

## Enhanced Intersystem Crossing in Three-Spin Systems: A Perturbation Theory Treatment

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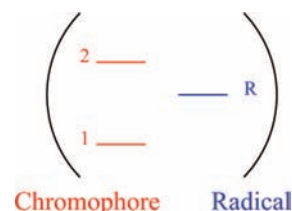
**Abstract:** We present a simple model for analyzing the spin dynamics of a three-spin system representing a photoexcited chromophore coupled to a stable radical species. Perturbation theory yields a Fermi's Golden Rule-type rate expression that describes the formation of a local triplet on the chromophore through spin exchange with the radical. The error introduced by perturbation theory is evaluated for a number of parameters. Finally, we explore the effect of different energetic and coupling parameters on the rate of triplet formation and suggest how this model can be used to tune the enhanced intersystem crossing in three-spin systems.

### Introduction

An exciting new direction in electron transfer research has focused on understanding and controlling the transfer not only of charge but also of spin.<sup>1</sup> In addition to interest for device purposes,<sup>2–4</sup> there are fundamental questions regarding the control and detection of spin systems.

We focus our attention on three-spin organic systems in which a chromophore is coupled to a doublet radical. Photoexcitation of the chromophore leads to a localized singlet excited state, which can convert to a triplet state. The different spin species can be observed via optical and magnetic resonance spectroscopy.<sup>5,6</sup> In the absence of coupling to the radical, this process can only occur via spin-flips, and the intersystem crossing is expected to be slow for organics with weak spin–orbit coupling. The presence of the radical, however, acts as a spin catalyst,<sup>7</sup> causing enhanced intersystem crossing (EISC).

In the following section, we present a model system for describing these spin-dynamical processes. Although the model ignores solvent effects, the general trends that follow from it should be relevant for intramolecular three-spin systems in which the chromophore and radical are bonded together in a rigid fashion, enabling the various spin exchange processes leading to EISC to occur rapidly.<sup>8–13</sup> We note that extensive theoretical work has been carried out on triplet-radical quenching in solution,<sup>14,15</sup> but that is a slightly different system than the one considered here. By constructing a simple model Hamiltonian of the Hubbard type, we are



**Figure 1.** Diagram of the states used in this work. The chromophore consists of sites 1 and 2 representing the HOMO and LUMO, respectively, while the radical is described by a single level R, the SOMO. Although we have drawn the radical level halfway between the HOMO and LUMO, our model does not depend on this arrangement.

able to extract the factors that produce the EISC and predict trends as a function of chemical functionality.

### Theory

We begin with a description of the three-spin system in terms of the picture shown in Figure 1. For this system, we can write the following model Hamiltonian to describe the energetics and dynamics:

$$\hat{H} = \sum_{\sigma=\uparrow,\downarrow} \sum_{j=1,2,R} \varepsilon_j \hat{n}_{j\sigma} + \sum_{j=1,2,R} U_j \hat{n}_j \hat{n}_j + \sum_{\sigma=\uparrow,\downarrow} K \hat{n}_{1\sigma} \hat{n}_{2\sigma} + \sum_{\sigma=\uparrow,\downarrow} [V_1 (\hat{c}_{1\sigma}^\dagger \hat{c}_{R\sigma} + \text{h.c.}) + V_2 (\hat{c}_{2\sigma}^\dagger \hat{c}_{R\sigma} + \text{h.c.})] \quad (1)$$

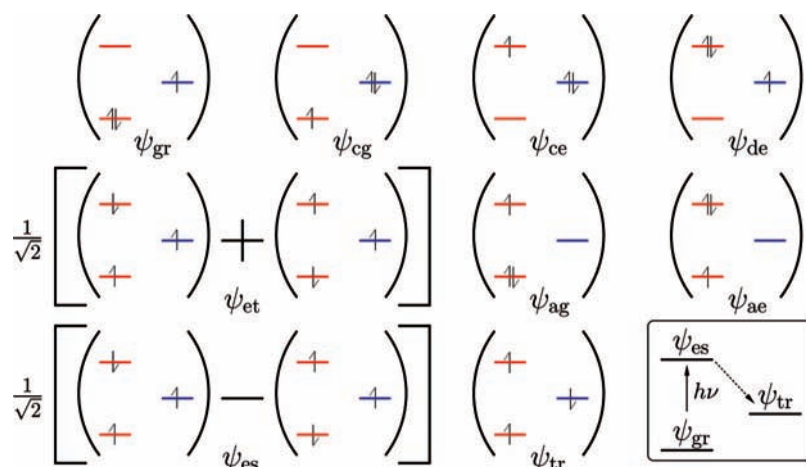
where the first term describes the unoccupied orbital energies ( $\varepsilon_{1,2,R}$ ), the second term the on-site repulsion ( $U_{1,2,R}$ ), the third term exchange stabilization ( $K$ ) between electrons of same spin on the chromophore, and the last term electron tunneling between the chromophore HOMO ( $V_1$ ) and LUMO ( $V_2$ ) and the radical. In eq 1,  $\hat{c}_i^\dagger$  and  $\hat{c}_i$  are creation and annihilation operators, respectively, acting on  $i$ , and  $\hat{n}_i = \hat{c}_i^\dagger \hat{c}_i$  is the number operator. Formally, eq 1 resembles the Hubbard model, but here exchange between levels 1 and 2 is included. We assume that the spin–orbit coupling is small, so triplet

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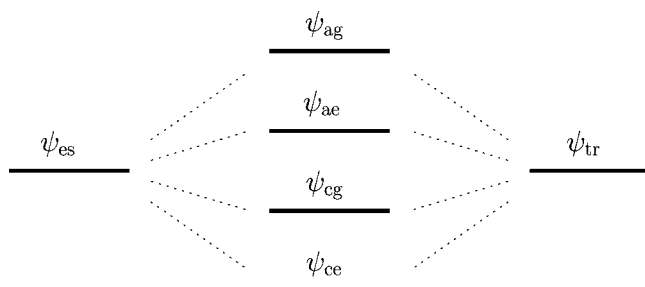
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**Figure 2.** Basis for the matrix Hamiltonian (eq 3). The states are labeled as follows: ground state ( $\psi_{\text{gr}}$ ), photoexcited triplet state ( $\psi_{\text{ct}}$ ), photoexcited singlet state ( $\psi_{\text{es}}$ ), cation chromophore ground state ( $\psi_{\text{cg}}$ ), cation chromophore excited state ( $\psi_{\text{ce}}$ ), anion chromophore ground state ( $\psi_{\text{ag}}$ ), anion chromophore excited state ( $\psi_{\text{ae}}$ ), chromophore doubly excited state ( $\psi_{\text{dc}}$ ), and chromophore triplet state ( $\psi_{\text{tr}}$ ). These are all of the three-electron states with  $M_S = +1/2$ . At the bottom right, the photoexcitation and intersystem crossing processes are diagrammed. States  $\psi_{\text{es}}$  and  $\psi_{\text{tr}}$  have  $m_s$  components of 0 and 1 respectively.



**Figure 3.** Second-order transitions that are included in the perturbation theory treatment (eq 16).

formation is due entirely to chromophore/radical coupling.

An obvious basis for this Hamiltonian is thus given by the nine states shown in Figure 2.<sup>16</sup> It should be noted that the total spin quantum number ( $M_S = +1/2$ ) remains constant throughout (no intersystem crossing is allowed), so the state labels ( $\psi_{\text{tr}}$ ,  $\psi_{\text{es}}$ , and  $\psi_{\text{gr}}$ ) in Figure 2 are fully adequate to describe all of the configurations in this spin manifold. In this basis, we can then write the Hamiltonian in matrix form:

$$\hat{\mathbf{H}} = \begin{pmatrix} \varepsilon_{\text{gr}} & V_1 & 0 & 0 & 0 & V_2 & 0 & 0 & 0 \\ V_1 & \varepsilon_{\text{cg}} & 0 & 0 & \frac{V_2}{\sqrt{2}} & 0 & 0 & \frac{-V_2}{\sqrt{2}} & V_2 \\ 0 & 0 & \varepsilon_{\text{cc}} & V_2 & \frac{V_1}{\sqrt{2}} & 0 & 0 & \frac{V_1}{\sqrt{2}} & V_1 \\ 0 & 0 & V_2 & \varepsilon_{\text{dc}} & 0 & 0 & V_1 & 0 & 0 \\ 0 & \frac{V_2}{\sqrt{2}} & \frac{V_1}{\sqrt{2}} & 0 & \varepsilon_{\text{et}} & \frac{V_1}{\sqrt{2}} & \frac{V_2}{\sqrt{2}} & 0 & 0 \\ V_2 & 0 & 0 & 0 & \frac{V_1}{\sqrt{2}} & \varepsilon_{\text{ag}} & 0 & \frac{V_1}{\sqrt{2}} & V_1 \\ 0 & 0 & 0 & V_1 & \frac{V_2}{\sqrt{2}} & 0 & \varepsilon_{\text{ae}} & \frac{-V_2}{\sqrt{2}} & V_2 \\ 0 & \frac{-V_2}{\sqrt{2}} & \frac{V_1}{\sqrt{2}} & 0 & 0 & \frac{V_1}{\sqrt{2}} & \frac{-V_2}{\sqrt{2}} & \varepsilon_{\text{es}} & 0 \\ 0 & V_2 & V_1 & 0 & 0 & V_1 & V_2 & 0 & \varepsilon_{\text{tr}} \end{pmatrix} \quad (2)$$

where

$$\varepsilon_{\text{gr}} = 2\varepsilon_1 + \varepsilon_{\text{R}} + U_1 \quad (3)$$

$$\varepsilon_{\text{cg}} = 2\varepsilon_{\text{R}} + \varepsilon_1 + U_{\text{R}} \quad (4)$$

$$\varepsilon_{\text{cc}} = 2\varepsilon_{\text{R}} + \varepsilon_2 + U_{\text{R}} \quad (5)$$

$$\varepsilon_{\text{dc}} = 2\varepsilon_2 + \varepsilon_{\text{R}} + U_2 \quad (6)$$

$$\varepsilon_{\text{et}} = \varepsilon_1 + \varepsilon_2 + \varepsilon_{\text{R}} \quad (7)$$

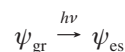
$$\varepsilon_{\text{ag}} = 2\varepsilon_1 + \varepsilon_2 + K + U_1 \quad (8)$$

$$\varepsilon_{\text{ae}} = 2\varepsilon_2 + \varepsilon_1 + K + U_2 \quad (9)$$

$$\varepsilon_{\text{es}} = \varepsilon_1 + \varepsilon_2 + \varepsilon_{\text{R}} \quad (10)$$

$$\varepsilon_{\text{tr}} = \varepsilon_1 + \varepsilon_2 + \varepsilon_{\text{R}} + K \quad (11)$$

Since the three-spin system is generated via photoexcitation of  $\psi_{\text{gr}}$ ,



the formal solution to the dynamics of this system is given by

$$\Psi(t) = e^{-i\hat{\mathbf{H}}t/\hbar} \psi_{\text{es}} \quad (12)$$

We seek an approximate analytical form for the rate of formation of the triplet state  $\psi_{\text{tr}}$  following photoexcitation. We rewrite the Hamiltonian as  $\hat{\mathbf{H}} = \hat{\mathbf{H}}_0 + \hat{\mathbf{V}}$ , where  $\hat{\mathbf{H}}_0$  consists of the diagonal terms in eq 2 and  $\hat{\mathbf{V}}$  the off-diagonal terms. Time-dependent perturbation theory is then invoked, and the lowest-order term in the perturbative expansion that connects the initial and final states is the second-order term. The next-higher-order terms that contribute are fourth-order terms, and we assume that the chromophore–radical coupling is weak, ensuring that these terms can be dropped and that the assumptions of second-order perturbation theory are valid. We thus have coefficients  $c_f(t)$  describing transitions between the initial (i) and final (f) states via an intermediate state (n) that are of the form<sup>17</sup>

$$\begin{aligned} c_f(t) &= \left(\frac{-i}{\hbar}\right)^2 \int_0^t dt' \int_0^{t'} dt'' V_{\text{in}} V_{\text{nf}} e^{i\omega_{\text{in}} t'} e^{i\omega_{\text{nf}} t''} \\ &= \frac{V_{\text{in}} V_{\text{nf}}}{\hbar^2 \omega_{\text{ni}}} \left[ \left( \frac{1 - e^{i\omega_{\text{nf}} t}}{\omega_{\text{fn}}} \right) - \left( \frac{1 - e^{i\omega_{\text{if}} t}}{\omega_{\text{fi}}} \right) \right] \quad (13) \end{aligned}$$

where  $\omega_{jk} = (E_j - E_k)/\hbar$  and  $V_{in}$  and  $V_{nr}$  are electronic coupling parameters. A Fermi's Golden Rule (FGR)-type expression can then be derived, and the rate of the  $i \rightarrow f$  transition ( $W_{i \rightarrow f}$ ) can be written as

$$W_{i \rightarrow f} = \frac{2\pi}{\hbar} \rho(E_i) |V_{in}|^2 |V_{nr}|^2 \frac{2}{(E_n - E_i)^2} \quad (14)$$

where  $\rho(E_i)$  is the density of final states evaluated at energy  $E_i$  (see the Supporting Information for details).

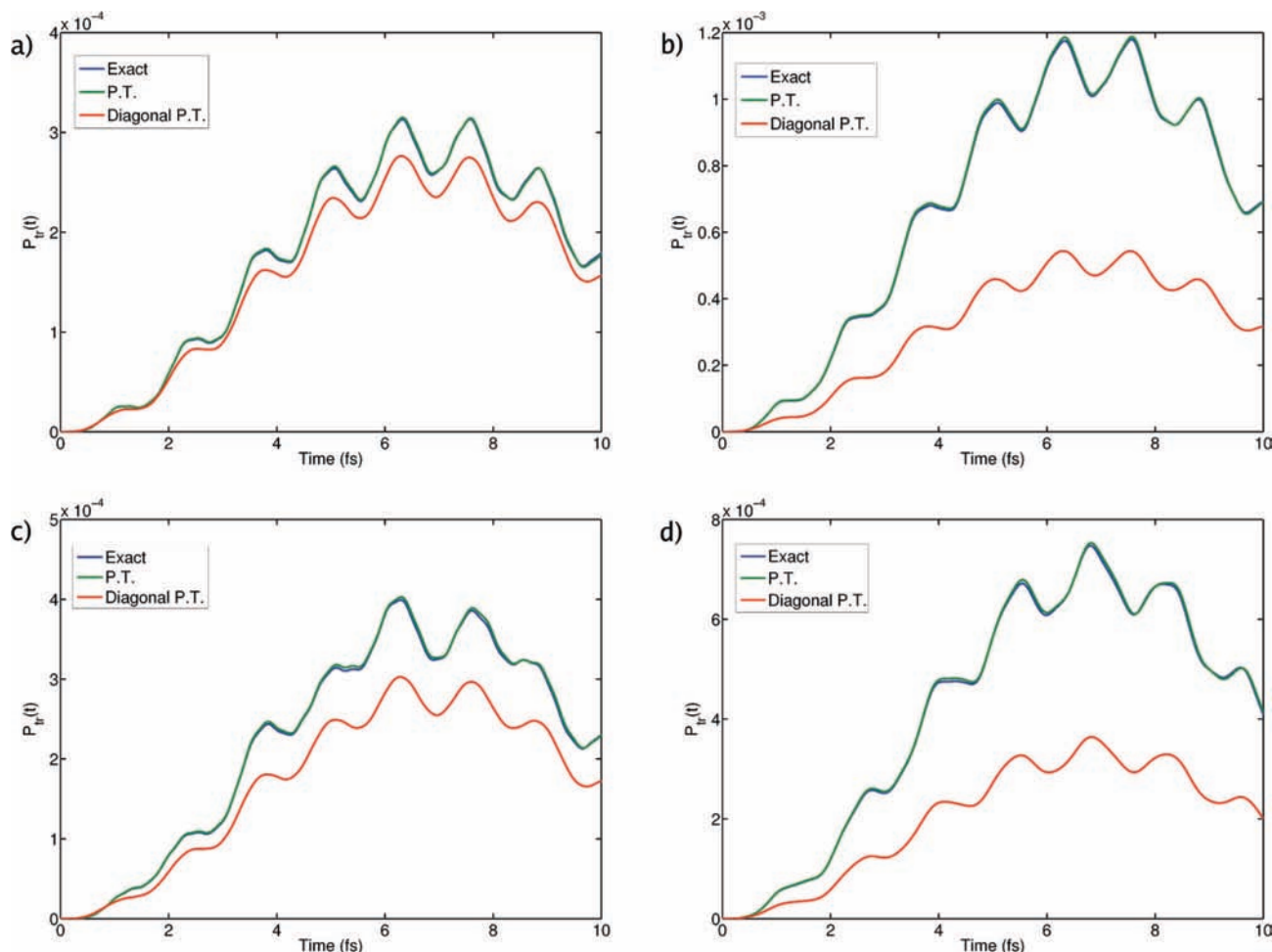
To extend this result to our slightly more complicated system, we reduce the full complexity of  $\hat{H}$  to the second-order processes that connect  $\psi_{es}$  and  $\psi_{tr}$ , as shown in Figure 3.<sup>18</sup> The time-dependent coefficient for the triplet state is given by

$$C_{tr}(t) = \left(\frac{-i}{\hbar}\right)^2 \left[ \int_0^t dt' \int_0^{t'} dt'' V_{es,ag} V_{ag,tr} e^{i\omega_{tr,ag}t'} e^{i\omega_{es,ag}t''} + \int_0^t dt' \int_0^{t'} dt'' V_{es,ae} V_{ae,tr} e^{i\omega_{tr,ae}t'} e^{i\omega_{es,ae}t''} + \int_0^t dt' \int_0^{t'} dt'' V_{es,cg} V_{cg,tr} e^{i\omega_{tr,cg}t'} e^{i\omega_{es,cg}t''} + \int_0^t dt' \int_0^{t'} dt'' V_{es,ce} V_{ce,tr} e^{i\omega_{tr,ce}t'} e^{i\omega_{es,ce}t''} \right] \quad (15)$$

which leads to

$$c_{tr}(t) = \frac{V_{es,ag} V_{tr,ag}}{\hbar^2 \omega_{es,ag}} \left( \frac{1 - e^{i\omega_{tr,ag}t}}{\omega_{tr,ag}} - \frac{1 - e^{i\omega_{tr,es}t}}{\omega_{tr,es}} \right) + \frac{V_{es,ae} V_{tr,ae}}{\hbar^2 \omega_{es,ae}} \left( \frac{1 - e^{i\omega_{tr,ae}t}}{\omega_{tr,ae}} - \frac{1 - e^{i\omega_{tr,es}t}}{\omega_{tr,es}} \right) + \frac{V_{es,cg} V_{tr,cg}}{\hbar^2 \omega_{es,cg}} \left( \frac{1 - e^{i\omega_{tr,cg}t}}{\omega_{tr,cg}} - \frac{1 - e^{i\omega_{tr,es}t}}{\omega_{tr,es}} \right) + \frac{V_{es,ce} V_{tr,ce}}{\hbar^2 \omega_{es,ce}} \left( \frac{1 - e^{i\omega_{tr,ce}t}}{\omega_{tr,ce}} - \frac{1 - e^{i\omega_{tr,es}t}}{\omega_{tr,es}} \right) \quad (16)$$

where  $V_{i,j}$  is the relevant off-diagonal term in eq 2. Equation 16 yields the exact time dependence of the triplet state within second-order perturbation theory, but it does not yield a tractable FGR expression for the rate of triplet formation. In order to simplify the FGR derivation, we drop the cross-terms in the expansion of  $|c_{tr}|^2$  (see the Supporting Information); physically, this is motivated by the assumption that triplet formation is dominated by "direct" two-step transitions from  $\psi_{es}$  to  $\psi_{tr}$  and that different pathways do not interfere to a great extent. Mathematically, we expect that this approximation is worst when  $V_1 = V_2$  and improves as these values become more different. Once we drop these cross-



**Figure 4.** Results using full perturbation theory (P.T., eq 16) and approximate perturbation theory (Diagonal P.T., leading to eqs 17 and 18) are compared with the exact quantum dynamics results for a number of different parameters by plotting the triplet population as a function of time. The initial state is  $\psi_{es}$ . In all of the examples,  $U_{1,2,R} = 5$  eV and  $K = -0.3$  eV. In (a),  $\epsilon_2 = 10$  eV,  $\epsilon_R = 8$  eV,  $V_1 = 0.1$  eV, and  $V_2 = 0.05$  eV. In (b),  $\epsilon_2 = 10$  eV,  $\epsilon_R = 8$  eV,  $V_1 = 0.1$  eV, and  $V_2 = 0.1$  eV. In (c),  $\epsilon_2 = 5$  eV,  $\epsilon_R = 8$  eV,  $V_1 = 0.1$  eV, and  $V_2 = 0.05$  eV. In (d),  $\epsilon_2 = 10$  eV,  $\epsilon_R = 2$  eV,  $V_1 = 0.1$  eV, and  $V_2 = 0.05$  eV. In all of the cases shown, the full perturbation theory result agrees almost perfectly with the exact solution. Additional comparisons are shown in Figure 1 in the Supporting Information.

terms, a sum of rates, each of the form of eq 14, can be written in FGR form as

$$W_{\text{es} \rightarrow \text{tr}} = \frac{2\pi}{\hbar} \rho(E_{\text{cs}}) |V_{\text{es, tr}}|^2 \quad (17)$$

where

$$\begin{aligned} |V_{\text{es, tr}}|^2 = & \frac{2|V_{\text{es, ag}}|^2 |V_{\text{tr, ag}}|^2}{(\epsilon_{\text{ag}} - \epsilon_{\text{es}})^2} + \frac{2|V_{\text{es, ae}}|^2 |V_{\text{tr, ae}}|^2}{(\epsilon_{\text{ae}} - \epsilon_{\text{es}})^2} + \\ & \frac{2|V_{\text{es, cg}}|^2 |V_{\text{tr, cg}}|^2}{(\epsilon_{\text{cg}} - \epsilon_{\text{es}})^2} + \frac{2|V_{\text{es, ce}}|^2 |V_{\text{tr, ce}}|^2}{(\epsilon_{\text{ce}} - \epsilon_{\text{es}})^2} \\ = & |V_1|^4 [(\epsilon_1 + K + U_1 - \epsilon_{\text{R}})^{-2} + (\epsilon_{\text{R}} + U_{\text{R}} - \epsilon_1)^{-2}] + \\ & |V_2|^4 [(\epsilon_2 + K + U_2 - \epsilon_{\text{R}})^{-2} + (\epsilon_{\text{R}} + U_{\text{R}} - \epsilon_2)^{-2}] \end{aligned} \quad (18)$$

Further simplification can be achieved by using the (qualitatively reasonable) approximation that the on-site repulsion terms are the same ( $U_{1,2,\text{R}} = U$ ) and setting  $\epsilon_1$  as the zero of energy, yielding

$$\begin{aligned} |V_{\text{es, tr}}|^2 = & |V_1|^4 [(K + U - \epsilon_{\text{R}})^{-2} + (\epsilon_{\text{R}} + U)^{-2}] + \\ & |V_2|^4 [(\epsilon_2 + K + U - \epsilon_{\text{R}})^{-2} + (\epsilon_{\text{R}} + U - \epsilon_2)^{-2}] \end{aligned} \quad (19)$$

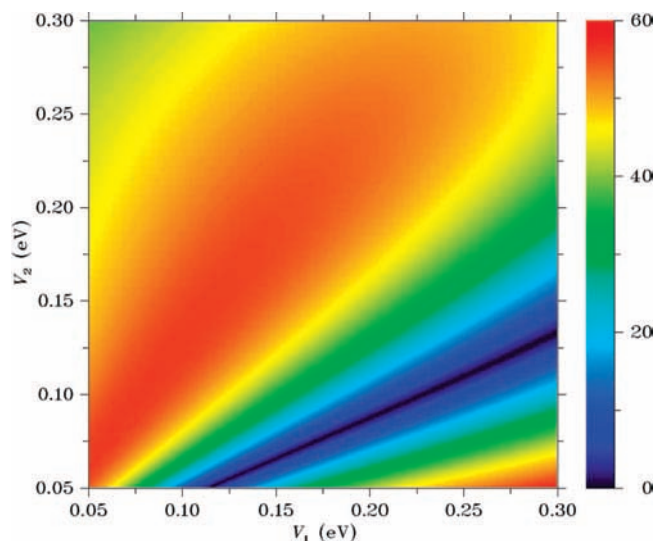
Equations 17, 18, and 19 are the main results of this work; they provide a simple expression for the rate of triplet formation upon photoexcitation in terms of the energetic parameters of the system. In the next section, we will compare these perturbation theory results with the exact quantum dynamics and discuss how these model parameters influence the EISC rates.

## Results and Discussion

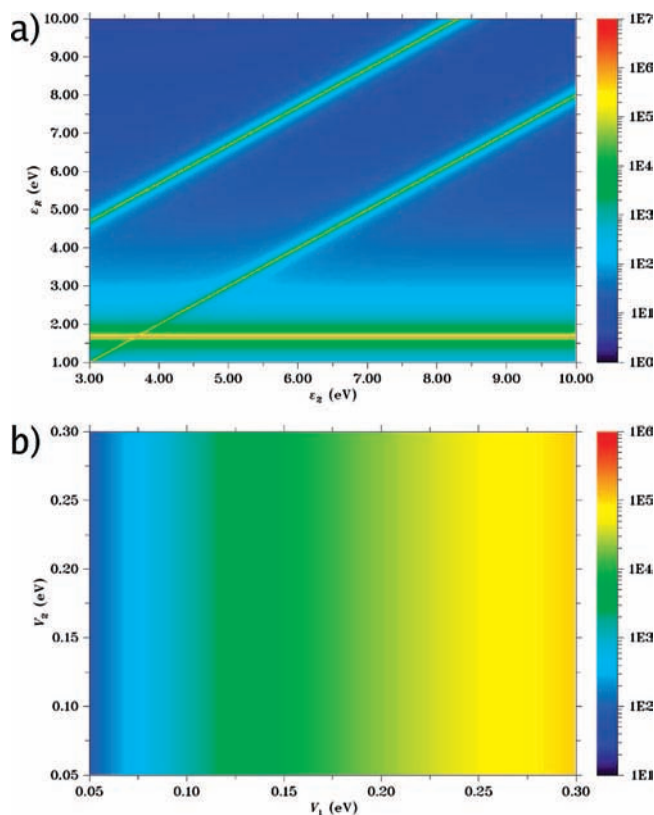
To obtain our rate expression in eqs 17 and 19, we made a number of approximations, and it is appropriate to examine their validity. For our rate expression to hold, the standard assumptions of Fermi's Golden Rule must hold: there must be a large overall density of states for the triplet, enabling a rate constant to be defined, and  $V_1$  and  $V_2$  should not vary much in the manifold of different triplet states.

We can compare the approximate results with the exact quantum dynamics given by eq 12 for a number of parameters. As shown in Figure 4, for the values of  $V_1$  and  $V_2$  we have used (which are small relative to the relevant energy gaps in the system), the full second-order perturbation theory result is in very good agreement with the exact treatment, as expected. Taking only the diagonal terms [i.e., making the approximation that  $(\sum x)^2 \approx \sum x^2$ , which leads to eq 17] yields slightly worse agreement with the exact quantum dynamics. It seems to perform reasonably well, however, in some parameter regimes. For example, when  $V_1$  and  $V_2$  differ by a significant amount, the cross-terms are small, and the diagonal approximation appears to be acceptable. For a more systematic examination of the approximation, we have plotted the percent error (defined as the difference in the triplet-state populations calculated with the approximate perturbation theory and the exact dynamics after a certain time has elapsed) as a function of  $V_1$  and  $V_2$ . This is shown in Figure 5 for  $t = 7$  fs. We see that the diagonal approximation is worst when  $V_1 = V_2$ , with a relative error of  $\sim 60\%$  for the parameters chosen, but when  $V_1 \approx 2.5V_2$ , this error drops to less than 10%. Thus, careful examination of the parameters for each system should be undertaken in order to assess the validity of the approximations leading to eq 17.

We can now make predictions regarding the dependence of the EISC rate on a number of different parameters in our



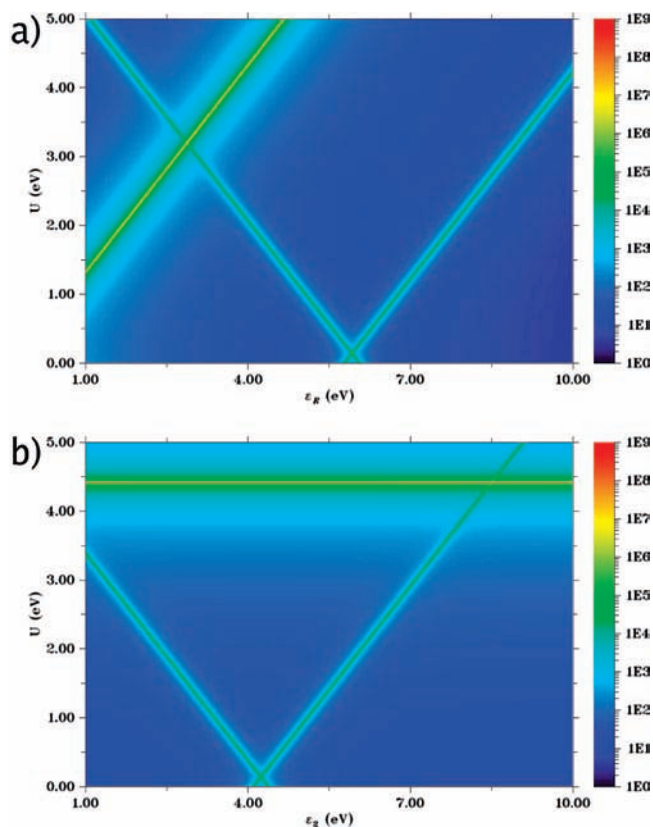
**Figure 5.** Percent error between the calculated triplet populations obtained from the diagonal perturbation theory and exact quantum dynamics results at  $t = 7$  fs, plotted as a function of  $V_1$  and  $V_2$  with the other parameter values chosen as  $\epsilon_2 = 10$  eV,  $\epsilon_{\text{R}} = 8$  eV,  $U = 5$  eV, and  $K = -0.3$  eV. The error is maximized when  $V_1 \approx V_2$  but drops significantly for  $V_1/V_2 \approx 2.5$  (dark-blue line). The error at  $t = 30$  fs is shown in Figure 2 in the Supporting Information.



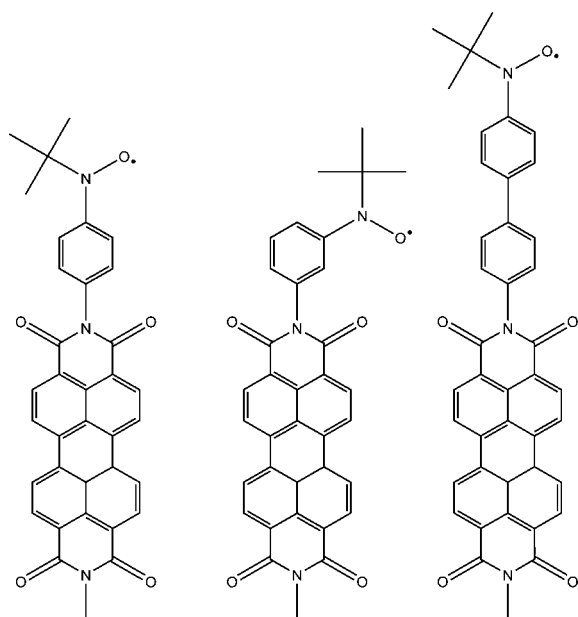
**Figure 6.** Plots of the FGR results (eq 17) assuming  $\rho(E_{\text{cs}}) = 0.04$  eV $^{-1}$ . The color bar has units of ns $^{-1}$ . In (a),  $V_1 = 0.15$  eV and  $V_2 = 0.06$  eV. In (b),  $\epsilon_2 = 6$  eV and  $\epsilon_{\text{R}} = 4$  eV. In both plots,  $K = -0.3$  eV and  $U = 2$  eV. The same trends are also seen in the exact quantum dynamics.

model. We examine the rate dependence on the energetic parameters  $\epsilon_2$  and  $\epsilon_{\text{R}}$  in Figure 6a. We see three sets of resonances that are expected from eq 19: two parallel lines that occur at  $\epsilon_{\text{R}} = \epsilon_2 - U$  and  $\epsilon_{\text{R}} = \epsilon_2 + U + K$  and a horizontal line at  $\epsilon_{\text{R}} = K + U$ . There is also a resonance at





**Figure 7.** FGR rate as a function of the system parameters, as in Figure 6. In (a),  $\varepsilon_2 = 6$  eV. In (b),  $\varepsilon_R = 4$  eV. In both plots,  $K = -0.3$  eV,  $V_1 = 0.15$  eV, and  $V_2 = 0.06$  eV.



**Figure 8.** A series of substituted perylene-3,4,9,10-tetracarboxylic diimide molecules in which excited-state singlet-to-triplet transitions could be studied with the model presented here.

$\varepsilon_R = -U$  that does not fall in the range of Figure 6a. These resonances could be probed experimentally by shifting  $\varepsilon_2$  through the addition of electron-donating groups on the chromophore. The effect of  $V_1$  and  $V_2$  is shown in Figure 6b. For the choice of parameters used, the rate is dominated by the magnitude of  $V_1$ . Finally, in Figure 7 we examine the

rate dependence on the energy levels  $\varepsilon_2$ ,  $\varepsilon_R$ , and  $U$ . We predict an interesting nonlinear dependence on the on-site repulsion energy, although  $U$  might be more difficult to engineer experimentally.

Although we have only discussed the predictions of our rate model in terms of various parameters, these parameters can be connected to experimental systems of interest. The relevant state energies can be calculated using electronic structure theory, and recent work in constrained density functional theory (CDFT) makes possible<sup>19</sup> the explicit construction of these charge- and spin-localized states. Electronic couplings can also be calculated with a number of methods, including CDFT,<sup>20,21</sup> generalized Mulliken–Hush,<sup>22,23</sup> or the corresponding orbital transformation.<sup>24</sup> Future work will compare theoretically determined rate constants to experimentally measured rates of triplet formation in three-spin systems. One series of molecules of particular interest are the perylene-3,4,9,10-tetracarboxylic diimide (PDI) derivatives shown in Figure 8.<sup>25</sup> The PDI chromophore is coupled to the nitroxide radical in a number of different ways, yielding a set of different energetic ( $\varepsilon_2$ ,  $\varepsilon_R$ ) and tunneling ( $V_1$ ,  $V_2$ ) parameters. The analysis given here should be useful in explaining differences in the rates of excited singlet state quenching through a combination of our FGR results and electronic structure calculations.

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**Supporting Information Available:** Appendix showing the derivation of the superexchange FGR expression; plots similar

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to those in Figure 4 but with larger values of  $V_1$  and  $V_2$ , showing the breakdown in the perturbation theory approximation; and a plot similar to Figure 5 showing the

percent error in the diagonal perturbation theory result calculated at  $t = 30$  fs. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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