Supporting Information:
Computational construction of the electronic Hamiltonian for photoinduced electron transfer and Redfield propagation.

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1 FMR

1.1 Non-bound fragments (FMR)

The idea in the FMR[1–3] formalism is to take advantage of the fact that atomic basis functions are often localized at the nuclei. This means, that the Fock matrix expressed in that atomic basis set, $\mathbf{F^{AO}}$, can be partitioned in submatrices involving only donor basis functions, $\mathbf{F}^{\mathbf{(AO)}}_{\mathbf{DD}}$, only acceptor basis functions, $\mathbf{F}^{\mathbf{(AO)}}_{\mathbf{AA}}$ and cross terms involving both, $\mathbf{F}^{\mathbf{(AO)}}_{\mathbf{DA}}$ and $\mathbf{F}^{\mathbf{(AO)}}_{\mathbf{AD}}$.

$$\mathbf{F^{AO}} = \tag{1}$$

$$\begin{bmatrix} \mathbf{F}^{\mathbf{(AO)}}_{\mathbf{DD}} & \mathbf{F}^{\mathbf{(AO)}}_{\mathbf{DA}} \\ \mathbf{F}^{\mathbf{(AO)}}_{\mathbf{AD}} & \mathbf{F}^{\mathbf{(AO)}}_{\mathbf{AA}} \end{bmatrix} \tag{2}$$

The goal is to get localized orbitals, which are constructed by diagonalization of the pure donor and acceptor blocks respectively. However, since the atomic basis set is not necessarily orthonormal, proceeding without a transformation of the basis set would lead to non-orthonormal orbitals. A Löwdin transformation[4] of the atomic basis set is made in order to get an orthogonal basis as close to the original basis set as possible in a least square sense[5,6]. The Löwdin transformed fock matrix is then

$$\mathbf{\bar{F}^{AO}} = \tag{3}$$

$$\begin{bmatrix} \mathbf{\bar{F}}^{\mathbf{(AO)}}_{\mathbf{DD}} & \mathbf{\bar{F}}^{\mathbf{(AO)}}_{\mathbf{DA}} \\ \mathbf{\bar{F}}^{\mathbf{(AO)}}_{\mathbf{AD}} & \mathbf{\bar{F}}^{\mathbf{(AO)}}_{\mathbf{AA}} \end{bmatrix} \tag{4}$$

$$= (\mathbf{S^{AO}})^{-\frac{1}{2}} \mathbf{F^{AO}} (\mathbf{S^{AO}})^{-\frac{1}{2}} \tag{5}$$

where $\mathbf{S^{AO}}$ is the overlap matrix in the atomic orbital basis. The localized orbitals of the donor and acceptor ($\{\phi_i^D\}$, $\{\phi_i^A\}$) are now constructed from the donor and acceptor blocks respectively as the orbitals that diagonalize them:

$$\phi^{\mathbf{D},\dagger} \mathbf{\bar{F}}^{\mathbf{(AO)}}_{\mathbf{DD}} \phi^{\mathbf{D}} = \varepsilon^{\mathbf{D}} \tag{6}$$

$$\phi^{\mathbf{A},\dagger} \mathbf{\bar{F}}^{\mathbf{(AO)}}_{\mathbf{AA}} \phi^{\mathbf{A}} = \varepsilon^{\mathbf{A}} \tag{7}$$

where $\varepsilon^{\mathbf{D/A}}$ is a diagonal matrix with the localized orbital energies on the diagonal. The localized orbitals are automatically orthonormal due to the orthonormalized atomic basis set from the Löwdin transformation. The Fock matrix is then expressed in this localized basis

$$\mathbf{F^{DA}} = \tag{8}$$

$$\begin{bmatrix} \varepsilon^{\mathbf{D}} & \mathbf{F}^{\mathbf{loc}}_{\mathbf{DA}} \\ \mathbf{F}^{\mathbf{loc}}_{\mathbf{AD}} & \varepsilon^{\mathbf{A}} \end{bmatrix} \tag{9}$$

The off-diagonal elements in $\mathbf{F}^{\mathbf{loc}}_{\mathbf{DA}}$ and $\mathbf{F}^{\mathbf{loc}}_{\mathbf{AD}}$ contain the electronic coupling elements between the donor and acceptor orbitals:

$$\mathbf{F}^{\mathbf{loc}}_{\mathbf{AD}} = \phi^{\mathbf{A},\dagger} \mathbf{\bar{F}}^{\mathbf{(AO)}}_{\mathbf{AD}} \phi^{\mathbf{D}} \tag{10}$$

$$\mathbf{F}^{\mathbf{loc}}_{\mathbf{DA}} = \phi^{\mathbf{D},\dagger} \mathbf{\bar{F}}^{\mathbf{(AO)}}_{\mathbf{DA}} \phi^{\mathbf{A}} \tag{11}$$

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† Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/cXCP00000x/

In total, the coupling element between orbital i and j in the localized basis is

$$F^{loc}_{DA,ij} = \phi_{\mathbf{i}}^{\dagger}(\mathbf{S}^{\mathbf{AO}})^{-\frac{1}{2}}\mathbf{F}^{\mathbf{AO}}(\mathbf{S}^{\mathbf{AO}})^{-\frac{1}{2}}\phi_{\mathbf{j}} \tag{12}$$

1.2 Bound fragments (FMR-B)

The formalism in FMR/POD can be extended to systems where a bridge is connecting the donor and acceptor fragment[7,8]. The Fock matrix in atomic basis is again ordered according to the fragments: this time a donor (D), bridge (B) and acceptor (A) part, and the corresponding crossterms, (Eqn. 14)

$$\mathbf{F}^{\mathbf{AO}} = \tag{13}$$

$$\begin{bmatrix} \mathbf{F}^{(\mathbf{AO})}_{\mathbf{DD}} & \mathbf{F}^{(\mathbf{AO})}_{\mathbf{DB}} & \mathbf{F}^{(\mathbf{AO})}_{\mathbf{DA}} \\ \mathbf{F}^{(\mathbf{AO})}_{\mathbf{BD}} & \mathbf{F}^{(\mathbf{AO})}_{\mathbf{BB}} & \mathbf{F}^{(\mathbf{AO})}_{\mathbf{BA}} \\ \mathbf{F}^{(\mathbf{AO})}_{\mathbf{AD}} & \mathbf{F}^{(\mathbf{AO})}_{\mathbf{AB}} & \mathbf{F}^{(\mathbf{AO})}_{\mathbf{AA}} \end{bmatrix} \tag{14}$$

Again, a Löwdin transformation of the atomic basis set is done in order to work with an orthonormal basis set:

$$\bar{\mathbf{F}}^{\mathbf{AO}} = \tag{15}$$

$$\begin{bmatrix} \bar{\mathbf{F}}^{(\mathbf{AO})}_{\mathbf{DD}} & \bar{\mathbf{F}}^{(\mathbf{AO})}_{\mathbf{DB}} & \bar{\mathbf{F}}^{(\mathbf{AO})}_{\mathbf{DA}} \\ \bar{\mathbf{F}}^{(\mathbf{AO})}_{\mathbf{BD}} & \bar{\mathbf{F}}^{(\mathbf{AO})}_{\mathbf{BB}} & \bar{\mathbf{F}}^{(\mathbf{AO})}_{\mathbf{BA}} \\ \bar{\mathbf{F}}^{(\mathbf{AO})}_{\mathbf{AD}} & \bar{\mathbf{F}}^{(\mathbf{AO})}_{\mathbf{AB}} & \bar{\mathbf{F}}^{(\mathbf{AO})}_{\mathbf{AA}} \end{bmatrix} = \tag{16}$$

$$(\mathbf{S}^{\mathbf{AO}})^{-\frac{1}{2}}\mathbf{F}^{\mathbf{AO}}(\mathbf{S}^{\mathbf{AO}})^{-\frac{1}{2}} \tag{17}$$

Since the bridge does not constitute a charge site in its own and cannot be unambiguously assigned to neither donor nor acceptor fragment, the basis functions belonging to the bridge is made available to both fragments. The matrices corresponding to the pure donor and acceptor matrices which were diagonalized to obtain the localized orbitals are highlighted in orange (donor: $\mathbf{F}^{\mathbf{D-B}}$) and green (acceptor: $\mathbf{F}^{\mathbf{B-A}}$) in (Eqn. 23)

$$\bar{\mathbf{F}}^{\mathbf{AO}} = \tag{18}$$

$$\begin{bmatrix} \bar{\mathbf{F}}^{(\mathbf{AO})}_{\mathbf{DD}} & \bar{\mathbf{F}}^{(\mathbf{AO})}_{\mathbf{DB}} & \bar{\mathbf{F}}^{(\mathbf{AO})}_{\mathbf{DA}} \\ \bar{\mathbf{F}}^{(\mathbf{AO})}_{\mathbf{BD}} & \bar{\mathbf{F}}^{(\mathbf{AO})}_{\mathbf{BB}} & \bar{\mathbf{F}}^{(\mathbf{AO})}_{\mathbf{BA}} \\ \bar{\mathbf{F}}^{(\mathbf{AO})}_{\mathbf{AD}} & \bar{\mathbf{F}}^{(\mathbf{AO})}_{\mathbf{AB}} & \bar{\mathbf{F}}^{(\mathbf{AO})}_{\mathbf{AA}} \end{bmatrix} \tag{19}$$

$$\bar{\mathbf{F}}^{\mathbf{D-B}} = \tag{20}$$

$$\begin{bmatrix} \bar{\mathbf{F}}^{(\mathbf{AO})}_{\mathbf{DD}} & \bar{\mathbf{F}}^{(\mathbf{AO})}_{\mathbf{DB}} \\ \bar{\mathbf{F}}^{(\mathbf{AO})}_{\mathbf{BD}} & \bar{\mathbf{F}}^{(\mathbf{AO})}_{\mathbf{BB}} \end{bmatrix} \tag{21}$$

$$\bar{\mathbf{F}}^{\mathbf{B-A}} = \tag{22}$$

$$\begin{bmatrix} \bar{\mathbf{F}}^{(\mathbf{AO})}_{\mathbf{BB}} & \bar{\mathbf{F}}^{(\mathbf{AO})}_{\mathbf{BA}} \\ \bar{\mathbf{F}}^{(\mathbf{AO})}_{\mathbf{AB}} & \bar{\mathbf{F}}^{(\mathbf{AO})}_{\mathbf{AA}} \end{bmatrix} \tag{23}$$

As in the non-bound case, the localized orbitals are now found as the orbitals that diagonalize the donor and acceptor matrices respectively (locally adiabatic states):

$$\phi^{\mathbf{D},\dagger}\bar{\mathbf{F}}^{\mathbf{D-B}}\phi^{\mathbf{D}} = \varepsilon^{\mathbf{D}} \tag{24}$$

$$\phi^{\mathbf{A},\dagger}\bar{\mathbf{F}}^{\mathbf{B-A}}\phi^{\mathbf{A}} = \varepsilon^{\mathbf{A}} \tag{25}$$

The orbitals on the acceptor and donor are expressed in terms of the Löwdin transformed basis set, so that each vector for a specific orbital is N_{AOs} long with $N_{AOs} = N_D + N_B + N_A$, where N_D is the number of atomic orbitals located at the donor, N_B is the number of atomic orbitals located at the bridge and N_A is the number of atomic orbitals located at the acceptor. For donor orbitals all coefficients relating to acceptor atomic orbitals are zero and for acceptor orbitals all coefficients relating to donor atomic orbitals are zero, i.e.

$$\phi_i^D \begin{bmatrix} c_{1i}^D \\ c_{2i}^D \\ \vdots \\ c_{(N_D+N_B)i}^D \\ 0 \\ \vdots \\ 0 \end{bmatrix} \qquad \phi_j^A = \begin{bmatrix} 0 \\ \vdots \\ 0 \\ c_{1j}^A \\ c_{2j}^A \\ \vdots \\ c_{(N_B+N_A)j}^A \end{bmatrix} \tag{26}$$

This procedure leads to $N_{loc} = N_D + 2N_B + N_A$ differenct localized orbitals, which can be collected in an $N_{AOs} \times N_{loc}$ dimensional matrix:

$$\mathbf{C^{full}} = \begin{bmatrix} \phi_1^D & \phi_2^D & \phi_3^D & \cdots & \phi_{N_D+N_B}^D & \phi_1^A & \phi_2^A & \phi_3^A & \cdots & \phi_{N_B+N_A}^A \end{bmatrix} \tag{27}$$

The Fock matrix in the localized basis is then:

$$\mathbf{\bar{F}^{D-B-A}} = \mathbf{C^{full,\dagger}\bar{F}^{AO}C^{full}} \tag{28}$$

In the non-bound case the initial Löwdin transformation of the atomic basis set made sure that the localized orbitals located at different sites were automatically orthogonal since no basis function contributes to both donor orbitals and acceptor orbitals. However, in FMR-B the bridge functions are shared between the fragments and localized orbitals located at different sites are not orthogonal. Hence, an additional Löwdin transformation is done for the states for which the coupling is to be calculated. The Fock matrix and overlap matrix for state i on the donor (ϕ_i^D) and state j on the acceptor (ϕ_j^A) is then:

$$\mathbf{\bar{F}_{i,j}^{D-B-A}} = \begin{bmatrix} \varepsilon_i^D & \bar{F}_{ij}^{D-B-A} \\ \bar{F}_{ji}^{D-B-A} & \varepsilon_j^A \end{bmatrix} \mathbf{S_{i,j}^{D-B-A}} = \begin{bmatrix} 1 & S_{ij}^{D-B-A} \\ S_{ji}^{D-B-A} & 1 \end{bmatrix} \tag{29}$$

where $S_{ij}^{D-B-A} = \phi_i^{D,\dagger}\phi_j^A$. The final Löwdin transformation can now be done on this 2-level system:

$$\mathbf{\widetilde{F}_{i,j}^{D-B-A}} = \tag{30}$$

$$(\mathbf{S_{i,j}^{D-B-A}})^{-\frac{1}{2}}\mathbf{\bar{F}_{i,j}^{D-B-A}}(\mathbf{S_{i,j}^{D-B-A}})^{-\frac{1}{2}} = \tag{31}$$

$$\begin{bmatrix} \tilde{\varepsilon}_i^D & \tilde{F}_{ij}^{D-B-A} \\ \tilde{F}_{ji}^{D-B-A} & \tilde{\varepsilon}_j^A \end{bmatrix} \tag{32}$$

and the localized orbital energies can be read of the diagonal ($\tilde{\varepsilon}_i^D, \tilde{\varepsilon}_j^A$), while the electronic coupling element between these localized orbitals are the off-diagonal elements ($\tilde{F}_{ij}^{D-B-A}$). The procedure for obtaining the localized electronic coupling elements is then as follows:

1. Rotate the ordered Fock matrix in atomic orbital basis into the locally adiabatic basis:

$$\mathbf{\bar{F}^{D-B-A}} = \mathbf{C^{full,\dagger}}(\mathbf{S^{AO}})^{-\frac{1}{2}}\mathbf{F^{AO}}(\mathbf{S^{AO}})^{-\frac{1}{2}}\mathbf{C^{full}} \tag{33}$$

2. Extract the relevant orbitals (e.g. homo from the donor fragment and homo from the acceptor fragment) and construct the two level Fock and overlap matrices in Eqn. 29

3. Orthonormalize the chosen orbitals using a Löwdin transformation to get localized orbital energies and couplings (Eqn. 32)

1.3 Multiple charge centers (FMR-B)

The FMR-B method is readily extended to multiple charge centers. In the case of a triad with a donor (D) connected through a bridge (B1) to the chromophore (An) which in turn is connected to an acceptor (Ac) via a second bridge (B2): D-B1-An-B2-Ac. The Fock matrix in atomic orbital basis can now be partitioned according to these five units as shown in Eqn. 35, and Löwdin transformed as in Eqn. 14 to yield $\mathbf{\bar{F}^{AO}}$.

$$\mathbf{F^{AO}} = \tag{34}$$

$$\begin{bmatrix} \mathbf{F}^{\mathbf{(AO)}}_{\mathbf{DD}} & \mathbf{F}^{\mathbf{(AO)}}_{\mathbf{DB1}} & \mathbf{F}^{\mathbf{(AO)}}_{\mathbf{DAn}} & \mathbf{F}^{\mathbf{(AO)}}_{\mathbf{DB2}} & \mathbf{F}^{\mathbf{(AO)}}_{\mathbf{DAc}} \\ \mathbf{F}^{\mathbf{(AO)}}_{\mathbf{B1D}} & \mathbf{F}^{\mathbf{(AO)}}_{\mathbf{B1B1}} & \mathbf{F}^{\mathbf{(AO)}}_{\mathbf{B1An}} & \mathbf{F}^{\mathbf{(AO)}}_{\mathbf{B1B2}} & \mathbf{F}^{\mathbf{(AO)}}_{\mathbf{B1Ac}} \\ \mathbf{F}^{\mathbf{(AO)}}_{\mathbf{AnD}} & \mathbf{F}^{\mathbf{(AO)}}_{\mathbf{AnB1}} & \mathbf{F}^{\mathbf{(AO)}}_{\mathbf{AnAn}} & \mathbf{F}^{\mathbf{(AO)}}_{\mathbf{AnB2}} & \mathbf{F}^{\mathbf{(AO)}}_{\mathbf{AnA}} \\ \mathbf{F}^{\mathbf{(AO)}}_{\mathbf{B2D}} & \mathbf{F}^{\mathbf{(AO)}}_{\mathbf{B2B1}} & \mathbf{F}^{\mathbf{(AO)}}_{\mathbf{B2An}} & \mathbf{F}^{\mathbf{(AO)}}_{\mathbf{B2B2}} & \mathbf{F}^{\mathbf{(AO)}}_{\mathbf{B2Ac}} \\ \mathbf{F}^{\mathbf{(AO)}}_{\mathbf{AcD}} & \mathbf{F}^{\mathbf{(AO)}}_{\mathbf{AcB1}} & \mathbf{F}^{\mathbf{(AO)}}_{\mathbf{AcAn}} & \mathbf{F}^{\mathbf{(AO)}}_{\mathbf{AcB2}} & \mathbf{F}^{\mathbf{(AO)}}_{\mathbf{AcAc}} \end{bmatrix} \tag{35}$$

In forming the localized orbitals for the three charge centers (donor, chromophore and acceptor), each charge center is allowed to expand across the neighbouring bridge units. The localized donor orbitals are formed by diagonalizing $\mathbf{\bar{F}^{D-B1}}$ (The orange square in Eqn. 36), the localized antenna orbitals are formed by diagonalizing $\mathbf{\bar{F}^{B1-An-B2}}$ (the purple square in Eqn. 36) and the localized acceptor orbitals are formed by diagonalizing $\mathbf{\bar{F}^{B2-Ac}}$ (the green square in Eqn. 36).

$$\mathbf{\bar{F}^{AO}} = \begin{bmatrix} \mathbf{\bar{F}}^{\mathbf{(AO)}}_{\mathbf{DD}} & \mathbf{\bar{F}}^{\mathbf{(AO)}}_{\mathbf{DB1}} & \mathbf{\bar{F}}^{\mathbf{(AO)}}_{\mathbf{DAn}} & \mathbf{\bar{F}}^{\mathbf{(AO)}}_{\mathbf{DB2}} & \mathbf{\bar{F}}^{\mathbf{(AO)}}_{\mathbf{DAc}} \\ \mathbf{\bar{F}}^{\mathbf{(AO)}}_{\mathbf{B1D}} & \mathbf{\bar{F}}^{\mathbf{(AO)}}_{\mathbf{B1B1}} & \mathbf{\bar{F}}^{\mathbf{(AO)}}_{\mathbf{B1An}} & \mathbf{\bar{F}}^{\mathbf{(AO)}}_{\mathbf{B1B2}} & \mathbf{\bar{F}}^{\mathbf{(AO)}}_{\mathbf{B1Ac}} \\ \mathbf{\bar{F}}^{\mathbf{(AO)}}_{\mathbf{AnD}} & \mathbf{\bar{F}}^{\mathbf{(AO)}}_{\mathbf{AnB1}} & \mathbf{\bar{F}}^{\mathbf{(AO)}}_{\mathbf{AnAn}} & \mathbf{\bar{F}}^{\mathbf{(AO)}}_{\mathbf{AnB2}} & \mathbf{\bar{F}}^{\mathbf{(AO)}}_{\mathbf{AnAc}} \\ \mathbf{\bar{F}}^{\mathbf{(AO)}}_{\mathbf{B2D}} & \mathbf{\bar{F}}^{\mathbf{(AO)}}_{\mathbf{B2B1}} & \mathbf{\bar{F}}^{\mathbf{(AO)}}_{\mathbf{B2An}} & \mathbf{\bar{F}}^{\mathbf{(AO)}}_{\mathbf{B2B2}} & \mathbf{\bar{F}}^{\mathbf{(AO)}}_{\mathbf{B2Ac}} \\ \mathbf{\bar{F}}^{\mathbf{(AO)}}_{\mathbf{AcD}} & \mathbf{\bar{F}}^{\mathbf{(AO)}}_{\mathbf{AcB1}} & \mathbf{\bar{F}}^{\mathbf{(AO)}}_{\mathbf{AcAn}} & \mathbf{\bar{F}}^{\mathbf{(AO)}}_{\mathbf{AcB2}} & \mathbf{\bar{F}}^{\mathbf{(AO)}}_{\mathbf{AcAc}} \end{bmatrix} \tag{36}$$

Having obtained the locally adiabatic orbitals for the triad, the procedure is the same as the one described above for the bridged donor-acceptor system (D-B-A).

2 Generalized Mulliken-Hush (GMH) theory

2.1 2-level treatment

The goal of GMH theory[9,10] is to create the best diabatic states as a combination of the calculated adiabatic states. A central assumption in GMH is that diabatic states localized at different sites have zero off-diagonal matrix element for the dipole moment ($\mu_{12}^{dia} = 0$). Also, one needs to define a central charge transfer direction ($\vec{v}$) which for a 2-state system is defined as the difference in initial and final adiabatic dipole vector: $\vec{v} = \vec{\mu}_{22}^{ad} - \vec{\mu}_{11}^{ad}$. Within a 2-state formalism, the dipole matrix projected onto this charge transfer direction is then:

$$\mu^{\mathbf{ad,v}} = \begin{bmatrix} \mu_{11}^{ad,v} & \mu_{12}^{ad,v} \\ \mu_{21}^{ad,v} & \mu_{22}^{ad,v} \end{bmatrix} \tag{37}$$

where $\mu_{ij}^{ad,v}$ is the projection of $\vec{\mu}_{ij}^{ad}$ onto $\vec{v}$: $\mu_{ij}^{ad,v} = \frac{\vec{\mu}_{ij}^{ad} \cdot \vec{v}}{|\vec{v}|}$. In the GMH the diatic states are defined as those with zero transition dipole moment ($\mu_{12}^{dia} = \mu_{21}^{dia} = 0$). The dipole moment matrix expressed in the diabatic basis is then:

$$\mu^{\mathbf{dia}} = \begin{bmatrix} \mu_{11}^{dia} & 0 \\ 0 & \mu_{22}^{dia} \end{bmatrix} \tag{38}$$

and can be found by diagonalizing the dipole moment matrix in the adiabatic basis:

$$\mathbf{C}^{\dagger} \mu^{\mathbf{ad,v}} \mathbf{C} = \mu^{\mathbf{dia}} \tag{39}$$

The hamiltonian in the diabatic basis ($\mathbf{H^{ad}}$) can then be found by using the transformation matrix ($\mathbf{C}$) on the hamiltonian in the aiabatic basis ($\mathbf{H^{ad}}$), which is diagonal:

$$\mathbf{H^{dia}} = \mathbf{C}^{\dagger} \mathbf{H^{ad}} \mathbf{C} \tag{40}$$

The procedure in GMH is summarized in Eqn. 41, which illustrates how one goes from adiabatic properties to diabatic properties.

$$\begin{aligned} \mu^{\mathbf{ad,v}} = \begin{bmatrix} \mu_{11}^{ad,v} & \mu_{12}^{ad,v} \\ \mu_{21}^{ad,v} & \mu_{22}^{ad,v} \end{bmatrix} \quad &\xrightarrow{\mathbf{C}} \quad \mu^{\mathbf{dia}} = \begin{bmatrix} \mu_{11}^{dia} & 0 \\ 0 & \mu_{22}^{dia} \end{bmatrix} \\ \mathbf{H^{ad}} = \begin{bmatrix} H_{11}^{ad} & 0 \\ 0 & H_{22}^{ad} \end{bmatrix} \quad &\xrightarrow{\mathbf{C}} \quad \mathbf{H^{dia}} = \begin{bmatrix} H_{11}^{dia} & H_{12}^{dia} \\ H_{21}^{dia} & H_{22}^{dia} \end{bmatrix} \end{aligned} \tag{41}$$

The electronic coupling element between the two diabatic states can then be read of as the off-diagonal elements: $H_{12}^{dia} = H_{21}^{dia}$.

3 System-Bath coupling sizes

As states in the article, the use of Redfield theory, include the second-order perturbation expansion in H_{SB}, is only valid if the size of the system-bath coupling is small. This is tested using the equation below.

$$\frac{C(\omega_n - \omega_m)}{2\pi(\omega_n - \omega_m)\hbar^2} \ll 1 \tag{42}$$

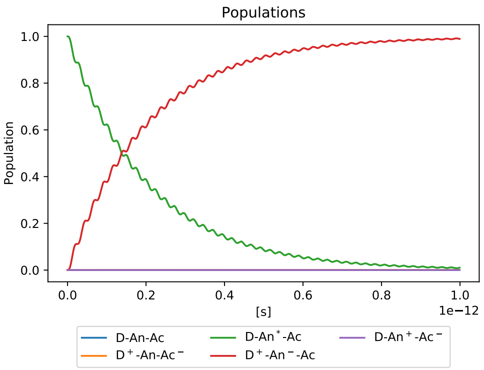
where $\omega_n - \omega_m$ is the difference in energy between initial and final state of the ET reaction.

Transition	$\frac{C(\omega_n-\omega_m)}{2\pi(\omega_n-\omega_m)\hbar^2}$
D-An*-Ac $\rightarrow$ D$^+$-An$^-$-Ac	6.10e-03
D-An*-Ac $\rightarrow$ D-An$^+$-Ac$^-$	3.90e-02
D-An*-Ac $\rightarrow$ D$^+$-An-Ac$^-$	3.62e-02
D$^+$-An$^-$-Ac $\rightarrow$ D-An$^+$-Ac$^-$	8.00e-03
D$^+$-An$^-$-Ac $\rightarrow$ D$^+$-An-Ac$^-$	2.88e-02
D-An$^+$-Ac$^-$ $\rightarrow$ D$^+$-An-Ac$^-$	2.46e-02

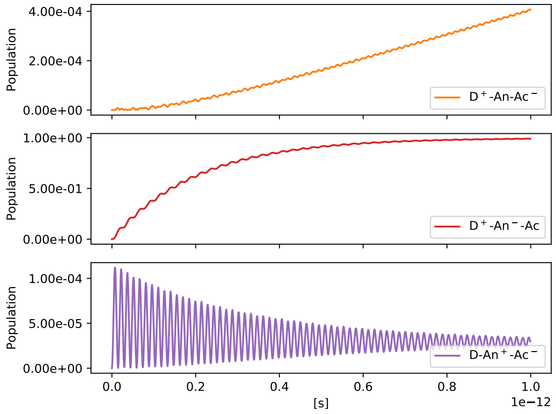
Table 1 Caption

4 GMH and FMR propagation of Individual Populations

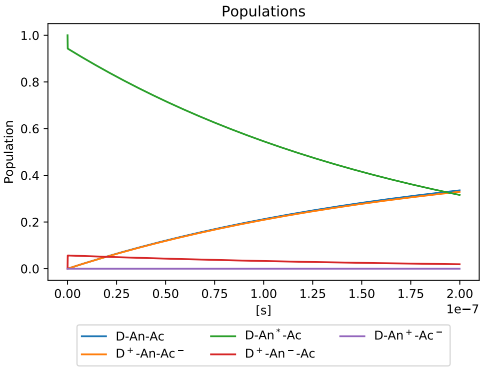
4.1 GMH



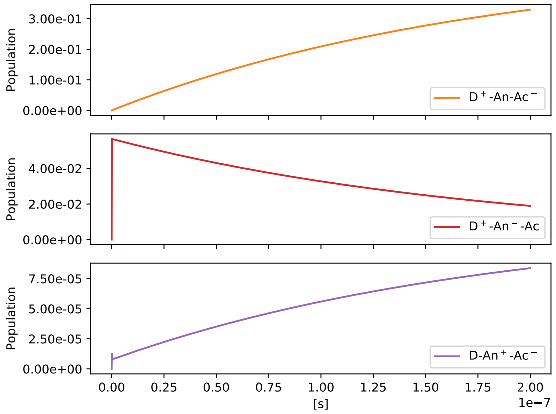
(a) 1 ps



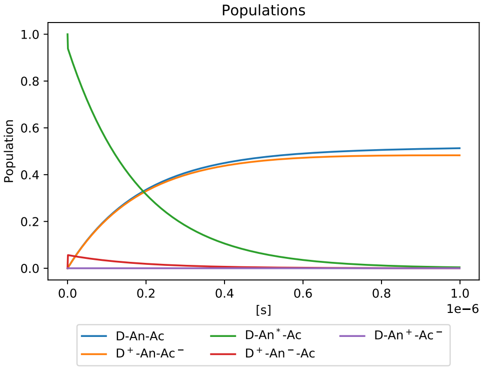
(b) 1 ps



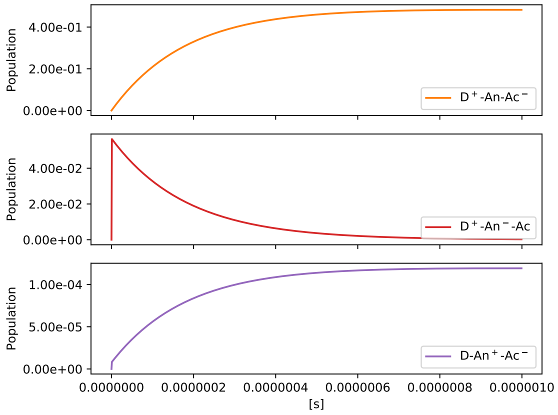
(a) 200 ns



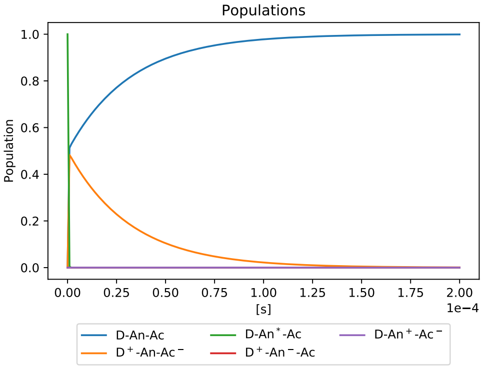
(b) 200 ns



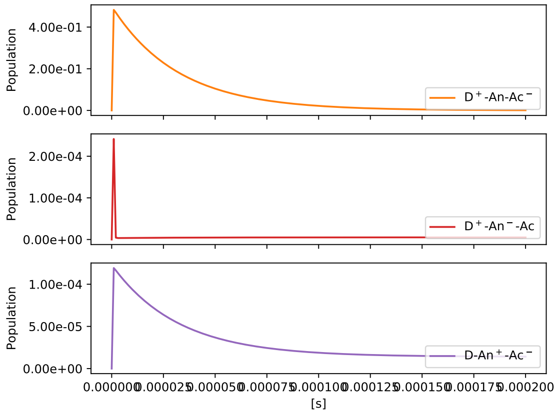
(a) 1 μs



(b) 1 μs

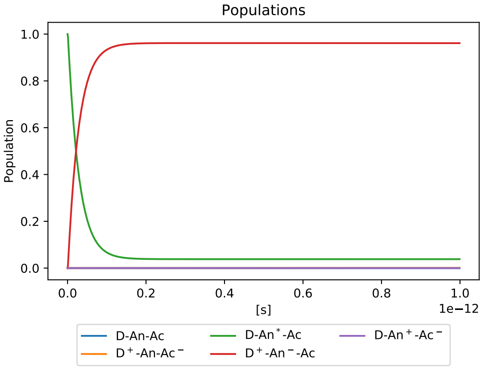


(a) 0.2 ms

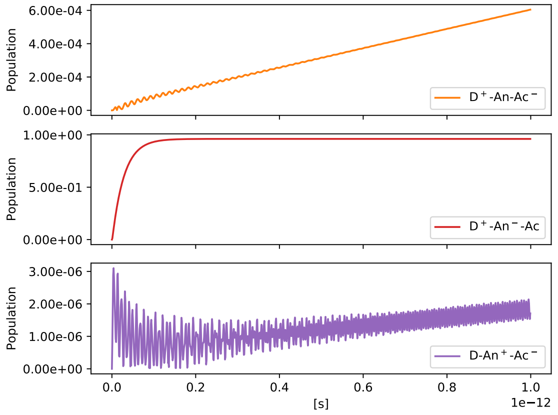


(b) 0.2 ms

4.2 FMR-B



(a) 1 ps



(b) 1 ps

5 Scripts for calculations of couplings and correlation funcitons

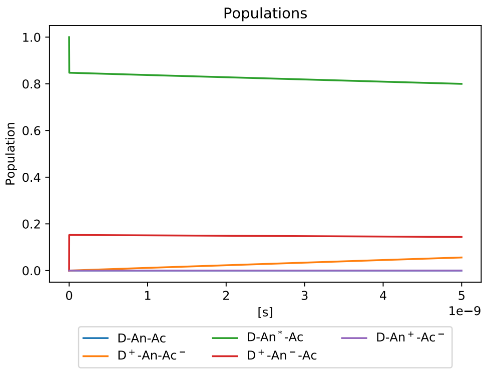
5.1 FMR

The FMR script for 3 charge sites separated by bridges is based on a Gaussian[11] output. Since the overlap matrix and the Fock matrix expressed in terms of the atomic orbital are needed the following keywords need to be added to the .com file:

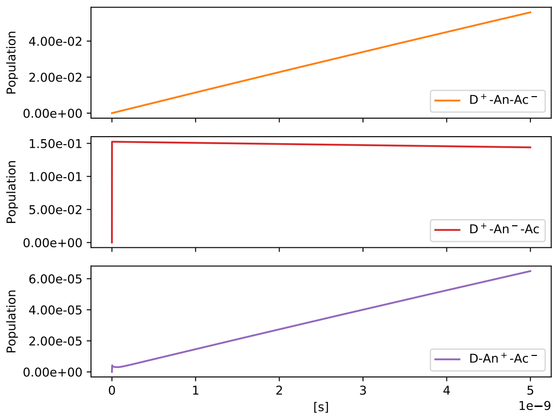
```
pop=full iop(3/33=1, 5/33=3)
```

The orbital couplings are calculated running the FMR script:

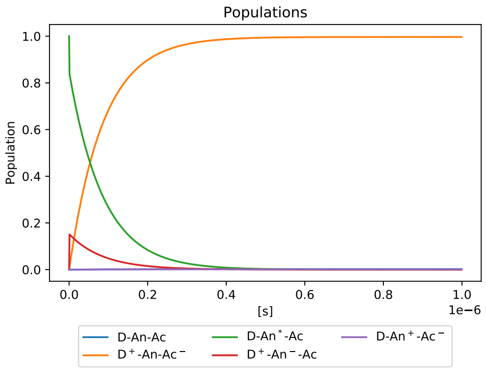
```
$ python FMR-B-DCA_systems.py guassia_outputfile.out
```



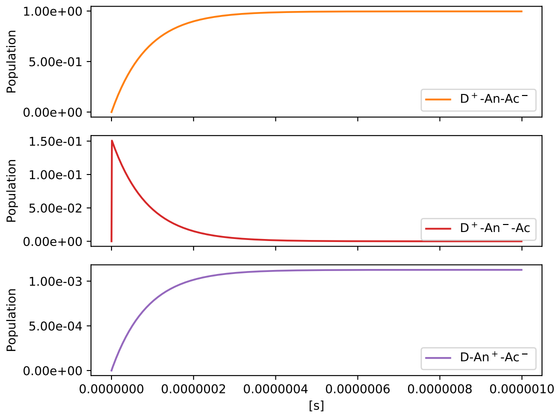
(a) 5 ns



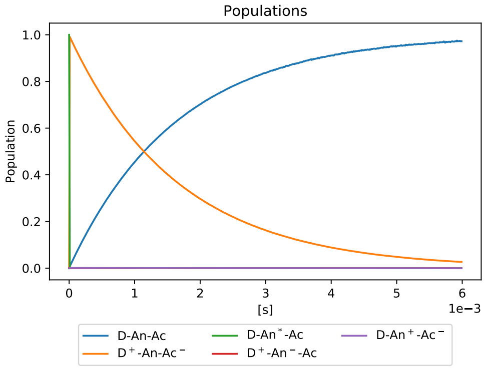
(b) 5 ns



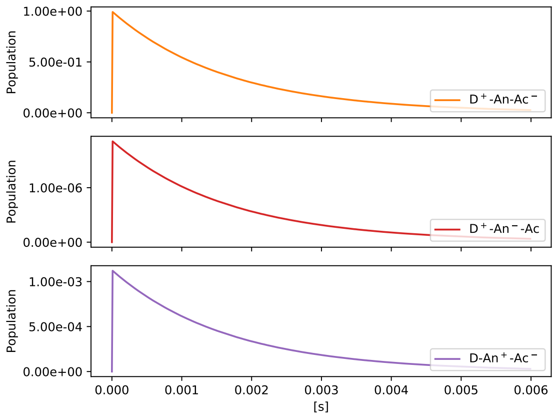
(a) 1 μs



(b) 1 μs



(a) 6 ms



(b) 6 ms

The script is based on 5 fragments: donor, bridge1, chromophore, bridge2, acceptor and the atoms should be ordered accordingly. The script needs the number of atoms in the molecule and this should be changed to fit the relevant system:

''

N_atoms_per_fragment = [22, 10, 38, 10, 30]

''

The script also needs the number of electrons to fill in each charge site in order to find the HOMO and LUMO index for that charge site. The number of electrons per fragment is automatically calculated but needs to be corrected for the number of bonds that are being broken for each site:

''

N_donor_electrons = electrons_per_fragment[0]+electrons_per_fragment[1]-1

```
N_chromophore_electrons = electrons_per_fragment[1]+electrons_per_fragment[2]+ electrons_per_fragment[3]-2
N_acceptor_electrons = electrons_per_fragment[3]+electrons_per_fragment[4]-1
```

"

Lastly, the orbitals that one wants to couple need to be specified in the part of the script that extracts the orbitals for example:

"

```
f_system_orthorgonal_homo =
donor_acceptor_orthorgonalize(C_full, f_diabatic, [homo_indexes[0], homo_indexes[1]])
```

"

chooses the HOMO of the first site (donor) to couple with the HOMO of the second site (chromophore).

5.2 GMH

For the GMH couplings, two different scripts are used: one for the coupling between two excited states (2_state_gmh.py) and one for the coupling between ground state and an excited state (2_state_gmh_groundtoexc.py). The scripts are based on the output of DALTON[12] calculations. Linear and response calculations are done in two separate calculations and the output files are respectively called: dalton_output_LR.out and dalton_output_QR.out. The calculation of dipole moments needs to be specified. For excited state - excited state calculations the script is called as:

```
$ python 2_state_gmh.py dalton_outut_LR.out state1 state2
```

where state1 and state2 are the two excited states that are chosen to form the adiabatic basis. For the recombination couplings (excited state to ground state) the script is called as:

```
$ python 2_state_gmh_groundtoexc.py dalton_output_LR.out dalton_output_QR.out excited_state
```

where "excited_state" is the adiabatic excited state chosen to as the adiabatic basis in addition to the ground state.

5.3 Correlation Function

The gradient on the excited state, needed for the calculation of the couplings to normal modes, is calculated with Gaussian[11]. To calculate the forces/gradient on the first excited state, the following keywords can be used

```
# td=(root=1) functional/basis-set force .
```

The .out files of the excited state gradients should be named f.ex.

name_root1.out

since then the gradient script will automatically name the .csv file of frequencies and couplings constants with the rootnumber.

5.4 Redfield Propagation

With the FMR-B/GMH couplings, the .csv files of γ parameters, and site energies calculated from Eq. 15, the Redfield propagation can be performed. The energies and couplings must be manually added to the Hamiltonian of either FMR-B or GMH. Correlation function .csv files should be in the same folder as the redfield_propagation.py script. The scrit is called as:

```
redfield_propagation.py plot_name
```

Notes and references

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