Nuances of Multi-Quantum excitation in solid state NMR of quadrupolar nuclei

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Supporting Information

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1 3Q excitation in spin 3/2

1.1 Scheme 1A

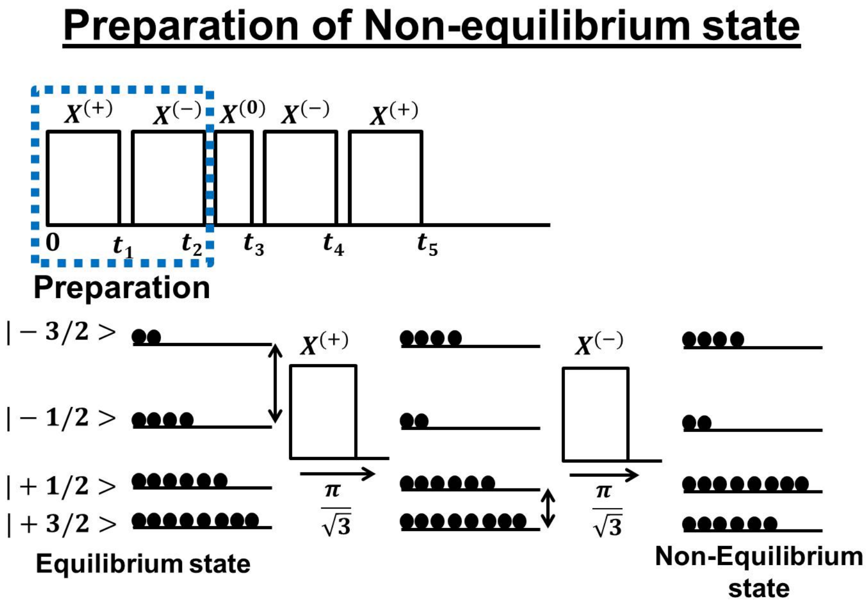

Figure 1: The figure illustrates the preparation of non-equilibrium state in a spin 3/2 system. The first two pulses (dotted blue box) are employed for preparing the non-equilibrium state, while the remaining pulses are employed for creating the desired MQ coherence. The redistribution of the spin population due to the preparatory pulses are depicted underneath. The duration between the pulses is 2 μs.

1.1.1 Density matrix calculations

To begin with, the Hamiltonian of an isolated quadrupolar spin system subjected to the Zeeman (H_z), Quadrupolar (H_Q) and the RF interaction (H_{RF}) is represented by

$$\begin{aligned} H &= H_Z + H_Q + H_{RF} \\ &= -\hbar\omega_0 I_z - \omega_Q(\alpha,\beta)[3I_z^2 - I(I+1)] - 2\hbar\omega_1\cos(\omega t)I_x. \end{aligned} \tag{1}$$

In the above equation 'ω_0' denotes the larmor frequency and 'ω_Q' depicts the quadropolar interaction $\left(\omega_Q(\alpha,\beta) = \frac{3C_Q}{2I(2I-1)}\left(\frac{3\cos^2\beta-1}{2} + \frac{\eta}{2}\sin^2\beta\cos 2\alpha\right)\right)$. The oscillating magnetic field is characterized by the frequency 'ω' and amplitude 'ω_1'. Since the magnitude of the quadrupolar interaction often exceeds the amplitude of the RF field ($\omega_Q > \omega_1$), the above Hamiltonian is transformed into the Zeeman-Quadrupolar (Z-Q) interaction frame[1] as defined below.

$$\tilde{H}_{RF}(t) = e^{\frac{i}{\hbar}H_z t}.e^{\frac{i}{\hbar}H_Q t}He^{-\frac{i}{\hbar}H_Q t}.e^{-\frac{i}{\hbar}H_z t} \tag{2}$$

To facilitate analytic description, operators of the kind $I_r^{(q)}$ were defined recently[2] to describe transitions in quadrupolar spin systems. In this representation, the index 'q' depicts the order of the excited coherence $|\Delta m| = q$ and 'r' the excitation frequency through the relation, $\omega = q\omega_0 + r\omega_Q$. Employing these operators, the RF Hamiltonian in the Z-Q interaction frame is represented by

$$\begin{aligned}\tilde{H}_{RF}(t) = -\frac{\hbar\omega_1}{2}\Big[2\Big\{\Big(I_0^{(1)}(a) + iI_0^{(1)}(s)\Big)e^{(it[\omega-\omega_0])} + \Big(I_0^{(1)}(a) - iI_0^{(1)}(s)\Big)e^{(-it[\omega-\omega_0])}\Big\} \\ +\sqrt{3}\Big\{\Big(I_{-1}^{(1)}(a) + iI_{-1}^{(1)}(s)\Big)e^{\left(it\left[\omega-\left\{\omega_0-\omega_Q(\alpha,\beta)\right\}\right]\right)} + \Big(I_{-1}^{(1)}(a) - iI_{-1}^{(1)}(s)\Big)e^{\left(-it\left[\omega-\left\{\omega_0-\omega_Q(\alpha,\beta)\right\}\right]\right)}\Big\} \\ +\sqrt{3}\Big\{\Big(I_{+1}^{(1)}(a) + iI_{+1}^{(1)}(s)\Big)e^{\left(it\left[\omega-\left\{\omega_0+\omega_Q(\alpha,\beta)\right\}\right]\right)} + \Big(I_{+1}^{(1)}(a) - iI_{+1}^{(1)}(s)\Big)e^{\left(-it\left[\omega-\left\{\omega_0+\omega_Q(\alpha,\beta)\right\}\right]\right)}\Big\}\Big].\end{aligned} \quad (3)$$

When the excitation frequency is chosen to $\omega = \omega_0 + \omega_Q$, the above equation reduces to an effective RF Hamiltonian as represented below.

$$\tilde{H}_{RF,eff} = -\hbar\omega_1\sqrt{3}I_{+1}^{(1)}(a) \quad (4)$$

For the sake of illustration, the above effective RF Hamiltonian (exclusive of the coefficients) will be symbolically represented by $X^{(+)}$ in the following sections. Subsequently, the equilibrium density operator in the conventional scheme is transformed by a frequency selective pulse ($X^{(+)}$) as represented below.

$$\begin{aligned}\tilde{\rho}(t_1) &= e^{-\frac{i}{\hbar}H_{RF,eff}t_1}\tilde{\rho}_{eq}(0)e^{\frac{i}{\hbar}H_{RF,eff}t_1} \\ \tilde{\rho}(t_1) &= e^{i\omega_1X^{(+)}t_1}\tilde{\rho}_{eq}(0)e^{-i\omega_1X^{(+)}t_1}\end{aligned} \quad (5)$$

Employing the operator relations summarized in recent literature[1, 2], a closed form solution for the density operator is obtained.

$$\tilde{\rho}(t_1) = I_z + I_{+1}^{(1)}(s)\sin\sqrt{3}\omega_1t_1 + I_{+0}^{(0)}\left(\cos\sqrt{3}\omega_1t_1 - 1\right) \quad (6)$$

When the amplitude of the RF pulse is adjusted to ($\sqrt{3}\omega_1t_1 = \pi$), the density operator reduces to a simpler form as described below.

$$\tilde{\rho}(t_1) = I_z - 2I_{+0}^{(0)} \quad (7)$$

The evolution of the density operator under a sequence of frequency selective pulses with filp angles ($\frac{\pi}{\sqrt{3}}, \frac{\pi}{4}, \frac{\pi}{\sqrt{3}}, \frac{\pi}{\sqrt{3}}$), respectively, is evaluated and described below.

$$\tilde{\rho}(t_2) = I_z - 2I_{+0}^{(0)} - 2I_{-0}^{(0)} \quad (8)$$

$$\tilde{\rho}(t_3) = I_z + 3I_0^{(1)}(s) - 2I_{+0}^{(0)} - 2I_{-0}^{(0)} - 3I_0^{(0)} \quad (9)$$

$$\tilde{\rho}(t_4) = I_z + 3I_{-1}^{(2)}(s) - 2I_{+0}^{(0)} - 3I_{-0}^{(0)} - 3I_0^{(0)} \quad (10)$$

$$\tilde{\rho}(t_5) = I_z + 3I_0^{(3)}(s) - 3I_{+0}^{(0)} - 3I_{-0}^{(0)} - 3I_0^{(0)} \quad (11)$$

1.1.2 Excitation of 3Q transitions in spin 3/2

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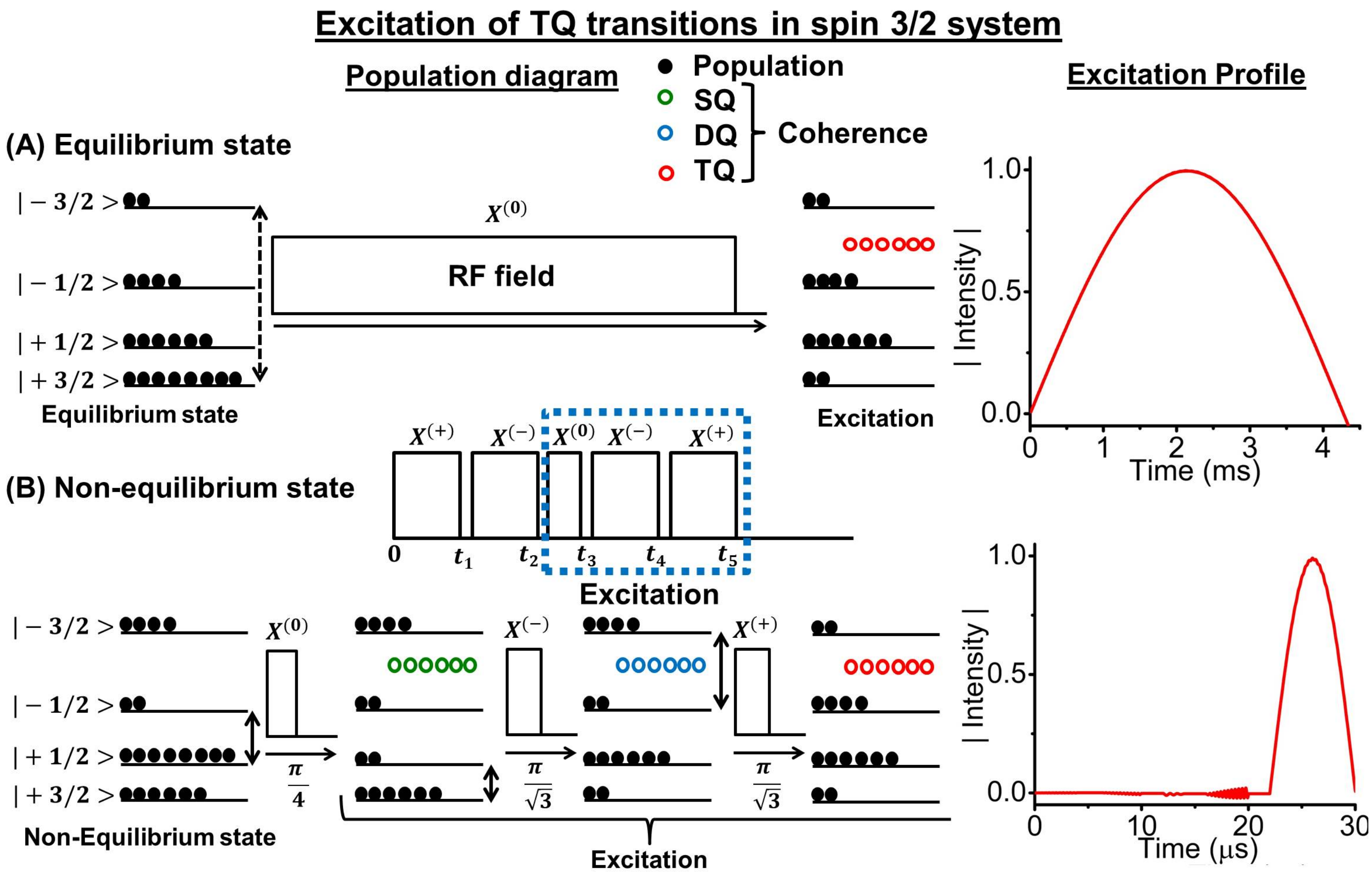


Figure 2: The figure depicts the efficiency of TQ excitation in spin 3/2 system employing **(A)** Equilibrium and **(B)** Non-Equilibrium state. On the left hand side, the population distribution before and after the pulse is depicted. In panel (A), the initial state corresponds to the Boltzmann distribution while in panel (B) the excitation is carried out from a non-equilibrium state. The resulting excitation profile (Single crystal) from the two schemes are depicted on the right hand side. The following parameters in the form of pulse amplitude ($\nu_{1,i}$ (kHz)), frequency offset ($\nu_{fo,i} = \nu_i - \nu_0$ (MHz)), the pulse duration ($\tau_i = t_i - t_{i-1}$ (μs)) were employed in the simulations i.e. ($\nu_{1,i}$, τ_i, $\nu_{fo,i}$). **(A)** (56, t, 0). **(B)** (72.2, 4, 1.5), (72.2, 4, -1.5), (62.5, 2, 0), (72.2, 4, -1.5), (72.2, t, 1.5). In above simulations the quadrupolar coupling constant $C_Q = 3$ MHz and $\eta = 0$.

1.2 Scheme 1B

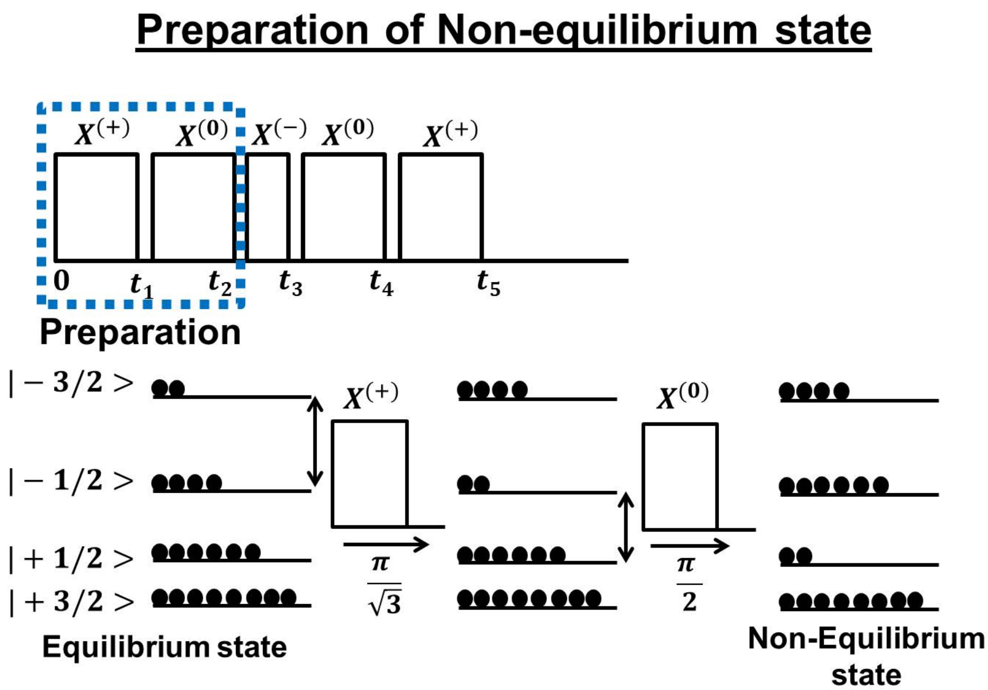


Figure 3: The figure illustrates the preparation of non-equilibrium state in a spin 3/2 system. The first two pulses (dotted blue box) are employed for preparing the non-equilibrium state, while the rest creates the desired coherence. The redistribution of the spin population due to the preparatory pulses are depicted underneath. The duration between the pulses is 2 μs.

1.2.1 Density matrix calculations

The evolution of the density operator under the pulse scheme 3B (see Figure 3) with flip-angles ($\frac{\pi}{\sqrt{3}}$, $\frac{\pi}{2}$, $\frac{\pi}{2\sqrt{3}}$, $\frac{\pi}{2}$, $\frac{\pi}{\sqrt{3}}$) is described below.

$$\tilde{\rho}(t_0) = I_z \tag{12}$$

$$\tilde{\rho}(t_1) = I_z - 2I_{+0}^{(0)} \tag{13}$$

$$\tilde{\rho}(t_2) = I_z - 2I_{+0}^{(0)} - 4I_0^{(0)} \tag{14}$$

$$\tilde{\rho}(t_3) = I_z + 3I_{-1}^{(1)}(s) - 3I_{-0}^{(0)} - 2I_{+0}^{(0)} - 4I_0^{(0)} \tag{15}$$

$$\tilde{\rho}(t_4) = I_z - 3I_{-1}^{(2)}(s) - 3I_{-0}^{(0)} - 2I_{+0}^{(0)} - 3I_0^{(0)} \tag{16}$$

$$\tilde{\rho}(t_5) = I_z - 3I_0^{(3)}(s) - 3I_{-0}^{(0)} - 3I_{+0}^{(0)} - 3I_0^{(0)} \tag{17}$$

1.2.2 Excitation of 3Q transitions in spin 3/2

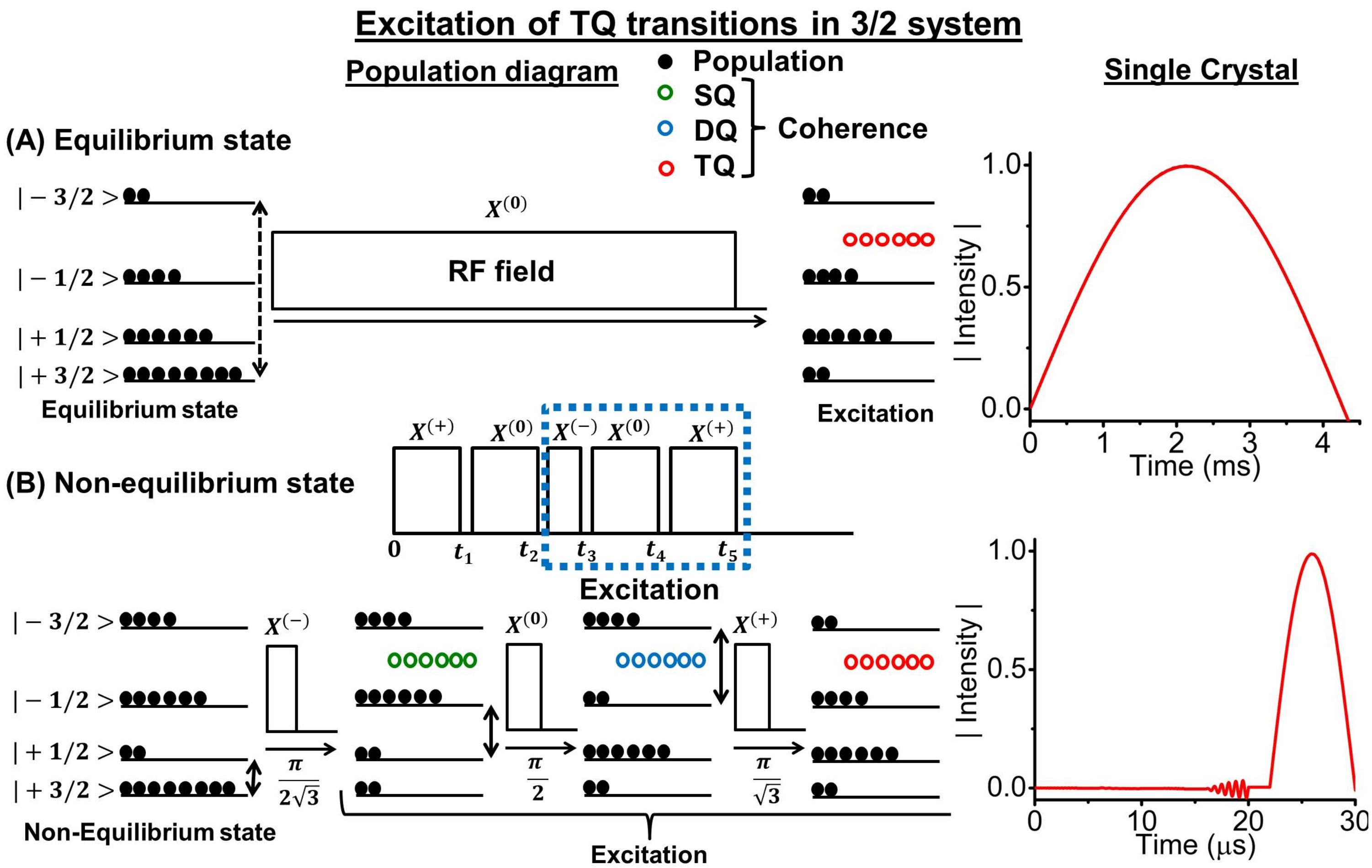


Figure 4: The figure depicts TQ excitation in spin 3/2 system employing **(A)** Equilibrium state and **(B)** Non-Equilibrium state. On the left hand side, the population distribution before and after the pulse is depicted. In panel (A), the initial state corresponds to the Boltzmann distribution, while in panel (B) the excitation is carried out from a non-equilibrium state. The resulting excitation profile (Single crystal) from the two schemes are depicted on the right hand side. The following parameters in the form of pulse amplitude ($\nu_{1,i}$ (kHz)), frequency offset ($\nu_{fo,i} = \nu_i - \nu_0$ (MHz)), the pulse duration ($\tau_i = t_i - t_{i-1}$ (μs)) were employed in the simulations i.e. ($\nu_{1,i}$, τ_i, $\nu_{fo,i}$). **(A)** (56, t, 0). **(B)** (72.2, 4, 1.5), (62.5, 4, 0), (72.2, 2, -1.5), (62.5, 4, 0), (72.2, t, 1.5). In above simulations the quadrupolar coupling constant is kept constant (see Figure 2).

2 Excitation of 5Q transitions in spin 5/2 system

2.1 Scheme 2A

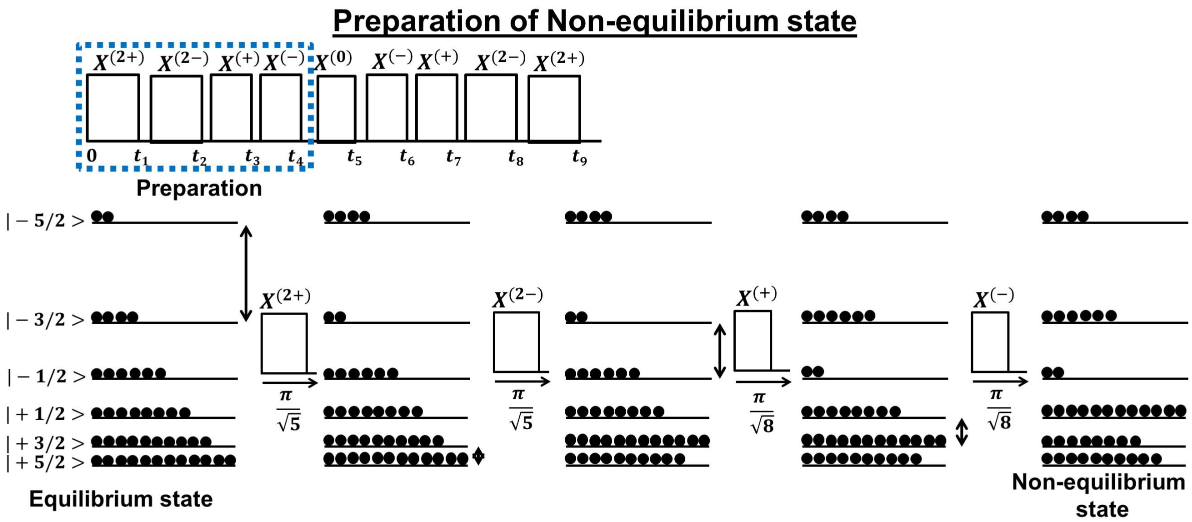
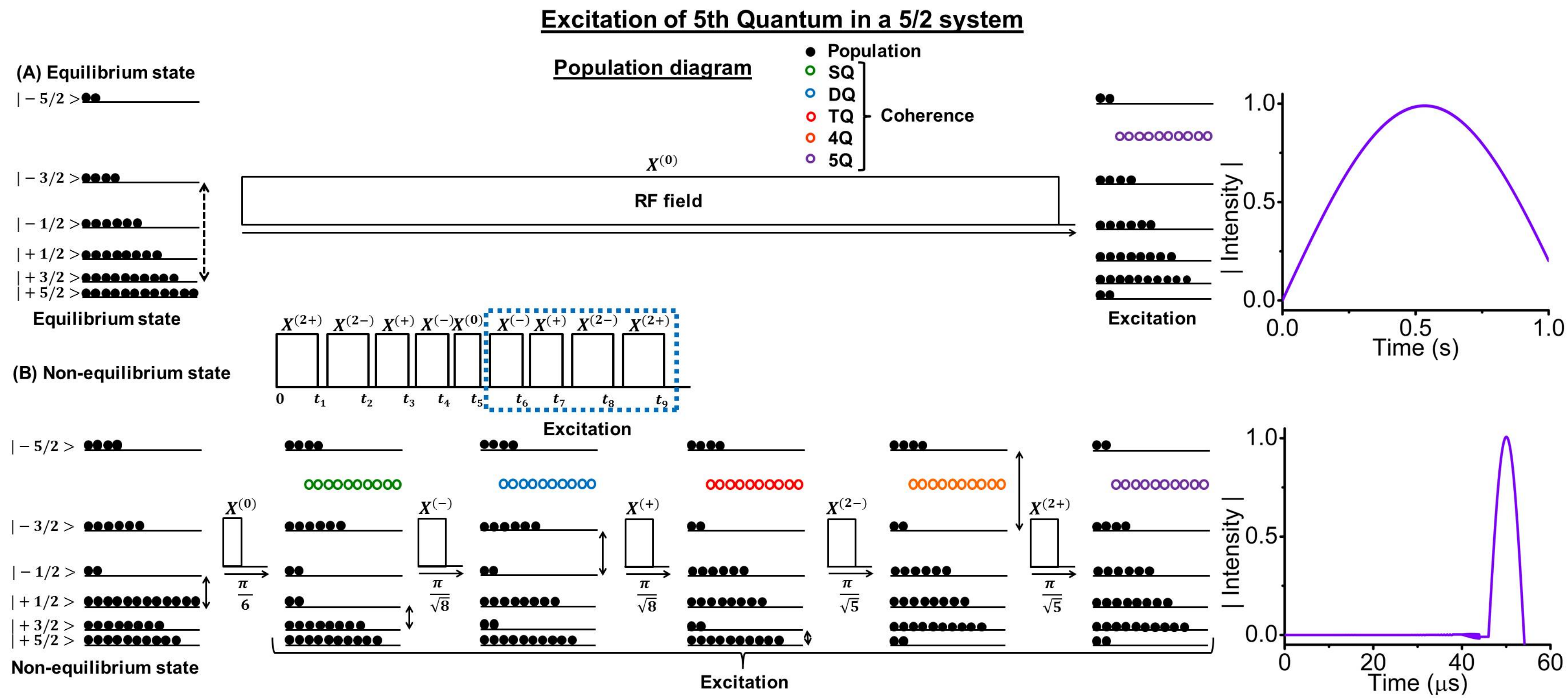


Figure 5: The figure illustrates the preparation of non-equilibrium state in a spin 5/2 system. The first four pulses (dotted blue box) are employed for preparing the non-equilibrium state, while the remaining pulses are employed to create the desired coherence. The redistribution of the spin population due to the preparatory pulses are depicted underneath the pulse scheme. The duration between the pulses is 2 μs.

2.1.1 Excitation of 5Q transition in spin 5/2 system



∞

Figure 6: The figure depicts the excitation of 5Q-transition in spin 5/2 system employing **(A)** Equilibrium and **(B)** Non-Equilibrium state for a spin-5/2 system. On the left hand side, the population distribution before and after the pulse is depicted. In panel (A), the initial state corresponds to the Boltzmann distribution while in panel (B) the excitation is carried out from a non-equilibrium state. The resulting excitation profile (Single crystal) from the two schemes are depicted on the right hand side. The following parameters in the form of pulse amplitude ($\nu_{1,i}$ (kHz)), frequency offset ($\nu_{fo,i} = \nu_i - \nu_0$ (MHz)), the pulse duration ($\tau_i = t_i - t_{i-1}$ (μs)) were employed in the simulations i.e. ($\nu_{1,i}$, τ_i, $\nu_{fo,i}$). **(A)** (100, t, 0). **(B)** (56, 4, 3), (56, 4, -3), (44.2, 4, 1.5), (44.2, 4, -1.5), (41.67, 2, 0), (44.2, 4, -1.5), (44.2, 4, 1.5), (56, 4, -3), (56, t, 3). In above simulations, the quadrupolar coupling constant $C_Q = 10$ MHz and $\eta = 0$.

2.2 Scheme 2B

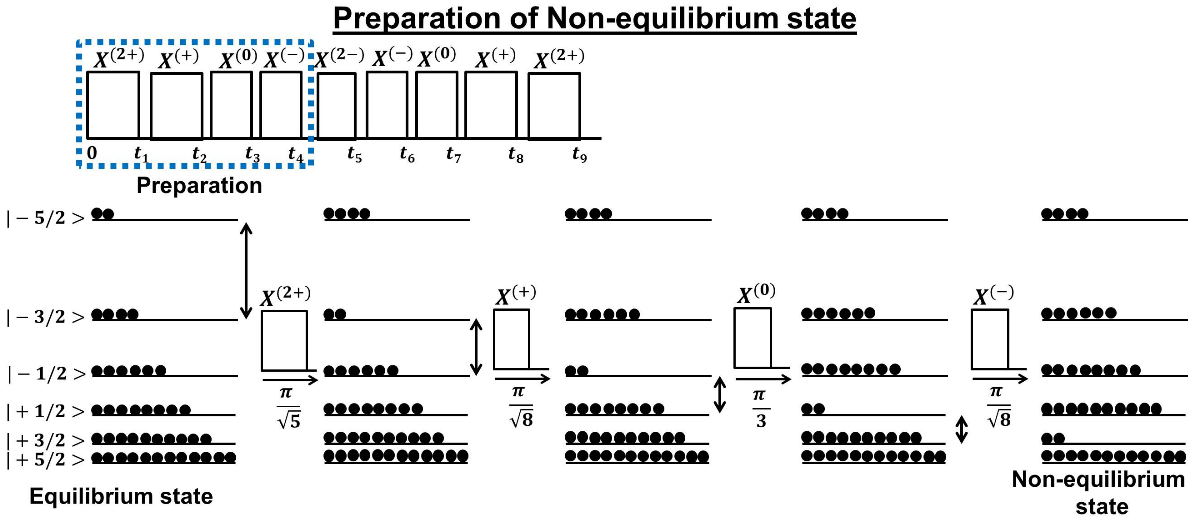


Figure 7: The figure illustrates the preparation of non-equilibrium state in a spin-5/2 system. The first four pulses (dotted blue box) are employed for preparing the non-equilibrium state, while the remaining pulses are employed to create the desired coherence. The redistribution of the spin population due to the preparatory pulses are depicted underneath. The duration between the pulses is 2 μs.

2.2.1 Excitation of 5Q transition in spin 5/2 system

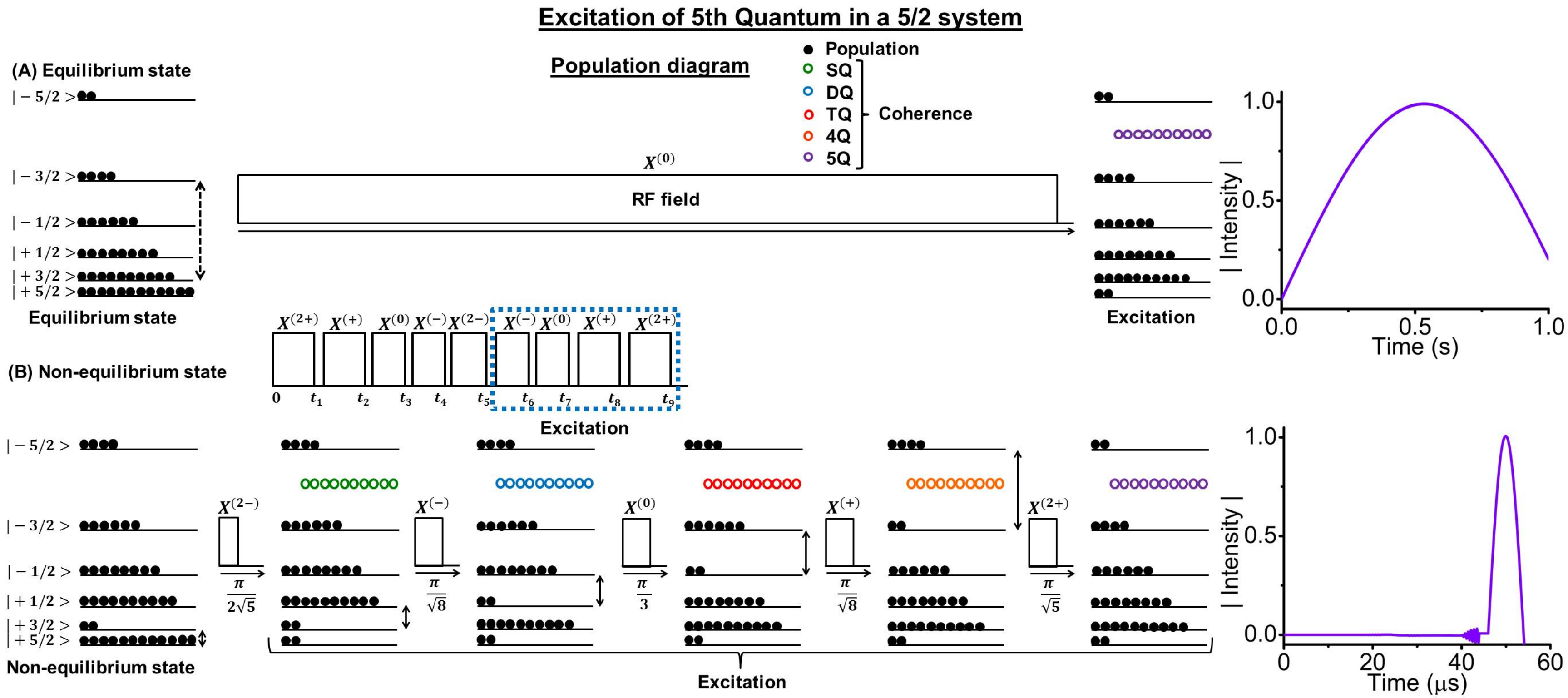


Figure 8: The figure depicts the excitation of 5Q-transition in spin 5/2 system employing **(A)** Equilibrium and **(B)** Non-Equilibrium state for a spin-5/2 system. On the left hand side, the population distribution before and after the pulse is depicted. In panel (A), the initial state corresponds to the Boltzmann distribution while in panel (B) the excitation is carried out from a non-equilibrium state. The resulting excitation profile (Single crystal) from the two schemes are depicted on the right hand side. The following parameters in the form of pulse amplitude ($\nu_{1,i}$ (kHz)), frequency offset ($\nu_{fo,i} = \nu_i - \nu_0$ (MHz)), the pulse duration ($\tau_i = t_i - t_{i-1}$ (μs)) were employed in the simulations i.e. ($\nu_{1,i}$, τ_i, $\nu_{fo,i}$). **(A)** (100, t, 0). **(B)** (56, 4, 3), (44.2, 4, 1.5), (41.67, 4, 0), (44.2, 4, -1.5), (56, 2, -3), (44.2, 4, -1.5), (41.67, 4, 0), (44.2, 4, 1.5), (56, t, 3). In above simulations the quadrupolar coupling constant is kept constant (see Figure 6).

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3 Comparision of TQ excitation in spin 3/2 and 5/2 systems

1 . Matrix representation of $T^{(3)3}$ operator in spin 3/2

$$T^{(3)3} = i \begin{pmatrix} 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix} \tag{18}$$

2 . Matrix representation of $T^{(3)3}$ operator in spin 5/2

$$T^{(3)3} = \frac{i}{3\sqrt{2}} \begin{pmatrix} 0 & 0 & 0 & \sqrt{5} & 0 & 0 \\ 0 & 0 & 0 & 0 & 2\sqrt{2} & 0 \\ 0 & 0 & 0 & 0 & 0 & \sqrt{5} \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \end{pmatrix} \tag{19}$$

As depicted in Figure 9, the efficieny of TQ excitation is lower in spin 5/2 in comparision to spin 3/2 i.e.,

$$\frac{TQ_{spin-5/2}}{TQ_{spin-3/2}} = \frac{2}{3}$$

The above result may also be deduced from the matrix elements of the $T^{(3)3}$ operator represented above.

$$\left\langle \frac{3}{2}, -\frac{3}{2} \right| T^{(3)3} \left| \frac{3}{2}, \frac{3}{2} \right\rangle = i$$

$$\left\langle \frac{5}{2}, -\frac{3}{2} \right| T^{(3)3} \left| \frac{5}{2}, \frac{3}{2} \right\rangle = \frac{2}{3} i$$

4 Frequency Sweep techniques

4.1 Single Frequency Sweep ($\mathbf{SFS_{I/O}}$)

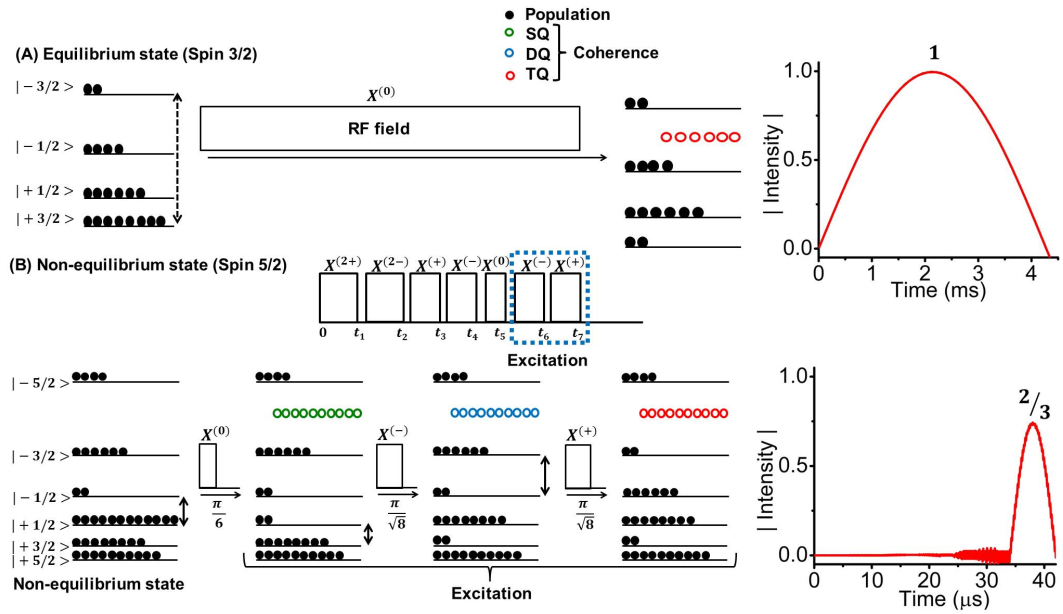

Figure 9: The figure depicts the excitation of 3Q transitions. Panel (A) depicts the excitation profile of TQ transition in a spin 3/2 system in a single pulse experiment whereas panel (B) depicts the TQ excitation profile in a spin 5/2 system employing frequency selective pulse scheme.

4.2 Double Frequency Sweep ($DFS_{I/O}$)

References

[1] R. Venkata SubbaRao, D. Srivastava, and R. Ramachandran, Phys. Chem. Chem. Phys. **15**, 2081 (2013).

[2] D. Srivastava, R. Venkata SubbaRao, and R. Ramachandran, Phys. Chem. Chem. Phys. **15**, 6699 (2013).

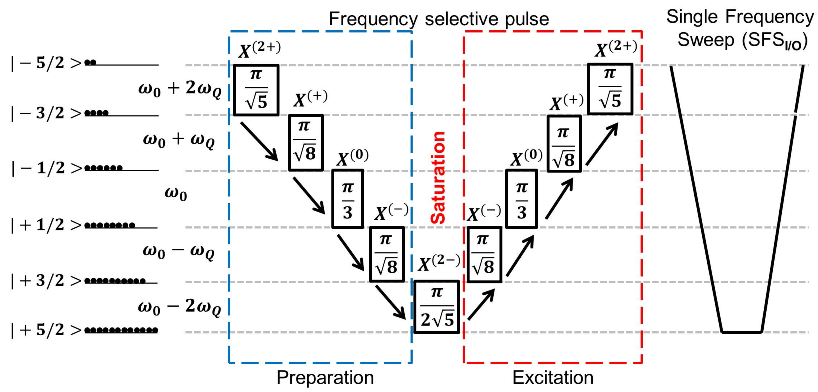

Figure 10: The figure depicts the excitation of 5Q transitions in a spin 5/2 system employing discrete frequency selective pulses and continuous frequency sweep techniques. The entire MQ experiment is divided into three stages. 1) Preparation, $[X^{(2+)}][X^{(+)}][X^{(0)}][X^{(-)}]$ 2) Saturation, $[X^{(2-)}]$ 3) Excitation, $[X^{(-)}][X^{(0)}][X^{(+)}][X^{(2+)}]$.

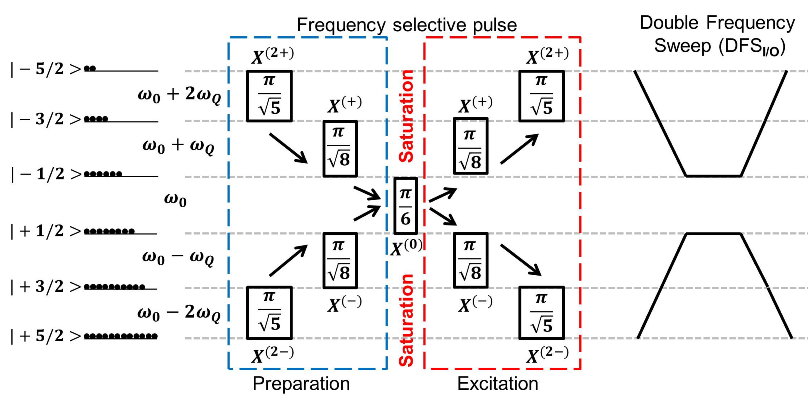

Figure 11: The figure depicts the excitation of 5Q transitions employing discreet frequency selective pulses and continuous frequency sweep techniques in a spin 5/2 system. The entire MQ experiment is divided into three stages. 1) Preparation, $[X^{(2+)}][X^{(2-)}][X^{(+)}][X^{(-)}]$ 2) Saturation, $[X^{(0)}]$ 3) Excitation, $[X^{(-)}][X^{(+)}][X^{(2-)}][X^{(2+)}]$.