An Analytical Formulation of CPMAS

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(Dated: November 29, 2021)

An exact expression for the cross polarization between two spin-1/2 particles is derived from the quantum Liouville equation. This is given in the form of two integrodifferential equations. These can be solved exactly in the static case (no sample spinning) and a powder average easily performed numerically. With magic angle spinning, the neglect of certain interference terms simplifies the numerical calculation. A further assumption decoupling the calculation of the sidebands gives a very simple formula that is capable of giving a qualitative interpretation of all experimental observations. Examples are given illustrating typical buildup curves and CPMAS matching profiles.

I. INTRODUCTION

The most frequently used technique to improve the sensitivity of nuclei with low gyromagnetic ratios and/or low isotopic abundances in solid-state NMR is the Hartmann-Hahn cross polarization (CP) in the rotating frame. With this technique, polarization can be transferred from sensitive and often abundant nuclear spins $I$ (e.g., protons) to the insensitive nuclear spins $S$ (e.g., $^{13}$C, $^{15}$N). It is driven by the flip-flop transitions where both dipolar coupled spins $I$ and $S$ change their magnetic quantum number in an energy conserving process. Since this transfer of polarization takes time to develop, CP can be observed only if the whole spin system has reasonably long relaxation times. The CP spin dynamics has already been discussed more than 25 years ago and since then has been the subject of a variety of additional studies. The polarization of the abundant $I$ spins (usually with a high gyromagnetic ratio) is spin-locked in the rotating frame by a radiofrequency (rf) field. When a second rf field of appropriate magnitude is then simultaneously applied to the dipolar coupled rare $S$ spins (usually with a low gyromagnetic ratio), flip-flop processes become energy conserving and thus allow the transfer of polarization from the $I$ spins to the unpolarized $S$ spins. An overview of the Cross Polarization under Magic Angle Spinning (CPMAS) can be found in a number of places, a partial list of which is Refs. The emphasis in this paper is on an exact theoretical formulation of CPMAS and no attempt is made to review the experimental methods and/or results that have been achieved using them.

Several theoretical approaches have been presented for the description of CPMAS. One such approach is based on there being a spin temperature, which assumes the spins are in thermal equilibrium in an appropriate rotating frame, the recent paper by Meier exemplifies how this approach can be used. Another method, due to Müller et al., resulted in an empirical fitting formula which has been extensively used by many workers. A third type of approach is based on the use of Floquet theory and a comprehensive program GAMMA has been written which can be used for treating spin dynamics and numerically solving the quantum Liouville equation. A method of describing the spin dynamics in terms of rotations by parts of the Hamiltonian has been used by Levitt and Zhang et al. Finally, there are methods that use the Morlet approach to nonequilibrium statistical mechanics. One method is based on projecting onto selected parts of the Hamiltonian whereas another uses standard approximation methods for estimating the memory kernel. In contrast to this variety of methods, the approach presented here utilizes the special nature of the Hamiltonian in the doubly rotating frame, and the specific properties of spin-1/2 systems to obtain an exact integrodifferential equation (correctly a pair of such equations) for the cross polarization. A solution of these equations is complicated by any time dependence of the dipolar coupling, while an exact solution is immediately available for a time independent and orientation fixed coupling constant. The powder average of the resulting solution can be done numerically.

While the spin temperature approach is very appealing in that it provides a relatively simple explanation for the qualitative behaviour of cross polarization, it has a number of weaknesses. First of all, it is noticed that the spin system suffers no (or at most negligible) relaxation during a cross polarization experiment. Thus there is no basis for an equilibrium to be obtained and thus no basis for assuming a thermal distribution. An argument might be made for ergodic behaviour but we do not find that appealing. Second, the thermal equilibrium is to be in the doubly rotating frame, in which the Hamiltonian must still be time dependent if magic angle spinning is performed. Thus a selection has to be made in some way to extract a time independent Hamiltonian in order to have a thermal distribution. Exactly how this is done is arbitrary. Thirdly, only one Hartmann-Hahn matching condition can be described at a time, after selecting out the right time independent Hamiltonian. The theory presented here is a purely dynamical theory (no relaxation is involved), is capable of treating the magic angle spinning exactly (approximations simplifying the calculation are made, but all time dependence could be included), and all four peaks of the CPMAS matching profile are obtained from the same calculation.

The paper starts by reviewing some relevant properties of spin-1/2 systems together with their rotational properties. These are used in Sec. III to examine the specific
The exponential superoperator in terms of the sum of products (including the identity) implies a total operator space

events are of course just part of the commutation relations. Setting the commutator superoperator for the other spin directions can be defined but are not needed in this work.

II. A SYSTEM OF TWO SPIN-1/2 PARTICLES

The spin operators for the two particles are labelled as $S_x, S_y, S_z$ and $I_x, I_y, I_z$. There are also the identities $1_S$ and $1_I$ for the respective spin spaces. As spin-1/2 particles, these operators satisfy the product conditions

$$S_x S_y = \frac{i}{2} S_z, \quad I_x I_y = \frac{i}{2} I_z,$$

and their cyclic permutations.

and the cyclic permutations. The first set of product conditions are of course just part of the commutation relations

$$[S_x, S_y]_+ = i S_z \quad [I_x, I_y]_+ = i I_z,$$

and their cyclic permutations. [Throughout this work, $\hbar$ is set equal to 1.] The four operators for each spin (including the identity) imply a total operator space of 16 dimensions, which exactly coincides with the dimension of a matrix representation of a system of two spin-1/2 particles. Thus any operator can be expressed in terms of the sum of products of $S$ and $I$ spin operators. For simplicity of presentation, the identity operators are usually not written explicitly. Thus the operator $S_z$ is understood to stand for the product $S_z I_1$, etc.

Another important property of spin operators (not just of spin-1/2) is that the commutator of a spin operator generates a rotation. Setting the commutator superoperator

$$S_z A \equiv [S_z, A]_-, \quad e^{iS_z S_z} S_x e^{iS_z S_z} = S_x \cos \theta + S_y \sin \theta$$

rotates the $S$-spin operator on which it acts (here $S_z$) about the $\hat{z}$ axis. $I_z$ is used to denote the corresponding commutator superoperator for $I_z$. Analogous commutator superoperators for the other spin directions can be defined but are not needed in this work.

III. NATURAL PARTITIONING OF THE OPERATOR SPACE IN THE DOUBLY-ROTATING TILTED FRAME

This is phrased in the tilted frame, namely the rf fields are labelled as being in the $\hat{z}$ direction and the spin operators of the truncated (often referred to as the secular part of the) dipolar hamiltonian lying along the $\hat{z}$ direction. Thus the hamiltonian is

$$H(t) = \omega_{11} I_z + \omega_{1S} S_z + 2 b(t) I_x S_x.$$  \hspace{1cm} (6)

The angular velocities $\omega_{11} = |\gamma_{1} B_{11}|$ and $\omega_{1S} = |\gamma_{S} B_{1S}|$ are proportional to the radio frequency field amplitudes $B_{11}$ and $B_{1S}$. In the laboratory frame, these rf fields are oscillating at the respective resonance Zeeman frequencies determined by a large static magnetic field in the $\hat{z}$ direction. $b(t)$ is the (possibly) time dependent heteronuclear dipolar coupling strength. Fundamentally this coupling strength depends on the angle $\theta$ between the vector $r$ pointing from the nucleus having its spin labelled $I$ to the nucleus whose spin is labelled $S$ relative to the Zeeman field direction $\hat{z}$, being explicitly given by

$$b(\theta) = b_0 (\cos^2 \theta - 1/3),$$  \hspace{1cm} (7)

where $b_0 = -3 \mu_0 \gamma_{1} \gamma_{S} \hbar/(8 \pi v^3)$ is the dipolar coupling constant. Ignoring any angular (rotational or vibrational) motion of the molecules in the chemical system, a time dependence arises only through the physical spinning of the sample about an axis at the magic angle. \[^{[1]}\] Then, the energy eigenvalues $\omega_{11} = |\gamma_{1} B_{11}|$ and $\omega_{1S} = |\gamma_{S} B_{1S}|$ are proportional to the radio frequency field amplitudes $B_{11}$ and $B_{1S}$. In the laboratory frame, these rf fields are oscillating at the respective resonance Zeeman frequencies determined by a large static magnetic field in the $\hat{z}$ direction. Thus $\theta$ becomes time dependent and $b(t)$ is written as a shorthand for $b(\theta(t))$. There is inherently a remaining orientation dependence of $b(t)$, associated with the original orientation $\theta(0)$ of $r$. In a powder sample there is a random distribution of such angles so an average over $\theta(0)$ needs to be made for such samples. But for the analysis of the spin dynamics, only the possible time dependence of $b(t)$ is important, so only this time dependence is explicitly displayed. Later on, when a powder sample is considered, the extra averaging over initial orientations (or its equivalent) is made.

It is also noted that, if $b$ is time independent (and has a fixed interspin orientation, $\theta$), the energy eigenvalues of this hamiltonian are $\pm (1/2) \sqrt{b^2 + (\omega_I \pm \omega_S)^2}$. These eigenvalues have been noted (at least) by Levitt, et al., but their method of solving the spin dynamics, as do some other treatments, for example, is based on a separation of the hamiltonian, Eq. (3), into two commuting parts. Neither the eigenvalues, nor their respective eigenvectors, seem to be standardly quoted in the literature. They are listed for reference in Appendix A. The method used in this paper does not explicitly use these eigenvalue properties nor the above noted separation of the hamiltonian, Eq. (6), into two commuting parts.

The purpose of this section is to catalog how the 16 spin operators behave under the action of the commutator superoperator $\mathcal{L}(t)$ for the hamiltonian,

$$\mathcal{L}(t) A \equiv [H(t), A]_- = \mathcal{L}_{rf} A + \mathcal{L}_{d}(t) A.$$  \hspace{1cm} (8)
This is listed as a sum of radio frequency and dipolar parts. It is to be shown that this set of operators is partitioned into four dynamically separate sets of operators. Crucial to this partitioning is the vanishing of commutators of the form

\[ [S_x I_x, S_y I_y] = S_x[I_x, S_y I_y] + [S_x S_y I_y] I_x = S_x S_y (iI_z) + i S_z I_y I_x = (i/2) S_x (iI_z) + i S_z (-i/2) I_z = 0. \] (9)

This relation is special to spin-1/2 systems since it depends on the special product conditions, Eq. (1), of the spin-1/2 operators.

Starting with the operator \( I_z \), the action of \( \mathcal{L}(t) \) on successively appearing operators is

\[ \mathcal{L} I_z = -2ib S_z I_y, \]
\[ \mathcal{L} S_y I_y = i \omega_1 S_y I_y - i \omega_1 S_x I_x + \frac{i}{2} b I_z, \]
\[ \mathcal{L} S_y I_x = -i \omega_1 S_y I_x - i \omega_1 S_y I_y, \]
\[ \mathcal{L} S_z I_x = i \omega_1 S_y I_x + i \omega_1 S_y I_y, \]
\[ \mathcal{L} S_z I_y = -i \omega_1 S_z I_x + i \omega_1 S_y I_y + \frac{i}{2} b S_z, \]
\[ \mathcal{L} S_z = -2ib S_y I_z. \] (10)

The possible time dependence of \( \mathcal{L} \) and \( b \) has not been indicated in these equations. This gives a closed set of 6 operators, namely \( I_z, S_z, S_x I_x, S_y I_y, S_y I_x \) and \( S_y I_y \). It is this set of operators that govern the behaviour of a CPMAS experiment. The set of commutators (10) have some special properties which are useful for the subsequent analysis. Specifically it is noticed that the dipolar hamiltonian acts only to couple the single 1-spin operators \( S_z \) and \( I_z \) to the product spin operators, whereas the rf operators act only on the product spin operators.

Another closed set consists of the identity \( 1_S I_I \) as its sole member, since this operator is unchanged by \( \mathcal{L} \). So it is a set all by its own. The same is true for the product operator \( S_z I_z \) since it commutes with both rf operators and, because of the commutator type of Eq. (3), it also commutes with the truncated dipolar operator. Finally there are the remaining 8 operators, which can easily be shown to be all dynamically coupled, so there is no further partitioning of the spin space.

Since the 16 operators span the operator space, any operator, and in particular the density operator \( \rho \), can be expressed as a linear combination of these operators [4]. For the CPMAS set of operators, the relevant space consists only of 6 operators plus the identity, the latter being retained in order that the density operator be normalized, namely that the trace over both spins (a total of four Dirac states) is consistent with Tr \( \rho = 1 \). Of these operators, only the identity has a finite trace, so \( \rho \) must have \( (1/4) 1_S I_I \) as one of its terms. Recognizing the expansion coefficients as proportional to the corresponding expectation values, the CPMAS density operator can thus be expressed as

\[ \rho = (1/4) 1_S I_I + S_z \langle S_z \rangle + I_z \langle I_z \rangle + 4S_z I_x \langle S_z I_x \rangle + 4S_y I_y \langle S_z I_y \rangle + 4S_y I_x \langle S_y I_x \rangle + 4S_y I_y \langle S_y I_y \rangle. \] (11)

Thus the study of the evolution of the density operator is equivalent to the study of the evolution of the expectation values of these observables.

It is appropriate to subdivide this set of operators further, namely into the set of 1-spin operators \( S_z \) and \( I_z \), plus the identity to preserve normalization, and the remaining set of 2-spin operators. Appropriate for this subdivision, a projection superoperator \( \mathcal{P} \) is defined that selects out the 1-spin part of the operator space, thus

\[ \mathcal{P} = (1/4) 1_S 1_I \mathrm{Tr} + S_z \mathrm{Tr} S_z + I_z \mathrm{Tr} I_z, \] (12)

where the trace is to be taken over both spin spaces. Necessarily, this superoperator is idempotent \( \mathcal{P}^2 = \mathcal{P} \), which determines the numerical factors. \( 1 - \mathcal{P} \) is written for the projector onto the remaining (2-spin) operators. Because of the commutation relations, it is noticed that

\[ \mathcal{P} \mathcal{L} \mathcal{P} = 0, \]
\[ (1 - \mathcal{P}) \mathcal{L}(1 - \mathcal{P}) = \mathcal{L}_{rf} = \omega_1 S + \omega_1 I, \]
\[ \mathcal{P} \mathcal{L}(1 - \mathcal{P}) = \mathcal{P} \mathcal{L}_I, \]
\[ (1 - \mathcal{P}) \mathcal{L} \mathcal{P} = \mathcal{L}_d \mathcal{P} \] (13)

separates the action of \( \mathcal{L} \) within the \( \mathcal{P} \) and \( 1 - \mathcal{P} \) spaces to be entirely due to the rf fields (vanishing for the \( \mathcal{P} \) space), while the coupling between these two subspaces is due solely to the dipolar hamiltonian. The retention of one projector in each of the subspace coupling cases serves to select which space is to be acted upon and which is to be mapped into. Again it is emphasized that any time dependence of the dipolar coupling strength has no effect on this separation of the different parts of \( \mathcal{L} \).

### IV. THE SPIN OPERATOR DYNAMICS FOR CROSS POLARIZATION

After a 90° pulse to align the \( I \)-spin along the \( \hat{z} \) axis (doubly rotating tilted frame), the time evolution of the expectation value \( \langle S_z \rangle \) of the \( S \)-spin is monitored experimentally. Thus the calculation is to use the value of \( \langle I_x \rangle(0) \) as the only nonzero spin expectation value as the initial condition and to calculate the consequent time dependence of \( \langle S_z \rangle(t) \). Since it is the expectation values of \( S_z \) and \( I_z \) that are of importance, it is the partition consisting of these two operators that is relevant for the analysis of these experiments. The projection superoperator \( \mathcal{P} \) defined above carries out this selection.

The density operator \( \rho \) for the spin system satisfies the quantum Liouville equation (von Neumann equation)

\[ i \frac{\partial \rho}{\partial t} = \mathcal{L} \rho = [H, \rho]_. \] (14)

Again \( \hbar \) is set to 1. The expectation value for any observable \( A \) is calculated as the trace \( \langle A \rangle = \mathrm{Tr} A \rho \) whose time dependence can be calculated according to

\[ \frac{\partial \langle A \rangle}{\partial t} = \mathrm{Tr} A \frac{\partial \rho}{\partial t} = -i \mathrm{Tr} A \mathcal{L} \rho = i \mathrm{Tr} (\mathcal{L} A) \rho, \] (15)
in the Schrödinger picture (first form) or Heisenberg picture (last form). From the commutation relations, it is a set of 6 coupled equations that must be solved in order to predict the time evolution of $\langle S_z(t) \rangle$. Since only the $S_z$ and $I_z$ part of the operator space reflects the experimentally observed quantities, a separation of the dynamics to emphasize these can be useful. The generalized master equation approach does this in a natural way. This method is summarized in the following subsection.

**A. Derivation of the generalized master equation**

The derivation of the generalized master equation is reviewed in its generality since there is no immediate simplification of the derivation by specializing the superoperators to the present case. Note, which is predictable by the time dependence of $L(t)$ is allowed for here, which is standardly not considered.

Define the relevant part of the density operator as $\rho_1 \equiv \mathcal{P}\rho$ and the irrelevant part as the remainder $\rho_2 \equiv (1-\mathcal{P})\rho$. Then these parts evolve according to

$$
\frac{d\rho_1(t)}{dt} = \mathcal{P}L(t)\rho(t) = \mathcal{P}L\mathcal{P}\rho_1(t) + \mathcal{P}L(t)(1-\mathcal{P})\rho_2(t),
$$
$$
\frac{d\rho_2(t)}{dt} = (1-\mathcal{P})L(t)\rho(t) = (1-\mathcal{P})L(1-\mathcal{P})\rho_2(t) + (1-\mathcal{P})L(t)\mathcal{P}\rho_1(t).
$$

Here the possible time dependence of the coupling superoperators $\mathcal{P}L(t)(1-\mathcal{P})$ and $(1-\mathcal{P})L(t)\mathcal{P}$ are explicitly displayed. Solve formally for $\rho_2(t)$,

$$
\rho_2(t) = e^{-(1-\mathcal{P})L(t)}\rho_2(0) - i \int_0^t e^{-(1-\mathcal{P})L(t-t')}L(t')\mathcal{P}\rho_1(t')dt'.
$$

Note that it is assumed that there is no time dependence of $(1-\mathcal{P})L(1-\mathcal{P})$, so the exponential evolution superoperator is correct as written. This is the case for the present problem. Substitute this equation for $\rho_2(t)$ back into the differential equation for $\rho_1(t)$,

$$
\frac{d\rho_1}{dt} = \mathcal{P}L\rho = \mathcal{P}L\mathcal{P}\rho_1 + \mathcal{P}L(1-\mathcal{P})e^{-(1-\mathcal{P})L(1-\mathcal{P})t}\rho_2(0)
$$
$$
- i \int_0^t \mathcal{P}L(t-t')e^{-(1-\mathcal{P})L(1-\mathcal{P})(t-t')}\times (1-\mathcal{P})L(t')\mathcal{P}\rho_1(t')dt'.
$$

This is the generalized master equation of Zwanzig, with an additional time dependence of the coupling superoperators. It describes the exact evolution of the relevant observables while taking into account the role of the irrelevant observables in this evolution by means of an integral over the time history (memory) of the relevant observables.

**B. Application of the generalized master equation**

For a cross polarization experiment involving spin-1/2 particles, the special properties, of the Liouville superoperator allows all projection superoperators to be dropped in the generalized master equation for $\rho_1(t)$. Moreover, the initial condition on the density operator

$$
\rho(0) = \rho_1(0) = (1/4)1_s1_I + I_z\langle I_z(0) \rangle
$$

lies entirely in the relevant space, so the generalized master equation reduces to

$$
\frac{d\rho_1(t)}{dt} = - \int_0^t L_d(t)e^{-iL_d(t-t')L_d(t')}\rho_1(t')dt'.
$$

This is exact for this system!

On taking the trace of this equation with $S_z$ and using the expansion

$$
\rho_1(t) = \mathcal{P}\rho(t) = (1/4)1_s1_I + S_z\langle S_z(t) \rangle + I_z\langle I_z(t) \rangle
$$

for $\rho_1(t)$, the equation of change for the expectation value $\langle S_z(t) \rangle$ is calculated to be

$$
\frac{d\langle S_z(t) \rangle}{dt} = - \int_0^t b(t)[K_{SS}(t-t')\langle S_z(t') \rangle + K_{SL}(t-t')\langle I_z(t') \rangle]dt'.
$$

Here the (possibly time dependent) dipolar coupling strengths are written out explicitly and it should be noted how they depend on different times. The memory kernel $K_{SS}(s)$ is defined as

$$
K_{SS}(s) = 4\text{Tr}[S_zS_zI_z]_e^{-i(\omega_1S_z+\omega_1I_z)s}S_zI_zS_z - 4\text{Tr}[S_yS_yI_z]e^{-i(\omega_1S_z+\omega_1I_z)s}(-i)S_yI_z
$$

$$
= 4\text{Tr}[S_yI_z[S_y\cos(\omega_1S_z)-S_x\sin(\omega_1S_z)]
$$

$$
\times [I_z\cos(\omega_1I_z)+I_y\sin(\omega_1I_z)]
$$

$$
= \cos(\omega_1S_z)\cos(\omega_1I_z)
$$

$$
\frac{1}{2}[\cos((\omega_1S_z+\omega_1I_z)s) + \cos((\omega_1S_z-\omega_1I_z)s)].
$$

In the first term the commutator $[S_z,S_zI_z]_c$ arises by using the invariance of the trace to interchange the order of commutation arising from $\text{Tr}S_zL_d\cdots$. The memory kernel $K_{SI}(s)$ is calculated in a similar manner to give

$$
K_{SI}(s) = (1/2)[\cos((\omega_1S_z+\omega_1I_z)s) - \cos((\omega_1S_z-\omega_1I_z)s)].
$$

The corresponding equation for $\langle I_z(t) \rangle$ is obtained by interchanging $S$ and $I$ labels on the various terms. Specifically this gives

$$
\frac{d\langle I_z(t) \rangle}{dt} = - \int_0^t b(t)[K_{IS}(t-t')\langle S_z(t') \rangle + K_{III}(t-t')\langle I_z(t') \rangle]dt'.
$$
The memory kernels
\[ K_{11}(s) = \frac{1}{2} [\cos(\omega_{1S} + \omega_{1r})s + \cos(\omega_{1S} - \omega_{1r})s], \]
\[ K_{1S}(s) = \frac{1}{2} [\cos(\omega_{1S} + \omega_{1r})s - \cos(\omega_{1S} - \omega_{1r})s], \]
are of the same form as the previous pair. As a consequence, the equations for \( \langle S_z \rangle \) and \( \langle I_z \rangle \) can be simplified when rewritten in terms of the sum and difference expectation values, namely
\[
\frac{\partial \langle S_z - I_z \rangle(t)}{\partial t} = - \int_0^t b(t)b(t') \cos(\Delta(t - t')) \langle S_z - I_z \rangle(t') dt',
\]
and
\[
\frac{\partial \langle S_z + I_z \rangle(t)}{\partial t} = - \int_0^t b(t)b(t') \cos(\Sigma(t - t')) \langle S_z + I_z \rangle(t') dt',
\]
(27)
(28)
involving the difference \( \Delta = \omega_{1S} - \omega_{1r} \) and sum \( \Sigma = \omega_{1S} + \omega_{1r} \) frequencies.

It is thus shown that the calculation of the cross polarization separates into two independent parts. This completes the part of the calculation which involves the spin operators, the remaining part of the calculation requires solving the two integrodifferential equations. In order to carry this out, it is necessary to specify the detailed time dependence of the dipolar coupling strength \( b(t) \). The static \([b(t) \text{ time independent}] \) and magic angle spinning cases are discussed in turn.

V. STATIC CROSS POLARIZATION

In the static case, the dipolar coupling strength \( b \) is time independent, but still depends on the angle \( \theta \) of the vector \( r \) separating the \( S \) and \( I \) spin particles and the direction \( \hat{z} \) of the static magnetic field. In a powder sample there is a random arrangement of this direction so an ensemble average of \( \langle S_z \rangle(t) \) over \( \theta \) needs to be taken. But this is to be done after \( \langle S_z \rangle \) has been calculated for each fixed direction.

A. Fixed orientation of the dipolar coupling strength

The expectation of the difference of the spins \( D(t) \equiv \langle S_z - I_z \rangle(t) \) is considered first. According to Eq. (27), this satisfies the integrodifferential equation
\[
\frac{\partial D(t)}{\partial t} = -b^2 \int_0^t \cos(\Delta(t - t')) D(t') dt'.
\]
(29)
Differentiating this equation gives
\[
\frac{\partial^2 D(t)}{\partial t^2} = -b^2 D(t) + b^2 \Delta \int_0^t \sin(\Delta(t - t')) D(t') dt',
\]
(30)
and differentiating again
\[
\frac{\partial^3 D(t)}{\partial t^3} = -b^2 \frac{\partial D(t)}{\partial t} + b^2 \Delta^2 \int_0^t \cos(\Delta(t - t')) D(t') dt' = -(b^2 + \Delta^2) \frac{\partial D(t)}{\partial t}.
\]
(31)
As a consequence, the time derivative of \( D(t) \) must satisfy
\[
\frac{\partial D(t)}{\partial t} = A \cos(ft) + B \sin(ft)
\]
(32)
where
\[
f = \sqrt{b^2 + \Delta^2}
\]
(33)
is the natural oscillation frequency for \( D(t) \). From the fact that \( \partial D(t)/\partial t \) vanishes at \( t = 0 \), as follows from Eq. (29), the coefficient \( A \) vanishes. At \( t = 0 \) the second derivative of \( D(t) \) equals \(-b^2 D(0) \), so \( B \) is given by \(-b^2 D(0)/f \). Consequently the derivative of \( D(t) \) is given by
\[
\frac{\partial D(t)}{\partial t} = -\frac{b^2}{f} D(0) \sin(ft).
\]
(34)
Integrating this result and choosing the integration constant so as to satisfy the initial condition, \( D(t) \) is determined to be
\[
D(t) = \frac{\Delta^2 + b^2 \cos(ft)}{b^2 + \Delta^2} D(0)
\]
(35)
Expressed in terms of the spin expectation values, note that \( D(0) = \langle I_z \rangle(0) \), this is
\[
\langle S_z - I_z \rangle(t) = \left[ \frac{b^2(1 - \cos(ft))}{b^2 + \Delta^2} - 1 \right] \langle I_z \rangle(0).
\]
(36)
An analogous calculation of the sum of the spin expectation values implies
\[
\langle S_z + I_z \rangle(t) = \left[ 1 - \frac{b^2(1 - \cos(Ft))}{b^2 + \Sigma^2} \right] \langle I_z \rangle(0),
\]
(37)
where the frequency \( F = \sqrt{b^2 + \Sigma^2} \) is natural for the sum of the spin expectation values. Finally, the sum of these results determines the time dependence of the \( S_z \) expectation value, experimentally referred to as the “buildup curve”, namely
\[
\langle S_z \rangle(t) = \frac{1}{2} b^2 \left[ \frac{1 - \cos(ft)}{b^2 + \Delta^2} - 1 - \cos(Ft) \right] \langle I_z \rangle(0).
\]
(38)
Thus it is seen that, for a constant \( b \) (specific orientation of the vector connecting the \( S \) and \( I \) spin particles), the time dependence of \( \langle S_z \rangle(t) \) is governed by a difference between oscillating terms. Actually, since \( \omega_{1S} \) and \( \omega_{1r} \) are both positive (they are the amplitudes of the radio frequency fields), the sum frequency \( \Sigma \) is larger than the magnitude of the difference frequency \( |\omega_{1S} - \omega_{1r}| \). As
a consequence, the amplitude $b^2/(b^2 + \Sigma^2)$ of the sum frequency contribution is smaller than the amplitude of the difference frequency contribution, implying that the rapid oscillations of the sum frequency are likely lost as noise on top of the slower oscillations of the difference frequency.

Equation (38) has been obtained by Levitt and Zhang et al. by using a sequence of rotations using effective spin operators based on a decomposition of the Hamiltonian into two commuting parts.

Experimentally, the matching profile is obtained by scanning the rf amplitude of the S-spin channel and the (relatively) longtime average of $\langle S_z(t) \rangle$ measured. This should be compared with

$$\langle S_z(t) \rangle_{\text{time average}} = \frac{1}{2} \left[ \frac{b^2}{b^2 + b^2} \right] \langle I_z \rangle(0). \quad (39)$$

This time average is dominated by the difference frequency term which, if the dominance is sufficient, implies that the experimental plot of $\langle S_z(t) \rangle_{\text{time average}}$ versus $\omega_{1S}$ is Lorentzian.

### B. Powder average

In a powder all orientations must be averaged over, so the cross polarization time dependence is

$$\langle S_z(t) \rangle_{\text{powder}} = \frac{1}{4} \int_0^\pi b^2(\theta) \left[ \frac{1 - \cos(f(\theta)t)}{b^2(\theta) + \Delta^2} \right] \sin \theta d\theta \langle I_z \rangle(0), \quad (40)$$

with an analogous expression for the time average. Note that since there is no $\phi$ dependence in $b$, the average over $\phi$ is unnecessary while the frequencies $f$ and $F$ are $\theta$ dependent through their dependence on $b(\theta)$. Figure 1 shows the effects of the angle averaging on the time dependence of $\langle S_z(t) \rangle$, two of the rapidly oscillating contributions to this powder average are also shown. Compare the corresponding depolarization curves in Ref. 6. The corresponding matching profile, namely a scan of the time and powder average $\langle S_z(t) \rangle_{\text{time-average, powder}}$ for different $\omega_{1S}$, is given in Fig. 2. A Lorentzian, peaked to have the same height and width at half height, is also plotted. This shows that the powder CP line shape is close to Lorentzian, but not quite.

### VI. CROSS POLARIZATION WITH MAGIC ANGLE SPINNING

The orientation of the vector $\mathbf{r}$ connecting the positions of the two spins is made time dependent by rotation about an axis $\hat{n}$ at a frequency of $\omega_r$. For magic angle spinning, the angle between the rotation axis $\hat{n}$ and the direction $\hat{x}$ of the static magnetic (Zeeman) field is $\arccos(1/\sqrt{3})$. At that angle the dipolar angle dependence is split into four time dependent parts, rather than the five parts for a general splitting of the order 2 spherical harmonics. Explicitly this time dependence is given by

$$b(t) = b_1^e e^{-2i\omega_r t} + b_1^e e^{-i\omega_r t} + b_1^e e^{i\omega_r t} + b_2 e^{2i\omega_r t}, \quad (41)$$

where

$$b_1 = \frac{\sqrt{2}}{3} b_0 \cos \theta_r \sin \theta_r e^{i\phi_r} \quad (42)$$

and

$$b_2 = \frac{1}{6} b_0 \sin^2 \theta_r e^{2i\phi_r} \quad (43)$$

are proportional to the spherical harmonics $Y_{21}(\theta_r, \phi_r)$ and $Y_{22}(\theta_r, \phi_r)$, expressed in terms of the angles $\theta_r, \phi_r$ defining the direction between the particles containing the spins with respect to the axis of rotation $\hat{n}$. A short discussion of how this splitting arises is given in Appendix B.
A. General formulation for magic angle spinning

The dipolar coupling strength \( b(t) \) enters into the integrodifferential equations \((24 \text{--} 25)\) for the cross polarization in the form of the product \( b(t)b(t') \). From the explicit time dependence given by Eq. (11), the product has a total of 16 different terms. Four of these are naturally combined into two simple forms involving the time difference \( t - t' \), while the remainder have a variety of time dependences. In detail, the combination of time dependences is

\[
\begin{align*}
 b(t)b(t') &= 2|b_2|^2 \cos(\omega_r(t - t')) + 2|b_2|^2 \cos(2\omega_r(t - t')) \\
 &\quad + b_2^* e^{2i\omega_r(t + t')} + b_2^* e^{i\omega_r(t + t')} + (b_2^*)^2 e^{-i\omega_r(t + t')} + (b_2^*)^2 e^{-2i\omega_r(t + t')} \\
 &\quad + b_1 b_2 \left[ e^{i\omega_r(2t + t')} + e^{i\omega_r(2t + 2t')} \right] + b_1 b_2^* \left[ e^{-i\omega_r(2t + t')} + e^{-i\omega_r(2t + 2t')} \right] \\
 &\quad + b_1 b_2^* \left[ e^{i\omega_r(-2t + t')} + e^{i\omega_r(-2t + 2t')} \right] + b_1^* b_2 \left[ e^{i\omega_r(2t - t')} + e^{i\omega_r(2t - 2t')} \right].
\end{align*}
\]

(44)

In the following it is assumed that only the terms involving the time difference \( t - t' \) are important, and the remainder act to produce a variety of interference effects. Retaining only these two terms, the frequency difference formula \((27)\) is approximated by

\[
\frac{\partial D(t)}{\partial t} = -2 \int_0^t \left[ |b_2|^2 \cos(\omega_r(t - t')) + |b_2|^2 \cos(2\omega_r(t - t')) \right] \cos(\Delta(t - t')) D(t') dt'
\]

(45)

where \( D(t) \) is again used as an abbreviation for \( \langle S_z - I_z \rangle(t) \). The integral in this equation is naturally divided up into four terms, whose generic definition is

\[
N_n(t) \equiv |b_n|^2 \int_0^t \cos((\Delta + n\omega_r)(t - t')) D(t') dt',
\]

(46)

with the obvious definition \(|b_{-n}|^2 = |b_n|^2\). A solution of Eq. (45) is required. This can be accomplished as in the static CP situation by using successive derivatives of Eq. (45), see Sec. B. But it is necessary to go up to the ninth derivative of \( D(t) \) before a sufficient number of terms are obtained in order to eliminate the \( N_n(t) \) ‘s. This calculation is described in Appendix C while an approximation is made in the following subsection that provides a simple analytical estimation of the cross polarization with magic angle spinning.

B. Independent Sideband Approximation

The idea here is that, near a Hartmann-Hahn matching condition, only one of the \( N_n(t) \) ‘s is of importance, that is, of appreciable magnitude. As a consequence, \( D(t) \) can be considered as a sum of four terms, each of which is determined by a separate equation. With a similar approximation for the \( \Sigma \) based \( G(t) \equiv \langle S_z + I_z \rangle(t) \), the total cross polarization is described as a sum of eight terms.

To implement this idea, \( D(t) \) is written as the sum

\[
D(t) = D_{-2}(t) + D_{-1}(t) + D_1(t) + D_2(t),
\]

(47)

each term of which is to be approximated as the solution of

\[
\frac{\partial D_n(t)}{\partial t} = -|b_n|^2 \int_0^t \cos((\Delta + n\omega_r)(t - t')) D_n(t') dt'.
\]

(48)

A decoupling of Eq. (45) has thus been accomplished. Since the equation for \( D_n(t) \) has the same structure as that of Eq. (23), so its solution is, according to Eq. (33),

\[
D_n(t) = \frac{(\Delta + n\omega_r)^2 + |b_n|^2 \cos(f_n t)}{|b_n|^2 + (\Delta + n\omega_r)^2} D(0),
\]

(49)

with an effective frequency given by

\[
f_n = \sqrt{|b_n|^2 + (\Delta + n\omega_r)^2}.
\]

(50)

On the basis that only one \( D_n(t) \) has a significant contribution when near a matching condition, it has been assumed that \( D_n(0) \) is well estimated by \( D(0) \). Adding in the corresponding approximation for \( \langle S_z + I_z \rangle(t) \) and doing some minor algebra, the complete time dependence of \( \langle S_z \rangle(t) \) is estimated by the sum of eight terms

\[
\langle S_z \rangle = \frac{1}{2} \sum_{n=-2,-1,1,2} |b_n|^2 \left[ \frac{1 - \cos(F_n t)}{|b_n|^2 + (\Delta + n\omega_r)^2} \right] I_z(0).
\]

(51)

Here the frequencies for the sum terms are given by

\[
F_n = \sqrt{|b_n|^2 + (\Sigma + n\omega_r)^2}.
\]

(52)
A powder average of this result is easily calculated since the $|b_n|^2$’s depend only on the single angle $\theta_r$. The time average of Eq. (53) is obtained by merely dropping the cosine terms, to give an estimation of the CPMAS matching profile.

Figures 3 and 4 illustrate the typical matching profiles that can be attained. Figure 3 exemplifies what is standardly observed in an experiment, namely four peaks at the shifted Hartmann-Hahn matching conditions $\omega_{1S} = \omega_{1I} + n\omega_r$ for $n=-2,-1,1$ and 2. These are due to the set of first terms in the sum of Eq. (51) [with the cosine term dropped to reflect the time average], associated with the conditions $\Delta + n\omega_r = 0$. In such a situation the second set of terms is small because $\Sigma + n\omega_r \gg \Delta + n\omega_r$. But if $2\omega_r > \omega_{1I}$ then $\omega_{1I} - 2\omega_r < 0$ and the matching condition $\Delta + 2\omega_r$ requires a negative $\omega_{1S}$. This is not experimentally possible ($\omega_{1S}$ measures the strength of an rf field) so this matching condition cannot be attained and the peak in the matching profile is absent. However, in this case, one of the second set of terms in Eq. (22) can have a small denominator, so a peak in the matching profile arises from that term. This gives a negative $\langle S_z \rangle(t)$ so the peak is negative. Figure 4 illustrates this case. The structure is emphasized by choosing a small $\omega_{1I}$ while a large $\omega_r$ is needed to allow the matching condition $\omega_{1S} = 2\omega_r - \omega_{1I}$ to be attained for positive $\omega_{1S}$. Meier has a figure of experimental data illustrating this kind of behavior, but for the 3-spin system CH$_2$. An even more interesting profile, which does not seem to have yet been observed experimentally, is when $\omega_{1I}$ is even smaller, so that two matching conditions are from the second term, namely $\Sigma - 2\omega_r = 0$ and $\Sigma - \omega_r = 0$, while the other two matching conditions are $\Delta - \omega_r = 0$ and $\Delta - 2\omega_r$. The result is a matching profile with two negative and two positive peaks. This is illustrated by the second profile shown in Fig. 4. It is clear that there can be at most only two negative peaks in a

FIG. 3: The CPMAS matching profile for a powder sample with $\omega_r = 10$ kHz and $\omega_{1I} = 60$ kHz. The solid line is for a dipolar coupling constant $b_0$ of 10 kHz and the dashed curve for a dipolar coupling constant of 1 kHz.

FIG. 4: The CPMAS matching profiles for a powder sample with a dipolar coupling constant $b_0$ of 10 kHz. The solid line is for $\omega_{1I} = 12$ kHz and $\omega_r = 10$ kHz while the dashed line is for $\omega_{1I} = 8$ kHz and $\omega_r = 11.34$ kHz.

VII. DISCUSSION

The special properties of spin-1/2 systems and the special nature of the hamiltonian, Eq. (1), have been used to give a formally exact method of calculating the cross polarization buildup curves and matching profiles for an isolated pair of spins. For the static case (no sample spinning), this can be expressed in closed form, Eq. (38), if the interspin direction is fixed, while a powder average can be easily calculated numerically, Eq. (41). These results have also been obtained by Levitt and Zhang et al. using a sequence of rotations based on a particular division of the hamiltonian into commuting parts. It is of note that the time dependence of the cross polarization is purely oscillatory if a single orientation of the dipolar coupling strength is involved. It is the sensitive dependence of the frequency of this oscillation on the orientation, which causes an enormous destructive interference in a powder sample. The decay-like nature of the envelope of the oscillations in a powder sample, see Fig. 1, arises from this destructive interference rather than from any spin relaxation (or spin diffusion), which of course is not included in the hamiltonian dynamics of an isolated system.

Magic angle spinning is formally easy to include, it is just a case of recognizing the correct time dependence of the dipolar coupling strengths in the integrodifferential equations (27) and (28). But how to obtain a general solution of these equations is not clear. Two simplifying approximations have been made. First, only those terms in the product of the dipolar coupling strengths, Eq. (14), are kept that depend on the time difference. It is assumed that the other time dependences lead to minor interference effects but that has not been explored. A method of solving the equations with the above single approximation is given in Appendix C, and been explored with
some calculations. The results found, which are not presented here, indicate that the solutions are qualitatively in agreement with those using the further approximation of Sec. 11. This second approximation assumes that only one term in Eq. (A11) is of importance in a range of $\omega_{1S}$ values. An analytic expression, Eq. (A13), for the cross polarization is then obtained for fixed interspin orientation, and it is in a form in which a powder average can easily be carried out numerically. Its form is very simple and it is immediately seen how the cross polarization is significant when the standard matching conditions $\Delta + n\omega_r = 0$ are met. It is also seen that there is another set of matching conditions, $\Sigma + n\omega_r = 0$ which can lead to an enhancement of the cross polarization, but now with $\langle S_z \rangle$ and $\langle I_z \rangle(0)$ having opposite signs. There can be at most two negative peaks in the matching profile, but there are always four physically possible matching conditions for a given $\omega_{1I}$ and $\omega_r$.

The method presented here, with the approximations, has the advantage that the qualitative behavior of experimental buildup curves and matching profiles can be given simple explanations. The quantitative connection between the dipolar coupling strength and the size and width of the matching profiles, and the oscillatory nature of the buildup curves is formally available. How well that can be done experimentally can also depend on the real physical system. The spin pair is never truly isolated, so small interactions can cause some more interference effects, and the surroundings afford relaxation. Such effects can surely influence the shape of the buildup curves, contributing to a more rapid closure of the envelope of the oscillations as time progresses. It would also affect the height of the matching profile peaks, but hopefully not perturb too much the position of the peaks.

It is interesting that the thermodynamic method can give the same formulas for the $\Delta$-based peaks in the matching profile as the independent sideband approximation, provided an $\omega_r$-dependent transformation is used to get a time independent rotating frame hamiltonian. However, this must be done one peak at a time whereas the present method gives all four peaks predicted by the same formalism and there is no question about any further frame transformation.

Of the previously introduced methods that we are aware of [1], interpreting cross polarization, the one used by Levin[2] and Zhang et al[3] seems the closest to being fundamentally based. But it does not seem to have been extended to include the magic angle spinning case. It is also not clear to us how that might be incorporated into their formalism. We see the formula introduced by Müller[2], and extensively used for fitting experimental buildup curves, as a very useful fitting tool. But since it inherently has exponential decays built into it, care should be taken when interpreting the parameters found in terms of physical quantities, since no relaxation is fundamental to the explanation of the buildup curves. We hasten to add that, as we indicated above, in a real system the spins are not truly isolated so relaxation effects are present and these can influence the detailed shapes of the experimental curves, but not their fundamental behavior.

Acknowledgments

This work was supported in part by the Natural Sciences and Engineering Research Council of Canada. The authors thank Professor C. A. Fyfe and Dr. A. Lewis for pointing out a number of references and for their support in trying to put this work into perspective. One of the authors (F. M., on leave from the University of Bucharest, Romania) would like to thank the Natural Sciences and Engineering Research Council of Canada for the award of a NATO Science Postdoctoral Fellowship held during the course of this work.

APPENDIX A: EIGENVALUES AND EIGENVECTORS OF $H$

This lists the eigenvectors and eigenvalues of the hamiltonian defined in Eq. (A1) for time independent $b$ and for fixed orientation. The basis $|mn\rangle$, $m, n = \pm 1/2$ used for this calculation is that of the simultaneous eigenvectors of $S_z$ and $I_z$, namely

$$S_z|mn\rangle = m|mn\rangle; \quad I_z|mn\rangle = n|mn\rangle. \quad (A1)$$

As a notation similar to Zhang’s[3], the quantities

$$\omega^\Sigma \equiv \sqrt{b^2 + \Sigma^2}; \quad \omega^\Delta \equiv \sqrt{b^2 + \Delta^2} \quad (A2)$$

are introduced. Then the eigenvectors, labelled with their respective energy eigenvalues are:

$$|\psi(1/2)\rangle_{\omega^\Delta} = \frac{b[1/2, -1/2] + (\omega^\Delta - \Delta)|1/2, 1/2\rangle}{\sqrt{b^2 + (\omega^\Delta - \Delta)^2}}$$

$$|\psi_{-1/2}\rangle_{\omega^\Delta} = \frac{b[-1/2, 1/2] - (\omega^\Delta - \Delta)|1/2, -1/2\rangle}{\sqrt{b^2 + (\omega^\Delta - \Delta)^2}}$$

$$|\psi(1/2)\rangle_{\omega^\Sigma} = \frac{b[1/2, 1/2] + (\omega^\Sigma - \Sigma)|1/2, -1/2\rangle}{\sqrt{b^2 + (\omega^\Sigma - \Sigma)^2}}$$

$$|\psi_{-1/2}\rangle_{\omega^\Sigma} = \frac{b[-1/2, -1/2] - (\omega^\Sigma - \Sigma)|1/2, 1/2\rangle}{\sqrt{b^2 + (\omega^\Sigma - \Sigma)^2}}$$

It is be noted that these are NOT the same as the eigenvalues and eigenvectors of Zhang’s $H^\Delta$ and/or $H^\Sigma$, arising from his decomposition of the hamiltonian of Eq. (A1), even taking into account the difference in the labelling of the coordinate axes.

The limits of these eigenvectors when $b \to 0$ and $\Delta \to 0$ or $\Sigma \to 0$ give respectively the eigenvectors of the rf hamiltonian and of the truncated dipolar hamiltonian. In particular, as $b \to 0$ with $\Delta > 0$, the expansion of $\omega^\Delta$ is

$$\omega^\Delta = \Delta \sqrt{1 + \frac{b^2}{\Delta^2}} \Delta + \frac{b^2}{2\Delta} + \cdots, \quad (A3)$$
while \( \omega^\Delta \to b \) as \( \Delta \to 0 \). As a consequence, the first listed eigenvector has the limits

\[
|\psi_{1/2\omega^\Delta}\rangle \to \begin{cases} 
|1/2, -1/2\rangle & \text{as } b \to 0 \text{ for } \Delta > 0 \\
| -1/2, 1/2\rangle & \text{as } b \to 0 \text{ for } \Delta < 0 \\
(1/\sqrt{2})[|1/2, -1/2\rangle + | -1/2, 1/2\rangle] & \text{as } \Delta \to 0.
\end{cases}
\]

The limits of the other eigenvectors are obtained in an analogous manner.

**APPENDIX B: MAGIC ANGLE SPINNING**

A vector based derivation is given for the effect of spinning the orientation dependent dipolar coupling strength. The rotation of any unit vector \( \hat{r} \) about an axis \( \hat{n} \) by an angle \( \chi \) produces the rotated vector

\[
\hat{r}' = \hat{n}\hat{n}\cdot\hat{r} + (\hat{r} - \hat{n}\hat{n}\cdot\hat{r}) \cos \chi + \hat{n}\times\hat{r} \sin \chi.
\]

The rotation of any unit vector \( \hat{n} \) along the Zeeman field direction \( \hat{x} \) is then

\[
\cos \theta = \hat{x}\cdot\hat{r}' = \hat{x}\cdot\hat{n}\hat{n}\cdot\hat{r} + (\hat{x}\cdot\hat{r} - \hat{x}\cdot\hat{n}\hat{n}\cdot\hat{r}) \cos \chi + \hat{x}\times\hat{n}\hat{n}\cdot\hat{r} \sin \chi.
\]

If the unit vector \( \hat{r} \) is expressed in a right handed coordinate frame based on the rotation axis \( \hat{n} \) and the \( \hat{x} - \hat{n} \) plane,

\[
\hat{r} = \hat{n}\cos \theta_r + \frac{\hat{x} - \hat{n}\hat{n}\cdot\hat{x}}{\sqrt{1 - (\hat{n}\hat{n}\cdot\hat{x})^2}} \sin \theta_r \cos \phi_r + \frac{\hat{n}\times\hat{x}}{\sqrt{1 - (\hat{n}\hat{n}\cdot\hat{x})^2}} \sin \theta_r \sin \phi_r,
\]

then

\[
\cos \theta = \hat{x}\cdot\hat{n}\cos \theta_r + \sqrt{1 - (\hat{n}\hat{n}\cdot\hat{x})^2} \sin \theta_r \cos(\phi_r + \chi).
\]

The angle dependence of the rotated dipolar coupling strength is then expressed by

\[
\begin{align*}
\cos^2 \theta - 1/3 &= (\hat{n}\hat{n}\cdot\hat{x})^2 \cos^2 \theta_r - 1/3 + [1 - (\hat{n}\hat{n}\cdot\hat{x})^2] \sin^2 \theta_r \cos^2(\phi_r + \chi) \\
&+ 2\hat{n}\hat{n}\cdot\hat{x}\sqrt{1 - (\hat{n}\hat{n}\cdot\hat{x})^2} \cos \theta_r \sin \theta_r \cos(\phi_r + \chi).
\end{align*}
\]

The trigonometric identity

\[
\cos^2(\phi_r + \chi) = \frac{1}{2} \cos 2(\phi_r + \chi) + 1
\]

simplifies this expression. Finally, if \( \hat{n}\hat{n}\cdot\hat{x} \) is chosen as \( 1/\sqrt{3} \) and the angle \( \chi \) is set equal to the \( \omega_r t \), the time dependence of the dipolar coupling strength is

\[
b_0 \left( \cos^2 \theta - \frac{1}{3} \right) = \frac{1}{3} \sin^2 \theta_r \cos[2(\phi_r + \omega_r t)] + \frac{2\sqrt{2}}{3} \cos \theta_r \sin \theta_r \cos(\phi_r + \omega_r t)
\]

\[
= b_2 e^{-2i\omega_r t} + b_1 e^{-i\omega_r t} + b_1 e^{i\omega_r t} + b_2 e^{2i\omega_r t},
\]

where \( b_1 \) and \( b_2 \) are given explicitly in Eqs. (12) and (13).

It is noted that the sum of the squares of the magnitudes of these parts of the coupling strengths, when averaged over all angles, preserves the total square of the coupling strength, namely

\[
\int \int b_0^2(\cos^2 \theta - \frac{1}{3})^2 \sin \theta d\theta d\phi = \int \int 2|b_1|^2 + 2|b_2|^2 \sin \theta \sin(t, d\theta, d\phi,
\]

\[
= \frac{8\pi}{45} b_0^2 = \frac{16\pi}{135} b_0^2 + \frac{8\pi}{135} b_0^2.
\]

Thus the contributions of the \( b_1 \) terms are twice those of the \( b_2 \) terms.

**APPENDIX C: COMPLETE SIDEBAND CALCULATION**

This appendix gives a method for carrying out the exact calculation of \( D(t) \) from Eq. (15). For this purpose,

the second derivative of \( N_n(t) \) is

\[
\frac{\partial^2 N_n(t)}{\partial t^2} = |b_n|^2 \frac{\partial D(t)}{\partial t} - (\Delta + n\omega_n)^2 N_n(t).
\]
Then the third derivative of \( D(t) \) can be expressed in terms of the first derivative and the \( N_n(t) \)’s, that is
\[
\frac{\partial^3 D(t)}{\partial t^3} = -\sum_n |b_n|^2 \frac{\partial D(t)}{\partial t} + \sum_n (\Delta + n\omega_n)^2 N_n(t). \tag{C2}
\]

Continuing in this way, the higher odd-ordered derivatives of \( D(t) \) can be calculated in terms of lower ordered derivatives and the \( N_n(t) \)’s. The first 4 equations obtained in this way (up to the \( 9 \)th order derivative) can be used to solve for the \( N_n(t) \)’s in terms of the derivatives of \( D(t) \). Substituting these into the equation for the \( 9 \)th order derivative produces a differential equation for \( D(t) \) of \( 9 \)th order, but with constant coefficients. Such an equation has 9 solutions of the form \( D(t) = e^{\lambda t} \), whose proper combination gives the time dependence of \( D(t) \).

To simplify this calculation, it is convenient to introduce the notation \( D^{(m)}(t) \) for the \( m \)th derivative of \( D(t) \), and the sums
\[
SS_m \equiv \sum_n (\Delta + n\omega) m |b_n|^2. \tag{C3}
\]

Then the needed equations for the higher odd-ordered derivatives of \( D(t) \) are
\[
D^{(5)}(t) = -SS_5 D^{(3)} - SS_2 D^{(1)} - \sum_n (\Delta + n\omega)^4 N_n(t)
\]
\[
D^{(7)}(t) = -SS_7 D^{(5)} + SS_2 D^{(3)} - SS_4 D^{(1)} + \sum_n (\Delta + n\omega)^6 N_n(t)
\]
\[
D^{(9)}(t) = -SS_9 D^{(7)} + SS_2 D^{(5)} - SS_4 D^{(3)} + SS_6 D^{(1)} - \sum_n (\Delta + n\omega)^8 N_n(t). \tag{C4}
\]

A formal inversion of the matrix of frequency powers multiplying the \( N_n(t) \)’s from the 4 odd-ordered derivatives \( D^{(1)}(t) \) to \( D^{(7)}(t) \) allows the \( N_n(t) \)’s to be expressed in terms of the \( D^{(m)}(t) \)’s. Substitution into the \( D^{(9)}(t) \) equation gives the desired differential equation for \( D(t) \). This involves only odd-ordered derivatives of \( D(t) \). If \( e^{\lambda t} \) is substituted in for \( D(t) \), this gives a fourth order polynomial in \( \lambda \) times a factor of \( \lambda \). The polynomial has 4 roots which must be negative since the spin dynamics is governed by the quantum Liouville equation (and thus the spin system must oscillate without any relaxation), and there is also the zero root from the multiplicative factor of \( \lambda \). The 4 eigenfrequencies \( \Omega_m \) (square roots of minus the polynomial roots) and the zero frequency determine the time dependence of \( D(t) \). A further simplification arises from noticing that \( N_n(0) = 0 \), which implies that all odd derivatives of \( D(t) \) vanish at \( t = 0 \). Thus \( D(t) \) must be an even function of \( t \) and can be expressed as the sum
\[
D(t) = A_0 + \sum_{m=1}^{4} A_m \cos(\Omega_m t). \tag{C5}
\]

The expansion coefficients \( A_m \) \( (m = 0 \cdots 4) \) still need to be determined.

The coefficients \( A_m \) are determined from the even-ordered derivatives \( D^{(2m)}(t) \) evaluated at \( t = 0 \). These can be found directly by differentiating Eqs. \( \text{(13)} \), \( \text{(2)} \) and \( \text{(4)} \), and evaluating them at \( t = 0 \). Specifically, the 5 required relations are
\[
A_0 + \sum_m A_m = D(0)
\]
\[
-\sum_m \Omega^2_m A_m = D^{(2)}(0) = -SS_0 D(0)
\]
\[
\sum_m \Omega^4_m A_m = D^{(4)}(0) = (SS_0^2 + SS_2) D(0)
\]
\[
-\sum_m \Omega^6_m A_m = D^{(6)}(0) = -[SS_0(2SS_0^2 + 2SS_2) + SS_4] D(0)
\]
\[
\sum_m \Omega^8_m A_m = D^{(8)}(0) = [SS_0(2SS_0^2 + 3SS_2) + 2SS_0SS_4 + SS_2^2 + SS_0] D(0). \tag{C6}
\]

These equations are to be solved for the expansion coefficients.

This determines the difference \( \langle S_z - I_z \rangle(t) = D(t) \) of the expectation values of the two spin operators. A calculation of the sum \( \langle S_z + I_z \rangle(t) = G(t) \) involves the same treatment, but with the sum frequency \( \Sigma \) replacing the difference frequency \( \Delta \) in all the above formulas. The cross polarization is given by one half the sum of these two quantities
\[
\langle S_z \rangle(t) = \frac{1}{2} |D(t) + G(t)|. \tag{C7}
\]

Note that \( G(0) = -D(0) = \langle I_z \rangle(0) \). To calculate the powder average CPMAS, the above computations need to be carried out for every possible orientation of the vector pointing from one spin to the other. A bonus of the approximation of retaining only the terms |\( b_1 |^2 \) and |\( b_2 |^2 \) in the product of the time dependent coupling strengths, Eq. \( \text{(14)} \), is that these quantities are independent of the angle \( \phi \) in the description of this orientation, so only the \( \theta_r \) average needs to be done. Thus the powder CPMAS is given by
\[
\langle S_z \rangle_{\text{powder}}(t) = \frac{1}{4} \int_{-1}^{1} [D(t) + G(t)] d \cos \theta_r. \tag{C8}
\]

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