Multi-modal spectroscopy of phase transitions

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To understand a phase transition, independent measurement of the value and variation in each physical parameter of a material’s Hamiltonian is vital. Conventional one-dimensional spectroscopy, which studies dynamical responses to fields, struggles to distinguish between different sources of noise. Multi-dimensional spectroscopy can avoid this issue and probe symmetry-specific Hamiltonian parameters by analyzing how the time delay between applied pulses (τ) affects the response. In this work, we present a spectroscopic technique based on the multi-dimensional paradigm which can measure a quadrupolar interaction (inversion symmetric) even in the presence of large magnetic noise (inversion asymmetric). Inversion symmetric combinations of spin operators are found to give clear sinusoidal responses in τ due to periodic refocusing. The time-scale on which the magnetization partially decays in τ provides a direct measure of the distribution of interaction strengths, even when the average value of the interaction is zero. This method independently measures the distributions of different forms of disorder, helping elucidate which microscopic symmetry drives a phase transition.

I. INTRODUCTION

The study of symmetry-breaking phase transitions is a cornerstone of condensed matter physics. Landau theory explains such transitions classically: symmetry-related degenerate ground states appear below a critical temperature, and the symmetry breaks as the system chooses one of these state over others [1]. The loss of symmetry is often understood through the definition of an order parameter: a (possibly observable) quantity which describes the magnitude of the symmetry-breaking in the material and encodes some macroscopic property of the system. Fluctuations of the order parameter around its zero value grow exponentially when approaching a critical temperature from above, making it an important indicator of the emerging phase [2]. In systems where the degenerate ground state manifolds are caused by frustration, e.g. “accidental” symmetries of the Hamiltonian, a different type of symmetry-breaking can occur. One specific ground state becomes preferred due to differences in low-energy fluctuations, a process known as order by disorder (ObD) [3, 4].

To understand both traditional and ObD symmetry-breaking phase transitions, one must first understand the origins and size of the associated fluctuations above the critical temperature. For example, consider multi-linear spin interactions in a nuclear Hamiltonian (e.g. $S^2$, $n > 1$), which can be caused by the anisotropic electric field gradients of materials with large atomic distortions or strong spin-orbit interactions. The most commonly studied of these interactions is the quadrupolar type ($S^2$), associated with an interaction strength $\omega_Q$, but order parameters of higher power terms are also possible [5]. Phases driven by octupolar ($S^3$) [6–8] and hexadecapolar ($S^4$) [9, 10] interactions have been examined in some materials, but here we focus here on the more common quadrupolar phase.

Many measurement techniques for lattice distortions or magnetism are usually only sensitive to the average atomic or electronic structure of the material [11–15]. For

FIG. 1. (a) Two-dimensional spectroscopy for a spin-3/2 nuclei with quadrupolar interaction strength $\omega_Q = 100$ kHz (and no noise, $\Gamma_Q = 0$) and magnetic (Zeeman) noise $\Gamma_Z = 300$ kHz. Values of $\tau$ that give local maxima in the echo amplitude are highlighted in red. The upper inset shows the echo pulse sequence, and the lower inset shows the two independent time-parameters, experiment time $t$ and integration time $\tau$. (b) Traditional echo spectra for two values of $\omega_Q$ (c) Echo amplitudes as a function of integration time $\tau$ for the same two values of $\omega_Q$. 
example, in neutron diffraction, the measurements of local structure requires high energy sources or extremely accurate scattering models (form factors) to access local information about the material [16–19]. Moreover, if multiple sources of disorder are present, e.g. lattice distortions, nuclear spin noise, and orbital magnetism, disentangling them can be challenging as they all contribute to the cross section [20]. This can leave lingering questions about the nature of the phase transition above the critical temperature.

Some of these shortcomings have been overcome in the few-spin case (molecular or “qubit” systems), due to developments in quantum information technology and chemical spectroscopy techniques [21–23]. One such approach is multi-dimensional spectroscopy, originally developed for magnetic resonance [24]. By taking Fourier transforms of experimental signals that depend on pulses occurring at multiple independent times, one obtains spectral information in a high-dimensional space (one dimension for each of the associated pulse or delay times), as shown in Fig. 1(a). The multi-dimensional approach has been leveraged in few-spin systems to extract different symmetry-specific terms in a Hamiltonian [25–27]. Our goal in this work is to translate these techniques, well known in quantum information and chemical spectroscopy, to the study of phase transitions in many body systems.

The introduced methodology distinguishes the noise from inversion symmetric ($S^n_i$, n even) and inversion asymmetric (n odd) terms in microscopic Hamiltonians. This noise, or distribution of the terms, can arise from both spatial or temporal variations. However, the temporal variations must occur on a time scale longer than the experiment time ($2\tau$) but much shorter than the total run-time of an integrated spectral acquisition (e.g. when the spectra is obtained from many repetitions of an identical experiment). We showcase this methodology for the characterization of phase transitions, providing an inverse transform that directly measures the distribution of symmetry breaking terms and not just their mean value.

In Section II we give a pedagogical introduction to multidimensional spectroscopy. We describe a specific two-dimensional spectroscopic technique for a spin-3/2 system with a quadrupolar interaction in Section III. A general derivation of the technique for arbitrary spin quantum numbers and Hamiltonians is outlined in Section IV. We summarize these results and discuss future applications and extensions in Section V.

II. MULTIDIMENSIONAL SPECTROSCOPY

The multidimensional spectroscopy technique has a rich history in chemistry, biology and quantum control [21, 22, 28–33]. It allows for the independent measurement of terms with different symmetry properties in the time-evolution Hamiltonian, and is most commonly implemented to investigate correlations between different energy levels in molecular or few-spin systems. Here we will consider only the simplest example, namely a two-dimensional spectroscopy with two applied pulses on a particle of spin $S$, with time $t_1$ between them and time $t_2$ between the final pulse and signal acquisition:

$$\langle S_z \rangle = \langle \psi | S_z | \psi \rangle$$

(1)

where $R_{\{1,2\}}$ are the first and second rotation operators, mediated by an external pulse, $U(t_i)$ is the time propagation operator of duration $t_i$, and $|\uparrow\rangle$ is the initial state, assumed to be maximal along the $z$-axis ($S_z |\uparrow\rangle = S |\uparrow\rangle$). We will assume for now that the Hamiltonian is diagonal in the $S_z$ basis, and consists of only diagonal entries, $H_{aa} \equiv h_a$, for $a \in \{-S, -S+1, \ldots, S-1, S\}$. This two-dimensional $(t_1, t_2)$ experiment, under unspecified rotations $R_1$ and $R_2$, yields a $\langle S_z \rangle$ of the form:

$$\langle S_z (t_1, t_2) \rangle = \sum_{a,b,c,\pm} C_{abc} e^{-i[(h_a-h_b)t_1+(h_b+1-h_a)t_2]}$$

(2)

for some constants $C_{abc}$, which depend on the initial state and rotation operators. Note that the indirect domain $(t_1)$ has no constraint on it’s phase terms, while the direct domain $(t_2)$ has it’s associated phase constrained by the selection rules of $S_z$ (e.g. $b \pm 1$). The two-dimensional Fourier transform, along each $t_i$ axis, $\langle S_z (\omega_1, \omega_2) \rangle$ can then be analyzed, and will reflect this constraint on the phases by encoding information about $h_{b\pm 1}$ along the $\omega_2$ axis.

Our proposed methodology considers the diagonal of this object, with $t_1 = t_2 = \tau$, and thus we will describe it as a $\tau$-spectroscopy method. This in contrast to analysis of measurements made solely by observing the direct domain $(t_2 \equiv \tau)$, which we will henceforth refer to as $t$-domain spectroscopy. We consider a Hamiltonian that consists of two parts, $H = H_1 + H_2$, with $H_1 \propto S_z$ and $H_2 \propto S_2$. Note that this means the two parts commute, $[H_1, H_2] = 0$, and we can assign eigenvalues $H_1 (|a\rangle) = k_a |a\rangle$ and $H_2 (|a\rangle) = g_a |a\rangle$, such that $h_a = k_a + g_a$. Our method utilizes a conventional Hahn spin echo, where one takes $R_2 = R_x(180^\circ)$. Then each Hamiltonian’s behavior under inversion of is given by $R_z^2 R_1 R_2 = -H_1$ and $R_z^1 R_2 R_2 = H_2$. Simplifying the time-propagation step, we have

$$U(t_2)R_2U(t_1)U(\tau)R_2U(\tau) = e^{-i\tau H}R_2 e^{-i\tau H}$$

$$= R_2 R_1 e^{-i\tau H} R_2 R_2 e^{-i\tau H}$$

$$= R_2 e^{-i(\tau(H_1+H_2))} e^{-i\tau(H_1+H_2)}$$

$$= R_2 e^{-i2\tau H_2}$$

(3)

The wavefunction at the echo is then given by

$$|\psi(2\tau)\rangle = R_2 e^{-i2\tau H_2} R_1 |\uparrow\rangle$$

(4)

This illustrates one of the key utilities of multi-dimensional spectroscopy: since $|\psi(2\tau)\rangle$ is independent
of odd terms in the Hamiltonian, \( H_1 \), it allows for measurement of inversion-symmetric terms, \( H_2 \), independent of the value or noise of non inversion-symmetric terms. For a more detailed derivation of this effect, we refer the reader to Appendix B.

Note that relaxing our assumption of a diagonal Hamiltonian does complicate things. One must either apply generalized rotation operators which act on the diagonalized basis, or derive corrections to the diagonal assumption (generally, only the coefficients \( C_a \) change). Although the first approach is easier to deal with conceptually, experimentally it is challenging: how does one determine the correct rotation if the Hamiltonian is not already known? Therefore, we will focus on the second approach when the Hamiltonian is not diagonal.

### III. QUADRUPOLAR SPIN 3/2

Spin 3/2 nuclei can couple strongly to higher magnetic moments, making them a useful probe of multipolar electronic phases. For this reason, we will focus on a spin 3/2 Hamiltonian in the presence of an electric field gradient (EFG), given by the Hamiltonian \([34]\) (see Appendix D):

\[
H = \omega_Z S_z + \frac{\omega_Q}{2} \left[ (3S_z^2 - S^2) + \eta(S_z^2 - S_y^2) \right]
\]

where \( \omega_Z \) is the precession frequency of the nuclei due to some external field (whose variations in space are called Zeeman, or magnetic noise), \( \omega_Q \) is the strength of a quadrupolar interaction in the rotating frame of the nuclei caused by a local electric field gradient, and \( \eta \) is a measure of the anisotropy of the quadrupolar interaction. We note that the quadrupolar interaction strength commonly used in the NMR literature is given by \( \omega_Q \equiv 3 \omega_Q \).

An EFG is most commonly caused by a distortion of the crystal lattice which removes a rotational symmetry. Near a phase transition, as the crystal transitions from the symmetric to distorted phase, the energies of the distorted symmetry-broken sites approach those of the symmetric sites. Due to this near degeneracy, the distorted structures begin to appear throughout the material, with thermal fluctuations allowing them to appear for short periods of time in small domains. The values of the associated order parameter, \( \omega_Q \), therefore acquire a broad distribution across the sample just before the critical temperature. However, estimating the distribution of \( \omega_Q \) just before the transition via traditional one-dimensional spectroscopic techniques is difficult: its average value is zero so only line broadening will be observed. Since the Hamiltonian term associated with \( \omega_Q \) is non-linear, the effect of the broadening on the acquired spectrum is not straightforward and may be difficult to evaluate and interpret if it is smaller than other forms of disorder in the system.

We will show that a careful analysis of Hahn echos of varying pulse separation times \( \tau \) reveals both the strength and distribution of \( \omega_Q \). Although other multidimensional spectral techniques exist which extract the average value of the quadrupolar interaction \([35]\), they do not provide a clear pathway to accessing the distribution of \( \omega_Q \).

#### A. Signal periodicity in \( \tau \)

The presence of even a small finite value of \( \omega_Q \) in Eq. 5 is associated with a symmetry-breaking phase, and our method provides an extremely sensitive probe of this parameter. This can be seen in a direct analysis of the dynamics of the Hamiltonian in Eq. 5. For simplicity, we will assume that the spinor starts in the \( m = 3/2 \) spin state, \( |\psi(0)\rangle = |S = 3/2, m = 3/2 \rangle \equiv (1, 0, 0, 0)^T \). Note that in Sec. IV we will generalize these results for a more realistic thermally mixed state. Our “experiment” is performed by applying the following four operations upon the \( m = 3/2 \) state:

1. Rotation into the \( x-y \) plane by a \( 90^\circ (\pi/2) \) rotation about the \( y \) axis, \( R_y(90^\circ) \)
2. Time evolution to time \( \tau \), via \( U(\tau) = e^{-iH \tau} \)
3. Rotation about the \( x \) axis by \( 180^\circ (\pi) \), to cancel any accumulated phase due to \( \omega_Z \), \( R_x(180^\circ) \)
4. Time evolution to time \( 2\tau \), given by the same \( U(\tau) \) as above.

Considering first the case where \( \eta = 0 \), we find \( H \) is a sum of the operators \( \{S^2, S_z, S_y^2\} \), and thus is already in a diagonal form

\[
H = \frac{1}{2} \text{diag}\{3\omega_Z + 3\omega_Q, \omega_Z - 3\omega_Q, -\omega_Z - 3\omega_Q, -3\omega_Z + 3\omega_Q\}
\]

so time propagation can be done by simply taking the complex exponent of each diagonal entry of \( H \) and applying it to each element of the state vector \( |\psi\rangle \).

We can calculate the final state \( |\psi(2\tau)\rangle \) as a product of these four operators as

\[
|\psi(2\tau)\rangle = e^{-iH \tau} R_x(180^\circ) e^{-iH \tau} R_y(90^\circ) |\psi(0)\rangle
\]

Tedious but straightforward calculations yield an expectation value of \( S_z \) at time \( 2\tau \) of

\[
\langle S_z(2\tau) \rangle = \frac{3}{4} [1 + \cos(6\omega_Q \tau)]
\]

which is in excellent agreement with the form of the numerical results of Fig. 1(c). We expect minima in the echo amplitude to occur when

\[
6\omega_Q \tau = \pi + 2\pi n
\]

and maxima when

\[
6\omega_Q \tau = 2\pi n
\]

for \( n \in \mathbb{Z} \).
Periodic dependence of the echo amplitudes on $\tau$ has been previously observed in quadrupolar systems [36–38], but it is much less common in the literature than the conventional one-dimensional ($t$-domain) spectroscopic techniques. In particular, our main result, how the $\tau$-dependence transforms under a distribution of $\omega_Q$, is not present in these previous works.

B. Traditional spectral effects

Before examining how other terms in the quadrupolar Hamiltonian affect the $\tau$-spectroscopy, we first discuss the spectra of Eq. (5) with $\eta = 0$ that is generated from a traditional $t$-domain spin echo. In Fig. 2(a), a typical spectrum obtained from the Fourier transform of a spin-echo with both Zeeman noise (variations in $\omega_T$) of linewidth $\Gamma_Z$ and a fixed quadrupolar interaction ($\omega_Q$) is shown. For our chosen pulsing condition (a 90° rotation about $y$), the quadrupolar term splits the spectrum into three peaks, one at the center with total spectral weight $0.5$, and two satellites at frequencies $\pm 3\omega_Q/(2\pi)$ with $0.25$ spectral weight each. The Zeeman noise then broadens each peak by its linewidth $\Gamma_Z$. However, when $\Gamma_Z > \omega_Q$, identifying the location of the satellite peaks is challenging, as shown in Fig. 1(b).

We next consider a sample where $\omega_Q$ varies in space, and assume that its distribution follows a Lorentzian distribution centered at $0$ with linewidth $\Gamma_Q$ as in Fig. 2(b). In this case, the clear three-peak signature of the quadrupolar interaction is lost. As the central peak of the quadrupolar interaction is independent of $\omega_Q$, the variation in $\omega_Q$ is invisible to half the spectral weight. This leads to a large central peak whose width is determined by $\Gamma_Z$ alone. The other half of the spectral weight (corresponding to the two satellite peaks of the quadrupolar interaction) forms a distribution whose width is dependent on $\Gamma_Q$. When $\Gamma_Z < \Gamma_Q$, the total spectrum can be approximated by a sum of two Lorentzians:

$$\tilde{L}_Q(\omega) + L_Z(\omega)$$

where

$$L_j(\omega) = \frac{\Gamma_j}{2\pi(\omega^2 + (\Gamma_j/2)^2)}$$

is a Lorentzian distribution of linewidth $\Gamma_j$ centered at zero frequency. Here we must modify the $\Gamma_Q$ Lorentzian according to $\tilde{L}_Q(\omega) = \frac{\Gamma_Z}{2\pi} L_Q(\frac{2\pi}{\Gamma_Z})$ to correctly account for how the splitting depends on $\omega_Q$. In particular, this means that the true linewidth is related to the observed spectral linewidth via $\Gamma_Q = \frac{2\pi}{\Gamma_Z} \Gamma_Q$. The spectra is therefore a non-Lorentzian distribution whose FWHM is slightly larger than $\Gamma_Z$. Importantly, when $\Gamma_Q \gg \Gamma_Z$, the broad nature of $\tilde{L}_Q$ relative to $L_Z$ makes it difficult to resolve fluctuations in the order parameter through the conventional spectral technique, motivating the need for an improved method.

C. Quadrupolar Asymmetry ($\eta \neq 0$)

Returning now to $\tau$-spectroscopy, if we consider the more general $\eta \neq 0$ case, we show how to probe not just the presence of multipolar order but also its anisotropy. With $\eta \neq 0$, the Hamiltonian consists of the operators $\{S_x^2, S_y^2, S_z^2\}$. It now has off-diagonal terms, but one can still perform the time-propagation in the diagonal basis of $H$. With the assistance of automated algebraic simplification in Mathematica [39], we obtain a closed-form solution for $\langle S_x(2\tau) \rangle$, but only for $\omega = 0$. We will also consider general cases of initial magnetization $m$, such that the initial state satisfies $S_z |\psi(0)\rangle = m |\psi(0)\rangle$. The expressions for the response at $2\tau$ when $\omega = 0$ are:

$$\langle S_x(2\tau) \rangle = A \cos(\xi \omega_Q \tau) + C$$

with coefficients for general $m$ easily summarized by introducing $\sigma = \text{sgn}(m)$:

$$\xi = 2\sqrt{3(3 + \eta^2)}$$

$$A = 3\sigma(3 + \eta)^2/\xi^2,$$

$$C = 3\sigma[(3 - \eta)^2 + 4\eta^2]/\xi^2, \quad |m| = 3/2$$

$$C = 3\sigma[(3 - \eta)^2 - 12]/\xi^2, \quad |m| = 1/2.$$
FIG. 3. (a) $\eta$ dependence of $\langle S_x(2\tau) \rangle$ in an $S = 3/2$ system for the $m = 3/2$ eigenstate, as a function of the unitless parameter $\omega_Q\tau$ for an ensemble with Zeeman ($\omega_Z$) noise of linewidth $\Gamma_Z = 0.1\omega_Q$. The black dots give the numerical results for each $\eta$, with a shifted origin indicated by the dashed black line, while the solid colored lines are fits to the form $A\cos(\omega_Q\tau) + C$. (b) Dependence of the ratio of the fitting parameters $A/C$ on the anisotropy parameter $\eta$ and magnetic noise $\Gamma_Z$. At $\eta = 0$, the fitting reproduces Eq. (8) for all $\Gamma_Z$.

(FIG. 3(a)). See Appendix A for details of the spin propagation simulations. The numerical results are then fit to the function $A\cos(\omega_Q\tau) + C$, and in Fig. 3(b) we find that the analytic result for $\omega_Z = 0$ agrees well with the numerical results when $\Gamma_Z \leq 0.1\omega_Q$. As $\Gamma_Z$ increases, the ratio $A/C$ decreases for all $\eta > 0$, going as low as $A/C \approx 1/2$ at $\eta = 1$. This provides information on not only the magnitude of the fluctuations in the order parameter ($\omega_Q$), but also on the anisotropy of the underlying distortions ($\eta$).

D. Pulse dependence ($\theta \neq 90^\circ$)

One can also modify the pulse strength in a nuclear magnetic resonance (NMR) experiment to change the effective angle $\theta$ that the spins undergo due to the $R_y$ and $R_z$ operators. We generalize $R_y$ to a $\theta$ pulse and $R_z$ to a $2\theta$ pulse, set to $\theta = 90^\circ$ in the previous discussions. A general analytic result for the $\langle \omega_Q\tau, \omega_Z, \eta, \theta \rangle$-dependence of the echo amplitude may be out or reach, so for now we consider $\omega_Z = \eta = 0$ and restrict $\tau$ to values that maximize or minimize the echo amplitude. We obtain the following formulas for the maxima

$$\langle S_x(2\tau) \rangle = \begin{cases} \frac{3}{4} \sin \theta, & 6\omega_Q\tau = 4\pi n \\ \frac{1}{2} \sin \theta \cos^2(2\theta), & 6\omega_Q\tau = 2\pi + 4\pi n \end{cases}$$

and for the minima a more complicated form

$$\langle S_x(2\tau) \rangle = \frac{3}{128} \left( 5\sin 7\theta + 17\sin 5\theta - 11\sin 3\theta - 23\sin \theta \right) \left( - \text{if } 6\omega_Q\tau = \pi + 4\pi n \right) + \left( \text{if } 6\omega_Q\tau = 3\pi + 4\pi n \right).$$

Note that the maxima simplify to a value of $3/2$ and the minima to a value of $0$ for the case $\theta = 90^\circ$, as expected from the analysis above.

To estimate the full $\tau$ dependence, and to include a distribution of frequencies $\omega_Z \neq 0$, we perform numerical tests and fit a modified version of the $90^\circ$ model. We find a generalization of Eq. (8), which includes an additional cosine term at half frequency, allows for good agreement:

$$\langle S_x(2\tau) \rangle = A\cos(6\omega_Q\tau) + B\cos(3\omega_Q\tau) + C.$$  \hspace{1cm} (17)

The half frequency term ($3\omega_Q$) is associated with the (1,3) and (2,2) elements of the $R_x(\theta)$ matrix, which can cause an additional refocusing of the echo and is maximized at $\theta = 60^\circ$. Earlier work on quadrupolar echoes, which accounted for generalization rotation matrices, derives this half-frequency term analytically (Eq. 22 of Ref. 37), but did not explicitly estimate the pulse-angle ($\theta$) dependence.

In Fig. 4, we plot the fitting results as a function of $\theta$, and recover Eq. (8) at $\theta = 90^\circ$. These results are symmetric about $\theta = 90^\circ$ due to the $z \rightarrow -z$ symmetry of the Hamiltonian, assuming the distribution of precession frequencies $\omega_Z$ is symmetric. As $\theta$ decreases (increases) from $90^\circ$, the constant term and $6\omega_Q$ term decrease while a $3\omega_Q$ term increases. At $\theta = 60^\circ$, the $3\omega_Q$ term dominates the fitted form. At $\theta \leq 40^\circ$, only the constant term is significant and $\langle S_x \rangle$ has little $\tau$-dependence. This precise $\theta$ dependence should be possible to directly observe in experiment, as the pulse angle $\theta$ can be assumed proportional to the total pulse strength (a product of the pulse power and duration). Observation of this $\theta$-dependence in $A, B, C$, as well as the appearance of a half-frequency component, permits a robust verification that the signal is caused by the quadrupolar parameter $\omega_Q$.

E. Sample tilt dependence ($\alpha \neq 0^\circ$)

Another way to extract evidence of the quadrupolar coupling is to study how the $\tau$ spectroscopy depends on the physical orientation of the sample relative to the vertical applied field. The quadrupolar interaction has a complicated dependence on the relative angle between a material’s principle axis systems (PAS) and the nuclear spin’s axes. This effect is derived in Appendix D for both a polar angle $\beta$ and azimuthal angle $\alpha$. Here we will just discuss the dependence on the azimuthal angle $\alpha$, which is the angle between the dominant axis of the PAS and the nuclear spin’s $\hat{z}$-axis.

We present simulations of the azimuthal angle-dependence of the magnetization, with $\beta = 0$ and $\eta = 0$, in Fig. 5. The angle dependence is fit well by a three-term function, with a variable quadrupolar frequency prefactor:

$$\langle S_x(2\tau) \rangle = A\cos(\xi\omega_Q\tau) + B\cos(\xi\omega_Q\tau/2) + C.$$  \hspace{1cm} (18)
This equation is a combination of the parameters introduced in Eq. 13 and Eq. 17. We find that both ξ and the relative weight of A and B depend strongly on α.

In an experiment, both the ξ and A/B ratio changes would manifest as effective changes to the measured ωQ frequency. Therefore, we also plot in Fig. 5b the effective quadrupolar prefactor ξc, defined as:

$$\xi_c \equiv \frac{|A| + |B|/2}{|A| + |B|}.$$  

(19)

This is chosen so that when A dominates the τ dependence of the signal, the effective frequency is just ξ. But when B dominates, the effective frequency is ξ/2, due to the half-frequency in B’s cosine argument.

F. Distributions of ωQ

Armed with a complete understanding of how specific values of ωQ, η, and θ affect the τ-dependence of the echoes, we can now turn to our main goal: understanding distributions of ωQ. We will show that when ωQ varies throughout a sample, a straightforward generalization of the periodic oscillations we have predicted for \( \langle S_x(2\tau) \rangle \) is possible.

Assume that each quadrupolar interaction term ωQ has a weighting g(ωQ) in our hypothetical sample, with normalization given by \( \int g(\omega_Q)d\omega_Q = 1 \). For an ωQ that varies in space or time, we assume for our simulations that each individual nuclei sees a constant, uniform value of ωQ and η, but that the overall sample provides, in aggregate, a random distribution of ωQ. For spatial variations, this is easily achieved if we assume our sample is large compared to the scale of the variations. For temporal variations, this is only achieved if the time-scale on which ωQ varies is longer than that of a single echo (2τ) but shorter than the time scale on which the experimental spectra is obtained via averaging.

Now, if the τ dependence of the response for a specific quadrupolar interaction strength is given by a kernel \( K(\omega_Q, \tau) \), we can estimate the τ-dependent intensity of the entire sample as

$$I(\tau) = \int g(\omega_Q)K(\omega_Q, \tau)d\omega_Q.$$  

(20)

The key here is that this transformation is linear in \( K \). So if we write \( K(\omega_Q, \tau) = \sum_j A_j \cos(n_j \omega_Q \tau) = \sum_j K_j \), then the final intensity will be \( I = \sum_j I_j \), where \( I_j \) is the \( g \)-transform of \( K_j \) (Eq. 20). For the \( S = 3/2 \) case (Eq. 8, with \( n_1 = 0 \) and \( n_2 = 6 \)) we have \( K_1 = 3/4 \) and \( K_2 = 3/4 \cos(6\omega_Q \tau) \). However, when generalizing to higher spins, more cosine terms will appear. To understand the τ-spectroscopy for all spins, let us consider the transform of a generalized function \( K_j = A \cos(n_j \omega_Q \tau) \). If we take the \( \omega_Q \) to be normally distributed with some mean \( \omega_Q \) and standard deviation \( \sigma_Q \), we obtain

$$I = \int \frac{1}{\sigma_Q \sqrt{2\pi}} e^{-\frac{(n\omega_Q - \omega_Q)^2}{\sigma_Q^2}} A \cos(n\omega_Q \tau)d\omega_Q$$  

$$= A e^{-\frac{1}{2}(n\sigma_Q)^2} \cos(n\omega_Q \tau).$$  

(21)

So we see that the oscillations in τ still have a frequency \( \omega_Q \) but decay like the inverse of the distribution of frequencies, \( (n\sigma_Q)^{-1} \). Now consider a Lorentzian dis-
distribution of frequencies, \( g(\omega_Q) = \frac{1}{2\pi} \frac{\Gamma_Q}{(\omega_Q - \omega_Q^0)^2 + (\Gamma_Q/2)^2} \). Then we obtain:

\[
\bar{I} = \int 2\pi \frac{\Gamma_Q}{(\omega_Q - \omega_Q^0)^2 + (\Gamma_Q/2)^2} A \cos(n\omega_Q\tau) d\omega_Q
= Ae^{-(n/2)\Gamma_Q\tau} \cos(n\omega_Q\tau).
\]

(22)

We can add a \( T_2 \) decay process to the \( \{S = 3/2, \theta = \pi/2, \eta = 0\} \) case by applying Eq. (21) or Eq. (22) to Eq. (8) and obtain realistic predictions of the \( \tau \)-dependent intensity:

\[
I(\tau) = \frac{I(0)}{2} \left( 1 + e^{-18(\pi/2)^2} \cos(6\omega_Q\tau) \right) e^{-2\tau/T_2}
\]

(23) or

\[
I(\tau) = \frac{I(0)}{2} \left( 1 + e^{-3\Gamma_Q\tau} \cos(6\omega_Q\tau) \right) e^{-2\tau/T_2}.
\]

(24)

The general behavior of these formulae are plotted in Fig. 6. Importantly, even for \( \omega_Q^0 = 0 \), the width of the distribution can be recovered from a \( \tau \) spectroscopy experiment. This is possible if the distribution’s decay rate is not larger than \( T_2 \) (e.g. \( \Gamma_Q \) or \( \sigma_Q \) are not too small), as a “plateau” will occur between the \( 1/T_Q \) decay time and the \( T_2 \) decay time. In other words, the presence of both orbital and magnetic noise leads to a two-step relaxation process. For \( \omega_Q \neq 0 \), we see the characteristic cosine variations, which clearly distinguish it from the \( \omega_Q^0 = 0 \) case.

We note that a dipole-dipole interaction can also cause a similar decay (e.g. two spin-1/2 nuclei with an \( S_z \otimes S_z \) interaction), but the dipole-dipole interaction will have a different angular response (\( \alpha, \beta \)) compared to the quadrupolar interaction’s (Appendix D).

To briefly outline how \( I(\tau) \) reacts to \( \eta \) and \( \theta \) variations, we consider the general form of the \( \tau \) dependence from Eq. (17). The rule of thumb is that the relative ratio of the constant term to the sum of cosine amplitudes gives the plateau height. As we saw in Fig. 3, \( \eta \) can modify the ratio of the cosine parameter to the constant, \( A/C \), depending on the relative size of \( \Gamma_Z \) to \( \Gamma_Q \). Increasing \( \eta \) also slightly modifies the cosine frequency through \( \xi \) in Eq. (14), making \( n_j \) in the the kernel \( K_j \) larger by up to 15%. For simplicity, we ignore this small correction to \( n_j \). Then the echo intensity, in terms of the \( A \) and \( C \) parameters, is:

\[
I(\tau, \eta) \propto \left( C(\eta) + A(\eta)e^{-3\pi\tau\cos(6\omega_Q\tau)} \right) e^{-2\tau/T_2}.
\]

(25)

Modifications to \( \theta \) are more complicated (Fig. 4(b)). At 60°, the large reduction in the constant term \( C \) means the decay associated with the \( 3\omega_Q \) cosine dominates, causing a lower plateau than at 90°, as seen in the dashed line of Fig. 6(b). This also leads to a slower effective decay time, and indeed the plateau occurs slightly later for the 60° pulse angle simulation. As \( \theta \) decreases further, the small amplitudes of both the cosine terms would lead to a case with only a \( \Gamma_Z \) decay. In terms of the \( A, B, \) and \( C \) parameters:

\[
I(\tau, \theta) \propto \left[ C + Ae^{-3\pi\tau\cos(6\omega_Q\tau)} + Be^{-3(3/2)\pi\tau\cos(3\omega_Q\tau)} \right] e^{-2\tau/T_2}.
\]

(26)

Finally, we note that as Eq. (20) is a classical linear inverse problem, it is possible to determine the distribution \( g(\omega_Q) \) from a \( \tau \) spectroscopy experiment even if \( g \) takes an arbitrary or unknown form. Let us consider the simplest form of \( \langle S_z(2\tau) \rangle \) (Eq. (8)) such that we have two kernels:

\[
K_1 = (3/4)
K_2 = (3/4) \cos(6\omega_Q\tau).
\]

(27)

Note that the intensity associated with the constant kernel is trivial, \( I_1 = \int_{-\infty}^{\infty} g(\omega_Q)(3/4)d\omega_Q = 3/4 = S/2 \), since \( g(\omega_Q) \) is assumed to be normalized. Therefore all of the spectral information must lie in \( I_2 \), which is of the form \( \int_{-\infty}^{\infty} g(\omega_Q) A \cos(n\omega_Q\tau)d\omega_Q \). This is just a cosine transform, and so we can easily write down the inverse transformation:

\[
g(\omega_Q) = \frac{2\pi}{A n} \int_{-\infty}^{\infty} I_2(\tau) \cos(n\tau\omega_Q)d\tau.
\]

(28)

We expect the initial intensity to be the magnitude of the spin, \( I(0) = S = 2I_1 \). Then, we can obtain \( I_2(\tau) \) via \( I = I_1 + I_2 = I(0)/2 + I_2 \). As mentioned previously, in experiments one observes an additional \( T_2 \) decay rate, \( e^{-2\tau/T_2} \), and so we can add this to our expected theoretical intensity and define \( I_{\text{exp}}(\tau) = I(\tau) e^{-2\tau/T_2} \). Putting both of these assumptions into Eq. (28), one can reconstruct the distribution \( g(\omega_Q) \) from \( I_{\text{exp}}(\tau) \) by evaluating:

\[
g(\omega_Q) \propto \int_0^m \left( I_{\text{exp}}(\tau)e^{2\tau/T_2} - \frac{I_{\text{exp}}(0)}{2} \right) \cos(6\omega_Q\tau)d\tau.
\]

(29)
Here we have set the lower integration limit to 0, as we assume the spin dynamics are symmetric in negative $\tau$ (i.e. that $g(\omega_Q)$ is an even function of $\omega_Q$). We have also set an upper limit of time $\tau_m$ which is assumed to be some multiple of $T_2$ such that $I_{\text{exp}}(\tau > \tau_m) \approx 0$. Note that $1/\tau_m$ will act as a low-frequency cutoff in the reconstruction of $g(\omega_Q)$, as the method cannot distinguish contributions to the distribution for $\omega_Q < 1/2T_2$.

IV. SPECTROSCOPY FOR GENERAL SPINS

We have seen that careful analysis of the $\tau$-dependence of a spin echo amplitude in the presence of a quadrupolar EFG can give information about the distribution of $\omega_Q$ and the asymmetry $\eta$. We will now generalize this technique for any spin to provide formulae up to $S = 7/2$. Derivations of these formulae, which depends on iterative equations generated via the $SU(2)$ spin representations, are provided in Appendix B and C.

A. Half-integer Spin

The explicit forms up to $S = 5/2$ (for a coherent initial state of maximum $S_z$ value, e.g. $m = S$) for the case $\eta = 0$ are:

- $S = 1/2 : \frac{1}{2}$
- $S = 3/2 : \frac{1}{2}[1 + \cos(6\omega_Q\tau)]$
- $S = 5/2 : \frac{1}{16}[3 + 4\cos(6\omega_Q\tau) + \cos(12\omega_Q\tau)]$.

In Fig. 7 we plot the shape of each of these functions for $S = 3/2$ up to $S = 11/2$, with the equations for higher spin included in App. B. Note that although the higher spins have a more complicated form, the higher frequency terms cancel to prevent any high-frequency oscillations. We expect that spectroscopy of $\omega_Q$ and its distribution should follow a similar methodology to the $S = 3/2$ case studied in detail in the previous section, but now a few additional frequencies with weak amplitudes should be visible. For $\omega_Q \neq 0$, this should be evident in the spectral transform of the $\tau$-dependent signal, $\langle S_x(2\tau) \rangle$. For $\omega_Q = 0$, additional plateaus will occur at earlier timescales than that associated with the $6\omega_Q\tau$ cosine, with values near the maximum amplitude $I(0)$ due to their relatively small prefactors. We also note that as the system becomes classical ($S \to \infty$), these equations represent smooth approximations of a sum of delta functions:

$$\lim_{S \to \infty} \langle S_x(2\tau) \rangle = \sum_{n=0}^{\infty} \delta(\omega_Q\tau - n\pi/3).$$

B. Integer Spin

The explicit forms for $\langle S_x(2\tau) \rangle$ for $S = 1$ and 2 (again assuming $m = S$) are:

$$S = 1 : \cos(3\omega_Q\tau)$$
$$S = 2 : \frac{1}{4}[3\cos(3\omega_Q\tau) + \cos(9\omega_Q\tau)]$$

and are plotted in Fig. 8, with the equations for higher spin included in App. C. As no constant term appears in these equations, a plateau between the largest cosine timescale and the $\Gamma_z$ timescale will not occur. If more than one cosine term exists ($S > 1$), one can try to measure the plateaus caused by two or more distinct $\omega_Q\tau$ decays, but this is difficult as they are separated by at most a factor of 3.

As before, when the system becomes classical ($S \to \infty$), these equations represent smooth approximations of a sum of delta functions, but now with an alternating sign:

$$\lim_{S \to \infty} \langle S_x(2\tau) \rangle = \sum_{n=0}^{\infty} (-1)^n \delta(\omega_Q\tau - n\pi/3).$$

C. Thermal Ensembles

To understand the effects of having an initial state that is a thermal mixture of different $S_z$ eigenvalues, instead of the pure state $|S, m = S\rangle$ cases considered before, we briefly illustrate the case of $S = 3/2$. After computing the response for general $m$ (App. B), we obtain

$$m = 3/2 : \frac{1}{2}[1 + \cos(6\omega_Q\tau)]$$
$$m = 1/2 : \frac{1}{2}[-1 + 3\cos(6\omega_Q\tau)]$$
$$m = -1/2 : \frac{1}{2}[-1 + 3\cos(6\omega_Q\tau)]$$
$$m = -3/2 : \frac{1}{2}[1 + \cos(6\omega_Q\tau)]$$

FIG. 7. Dependence of $\langle S_x(2\tau) \rangle$ on $\omega_Q\tau$ for different half-integer spins, indicated by different colors. The y-axis is normalized.
which satisfy the inversion symmetry constraint
\[ \langle S_x(2\tau) \rangle_m = -\langle S_x(2\tau) \rangle_{-m}. \]  

When the nuclear Zeeman interaction dominates, we expect the thermal state to be a mixed state represented by a block diagonal density matrix of the form
\[ \rho = \frac{1}{Z} \sum_m e^{-\beta H_m} \langle S, m | S, m \rangle = \sum_m \rho_m, \]  
where \( \rho_m = e^{-\beta H_m} \langle S, m | S, m \rangle \), with relative energies \( H_m = B_0 m \), inverse temperature \( \beta = 1/T \), and partition function \( Z = \sum_m e^{-\beta H_m} \). The amount of mixing depends solely on the product \( B_0 \beta \), which for most experiments is very small (the temperature is much larger than the magnetic level splittings), and thus a large amount of mixing is generally expected.

As each element of the density matrix should preccess independently of the others, we can simply use the relative weightings of each state to define an average spin-echo profile:
\[ \langle S_x(2\tau) \rangle_{Th} = \sum_m p_m \langle S_x(2\tau) \rangle_m \]  
where \( p_m = \frac{1}{Z} e^{-\beta H_m} \). For example, for the \( S = 3/2 \) case here, if we assume a moderately high temperature such that \( p_{3/2} \approx 0.28 \) and \( p_{1/2} \approx 0.26 \) (and that \( p_{-1/2} \approx 0.24 \) and \( p_{-3/2} \approx 0.22 \)), one obtains \( \langle S_x(2\tau) \rangle_{Th} = \frac{1}{8} \left( 1 + \frac{3}{2} \cos(6\omega_Q\tau) \right) \). Remember, only the relative amplitude between the constant and cosine term are measurable, and not the overall amplitude. So, compared to the coherent \( m = 3/2 \) state, the only change for the thermal mixture is that the cosine term is 50% larger. That is to say, the plateau will occur at a relative amplitude smaller than 1/2 (similar to the effect of \( \theta \neq 90^\circ \) in Fig. 6), but still reveal the distribution of any inversion-symmetric interactions.

V. CONCLUSIONS

We have developed a methodology for the determination of the mean-value and distribution of even-powered spin interactions \( \langle S^n \rangle \) in a solid state system. We have focused on the quadrupolar Hamiltonian \( (n = 2) \), and provided closed form equations for general spins. Even when the average value of \( \omega_Q \) is zero, the effective linewidth of the distribution \( \Gamma_Q \) is obtained from this straightforward \( \tau \)-spectroscopy if the quadrupolar timescale \( \Gamma_Q^{-1} \) or \( \sigma_Q^{-1} \) is smaller than the magnetic disorder timescale \( \Gamma_Z^{-1} \). Considering anisotropic \( (\eta \neq 0) \), pulse-angle \( (\theta \neq 0) \), or tilt-angle \( (\alpha \neq 0) \) effects, we find the relative weighting of the \( \tau \)-dependent and \( \tau \)-independent terms change, which appears in experiments as a variable plateau height in the \( \tau \)-spectroscopy (the ratio \( A/C \)). We also note that implementing an effective experiment for integer spin will be difficult as no \( \tau \)-independent term appears, suggesting a more sophisticated pulse-protocol should be developed in these cases.

Our methodology easily extracts the variations in the multipolar order parameter and its anisotropy, even when its average value is zero, giving valuable information about temperature-dependent fluctuations that drive a phase transition. This provides invaluable physical insight into the mechanisms which drive magnetic frustration caused by the interplay of multiple interactions. At the same time, the technique reveals any inversion or time-reversal symmetry among local interactions, giving direct evidence on the form of the microscopic Hamiltonian.

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Appendix A: Simulation details

The simulations of the quadrupolar spin echos were performed using the QuTiP python package [40, 41], by way of its master equation solver mesolve. This method, which solves the Lindblad master equation, determines the spin dynamics by solving the differential equations acting on the spin’s density matrix, \( \rho(t) \). To apply the external magnetic field, we assume instantaneous pulsing. This means that, instead of applying a finite magnetic field along a specific axis for a finite number of time steps, we instead apply a single rotation operator at a specified
time-step ($\tau$) before continuing time-propagation via me-
solve, e.g. $\rho(t') = e^{-i\theta S_x} \rho(t) e^{i\theta S_x}$ for a $\theta$ pulse about the
x axis. To account for variations in the precession fre-
cuency $\omega_z$, we sample its distribution (a Lorentzian with
FWHM $\Gamma_z$) uniformly. The total dynamics of all the
spins together are then given by the sum of the dyna-
ics at each sampled point on the distribution, weighted
by the distribution’s value at each sample. We confirmed
that a random sampling of the frequencies converges to
the result obtained from this (more efficient) integrated
sampling.

Appendix B: Half-integer Spin

We begin with a review of the standard $SU(2)$ rep-
resentation structure for general spin. We will choose the
$S_z$ operator as the diagonal matrix with descending ele-
ments $\{S, S-1, \ldots, -S+1, -S\}$. The operators $S_x$ and
$S_y$ can be determined from the sum or difference of the
related operators $S_{\pm} = S_x \pm i S_y$. The momenta
raising/lowering operators $S_{\pm}$ are zero except for the terms
given by

$$\langle S, j \pm 1 | S_{\pm} | S, j \rangle = \sqrt{S(S+1) - j(j \pm 1)}.$$  \hspace{1cm} (B1)

The general form of $S_x$ and $S_{\pm}$ in the $z$ basis are therefore

$$S_x = \frac{i}{2} \begin{pmatrix} 0 & a_S^x & 0 & \cdots \\ a_S^x & 0 & a_S^{-1} & 0 \\ 0 & a_S^{-1} & 0 & \cdots \\ \vdots & \vdots & \vdots & \ddots \\ \end{pmatrix},$$  \hspace{1cm} (B2)

$$S_y = \frac{i}{2} \begin{pmatrix} 0 & -a_S^y & 0 & \cdots \\ a_S^y & 0 & -a_S^{-1} & 0 \\ 0 & a_S^{-1} & 0 & \cdots \\ \vdots & \vdots & \vdots & \ddots \\ \end{pmatrix},$$

with $a_S^z = \sqrt{S(S+1) - j(j-1)}$. Note that these
matrices are symmetric about their center because $a_S^z = a_S^{j+1}$. To estimate the spin echo, we need to know the initial state, which is given by a 90° ro-
tation about the $y$-axis from the $\langle S_z \rangle = m$ state,
$|\psi_0\rangle = \mathcal{R}_S(90°) |S, m\rangle$. We will also need the op-
erator which performs a 180° rotation about the $x$-axis.
Thankfully, the latter is quite simple in this basis

$$\mathcal{R}_S(180°) = i^{2S+2} \begin{pmatrix} 0 & 1 & 0 & \cdots \\ 1 & 0 & 0 & \cdots \\ 0 & 0 & 1 & \cdots \\ \vdots & \vdots & \vdots & \ddots \\ \end{pmatrix},$$  \hspace{1cm} (B3)

but $|\psi_0\rangle$ must be determined from a set of iterative equa-
tions. The easiest way to obtain $|\psi_0\rangle = \sum_m \psi_m |S, m\rangle$ is to
realize it must be an eigenvector of $S_x$ with a specific

\[
\frac{1}{2} \begin{pmatrix} 0 & a_S & 0 & \cdots \\ a_S & 0 & a_S^{-1} & 0 \\ a_S^{-1} & 0 & 0 & \cdots \\ \vdots & \vdots & \vdots & \ddots \\ \end{pmatrix} \begin{pmatrix} \psi_S \\ \psi_{S-1} \\ \psi_{S-2} \\ \vdots \end{pmatrix} = m \begin{pmatrix} \psi_S \\ \psi_{S-1} \\ \psi_{S-2} \\ \vdots \end{pmatrix}
\]

where we have begun to suppress the superscript $S$ for
simplicity. For the pure state we assumed in the analysis
of the main paper, this was taken to be the maximum,
m = S, but for thermal states we will want to consider a
general distribution of different $m$ values. To summarize
the first three lines:

$$a_S \psi_{S-1} = 2m \psi_S,$$

$$a_S \psi_S + a_{S-1} \psi_{S-2} = 2m \psi_{S-1},$$  \hspace{1cm} (B5)

$$a_{S-1} \psi_{S-1} + a_{S-2} \psi_{S-3} = 2m \psi_{S-2}.$$  

Ignoring the overall normalization of $|\psi_0\rangle$ for now, we can
set $\psi_S = 1$. The first line then gives us $\psi_{S-1} = 2m/a_S$. The rest of the $\psi_j$ are given by the recursion relationship

$$\psi_j = \frac{1}{a_{j+1}} (2m \psi_{j+1} - a_{j+2} \psi_{j+2})$$  \hspace{1cm} (B6)

and note there is an inversion symmetry $\psi_j = \psi_{-j}$. Now
we assume our Hamiltonian is a diagonal matrix, \(\mathcal{H} = \text{diag} \{h_S, h_{S-1}, \ldots, h_{-S}\}\) for general elements
$h_j$. The corresponding time propagator is $U(\tau) = \text{diag} \{e^{-i h_S \tau}, e^{-i h_{S-1} \tau}, \ldots, e^{-i h_{-S} \tau}\}$ and we can write the final (echo) state as

$$|2\tau\rangle = U(\tau) \mathcal{R}_x(\pi) U(\tau) |\psi_0\rangle.$$  \hspace{1cm} (B7)

As $\mathcal{R}_x(\pi)$ simply inverts a state vector and multiplies it
by $\pm i$, we can quickly write down the final state as

$$|2\tau\rangle = \text{diag} \left\{ i(-1)^{S+1/2} \psi_j e^{-i(h_j+h_{-j})\tau} \right\} = \text{diag} \{F_j\}. \hspace{1cm} (B8)$$

As $\psi_j = \psi_{-j}$, this state vector is symmetric about its
center, and as the operator $S_x$ is as well, we only need to
evaluate half of the terms in inner product $\langle 2\tau | S_x | 2\tau \rangle$, e.g. from $S$ to $j = 1/2$. Taking special note of
the structure caused by the off-diagonal terms of $S_x$ (we
have grouped the product terms from the inner product
in brackets) we obtain

\[
\frac{1}{2} \langle 2\tau | S_x | 2\tau \rangle = \begin{cases} a_S F_S^1 F_{S-1} \\
+ a_S F_{S-1}^1 F_s + a_{S-1} F_{S-1}^1 F_{S-2} \\
+ a_{S-1} F_{S-2}^1 F_{S-1} + a_{S-2} F_{S-2}^1 F_{S-3} \\
+ \cdots + a_3 F_{1/2}^1 F_{1/2} + a_{1/2} F_{1/2}^1 F_{-1/2} \end{cases}.
\]

Notice that by grouping across adjacent brackets, this is a
sum of conjugate pairs except for an unpaired $j = 1/2$.
with \( \lambda_j = 1 \) if \( j = 1/2 \), and \( \lambda_j = 2 \) otherwise. The exponential term and its conjugate is simply \( 2 \cos(\cdot) \) of the argument, except for the \( j = 1/2 \) case where the argument is 0 and there is no conjugate pair. To evaluate the argument of the cosines, we define the matrix \( W_j \) such that \( W_S = \text{diag} \{-1, 1, 0, \ldots, 0, 1, -1\} \), \( W_{S-1} = \text{diag} \{0, -1, 0, \ldots, 0, 1, -1, 0\} \), and so forth. This yields cosine arguments of \( \omega_j \tau \) where \( \omega_j \equiv \text{Tr}(W_j \mathcal{H}) \), remembering that \( \mathcal{H} \) is diagonal. The final (general) equation for the echo magnitude is then given by

\[
\langle S_x(2\tau) \rangle = C \sum_{j=1/2}^S \lambda_j a_j \psi_j \psi_{j-1} \cos(\omega_j \tau). \tag{B11}
\]

To help simplify, we define the prefactor variable \( \tilde{A}_j^S = \lambda_j a_j \psi_j \psi_{j-1}^\dagger \), and note that since \( \langle S_x(0) \rangle = S \) we can derive the normalization factor by setting \( \tau = 0 \) in the above expression, yielding \( S = C \sum_{j=1/2}^S \tilde{A}_j^S \). This normalization is necessary as a final step, as we never normalized \( |\psi_0\rangle \), and doing so from the recursive relation would be tedious.

The Hamiltonian \( \mathcal{H} \) only enters this final expression linearly in the definitions of \( \omega_j \). If we write \( \mathcal{H}_{\text{diag}} = \mathcal{H}_1 + \mathcal{H}_2 \), then the final \( \omega_j = \omega_j^{(1)} + \omega_j^{(2)} \), e.g. the frequencies add linearly. Let us consider some general Hamiltonian terms then. First, we can quickly see that any identity term \( \mathcal{H} \propto \text{Id} \) must yield \( \omega_j = 0 \) for all \( j \) (which is reassuring, as constants should not affect the dynamics of observables). Similarly, if \( \mathcal{H} = \mathcal{S}_z \), its antisymmetry yields \( \omega_j = 0 \). However, for \( \mathcal{H} = \mathcal{S}_z^2 \), its symmetric (but non-constant) elements are \( \{j^2\} \) and we have \( |\omega_j| = 2(j^2 - (j - 1)^2) = 4j - 2 \). Now consider the quadrupolar Hamiltonian (for general \( S \)):

\[
\mathcal{H}_Q = \omega_2 \mathcal{S}_z + \frac{\omega^2}{2} (3\mathcal{S}_z^2 + \mathcal{S}^2). \tag{B12}
\]

Since \( \mathcal{S}^2 \propto \text{Id} \), \( \mathcal{S}_z^2 \) and \( \mathcal{S}_z \) both give no contribution to \( \omega_j \), and we need only consider the \( \mathcal{S}_z^2 \) contribution:

\[
\omega_j^{\mathcal{H}_Q} = 3\omega_Q(2j - 1). \tag{B13}
\]

We now have everything needed to derive expressions of \( \langle S_x(2\tau) \rangle \) for general \( S \), which are explicitly given up to \( S = 11/2 \) (for \( m = S \)) by:

\[
\begin{align*}
S &= 1/2 : \frac{1}{2} \\
S &= 3/2 : \frac{1}{2} \left[ 1 + \cos(6\omega_Q \tau) \right] \\
S &= 5/2 : \frac{1}{2} \left[ 3 + 4 \cos(6\omega_Q \tau) + \cos(12\omega_Q \tau) \right] \\
S &= 7/2 : \frac{1}{6} \left[ 10 + 15 \cos(6\omega_Q \tau) + 6 \cos(12\omega_Q \tau) + \cos(18\omega_Q \tau) \right] \\
S &= 9/2 : \frac{9}{256} \left[ 35 + 60 \cos(6\omega_Q \tau) + 28 \cos(12\omega_Q \tau) + 8 \cos(18\omega_Q \tau) + \cos(24\omega_Q \tau) \right] \\
S &= 11/2 : \frac{11}{1024} \left[ 120 + 210 \cos(6\omega_Q \tau) + 120 \cos(12\omega_Q \tau) + 45 \cos(18\omega_Q \tau) + 10 \cos(24\omega_Q \tau) + \cos(30\omega_Q \tau) \right]. \tag{B14}
\end{align*}
\]

Appendix C: Integer Spin

For integer spin, the \( S_i \) matrices and initial state \( \psi_0 \) now have a term at their center \( j = 0 \) that is not related to any other by symmetry. However, the rest of the derivation is identical, and the final dot product now looks like:

\[
\langle 2\tau | S_x | 2\tau \rangle = \left[ a_S F_S \right] + \left[ a_S F_S^\dagger F_S - a_S F_S^\dagger F_S \right] + \ldots + \left[ a_1 F_1 \right] + \left[ a_0 F_0 \right] + \left[ a_{-1} F_{-1} \right] + \left[ a_{-2} F_{-2} \right] + \ldots
\]

\[
\text{So unlike in the half-integer case, every term has a hermitian conjugate. Remembering the symmetry } a_j = a_{-j+1} \text{ and } F_j = -F_{-j}, \text{ we can simplify as:}
\]

\[
\langle S_x(2\tau) \rangle = 2 \sum_{j=1}^{S} a_j \psi_j \psi_{j-1} \times \left[ e^{-i(h_j + h_{j-1} + h_{j-1}) \tau} + \text{h.c.} \right] \tag{C2}
\]

where \( \tilde{A}_j^S = a_j \psi_j \psi_{j-1} \), i.e. we no longer need the special function \( n_j \) to single out the unpaired term. The generating matrices \( W_j \) are mostly the same (but with an extra 0 at the center), and a special form shows up for \( j = 1 \): \( W = \text{diag} \{0, -1, 2, -1, 0, \ldots\} \). This still leads to the same conditions: \( \omega_j = 0 \) for any Hamiltonian proportional to \( \text{Id} \) or \( \mathcal{S}_z \), and \( \omega_j = 4j - 2 \) for Hamiltonians proportional to \( \mathcal{S}_z^2 \). However, as \( j \) is now an integer,
\( \omega_j \neq 0 \) for any \( j \) under \( S_j^2 \), and so we will not have a constant term in our expressions for \( \langle S \rangle \).

The expressions for \( S \) up to 5 are (for \( m = S \)):

\[
S = 1 : \cos(3\omega Q \tau) \\
S = 2 : \frac{2}{7} [3 \cos(3\omega Q \tau) + \cos(9\omega Q \tau)] \\
S = 3 : \frac{3}{16} [10 \cos(3\omega Q \tau) + 5 \cos(9\omega Q \tau) + \cos(15\omega Q \tau)]. \\
S = 4 : \frac{4}{64} [35 \cos(3\omega Q \tau) + 21 \cos(9\omega Q \tau) + 7 \cos(15\omega Q \tau) + \cos(21\omega Q \tau)] \\
S = 5 : \frac{5}{256} [126 \cos(3\omega Q \tau) + 84 \cos(9\omega Q \tau) + 36 \cos(15\omega Q \tau) + 9 \cos(21\omega Q \tau) + \cos(27\omega Q \tau)].
\]

\section*{Appendix D: Derivation of \( H_Q(\alpha, \beta) \)}

We define our quadrupolar frequency as:

\[
\omega_Q = \frac{eqV_{zz}}{S(2S-1)} \tag{D1}
\]

where \( V_{zz} \equiv eq \) is the largest component of the EFG in the principle axis system (PAS, the basis choice where \( V_{ij} = \partial E_q/\partial x_i \) is diagonal) and \( eq \) is introduced to parameterize the nuclear coupling to the EFG. In principle neither \( eq \) or \( eq \) needs to be measured independently, as only their product enters into the observable \( \omega_Q \). We also define the asymmetry parameter as

\[
\eta = \frac{V_{xx} - V_{yy}}{V_{zz}} \tag{D2}
\]

where again \( V_{ij} \) is in the PAS.

We now derive how \( H_Q \) changes if the material is rotated such that the laboratory frame does not align with the PAS. Consider the material originally aligned with the PAS. It then undergoes two rotations: first, a rotation about \( z \)-axis by \( \beta \), and then a rotation about the \( y \)-axis by \( \alpha \). The EFG \( (V_{ij}) \), which was originally diagonal in the PAS, now has components:

\[
\begin{align*}
V_{xx} &= \frac{eQ}{2} (2 \sin^2 \alpha - \cos^2 \alpha(1 - \eta \cos 2\beta)) \\
V_{yy} &= -\frac{eQ}{2} (1 + \eta \cos 2\alpha) \\
V_{zz} &= \frac{eQ}{2} (2 \cos^2 \alpha - \sin^2 \alpha(1 - \eta \cos 2\beta)) \\
V_{xy} &= -\frac{eQ}{2} \eta \cos \alpha \sin 2\beta \\
V_{xz} &= \frac{eQ}{2} \eta \sin \alpha \sin 2\beta \\
V_{yz} &= \frac{eQ}{4} \sin 2\alpha(3 - \eta \cos 2\beta).
\end{align*}
\]

and \( V \) is still symmetric and traceless. The quadrupolar Hamiltonian for a spin in the presence of an EFG can be written via a dyadic inner product over spherical harmonics as [34]:

\[
H_Q = Q^{(2)} \cdot \nabla E^{(2)} = \sum_{m=-2}^{2} (-1)^m Q_m^{(2)} \nabla E_{-m}^{(2)}. \tag{D4}
\]

The nuclear spin terms are given by

\[
\begin{align*}
Q^{(2)}_0 &= A(3S_z^2 - S^2) \\
Q^{(2)}_{\pm 1} &= \pm A \sqrt{\frac{3}{2}} (S_zS_y + S_yS_z) \\
Q^{(2)}_{\pm 2} &= A \sqrt{\frac{5}{2}} S_z^2
\end{align*}
\]

with \( A = eq/(2S(2S-1)) \). The EFG components are

\[

\begin{align*}
\nabla E_0^{(2)} &= \frac{1}{2} V_{zz} \\
\nabla E_{\pm 1}^{(2)} &= \frac{1}{\sqrt{6}} (V_{xz} \pm iV_{yz}) \\
\nabla E_{\pm 2}^{(2)} &= -\frac{1}{\sqrt{6}} (V_{xx} - V_{yy} \pm 2iV_{xy}).
\end{align*}
\]

By combining the dyadic expression for \( H_Q \) with the basis transformation for \( V_{ij} \), we obtain:

\[
H_Q(\beta, \alpha) = \frac{\omega_Q}{2} \left[ \frac{3 \cos^2 \alpha - 1}{2} + \frac{\eta}{2 \sin^2 \alpha} \cos 2\beta \right] (3S_z^2 - S^2) + \frac{3 \sin^2 \alpha + \frac{1}{2} \cos^2 \alpha}{2} \cos 2\beta \left( S_z^2 - S_y^2 \right) \\
+ \frac{\eta \cos \alpha \sin 2\beta (S_zS_y + S_yS_z)}{4} - \frac{\sin 2\alpha}{4} (3 - \eta \cos 2\beta) (S_zS_x + S_xS_z) + \frac{\eta}{2} \sin \alpha \sin 2\beta (S_yS_x + S_xS_y). \tag{D7}
\]

This reproduces the Hamiltonian in the PAS (Eq. 5) when \( \alpha = \beta = 0 \).
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