

# PRODUCT OPERATOR FORMALISM FOR THE DESCRIPTION OF NMR PULSE EXPERIMENTS

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(Received 29 March 1983)

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## 1. INTRODUCTION

In recent years, an astonishing variety of pulse techniques has been developed with the aim of enhancing the information content or the sensitivity of NMR spectra in both solution and solid phases.<sup>(1-39)</sup> For the design and analysis of new techniques two approaches have been pursued in the field of "spin engineering". Many of the original concepts were based on simplified *classical or semiclassical vector models* which have inherently severe limitations for describing more sophisticated techniques; for example, those involving multiple quantum coherence. On the other hand, for a full analysis of arbitrarily complex pulse experiments applied to large spin systems, the heavy machinery of *density operator theory* has been put into action, often at the expense of physical intuition.

We present here an approach which follows a middle course. It is founded on density operator theory but retains the intuitive concepts of the classical or semiclassical vector models. The formalism systematically uses product operators to represent the state of the spin system.

In Section 2 we discuss the relation of product operators to vector models and density operator theory. In the following three sections, we develop the nomenclature of product operators, the relationship between operators and vector pictures, and the rules for the evolution under shifts, couplings and pulses. Combinations of evolution intervals and rf pulses are treated in Section 6 in terms of "composite rotations". Magnetically equivalent nuclei are discussed in Section 7. The scalar coupling to nuclei with spin  $S > 1/2$  and the effects of quadrupolar couplings in anisotropic phase are the subject of Section 8. In Section 9, multiple-quantum coherence is discussed in terms of shift operators and of single-spin operators. Guidelines are indicated in Section 10 for deriving the observable magnetization, in particular the amplitudes and phases of multiplets. Selective pulses are briefly mentioned in Section 11. Finally, we treat in Sections 12–15 some examples involving coherence transfer such as two-dimensional correlation spectroscopy, relayed magnetization transfer, multiple quantum filters, 2D exchange spectroscopy, and systems with non-uniform spin temperature in the context of flip angle effects.

## 2. APPROACHES FOR THE ANALYSIS OF PULSE EXPERIMENTS

### 2.1. Classical Vector Models

In systems containing only isolated nuclei without spin–spin coupling (and without quadrupolar coupling), the magnetization can be described in terms of Bloch equations as a classical vector moving in three-dimensional space. This approach is satisfactory to describe many basic experiments of Fourier spectroscopy,<sup>(1)</sup> including spin-echoes,<sup>(2)</sup>  $T_1$  measurements,<sup>(3)</sup> "DANTE" sequences,<sup>(9,10)</sup> composite pulses,<sup>(27,28)</sup> measurement of slow chemical exchange<sup>(22,38)</sup> and spin imaging.<sup>(39)</sup>

### 2.2. Semiclassical Vector Models

In multi-level systems, it is possible to assign a vector to each individual transition. The effects of selective pulses and precession can still be understood on classical grounds. However, non-classical extensions are necessary to describe the transfer of coherence from one transition to another.<sup>(6)</sup> In this context, the substitution of non-selective pulses by pulse cascades has proved to be convenient.<sup>(40)</sup> Semiclassical vector models, though successful for many experiments, including heteronuclear 2D spectroscopy<sup>(14–16)</sup> and other polarization transfer experiments,<sup>(17–19)</sup> must be handled with care. In particular vector models do not adequately reflect the interdependence of  $z$ -components belonging to single transitions that share common energy levels.

### 2.3. Density Operator Approach

In contrast to semiclassical treatments, the quantum mechanical approach does not deal directly with observable magnetization, but rather with the state of the spin system, irrespective of the observable that will be finally detected.<sup>(41–43)</sup> The state of the system is expressed either by the wave function  $\psi(t)$  or by the density operator  $\sigma(t)$ .

If relaxation is disregarded, the time evolution of the density operator is described by the Liouville–von Neumann equation

$$\dot{\sigma}(t) = -i[\mathcal{H}(t), \sigma(t)]. \quad (1)$$

The Hamiltonian includes chemical shift terms, coupling terms and interactions with time-dependent external radio-frequency fields. It can be made time-independent within a finite time segment by selecting a suitable rotating frame. The time evolution can then be expressed by a sequence of unitary transformations of the type:

$$\sigma(t + \tau_1 + \tau_2) = \exp\{-i\mathcal{H}_2\tau_2\} \exp\{-i\mathcal{H}_1\tau_1\} \sigma(t) \exp\{+i\mathcal{H}_1\tau_1\} \exp\{+i\mathcal{H}_2\tau_2\} \quad (2)$$

with the propagators  $\exp\{-i\mathcal{H}_k\tau_k\}$ . This equation applies to any sequence of intervals  $\tau_k$  with constant external fields, or alternatively to  $\tau_k$  intervals where a time-independent average Hamiltonian  $\bar{\mathcal{H}}_k$  can be defined.

Having computed the time evolution of the density operator  $\sigma(t)$ , the observable magnetization components can be evaluated from the trace relations:

$$M_x(t) = \mathcal{N}\gamma\hbar \text{Tr} \{F_x\sigma(t)\}; \quad M_y(t) = \mathcal{N}\gamma\hbar \text{Tr} \{F_y\sigma(t)\} \quad (3)$$

with the number of nuclei per unit volume  $\mathcal{N}$  and the observable operators

$$F_x = \sum_k I_{kx}; \quad F_y = \sum_k I_{ky} \quad (4)$$

which are evaluated by summation over all spins  $k$  of one particular kind (for example protons, carbon-13, etc.). We shall discuss the implications of these trace relations in Section 10, with particular emphasis on the behaviour of individual multiplet components in coupled spin systems.

The evaluation of expectation values according to eqns. (3) takes place in the so-called "Schrödinger representation" where the state of the system represented by the density operator  $\sigma(t)$  is time-dependent, while the observable operators are time-independent. Sometimes, it is more convenient to transfer the time dependence to the observable operator, e.g.  $F_x$ , in the sense

$$\begin{aligned} M_x(t) &= \mathcal{N}\gamma\hbar \text{Tr} \{F_x(U(t)\sigma(0)U^{-1}(t))\} \\ &= \mathcal{N}\gamma\hbar \text{Tr} \{(U^{-1}(t)F_xU(t))\sigma(0)\} \\ &= \mathcal{N}\gamma\hbar \text{Tr} \{F_x(t)\sigma(0)\}. \end{aligned} \quad (5)$$

Attributing the time-dependence to the operators amounts to using the so-called "Heisenberg representation",<sup>(44)</sup> where in analogy to eqn. [2] the evolution is described by

$$F_x(t + \tau_1 + \tau_2) = \exp \{i\mathcal{H}_1\tau_1\} \exp \{i\mathcal{H}_2\tau_2\} F_x(t) \exp \{-i\mathcal{H}_2\tau_2\} \exp \{-i\mathcal{H}_1\tau_1\}. \quad (6)$$

Note the opposite order of the propagators. The Heisenberg representation, though it provides less intuitive insight, is of advantage when the evolution should be discussed for various initial conditions  $\sigma(0)$ . As long as relaxation is not considered both representations are only trivially different. However, for proper consideration of relaxation and exchange processes it is necessary to work in the Schrödinger representation. In the following, we use only the "natural" Schrödinger representation although the formalism can equally well be applied to the Heisenberg representation.

When eqn. (2) is expressed in terms of explicit matrices the unitary transformations amount to multiplications of matrices with dimension  $2^N \times 2^N$  for  $N$  spins with  $I = 1/2$ . In the eigenbasis of the unperturbed Hamiltonian, the elements of the density matrix have a simple physical meaning: a diagonal element  $\sigma_{ii}(t)$  represents the population  $P_i(t)$  of energy level  $i$ , while an off-diagonal element  $\sigma_{ij}$  represents coherence belonging to the transition  $(i, j)$ . Free precession can be readily described in the eigenbase, since the propagator  $\exp \{-i\mathcal{H}\tau\}$  is represented by a diagonal matrix, but the matrix elements of pulse operators cause complicated mixing of the matrix elements of  $\sigma(t)$ .<sup>(5,6)</sup> Explicit matrix representations tend to be cumbersome for systems with more than a few coupled spins.

#### 2.4. Product Operator Formalism

For the evaluation of eqns. (2)–(6) the density operator  $\sigma$  may be expressed as a linear combination of base operators  $B_s$ :<sup>(41)</sup>

$$\sigma(t) = \sum_s b_s(t)B_s. \quad (7)$$

The complexity of practical calculations greatly depends on the choice of the set  $\{B_s\}$ . The use of irreducible tensor operators as base operators has been proposed elsewhere.<sup>(45,46)</sup> Single transition operators,<sup>(47,48)</sup> which are useful to describe selective excitation, can also be used as base operators, but in the case of non-selective excitation retain much of the complexity of explicit matrix calculations.

To provide at the same time physical insight and computational convenience, we propose to express the density operator systematically in terms of product operators:

$$B_s = 2^{(q-1)} \prod_{k=1}^N (I_{kx})^{a_k} \quad (8)$$