INTRODUCTION

This book is about the study of stochastic, i.e., random processes in magnetic resonance. In particular, a certain method for calculating the effect of such processes on magnetic resonance line shapes is treated in detail. This method is known as the stochastic Liouville method. Relevant stochastic processes are various diffusion or exchange processes. They are responsible for broadening of spectral lines in some cases, narrowing such lines in other cases, shifting lines, merging and separating lines. It is therefore of great importance to be able to calculate the outcome of an experiment when such random processes are operating. This usually requires some kind of semi-classical equation for the density matrix, in the context of quantum mechanics. The reason for this will now be explained.

A rigorous account of many physical problems, magnetic resonance included, must make use of quantum mechanical concepts. In standard quantum theory one deals with wave functions of given physical systems. However, very often practical situations arise where such a standard treatment is inadequate. For complex systems (e.g. various solids) or macroscopic incoherent assemblies of many small quantum systems (e.g. paramagnetic species in a liquid solution), one needs to describe the experimentally accessible quantum systems by a density matrix rather than by a wave function. This is true even when the relevant system has no interactions with its environment. Moreover, in many physical situations the interesting system has non-negligible interactions with its surroundings. These interactions are often complicated and changing with time. In particular, for many quantum mechanical systems the influence of the environment takes the form of random processes acting on the system. To describe the system properly it is then not sufficient to use the density matrix formalism. This formalism has to be augmented with a semi-classical treatment of the effect of the random processes on the system of interest. In magnetic resonance this is often the case.

There are two main approaches to the calculation of the effect of random processes on magnetic resonance experiments. Both of them lead to a semi-classical equation of motion for the quantum mechanical density matrix. Each of these equations is a mathematical tool for simulating of the behavior of some quantum systems, in which one can describe some features "exactly" - with a quantum mechanical density matrix, and some features approximately with classical stochastic (random) processes. Such a formalism is useful in magnetic resonance, because a quantum description is necessary (and can be given) to the spin system in order to analyze its observed transitions, but there may be many processes affecting the spins indirectly. It is very difficult to describe these processes fully, and it is not needed in practice - one only needs a method to account for the effect of these processes on the spins.

One approach is the Bloch-Redfield treatment, based mainly on perturbation theory, valid for relatively fast random motions with a relatively small effect on the interactions. Such a theory is often useful in NMR (nuclear magnetic resonance), where time scales are relatively long, so the diffusion processes are usually fast on the NMR time scale. The quantum mechanical description of chemical exchange processes, which is not limited to the fast motion regime, is closely related to this approach.

The other approach was initially developed mainly by Kubo, and then further developed and applied to magnetic resonance mainly by Freed. In this method, the emphasis is on a relatively detailed treatment of the stochastic process, without the restriction to fast motions. The resulting equation, known as the stochastic Liouville equation, is applicable to a broad range of problems in magnetic resonance. The "Stochastic Liouville Equation" (SLE) is a stochastic version of the Liouville - von Neumann equation, which is an exact quantum mechanical equation of motion for the density matrix.

This equation is valid even for relatively slow random processes, and is therefore especially suitable for EPR (electron paramagnetic resonance), where the natural time scale is short so that the random processes are not usually fast on this time scale. Many papers on the subject, mainly by Freed's group, have shown that this approach is indeed useful for a very wide variety of experimental situations in magnetic resonance.

The purpose of the book is to present a unified treatment of the different relaxation theories of magnetic resonance, with an emphasis on the stochastic Liouville equation, on which it is difficult to find introductory material at the textbook level. The unified presentation makes it possible to put that equation and the resulting relaxation theory in a proper perspective. As a background to this theoretical discussion, a brief review is given of the theory of the quantum mechanical density matrix. Some introductory mathematical material is reviewed in the Appendices. The general theoretical part of the book is followed by a fairly detailed treatment of some applications of the theory. The final chapter gives a brief introduction to the relevant experimental methods for which the theory has been applied.

An overview of the contents of the book is now given. Chapter I begins with a very brief review of the subject of Liouville's equation in classical mechanics, which is in a sense a precursor of the Liouville-von Neumann equation. The basic formalism of quantum mechanics is then introduced, leading to the main subject of the chapter - the quantum mechanical density matrix and its equation of motion. Examples are given, illustrating the actual application of the formalism in magnetic resonance.

Chapter II starts with the phenomenological Bloch equations, which give a simple classical description of magnetic resonance. This is followed by a quantum mechanical treatment of elementary magnetic resonance, and by some definitions needed for the treatment of stochastic processes. These subjects serve as an introduction to the main part of the chapter, which is the well known relaxation theory in magnetic resonance, due to Bloch and Redfield. This theory, as well as its introductory subjects, have received excellent coverage in several books. They are included here as a background for the following chapters, and in order to make it possible to compare the different relaxation theories described in the present book. Examples are given of stochastic processes which are relevant in this context.

Chapter III deals with the subject of chemical exchange processes, both intra-molecular and inter-molecular, with an emphasis on the former. The main features here are the comparison of the theory with the standard Bloch-Redfield relaxation equations, and the use of various types of symmetry properties to simplify the treatment, both on the theoretical level of deriving selection rules and on the practical level of numerical computations.

Chapter IV develops in a fairly general context the stochastic Liouville equation. This is done first by constructing a relaxation theory in which a relaxation function or operator play the central role, and then by an alternative approach, in which a statistical distribution function plays a central role. Both the classical and quantum mechanical versions of the equation are derived, and their applicability to magnetic resonance is demonstrated. At the same time the relationship between these equations and the formalism developed in the previous two chapters is discussed.

In chapter V several methods for solving the SLE are described. Following the general method of cumulants some numerical methods are presented. The emphasis in this Chapter is on the method of eigenfunctions, which is used in the subsequent formal development in the rest of the book. An application of this method to a problem in nuclear magnetic resonance is included here. The equations result in each case in a set of coupled algebraic equations, which is often of very large dimensions. Therefore a special section is devoted to some numerical techniques which can handle such problems, cutting down the size of numerical computations to a minimum.

Applications of the general theory (with the method of eigenfunctions) to several typical cases in CW EPR are described in chapter VI. The main purpose of this treatment is to develop the relevant equations for these cases, mostly for non-saturated lines. Some typical examples are given for EPR doublets and for photoexcited EPR triplets. A discussion of the special expression for the line shape of transient species is included, which is especially important for photoexcited triplets. The theoretical treatment is followed by some examples of relevant experimental results. Finally, applications to NMR are briefly discussed.

Chapter VII indicates how the theory is extended to more general types of experiments. This includes the study of saturated lines and double resonance methods such as ELDOR and ENDOR, as well as multiple pulse methods. Here, too, the theory is supplemented by some experimental examples.

Chapter VIII is a short introduction to experimental methods in magnetic resonance, for which the theory in this book is relevant. The main emphasis is on methods in EPR, particularly some modern methods which are useful in EPR, where the study of stochastic processes may require a formalism such as that treated in the present book.

The Appendices present some mathematical details which are needed as a background to some of the material in this book. The first four appendices deal with various aspects of angular momentum theory in quantum mechanics. This theory is of fundamental importance in the study of magnetic resonance, including the particular subjects treated here. The fifth one includes some elementary definitions and results in group theory, relevant to the discussion of symmetries in Chapter III.

We would like to emphasize that the book is not intended to give a comprehensive review of the vast existing literature on the subjects treated in this book. Certain aspects of the subject matter have been selected so as to construct a coherent framework, to develop and clarify the central points. Consequently, we have not attempted to refer to all important work on the SLE. Rather, in each chapter only a few references are given, either because they are directly related to the material included in that chapter, or because they can serve as typical examples of concepts or applications discussed in that chapter. However, some of the references are review articles which do have a comprehensive bibliography, so the interested reader may use these in order to find out about additional work that has been done on the study of stochastic processes by means of the SLE.

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