Singlet Fission in Carotenoid Dimers - The Role of the Exchange and Dipolar Interactions Supplementary Information

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1. Matrix Representation of the Reduced Two-Triplet Hamiltonian, eqn. (29)

Here we give the matrix representation, in the spin-coupled basis $|S, M_S\rangle$, of the exchange interactions (introduced in the reduced two-triplet Hamiltonian (eqn. (29) in the main paper)), and the dipolar and Zeeman interactions. We take the axis of spin quantisation to be parallel to the principal axis $\mathbf{Z}$. We use the notation $B_i \equiv B_x + iB_y$ and $B_i^* \equiv B_x - iB_y$. The order of the basis functions is

$$\{|0,0\rangle, |2,0\rangle, |2,-2\rangle, |2,+2\rangle, |2,-1\rangle, |2,+1\rangle, |1,0\rangle, |1,-1\rangle, |1,+1\rangle\},$$

where the basis functions are defined by eqn. (2) of the main paper (taking $i \equiv A$ and $j \equiv B$).

$$\mathbf{H}_{\text{dipolar}} = \begin{bmatrix} 0 & \frac{\sqrt{8}}{3}D & \frac{2}{\sqrt{3}}E & \frac{2}{\sqrt{3}}E & 0 & 0 & 0 & 0 & 0 \\ \frac{\sqrt{8}}{3}D & -\frac{2}{3}D & \frac{2}{\sqrt{6}}E & \frac{2}{\sqrt{6}}E & 0 & 0 & 0 & 0 & 0 \\ \frac{2}{\sqrt{3}}E & \frac{2}{\sqrt{6}}E & \frac{2}{3}D & 0 & 0 & 0 & 0 & 0 & 0 \\ \frac{2}{\sqrt{3}}E & \frac{2}{\sqrt{6}}E & 0 & \frac{2}{3}D & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & -\frac{1}{3}D & E & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & E & -\frac{1}{3}D & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & \frac{2}{3}D & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & -\frac{1}{3}D & -E \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & -E & -\frac{1}{3}D \end{bmatrix} \tag{1}$$

$$\frac{\mathbf{H}_{\text{Zeeman}}}{\mu_B g} = \begin{bmatrix} 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & \frac{3}{\sqrt{6}}B_i^* & \frac{3}{\sqrt{6}}B_i & 0 & 0 & 0 \\ 0 & 0 & -2B_z & 0 & B_i & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 2B_z & 0 & B_i^* & 0 & 0 & 0 \\ 0 & \frac{3}{\sqrt{6}}B_i & B_i^* & 0 & -B_z & 0 & 0 & 0 & 0 \\ 0 & \frac{3}{\sqrt{6}}B_i^* & 0 & B_i & 0 & B_z & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & \frac{1}{\sqrt{2}}B_i^* & \frac{1}{\sqrt{2}}B_i \\ 0 & 0 & 0 & 0 & 0 & 0 & \frac{1}{\sqrt{2}}B_i & -B_z & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & \frac{1}{\sqrt{2}}B_i^* & 0 & B_z \end{bmatrix} \tag{2}$$

$$\mathbf{H}_{\text{exchange}} = \begin{bmatrix} -2J_1 - 4J_2 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & J_1 - J_2 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & J_1 - J_2 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & J_1 - J_2 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & J_1 - J_2 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & J_1 - J_2 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & -J_1 - J_2 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & -J_1 - J_2 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & -J_1 - J_2 \end{bmatrix} \tag{3}$$

2. Derivation of the Lindblad Rate Constants

Below we present the derived relative rates of population transfer between the coupled-spin states $|S, M_S\rangle$. We use the notation $\gamma_1 \equiv \frac{1}{T_1}$ and $\gamma_2 \equiv \frac{1}{T_2}$. The relative rates are the values that the multiplicative factor r_p takes in the main text (see Section 2.3 and eqn. (22)).

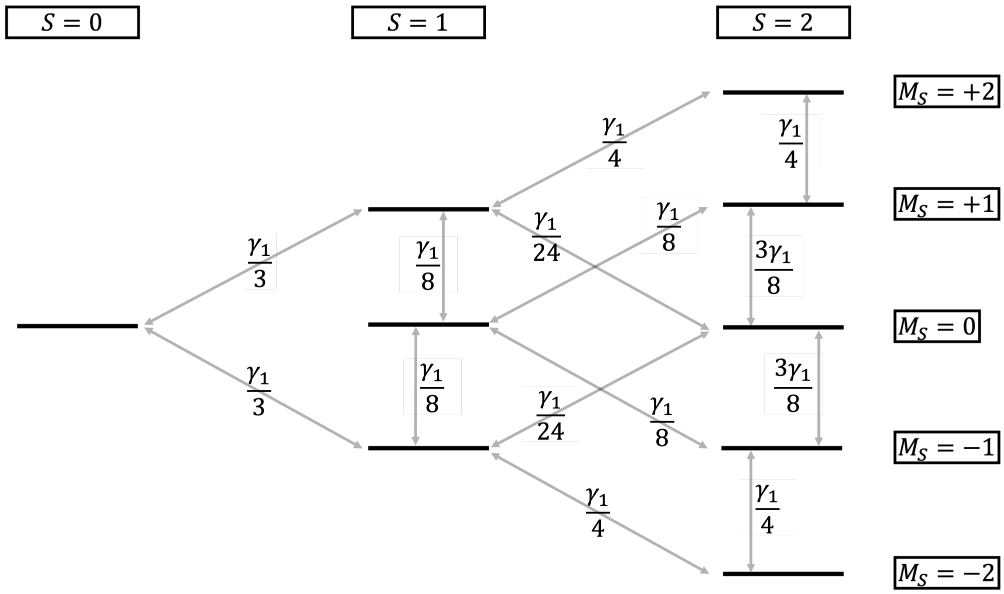

Figure 1: The derived relative rates of population transfer (i.e., r_p) between the spin-coupled basis states as a result of longitudinal spin-dephasing.

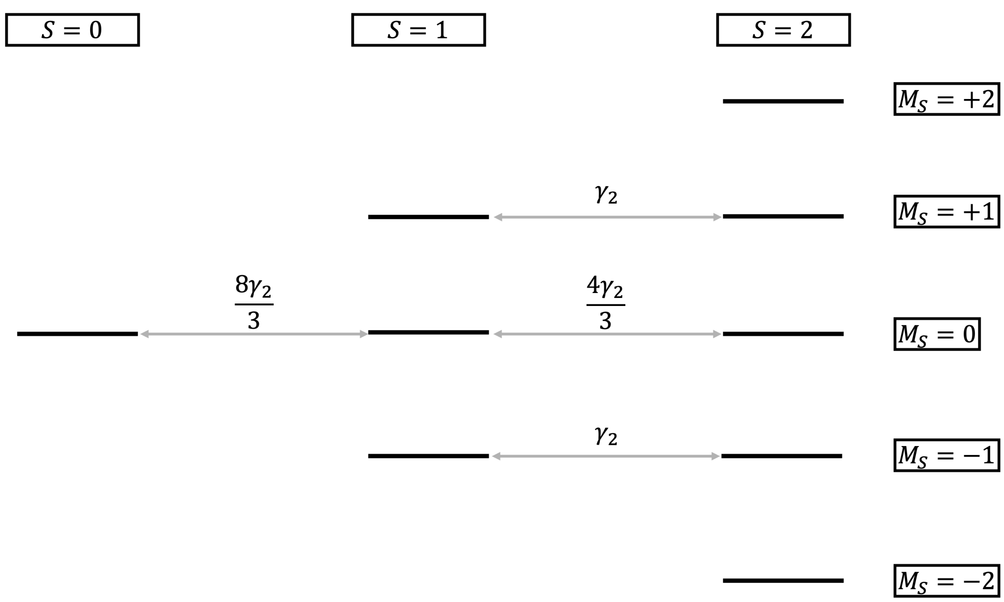

Figure 2: The derived relative rates of population transfer (i.e., r_p) between the spin-coupled basis states as a result of transverse spin-dephasing.