Singlet States: Preparation and Detection (near-equivalence)

1. Hamiltonian in the Singlet and Triplet basis

When in the presence of near equivalence, singlet and triplet states are good eigenstates of the spin Hamiltonian even in high magnetic fields. Therefore, when discussing near-equivalence, it is better to work directly in the singlet-triplet basis. The singlet-triplet basis has been derived in Eq. 1.13 of Lecture 5 and it is here rearranged as:

\[
\begin{align*}
|T_+\rangle &= |\alpha\alpha\rangle \\
|T_0\rangle &= \frac{1}{\sqrt{2}}(|\alpha\beta\rangle + |\beta\alpha\rangle) \\
|S_0\rangle &= \frac{1}{\sqrt{2}}(|\alpha\beta\rangle - |\beta\alpha\rangle) \\
|T_\mp\rangle &= |\beta\beta\rangle
\end{align*}
\] (1.1)

The Hamiltonian for a system of two spin-1/2 nuclei has also been introduced in Lecture 5 as:

\[
H = H_{CS,\Sigma} + H_{CS,\Delta} + H_J = \frac{1}{2} \Sigma \omega (I_{1,z} + I_{2,z}) + \frac{1}{2} \Delta \omega (I_{1,z} - I_{2,z}) + \omega J_1 \cdot I_2
\] (1.2)

Its representation in the singlet-triplet basis of Eq. 1.1 has the following form:

\[
\begin{pmatrix}
\frac{1}{2} \Sigma \omega + \frac{1}{4} \omega_j & 0 & 0 & 0 \\
0 & \frac{1}{4} \omega_j & \frac{1}{2} \Delta \omega & 0 \\
0 & \frac{1}{2} \Delta \omega & -\frac{3}{4} \omega_j & 0 \\
0 & 0 & 0 & -\frac{1}{2} \Sigma \omega + \frac{1}{4} \omega_j
\end{pmatrix}
\] (1.3)

The evolution of the singlet and the central triplet is inter-connected.

2. Fictitious spin-1/2 operators

Given two spin states |1⟩ and |2⟩, it is possible to define the following set of fictitious spin-1/2 operators:

\[
\begin{align*}
I^x_1 &= \frac{1}{2}(|1⟩⟨2| + |2⟩⟨1|) \\
I^y_1 &= \frac{1}{2}(|1⟩⟨2| - |2⟩⟨1|) \\
I^z_1 &= \frac{1}{2}(|1⟩⟨1| - |2⟩⟨2|) \\
E^{z2} &= |1⟩⟨1| + |2⟩⟨2|
\end{align*}
\] (2.1)

Since the outer triplet states (T±1) are disconnected from the subspace made by the central triplet (T0) and the singlet (S0) states, it is convenient to treat these subspaces as separate and introduce two sets of fictitious spin-1/2 operators as:
These operators satisfy the following commutation rules:

\[
[I^x, I^y] = \begin{cases} 
0 & \alpha \neq \beta \\
-2i \alpha & (cyclic) \quad \alpha = \beta 
\end{cases}
\]  

and have the following matrix representation in the singlet-triplet basis of Eq.1.1:

\[
\begin{align*}
I^{S_0}_x &= \frac{1}{2} \begin{pmatrix} 
0 & 0 & 0 & 0 \\
0 & 0 & 1 & 0 \\
0 & 1 & 0 & 0 \\
0 & 0 & 0 & 0 
\end{pmatrix}, & I^{S_0}_y &= \frac{1}{2} \begin{pmatrix} 
0 & 0 & 0 & 0 \\
0 & 0 & -i & 0 \\
i & 0 & 0 & 0 \\
0 & 0 & 0 & 0 
\end{pmatrix} \\
I^{S_0}_z &= \frac{1}{2} \begin{pmatrix} 
0 & 0 & 0 & 0 \\
0 & 0 & 0 & 1 \\
0 & -1 & 0 & 0 \\
0 & 0 & 0 & 0 
\end{pmatrix}, & E^{S_0} &= \begin{pmatrix} 
0 & 0 & 0 & 0 \\
0 & 1 & 0 & 0 \\
0 & 0 & 1 & 0 \\
0 & 0 & 0 & 0 
\end{pmatrix} \\
I^{T_0}_x &= \frac{1}{2} \begin{pmatrix} 
0 & 0 & 0 & 1 \\
0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 \\
1 & 0 & 0 & 0 
\end{pmatrix}, & I^{T_0}_y &= \frac{1}{2} \begin{pmatrix} 
0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 \\
is & 0 & 0 & 0 \\
0 & 0 & 0 & 0 
\end{pmatrix} \\
I^{T_0}_z &= \frac{1}{2} \begin{pmatrix} 
1 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 \\
0 & 0 & 0 & -1 
\end{pmatrix}, & E^{T_0} &= \begin{pmatrix} 
1 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 \\
0 & 0 & 0 & 1 
\end{pmatrix}
\end{align*}
\]  

3. Spin Hamiltonian in the fictitious spin-1/2 operators representation

The set of fictitious operators introduced in Sec. 2 can be used to rewrite the Hamiltonian in Eq. 1.3 as follows:
\[ H = H^{S^h} + H^{T^f_i} \]
\[ H^{S^h} = \Delta_s \hat{I}^S_{s^h} + \omega_s \hat{I}^S_{s^h} - \frac{\omega_s}{4} \hat{E}^{S^h} \]
\[ H^{T^f_i} = \sum_j \hat{J}^{T^f_i}_j + \frac{\omega_j}{4} \hat{E}^{T^f_i} \]  

(3.1)

The first two terms of \( H^{S^h} \) in Eq. 3.1 can be visualized in the Bloch-sphere of the \( S_0T_0 \) subspace as sketched in Fig. 1:

![Bloch sphere](image)

It is then evident that it can be described as composed by an effective field of strength:

\[ \omega_{s^{h}} = \sqrt{\Delta_{s}^2 + \omega_{s}^2} \]  

(3.2)

tilted about the \( y \)-axis by the angle \( \theta \) given by:

\[ \theta = \arctan \left( \frac{\Delta_s}{\omega_s} \right) \]  

(3.3)

i.e.:

\[ H_{s^{h}} = \omega_{s^{h}} \hat{R}_{s^{h}}(\theta) \hat{I}^{S^h} - \frac{\omega_s}{4} \hat{E}^{S^h} \]  

(3.4)

**4. Free Evolution under \( H^{S^h} \) and \( H^{T^f_i} \)**

The free evolution under the Hamiltonian is readily obtained by exponentiation:

\[ U(\tau) = \exp(-iH\tau) = U^{S^h}(\tau)U^{T^f_i}(\tau) = \exp\left(-i\frac{\omega_s}{4} \tau \left( \hat{E}^{S^h} - \hat{E}^{T^f_i} \right) \right) \hat{R}_{s^{h}}(\theta) \hat{R}_{s^{h}}(\omega_s \tau) \hat{R}_{s^{h}}(-\theta) \hat{R}_{s^{h}}(\Sigma_s \tau) \]

\[ U^{S^h}(\tau) = \exp(-iH_{s^{h}}\tau) = \exp\left(i\frac{\omega_s}{4} \tau \hat{E}^{S^h} \right) \hat{R}_{s^{h}}(\theta) \hat{R}_{s^{h}}(\omega_s \tau) \hat{R}_{s^{h}}(-\theta) \]  

(4.1)

\[ U^{T^f_i}(\tau) = \exp(-iH_{T^f_i}\tau) = \exp\left(-i\frac{\omega_j}{4} \tau \hat{E}^{T^f_i} \right) \hat{R}_{s^{h}}(\Sigma_s \tau) \]

In the presence of near magnetic equivalence (\( \Delta_s, \Sigma_s \ll \omega_j \)), \( \theta \) is very small and therefore the rotation about the \( y \)-axis of the \( S_0T_0 \) subspace is negligibly small. In these conditions very little triplet is converted into singlet, i.e. free evolution is not efficient to populate singlet states, therefore
the singlet preparation methods used in the case of strong or weak coupling are not of any practical use when in the presence of nearly equivalent nuclei.

5. Effect of a $\pi$-pulse in the $S_0T_0$ and $T_1T_1$ subspaces

Later on we will make use of $\pi$-pulses. The way they works in the two subspaces is not trivial but can be analyzed by taking the matrix representation of the propagator for a $\pi$-pulse in the singlet-triplet basis (note that the choice of the phase of the $\pi$-pulse, will be irrelevant in our purposes):

$$R_s(\pi) = \exp(-i\pi I_z) = \begin{pmatrix} 0 & 0 & 0 & -1 \\ 0 & -1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ -1 & 0 & 0 & 0 \end{pmatrix}$$ (5.1)

The $\pi$-pulse changes the sign of $T_0$ leaving $S_0$ unaltered. It also interchanges the two outer triplet states. This is equivalent to a $\pi$ rotation about the z-axis of the $S_0T_0$ subspace followed by a $\pi$ rotation about the x-axis of the $T_1T_1$ subspace as:

$$-i\{R^{S_0}_{x} (\pi) R^{T_1}_{z} (\pi)\} = \begin{pmatrix} 0 & 0 & 0 & -1 \\ 0 & -1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ -1 & 0 & 0 & 0 \end{pmatrix} = R_s(\pi)$$ (5.2)

6. Evolution through a J-synchronized spin-echo

Singlet-triplet transitions are more efficiently stimulated via $J$-synchronized spin echoes of the form: $\tau - \pi - \tau$. The propagator through a spin echo is readily written in the two subspaces as:

$$U^{S_0}_{\text{echo}}(2\tau) = -iU^{S_0}_{\text{es}}(\tau)R^{S_0}_{x}(\pi)U^{S_0}_{\text{es}}(\tau)$$
$$U^{T_1}_{\text{echo}}(2\tau) = -iU^{T_1}_{\text{es}}(\tau)R^{T_1}_{z}(\pi)U^{T_1}_{\text{es}}(\tau)$$

(6.1)

Using Eq. 4.1, the total propagator for the echo becomes:

$$U_{\text{echo}}(2\tau) = U^{S_0}_{\text{echo}}(\tau)U^{T_1}_{\text{echo}}(\tau)$$
$$U^{S_0}_{\text{echo}}(2\tau) = -i\exp\left(i\frac{\omega_s}{2}\tau E^{S_0}\right)\tilde{R}^{S_0}(\theta)\tilde{R}^{S_0}(\omega_s\tau)\tilde{R}^{S_0}(\pi)\tilde{R}^{S_0}(\theta)\tilde{R}^{S_0}(\omega_s\tau)\tilde{R}^{S_0}(\pi)$$
$$U^{T_1}_{\text{echo}}(2\tau) = -i\exp\left(-i\frac{\omega_j}{2}\tau E^{T_1}\right)\tilde{R}^{T_1}(\Sigma_{\tau})\tilde{R}^{T_1}(\pi)\tilde{R}^{T_1}(\Sigma_{\tau})$$

(6.2)

By choosing $\tau = \pi/(2\omega_s)$, (hence the term $J$-synchronized), Eq. 6.2 reduces to:

$$U^{S_0}_{\text{echo}}(2\tau) = -i\exp\left(i\frac{\omega_s}{2}\tau E^{S_0}\right)\tilde{R}^{S_0}(\theta)\tilde{R}^{S_0}(\pi/2)\tilde{R}^{S_0}(\pi)\tilde{R}^{S_0}(\theta)\tilde{R}^{S_0}(\pi/2)\tilde{R}^{S_0}(\pi)$$
$$U^{T_1}_{\text{echo}}(2\tau) = -i\exp\left(-i\frac{\omega_j}{2}\tau E^{T_1}\right)\tilde{R}^{T_1}(\Sigma_{\tau}/(2\omega_s))\tilde{R}^{T_1}(\pi)\tilde{R}^{T_1}(\Sigma_{\tau}/(2\omega_s))$$

(6.3)

For small values of $\theta$ (as would be valid in near magnetic equivalence conditions, $\Delta, \Sigma_s \ll \omega_j$) the $S_0T_0$ propagator in Eq. 6.3 can be approximated by a rotation of $2\theta$ around the x-axis of the $S_0T_0$
subspace (see Fig. 2 and Appendix C for proof). At the same time the $T_1T_{-1}$ propagator in Eq. 6.3 can be approximated by a rotation of $\pi$ about the x-axis of the $T_1T_{-1}$ subspace:

$$U_{\text{echo}}^{S_0}(2\tau) \sim \exp\left(i\frac{\beta\tau E_{S_0}}{2}\right) \hat{R}_x(2\theta)$$

$$U_{\text{echo}}^{T_1}(2\tau) \sim \exp\left(-i\frac{\omega_T}{2}\tau E_{T_1}\right) \hat{R}_z(\pi)$$

$$U_{\text{echo}}^{T_{-1}}(2\tau) \sim -\exp\left(i\frac{\omega_{T_{-1}}}{2}\tau E_{T_{-1}}\right) \exp\left(-i\frac{\omega_{T_{-1}}}{2}\tau E_{T_{-1}}\right) \hat{R}_z(2\theta) \hat{R}_z(\pi)$$

(6.4)

By repeating a single echo for $n$ times one obtains a total rotation of $2\theta n$. If $n$ is chosen to satisfy $2\theta n = \pi$ it is then possible to fully convert $T_0$ into $S_0$, i.e. to realize a $\pi$ rotation around the x-axis of the $S_0T_0$ subspace (see Fig. 2).

![Figure 2](image)

Figure 2 (picture from M. C. D. Tayler’s PhD thesis)

The total propagator under $n$ echoes is therefore:

$$\left(U_{\text{echo}}(2\tau)\right)^n \sim \exp\left(-in\frac{\pi}{4}(E_{T_{-1}} - E_{S_0})\right) \left[\hat{R}_z(\pi)\right]^n \hat{R}_z(\pi)$$

(6.5)

A note about $\pi$-rotations: The effect of the rotation superoperators on the subspaces is a bit tricky since the rotation adds a phase according to:

$$\hat{R}_x^{S_0}(\pi)|S_0\rangle = -i|T_0\rangle; \quad \hat{R}_x^{S_0}(\pi)|T_0\rangle = -i|S_0\rangle$$

$$\left[\hat{R}_z^{T_{-1}}(\pi)\right]^n |T_{-1}\rangle = -i^n |T_{-1}\rangle; \quad \left[\hat{R}_z^{T_1}(\pi)\right]^n |T_1\rangle = -i^n |T_1\rangle$$

(6.6)

7. M2S pulse sequences\(^2^3\)

J-synchronized echoes are building blocks of more sophisticated pulse sequences that are able to convert magnetization into singlet order (M2S) and viceversa (S2M). Figure 3 sketches a M2S pulse sequence.
The sequence starts with a $90_\circ$ pulse that converts longitudinal polarization (normalized) into triplet-triplet coherences. Readily:

$$\frac{1}{\sqrt{2}} I_z = \frac{1}{\sqrt{2}} \left( |\alpha\alpha\rangle \langle \alpha\alpha| - |\beta\beta\rangle \langle \beta\beta| \right) = \frac{1}{\sqrt{2}} \left[ |T_\circ\rangle \langle T_\circ| - |T_-\rangle \langle T_-| \right]$$

$$\frac{1}{\sqrt{2}} I_z = \frac{1}{\sqrt{2}} \left( |T_\circ\rangle + |T_-\rangle \right)$$

A J-synchronized spin echo train, made by an even number of echoes such that $n = \pi/(2\theta)$ (i.e. a 180 degrees rotation in the $S_0T_0$ subspace) follows. It swaps $T_0$ with $S_0$ according to Eq. 6.6:

$$\frac{1}{2} \left[ (|T_\circ\rangle + |T_-\rangle) \langle T_\circ| + |T_-\rangle \langle T_-| \right] \rightarrow \begin{cases} \frac{i}{2} \left[ (|T_\circ\rangle + |T_-\rangle) \langle S_0| - |S_0\rangle \langle T_\circ + T_-| \right] & n = \text{even} \\ \frac{i}{2} \left[ (|T_\circ\rangle + |T_-\rangle) \langle S_0| + |S_0\rangle \langle T_\circ + T_-| \right] & n = \text{odd} \end{cases}$$

In practice $n$ is always chosen as even since later on one need to repeat the same echo train with half the number of echoes.

A $90_\circ$ pulse is then applied. It converts $T_{\pm 1}$ into $T_0$ and vice versa leaving the singlet untouched, i.e.:

$$|T_\circ\rangle + |T_-\rangle \rightarrow i\sqrt{2}|T_0\rangle$$

$$|T_0\rangle \rightarrow -\frac{i}{\sqrt{2}} (|T_\circ\rangle + |T_-\rangle)$$

$$|S_0\rangle \rightarrow |S_0\rangle$$

Therefore Eq. 7.2 evolves as:

$$\begin{cases} \frac{i}{2} \left[ (|T_\circ\rangle + |T_-\rangle) \langle S_0| - |S_0\rangle \langle T_\circ + T_-| \right] & n = \text{even} \\ \frac{i}{2} \left[ (|T_\circ\rangle + |T_-\rangle) \langle S_0| + |S_0\rangle \langle T_\circ + T_-| \right] & n = \text{odd} \end{cases} \rightarrow \begin{cases} \frac{1}{\sqrt{2}} \left[ |T_0\rangle \langle S_0| + |S_0\rangle \langle T_\circ| \right] = \sqrt{2} T_{S_0}^{T_\circ} & n = \text{even} \\ \frac{1}{\sqrt{2}} \left[ |T_0\rangle \langle S_0| - |S_0\rangle \langle T_\circ| \right] = i\sqrt{2} T_{S_0}^{T_\circ} & n = \text{odd} \end{cases}$$

Figure 3 (picture from M. C. D. Tayler’s PhD thesis)
Successively, the system is left to evolve under the internal Hamiltonian for a \( \tau \). The effect of a free evolution is described in Eq. 4.1. It approximates a rotation of 90 degrees about the z-axis of the \( S_0T_0 \) subspace, therefore giving:

\[
\sqrt{2} I_z^{S_0T_0} \xrightarrow{U(\tau)} \sqrt{2} I_y^{S_0T_0} \quad n = \text{even}
\]  

(7.5)

A second spin echo train, composed by half the number of echoes (\( n' = n/2 \)), follows. It results in a 90 degrees rotation about the x-axis of the \( S_0T_0 \) subspace.

\[
\sqrt{2} I_y^{S_0T_0} \xrightarrow{(U_{\text{echo}}(2\tau))^{n/2}} \sqrt{2} I_z^{S_0T_0}
\]  

(7.6)

The term \( I_z^{S_0T_0} \) is exactly what we were looking for. It corresponds to a population difference across the singlet state \( S_0 \) and the central triplet \( T_0 \) (see Eq. 2.2). This demonstrates that M2S is able to convert magnetization into singlet spin order. The opposite conversion, from singlet order to longitudinal magnetization, can be obtained by time reversal of the M2S scheme (named S2M). The same arguments used here can be used to prove how S2M sequences works.

8. Efficiency of the M2S conversion

To work out the efficiency of the proposed M2S scheme in converting longitudinal magnetization into singlet order, two more calculations need to be done. Firstly, we need to find out what is the maximum conversion factor allowed by theory, and secondly, how much of this is achieved by M2S in ideal conditions. The maximum transfer amplitude between two operators under the unitary transformation \( \hat{U} \) can be calculated by the equation introduced by Sørensen:\n
\[
A_{A \rightarrow B}^{\text{max}} = \left| \frac{\text{Tr}(O_B^{*} \hat{U} O_A)}{\text{Tr}(O_B^{*} O_B)} \right|_{\text{max}} = \frac{\Lambda_B \cdot \Lambda_A}{\Lambda_B \cdot \Lambda_B}
\]  

(8.1)

where \( \Lambda_A, \Lambda_B \) are ordered list of eigenvalues of the corresponding operators \( O_A, O_B \). In our case we need to consider the following two transformations:

\[
\begin{align*}
\frac{I_z}{\sqrt{2}} & \xrightarrow{\text{M2S}} \sqrt{2} I_z^{S_0T_0} \\
\sqrt{2} I_z^{S_0T_0} & \xrightarrow{\text{S2M}} \frac{I_z}{\sqrt{2}}
\end{align*}
\]  

(8.2)

The eigenvalues of the two operators are readily calculated, as both are diagonal in the singlet-triplet basis:

\[
\frac{I_z}{\sqrt{2}} = \frac{1}{\sqrt{2}} \begin{pmatrix}
1 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 \\
0 & 0 & 0 & -1
\end{pmatrix} \Rightarrow \Lambda = \begin{pmatrix}
1 \\
0 \\
0 \\
-1
\end{pmatrix}
\]  

(8.3)

\[
\sqrt{2} I_z^{S_0T_0} = \frac{1}{\sqrt{2}} \begin{pmatrix}
0 & 0 & 0 & 0 \\
0 & 1 & 0 & 0 \\
0 & 0 & -1 & 0 \\
0 & 0 & 0 & 0
\end{pmatrix} \Rightarrow \Lambda = \begin{pmatrix}
1 \\
0 \\
0 \\
-1
\end{pmatrix}
\]  

(8.3)
Eq. 8.1 gives 1 for both of the path in Eq. 8.2, meaning that both transformations can be accomplished with 100% efficiency. Note that normalization factors must be used. We can now use Eq. 8.1 to calculate how much of this efficiency can be theoretically achieved by M2S and S2M sequences as:

\[
\frac{\text{Tr} \left( \sqrt{2} I_{z}^{S_{0}+} \cdot \text{M2S} \cdot I_{z} / \sqrt{2} \right)}{\text{Tr} \left( \sqrt{2} I_{z}^{S_{0}+} \cdot \sqrt{2} I_{z}^{S_{0}} \right)} = \frac{\text{Tr} \left( \sqrt{2} I_{z}^{S_{0}+} \cdot \sqrt{2} I_{z}^{S_{0}} \right)}{\text{max} \left( \text{Tr} \left( \sqrt{2} I_{z}^{S_{0}+} \cdot \sqrt{2} I_{z}^{S_{0}} \right) \right)} = 1 \quad (8.4)
\]

which confirms that the M2S sequence achieves the maximum allowed conversion. The same is true for S2M.

A final issue is worth noting. Despite we prepare the operator \( I_{z}^{S_{0}} \) which represents a population difference between the singlet and the central triplet state, for system where \( T_{S} \gg T_{1} \) the populations of the three triplet states equilibrates within a few \( T_{1} \). From that point onwards we are then left with the following state:

\[
\mathbf{S} = \frac{\sqrt{3}}{2} \left( |S_{0}\rangle \langle S_{0}| - \frac{1}{3} \sum_{m=-1}^{1} |T_{m}\rangle \langle T_{m}| \right) \quad (8.5)
\]

representing the singlet order (normalized), i.e. the difference between the singlet population and the mean triplet population. For this state we have the following matrix representation:

\[
\mathbf{S} = \frac{\sqrt{3}}{2} \begin{pmatrix}
1 & 0 & 0 & 0 \\
0 & -1/3 & 0 & 0 \\
0 & 0 & -1/3 & 0 \\
0 & 0 & 0 & -1/3 \\
\end{pmatrix} \Rightarrow \Lambda = \begin{pmatrix}
-1/(2\sqrt{3}) \\
-1/(2\sqrt{3}) \\
-1/(2\sqrt{3}) \\
\sqrt{3}/2 \\
\end{pmatrix} \quad (8.6)
\]

For this state Eq. 8.1 gives \( A_{\text{M2S}}^{\text{max}} = \sqrt{2/3} \). The M2S realizes the same transformation with the maximum allowed efficiency:

\[
\frac{\text{Tr} \left( \mathbf{S}^{+} \cdot \text{M2S} \cdot I_{z} / \sqrt{2} \right)}{\text{Tr} \left( \mathbf{S}^{+} \cdot \mathbf{S} \right)} = \frac{1}{\sqrt{2}} \frac{\text{Tr} \left( \mathbf{S}^{+} \cdot |S_{0}\rangle \langle S_{0}| - \mathbf{S}^{+} \cdot |T_{0}\rangle \langle T_{0}| \right)}{\text{Tr} \left( \mathbf{S}^{+} \cdot \mathbf{S} \right)} = \sqrt{2/3} \quad (8.7)
\]

An identical factor is found for the inverse transformation (S2M). This means that (1-2/3)=1/3 of polarization is lost in going from longitudinal magnetization to singlet order and back again.

**Appendix C.**

In this appendix we will demonstrate how the approximation used from Eq. 6.3 to Eq. 6.4 works.

The task is to demonstrate the following equality:

\[
\tilde{R}_{\phi}(\theta) \tilde{R}_{\phi}(\pi/2) \tilde{R}_{\phi}(-\theta) \tilde{R}_{\phi}(\pi) \tilde{R}_{\phi}(\theta) \tilde{R}_{\phi}(\pi/2) \tilde{R}_{\phi}(-\theta) \sim -\tilde{R}_{\phi}(2\theta) \quad \text{for} \quad \theta \ll 1 \\
(C.1)
\]

Lecture 8: pg. 8
We do that working out the “sandwich” denoted by the curly brackets in Eq. C.1 first. For this we use the trick of inserting a pair of extra rotation. This allows to reduce the sandwich of Eq. C.1 as:

\[
\hat{R}^{xT}_{y}(-\theta)\hat{R}^{xT}_{z}(\pi)\hat{R}^{xT}_{y}(\theta)\hat{R}^{xT}_{z}(\pi)\hat{R}^{xT}_{y}(-\theta)\hat{R}^{xT}_{z}(\pi) = \hat{R}^{xT}_{y}(-2\theta)\hat{R}^{xT}_{z}(\pi)
\]

(\text{C.2})

that goes back into Eq. C.1 that now simplifies to:

\[
\hat{R}^{xT}_{y}(\theta)\hat{R}^{xT}_{z}(\pi/2)\hat{R}^{xT}_{y}(-2\theta)\hat{R}^{xT}_{z}(\pi)\hat{R}^{xT}_{y}(\pi/2)\hat{R}^{xT}_{z}(\pi) - \hat{R}^{xT}_{y}(2\theta) \quad \text{for } \theta \ll 1
\]

(\text{C.3})

We apply the same trick of adding a pair of extra rotation to solve the ‘sandwich’ in curly brackets of Eq. C.3 as:

\[
\hat{R}^{xT}_{y}(\pi/2)\hat{R}^{xT}_{z}(-2\theta)\hat{R}^{xT}_{y}(\pi/2)\hat{R}^{xT}_{z}(\pi)\hat{R}^{xT}_{y}(\pi/2)\hat{R}^{xT}_{z}(\pi) - \hat{R}^{xT}_{y}(2\theta)
\]

(\text{C.4})

The result in Eq. C.4 is included into Eq. C.3 that now simplifies as:

\[
-\hat{R}^{xT}_{y}(\theta)\hat{R}^{xT}_{z}(2\theta)\hat{R}^{xT}_{y}(-\theta) ~ -\hat{R}^{xT}_{y}(2\theta) \quad \text{for } \theta \ll 1
\]

(\text{C.5})

which can be demonstrated using the first order terms in \(\theta\) in the series expansion equation for the exponential involved in the rotation superoperators:

\[
\hat{R}^{xT}_{y}(\theta)\hat{R}^{xT}_{z}(2\theta)\hat{R}^{xT}_{y}(-\theta) = e^{-i\theta J_{y}^{xT}} e^{-2i\theta J_{z}^{xT}} e^{i\theta J_{y}^{xT}} = \left(E^{xT}_{y} - i\theta T_{y}^{xT}\right)\left(E^{xT}_{z} - i2\theta T_{z}^{xT}\right)\left(E^{xT}_{y} + i\theta T_{y}^{xT}\right) \equiv E^{xT}_{y} - i2\theta T_{z}^{xT}
\]

(\text{C.6})

References:


