Supporting Information

Quantum Mechanical Theory of Dynamic Nuclear Polarization in Solid Dielectrics

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Section I – Symbols used in the text

δ - homogeneous line width of EPR spectrum
Δ - inhomogeneous breadth of EPR spectrum
ω_{1S} - strength of the microwave irradiation field
ω_M - microwave irradiation frequency
ω_{0S_i} - Larmor frequency of electron *i*
ω_{0I} - nuclear Larmor frequency
γ_S - electron gyromagnetic ratio
γ_I - nuclear gyromagnetic ratio
B_0 - static magnetic field

Section II – Commutator relations (Eq.44)

1) $M_{\Delta x}$ commutes with both $S_{\Delta z}I_z$ and $S_{1z}S_{2z}$ since

$$\begin{aligned} S_{\Delta z}I_z &= \frac{1}{4}(E_{M\Sigma} - E_{M\Delta}) \\ S_{1z}S_{2z} &= \frac{1}{4}(E_{S\Sigma} - E_{M\Sigma} - E_{M\Delta}) \end{aligned} \tag{S1}$$

2) From the definitions in Table 1, it follows that

$$S_\Delta^{\pm} S_{\Sigma z} = S_1^{\pm} S_2^{\mp} \cdot \tfrac{1}{2}(S_{1z} + S_{2z}) = 0 \tag{S2}$$

Therefore,

$$M_{\Delta x} S_{\Sigma z} = \tfrac{1}{2}(S_\Delta^+ I^- + S_\Delta^- I^+) S_{\Sigma z} = 0 \tag{S3}$$

3) Based on the results of Eq. S3, it also follows that

$$\left[M_{\Delta x}, S_{\Sigma z} I_z \right] = M_{\Delta x} S_{\Sigma z} I_z - S_{\Sigma z} I_z M_{\Delta x} = 0 \tag{S4}$$

$$[M_{\Delta x}, E_{S\Sigma} I_z] = M_{\Delta x} E_{S\Sigma} I_z - E_{S\Sigma} I_z M_{\Delta x} = 4(M_{\Delta x} S_{\Sigma z}^2 I_z - S_{\Sigma z}^2 I_z M_{\Delta x}) = 0 \tag{S5}$$

4) Going back to the definitions in Table 1, the following commutator relation can also be obtained:

$$\begin{aligned} [M_{\Delta x}, M_{\Sigma z}] &= \tfrac{1}{4}[S_\Delta^+ I^- + S_\Delta^- I^+, S_{\Delta z} + E_{S\Delta} I_z] \\ &= \tfrac{1}{4}(-S_\Delta^+ I^- + S_\Delta^- I^+ + S_\Delta^+ I^- - S_\Delta^- I^+) \\ &= 0. \end{aligned} \tag{S6}$$

Section III – The CE Microwave Hamiltonian in the EBS

To obtain the effective microwave excitations for DNP, the microwave Hamiltonian $\tilde{\tilde{H}}_M = 2\omega_{1S}(S_{1x} + S_{2x})\cos(\omega_M t)$ for the two electrons needs to be transformed from the PSB to the EBS using the unitary transformations U_ζ (Eq. 33) and U_ξ (Eq.45):

$$\tilde{\tilde{H}}_M = 2\omega_{1S}\cos(\omega_M t)\cdot U_\xi U_\zeta (S_{1x} + S_{2x}) U_\zeta^{-1} U_\xi^{-1} \qquad \text{(S7 = 51)}$$

First, we evaluate the effect of U_ζ, which is given by the following expression:

$$U_\zeta = \exp[i\zeta_\alpha S_{\Delta y} I^\alpha + i\zeta_\beta S_{\Delta y} I^\beta], \qquad \text{(S8 = 33)}$$

Let, $U_\phi = e^{i\phi S_{\Delta y}} = \exp[\frac{1}{2}\phi(S_1^+ S_2^- - S_1^- S_2^+)]$, where ϕ represents ζ_α or ζ_β in Eq. S8. Then,

$$\begin{aligned} U_\phi S_{1z} U_\phi^{-1} &= U_\phi (S_{\Sigma z} + S_{\Delta z}) U_\phi^{-1} \\ &= S_{\Sigma z} + S_{\Delta z}\cos\phi - S_{\Delta x}\sin\phi \\ &= \tfrac{1}{2}(S_{1z} + S_{2z}) + \tfrac{1}{2}(S_{1z} - S_{2z})\cos\phi - \tfrac{1}{2}(S_1^+ S_2^- + S_1^- S_2^+)\sin\phi, \end{aligned} \qquad \text{(S9)}$$

$$\begin{aligned} U_\phi S_1^+ U_\phi^{-1} &= S_1^+ + \tfrac{\phi}{2}(2S_{1z}S_2^+) + (\tfrac{\phi}{2})^2 \tfrac{1}{2!}(-S_1^+) + (\tfrac{\phi}{2})^3 \tfrac{1}{3!}(-2S_{1z}S_2^+) + \ldots \\ &= S_1^+ \cos\tfrac{\phi}{2} + 2S_{1z}S_2^+ \sin\tfrac{\phi}{2}, \end{aligned} \qquad \text{(S10)}$$

$$\begin{aligned} U_\phi S_1^- U_\phi^{-1} &= S_1^- + \tfrac{\phi}{2}(2S_{1z}S_2^-) + (\tfrac{\phi}{2})^2 \tfrac{1}{2!}(-S_1^-) + (\tfrac{\phi}{2})^3 \tfrac{1}{3!}(-2S_{1z}S_2^-) + \ldots \\ &= S_1^- \cos\tfrac{\phi}{2} + 2S_{1z}S_2^- \sin\tfrac{\phi}{2}. \end{aligned} \qquad \text{(S11)}$$

Similarly,

$$\begin{aligned} U_\phi S_{2z} U_\phi^{-1} &= U_\phi (S_{\Sigma z} - S_{\Delta z}) U_\phi^{-1} \\ &= S_{\Sigma z} - S_{\Delta z}\cos\phi + S_{\Delta x}\sin\phi \\ &= \tfrac{1}{2}(S_{1z} + S_{2z}) - \tfrac{1}{2}(S_{1z} - S_{2z})\cos\phi + \tfrac{1}{2}(S_1^+ S_2^- + S_1^- S_2^+)\sin\phi, \end{aligned} \qquad \text{(S12)}$$

$$\begin{aligned} U_\phi S_2^+ U_\phi^{-1} &= S_2^+ + \tfrac{\phi}{2}(-2S_1^+ S_{2z}) + (\tfrac{\phi}{2})^2 \tfrac{1}{2!}(-S_2^+) + (\tfrac{\phi}{2})^3 \tfrac{1}{3!}(2S_1^+ S_{2z}) + \ldots \\ &= S_2^+ \cos\tfrac{\phi}{2} - 2S_1^+ S_{2z} \sin\tfrac{\phi}{2}, \end{aligned} \qquad \text{(S13)}$$

$$U_\phi S_2^- U_\phi^{-1} = S_2^- + \tfrac{\phi}{2}(-2S_1^- S_{2z}) + (\tfrac{\phi}{2})^2 \tfrac{1}{2!}(-S_2^-) + (\tfrac{\phi}{2})^3 \tfrac{1}{3!}(2S_1^- S_{2z}) + ... \\ = S_2^- \cos\tfrac{\phi}{2} - 2S_1^- S_{2z} \sin\tfrac{\phi}{2}, \tag{S14}$$

Combining these results, leads to Eq. 52:

$$\begin{aligned} \widetilde{H}_M &= U_\zeta (S_{1x} + S_{2x}) U_\zeta^{-1} \\ &= S_{1x}(I^\alpha \cos\tfrac{\zeta_\alpha}{2} + I^\beta \cos\tfrac{\zeta_\beta}{2}) + 2S_{1z}S_{2x}(I^\alpha \sin\tfrac{\zeta_\alpha}{2} + I^\beta \sin\tfrac{\zeta_\beta}{2}) \\ &+ S_{2x}(I^\alpha \cos\tfrac{\zeta_\alpha}{2} + I^\beta \cos\tfrac{\zeta_\beta}{2}) - 2S_{1x}S_{2z}(I^\alpha \sin\tfrac{\zeta_\alpha}{2} + I^\beta \sin\tfrac{\zeta_\beta}{2}) \\ &= \tfrac{1}{2}(S_{1x} + S_{2x})(c_\alpha + c_\beta) + (S_{1x} + S_{2x}) I_z (c_\alpha - c_\beta) \\ &+ (S_{1z}S_{2x} - S_{1x}S_{2z})(s_\alpha + s_\beta) + 2(S_{1z}S_{2x} - S_{1x}S_{2z}) I_z (s_\alpha - s_\beta), \end{aligned} \tag{S15 = 52}$$

$$c_\alpha = \cos\frac{\zeta_\alpha}{2}, c_\beta = \cos\frac{\zeta_\beta}{2}, s_\alpha = \sin\frac{\zeta_\alpha}{2}, s_\beta = \sin\frac{\zeta_\beta}{2}. \tag{S16 = 53}$$

Next, we evaluate the effect of U_ξ, which is given in Eq.45, i.e.

$$U_\xi = \exp[i\xi M_{\Delta y}], \tag{S17 = 45}$$

Let $U_\chi = e^{i\chi M_{\Delta y}} = \exp[\tfrac{1}{2}\chi(S_1^+ S_2^- I^- - S_1^- S_2^+ I^+)]$, where χ represents ξ in Eq. 45. Then we can derive the following intermediate expressions:

$$\begin{aligned} U_\chi I_z U_\chi^{-1} &= U_\chi (E_{S\Sigma} I_z + E_{S\Delta} I_z) U_\chi^{-1} = U_\chi (E_{S\Sigma} I_z + M_{\Sigma z} - M_{\Delta z}) U_\chi^{-1} \\ &= E_{S\Sigma} I_z + M_{\Sigma z} - M_{\Delta z} \cos\chi + M_{\Delta x} \sin\chi \\ &= \tfrac{1}{4}S_{1z} - \tfrac{1}{4}S_{2z} + \tfrac{3}{4}I_z + S_{1z}S_{2z}I_z \\ &- (\tfrac{1}{4}S_{1z} - \tfrac{1}{4}S_{2z} - \tfrac{1}{4}S_{2z} + S_{1z}S_{2z}I_z)\cos\chi \\ &+ \tfrac{1}{2}(S_1^+ S_2^- I^- + S_1^- S_2^+ I^+)\sin\chi, \end{aligned} \tag{S18}$$

$$\begin{aligned} U_\chi I^+ U_\chi^{-1} &= I^+ + \tfrac{\chi}{2}(-2S_1^+ S_2^- I_z) + (\tfrac{\chi}{2})^2 \tfrac{1}{2!}(\tfrac{-1}{2} I^+ + 2S_{1z}S_{2z}I^+) \\ &+ (\tfrac{\chi}{2})^3 \tfrac{1}{3!}(2S_1^+ S_2^- I_z) + (\tfrac{\chi}{2})^4 \tfrac{1}{4!}(\tfrac{1}{2} I^+ - 2S_{1z}S_{2z}I^+) + ... \\ &= \tfrac{1}{2} I^+ + 2S_{1z}S_{2z}I^+ \\ &+ (\tfrac{1}{2} I^+ - 2S_{1z}S_{2z}I^+)\cos\tfrac{\chi}{2} - 2S_1^+ S_2^- I_z \sin\tfrac{\chi}{2}, \end{aligned} \tag{S19}$$

$$
\begin{aligned}
U_\chi I^- U_\chi^{-1} &= I^- + \tfrac{\chi}{2}(-2S_1^- S_2^+ I_z) + (\tfrac{\chi}{2})^2 \tfrac{1}{2!}(\tfrac{-1}{2} I^- + 2S_{1z} S_{2z} I^-) \\
&\quad + (\tfrac{\chi}{2})^3 \tfrac{1}{3!}(2S_1^- S_2^+ I_z) + (\tfrac{\chi}{2})^4 \tfrac{1}{4!}(\tfrac{1}{2} I^- - 2S_{1z} S_{2z} I^-) + \ldots \\
&= \tfrac{1}{2} I^- + 2S_{1z} S_{2z} I^- \\
&\quad + (\tfrac{1}{2} I^- - 2S_{1z} S_{2z} I^-)\cos\tfrac{\chi}{2} - 2S_1^- S_2^+ I_z \sin\tfrac{\chi}{2}.
\end{aligned} \tag{S20}
$$

Further,

$$
\begin{aligned}
U_\chi S_{1z} U_\chi^{-1} &= U_\chi (S_{\Sigma z} + M_{\Sigma z} + M_{\Delta z}) U_\chi^{-1} \\
&= S_{\Sigma z} + M_{\Sigma z} + M_{\Delta z}\cos\chi - M_{\Delta x}\sin\chi \\
&= \tfrac{3}{4} S_{1z} + \tfrac{1}{4} S_{2z} + \tfrac{1}{4} I_z - S_{1z} S_{2z} I_z \\
&\quad + (\tfrac{1}{4} S_{1z} - \tfrac{1}{4} S_{2z} - \tfrac{1}{4} S_{2z} + S_{1z} S_{2z} I_z)\cos\chi \\
&\quad - \tfrac{1}{2}(S_1^+ S_2^- I^- + S_1^- S_2^+ I^+)\sin\chi,
\end{aligned} \tag{S21}
$$

$$
\begin{aligned}
U_\chi S_1^+ U_\chi^{-1} &= S_1^+ + \tfrac{\chi}{2}(2S_{1z} S_2^+ I^+) + (\tfrac{\chi}{2})^2 \tfrac{1}{2!}(\tfrac{-1}{2} S_1^+ - 2S_1^+ S_{2z} I_z) \\
&\quad + (\tfrac{\chi}{2})^3 \tfrac{1}{3!}(-2S_{1z} S_2^+ I^+) + (\tfrac{\chi}{2})^4 \tfrac{1}{4!}(\tfrac{1}{2} S_1^+ + 2S_1^+ S_{2z} I_z) + \ldots \\
&= \tfrac{1}{2} S_1^+ - 2S_1^+ S_{2z} I_z \\
&\quad + (\tfrac{1}{2} S_1^+ + 2S_1^+ S_{2z} I_z)\cos\tfrac{\chi}{2} + 2S_{1z} S_2^+ I^+ \sin\tfrac{\chi}{2},
\end{aligned} \tag{S22}
$$

$$
\begin{aligned}
U_\chi S_1^- U_\chi^{-1} &= S_1^- + \tfrac{\chi}{2}(2S_{1z} S_2^- I^-) + (\tfrac{\chi}{2})^2 \tfrac{1}{2!}(\tfrac{-1}{2} S_1^- - 2S_1^- S_{2z} I_z) \\
&\quad + (\tfrac{\chi}{2})^3 \tfrac{1}{3!}(-2S_{1z} S_2^- I^-) + (\tfrac{\chi}{2})^4 \tfrac{1}{4!}(\tfrac{1}{2} S_1^- + 2S_1^- S_{2z} I_z) + \ldots \\
&= \tfrac{1}{2} S_1^- - 2S_1^- S_{2z} I_z \\
&\quad + (\tfrac{1}{2} S_1^- + 2S_1^- S_{2z} I_z)\cos\tfrac{\chi}{2} + 2S_{1z} S_2^- I^- \sin\tfrac{\chi}{2}.
\end{aligned} \tag{S23}
$$

Finally,

$$
\begin{aligned}
U_\chi S_{2z} U_\chi^{-1} &= U_\chi (S_{\Sigma z} - M_{\Sigma z} - M_{\Delta z}) U_\chi^{-1} \\
&= S_{\Sigma z} - M_{\Sigma z} - M_{\Delta z}\cos\chi + M_{\Delta x}\sin\chi \\
&= \tfrac{1}{4} S_{1z} + \tfrac{3}{4} S_{2z} - \tfrac{1}{4} I_z + S_{1z} S_{2z} I_z \\
&\quad - (\tfrac{1}{4} S_{1z} - \tfrac{1}{4} S_{2z} - \tfrac{1}{4} S_{2z} + S_{1z} S_{2z} I_z)\cos\chi \\
&\quad + \tfrac{1}{2}(S_1^+ S_2^- I^- + S_1^- S_2^+ I^+)\sin\chi.
\end{aligned} \tag{S24}
$$

$$
\begin{aligned}
U_\chi S_2^+ U_\chi^{-1} &= S_2^+ + \tfrac{\chi}{2}(-2S_1^+ S_{2z} I^-) + (\tfrac{\chi}{2})^2 \tfrac{1}{2!}(\tfrac{-1}{2} S_2^+ + 2S_{1z} S_2^+ I_z) \\
&\quad + (\tfrac{\chi}{2})^3 \tfrac{1}{3!}(2S_1^+ S_{2z} I^-) + (\tfrac{\chi}{2})^4 \tfrac{1}{4!}(\tfrac{1}{2} S_2^+ - 2S_{1z} S_2^+ I_z) + \ldots \\
&= \tfrac{1}{2} S_2^+ + 2S_{1z} S_2^+ I_z \\
&\quad + (\tfrac{1}{2} S_2^+ - 2S_{1z} S_2^+ I_z)\cos\tfrac{\chi}{2} - 2S_1^+ S_{2z} I^- \sin\tfrac{\chi}{2},
\end{aligned} \tag{S25}
$$

$$
\begin{aligned}
U_\chi S_2^- U_\chi^{-1} &= S_2^- + \tfrac{\chi}{2}(-2S_1^- S_{2z} I^+) + (\tfrac{\chi}{2})^2 \tfrac{1}{2!}(\tfrac{-1}{2} S_2^- + 2S_{1z} S_2^- I_z) \\
&\quad + (\tfrac{\chi}{2})^3 \tfrac{1}{3!}(2S_1^- S_{2z} I^+) + (\tfrac{\chi}{2})^4 \tfrac{1}{4!}(\tfrac{1}{2} S_2^- - 2S_{1z} S_2^- I_z) + \ldots \\
&= \tfrac{1}{2} S_2^- + 2S_{1z} S_2^- I_z \\
&\quad + (\tfrac{1}{2} S_2^- - 2S_{1z} S_2^- I_z)\cos\tfrac{\chi}{2} - 2S_1^- S_{2z} I^+ \sin\tfrac{\chi}{2}.
\end{aligned} \tag{S26}
$$

Before we use the expressions above (Eq. S18 to S26), it is convenient to rewrite $\tilde{H}_M$ (Eq. 52, S15) taking advantage of the following commutator relation:

$$
\begin{aligned}
&[M_{\Delta y}, S_{1z} I_z] = [M_{\Delta y}, S_{1z} S_{2z}] = [M_{\Delta y}, S_{2z} I_z] = 0, \\
&S_{1x} = -2i S_{1y} S_{1z}, \quad S_{2x} = -2i S_{2y} S_{2z}.
\end{aligned} \tag{S27 = 54}
$$

The new, more convenient form of $\tilde{H}_M$ is therefore,

$$
\begin{aligned}
\tilde{H}_M &= \tfrac{1}{2}(c_\alpha + c_\beta)(S_{1x} + S_{2x}) - 2i(c_\alpha - c_\beta)(S_{1y} S_{1z} I_z + S_{2y} S_{2z} I_z) \\
&\quad + 2i(s_\alpha + s_\beta)(S_{1y} - S_{2y}) S_{1z} S_{2z} - 2(s_\alpha - s_\beta)(S_{1x} S_{2z} I_z - S_{2x} S_{1z} I_z).
\end{aligned} \tag{S28 = 55}
$$

Now, we can evaluate the effect of the second unitary transformation U_ξ:

$$
\begin{aligned}
U_\xi \tilde{H}_M U_\xi^{-1} = (c_\alpha + c_\beta)\{&\tfrac{1}{4}(S_{1x}+S_{2x}) - (S_{1x}S_{2z} - S_{1z}S_{2x})I_z \\
&+[\tfrac{1}{4}(S_{1x}+S_{2x}) + (S_{1x}S_{2z} - S_{1z}S_{2x})I_z]\cos\tfrac{\xi}{2} \\
&+\tfrac{1}{2}[S_{1z}(S_2^+I^+ + S_2^-I^-) - (S_1^+I^- + S_1^-I^+)S_{2z}]\sin\tfrac{\xi}{2}\} \\
+\tfrac{1}{2}(c_\alpha - c_\beta)\{&(S_{1x}+S_{2x})I_z - (S_{1x}S_{2z} - S_{1z}S_{2x}) \\
&+[(S_{1x}+S_{2x})I_z + (S_{1x}S_{2z} - S_{1z}S_{2x})]\cos\tfrac{\xi}{2} \\
&+\tfrac{1}{2}(S_2^+I^+ + S_2^-I^- + S_1^+I^- + S_1^-I^+)\sin\tfrac{\xi}{2}\} \\
+\tfrac{1}{2}(s_\alpha + s_\beta)\{&(S_{1x}+S_{2x})I_z - (S_{1x}S_{2z} - S_{1z}S_{2x}) \\
&-[(S_{1x}+S_{2x})I_z + (S_{1x}S_{2z} - S_{1z}S_{2x})]\cos\tfrac{\xi}{2} \\
&-\tfrac{1}{2}(S_2^+I^+ + S_2^-I^- + S_1^+I^- + S_1^-I^+)\sin\tfrac{\xi}{2}\} \\
+(s_\alpha - s_\beta)\{&\tfrac{1}{4}(S_{1x}+S_{2x}) - (S_{1x}S_{2z} - S_{1z}S_{2x})I_z \\
&-[\tfrac{1}{4}(S_{1x}+S_{2x}) + (S_{1x}S_{2z} - S_{1z}S_{2x})I_z]\cos\tfrac{\xi}{2} \\
&-\tfrac{1}{2}[S_{1z}(S_2^+I^+ + S_2^-I^-) - (S_1^+I^- + S_1^-I^+)S_{2z}]\sin\tfrac{\xi}{2}\}.
\end{aligned}
\quad \text{(S29 =56)}
$$

The result of this transformation is $\tilde{\tilde{H}}_M$. For bookkeeping purposes, the operators in $\tilde{\tilde{H}}_M$ can be grouped into six terms:

$$\tilde{\tilde{H}}_M = 2\omega_{1S}\cos(\omega_M t)\cdot(\tilde{\tilde{H}}_M^1 + \tilde{\tilde{H}}_M^2 + \tilde{\tilde{H}}_M^3 + \tilde{\tilde{H}}_M^4 + \tilde{\tilde{H}}_M^5 + \tilde{\tilde{H}}_M^6) \quad \text{(S30 = 57)}$$

$$\tilde{\tilde{H}}_M^1 = \tilde{\tilde{h}}_1(S_{1x}+S_{2x}),\ \tilde{\tilde{h}}_1 = \tfrac{1}{4}[(c_\alpha + c_\beta + s_\alpha - s_\beta) + (c_\alpha + c_\beta - s_\alpha + s_\beta)\cos\tfrac{\xi}{2}] \quad \text{(S31)}$$

$$\tilde{\tilde{H}}_M^2 = \tilde{\tilde{h}}_2(S_{1x}+S_{2x})I_z,\ \tilde{\tilde{h}}_2 = \tfrac{1}{2}[(c_\alpha - c_\beta + s_\alpha + s_\beta) + (c_\alpha - c_\beta - s_\alpha - s_\beta)\cos\tfrac{\xi}{2}] \quad \text{(S32)}$$

$$\tilde{\tilde{H}}_M^3 = \tilde{\tilde{h}}_3(S_{1x}S_{2z} - S_{1z}S_{2x}),\ \tilde{\tilde{h}}_3 = \tfrac{1}{2}[(-c_\alpha + c_\beta - s_\alpha - s_\beta) + (c_\alpha - c_\beta - s_\alpha - s_\beta)\cos\tfrac{\xi}{2}] \quad \text{(S33)}$$

$$\tilde{\tilde{H}}_M^4 = \tilde{\tilde{h}}_4(S_{1x}S_{2z} - S_{1z}S_{2x})I_z,\ \tilde{\tilde{h}}_4 = [(-c_\alpha - c_\beta - s_\alpha + s_\beta) + (c_\alpha + c_\beta - s_\alpha + s_\beta)\cos\tfrac{\xi}{2}] \quad \text{(S34)}$$

$$\tilde{\tilde{H}}_M^5 = \tilde{\tilde{h}}_5(S_2^+I^+ + S_2^-I^- + S_1^+I^- + S_1^-I^+),\ \tilde{\tilde{h}}_5 = \tfrac{1}{4}(c_\alpha - c_\beta - s_\alpha - s_\beta)\sin\tfrac{\xi}{2} \quad \text{(S35)}$$

$$\tilde{\tilde{H}}_M^6 = \tilde{\tilde{h}}_6[(S_2^+I^+ + S_2^-I^-)S_{1z} - (S_1^+I^- + S_1^-I^+)S_{2z}],\ \tilde{\tilde{h}}_6 = \tfrac{1}{2}(c_\alpha + c_\beta - s_\alpha + s_\beta)\sin\tfrac{\xi}{2} \quad \text{(S36)}$$

Section IV – Detailed expressions for the terms in Eq. 61

$$\begin{aligned}\tilde{\tilde{H}}_M^{1*} = \tfrac{1}{2}\tilde{\tilde{h}}_1\{ & S_1^+S_2^\alpha I^\alpha e^{i(\tilde{\tilde{\omega}}_{0S_1}+\frac{D_d}{2}+\frac{\tilde{\tilde{A}}_1}{2}+\frac{\tilde{\tilde{V}}}{4})t} + S_1^-S_2^\alpha I^\alpha c.c. + S_2^+S_1^\alpha I^\alpha e^{i(\tilde{\tilde{\omega}}_{0S_2}+\frac{D_d}{2}+\frac{\tilde{\tilde{A}}_2}{2}+\frac{\tilde{\tilde{V}}}{4})t} + S_2^-S_1^\alpha I^\alpha c.c. \\ & + S_1^+S_2^\alpha I^\beta e^{i(\tilde{\tilde{\omega}}_{0S_1}+\frac{D_d}{2}-\frac{\tilde{\tilde{A}}_1}{2}-\frac{\tilde{\tilde{V}}}{4})t} + S_1^-S_2^\alpha I^\beta c.c. + S_2^+S_1^\alpha I^\beta e^{i(\tilde{\tilde{\omega}}_{0S_2}+\frac{D_d}{2}-\frac{\tilde{\tilde{A}}_2}{2}-\frac{\tilde{\tilde{V}}}{4})t} + S_2^-S_1^\alpha I^\beta c.c. \\ & + S_1^+S_2^\beta I^\alpha e^{i(\tilde{\tilde{\omega}}_{0S_1}-\frac{D_d}{2}+\frac{\tilde{\tilde{A}}_1}{2}-\frac{\tilde{\tilde{V}}}{4})t} + S_1^-S_2^\beta I^\alpha c.c. + S_2^+S_1^\beta I^\alpha e^{i(\tilde{\tilde{\omega}}_{0S_2}-\frac{D_d}{2}+\frac{\tilde{\tilde{A}}_2}{2}-\frac{\tilde{\tilde{V}}}{4})t} + S_2^-S_1^\beta I^\alpha c.c. \\ & + S_1^+S_2^\beta I^\beta e^{i(\tilde{\tilde{\omega}}_{0S_1}-\frac{D_d}{2}-\frac{\tilde{\tilde{A}}_1}{2}+\frac{\tilde{\tilde{V}}}{4})t} + S_1^-S_2^\beta I^\beta c.c. + S_2^+S_1^\beta I^\beta e^{i(\tilde{\tilde{\omega}}_{0S_2}-\frac{D_d}{2}-\frac{\tilde{\tilde{A}}_2}{2}+\frac{\tilde{\tilde{V}}}{4})t} + S_2^-S_1^\beta I^\beta c.c.\}\end{aligned} \tag{S31}$$

$$\begin{aligned}\tilde{\tilde{H}}_M^{2*} = \tfrac{1}{4}\tilde{\tilde{h}}_2\{ & S_1^+S_2^\alpha I^\alpha e^{i(\tilde{\tilde{\omega}}_{0S_1}+\frac{D_d}{2}+\frac{\tilde{\tilde{A}}_1}{2}+\frac{\tilde{\tilde{V}}}{4})t} + S_1^-S_2^\alpha I^\alpha c.c. + S_2^+S_1^\alpha I^\alpha e^{i(\tilde{\tilde{\omega}}_{0S_2}+\frac{D_d}{2}+\frac{\tilde{\tilde{A}}_2}{2}+\frac{\tilde{\tilde{V}}}{4})t} + S_2^-S_1^\alpha I^\alpha c.c. \\ & - S_1^+S_2^\alpha I^\beta e^{i(\tilde{\tilde{\omega}}_{0S_1}+\frac{D_d}{2}-\frac{\tilde{\tilde{A}}_1}{2}-\frac{\tilde{\tilde{V}}}{4})t} - S_1^-S_2^\alpha I^\beta c.c. - S_2^+S_1^\alpha I^\beta e^{i(\tilde{\tilde{\omega}}_{0S_2}+\frac{D_d}{2}-\frac{\tilde{\tilde{A}}_2}{2}-\frac{\tilde{\tilde{V}}}{4})t} - S_2^-S_1^\alpha I^\beta c.c. \\ & + S_1^+S_2^\beta I^\alpha e^{i(\tilde{\tilde{\omega}}_{0S_1}-\frac{D_d}{2}+\frac{\tilde{\tilde{A}}_1}{2}-\frac{\tilde{\tilde{V}}}{4})t} + S_1^-S_2^\beta I^\alpha c.c. + S_2^+S_1^\beta I^\alpha e^{i(\tilde{\tilde{\omega}}_{0S_2}-\frac{D_d}{2}+\frac{\tilde{\tilde{A}}_2}{2}-\frac{\tilde{\tilde{V}}}{4})t} + S_2^-S_1^\beta I^\alpha c.c. \\ & - S_1^+S_2^\beta I^\beta e^{i(\tilde{\tilde{\omega}}_{0S_1}-\frac{D_d}{2}-\frac{\tilde{\tilde{A}}_1}{2}+\frac{\tilde{\tilde{V}}}{4})t} - S_1^-S_2^\beta I^\beta c.c. - S_2^+S_1^\beta I^\beta e^{i(\tilde{\tilde{\omega}}_{0S_2}-\frac{D_d}{2}-\frac{\tilde{\tilde{A}}_2}{2}+\frac{\tilde{\tilde{V}}}{4})t} - S_2^-S_1^\beta I^\beta c.c.\}\end{aligned} \tag{S32}$$

$$\begin{aligned}\tilde{\tilde{H}}_M^{3*} = \tfrac{1}{4}\tilde{\tilde{h}}_3\{ & S_1^+S_2^\alpha I^\alpha e^{i(\tilde{\tilde{\omega}}_{0S_1}+\frac{D_d}{2}+\frac{\tilde{\tilde{A}}_1}{2}+\frac{\tilde{\tilde{V}}}{4})t} + S_1^-S_2^\alpha I^\alpha c.c. - S_2^+S_1^\alpha I^\alpha e^{i(\tilde{\tilde{\omega}}_{0S_2}+\frac{D_d}{2}+\frac{\tilde{\tilde{A}}_2}{2}+\frac{\tilde{\tilde{V}}}{4})t} - S_2^-S_1^\alpha I^\alpha c.c. \\ & + S_1^+S_2^\alpha I^\beta e^{i(\tilde{\tilde{\omega}}_{0S_1}+\frac{D_d}{2}-\frac{\tilde{\tilde{A}}_1}{2}-\frac{\tilde{\tilde{V}}}{4})t} + S_1^-S_2^\alpha I^\beta c.c. - S_2^+S_1^\alpha I^\beta e^{i(\tilde{\tilde{\omega}}_{0S_2}+\frac{D_d}{2}-\frac{\tilde{\tilde{A}}_2}{2}-\frac{\tilde{\tilde{V}}}{4})t} - S_2^-S_1^\alpha I^\beta c.c. \\ & - S_1^+S_2^\beta I^\alpha e^{i(\tilde{\tilde{\omega}}_{0S_1}-\frac{D_d}{2}+\frac{\tilde{\tilde{A}}_1}{2}-\frac{\tilde{\tilde{V}}}{4})t} - S_1^-S_2^\beta I^\alpha c.c. + S_2^+S_1^\beta I^\alpha e^{i(\tilde{\tilde{\omega}}_{0S_2}-\frac{D_d}{2}+\frac{\tilde{\tilde{A}}_2}{2}-\frac{\tilde{\tilde{V}}}{4})t} + S_2^-S_1^\beta I^\alpha c.c. \\ & - S_1^+S_2^\beta I^\beta e^{i(\tilde{\tilde{\omega}}_{0S_1}-\frac{D_d}{2}-\frac{\tilde{\tilde{A}}_1}{2}+\frac{\tilde{\tilde{V}}}{4})t} - S_1^-S_2^\beta I^\beta c.c. + S_2^+S_1^\beta I^\beta e^{i(\tilde{\tilde{\omega}}_{0S_2}-\frac{D_d}{2}-\frac{\tilde{\tilde{A}}_2}{2}+\frac{\tilde{\tilde{V}}}{4})t} + S_2^-S_1^\beta I^\beta c.c.\}\end{aligned} \tag{S33}$$

$$\begin{aligned}\tilde{\tilde{H}}_M^{4*} = \tfrac{1}{8}\tilde{\tilde{h}}_4\{ & S_1^+S_2^\alpha I^\alpha e^{i(\tilde{\tilde{\omega}}_{0S_1}+\frac{D_d}{2}+\frac{\tilde{\tilde{A}}_1}{2}+\frac{\tilde{\tilde{V}}}{4})t} + S_1^-S_2^\alpha I^\alpha c.c. - S_2^+S_1^\alpha I^\alpha e^{i(\tilde{\tilde{\omega}}_{0S_2}+\frac{D_d}{2}+\frac{\tilde{\tilde{A}}_2}{2}+\frac{\tilde{\tilde{V}}}{4})t} - S_2^-S_1^\alpha I^\alpha c.c. \\ & - S_1^+S_2^\alpha I^\beta e^{i(\tilde{\tilde{\omega}}_{0S_1}+\frac{D_d}{2}-\frac{\tilde{\tilde{A}}_1}{2}-\frac{\tilde{\tilde{V}}}{4})t} - S_1^-S_2^\alpha I^\beta c.c. + S_2^+S_1^\alpha I^\beta e^{i(\tilde{\tilde{\omega}}_{0S_2}+\frac{D_d}{2}-\frac{\tilde{\tilde{A}}_2}{2}-\frac{\tilde{\tilde{V}}}{4})t} + S_2^-S_1^\alpha I^\beta c.c. \\ & - S_1^+S_2^\beta I^\alpha e^{i(\tilde{\tilde{\omega}}_{0S_1}-\frac{D_d}{2}+\frac{\tilde{\tilde{A}}_1}{2}-\frac{\tilde{\tilde{V}}}{4})t} - S_1^-S_2^\beta I^\alpha c.c. + S_2^+S_1^\beta I^\alpha e^{i(\tilde{\tilde{\omega}}_{0S_2}-\frac{D_d}{2}+\frac{\tilde{\tilde{A}}_2}{2}-\frac{\tilde{\tilde{V}}}{4})t} + S_2^-S_1^\beta I^\alpha c.c. \\ & + S_1^+S_2^\beta I^\beta e^{i(\tilde{\tilde{\omega}}_{0S_1}-\frac{D_d}{2}-\frac{\tilde{\tilde{A}}_1}{2}+\frac{\tilde{\tilde{V}}}{4})t} + S_1^-S_2^\beta I^\beta c.c. - S_2^+S_1^\beta I^\beta e^{i(\tilde{\tilde{\omega}}_{0S_2}-\frac{D_d}{2}-\frac{\tilde{\tilde{A}}_2}{2}+\frac{\tilde{\tilde{V}}}{4})t} - S_2^-S_1^\beta I^\beta c.c.\}\end{aligned} \tag{S34}$$

$$\begin{aligned}\tilde{\tilde{H}}_M^{5*} = \tilde{\tilde{h}}_5\{ & S_2^+I^+S_1^\alpha e^{i(\tilde{\tilde{\omega}}_{0S_2}+\frac{D_d}{2}-\tilde{\tilde{\omega}}_{0I}+\frac{\tilde{\tilde{A}}_1}{2})t} + S_2^-I^-S_1^\alpha c.c. + S_1^+I^-S_2^\alpha e^{i(\tilde{\tilde{\omega}}_{0S_1}+\frac{D_d}{2}+\tilde{\tilde{\omega}}_{0I}-\frac{\tilde{\tilde{A}}_2}{2})t} + S_1^-I^+S_2^\alpha c.c. \\ & + S_2^+I^+S_1^\beta e^{i(\tilde{\tilde{\omega}}_{0S_2}-\frac{D_d}{2}-\tilde{\tilde{\omega}}_{0I}-\frac{\tilde{\tilde{A}}_1}{2})t} + S_2^-I^-S_1^\beta c.c. + S_1^+I^-S_2^\beta e^{i(\tilde{\tilde{\omega}}_{0S_1}-\frac{D_d}{2}+\tilde{\tilde{\omega}}_{0I}+\frac{\tilde{\tilde{A}}_2}{2})t} + S_1^-I^+S_2^\beta c.c.\}\end{aligned} \tag{S35}$$

$$\begin{aligned}\tilde{\tilde{H}}_M^{6*} = \tfrac{1}{2}\tilde{\tilde{h}}_6\{ & S_2^+I^+S_1^\alpha e^{i(\tilde{\tilde{\omega}}_{0S_2}+\frac{D_d}{2}-\tilde{\tilde{\omega}}_{0I}+\frac{\tilde{\tilde{A}}_1}{2})t} + S_2^-I^-S_1^\alpha c.c. - S_1^+I^-S_2^\alpha e^{i(\tilde{\tilde{\omega}}_{0S_1}+\frac{D_d}{2}+\tilde{\tilde{\omega}}_{0I}-\frac{\tilde{\tilde{A}}_2}{2})t} - S_1^-I^+S_2^\alpha c.c. \\ & - S_2^+I^+S_1^\beta e^{i(\tilde{\tilde{\omega}}_{0S_2}-\frac{D_d}{2}-\tilde{\tilde{\omega}}_{0I}-\frac{\tilde{\tilde{A}}_1}{2})t} - S_2^-I^-S_1^\beta c.c. + S_1^+I^-S_2^\beta e^{i(\tilde{\tilde{\omega}}_{0S_1}-\frac{D_d}{2}+\tilde{\tilde{\omega}}_{0I}+\frac{\tilde{\tilde{A}}_2}{2})t} + S_1^-I^+S_2^\beta c.c.\}\end{aligned} \tag{S36}$$

Section V – Example 3 (Eq. 80 to 83)

Letting

$$\tilde{\tilde{H}}_{M3}^{eff*} = S_{1x} S_2^{\alpha} I^{\alpha} + \tfrac{1}{2} S_1^{\alpha}(S_2^{+} I^{+} + S_2^{-} I^{-}) = S_{1x} I_{2\Sigma}^{\alpha} + S_1^{\alpha} I_{2\Sigma x}, \tag{S37 = 80}$$

we obtain

$$\begin{aligned}&[\tilde{\tilde{H}}_{M3}^{eff*}, S_{1z} + S_{2z}] \\ &= -iS_{1y} S_2^{\alpha} I^{\alpha} - \tfrac{1}{2} S_1^{\alpha}(S_2^{+} I^{+} - S_2^{-} I^{-}),\end{aligned} \tag{S38 = 81}$$

$$\begin{aligned}&[\tilde{\tilde{H}}_{M3}^{eff*}, [\tilde{\tilde{H}}_{M3}^{eff*}, S_{1z} + S_{2z}]] \\ &= [\tilde{\tilde{H}}_{M3}^{eff*}, iS_{1y} S_2^{\alpha} I^{\alpha} + \tfrac{1}{2} S_1^{\alpha}(S_2^{+} I^{+} - S_2^{-} I^{-})] \\ &= [S_{1x} I_{2\Sigma}^{\alpha} + S_1^{\alpha} I_{2\Sigma x}, iS_{1y} I_{2\Sigma}^{\alpha} + iS_1^{\alpha} I_{2\Sigma y}] \\ &= i(S_{1x} I_{2\Sigma}^{\alpha} S_{1y} I_{2\Sigma}^{\alpha} + S_{1x} I_{2\Sigma}^{\alpha} S_1^{\alpha} I_{2\Sigma y} + S_1^{\alpha} I_{2\Sigma x} S_{1y} I_{2\Sigma}^{\alpha} + S_1^{\alpha} I_{2\Sigma x} S_1^{\alpha} I_{2\Sigma y} \\ &\quad - S_{1y} I_{2\Sigma}^{\alpha} S_{1x} I_{2\Sigma}^{\alpha} - S_{1y} I_{2\Sigma}^{\alpha} S_1^{\alpha} I_{2\Sigma x} - S_1^{\alpha} I_{2\Sigma y} S_{1x} I_{2\Sigma}^{\alpha} - S_1^{\alpha} I_{2\Sigma y} S_1^{\alpha} I_{2\Sigma x}) \\ &= i(\tfrac{i}{2} S_{1z} I_{2\Sigma}^{\alpha} + \tfrac{1}{2} S_1^{-} \tfrac{1}{2i} I_{2\Sigma}^{+} + \tfrac{1}{2i} S_1^{+} \tfrac{1}{2} I_{2\Sigma}^{-} + S_1^{\alpha} \tfrac{i}{2} I_{2\Sigma z} \\ &\quad - \tfrac{-i}{2} S_{1z} I_{2\Sigma}^{\alpha} - \tfrac{-1}{2i} S_1^{-} \tfrac{1}{2} I_{2\Sigma}^{+} - \tfrac{1}{2} S_1^{+} \tfrac{-1}{2i} I_{2\Sigma}^{-} - S_1^{\alpha} \tfrac{-i}{2} I_{2\Sigma z}) \\ &= -S_{1z} I_{2\Sigma}^{\alpha} + \tfrac{1}{2} S_1^{-} I_{2\Sigma}^{+} + \tfrac{1}{2} S_1^{+} I_{2\Sigma}^{-} - S_1^{\alpha} I_{2\Sigma z} \\ &= -S_1^{\alpha} S_2^{\alpha} I^{\alpha} + \tfrac{1}{2} S_1^{\beta} S_2^{\alpha} I^{\alpha} + \tfrac{1}{2} S_1^{\alpha} S_2^{\beta} I^{\beta} + \tfrac{1}{2}(S_1^{+} S_2^{-} I^{-} + S_1^{-} S_2^{+} I^{+}),\end{aligned} \tag{S39 = 82}$$

$$
\begin{aligned}
&[\tilde{\tilde{H}}_{M3}^{eff*},[\tilde{\tilde{H}}_{M3}^{eff*},[\tilde{\tilde{H}}_{M3}^{eff*},S_{1z}+S_{2z}]]] \\
&=[\tilde{\tilde{H}}_{M3}^{eff*},-S_1^{\alpha}S_2^{\alpha}I^{\alpha}+\tfrac{1}{2}S_1^{\beta}S_2^{\alpha}I^{\alpha}+\tfrac{1}{2}S_1^{\alpha}S_2^{\beta}I^{\beta}+\tfrac{1}{2}(S_1^{+}S_2^{-}I^{-}+S_1^{-}S_2^{+}I^{+})] \\
&=[S_{1x}I_{2\Sigma}^{\alpha}+S_1^{\alpha}I_{2\Sigma x},-S_{1z}I_{2\Sigma}^{\alpha}+\tfrac{1}{2}S_1^{-}I_{2\Sigma}^{+}+\tfrac{1}{2}S_1^{+}I_{2\Sigma}^{-}-S_1^{\alpha}I_{2\Sigma z}] \\
&=-S_{1x}I_{2\Sigma}^{\alpha}S_{1z}I_{2\Sigma}^{\alpha}+S_{1x}I_{2\Sigma}^{\alpha}\tfrac{1}{2}S_1^{-}I_{2\Sigma}^{+}+S_{1x}I_{2\Sigma}^{\alpha}\tfrac{1}{2}S_1^{+}I_{2\Sigma}^{-}-S_{1x}I_{2\Sigma}^{\alpha}S_1^{\alpha}I_{2\Sigma z} \\
&-S_1^{\alpha}I_{2\Sigma x}S_{1z}I_{2\Sigma}^{\alpha}+S_1^{\alpha}I_{2\Sigma x}\tfrac{1}{2}S_1^{-}I_{2\Sigma}^{+}+S_1^{\alpha}I_{2\Sigma x}\tfrac{1}{2}S_1^{+}I_{2\Sigma}^{-}-S_1^{\alpha}I_{2\Sigma x}S_1^{\alpha}I_{2\Sigma z} \\
&+S_{1z}I_{2\Sigma}^{\alpha}S_{1x}I_{2\Sigma}^{\alpha}-\tfrac{1}{2}S_1^{-}I_{2\Sigma}^{+}S_{1x}I_{2\Sigma}^{\alpha}-\tfrac{1}{2}S_1^{+}I_{2\Sigma}^{-}S_{1x}I_{2\Sigma}^{\alpha}+S_1^{\alpha}I_{2\Sigma z}S_{1x}I_{2\Sigma}^{\alpha} \\
&+S_{1z}I_{2\Sigma}^{\alpha}S_1^{\alpha}I_{2\Sigma x}-\tfrac{1}{2}S_1^{-}I_{2\Sigma}^{+}S_1^{\alpha}I_{2\Sigma x}-\tfrac{1}{2}S_1^{+}I_{2\Sigma}^{-}S_1^{\alpha}I_{2\Sigma x}+S_1^{\alpha}I_{2\Sigma z}S_1^{\alpha}I_{2\Sigma x} \\
&=\tfrac{i}{2}S_{1y}I_{2\Sigma}^{\alpha}+\tfrac{1}{4}S_1^{\alpha}I_{2\Sigma}^{+}+0-\tfrac{1}{4}S_1^{-}I_{2\Sigma}^{\alpha} \\
&-\tfrac{1}{4}S_1^{\alpha}I_{2\Sigma}^{-}+0+\tfrac{1}{4}S_1^{+}I_{2\Sigma}^{\alpha}+\tfrac{i}{2}S_1^{\alpha}I_{2\Sigma y} \\
&+\tfrac{i}{2}S_{1y}I_{2\Sigma}^{\alpha}+0-\tfrac{1}{4}S_1^{\alpha}I_{2\Sigma}^{-}+\tfrac{1}{4}S_1^{+}I_{2\Sigma}^{\alpha} \\
&+\tfrac{1}{4}S_1^{\alpha}I_{2\Sigma}^{+}-\tfrac{1}{4}S_1^{-}I_{2\Sigma}^{\alpha}+0+\tfrac{i}{2}S_1^{\alpha}I_{2\Sigma y} \\
&=2iS_{1y}I_{2\Sigma}^{\alpha}+2iS_1^{\alpha}I_{2\Sigma y} \\
&=2[iS_{1y}S_2^{\alpha}I^{\alpha}+\tfrac{1}{2}S_1^{\alpha}(S_2^{+}I^{+}-S_2^{-}I^{-})].
\end{aligned}
\qquad \text{(S40 = 83)}
$$

Section VI – Example 4 (Eq. 89 to 92)

Letting

$$
\tilde{\tilde{H}}_{M4}^{eff*}=S_{1x}S_2^{\beta}I^{\beta}+\tfrac{1}{2}S_1^{\alpha}(S_2^{+}I^{+}+S_2^{-}I^{-})=S_{1x}I_{2\Sigma}^{\beta}+S_1^{\alpha}I_{2\Sigma x}, \qquad \text{(S41 = 89)}
$$

we obtain

$$
\begin{aligned}
&[\tilde{\tilde{H}}_{M4}^{eff*},S_{1z}+S_{2z}] \\
&=-iS_{1y}S_2^{\beta}I^{\beta}-\tfrac{1}{2}S_1^{\alpha}(S_2^{+}I^{+}-S_2^{-}I^{-}),
\end{aligned}
\qquad \text{(S42 = 90)}
$$

$$
\begin{aligned}
&[\tilde{\tilde{H}}_{M4}^{eff*},[\tilde{\tilde{H}}_{M4}^{eff*},S_{1z}+S_{2z}]] \\
&=[\tilde{\tilde{H}}_{M4}^{eff*},iS_{1y}S_2^{\beta}I^{\beta}+\tfrac{1}{2}S_1^{\alpha}(S_2^{+}I^{+}-S_2^{-}I^{-})] \\
&=[S_{1x}I_{2\Sigma}^{\beta}+S_1^{\alpha}I_{2\Sigma x},iS_{1y}I_{2\Sigma}^{\beta}+iS_1^{\alpha}I_{2\Sigma y}] \\
&=i(S_{1x}I_{2\Sigma}^{\beta}S_{1y}I_{2\Sigma}^{\beta}+S_{1x}I_{2\Sigma}^{\beta}S_1^{\alpha}I_{2\Sigma y}+S_1^{\alpha}I_{2\Sigma x}S_{1y}I_{2\Sigma}^{\beta}+S_1^{\alpha}I_{2\Sigma x}S_1^{\alpha}I_{2\Sigma y} \\
&-S_{1y}I_{2\Sigma}^{\beta}S_{1x}I_{2\Sigma}^{\beta}-S_1^{\alpha}I_{2\Sigma y}S_{1x}I_{2\Sigma}^{\beta}-S_{1y}I_{2\Sigma}^{\beta}S_1^{\alpha}I_{2\Sigma x}-S_1^{\alpha}I_{2\Sigma y}S_1^{\alpha}I_{2\Sigma x}) \\
&=i(\tfrac{i}{2}S_{1z}I_{2\Sigma}^{\beta}-\tfrac{1}{4i}S_1^{-}I_{2\Sigma}^{-}+\tfrac{1}{4i}S_1^{+}I_{2\Sigma}^{+}+\tfrac{i}{2}S_1^{\alpha}I_{2\Sigma z} \\
&+\tfrac{i}{2}S_{1z}I_{2\Sigma}^{\beta}-\tfrac{1}{4i}S_1^{+}I_{2\Sigma}^{+}+\tfrac{1}{4i}S_1^{-}I_{2\Sigma}^{-}+\tfrac{i}{2}S_1^{\alpha}I_{2\Sigma z}) \\
&=-S_{1z}I_{2\Sigma}^{\beta}-S_1^{\alpha}I_{2\Sigma z} \\
&=-S_{1z}S_2^{\beta}I^{\beta}-\tfrac{1}{2}S_1^{\alpha}(S_2^{\alpha}I^{\alpha}-S_2^{\beta}I^{\beta}),
\end{aligned}
\qquad \text{(S44 = 91)}
$$

$$
\begin{aligned}
&[\tilde{\tilde{H}}_{M4}^{eff*},[\tilde{\tilde{H}}_{M4}^{eff*},[\tilde{\tilde{H}}_{M4}^{eff*},S_{1z}+S_{2z}]]] \\
&=[\tilde{\tilde{H}}_{M4}^{eff*},S_{1z}S_2^{\beta}I^{\beta}+\tfrac{1}{2}S_1^{\alpha}(S_2^{\alpha}I^{\alpha}-S_2^{\beta}I^{\beta})] \\
&=[S_{1x}I_{2\Sigma}^{\beta}+S_1^{\alpha}I_{2\Sigma x},S_{1z}I_{2\Sigma}^{\beta}+S_1^{\alpha}I_{2\Sigma z}] \\
&=S_{1x}I_{2\Sigma}^{\beta}S_{1z}I_{2\Sigma}^{\beta}+S_{1x}I_{2\Sigma}^{\beta}S_1^{\alpha}I_{2\Sigma z}+S_1^{\alpha}I_{2\Sigma x}S_{1z}I_{2\Sigma}^{\beta}+S_1^{\alpha}I_{2\Sigma x}S_1^{\alpha}I_{2\Sigma z} \\
&-S_{1z}I_{2\Sigma}^{\beta}S_{1x}I_{2\Sigma}^{\beta}-S_1^{\alpha}I_{2\Sigma z}S_{1x}I_{2\Sigma}^{\beta}-S_{1z}I_{2\Sigma}^{\beta}S_1^{\alpha}I_{2\Sigma x}-S_1^{\alpha}I_{2\Sigma z}S_1^{\alpha}I_{2\Sigma x} \\
&=\tfrac{-i}{2}S_{1y}I_{2\Sigma}^{\beta}-\tfrac{1}{4}S_1^{-}I_{2\Sigma}^{\beta}+\tfrac{1}{4}S_1^{\alpha}I_{2\Sigma}^{+}-\tfrac{i}{2}S_1^{\alpha}I_{2\Sigma y} \\
&-\tfrac{i}{2}S_{1y}I_{2\Sigma}^{\beta}+\tfrac{1}{4}S_1^{+}I_{2\Sigma}^{\beta}-\tfrac{1}{4}S_1^{\alpha}I_{2\Sigma}^{-}-\tfrac{i}{2}S_1^{\alpha}I_{2\Sigma y} \\
&=-\tfrac{i}{2}S_{1y}I_{2\Sigma}^{\beta}-\tfrac{i}{2}S_1^{\alpha}I_{2\Sigma y} \\
&=-\tfrac{i}{2}S_{1y}S_2^{\beta}I^{\beta}-\tfrac{1}{4}S_1^{\alpha}(S_2^{+}I^{+}-S_2^{-}I^{-}).
\end{aligned}
\qquad \text{(S45 = 92)}
$$

Section VII – Experimental methods

DNP experiments were performed at 211 MHz ^{1}H Larmor frequency (140 GHz EPR frequency) in a custom designed spectrometer (courtesy of D. J. Ruben, Francis Bitter Magnet Laboratory, Massachusetts Institute of Technology, Cambridge, MA) equipped with a home-built 4 mm low temperature MAS probe and a superconducting sweep coil. The MW source was a custom built gyrotron capable of delivering 10 W of continuous-wave MW irradiation. The samples contained 40 mM trityl (for the SE) or 10 mM

TOTAPOL (for the CE) dispersed in a glycerol-d_8/D_2O/H_2O (60:25:15 w/w/w) matrix, also containing 2M ^{13}C-urea. Experiments were performed at 90 K, in sapphire rotors, $\omega_r/2\pi$ = 5 kHz. The enhanced ^{1}H signal of the sample was used for recording the DNP enhancement profiles and the enhancement was defined as the difference between the ^{1}H signals with MW on and off.