Optimal excitation of $^{23}$Na nuclear spins in the presence of residual quadrupolar coupling and quadrupolar relaxation

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Optimal control theory is applied for designing pulse sequences to optimally excite a spin-3/2 system with residual quadrupolar coupling in the presence of quadrupolar relaxation. A homogeneous form of the master equation is constructed to simulate the dynamics of the spin system, and a general optimization procedure with a homogeneous form of the equation of motion is described. The optimized pulses are tested with $^{23}$Na NMR, and their performance is compared with that of pulses optimized in the absence of relaxation. © 2009 American Institute of Physics [doi:10.1063/1.3253970]

I. INTRODUCTION

Relaxation is a phenomenon by which a spin system loses its coherence and establishes equilibrium with its environment. Relaxation can provide useful information on the dynamics and structure of molecules (e.g., NOESY, ROESY, and TROSY experiments). On the other hand, relaxation limits the sensitivity and resolution in spectroscopy and imaging. Relaxation effects cannot easily be quenched by the application of rf pulses. Notable exceptions are the application of lifetime prolonging pulse sequences, in which, for example, spin-lock pulses are used to extend the lifetime of quasi-singlet states. With a suitable basis set, one may regard this effect as a special case of channeling the magnetization through decoherence-minimized trajectories. Recently, optimal control theory has been applied for the enhanced excitation or conversion of magnetization in single and coupled spin-1/2 systems with relaxation, whereby the coherent evolution can be guided in such a way as to minimize the effect of relaxation on the magnetization.

For quadrupolar nuclei ($I > \frac{1}{2}$), numerical optimizations based on optimal control theory have been applied to multiple-quantum magic-angle spinning experiments to significantly improve the sensitivity in solids.

For $I > \frac{1}{2}$ nuclei in solution, however, quadrupolar relaxation is typically dominant and may limit the application of quadrupolar NMR and magnetic resonance imaging (MRI). For example, sodium ions are easily accessible in tissues and may be useful for MRI with the advent of high-field scanners. The quadrupolar relaxation together with the low sensitivity of sodium compared to $^{1}$H is the main bottleneck preventing $^{23}$Na MRI from being a more prevailing tool. Recently, optimal control theory was applied for designing pulse sequences, which optimally excite the signal of a spin 3/2 with residual quadrupolar coupling in the intermediate rf-power regime ($\omega_0 \sim \omega_Q$). We also demonstrated that the quadrupolar jump-and-return sequence, which was derived from the optimal pulse sequence, can produce a good MRI contrast, discriminating free from bound sodium ions. Although these pulse sequences can optimally excite the central transition of a spin 3/2 in an ideal situation, they may not be as efficient as expected in practice when the relaxation times are comparable to their durations.

In this paper, we extend our previous work and design pulse sequences for optimally exciting the signal of a spin 3/2 in the presence of quadrupolar relaxation. The master equation is transformed into a homogeneous form, and a general optimization procedure is presented based on optimal control theory. The pulses optimized with and without relaxation are compared and are tested with $^{23}$Na NMR.

II. METHOD

The dynamics of the density operator with relaxation can be described by the master equation

$$\frac{d}{dt} \rho(t) = -i \left[ \mathcal{H}, \rho(t) \right] - \hat{\Gamma}\{\rho(t) - \rho^h\},$$  \hspace{1cm} (1)

where $\mathcal{H}$ is the spin Hamiltonian, $\hat{\Gamma}$ is the relaxation super-operator, $\rho(t)$ is the density operator at time $t$, and $\rho^h$ is the density operator in the thermal equilibrium state. In terms of matrix elements, the above equation can be written as

$$\frac{d}{dt} \rho_{jk} = -i \sum_m \left( \mathcal{H}_{jm} \rho_{mk} - \rho_{jm} \mathcal{H}_{mk} \right) - \sum_{m,n} \Gamma_{jk,mn} (\rho_{mn} - \rho_{mn}^h),$$  \hspace{1cm} (2)

$$= \sum_{m,n} \left[ -i \left( \mathcal{H}_{jm} \delta_{kn} - \mathcal{H}_{ak} \delta_{jm} \right) - \Gamma_{jk,mn} \right] \rho_{mn} + \sum_{m,n} \Gamma_{jk,mn} \rho_{mn}^h,$$  \hspace{1cm} (3)
\[
\sum_{m,n} (-\imath H_{jk,mn} - \Gamma_{jk,mn}) P_{mn} + \sum_{m,n} \Gamma_{jk,mn} \rho_{mn},
\]

where \( \delta \) is the Kronecker delta and \( H_{jk,mn} = \mathcal{H}_{jm} \delta_{(m,n)} - \mathcal{H}_{jk} \delta_{(m,n)} \) with which we define the Hamiltonian superoperator \( \hat{H} \). Since \( \frac{d}{dt} \rho_{mn} = 0 \) for all \( m \)'s and \( n \)'s, one can transform the master equation into a homogeneous form by concatenating the elements of \( \rho^h \) and \( \rho \) into one state vector with \( D^2 + K \) elements, where \( D \) is the dimensionality the spin system, \( K \) the number of nonzero elements of the thermal density matrix \( \rho^h \), and subsequently rearranging the elements of the superoperators according to

\[
\frac{d}{dt} \begin{pmatrix}
\rho_{jk}^{th} \\
\rho_{jk}\end{pmatrix}_{D^2 \times 1}
= -\begin{pmatrix}
\begin{bmatrix} 0_{K \times K} & \mathbf{0}_{D^2 \times K} \\
-\Gamma_{jk,mn} & \mathbf{1}_{D^2 \times D^2}
\end{bmatrix} & \mathbf{1}_{D^2 \times D^2} \\
\end{bmatrix}
\end{pmatrix}
\begin{pmatrix}
\rho_{mn}^{th} \\
\rho_{mn}\end{pmatrix}_{D^2 \times 1},
\]

where \( \square \) indicates that the region is filled with the elements of the operator inside with the size of the region indicated as a subscript. The arrangement of the elements of the superoperators depends on the order of the elements of \( \rho^h \) and \( \rho \) in the concatenated state vector such that Eq. (5) reproduces Eq. (4). This homogeneous form of Eq. (5) makes it convenient to evaluate the evolution of a given spin system \(^{16}\) and provides the optimization procedure with a general algorithm as seen below.

Equation (5) can be written as

\[
\frac{d}{dt} \mu(t) = -P(t) \mu(t),
\]

where \( \mu(t) \) is a vector describing the state of a system and \( P(t) \) is composed of a time-independent part \( P_0 \) and the parts \( P_k \) corresponding to the available control parameters \( u_k(t) \), according to \( P(t) = P_0 + \sum_k P_k u_k(t) \). For example, the relaxation superoperator \( \hat{1} \) and quadrupolar Hamiltonian \( \mathcal{H}_q = \pi \rho^h_0 [3 \mathbf{I} - \mathbf{I}(\mathbf{I} + 1)] \) contribute to \( P_0 \), and \( I_1 \) and \( I_2 \) consist of the \( P_k \)'s with time-varying applied rf fields (see Appendix). Using optimal control theory procedures as outlined in Skinner et al. \(^{17}\) one can build a general procedure for optimization.

Using the general procedures outlined in the Pontryagin maximum principle, \(^{18}\) one defines a vector Lagrange multiplier \( \lambda \), \(^{19-21}\) and a quantity \( h \) as

\[
h = \lambda \frac{d \mu}{dt} + \frac{d \mu^\dagger}{dt} \lambda = -\lambda^\dagger P \mu - \mu^\dagger P \lambda,
\]

where \( \dagger \) indicates the Hermitian adjoint and Eq. (6) was used to replace \( d \mu^\dagger/dt \) and \( d \mu/dt \). Then, it is straightforward to verify that the equation of motion for \( \mu \) is given by \( d \mu/dt = \partial h / \partial \lambda \).\(^{17}\) The equation of motion for \( \lambda^\dagger \) is given by

\[
\frac{d \lambda^\dagger}{dt} = -\partial h / \partial \mu = \lambda^\dagger P.
\]

According to optimal control theory \(^{18,22,23}\) \( h \) becomes stationary throughout the motion of the vector \( \mu \) when the control parameters \( u_k \) are optimal. In other words, with \( u_k \) optimal.

As a cost function to be minimized, we use

\[
\Phi = |C^f | \mu(t_f) - a |
\]

where \( t_f \) is the end of a time interval during which the vector \( \mu \) evolves, \( a \) is the targeted value that we want the quantity \( C^f | \mu(t_f) \) to be, where \( C^f \) is the row vector of a desired state at the end. This cost function gives more freedom to design pulse sequences than the simpler one \( C^f | \mu(t_f) \). For example, one can design a pulse sequence for explicitly suppressing some components in the final state by setting \( a \) to zero. If the quantity \( C^f | \mu(t_f) \) is bounded, setting \( a \) to a number outside the bound would give the same result as setting \( a \) to the bound.

We can design the control parameters \( u_k(t) \) such that they correspond to \( N \) discrete time steps. In each time step, the control parameters are constant, and \( P(t) \) is time independent. Then, one can solve the equations of motion, Eqs. (6) and (8), in each time step and express \( \mu(t) \) and \( \lambda^\dagger(t) \) in a simple way

\[
\mu(t_j) = \exp[-P(t_j) \Delta t] \cdots \exp[-P(t_1) \Delta t] \mu(0),
\]

\[
\lambda^\dagger(t_j) = \lambda^\dagger(t_j) \exp[-P(t_j) \Delta t] \cdots \exp[-P(t_{j+1}) \Delta t],
\]

where \( \Delta t = t_f / N \), \( t_j \) indicates the time interval between \( t = (j-1) \Delta t \) and \( t = j \Delta t \), and \( P(t) \) is the time-independent operator representing the motion of a vector \( \mu \) during that time interval. Then, one can estimate the gradient in the cost function when a control parameter \( u_k(t_j) \) changes as

\[
\frac{\partial \Phi}{\partial u_k(t_j)} = \frac{\partial}{\partial u_k(t_j)} |\lambda^\dagger(t_j) | \mu(t_j) - a |
\]

\[
= \frac{\partial}{\partial u_k(t_j)} |\lambda^\dagger(t_j) \exp[-P(t_j) \Delta t] \mu(t_{j-1}) - a |
\]

\[
= \text{sign}(\lambda^\dagger(t_j) \mu(t_j) - a) \Delta t \lambda^\dagger(t_j) P \mu(t_j).
\]

This gradient information can be used to iteratively reduce the value of the cost function \( \Phi \). We used the conjugate
Taking these pulses as the initial guesses and including the Redfield matrix for quadrupolar relaxation, the optimization was then performed for individual pulse durations. The desired state $C_f$ is a rearranged row vector whose elements are all zeros except those corresponding to $\rho_{1,2,1,2}$ and $\rho_{1,2,1,2}$. From the operator $I_x$ of a spin 3/2, the values of these elements were determined to be 1. The constant $a$ in the cost function $\Phi$ of Eq. (10) was set to 0.6 in order to maximize the intensity of the central peak. Since this is the theoretical maximum, any values of $a$ larger than 0.6 would produce the same results as mentioned above. The results, shown as the filled circles in Fig. 1, did not show a uniform performance through different pulse durations, but there were long pulses exciting the central peak ($\sim 0.51$) as much as the short pulses with $f_0\tau \sim 0.5$ did. We selected one of those long pulses, the pulse at $f_0\tau = 3.5$, as a new initial guess and found optimized pulses by decreasing the pulse duration. This second set of optimized pulses, shown as the filled triangles in Fig. 1, excelled the central peak most ($\sim 0.53$) when $f_0\tau = 1.4$.

Contrary to the coherent case, it is not straightforward to find the theoretical upper bound in the presence of quadrupolar relaxation. Starting from the best pulse mentioned above, the pulse duration was increased by zero padding and the optimization was performed again in an effort to produce better pulses (at the expense of longer duration). Those pulses are shown as the filled rectangles in Fig. 1. The performance was increased only slightly with this procedure (less than 1%), indicating that the shorter pulses were indeed already near optimal.

IV. EXPERIMENTAL TEST

The optimized pulses were tested on a sample of filamentous Pf1 bacteriophage. The original Pf1 bacteriophage sample (ASLA Biotech) with its concentration of $53 \pm 4$ mg/ml was diluted to $15 \pm 1$ mg/ml by adding phosphate buffered saline solution (Aldrich, pH 7.4). After dilution, the concentration of sodium ions in Pf1 bacteriophage was measured to be 70 mM by comparing its $^{23}$Na NMR signal with that of a 50 mM NaCl aqueous solution. The quadrupolar splitting $f_q$ of the $^{23}$Na ions in the Pf1 solution was measured to be 205 Hz, which was used in performing optimization and pulse calibration procedures. The $T_1$ and $T_2$ relaxation times were measured for the individual peaks. For the satellite peaks, $T_1$ and $T_2$ were respectively 46.6 and 8.2 ms. For the central peak, $T_1$ and $T_2$ were 43.9 and 44.4 ms, respectively. From these measurements, we could obtain the values of the spectral density $J(0)$, $J(\omega)$, and $J(2\omega)$. Although the $T_1$ decay curve of the central peak from the inversion recovery experiment should be biexponential, it was found to be almost single exponential, which is confirmed by the almost identical values of $J(\omega)$ and $J(2\omega)$. All the experiments were performed on a Bruker Avance 500 MHz spectrometer.

Figure 2 shows the intensities of the central peak from the Pf1 solution excited by optimized pulses, together with a single exponential decay curve with the decay time constant 44 ms, which is the $T_2$ of the central peak measured by a
spin-echo pulse sequence. The pulses optimized with relaxation gave consistently higher intensities (except for the first one).

Figure 3 shows selected spectra and pulses from the experimental results. The thermal equilibrium spectrum excited using a 7.2 μs 90° pulse is shown in Fig. 3(a). The spectra excited by the optimized pulses revealed that the satellite peaks were suppressed and the central transition signal increased. Although the resulting spectra in Figs. 3(b) and 3(c) look very different as seen in Figs. 3(b′) and 3(c′). As discussed earlier, the intensity achieved with relaxation optimization is higher.

V. DISCUSSION

In order to gain insight into how optimal control finds optimal pulses, we decompose the density operator as it evolves during the pulse sequences of Figs. 3(b′) and 3(c′) into spherical tensor operators (Fig. 4). When quadrupolar relaxation is included in the pulse optimizations [Fig. 3(b′)], the spin system stays longer in the $T_{1,0} = I_z$ state as seen in Fig. 4(a), and the intensities of the double-quantum and triple-quantum coherences are kept low in the beginning. The final states are almost the same for the two pulses except for differences in the central transition and the triple-quantum coherences [Fig. 4(g)]. One interesting behavior is that the $T_{2,0}$ component is always zero for both pulses. The trajectories can be understood by considering that the Redfield matrix describing the quadrupolar relaxation connects

![Figure 2](image_url)  
**FIG. 2.** Experimentally measured intensities of the central peak excited by the pulses optimized with (circle) and without (rectangle) relaxation. The dashed line represents a single exponential decay curve $\exp(-t/T_2)$ with $T_2=44$ ms.

![Figure 3](image_url)  
**FIG. 3.** (a) $^{23}$Na NMR spectrum of sodium ions in Pf1 bacteriophage recorded by a 7.2 μs 90° pulse at the thermal equilibrium state. Spectra recorded by pulses optimized (b) without and (c) with quadrupolar relaxation. The corresponding shaped pulses are shown in (b′) and (c′).
only coherences of the same order, and that the values of the spectral density for our Pf1 sample obey $J(0) > J(\omega) \sim J(2\omega)$. Hence we expect that coherences which include $J(0)$ into their decay constants would be avoided. For example, the fact that $J(0)$ does not contribute to the decay of the triple-quantum coherences could explain why the pulse optimized with relaxation excites and keeps the triple-quantum coherences. The $T_{2,0}$ component further is not favorable to the pulse optimized with relaxation because it decays almost two times faster than the other zeroth order coherences $T_{1,0}$ and $T_{3,0}$. However, the $T_{2,0}$ component is not excited at all even with the pulse optimized without relaxation.

There are further two kinds of coherences with faster relaxation: the single-quantum satellite transitions and the double-quantum coherences. As seen in Figs. 4(d), 4(f), and 4(g), the $T_{2,1}$, $T_{2,2}$, and $T_{3,2}$ components are avoided initially and excited later by the pulse optimized with relaxation. The likely reason why we do not see a noticeable change in the $T_{3,1}$ component [Fig. 4(e)] between the optimizations with and without relaxation is that the $T_{3,1}$ component contributes to the central transition, which is what is selected for detection.

The application of rf irradiation could, in principle, alter the Redfield relaxation matrix. If we assume that neither the rf field nor the density matrix change too much during the correlation time, then the rf field does not change the secular approximation significantly in the derivation of the Redfield matrix. The error made by this assumption is hence negligible. Most high-field liquid state NMR situations would satisfy this condition, except in cases where several near-equivalent nuclear spins are considered. Another issue is that $\rho^{25}$ may not simply be $I_{1}$ [Eq. (1)] in the presence of the rf field, although significant deviations would only be seen for some extreme cases, for example, when the line width is comparable to the resonance frequency.

**VI. CONCLUSION**

Optimal control theory has been applied to the optimal excitation of a spin-3/2 system in the presence of quadrupolar relaxation. The homogeneous form of the master equation including the Redfield relaxation matrix is constructed and a general algorithm to perform optimization with such an equation is described. The pulses optimized with relaxation take different pathways of evolution than the pulses optimized without relaxation, which gives clues as to how to construct relaxation-optimized sequences in the quadrupolar case. These excitation schemes were experimentally tested with $^{23}$Na NMR on a sample of Pf1 bacteriophage, which showed that optimal control could partly compensate for the
effect of relaxation. Such approaches can be useful for quadrupolar NMR and MRI, in particular for sensitivity and resolution enhancement.

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APPENDIX: SUPEROPERATORS

The superoperators $\hat{H}$ and $\hat{I}$ to fill in Eq. (1) for a spin-3/2 system are given below, for which the elements of the density operator $\rho$ are rearranged as follows:

$$
\begin{pmatrix}
\rho_{3/2,3/2}, & \rho_{1/2,1/2}, & \rho_{-1/2,-1/2}, & \rho_{-3/2,-3/2}, & \rho_{3/2,1/2}, & \rho_{1/2,-1/2}, & \rho_{-1/2,-3/2}, \\
\rho_{1/2,3/2}, & \rho_{-1/2,1/2}, & \rho_{-3/2,-1/2}, & \rho_{3/2,1/2}, & \rho_{1/2,-3/2}, & \rho_{-1/2,3/2}, & \rho_{3/2,-1/2}, \\
\rho_{3/2,3/2}, & \rho_{1/2,1/2}, & \rho_{-1/2,-1/2}, & \rho_{-3/2,-3/2}, & \rho_{3/2,1/2}, & \rho_{1/2,-1/2}, & \rho_{-1/2,-3/2}
\end{pmatrix}
$$

For a spin-3/2 system, we consider the quadrupolar coupling and interaction with applied rf fields. The Zeeman Hamiltonian can be removed by describing the spin dynamics in the rotating frame. The superoperator form of the quadrupolar Hamiltonian is given by

$$
\hat{H}_Q = \pi f_Q \text{diag}(0,0,0,0,2,0,-2,0,2,0,-2,2,0,0),
$$

where $f_Q$ is a peak splitting in the NMR spectrum and diag(...) means a diagonal matrix with specified diagonal elements. The superoperator of the interaction with applying rf fields can be written as

$$
\hat{I}_x = \omega_{1} \hat{I}_x + \omega_{2} \hat{I}_y,
$$

where two superoperators $\hat{I}_x$ and $\hat{I}_y$ are respectively given as

$$
\begin{pmatrix}
0 & 0 & 0 & 0 & -\frac{\sqrt{3}}{2} & 0 & 0 & \frac{\sqrt{3}}{2} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & \frac{\sqrt{3}}{2} & -1 & 0 & -\frac{\sqrt{3}}{2} & 1 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & -\frac{\sqrt{3}}{2} & 0 & 0 & 0 & 0 & 0 & 0 \\
-\frac{\sqrt{3}}{2} & -\frac{\sqrt{3}}{2} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & -1 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & -\frac{\sqrt{3}}{2} & -\frac{\sqrt{3}}{2} & 0 & 0 & 0 & 0 \\
0 & 0 & -\frac{\sqrt{3}}{2} & \frac{\sqrt{3}}{2} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 \\
\frac{\sqrt{3}}{2} & -\frac{\sqrt{3}}{2} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 \\
0 & 1 & -1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & -\frac{\sqrt{3}}{2} & -\frac{\sqrt{3}}{2} & 0 & 0 \\
0 & 0 & \frac{\sqrt{3}}{2} & -\frac{\sqrt{3}}{2} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & -1 & 0 & 0 \\
0 & 0 & 0 & 0 & -1 & \frac{\sqrt{3}}{2} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & -\frac{\sqrt{3}}{2} & 0 \\
0 & 0 & 0 & 0 & 0 & -\frac{\sqrt{3}}{2} & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \frac{\sqrt{3}}{2} & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \frac{\sqrt{3}}{2} & 0 & 0 & 0 & -\frac{\sqrt{3}}{2} \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & -\frac{\sqrt{3}}{2} & \frac{\sqrt{3}}{2} & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & \frac{\sqrt{3}}{2} & -\frac{\sqrt{3}}{2} & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \frac{\sqrt{3}}{2} & -\frac{\sqrt{3}}{2} & 0 & 0 & 0 & 0
\end{pmatrix}
$$

(A1)
The Redfield matrix $\hat{\mathcal{I}}$ is given as

$$
\hat{\mathcal{I}}_j = 
\begin{pmatrix}
0 & 0 & 0 & 0 & -\frac{i\sqrt{3}}{2} & 0 & 0 & -\frac{i\sqrt{3}}{2} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & \frac{i\sqrt{3}}{2} & -i & 0 & \frac{i\sqrt{3}}{2} & -i & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & -i & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & \frac{i\sqrt{3}}{2} & 0 & \frac{i\sqrt{3}}{2} & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & -i & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & \frac{i\sqrt{3}}{2} & 0 & \frac{i\sqrt{3}}{2} & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & -i & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & \frac{i\sqrt{3}}{2} & 0 & \frac{i\sqrt{3}}{2} & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & -i & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & \frac{i\sqrt{3}}{2} & 0 & \frac{i\sqrt{3}}{2} & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & -i \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & \frac{i\sqrt{3}}{2} & 0 & \frac{i\sqrt{3}}{2} & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & \frac{i\sqrt{3}}{2} & 0 & \frac{i\sqrt{3}}{2} & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & -i & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & \frac{i\sqrt{3}}{2} & 0 & \frac{i\sqrt{3}}{2} & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & -i \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & \frac{i\sqrt{3}}{2} & 0 & \frac{i\sqrt{3}}{2} & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0
\end{pmatrix}
$$

The Redfield matrix $\hat{\mathcal{I}}$ is given as
\[
I^e = \begin{pmatrix}
e - b - c & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
- b & e & 0 & - c & 0 & 0 & 0 & 0 & 0 & 0 \\
- c & 0 & e - b & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & - c & - b & e & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & d & 0 & - c & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & e & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & - c & 0 & d & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & b & d & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & b & d \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & e \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & e \\
\end{pmatrix}
\] (A3)

where \(a = 3J(0), \quad b = 3J(\omega), \quad c = 3J(2\omega), \quad d = 3J(0) + J(\omega) + J(2\omega), \) and \(e = 3J(\omega) + J(2\omega).\)

Using the superoperators given above, the homogeneous form of the master equation can be constructed according to Eq. (5). The quadrupolar coupling and Redfield matrix consist of the time-independent part of \(P(t)\) in Eq. (6) or \(P_0\), which is given as

\[
P_0 = \begin{pmatrix}
0 & 0 \\
0 & 0 \\
- \hat{\Gamma} & 1 \hat{H} + \hat{\Gamma} \\
\end{pmatrix},
\] (A4)

and the interaction with applying rf fields consists of the parts of \(P\) corresponding to the available control parameters \(\omega_{1,z}(t)\) and \(\omega_{1,y}(t)\) or \(P_k\)'s, which can be constructed as

\[
\begin{pmatrix}
0 & 0 \\
0 & 0 \\
\hat{I}_x & \hat{I}_y \\
\end{pmatrix}
\text{ and }
\begin{pmatrix}
0 & 0 \\
0 & 0 \\
\hat{I}_y & \hat{I}_x \\
\end{pmatrix}
\] (A5)

for \(\omega_{1,z}(t)\) and \(\omega_{1,y}(t)\), respectively.


25. *www.mathworks.com*