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Effective Hamiltonians in Floquet theory of magic angle spinning using van Vleck transformation

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In this article, we propose to use van Vleck's contact transformation method for the study of time-dependent interactions in solid state nuclear magnetic resonance (NMR) by Floquet theory [A. Schmidt and S. Vega, *J. Chem. Phys.* **96**, 2655 (1992)]. Floquet theory has been used for studying the spin dynamics of magic angle spinning (MAS) NMR experiments. The contact transformation method is an operator method in time-independent perturbation theory and has been used to obtain effective Hamiltonians in molecular spectroscopy. Here the above method is combined with Floquet theory to study the dynamics of a dipolar coupled spin ($I=1/2$) system. In order to determine the frequencies and intensities of bands in MAS spectra, we need to diagonalize the Floquet-Hamiltonian matrix. This is generally done numerically, by truncating the infinite dimensional Floquet-Hamiltonian matrix. Here we propose an effective Floquet-Hamiltonian for the system. We demonstrate the application of the above method to a homonuclear dipolar coupled spin system ($I=1/2$). The eigenvalues obtained from the above are compared with those obtained using numerical diagonalization. The eigenvalues of the effective Hamiltonian compare quite well with those computed using numerical diagonalization of Floquet matrices. © 2001 American Institute of Physics. [DOI: 10.1063/1.1354147]

I. INTRODUCTION

In nuclear magnetic resonance (NMR) spectroscopy, spectra obtained from solids are broader and much more complex compared to that of liquids. In liquids, rapid isotropic motions of the nuclei average out the anisotropic interactions effectively to zero, whereas in the case of solids these interactions are not averaged out.^{1,2} The technique of magic angle spinning (MAS)^{3,4} is used to reduce or effectively remove these anisotropic interactions. In this technique the sample is rotated about an axis inclined at an angle $\beta = 54.7^\circ$ with respect to the external magnetic field. The internal Hamiltonians which are time independent, do become time dependent under sample spinning. The theoretical treatment of time dependent Hamiltonians is given either by the use of average Hamiltonian theory⁵⁻⁷ or by the use of Floquet theory.⁸⁻²² If Hamiltonians at different times commute with each other (e.g., the chemical shift anisotropy and the dipolar interaction of an isolated heteronuclear pair), the problem becomes simplified. The situation becomes complicated when Hamiltonians at different times do not commute (e.g., multispin homonuclear dipolar Hamiltonian). To explain such complicated systems several formal theoretical treatments have been proposed by various research groups. We follow the Floquet formalism here. Theoretical analyses of homonuclear dipolar coupled MAS systems have been

given earlier.^{17,23,24} The time-dependent Hamiltonian is transformed in these analyses, to a time-independent Hamiltonian known as Floquet-Hamiltonian and expressed in a matrix form using an infinite dimensional basis set. The basis set is a direct product of the spin basis (which is finite) and a Fourier index (which can take infinite values in principle). In the transformed basis, the Hamiltonian matrix does not contain any time-dependent coefficients however, and as a result, the evolution of the system in time can be studied by simpler algebraic/numerical methods. Such transformations are possible only for periodically time-dependent Hamiltonians.

Vega and his co-workers have made seminal contributions in the application of Floquet theory to study the dynamics of various MAS experiments.⁹⁻¹⁹ There are a number of excellent review articles¹⁴⁻¹⁶ which describe the use of Floquet theory in solid state NMR. In this article, we follow the methodology and notation due to Schmidt and Vega.¹⁷ We study the homonuclear dipolar coupled spin system by applying contact transformation to the Floquet-Hamiltonian.

To follow the evolution of the coupled spin system we need to diagonalize the Floquet-Hamiltonian matrix. Instead of diagonalizing the Floquet-Hamiltonian numerically, we employ the method of contact transformation well known in molecular spectroscopy²⁵ where it has been used extensively to obtain effective rotational Hamiltonians for vibrational states from the rovibrational (Watson) Hamiltonian.²⁵⁻²⁸ The role of contact transformations in establishing the equiva-

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lence between the average Hamiltonian theory approach and the Floquet theory approach for solid state NMR has been discussed by other researchers.^{29–33} The advantage of van Vleck transformation is that it provides *effective Floquet–Hamiltonians* which incorporate various orders of perturbation corrections explicitly as operators. We illustrate this by applying the method to a homonuclear dipolar coupled two-spin ($I=1/2$) system.

A brief introduction to the method of contact transformation is given in Sec. II. The application of Floquet theory to a pair of homonuclear dipolar coupled spin system is given in Sec. III. In Sec. IV we use the contact transformation method to diagonalize the Floquet–Hamiltonian for a homonuclear dipolar coupled spin system described in Sec. III. In Sec. V we present the results of contact transformation method followed by conclusion in Sec. VI.

II. THE METHOD OF CONTACT TRANSFORMATION

The method of contact transformations proposes a series of unitary transformations to diagonalize a Hamiltonian containing a zero order Hamiltonian and a series of other interaction Hamiltonians whose magnitudes decrease in an appropriately chosen order-of-magnitude scheme. The transformation is done on the Hamiltonian so that by successive applications one obtains a Hamiltonian whose diagonal operators incorporate corrections from the interaction Hamiltonians. It is an *operator transformation* which, in principle, leads to better, *effective Hamiltonians*. The contact transformation method is formally equivalent to the traditional and more commonly known Rayleigh–Schrödinger perturbation theory which provides corrections to zero order eigenvalues and eigenvectors. The important aspect of the transformation, however, is that it is possible to obtain *effective Hamiltonians*. The unitary transformations are chosen in such a way that the off-diagonal operators due to interaction Hamiltonians are folded back to give diagonal contributions to the zero order Hamiltonian. As a result, one obtains a new Hamiltonian which is more effective, i.e., its eigenvalues are closer to the eigenvalues of the overall, untransformed Hamiltonian.

The steps involved in the transformation may be represented as follows:

$$\hat{H} = UHU^{-1} = e^{i\lambda^n S_n} \dots e^{i\lambda^2 S_2} e^{i\lambda S_1} H e^{-i\lambda S_1} e^{-i\lambda^2 S_2} \dots e^{-i\lambda^n S_n}, \quad (1)$$

where S_n 's are Hermitian operators, U is a product of unitary transformations given by the exponential, \hat{H} is the transformed Hamiltonian, H is the untransformed Hamiltonian which is considerably off diagonal, and λ is the perturbation parameter which is set to unity after performing the expansion.

It must be noted here that successive contact transformations through S_1, S_2 , etc. affect terms in the Hamiltonian corresponding to various powers of λ , the perturbation parameter. If we write the untransformed Hamiltonian as

$$H = H_0 + \lambda H_1 + \lambda^2 H_2 \dots, \quad (2)$$

where H_0 is the zero order Hamiltonian and H_1, H_2 , etc. are perturbing (interaction) Hamiltonians with decreasing orders of magnitude, then, the transformed Hamiltonian $H^{(1)}$ obtained after first transformation is given by

$$\begin{aligned} H^{(1)} &= U_1 H U_1^{-1} = e^{i\lambda S_1} H e^{-i\lambda S_1} \\ &= H_0^{(1)} + \lambda H_1^{(1)} + \lambda^2 H_2^{(1)} + \dots \end{aligned} \quad (3)$$

The operator S_1 is chosen such that $H^{(1)}$ has no off-diagonal elements to order λ . This is done as follows:

$$\begin{aligned} H^{(1)} &= U_1 H U_1^{-1} = H_0^{(1)} + \lambda H_1^{(1)} + \lambda^2 H_2^{(1)} + \dots \\ &= H_0 + \lambda(H_1 + i[S_1, H_0]) \\ &\quad + \lambda^2(H_2 + i[S_1, H_1] - \frac{1}{2}[S_1, [S_1, H_0]]) \dots \end{aligned} \quad (4)$$

By equating powers of λ on both sides we get the following expressions:

$$\begin{aligned} H_0^{(1)} &= H_0, \\ H_1^{(1)} &= H_1 + i[S_1, H_0], \\ H_2^{(1)} &= H_2 + i[S_1, H_1] - \frac{1}{2}[S_1, [S_1, H_0]]. \end{aligned} \quad (5)$$

The general term $H_n^{(1)}$ is given by

$$H_n^{(1)} = H_n + \sum_{m=0}^{n-1} \frac{i^{n-m}}{(n-m)!} \underbrace{[S_1, [S_1, \dots [S_1, H_m] \dots]]}_{n-m}. \quad (6)$$

The above procedure is repeated to perform a second contact transformation on $H^{(1)}$. The transformation function S_2 is chosen such that the quantity

$$H_0^{(2)} + \lambda H_1^{(2)} + \lambda^2 H_2^{(2)}$$

is diagonal to order λ^2 . Successive contact transformations are represented by the product of U 's as

$$U = U_n U_{n-1} \dots U_2 U_1, \quad (7)$$

where $U_n = e^{i\lambda^n S_n}$ and the transformed Hamiltonians are given in terms of earlier ones by

$$H^{(n)} = e^{i\lambda^n S_n} H^{(n-1)} e^{-i\lambda^n S_n}. \quad (8)$$

An important aspect of this method is the determination of the transformation function “ S .” To determine S_1 the equation to be solved is

$$H_1^{(1)} = H_1 + i[S_1, H_0], \quad (9)$$

where H_1 may contain both diagonal and off-diagonal terms. In the above equation, the diagonal terms are not considered. The operator S_1 is chosen such that the transformed Hamiltonian $H_1^{(1)}$ does not contain any off-diagonal terms to order λ . That is, S_1 is chosen such that the commutator $i[S_1, H_0]$ compensates the off-diagonal terms present in H_1 . Since H_0 is diagonal, this implies that S_1 is off diagonal. The transformed Hamiltonian contains corrections to the eigenvalues of the zero order Hamiltonian H_0 . This will also be the dominant correction provided H_1, H_2 , etc. decrease in mag-

nitude rapidly when compared to H_0 . The transformed Hamiltonian which includes corrections to order λ^2 is given by

$$H_2^{(1)} = H_2 + i[S_1, H_1] - \frac{1}{2}[S_1, [S_1, H_0]].$$

It is the diagonal part of the above equation which is the effective Hamiltonian if terms of order λ^2 and higher which are off diagonal in the basis of the zero order Hamiltonian can be neglected.

III. FLOQUET THEORY FOR A DIPOLAR COUPLED TWO SPIN SYSTEM WITH $I = 1/2$

We use the Hamiltonian for a dipolar coupled spin pair ($I = 1/2$) under MAS condition given by Schmidt and Vega¹⁷

$$H(t) = -\omega^1(t)I_z^1 - \omega^2(t)I_z^2 + \omega_d(t)[I_z^1 I_z^2 - \frac{1}{4}(I_+^1 I_-^2 + I_-^1 I_+^2)], \quad (10)$$

where the J -coupling term has been neglected for the sake of simplicity. The terms $\omega^i(t)$ and $\omega_d(t)$ are due to the chemical shift interaction and dipolar interactions respectively and are given by

$$\omega^i(t) = \omega^i[g_1^i \cos(\omega_r t + \phi_1^i) + g_2^i \cos(2\omega_r t + \phi_2^i)] + \Delta\omega^i, \quad (11)$$

$$\omega_d(t) = \omega_{12}[G_1 \cos(\omega_r t + \phi_1) + G_2 \cos(2\omega_r t + \phi_2)], \quad (12)$$

where

$$\Delta\omega^i = \sigma_0^i \omega_0, \quad \sigma_0^i = \frac{1}{3}(\sigma_{11}^i + \sigma_{22}^i + \sigma_{33}^i),$$

and

$$\omega^i = \sigma_{33}^i \omega_0 - \Delta\omega^i.$$

In the above, ω_0 is the Larmor frequency. The Hamiltonian above is time dependent and periodic and has been studied using Floquet theory. The time-dependent coefficients are expanded in a Fourier series and a new basis is constructed which is the direct product of the spin operator basis and a basis denoting the Fourier index. The new product basis is infinite dimensional and the Hamiltonian is expressed in this basis using a set of operators to form what is known as the Floquet–Hamiltonian. The form of the Floquet–Hamiltonian used here for a dipolar coupled ($I = 1/2$) spin system is given as follows:

$$H_F = H_F^{11} + H_F^{22} + H_F^{33} + H_F^{44} + H_F^{23}, \quad (13)$$

where the superscripts 1, 2, 3, and 4 denote the two-spin product basis functions $|\alpha\alpha\rangle$, $|\alpha\beta\rangle$, $|\beta\alpha\rangle$, and $|\beta\beta\rangle$, respectively. The Floquet–Hamiltonian is represented by the operators N^{pp} , X_n^{pq} , Y_n^{pq} , and Z_n^{pp} which are all of infinite dimension. Using these operators, the Floquet–Hamiltonian is given by the expressions

$$H_F^{pp} = \omega_r N^{pp} + \sum_{n=-2}^{n=2} z_n^{pp} Z_n^{pp} \quad (14)$$

and

$$H_F^{23} = \sum_{n=-2, n \neq 0}^{n=2} x_n^{23} X_n^{23}. \quad (15)$$

The Floquet–Hamiltonian H_F consists of five terms. Four of the five terms H_F^{11} , H_F^{22} , H_F^{33} , and H_F^{44} are block diagonal. Each of these block diagonal matrices contains the Z_n^{pp} operators which connect the Floquet states differing in the Fourier index “ n ” but connecting the same spin basis states. H_F^{23} is an off-diagonal term which is similar to the flip-flop terms present in the dipolar Hamiltonian. This Hamiltonian is represented by means of the operators X_n^{pq} which connect different Floquet states, namely $|p, m\rangle$, with $|q, n+m\rangle$ differing in the Fourier index n as well as the spin basis.

To follow the evolution of the coupled spin system the standard procedure is to diagonalize the Floquet–Hamiltonian matrix. The diagonalization of the Floquet–Hamiltonian is performed numerically which requires a truncation of the infinite dimensional matrix. Perturbation theory calculations have also been employed to study such problems.^{20–22} In the method of contact transformation we use the same perturbation treatment, but instead of calculating the correction terms we calculate an effective Hamiltonian. In numerical treatments for diagonalizing Floquet–Hamiltonian, a variational approach has been used to determine the convergence of the required eigenvalues.

IV. APPLICATION OF THE CONTACT TRANSFORMATION PROCEDURE

We use the following Hamiltonian for a pair of spin $1/2$ s,

$$H = \sum_{p=1}^4 \omega_r N^{pp} + \sum_{p=1}^4 \sum_{n=-2}^2 z_n^{pp} Z_n^{pp} + \sum_{n=-2, n \neq 0}^2 x_n^{23} X_n^{23}. \quad (16)$$

The above Hamiltonian is split into a zero order Hamiltonian and interaction terms as

$$H_0 = \sum_{p=1}^4 \omega_r N^{pp} - \frac{\Delta\omega^1 - \Delta\omega^2}{2} (Z_0^{22} - Z_0^{33}) - \frac{(\Delta\omega^1 + \Delta\omega^2)}{2} (Z_0^{11} - Z_0^{44}), \quad (17)$$

$$H_1 = \sum_{p=1}^4 \sum_{n=-2, n \neq 0}^2 z_n^{pp} Z_n^{pp} + \sum_{n=-2, n \neq 0}^2 x_n^{23} X_n^{23}, \quad (18)$$

where the values for z_0^{pp} ($p = 1, 4$) have been substituted. The zero order Hamiltonian has matrix elements between Floquet states having the *same* Fourier index. The perturbing Hamiltonian has matrix elements between Floquet states which have *different* Fourier indices. The Floquet–Hamiltonian is represented as blocks of four by four matrices with each block having a different Fourier index. The transformation function S_1 is obtained by solving the equation given below,

$$H_1^{(1)} = H_1 + i[S_1, H_0]. \quad (19)$$

The transformation function S_1 can be expressed in terms of a linear combination of all spin operators used to describe the system. It is chosen in such a way that the commutator $i[S_1, H_0]$ compensates the off-diagonal terms present in H_1 . The S_1 function is written using the complete set of operators (which are relevant to the problem of interest) as follows:

$$S_1 = i \sum_{j=1}^4 \sum_{n=-2, n \neq 0}^2 K_n^j Z_n^{jj} - i \sum_{n=-2, n \neq 0}^2 (C_n X_n^{23} + i B_n Y_n^{23}), \tag{20}$$

where the constants K_n^j , C_n , and B_n are to be determined. The Appendix describes the procedure and the details of evaluation of the various constants. Using the expression for S_1 , we evaluate corrections to the diagonal term of Hamiltonian as

$$H_2^{(1)} = H_2 + i[S_1, H_1] - \frac{1}{2}[S_1, [S_1, H_0]]. \tag{21}$$

In our case $H_2 = 0$ and H_1 is off diagonal, so the final form of the equation becomes

$$H_2^{(1)} = \frac{i}{2}[S_1, H_1]. \tag{22}$$

Since S_1 and H_1 are off diagonal, the product of two off-diagonal terms gives rise to a correction in the diagonal term. Matrix elements of the corrected Hamiltonian using a suitable basis set are identical to the corrections to the appropriate diagonal elements of the zero order Hamiltonian calculated using Rayleigh–Schrödinger perturbation theory (and the same basis set).^{15,16,20–22,24} *The advantage of this procedure, however, is that the correction is in the form of operators and therefore permits us to define new, effective Hamiltonians which can be employed gainfully in pulse dynamics of rotating solids.*

In the evaluation of the commutator $[S_1, H_1]$, by restricting ourselves to the evaluation of the diagonal correction terms only for the moment, we obtain the following transformed Hamiltonian:

$$H_2^{(1)} = iA_1 Y_0^{23} - A_2 X_0^{23} + A_3 (Z_0^{22} - Z_0^{33}), \tag{23}$$

where A_1 , A_2 , and A_3 are the corresponding coefficients associated with the operators, respectively, and are given in the Appendix (“Diagonal” means here “diagonal with respect to the Fourier index”). When we evaluate matrix elements of the correction terms we note that the $|\alpha\alpha n\rangle$ and $|\beta\beta n\rangle$ states are unaffected by this transformation. The matrix elements which are modified are the terms $|\alpha\beta n\rangle$ and $|\beta\alpha n\rangle$ which have correction terms from the flip-flop terms involved in the dipolar Hamiltonian. The final form of the transformed Hamiltonian $H^{(1)}$ is given as follows:

$$H^{(1)} \approx H_0^{(1)} + H_1^{(1)} + H_2^{(2)}, \tag{24}$$

where $H_0^{(1)} = H_0$, $H_1^{(1)} = 0$, and $H_2^{(2)} = iA_1 Y_0^{23} - A_2 X_0^{23} + A_3 (Z_0^{22} - Z_0^{33})$. Next we perform a second transformation on the transformed Hamiltonian. For this case, the diagonal terms present in $H_2^{(1)}$ are taken as H_0 and the off-diagonal terms present in $H_2^{(1)}$ are taken as the perturbing term H_1 . Let the Hamiltonian H be represented as follows:

$$H = H_0 + H_1, \tag{25}$$

where

$$H_0 = \sum_{p=1}^4 \omega_r N^{pp} + \left(A_3 - \frac{\Delta\omega}{2} \right) [Z_0^{22} - Z_0^{33}] + iA_1 Y_0^{23} - A_2 X_0^{23}, \tag{26}$$

$$H_1 = \sum_{n=-2, n \neq 0}^2 F_n (Z_n^{22} - Z_n^{33}) + \sum_{n=-2, n \neq 0}^2 (iD_n Y_n^{23} + U_n X_n^{23}).$$

TABLE I. Coefficients of the transformed Hamiltonian after one transformation.

D_1	$-\frac{1}{8\omega_r} x_{-1}^{23} (z_2^{22} - z_2^{33}) + \frac{1}{4\omega_r} x_{-1}^{23} (z_{-1}^{22} - z_{-1}^{33}) - \frac{1}{4} C_2 (z_{-1}^{22} - z_{-1}^{33}) - \frac{1}{4} C_{-1} (z_2^{22} - z_2^{33})$
D_2	$-\frac{1}{4\omega_r} x_1^{23} (z_1^{22} - z_1^{33}) - \frac{1}{4} C_1 (z_1^{22} - z_1^{33})$
D_{-1}	$\frac{1}{8\omega_r} x_1^{23} (z_{-2}^{22} - z_{-2}^{33}) - \frac{1}{4\omega_r} x_{-2}^{23} (z_1^{22} - z_1^{33}) - \frac{1}{4} C_{-2} (z_1^{22} - z_1^{33}) - \frac{1}{4} C_1 (z_{-2}^{22} - z_{-2}^{33})$
D_{-2}	$\frac{1}{4\omega_r} x_{-1}^{23} (z_{-1}^{22} - z_{-1}^{33}) - \frac{1}{4} C_{-1} (z_{-1}^{22} - z_{-1}^{33})$
F_{-1}	$\frac{1}{2} (B_1 x_{-2}^{23} + B_{-2} x_1^{23})$
F_1	$\frac{1}{2} (B_2 x_{-1}^{23} + B_{-1} x_2^{23})$
F_2	$\frac{1}{2} (B_1 x_1^{23})$
F_{-2}	$\frac{1}{2} (B_{-1} x_{-1}^{23})$
U_{-1}	$\frac{1}{4} (-B_1 (z_{-2}^{22} - z_{-2}^{33}) - B_{-2} (z_1^{22} - z_1^{33}))$
U_1	$\frac{1}{4} (-B_{-1} (z_2^{22} - z_2^{33}) - B_2 (z_{-1}^{22} - z_{-1}^{33}))$
U_2	$-\frac{1}{4} B_1 (z_1^{22} - z_1^{33})$
U_{-2}	$-\frac{1}{4} B_{-1} (z_{-1}^{22} - z_{-1}^{33})$

The Z_0^{11} and Z_0^{44} terms are dropped from H_0 . The constants involved in H_1 are given in Table I. The transformation function S_2 is given as follows:

$$S_2 = \sum_{n=-2, n \neq 0}^2 M_n Y_n^{23} + i \sum_{n=-2, n \neq 0}^2 P_n (Z_n^{22} - Z_n^{33}) + i \sum_{n=-2, n \neq 0}^2 R_n X_n^{23}. \tag{27}$$

The constants involved in the transformation function S_2 can be obtained by the same procedure as described earlier and are given in Table II. Next we evaluate the corrections to the diagonal terms,

$$H_2^{(2)} \approx \frac{i}{2}[S_2, H_1]. \tag{28}$$

In the evaluation of the above commutator relation, we restrict ourselves only to corrections to diagonal terms. The diagonal part of $H_2^{(2)}$ is given below,

$$H_2^{(2)} = -\frac{1}{2} X_0^{23} \sum_{n=1}^2 (M_n F_{-n} + M_{-n} F_n + P_n D_{-n} + P_{-n} D_n) + \frac{i}{2} Y_0^{23} \sum_{n=1}^2 (R_n F_{-n} + R_{-n} F_n - P_n U_{-n} - P_{-n} U_n) + \frac{1}{2} [Z_0^{22} - Z_0^{33}] \sum_{n=1}^2 (R_n D_{-n} + R_{-n} D_n - M_n U_{-n} - M_{-n} U_n),$$

TABLE II. Coefficients of the transformation function S_2 . The following notations have been used below: $d=D_1$, $f=F_1$, $e=A_1$, $a=\omega_r$, $b=A_2$, $c=(A_3-\Delta\omega/2)$, $d_3=D_{-1}$, $f_3=F_{-1}$, $d_4=D_{-2}$, $f_4=F_{-2}$, $d_2=D_2$, $f_2=F_2$, and $n=U_1$, $n_2=U_2$, $n_3=U_{-1}$, $n_4=U_{-2}$.

R_1	$(-cbf+ebd+eaf-cda+nb^2-na^2)/(-a(e^2-c^2-b^2+a^2))$
M_1	$(neb+fab-cef+nca+de^2+da^2)/(-a(e^2-c^2-b^2+a^2))$
P_1	$(-bad-bcn+fc^2-dec-fa^2-ane)/(-a(e^2-c^2-b^2+a^2))$
M_2	$(2f_2ab+ebn_2-cef_2+2can_2+d_2e^2+4d_2a^2)/(2a(c^2-e^2+b^2-4a^2))$
R_2	$(-cbf_2+ebd_2+2eaf_2-2acd_2+n_2b^2-4n_2a^2)/(2a(c^2-e^2+b^2-4a^2))$
P_2	$(-2abd_2-bcn_2+f_2c^2-ced_2-4f_2a^2-2n_2ae)/(2a(c^2-e^2+b^2-4a^2))$
R_{-1}	$(ebd_3-cbf_3-eaf_3+cad_3+n_3b^2-n_3a^2)/(a(e^2-c^2-b^2+a^2))$
M_{-1}	$(ebn_3-f_3ab-cef_3-n_3ca+d_3e^2+d_3a^2)/(a(e^2-c^2-b^2+a^2))$
P_{-1}	$(bad_3-bcn_3+c^2f_3-d_3ce-f_3a^2+ae n_3)/(a(e^2-c^2-b^2+a^2))$
R_{-2}	$(-cbf_4+ebd_4-2eaf_4+2acd_4+n_4e^2-4n_4a^2)/(-2a(c^2-e^2+b^2-4a^2))$
M_{-2}	$(-2abf_4+ebn_4-ecf_4-2acn_4+d_4e^2+4a^2d_4)/(-2a(c^2-e^2+b^2-4a^2))$
P_{-2}	$(2abd_4-bcn_4+c^2f_4-d_4ce-4f_4a^2+2eae n_4)/(-2a(c^2-e^2+b^2-4a^2))$

where all the constants are tabulated in Tables I and II. The final form of the diagonal, effective Hamiltonian after two transformations is given below,

$$\begin{aligned}
 H_{\text{eff}} = & \sum_{p=1}^4 \omega_r N^{pp} + \left(A_1 + \frac{1}{2} \sum_{n=1}^2 (R_n F_{-n} + R_{-n} F_n \right. \\
 & \left. - P_n U_{-n} - P_{-n} U_n) \right) iY_0^{23} + \left(A_3 - \frac{\Delta\omega}{2} \right. \\
 & \left. + \frac{1}{2} \sum_{n=1}^2 (R_{-n} D_n + R_n D_{-n} - M_n U_{-n} - M_{-n} U_n) \right) \\
 & \times [Z_0^{22} - Z_0^{33}] - \left(A_2 + \frac{1}{2} \sum_{n=1}^2 (M_{-n} F_n + M_n F_{-n} \right. \\
 & \left. + P_{-n} D_n + P_n D_{-n}) \right) X_0^{23}. \tag{29}
 \end{aligned}$$

TABLE III. Comparison between eigenvalues of the effective and the untransformed Hamiltonians for a rotor frequency of 10 KHz.^{a,b}

Zero order	First transformation	Second transformation	Numerical diagonalization
7.387	7.387	7.387	7.387
8.040	8.487	8.488	8.470
11.960	11.513	11.512	11.530
12.612	12.612	12.612	12.612

^a $\omega_D = -24.53$ KHz.

^bThe values given here are for $n=0$. All eigenvalues for a given n are generated from the above using the relation, $E_i^n = E_i^0 + n\omega_r$, where ω_r is the rotor frequency.

TABLE IV. Comparison between eigenvalues of the effective and the untransformed Hamiltonians for a rotor frequency of 20 KHz.^{a,b}

Zero order	First transformation	Second transformation	Numerical diagonalization
17.387	17.387	17.387	17.387
18.040	18.139	18.139	18.143
21.960	21.861	21.861	21.857
22.612	22.612	22.612	22.612

^a $\omega_D = -24.53$ KHz.

^bThe values given here are for $n=0$. All eigenvalues for a given n are generated from the above using the relation, $E_i^n = E_i^0 + n\omega_r$, where ω_r is the rotor frequency.

The perturbation correction terms are given in terms of operators and we have an effective Hamiltonian H_{eff} which is a simplified solution to the problem of finding the eigenvalues of the Floquet Hamiltonian.

V. RESULTS

In the previous section we obtained perturbation corrections in terms of operators using contact transformation. For interactions between several spins, this method simplifies the calculation of eigenvalues in that the matrix which needs to be diagonalized has the spin dimension only, i.e., for each Fourier index we have an effective Hamiltonian analogous to an effective rotational Hamiltonian for each vibrational state in a semirigid polyatomic molecule. The obvious advantage of such a procedure is that the Hamiltonians should prove themselves to be useful in the study of multiple pulse dynamics of rotating solids. The other advantage is that they can be programmed with considerable ease and require smaller dimensional matrices, an advantage that becomes quite significant as the number of spins coupled to each other becomes larger.

We have compared the results of our method with the numerical diagonalization of a Floquet-Hamiltonian for two coupled spins with $I=1/2$. In our calculations involving numerical diagonalization before transformation, the order of truncation was determined by the convergence of the smallest eigenvalues and a matrix of dimensions 204×204 was employed. In the method of contact transformation the diagonal blocks (of dimension 4×4) for each Fourier index n were diagonalized to obtain the eigenvalues. In Tables III-V, comparisons are made between the eigenvalues ob-

TABLE V. Comparison between eigenvalues of the effective and the untransformed Hamiltonians for a rotor frequency of 30 KHz.^{a,b}

Zero order	First transformation	Second transformation	Numerical diagonalization
27.387	27.387	27.387	27.387
28.040	28.083	28.083	28.085
31.960	31.917	31.917	31.915
32.612	32.612	32.612	32.612

^a $\omega_D = -24.53$ KHz.

^bThe values given here are for $n=0$. All eigenvalues for a given n are generated from the above using the relation, $E_i^n = E_i^0 + n\omega_r$, where ω_r is the rotor frequency.

TABLE VI. Parameters used for the calculation of eigenvalues.

α_1	0°
β_1	-90°
γ_1	0°
η_1	-0.3217
ω^1	-3.7547 KHz
α_2	0°
β_2	0°
γ_2	0°
η_2	-0.5508
ω^1	-1.188 KHz
$\Delta\omega$	7.8387 KHz
ω_{12}	-4.53 KHz
ω_0	50.329 MHz
θ_D	45°
ϕ_D	30°

tained from zero order Hamiltonian, the block-diagonal part of the transformed Hamiltonian after a single transformation, the block-diagonal part of the transformed Hamiltonian after two transformations and (variational) numerical diagonalization of the untransformed Hamiltonian. Three sets of eigenvalues were calculated in Tables III–V and these correspond to three different rotor speeds. The agreement between perturbation correction using the transformation method, and the eigenvalues obtained by diagonalization of the Floquet–Hamiltonian matrix numerically, is better with higher rotor speeds. This is evident from the fact that the zero order block matrices (eigenvalues of H_0) are separated from each other more with increased rotor speeds. It is clear from the Tables III–V that the eigenvalues obtained from contact transformation are in good agreement with the converged eigenvalues obtained using numerical diagonalization employing a much bigger basis set. Table VI contains a list of parameters employed by us for the calculation of eigenvalues.

VI. CONCLUSIONS

In this article we have proposed the use of the method of contact transformation for doing perturbation theory calculations on MAS Hamiltonians. Though this method has been widely applied in the branch of molecular spectroscopy, its application to MAS and the derivation of effective Floquet–Hamiltonian have been given by us for the first time, to the best of our knowledge. The main usefulness of this method is that it can provide effective Hamiltonians and thereby simplify the calculations of eigenvalues of Floquet–Hamiltonian matrix. The eigenvalues obtained from this method are in good agreement with those obtained from numerical diagonalization. This method would be very useful when we treat systems in which many spins are coupled. Very often many spin Hamiltonians can be expressed as a series of terms of decreasing magnitude as in Eq. (2). A sequence of contact transformations can be quite effective here, since we are able to correct the zero order Hamiltonian successively through determining S_1, S_2 , etc, with S_i not affecting $S_j (i > j)$ since S_j has already been determined.

In many spin coupled systems numerical diagonalization becomes quite difficult due to large dimensions of matrices. The method of contact transformation gives the corrections

in terms of operators and permits us to restrict to the spin basis only, thereby reducing the size of matrices to be diagonalized in such systems.

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APPENDIX: DETERMINATION OF THE TRANSFORMATION OPERATOR S_1

To determine the constants in the transformation function we need to solve the equation

$$H_1 + i[S_1, H_0] = 0.$$

S_1 is expanded as a linear combination of all the relevant linearly independent operators to give

$$S_1 = i \sum_{j=1}^4 \sum_{n=-2, n \neq 0}^2 K_n^j Z_n^{jj} - i \sum_{n=-2, n \neq 0}^2 (C_n X_n^{23} + i B_n Y_n^{23}), \quad (\text{A1})$$

where H_0 and H_1 are given as follows:

$$H_0 = \sum_{p=1}^4 \omega_r N^{pp} - \frac{\Delta\omega^1 - \Delta\omega^2}{2} [Z_0^{22} - Z_0^{33}] - \frac{(\Delta\omega^1 + \Delta\omega^2)}{2} [Z_0^{11} - Z_0^{44}], \quad (\text{A2})$$

$$H_1 = \sum_{p=1}^4 \sum_{n=-2, n \neq 0}^2 z_n^{pp} Z_n^{pp} + \sum_{n=-2, n \neq 0}^2 x_n^{23} X_n^{23}.$$

The commutator in the above equation is evaluated using the commutation properties of Floquet spin operators as given in Appendix A of Schmidt and Vega.¹⁷ Collecting all nonzero coefficients of every operator and realizing that the Hamiltonian H_1 does not contain any Y_n^{23} operator, we arrive at the following expression for $H^{(1)}$ which is set to zero:

$$H^{(1)} = \sum_{j=1,4} [z_1^{jj} Z_1^{jj} + z_{-1}^{jj} Z_{-1}^{jj} + z_2^{jj} Z_2^{jj} + z_{-2}^{jj} Z_{-2}^{jj}] - \omega_r (K_1^j Z_1^{jj} - K_{-1}^j Z_{-1}^{jj} + 2K_2^j Z_2^{jj} - 2K_{-2}^j Z_{-2}^{jj}) + \sum_{n=-2, n \neq 0}^2 [C_n \omega_r n X_n^{23} - B_n z_0 X_n^{23} + x_n^{23} X_n^{23} + i B_n \omega_r n Y_n^{23} - i C_n z_0 Y_n^{23}] = 0. \quad (\text{A3})$$

From the above we arrive at the following expressions for all nonzero constants:

$$K_1^1 = \frac{z_1^{11}}{\omega_r}, \quad K_{-1}^1 = -\frac{z_{-1}^{11}}{\omega_r},$$

$$K_2^1 = \frac{z_2^{11}}{2\omega_r}, \quad K_{-2}^1 = -\frac{z_{-2}^{11}}{2\omega_r},$$

$$K_1^4 = \frac{z_1^{44}}{\omega_r}, \quad K_{-1}^4 = -\frac{z_{-1}^{44}}{\omega_r},$$

$$K_2^4 = \frac{z_2^{44}}{2\omega_r}, \quad K_{-2}^4 = -\frac{z_{-2}^{44}}{2\omega_r},$$

$$K_1^2 = \frac{z_1^{22}}{\omega_r}, \quad K_{-1}^2 = -\frac{z_{-1}^{22}}{\omega_r},$$

$$K_2^2 = \frac{z_2^{22}}{2\omega_r}, \quad K_{-2}^2 = -\frac{z_{-2}^{22}}{2\omega_r},$$

$$K_1^3 = \frac{z_1^{33}}{\omega_r}, \quad K_{-1}^3 = -\frac{z_{-1}^{33}}{\omega_r},$$

$$K_2^3 = \frac{z_2^{33}}{2\omega_r}, \quad K_{-2}^3 = -\frac{z_{-2}^{33}}{2\omega_r},$$

$$C_1 = \frac{-x_1^{23}\omega_r}{(\omega_r^2 - z_0^2)}, \quad C_2 = \frac{-2x_2^{23}\omega_r}{(4\omega_r^2 - z_0^2)},$$

$$B_1 = \frac{C_1 z_0}{\omega_r}, \quad B_2 = \frac{C_2 z_0}{2\omega_r},$$

$$C_{-1} = \frac{x_{-1}^{23}\omega_r}{(\omega_r^2 - z_0^2)}, \quad C_{-2} = \frac{2x_{-2}^{23}\omega_r}{(4\omega_r^2 - z_0^2)},$$

$$B_{-1} = \frac{-C_{-1} z_0}{\omega_r}, \quad B_{-2} = \frac{-C_{-2} z_0}{2\omega_r},$$

where $z_0 = -(\Delta\omega^1 - \Delta\omega^2)/2$.

S_1 is then substituted in the expression for $H_2^{(1)}$ [Eq. (23)] leading to Eq. (24). The constants A_1 , A_2 , and A_3 are given by

$$A_1 = -\frac{z_1^{22} - z_1^{33}}{4} \left[\frac{x_{-1}^{23}}{\omega_r} + C_{-1} \right] - \frac{z_2^{22} - z_2^{33}}{4} \left[\frac{x_{-2}^{23}}{2\omega_r} + C_{-2} \right] \\ + \frac{z_{-1}^{22} - z_{-1}^{33}}{4} \left[\frac{x_1^{23}}{\omega_r} - C_1 \right] + \frac{z_{-2}^{22} - z_{-2}^{33}}{4} \left[\frac{x_2^{23}}{2\omega_r} - C_2 \right],$$

$$A_2 = -\frac{1}{4} [B_1(z_{-1}^{22} - z_{-1}^{33}) + B_{-1}(z_1^{22} - z_1^{33}) \\ + B_2(z_{-2}^{22} - z_{-2}^{33}) + B_{-2}(z_2^{22} - z_2^{33})],$$

and

$$A_3 = \frac{1}{2} (B_1 x_{-1}^{23} + B_{-1} x_1^{23} + B_2 x_{-2}^{23} + B_{-2} x_2^{23}).$$

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