HOMO} \rightarrow \text{LUMO}) - (\text{HOMO}-1 \rightarrow \text{LUMO} + 1)|$ ) for the supermolecular TDA calculations are shown in Figure 3



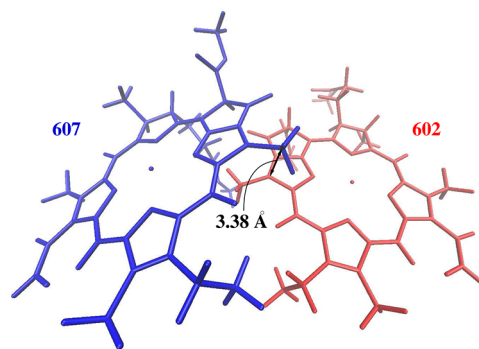
**Figure 3.** Differences between contribution weights of the two largest orbital transitions in the lower excitation in the supermolecular TDA calculations in the 2-pyridone dimer plotted with respect to the displacement for B3LYP/TZP with different amount of exact exchange (HF).

for displacements of up to 5 Å. At larger distances, we observe a localization of the frontier orbitals on the pigments, so that this analysis, which is based on the assumption of delocalized orbitals, is not applicable. For displacements larger than 2–3 Å,  $\Delta w$  is almost zero, which indicates negligible interchromophore charge-transfer contributions. Its value at short distances is largely dependent on the amount of exact exchange applied: With 100% exact exchange only a minor increase is observed. The largest values for  $\Delta w$  are obtained with 20% exact exchange, while 0% and 50% exact exchange yield intermediate results. Thus, there is no clear correlation of the deviation to the amount of exact exchange.

In conclusion, several findings support the assumption that the charge-transfer problem is one of the main error sources for the calculation of exciton splitting energies with supermolecular TDDFT and TDA, namely, (i) the nonsystematic behavior of the interchromophore transitions and the exciton splitting energies with respect to the amount of the exact exchange applied, (ii) the strong dependence on the percentage of exact exchange, and (iii) the best resemblance of the ideal, neutral picture in case of 100% exact exchange. The charge-transfer failure of TDDFT has, thus, a large contribution to the deviations between the supermolecular and FDEC calculations at close distances.

For comparison, CC2 calculations were performed. We find, in agreement with refs 12, 13, 16, that the exciton splittings calculated with high amounts of exact exchange agree well with the wavefunction-based reference values. The CC2/cc-pVTZ excitonic splitting of the same ground state structure as applied here amounts to 0.136 eV,<sup>12</sup> which fits very well to our CC2/TZVP result (0.135 eV), and also to the FDEC-TDA calculations with large percentages of exact exchange (50%: 0.131 eV; 100%: 0.139 eV). The deviation of this value from the much smaller experimental one of 0.005 eV was explained by vibrational quenching<sup>54</sup> or by a reinterpretation as a tunneling splitting in the adiabatic potential energy surface of the lowest state exhibiting two minima.<sup>55</sup> After scaling the exciton splitting by the vibrational quenching factor calculated for the 2-pyridone dimer in ref 54 (0.019), the theoretical exciton splittings agree well with the experimental ones.<sup>54</sup> For larger distances, the CC2 calculations closely resemble those of supermolecular and FDEC-TDA calculations with 20% exact exchange.

**3.2. Chlorophyll Dimer from LHC-II.** In order to investigate the effect of the exact exchange for an example of biological interest, we have chosen the pair of chlorophyll *a* residues 602 and 607 from the pea light-harvesting complex II (LHC-II, pdb entry 2BHW<sup>56</sup>). The model applied here is shown in Figure 4. We truncated the phytol-chains and kept all

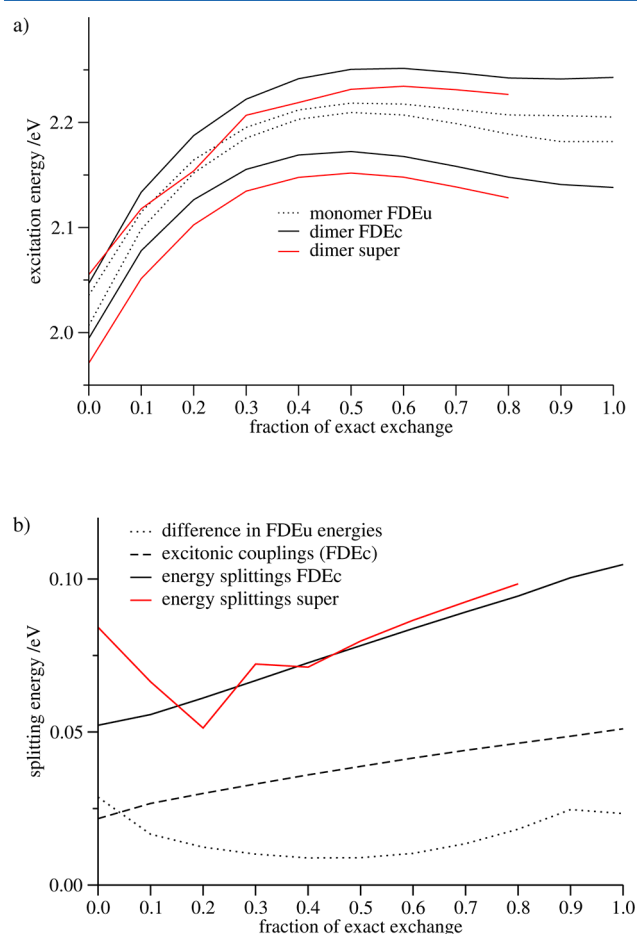


**Figure 4.** Applied model for the pair of chlorophyll *a* residues (602 and 607) from LHC-II.

heavy atoms constrained to the crystal structure during the optimization of the hydrogen atoms (BP86/TZP). In this technical test we refrain from investigating structural effects. For a more detailed analysis of the actual mechanism in the biological system, a reoptimization of the structural parameters is usually recommended.<sup>57</sup> The exciton coupling between the so-called  $Q_y$  transitions within this pair of chlorophylls is the largest within the chlorophyll network in LHC-II and has been investigated previously with different theoretical ap-

proaches.<sup>58–61</sup> This example thus provides an ideal testbed for our approach.

In Figure 5a, the  $Q_y$  excitations of the chlorophyll residues and the dimer are plotted with respect to the fraction of exact



**Figure 5.** (a) Lowest excitation energies and (b) energy splittings of the chlorophyll *a* dimer 602–607 in LHC-II obtained in FDEu, FDEc, and supermolecular TDA calculations with the B3LYP functional with varying amount of exact exchange. Note that for 90% and 100% exact exchange convergence problems occurred during the supermolecular calculations, so that these values are not given.

exchange used in the exchange–correlation functional. The excitation energies increase with increasing amount of exact exchange until they reach a maximum at 50% exact exchange. For higher percentages, the excitation energies are slightly decreasing. Supermolecular calculations were performed for comparison. For the lower, intense excitation, the supermolecular calculations lead to excitation energies which lie systematically about 0.02 eV below the corresponding FDEc values. The deviations between the supermolecular and the FDEc calculations for the higher, less intense excitation are less systematic. This is particularly pronounced for low percentages of exact exchange. This observation might be related to the charge-transfer failure of standard TDDFT, as explained above. For higher percentages of exact exchange we again observe an almost constant energy offset of about 0.02 eV. This offset is most probably due to the limited number of states included in the FDEc calculations: As shown in ref 35, the exciton splitting in FDEc usually converges faster with respect to the number of

coupled states considered than the energies of the exciton states.

For better comparison, we have plotted the corresponding energy splittings and excitonic coupling constants in Figure 5b. The FDEc splitting energies as well as the excitonic coupling constants depend almost linearly on the amount of exact exchange. In contrast to this, the differences in FDEu excitation energies display a minimum at 50% exact exchange, which coincides with the maximum in total excitation energies. For low percentages of exact exchange, the splitting energies calculated with the supermolecular approach deviate in a rather nonsystematic way from those obtained in FDEc calculations. Starting at 40% exact exchange, a similar near-linear dependence is observed for both methods. The resulting slope is only slightly higher in the supermolecular case. Thus, the major effect of the exact exchange is already captured by its inclusion solely in the intrasubsystem part in the FDEc-TDA calculations—in spite of the rather close distance.

We conclude that the sensitivity of calculated exciton splitting energies on the amount of exact exchange is mainly due to the resulting change in the transition densities, rather than the accounting for the direct Dexter-type coupling. In the following, we demonstrate that the amount of exact exchange has in fact a strong effect on the local transition densities. This is done by analyzing the oscillator strengths, which are calculated directly from the transition densities. Thus, changes in the transition densities can be monitored by changes in the oscillator strengths, as done in Figure 6a. The oscillator strengths are slowly increased by about a factor of 2 for both chlorophyll pigments when increasing the amount of exact exchange from 0% to 100%. This clearly indicates that also the transition densities change when increasing the amount of exact exchange.

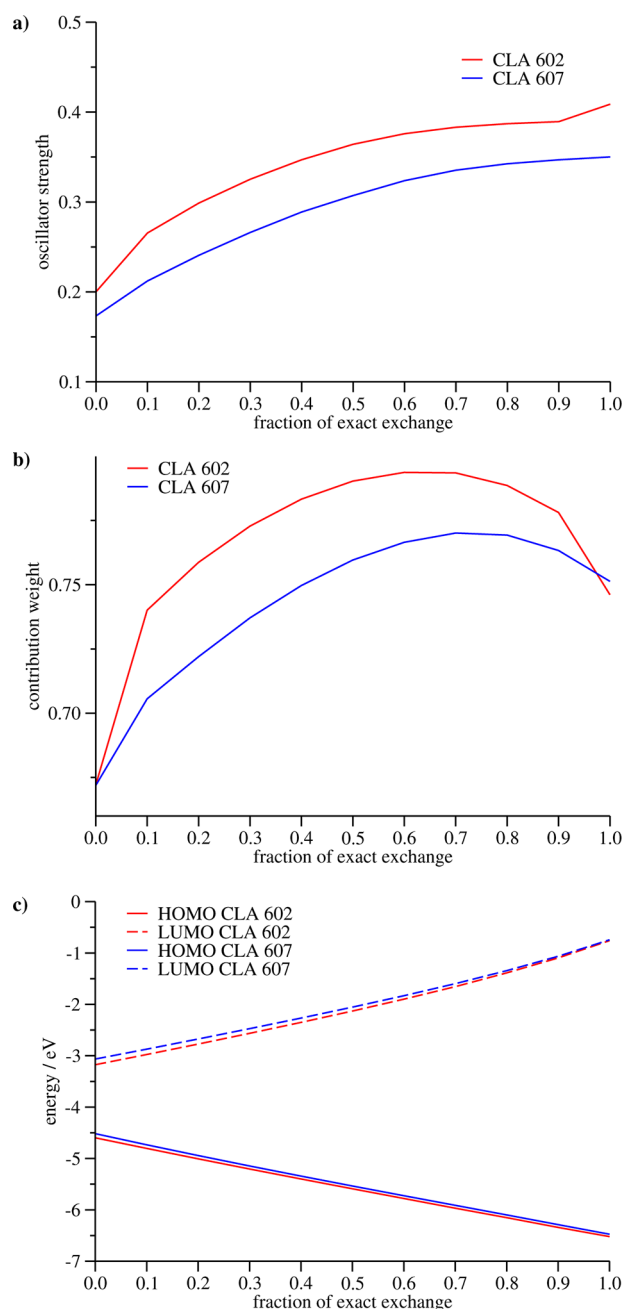
The transition density in TDA is calculated as

$$\rho^t = \sum_{ai} c_{ai} \phi_a \phi_i \quad (7)$$

where  $\phi_i$  and  $\phi_a$  are real occupied and virtual molecular orbitals and  $c_{ai}$  are the expansion coefficients. To illustrate the origins of the change of the transition densities we also show the weight of the main orbital transition in the lowest excitation in chlorophyll *a*, which is the one between the HOMO and LUMO, in Figure 6b. The contribution weight of the HOMO–LUMO transition changes only moderately between 0.67 and 0.79. Additionally, we monitor the change in the molecular orbital energies in Figure 6c. While the energy of the HOMO decreases, that of the LUMO increases with increasing amount of exact exchange. Thus, the HOMO–LUMO gap is increased. The impact of the exact exchange on the molecular orbitals can be rationalized by the different character of the LUMO in pure Kohn–Sham and pure Hartree–Fock theory: In Hartree–Fock theory, the virtual orbitals experience a potential for an additional electron, whereas in pure Kohn–Sham theory, they correspond to excited one-particle Kohn–Sham states, since they are obtained in the same effective potential as the occupied orbitals. Overall, these observations indicate a rather strong dependence of the transition density on the amount of exact exchange, even though the character of the excitation is largely maintained.

#### 4. DISCUSSION AND CONCLUSIONS

We have shown that, in both cases, the 2-pyridone dimer and the chlorophyll dimer, the FDEc scheme results in a more



**Figure 6.** (a) Oscillator strengths, (b) contribution weight of the HOMO–LUMO transition to the  $Q_y$  excitation, and (c) orbital energies of the frontier orbital of the chlorophyll *a* pigments 602 and 607 of the LHC-II calculated with B3LYP/TZP with varying amount of exact exchange.

systematic dependence of calculated energy splittings on the amount of exact exchange than the supermolecular calculations. Rather good agreement is obtained for high percentages of exact exchange. The inclusion of exact exchange in TDDFT calculations of dimers can affect (i) the (local) ground state and transition densities and (ii) the coupling mechanism by allowing for direct Dexter-type coupling. The latter is (partly) included in the supermolecular calculations with hybrid functionals but is absent in the FDEc scheme, even if hybrid functionals are used in the intrasubsystem calculations. Thus, the close resemblance of the supermolecular and FDEc calculations with the same fraction of exact exchange suggests

that the sensitivity of TDDFT exciton splittings on the amount of exact exchange can to a large extent be explained by a pseudo exchange effect, that is an increased Coulomb coupling due to changes in the transition densities, rather than by a direct Dexter-type exchange mechanism. This finding is supported by the strong increase in oscillator strengths of the underlying local excitations. As far as previous recommendations of hybrid functionals for exciton couplings are concerned, we can refine this statement in the following way: In calculations based on monomer transitions it appears more important to include exact exchange in the calculations of the monomer transitions than in the actual coupling step. The examples presented in this work do not yet allow a generalization to a universal applicable recommendation on the amount of exact exchange. In a previous study we found that a good description of underlying local excitations is essential to obtain reliable excitonic splitting in the FDEc framework.<sup>38</sup> Thus one might speculate that this also holds for the amount of exact exchange to be chosen; it should be similar to that for reliable local excitations.

As a side aspect, we observe again that FDEc calculations can be advantageous over supermolecular calculations, as they prevent the admixture of poorly described charge-transfer states between the subsystems into the states of interest. In particular in supermolecular calculations for larger systems the density of states is usually quite high, so that the state of interest is not always easy to identify. This interpretation is largely simplified when using the FDEc scheme, which allows one to trace the delocalized excitations back to localized excitations on the subsystems.

The most important practical consequence of our findings is probably that the time-consuming step of supermolecular hybrid-DFT calculations or of hybrid-DFT intersubsystem couplings in perturbative approaches can be avoided. The computational cost of the exact exchange part scales with the fourth power of the system size in supermolecular calculations if no special prescreening is applied, while it scales linearly with the number of subsystems in FDE, if it is only used for the intrasubsystem part. Thus, with FDEc-TDA it is possible to include the major contribution of the exact exchange also for larger dye-aggregates, for which supermolecular hybrid DFT calculations are out of reach.

## ■ ASSOCIATED CONTENT

### 📄 Supporting Information

More detailed discussion of the computations and a comparison of supermolecular TDA and TDDFT calculations, including an additional figure. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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### 📝 Notes

The authors declare no competing financial interest.

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