OOP-ESEEM for CISS of photo-generated radical pairs

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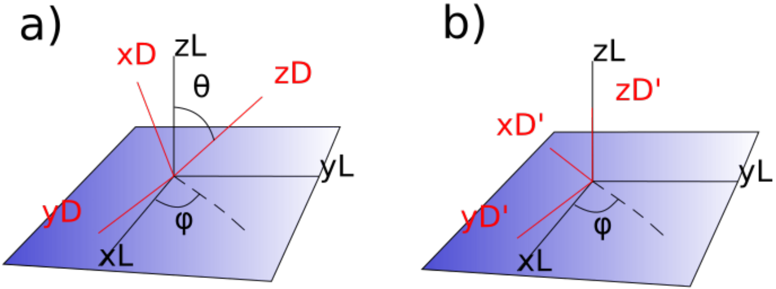
Euler angles

- χ axis $\equiv$ dipolar axis $\equiv$ zD
- initial condition: $|\uparrow\downarrow(\mathbf{n})\rangle$
- change of coordinate system: from dipolar frame (D) to laboratory frame (L)



$$R = R_2 \circ R_1,$$

$$R_1 = R_{yD}(\theta),\ R_2 = R_{zD'}(\pi - \varphi)$$

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

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

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$$R_1 = e^{\left[i(S_{y,A}+S_{y,B})\theta\right]},\ R_2 = e^{\left[i(S_{z,A}+S_{z,B})(\pi-\phi)\right]}$$

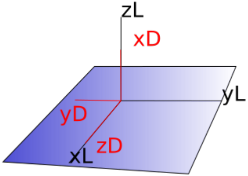
$$\rho|_L = R_2^{-1} R_1^{-1} \rho|_D R_1 R_2$$

Euler angles

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

Euler angles

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



If $\theta = \pi/2$ and $\phi = \pi$:
$\rho|_L = [-S_{xx} + S_{x,A} - S_{x,B}]/2$

Hamiltonian and pulse sequence

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

Hamiltonian and pulse sequence

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

- Transform to the eigenbasis (therefore $\mathcal{H}$ becomes diagonal):

$$U_\xi = e^{[i(S_{xy}-S_{yx})\xi/2]}$$

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

with $\xi = \arctan[(d+2J)/(\Omega_A-\Omega_B)]$, $\Omega_S = (\Omega_A+\Omega_B)/2$,
$q' = [(\Omega_A-\Omega_B)\cos(\xi) - (d+2J)\sin(\xi)]/2$.

Hamiltonian and pulse sequence

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- Transform to the eigenbasis (therefore $\mathcal{H}$ becomes diagonal):

$$U_\xi = e^{[i(S_{xy} - S_{yx})\xi/2]}$$

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

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

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

Hamiltonian and pulse sequence

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

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In the rotating frame:

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The pulse sequence consists in: lightflash-T-β_x-τ-π_x-τ-echo.

Evolution for isolated operators: part 1

Part 1: lightflash and free evolution for time T.

1. Transform the operator to the eigenbasis of $\mathcal{H}$
2. Propagation: $\exp[-i\mathcal{H}T]\rho\exp[i\mathcal{H}T]$
3. Fast oscillating approx.: drop all the term $\propto$ sinusoidal of q'

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

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

Evolution for isolated operators: part 1

After part 1 of the pulse sequence:

Initial operator		After part 1
S_{zz}	$\rightarrow$	S_{zz}
$S_{xx} + S_{yy}$	$\rightarrow$	$\sin(\xi)(S_{z,A} - S_{z,B})$
$S_{z,A} - S_{z,B}$	$\rightarrow$	$\cos(\xi)(S_{z,A} - S_{z,B})$
$S_{xx} - S_{yy}$	$\rightarrow$	$S_{xx} - S_{yy}$
$S_{xy} + S_{yx}$	$\rightarrow$	$S_{xy} + S_{yx}$
$S_{xz} + S_{zx}$	$\rightarrow$	0
$S_{yz} + S_{zy}$	$\rightarrow$	0
$S_{x,A} - S_{x,B}$	$\rightarrow$	0
$S_{y,A} - S_{y,B}$	$\rightarrow$	0

Evolution for isolated operators: part 2

Part 2: β_x pulse.

1. Transform back to cartesian basis (inverse of transformation to the eigenbasis of $\mathcal{H}$)
2. Pulse along x-axis with flipping angle β
3. Transform to the eigenbasis of $\mathcal{H}$

Evolution for isolated operators: part 2

Part 2: β_x pulse.

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- The initial operators S_{zz}, $S_{xx} + S_{yy}$, $S_{z,A} - S_{z,B}$, $S_{xx} - S_{yy}$: get terms proportional to: S_{zz}, S_{xx}, S_{yy}, $S_{z,A} - S_{z,B}$ $S_{yz} + S_{zy}$, $S_{y,A} - S_{y,B}$
- The initial operator $S_{xy} + S_{yx}$ gets terms proportional to $S_{xy} + S_{yx}$, $S_{xz} + S_{zx}$, $S_{x,A} - S_{x,B}$

Evolution for isolated operators: part 3

Part 3: free evolution for time τ, π_x-pulse, free evolution for τ.

1. Free evolution (propagation: $\exp[-i\mathcal{H}T]\rho\exp[i\mathcal{H}T]$)
2. Transform to cartesian basis
3. π_x-pulse
4. Transform to eigenbasis of $\mathcal{H}$
5. Free evolution (propagation: $\exp[-i\mathcal{H}T]\rho\exp[i\mathcal{H}T]$)
6. Fast oscillating approx.: drop all the term $\propto$ sinusoidal of q'
7. Transform to cartesian basis

Evolution for isolated operators: part 3

Part 3: free evolution for time τ, π_x-pulse, free evolution for τ.

1. Free evolution (propagation: $\exp[-i\mathcal{H}T]\rho\exp[i\mathcal{H}T]$)
2. Transform to cartesian basis
3. π_x-pulse
4. Transform to eigenbasis of $\mathcal{H}$
5. Free evolution (propagation: $\exp[-i\mathcal{H}T]\rho\exp[i\mathcal{H}T]$)
6. Fast oscillating approx.: drop all the term $\propto$ sinusoidal of q'
7. Transform to cartesian basis

- This part of the sequence does not change the quantum order of the operators
- To get the signal at the end we do: $\mathrm{Tr}[\rho(S_{x,A}+S_{x,B})]$ and $\mathrm{Tr}[\rho(S_{y,A}+S_{y,B})]$

→ We evolve each pathway separately (only single quantum operators)

→ We look at the terms proportional to $(S_{x,A}+S_{x,B})$ and $(S_{y,A}+S_{y,B})$ after the evolution

Evolution for isolated operators: part 3

All the pathways that appear at the end of part 2:

$$\begin{array}{rcr} \underline{S_{zz}} & \underline{S_{xx}} & \underline{S_{yy}} \\ \underline{S_{z,A} - S_{z,B}} & S_{yz} + S_{zy} & S_{y,A} - S_{y,B} \\ \underline{S_{xy} + S_{yx}} & S_{xz} + S_{zx} & S_{x,A} - S_{x,B} \end{array}$$

- The pathways $S_{yz} + S_{zy}$ and $S_{y,A} - S_{y,B}$ get one term that is proportional to $S_{x,A} + S_{x,B}$ $\rightarrow$ out-of-phase EPR signal
- The pathways $S_{xz} + S_{zx}$ and $S_{x,A} - S_{x,B}$ get one term that is proportional to $S_{y,A} + S_{y,B}$ $\rightarrow$ in-phase EPR signal

Evolution for isolated operators: results

Initial operator	EPR signal
S_{zz}	$\rightarrow$out-of-phase
$S_{xx}+S_{yy}$	$\rightarrow$out-of-phase
$S_{z,A}-S_{z,B}$	$\rightarrow$out-of-phase
$S_{xx}-S_{yy}$	$\rightarrow$out-of-phase
$S_{xy}+S_{yx}$	$\rightarrow$in-phase
$S_{xz}+S_{zx}$	$\rightarrow 0$
$S_{yz}+S_{zy}$	$\rightarrow 0$
$S_{x,A}-S_{x,B}$	$\rightarrow 0$
$S_{y,A}-S_{y,B}$	$\rightarrow 0$

$\rho_{\uparrow\uparrow/\downarrow\downarrow}=[S_{zz}\pm(S_{z,A}+S_{z,B})]/2 \rightarrow$ out-of-phase
$\rho_{T_0/S}=[-S_{zz}\pm(S_{xx}+S_{yy})]/2 \rightarrow$ out-of-phase
$\rho_{\uparrow\downarrow/\downarrow\uparrow}=[-S_{zz}\pm(S_{z,A}-S_{z,B})]/2 \rightarrow$ out-of-phase

Evolution for isolated operators: results

$$
\begin{aligned}
E_x(S_{zz}) &= \cos^2(\xi)\sin[2(d-J)\tau]\sin(2\beta),\\
E_x(S_{xx}+S_{yy}) &= \cos^2(\xi)\sin^2(\xi)\sin[2(d-J)\tau][2\sin(\beta)-\sin(2\beta)],\\
E_x(S_{z,A}-S_{z,B}) &= \cos^3(\xi)\sin(\xi)\sin[2(d-J)\tau][2\sin(\beta)-\sin(2\beta)],\\
E_x(S_{xx}-S_{yy}) &= \sin[2(d-J)\tau]\cos^2(\xi)\sin(2\beta),
\end{aligned}
$$

$$
E_y(S_{xy}+S_{yx}) = -2\cos^2(\xi)\sin(\beta)\sin[2(d-J)\tau].
$$

Evolution for isolated operators: results

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

In-phase signal, maximum at
$\theta = \pi/2$, $\phi = \pi/4$