

Multipole-multimode Floquet theory in nuclear magnetic resonance

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In this paper, we present a new analytical approach for describing the spin dynamics of synchronous and asynchronous time-dependent modulations in solid-state nuclear magnetic resonance experiments. The approach, based on multimode Floquet theory, employs the multipole operator basis of Sanctuary for spin description and illustrates the time evolution in the Floquet–Liouville space using the effective Hamiltonians obtained from the contact (or van Vleck) transformation procedure. Since the Hamiltonian and the density operator are expressed in terms of irreducible tensor operators, extensions to higher spin magnitudes ($I > 1/2$) and multiple spins are quite straightforward and permit analytical treatments for many problems. We outline the general underlying principles involved in this approach with a brief mention of its potential application in other branches of spectroscopy. © 2005 American Institute of Physics. [DOI: 10.1063/1.1875092]

I. INTRODUCTION

The combination of magic angle spinning (MAS) (Ref. 1) and multiple pulse techniques^{2,3} has established solid-state nuclear magnetic resonance (SSNMR) spectroscopy as a powerful tool for investigating molecular structure and dynamics in biological solids such as membrane proteins^{4,5} and amyloid aggregates,^{6,7} systems that are generally intractable to study with conventional diffraction or solution nuclear magnetic resonance (NMR) techniques. The development of homonuclear and heteronuclear recoupling techniques^{8–10} and their use in combination with multidimensional chemical shift correlation spectroscopy has provided complete spectral assignments in many cases in addition to supplying constraints on internuclear distances and molecular torsion angles.^{11–14} In many cases these experiments involve selective isotopic enrichment of the sample and employ recoupling techniques, which are selective and site specific. The experimental results are interpreted using approximate theoretical models (usually involving two spins) within the framework of average Hamiltonian theory (AHT).^{15,16}

More recently, uniformly ¹³C, ¹⁵N labeled samples and broadband recoupling techniques are finding frequent use in structural and dynamic investigations. In these cases interpretation of the experimental data with the theory developed for isolated spin pairs can lead to erroneous or inaccurate interpretations. Further, complications due to interference effects between the sample spinning and multiple pulse trains (a condition encountered when the spinning frequency and rf irradiation occur on comparable time scales) limit the utility of AHT in describing the experimental results.¹⁷ Such issues have limited our understanding of the phenomena of heteronuclear decoupling,¹⁸ which involves multiple spins (in the form of strongly coupled protons) in addition to the observed nuclei. Furthermore, polarization transfer experiments in-

volving multiple spins, require a description of the spin system in the operator space¹⁹ (or Liouville space) to incorporate the coherent effects due to the spin Hamiltonian as well as the incoherent effects due to relaxation. Since the density operator²⁰ is analogous to the spin eigenfunctions in the state space, the choice of an appropriate basis that spans the entire operator space has often remained elusive for theoretical treatments involving higher spin magnitudes and multiple spins. Although many bases exist in the literature,^{21,22} their applications are specific and inadequate for describing both multiple spins as well as higher spin ($I > 1/2$) systems. This motivated the development of alternate formalisms for describing multiple pulse MAS NMR experiments involving spins of arbitrary magnitude. To this end theoretical treatments such as Floquet theory^{23–30} and secular averaging theory³¹ could be employed with suitable modifications as alternatives to AHT for describing the underlying dynamics in MAS experiments. In this paper we confine our attention to a modified Floquet description of MAS experiments.

Using Floquet theorem, Shirley proposed a general description in the form of Floquet theory²³ for studying periodically time-dependent phenomena in quantum systems. In this approach, a time-dependent (usually periodic) Hamiltonian, represented in a finite dimensional basis set, is transformed into a time-independent Hamiltonian (usually referred as Floquet Hamiltonian) represented in an infinite dimensional basis set via Fourier series expansion. Vega and co-workers introduced the Floquet operators^{27,32} for studying the time evolution during MAS in the Floquet-state space. Subsequently, the Floquet approach was formulated into a Fourier state representation by Levante *et al.*²⁸ and to an integral representation by Filip *et al.*²⁹ Although the Floquet approach describes the time evolution of the spin system under a time-independent Hamiltonian, the infinite dimensionality involved in the description often complicates its practical application in solid-state NMR. The standard approach in such cases generally involves the numerical diagonalization of the truncated Floquet Hamiltonian matrix

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(where the order of truncation is fixed based on the convergence of the eigenvalues for increasing matrix dimensions). Although such an approach yields results, it limits the physical insights into the spin dynamic problem. This limitation provides the motivation to develop analytical methods (e.g., perturbation theory) to solve the above problem. Thus the main points of this paper are twofold. First, we propose and illustrate the utility of employing the multipole basis³³ as an improved alternative to the current bases employed both in the Floquet as well as AHT spin description. Second, for experiments involving multiple asynchronous time modulations, we highlight the importance of the effective Floquet Hamiltonians (obtained via van Vleck transformation) in describing the dynamics in the extended Floquet–Liouville space.

An outline of the paper is as follows. In Sec. II A, we briefly describe the advantages of the multipole theory with suitable modifications to treat multiple spins in the operator space. The application of the multipole operator basis in multimode Floquet theory (MMFT) is discussed in Sec. II B, followed in Sec. II C by a brief illustration of the effective Hamiltonians obtained via the van Vleck transformation method. In Sec. II D we elucidate the advantages associated with the MMFT approach in describing the spin dynamics in the Floquet–Liouville space. The final section of the paper summarizes our conclusions.

II. THEORY

A. Background: Multipole NMR

The multipole theory proposed by Sanctuary^{33–37} to treat spin dynamics in NMR differs from the usual approaches in that the dynamics is described in the operator space (or Liouville space) with an explicit time-dependent density operator. Other theoretical treatments¹⁹ describe the dynamics with an explicit time dependence on the operator(s). The latter method has gained wide acceptance and is at times a convenient approach for describing the dynamical behavior; it is often limited to calculations involving only the experimentally detectable magnetization (or polarizations). Additionally, it fails to provide insights into multiple-quantum NMR phenomena and polarization transfer experiments that involve relaxation in addition to the observed spin dynamics. Further, in spite of the spin Hamiltonian being described in terms of irreducible tensor operators, it is not yet common practice to express the spin basis in terms of operators, which are also irreducible under rotations,^{38–41} though some examples of this exist in the literature.^{42–46} This approach has been exploited extensively in the multipole formalism, where the basis operators are deliberately chosen to be invariant under the rotation group SO(3), thereby extending their range of applicability from single spins (of arbitrary magnitudes) to multiple spins.

The general time evolution of a spin system is described by the Liouville equation,

$$i\hbar \frac{d\rho(t)}{dt} = [H, \rho(t)], \quad (1)$$

where H represents the spin Hamiltonian operator and, for the sake of illustration, is assumed to be time independent.

In the multipole approach^{33–37} the density operator for an N spin system is represented by

$$\rho(t) = \frac{1}{N} \sum_{\substack{k,q,\{K\} \\ \text{all } k_1, k_2, \dots, k_N}} \Phi_{q,\{K\}}^{(k)}(k_1, k_2, \dots, k_N, t) \times T_{\{K\}}^{(k)q}(k_1, k_2, \dots, k_N), \quad (2)$$

where $\Phi_{q,\{K\}}^{(k)}(k_1, k_2, \dots, k_N, t)$ represents the time-dependent spin polarization and $T_{\{K\}}^{(k)q}(k_1, k_2, \dots, k_N)$ the corresponding irreducible spin tensor operator with labels k , q , and $\{K\}$ defining the configuration of the spin polarization (i.e., the rank, coherence order, and number of spins involved, etc.) in the operator space. The superscript k denotes the total rank of the spherical tensor and ranges from $0 \leq k \leq 2I$, with I representing the total spin angular momentum of the system (i.e., $I = I_1 + I_2 + \dots + I_N$). The total rank k essentially describes the number of ways in which the spin angular momentum vectors are coupled in describing the system. The subscript q represents the component of the spherical tensor associated with a particular rank k (whose values range from $-k \leq q \leq k$) and is directly associated with the coherence order. Depending on the coupling scheme (i.e., coupling of angular momentum vectors), the spin system is further described by a set of intermediate angular momentum vectors represented by $\{K\}$ (i.e., for an N spin system, $N-2$ intermediate coupling constants are defined, $\{K\} = \{K_1, \dots, K_{N-2}\}$). The individual ranks of the spins involved are described by the indices k_1, k_2, \dots, k_N ; each of whose values ranges from 0 to $2I_i$. For convenience, the following compact notation employed by Sanctuary *et al.*³⁷ will be employed in this paper:

$$\rho(t) = \frac{1}{N} \sum_{k,q,\bar{\alpha}} \Phi_q^{(k)}(\bar{\alpha}, t) T^{(k)q}(\bar{\alpha}), \quad (3)$$

where $\bar{\alpha}$ is representative of all the quantum numbers illustrated previously for the description in the operator space. In a similar vein the Hamiltonian of the system is also expressed in the same basis as that of the density operator and is represented by

$$H = \sum_{l,m,\bar{\alpha}} C_{lm(\bar{\alpha})} T^{(l)m}(\bar{\alpha}), \quad (4)$$

where l and m denote the rank and component of the tensor, respectively, with $l \leq 2$ being the standard case in NMR experiments. The interaction parameters corresponding to the Zeeman, dipole-dipole, and quadrupolar interactions are represented by the $C_{lm(\bar{\alpha})}$ coefficients.

Substituting $\rho(t)$ and H in the Liouville equation [Eq. (1)], yields a set of differential equations spanning the entire operator space,

$$i\hbar \frac{d}{dt} \Phi_q^{(k)}(\bar{\alpha}, t) = \sum_{k', q', \alpha'} \sum_{l, m, \alpha_1} C_{lm}(\bar{\alpha}_1) \text{Tr} \left\{ T^{(k)-q}(\bar{\alpha}) \right. \\ \left. \times L^{(l)m}(\bar{\alpha}_1) T^{(k')q'}(\bar{\alpha}') \right\} \Phi_{q'}^{(k')}(\bar{\alpha}', t), \quad (5)$$

where $L^{lm}(\bar{\alpha}_1) = [T^{lm}(\bar{\alpha}_1)]$ corresponds to the Liouville superoperator. The above equation can be conveniently reexpressed in matrix form as

$$i\hbar \frac{d}{dt} \Phi_q^{(k)}(\bar{\alpha}, t) = [A]_{kq, k'q'} \Phi_{q'}^{(k')}(\bar{\alpha}', t), \quad (6)$$

wherein the spin polarizations $\Phi_q^{(k)}(\bar{\alpha}, t)$ are represented by column vectors with $[A]$ representing the supermatrix whose elements are evaluated using the Wigner–Eckart theorem.^{47,48} The various steps involved in the evaluation of the elements of the supermatrix are explained in detail in Appendix A. In contrast to other existing basis, the symmetry embedded in the multipole basis reduces the problem to a set of coupled first-order differential equations whose solutions depend on the appropriate initial conditions, $\Phi_q^{(k)}(\bar{\alpha})[0]$ [at time $t=0$, the $\Phi_q^{(k)}(\bar{\alpha}, t)$ terms represent a scalar coefficient (i.e., $\Phi_q^{(k)}(\bar{\alpha}, 0)$],

$$\Phi_i(t) = \sum_{j,k} \zeta_{ik} e^{i\lambda_k t} \zeta_{kj}^{-1} \Phi_j(0), \quad (7)$$

with ζ_{ik} and λ_k representing the eigenvectors and eigenvalues, respectively.

In the absence of rf fields, the supermatrix $[A]$ is block diagonal, thereby constraining the dynamics to a particular coherence order q in the operator space. Using this approach, Sanctuary *et al.*³⁷ derived analytical expressions for single spin systems to explain several interesting experimental situations. Since the entire formalism relies on spin angular momentum algebra, extensions to $I > 1/2$ and multiple spin systems are relatively straightforward.

However, in the presence of rf fields, the spin dynamics is described in the entire operator space (mainly due to the mixing of coherences of various orders, i.e., the tensors now orient in the $(2k+1)$ -dimensional space),⁴⁹ thereby restricting analytical treatments to two spins. In such cases, the standard approach involves the use of numerical methods to diagonalize the supermatrix at the expense of analytical insights. This provides the motivation for the development of an analytical theory of spin dynamics in such cases.

To address this problem, we propose an analytical treatment based on the concept of effective Hamiltonians obtained using the van Vleck or contact transformation method. The contact transformation method is an operator equivalent of standard perturbation theory in which perturbation corrections are obtained in terms of effective Hamiltonians. This differs from traditional perturbation theory where corrections are expressed in terms of matrix elements. Using the effective Hamiltonians, calculations of the spin dynamics is constrained in a lesser dimension corresponding to a particular coherence order rather than the entire operator (or Liouville) space. Such simplifications facilitate the study of multiple-quantum coherences and multiple-quantum phenomena in

general. This is in contrast to the standard multipole approach, which involves a description in the entire operator space under rf irradiation.

In cases where the Hamiltonians are explicitly time dependent (as is true for MAS experiments) special theoretical approaches (such as Floquet theory) are required to solve the above set of differential equations involving time-dependent coefficients. In the following section, we illustrate the application and utility of the multipole based multimode Floquet theory^{24,25} for studying the dynamics under asynchronous time modulations.

B. MMFT

The nuclear spin Hamiltonian in the rf interaction frame in multiple pulse SSNMR experiments involve explicit time-dependent coefficients due both to MAS as well as the rf irradiation. Such periodic time-dependent (with multiple time modulations) phenomena are easily analyzed using Floquet theory as opposed to the average Hamiltonian approach, which is valid only for time modulations which are linearly dependent and occur on different time scales. Furthermore, existing bases employed in theoretical treatments [both in Floquet theory^{27,29,50} and AHT (Ref. 3)] do not provide analytical insights beyond two spins and are often difficult to extend to multiple spins and $I > 1/2$ systems. To this end the MMFT approach seems a viable alternative for describing both coherent as well as incoherent effects observed in solid-state NMR experiments.

By integrating the multipole formalism of Sanctuary with Shirley's Floquet approach, it is possible to expand any periodic time-dependent spin Hamiltonian as well as the density operator in a Fourier series,

$$H(t) = \sum_{n_1 \rightarrow m = -\infty}^{\infty} H_{n_1 \rightarrow m} e^{it\omega.n}, \quad (8)$$

$$\rho(t) = \sum_{n_1 \rightarrow m = -\infty}^{\infty} \sum_{k, q, \bar{\alpha}} \Phi_{q, n_1 \rightarrow m}^{(k)}(\bar{\alpha}, t) T^{(k)q}(\bar{\alpha}) e^{it\omega.n}, \quad (9)$$

where we have used the following notation: $n_1 \rightarrow m = n_1, n_2, \dots, n_m$, $A_{n_1 \rightarrow m} = A_{n_1, n_2, \dots, n_m}$, $\omega = \{\omega_1, \omega_2, \dots, \omega_m\}$, $n = \{n_1, n_2, \dots, n_m\}$, $\omega.n = \omega_1 n_1 + \omega_2 n_2 + \dots + \omega_m n_m$. Note that n_i , ω_i represent the Fourier index and frequency associated with a particular time modulation, respectively. Using the same procedure, the Liouville superoperator may be expressed as

$$L(t) = \sum_{n_1 \rightarrow m = -\infty}^{\infty} L(\bar{\alpha}_1)_{n_1 \rightarrow m}^{(l)m} e^{it\omega.n}. \quad (10)$$

Substituting the Fourier expansions of the density operator $\rho(t)$ and the Liouville super operator $L(t)$ in Eq. (1), a new set of coupled differential equations spanning an infinite dimensional vector space (or Floquet–Liouville space), with time-independent coefficients are obtained,

$$i\hbar \frac{d}{dt} \Phi(\bar{\alpha}, t)_{q, n_1 \rightarrow m}^{(k)} = \sum_{n'_1 \rightarrow m = -\infty}^{\infty} \sum_{k', q', \bar{\alpha}', l, m, \bar{\alpha}_1} \sum_{l, m, \bar{\alpha}_1} (\text{Tr}\{T^{(k)-q}(\bar{\alpha}) \times L(\bar{\alpha}_1)_{n_1 \rightarrow m}^{lm} T^{(k')q'}(\bar{\alpha}')\} + (n \cdot \omega) \delta) \Phi(\bar{\alpha}', t)_{q', n'_1 \rightarrow m}^{(k')} \quad (11)$$

In the above expression $\delta = \delta_{n_1, n'_1} \dots \delta_{n_m, n'_m} \delta_{k, k'} \delta_{q, q'} \delta_{k_1, k'_1} \dots \delta_{k_N, k'_N} \delta_{\{K\}, \{K'\}}$ and $\delta_{\{K\}, \{K'\}}$ implies $\delta_{K_1, K'_1} \delta_{K_2, K'_2} \dots \delta_{K_{N-2}, K'_{N-2}}$ with K referring to the intermediate coupling of the angular momentum vectors. The above equation differs from the one derived using the wave function approach [Eq. (B5), Appendix B], in the sense that all the basis functions and operators are described in terms of irreducible tensor operators which, in addition to simplifying the description of interactions involving multiple spins (of arbitrary spin magnitudes), also provides physical insights in to the spin dynamical problem of interest. The notation $L(\bar{\alpha}_1)_{n_1 \rightarrow m}^{(l)m}$ refers to $L(\bar{\alpha}_1)_{n_1 \rightarrow m}^{(l)m}$ and includes the interaction coefficients as well as the spin and Fourier operators. The above equation [i.e., Eq. (11)] can be reexpressed in matrix notation,

$$i\hbar \frac{d}{dt} \Phi_{q, n_1 \rightarrow m}^{(k)}(\bar{\alpha}, t) = [[A]_{kq, k'q'}]_{n_1 \rightarrow m, n'_1 \rightarrow m} \Phi_{q', n'_1 \rightarrow m}^{(k')}(\bar{\alpha}', t),$$

where $[[A]_{kq, k'q'}]_{n_1 \rightarrow m, n'_1 \rightarrow m}$ represents the supermatrix defined in the infinite dimensional Floquet–Liouville space. Subsequently, the Floquet density operator and the Hamiltonian operator may be represented by

$$\rho_F(t) = \sum_{n_1 \rightarrow m = -\infty}^{\infty} \sum_{k, q, \bar{\alpha}} \Phi_{q, n_1 \rightarrow m}^{(k)}(\bar{\alpha}, t) T^{(k)q}(\bar{\alpha}) F_{r_1}^1 F_{r_2}^2 \dots F_{r_m}^m, \quad (12)$$

$$H_F = \sum_{r_1 \rightarrow m = -\infty}^{\infty} \sum_{k, q, \bar{\alpha}} T^{(k)q}(\bar{\alpha}) F_{r_1}^1 F_{r_2}^2 \dots F_{r_m}^m + \sum_{i=1}^m \omega_i N^i. \quad (13)$$

The Floquet Hamiltonian described above is represented using an operator basis constructed by the direct product of operators defined both in the spin ($T^{(k)q}$) as well as the Fourier dimensions ($F_{r_m}^m$, corresponding to m th time modulation) with the off-diagonality represented by the indices q and r_m , respectively. Using these operators, the Floquet Hamiltonian is schematically represented by (see Fig. 1) where each element $[H_i]$ corresponds to a matrix, defined in the Liouville space and is off-diagonal, both in the spin as well as in the Fourier dimension. The infinite dimensionality results from the Fourier decomposition of both the density operator as well as the Liouville super operator and is often solved numerically by truncating the dimension of the Floquet Hamiltonian matrix.

We believe that the technique proposed here continues to provide analytical insights in spite of the infinite dimensionality of the problem. To validate this claim we describe an analytical solution in the form of effective Hamiltonians obtained via contact or van Vleck transformation procedure. In addition to the infinite dimensionality, the complexity in-

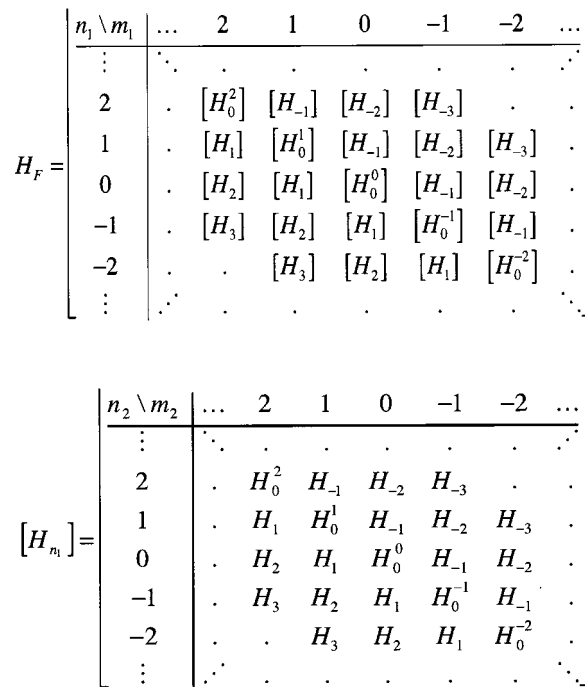


FIG. 1. Representation of the Floquet Hamiltonian involving two time modulations.

involved in the diagonalization of the Floquet Hamiltonian using perturbation theory lies in the off-diagonality both in the Fourier as well as in the spin dimension. This necessitates a description in the entire Floquet–Liouvilian space, and often becomes intractable for analytical treatments beyond two spins unless the correct choice of basis is made. In the following section we illustrate the effective Hamiltonian approach via van Vleck transformation and the underlying advantages associated in the spin dynamical calculations.

C. Effective Hamiltonians via van Vleck or contact transformation method

The contact transformation method is an operator transformation based on the standard perturbation theory, wherein perturbation corrections to the zero-order eigenvalues and eigenvectors are obtained by means of effective Hamiltonians rather than in terms of matrix elements. Using the contact transformation method, effective Hamiltonians have been obtained both in the static^{51,52} as well as in the MAS case.^{30,50} The method essentially involves a series of unitary transformations which diagonalize a Hamiltonian containing a zero order and a series of other interaction terms whose magnitudes decrease in an appropriately chosen order of magnitude scheme. In order to apply the contact transformation procedure, the Floquet Hamiltonian represented in Eq. (13) is divided in to a sum involving a zero-order Hamiltonian and a series of other interaction terms (or perturbations). For the sake of illustration, we consider here only a single perturbing term H_1 ,

$$H_F = H_0 + H_1. \quad (14)$$

The zero-order Hamiltonian H_0 is chosen to contain operators which are diagonal in the spin as well as the Fourier

dimension (i.e., time-independent terms), represented below,

$$H_0 = \sum_{\bar{\alpha}, k} G_0(\bar{\alpha}) T^{(k)0}(\bar{\alpha}) F_0^{(1)} F_0^{(2)} \dots F_0^{(m)} + \sum_{i=1}^m \omega_i N^i, \quad (15)$$

and $G_0(\bar{\alpha})$ is representative of the time-independent spin interaction coefficients such as the scaled isotropic chemical shifts (due to rf irradiation), J -coupling constants, etc. The perturbing Hamiltonian H_1 contains operators, which are off-diagonal either in the spin or the Fourier or in both dimensions

$$H_1 = \sum_{r_1 \rightarrow m} \sum_{k, q, \bar{\alpha}} G_{r_1 \rightarrow m}(\bar{\alpha}, q) T^{(k)q}(\bar{\alpha}) F_{r_1}^{(1)} F_{r_2}^{(2)} \dots F_{r_m}^{(m)}. \quad (16)$$

The nonzero $G_{r_1 \rightarrow m}(\bar{\alpha}, q)$ coefficients illustrated above involve interaction parameters dependent on MAS or rf irradiation or both. The $T^{(k)q}(\bar{\alpha}) (q \neq 0)$ operators represent the off-diagonality in the spin dimension, while $F_{r_m}^{(m)}$ the off-diagonality in the Fourier dimension associated with the m th modulation. In general, it is always preferable to arrange the interaction terms in a series of perturbations based on their coherence orders. Such an approach often simplifies further calculations and also assists in averting accidental degeneracy's present in the system.

The effective Floquet Hamiltonian H_F^{eff} is obtained by transforming the highly off-diagonal Floquet Hamiltonian H_F using an unitary transformation,

$$H_F^{eff} = U_1 H_F U_1^{-1} = e^{i\lambda S_1} H_F e^{-i\lambda S_1} = H_0^{(1)} + H_1^{(1)} + H_2^{(1)} + \dots,$$

$$H_0^{(1)} = H_0,$$

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

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

$$H_n^{(1)} = H_n + \sum_{m=0}^{n-1} \frac{i^{n-m}}{(n-m)!} \underbrace{[S_1, [S_1 \dots [S_1, H_m] \dots]]}_{n-m}. \quad (17)$$

In the above equation the terms H_1, H_2, \dots, H_n represent the perturbations present in the original Hamiltonian (i.e., $H_F = H_0 + \lambda H_1 + \lambda^2 H_2 + \dots + \lambda^n H_n$, wherein λ represents the perturbation parameter).

The transformation function S_1 is generally expressed as a linear combination of spin operators (with suitable coefficients) employed in the description of the perturbing Hamiltonian. For example, if the perturbing Hamiltonian H_1 consists of single quantum operators ($q = \pm 1$), the transformation function should in principle involve a linear combination of all single quantum spin operators employed,

$$S_1 = i \sum_{r_1 \rightarrow m} \sum_{k, q, \bar{\alpha}} C_{r_1 \rightarrow m}(\bar{\alpha}, q) T^{(k)q}(\bar{\alpha}) F_{r_1}^{(1)} F_{r_2}^{(2)} \dots F_{r_m}^{(m)}, \quad (18)$$

and $C_{r_1 \rightarrow m}(\bar{\alpha}, q)$ corresponds to a set of coefficients (dependent on both the spin as well as Fourier coefficients) suitably

chosen to compensate the off-diagonality in the perturbing Hamiltonian H_1 . The $C_{r_1 \rightarrow m}(\bar{\alpha}, q)$ coefficients corresponding to each operator in the transformation function are obtained by solving the following equation:

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

and may be represented in general as

$$C_{r_1 \rightarrow m}(\bar{\alpha}, q) \approx \frac{G_{r_1 \rightarrow m}(\bar{\alpha}, q)}{n_1 \omega_1 + n_2 \omega_2 + \dots + n_m \omega_m + q G_0(\bar{\alpha})} \quad (20)$$

with $G_0(\bar{\alpha})$, $G_{r_1 \rightarrow m}(\bar{\alpha}, q)$ being the coefficients associated with the zero order and the perturbing Hamiltonian, respectively. The $C_{r_1 \rightarrow m}(\bar{\alpha}, q)$ coefficients in addition to compensating the off-diagonality in H_1 , also compensate the residual off-diagonality due to the commutator expression $[S_1, H_0]$. The second-order or diagonal corrections to the zero-order Hamiltonian are obtained by evaluating Eq. (21),

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

Since $H_2 = 0$, the above equation reduces to $H_2^{(1)} = (i/2)[S_1, H_1]$.

The diagonal corrections (diagonal in both spin as well as the Fourier dimension) to the zero-order Hamiltonian are obtained only by evaluating commutator relations of the type given below:

$$[T^{(k)q}(\alpha) F_{r_1}^1 F_{r_2}^2 \dots F_{r_m}^m, T^{(k')-q}(\alpha') F_{-r_1}^1 F_{-r_2}^2 \dots F_{-r_m}^m] \quad (22a)$$

or

$$[T_{r_1, r_2, \dots, r_m}^{(k)q}(\alpha), T_{-r_1, -r_2, \dots, -r_m}^{(k')-q}(\alpha')]. \quad (22b)$$

In order to evaluate Eq. (22) the following relations among the Fourier operators were employed:

$$F_l^m F_n^m = F_{l+n}^m, \quad (23a)$$

$$[F_l^m, N^m] = l F_l^m, \quad (23b)$$

$$[F_l^m, F_l^{m'}] = 0, \quad (23c)$$

$$[F_l^m, F_n^m] = 0. \quad (23d)$$

The commutator relations among the spin operators $[T^{(k)q}(\alpha), T^{(k')-q}(\alpha')]$ are evaluated using the relation illustrated in Appendix A.

$$H_F^{eff} \approx \begin{bmatrix} n_1 \setminus m_1 & \dots & 2 & 1 & 0 & -1 & -2 & \dots \\ \vdots & \ddots & \cdot & \cdot & \cdot & \cdot & \cdot & \ddots \\ 2 & \cdot & [H_0^2]^\dagger & \cdot & \cdot & \cdot & \cdot & \cdot \\ 1 & \cdot & \cdot & [H_0^1]^\dagger & \cdot & \cdot & \cdot & \cdot \\ 0 & \cdot & \cdot & \cdot & [H_0^0]^\dagger & \cdot & \cdot & \cdot \\ -1 & \cdot & \cdot & \cdot & \cdot & [H_0^{-1}]^\dagger & \cdot & \cdot \\ -2 & \cdot & \cdot & \cdot & \cdot & \cdot & [H_0^{-2}]^\dagger & \cdot \\ \vdots & \ddots & \cdot & \cdot & \cdot & \cdot & \cdot & \ddots \end{bmatrix}$$

FIG. 2. Representation of the effective Floquet Hamiltonian obtained from the contact transformation method. Each block corresponds to a matrix defined in the operator space.

The effective Hamiltonian so obtained ($H_F^{eff} \approx H_0 + H_2^{(1)}$) incorporates all the corrections (to appropriate orders) in terms of operators (which are diagonal in both the spin as well as the Fourier dimension) and is block diagonal in this approach (see Fig. 2),

The eigenvector coefficients associated with each of these block matrices $[H_0^i]^*$ in the effective Hamiltonian are identical to one another and differ only in their representation in the Floquet Liouville space. Since the Floquet eigenvalues differ only by integer multiples of the various modulation frequencies, the eigenvalues corresponding to the various blocks $[H_0^i]^*$ can in principle be obtained by just diagonalizing the superblock $[H_0^0]^*$ (whose Fourier indices are simultaneously zero). The importance of the effective

Hamiltonians in the spin dynamical calculations will be described in the following section.

D. Spin dynamics in the Floquet–Liouville space

The Floquet modes, which are coupled in the untransformed Floquet Hamiltonian representation Eq. (24a) are uncoupled in the representation Eq. (24b) employing the effective Floquet Hamiltonians derived using the van Vleck transformation method. This simplifies the calculations to a great extent in the Floquet–Liouville space, since the time evolution of the multimode spin polarizations $\Phi_{q,n_1 \rightarrow m}^{(k)}(\alpha, t)$ can now be described using a set of differential equations corresponding to a particular mode independent of other modes. This may be schematically illustrated as follows:

$$i\hbar \frac{d}{dt} \begin{bmatrix} \vdots \\ \Phi^{(2)}(t) \\ \Phi^{(1)}(t) \\ \Phi^{(0)}(t) \\ \Phi^{(-1)}(t) \\ \Phi^{(-2)}(t) \\ \vdots \end{bmatrix} = \begin{bmatrix} \ddots & \ddots & \ddots & & & & \\ \ddots & [A_0]_2 & [A_1] & [A_2] & & & \\ \ddots & [A_{-1}] & [A_0]_1 & [A_1] & [A_2] & & \\ & [A_{-2}] & [A_{-1}] & [A_0]_0 & [A_1] & [A_2] & \\ & & [A_{-2}] & [A_{-1}] & [A_0]_{-1} & [A_1] & \\ & & & [A_{-2}] & [A_{-1}] & [A_0]_{-2} & \\ \ddots & & & & \ddots & \ddots & \ddots \end{bmatrix} \begin{bmatrix} \vdots \\ \Phi^{(2)}(t) \\ \Phi^{(1)}(t) \\ \Phi^{(0)}(t) \\ \Phi^{(-1)}(t) \\ \Phi^{(-2)}(t) \\ \vdots \end{bmatrix}, \quad (24a)$$

$$i\hbar \frac{d}{dt} \begin{bmatrix} \vdots \\ \Phi^{(2)}(t) \\ \Phi^{(1)}(t) \\ \Phi^{(0)}(t) \\ \Phi^{(-1)}(t) \\ \Phi^{(-2)}(t) \\ \vdots \end{bmatrix} = \begin{bmatrix} \ddots & & & & & & \\ & [A_0]_2^* & & & & & \\ & & [A_0]_1^* & & & & \\ & & & [A_0]_0^* & & & \\ & & & & [A_0]_{-1}^* & & \\ & & & & & [A_0]_{-2}^* & \\ \ddots & & & & & & \ddots \end{bmatrix} \begin{bmatrix} \vdots \\ \Phi^{(2)}(t) \\ \Phi^{(1)}(t) \\ \Phi^{(0)}(t) \\ \Phi^{(-1)}(t) \\ \Phi^{(-2)}(t) \\ \vdots \end{bmatrix}, \quad (24b)$$

where the multimode spin polarizations are represented by $\Phi^{(i)}(t)$ with the superscript indicating the Fourier index associated with a particular mode. Each of these modes $\Phi^{(i)}(t)$ [Eq. (25)], in turn represent, column vectors corresponding to the spin polarizations $\Phi_q^{(k)}(\alpha, t)$ defined in the operator (or Liouville) space

$$\Phi^{(i)}(t) = \begin{bmatrix} \Phi_q^{(k)}(\alpha, t) \\ \vdots \\ \vdots \\ \vdots \\ \vdots \\ \vdots \\ \vdots \\ \vdots \\ \vdots \\ \Phi_{-q}^{(k)}(\alpha, t) \end{bmatrix}. \quad (25)$$

The highly off-diagonal supermatrix $[[A]_{kq, k'q'}]_{n_1 \rightarrow m, n'_1 \rightarrow m}$ [given in Eq. (11)] is transformed under van Vleck transfor-

mation into block diagonal matrices $[A_b]_c^*$, where the index b represents the difference in the Fourier indices between the modes and c the Fourier index in the Floquet–Liouville space. Each of these matrices $[A_b]_c^*$ represent a supermatrix, which is block diagonal within the operator space corresponding to a particular coherence order q . This may be schematically represented as (see Fig. 3).

Since the multimode spin polarizations are uncoupled, their time evolution can be described using a set of differential equations pertaining to a particular mode in the operator space, i.e.,

$$i\hbar \frac{d}{dt} \Phi^{(i)}(t) = [A]_i \Phi^{(i)}(t), \quad (26)$$

$$\Phi_a^{(i)}(t) = \sum_{jk} \Gamma_{ak}^{(i)} e^{i\lambda_k^{(i)} t} [\Gamma_{kj}^{(i)}]^{-1} \Phi_j^{(i)}(0). \quad (27)$$

In the above expression $\Gamma_{ak}^{(i)}$ and $\lambda_k^{(i)}$ represent the eigenvectors and eigenvalues corresponding to a particular mode (de-

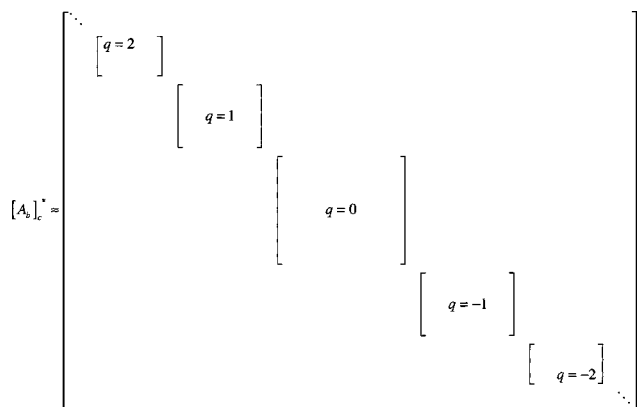


FIG. 3. The Hamiltonian in the operator space is block diagonal corresponding to the coherence order.

noted by the superscript), respectively. The subscript in $\Phi_a^{(i)}(t)$ is representative of all the quantum numbers (such as the rank, component, etc.) employed in the description of the spin polarization in the operator space. Since the eigenvectors corresponding to different modes are identical, with the eigenvalues differing only by integer multiples of the modulating frequencies, Eq. (27) in principle can be reexpressed as

$$\Phi_a^{(i)}(t) = \sum_{jk} \Gamma_{ak} e^{it(\lambda_k + \omega_n)} \Gamma_{kj}^{-1} \Phi_j^{(i)}(0), \quad (28)$$

where λ_k represents the eigenvalues corresponding to the supermatrix $[A_0]_0^*$. The term $\Phi_j^{(i)}(0)$ represents the initial condition for the spin polarizations within the operator space corresponding to a particular Fourier mode (represented by the superscript i).

The initial condition at time $t=0$ involves only those Floquet modes whose Fourier indices are zero, i.e., $\rho(0) = \Phi^{(0)}(0)$. This choice of the initial condition is appropriate as no evolution takes place at $t=0$, and is in agreement with other standard theoretical approaches employed for spin description in a finite dimensional space. Since the Floquet Hamiltonian has been transformed into a new frame (in which it is diagonal), it becomes essential for the initial condition, $\rho(0)$, to be described in a common frame. This may be illustrated by the following transformation:

$$\tilde{\rho}(0) = e^{i\lambda S_1} \rho(0) e^{-i\lambda S_1} = \rho(0) + [S_1, \rho(0)] + \dots \quad (29)$$

In this new frame, in addition to the $\Phi^{(0)}(0)$ term, initial conditions for other multimode polarizations $[\Phi^{(i)}(0), i \neq 0]$ result from the evaluation of higher-order terms in Eq. (28) (such as $[S_1, \rho(0)] + \dots$). However, these multimode polarizations ($\Phi^{(i)}(0), i \neq 0$) are scaled accordingly (by a factor $1/n_1\omega_1 + n_2\omega_2 + \dots + n_m\omega_m$, due to the transformation function S_1), thereby minimizing their contributions in the Floquet–Liouville space. This enables an approximate description of the spin dynamics in a reduced subspace, corresponding to the superblock $[A_0]_0^*$ (commonly referred as fast spinning regime in solid-state NMR), and is illustrated below:

$$i\hbar \frac{d}{dt} \Phi^{(0)}(t) = [A_0]_0^* \Phi^{(0)}(t), \quad (30)$$

$$\Phi_a^{(0)}(t) = \sum_{jk} \Gamma_{ak} e^{i\lambda_k t} \Gamma_{kj}^{-1} \Phi_j^{(0)}(0).$$

This is analogous to the standard description of polarization transfer experiments described in a finite dimensional vector space. For sideband simulations (usually observed in the slow spinning regime), higher-order terms in the expansion of $\tilde{\rho}(0)$ become significant and the spin polarizations are evaluated with suitable modifications given below:

$$\Phi(t) = \sum_{i=-\infty}^{\infty} \Phi^{(i)}(t), \quad (31)$$

$$\Phi_a^{(i)}(t) = \sum_{jk} \Gamma_{ak} e^{i\lambda_k t} \Gamma_{kj}^{-1} \Phi_j^{(i)}(0) e^{it\omega_n}.$$

The symmetry embedded in the multipole basis further renders the supermatrix $[A_0]_0^*$ block diagonal and simplifies the evaluation of Eq. (30) (corresponding to a particular coherence order q) in the operator (or Liouville) space. Such simplifications within the operator (or Liouville) space facilitate spin dynamical calculations involving higher spin magnitudes (e.g., quadrupolar nuclei) and multiple spins in addition to providing valuable insights into the dynamical behavior of spin systems of interest. This is in contrast to other traditional approaches employed in Floquet theory, which often describe the calculations in the truncated Floquet–Liouville space with limited physical insight into the spin dynamical problem. Hence, the choice of multipole basis in conjunction with the effective Hamiltonians obtained using the van Vleck transformation method appears to be an attractive solution for describing the spin dynamics in complex systems. The application of this theory in understanding the nuances of heteronuclear decoupling and other solid-state NMR experiments are described in the accompanying manuscript.

III. CONCLUSIONS

In summary we have introduced a novel approach based on multimode Floquet theory for predicting the spin dynamics in solid-state NMR experiments involving multiple time modulations on arbitrary and even competing time scales. The MMFT approach describes the spin dynamics in the Floquet–Liouville space using the effective Hamiltonians obtained from the contact transformation besides employing irreducible spherical tensor operators (or multipole operators) as basis functions or operators for spin description. Since the multipole operators are built on the principles of angular momentum, its application towards higher spin magnitudes (e.g., quadrupolar systems) and extensions to multiple spin systems are quite straightforward and elegant for analytical treatments. This is in contrast to other currently existing bases in NMR, which are both inadequate in treating the dynamics beyond two spins as well as for higher spin magnitudes.

The difficulties encountered in dealing with the Floquet–Liouvillian space are significantly reduced when compared with traditional Floquet calculations, involving a description of the entire Floquet–Liouville space. Such simplifications result from the van Vleck or contact transformation procedure, involving the perturbation corrections (both in the spin space as well as the Fourier space) in terms of operators thereby leading to effective Hamiltonians. Moreover, calculations involving arbitrary number of spins (of any magnitude) require a single commutator relation (given in Appendix A) in contrast to other methods, which involve the evaluation of multiple commutator relations and are often intractable beyond two spins. The theoretical approach illustrated here has tremendous potential for studying a wide range of NMR phenomena involving synchronous/asynchronous time modulations and will be illustrated in future publications. The MMFT approach provides a general framework for studying the effects of relaxation along with the spin dynamics in the operator space. A rigorous description of relaxation processes using the MMFT approach will be described elsewhere.

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APPENDIX A: LIOUVILLE SUPERMATRIX

The appendix presents an approach for evaluating the matrix elements of the supermatrix using the commutator relations among the irreducible spherical tensor operators. The approach is quite general for multiple spins of arbitrary spin magnitude.

The general procedure for evaluating Eq. (5),

$$i\hbar \frac{d}{dt} \Phi_q^{(k)}(\bar{\alpha}, t) = \sum_{k', q', \bar{\alpha}'} \sum_{l, m, \bar{\alpha}_1} C_{lm}(\bar{\alpha}_1) \text{Tr}\{T^{(k)-q}(\bar{\alpha}) \times L^{(l)m}(\bar{\alpha}_1) T^{(k')q'}(\bar{\alpha}')\} \Phi_{q'}^{(k')}(\bar{\alpha}', t), \quad (\text{A1})$$

has already been derived explicitly for single spin systems and briefly for multispin systems by Sanctuary *et al.*³⁷ For the sake of clarity and continuity we elaborate here the spin dynamics involving multiple spins. The solution to Eq. (A1) lies in the evaluation of the commutator relation involving the irreducible tensor operators and has been derived in general for arbitrary number of spins by Sanctuary *et al.*³⁷ Here we repeat the same expression (with appropriate typographical corrections) for the sake of interested readers,

$$\begin{aligned} [T_{\{L\}}^{(l)m}(l_1, l_2, \dots, l_N), T_{\{K'\}}^{(k')q'}(k'_1, k'_2, \dots, k'_N)] = & \sum_{\text{all } k''_N, K''_{N-2}, k'', q''} 2\phi_{i=1 \rightarrow N}(l_i k'_i k''_i) (-1)^{2(l_1 + l_2 + \dots + l_N)} \\ & \times (i)^{l_1 + l_2 + \dots + l_N} (i)^{k'_1 + k'_2 + \dots + k'_N} (i)^{k''_1 + k''_2 + \dots + k''_N} \\ & \sqrt{\prod_{i=1}^{N-2} (2L_i + 1) \prod_{i=1}^{N-2} (2K'_i + 1) \prod_{i=1}^{N-2} (2K''_i + 1) \prod_{i=1}^N (2l_i + 1) \prod_{i=1}^N (2k'_i + 1) \prod_{i=1}^N (2k''_i + 1)} \\ & \times \sqrt{(2l + 1)(2k' + 1)(2k'' + 1)} \begin{Bmatrix} k''_1 & l_1 & k'_1 \\ I_1 & I_1 & I_1 \end{Bmatrix} \begin{Bmatrix} k'_2 & l_2 & k'_2 \\ I_2 & I_2 & I_2 \end{Bmatrix} \dots \begin{Bmatrix} k''_N & l_N & k'_N \\ I_N & I_N & I_N \end{Bmatrix} \\ & \times \begin{Bmatrix} l_1 & l_2 & L_1 \\ k'_1 & k'_2 & K'_1 \end{Bmatrix} \begin{Bmatrix} L_1 & l_3 & L_2 \\ K'_1 & k'_3 & K'_2 \end{Bmatrix} \dots \begin{Bmatrix} L_{N-2} & l_N & l \\ K'_{N-2} & k'_N & k' \end{Bmatrix} \\ & \times \begin{Bmatrix} k''_1 & k''_2 & K''_1 \\ k''_1 & k''_2 & K''_1 \end{Bmatrix} \begin{Bmatrix} K''_1 & k''_3 & K''_2 \\ K''_1 & k''_3 & K''_2 \end{Bmatrix} \dots \begin{Bmatrix} K''_{N-2} & k''_N & k'' \\ K''_{N-2} & k''_N & k'' \end{Bmatrix} \\ & \times (-1)^{k'' - q''} \begin{pmatrix} l & k' & k'' \\ m & q' & -q'' \end{pmatrix} T_{\{K''\}}^{(k'')q''}(k''_1, k''_2, \dots, k''_N). \end{aligned} \quad (\text{A2})$$

In the above expression the notations

$$\begin{pmatrix} l & k' & k'' \\ m & q' & -q'' \end{pmatrix}, \begin{Bmatrix} k''_n & l_n & k'_n \\ I_n & I_n & I_n \end{Bmatrix}, \begin{Bmatrix} l_1 & l_2 & L_1 \\ k'_1 & k'_2 & K'_1 \\ k''_1 & k''_2 & K''_1 \end{Bmatrix}$$

correspond to the Wigner-3j, Wigner-6j, Wigner-9j symbols, respectively, and have been well documented in the literature. The selection rule for the above commutator relation is

defined by the coefficient $\phi_{i=1 \rightarrow n}(l_i k'_i k''_i)$, which has the following definition:

$$\begin{aligned} \phi_{i=1 \rightarrow n}(l_i k'_i k''_i) = & 1 \quad \text{if } \sum_{i=1}^N l_i + k'_i + k''_i = \text{odd} \\ & = 0 \quad (\text{otherwise}) \end{aligned} \quad (\text{A3})$$

and is quite general for multiple spins of arbitrary spin magnitudes.

In order to generate the differential equations corresponding to a given set of $k, q, k_1, k_2, \dots, k_N, \{K\}$ coefficients, the summation index on the right-hand side of the commutator expression is restricted to a particular set of coefficients corresponding to the left-hand side of Eq. (A1), i.e., $k''=k, q''=q, k_1''=k_1, k_2''=k_2, \dots, k_M''=k_M, \{K''\}=\{K\}$, and the various terms in the Hamiltonian operator (represented by the operator $T_{\{L\}}^{(l)m}(l_1, l_2, \dots, l_n)$) corresponding to different sets of interactions (represented by means of different sets of $l, m, l_1, l_2, \dots, l_N, \{L\}$ values) are evaluated for a given value of $k', q', k_1', k_2', \dots, k_N', \{K'\}$. This is then repeated for different sets of $k', q', k_1', k_2', \dots, k_N', \{K'\}$ values in order to generate other matrix elements along a row. The preceding two steps are repeated for each such values of $k, q, k_1, k_2, \dots, k_N, \{K\}$ to generate the entire matrix.

APPENDIX B: FLOQUET-STATE SPACE DESCRIPTION

The time evolution of a N -spin system in state space under a time-dependent Hamiltonian (with multiple time modulations) is represented by the Schrodinger equation

$$i\hbar \frac{d|\Psi(t)\rangle}{dt} = H(t)|\Psi(t)\rangle, \quad (\text{B1})$$

where the state function $|\Psi(t)\rangle$ is described by a set of orthonormal basis functions $|\Phi_i\rangle$, usually expressed as

$$|\Psi(t)\rangle = \sum_{i=1}^N C_i(t)|\Phi_i\rangle. \quad (\text{B2})$$

Using Floquet theorem and Shirley's approach the above state function and the periodic time-dependent Hamiltonian can be reexpressed via Fourier series expansion as follows:

$$H(t) = \sum_{n_1 \rightarrow m = -\infty}^{\infty} H_{n_1 \rightarrow m} e^{i\omega \cdot n}, \quad (\text{B3})$$

$$|\Psi(t)\rangle = \sum_{n_1 \rightarrow \infty = -\infty}^{\infty} \sum_{j=1}^N C_{jn_1 \rightarrow m}(t) |\Phi_j\rangle e^{i\omega \cdot n}. \quad (\text{B4})$$

On substitution in Eq. (B1) a set of differential equations spanning an infinite dimensional vector space is obtained,

$$\begin{aligned} & \sum_{n_1 \rightarrow m = -\infty}^{\infty} \sum_{j=1}^N \left[i\hbar \frac{d}{dt} C_{jn_1 \rightarrow m}(t) - (n_1\omega_1 + n_2\omega_2 + \dots + n_m\omega_m) C_{jn_1 \rightarrow m}(t) \right] |\Phi_j\rangle e^{i(n_1\omega_1 + n_2\omega_2 + \dots + n_m\omega_m)t} \\ &= \sum_{n_1' \rightarrow m = -\infty}^{\infty} H_{n_1' \rightarrow m} e^{i(n_1'\omega_1 + n_2'\omega_2 + \dots + n_m'\omega_m)t} \sum_{r_1 \rightarrow m = -\infty}^{\infty} \sum_{l=1}^N C_{lr_1 \rightarrow m}(t) |\Phi_l\rangle e^{i(r_1\omega_1 + r_2\omega_2 + \dots + r_m\omega_m)t}. \end{aligned} \quad (\text{B5})$$

Equating the exponential powers for each time modulations on both sides of the equation (i.e., $n_i = n_i' + r_i$) and rearranging we get the following set of differential equations:

$$\begin{aligned} i\hbar \frac{dC_{jn_1 \rightarrow m}(t)}{dt} &= \sum_{r_1 \rightarrow m = -\infty}^{\infty} \left\{ \sum_{l=1}^N H_{n_1 \rightarrow m - r_1 \rightarrow m}^{jl} \right. \\ & \left. + (\omega \cdot n) \delta_{n_p, r_1} \dots \delta_{n_m, r_m} \delta_{j,l} \right\} C_{lr_1 \rightarrow m}(t), \end{aligned} \quad (\text{B6})$$

where we have employed the notation $H_{n_1 \rightarrow m - r_1 \rightarrow m}^{jl} = \langle \Phi_j | H_{n_1 - r_1, \dots, n_m - r_m}^{jl} | \Phi_l \rangle$. Using the Floquet basis states $|n_{1 \rightarrow m} \Phi_j\rangle$ (which are constructed by a direct product of the spin basis with the Fourier basis states, i.e., $|n_{1 \rightarrow m}, \Phi_j\rangle = |\Phi_j\rangle \otimes |n_1\rangle \otimes |n_2\rangle \dots \otimes |n_m\rangle$) the state function in the Floquet space is defined as

$$|\Psi^F(t)\rangle = \sum_{n_1 \rightarrow m = -\infty}^{\infty} \sum_{j=1}^N C_{jn_1 \rightarrow m}(t) |n_{1 \rightarrow m}, \Phi_j\rangle. \quad (\text{B7})$$

Subsequently the Floquet Hamiltonian is defined via its matrix elements as

$$\begin{aligned} & \langle \Phi_j | n_1 \dots n_m | H_F | \Phi_l | r_1 \dots r_m \rangle \\ &= H_{n_1 \rightarrow m - r_1 \rightarrow m}^{jl} + (\omega \cdot n) \delta_{n_1, r_1} \dots \delta_{n_m, r_m} \delta_{j,l}. \end{aligned} \quad (\text{B8})$$

The Floquet Hamiltonian is represented by a direct product involving the spin (represented by T^{jl}) and the Fourier operators³² ($F_{n_m}^m$), i.e., $T^{jl} \otimes F_{n_1}^1 \otimes F_{n_2}^2 \dots \otimes F_{n_m}^m$ and may be represented by

$$H_F = C^{jl} T^{jl} F_{r_1 - n_1}^1 F_{r_2 - n_2}^2 \dots F_{r_m - n_m}^m + \sum_{i=1}^m \omega_i N_i, \quad (\text{B9})$$

where C^{jl} represents the coefficients involved in the Hamiltonian.

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