OOP-ESEEM for CISS of photo-generated radical pairs

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Chapter 1

Initial rotation of the spin wavefunction

1.1 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:

$$\mathcal{H} = \Omega_A S_{z,A} + \Omega_B S_{z,B} + (d - J)S_{zz} - \frac{d + 2J}{2}(S_{xx} + S_{yy}), \tag{1.1}$$

where $S_{pq} = 2S_pS_q$, $p, q = x, y, z$, $d = \tilde{d}(1 - 3\cos(\theta)^2)$, $\tilde{d} = \frac{\mu_0}{4\pi h}\frac{g_A g_B \mu_e^2}{r_{AB}^3}$.

1.2 Rotation of wavefunction after CISS electron transfer

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

$$\rho_{\uparrow\downarrow} = |\uparrow\downarrow\rangle\langle\uparrow\downarrow| = \frac{1}{2}\left(\frac{1}{2}\mathbb{1} - S_{zz} + S_{z,A} - S_{z,B}\right). \tag{1.2}$$

We will neglect terms proportional to the identity matrix, since these are invariant under rotations.
In the laboratory frame this state can be expressed applying to the initial state three rotations of Euler angles, as it is usually done in EPR to transform from the molecular frame to the laboratory frame: one rotation around the z-axis, the second one around the new y-axis, and the third around the new z-axis. Since the initial state $|\uparrow\downarrow\rangle$ is invariant under rotations along the

z-axis (because the commutator $[S_{z,A} + S_{z,B}, \rho_{\uparrow\downarrow}] = 0$), then the first rotation can be neglected. This means that in our case the initial rotation boils down to one rotation around the y-axis of polar angle θ and one around the new z-axis of azimuthal angle ϕ. Calling ϕ the azimuthal angle, one can write: $\mathbf{n} = \sin(\theta)\cos(\phi)\mathbf{x} + \sin(\theta)\sin(\phi)\mathbf{y} + \cos(\theta)\mathbf{z}$. If we call η the plane containing both $\mathbf{n}$ and the z-axis, the normal to η will be $\sin(\phi)\mathbf{x} - \cos(\phi)\mathbf{y}$. This is easy to verify for particular cases: if $\mathbf{n} = \mathbf{y}$ ($\mathbf{n} = \mathbf{x}$), then $\phi = \pi/2$ ($\phi = 0$), therefore η coincides with the yz-plane (xz-plane) and its normal is the positive direction of the x-axis (negative direction of the y-axis). Applying a rotation of angle θ along the perpendicular to α, one brings $\mathbf{n}$ to the z-axis.
The rotation around the y-axis consists of a transformation using the operator $\exp\left[i(S_{y,A} + S_{y,B})\theta\right]$. Splitting the rotation of $\rho_{\uparrow\downarrow}$ in steps, one obtains

$$\begin{aligned} S_{zz} &\to \cos^2(\theta)S_{zz} + \sin^2(\theta)S_{xx} + \frac{1}{2}\sin(2\theta)(S_{xz} + S_{zx}) \\ S_{z,A} - S_{z,B} &\to \cos(\theta)(S_{z,A} - S_{z,B}) + \sin(\theta)(S_{x,A} - S_{x,B}). \end{aligned} \tag{1.3}$$

Therefore the density matrix after the first rotation is:

$$\begin{aligned} \rho_{\uparrow\downarrow} = -\frac{1}{2}\cos^2(\theta)S_{zz} - \frac{1}{2}\sin^2(\theta)S_{xx} - \frac{1}{4}\sin(2\theta)(S_{xz} + S_{zx}) \\ + \frac{1}{2}\cos(\theta)(S_{z,A} - S_{z,B}) + \frac{1}{2}\sin(\theta)(S_{x,A} - S_{x,B}). \end{aligned} \tag{1.4}$$

Rotating the terms appearing in Eq. 1.4 around the new z-axis one obtains:

$$\begin{aligned} S_{zz} &\to S_{zz} \\ S_{xx} &\to \cos^2(\phi)S_{xx} + \sin^2(\phi)S_{yy} + \frac{1}{2}\sin(2\phi)(S_{xy} + S_{yx}) \\ S_{xz} + S_{zx} &\to \cos(\phi)(S_{xz} + S_{zx}) + \sin(\phi)(S_{yz} + S_{zy}) \\ S_{z,A} - S_{z,B} &\to S_{z,A} - S_{z,B} \\ S_{x,A} - S_{x,B} &\to \cos(\phi)(S_{x,A} - S_{x,B}) + \sin(\phi)(S_{y,A} - S_{y,B}). \end{aligned} \tag{1.5}$$

Therefore the density matrix after these two rotations is:

$\theta = \frac{\pi}{2}$

$$\begin{aligned} \rho_{\uparrow\downarrow} = &-\frac{1}{2}\cos^2(\theta)S_{zz} \\ &-\frac{1}{2}\sin^2(\theta)\cos^2(\phi)S_{xx} \quad \tfrac{1}{2} \\ &-\frac{1}{2}\sin^2(\theta)\sin^2(\phi)S_{yy} \quad \tfrac{1}{2} \\ &-\frac{1}{4}\sin^2(\theta)\sin(2\phi)(S_{xy} + S_{yx}) \\ &-\frac{1}{4}\sin(2\theta)\cos(\phi)(S_{xz} + S_{zx}) \\ &-\frac{1}{4}\sin(2\theta)\sin(\phi)(S_{yz} + S_{zy}) \\ &+\frac{1}{2}\cos(\theta)(S_{z,A} - S_{z,B}) \\ &+\frac{1}{2}\sin(\theta)\cos(\phi)(S_{x,A} - S_{x,B}) \\ &+\frac{1}{2}\sin(\theta)\sin(\phi)(S_{y,A} - S_{y,B}). \end{aligned} \tag{1.6}$$

Eq. 1.6 describes the initial density matrix when one wants to calculate EPR signals from a specific orientation of the sample, defined by the angles θ and ϕ. 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 of Eq. 2.2 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. If the g-factor is not rhombic, one can do the integral of ϕ, obtaining:~~

both g_i axial and axis $\parallel \vec{d}$?

$$\rho_{\uparrow\downarrow} = \cancel{\pi}\,\frac{1}{2}\left[-\cos^2(\theta)S_{zz} - \frac{1}{2}\sin^2(\theta)(S_{xx} + S_{yy}) + \cos(\theta)(S_{z,A} - S_{z,B})\right]. \quad (1.7)$$

?

Note that, for the initial state:

$$\rho_{\downarrow\uparrow} = |\downarrow\uparrow\rangle\langle\downarrow\uparrow| = \frac{1}{2}\left(\frac{1}{2}\mathbb{1} - S_{zz} - S_{z,A} + S_{z,B}\right), \quad (1.8)$$

the density matrix after the two rotations is:

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

equal to Eq. 1.6 but with different sign for the last three terms. This is the same as setting $\theta \to \theta + \pi$ in Eq. 1.6. After the integral of ϕ, one obtains:

$$\rho_{\downarrow\uparrow} = \pi\left[-\cos^2(\theta)S_{zz} - \frac{1}{2}\sin^2(\theta)(S_{xx} + S_{yy}) - \cos(\theta)(S_{z,A} - S_{z,B})\right]. \quad (1.10)$$

Now we proceed in calculating the OOP-ESEEM signal separately for the operators that appear in Eqq. 1.6, 1.7, 1.9, 1.10: S_{zz}, $\underline{(S_{xx} + S_{yy})}$, $(S_{z,A} - S_{z,B})$, $\underline{S_{yy}}$, S_{xx}, $(S_{xy} + S_{yx})$, $(S_{xz} + S_{zx})$, $(S_{yz} + S_{zy})$, $(S_{x,A} - S_{x,B})$, $(S_{x,A} - S_{x,B})$.

?

Chapter 2

OOP-ESEEM signal for various initial operators

2.1 OOP-ESEEM sequence

We follow the derivation in [1].
The pulse sequence is lightflash-T-β_x-τ-π_x-τ-echo.

2.2 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. 1.1.

2.2.1 Transformation to the eigenbasis

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

$$\mathcal{H} = \Omega_S(S_{z,A} + S_{z,B}) + q'(S_{z,A} - S_{z,B}) + (d - J)S_{zz}. \tag{2.1}$$

In a rotating frame with frequency Ω_S:

$$\mathcal{H} = q'(S_{z,A} - S_{z,B}) + (d - J)S_{zz}. \tag{2.2}$$

The operators that appear in Eq. 1.7 (they will be called for shortness $\rho 1 = S_{zz}$, $\rho 2 = S_{xx} + S_{yy}$, $\rho 3 = S_{z,A} - S_{z,B}$, $\rho 4 = S_{xx}$, $\rho 5 = S_{yy}$, $\rho 6 = (S_{xy} + S_{yx})$, $\rho 7 = (S_{xz} + S_{zx})$, $\rho 8 = (S_{yz} + S_{zy})$, $\rho 9 = (S_{x,A} - S_{x,B})$, $\rho 10 = (S_{y,A} - S_{y,B})$

unfortunately S_{xx} and S_{yy} don't appear with identical prefactors ($\cos^2\phi$ vs. $\sin^2\phi$)

$\cos^2\phi\, S_{xx} + \sin^2\phi\, S_{yy} = \frac{1}{2}\left[(\cos^2\phi + 1 - \sin^2\phi)S_{xx} + (\sin^2\theta + 1 - \cos^2\phi)S_{yy}\right]$

$= \frac{1}{2}\left[\cos^2\phi(S_{xx} - S_{yy}) - \sin^2\phi(S_{xx} - S_{yy}) + S_{xx} + S_{yy}\right] =$

$$-\frac{1}{2}\left[\cos 2\phi\,(S_{xx}-S_{yy}) + (S_{xx}+S_{yy})\right]$$

Better take $(S_{xx}+S_{yy}), (S_{xx}-S_{yy}), (S_{za}-S_{zb})$ instead of $S_1 - S_5$; $(S_{xx}-S_{yy})$ is inert under transformation to the eigenbasis and appears anyway later in S_{45}!

transform to the eigenbasis of the Hamiltonian as follows:

$\cos^2\frac{\xi}{2} - \sin^2\frac{\xi}{2} = \cos\xi$!

$$
\begin{aligned}
\rho 1 \to & S_{zz}, \quad \cdot\left(-\tfrac{1}{2}\right)\cos^2\Theta\\
\rho 2 \to & \cos(\xi)(S_{xx}+S_{yy}) + \sin(\xi)(S_{z,A}-S_{z,B}), \quad -\tfrac{1}{4}\sin^2\Theta\\
\rho 3 \to & \cos(\xi)(S_{z,A}-S_{z,B}) - \sin(\xi)(S_{xx}+S_{yy}), \quad \cdot\left(-\tfrac{1}{2}\cos\Theta\right)\\
\rho 4 \to & \cos^2(\xi/2)S_{xx} - \sin^2(\xi/2)S_{yy} + \frac{1}{2}\sin(\xi)(S_{z,A}-S_{z,B}),\\
& (S_{xx}-S_{yy}) \to (S_{xx}-S_{yy}) \quad \tfrac{1}{2}\sin^2\Theta\cos 2\phi\\
\rho 5 \to & -\sin^2(\xi/2)S_{xx} + \cos^2(\xi/2)S_{yy} + \frac{1}{2}\sin(\xi)(S_{z,A}-S_{z,B}),\\
\rho 6 \to & S_{xy}+S_{yx},\\
\rho 7 \to & \cos(\xi/2)(S_{xz}+S_{zx}) - \sin(\xi/2)(S_{x,A}-S_{x,B}),\\
\rho 8 \to & \cos(\xi/2)(S_{yz}+S_{zy}) - \sin(\xi/2)(S_{y,A}-S_{y,B}),\\
\rho 9 \to & \cos(\xi/2)(S_{x,A}-S_{x,B}) + \sin(\xi/2)(S_{xz}+S_{zx}),\\
\rho 10 \to & \cos(\xi/2)(S_{y,A}-S_{y,B}) + \sin(\xi/2)(S_{yz}+S_{zy}).
\end{aligned}
\tag{2.3}
$$

$H = q'(S_{z,a}-S_{z,b}) + d_{eff} S_{zz}$

2.2.2 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. 2.2. They transform as:

all q are q'

$$
\begin{aligned}
\rho 1 \to & S_{zz},\\
\rho 2 \to & \cos(\xi)\cos(2qT)(S_{xx}+S_{yy}) + \cos(\xi)\sin(2qT)(S_{xy}+S_{yx})\\
& + \sin(\xi)(S_{z,A}-S_{z,B}),\\
\rho 3 \to & \cos(\xi)(S_{z,A}-S_{z,B}) - \sin(\xi)\cos(2qT)(S_{xx}+S_{yy})\\
& + \sin(\xi)\sin(2qT)(S_{xy}-S_{yx}),\\
\rho 4 \to & \frac{1}{2}\cancel{\cos^2(\xi/2)}S_{xx} - \frac{1}{2}\cancel{\cos^2(\xi/2)}S_{yy} \quad \tfrac{1}{2}(S_{xx}-S_{yy})\\
& + \frac{1}{2}\cos(\xi)\left[\cos(2qT)(S_{xx}+S_{yy}) - \frac{1}{2}\cancel{\cos^2(\xi/2)}\sin(2qT)(S_{xy}-S_{yx})\right]\\
& \cancel{- \frac{1}{2}\sin^2(\xi/2)S_{yy} + \frac{1}{2}\sin^2(\xi/2)S_{xx}}\\
& \cancel{- \frac{1}{2}\sin^2(\xi/2)\cos(2qT)(S_{xx}+S_{yy}) + \frac{1}{2}\sin^2(\xi/2)\sin(2qT)(S_{xy}-S_{yx})}\\
& + \frac{1}{2}\sin(\xi)(S_{z,A}-S_{z,B}),\\
\rho 5 \to & -\frac{1}{2}\cancel{\sin^2(\xi/2)}S_{xx} + \frac{1}{2}\cancel{\sin^2(\xi/2)}S_{yy} \quad -\tfrac{1}{2}(S_{xx}-S_{yy})\\
& \cancel{- \frac{1}{2}\sin^2(\xi/2)\cos(2qT)(S_{xx}+S_{yy}) + \frac{1}{2}\sin^2(\xi/2)\sin(2qT)(S_{xy}-S_{yx})}\\
& \cancel{+ \frac{1}{2}\cos^2(\xi/2)S_{yy} - \frac{1}{2}\cos^2(\xi/2)S_{xx}}\\
& + \frac{1}{2}\cos(\xi)\left[\cos(2qT)(S_{xx}+S_{yy}) - \cancel{\frac{1}{2}\cos^2(\xi/2)}\sin(2qT)(S_{xy}-S_{yx})\right]\\
& + \frac{1}{2}\sin(\xi)(S_{z,A}-S_{z,B}),\\
\rho 6 \to & S_{xy}+S_{yx},
\end{aligned}
\tag{2.4}
$$

$(S_{za} - S_{zb})\,qT$ $\quad$ $T\,d\omega\,\xi\,S_{zz}$

$$
\begin{aligned}
\rho7 \to & [-\sin(\xi/2)\cos[(d-J)T]\boxed{\cos(qT)} - \cos(\xi/2)\sin[(d-J)T]\boxed{\sin(qT)}]\boxed{(S_{x,A} - S_{x,B})} \\
& + [-\cos(\xi/2)\sin[(d-J)T]\sin(qT) + \sin(\xi/2)\cos[(d-J)T]\cos(qT)](S_{xz} + S_{zx}) \\
& + [\cos(\xi/2)\sin[(d-J)T]\cos(qT) + \sin(\xi/2)\cos[(d-J)T]\sin(qT)](S_{yz} - S_{zy}) \\
& + [\cos(\xi/2)\cos[(d-J)T]\cos(qT) + \sin(\xi/2)\sin[(d-J)T]\cos(qT)](S_{y,A} + S_{y,B}) \\
\rho8 \to & [-\sin(\xi/2)\cos[(d-J)T]\cos(qT) - \cos(\xi/2)\sin[(d-J)T]\sin(qT)](S_{y,A} - S_{y,B}) \\
& + [\sin(\xi/2)\sin[(d-J)T]\sin(qT) + \cos(\xi/2)\cos[(d-J)T]\cos(qT)](S_{yz} + S_{zy}) \\
& + [-\cos(\xi/2)\cos[(d-J)T]\sin(qT) + \sin(\xi/2)\sin[(d-J)T]\cos(qT)](S_{xz} - S_{zx}) \\
& + [-\cos(\xi/2)\sin[(d-J)T]\cos(qT) + \sin(\xi/2)\cos[(d-J)T]\sin(qT)](S_{x,A} + S_{x,B}) \\
\rho9 \to & [-\cos(\xi/2)\cos[(d-J)T]\cos(qT) - \sin(\xi/2)\sin[(d-J)T]\sin(qT)](S_{x,A} - S_{x,B}) \\
& + [-\cos(\xi/2)\sin[(d-J)T]\sin(qT) + \sin(\xi/2)\cos[(d-J)T]\cos(qT)](S_{xz} + S_{zx}) \\
& + [\cos(\xi/2)\sin[(d-J)T]\cos(qT) + \sin(\xi/2)\cos[(d-J)T]\sin(qT)](S_{yz} - S_{zy}) \\
& + [\cos(\xi/2)\cos[(d-J)T]\sin(qT) + \sin(\xi/2)\sin[(d-J)T]\cos(qT)](S_{y,A} + S_{y,B}), \\
\rho10 \to & [-\cos(\xi/2)\cos[(d-J)T]\cos(qT) - \sin(\xi/2)\sin[(d-J)T]\sin(qT)](S_{y,A} - S_{y,B}) \\
& + [-\cos(\xi/2)\sin[(d-J)T]\sin(qT) + \sin(\xi/2)\cos[(d-J)T]\cos(qT)](S_{yz} + S_{zy}) \\
& + [-\cos(\xi/2)\sin[(d-J)T]\cos(qT) - \sin(\xi/2)\cos[(d-J)T]\sin(qT)](S_{xz} - S_{zx}) \\
& + [-\cos(\xi/2)\cos[(d-J)T]\sin(qT) - \sin(\xi/2)\sin[(d-J)T]\cos(qT)](S_{x,A} + S_{x,B}).
\end{aligned}
\tag{2.5}
$$

Neglecting the sinusoidal terms containing q':

$$
\begin{aligned}
\rho1 \to & S_{zz}, \\
\rho2 \to & \sin(\xi)(S_{z,A} - S_{z,B}), \\
\rho3 \to & \cos(\xi)(S_{z,A} - S_{z,B}), \\
\rho4 \to & \frac{1}{2}(S_{xx} - S_{yy}) + \frac{1}{2}\sin(\xi)(S_{z,A} - S_{z,B}), \\
\rho5 \to & -\frac{1}{2}(S_{xx} - S_{yy}) + \frac{1}{2}\sin(\xi)(S_{z,A} - S_{z,B}), \\
\rho6 \to & S_{xy} + S_{yx}, \\
\rho7 \to & 0, \\
\rho8 \to & 0, \\
\rho9 \to & 0, \\
\cancel{\rho10 \to} & \cancel{0.}
\end{aligned}
\tag{2.6}
$$

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 ~~OOP-ESEEM~~ signal.
From here we define $\rho23 = A_\xi(S_{z,A} - S_{z,B})$ to express $\rho2 = \rho23(A_\xi = \sin(\xi))$ and $\rho3 = \rho23(A_\xi = \cos(\xi))$ and $\rho45 = \pm\frac{1}{2}(S_{xx} - S_{yy}) + \frac{1}{2}\sin(\xi)(S_{z,A} - S_{z,B})$ to express $\rho4$ and $\rho5$ in a compact way.

2.3 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.

2.3.1 Transformation to the product basis

This is the inverse of the transformation in Sec. 2.2.1. The operators from Eq. 2.6 transform as follows:

$$
\begin{aligned}
\rho 1 \to & S_{zz}, \\
\rho 23 \to & A_\xi \cos(\xi)(S_{z,A} - S_{z,B}) + A_\xi \sin(\xi)(S_{xx} + S_{yy}), \\
\rho 45 \to & \frac{1}{2}[\pm 1 + \sin^2(\xi)]S_{xx} + \frac{1}{2}[\mp 1 + \sin^2(\xi)]S_{yy} + \frac{1}{4}\sin(2\xi)(S_{z,A} - S_{z,B}) \\
\rho 6 \to & S_{xy} + S_{yx}.
\end{aligned}
\tag{2.7}
$$

2.3.2 Microwave pulse of turning angle β

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

$$
\begin{aligned}
\rho 1 \to & \cos^2(\beta)\cancel{S_{zz}} + \sin^2(\beta)\cancel{S_{yy}} - \frac{1}{2}\sin(2\beta)(S_{yz} + S_{zy}), \quad \cdot\,(-\cos^2\theta) \\
\rho 23 \to & \cos(\beta)A_\xi \cos(\xi)\cancel{(S_{z,A} - S_{z,B})} - \sin(\beta)A_\xi \cos(\xi)(S_{y,A} - S_{y,B}) \\
& + \cos^2(\beta)A_\xi \sin(\xi)\cancel{S_{yy}} + \sin^2(\beta)A_\xi \sin(\xi)\cancel{S_{zz}} \\
& + \frac{1}{2}\sin(2\beta)A_\xi \sin(\xi)(S_{yz} + S_{zy}) \\
& + A_\xi \sin(\xi)\cancel{S_{xx}}, \\
\rho 45 \to & \frac{1}{2}[\pm 1 + \sin^2(\xi)]S_{xx} \\
& + \frac{1}{2}\cos^2(\beta)[\mp 1 + \sin^2(\xi)]\cancel{S_{yy}} + \frac{1}{2}\sin^2(\beta)[\mp 1 + \sin^2(\xi)]\cancel{S_{zz}} \\
& + \frac{1}{4}\sin(2\beta)[\mp 1 + \sin^2(\xi)](S_{yz} + S_{zy}) \\
& + \frac{1}{4}\cos(\beta)\sin(2\xi)\cancel{(S_{z,A} - S_{z,B})} - \frac{1}{4}\sin(\beta)\sin(2\xi)(S_{y,A} - S_{y,B}) \\
\rho 6 \to & \cos(\beta)\cancel{(S_{xy} + S_{yx})} + \sin(\beta)(S_{xz} + S_{zx}).
\end{aligned}
\tag{2.8}
$$

2.3.3 Transformation to the eigenbasis

Transforming back to the eigenbasis one obtains:

$$
\begin{aligned}
\rho 1 \rightarrow & \cos^2(\beta) S_{zz} \\
& + \sin^2(\beta)\cos^2(\xi) S_{yy} \\
& - \sin^2(\beta)\sin^2(\xi) S_{xx} \\
& + \frac{1}{2}\sin^2(\beta)\sin(\xi)(S_{z,A} - S_{z,B}) \\
& - \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 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}) \\
& - \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}) \\
& + \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} \\
& + \frac{1}{2}\cos^2(\beta) A_\xi \sin^2(\xi)(S_{z,A} - S_{z,B}) \\
& + \sin^2(\beta) A_\xi \sin(\xi) S_{zz} \\
& + \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}) \\
& + A_\xi \sin(\xi)\cos^2(\xi/2) S_{xx} - A_\xi \sin(\xi)\sin^2(\xi/2) S_{yy} \\
& + \frac{1}{2} A_\xi \sin^2(\xi)(S_{z,A} - S_{z,B}), \\
\rho 45 \rightarrow & \frac{1}{2}[\pm 1 + \sin^2(\xi)]\cos^2(\xi/2) S_{xx} - \frac{1}{2}[\pm 1 + \sin^2(\xi)]\sin^2(\xi/2) S_{yy} \\
& + \frac{1}{4}[\pm 1 + \sin^2(\xi)]\sin(\xi)(S_{z,A} - S_{z,B}) \\
& + \frac{1}{2}\cos^2(\beta)[\mp 1 + \sin^2(\xi)]\cos^2(\xi/2) S_{yy} - \frac{1}{2}\cos^2(\beta)[\mp 1 + \sin^2(\xi)]\sin^2(\xi/2) S_{xx} \\
& + \frac{1}{4}\cos^2(\beta)[\mp 1 + \sin^2(\xi)]\sin(\xi)(S_{z,A} - S_{z,B}) \\
& + \frac{1}{2}\sin^2(\beta)[\mp 1 + \sin^2(\xi)] S_{zz} \\
& + \frac{1}{4}\sin(2\beta)[\mp 1 + \sin^2(\xi)]\cos(\xi/2)(S_{yz} + S_{zy}) - \frac{1}{4}\sin(2\beta)[\mp 1 + \sin^2(\xi)]\sin(\xi/2)(S_{y,A} - S_{y,B}) \\
& + \frac{1}{4}\cos(\beta)\sin(2\xi)\cos(\xi)(S_{z,A} - S_{z,B}) - \frac{1}{4}\cos(\beta)\sin(2\xi)\sin(\xi)(S_{xx} + S_{yy}) \\
& - \frac{1}{4}\sin(\beta)\sin(2\xi)\cos(\xi/2)(S_{y,A} - S_{y,B}) - \frac{1}{4}\sin(\beta)\sin(2\xi)\sin(\xi/2)(S_{yz} + S_{zy}), \\
\rho 6 \rightarrow & \cos(\beta)(S_{xy} + S_{yx}) \\
& + \sin(\beta)\cos(\xi/2)(S_{xz} + S_{zx}) - \sin(\beta)\sin(\xi/2)(S_{x,A} - S_{x,B}).
\end{aligned}
\tag{2.9}
$$

We can rewrite these as:

$$
\begin{aligned}
\rho 1 \rightarrow & \cos^2(\beta) S_{zz} \\
& + \sin^2(\beta)\cos^2(\xi) S_{yy} \\
& - \sin^2(\beta)\sin^2(\xi) S_{xx} \\
& + \frac{1}{2}\sin^2(\beta)\sin(\xi)(S_{z,A} - S_{z,B}) \\
& - \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 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}) \\
& + \sin^2(\beta) A_\xi \sin(\xi) S_{zz} \\
& + \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} \\
& + \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} \\
& + \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}) \\
& + \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 45 \rightarrow & \left[\frac{1}{2}[\pm 1 + \sin^2(\xi)]\cos^2(\xi/2) - \frac{1}{2}\cos^2(\beta)[\mp 1 + \sin^2(\xi)]\sin^2(\xi/2) - \frac{1}{4}\cos(\beta)\sin(2\xi)\sin(\xi)\right] S_{xx} \\
& + \left[\frac{1}{2}[\pm 1 + \sin^2(\xi)]\sin^2(\xi/2) + \frac{1}{2}\cos^2(\beta)[\mp 1 + \sin^2(\xi)]\cos^2(\xi/2) - \frac{1}{4}\cos(\beta)\sin(2\xi)\sin(\xi)\right] S_{yy} \\
& + \left[\frac{1}{4}[\pm 1 + \sin^2(\xi)]\sin(\xi) + \frac{1}{4}\cos^2(\beta)[\mp 1 + \sin^2(\xi)]\sin(\xi) + \frac{1}{4}\cos(\beta)\sin(2\xi)\cos(\xi)\right](S_{z,A} - S_{z,B}) \\
& + \frac{1}{2}\sin^2(\beta)[\mp 1 + \sin^2(\xi)] S_{zz} \\
& + \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](S_{yz} + S_{zy}) \\
& + \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](S_{y,A} - S_{y,B}), \\
\rho 6 \rightarrow & \cos(\beta)(S_{xy} + S_{yx}) \\
& + \sin(\beta)\cos(\xi/2)(S_{xz} + S_{zx}) - \sin(\beta)\sin(\xi/2)(S_{x,A} - S_{x,B}).
\end{aligned}
\tag{2.10}
$$

Arrived at this point we will calculate each pathway separately.

2.4 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 ~~scalar~~ 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:

$$\begin{aligned}
S_{y,A}-S_{y,B} \rightarrow & [-\cos(\xi)\sin(\xi/2)\sin[2(d-J)\tau] \\
& +\cos^2(\xi/2)\sin(\xi/2)\sin[2(d-J)\tau]\cos(2q'\tau) \\
& -\sin(\xi)\sin(\xi/2)\cos[2(d-J)\tau]\sin(2q'\tau)](S_{x,A}+S_{x,B}), \\
S_{yz}+S_{zy} \rightarrow & [-\cos(\xi)\cos(\xi/2)\sin[2(d-J)\tau] \\
& -\sin(\xi/2)\sin(\xi)\sin[2(d-J)\tau]\cos(2q'\tau) \\
& +2\sin(\xi/2)\cos^2(\xi/2)\cos[2(d-J)\tau]\sin(2q'\tau)](S_{x,A}+S_{x,B}), \\
S_{x,A}-S_{x,B} \rightarrow & [-\cos(\xi)\sin(\xi/2)\sin[2(d-J)\tau] \\
& +2\cos^2(\xi/2)\sin(\xi/2)\sin[2(d-J)\tau]\cos[\overset{2q'}{2(d-J)}\tau] \quad ? \\
& -\sin(\xi)\sin(\xi/2)\cos[2(d-J)\tau]\sin(2q'\tau)](S_{y,A}+S_{y,B}), \\
S_{xz}+S_{zx} \rightarrow & [-\cos(\xi)\cos(\xi/2)\sin[2(d-J)\tau] \\
& -\sin(\xi/2)\sin(\xi)\sin[2(d-J)\tau]\cos(2q'\tau) \\
& +2\sin(\xi/2)\cos^2(\xi/2)\cos[2(d-J)\tau]\sin(2q'\tau)](S_{y,A}+S_{y,B}).
\end{aligned} \tag{2.11}$$

Neglecting the fast decaying terms including q:

$$\begin{aligned}
S_{y,A}-S_{y,B} \rightarrow & [-\cos(\xi)\sin(\xi/2)\sin[2(d-J)\tau]](S_{x,A}+S_{x,B}) \\
S_{yz}+S_{zy} \rightarrow & [-\cos(\xi)\cos(\xi/2)\sin[2(d-J)\tau]](S_{x,A}+S_{x,B}), \\
S_{x,A}-S_{x,B} \rightarrow & [-\cos(\xi)\sin(\xi/2)\sin[2(d-J)\tau]](S_{y,A}+S_{y,B}), \\
S_{xz}+S_{zx} \rightarrow & [-\cos(\xi)\cos(\xi/2)\sin[2(d-J)\tau]](S_{y,A}+S_{y,B}).
\end{aligned} \tag{2.12}$$

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

Plugging the pathways in Eq. 2.12 in Eq. 2.10 and neglecting all the non-single-quantum operators, one obtains:

S_{zz}

$$
\begin{aligned}
\rho 1 \rightarrow & -\frac{1}{2}\sin(2\beta)\cos(\xi/2)[-\cos(\xi)\cos(\xi/2)\sin[2(d-J)\tau]](S_{x,A}+S_{x,B}),\\
& +\frac{1}{2}\sin(2\beta)\sin(\xi/2)[-\cos(\xi)\sin(\xi/2)\sin[2(d-J)\tau]](S_{x,A}+S_{x,B}),\\
\rho 2 \rightarrow & + \left[-\sin(\beta)A_\xi\cos(\xi)\cos(\xi/2) - \frac{1}{2}\sin(2\beta)A_\xi\sin(\xi)\sin(\xi/2)\right]\\
& \times[-\cos(\xi)\sin(\xi/2)\sin[2(d-J)\tau]](S_{x,A}+S_{x,B})\\
& + \left[-\sin(\beta)A_\xi\sin(\xi)\sin(\xi/2) + \frac{1}{2}\sin(2\beta)A_\xi\sin(\xi)\cos(\xi/2)\right]\\
& \times[-\cos(\xi)\cos(\xi/2)\sin[2(d-J)\tau]](S_{x,A}+S_{x,B})\\
\rho 4 \rightarrow & + \left[\frac{1}{4}\sin(2\beta)[\mp 1+\sin^2(\xi)]\cos(\xi/2) - \frac{1}{4}\sin(\beta)\sin(2\xi)\sin(\xi/2)\right]\\
& \times[-\cos(\xi)\cos(\xi/2)\sin[2(d-J)\tau]](S_{x,A}+S_{x,B})\\
& + \left[-\frac{1}{4}\sin(2\beta)[\mp 1+\sin^2(\xi)]\sin(\xi/2) - \frac{1}{4}\sin(\beta)\sin(2\xi)\cos(\xi/2)\right]\\
& \times[-\cos(\xi)\sin(\xi/2)\sin[2(d-J)\tau]](S_{x,A}+S_{x,B}),\\
\rho 6 \rightarrow & + \sin(\beta)\cos(\xi/2)[-\cos(\xi)\cos(\xi/2)\sin[2(d-J)\tau]](S_{y,A}+S_{y,B})\\
& - \sin(\beta)\sin(\xi/2)[-\cos(\xi)\sin(\xi/2)\sin[2(d-J)\tau]](S_{y,A}+S_{y,B}).
\end{aligned}
\tag{2.13}
$$

$= 0$?

$-\cos^2\frac{\xi}{2} + \sin^2\frac{\xi}{2} = -\cos\xi$

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 $T+2\tau$:

$$
\begin{aligned}
E_x(S_{zz}) =& \cos^2(\xi)\sin[2(d-J)\tau]\sin(2\beta),\\
E_x(S_{xx}+S_{yy}) =& \cos^2(\xi)\sin^2(\xi)\sin[2(d-J)\tau][2\sin(\beta)-\sin(2\beta)],\\
E_x(S_{z,A}-S_{z,B}) =& \cos^3(\xi)\sin(\xi)\sin[2(d-J)\tau][2\sin(\beta)-\sin(2\beta)],\\
E_x(S_{xx}) =& \sin[2(d-J)\tau]\left[\sin(\beta)\cos^2(\xi)\sin^2(\xi)+\frac{1}{2}\sin(2\beta)\cos^4(\xi)\right],\\
E_x(S_{yy}) =& \sin[2(d-J)\tau]\left[\sin(\beta)\cos^2(\xi)\sin^2(\xi)-\frac{1}{2}\sin(2\beta)\cos^2(\xi)[1+\sin^2(\xi)]\right],\\
E_x(S_{xy}+S_{yx}) =& 0,
\end{aligned}
\tag{2.14}
$$

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

$$
\begin{aligned}
E_y(S_{zz}) =& E_y(S_{xx}+S_{yy}) = E_y(S_{z,A}-S_{z,B}) = E_y(S_{xx}) = E_y(S_{yy}) = 0,\\
E_y(S_{xy}+S_{yx}) =& 2\cos^2(\xi)\sin(\beta)\sin[2(d-J)\tau].
\end{aligned}
\tag{2.15}
$$

$-$? !

Arrived at this point, we can check if part of 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:

$$\begin{aligned} E_x(\rho_S) = &-\frac{1}{2}\sin[2(d-J)\tau] \\ &\times \left[2\sin(\beta)\cos^2(\xi)\sin^2(\xi) + \sin(2\beta)[\cos^2(\xi) - \cos^2(\xi)\sin^2(\xi)]\right] \\ &= -\frac{1}{2}\sin[2(d-J)\tau]\left[\frac{1}{2}\sin(\beta)\sin^2(2\xi) + \sin(2\beta)\cos^4(\xi)\right], \end{aligned} \tag{2.16}$$

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

Chapter 3

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

3.1 OOP-ESEEM for $|\uparrow\downarrow\rangle$ state

Using the results obtained in Eq. 2.14 and the expression in Eq. 1.2, one obtains that the OOP-ESEEM signal for a $|\uparrow\downarrow\rangle$ state is:

$$E_x = \frac{1}{2}\cos(\xi)^2 \sin[2(d-J)\tau]\left[\sin(\beta)\sin(2\xi) - \sin(2\beta)\frac{2+\sin(2\xi)}{2}\right]. \tag{3.1}$$

For initial $|\downarrow\uparrow\rangle$ state, using Eq. 1.8, one obtains:

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

Notice that this last equation could also be obtained from Eq. 1.6 for $\theta = \pi$. Moreover Eqq. 3.1 and 3.2 have a stronger symmetry, since ~~one~~ they can be obtained from the other with the transformation $\xi \to -\xi$.

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

Inserting the results obtained in Eqq. 2.14 and 2.15 in the expression obtained in Eq. 1.6 one obtains:

$$\begin{aligned}
E_x = &\frac{1}{2}\sin[2(d-J)\tau] \\
&\left[\sin(\beta)\left(-\frac{1}{2}\sin^2(\theta)\cos^2(\xi)\sin^2(\xi) + 2\cos(\theta)\cos^3(\xi)\sin(\xi)\right)\right. \\
&+\sin(2\beta)\Bigg(-\cos^2(\theta)\cos^2(\xi) + \frac{1}{4}\sin^2(\theta)\cos^2(\xi)\sin^2(\xi) \\
&\left.+\frac{1}{4}\sin^2(\theta)\cos^2(\xi)[\cos^2(\phi) - \sin^2(\phi)] - \cos(\theta)\cos^3(\xi)\sin(\xi)\Bigg)\right].
\end{aligned} \tag{3.3}$$

3.3 OOP-ESEEM for powder spectrum

To obtain the powder spectrum, one would take the integral over θ and ϕ of Eq. 3.3. 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:

? no, because d and ξ depend on θ, φ

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

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. 3.3 over ϕ, therefore multiplying everything by a factor of 2π:

$$\begin{aligned} E_x =& \pi\sin[2(d-J)\tau] \\ & \Bigg[-\sin(\beta)\sin^2(\theta)\cos^2(\xi)\sin^2(\xi) \\ & + \sin(2\beta)\Bigg(-\cos^2(\theta)\cos^2(\xi) + \frac{1}{2}\sin^2(\theta)\cos^2(\xi)\sin^2(\xi)\Bigg)\Bigg]. \end{aligned} \tag{3.5}$$

This is the same as plugging the results of Eq. 2.14 in Eq. 1.7.
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).

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

Fig. 3.1 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):

$$\begin{aligned} J =& 0.1 \text{ MHz}, \\ \tilde{d} =& 26/r_{AB}^3 \text{ MHz nm}^3, \\ r_{AB} =& 2.48 \text{ nm}, \\ g_A =& [2.0034, 2.0041, 2.0043], \\ g_B =& [2.0031, 2.0044, 2.0046]. \end{aligned} \tag{3.6}$$

Note: in The OOP-ESEEM expected for the donor-chiral bridge-acceptor system used in such reference for initial singlet state using Eq. 2.16, for initial up-down and down-up states, for initial mixture of up-down and down-up states using Eq. 3.1 and for a powder sample using the numerical integration of Eq. 3.4.

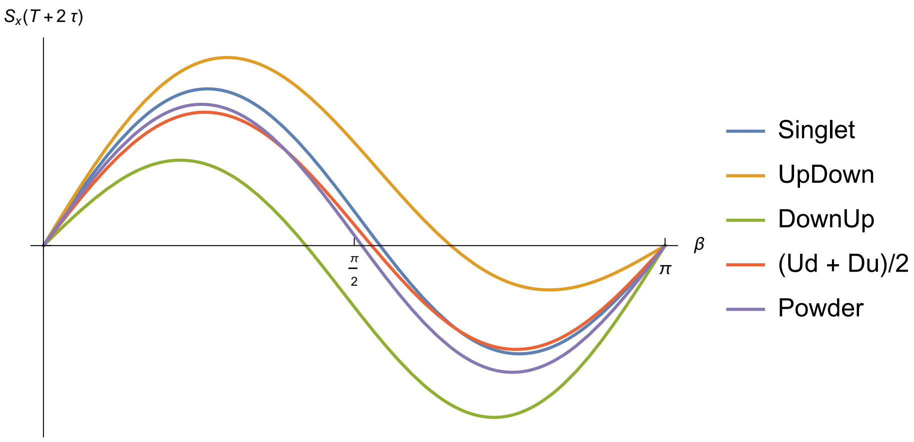

Figure 3.1: OOP-ESEEM signal using the parameters in Eq. 3.6 for initial singlet state ($\theta = 0$), $|\uparrow\downarrow\rangle$ state and $|\downarrow\uparrow\rangle$ and their sum ($\theta = 0$) and for powder average at $\tau = 2\ \mu$s.

3.5 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:

$$\begin{aligned} J =& 0.03 \text{ MHz}, \\ \tilde{d} =& -3 \text{ MHz}, \\ g_A =& [2.0033, 2.0024, 2.0020], \\ g_B =& [2.0065, 2.0053, 2.0022]. \end{aligned} \tag{3.7}$$

The OOP-ESEEM signal dependence on β is shown in Fig. 3.2.

3.6 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. 3.6. No clear dependence from τ is present.

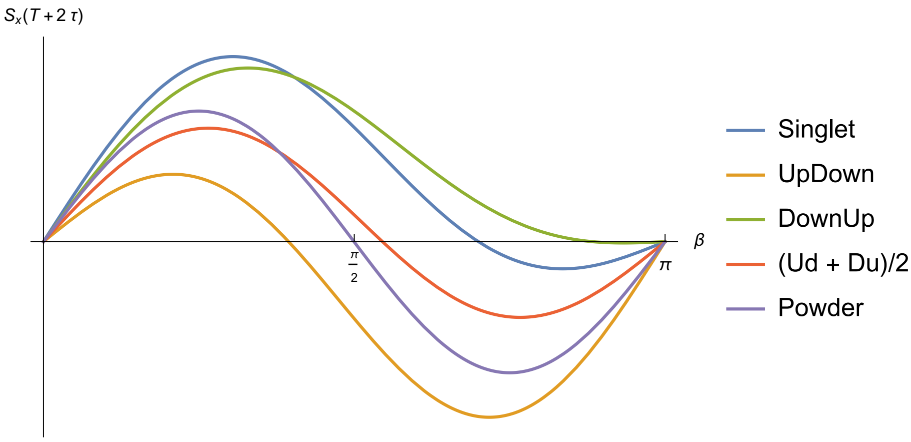

Figure 3.2: OOP-ESEEM signal using the parameters in Eq. 3.7 for initial singlet state ($\theta = 0$), $|\uparrow\downarrow\rangle$ state and $|\downarrow\uparrow\rangle$ and their sum ($\theta = 0$) and for powder average at $\tau = 2\ \mu$s.

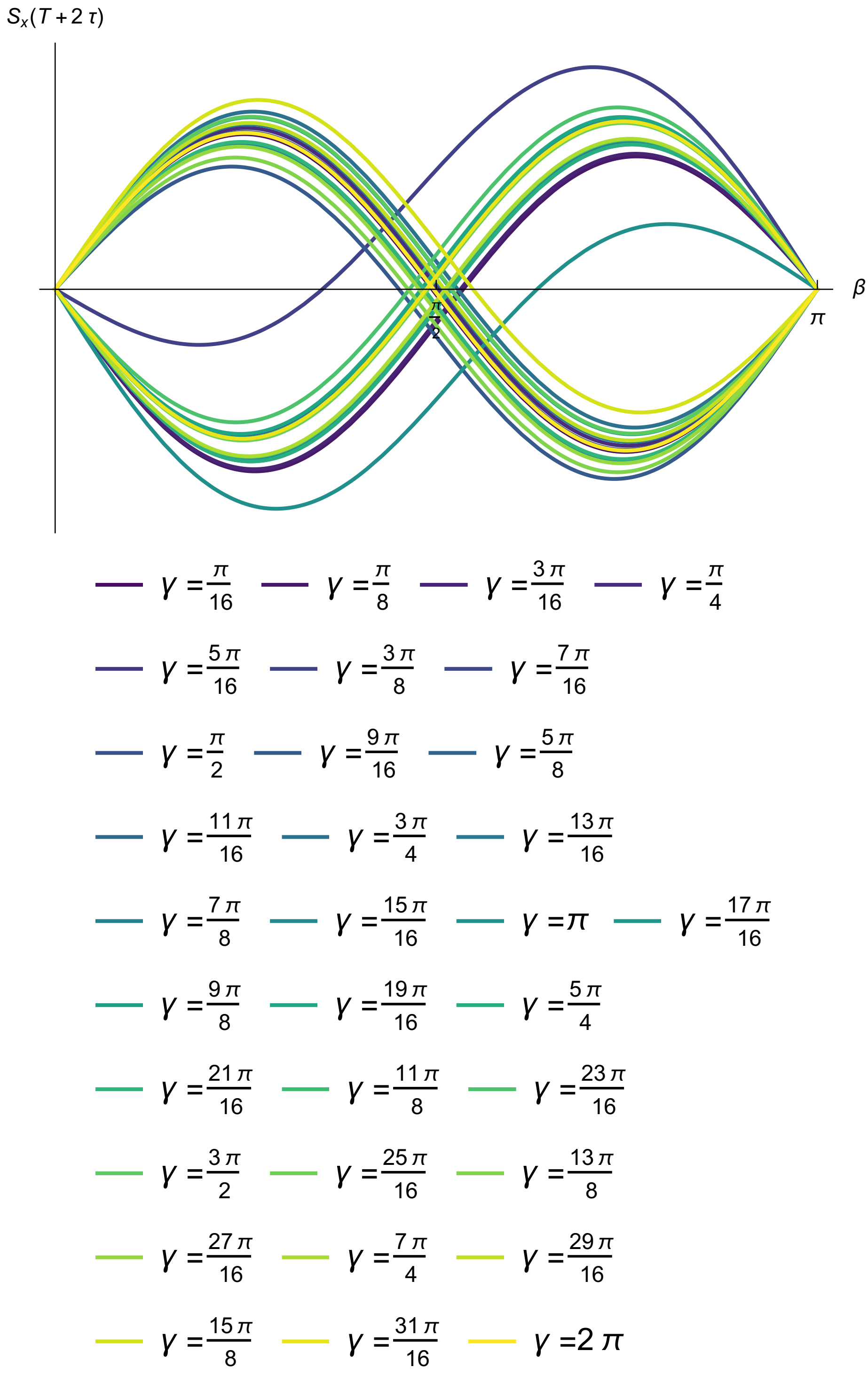

Figure 3.3: OOP-ESEEM signal using the parameters in Eq. 3.6 for powder average at $\gamma = 2(d-J)\tau = 2\pi \cdot n/32$, $n = 1, 2 \ldots 32$.

Bibliography

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[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).

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