

Product Operator Formalism: A Brief Introduction

Micholas D. Smith
Physics Department, Drexel University, Philadelphia, PA 19104

May 14, 2010

Abstract

Multiple spin systems allow for the presence of quantum coherence and spin-spin coupling interactions. Traditionally, density operator formalism is used to describe these systems; however, the use of this formalism often clouds intuition making it a cumbersome tool. Here we introduce a third formalism constructed from the density operator formalism with a direct connection to a non-classical intuitive vector-like representation. After introducing the method, a simple example of its use is given when describing the COSY 2D-NMR experiment.

Introduction

When describing spin systems generally two approaches are used: the classical vector formalism [1] or the density operator formalism [2]. Here we seek to briefly introduce the product operator formalism developed by Sørensen [3], as an alternative to the standard approaches. In Sect. 1 and 2, we describe the classical vector and density operator formalisms. In Sect. 3 we introduce the product operators for a two spin system. In Sect. 4 we describe the derivation of the product operator formalism from the density operator formalism. In Sect. 5 we introduce the non-classical vector-like interpretation of the product operator formalism. In the final section we present a working example of the product operator formalism applied to the Correlation Spectroscopy (COSY) NMR experimental technique.

Classical Vector Formalism

The classical vector approach is rooted in the idea of equating a classically precessing charged particle in a magnetic field with that of a particle with some spin, all interactions between the ‘spinning’ particle and any external interactions (outside of the field the particle is ‘spinning’ in) are described by a torque being exerted on the particle. Extending on these same principles, the Bloch equations can also be derived (see Mirau [1]) to directly connect the classical model with observable changes in magnetization. A problem occurs at this point in that the inclusion of a second spin to allow for spin-spin interactions is not a direct extension, and worse will not be able to account for coherence between different spin systems.

Density Operator Formalism

Density operator formalism, in contrast to the classical vector formalism, is rooted in quantum mechanics. The density operator¹ is defined by:

$$\begin{aligned}\rho_{nq} &= \langle q | \rho \rangle \cdot \langle n | \rho \rangle \\ \rho_{nn} &= |\langle \rho | n \rangle|^2 = P_n \\ \text{Tr}(\rho) &= 1\end{aligned}\tag{1}$$

Where ρ is the density operator (matrix), ψ is the wave function of the system, n and q are states of the system, and P_n is the probability of finding the system in the n^{th} state. The system is further divided into mixed states and pure

¹ There also exists an alternative definition based on the use of the projection operator. See Liboff [4]

states where the mixed states are the combinations of n and q states, who's ensemble averages are the off-diagonal terms in the matrix, while the diagonal terms represent the probability of finding the system in one of the pure states.

To make use of the density operator the time evolution must also be defined, but to do this it is necessary to have an expression for the Hamiltonian of the system. For a spin system the Hamiltonian is defined as:

$$H = H_{\text{external-field}} + H_{\text{coupling-interactions}}$$

$$H = \sum_i \mu_i \cdot B + \sum_i \sum_j J_{ij} I_i \cdot I_j \quad (2)$$

Where I_i represents the spin associated with the i^{th} particle, J_{ij} is the coupling constant between the spins, μ_i is the magnetic dipole of the i^{th} particle and B is the magnetic field. With the Hamiltonian defined, the time evolution of the density operator is defined (assuming any relaxation times from state transitions are instantaneous) is:

$$\dot{\rho} = i[H(t), \rho(t)] \quad (3)$$

Which can be solved by a sequence of matrix exponentiation's in the form of a sequence of unitary transformations. Additionally, (3) implies that as time progresses, the off-diagonal terms will influence the probabilities of the pure states. With the time evolution defined, the last detail needed is to note the relationship between an observable quantity and the density operator, which is given by:

$$\text{Tr}(\rho \hat{O}) = \langle O \rangle \quad (4)$$

Where $\langle O \rangle$ is an observable and \hat{O} is the operator associated with O .

In the case of measuring magnetization of a spin system in the density operator formalism we use the "recipe" of solving equation (3) and applying the magnetization operator (e.g. the spin operator with a scaling factor) into equation (4). The issue here is as the number of spins (N) increases the dimensions of the matrices to multiply increases by $2^N \times 2^N$ [3], so the ability to do "back of the envelope" calculations quickly diminishes.

Product Operator Formalism

Product operator formalism follows from introducing a set of operator consisting of an identity operator, directional operators for each state, and combinations of products of directional operators. For a spin $\frac{1}{2}$ system made up of two particles we can generate sixteen different operators, which are as follows [3]:

I_{kz} : Longitudinal magnetization of spin k (or l)

I_{kx} : In-phase x-magnetization of spin k (or l)

I_{ky} : In-phase y-magnetization of spin k (or l)

$2I_{kx}I_{lz}$: x-magnetization of spin k antiphase with respect to spin l

$2I_{ky}I_{lz}$: y-magnetization of spin k antiphase with respect to spin l

$2I_{kx}I_{lx}$, $2I_{ky}I_{ly}$, $2I_{kx}I_{ly}$, and $2I_{ky}I_{lx}$: two spin coherence of spins k and l

$2I_{kz}I_{lz}$: Longitudinal two-spin order of spins k and l.

0.5E: Identity operator

Additionally, the number of operators can be increased to allow for a system of arbitrary number of spins by including third, fourth, n^{th} product operators made up of combinations of the three directional operators.

In practice to describe interactions with the product operators the initial state is represented as a series of operators being acted on is placed to the left of an arrow with the operator acting on the initial state placed above the arrow and their results are computed using a look-up table, such as in figure one [from 5]:

$$\begin{array}{l}
I_{1z} \xrightarrow{90^\circ I_x} -I_{1y} \quad I_{1x} \xrightarrow{90^\circ I_x} I_{1x} \quad I_{1y} \xrightarrow{90^\circ I_x} I_{1z} \quad I_{1x} \xrightarrow{\pi J 2 I_{1y} I_{2z}} I_{1x} \cos \pi t + 2 I_{1y} I_{2z} \sin \pi t \\
I_{1z} \xrightarrow{90^\circ I_y} I_{1x} \quad I_{1x} \xrightarrow{90^\circ I_y} -I_{1z} \quad I_{1y} \xrightarrow{90^\circ I_y} I_{1y} \quad -I_{1x} \xrightarrow{\pi J 2 I_{1y} I_{2z}} -I_{1x} \cos \pi t - 2 I_{1y} I_{2z} \sin \pi t \\
I_{1z} \xrightarrow{90^\circ I_x} I_{1y} \quad I_{1x} \xrightarrow{90^\circ I_x} I_{1x} \quad I_{1y} \xrightarrow{90^\circ I_x} -I_{1z} \quad I_{1y} \xrightarrow{\pi J 2 I_{1y} I_{2z}} I_{1y} \cos \pi t - 2 I_{1x} I_{2z} \sin \pi t \\
I_{1z} \xrightarrow{90^\circ I_y} -I_{1x} \quad I_{1x} \xrightarrow{90^\circ I_y} I_{1z} \quad I_{1y} \xrightarrow{90^\circ I_y} I_{1y} \quad -I_{1y} \xrightarrow{\pi J 2 I_{1y} I_{2z}} -I_{1y} \cos \pi t + 2 I_{1x} I_{2z} \sin \pi t \\
2 I_{1x} I_{2z} \xrightarrow{90^\circ I_y} -2 I_{1y} I_{2z} \quad 2 I_{1x} I_{2z} \xrightarrow{\pi J 2 I_{1y} I_{2z}} 2 I_{1x} I_{2z} \cos \pi t + I_{1y} \sin \pi t \\
2 I_{1x} I_{2z} \xrightarrow{90^\circ I_x} -2 I_{1x} I_{2z} \quad -2 I_{1x} I_{2z} \xrightarrow{\pi J 2 I_{1y} I_{2z}} -2 I_{1x} I_{2z} \cos \pi t - I_{1y} \sin \pi t \\
2 I_{1y} I_{2z} \xrightarrow{90^\circ I_x} 2 I_{1y} I_{2z} \quad 2 I_{1y} I_{2z} \xrightarrow{\pi J 2 I_{1y} I_{2z}} 2 I_{1y} I_{2z} \cos \pi t - I_{1x} \sin \pi t \\
-2 I_{1y} I_{2z} \xrightarrow{90^\circ I_x} -2 I_{1y} I_{2z} \quad -2 I_{1y} I_{2z} \xrightarrow{\pi J 2 I_{1y} I_{2z}} -2 I_{1y} I_{2z} \cos \pi t + I_{1x} \sin \pi t \\
I_{1z} \xrightarrow{\pi J 2 I_{1y} I_{2z}} I_{1z}
\end{array}$$

Figure (1)

$$\begin{array}{l}
I_{1x} \xrightarrow{\Omega I_z} I_{1x} \cos \Omega t + I_{1y} \sin \Omega t \quad -I_{1x} \xrightarrow{\Omega I_z} -I_{1x} \cos \Omega t - I_{1y} \sin \Omega t \quad I^+ = I_x + i I_y \\
I_{1y} \xrightarrow{\Omega I_z} I_{1y} \cos \Omega t - I_{1x} \sin \Omega t \quad -I_{1y} \xrightarrow{\Omega I_z} -I_{1y} \cos \Omega t + I_{1x} \sin \Omega t \quad I^- = I_x - i I_y \\
I_{1z} \xrightarrow{\Omega I_z} I_{1z} \quad I^+ = \frac{1}{2}(I^+ + I^-) \\
I^+ = \frac{1}{2}(I^+ - I^-) \\
2 I_{1x} I_{2z} = I_{2z} (I^+ + I^-) \\
I^+ \xrightarrow{90^\circ I_x} \frac{1}{2}(I^+ + I^-) + i I_z \\
I^- \xrightarrow{90^\circ I_x} \frac{1}{2}(I^+ + I^-) - i I_z \\
I^+ \xrightarrow{\Omega I_z} I^+ e^{-i\Omega t} \\
I^- \xrightarrow{\Omega I_z} I^- e^{+i\Omega t}
\end{array}$$

Where Ω is an arbitrary “pulse” frequency and J is a spin-coupling constant.

Connection between Product Operator and Density Operator Formalism

To best understand where the tables for computation are derived from, it is necessary to return to the density operator formalism. Product operators are in actuality a special choice of a linear combination of operators to define a basis for the density operator. The product operators are chosen such that the operators in the linear combination that make up the density operator are from the product [3]:

$$B_s = 2^{q-1} \prod_{k=1}^N (I_{kv})^{a_{sk}} \quad (5)$$

Where N is the total number of $I=1/2$ nuclei in the system, k represents what nucleus, v represents either the x , y , or z direction, q is the number of single-spin operators, and a_{sk} is equal to either one or zero depending on if it is the q nuclei or the $N-q$ remaining nuclei. Additionally, the operators are not normalized, complete a basis set for spin $1/2$ systems of 4^N operators, and are constructed to be orthogonal with respect to the formation of the trace (thus maintaining the probability interpretation associated with the diagonal found in the density operator formalism). The most direct way to visualize the product operators, following their definition above, is to note that the direct product of the 2×2 Pauli Matrices for two separate systems with spin $1/2$ will give the sixteen operators listed above in their matrix form.

In addition to the above connection to density operator formalism, it is also found that the time evolution of the product operators is generated from [3]:

$$\exp(-i\phi B_r) B_s \exp(i\phi B_r) = \sum_t b_{ts}(r, \phi) B_t \quad (6)$$

The benefit of this is that the term within the exponential can be expressed in terms related to resonance frequency shifts or scalar coupling for the spin system (as will be clear in section 5).

Graphical Connection between Product Operator and Vector Formalism

Multiple graphic representations have been developed for dealing with product operators; however, the most straightforward and flexible representation is presented in Donne [6]. The figure below (from [6]) is a complete listing of the product operators of a spin $\frac{1}{2}$ system with two interacting particles in a ‘quasi-vector’ picture.

The premise behind the ‘quasi-vector’ graphical representation is that a single particle (a single spin) is represented by a two headed arrow, and two particles (two-spin operators) are two double headed arrows. Additionally, the arrows are labeled according to which particle they represent. During use, the evolutions are illustrated by rotations associated with other operators operating on the described system.

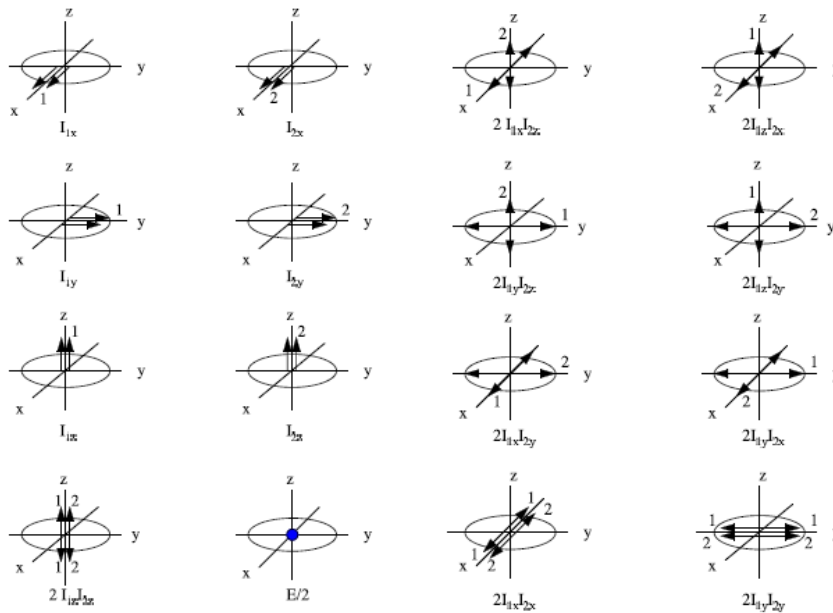


Figure (2)

Figure 8.2: Non-classical vectors for the 16 operators of a weakly-coupled two-spin system. One-spin operators are represented by two single-headed arrows along their corresponding axes. Two-spin operators are represented by two double-headed arrows along their corresponding axes. The arrows are also labeled by their spin identities (i.e., spin 1 or spin 2). The zero-spin operator $E/2$ is included for completeness.

For instance, if the operator representing two spins along the z-direction is the initial state and a pulse selecting the first x-direction of only one of the particles is used, only the particle influenced by the pulse is affected and rotates according to the right hand rule (i.e. aligns with the y-axis). The benefit of this is that the interactions between the particles are still described by the product operators above or a linear combination of them, without needing to proceed with matrix multiplications.

In addition to the rotations associated with non-coupling interactions, as described above, the graphical representation can also tackle the weakly coupled evolutions, unlike the standard vector model. A modulating factor (either a sine or cosine) terms is simply added to the rotations, this changes the degree of rotation according to [6]:

$$\begin{aligned}
 I_{1x} &\xrightarrow{\pi J_{12} \tau 2I_{1z} I_{2z}} I_{1x} \cos(\pi J_{12} \tau) - 2I_{1y} I_{2z} \sin(\pi J_{12} \tau) \\
 I_{1y} &\xrightarrow{\pi J_{12} \tau 2I_{1z} I_{2z}} I_{1y} \cos(\pi J_{12} \tau) + 2I_{1x} I_{2z} \sin(\pi J_{12} \tau) \\
 2I_{1x} I_{2z} &\xrightarrow{\pi J_{12} \tau 2I_{1z} I_{2z}} 2I_{1x} I_{2z} \cos(\pi J_{12} \tau) - I_{1y} \sin(\pi J_{12} \tau) \\
 2I_{1y} I_{2z} &\xrightarrow{\pi J_{12} \tau 2I_{1z} I_{2z}} 2I_{1y} I_{2z} \cos(\pi J_{12} \tau) + I_{1x} \sin(\pi J_{12} \tau)
 \end{aligned}$$

Figure (3)

Application of Product Operator Formalism: The COSY Experiment

The Correlation Spectroscopy (COSY) experimental technique in 2D-NMR is used to transfer coherence between homonuclear samples. The COSY procedure follows by first applying a set of pulses to transform z-magnetization into transverse magnetization, spin-spin coupling then develops with antiphase magnetization of one nucleus with respect to the other nuclei. Once the antiphase magnetization develops, a repeat of the first pulse is applied which then will cause the system to develop evolutions in resonance frequencies (the chemical shift) and spin-spin coupling. The end result of the procedure is the development of a 2D-NMR spectrum with cross-peaks representing allylic coupling.

To describe this process in the classical vector formalism is impossible, and to describe the system in the standard density operator formalism is cumbersome to arrive at the description of the cross peaks; however, the product operator formalism can simply describe the system and immediately arrive at the cross peaks. The description arrives from the following (from [5]):

$$\begin{aligned}
 I_{1z} + I_{2z} &\xrightarrow{I_x} -I_{1y} - I_{2y} \xrightarrow{\Omega_1 t_1 I_{1z}} I_{1x} \sin \Omega_1 t_1 - I_{1y} \cos \Omega_1 t_1 \\
 &\xrightarrow{\pi J t_1 2 I_{1z} I_{2z}} 2 I_{1y} I_{2y} \sin \Omega_1 t_1 \sin \pi J t_1 \xrightarrow{I_x} 2 I_{1z} I_{2y} \sin \Omega_1 t_1 \sin \pi J t_1 \\
 &\xrightarrow{\Omega_2 t_2 I_{1z}} \xrightarrow{\pi J t_2 2 I_{1z} I_{2z}} I_{2y} \sin \Omega_1 t_1 \sin \pi J t_1 \sin \Omega_2 t_2 \sin \pi J t_2
 \end{aligned}$$

Figure (4)

Where the final result describes the cross-peaks found when running the COSY experiment².

Conclusion

In this paper we briefly reviewed the classical vector and density operator formalism for describing spin systems, and proceeded to introduce a third formalism, product operator formalism, for discussing spin systems. We then described the connections between the traditional formalisms and the product operator formalism. Finally, an example use of the product operator formalism was presented. With this brief introduction, it is hoped that the product operator formalism will be implemented with discussing spin systems in the physics community.

References

1. Mirau, P.A, *A Practical Guide to Understanding the NMR of Polymers*. Wiley-Interscience, Hoboken, 2005, pp. 1-418
2. Fano, U. "Description of States in Quantum Mechanics by Density Matrix and Operator Techniques." *Rev. Mod. Phys.* 1957 29, pp. 74-93
3. Sørensen O.W, Eich G. W, Levitt M. H, Bodenhausen G, and Ernst R. R, "Product operator formalism for the description of NMR pulse experiments," *Prog. Nucl. Magn. Reson. Spectrosc.*, 1983, 16, pp. 163–192.
4. Liboff, R. L. *Introductory Quantum Mechanics* 4th edition. Addison-Wesley, San Francisco, 2003, pp. 480-578
5. Berger, S. and Sigmar Braun. *200 and More NMR Experiments: A Practical Course*. Wiley-VCH, Weinheim, 2004, pp. 1-838

² See [6] for the graphical representation of the COSY experimental procedure

6. Donne, D. G. and David G. Gorenstein. "Chapter 8: A Pictorial Representation of Product Operator Formalism: Non-Classical Vector Diagrams for Multidimensional NMR."
<http://www.biophysics.org/Porals/1/PDFs/Education/donne.pdf> (accessed April 2010).
7. Spiess, C. E. "A Simplified Approach to Product Operator Formalism." *J. Chem. Ed.* 2004, 81, 1, pp. 134- 137
8. Van De Ven, F. J. M. and C.W. Hilbers. "A Simple Formalism for the Description of Multiple-Pulse Experiments. Application to a Weakly Coupled Two-Spin ($I = 1/2$) System." *J. Mag. Res.* 1983, 53, pp. 512-520