

OOP-ESEEM for CISS of photo-generated radical pairs

Gianluca Marcozzi

August 5, 2024

Chapter 1

Rotated initial density matrix: change of reference frame

1.1 Definition of angles and initial density matrix

The angle between the external magnetic field B_0 and the chirality axis \mathbf{n}_D is exactly θ , that is the angle of the dipolar interaction, because the direction of the dipolar interaction is also along \mathbf{n}_D . In case of maximal spin polarization (100% CISS), the wavefunction after electron transfer will be $|\uparrow\downarrow(\mathbf{n}_D)\rangle$, that is $|\uparrow\downarrow\rangle$ along the direction of the dipolar vector. In the dipolar D-frame, that is a frame having \mathbf{n}_D as z -axis, the initial density matrix is:

$$\rho|_D = \rho_{\uparrow\downarrow} = |\uparrow\downarrow\rangle\langle\uparrow\downarrow| = \frac{1}{2} \left(\frac{1}{2}\mathbb{1} - S_{zz} + S_{z,A} - S_{z,B} \right). \quad (1.1)$$

We will neglect terms proportional to the identity matrix, since these are invariant under rotations.

1.2 Euler angles

Let us derive the Euler angles of interest to express the initial density matrix, that in Eq. 1.1 is expressed in the D-frame coordinate system, in the laboratory coordinate system. Without loss of generality, we assume that in the laboratory frame the dipolar vector is equal to: $\mathbf{n}_D|_L = [\sin(\theta)\cos(\phi), \sin(\theta)\sin(\phi), \cos(\theta)]_L$. Since we take $\mathbf{n}_D \equiv z^{(D)}$, in the dipolar frame $\mathbf{n}_D|_D = [0, 0, 1]_D$. Notice that the $x^{(D)}y^{(D)}$ -plane is perpendicular to \mathbf{n}_D , $x^{(D)}$ and $y^{(D)}$ are orthogonal, but the exact direction of these two versors is not defined because the starting condition in Eq. 1.1 is invariant under rotations around \mathbf{n}_D .

Finding the transformation that applied to the base vectors of one frame result in the base vectors of the other frame is the same that one need to transform

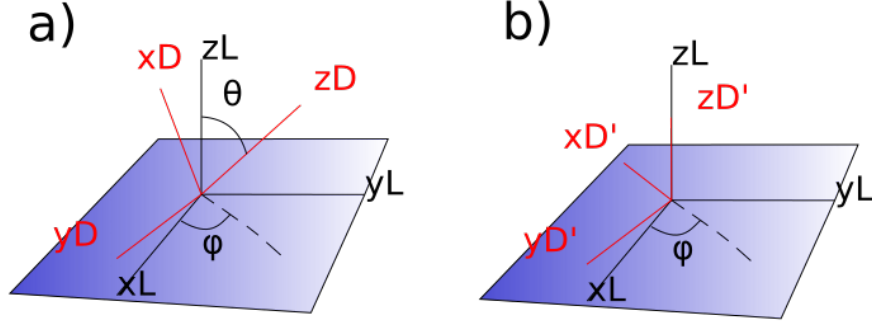


Figure 1.1: Sketch of the laboratory and dipolar frame. a) Initial situation with $y^{(D)}$ on the $x^{(L)}y^{(L)}$ -plane. b) Situation after the first rotation, which is around $y^{(D)}$ and with angle θ . From here another rotation around $z'^{(D)}$ of angle $\pi - \phi$ makes the two coordinate frames coincide.

coordinate systems. Following the zyz convention, to bring the D-frame axes to the laboratory axes we have to apply three rotations with Euler angles (α, β, γ) around the z-, y-, and z-axis respectively (consecutively, always taking the new axes as the frame of reference). In our case, we can arbitrarily choose to have the $y^{(D)}$ -axis on the $x^{(L)}y^{(L)}$ -plane because of the invariance of the initial density matrix. In this way, only two rotations are necessary. As shown in Fig. 1.1, applying a first rotation around $y^{(D)}$ of angle θ one brings $\mathbf{n}_D \equiv z^{(D)}$ to the $z^{(L)}$ -axis, hence also making the $x'^{(D)}y'^{(D)}$ -plane coincide with the $x^{(L)}y^{(L)}$ -plane. With a second rotation around $z'^{(D)} \equiv z^{(L)}$ of angle $\pi - \phi$ one brings $x'^{(D)}$ on $x^{(L)}$ and also $y'^{(D)}$ on $y^{(L)}$.

This means that the Euler angles β and γ to bring the D-frame to the L-frame are equivalent to the angles θ and $\pi - \phi$, respectively. Note that we are transforming from the dipolar frame to the laboratory frame, while usually in the EPR literature the Euler angles are defined as the ones going from the laboratory frame to the molecular one.

The transformation for Euler angles (α, β, γ) , which would consist of the multiplication between the three rotation matrices, would be:

$$\begin{bmatrix} \cos(\gamma) & \sin(\gamma) & 0 \\ -\sin(\gamma) & \cos(\gamma) & 0 \\ 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} \cos(\theta) & 0 & -\sin(\theta) \\ 0 & 1 & 0 \\ \sin(\theta) & 0 & \cos(\theta) \end{bmatrix} \begin{bmatrix} \cos(\alpha) & \sin(\alpha) & 0 \\ -\sin(\alpha) & \cos(\alpha) & 0 \\ 0 & 0 & 1 \end{bmatrix}. \quad (1.2)$$

In our case, we apply two rotations only and, keeping in mind that $\cos(\pi - \phi) = -\cos(\phi)$ and $\sin(\pi - \phi) = \sin(\phi)$, one obtains the rotation matrix:

$$\begin{bmatrix} -\cos(\phi) & \sin(\phi) & 0 \\ -\sin(\phi) & -\cos(\phi) & 0 \\ 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} \cos(\theta) & 0 & -\sin(\theta) \\ 0 & 1 & 0 \\ \sin(\theta) & 0 & \cos(\theta) \end{bmatrix} = \begin{bmatrix} -\cos(\theta)\cos(\phi) & \sin(\phi) & \sin(\theta)\cos(\theta) \\ -\cos(\theta)\sin(\phi) & -\cos(\phi) & \sin(\theta)\sin(\theta) \\ \sin(\theta) & 0 & \cos(\theta) \end{bmatrix} \quad (1.3)$$

One can check quickly if the derivation is correct by applying the rotations (which correspond to a change in reference frame) to $\mathbf{n}_D|_D = [0, 0, 1]_D$:

$$\begin{bmatrix} -\cos(\theta)\cos(\phi) & \sin(\phi) & \sin(\theta)\cos(\theta) \\ -\cos(\theta)\sin(\phi) & -\cos(\phi) & \sin(\theta)\sin(\phi) \\ \sin(\theta) & 0 & \cos(\theta) \end{bmatrix} \begin{bmatrix} 0 \\ 0 \\ 1 \end{bmatrix} = \begin{bmatrix} \cos(\phi)\sin(\theta) \\ \sin(\phi)\sin(\theta) \\ \cos(\theta) \end{bmatrix} \quad (1.4)$$

As expected, the vector $[0, 0, 1]_D$ is transformed to $[\sin(\theta)\cos(\phi) + \sin(\theta)\sin(\phi) + \cos(\theta)]_L$ by the change of reference frame.

1.3 Rotation of isolated operators

In order to express the initial density matrix from any dipolar frame to the laboratory coordinate system we apply the rotations found in the previous chapter to a collection of operators that recur usually. We are now considering rotations of spin-operators, therefore any rotation around the x -, y - or z -axis of given angle δ consists of a transformation using the operator $\exp[i(S_{p,A} + S_{p,B})\delta]$, where $p = x, y, z$ respectively. Therefore, considering a density matrix ρ , the transformation from D-frame coordinates to L-frame coordinates is equal to:

$$\rho|_L = R_z^{-1}(\gamma)R_y^{-1}(\beta)\rho|_D R_y(\beta)R_z(\gamma), \quad (1.5)$$

where the Euler angles are $\beta = \theta$ and $\gamma = \pi - \phi$.

We consider now the following operators:

- S_{zz} ,
- S_{xx} ,
- S_{yy} ,
- $S_{z,A} - S_{z,B}$,
- $S_{z,A} + S_{z,B}$.

Any triplet state, singlet state, $|\uparrow\downarrow\rangle$ and $|\downarrow\uparrow\rangle$ can be expressed as a linear combination of the previous states.

Applying the first rotation (around the y -axis of the D-frame with angle $\beta = \theta$) to these operators, one obtains:

$$\begin{aligned} S_{zz} &\rightarrow \cos^2(\theta)S_{zz} + \sin^2(\theta)S_{xx} + \frac{1}{2}\sin(2\theta)(S_{xz} + S_{zx}), \\ S_{xx} &\rightarrow \cos^2(\theta)S_{xx} + \sin^2(\theta)S_{zz} - \frac{1}{2}\sin(2\theta)(S_{xz} + S_{zx}), \\ S_{yy} &\rightarrow S_{yy}, \\ S_{z,A} - S_{z,B} &\rightarrow \cos(\theta)(S_{z,A} - S_{z,B}) + \sin(\theta)(S_{x,A} - S_{x,B}), \\ S_{z,A} + S_{z,B} &\rightarrow \cos(\theta)(S_{z,A} + S_{z,B}) + \sin(\theta)(S_{x,A} + S_{x,B}). \end{aligned} \quad (1.6)$$

Applying the second rotation (around the z -axis of the new frame with angle γ) to the expressions just obtained, one gets that the operators after the complete

transformation are:

$$\begin{aligned}
S_{zz} &\rightarrow \cos^2(\theta)S_{zz} \\
&\quad + \sin^2(\theta)\cos^2(\gamma)S_{xx} + \sin^2(\theta)\sin^2(\gamma)S_{yy} \\
&\quad + \frac{1}{2}\sin^2(\theta)\sin(2\gamma)(S_{xy} + S_{yx}) \\
&\quad + \frac{1}{2}\sin(2\theta)\cos(\gamma)(S_{xz} + S_{zx}) + \frac{1}{2}\sin(2\theta)\sin(\gamma)(S_{yz} + S_{zy}), \\
S_{xx} &\rightarrow \cos^2(\theta)\cos^2(\gamma)S_{xx} + \cos^2(\theta)\sin^2(\gamma)S_{yy} \\
&\quad + \frac{1}{2}\cos^2(\theta)\sin(2\gamma)(S_{xy} + S_{yx}) \\
&\quad + \sin^2(\theta)S_{zz} \\
&\quad - \frac{1}{2}\sin(2\theta)\cos(\gamma)(S_{xz} + S_{zx}) - \frac{1}{2}\sin(2\theta)\sin(\gamma)(S_{yz} + S_{zy}), \\
S_{yy} &\rightarrow \cos^2(\gamma)S_{yy} + \sin^2(\gamma)S_{xx} \\
&\quad - \frac{1}{2}\sin^2(\theta)\sin(2\gamma)(S_{xy} + S_{yx}) \\
S_{z,A} - S_{z,B} &\rightarrow \cos(\theta)(S_{z,A} - S_{z,B}) \\
&\quad + \sin(\theta)\cos(\gamma)(S_{x,A} - S_{x,B}) + \sin(\theta)\sin(\gamma)(S_{y,A} - S_{y,B}), \\
S_{z,A} + S_{z,B} &\rightarrow \cos(\theta)(S_{z,A} + S_{z,B}) \\
&\quad + \sin(\theta)\cos(\gamma)(S_{x,A} + S_{x,B}) + \sin(\theta)\sin(\gamma)(S_{y,A} + S_{y,B}).
\end{aligned} \tag{1.7}$$

Since $\gamma = \pi - \phi$, using the fact that:

$$\cos(\pi - \phi) = -\cos(\phi),$$

$$\cos^2(\pi - \phi) = [-\cos(\phi)]^2 = \cos^2(\phi),$$

$$\sin(\pi - \phi) = \sin(\phi),$$

$$\sin^2(\pi - \phi) = [\sin(\phi)]^2 = \sin^2(\phi),$$

$$\sin(2(\pi - \phi)) = \sin(2\pi - 2\phi) = \sin(-2\phi) = -\sin(2\phi),$$

the previous expressions can be rewritten as:

$$\begin{aligned}
S_{zz} &\rightarrow \cos^2(\theta)S_{zz} \\
&\quad + \sin^2(\theta)\cos^2(\phi)S_{xx} + \sin^2(\theta)\sin^2(\phi)S_{yy} \\
&\quad - \frac{1}{2}\sin^2(\theta)\sin(2\phi)(S_{xy} + S_{yx}) \\
&\quad - \frac{1}{2}\sin(2\theta)\cos(\phi)(S_{xz} + S_{zx}) + \frac{1}{2}\sin(2\theta)\sin(\phi)(S_{yz} + S_{zy}), \\
S_{xx} &\rightarrow \cos^2(\theta)\cos^2(\phi)S_{xx} + \cos^2(\theta)\sin^2(\phi)S_{yy} \\
&\quad - \frac{1}{2}\cos^2(\theta)\sin(2\phi)(S_{xy} + S_{yx}) \\
&\quad + \sin^2(\theta)S_{zz} \\
&\quad + \frac{1}{2}\sin(2\theta)\cos(\phi)(S_{xz} + S_{zx}) - \frac{1}{2}\sin(2\theta)\sin(\phi)(S_{yz} + S_{zy}), \\
S_{yy} &\rightarrow \cos^2(\phi)S_{yy} + \sin^2(\phi)S_{xx} \\
&\quad + \frac{1}{2}\sin^2(\theta)\sin(2\phi)(S_{xy} + S_{yx}) \\
S_{z,A} - S_{z,B} &\rightarrow \cos(\theta)(S_{z,A} - S_{z,B}) \\
&\quad - \sin(\theta)\cos(\phi)(S_{x,A} - S_{x,B}) + \sin(\theta)\sin(\phi)(S_{y,A} - S_{y,B}), \\
S_{z,A} + S_{z,B} &\rightarrow \cos(\theta)(S_{z,A} + S_{z,B}) \\
&\quad - \sin(\theta)\cos(\phi)(S_{x,A} + S_{x,B}) + \sin(\theta)\sin(\phi)(S_{y,A} + S_{y,B}).
\end{aligned} \tag{1.8}$$

We will now use these results to obtain the initial density matrix expressed in the laboratory frame.

1.4 Initial density matrix in the laboratory coordinate system

Using the results obtained in Eq. 1.8, the initial density matrix in Eq. 1.1 in the laboratory coordinate system is equal to:

$$\begin{aligned}
\rho_{\uparrow\downarrow}|_L = & -\frac{1}{2}\cos^2(\theta)S_{zz} \\
& -\frac{1}{2}\sin^2(\theta)\cos^2(\phi)S_{xx} \\
& -\frac{1}{2}\sin^2(\theta)\sin^2(\phi)S_{yy} \\
& +\frac{1}{4}\sin^2(\theta)\sin(2\phi)(S_{xy}+S_{yx}) \\
& +\frac{1}{4}\sin(2\theta)\cos(\phi)(S_{xz}+S_{zx}) \\
& -\frac{1}{4}\sin(2\theta)\sin(\phi)(S_{yz}+S_{zy}) \\
& +\frac{1}{2}\cos(\theta)(S_{z,A}-S_{z,B}) \\
& -\frac{1}{2}\sin(\theta)\cos(\phi)(S_{x,A}-S_{x,B}) \\
& +\frac{1}{2}\sin(\theta)\sin(\phi)(S_{y,A}-S_{y,B}).
\end{aligned} \tag{1.9}$$

Note that, for the initial state:

$$\rho|_D = \rho_{\downarrow\uparrow} = |\downarrow\uparrow\rangle\langle\downarrow\uparrow| = \frac{1}{2}\left(\frac{1}{2}\mathbb{1} - S_{zz} - S_{z,A} + S_{z,B}\right), \tag{1.10}$$

the density matrix after in the laboratory frame is:

$$\begin{aligned}
\rho_{\downarrow\uparrow}|_L = & -\frac{1}{2}\cos^2(\theta)S_{zz} \\
& -\frac{1}{2}\sin^2(\theta)\cos^2(\phi)S_{xx} \\
& -\frac{1}{2}\sin^2(\theta)\sin^2(\phi)S_{yy} \\
& +\frac{1}{4}\sin^2(\theta)\sin(2\phi)(S_{xy}+S_{yx}) \\
& +\frac{1}{4}\sin(2\theta)\cos(\phi)(S_{xz}+S_{zx}) \\
& -\frac{1}{4}\sin(2\theta)\sin(\phi)(S_{yz}+S_{zy}) \\
& -\frac{1}{2}\cos(\theta)(S_{z,A}-S_{z,B}) \\
& +\frac{1}{2}\sin(\theta)\cos(\phi)(S_{x,A}-S_{x,B}) \\
& -\frac{1}{2}\sin(\theta)\sin(\phi)(S_{y,A}-S_{y,B}),
\end{aligned} \tag{1.11}$$

equal to Eq. 1.9 but with opposite sign for the last three terms. This is the same as setting $\theta \rightarrow \theta + \pi$ in Eq. 1.9.

If one wants to compute the powder averaged signal, one would firstly calculate the contributions given by each one of these terms and then compute the integral over ϕ and θ . One must also keep in mind that there are terms in the Hamiltonian that are angular dependent, in particular θ is present in the expression for the dipolar coupling and the resonance frequencies Ω_A and Ω_B in case of non-isotropic g-factor, while ϕ only appears in the resonance frequencies in case of rhombic g-factor.

Notice that the singlet state is invariant under change of reference frame because $\rho_S = -(S_{zz} + S_{xx} + S_{yy})/2$.

An additional example to check that the transformation is correct: let's consider the $|\uparrow\downarrow\rangle$ state aligned along the $x^{(L)}$ axis. In this case $\theta = \pi/2$ and $\phi = \pi$, therefore if we express the state in the laboratory coordinates using Eq. 1.9 one gets $(-S_{xx} + S_{x,A} - S_{x,B})/2$, which is the same as Eq. 1.1 where $z \rightarrow x$, as expected.

Now we proceed in calculating the ESEEM signal separately for the operators that appear in Eq. 1.9. Since S_{xx} and S_{yy} appear with different prefactors, we will calculate the signals for the sum and the difference of these operators instead. The list of operators under investigation is: S_{zz} , $(S_{xx} + S_{yy})$, $(S_{z,A} - S_{z,B})$, $(S_{xx} - S_{yy})$, $(S_{xy} + S_{yx})$, $(S_{xz} + S_{zx})$, $(S_{yz} + S_{zy})$, $(S_{x,A} - S_{x,B})$, $(S_{y,A} - S_{y,B})$.

Chapter 2

OOP-ESEEM signal for various initial operators

2.1 Spin-Hamiltonian

Assuming that the magnetic field is along the z -axis, $\mathbf{B}_0 = B_0 \mathbf{z}$, one can write the Hamiltonian of the system as:

$$\mathcal{H} = \sum_{j=A,B} \Omega_j S_{z,j} + S_A \cdot \mathbf{D} \cdot S_B + S_A \cdot \mathbf{J} \cdot S_B. \quad (2.1)$$

Following [1], we rewrite this expression as:

$$\mathcal{H} = \Omega_A S_{z,A} + \Omega_B S_{z,B} + (d - J) S_{zz} - \frac{d + 2J}{2} (S_{xx} + S_{yy}), \quad (2.2)$$

where $S_{pq} = 2S_p S_q$, $p, q = x, y, z$, $\Omega_j = g_j \frac{\mu_B B_0}{\hbar} - \omega_{MW}$, $d = \tilde{d}(1 - 3 \cos(\theta)^2)$, $\tilde{d} = \frac{\mu_0}{4\pi\hbar} \frac{g_A g_B \mu_e^2}{r_{AB}^3}$. In the cartesian basis, remembering that $S_{pq} = 2S_p S_q$, the \mathbf{D} and \mathbf{J} tensors are diagonal with elements $[-d, -d, 2d]$ and $[-2J, -2J, -2J]$ respectively.

2.2 OOP-ESEEM sequence

We follow the derivation in [1].

The pulse sequence is lightflash-T- β_x - τ - π_x - τ -echo.

2.3 Free evolution for time T

To calculate the free evolution of the operators it is convenient to transform to the eigenbasis of the spin-Hamiltonian in Eq. 2.2.

2.3.1 Transformation to the eigenbasis

The transformation to the eigenbasis is equal to $\exp[i(S_{xy} - S_{yx})\xi/2]$, where ξ is the mixing angle $\xi = \arctan[(d + 2J)/(\Omega_A - \Omega_B)]$. In this basis the Hamiltonian is:

$$\mathcal{H} = \Omega_S(S_{z,A} + S_{z,B}) + q'(S_{z,A} - S_{z,B}) + (d - J)S_{zz}, \quad (2.3)$$

with $\Omega_S = (\Omega_A + \Omega_B)/2$, $q' = [(\Omega_A - \Omega_B) \cos(\xi) - (d + 2J) \sin(\xi)]/2$. In a frame rotating with frequency Ω_S :

$$\mathcal{H} = q'(S_{z,A} - S_{z,B}) + (d - J)S_{zz}. \quad (2.4)$$

The operators under investigation mentioned in the previous chapter are:

- $\rho 1 = S_{zz}$,
- $\rho 2 = S_{xx} + S_{yy}$,
- $\rho 3 = S_{z,A} - S_{z,B}$,
- $\rho 4 = S_{xx} - S_{yy}$,
- $\rho 5 = S_{xy} + S_{yx}$,
- $\rho 6 = S_{xz} + S_{zx}$,
- $\rho 7 = S_{yz} + S_{zy}$,
- $\rho 8 = S_{x,A} - S_{x,B}$,
- $\rho 9 = S_{y,A} - S_{y,B}$.

They transform to the eigenbasis of the Hamiltonian as follows:

$$\begin{aligned} \rho 1 &\rightarrow S_{zz}, \\ \rho 2 &\rightarrow \cos(\xi)(S_{xx} + S_{yy}) + \sin(\xi)(S_{z,A} - S_{z,B}), \\ \rho 3 &\rightarrow \cos(\xi)(S_{z,A} - S_{z,B}) - \sin(\xi)(S_{xx} + S_{yy}), \\ \rho 4 &\rightarrow S_{xx} - S_{yy}, \\ \rho 5 &\rightarrow S_{xy} + S_{yx}, \\ \rho 6 &\rightarrow \cos(\xi/2)(S_{xz} + S_{zx}) - \sin(\xi/2)(S_{x,A} - S_{x,B}), \\ \rho 7 &\rightarrow \cos(\xi/2)(S_{yz} + S_{zy}) - \sin(\xi/2)(S_{y,A} - S_{y,B}), \\ \rho 8 &\rightarrow \cos(\xi/2)(S_{x,A} - S_{x,B}) + \sin(\xi/2)(S_{xz} + S_{zx}), \\ \rho 9 &\rightarrow \cos(\xi/2)(S_{y,A} - S_{y,B}) + \sin(\xi/2)(S_{yz} + S_{zy}). \end{aligned} \quad (2.5)$$

2.3.2 Free evolution for time T

Under free evolution for a time T, the operators in the previous equations must be propagated using the Hamiltonian in Eq. 2.4. They transform as:

$$\begin{aligned}
\rho 1 &\rightarrow S_{zz}, \\
\rho 2 &\rightarrow \cos(\xi) \cos(2q'T)(S_{xx} + S_{yy}) + \cos(\xi) \sin(2q'T)(S_{xy} + S_{yx}) \\
&\quad + \sin(\xi)(S_{z,A} - S_{z,B}), \\
\rho 3 &\rightarrow \cos(\xi)(S_{z,A} - S_{z,B}) - \sin(\xi) \cos(2q'T)(S_{xx} + S_{yy}) \\
&\quad + \sin(\xi) \sin(2q'T)(S_{xy} - S_{yx}), \\
\rho 4 &\rightarrow S_{xx} - S_{yy}, \\
\rho 5 &\rightarrow S_{xy} + S_{yx}, \\
\rho 6 &\rightarrow [-\sin(\xi/2) \cos[(d-J)T] \cos(q'T) - \cos(\xi/2) \sin[(d-J)T] \sin(q'T)](S_{x,A} - S_{x,B}) \\
&\quad + [-\cos(\xi/2) \sin[(d-J)T] \sin(q'T) + \sin(\xi/2) \cos[(d-J)T] \cos(q'T)](S_{xz} + S_{zx}) \\
&\quad + [\cos(\xi/2) \sin[(d-J)T] \cos(q'T) + \sin(\xi/2) \cos[(d-J)T] \sin(q'T)](S_{yz} - S_{zy}) \\
&\quad + [\cos(\xi/2) \cos[(d-J)T] \sin(q'T) + \sin(\xi/2) \sin[(d-J)T] \cos(q'T)](S_{y,A} + S_{y,B}) \\
\rho 7 &\rightarrow [-\sin(\xi/2) \cos[(d-J)T] \cos(q'T) - \cos(\xi/2) \sin[(d-J)T] \sin(q'T)](S_{y,A} - S_{y,B}) \\
&\quad + [\sin(\xi/2) \sin[(d-J)T] \sin(q'T) + \cos(\xi/2) \cos[(d-J)T] \cos(q'T)](S_{yz} + S_{zy}) \\
&\quad + [-\cos(\xi/2) \cos[(d-J)T] \sin(q'T) + \sin(\xi/2) \sin[(d-J)T] \cos(q'T)](S_{xz} - S_{zx}) \\
&\quad + [-\cos(\xi/2) \sin[(d-J)T] \cos(q'T) + \sin(\xi/2) \cos[(d-J)T] \sin(q'T)](S_{x,A} + S_{x,B}) \\
\rho 8 &\rightarrow [-\cos(\xi/2) \cos[(d-J)T] \cos(q'T) - \sin(\xi/2) \sin[(d-J)T] \sin(q'T)](S_{x,A} - S_{x,B}) \\
&\quad + [-\cos(\xi/2) \sin[(d-J)T] \sin(q'T) + \sin(\xi/2) \cos[(d-J)T] \cos(q'T)](S_{xz} + S_{zx}) \\
&\quad + [\cos(\xi/2) \sin[(d-J)T] \cos(q'T) + \sin(\xi/2) \cos[(d-J)T] \sin(q'T)](S_{yz} - S_{zy}) \\
&\quad + [\cos(\xi/2) \cos[(d-J)T] \sin(q'T) + \sin(\xi/2) \sin[(d-J)T] \cos(q'T)](S_{y,A} + S_{y,B}), \\
\rho 9 &\rightarrow [-\cos(\xi/2) \cos[(d-J)T] \cos(q'T) - \sin(\xi/2) \sin[(d-J)T] \sin(q'T)](S_{y,A} - S_{y,B}) \\
&\quad + [-\cos(\xi/2) \sin[(d-J)T] \sin(q'T) + \sin(\xi/2) \cos[(d-J)T] \cos(q'T)](S_{yz} + S_{zy}) \\
&\quad + [-\cos(\xi/2) \sin[(d-J)T] \cos(q'T) - \sin(\xi/2) \cos[(d-J)T] \sin(q'T)](S_{xz} - S_{zx}) \\
&\quad + [-\cos(\xi/2) \cos[(d-J)T] \sin(q'T) - \sin(\xi/2) \sin[(d-J)T] \cos(q'T)](S_{x,A} + S_{x,B}).
\end{aligned} \tag{2.6}$$

Neglecting the sinusoidal terms containing q' , that will never be refocused due to the fact that the $T \neq \tau$ in the pulse sequence:

$$\begin{aligned}
\rho 1 &\rightarrow S_{zz}, \\
\rho 2 &\rightarrow \sin(\xi)(S_{z,A} - S_{z,B}), \\
\rho 3 &\rightarrow \cos(\xi)(S_{z,A} - S_{z,B}), \\
\rho 4 &\rightarrow S_{xx} - S_{yy}, \\
\rho 5 &\rightarrow S_{xy} + S_{yx}, \\
\rho 6 &\rightarrow 0, \\
\rho 7 &\rightarrow 0, \\
\rho 8 &\rightarrow 0, \\
\rho 9 &\rightarrow 0.
\end{aligned} \tag{2.8}$$

This means that the operators $(S_{xz} + S_{zx})$, $(S_{yz} + S_{zy})$, $(S_{x,A} - S_{x,B})$ and $(S_{y,A} - S_{y,B})$ give no signal.

From here we define $\rho_{23} = A_\xi(S_{z,A} - S_{z,B})$ to express $\rho_2 = \rho_{23}(A_\xi = \sin(\xi))$ and $\rho_3 = \rho_{23}(A_\xi = \cos(\xi))$ and $\rho_{45} = \pm \frac{1}{2}(S_{xx} - S_{yy}) + \frac{1}{2}\sin(\xi)(S_{z,A} - S_{z,B})$ to express ρ_4 and ρ_5 in a compact way.

2.4 Microwave pulse

The microwave pulse is equal to a transformation $\exp[i(S_{x,A} + S_{x,B})\beta]$ in the product basis, therefore it is convenient to bring the density matrices back to this basis, apply the pulse and then transform back again to the eigenbasis.

2.4.1 Transformation to the product basis

This is the inverse of the transformation in Sec. 2.3.1. The operators from Eq. 2.8 transform as follows:

$$\begin{aligned}\rho_1 &\rightarrow S_{zz}, \\ \rho_{23} &\rightarrow A_\xi \cos(\xi)(S_{z,A} - S_{z,B}) + A_\xi \sin(\xi)(S_{xx} + S_{yy}), \\ \rho_4 &\rightarrow S_{xx} - S_{yy} \\ \rho_5 &\rightarrow S_{xy} + S_{yx}.\end{aligned}\tag{2.9}$$

2.4.2 Microwave pulse of turning angle β

Applying the transformation $\exp[i(S_{x,A} + S_{x,B})\beta]$ to the previous operators:

$$\begin{aligned}\rho_1 &\rightarrow \cos^2(\beta)S_{zz} + \sin^2(\beta)S_{yy} - \frac{1}{2}\sin(2\beta)(S_{yz} + S_{zy}), \\ \rho_{23} &\rightarrow \cos(\beta)A_\xi \cos(\xi)(S_{z,A} - S_{z,B}) - \sin(\beta)A_\xi \cos(\xi)(S_{y,A} - S_{y,B}) \\ &\quad + \cos^2(\beta)A_\xi \sin(\xi)S_{yy} + \sin^2(\beta)A_\xi \sin(\xi)S_{zz} \\ &\quad + \frac{1}{2}\sin(2\beta)A_\xi \sin(\xi)(S_{yz} + S_{zy}) \\ &\quad + A_\xi \sin(\xi)S_{xx}, \\ \rho_4 &\rightarrow S_{xx} \\ &\quad - \cos^2(\beta)S_{yy} - \sin^2(\beta)S_{zz} - \frac{1}{2}\sin(2\beta)(S_{yz} + S_{zy}), \\ \rho_5 &\rightarrow \cos(\beta)(S_{xy} + S_{yx}) + \sin(\beta)(S_{xz} + S_{zx}).\end{aligned}\tag{2.10}$$

2.4.3 Transformation to the eigenbasis

Transforming back to the eigenbasis one obtains:

$$\begin{aligned}
\rho 1 &\rightarrow \cos^2(\beta) S_{zz} \\
&\quad + \sin^2(\beta) \cos^2(\xi) S_{yy} \\
&\quad - \sin^2(\beta) \sin^2(\xi) S_{xx} \\
&\quad + \frac{1}{2} \sin^2(\beta) \sin(\xi) (S_{z,A} - S_{z,B}) \\
&\quad - \frac{1}{2} \sin(2\beta) \cos(\xi/2) (S_{yz} + S_{zy}), \\
&\quad + \frac{1}{2} \sin(2\beta) \sin(\xi/2) (S_{y,A} - S_{y,B}), \\
\rho 23 &\rightarrow \cos(\beta) A_\xi \cos(\xi) \cos(\xi) (S_{z,A} - S_{z,B}) - \cos(\beta) A_\xi \cos(\xi) \sin(\xi) (S_{xx} + S_{yy}) \\
&\quad - \sin(\beta) A_\xi \cos(\xi) \cos(\xi/2) (S_{y,A} - S_{y,B}) - \frac{1}{2} \sin(\beta) A_\xi \cos(\xi) \sin(\xi/2) (S_{yz} + S_{zy}) \\
&\quad + \cos^2(\beta) A_\xi \sin(\xi) \cos^2(\xi/2) S_{yy} - \cos^2(\beta) A_\xi \sin(\xi) \sin^2(\xi/2) S_{xx} \\
&\quad + \frac{1}{2} \cos^2(\beta) A_\xi \sin^2(\xi) (S_{z,A} - S_{z,B}) \\
&\quad + \sin^2(\beta) A_\xi \sin(\xi) S_{zz} \\
&\quad + \frac{1}{2} \sin(2\beta) A_\xi \sin(\xi) \cos(\xi/2) (S_{yz} + S_{zy}) - \frac{1}{2} \sin(2\beta) A_\xi \sin(\xi) \sin(\xi/2) (S_{y,A} - S_{y,B}) \\
&\quad + A_\xi \sin(\xi) \cos^2(\xi/2) S_{xx} - A_\xi \sin(\xi) \sin^2(\xi/2) S_{yy} \\
&\quad + \frac{1}{2} A_\xi \sin^2(\xi) (S_{z,A} - S_{z,B}), \\
\rho 4 &\rightarrow \cos^2(\xi/2) S_{xx} - \sin^2(\xi/2) S_{yy} + \frac{1}{2} \sin(\xi) (S_{z,A} - S_{z,B}) \\
&\quad - \cos^2(\beta) \cos^2(\xi/2) S_{yy} + \cos^2(\beta) \sin^2(\xi/2) S_{xx} - \frac{1}{2} \cos^2(\beta) \sin(\xi) (S_{z,A} - S_{z,B}) \\
&\quad - \sin^2(\beta) S_{zz} \\
&\quad - \frac{1}{2} \sin(2\beta) \cos(\xi/2) (S_{yz} + S_{zy}) + \frac{1}{2} \sin(2\beta) \sin(\xi/2) (S_{y,A} - S_{y,B}), \\
\rho 5 &\rightarrow \cos(\beta) (S_{xy} + S_{yx}) \\
&\quad + \sin(\beta) \cos(\xi/2) (S_{xz} + S_{zx}) - \sin(\beta) \sin(\xi/2) (S_{x,A} - S_{x,B}).
\end{aligned} \tag{2.11}$$

We can rewrite these as:

$$\begin{aligned}
\rho 1 &\rightarrow \cos^2(\beta) S_{zz} \\
&\quad + \sin^2(\beta) \cos^2(\xi) S_{yy} \\
&\quad - \sin^2(\beta) \sin^2(\xi) S_{xx} \\
&\quad + \frac{1}{2} \sin^2(\beta) \sin(\xi) (S_{z,A} - S_{z,B}) \\
&\quad - \frac{1}{2} \sin(2\beta) \cos(\xi/2) (S_{yz} + S_{zy}), \\
&\quad + \frac{1}{2} \sin(2\beta) \sin(\xi/2) (S_{y,A} - S_{y,B}), \\
\rho 23 &\rightarrow \left[\cos(\beta) \cos^2(\xi) A_\xi + \frac{1}{2} \cos^2(\beta) A_\xi \sin^2(\xi) + \frac{1}{2} A_\xi \sin^2(\xi) \right] (S_{z,A} - S_{z,B}) \\
&\quad + \sin^2(\beta) A_\xi \sin(\xi) S_{zz} \\
&\quad + \left[-\cos(\beta) A_\xi \cos(\xi) \sin(\xi) + A_\xi \sin(\xi) \cos^2(\xi/2) - \cos^2(\beta) A_\xi \sin(\xi) \sin^2(\xi/2) \right] S_{xx} \\
&\quad + \left[-\cos(\beta) A_\xi \cos(\xi) \sin(\xi) - A_\xi \sin(\xi) \sin^2(\xi/2) + \cos^2(\beta) A_\xi \sin(\xi) \cos^2(\xi/2) \right] S_{yy} \\
&\quad + \left[-\sin(\beta) A_\xi \cos(\xi) \cos(\xi/2) - \frac{1}{2} \sin(2\beta) A_\xi \sin(\xi) \sin(\xi/2) \right] (S_{y,A} - S_{y,B}) \\
&\quad + \left[-\frac{1}{2} \sin(\beta) A_\xi \cos(\xi) \sin(\xi/2) + \frac{1}{2} \sin(2\beta) A_\xi \sin(\xi) \cos(\xi/2) \right] (S_{yz} + S_{zy}), \\
\rho 4 &\rightarrow [\cos^2(\xi/2) + \cos^2(\beta) \sin^2(\xi/2)] S_{xx} \\
&\quad + [-\sin^2(\xi/2) - \cos^2(\beta) \cos^2(\xi/2)] S_{yy} \\
&\quad + \frac{1}{2} \sin(\xi) [1 - \cos^2(\beta)] (S_{z,A} - S_{z,B}) \\
&\quad - \sin^2(\beta) S_{zz} \\
&\quad - \frac{1}{2} \sin(2\beta) \cos(\xi/2) (S_{yz} + S_{zy}) \\
&\quad + \frac{1}{2} \sin(2\beta) \sin(\xi/2) (S_{y,A} - S_{y,B}), \\
\rho 5 &\rightarrow \cos(\beta) (S_{xy} + S_{yx}) \\
&\quad + \sin(\beta) \cos(\xi/2) (S_{xz} + S_{zx}) - \sin(\beta) \sin(\xi/2) (S_{x,A} - S_{x,B}).
\end{aligned} \tag{2.12}$$

Arrived at this point we will calculate each pathway separately.

2.5 Free evolution for time τ , π -pulse, free evolution for time τ

The sequence of free evolution, transformation to product basis, π -pulse, transformation to eigenbasis, time evolution and transformation to product basis do not change the quantum order of the operators. Given the fact that at the end we will take the trace of the product between the density matrices and the $(S_{x,A} + S_{x,B})$ and the $(S_{y,A} + S_{y,B})$ (which are single quantum operators), then we can focus only on the single quantum operators that appear in the previous equation, that is $(S_{yz} + S_{zy})$, $(S_{y,A} - S_{y,B})$, $(S_{xz} + S_{zx})$ and $(S_{x,A} - S_{x,B})$.

Moreover, after all the sequence, the trace will eliminate all terms where operators appear that are different from $(S_{x,A} + S_{x,B})$ and $(S_{y,A} + S_{y,B})$. Therefore the terms in which we are interested after this sequence are:

$$\begin{aligned}
S_{y,A} - S_{y,B} &\rightarrow [-\cos(\xi) \sin(\xi/2) \sin[2(d-J)\tau] \\
&\quad + \cos^2(\xi/2) \sin(\xi/2) \sin[2(d-J)\tau] \cos(2q'\tau) \\
&\quad - \sin(\xi) \sin(\xi/2) \cos[2(d-J)\tau] \sin(2q'\tau)](S_{x,A} + S_{x,B}), \\
S_{yz} + S_{zy} &\rightarrow [-\cos(\xi) \cos(\xi/2) \sin[2(d-J)\tau] \\
&\quad - \sin(\xi/2) \sin(\xi) \sin[2(d-J)\tau] \cos(2q'\tau) \\
&\quad + 2 \sin(\xi/2) \cos^2(\xi/2) \cos[2(d-J)\tau] \sin(2q'\tau)](S_{x,A} + S_{x,B}), \\
S_{x,A} - S_{x,B} &\rightarrow [-\cos(\xi) \sin(\xi/2) \sin[2(d-J)\tau] \\
&\quad + 2 \cos^2(\xi/2) \sin(\xi/2) \sin[2(d-J)\tau] \cos(2q'\tau) \\
&\quad - \sin(\xi) \sin(\xi/2) \cos[2(d-J)\tau] \sin(2q'\tau)](S_{y,A} + S_{y,B}), \\
S_{xz} + S_{zx} &\rightarrow [-\cos(\xi) \cos(\xi/2) \sin[2(d-J)\tau] \\
&\quad - \sin(\xi/2) \sin(\xi) \sin[2(d-J)\tau] \cos(2q'\tau) \\
&\quad + 2 \sin(\xi/2) \cos^2(\xi/2) \cos[2(d-J)\tau] \sin(2q'\tau)](S_{y,A} + S_{y,B}).
\end{aligned} \tag{2.13}$$

Neglecting the fast decaying terms including q' :

$$\begin{aligned}
S_{y,A} - S_{y,B} &\rightarrow [-\cos(\xi) \sin(\xi/2) \sin[2(d-J)\tau]](S_{x,A} + S_{x,B}) \\
S_{yz} + S_{zy} &\rightarrow [-\cos(\xi) \cos(\xi/2) \sin[2(d-J)\tau]](S_{x,A} + S_{x,B}), \\
S_{x,A} - S_{x,B} &\rightarrow [-\cos(\xi) \sin(\xi/2) \sin[2(d-J)\tau]](S_{y,A} + S_{y,B}), \\
S_{xz} + S_{zx} &\rightarrow [-\cos(\xi) \cos(\xi/2) \sin[2(d-J)\tau]](S_{y,A} + S_{y,B}).
\end{aligned} \tag{2.14}$$

2.5.1 Projection on $S_{x,A} + S_{x,B}$ and $S_{y,A} + S_{y,B}$

Plugging the pathways in Eq. 2.14 in Eq. 2.12 and neglecting all the non-single-quantum operators, one obtains:

$$\begin{aligned}
\rho 1 &\rightarrow -\frac{1}{2} \sin(2\beta) \cos(\xi/2) [-\cos(\xi) \cos(\xi/2) \sin[2(d-J)\tau]] (S_{x,A} + S_{x,B}), \\
&\quad + \frac{1}{2} \sin(2\beta) \sin(\xi/2) [-\cos(\xi) \sin(\xi/2) \sin[2(d-J)\tau]] (S_{x,A} + S_{x,B}), \\
\rho 23 &\rightarrow + \left[-\sin(\beta) A_\xi \cos(\xi) \cos(\xi/2) - \frac{1}{2} \sin(2\beta) A_\xi \sin(\xi) \sin(\xi/2) \right] \\
&\quad \times [-\cos(\xi) \sin(\xi/2) \sin[2(d-J)\tau]] (S_{x,A} + S_{x,B}) \\
&\quad + \left[-\sin(\beta) A_\xi \sin(\xi) \sin(\xi/2) + \frac{1}{2} \sin(2\beta) A_\xi \sin(\xi) \cos(\xi/2) \right] \\
&\quad \times [-\cos(\xi) \cos(\xi/2) \sin[2(d-J)\tau]] (S_{x,A} + S_{x,B}) \\
\rho 4 &\rightarrow + \left[\frac{1}{4} \sin(2\beta) [\mp 1 + \sin^2(\xi)] \cos(\xi/2) - \frac{1}{4} \sin(\beta) \sin(2\xi) \sin(\xi/2) \right] \\
&\quad \times [-\cos(\xi) \cos(\xi/2) \sin[2(d-J)\tau]] (S_{x,A} + S_{x,B}) \\
&\quad + \left[-\frac{1}{4} \sin(2\beta) [\mp 1 + \sin^2(\xi)] \sin(\xi/2) - \frac{1}{4} \sin(\beta) \sin(2\xi) \cos(\xi/2) \right] \\
&\quad \times [-\cos(\xi) \sin(\xi/2) \sin[2(d-J)\tau]] (S_{x,A} + S_{x,B}), \\
\rho 6 &\rightarrow + \sin(\beta) \cos(\xi/2) [-\cos(\xi) \cos(\xi/2) \sin[2(d-J)\tau]] (S_{y,A} + S_{y,B}) \\
&\quad - \sin(\beta) \sin(\xi/2) [-\cos(\xi) \sin(\xi/2) \sin[2(d-J)\tau]] (S_{y,A} + S_{y,B}).
\end{aligned} \tag{2.15}$$

Computing the math and projecting (there is a factor of 2 because of $Tr[(S_{x,A} + S_{x,B})(S_{x,A} + S_{x,B})] = Tr[(S_{y,A} + S_{y,B})(S_{y,A} + S_{y,B})] = 2$), one obtains the following results E_x for the magnetization along the x -axis at time equal to $T + 2\tau$:

$$\begin{aligned}
E_x(S_{zz}) &= \cos^2(\xi) \sin[2(d-J)\tau] \sin(2\beta), \\
E_x(S_{xx} + S_{yy}) &= \cos^2(\xi) \sin^2(\xi) \sin[2(d-J)\tau] [2 \sin(\beta) - \sin(2\beta)], \\
E_x(S_{z,A} - S_{z,B}) &= \cos^3(\xi) \sin(\xi) \sin[2(d-J)\tau] [2 \sin(\beta) - \sin(2\beta)], \\
E_x(S_{xx}) &= \sin[2(d-J)\tau] \left[\sin(\beta) \cos^2(\xi) \sin^2(\xi) + \frac{1}{2} \sin(2\beta) \cos^4(\xi) \right], \\
E_x(S_{yy}) &= \sin[2(d-J)\tau] \left[\sin(\beta) \cos^2(\xi) \sin^2(\xi) - \frac{1}{2} \sin(2\beta) \cos^2(\xi) [1 + \sin^2(\xi)] \right], \\
E_x(S_{xy} + S_{yx}) &= 0,
\end{aligned} \tag{2.16}$$

and for E_y magnetization along the y -axis at time equal to $T + 2\tau$:

$$\begin{aligned}
E_y(S_{zz}) &= E_y(S_{xx} + S_{yy}) = E_y(S_{z,A} - S_{z,B}) = E_y(S_{xx} - S_{yy}) = 0, \\
E_y(S_{xy} + S_{yx}) &= -2 \cos^2(\xi) \sin(\beta) \sin[2(d-J)\tau].
\end{aligned} \tag{2.17}$$

We can use these results to obtain the ESEEM signal from various initial density matrices in the next chapter.

Chapter 3

ESEEM for various initial states

3.1 OOP-ESEEM for singlet state

We check if the calculations are correct comparing our results with the ones from Jeschke and Bittl [1]. In order to do this, we write explicitly the OOP-ESEEM signal for a singlet state. Since $\rho_S = 1/2(-S_{zz} - S_{xx} - S_{yy})$, the expected OOP-ESEEM signal is:

$$\begin{aligned} E_x(\rho_S) &= -\frac{1}{2} \sin[2(d-J)\tau] \\ &\times [2 \sin(\beta) \cos^2(\xi) \sin^2(\xi) + \sin(2\beta) [\cos^2(\xi) - \cos^2(\xi) \sin^2(\xi)]] \\ &= -\frac{1}{2} \sin[2(d-J)\tau] \left[\frac{1}{2} \sin(\beta) \sin^2(2\xi) + \sin(2\beta) \cos^4(\xi) \right], \quad (3.1) \end{aligned}$$

as reported in Ref. [1] in Eq. 9.

3.2 OOP-ESEEM for $|\uparrow\downarrow\rangle$ and $|\downarrow\uparrow\rangle$ state

Using the results obtained in Eq. 2.16 and the expression in Eq. 1.1, one obtains that the OOP-ESEEM signal for a $|\uparrow\downarrow\rangle$ state is:

$$E_x = \frac{1}{2} \cos(\xi)^2 \sin[2(d-J)\tau] \left[\sin(\beta) \sin(2\xi) - \sin(2\beta) \frac{2 + \sin(2\xi)}{2} \right]. \quad (3.2)$$

For initial $|\downarrow\uparrow\rangle$ state, using Eq. 1.10, one obtains:

$$E_x = -\frac{1}{2} \cos(\xi)^2 \sin[2(d-J)\tau] \left[\sin(\beta) \sin(2\xi) + \sin(2\beta) \frac{2 - \sin(2\xi)}{2} \right]. \quad (3.3)$$

Eq. 3.2 and 3.3 have are symmetric under the transformation $\xi \rightarrow -\xi$.

3.3 ESEEM for rotated $|\uparrow\downarrow\rangle$ and $|\downarrow\uparrow\rangle$ state

Inserting the results obtained in Eqq. 2.16 and 2.17 in the expression obtained in Eq. 1.9 one obtains for a rotated $|\uparrow\downarrow\rangle$ state:

$$\begin{aligned}
 E_x &= \frac{1}{2} \sin[2(d-J)\tau] \\
 &\quad \left[\sin(\beta) \left(-\frac{1}{2} \sin^2(\theta) \cos^2(\xi) \sin^2(\xi) + 2 \cos(\theta) \cos^3(\xi) \sin(\xi) \right) \right. \\
 &\quad + \sin(2\beta) \left(-\cos^2(\theta) \cos^2(\xi) + \frac{1}{4} \sin^2(\theta) \cos^2(\xi) \sin^2(\xi) \right. \\
 &\quad \left. \left. + \frac{1}{4} \sin^2(\theta) [\cos^2(\phi) - \sin^2(\phi)] \cos^2(\xi) - \cos(\theta) \cos^3(\xi) \sin(\xi) \right) \right], \\
 E_y &= -\frac{1}{2} \sin[2(d-J)\tau] \sin^2(\theta) \sin(2\phi) \cos^2(\xi) \sin(\beta).
 \end{aligned} \tag{3.4}$$

For a rotated $|\downarrow\uparrow\rangle$ state, only the contributions coming from the initial $S_{z,A} - S_{z,B}$ term have opposite sign, therefore one obtains:

$$\begin{aligned}
 E_x &= \frac{1}{2} \sin[2(d-J)\tau] \\
 &\quad \left[\sin(\beta) \left(-\frac{1}{2} \sin^2(\theta) \cos^2(\xi) \sin^2(\xi) - 2 \cos(\theta) \cos^3(\xi) \sin(\xi) \right) \right. \\
 &\quad + \sin(2\beta) \left(-\cos^2(\theta) \cos^2(\xi) + \frac{1}{4} \sin^2(\theta) \cos^2(\xi) \sin^2(\xi) \right. \\
 &\quad \left. \left. + \frac{1}{4} \sin^2(\theta) [\cos^2(\phi) - \sin^2(\phi)] \cos^2(\xi) + \cos(\theta) \cos^3(\xi) \sin(\xi) \right) \right], \\
 E_y &= -\frac{1}{2} \sin[2(d-J)\tau] \sin^2(\theta) \sin(2\phi) \cos^2(\xi) \sin(\beta).
 \end{aligned} \tag{3.5}$$

Expected signal for theta = pi/2, phi = pi/4

Chapter 4

This chapter must be reviewed

4.1 OOP-ESEEM for powder spectrum

To obtain the powder spectrum, one would take the integral over θ and ϕ of Eq. ?? . It must be highlighted that both the dipolar coupling $d = \tilde{d}(1 - 3\cos(\theta)^2)$ and the mixing angle $\xi = \arctan[(d + 2J)/(\Omega_A - \Omega_B)]$ depend on θ . Moreover in case of rhombic g-tensor ξ has an additional dependence on the azimuthal angle ϕ , that enters in the expression for the resonance frequencies. This integration can only be done numerically.

Some consideration about symmetry: the terms proportional to $\cos(\theta)$ and the one proportional to $[\cos^2(\phi) - \sin^2(\phi)]$ will average to 0 after the integration, therefore these can be neglected, giving:

$$E_x = \frac{1}{2} \sin[2(d - J)\tau] \left[-\sin(\beta) \sin^2(\theta) \cos^2(\xi) \sin^2(\xi) + \sin(2\beta) \left(-\cos^2(\theta) \cos^2(\xi) + \frac{1}{4} \sin^2(\theta) \cos^2(\xi) \sin^2(\xi) \right) \right]. \quad (4.1)$$

In the case of non-rhombic g-tensor, the expression becomes independent of ϕ (which enters otherwise in the definition of ξ) and one can integrate Eq. ?? over ϕ , therefore multiplying everything by a factor of 2π :

$$E_x = \pi \sin[2(d - J)\tau] \left[-\sin(\beta) \sin^2(\theta) \cos^2(\xi) \sin^2(\xi) + \sin(2\beta) \left(-\cos^2(\theta) \cos^2(\xi) + \frac{1}{2} \sin^2(\theta) \cos^2(\xi) \sin^2(\xi) \right) \right]. \quad (4.2)$$

This is the same as plugging the results of Eq. 2.16 in Eq. ??.

Note that, while the previously obtained OOP-ESEEM signals for single orientations are proportional to the term $\sin[2(d - J)\tau]$, therefore the shape of the β

dependence is just scaled at different times τ , the powder averaged signal will change shape because it is not directly proportional to $\sin[2(d - J)\tau]$ (due to different terms having different θ dependencies and being summed).

4.2 OOP-ESEEM for donor-chiral bridge-acceptor system

Fig. 4.1 shows the dependence of the signal from the flip-angle β for a system having parameters equal to the ones reported in Ref. [2], that is (notice that J and \tilde{d} values are adjusted to the mathematical convention used here):

$$\begin{aligned} J &= 0.1 \text{ MHz}, \\ \tilde{d} &= 26/r_{AB}^3 \text{ MHz nm}^3, \\ r_{AB} &= 2.48 \text{ nm}, \\ g_A &= [2.0034, 2.0041, 2.0043], \\ g_B &= [2.0031, 2.0044, 2.0046]. \end{aligned} \tag{4.3}$$

Note: in The OOP-ESEEM expected for the donor-chiral bridge-acceptor system used in such reference for initial singlet state using Eq. 3.1, for initial up-down and down-up states, for initial mixture of up-down and down-up states using Eq. ?? and for a powder sample using the numerical integration of Eq. 4.1.

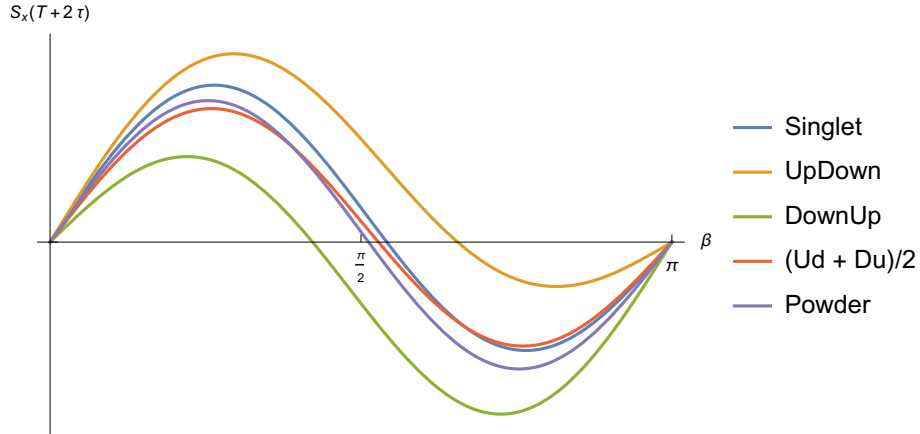


Figure 4.1: OOP-ESEEM signal using the parameters in Eq. 4.3 for initial singlet state ($\theta = 0$), $|\uparrow\downarrow\rangle$ state and $|\downarrow\uparrow\rangle$ and their sum ($\theta = 0$) and for powder average at $\tau = 2 \mu\text{s}$.

4.3 OOP-ESEEM for PS-I system

For Photosystem I, one can use the values reported at page 45 and page 100 of Ref. [3], that is:

$$\begin{aligned} J &= 0.03 \text{ MHz}, \\ \tilde{d} &= -3 \text{ MHz}, \\ g_A &= [2.0033, 2.0024, 2.0020], \\ g_B &= [2.0065, 2.0053, 2.0022]. \end{aligned} \tag{4.4}$$

The OOP-ESEEM signal dependence on β is shown in Fig. 4.2.

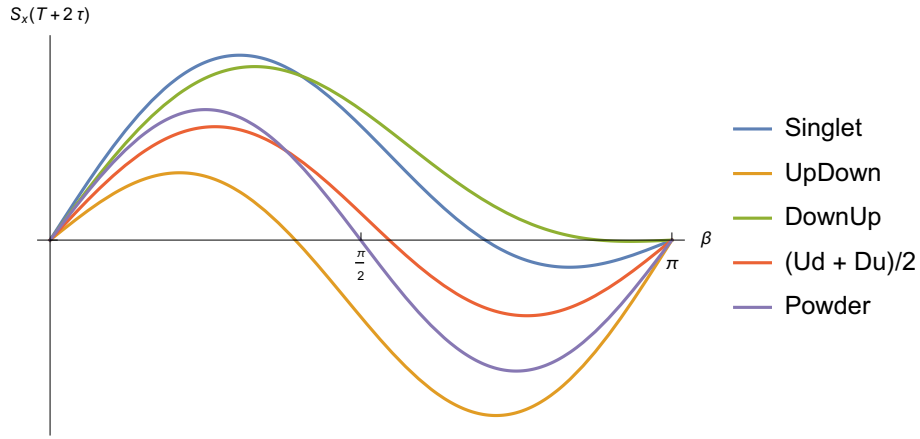


Figure 4.2: OOP-ESEEM signal using the parameters in Eq. 4.4 for initial singlet state ($\theta = 0$), $|\uparrow\downarrow\rangle$ state and $|\downarrow\uparrow\rangle$ and their sum ($\theta = 0$) and for powder average at $\tau = 2 \mu s$.

4.4 OOP-ESEEM powder signal dependence on time τ

As mentioned earlier, the OOP-ESEEM dependence on β is directly proportional to $\sin[2(d - J)\tau]$, meaning that at different times the shape of the curve is preserved and the only thing changing is the multiplication factor. For a powder average this does not hold. In Fig. the OOP-ESEEM dependence on β for different τ values is shown using the parameters of Eq. 4.3. No clear dependence from τ is present.

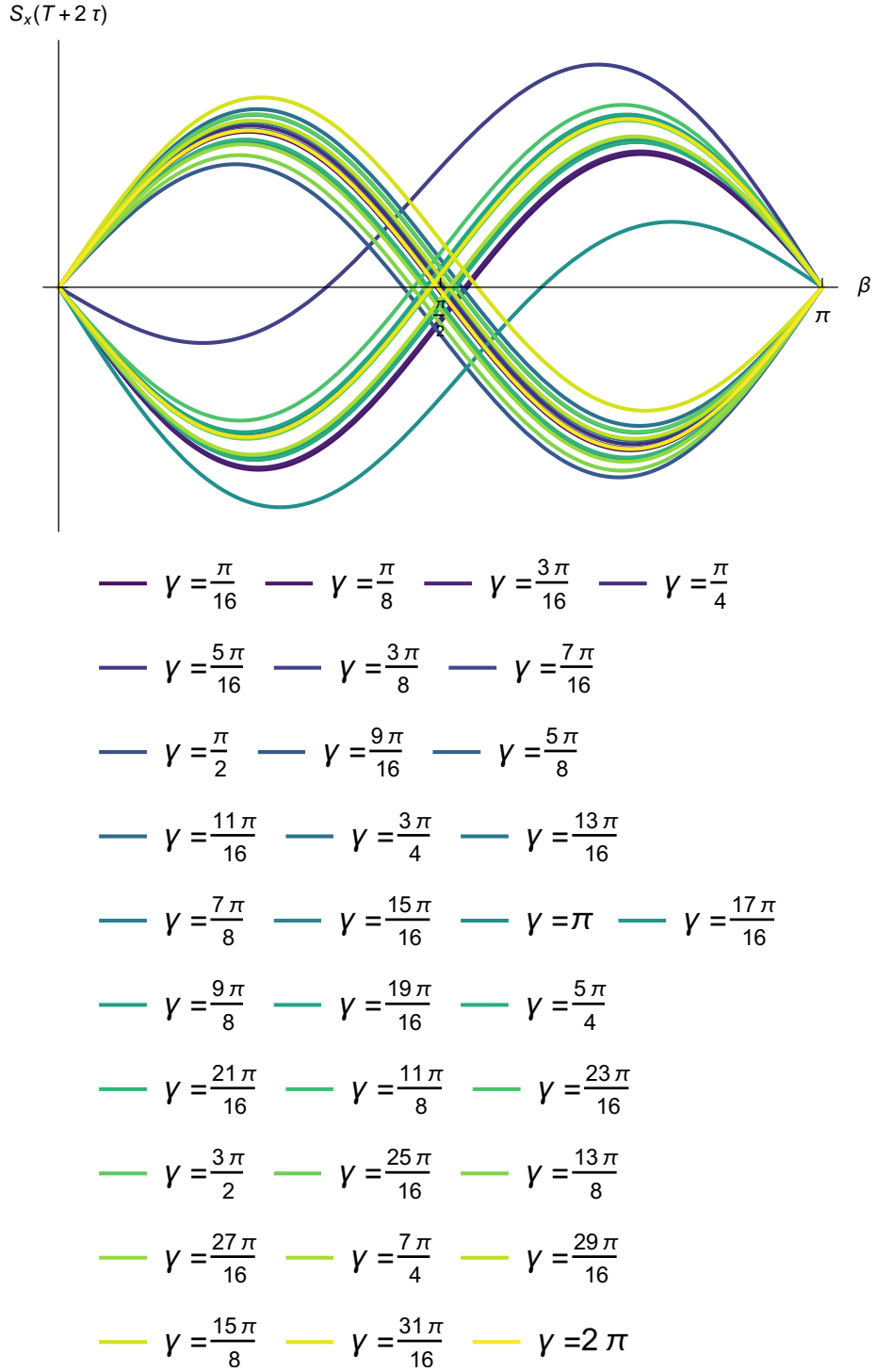


Figure 4.3: OOP-ESEEM signal using the parameters in Eq. 4.3 for powder average at $\gamma = 2(d - J)\tau = 2\pi \cdot n/32$, $n = 1, 2, \dots, 32$.

Bibliography

- [1] Gunnar Jeschke and Robert Bittl. “Electron Spin Echo Envelope Modulation by Electronic Spin–Spin Interactions in Radical Pairs Undergoing Electron Transfer”. In: *Chemical Physics Letters* 294.4-5 (Sept. 1998), pp. 323–331. ISSN: 00092614. DOI: 10.1016/S0009-2614(98)00883-5. URL: <https://linkinghub.elsevier.com/retrieve/pii/S0009261498008835> (visited on 01/16/2024).
- [2] Hannah J. Eckvahl et al. “Direct Observation of Chirality-Induced Spin Selectivity in Electron Donor–Acceptor Molecules”. In: *Science* 382.6667 (Oct. 13, 2023), pp. 197–201. ISSN: 0036-8075, 1095-9203. DOI: 10.1126/science.adj5328. URL: <https://www.science.org/doi/10.1126/science.adj5328> (visited on 01/25/2024).
- [3] “Pulsed and transient electron paramagnetic resonance spectroscopy on light induced radical pairs in photosynthetic reaction centers”. Aachen: Shaker, 1998.