Appendix C:

Triplet Pair Spin Operators and Spin Hamiltonian

Triplet Pair Spin Operators

The triplet pair eigenstates may be constructed by standard rules of angular momentum addition as we will show below. We first begin by defining the $|\alpha\rangle$ and $|\beta\rangle$ basis functions in matrix form in addition to the Pauli matrices for the Cartesian components of a single electron spin operator that operate on these basis functions.[1,2]

$$|\alpha\rangle = \begin{bmatrix} 1 \\ 0 \end{bmatrix}$$

$$|\beta\rangle = \begin{bmatrix} 0 \\ 1 \end{bmatrix}$$

$$\hat{S}_x = \frac{1}{2}\begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix}$$

$$\hat{S}_y = \frac{1}{2}\begin{bmatrix} 0 & -i \\ i & 0 \end{bmatrix}$$

$$\hat{S}_z = \frac{1}{2}\begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix}$$

From here, there are two potential routes to generating the triplet pair eigenstates. The first is the traditional route used by Merrifield by defining two sets of triplet eigenfunctions and corresponding spin operators and taking their tensor products to generate the nine triplet pair eigenstates.[3,4] The second was outlined by Scholes in 2015, by generating the spin operators for four electron basis functions and factoring the uncoupled basis into the triplet pair basis assuming the two triplets are distinguishable.[5]

To define the triplet pair states in the vein of Merrifield, we must first construct triplet eigenstates and spin operators in the coupled two-electron basis. For two electrons, we can define

the uncoupled set of basis states as the tensor (Kronecker) product, denoted by $\otimes$, of the individual $|\alpha\rangle$ and $|\beta\rangle$ basis functions:

$$|\alpha\alpha\rangle = |\alpha\rangle \otimes |\alpha\rangle = \begin{bmatrix}1\\0\end{bmatrix} \otimes \begin{bmatrix}1\\0\end{bmatrix} = \begin{bmatrix}1\\0\\0\\0\end{bmatrix}$$

$$|\alpha\beta\rangle = |\alpha\rangle \otimes |\beta\rangle = \begin{bmatrix}1\\0\end{bmatrix} \otimes \begin{bmatrix}0\\1\end{bmatrix} = \begin{bmatrix}0\\1\\0\\0\end{bmatrix}$$

$$|\beta\alpha\rangle = |\beta\rangle \otimes |\alpha\rangle = \begin{bmatrix}0\\1\end{bmatrix} \otimes \begin{bmatrix}1\\0\end{bmatrix} = \begin{bmatrix}0\\0\\1\\0\end{bmatrix}$$

$$|\beta\beta\rangle = |\beta\rangle \otimes |\beta\rangle = \begin{bmatrix}0\\1\end{bmatrix} \otimes \begin{bmatrix}0\\1\end{bmatrix} = \begin{bmatrix}0\\0\\0\\1\end{bmatrix}$$

The spin operators in the uncoupled basis are similarly constructed by summing over the following Kronecker products where $\mathbf{I_2}$ represents the 2x2 identity matrix, $\hat{S}_{x,y,z}$ represents the total two-electron spin operator for each Cartesian coordinate, and $\hat{S}_{1x,y,z}$ and $\hat{S}_{2x,y,z}$ represent the Cartesian spin operators for electron 1 and 2, respectively:

$$\hat{S}_{Tot\,x,y,z} = \hat{S}_{1x,y,z} \otimes \boldsymbol{I_2} + \boldsymbol{I_2} \otimes \hat{S}_{2x,y,z}$$

$$\hat{S}_x = \hat{S}_{1x} \otimes \boldsymbol{I_2} + \boldsymbol{I_2} \otimes \hat{S}_{2x} = \frac{1}{2}\begin{bmatrix}0 & 1\\1 & 0\end{bmatrix} \otimes \begin{bmatrix}1 & 0\\0 & 1\end{bmatrix} + \frac{1}{2}\begin{bmatrix}1 & 0\\0 & 1\end{bmatrix} \otimes \begin{bmatrix}0 & 1\\1 & 0\end{bmatrix}$$

$$\hat{S}_x = \frac{1}{2}\begin{bmatrix}0 & 0 & 1 & 0\\0 & 0 & 0 & 1\\1 & 0 & 0 & 0\\0 & 1 & 0 & 0\end{bmatrix} + \frac{1}{2}\begin{bmatrix}0 & 1 & 0 & 0\\1 & 0 & 0 & 0\\0 & 0 & 0 & 1\\0 & 0 & 1 & 0\end{bmatrix} = \frac{1}{2}\begin{bmatrix}0 & 1 & 1 & 0\\1 & 0 & 0 & 1\\1 & 0 & 0 & 1\\0 & 1 & 1 & 0\end{bmatrix}$$

$$\hat{S}_y = \hat{S}_{1y} \otimes \boldsymbol{I_2} + \boldsymbol{I_2} \otimes \hat{S}_{2y} = \frac{1}{2}\begin{bmatrix} 0 & -i \\ i & 0 \end{bmatrix} \otimes \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix} + \frac{1}{2}\begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix} \otimes \begin{bmatrix} 0 & -i \\ i & 0 \end{bmatrix}$$

$$\hat{S}_y = \frac{1}{2}\begin{bmatrix} 0 & 0 & -i & 0 \\ 0 & 0 & 0 & -i \\ i & 0 & 0 & 0 \\ 0 & i & 0 & 0 \end{bmatrix} + \frac{1}{2}\begin{bmatrix} 0 & -i & 0 & 0 \\ i & 0 & 0 & 0 \\ 0 & 0 & 0 & -i \\ 0 & 0 & i & 0 \end{bmatrix} = \frac{1}{2}\begin{bmatrix} 0 & -i & -i & 0 \\ i & 0 & 0 & -i \\ i & 0 & 0 & -i \\ 0 & i & i & 0 \end{bmatrix}$$

$$\hat{S}_z = \hat{S}_{1z} \otimes \boldsymbol{I_2} + \boldsymbol{I_2} \otimes \hat{S}_{2z} = \frac{1}{2}\begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix} \otimes \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix} + \frac{1}{2}\begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix} \otimes \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix}$$

$$\hat{S}_z = \frac{1}{2}\begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & -1 \end{bmatrix} + \frac{1}{2}\begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & -1 \end{bmatrix} = \frac{1}{2}\begin{bmatrix} 2 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & -2 \end{bmatrix} = \begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & -1 \end{bmatrix}$$

$$\hat{S}^2 = \hat{S}_x + \hat{S}_y + \hat{S}_z = \begin{bmatrix} 2 & 0 & 0 & 0 \\ 0 & 1 & 1 & 0 \\ 0 & 1 & 1 & 0 \\ 0 & 0 & 0 & 2 \end{bmatrix}$$

As can be seen, the $\hat{S}^2$ operator is not diagonal in the uncoupled basis. Specifically, $|\alpha\beta\rangle$ and $|\beta\alpha\rangle$ are not eigenstates, i.e. they are not states of pure spin multiplicity. The elements $\langle\alpha\alpha|\hat{S}^2|\alpha\alpha\rangle$ and $\langle\beta\beta|\hat{S}^2|\beta\beta\rangle$ are both 2, consistent with the expected eigenvalue S(S+1) for a triplet S = 1, and the corresponding matrix elements of the $\hat{S}_z$ operator give m_s values of +1 and -1, respectively. We can diagonalize the $\hat{S}^2$ matrix to retrieve the eigenvalues and associated eigenvectors:

$$\hat{S}^2 = \begin{bmatrix} 0 & 0 & 0 & 0 \\ 0 & 2 & 0 & 0 \\ 0 & 0 & 2 & 0 \\ 0 & 0 & 0 & 2 \end{bmatrix}$$

$$eigenvectors: \frac{1}{\sqrt{2}}\begin{bmatrix} 0 \\ 1 \\ -1 \\ 0 \end{bmatrix}, \begin{bmatrix} 1 \\ 0 \\ 0 \\ 0 \end{bmatrix}, \frac{1}{\sqrt{2}}\begin{bmatrix} 0 \\ 1 \\ 1 \\ 0 \end{bmatrix}, \begin{bmatrix} 0 \\ 0 \\ 0 \\ 1 \end{bmatrix}$$

This provides us a set of eigenvectors in the coupled spin basis $|S,M\rangle$ that are pure singlet and triplet functions (S = 0 and S=1 respectively):

$$|0,0\rangle = |S\rangle = \frac{1}{\sqrt{2}}(|\alpha\beta\rangle - |\beta\alpha\rangle)$$

$$|1,0\rangle = |T_0\rangle = \frac{1}{\sqrt{2}}(|\alpha\beta\rangle + |\beta\alpha\rangle)$$

$$|1,+1\rangle = |T_+\rangle = |\alpha\alpha\rangle$$

$$|1,-1\rangle = |T_-\rangle = |\beta\beta\rangle$$

From these eigenvectors we can construct a rotation matrix to transform the individual Cartesian spin operators into the coupled $|S,M\rangle$ basis; alternatively, we can directly construct the matrix from the Clebsch-Gordon coefficients:

$$R = \begin{bmatrix} 0 & 1 & 0 & 0 \\ {}^{1}/_{\sqrt{2}} & 0 & {}^{1}/_{\sqrt{2}} & 0 \\ {}^{-1}/_{\sqrt{2}} & 0 & {}^{1}/_{\sqrt{2}} & 0 \\ 0 & 0 & 0 & 1 \end{bmatrix}$$

$$\hat{S}_{x,y,z}^{|S,M\rangle} = R' * \hat{S}_{x,y,z} * R$$

$$\hat{S}_x^{|S,M\rangle} = \begin{bmatrix} 0 & 0 & 0 & 0 \\ 0 & 0 & {}^{1}/_{\sqrt{2}} & 0 \\ 0 & {}^{1}/_{\sqrt{2}} & 0 & {}^{1}/_{\sqrt{2}} \\ 0 & 0 & {}^{1}/_{\sqrt{2}} & 0 \end{bmatrix}$$

$$\hat{S}_y^{|S,M\rangle} = \begin{bmatrix} 0 & 0 & 0 & 0 \\ 0 & 0 & -i/\sqrt{2} & 0 \\ 0 & i/\sqrt{2} & 0 & -i/\sqrt{2} \\ 0 & 0 & i/\sqrt{2} & 0 \end{bmatrix}$$

$$\hat{S}_z^{|S,M\rangle} = \begin{bmatrix} 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & -1 \end{bmatrix}$$

As can be seen, the spin operators in the coupled $|S, M\rangle$ basis are block diagonal – no matrix elements connect the singlet and triplet eigenfunctions. Furthermore, all elements associated with the $|S\rangle$ eigenstate are 0, which makes sense because all components of the net spin vector should sum to zero for a singlet. As a result, we will truncate the matrices to carry forward only the triplet eigenstates to generate the triplet pair functions:

$$\hat{S}_{Tx} = \begin{bmatrix} 0 & 1/\sqrt{2} & 0 \\ 1/\sqrt{2} & 0 & 1/\sqrt{2} \\ 0 & 1/\sqrt{2} & 0 \end{bmatrix}$$

$$\hat{S}_{Ty} = \begin{bmatrix} 0 & -i/\sqrt{2} & 0 \\ i/\sqrt{2} & 0 & -i/\sqrt{2} \\ 0 & i/\sqrt{2} & 0 \end{bmatrix}$$

$$\hat{S}_{Tz} = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & -1 \end{bmatrix}$$

$$basis\ functions: |1,+1\rangle = |+\rangle = \begin{bmatrix} 1 \\ 0 \\ 0 \end{bmatrix}, |1,0\rangle = |0\rangle = \begin{bmatrix} 0 \\ 1 \\ 0 \end{bmatrix}, |1,-1\rangle = |-\rangle = \begin{bmatrix} 0 \\ 0 \\ 1 \end{bmatrix}$$

We then take the Kronecker products of our triplet basis functions to generate uncoupled triplet pair basis states.

$$|+\,+\rangle = |+\rangle \otimes |+\rangle = \begin{bmatrix}1\\0\\0\end{bmatrix} \otimes \begin{bmatrix}1\\0\\0\end{bmatrix} = \begin{bmatrix}1\\0\\0\\0\\0\\0\\0\\0\\0\end{bmatrix}$$

$$|+0\rangle = |+\rangle \otimes |0\rangle = \begin{bmatrix}1\\0\\0\end{bmatrix} \otimes \begin{bmatrix}0\\1\\0\end{bmatrix} = \begin{bmatrix}0\\1\\0\\0\\0\\0\\0\\0\\0\end{bmatrix}$$

$$|+\,-\rangle = |+\rangle \otimes |-\rangle = \begin{bmatrix}1\\0\\0\end{bmatrix} \otimes \begin{bmatrix}0\\0\\1\end{bmatrix} = \begin{bmatrix}0\\0\\1\\0\\0\\0\\0\\0\\0\end{bmatrix}$$

$$|0\,+\rangle = |0\rangle \otimes |+\rangle = \begin{bmatrix}0\\1\\0\end{bmatrix} \otimes \begin{bmatrix}1\\0\\0\end{bmatrix} = \begin{bmatrix}0\\0\\0\\1\\0\\0\\0\\0\\0\end{bmatrix}$$

$$|00\rangle = |0\rangle \otimes |0\rangle = \begin{bmatrix}0\\1\\0\end{bmatrix} \otimes \begin{bmatrix}0\\1\\0\end{bmatrix} = \begin{bmatrix}0\\0\\0\\0\\1\\0\\0\\0\\0\end{bmatrix}$$

$$|0-\rangle = |0\rangle \otimes |-\rangle = \begin{bmatrix}0\\1\\0\end{bmatrix} \otimes \begin{bmatrix}0\\0\\1\end{bmatrix} = \begin{bmatrix}0\\0\\0\\0\\0\\1\\0\\0\\0\end{bmatrix}$$

$$|-+\rangle = |-\rangle \otimes |+\rangle = \begin{bmatrix}0\\0\\1\end{bmatrix} \otimes \begin{bmatrix}1\\0\\0\end{bmatrix} = \begin{bmatrix}0\\0\\0\\0\\0\\0\\1\\0\\0\end{bmatrix}$$

$$|-0\rangle = |-\rangle \otimes |0\rangle = \begin{bmatrix}0\\0\\1\end{bmatrix} \otimes \begin{bmatrix}0\\1\\0\end{bmatrix} = \begin{bmatrix}0\\0\\0\\0\\0\\0\\0\\1\\0\end{bmatrix}$$

$$|--\rangle = |-\rangle \otimes |-\rangle = \begin{bmatrix}0\\0\\1\end{bmatrix} \otimes \begin{bmatrix}0\\0\\1\end{bmatrix} = \begin{bmatrix}0\\0\\0\\0\\0\\0\\0\\0\\1\end{bmatrix}$$

We build triplet pair spin operators in analogous fashion by the following summation of Kronecker products:

$$\hat{S}_{TTx,y,z} = \hat{S}_{Tx,y,z} \otimes \boldsymbol{I}_3 + \boldsymbol{I}_3 \otimes \hat{S}_{Tx,y,z}$$

$$\hat{S}_{TTx} = \begin{bmatrix}
0 & {}^{1}/_{\sqrt{2}} & 0 & {}^{1}/_{\sqrt{2}} & 0 & 0 & 0 & 0 & 0 \\
{}^{1}/_{\sqrt{2}} & 0 & {}^{1}/_{\sqrt{2}} & 0 & {}^{1}/_{\sqrt{2}} & 0 & 0 & 0 & 0 \\
0 & {}^{1}/_{\sqrt{2}} & 0 & 0 & 0 & {}^{1}/_{\sqrt{2}} & 0 & 0 & 0 \\
{}^{1}/_{\sqrt{2}} & 0 & 0 & 0 & {}^{1}/_{\sqrt{2}} & 0 & {}^{1}/_{\sqrt{2}} & 0 & 0 \\
0 & {}^{1}/_{\sqrt{2}} & 0 & {}^{1}/_{\sqrt{2}} & 0 & {}^{1}/_{\sqrt{2}} & 0 & {}^{1}/_{\sqrt{2}} & 0 \\
0 & 0 & {}^{1}/_{\sqrt{2}} & 0 & {}^{1}/_{\sqrt{2}} & 0 & 0 & 0 & {}^{1}/_{\sqrt{2}} \\
0 & 0 & 0 & {}^{1}/_{\sqrt{2}} & 0 & 0 & 0 & {}^{1}/_{\sqrt{2}} & 0 \\
0 & 0 & 0 & 0 & {}^{1}/_{\sqrt{2}} & 0 & {}^{1}/_{\sqrt{2}} & 0 & {}^{1}/_{\sqrt{2}} \\
0 & 0 & 0 & 0 & 0 & {}^{1}/_{\sqrt{2}} & 0 & {}^{1}/_{\sqrt{2}} & 0
\end{bmatrix}$$

$$\hat{S}_{TTy} = \begin{bmatrix} 0 & -i/\sqrt{2} & 0 & -i/\sqrt{2} & 0 & 0 & 0 & 0 & 0 \\ i/\sqrt{2} & 0 & -i/\sqrt{2} & 0 & -i/\sqrt{2} & 0 & 0 & 0 & 0 \\ 0 & i/\sqrt{2} & 0 & 0 & 0 & -i/\sqrt{2} & 0 & 0 & 0 \\ i/\sqrt{2} & 0 & 0 & 0 & -i/\sqrt{2} & 0 & -i/\sqrt{2} & 0 & 0 \\ 0 & i/\sqrt{2} & 0 & i/\sqrt{2} & 0 & -i/\sqrt{2} & 0 & -i/\sqrt{2} & 0 \\ 0 & 0 & i/\sqrt{2} & 0 & i/\sqrt{2} & 0 & 0 & 0 & -i/\sqrt{2} \\ 0 & 0 & 0 & i/\sqrt{2} & 0 & 0 & 0 & -i/\sqrt{2} & 0 \\ 0 & 0 & 0 & 0 & i/\sqrt{2} & 0 & i/\sqrt{2} & 0 & -i/\sqrt{2} \\ 0 & 0 & 0 & 0 & 0 & i/\sqrt{2} & 0 & i/\sqrt{2} & 0 \end{bmatrix}$$

$$\hat{S}_{TTz} = \begin{bmatrix} 2 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & -1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & -2 \end{bmatrix}$$

$$\hat{S}_{TT}^2 = \hat{S}_{TTx}^2 + \hat{S}_{TTy}^2 + \hat{S}_{TTz}^2 = \begin{bmatrix} 6 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 4 & 0 & 2 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 2 & 0 & 2 & 0 & 0 & 0 & 0 \\ 0 & 2 & 0 & 4 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 2 & 0 & 4 & 0 & 2 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 4 & 0 & 2 & 0 \\ 0 & 0 & 0 & 0 & 2 & 0 & 2 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 2 & 0 & 4 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 6 \end{bmatrix}$$

By diagonalizing the $\hat{S}_{TT}^2$ matrix, we retrieve the pure spin eigenvectors and eigenvalues:

$$\hat{S}_{TT}^2 = \begin{bmatrix} 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 2 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 2 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 2 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 6 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 6 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 6 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 6 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 6 \end{bmatrix}$$

$$eigenvectors\colon \frac{1}{\sqrt{3}}\begin{bmatrix} 0 \\ 0 \\ 1 \\ 0 \\ -1 \\ 0 \\ 1 \\ 0 \\ 0 \end{bmatrix}, \frac{1}{\sqrt{2}}\begin{bmatrix} 0 \\ 1 \\ 0 \\ -1 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \end{bmatrix}, \frac{1}{\sqrt{2}}\begin{bmatrix} 0 \\ 0 \\ 1 \\ 0 \\ 0 \\ 0 \\ -1 \\ 0 \\ 0 \end{bmatrix}, \frac{1}{\sqrt{2}}\begin{bmatrix} 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 1 \\ 0 \\ -1 \\ 0 \end{bmatrix}, \begin{bmatrix} 1 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \end{bmatrix}, \frac{1}{\sqrt{2}}\begin{bmatrix} 0 \\ 1 \\ 0 \\ 1 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \end{bmatrix}, \frac{1}{\sqrt{6}}\begin{bmatrix} 0 \\ 0 \\ 1 \\ 0 \\ 2 \\ 0 \\ 1 \\ 0 \\ 0 \end{bmatrix}, \frac{1}{\sqrt{2}}\begin{bmatrix} 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 1 \\ 0 \\ 1 \\ 0 \end{bmatrix}, \begin{bmatrix} 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 1 \end{bmatrix}$$

We can rotate the $\hat{S}_{TTz}$ matrix into this new basis to specify the associated m_s values with each eigenvector, which leads to the following triplet pair eigenstates expanded in the basis of uncoupled triplet product states. As can be seen, we expect one state of pure singlet character, three of triplet character, and five of quintet character.

$$\left|\,{}^1TT\right\rangle = \frac{1}{\sqrt{3}}(|00\rangle - |+-\rangle - |-+\rangle)$$

$$\left|\,{}^3TT_{+1}\right\rangle = \frac{1}{\sqrt{2}}(|+0\rangle - |0+\rangle)$$

$$\left|\,{}^3TT_{0}\right\rangle = \frac{1}{\sqrt{2}}(|+-\rangle - |-+\rangle)$$

$$\left|\,{}^3TT_{-1}\right\rangle = \frac{1}{\sqrt{2}}(|0-\rangle - |-0\rangle)$$

$$\left|\,{}^5TT_{+2}\right\rangle = |++\rangle$$

$$\left|\,^5TT_{+1}\right\rangle = \frac{1}{\sqrt{2}}(|+0\rangle + |0+\rangle)$$

$$\left|\,^5TT_{0}\right\rangle = \frac{1}{\sqrt{6}}(2|00\rangle + |+-\rangle + |-+\rangle)$$

$$\left|\,^5TT_{-1}\right\rangle = \frac{1}{\sqrt{2}}(|0-\rangle + |-0\rangle)$$

$$\left|\,^5TT_{-2}\right\rangle = |--\rangle$$

Triplet Pair Spin Hamiltonian

We define the spin Hamiltonian similarly to previous reports.[6–9] In the conceptualization of the spin Hamiltonian, we consider the four unpaired electron spin system with electrons 1 and 2 localized on triplet A, and electrons 3 and 4 are localized on triplet B. At zero-field, we will consider the intratriplet magnetic dipolar interactions, $\widehat{H}_{zfs}$, and the intertriplet exchange interaction, $\widehat{H}_{ex}$. The intratriplet exchange, intertriplet dipolar interactions are excluded, and spin-orbit coupling, typically weak in these organic chromophores, is neglected.

The intratriplet exchange interaction serves to split the energies of the excited singlet S_1 and excited triplet T_1 states by a large energy – in pentacene around 1.2 eV – which is necessary for singlet fission to be thermodynamically accessible. When considering the triplet pair states, we make the assumption that the singly excited singlet state does not interact substantially with the triplets, an assumption that underlies our construction of the triplet pair spin operators when we carry forward only the triplet subspace from the individual triplet operators. For the intertriplet interactions, the exchange is typically dominant, so we disregard the magnetic dipolar interactions between electrons localized on separate chromophores, although these can be included as well.

We define the spin Hamiltonian below as a summation over the three interactions:

$$\hat{H} = \hat{H}_{zee} + \hat{H}_{zfs} + \hat{H}_{ex}$$

The total Zeeman Hamiltonian, $\hat{H}_{zee}$, can be constructed from the Kronecker product of the individual Zeeman Hamiltonians defined for triplets A and B that are expressed in terms of the triplet spin operators.

$$\hat{H}_{zee}^{A,B} = \mu_B \boldsymbol{B^T} \cdot \boldsymbol{g^{A,B}} \cdot \boldsymbol{S^{A,B}} = \mu_B \sum_{i,j=x,y,z} B_i g_{ij}^{A,B} \hat{S}_j^{A,B}$$

$$\hat{H}_{zee} = \hat{H}_{zee}^{A} \otimes I_3 + I_3 \otimes \hat{H}_{zee}^{B}$$

$$\boldsymbol{g^{A,B}} = R^{A,B} \boldsymbol{g} {R^{A,B}}^T$$

$$\boldsymbol{g} = \begin{bmatrix} g_x & 0 & 0 \\ 0 & g_y & 0 \\ 0 & 0 & g_z \end{bmatrix}$$

Here, μ_B is the Bohr magneton. $\boldsymbol{B^T}$ is the external magnetic field vector defined by the x-, y-, and z-components of the field. $\boldsymbol{g^{A,B}}$ is the g tensor defined for each triplet that describes the coupling between the spin angular momentum and the externally applied field. The g tensor can be defined in its principal frame $\boldsymbol{g}$. In general, the principal axes of the two spin systems will not be aligned with each other nor the externally applied field. As a result, the g tensor can be rotated using three Euler angles by the rotation matrices $R^{A,B}$.

The total zero-field splitting Hamiltonian $\hat{H}_{zfs}$ may similarly be constructed over the Kronecker sum of the individual triplet zero-field splitting Hamiltonians $\hat{H}_{zfs}^{A,B}$.

$$\hat{H}_{zfs}^{A,B} = \boldsymbol{S^{A,B^T}} \cdot \boldsymbol{D^{A,B}} \cdot \boldsymbol{S^{A,B}} = \sum_{i,j=x,y,z} \hat{S}_i^{A,B} \cdot D_{ij}^{A,B} \cdot \hat{S}_j^{A,B}$$

$$\hat{H}_{zfs} = \hat{H}_{zfs}^{A} \otimes I_3 + I_3 \otimes \hat{H}_{zfs}^{B}$$

$$\boldsymbol{D^{A,B}} = R^{A,B}\boldsymbol{D}R^{A,B^T}$$

$$\boldsymbol{D} = \begin{bmatrix} D_x & 0 & 0 \\ 0 & D_y & 0 \\ 0 & 0 & D_z \end{bmatrix} = \begin{bmatrix} -\frac{1}{3}D + E & 0 & 0 \\ 0 & -\frac{1}{3}D - E & 0 \\ 0 & 0 & \frac{2}{3}D \end{bmatrix}$$

Here, $\boldsymbol{D^{A,B}}$ is the molecular D tensor for triplets A and B. Similarly, to the g tensor, the D tensor may be written in its principal frame as $\boldsymbol{D}$. The D tensor arising from magnetic dipolar coupling is traceless (i.e. $Tr(\boldsymbol{D}) = D_x + D_y + D_z = 0$) and as a result, the tensor can be parametrized using only two values: $D = \frac{3}{2}D_z$ and $E = \frac{1}{2}(D_x - D_y)$. As with the g tensor, the D tensor is defined in the molecular frame, and principal axes for each triplet may not be aligned with each other or the magnetic field. As a result, we can apply an arbitrary rotation $R^{A,B}$ to the D tensor to define a particular intertriplet orientation as well as the orientations with respect to the applied field.

To describe the exchange interaction between triplets A and B, we define the exchange Hamiltonian $\hat{H}_{ex}$ as follows:[10]

$$\hat{H}_{ex} = \hat{\boldsymbol{S}}^{\boldsymbol{A^T}} \cdot \boldsymbol{J} \cdot \hat{\boldsymbol{S}}^{\boldsymbol{B}} = \sum_{i,j=x,y,z} J_{ij}\hat{S}_i^A \otimes \hat{S}_j^B$$

In molecular systems, the isotropic exchange is typically the dominant portion of the exchange interaction. Accordingly, we can simplify the expression for $\hat{H}_{ex}$ as follows where we define the scalar exchange coupling constant as $J_{iso} = J$.

$$\hat{H}_{ex} = J(\hat{S}_x^A \otimes \hat{S}_x^B + \hat{S}_y^A \otimes \hat{S}_y^B + \hat{S}_z^A \otimes \hat{S}_z^B)$$

We will provide an illustrative example of the construction of the spin Hamiltonian matrix representation under the assumption that the molecular axes of the two triplets, and their respective g and D tensor principal axes, are aligned with each other. We use a general magnetic field vector $\boldsymbol{B^T} = [B_x \quad B_y \quad B_z]$ and use the triplet Cartesian spin operators we defined previously.

$$\hat{H}_{zee}^{A,B} = \mu_B [B_x \quad B_y \quad B_z] \cdot \begin{bmatrix} g_x & 0 & 0 \\ 0 & g_y & 0 \\ 0 & 0 & g_z \end{bmatrix} \cdot \begin{bmatrix} \hat{S}_x^{A,B} \\ \hat{S}_y^{A,B} \\ \hat{S}_z^{A,B} \end{bmatrix} = \mu_B (B_x g_x \hat{S}_x^{A,B} + B_y g_y \hat{S}_y^{A,B} + B_z g_z \hat{S}_z^{A,B})$$

$$\hat{H}_{zee}^{A,B} = \mu_B \left(B_x g_x \frac{1}{\sqrt{2}} \begin{bmatrix} 0 & 1 & 0 \\ 1 & 0 & 1 \\ 0 & 1 & 0 \end{bmatrix} + B_y g_y \frac{i}{\sqrt{2}} \begin{bmatrix} 0 & -1 & 0 \\ 1 & 0 & -1 \\ 0 & 1 & 0 \end{bmatrix} + B_z g_z \begin{bmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & -1 \end{bmatrix} \right)$$

$$\hat{H}_{zee}^{A,B} = \begin{bmatrix} \mu_B g_z B_z & \frac{1}{\sqrt{2}} \mu_B (g_x B_x - i g_y B_y) & 0 \\ \frac{1}{\sqrt{2}} \mu_B (g_x B_x + i g_y B_y) & 0 & \frac{1}{\sqrt{2}} \mu_B (g_x B_x - i g_y B_y) \\ 0 & \frac{1}{\sqrt{2}} \mu_B (g_x B_x + i g_y B_y) & -\mu_B g_z B_z \end{bmatrix}$$

Using the triplet Zeeman Hamiltonians, we can construct the triplet pair Zeeman Hamiltonian and rotate it into the coupled basis. As we defined the spin operators, the rows and columns are ordered from lowest to highest multiplicity (e.g S = 0, S = 1, S = 2) and highest M_s value to lowest (e.g. M_s = +2, M_s = +1, M_s = 0, M_s = -1, M_s = -2).

$$\hat{H}_{zee} = \hat{H}_{zee}^A \otimes I_3 + I_3 \otimes \hat{H}_{zee}^B$$

$$\hat{H}_{zee}$$

$$= \begin{bmatrix} 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & \mu_B g_z B_z & \frac{1}{\sqrt{2}}\mu_B(g_x B_x - i g_y B_y) & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & \frac{1}{\sqrt{2}}\mu_B(g_x B_x + i g_y B_y) & 0 & \frac{1}{\sqrt{2}}\mu_B(g_x B_x - i g_y B_y) & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & \frac{1}{\sqrt{2}}\mu_B(g_x B_x + i g_y B_y) & -\mu_B g_z B_z & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 2\mu_B g_z B_z & \mu_B(g_x B_x - i g_y B_y) & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & \mu_B(g_x B_x + i g_y B_y) & \mu_B g_z B_z & \mu_B(g_x B_x - i g_y B_y) & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & \mu_B(g_x B_x + i g_y B_y) & 0 & \frac{\sqrt{6}}{2}\mu_B(g_x B_x - i g_y B_y) & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & \frac{\sqrt{6}}{2}\mu_B(g_x B_x + i g_y B_y) & -\mu_B g_z B_z & \mu_B(g_x B_x - i g_y B_y) \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & \mu_B(g_x B_x + i g_y B_y) & -2\mu_B g_z B_z \end{bmatrix}$$

In the limit of an isotropic g-tensor ($g_x = g_y = g_z = g_e = g$), $\hat{H}_{zee}$ is independent of the orientation of the molecular frame with respect to the external field. As a result, we can take the magnetic field vector purely along the quantization axis B_z (i.e. $B_z = B$) and obtain a simplified, diagonal $\hat{H}_{zee}$:

$$\hat{H}_{zee} = \begin{bmatrix} 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & \mu_B g B & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & -\mu_B g B & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 2\mu_B g B & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & \mu_B g B & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & -\mu_B g B & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & -2\mu_B g B \end{bmatrix}$$

We next compute the zero-field splitting Hamiltonian $\hat{H}_{zfs}$ and rotate it into the coupled basis.

$$\widehat{H}_{zfs}^{A,B} = \begin{bmatrix} \hat{S}_x^{A,B} & \hat{S}_y^{A,B} & \hat{S}_z^{A,B} \end{bmatrix} \cdot \begin{bmatrix} -\frac{1}{3}D + E & 0 & 0 \\ 0 & -\frac{1}{3}D - E & 0 \\ 0 & 0 & \frac{2}{3}D \end{bmatrix} \cdot \begin{bmatrix} \hat{S}_x^{A,B} \\ \hat{S}_y^{A,B} \\ \hat{S}_z^{A,B} \end{bmatrix}$$

$$= \left(-\frac{1}{3}D + E\right)\hat{S}_x^{A,B^2} + \left(-\frac{1}{3}D - E\right)\hat{S}_y^{A,B^2} + \frac{2}{3}D\hat{S}_z^{A,B^2}$$

$$= D\left(\hat{S}_z^{A,B^2} - \frac{1}{3}\hat{S}^2\right) + E(\hat{S}_x^{A,B^2} - \hat{S}_y^{A,B^2})$$

$$\widehat{H}_{zfs}^{A,B} = \begin{bmatrix} \frac{1}{3}D & 0 & E \\ 0 & -\frac{2}{3}D & 0 \\ E & 0 & \frac{1}{3}D \end{bmatrix}$$

$$\widehat{H}_{zfs} = \begin{bmatrix} \frac{1}{3}D & 0 & E \\ 0 & -\frac{2}{3}D & 0 \\ E & 0 & \frac{1}{3}D \end{bmatrix} \otimes \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} + \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \otimes \begin{bmatrix} \frac{1}{3}D & 0 & E \\ 0 & -\frac{2}{3}D & 0 \\ E & 0 & \frac{1}{3}D \end{bmatrix}$$

$$\hat{H}_{zfs} = \begin{bmatrix} 0 & 0 & 0 & 0 & \frac{2}{\sqrt{3}}E & 0 & \frac{2\sqrt{2}}{3}D & 0 & \frac{2}{\sqrt{3}}E \\ 0 & -\frac{1}{3}D & 0 & -E & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & \frac{2}{3}D & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & -E & 0 & -\frac{1}{3}D & 0 & 0 & 0 & 0 & 0 \\ \frac{2}{\sqrt{3}}E & 0 & 0 & 0 & \frac{2}{3}D & 0 & \frac{\sqrt{6}}{3}E & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & -\frac{1}{3}D & 0 & E & 0 \\ \frac{2\sqrt{2}}{3}D & 0 & 0 & 0 & \frac{\sqrt{6}}{3}E & 0 & -\frac{2}{3}D & 0 & \frac{\sqrt{6}}{3}E \\ 0 & 0 & 0 & 0 & 0 & E & 0 & -\frac{1}{3}D & 0 \\ \frac{2}{\sqrt{3}}E & 0 & 0 & 0 & 0 & 0 & \frac{\sqrt{6}}{3}E & 0 & \frac{2}{3}D \end{bmatrix}$$

As shown above, $\hat{H}_{zfs}$ is not diagonal in the coupled basis. Thus, the eigenstates of the total spin Hamiltonian $\hat{H}$ will not all strictly be of pure spin multiplicity S or M_S. In the limit of large exchange ($J \gg D$) or high magnetic fields, the zero-field splitting becomes a small contribution to the overall spin Hamiltonian, and thus the eigenstates of $\hat{H}$ approach the pure spin coupled basis we obtained by diagonalization of the $\hat{S}^2$ operator. Still, by examination of $\hat{H}_{zfs}$, there are off-diagonal elements connecting the $\left|\,^1(TT)_0\right\rangle$ state with $\left|\,^5(TT)_0\right\rangle$ depending on the parameter D and $\left|\,^5(TT)_{\pm 2}\right\rangle$ depending on the parameter E. If the initially generated triplet pair state of singlet fission is the pure singlet state $\left|\,^1(TT)_0\right\rangle$, these off-diagonal elements allow for the population of the quintet sublevels, which we can probe by EPR spectroscopy.

Last, we construct the exchange Hamiltonian $\hat{H}_{ex}$ using only the isotropic component of the J tensor and rotate it into the coupled basis.

$$\widehat{H}_{ex} = J\left(\frac{1}{\sqrt{2}}\begin{bmatrix}0 & 1 & 0\\ 1 & 0 & 1\\ 0 & 1 & 0\end{bmatrix}\otimes\frac{1}{\sqrt{2}}\begin{bmatrix}0 & 1 & 0\\ 1 & 0 & 1\\ 0 & 1 & 0\end{bmatrix}+\frac{i}{\sqrt{2}}\begin{bmatrix}0 & -1 & 0\\ 1 & 0 & -1\\ 0 & 1 & 0\end{bmatrix}\otimes\frac{i}{\sqrt{2}}\begin{bmatrix}0 & -1 & 0\\ 1 & 0 & -1\\ 0 & 1 & 0\end{bmatrix}\ldots\right.$$

$$\left.+\begin{bmatrix}1 & 0 & 0\\ 0 & 0 & 0\\ 0 & 0 & -1\end{bmatrix}\otimes\begin{bmatrix}1 & 0 & 0\\ 0 & 0 & 0\\ 0 & 0 & -1\end{bmatrix}\right)$$

$$\widehat{H}_{ex} = \begin{bmatrix}-2J & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0\\ 0 & -J & 0 & 0 & 0 & 0 & 0 & 0 & 0\\ 0 & 0 & -J & 0 & 0 & 0 & 0 & 0 & 0\\ 0 & 0 & 0 & -J & 0 & 0 & 0 & 0 & 0\\ 0 & 0 & 0 & 0 & J & 0 & 0 & 0 & 0\\ 0 & 0 & 0 & 0 & 0 & J & 0 & 0 & 0\\ 0 & 0 & 0 & 0 & 0 & 0 & J & 0 & 0\\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & J & 0\\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & J\end{bmatrix}$$

The isotropic exchange Hamiltonian is diagonal in the coupled basis. As can be observed, the S = 0 singlet state will be separated from the S = 1 triplets by J and by the S = 2 quintet manifold by $3J$. By the convention chosen, a positive J value places the singlet state lowest in energy.

We can then write the total spin Hamiltonian with the magnetic field aligned along the molecular z-axis.

$$\begin{bmatrix}-2J & 0 & 0 & 0 & \frac{2}{\sqrt{3}}E & 0 & \frac{\sqrt{6}}{3}D & 0 & \frac{2}{\sqrt{3}}E\\ 0 & \mu_B gB-\frac{1}{3}D-J & 0 & -E & 0 & 0 & 0 & 0 & 0\\ 0 & 0 & \frac{2}{3}D-J & 0 & 0 & 0 & 0 & 0 & 0\\ 0 & -E & 0 & -\mu_B gB-\frac{1}{3}D-J & 0 & 0 & 0 & 0 & 0\\ \frac{2}{\sqrt{3}}E & 0 & 0 & 0 & 2\mu_B gB+\frac{2}{3}D+J & 0 & \frac{\sqrt{6}}{3}E & 0 & 0\\ 0 & 0 & 0 & 0 & 0 & \mu_B gB-\frac{1}{3}D+J & 0 & E & 0\\ \frac{\sqrt{6}}{3}D & 0 & 0 & 0 & \frac{\sqrt{6}}{3}E & 0 & -\frac{2}{3}D+J & 0 & \frac{\sqrt{6}}{3}E\\ 0 & 0 & 0 & 0 & 0 & E & 0 & -\mu_B gB-\frac{1}{3}D+J & 0\\ \frac{2}{\sqrt{3}}E & 0 & 0 & 0 & 0 & 0 & \frac{\sqrt{6}}{3}E & 0 & -2\mu_B gB+\frac{2}{3}D+J\end{bmatrix}$$

Citations

(1) Weil, J. A.; Bolton, J. R. Basic Principles of Paramagnetic Resonance. In *Electron Paramagnetic Resonance*; John Wiley & Sons, Ltd, 2006; pp 1–35. https://doi.org/10.1002/9780470084984.ch1.
(2) McWeeny, R. *Spins in Chemistry*; Dover Publications, 2004.
(3) Merrifield, R. E. Magnetic Effects on Triplet Exciton Interactions. *Pure and Applied Chemistry* **1971**, *27* (3), 481–498. https://doi.org/10.1351/pac197127030481.
(4) Benk, H.; Sixl, H. Theory of Two Coupled Triplet States. *Molecular Physics* **1981**, *42* (4), 779–801. https://doi.org/10.1080/00268978100100631.
(5) Scholes, G. D. Correlated Pair States Formed by Singlet Fission and Exciton–Exciton Annihilation. *J. Phys. Chem. A* **2015**, *119* (51), 12699–12705. https://doi.org/10.1021/acs.jpca.5b09725.
(6) Collins, M. I.; McCamey, D. R.; Tayebjee, M. J. Y. Fluctuating Exchange Interactions Enable Quintet Multiexciton Formation in Singlet Fission. *J. Chem. Phys.* **2019**, *151* (16), 164104. https://doi.org/10.1063/1.5115816.
(7) Smyser, K. E.; Eaves, J. D. Singlet Fission for Quantum Information and Quantum Computing: The Parallel JDE Model. *Sci Rep* **2020**, *10* (1), 18480. https://doi.org/10.1038/s41598-020-75459-x.
(8) Lewis, S. G.; Smyser, K. E.; Eaves, J. D. Clock Transitions Guard against Spin Decoherence in Singlet Fission. *J. Chem. Phys.* **2021**, *155* (19), 194109. https://doi.org/10.1063/5.0069344.
(9) Bayliss, S. L.; Weiss, L. R.; Kraffert, F.; Granger, D. B.; Anthony, J. E.; Behrends, J.; Bittl, R. Probing the Wave Function and Dynamics of the Quintet Multiexciton State with Coherent Control in a Singlet Fission Material. *Phys. Rev. X* **2020**, *10* (2), 021070. https://doi.org/10.1103/PhysRevX.10.021070.
(10) Bencini, A.; Gatteschi, D. *EPR of Exchange Coupled Systems*; Courier Corporation, 2012.