Predicting Accurate Electronic Excitation Transfer Rates via Marcus Theory with Boys or Edmiston–Ruedenberg Localized Diabatization

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We model the triplet—triplet energy-transfer experiments from the Closs group [Closs, G. L.; et al. J. Am. Chem. Soc. 1988, 110, 2652.] using a combination of Marcus theory and either Boys or Edmiston–Ruedenberg localized diabatization, and we show that relative and absolute rates of electronic excitation transfer may be computed successfully. For the case where both the donor and acceptor occupy equatorial positions on a rigid cyclohexane bridge, we find $\beta_{calc} = 2.8$ per C–C bond, compared with the experimental value $\beta_{exp} = 2.6$. This work highlights the power of using localized diabatization methods as a tool for modeling nonequilibrium processes.

1. Introduction: Modeling The Closs Experiments

Twenty years ago, in a series of elegant experiments, Closs and co-workers1,2 measured the rates of electronic excitation transfer (EET) or electron transfer (ET) from either benzophenone or biphenyl to naphthalene across a variety of bridge molecules at room temperature. Several conclusions were immediately clear from their results. First, for a rigid bridge molecule, the rate of triplet EET decayed exponentially with the number of bridging covalent bonds, consistent with the superexchange mechanism. Second, the rate of triplet EET was roughly proportional to the rate of electron transfer times the rate of hole transfer (with a properly dimensioned coefficient to account for solvation and reorganization). Thus, the Closs experiments reinforced the idea that ET and EET could and should be considered within the same theoretical framework.

In this article, we will computationally model the Closs EET experiments, and we will show that experimental EET rates may be successfully calculated when we combine Marcus theory3,4 with straightforward techniques from ab initio electronic structure theory. These techniques might be labeled localized diabatization, and they are very similar to orbital localization techniques from quantum chemistry.5 Intriguingly, these methods can be applied to both ET and EET equivalently; in a future paper, we will calculate the corresponding ET results and compare them with experimental values. Computational studies of ET in cyclohexane-bridged systems have been reported previously by Braga and Larsson6 and Koga, Sameshima, and Morokuma.7 The latter work also addresses EET partially.

An outline of this paper is as follows. In section 2, we will present the necessary theoretical background for modeling EET in terms of Marcus theory for real, three-dimensional chemical systems and discuss localized diabatization. In section 3, we present numerical results for the range of bridge molecules considered by Closs and co-workers. In section 4, we discuss our findings before concluding in section 5.

2. Theory

2.1. Marcus Theory Applied to Electronic Excitation Transfer (EET). According to Marcus theory, in the nonadiabatic high-temperature or activated crossing limit, the rate of EET in a condensed environment is8,9

$$k_{\text{ET-F}} = \frac{2\pi}{h} |H_{\text{IF}}|^2 \sqrt{\frac{1}{4\pi k_B T \omega}} \exp{-\left(\frac{\Delta G^0}{k_B T}\right)^2 / 4\pi k_B T \omega}$$

(1)

Here, “I” represents the initial state of the system, “F” represents the final state of the system, and $H_{\text{IF}}$ is the diabatic electronic coupling matrix element between the two electronic states. $\Delta G^0$ is the total change in free energy between the final and initial states ($E_F - E_I$, ignoring entropy changes), and $\lambda$ is the reorganization energy, which accounts for the motion of solvent and other nuclei. Equation 1 is valid in both the Dexter10 and Forster11,12 limits of EET, but as we will see, the experiments here are in the Dexter regime.

In order to derive eq 1, several assumptions have been made. First, one assumes that the potential energy surfaces for the nuclear vibrational modes are two shifted parabolas. Second, one assumes the validity of the golden rule or first-order time-dependent perturbation theory. Third and finally, we take the high-temperature or activated crossing limit, $k_B T \gg (\hbar \omega)^2 / 4\pi$, where $\omega$ is the maximum frequency for any nuclear vibrational mode coupled to the electronic system.8,9,13 This last assumption is usually not valid for EET events, as discussed in section 3.3. As a practical matter, standard Marcus theory can be derived easily if one assumes that all nuclear coordinates may be grouped together into one effective reaction coordinate. In this case, $\omega$ is chosen to be the frequency of that reaction coordinate, and eq 1 follows from transition-state theory.8 More elaborate versions of Marcus theory exist.14

Given the above assumptions, it is clear that the Marcus equation applies rigorously only for a model Hamiltonian. For a real system that can be experimentally probed, the necessary assumptions can be only approximately true. As a result, even

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if we are willing to assume that the golden rule applies, three new problems arise for practical predictions of EET rates:

(1) Starting with rigorous ab initio calculations of adiabatic electronic states \(|\Phi_{i,F}\rangle\), how do we define the diabatic states \(|\Xi_{j}\rangle\) that represent the initial and final states of the EET process? Intuitively, for the initial state, the electronic excitation should be localized on the donor, and for the final state, the electronic excitation should be on the acceptor, \(|\Xi_{1}\rangle = |AD^+\rangle\) and \(|\Xi_{F}\rangle = |A^+D\rangle\). How can such states be constructed for intramolecular EET where, in general, the adiabatic states \(|\Phi_{i,F}\rangle\) are mixtures of the initial and final states \(|\Xi_{1}\rangle,|\Xi_{F}\rangle|\)?

(2) For physical problems, the potential energy surfaces will not be parabolas, and the diabatic coupling \(H_{IB}\) will not be constant. By definition, a varying \(H_{IB}\) is a violation of the so-called Condon approximation. Thus, at what geometry should we calculate \(H_{IB}\) in order to best match experiment?\(^8\)

(3) Because calculations are most easily done in vacuum, how can we best and most easily approximate the reorganization energy?\(^9\)

In this paper, we will solve the first problem by constructing diabatic states using localized diabatization algorithms, in particular the Boys and Edmiston–Ruedenberg (ER) formalisms. As described in detail previously\(^5,15\) and briefly below, these diabatic states arise when one assumes that there are external electrostatic interactions stabilizing the localization of either charge or energy excitation.

For the second problem, we will test the Condon approximation by choosing different molecular geometries and comparing the resulting different values of \(H_{IB}\). According to the Condon approximation, over regions of nuclear configuration space where the electronic energies of adiabatic states do not change significantly, the electronic coupling \(H_{IB}\) should be constant. Our general conclusion will be that, for rigid bridge molecules, the Condon approximation is nearly satisfied. For small and flexible bridge molecules, especially when torsional angles are not fixed, the Condon approximation can be badly violated, and standard Marcus theory may be inapplicable or need correction. This conclusion agrees with previous ET results.\(^7\)

Finally, regarding the reorganization energy, we note that because charge is never displaced from one basin to another, we expect that reorganization energies should be relatively constant for EET. More generally, we will calculate optimized nuclear geometries corresponding to electronic configurations \(|AD^+\rangle\) and \(|A^+D\rangle\) by biasing the initial guess geometry and then minimizing the energy. Using the resulting optimized geometries, we can calculate precise reorganization energies and energy shifts. We will find that reorganization energies are not important for modeling the relative EET rates in the Closs experiments. If, however, we do calculate the reorganization energies, absolute EET rates may also be calculated with some success.

### 2.2. Brief Review of Localized Diabatization and the Diabatic Coupling \(H_{IB}\)

Before applying Marcus theory to the EET experiments of Closs and co-workers, we briefly review how localized diabatization is implemented for a real chemical system. This is how we solve problem (1) above.

#### 2.2.1. Boys and ER Diabatization

By definition, for any problem in quantum mechanics, the adiabatic states of a system \(|\Phi_{i}\rangle\) are those electronic states that diagonalize the electronic Hamiltonian, assuming that the nuclei are fixed

\[
    H(r) = H_{\text{m}}(r) + H_{\text{el}}(r;R)
\]

In eqs 2 and 3, \(r\) represents electronic coordinates, and \(R\) represents nuclear coordinates.

When external degrees of freedom are present (either from a bath of solvent or from nuclear vibrations), the adiabatic states of the system may not be stationary. Moreover, the adiabatic states may not represent the initial or final states of an ET or EET process. In such cases, one standard approach to describe the electronic stationary states of the system is to rotate the adiabatic states into a set of diabatic states \(|\Xi_{j}\rangle\)

\[
    |\Xi_{j}\rangle = \sum_{i=1}^{N_{\text{states}}} |\Phi_{i}\rangle U_{ji} \quad i = 1...N_{\text{states}}
\]

Several techniques have been previously introduced for generating the rotation matrix \(U\) using a variety of different approaches. Early techniques searched for the crossing seam\(^16,17\) where

\[
    U = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 & -1 \\ 1 & 1 \end{pmatrix}
\]

and then used a splitting criterion to calculate the diabatic coupling. This technique effectively localizes an electron on the donor and acceptor,\(^18\) which can be seen most easily when one freezes all but one electron. More recently, a new group of methods have allowed diabatic couplings to be calculated at arbitrary nuclear geometries. Examples of such methods in the context of electron transfer include generalized Mulliken Hush (GMH)\(^{19,20}\) and fragment charge difference (FCD),\(^21\) and in the context of energy transfer, fragment energy difference (FED).\(^{22-24}\)

We have previously argued that, on the basis of different models of system–bath coupling, one correct prescription for constructing such diabatic states is to use Boys, Edmiston–Ruedenberg (ER), or von Niessen–Edmiston–Ruedenberg (VNER) localization.\(^5,15\) These three techniques make different assumptions about system–solvent interactions that all lead to localization of some kind.

- Boys diabatization presumes that the bath exerts a linear electrostatic potential on the system.
- ER diabatization presumes that the bath exerts an electrostatic potential that responds linearly to the field of the system.
- Like ER diabatization, VNER diabatization presumes that the bath exerts an electrostatic potential that responds linearly to the field of the system, only with the extra stipulation that system charges and bound charges interact via a delta function potential (rather than by Coulomb’s law).

As a practical matter, the assumptions above lead to rotation matrices \(U\) characterized by maximizing three different localizing functions\(^5\)

\[
    f_{\text{Boys}}(U) = f_{\text{Boys}}(|\Xi_{j}\rangle) = \sum_{i,j=1}^{N_{\text{states}}} |\langle \Xi_{i}|\hat{\mu}|\Xi_{j}\rangle|^2
\]

\[
    f_{\text{VNER}}(U) = f_{\text{VNER}}(|\Xi_{j}\rangle) = \sum_{i,j=1}^{N_{\text{states}}} |\langle \Xi_{i}|\hat{\phi}_{\text{ext}}|\Xi_{j}\rangle|^2
\]

\[
    f_{\text{ER}}(U) = f_{\text{ER}}(|\Xi_{j}\rangle) = \sum_{i,j=1}^{N_{\text{states}}} |\langle \Xi_{i}|\hat{\phi}_{\text{ext}}|\Xi_{j}\rangle|^2
\]

\[
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\]
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\[ f_{\text{ER}}(U) = \sum_{i=1}^{N_{\text{states}}} \int d\mathbf{r}_2 \int d\mathbf{r}_1 \frac{\langle \Xi_i | \hat{\rho}(\mathbf{r}_2) \Xi_j \rangle \langle \Xi_j | \hat{\rho}(\mathbf{r}_1) \Xi_i \rangle}{|\mathbf{r}_1 - \mathbf{r}_2|} \]  (6)

\[ f_{\text{VNER}}(U) = \sum_{i=1}^{N_{\text{states}}} \int d\mathbf{r} \langle \Xi_i | \hat{\rho}(\mathbf{r}) \Xi_j \rangle - \langle \Xi_j | \hat{\rho}(\mathbf{r}) \Xi_i \rangle^2 \]  (7)

where the density operator at position \( \mathbf{r} \) is defined to be \( \hat{\rho}(\mathbf{r}) \)

\[ \hat{\rho}(\mathbf{r}) = \sum_{j=1}^{\text{All Electrons}} \delta(\mathbf{r} - \mathbf{r}_{ij}) \]  (8)

and \( \mathbf{r}_{ij} \) is the position of the \( j \)th electron. From the form of eqs 5 - 7, it is clear that these diabatization algorithms correspond exactly to the localization routines that are standard tools in quantum chemistry for generating localized orbitals.25-31

Note that because the Boys algorithm separates charge according to eq 5, it is applicable only to ET and not to EET (since charge never separates in EET). As such, the ER algorithm is more powerful than the Boys approach for it describes both ET and EET equivalently. Nevertheless, in order to produce and compare two independent localization algorithms for EET, in this paper, we have implemented both ER diabatization and a modified Boys algorithm that is applicable to EET for CIS or TD-DFT adiabatic states. To generate this modified Boys method, we localize separately the electronic excitation and de-excitations of the excited states relative to the ground state. More concretely, we maximize the occupied—virtual separated Boys function (BoysOV) by separating the dipole operator into occupied and virtual components, \( \mu = \mu^{\text{occ}} + \mu^{\text{virt}} \)

\[ f_{\text{BoysOV}}(U) = \sum_{i=1}^{N_{\text{states}}} \langle \Xi_i | \hat{\mu}^{\text{occ}} \Xi_j \rangle - \langle \Xi_j | \hat{\mu}^{\text{occ}} \Xi_i \rangle^2 + \langle \Xi_i | \hat{\mu}^{\text{virt}} \Xi_j \rangle - \langle \Xi_j | \hat{\mu}^{\text{virt}} \Xi_i \rangle^2 \]  (9)

All of the mathematical details behind eq 9 are given in the Appendix, section 1. Note that the decomposition \( \mu = \mu^{\text{occ}} + \mu^{\text{virt}} \) works only for CIS or TD-DFT excited states.

Physically, according to eq 9, one assumes that holes and electrons may encounter different electrostatic fields; this assumption is not particularly reasonable, but because the final goal is primarily to produce diabatic states with localized electronic excitation, this algorithm may be sufficient. Furthermore, we can and will compare this algorithm versus rigorous ER localization for confirmation of its validity. Because an algorithm for implementing ER diabatization has already been published,7 we provide only a few additional computational details needed for large molecules in section 2 of the Appendix.

2.2.2. Diabatic Coupling \( H_{\text{IF}} \). Once the diabatic states of the system are known, the diabatic coupling that appears in eq 1 can be computed easily by changing representation. More specifically, if we have \( n \) electronic states, let the adiabatic energies be denoted \( \epsilon_i (i = 1, ..., n) \), and let the adiabatic states be denoted \( |\Phi_i \rangle \), so that

\[ \langle \Phi_i | H^{\text{el}} | \Phi_j \rangle = \delta_{ij} \epsilon_i \]  (10)

When the diabatic states (|\Xi_i \rangle) are defined by the transformation \( U \) in eq 4, the diabatic couplings are simply the off-diagonal terms in the transformed Hamiltonian

\[ \langle \Xi_i | H^{\text{el}} | \Xi_j \rangle = \sum_{kl} U_{ki}(\langle \Phi_k | H^{\text{el}} | \Phi_l \rangle) U_{lj} \]  (11)

For the two-state problem, with initial state I and final state \( F \), the mathematical transformation can be written explicitly. Let \( U \) be parametrized by a mixing angle \( \theta \)

\[ U = \begin{pmatrix} \cos(\theta) & -\sin(\theta) \\ \sin(\theta) & \cos(\theta) \end{pmatrix} \]  (12)

Now, if we transform to the diabatic representation, the Hamiltonian becomes

\[ H^{\text{IF}} = \begin{pmatrix} \cos(\theta) & \sin(\theta) \\ -\sin(\theta) & \cos(\theta) \end{pmatrix} \begin{pmatrix} \epsilon_1 & 0 \\ 0 & \epsilon_2 \end{pmatrix} \begin{pmatrix} \cos(\theta) & -\sin(\theta) \\ \sin(\theta) & \cos(\theta) \end{pmatrix} \]  (13)

and the off-diagonal element \( H_{\text{IF}} \) is

\[ H_{\text{IF}}^{\text{def}} \equiv \langle \Xi_i | H^{\text{el}} | \Xi_j \rangle = \frac{1}{2} \sin(2\theta)(\epsilon_2 - \epsilon_1) \]  (14)

Thus, solving for the adiabatic-to-diabatic transformation matrix \( U \) automatically yields a value for \( H_{\text{IF}} \) to be used in the context of Marcus theory.

In the next section, we will provide \( H_{\text{IF}} \) values (and mixing angles \( \theta \)) for the Closs experiments. We will show that they match up very well with experimental EET rates.

3. Numerical Results: The Closs Experiments

The experimental results found by Closs and co-workers are listed in Table 1 along with our calculated \( H_{\text{IF}} \) values. Note that for these experiments, the EET occurred between triplet states; the triplet EET donor was benzophenone, and the triplet EET acceptor was naphthalene. In our work, for simplicity, we have substituted benzaldehyde for benzophenone; see Figure 1.

The \( H_{\text{IF}} \) values in Table 1 were generated according to the theory presented above. More specifically, the following steps were implemented using the ab initio quantum chemistry package Q-Chem:22

1. For a fixed donor—bridge—acceptor geometry of the system, the Hartree–Fock (HF) orbitals for the singlet ground state were computed.
2. A CIS triplet calculation was performed to find the lowest two adiabatic excited triplet states, \( T_1 \) and \( T_2 \). These states were easily shown to have \( \pi \rightarrow \pi^* \) character.
3. The two low-lying adiabatic triplet states were rotated together using either ER (eq 6) or BoysOV (eq 9) diabatization to generate the mixing angle \( \theta \) and \( H_{\text{IF}} \) (eq 14).
4. In order to be assured of meaningful results, the steps above were repeated while increasing the threshold for CIS convergence. A converged \( H_{\text{IF}} \) required a CIS relative error (in diagonalization) sometimes as small as \( 10^{-8} \), mostly when the mixing angle \( \theta \) was very small.
In order to check the Condon approximation, the nuclear geometry of the system was changed, and the steps above were repeated. We also verified that our results did not depend on basis set.

Before analyzing the physical meaning of the numbers in Table 1, we note that in all calculations for this paper, the ER and BoysOV algorithms gave nearly identical diabatic couplings; the differences are usually well within 10%. For this reason, often, we will present only results from the BoysOV algorithm.

3.1. Choice of Geometry. Before calculating an $H_{IF}$ value, the obvious question is: at what geometry should we be calculating it? According to the Condon approximation, the value of $H_{IF}$ should be independent of geometry, but is this true in practice?

In Table 1, we check the Condon approximation by listing $H_{IF}$ values at three different geometries, (i) the singlet ground-state geometry, (ii) the $T_1$ (first excited triplet state)-optimized geometry where the excitation is on the acceptor A*D, and (iii) the $T_1$ optimized geometry where the excitation is on the donor AD*. We note that, in almost all cases, our computed $H_{IF}$ values depend very weakly on the geometry of the molecule. This is true for all of the equatorial-equatorial-substituted molecules and for most of the equatorial-axial-substituted ones. The most extraordinary exception to this rule is the case where the bridge is a flexible CH$_2$ group; in this case, $H_{IF}$ changes dramatically, which is a violation of the Condon approximation, which will be discussed in section 4.2. For all other structures, there are rigid cyclohexane bridges between D and A, and we find that the Condon approximation is pretty good near the basin of the ground-state geometry.

Thus, for the moment, we are satisfied that we may predict EET rates (using eq 1) that will not depend strongly on molecular geometry within restricted geometric neighborhoods.

3.2. Relative EET Rates with Different Bridge Molecules. Going beyond the Condon approximation, by comparing the experimental and computational data in Table 1, we see that the experimental rate of triplet-triplet energy transfer is highly correlated with our computational value of $H_{IF}$. In order to make this correlation as clear as possible, in Figures 2 and 4, we plot the logarithm of the experimental EET rate versus the $H_{IF}$ value. We do this separately for the case where (i) D/A are both equatorial or (ii) D/A are a combination of equatorial/axial.

| Symbol | Compound | $k_{TT}^{ER}$ (1/s) | $|\theta|$ (rad) | $|H_{IF}|$ (meV) | $|H_{IF}|$ (meV) | $|H_{IF}|$ (meV) | $|H_{IF}|$ (meV) |
|--------|----------|---------------------|----------------|-----------------|----------------|----------------|----------------|
| Diabatization Algorithm | | ER | ER | BoysOV | BoysOV | BoysOV | BoysOV |
| Geometry optimized | | Ground State | Ground State | Ground State | Ground State | $T_1$ | $T_1$ |
| Basis | | 6-31G** | 6-31G** | 6-31G** | cc-pVTZ | 6-31G** | 6-31G** |
| D-2,6ee | | 3.1 $\times 10^6$ | 3.9 $\times 10^{-5}$ | 0.020 | 0.020 | 0.019 | 0.020 | 0.022 |
| D-2,7ee | | 9.1 $\times 10^7$ | 3.3 $\times 10^{-4}$ | 0.17 | 0.17 | 0.16 | 0.17 | 0.18 |
| C-1,4ee | | 1.3 $\times 10^9$ | 1.1 $\times 10^{-3}$ | 0.56 | 0.56 | 0.57 | 0.61 | 0.60 |
| C-1,3ee | | 7.7 $\times 10^9$ | 3.2 $\times 10^{-3}$ | 1.5 | 1.5 | 1.4 | 1.6 | 1.6 |
| D-2,6ae | | 1.3 $\times 10^5$ | 2.2 $\times 10^{-6}$ | 0.0010 | 0.0011 | 0.0011 | 0.0013 | 0.0017 |
| D-2,6ea | | 7 $\times 10^5$ | 4.4 $\times 10^{-6}$ | 0.0022 | 0.0019 | 0.0019 | < 0.0001* | 0.0024 |
| D-2,7ae | | 1.1 $\times 10^7$ | 1.0 $\times 10^{-4}$ | 0.049 | 0.052 | 0.053 | 0.058 | 0.054 |
| D-2,7ea | | 1.5 $\times 10^7$ | 1.0 $\times 10^{-4}$ | 0.047 | 0.045 | 0.045 | 0.032 | 0.050 |
| C-1,4ea | | 4 $\times 10^7$ | 5.2 $\times 10^{-5}$ | 0.026 | 0.034 | 0.037 | 0.066 | 0.043 |
| C-1,3ea | | 3.3 $\times 10^9$ | 9.4 $\times 10^{-4}$ | 0.51 | 0.53 | 0.56 | 0.66 | 0.63 |
| M | | 5 $\times 10^{10}$ | 1.2 $\times 10^{-3}$ | 0.56 | 0.64 | 0.79 | 6.0 | 3.1 |

* This infinitesimal coupling element designated with * is difficult to converge as the CIS error decreases; as such, here, we can only estimate an upper bound from our data.

![Figure 1](image-url)  
**Figure 1.** The donor (benzaldehyde) and acceptor (napthalene) fragments that are treated computationally in this article.
For the equatorial—equatorial data (Figure 2), note that the experimental and theoretical numbers are well fitted using linear interpolation with a slope of 1.8. Here, we plot \( H_B \) values at the singlet ground-state geometry. Because the linear fit is so good and the slope is close to 2 (which corresponds to \( \log(\beta) \)), it follows from this data that the golden rule (and time-dependent perturbation theory) applies to the relative rate of EET, and the reorganization energy is nearly constant across the different bridge molecules. As a confirmation of this claim, in Figure 3, we plot both the logarithm of the experimental rate constants and \( H_B \) versus the number of C–C bonds between the donor and acceptor. The curves are striking; we predict that the rate of transfer falls off exponentially (as in Dexter transfer) with and acceptor.

Predicting Accurate Electronic Excitation Transfer

**Figure 2.** In blue, we plot \( \log(\beta) \) versus the experimental rate constant \( \log(k_{\text{ET}}) \) for triplet–triplet energy transfer when D and A both occupy equatorial positions on cyclohexane. A line fit is also drawn in dotted black with a slope close to 2, showing that the reorganization energy must be nearly constant for this group of molecules. All diabatic couplings are computed at the singlet ground-state geometry with BoysOV localization and basis 6-31G**.

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For the equatorial—equatorial data (Figure 2), note that the experimental and theoretical numbers are well fitted using linear interpolation with a slope of 1.8. Here, we plot \( H_B \) values at the singlet ground-state geometry. Because the linear fit is so good and the slope is close to 2 (which corresponds to \( \log(\beta) \)), it follows from this data that the golden rule (and time-dependent perturbation theory) applies to the relative rate of EET, and the reorganization energy is nearly constant across the different bridge molecules. As a confirmation of this claim, in Figure 3, we plot both the logarithm of the experimental rate constants and \( H_B \) versus the number of C–C bonds between the donor and acceptor. The curves are striking; we predict that the rate of transfer falls off exponentially (as in Dexter transfer) with and acceptor.

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why our absolute rates are not as accurate as possible for the D-2,6ae and D-2,6ea molecules.

4. Discussion

4.1. Small Mixing Angles and the Condon Principle. The central conclusion of this article is that, together with Marcus theory, the BoysOV and ER localized diabatization algorithms predict EET rates with encouraging success. Admittedly, the near-linear curve in Figure 2 is possible only because the bridge molecules are so rigid that the reorganization energy is effectively constant for the series of molecules considered here. Even with this advantage, however, we were nevertheless surprised that such an excellent correlation between the EET rate and $H_{IF2}$ could be achieved using mixing angles as small as those listed in Table 1. In fact, we had expected that, in order to find reasonable diabatic couplings, we would need to find the region of the avoided crossing where mixing angles are necessarily large.

As Figure 2 shows, however, meaningful relative diabatic couplings can be found for the molecules in this paper using only the singlet ground-state geometry, for which the excitation energy of the first excited state T1 is almost entirely confined to the acceptor and the excitation energy of the second excited state T2 is almost entirely confined to the donor. Thus, whereas mixing angles under $1 \times 10^{-3}$ might usually be ignored computationally, our research suggests that even these small diabatic couplings can be quite meaningful for EET rates.

In the future, it will be crucial to investigate why and where the Condon approximation fails for a broad series of donors, bridges, and acceptors, so that we may gain experience for choosing the optimal geometry for $H_{IF}$. In particular, when, if ever, must we optimize the transition-state geometry and search for the avoided crossing? We will surely save a great deal of computational effort if we can safely use the ground-state geometry exclusively for $H_{IF}$ calculations of EET.

4.2. Failure of the Condon Principle for a Flexible Bridge. One case where we have already demonstrated a failure of the Condon approximation is for a flexible CH2 bridge. In this case, for changes in molecular geometry corresponding to electronic relaxation, we found that the $H_{IF}$ value changed by a factor of more than 10 for compound M in Table 1. This failure of the Condon approximation presents a serious obstacle to using standard Marcus theory in order to predict experimental EET rates. For this reason, we now want to analyze why the Condon approximation fails badly in this case, so that we may better anticipate when standard Marcus theory may be applied.
In Figures 6 and 7, we overlay the optimized A*D and AD* geometries for the molecules with CH2 and C-1,4ee bridges. One explanation from these figures is clear to the eye. On the one hand, when the flexible molecule changes from A to AD*, the diabatic coupling as we interpolate linearly from the initial to final state for both rigid and flexible molecules. Moreover, the form of eq 14 suggests that the diabatic coupling $H_{IF}$ might show a peak in the vicinity of the avoided crossing, where the angle $\theta$ is presumably maximized. Is it possible that the A*D optimized geometry of the flexible molecule lies close to the avoided crossing and that this explains the apparent failure of the Condon approximation?

In order to refute this explanation, in Figures 8 and 9, we plot the diabatic coupling as we interpolate linearly from the initial to final state for both rigid and flexible molecules. Mathematically, if $R_I$ represents the optimized geometry of AD* and $R_F$ represents the optimized geometry of A*D, we consider the value of $H_{IF}$ along the path

$$R(\zeta) = R_I + \zeta^* (R_F - R_I) \quad (15)$$

On the left-hand side of Figures 8 and 9, along this interpolated path in nuclear configuration space, we see an avoided crossing, whereby the first adiabatic excited state switches from D*A to AD* and there is a peak in the mixing parameters $\lambda$ and $\Delta G^\circ$.
angle $\theta$. In Figures 10 and 11, we show attachment/detachment plots$^{37}$ for the first two excited triplet states when the flexible molecule sits nearly at the avoided crossing, both before and after we apply our localized diabatization algorithm. At this avoided crossing geometry, the two adiabatic states have delocalized attachment/detachment density, and the mixing angle is $\pi/4$. After localized diabatization, the attachment/detachment densities are localized on either the donor or the acceptor molecule.

On the right-hand side of Figures 8 and 9, we plot the corresponding values of the diabatic couplings $H_{IF}$ along the same interpolation path. We conclude that the failure of the Condon approximation for the flexible bridge has very little to do with the avoided crossing. On the contrary, the diabatic coupling is nearly constant in both cases near the avoided crossing, which mirrors previous results in electron transfer.$^{38}$ From the graphs, we find that the diabatic coupling grows for the flexible bridge as the energy

Figure 8. Donor−CH$_2$−acceptor: On the left-hand side, the energies of the adiabatic first and second excited states are plotted, along with the mixing angle $\theta$ along the coordinate $\zeta$ in eq 15. $\zeta = 0$ corresponds to AD*, and $\zeta = 1$ corresponds to A*D. On the right-hand side, the corresponding value of $H_{IF}$ is plotted. The dip in $H_{IF}$ at $\zeta = 0.04$ is distinctly to the left of the avoided crossing at $\zeta = 0.16$. The value of $H_{IF}$ grows rapidly far away from the avoided crossing.

Figure 9. Donor−C-1,4ee−acceptor: On the left-hand side, the energies of the adiabatic first and second excited states are plotted, along with the mixing angle $\theta$ along the coordinate $\zeta$ in eq 15. $\zeta = 0$ corresponds to AD*, and $\zeta = 1$ corresponds to A*D. On the right-hand side, the corresponding value of $H_{IF}$ is plotted.

Figure 10. Attachment/detachment plots for the adiabatic excited triplet states near the avoided crossing; see section 4.2. The molecule here is donor−CH$_2$−acceptor.
of the adiabatic $T_1$ and $T_2$ states grows, and the molecule is exploring a twisting motion.

Overall, these examples suggest that for donor–bridge–acceptor systems with rigid bridges, as opposed to flexible bridges, the Condon approximation for EET is a realistic approximation. For a flexible bridge, a more elaborate theoretical framework is necessary.

5. Conclusions

The results of section 3 show that implementation of either BoysOV or ER localized diabatization gives diabatic coupling elements ($H_{di}$) and EET rates that match up well with experiment. For the equatorial–equatorial case in Figure 3, we find $\beta_{\text{eq}} = 2.8$ per C–C bond, compared with the experimental value $\beta_{\text{exp}} = 2.6$. Because many of the coupling elements in this paper were evaluated at the ground-state geometry of the molecule rather than near the avoided crossing between the two excited states, we may also conclude that, for some cases with rigid bridge molecules, the relative $H_{di}$ values can be obtained without worrying too much about the exact geometry of the molecule.

Future research will benefit greatly from exploring the geometric dependence of $H_{di}(R)$ in more detail for a broad series of EET or ET reactions. Because the BoysOV and ER algorithms are computationally inexpensive and can be implemented in a black box format, we believe that they will be very useful tools for future computational studies of nonequilibrium transfer reactions.

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Appendix

Most of the computational details necessary for implementing ER localization for CIS states have been published previously. For completeness, we now add a few more details regarding how occupied–virtual separated Boys and ER localization routines were implemented for the calculations presented above. We use the notation from section 2.2. For this appendix, many-electron states are indexed with capital letters {$I,J,K,L,M$} and molecular spin orbitals are indexed by lower-case letters; {$i,j$} identify occupied orbitals, {$a,b$} identify virtual orbitals, and {$p,q,r,s$} identify either occupied or virtual orbitals.

1. Occupied-Virtual Separated Boys Localized Diabatization.

For standard Boys localization, we maximize the sum

$$f_{\text{Boys}}(U) = f_{\text{Boys}}(\{\Xi_i\}) = \sum_{I,J=1}^{N_{\text{states}}}(\langle \Xi_I | \Sigma | \Xi_J \rangle - \langle \Xi_I | \Sigma | \Xi_J \rangle)^2$$

(16)

The usual approach for optimizing the function above is to use the method of Jacobi sweeps. For this approach, the only necessary input is the expectation value of the dipole operators in the basis of adiabatic states, e.g., in the $x$ direction, $\langle \Phi \rangle | x \rangle | \Phi \rangle$. From these dipole matrices, one may compute the expectation value in any diabatic basis

$$\langle \Xi_I | x \rangle | \Xi_J \rangle = \sum_{KL} U_{KL} \langle \Phi_K | x \rangle | \Phi_L \rangle U_{IJ}$$

(17)

More concretely, let us assume that we have performed a restricted, closed-shell HF calculation. Singlet CIS states are of the form

$$| \Phi_j^{\text{sing}} \rangle = \sum_{ia} t_i^a (c_i^\dagger c_i) | \Phi_{\text{HF}} \rangle$$

(18)

and triplet CIS states are of the form

$$| \Phi_j^{\text{trip}} \rangle = \sum_{ia} t_i^a (c_i^\dagger c_j - c_j^\dagger c_i) | \Phi_{\text{HF}} \rangle$$

(19)

For either case, the corresponding dipole matrices of the adiabatic states are

$$\langle \Phi_j | x | \Phi_I \rangle = 2 \left( \delta_{IJ} \sum_i X_{ii} \right) - \sum_{ai} t_i^a t_i^a X_{ij} + \sum_{iba} t_i^a t_i^b X_{ab}$$

(20)

For occupied–virtual separated Boys localization, we split apart the dipole matrices into occupied and virtual components, i.e., $X = X^{\text{occ}} + X^{\text{virt}}$. This decomposition can be justified by expressing $X$ in second-quantized form as $X = \sum_{i} X_{ii} c_i^\dagger c_i$, and then using the fact that the one-electron density matrix for CIS states is block diagonal; see eq 27. The result is

$$\langle \Phi_j | x^{\text{occ}} | \Phi_I \rangle = 2 \left( \delta_{IJ} \sum_i X_{ii} \right) - \sum_{ai} t_i^a t_i^a X_{ij}$$

(21)

$$\langle \Phi_j | x^{\text{virt}} | \Phi_I \rangle = 2 \sum_{iba} t_i^a t_i^b X_{ab}$$

(22)

and we maximize the localization of each component
\[ f_{\text{BoysOV}}(U) = f_{\text{BoysOV}}(\{\Xi_i\}) = \sum_{IJ=1}^{N_{\text{states}}} (\Xi_i|\hat{\rho}(\Xi_i)|\Xi_J) - (\Xi_J|\hat{\rho}(\Xi_i)|\Xi_i) \]
\[ + l(\Xi_i|\hat{\rho}(\Xi_J)|\Xi_i) - (\Xi_J|\hat{\rho}(\Xi_J)|\Xi_i) \]  
(23)

Effectively, maximizing eq 23 moves apart the centers of “particle” or virtual excitations and also the centers of the “hole” or occupied de-excitation of the CIS states. We note that this algorithm was suggested to us recently by Klaus Ruedenberg. In general, we much prefer the ER method to this BoysOV approach because (i) the physical meaning of the BoysOV diabatic states is not clear, (ii) ER works both for ET and EET while BoysOV works for only for EET and Boys works only for ET, and (iii) BoysOV diabatic states are defined only for CIS excited states and are not easily extended to other prototypical excited states.

2. Computational Implementation of ER Localized Diabatization. A complete algorithm for applying ER localized diabatization to CIS adiabatic states has already been published.3 As described previously, in order to implement ER for large systems, the bottleneck is computing the self-interaction four-tensor in the basis of adiabatic states

\[ R_{JKLM} = \sum_{rs} \int \int \langle \Phi_J|\hat{\rho}(\Xi_i)|\Phi_K \rangle \langle \Xi_i|\hat{\rho}(\Xi_j)|\Xi_M \rangle \]
\[ = \sum_{rs} D^{JK}_{rs} (rs|pq) D^{LM}_{pq} \]  
(24)

where \((rs|pq)\) is the two-electron Coulomb matrix element in chemists’ notation and the density matrix \(D\) is

\[ D^{JK}_{rs} = \langle \Phi_J|c_r c_s |\Phi_K \rangle \]
\[ = \left\{ \begin{array}{ll}
  \sum_{t_1 t_2} \delta_{t_1 t_2}^{r_1 r_2 K_1} & r, s = \text{virtual} \\
  - \sum_{t_1 t_2} \delta_{t_1 t_2}^{r_1 s_2 K_1} \delta_{r_1 s_2} & r, s = \text{occupied}
\end{array} \right. \]  
(27)

Here \(c^\dagger\) and \(c\) are creation and annihilation operators for orbitals \(r\) and \(s\). We compute the Coulomb integral in eq 25 using the resolution of the identity (RI) approximation,39 with error measured in the Coulomb metric for variational stability40

\[ (rs) = \sum_{XY} (rs|XY)(XY)^{-1}(XI) = \sum_X C_{rs}^X (X) \]  
(28)

and

\[ (rs|pq) = \sum_{XY} C_{rs}^X (XY) C_{pq}^Y \]  
(29)

Here \(X\) and \(Y\) are auxiliary basis fitting functions, in this implementation chosen to be the high-quality fitting sets provided by Ahlrichs and co-workers.41 The fitting basis functions are of the same form as the atomic orbital basis set. (Note the change in capitalized notation here only.)

In general, a minor simplification to eq 29 can be made by computing

\[ B_{rs}^X = \sum_Y C_{rs}^X Y (X) \]  
(30)

so that

\[ (rs|pq) = \sum_X B_{rs}^X B_{pq}^X \]  
(31)

In our implementation, we perform the contraction over the density matrix before the fitting step

\[ R_{JK}^{X} = \sum_{pq} D_{pq}^{JK} (pq|X) \]
\[ \tilde{B}_{JK}^{X} = \sum_X R_{JK}^{X} Y (X)^{-1/2} \]  
(32)

(33)

to set up the final contraction step

\[ R_{JKLM} = \sum_X \tilde{B}_{JKLM}^{X} \]  
(34)

As there will be few many-electron states \(\{J, K, L, \ldots\}\), the most time-consuming steps are the computation of the molecular orbital basis set integrals \((pq|JK)\) (scaling to the fourth power of basis set size). Potentially, converting the density matrix \(D_{pq}^{JK}\) into the atomic orbital basis representation could provide additional performance improvement.

References and Notes


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