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Constrained Density Functional Theory*

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**Triplet Excitation Energy Transfer with Constrained Density  
Functional Theory**

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9 **Triplet Excitation Energy Transfer with Constrained**  
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11 **Density Functional Theory**  
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16 Sina Yeganeh, and Troy Van Voorhis\*

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19 *Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts*

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## Abstract

We study the electronic coupling matrix element for triplet excitation energy transfer processes with a number of different computational methods. For the first time, constrained density functional theory (CDFT) is applied to the problem of energy transfer, and results are compared with direct coupling calculations of broken symmetry and fragment densities, as well as the splitting method. A naïve calculation of the electronic coupling using diabatic and adiabatic energy differences is shown to yield erroneous results due to the fractional spin error present in both Hartree-Fock and commonly used DFT exchange-correlation functionals. Some potential issues concerning the splitting method with triplet references within Hartree-Fock and DFT are discussed. We find that only methods that compute the matrix element directly (either from CDFT, broken symmetry, or fragment states) appear to be robust. Several illustrative examples are presented.

## 1 Introduction

Energy transfer is an important process in both natural and synthetic systems. For example, triplet excitation energy transfer (TEET) plays an important role in photosynthesis<sup>1</sup> where carotenoids prevent oxidation due to triplet-state chlorophyll via energy transfer.<sup>2</sup> Studying TEET can also yield new insights into electron transfer as similar factors (exchange, overlap) govern both, and in fact TEET has been modelled as a double electron exchange reaction.<sup>3,4</sup> In organic electronics,<sup>5</sup> energy transfer is a key process in organic photovoltaic (OPV) and light emitting diode (OLED) devices. Designing OLEDs requires in particular a clear understanding of TEET as spin statistics imply 75% of the created excitons will be phosphorescent rather than luminescent. In OPVs, some donor/acceptor materials have significant triplet exciton populations, and engineering greater fractions of triplet excitons might be a route to improving the short exciton diffusion lengths in these devices.<sup>6,7</sup> Thus, TEET in synthetically designed systems has been an active area of interest for experimentalists.<sup>8-12</sup>

Within the approximations inherent to Fermi's golden rule (FGR), the nonadiabatic TEET rate

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4 can be written as

$$k_{\text{TEET}} = \frac{2\pi}{\hbar} |V_{if}|^2 (\text{DWFC}) \quad (1)$$

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8 where DWFC refers to the density-weighted Franck-Condon factors, and  $V_{if}$ , the subject of this  
9 work, is the electronic coupling between initial and final states of the energy transfer process.  
10 The Franck-Condon factors can be derived for classical<sup>13</sup> or quantum harmonic oscillators,<sup>14</sup> and  
11 multiple vibrational modes<sup>15</sup> as well as anharmonic effects<sup>16,17</sup> can be considered. These factors  
12 are important for a quantitative calculation of the reaction rate, but here we are primarily concerned  
13 with deducing the distance dependence of energy transfer, which lies mainly in the electronic  
14 coupling. Although TEET is an overall spin-conserving process, the Coulomb interaction, which  
15 leads to the usual  $R^{-3}$  distance dependence in Förster theory,<sup>18</sup> is only weakly allowed by spin-  
16 orbit coupling and can be neglected.<sup>19</sup> Therefore, TEET is primarily mediated by the remaining  
17 interaction terms, exchange and orbital overlap, resulting in exponential decay of the TEET rate as  
18 donor and acceptor are separated.<sup>20-22</sup>

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33 The electronic coupling for the energy transfer from excited state donor,  $D^*$ , to ground state  
34 acceptor, A, can be written as

$$V_{if} = \langle DA^* | \hat{H} | D^* A \rangle \quad (2)$$

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38 where  $\hat{H}$  is the electronic Hamiltonian for the donor and acceptor, and the interactions between  
39 them. The states  $|D^*A\rangle$  and  $|DA^*\rangle$  are diabatic-like, representing excitations localized on different  
40 molecules (intermolecular TEET) or different parts of the same molecule (intramolecular TEET).  
41 The identification of these diabatic states, either implicitly or explicitly, is the main task in calcu-  
42 lating the electronic coupling.  
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In this paper, we begin by describing the transformation from the adiabatic states of quantum  
chemistry to the diabatic states necessary for FGR-type rate expressions. We then describe how  
we identify the diabatic states for localized triplet excited states using constrained density func-  
tional theory (CDFT).<sup>23,24</sup> With diabatic states in hand, we can calculate the electronic coupling  
directly. Using the diabatic-adiabatic energy gap provides an alternative approach; however, we

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3 find that this method fails due to the fractional spin error in single-reference methods, and we dis-  
4 cuss the reasons for this failure as well as its effects on TEET calculations in terms of ensemble  
5 DFT. Some cautionary notes are also raised for care in selecting adiabatic states in the splitting  
6 method. Finally, we examine chemical systems of interest, from a simple system consisting of  
7 two formaldehyde chromophores to a larger intramolecular TEET system of porphyrin moieties  
8 studied experimentally by Albinsson and co-workers.<sup>11,25,26</sup>  
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## 18 **2 Background**

### 21 **2.1 Diabatic-Adiabatic Transformations**

22 We present a brief background to the subject of diabatic states and their construction from adi-  
23 abatic states. For a more in-depth discussion, we refer to existing literature.<sup>24,27,28</sup> Within the  
24 Born-Oppenheimer approximation, adiabatic states are those which remain an eigenstate of the  
25 electronic Hamiltonian as a slowly varying perturbation (e.g. change along some reaction coordi-  
26 nate) is applied. These are the familiar output of quantum chemical calculations where the ground  
27 and excited states are well-defined at all coordinates. On the other hand, a diabatic state is one  
28 which remains qualitatively similar in its electronic character even at vastly different nuclear con-  
29 figurations. For example, in an alkali halide compound, XY, the ground adiabatic state would  
30 change smoothly from being mainly ionic at close separations to covalent at the dissociative limit;  
31 on the other hand, the two diabatic states would remain similar at all internuclear separations,  
32 corresponding to  $X^+Y^-$  and XY.  
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47 In computational quantum chemistry, the Born-Oppenheimer approximation is nearly always  
48 invoked, and adiabatic states are obtained. Although in general there is not a unique transformation  
49 to diabatic states,<sup>29</sup> approximate diabatic states can be obtained via rotations of the adiabatic states.  
50 For two states, this transformation can be represented by the following generalized eigenvalue  
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equation,

$$\begin{pmatrix} \epsilon_i & H_{if} \\ H_{if} & \epsilon_f \end{pmatrix} \begin{pmatrix} c_{i\pm} \\ c_{f\pm} \end{pmatrix} = \epsilon_{\pm} \begin{pmatrix} 1 & S_{if} \\ S_{if} & 1 \end{pmatrix} \begin{pmatrix} c_{i\pm} \\ c_{f\pm} \end{pmatrix} \quad (3)$$

where  $\epsilon_{i,f}$  are the diabatic state energies,  $H_{if}/S_{if}$  are the diabatic state coupling/overlap,  $c_{i,f}$  are the eigenvector coefficients from which the rotation angle between diabatic-adiabatic states can be obtained, and  $\epsilon_{\pm}$  are the two adiabatic state energies. In general the diabatic states obtained will not be orthogonal, so to obtain the electronic coupling matrix element required for the FGR expression (Eqn. 1), a symmetric orthogonalization is carried out to yield

$$V_{if} = \frac{H_{if} - S_{if}(\epsilon_i + \epsilon_f)/2}{1 - S_{if}^2} \quad (4)$$

We can solve the eigenvalue equation and examine the result in a number of cases. If there is some symmetry in the system (such as identical monomers in an intermolecular TEET) such that  $\epsilon_i = \epsilon_f$ , the coupling can be written,

$$V_{if} = \frac{\epsilon_- - \epsilon_+}{2} \quad (5)$$

and this result is commonly referred to as the splitting method. For symmetric systems, this result tells us that simply calculating the two appropriate adiabatic states and taking half their energy splitting yields the electronic coupling. Generally, a singlet ground-state reference is used and CIS, TDHF, or TDDFT (within the Tamm-Dancoff (TDA) or random phase (RPA) approximations) are used to obtain the  $T_1$  and  $T_2$  energies. Taking half the difference between these two values yields the desired coupling.

In another limiting case, when the overlap between diabatic states is negligible ( $S_{if} \approx 0$ ), the coupling reduces to

$$V_{if} = \sqrt{(\epsilon_i - \epsilon_+)(\epsilon_f - \epsilon_+)} \quad (6)$$

We see that only one adiabatic state ( $T_1$ ) is required in addition to the two diabatic state energies; in the case of symmetric diabats and negligible overlap,  $V_{if} = \epsilon_i - \epsilon_+$ .

Finally, some algebra yields the coupling in the general case:

$$V_{if} = \frac{\sqrt{(\epsilon_i - \epsilon_+)(\epsilon_f - \epsilon_+)} + S_{if}(\epsilon_+ - (\epsilon_i + \epsilon_f)/2)}{1 - S_{if}^2} \quad (7)$$

where  $S_{if}$  can be obtained by direct calculation of the overlap between the two diabatic states, or through the analytic expression

$$S_{if} = \frac{\sqrt{(\epsilon_i - \epsilon_+)(\epsilon_f - \epsilon_+)} + \sqrt{(\epsilon_i - \epsilon_-)(\epsilon_f - \epsilon_-)}}{\epsilon_- - \epsilon_+} \quad (8)$$

An alternative path to  $V_{if}$  can be found by directly obtaining diabatic states and explicitly calculating the coupling. One method for obtaining such diabatic states for TEET is CDFT, as discussed next.

## 2.2 Constrained Density Functional Theory

We introduce CDFT<sup>23</sup> as a constructive method to yield diabatic states for calculating TEET rates. More in-depth discussion can be found in the literature.<sup>24</sup> In CDFT an appropriately chosen constraint is added to the usual energy functional,  $E[\rho]$ , forcing the ground state of the constrained system to converge to the desired diabatic state. The constraint is enforced during SCF optimization via a Lagrange multiplier,  $V_c$ . The variational principle is then applied to  $W[\rho]$ :

$$W[\rho] = E[\rho] + V_c \left( \sum_{\sigma}^{\alpha, \beta} \int d\mathbf{r} w_c^{\sigma}(\mathbf{r}) \rho^{\sigma}(\mathbf{r}) - N_c \right) \quad (9)$$

where  $N_c$  is the desired constraint value, and  $w_c$  serves as the weight function that determines the constraint. Here we make use of Becke's atomic partitioning scheme<sup>30</sup> to define  $w_c$ .

By setting  $w_c^{\alpha} \neq w_c^{\beta}$ , spin constraints can be defined; setting  $w_c^{\alpha} = 1$  and  $w_c^{\beta} = -1$  in a region where the excitation is to be localized, and concurrently setting  $N_c$  to 2 will result in a localized triplet. With an appropriate choice of constraint regions, this yields the desired diabatic states for describing TEET (see Figure 1). One additional note should be made regarding



the choice of the constraint value,  $N_c$ . For an intermolecular charge or spin localized state where the fragments are considerably separated, integer choice of  $N_c$  is appropriate; however, when the fragments are close together or in an intramolecular localized state, strictly integer values of  $N_c$  are no longer appropriate, and a promolecule approach is needed to obtain  $N_c$ .<sup>24,31,32</sup> For our calculations here, we generally make use of this promolecule correction, although the coupling results do not change significantly in most cases. Finally, we note that since HF can be formulated as an exchange-correlation functional within generalized Kohn-Sham (KS) DFT, the CDFT approach outlined above can readily become a constrained HF (CHF) method.

With diabatic states from CDFT, we can now compute the diabatic coupling. The most obvious approach is to directly evaluate the non-orthogonal coupling with CDFT providing the  $|DA^*\rangle$  and  $|D^*A\rangle$  states. While this prescription is appropriate for CHF, in CDFT it requires evaluating 1 and 2-electron matrix elements over diabatic wavefunctions constructed from KS orbitals and is thus questionable. An alternative approach is to rewrite the matrix element to avoid requiring two-body matrix elements:<sup>24,33</sup>

$$\begin{aligned}
 H_{if} &= \langle DA^* | \hat{H} + V_c^{D^*A} w_c - V_c^{D^*A} w_c | D^*A \rangle \\
 &= (E + V_c^{D^*A} N_c) S_{if} - V_c^{D^*A} \langle DA^* | w_c | D^*A \rangle
 \end{aligned}
 \tag{10}$$

where we have reduced the coupling dependence on the KS orbitals to a zero-electron overlap term,  $S_{if}$ , and the one-body matrix element over the weight function. We refer to this method as the CDFT coupling.

Finally, from the discussion on diabatic-adiabatic transformations in Section 2.1, we saw in Eqn. 7 that the diabatic coupling could be calculated from two diabatic and one adiabatic state energies, without any explicit calculation of the coupling matrix element between the diabatic states. Using CHF/CDFT to obtain  $\epsilon_{i,f}$  and  $S_{if}$  while obtaining the adiabatic energy,  $\epsilon_+$ , from the ground-state triplet energy of the system, we should be able to obtain an alternative estimate of the electronic coupling. We term this method CDFT- $\Delta$ . As we find, however, the requirement of

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3 accurate adiabatic state energies causes difficulties in applying this method.<sup>33</sup>  
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## 7 8 **2.3 Fractional Spin** 9

10 Fractional charge error has been widely discussed in the context of density functional theory. The  
11 key point is that the self-interaction error (SIE) in commonly used exchange-correlation function-  
12 als causes an excessive delocalization of the electronic density, leading to, among other errors, too  
13 low barriers, too large polarizabilities, and overestimation of conductance in molecular electronics  
14 calculations.<sup>34</sup> An alternative view of this delocalization error<sup>35</sup> is based on the ensemble DFT  
15 proof that the true functional should yield a linear dependence of the total energy on the electron  
16 number between adjacent integer values,<sup>36</sup> with the slope of  $E(N)$  being proportional to either  
17 the ionization potential or electron affinity on either side of integer electron number. SIE, how-  
18 ever, causes approximate functionals to display nonlinear *convex* dependence on fractional charge,  
19 resulting in a too low, overly delocalized, description of systems. As system size increases, this  
20 delocalization error grows. Although HF does not possess a similar SIE, energies have an incor-  
21 rect *concave* dependence on electron number, resulting in a localization error, which saturates with  
22 increasing system size.<sup>34</sup>  
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36 A closely related, although less discussed, issue is fractional spin error.<sup>37</sup> Consider a hydrogen  
37 atom, usually pictured as containing one spin-up (or spin-down) electron. Next, imagine a hydro-  
38 gen atom which contains half a spin-up and half a spin-down electron. The exact functional should  
39 give the same energy for all these configurations.<sup>37</sup> However, approximate functionals (and HF)  
40 all yield large deviations from this exact condition. This failure results from the inability of mean-  
41 field HF and DFT functionals to describe the multiconfigurational nature of the half-up half-down  
42 state. Thus fractional spin error can be regarded as a static correlation error which arises when  
43 describing these degenerate states. In previous studies, the fractional spin error for both HF and  
44 DFT functionals has resulted in improper concave behavior (see Figure 2), although as we will see  
45 later this is not always the case in molecular systems.  
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57 For our interests in TEET, we will be concerned with a slightly different form of the fractional  
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3 spin error: we will study delocalized spin across a dimer. Locally these delocalized solutions will  
4 look like they have fractional spin: each monomer will be approximately 50% singlet and 50%  
5 triplet in character. On the other hand, the localized solutions will correspond to the end points,  
6 with one monomer entirely singlet and the other triplet. Thus, the extreme points in Figure 2  
7 correspond to all singlet or all triplet, with intermediate points a mixture of the two configurations.  
8 Regardless of whether the mid-point or end-points are taken, the energy of the system should be  
9 the same. However, this is not the case in HF or DFT, and thus the energy of a delocalized spin  
10 configuration is expected to be incorrect. Thus, we expect that adiabatic triplet state energies  
11 for dimer systems will be of questionable accuracy, and electronic coupling methods that rely  
12 upon these states and their energies will likewise be flawed. As TEET couplings are generally  
13 small, it is not surprising that this fractional spin error will be calamitous for the CDFT- $\Delta$  method.  
14 Additionally, the incorrect concavity in Figure 2 suggests that linear-response calculations from a  
15 triplet-reference dimer system will be in error.  
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## 32 **3 Results**

### 34 **3.1 Coupling Methods**

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36 Before discussing the results of TEET coupling calculations with CDFT, we introduce some of the  
37 methods we use for comparison. The different methods can be separated into two categories based  
38 on the way they construct the diabatic coupling and the reference states used. In the first category,  
39 adiabatic-based methods, the singlet ground state reference is usually used, and information about  
40 the triplet excited states is obtained through linear response. The simplest, and most oft-used,  
41 example is the splitting method, applicable to systems with symmetry conditions such that the two  
42 diabatic energies are the same. For TEET, generally CIS/TDDFT-TDA or TDHF/TDDFT-RPA  
43 calculations are performed with the singlet reference, and the two lowest triplet state energies yield  
44 the coupling via Eqn. 5. Alternatively, post-HF excited state methods (such as equation-of-motion  
45 coupled cluster) can be used for more accurate adiabatic energies. This method, in addition to the  
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necessity of symmetry, also requires an appropriate selection of adiabatic states; for this reason, HF, rather than DFT, is often used, as TDDFT can yield spurious low-lying charge-transfer states in dimer calculations, which would result in incorrect splitting values of the coupling.<sup>38-40</sup> A new method, fragment excitation difference (FED),<sup>41</sup> can also be used for TEET, even in asymmetric systems. It is based upon similar ideas as the fragment charge difference method for electron transfer coupling elements,<sup>42</sup> and like the splitting method relies upon accurate adiabatic state energies as well as transition densities from CIS/TDDFT. As in CDFT, it requires the specification of the donor and acceptor regions. We note that for splitting and FED, an alternative approach would be to begin with the triplet ground state and perform excited state calculations to the first excited state - this approach fails however, yielding drastically overestimated TEET couplings. We discuss the source of this behavior further in Section 3.2. CDFT- $\Delta$  can also roughly be placed in this category, as it makes use of both adiabatic and diabatic energies.

The second category consists of direct coupling methods with explicit calculation of the triplet state, and the CDFT coupling method falls into this category. In addition, we will compare our CDFT results with the broken symmetry (BS) method.<sup>43</sup> Here, approximate diabatic states are obtained by forcing the self-consistent field iterations to converge to a UHF/UKS state with the excess spin localized on one fragment. This is usually readily done in HF calculations, but can be considerably more challenging in pure DFT calculations, where the system often converges to the delocalized solution. Once these diabatic states are obtained, the electronic coupling is obtained by evaluating

$$H_{if} = \langle DA^* | \hat{H} | D^*A \rangle \quad (11)$$

$$S_{if} = \langle DA^* | D^*A \rangle \quad (12)$$

and applying Eqn. 4 to obtain  $V_{if}$  for orthogonal states. An approximate and computationally cheap alternative for obtaining the TEET coupling is the fragment method. Here, a diabatic state is obtained by forming the block diagonal density matrix from the combination of two isolated

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3 monomer calculations; one monomer in its singlet ground state, and the other in its triplet ground  
4 state. The coupling is once again obtained from Eqn. 11. As this requires separate calculations of  
5 the donor/acceptor fragments, this method is best suited for intermolecular TEET.  
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### 10 11 **3.2 TEET in Stacked Formaldehyde and Naphthalene**

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14 We now turn to benchmarking our CDFT method. As a first simple example, we study a stacked  
15 formaldehyde dimer. The electronic coupling matrix element for TEET from one formaldehyde  
16 to another in a parallel stacked configuration is calculated while varying the separation distance.  
17 From Dexter theory, we expect an exponential distance dependence of this coupling, with the de-  
18 cay of  $V_{if}$  equal to  $\beta/2$ , where  $\beta$  is the usual attenuation factor for exponentially decaying rates.  
19 In our calculations, the 6-31G\*\* basis set and a development version of Q-Chem were used.<sup>44</sup> For  
20 the CHF/CDFT- $\Delta$  method, truly adiabatic states were obtained by enforcing symmetry in the SCF  
21 convergence. HF and DFT (PBE functional)<sup>45</sup> calculations were carried out. In Figure 3, we see  
22 that for HF the splitting, BS, and CHF coupling methods all decay exponentially with similar  $\beta$   
23 values. For PBE, we see similar  $\beta$  for the CDFT coupling and splitting method (BS states could  
24 not be obtained in PBE). For both HF and PBE, however, the CHF/CDFT- $\Delta$  result is qualitatively  
25 different, yielding a different slope and non-zero coupling at infinite distances! The CHF- $\Delta$  result  
26 (not shown) was much larger than the other methods, yielding a coupling that grew from 3000 to  
27 5000 meV as the distance *increased*. As the  $\Delta$  calculation uses the same diabatic state as in direct  
28 coupling CHF/CDFT, the adiabatic state energy seems to be the culprit. Additionally, the split-  
29 ting method was applied to calculations from the triplet reference (not shown); we find a coupling  
30 that is several orders of magnitude too large ( $\approx 1000$  meV) and nearly constant with separation.  
31 Although the CHF/CDFT, BS, and splitting methods all yield similar slopes for the coupling, the  
32 absolute magnitudes differ. The difference between the diabatic and adiabatic-based schemes can  
33 be explained by the fact that diabats cannot be uniquely obtained from adiabats, and using the two  
34 lowest lying adiabatic states does not guarantee an adequate basis for the transformation. Com-  
35 paring different diabatic schemes, such as CDFT and BS, we find that the choice of diabatization  
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4 procedure can affect the TEET coupling.

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6 Next, we turn to  $\pi$ -stacked naphthalene dimer, and using both HF and PBE (6-31G\*\*), we  
7 calculate the TEET coupling with CHF/CDFT coupling and  $\Delta$ , as well as the splitting and fragment  
8 methods. As shown in Figure 4, we find that CHF/CDFT, splitting, and fragment methods all yield  
9 exponential decay, with similar slopes. Once again the CHF/CDFT- $\Delta$  result is much too large and  
10 qualitatively incorrect (not shown), with an anomalous rise in the coupling as a function of distance  
11 for PBE. The magnitude of the TEET coupling is considerably larger than in formaldehyde dimer,  
12 as expected for the more delocalized,  $\pi$ -conjugated naphthalene system.  
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20 For both formaldehyde and naphthalene, as well as other test systems not discussed here,  
21 we found that the CHF/CDFT- $\Delta$  method yielded qualitatively incorrect (non-exponential, non-  
22 vanishing) coupling. The origin of this error is the adiabatic state energy, i.e. the ground-state  
23 triplet energy calculated with either HF or DFT functionals. For a symmetric system with infinite  
24 donor-acceptor separation, the energy of the diabatic state (with triplet localized on one site) should  
25 exactly equal the energy of the ground adiabatic state (with triplet delocalized over both), leading to  
26 zero coupling as expected. This is a consequence of the constancy condition for fractional spin,<sup>37</sup>  
27 discussed earlier for hydrogen atom. Here the constancy condition for a single molecule can be  
28 written for an electron density,  $\rho$ , as  
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$$\rho(\gamma) = \gamma\rho_{S_0} + (1 - \gamma)\rho_{T_1} \quad (13)$$

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43 where  $\gamma: [0, 1]$  represents the fraction of singlet density, and  $\rho_{S_0}$  and  $\rho_{T_1}$  are the ground state singlet  
44 and triplet densities, respectively. The energy of this ensemble density should vary linearly as a  
45 function of  $\gamma$ , with  $E[\rho(1)] - E[\rho(0)]$  equal to the singlet-triplet gap for the isolated molecule. As  
46 we will see, this is not generally the case with HF and DFT functionals.  
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52 In Figure 5,  $E[\rho(\gamma)]$  is calculated for formaldehyde, naphthalene, and lithium fluoride with the  
53 6-311+G\*\* basis and a number of different exchange-correlation functionals. To aid the eye, the  
54 linear change in energy from singlet to triplet expected from the exact condition is differenced to  
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4 yield a symmetric curve, so that the exact result should be a flat line; in this way, deviations from  
5 constant energy are more easily seen. Thus we plot

$$\bar{E}[\rho(\gamma)] = E[\rho(\gamma)] - \gamma(E[\rho(1)] - E[\rho(0)]) \quad (14)$$

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13 In Figure 5a-b, for formaldehyde and naphthalene, we find that HF has the largest fractional spin  
14 error and incorrect concavity, and LDA has much smaller (but still slight) concavity; these trends  
15 are the same as seen previously for atomic and molecular systems.<sup>37</sup> The other functionals lie  
16 between these two, with hybrid functionals having larger deviations than the pure PBE functional.  
17 In Figure 5c for LiF, however, we find that while HF remains concave, the DFT functionals have  
18 an opposite error with incorrect convex behavior.

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21 The results in Figure 5 suggest that the adiabatic triplet energy in most cases will be too high,  
22 and Eqn. 7 will yield too large of a coupling. The magnitude of this error at infinite separation  
23 can be approximated from  $\bar{E}[\rho(\frac{1}{2})] - \bar{E}[\rho(0)]$ , and this error estimate is in qualitative agreement  
24 with the overestimation of the coupling from the CHF/CDFT- $\Delta$  method. For LiF, we expect that  
25 the DFT adiabatic triplet energy will be too low in energy, and the coupling will once again be too  
26 large (but with opposite sign).

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29 The behavior described above might also explain the failing of the splitting method when ap-  
30 plied to calculations from the triplet reference, as discussed briefly in Section 3.1. In a dimer  
31 system, a TDHF or TDDFT calculation from the triplet ground state should yield a low-lying  
32 spin-conserving excitation, the magnitude of which should approach zero exponentially as the  
33 molecules are separated. In all calculations we attempted, however, this behavior was not seen.  
34 Instead, the lowest lying triplet excitation was much larger than expected and stayed roughly con-  
35 stant as separation was increased. This can be explained from Figure 5 - within the linear response  
36 formulation<sup>46</sup> of TDDFT, the RPA equations yield the excited state energies of the system as the  
37 eigenvalues of a generalized eigenvalue equation for a matrix,  $\Gamma$ . This  $\Gamma$  matrix can be shown<sup>47</sup> to  
38 operate as the second derivative of the energy with respect to orbital rotations:  $\frac{\partial^2 E}{\partial c_{ia} \partial c_{jb}}$ . For systems

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3 with concave behavior (such as formaldehyde and naphthalene), a linear response calculation from  
4 the delocalized adiabatic state,  $\rho(\frac{1}{2})$ , will fail, resulting in imaginary roots. Thus, a TDHF/TDDFT  
5 calculation from the triplet reference requires that the partial derivative be evaluated at the left/right  
6 extremes of the plot ( $\gamma = 0, 1$ ). At these points, the second derivative for the exact functional should  
7 be zero, yielding a doubly degenerate triplet ground state at infinite separation; for approximate  
8 functionals, however, the second derivative can be quite large due to incorrect concavity, and too  
9 large excitation energies result.  
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12 It has been pointed out previously that SIE and fractional charge error make the CDFT- $\Delta$   
13 method inapplicable for calculating the electronic coupling between charge-transfer diabats.<sup>48</sup>  
14 From our calculations we conclude that a similar failing of the exact constancy conditions for  
15 fractional spin leads to errors when using the CHF/CDFT- $\Delta$  method for TEET as well.  
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### 18 **3.3 Intramolecular TEET in Biporphyrins**

19 Finally, as a more chemically interesting example, we examine a series of biporphyrin molecules  
20 studied experimentally and theoretically by Eng et al.<sup>11</sup> As shown in Figure 6, the separation  
21 between a free base ( $H_2P$ ) and zinc ( $ZnP$ ) porphyrin was increased by adding oligophenylene  
22 ethynylene units. The rate of TEET was measured from transient absorption studies, and an at-  
23 tenuation factor of  $\beta = 0.45 \text{ \AA}^{-1}$  was found. In addition, TDDFT calculations (6-31G\*, B3LYP)  
24 were carried out and the splitting method was used to estimate  $\beta$ ; to make the splitting method ap-  
25 plicable, symmetric analogues of the experimental system were calculated with  $H_2P-H_2P$  yielding  
26  $\beta = 0.32 \text{ \AA}^{-1}$ , while  $ZnP-ZnP$  was found to have  $\beta = 0.19 \text{ \AA}^{-1}$ , both in a planar geometry. Using  
27 Boltzmann-weighted geometries, rather than assuming planarity, yielded a slightly larger value for  
28  $\beta$  in each case.  
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31 We perform the TEET coupling calculation for the *asymmetric* system, as well as the sym-  
32 metric analogues, with CDFT. After geometry optimizing (with symmetry constraints forcing the  
33 molecule to remain planar), we calculated the localized triplet diabatic states and the coupling  
34 with our CDFT method (6-31G\*, B3LYP). Our results are summarized in Table 1 and plotted in  
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3 Figure 7. For the mixed system, we find  $\beta = 0.50 \text{ \AA}^{-1}$ , in good agreement with the experimental  
4 result. In contrast with the splitting result, we find that the ligands in the porphyrins (Zn or H<sub>2</sub>)  
5 have little effect on the distance dependence of the electronic coupling (or its overall magnitude).  
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## 10 11 12 **4 Conclusions**

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15 In the preceding, we have discussed the various methods available for calculation of the electronic  
16 coupling in energy transfer of triplet excited states. These can be divided roughly into two classes;  
17 those based on energy-gap expressions for the coupling, and those based on the triplet state and  
18 direct coupling from diabatic states. In the former, the splitting method, for symmetric systems,  
19 and FED provide a means of obtaining the electronic coupling for triplet transfer via linear response  
20 calculations of the triplet excited states. These methods thus require an accurate value of the triplet  
21 energy levels. Although not discussed here, we note recent work which has found that TDDFT  
22 errors for triplet excited states are in general larger than for singlets.<sup>49</sup> In addition to quantitative  
23 errors in the triplet excitation spectrum, there is also the potential for the lowest calculated triplet  
24 excited states to be qualitatively incorrect due to artificially low-lying charge-transfer<sup>38–40</sup> or other  
25 intruder states.<sup>50</sup> If these adiabatic states are chosen, the diabatic-adiabatic transformation will fail  
26 to yield the appropriate electronic coupling.  
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40 Another class of methods for computing electronic coupling are based on defining some addi-  
41 tional operator which represents the degree of excitation-localization; by maximizing this operator,  
42 the rotation matrix from the computed adiabatic states to the desired diabatic states is derived. The  
43 FED method can also be classified in this way. Additionally, a recently proposed approach by  
44 Subotnik et al. makes use of orbital localization techniques to localize states and can yield electron  
45 and energy transfer couplings.<sup>51,52</sup>  
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52 The second class of electronic coupling methods discussed in this work is based on calculating  
53 triplet diabatic states directly. Both perturbative (fragment) and supramolecular (CDFT and broken  
54 symmetry) approaches were discussed. We proposed a new approach for TEET coupling, where  
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3 CDFT provides the necessary diabatic states, and the expression in Eqn. 10 is used to obtain the  
4 coupling. Unlike other direct coupling methods, CDFT can be applied to both inter and intramolec-  
5 ular TEET and has a robust optimization method for converging to the diabatic state. In addition,  
6 directly evaluating the coupling matrix element from the CDFT diabats avoids any potential issues  
7 from fractional spin error.  
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13 Finally, we found that the fractional spin error present in HF and commonly-used DFT func-  
14 tionals can contaminate the coupling in triplet reference calculations if one is not careful. The  
15 adiabatic triplet state energy is incorrect, and even small deviations result in relatively large errors  
16 in the coupling. Thus, we conclude that direct coupling schemes, in which the electronic coupling  
17 is calculated by directly evaluating the matrix element between diabats, are a more robust choice  
18 for TEET. Looking forward, there are a number of related avenues of interest. One important  
19 question is what the best diabatic method for FGR-type rate expressions is; although there is not  
20 generally a unique set of diabatic states, can we construct some criterion for the best diabatiza-  
21 tion scheme for evaluating the electronic coupling matrix element in TEET? Also, Franck-Condon  
22 factors for TEET can be calculated, which when combined with the electronic coupling, provide  
23 the main parameters necessary for calculating the excitation transfer rate. We are also interested  
24 in applying this CDFT coupling scheme to study energy transfer in disordered organic materials  
25 using QM/MM methods;<sup>53</sup> including environment effects will provide a better understanding of  
26 exciton transfer processes in OLEDs and OPVs and can aid in the engineering of organic electronic  
27 devices.  
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## 45 46 **Acknowledgement**

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50 DOE (DE-FG02-07ER46474). We would also like to acknowledge the honoree of this special  
51 issue, Mark Ratner, an excellent mentor, colleague, scientist, and friend.  
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## References

- (1) Takiff, L.; Boxer, S. G. *J. Am. Chem. Soc.* **1988**, *110*, 4425–4426.
- (2) Gust, D.; Moore, T. A.; Moore, A. L. *Acc. Chem. Res.* **1993**, *26*, 198–205.
- (3) Closs, G. L.; Johnson, M. D.; Miller, J. R.; Piotrowiak, P. *J. Am. Chem. Soc.* **1989**, *111*, 3751–3753.
- (4) Closs, G. L.; Piotrowiak, P.; MacInnis, J. M.; Fleming, G. R. *J. Am. Chem. Soc.* **1988**, *110*, 2652–2653.
- (5) Forrest, S. R. *Nature* **2004**, *428*, 911–918.
- (6) Luhman, W. A.; Holmes, R. J. *Appl. Phys. Lett.* **2009**, *94*, 153304.
- (7) Shao, Y.; Yang, Y. *Adv. Mater.* **2005**, *17*, 2841–2844.
- (8) Terenin, A.; Ermolaev, V. *Trans. Faraday Soc.* **1956**, *52*, 1042–1052.
- (9) Harriman, A.; Khatyr, A.; Ziessel, R.; Benniston, A. C. *Angew. Chem., Int. Ed.* **2000**, *39*, 4287–4290.
- (10) Harriman, A.; Ziessel, R. In *Carbon-Rich Compounds*; Haley, M. M., Tykwinski, R. R., Eds.; 2006; Chapter 2, pp 26–89.
- (11) Eng, M. P.; Ljungdahl, T.; Martensson, J.; Albinsson, B. *J. Phys. Chem. B* **2006**, *110*, 6483–6491.
- (12) Merkel, P. B.; Dinnocenzo, J. P. *J. Phys. Chem. A* **2008**, *112*, 10790–10800.
- (13) Marcus, R. A. *J. Chem. Phys.* **1956**, *24*, 966–978.
- (14) Manneback, C. *Physica* **1951**, *17*, 1001–1010.
- (15) Jortner, J. *J. Chem. Phys.* **1976**, *64*, 4860–4867.

- 1  
2  
3  
4 (16) Søndergaard, N. C.; Ulstrup, J.; Jortner, J. *Chem. Phys.* **1976**, *17*, 417–422.  
5  
6  
7 (17) Yeganeh, S.; Ratner, M. A. *J. Chem. Phys.* **2006**, *124*, 044108.  
8  
9  
10 (18) Förster, T. *Ann. Phys. (Leipzig)* **1948**, *437*, 55–75.  
11  
12 (19) Scholes, G. D. *Annu. Rev. Phys. Chem.* **2003**, *54*, 57–87.  
13  
14  
15 (20) Dexter, D. L. *J. Chem. Phys.* **1953**, *21*, 836–850.  
16  
17  
18 (21) Naqvi, K. R.; Steel, C. *Chem. Phys. Lett.* **1970**, *6*, 29–32.  
19  
20  
21 (22) Salem, L. *Discuss. Faraday Soc.* **1965**, *40*, 150–163.  
22  
23  
24 (23) Wu, Q.; Van Voorhis, T. *Phys. Rev. A* **2005**, *72*, 024502.  
25  
26  
27 (24) Van Voorhis, T.; Kowalczyk, T.; Kaduk, B.; Wang, L.-P.; Cheng, C.-L.; Wu, Q. *Annu. Rev.*  
28 *Phys. Chem.* **2010**, *61*, 149–170.  
29  
30  
31 (25) Eng, M. P.; Albinsson, B. *Angew. Chem., Int. Ed.* **2006**, *45*, 5626–5629.  
32  
33  
34 (26) Eng, M. P.; Albinsson, B. *Chem. Phys.* **2009**, *357*, 132–139.  
35  
36  
37 (27) Newton, M. D. *Chem. Rev.* **1991**, *91*, 767–792.  
38  
39  
40 (28) Hsu, C. P. *Acc. Chem. Res.* **2009**, *42*, 509–518.  
41  
42  
43 (29) Mead, C. A.; Truhlar, D. G. *J. Chem. Phys.* **1982**, *77*, 6090–6098.  
44  
45  
46 (30) Becke, A. D. *J. Chem. Phys.* **1988**, *88*, 2547–2553.  
47  
48  
49 (31) Wu, Q.; Cheng, C. L.; Van Voorhis, T. *J. Chem. Phys.* **2007**, *127*, 164119.  
50  
51  
52 (32) Wu, Q.; Kaduk, B.; Van Voorhis, T. *J. Chem. Phys.* **2009**, *130*, 034109.  
53  
54  
55 (33) Wu, Q.; Van Voorhis, Q. *J. Chem. Phys.* **2006**, *125*, 164105.  
56  
57  
58 (34) Cohen, A. J.; Mori-Sanchez, P.; Yang, W. T. *Science* **2008**, *321*, 792–794.  
59  
60

- 1  
2  
3  
4 (35) Vydrov, O. A.; Scuseria, G. E.; Perdew, J. P. *J. Chem. Phys.* **2007**, *126*, 154109.  
5  
6  
7 (36) Perdew, J. P.; Parr, R. G.; Levy, M.; Balduz, J. L. *Phys. Rev. Lett.* **1982**, *49*, 1691–1694.  
8  
9  
10 (37) Cohen, A. J.; Mori-Sanchez, P.; Yang, W. T. *J. Chem. Phys.* **2008**, *129*, 121104.  
11  
12 (38) Dreuw, A.; Head-Gordon, M. *J. Am. Chem. Soc.* **2004**, *126*, 4007–4016.  
13  
14  
15 (39) Dreuw, A.; Head-Gordon, M. *Chem. Rev.* **2005**, *105*, 4009–4037.  
16  
17  
18 (40) Fink, R. F.; Pfister, J.; Zhao, H. M.; Engels, B. *Chem. Phys.* **2008**, *346*, 275–285.  
19  
20  
21 (41) Hsu, C.-P.; You, Z.-Q.; Chen, H.-C. *J. Phys. Chem. C* **2008**, *112*, 1204–1212.  
22  
23  
24 (42) Voityuk, A. A.; Rosch, N. *J. Chem. Phys.* **2002**, *117*, 5607–5616.  
25  
26  
27 (43) You, Z.-Q.; Hsu, C.-P.; Fleming, G. R. *J. Chem. Phys.* **2006**, *124*, 044506–10.  
28  
29  
30 (44) Shao, Y. et al. *Phys. Chem. Chem. Phys.* **2006**, *8*, 3172–3191.  
31  
32  
33 (45) Perdew, J. P.; Burke, K.; Ernzerhof, M. *Phys. Rev. Lett.* **1996**, *77*, 3865–3868.  
34  
35 (46) Casida, M. E. Time-dependent density functional response theory for molecules. In *Recent*  
36 *Advances in Density Functional Methods*; Chong, D. E., Ed.; World Scientific: Singapore,  
37 1995; Vol. 1, pp 155–1592.  
38  
39  
40  
41  
42 (47) McWeeny, R. *Methods of Molecular Quantum Mechanics*; Academic Press: London, 1992.  
43  
44  
45 (48) Ding, F.; Wang, H.; Wu, Q.; Van Voorhis, T.; Chen, S.; Konopelski, J. P. *J. Phys. Chem. A*  
46 **2010**, *114*, 6039–6046.  
47  
48  
49  
50 (49) Jacquemin, D.; Perpeite, E. A.; Ciofini, I.; Adamo, C. *J. Chem. Theory Comput.* **2010**, *6*,  
51 1532–1537.  
52  
53  
54  
55 (50) Curutchet, C.; Mennucci, B. *J. Am. Chem. Soc.* **2005**, *127*, 16733–16744.  
56  
57  
58 (51) Subotnik, J. E.; Yeganeh, S.; Cave, R. J.; Ratner, M. A. *J. Chem. Phys.* **2008**, *129*, 244101.  
59  
60

1  
2  
3  
4 (52) Subotnik, J. E.; Vura-Weis, J.; Sodt, A. J.; Ratner, M. A. *J. Phys. Chem. A* **2010**, Article  
5 ASAP.  
6

7  
8 (53) Difley, S.; Wang, L.-P.; Yeganeh, S.; Yost, S. R.; Van Voorhis, T. *Acc. Chem. Res.* **2010**, *43*,  
9 995–1004.  
10  
11  
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**Table 1: The extrapolated  $\beta$  values for the biporphyrin system in Figure 6 are tabulated.**  
<sup>a</sup>Calculated splitting and experimental values from Ref. 11 are also shown.

$\beta$ ( $\text{\AA}^{-1}$ )	Splitting <sup>a</sup>	CDFT	expt. <sup>a</sup>
H <sub>2</sub> -H <sub>2</sub>	0.32	0.53	-
Zn-Zn	0.19	0.51	-
Zn-H <sub>2</sub>	-	0.50	0.45

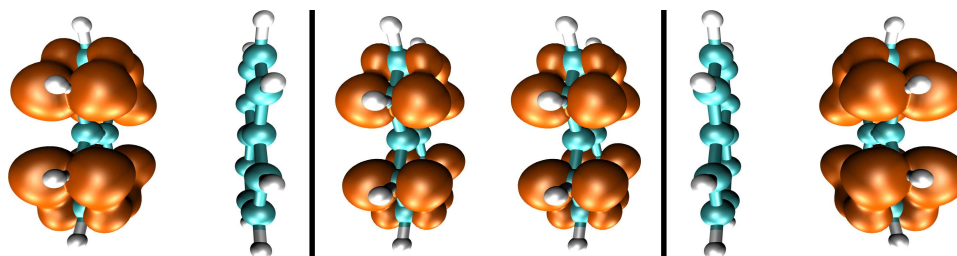


Figure 1: Spin density ( $\rho^\alpha - \rho^\beta$ ) is plotted for naphthalene dimer in adiabatic (center) and diabatic (left/right) representations. Methods for computing the electronic coupling either obtain adiabatic states and indirectly calculate the coupling, or (as in CDFT) directly obtain diabatic states and evaluate the coupling matrix element between them.

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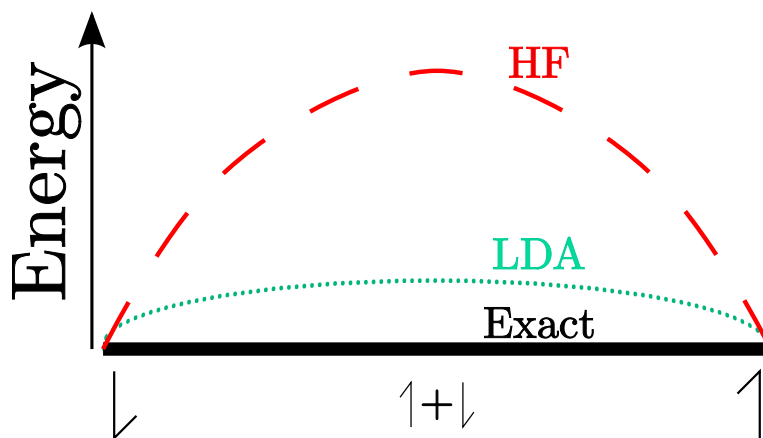


Figure 2: A sketch of the fractional spin error in atomic hydrogen. While the exact functional should yield a constant energy for all configurations of partial up and down spin, both HF and LDA display concave behavior due to the single determinant description in both methods.

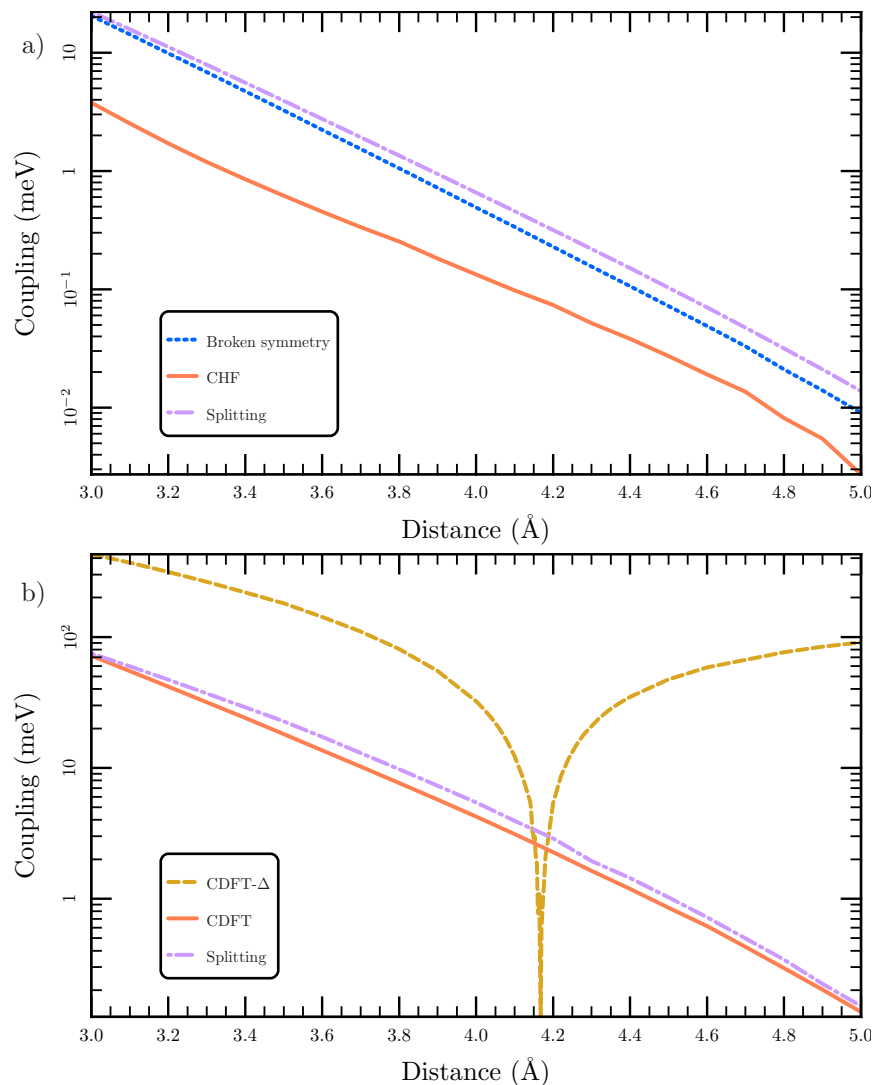


Figure 3: The electronic coupling for TEET in stacked formaldehyde is shown with a number of different methods. For HF (a), the broken symmetry method, CHF coupling, and HF splitting are shown. For PBE (b), CDFT- $\Delta$ , CDFT coupling, and splitting are shown - broken symmetry was inapplicable as the diabatic states could not be obtained. The absolute value of the coupling is plotted; hence the discontinuity in the CDFT- $\Delta$  result corresponds to a change in sign.

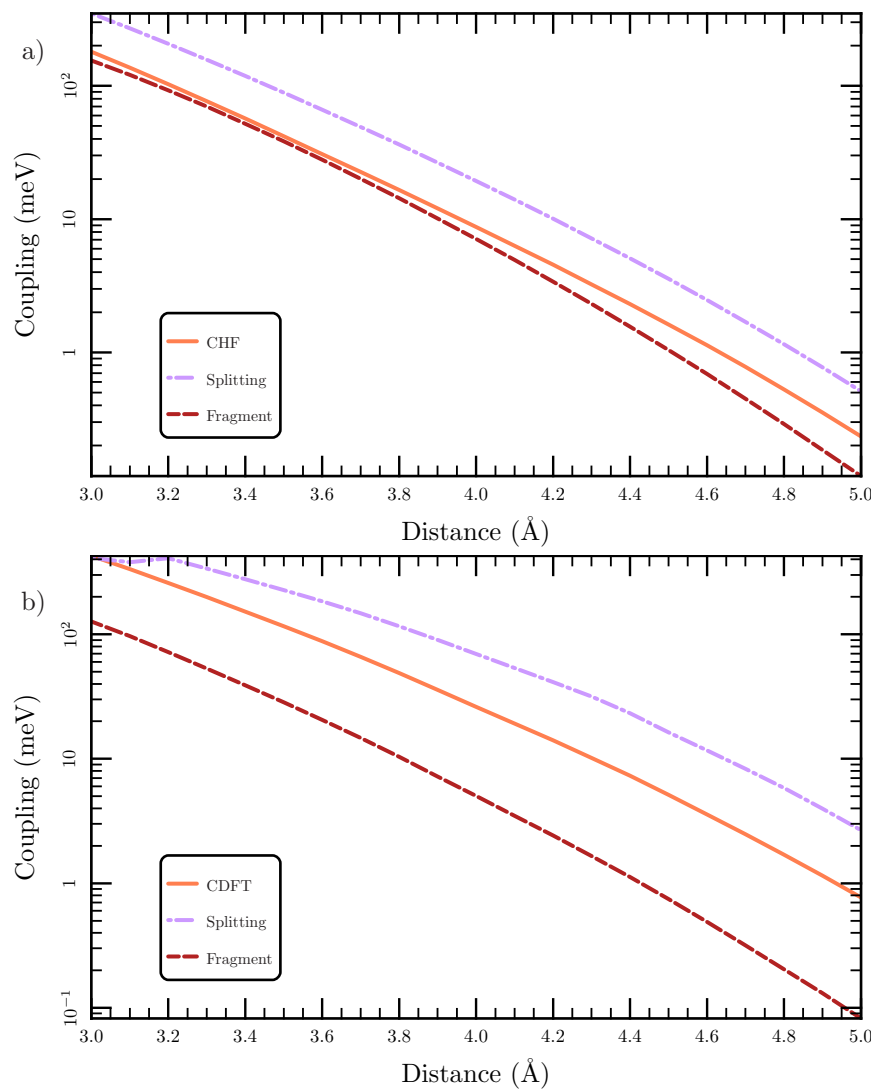


Figure 4: The TEET electronic coupling for a pair of  $\pi$ -stacked naphthalene molecules is shown with a number of different methods for HF (a) and PBE (b). The CHF/CDFT coupling, splitting, and fragment method results are plotted.

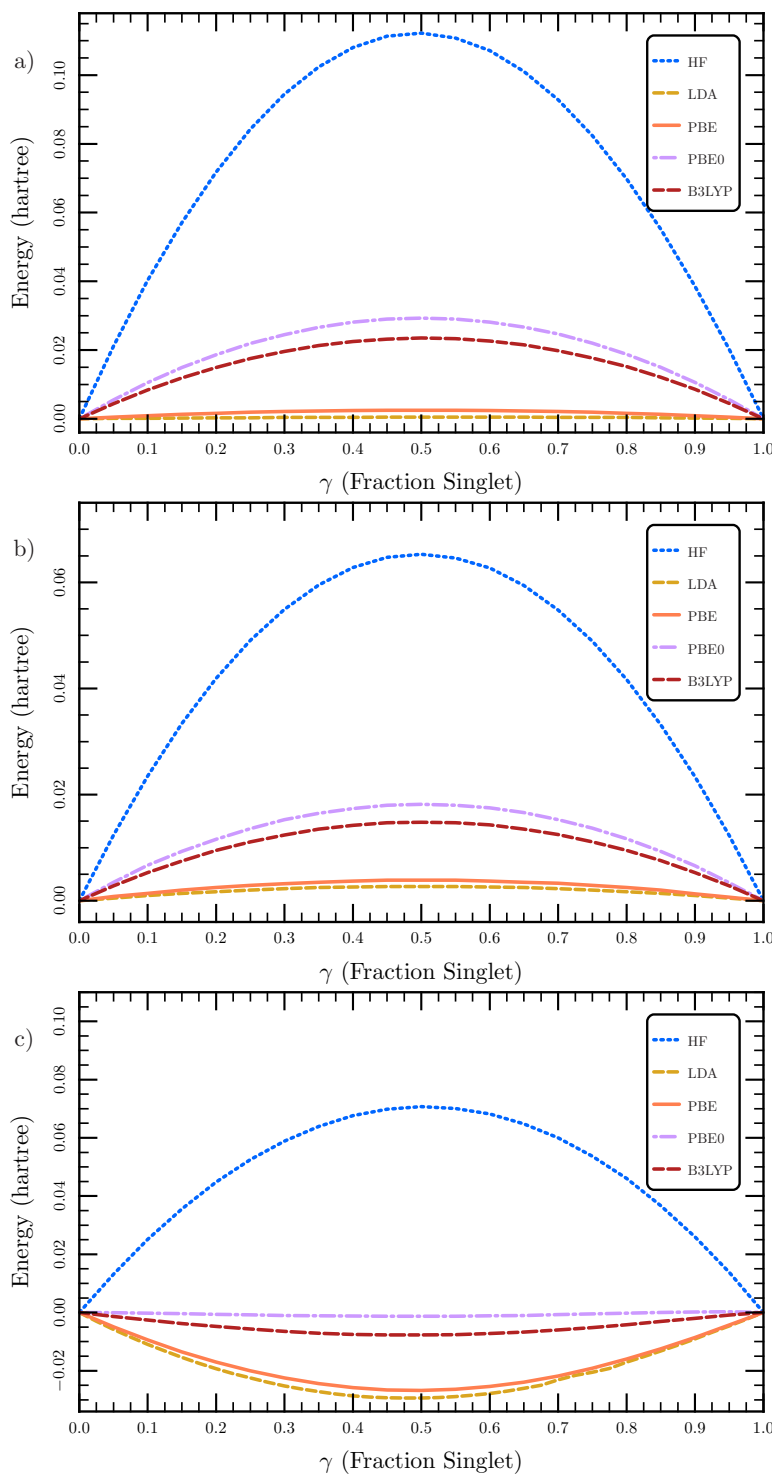


Figure 5: The ensemble density energy, Eqn. 14, is plotted for (a) formaldehyde, (b) naphthalene, and (c) lithium fluoride. Deviation from a flat line,  $\bar{E}[\gamma] = 0$ , is evidence of fractional spin error.

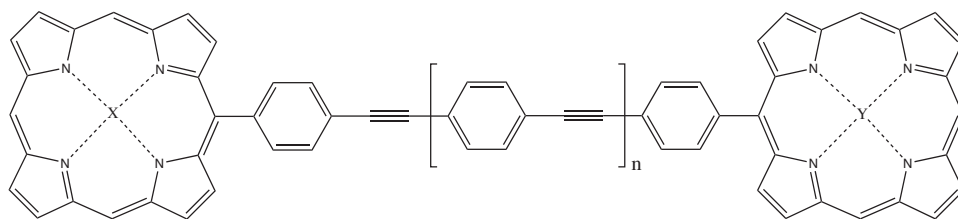


Figure 6: Structure of biporphyrin series studied here. The experimental system (Ref. 11) had side-chains which are omitted in our calculation. The experimental system has  $X = \text{Zn}$  and  $Y = \text{H}_2$ . The number of bridge units,  $n$ , is varied from 0 to 3.

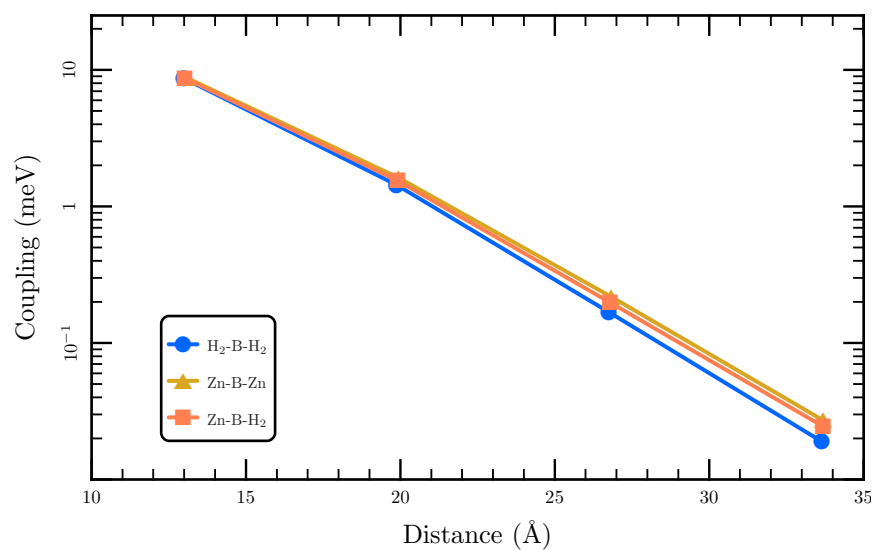
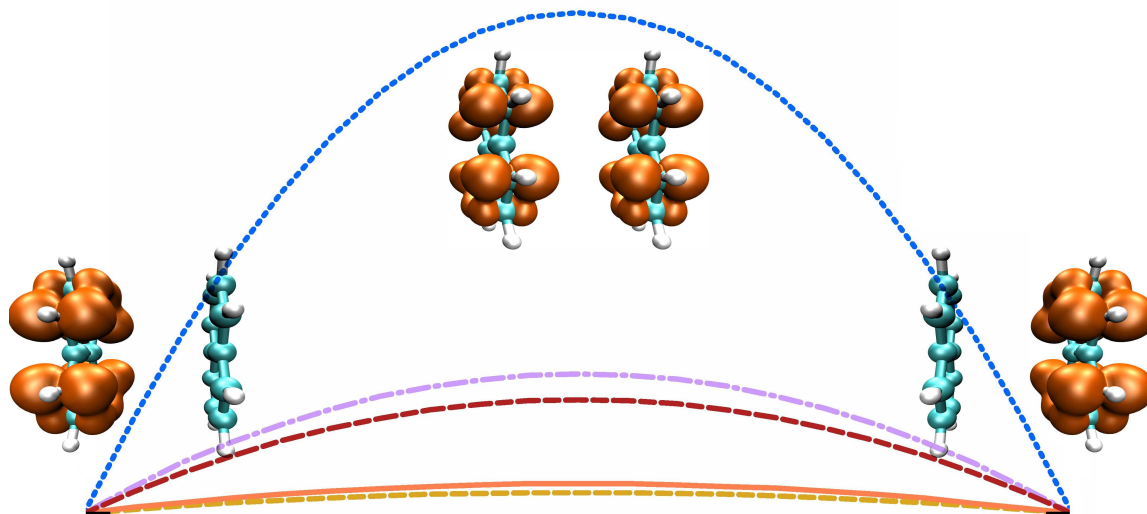


Figure 7: The TEET electronic coupling for the biporphyrin systems in Figure 6 is plotted. Calculations with CDFT (6-31G\*, B3LYP) are shown. Calculated  $\beta$  values are found in Table 1.



Graphical Table of Contents Entry

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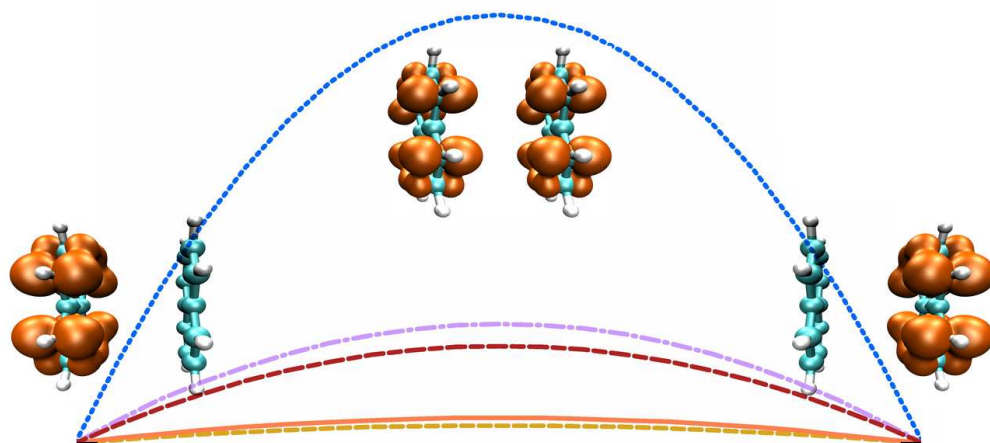


Table of Content Figure  
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