Generalised magnetisation-to-singlet-order transfer in nuclear magnetic resonance

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I. M2S EVOLUTION DELAY

We start by the assumption of equation 26 of the main text

$$n^*\xi^{12} = \pi/2. \tag{1}$$

The propagator for the $2n$ fold echo propagator may then be expressed as follows

$$\{U_{\mathrm{SE}}(\tau_1^*)\}^{2n^*} = \Phi^{12}(2n^*\pi/2)\Phi^{34}(2n^*\pi/2)\Phi^{34}(2n^*\tau_1^*\omega_e\cos(\theta_{\mathrm{ST}}))R_x^{12}(\pi)R_z^{34}(2n^*\pi). \tag{2}$$

Similarly the the n fold echo propagator becomes

$$\{U_{\mathrm{SE}}(\tau_1^*)\}^{n^*} = \Phi^{12}(n^*\pi/2)\Phi^{34}(n^*\pi/2)\Phi^{34}(n^*\tau_1^*\omega_e\cos(\theta_{\mathrm{ST}}))R_x^{12}(\pi/2)R_z^{34}(n^*\pi). \tag{3}$$

Ignoring the initial 90_y pulse the total propagator of the M2S sequence reads as

$$U_{\mathrm{M2S}} = \{U_{\mathrm{SE}}(\tau_1^*)\}^{n^*}U_0(\tau_2)R_x(\pi/2)\{U_{\mathrm{SE}}(\tau_1^*)\}^{2n^*} \tag{4}$$

Application of the M2S propagator to $Q_a = I_x/2 = I_x^{23}$ leads to

$$\begin{aligned} U_{\mathrm{M2S}}I_x^{23}U_{\mathrm{M2S}}^\dagger =& I_x^{12}\big(\cos(n^*(\pi+2\tau_1^*\omega_e\cos(\theta_{\mathrm{ST}}))(\cos^2(\theta_{\mathrm{ST}})\cos(\tau_2\omega_e)+\sin^2(\theta_{\mathrm{ST}})) \\ &- \cos(\theta_{\mathrm{ST}})\sin(\tau_2\omega_e)\sin(n^*(\pi+2\tau_1^*\omega_e\cos(\theta_{\mathrm{ST}}))\big) \\ &+ I_y^{12}\sin(\theta_{\mathrm{ST}})\big(2\cos(\theta_{\mathrm{ST}})\cos(n^*(\pi+2\tau_1^*\omega_e\cos(\theta_{\mathrm{ST}}))\sin^2(\tau_2\omega_e/2) \\ &+ \sin(\tau_2\omega_e)\sin(n^*(\pi+2\tau_1^*\omega_e\cos(\theta_{\mathrm{ST}}))\big) \\ &- I_z^{12}\big(\cos(\theta_{\mathrm{ST}})\sin(\tau_2\omega_e)\cos(n^*(\pi+2\tau_1^*\omega_e\cos(\theta_{\mathrm{ST}})) \\ &+ \cos(\tau_2\omega_e)\sin(n^*(\pi+2\tau_1^*\omega_e\cos(\theta_{\mathrm{ST}}))\big). \end{aligned} \tag{5}$$

Within the single transition operator formalism the singlet order operator takes the form

$$Q_b = -\frac{4}{3}\mathbf{I}_1\cdot\mathbf{I}_2 = \frac{4}{3}I_z^{12} + \frac{1}{3}(\mathbb{1}^{12} - \mathbb{1}^{34}). \tag{6}$$

The expectation value $\langle Q_a \xrightarrow{\mathrm{M2S}} Q_b\rangle$ is then easily seen to equal

$$\begin{aligned} \langle Q_a \xrightarrow{\mathrm{M2S}} Q_b\rangle = -\big(&\cos(\theta_{\mathrm{ST}})\sin(\tau_2\omega_e)\cos(n^*(\pi+2\tau_1^*\omega_e\cos(\theta_{\mathrm{ST}})) \\ &+ \cos(\tau_2\omega_e)\sin(n^*(\pi+2\tau_1^*\omega_e\cos(\theta_{\mathrm{ST}}))\big). \end{aligned} \tag{7}$$

The expectation value is maximised for

$$\tau_2^* = \omega_e^{-1}\tan^{-1}(\cos(\theta_{\mathrm{ST}})\cot(2n^*\tau_1^*\omega_e\cos(\theta_{\mathrm{ST}}))), \tag{8}$$

which is the result given in the main text.

II. IN DETAIL GM2S ANALYSIS

Starting from equation 30 of the main text we recall that the optimal echo delay τ_1 for the gM2S equals

$$\tau_1^* = 2\omega_e^{-1}\tan^{-1}(1/\sqrt{\cos(2\theta_{\mathrm{ST}})+\sin(2\theta_{\mathrm{ST}})}), \tag{9}$$

so that the effective rotation axis reduces to

$$\mathbf{n}_{\mathrm{gM2S}} = \frac{1}{\sqrt{2}}\begin{bmatrix}1\\0\\1\end{bmatrix} \tag{10}$$

and the effective rotation angle ξ_{gM2S} is given by

$$\xi_{\mathrm{gM2S}} = 2\sec^{-1}\left(\frac{\cos(\theta_{\mathrm{ST}})+\sin(\theta_{\mathrm{ST}})}{\sqrt{\cos(2\theta_{\mathrm{ST}})+\sin(2\theta_{\mathrm{ST}})}}\right). \tag{11}$$

The effective propagator in the $\{1,2\}$ subspace is then alternatively given by

$$U_{\mathrm{SE}}^{12}(\tau_1^*) = R_{\mathbf{n}}^{12}(\xi) = R_y^{12}(\pi/4)R_z^{12}(\xi_{\mathrm{gM2S}})R_y^{12}(-\pi/4). \tag{12}$$

The n-fold application of a gM2S echo may then be expressed as follows

$$\begin{aligned}\{U_{\mathrm{SE}}^{12}(\tau_1^*)\}^n &= \exp\{-in\xi_{\mathrm{gM2S}}\,\mathbf{n}_{\mathrm{gM2S}}\cdot\mathbf{I}^{12}\},\\ \{U_{\mathrm{SE}}^{34}(\tau_1^*)\}^n &= i^n\Phi^{34}(n\tau_1^*\cos(\theta_{\mathrm{ST}})\omega_e)R_z^{34}(n\pi).\end{aligned} \tag{13}$$

Assuming that $n^*\xi_{\mathrm{gM2S}} = \pi$ the n-fold echo propagator simplifies to

$$\begin{aligned}\{U_{\mathrm{SE}}^{12}(\tau_1^*)\}^{n^*} &= R_y^{12}(\pi/4)R_z^{12}(\pi)R_y^{12}(-\pi/4) = R_y^{12}(\pi/2)R_z^{12}(\pi),\\ \{U_{\mathrm{SE}}^{34}(\tau_1^*)\}^{n^*} &= i^{n^*}\Phi^{34}(n^*\tau_1^*\cos(\theta_{\mathrm{ST}})\omega_e)R_z^{34}(n^*\pi),\\ \{U_{\mathrm{SE}}(\tau_1^*)\}^{n^*} &= i^{n^*}R_y^{12}(\pi/2)R_z^{12}(\pi)\Phi^{34}(n^*\tau_1^*\cos(\theta_{\mathrm{ST}})\omega_e)R_z^{34}(n^*\pi)\end{aligned} \tag{14}$$

The relations above indicate that a full $|1\rangle$-$|2\rangle$ inversion is not possible by a simple $2n^*$-fold application of a gM2S echo

$$\{U_{\mathrm{SE}}^{12}(\tau_1^*)\}^{2n^*} = R_y^{12}(\pi/2)R_z^{12}(\pi)R_y^{12}(\pi/2)R_z^{12}(\pi) = -R_y^{12}(\pi/2)R_y^{12}(-\pi/2) = -\mathbb{1}^{12}. \tag{15}$$

The phase shift $R_z^{12}(\pi)$ may be removed by application of an additional $R_y(\pi)$ pulse

$$R_y(\pi) = iR_z^{12}(\pi)R_z^{34}(\pi). \tag{16}$$

The gM2S strategy for a full $|1\rangle$-$|2\rangle$ inversion is then given by

$$\begin{aligned}
&\{U_{\mathrm{SE}}(\tau_1^*)\}^{n^*}R_y(\pi)\{U_{\mathrm{SE}}(\tau_1^*)\}^{n^*}\\
=&i(\{U_{\mathrm{SE}}^{12}(\tau_1^*)\}^{n^*}R_z^{12}(\pi)\{U_{\mathrm{SE}}^{12}(\tau_1^*)\}^{n^*})(\{U_{\mathrm{SE}}^{34}(\tau_1^*)\}^{n^*}R_z^{34}(\pi)\{U_{\mathrm{SE}}^{34}(\tau_1^*)\}^{n^*})\\
=&i^{2n^*+1}(R_y^{12}(\pi)R_z^{12}(3\pi))(\Phi^{34}(2n^*\tau_1^*\cos(\theta_{\mathrm{ST}})\omega_e)R_z^{34}((2n^*+1)\pi)).
\end{aligned} \tag{17}$$

Let us define the following propagator blocks

$$U_{\mathrm{A}} = \{U_{\mathrm{SE}}(\tau_1^*)\}^{n^*}R_y(\pi)\{U_{\mathrm{SE}}(\tau_1^*)\}^{n^*}, \quad U_{\mathrm{B}} = U_0(\tau_2)R_x(\pi/2), \quad U_{\mathrm{C}} = \{U_{\mathrm{SE}}(\tau_1^*)\}^{n^*} \tag{18}$$

and the following initial and final state

$$Q_a = I_x/2 = I_x^{23}, \quad Q_b = -\frac{4}{3}\mathbf{I}_1\cdot\mathbf{I}_2 = \frac{4}{3}I_z^{12} + \frac{1}{3}(\mathbb{1}^{12} - \mathbb{1}^{34}). \tag{19}$$

We are then interested in the expectation value

$$\langle Q_a \xrightarrow{\mathrm{gM2S}} Q_b\rangle = \langle Q_b(U_{\mathrm{C}}U_{\mathrm{B}}U_{\mathrm{A}})Q_a(U_{\mathrm{C}}U_{\mathrm{b}}U_{\mathrm{A}})^\dagger\rangle = \mathrm{Tr}\{Q_b(U_{\mathrm{C}}U_{\mathrm{B}}U_{\mathrm{A}})Q_a(U_{\mathrm{C}}U_{\mathrm{B}}U_{\mathrm{A}})^\dagger\} \tag{20}$$

The expectation value may be calculated by splitting the propagators conveniently

$$\begin{aligned}
&R_x(\pi/2)U_{\mathrm{A}}Q_aU_{\mathrm{A}}^\dagger R_x(-\pi/2)\\
&= (-1)^{n^*}R_x(\pi/2)(\cos(2n^*\tau_1^*\omega_e\cos(\theta_{\mathrm{ST}}))I_x^{13} - \sin(2n^*\tau_1^*\omega_e\cos(\theta_{\mathrm{ST}}))I_y^{13})R_x(-\pi/2)\\
&= -(-1)^{n^*}(\cos(2n^*\tau_1^*\omega_e\cos(\theta_{\mathrm{ST}}))I_y^{12} + \sin(2n^*\tau_1^*\omega_e\cos(\theta_{\mathrm{ST}}))I_x^{12})
\end{aligned} \tag{21}$$

and

$$\begin{aligned}
&U_0^\dagger(\tau_2)U_{\mathrm{C}}^\dagger Q_bU_{\mathrm{C}}U_0(\tau_2)\\
&= U_0^\dagger(\tau_2)(\frac{4}{3}I_x^{12} + \frac{1}{3}(\mathbb{1}^{12} - \mathbb{1}^{34}))U_0(\tau_2)\\
&= \frac{4}{3}((\cos^2(\theta_{\mathrm{ST}})\cos(\tau_2\omega_e) + \sin^2(\theta_{\mathrm{ST}}))I_x^{12} + \cos(\theta_{\mathrm{ST}})\sin(\tau_2\omega_e)I_y^{12} - \sin(2\theta_{\mathrm{ST}})\sin^2(\frac{1}{2}\tau_2\omega_e)I_z^{12})\\
&+ \frac{1}{3}(\mathbb{1}^{12} - \mathbb{1}^{34}).
\end{aligned} \tag{22}$$

The expressions above lead to the following singlet amplitude

$$\begin{aligned}
&\langle Q_a \xrightarrow{\mathrm{gM2S}} Q_b\rangle\\
&= -\frac{2}{3}(-1)^{n^*}\Bigg(\cos(\theta_{\mathrm{ST}})\sin(\tau_2\omega_e)\cos(2n^*\tau_1^*\omega_e\cos(\theta_{\mathrm{ST}}))\\
&+ (\cos^2(\theta_{\mathrm{ST}})\cos(\tau_2\omega_e) + \sin^2(\theta_{\mathrm{ST}}))\sin(2n^*\tau_1^*\omega_e\cos(\theta_{\mathrm{ST}}))\Bigg).
\end{aligned} \tag{23}$$

The optimal value for τ_2 may be expressed as a superposition of the solutions for $n = 1$, $n = 2k$ and $n = 2k + 1$ with $k \in \mathbb{Z}^+$. A bit of algebra shows that the optimal evolution delay τ_2^* is then given by

$$\tau_2^* = \omega_e^{-1} |\tan^{-1}(\cot(2n^* \tau_1^* \omega_e \cos(\theta_{\mathrm{ST}})) \sec(\theta_{\mathrm{ST}}))| + 2\pi\omega_e^{-1}\delta_{1n^*}. \tag{24}$$

III. FIELD INHOMOGENEITY EFFECTS ON GM2S AND ADAPT

Conventional NMR experiments are conducted on bulk samples displaying a distribution of resonance offsets and nutation frequencies. Efficient singlet order excitation within the bulk therefore requires a certain degree of robustness against B_0 and B_1 mismatch. A numerical comparison between the robustness of the gM2S and ADAPT sequence against B_0 and B_1 mismatch is given in figure 1.

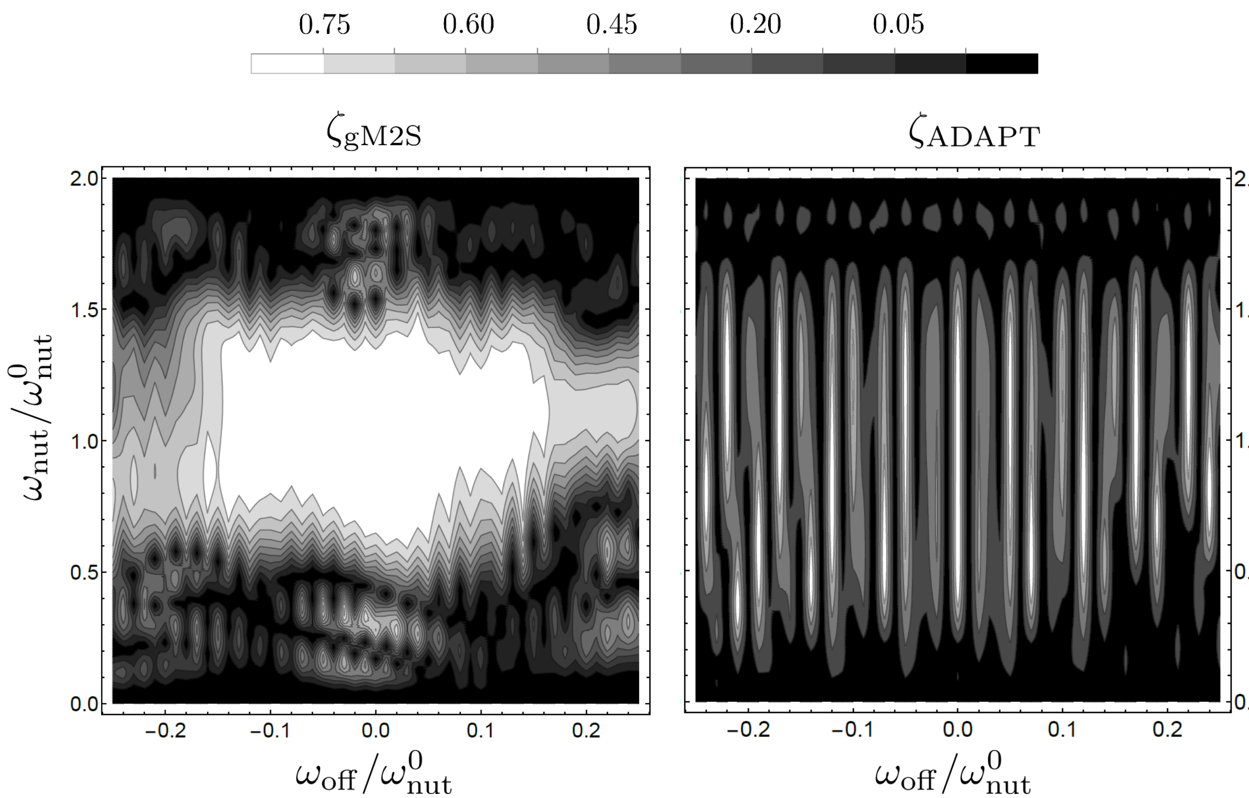

Figure 1. Singlet order excitation efficiency for gM2S and ADAPT_{90} as a function of the relative resonance offset ($\omega_{\text{off}}/\omega_{\text{nut}}^0$) and the relative nutation frequency ($\omega_{\text{nut}}/\omega_{\text{nut}}^0$) for a singlet-triplet mixing angle of $\theta_{\text{ST}} = \pi/4$. The nominal nutation frequency $\omega_{\text{nut}}^0/(2\pi)$ is 5 kHz. For both, gM2S and ADAPT, all radio frequency pulses have been replaced by their composite counterparts as described in the main text.

As the contour plot in figure 1 shows, the singlet order excitation efficiency for the ADAPT sequence rapidly drops off as the offset mismatch increases. Although the ADAPT shows some sort of periodicity in offset mismatches, there is clearly no robustness against B_0

inhomogeneities. Since the ADAPT sequence does not utilise spin echoes as its elementary building blocks, it does not possess any sort of compensation behaviour against uncertainties in the resonance frequency of the spins and the nutation frequency. The ADAPT sequence can therefore not be considered a viable option for singlet order excitation in the intermediate regime. The gM2S sequence on the other hand does not suffer from these shortcomings as it is build around echo based singlet order excitation. The gM2S sequence provides efficient singlet order excitation efficiency for relative resonance offsets between $[-0.15, +0.15]$ and relative nutation frequencies between $[+0.5, +1.5]$.