Constants of motion in NMR spectroscopy

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Abstract

We present a general method for constructing a subset of the constants of motion in terms of products of spin operators. These operators are then used to give insight into the multi-spin orders comprising the quasi-equilibrium state formed under a Jeener–Broekaert sequence in small, dipolar-coupled, spin systems. We further show that constants of motion that represent single-quantum coherences are present due to the symmetry of the dipolar Hamiltonian under $180°$ spin rotations, and that such coherences contribute a DC component to the FID which vanishes in the absence of the flip-flop terms and is only present for spin clusters with an odd number of spins.

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1. Introduction

In closed quantum systems, constants of motion other than the total energy are expected, and these additional constants of motion can lead to non-ergodic behavior. Examples of this are the unequal redistribution of magnetization under spin diffusion [1–3] or in the unequal redistribution of energy between equivalent phase space locations for energy redistribution in molecules [4]. Characterizing these additional constants of motion can therefore give insight into the origins of these non-ergodic processes.

For a given Hamiltonian $\widehat{H}$, the constants of motion are simply the projection operators onto degenerate eigenstates of $\widehat{H}$, and any linear combination of such operators. Given the set of eigenstates for $\widehat{H}$, $|\varepsilon_k\rangle$ (where $\widehat{H}|\varepsilon_k\rangle = \varepsilon_k|\varepsilon_k\rangle$), the projection operator, $\widehat{P}_{k,j} = |\varepsilon_k\rangle\langle\varepsilon_j|$, is a constant of motion only if $\varepsilon_j = \varepsilon_k$, since:

$$\frac{\mathrm{d}\widehat{P}_{k,j}}{\mathrm{d}t} = -\mathrm{i}[\widehat{H}, \widehat{P}_{k,j}]$$
$$= -\mathrm{i}(\varepsilon_k - \varepsilon_j)\widehat{P}_{k,j}. \tag{1}$$

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In the absence of degeneracies, the projection operators $\widehat{P}_{k,k}$ and their linear combinations are the only constants of motion.

In many systems, the exact eigenvectors and corresponding eigenvalues are not explicitly known, and hence the full set of constants of motion are also not known. However, a set of operators which represent a subset of the possible constants of motion can be constructed from the Hamiltonian, $\widehat{H}$, itself. Since $[\widehat{H}, \widehat{H}] = 0$, the operator $\widehat{H}$ is a constant of motion. Additionally, any function of $\widehat{H}$ is also a constant of motion. Defining the coefficient, $\lambda_{\widehat{A},\widehat{B}}$, for operators $\widehat{A}$ and $\widehat{B}$,

$$\lambda_{\widehat{A},\widehat{B}} = \frac{\mathrm{Trace}(\widehat{A}^\dagger\widehat{B})}{\mathrm{Trace}(\widehat{A}^\dagger\widehat{A})} \tag{2}$$

a set of orthogonal operators which are constants of motion can be constructed using a Gram-Schmidt orthogonalization procedure as follows:

$$\widehat{B}_0 = \widehat{1},$$

$$\widehat{B}_n = \widehat{H}^n - \sum_{k=0}^{n-1} \lambda_{\widehat{B}_k, \widehat{H}^n}\widehat{B}_k, \tag{3}$$

where the orthogonality condition is given by $\lambda_{\widehat{B}_k, \widehat{B}_j} = \delta_{k,j}$. The operators constructed using Eq. (3) represent linear combinations of the projection operators, $\widehat{P}_{k,k}$. If there are only $k \leqslant \mathrm{Dim}[\widehat{H}]$ distinct eigenvalues of $\widehat{H}$, then only k such linearly independent operators can be formed.

An arbitrary density matrix, $\widehat{\rho}$, can be written as

$$\widehat{\rho} = \widehat{\rho}_{\mathrm{QE}} + \widehat{\rho}_{\mathrm{Rest}}, \tag{4}$$

where $\widehat{\rho}_{\mathrm{QE}}$ represents the part of $\widehat{\rho}$ which does not evolve under $\widehat{H}$, sometimes referred to as a quasi-equilibrium [1–3,5,6]. In general, $\widehat{\rho}_{\mathrm{QE}}$ can be written as

$$\widehat{\rho}_{\mathrm{QE}} = \sum_k \beta_{\widehat{B}_k} \widehat{B}_k + \widehat{\rho}_{\mathrm{QE,Degeneracies}}, \tag{5}$$

where the operators $\widehat{B}_k$ are constructed using Eq. (3), $\beta_{\widehat{B}_k} = \lambda_{\widehat{B}_k,\widehat{\rho}}$ and $\widehat{\rho}_{\mathrm{QE,Degeneracies}}$ represent the constants of motion due to projection operators between degenerate states, $\widehat{P}_{k,j}$ for $k \neq j$, which cannot be created using the Hamiltonian, $\widehat{H}$, itself.

Applications of Eq. (3) to dipolar-coupled spin systems are presented in this work. In particular, constants of motion generated using Eq. (3) are used to analyze the quasi-equilibrium state formed under a Jeener–Broekaert (JB) sequence, and it is demonstrated that multi-spin order other than dipolar order can be generated in small spin systems. It is also argued that such multi-spin order decreases as the size of the spin system increases, where only dipolar and Zeeman order are expected in the thermodynamic limit. Using the symmetry of the dipolar Hamiltonian under 180° rotations, it is further demonstrated that long-lived single-quantum coherences can exist in systems with an odd number of spins, and such long-lived coherences can contribute a DC component to the FID after a simple excitation of the equilibrium Zeeman order.

2. Constants of motion for the dipolar Hamiltonian, $\widehat{H}_D$

Consider the case of high-field NMR for a set of dipolar-coupled spins with $I = 1/2$. The secular dipolar Hamiltonian (written in the rotating frame) is given by

$$\widehat{H}_D = \sum_{i<j} D_{ij}(3I_Z^i I_Z^j - \vec{I}^i \cdot \vec{I}^j)$$
$$= \sum_{i<j} \widehat{H}_D^{ij}. \tag{6}$$

Since $[\widehat{H}_D, \widehat{I}_Z] = 0$, where $\widehat{I}_Z = \sum_{i=1}^N \widehat{I}_Z^i$, a set of simultaneous eigenstates, $|\varepsilon, m\rangle$, for $\widehat{H}_D$ and $\widehat{I}_Z$ can be found which satisfy the following relations:

$$\widehat{H}_D|\varepsilon, m\rangle = \varepsilon|\varepsilon, m\rangle, \tag{7}$$
$$\widehat{I}_Z|\varepsilon, m\rangle = m|\varepsilon, m\rangle. \tag{8}$$

The projection operators onto the above eigenstates, $\widehat{F}_{\varepsilon,m} = |\varepsilon, m\rangle\langle\varepsilon, m|$, form a set of 2^N constants of motion, where N is the number of spins. However, an additional set of constants of motion can be constructed due to the symmetry of $\widehat{H}_D$ under a 180° rotation: $\widehat{R}^\dagger(\pi, \phi)\widehat{H}_D\widehat{R}(\pi, \phi) = \widehat{H}_D$ where $\widehat{R}(\theta, \phi) = \exp[i\theta(\widehat{I}_X \cos(\phi) + \widehat{I}_Y \sin(\phi))]$. Thus for any given state, $|\varepsilon, m\rangle$, there is another state (for $m \neq 0$) which has the same energy ε and is given by $|\varepsilon, -m\rangle \propto \widehat{R}(\pi, \phi)|\varepsilon, m\rangle$.

(For $m = 0$, it is possible that $|\varepsilon, 0\rangle \propto \widehat{R}(\pi, \phi)|\varepsilon, 0\rangle$.) An additional set of constants of motion, $\widehat{C}_{\varepsilon,m} = |\varepsilon, m\rangle\langle\varepsilon, -m|$, can therefore be created which represent $2m$-quantum coherences which do not evolve under $\widehat{H}_D$. The possible observation of the $\widehat{C}_{\varepsilon,m}$ constants of motion will be discussed in the last section.

Using both $\widehat{H}_D$ and $\widehat{I}_Z$ in Eq. (3), operators corresponding to linear combinations of the projection operators, $\widehat{F}_{\varepsilon,m}$, can be constructed. Labeling the identity operator as $\widehat{E}_0 = \widehat{1}$, the next two constants of motion constructed using $\widehat{H}_D$ are

$$\widehat{E}_1 = \widehat{H}_D - \lambda_{\widehat{E}_0,\widehat{H}_D}\widehat{E}_0$$
$$= \widehat{H}_D,$$
$$\widehat{E}_2 = \widehat{H}_D^2 - \lambda_{\widehat{E}_1,\widehat{H}_D^2}\widehat{E}_1 - \lambda_{\widehat{E}_0,\widehat{H}_D^2}\widehat{E}_0$$
$$= \widehat{H}_D^2 + \frac{M_3 - 3B_3}{2M_2}\widehat{E}_1 - \frac{3}{8}M_2\widehat{E}_0, \tag{9}$$

where the various coefficients are defined by

$$M_n = \sum_{i<j} D_{ij}^n,$$
$$B_3 = \sum_{i<j<k} D_{ij}D_{ik}D_{jk}. \tag{10}$$

All the $\widehat{E}$ operators constructed using Eq. (3) can be expressed in terms of operators composed of an even number of spin terms (e.g., $\widehat{I}_Z^i\widehat{I}_Z^j\widehat{I}_Z^k\widehat{I}_Z^l$). In particular, $\widehat{E}_1$ corresponds to dipolar order, and $\widehat{E}_2$ contains both four-spin and two-spin order. These operators, which represent linear combinations of the projection operators $\widehat{F}_{\varepsilon,m}$, cannot distinguish between the projection operators $\widehat{F}_{\varepsilon,m}$ and $\widehat{F}_{\varepsilon,-m}$. However, $\widehat{I}_Z$ can distinguish between $\widehat{F}_{\varepsilon,\pm m}$, since $\widehat{I}_Z\widehat{F}_{\varepsilon,\pm m} = \pm m\widehat{F}_{\varepsilon,\pm m}$. An additional set of constants of motion can be found by simply multiplying the $\widehat{E}$ operators by $\widehat{I}_Z$, and subsequently applying a Gram-Schmidt orthogonalization process (Eq. (3)). The first two operators formed in this way are given by

$$\widehat{O}_1 = \widehat{I}_Z,$$
$$\widehat{O}_2 = \widehat{H}_D\widehat{I}_Z - \lambda_{\widehat{O}_1,\widehat{H}_D\widehat{I}_Z}\widehat{O}_1$$
$$= \widehat{H}_D\widehat{I}_Z - \frac{M_1}{N}\widehat{O}_1. \tag{11}$$

The $\widehat{O}$ operators contain only operators comprised of an odd number of spin terms (which makes them trivially orthogonal to the $\widehat{E}$ constants of motion). Specifically, the operator $\widehat{O}_1$ corresponds to Zeeman order, and the operator $\widehat{O}_2$ contains both three-spin and one-spin order. Additional constants of motion can be generated using Eq. (3), although mathematical expressions for these operators quickly become complicated.