THE METHOD OF PROJECTION OPERATORS IN THE THEORY OF PULSED NMR PROCESSES WITH SELECTIVE IRRADIATION

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The method of projection operators is applied to the theory of pulsed nuclear magnetic resonance processes with selective irradiation. The use of the projection operator method alone and in combination with the known one-transition operator method is considered. In particular, general formulas are derived that describe the evolution of the density operator in the case of arbitrary first-order spectra.

1. INTRODUCTION

The theory of pulsed NMR processes reduces to calculating the density operator. The calculation is broken up into consecutive stages corresponding to periods of pulse action and to periods of free evolution of the nuclear system. The description of the wide-band pulse action is straightforward because the corresponding Hamiltonian is linear and the transformation of the spin operators entering the density operator is a transformation of rotation. The periods of free evolution are determined by a nonlinear Hamiltonian. In [1] the method of projection operators was suggested and applied to obtain general formulas defining the scalar interaction-induced evolution of spin operators for the case of arbitrary first-order spectra (such for the most part are spectra observed with modern equipment with strong constant fields). To have a mathematical apparatus for calculating any pulsed process it remains to investigate pulse actions with selective irradiation. This problem is considered in the present paper. As in [1], the method of projection operators is used. Considered are two versions: the method of projection operators in combination with the well-known method of one-transition operators (the method of a false spin) and the independent method of projection operators. As a result, general formulas are derived that describe the evolution of the system under selective irradiation (Section 4). The combined method (Section 3) is illustrated by the calculation of two well-known effects.

2. THE GENERAL FORMULATION OF THE METHOD IN APPLICATION TO SELECTIVE IRRADIATION

Consider the evolution of the density operator under the action of a Hamiltonian $\mathcal{H} = \mathcal{H}_0 + V$ (in a rotating coordinate system), where $\mathcal{H}_0$ is the spin Hamiltonian of the system, which has eigenvectors $|i\rangle$, V is the interaction Hamiltonian with a variable field: $V = -\gamma H_1 I_x$, and H_1 is the Hamiltonian of the variable field. With selective irradiation is suffices to keep in the Hamiltonian $V = \sum_{i,k} P_i V P_k$ (P_i are projection operators) its part

$$V' = P_1 V P_2 + P_2 V P_1. \tag{1}$$

It is assumed here that the frequency of the variable field is close to that of the single transition $|1\rangle \rightarrow |2\rangle$, and, as a consequence of the relation $\gamma H_1 \ll |E_i - E_k|$ other transitions are not excited. Because of the limited size of the paper, the proof of the applicability of expression (1) is not presented here, but its meaning is quite evident. Using the identity $P_i = |i\rangle\langle i|$, we obtain for (1) the formula

$$-\gamma H_1 \langle 1|I_x|2\rangle (|1\rangle\langle 2| + |2\rangle\langle 1|). \tag{2}$$

We assume that the frequency of the variable field is exactly at resonance with the transition $|1\rangle \rightarrow |2\rangle$, which is equivalent to the fact that the energies in the rotating coordinate system coincide: $E_1 = E_2$. As a

result, $\mathcal{H}_0$ contains the operator $E(|1\rangle\langle 1| + |2\rangle\langle 2|)$ and commutes with V' and with the transformed density operator I_z. Therefore $\mathcal{H}_0$ does not affect the result, and it suffices to calculate the expression

$$\exp\{-iV't\}I_z \exp\{iV't\}. \tag{3}$$

The version with the $(E_1 \neq E_2)$ detuning was also calculated, but, for the sake of brevity, is not present here.

To calculate (3) it suffices to employ the expansion with respect to the projection operators:

$$\exp\left\{\frac{1}{2}i\varphi a_{12}\right\} = P_0(a_{12}) + P_1(a_{12})\exp\left\{\frac{1}{2}i\varphi\right\} + P_{-1}(a_{12})\exp\left\{-\frac{1}{2}i\varphi\right\}, \tag{4}$$

where $\varphi = 2\gamma H_1\langle 1|I_x|2\rangle t$, $a_{12} = |1\rangle\langle 2| + |2\rangle\langle 1|$, and the projection operators for the eigenvalues of the operator a_{12}, which are equal to 0, 1, and -1, are given by the formulas

$$P_0(a_{12}) = (1 - a_{12})(1 + a_{12}), \qquad P_1(a_{12}) = \frac{1}{2}a_{12}(a_{12} + 1), \qquad P_{-1}(a_{12}) = \frac{1}{2}a_{12}(a_{12} - 1). \tag{5}$$

If there are several transitions at resonance (when, e. g., the number of equivalent nuclei in a system is more than one), then the original expression (1) must be supplemented with the corresponding projection operators.

3. THE PROJECTION OPERATOR METHOD IN COMBINATION WITH THE ONE-TRANSITION OPERATOR METHOD

The operators $c_{ik} = |i\rangle\langle k|$ are called one-transition operators. The one-transition operator method (or the equivalent technique of false spin) in application to NMR was proposed in [2–5]. The original idea belongs to Feynman et al. [6]. The term "false spin" arose because, e. g., the matrix of the operator $a_{12} = c_{12} + c_{21}$ in the basis $|1\rangle$, $|2\rangle$ coincides with the Pauli matrix σ_1, and the operators $-i(|1\rangle\langle 2| - |2\rangle\langle 1|)$ and $|1\rangle\langle 1| - |2\rangle\langle 2|$ correspond to the other two Pauli matrices. In the calculation involving one-transition operators it is convenient to use the identity $c_{ik}c_{k'j} = c_{ij}\delta_{kk'}$. Then expressions (5) are brought to the form

$$P_0 = 1 - c_{11} - c_{22}, \qquad P_1 = \frac{1}{2}(c_{11} + c_{22} + c_{12} + c_{21}), \qquad P_{-1} = \frac{1}{2}(c_{11} + c_{22} - c_{12} - c_{21}).$$

As an example, consider a two-spin system AX; the nuclei A and X will be denoted by the respective indices 1 and 2. The states $|m_1, m_2\rangle$ (where m_1 and m_2 are the values of the z-projections of the spins) are indexed in the following way: $|1\rangle = |-1/2, -1/2\rangle$, $|2\rangle = |1/2, -1/2\rangle$, $|3\rangle = |-1/2, 1/2\rangle$, and $|4\rangle = |1/2, 1/2\rangle$. We calculate the density operator (3) for the selective transition $|1\rangle \rightarrow |2\rangle$. The calculation using expansion (4) results in the formula:

$$F = \exp\left\{\frac{1}{2}i\varphi(c_{12} + c_{21})\right\}I_{1z} \exp\left\{-\frac{1}{2}i\varphi(c_{12} + c_{21})\right\}$$
$$= \frac{1}{2}(-c_{33} + c_{44}) + \frac{1}{2}(-c_{11} + c_{22})\cos\varphi + \frac{1}{2}i(-c_{21} + c_{12})\sin\varphi. \tag{6}$$

The formula takes into account that the transformation only affects the spin of the nucleus A: $I_{1z} = (1/2)(-c_{11} + c_{22} - c_{33} + c_{44})$, while the spin $I_{2z} = (1/2)(-c_{11} - c_{22} + c_{33} + c_{44})$ remains unchanged. The presence of the operators c_{21} and c_{12} in (6) testifies to the appearance of the one-quantum coherence in the $1 \rightarrow 2$ transition, which corresponds to the magnetization precession at the frequency of this transition.

If after that a second selective pulse is applied to the system, this time at the frequency of the $2 \rightarrow 4$ transition, the calculation leads to the appearance of one-transition operators in the density operator, which in this case correspond to the two-quantum coherence (c_{14} and c_{41}). If that second pulse was a π-pulse, the operators of the one-quantum coherence disappear.

We consider in more detail the effect of the second wide-band pulse at the subspectrum X frequencies, i.e., on the $2 \to 4$ and $1 \to 3$ transitions. The problem reduces to calculating the expression

$$\exp\{i\chi I_{2x}\}F\exp\{-i\chi I_{2x}\}. \tag{7}$$

Here it suffices to use the expansion $\exp\{i\chi I_{2x}\} = \cos(\chi/2) + 2iI_{2x}\sin(\chi/2)$ and the corresponding complex conjugate expression (they are valid for the spin 1/2). For brevity, we immediately set $\chi = \pi$ (a π-pulse), then (7) is reduced to the form $4I_{2x}FI_{2x}$, and, by virtue of (6), the last expression results in

$$\frac{1}{2}\big[-c_{11} + c_{22} + (-c_{33} + c_{44})\cos\varphi + i(c_{34} - c_{43})\sin\varphi\big].$$

Here the appearance of the operators c_{34} and c_{43} instead of c_{12} and c_{21} in formula (6) is characterized as transfer of coherence, i.e., the transformation of the magnetization that precesses with frequency $\omega_1 - J/2$ into magnetization precessing with frequency $\omega_1 + J/2$.

The calculations by the proposed technique, presented here without details, are rather cumbersome even for the simplest version (a two-spin system) considered here. In the next section we propose another procedure, which does not involve one-transition operators and which makes particularly noticeable the advantages of the use of projection operators.

4. THE PROJECTION OPERATOR METHOD AS APPLIED TO AN ARBITRARY FIRST-ORDER SPECTRUM

We consider an arbitrary subspectrum $\{I_1, I_2\}$ of the spectrum $A_p X_q$ and calculate the result of selective irradiation at the frequency of the subspectrum A corresponding to the transitions $|m_1 - 1, m_2\rangle \to |m_1, m_2\rangle$ (the projection m_2 is fixed, and the transition frequencies are the same for all values of m_1). It is clear that in this case the operator realizing the transition is $I_{1x}P_{m_2}$, where $P_{m_2} = P_{m_2}(I_{2z})$ is a projection operator. If at an intermediate time the density operator is a linear combination of products of spin operators, then to determine the effect of a selective pulse it suffices to examine its effect on the operators I_{1x} and I_{1y} and also on I_{2x} and I_{2y} (it does not affect the other operators). The solution to this problem for I_{1x} and I_{1y} is given by the relation

$$\exp\{i\varphi I_{1x}P_{m_2}\}I_{1x}\exp\{-i\varphi I_{1x}P_{m_2}\} = I_{1x}(1 - P_{m_2}) + (I_{1x}\cos\varphi + I_{1y}\sin\varphi)P_{m_2}, \tag{8}$$

$$\exp\{i\varphi I_{1x}P_{m_2}\}I_{1y}\exp\{-i\varphi I_{1x}P_{m_2}\} = I_{1y}(1 - P_{m_2}) + (I_{1y}\cos\varphi - I_{1x}\sin\varphi)P_{m_2}. \tag{9}$$

The proof of (8) and (9) can be obtained, for instance, by using the commutators

$$\begin{aligned}[I_{1x}P_{m_2}, I_{1x}] &= -iI_{1y}P_{m_2}, \\ [I_{1x}P_{m_2}, I_{1y}] &= iI_{1x}P_{m_2}.\end{aligned} \tag{10}$$

Introducing the notation $I_{1x}(\varphi)$ and $I_{1y}(\varphi)$ for the left-hand sides of (8) and (9) and using the commutators (10), we obtain for $I_{1x}(\varphi)$ and $I_{1y}(\varphi)$ a system of first-order differential equations whose solution with the corresponding initial conditions results in identities (8) and (9).

However, a still simpler derivation of (8) and (9) can be performed by introducing the projection operators P_0 and P_1 as functions of the projection operator P_{m_2} whose eigenvalues are 0 and 1. Then we have $\exp\{i\varphi I_{1x}P_{m_2}\} = P_0 + P_1\exp\{i\varphi I_{1x}\}$, where $P_0 = 1 - P_{m_2}$ and $P_1 = P_{m_2}$. Using this expression and its complex conjugate and also the identity $P_{m_2}^2 = P_{m_2}$ and the ordinary rotation formulas we immediately obtain (8) and (9).

In a similar way we prove the relation

$$\begin{aligned}\exp\{i\varphi I_{1x}P_{m_2}\}I_{2x}\exp\{-i\varphi I_{1x}P_{m_2}\} &= I_{2x} - P_{m_2}I_{2x} - I_{2x}P_{m_2} \\ &+ P_{m_2}I_{2x}\exp\{i\varphi I_{1x}\} + I_{2x}P_{m_2}\exp\{-i\varphi I_{1x}\},\end{aligned} \tag{11}$$

and then substitute the expansion

$$\exp\{i\varphi I_{1x}\} = \sum_{m_1}P_{m_1}(I_{1x})\exp\{i\varphi m_1\}$$

3

and the corresponding complex conjugate expression into (11). In the derivation of formula (11) the identity $P_{m_2}I_{2x}P_{m_2} = 0$ is taken into account. The formula for I_{2y} is obtained from (11) by replacing the indices "$2x$" by "$2y$".

Formulas (8) and (9) can also be generalized to the subspectra $\{I_1, I_2, \ldots, I_n\}$ for an arbitrary first-order spectrum of systems consisting of an arbitrary number of groups of equivalent nuclei. In this case we have

$$\exp\{i\varphi I_{kx}P'\}I_{kz}\exp\{-i\varphi I_{kx}P'\} = I_{kz}(1 - P') + (I_{kz}\cos\varphi + I_{ky}\sin\varphi)P',$$
$$\exp\{i\varphi I_{kx}P'\}I_{ky}\exp\{-i\varphi I_{kx}P'\} = I_{ky}(1 - P') + (I_{ky}\cos\varphi - I_{kz}\sin\varphi)P',$$

where

$$P' = \prod_{j(\neq k)} P_{m_j}.$$

At the end of Section 3 it was shown that the effect on the AX system of a wide-band pulse after a selective pulse leads to transfer of coherence. The resulting general formula makes it possible to obtain a generalization to the case of an arbitrary spectrum. Indeed, as follows from (8), for $\varphi = \pi/2$ the original density operator I_{1z} turns into $I_{1y}P_{m_2}$. The action of the subsequent wide-band π-pulse at the frequencies of the second subspectrum transforms I_{2z} into $-I_{2z}$, i.e., $P_{m_2}(I_{2z})$ turns into $P_{m_2}(-I_{2z})$. From the explicit expression

$$P_{m_2}(I_{2z}) = \prod_{m_2'(\neq m_2)} \frac{I_{2z} - m_2'}{m_2 - m_2'}$$

for the projection operator it follows that $P_{m_2}(-I_{2z}) = P_{-m_2}(I_{2z})$. Thus, the magnetization precession at a frequency $\omega_1 + Jm_2$ (where J is the spin-spin coupling constant) is transformed into precession with a frequency $\omega_1 - Jm_2$. A similar effect also exists in the case of a system with an arbitrary number of groups of equivalent nuclei.

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