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The Density Matrix Formalism

1. INTRODUCTION

Only the simplest NMR pulse sequences can be properly described and understood with the help of the vector representation (or handwaving) alone. All two-dimensional experiments require the density matrix formalism. Even some one-dimensional NMR sequences (see Part II.12) defy the vector treatment because this approach cannot account for the polarization transfer. The goal of Part I is to show how the density matrix can be used to understand a specific NMR pulse sequence. A "math reminder" is given in Appendix A for those who may need it. After becoming familiar with the use of the density matrix as a tool, the reader may find enough motivation to go to Appendix B which deals with the quantum-mechanical meaning of the density matrix.

2. THE DENSITY MATRIX

Before entering the formal treatment of the density matrix (see Appendix B) let us build an intuitive picture. We begin with the simple system of two spin 1/2 nuclei, A and X, with its four energy levels E_1 to E_4 (Figure I.1) generally described in introductory NMR textbooks. We assume here (and throughout the book) a negative gyromagnetic ratio, \checkmark . This explains the spin angular momentum orientation against the field in the lowest energy level E_4 . Of course, in this state the magnetic moment is oriented with the field.

2 Density Matrix Treatment

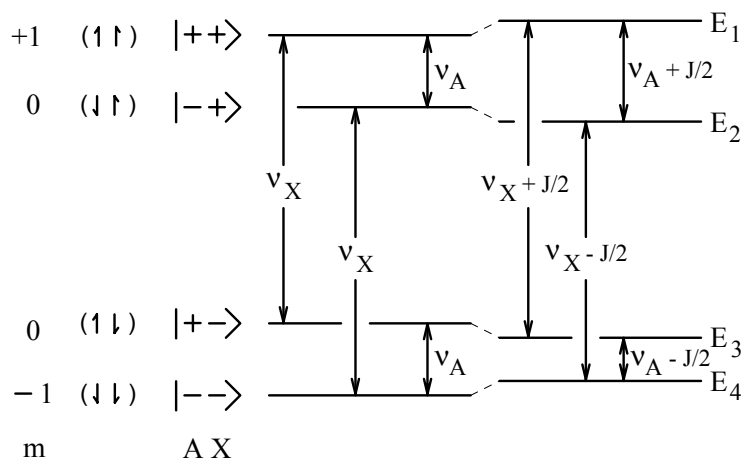


Figure I.1. Energy levels of an uncoupled (left) and coupled (right) heteronuclear AX system. The first column contains the total magnetic quantum number, m . Transition (precession) frequencies ν_A and ν_X and the coupling constant J are expressed in Hz.

The possible connections between the four quantum states represented by the "kets"

$$|++\rangle, |-\rangle, |+\rangle, |--\rangle,$$

are shown in Table I.1 (we assign the first symbol in the ket to nucleus A and the second, to nucleus X).

This is the general form of the density matrix for the system shown in Figure I.1. It can be seen that the off-diagonal elements of the matrix connect pairs of different states. These matrix elements are called "coherences" (for a formal definition see Appendix B) and are labeled according to the nature of the transitions between the corresponding states. For instance, in the transition

$$|++\rangle \rightarrow |-\rangle$$

only the nucleus A is flipped. The corresponding matrix element will represent a *single quantum coherence* implying an A transition and will be labeled $1Q_A$. We thus find two $1Q_A$ and two $1Q_X$ coherences (the matrix elements on the other side of the diagonal do not represent other coherences; they are mirror images of the ones indicated above the diagonal). There is also one *double-quantum coherence*, $2Q_{AX}$,

related to the transition

$$|++\rangle \rightarrow |--\rangle.$$

The *zero-quantum coherence* ZQ_{AX} can be considered as representing a flip-flop transition $E_2 \rightarrow E_3$. The name of this coherence does not necessarily imply that the energy of the transition is zero.

The diagonal elements represent populations.

Table I.1. Translation of the Classical Representation of a Two-spin System into a Density Matrix Representation

$ AX\rangle$	$ ++\rangle$	$ -+\rangle$	$ +-\rangle$	$ --\rangle$
$ ++\rangle$	P_1	$1Q_A$	$1Q_X$	$2Q_{AX}$
$ -+\rangle$		P_2	ZQ_{AX}	$1Q_X$
$ +-\rangle$			P_3	$1Q_A$
$ --\rangle$				P_4

The density matrix contains complete information about the status of the ensemble of spins at a given time. Populations and macroscopic magnetizations can be derived from the elements of the density matrix, as we will see later. The reciprocal statement is not true: given the magnetization components and populations we do not have enough information to write all the elements of the density matrix. The extra information contained in the density matrix enables us to understand the NMR sequences which cannot be fully described by vector treatment.