

4. Theory of Spin Correlated Radical Pairs

A radical pair generated by a light flash consists of two unpaired electron spins spaced at a certain distance which are coupled to each other. The spins are correlated because they originate from the primary donor that has been photo-excited to a singlet state. The time constant for the generation of such radical pairs is usually about 10^{-10} s and is fast compared to the time scale of all magnetic interactions within the radical pair or its precursors. To describe the observed behaviour in EPR experiments it is necessary to determine the energy levels, transition probabilities, population differences and spin dynamics for such a spin pair.

4.1 Hamiltonian for the two-spin system

The following interactions have to be included in the Hamiltonian:

The Zeeman interaction \hat{H}_{Z1} and \hat{H}_{Z2} of each electron with the external magnetic field,

The Hyperfine interaction \hat{H}_{hfs} between each electron and surrounding nuclei,

The Spin-spin interaction \hat{H}_{SS} between the two electrons.

The spin Hamiltonian for this system can be expressed as [50, 51]:

$$\hat{H}_0 = \hat{H}_{Z1} + \hat{H}_{Z2} + \hat{H}_{hfs} + \hat{H}_{SS}$$

If the high field approximation is applied (that means all other interactions are small compared to the Zeeman interaction), the Hamiltonian is given by [52]:

$$\hat{H}_0 = g_1 \mathbf{b}B_0 \hat{S}_{1z} + g_2 \mathbf{b}B_0 \hat{S}_{2z} + \sum_{i,j} A_{ij} \hat{S}_{iz} \hat{I}_{jz} + \frac{3}{2} d(\hat{S}_z^2 - \frac{1}{3} \hat{S}^2) - 2J\hat{S}_1\hat{S}_2$$

$$H_1 = \hbar \mathbf{w}_1 (S_{1x} + S_{2x})$$

Then the magnetic field B_0 defines the principal direction (z-axis) and may have arbitrary orientation with respect to the geometry of radical pair, g_1 and g_2 are the two effective g -values of the electron spins and d is the effective dipolar coupling along the field axis. The isotropic hfs between electron i and proton j is given by A_{ij} .

With the elements $\hat{H}_{ij} = \langle i | \hat{H}_0 | j \rangle$, the following matrix representation of \hat{H}_0 in the singlet-triplet high field spin state basis is obtained:

$$\hat{H}_0 = \begin{array}{cccc} & |T_+\rangle & |S\rangle & |T_0\rangle & |T_-\rangle \\ \mathbf{w}_0 - J/2 + d/2 & & 0 & 0 & 0 \\ 0 & 3J/2 & \Delta\mathbf{w} & & 0 \\ 0 & \Delta\mathbf{w} & -J/2 - d & & 0 \\ 0 & 0 & 0 & \mathbf{w}_0 - J/2 + d/2 & \end{array}$$

in which \mathbf{w}_0 and $\Delta\mathbf{w}$ are respectively half the sum and half the difference of the Larmor frequencies of the two electrons in the absence of spin-spin coupling:

$$\mathbf{w}_0 = \frac{1}{2} \mathbf{b}B_0 (g_1 + g_2) + \frac{1}{2} \sum_j (A_{1j} + A_{2j}) m_j$$

$$\Delta\mathbf{w} = \frac{1}{2} \mathbf{b}B_0 (g_1 - g_2) + \frac{1}{2} \sum_j (A_{1j} - A_{2j}) m_j$$

and $m_j \in \left\{ +\frac{1}{2}; -\frac{1}{2} \right\}$ denotes the projection of the spin state of nucleus j onto the axis

of B_0 .

4.2 Eigenvalues and eigenstates of the system

Usually, the two g -factors differ from each other ($\Delta\mathbf{w} \neq 0$) and the Hamiltonian has to be diagonalized. The triplet sublevels $|T_+\rangle$ and $|T_-\rangle$ are eigenfunctions of \hat{H}_0 because all

off-diagonal elements involving these states vanish. The remaining eigenfunctions $|2\rangle$ and

$|3\rangle$ can be expressed as linear combinations between $|S\rangle$ and $|T_0\rangle$, that is:

$$\begin{aligned} |1\rangle &= |T_+\rangle \\ |2\rangle &= c_{22}|S\rangle + c_{23}|T_0\rangle \\ |3\rangle &= c_{32}|S\rangle + c_{33}|T_0\rangle \\ |4\rangle &= |T_-\rangle \end{aligned}$$

or, writing in matrix form:

$$\begin{pmatrix} |1\rangle \\ |2\rangle \\ |3\rangle \\ |4\rangle \end{pmatrix} = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & c_{22} & c_{23} & 0 \\ 0 & c_{32} & c_{33} & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} |T_+\rangle \\ |S\rangle \\ |T_0\rangle \\ |T_-\rangle \end{pmatrix} = U \begin{pmatrix} |T_+\rangle \\ |S\rangle \\ |T_0\rangle \\ |T_-\rangle \end{pmatrix}$$

There matrix U contains the coefficients c_{ij} and is a unitary matrix ($UU^T = 1$). According

to the method of Jacobi, the matrix elements U_{ij} with $(i, j = 2, 3)$ can be expressed by the

sine or cosine of an angle \mathbf{a} :

$$U = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & c_{22} & c_{23} & 0 \\ 0 & c_{32} & c_{33} & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix} = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & \cos \mathbf{a} & \sin \mathbf{a} & 0 \\ 0 & -\sin \mathbf{a} & \cos \mathbf{a} & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix}$$

U transforms the Hamiltonian into its diagonal form by a simple coordinate rotation with

angle \mathbf{a} [53]:

$$\hat{H}_0^{diag} = U\hat{H}_0U^T = \begin{array}{cccc} & |1\rangle & |2\rangle & |3\rangle & |4\rangle \\ E_1 & 0 & 0 & 0 & \\ 0 & E_2 & 0 & 0 & \\ 0 & 0 & E_3 & 0 & \\ 0 & 0 & 0 & E_4 & \end{array}$$

Finally, the following energy values and eigenfunctions for a spin correlated radical pair

are derived [54, 55]:

$$\begin{aligned}
 E_1 &= \mathbf{w}_0 - (J - d)/2 & |1\rangle &= |T_+\rangle \\
 E_2 &= \Omega + (J - d)/2 & |2\rangle &= \cos \mathbf{a} |S\rangle + \sin \mathbf{a} |T_0\rangle \\
 E_3 &= -\Omega + (J - d)/2 & |3\rangle &= -\sin \mathbf{a} |S\rangle + \cos \mathbf{a} |T_0\rangle \\
 E_4 &= -\mathbf{w}_0 - (J - d)/2 & |4\rangle &= |T_-\rangle
 \end{aligned}$$

where Ω is the singlet triplet mixing frequency:

$$\Omega^2 = \Delta \mathbf{w}^2 + (J + d/2)^2$$

and the singlet-triplet mixing angle \mathbf{a} is defined by

$$\sin(2\mathbf{a}) = \frac{\Delta \mathbf{w}}{\Omega}; \quad \cos(2\mathbf{a}) = \frac{J + d/2}{\Omega};$$

Neglecting the hyperfine interaction for the moment, inspection of the equations show that for a coupled two-spin system, four energy levels are expected as shown in Figure 4.1. Since the observed radical pair is generated in a pure singlet state, the system starts out with the population only in the two middle levels, $|2\rangle$ and $|3\rangle$, as indicated by the bold bars in Figure 4.1.

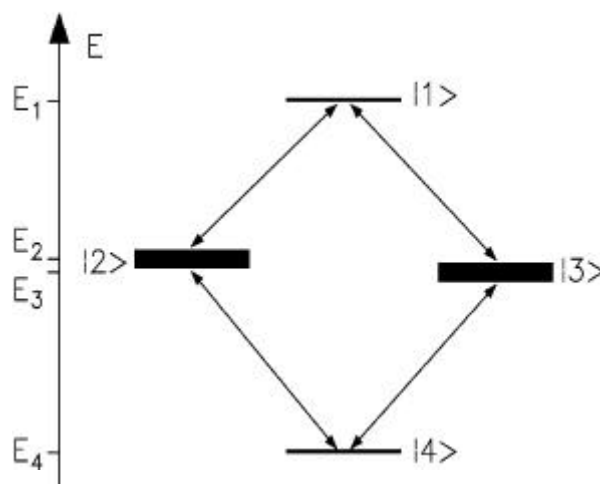


Figure 4.1. Energy scheme for a coupled two electrons system. The arrow marks the allowed single quantum transitions between the energy levels.

4.3 Transition frequencies and intensities

Since all eigenfunctions contain at least partial triplet character, four single-quantum transitions with $|\Delta m_s| = 1$ between the energy levels are possible. The corresponding transition frequencies are determined by:

$$\mathbf{w}_{12} = E_1 - E_2 = \mathbf{w}_0 - (J - d) - \Omega$$

$$\mathbf{w}_{34} = E_3 - E_4 = \mathbf{w}_0 + (J - d) - \Omega$$

$$\mathbf{w}_{13} = E_1 - E_3 = \mathbf{w}_0 - (J - d) + \Omega$$

$$\mathbf{w}_{24} = E_2 - E_4 = \mathbf{w}_0 + (J - d) + \Omega$$

The intensity I_{ij} of the EPR transition is proportional to the population difference between the energy levels i and j $-\Delta n_{ij} = -(n_i - n_j)$, scaled by the transition probability

$$W_{ij} \propto \langle i | \hat{H}_1 | j \rangle^2 \text{ [56].}$$

$$I_{ij} \propto -\Delta n_{ij} W_{ij}$$

The operator \hat{H}_1 represents the interaction between the spins and the magnetic field of the microwave radiation which is conventionally assumed to be polarised along the x-direction. In the rotating frame it is given by $H_1 = \hbar \mathbf{w}_1 (S_{1x} + S_{2x})$. Here, \mathbf{w}_1 is the amplitude of the microwave field in frequency units. The operator S_x induces transitions between the triplet sublevels. The transition probabilities are thus proportional to the triplet character of the eigenstates $|2\rangle$ and $|3\rangle$:

$$\langle 1 | \hat{S}_x | 2 \rangle^2 = \frac{1}{2} \sin^2 \mathbf{a}$$

$$\langle 3 | \hat{S}_x | 4 \rangle^2 = \frac{1}{2} \cos^2 \mathbf{a}$$

$$\langle 1 | \hat{S}_x | 3 \rangle^2 = \frac{1}{2} \cos^2 \mathbf{a}$$

$$\langle 2 | \hat{S}_x | 4 \rangle^2 = \frac{1}{2} \sin^2 \mathbf{a}$$

The final expression for the EPR line intensities is:

$$I_{12} = -I_{34} = I_{13} = -I_{24} \propto \frac{1}{2} \sin^2 \alpha \cos^2 \alpha \sin^2 \Omega t$$

As can be seen, four lines with equal intensity but different polarisation are expected. If a fixed orientation of the radical pair with respect to the magnetic field is considered and line broadening is neglected, the resonance lines and transition intensities can be visualised in the simple stick spectrum Figure 4.2. Both line pairs are symmetrically distributed around the g -factor of the single spins. The separation within each line pair is given by the spin-spin coupling $2(J-d)$. Hence, the polarisation pattern depends on the sign of the spin-spin coupling.

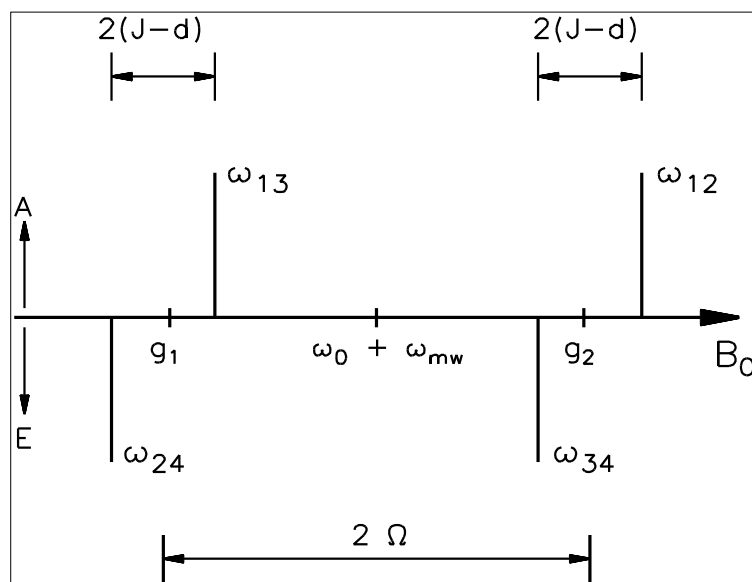
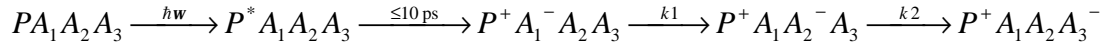


Figure 4.1 Stick spectrum for a spin-correlated radical pair. The separation between the two line pairs is governed by the g -shift between the two radicals. The difference within each line pair is given by $2(J-d)$.

4.4 Theoretical description of consecutive radical pairs [57].

The light induced charge separation in photosynthetic reaction centers follows the general scheme:



k_1 and k_2 are the rate constants of the electron transfer from A_1^- to A_2 and from A_2^- to A_3 , respectively. In PS I the lifetime of the charge separated states span several orders of magnitude and only those states which have an influence on the EPR signals should be conceded. To illustrate the general approach of the theoretical consideration, the two radical pairs $P^+A_1^-$ and $P^+A_2^-$ (RP1 and RP2) can be discussed. In addition to the forward electron transfer, charge recombination via back electron transfer to donor is included as k_s recombination rate from singlet, k_T recombination rate from triplet states. The equation of motion of the density matrices ρ_1 and ρ_2 , corresponding to RP1 and RP2 are:

$$\begin{aligned} \frac{\partial \mathbf{r}_1}{\partial t} &= L_1 \mathbf{r}_1 - K \mathbf{r}_1 - k_1 \mathbf{r}_1 \\ \frac{\partial \mathbf{r}_2}{\partial t} &= L_2 \mathbf{r}_2 + k_1 \mathbf{r}_1 - k_2 \mathbf{r}_2 \end{aligned}$$

where L_1 and L_2 describe the spin evolution in the Liouville representation, and the operator K describes the recombination of RP1:

$$\begin{aligned} L_1 \mathbf{r}_1 &= -i\hbar^{-1} [H_1, \mathbf{r}_1] \\ K \mathbf{r}_1 &= \frac{k_S (P_S \mathbf{r}_1 + \mathbf{r}_1 P_S)}{2} + \frac{k_T (P_T \mathbf{r}_1 + \mathbf{r}_1 P_T)}{2} \end{aligned}$$

where P_S and P_T are projection operators on to the singlet and triplet states.

