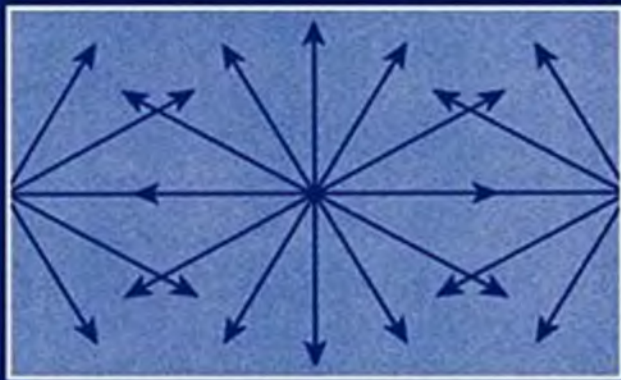


PHYSICS OF ATOMS AND MOLECULES

# *Density Matrix Theory and Applications*

SECOND EDITION



*Karl Blum*



*Density Matrix  
Theory and  
Applications*  
Second Edition

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*Plenum Press • New York and London*

Blum, Karl, 1937-

Density matrix theory and applications / Karl Blum. -- 2nd ed.

p. cm. -- (Physics of atoms and molecules)

Includes bibliographical references and index.

ISBN 0-306-45341-X

I. Density matrices. I. Title. II. Series.

QC174.L17.D44B55 1996

630.1'22--dc20

96-21443

CIP

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ISBN 0-306-45341-X

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A Division of Plenum Publishing Corporation  
233 Spring Street, New York, N. Y. 10013

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10987654321

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Printed in the United States of America

## *Preface to the First Edition*

Quantum mechanics has been mostly concerned with those states of systems that are represented by state vectors. In many cases, however, the system of interest is incompletely determined; for example, it may have no more than a certain probability of being in the precisely defined dynamical state characterized by a state vector. Because of this incomplete knowledge, a need for statistical averaging arises in the same sense as in classical physics.

The density matrix was introduced by J. von Neumann in 1927 to describe statistical concepts in quantum mechanics. The main virtue of the density matrix is its analytical power in the construction of general formulas and in the proof of general theorems. The evaluation of averages and probabilities of the physical quantities characterizing a given system is extremely cumbersome without the use of density matrix techniques. The representation of quantum mechanical states by density matrices enables the maximum information available on the system to be expressed in a compact manner and hence avoids the introduction of unnecessary variables. The use of density matrix methods also has the advantage of providing a uniform treatment of all quantum mechanical states, whether they are completely or incompletely known.

Until recently the use of the density matrix method has been mainly restricted to statistical physics. In recent years, however, the application of the density matrix has been gaining more and more importance in many other fields of physics. For example, in modern atomic physics, density matrix techniques have become an important tool for describing the various quantum mechanical interference phenomena which are of importance in scattering theory, quantum beat spectroscopy, optical pumping, and laser physics. This book proposes to introduce the reader to the methods of density matrix theory with an emphasis on their application in atomic (and nuclear) physics. It is aimed at beginners and not experts. All the basic concepts are therefore discussed in detail and all the steps in the calculations are explained. As background, a standard one-year course in quantum mechanics is assumed, as is knowledge of the elements of statistical mechanics. Some background in modern atomic physics and scattering theory would also be helpful. For Chapters 4–6 the reader should have a working knowledge of angular momentum the-

ory. Otherwise the treatment is begun from the lowest level possible. Some topics of contemporary interest are covered in sufficient detail to make the book also useful to those readers engaged in research in the fields of atomic or nuclear physics, laser physics, and physical chemistry.

The book can be divided into three main parts. In the first three chapters the basic concepts and methods of density matrix theory are introduced. In order to do this, some of the fundamental ideas of quantum mechanics and statistics are discussed. In particular, a clear understanding of pure and mixed quantum mechanical states is important. This is best achieved by considering simple systems. For this reason Chapter 1 is restricted to a discussion of the polarization states of spin-1/2 particles and photons, which enables all the basic concepts to be introduced in a simple way. The density matrix is first introduced as the counterpart of the distribution function of classical statistical mechanics, that is, by considering how many systems are in an ensemble with given wave functions. Then, after some of its basic properties are discussed, another aspect of the density matrix is considered: By introducing a convenient parametrization it is shown that the density matrix is the most convenient way of collecting all parameters of interest for a given experimental setup and of describing their behavior from an operational point of view.

In Chapter 2 these results are generalized to systems with more than two degrees of freedom and the basic properties of the density matrix derived in a more systematic way. The concept of coherence, which will be of central importance for the discussion of quantum mechanical interference phenomena in the following chapters is introduced. The properties of the time evolution operators are then reviewed and the basic equations of motion for statistical mixtures derived and illustrated with some examples.

In Chapter 3 another important aspect of the density matrix is introduced. Often, one is only interested in a few of many degrees of freedom of a quantum system, for example, when only one of several interacting systems is observed. In Sections 3.1 and 3.2 it is shown that, in general, it is impossible to find a wave function which depends only on the variables of the system of interest and not on those of all other systems as well. By averaging over all unobserved degrees of freedom a density matrix is obtained which describes the behavior of the system of interest. It is then shown that this "reduced" density matrix is the most general description of an open quantum mechanical system. The consequence of these general results are illustrated in Sections 3.3 and 3.4 with particular emphasis on the quantum mechanical theory of coherence. Finally, in Section 3.5 the reduced density matrix of atoms excited by electron impact is constructed and discussed in detail.

The subjects discussed in this chapter are related to the quantum mechanical theory of measurement. The questions raised here have attracted a great deal of interest from physicists in recent years.



The second part of the book (Chapters 4–6) is devoted to the application of the irreducible tensor method in density matrix theory. Quantum mechanical calculations for systems having symmetry can be divided into two parts. The first part consists of deriving as much information as possible from the symmetry requirements. The second part consists of calculating the dynamical quantities for which no information can be obtained from symmetry considerations. Often these two parts are tangled. The irreducible tensor method is designed to separate dynamical and geometrical elements and to provide a well-developed and efficient way of making use of the symmetry.

In Sections 4.2 and 4.3 the basic properties of tensor operators are discussed and the irreducible components of the density matrix (state multipoles, statistical tensors) are introduced. Sections 4.4–4.6 give various applications of the method, while Section 4.7 is devoted to a discussion of the time evolution of state multipoles in the presence of external perturbations.

The formalism developed up to this point is then applied in Chapters 5 and 6 to various problems of relevance to modern atomic spectroscopy, including the theory of quantum beats, electron-photon angular correlations, and the depolarization of the emitted radiation caused by fine and hyperfine interaction and magnetic fields. Throughout these chapters the discussion of quantum interference phenomena in atomic physics is based on the concept of “perturbation coefficients” developed by nuclear physicists in order to describe perturbed angular correlations. This formalism allows a very economic interpretation of experiments.

The last part of the book (Chapter 7) can be read independently of Chapters 4–6 (except some parts of Sections 7.5 and 7.6). In this chapter we discuss the density matrix approach to irreversible processes relating reversible and irreversible dynamics via generalized Master equations. Throughout this chapter the Markoff approximation is used. In Section 7.1 the fundamental concepts are introduced and the basic equations derived by considering the interaction between a “small” dynamic system and a “large” one (“heat bath”). Irreversibility is introduced by assuming that the bath remains in thermal equilibrium at constant temperature, irrespective of the amount of energy and information diffusing into it from the dynamic system. The special case of rate equations (Pauli’s Master equation) is considered in Section 7.2. The formalism is then applied to some simple examples in radio- and microwave spectroscopy. In order to illustrate the use of Master equation techniques in quantum electronics we consider the interaction between electromagnetic fields and two-level atoms. The corresponding Master equation is discussed in detail and the effects of relaxation interactions on the emitted line are described. In Section 7.4, the Bloch equations are derived and applied to magnetic resonance phenomena. It is shown that the density matrix method enables both longitudinal and transverse relaxation to be treated in a natural way, thereby avoiding the shortcomings of semiclassical theories. The

usefulness of the Bloch equations for a description of the interaction between atoms or molecules and laser or maser fields is briefly considered.

The discussion of the general formalism is then continued by deriving the general properties of the relaxation matrix in Section 7.5. The discussion of the Liouville formalism in Section 7.6 is restricted to the basic concepts. Finally, in Section 7.7, the response of a quantum system to an external field is considered. Here, an expression is derived by approximating the exact equation of motion of the density matrix in retaining only terms linear in the field strength. This method is closely related to the theory of retarded Green's functions and is of importance for the investigation of transport phenomena.

The theory and application of the density matrix have been well summarized by various authors. Here, we mention in particular the review papers by Fano (1957) and ter Haar (1961). Some textbooks on quantum mechanics outline the formalism (Messiah, 1965; Roman, 1965; Gottfried, 1966). These sources (and many others which are acknowledged in the appropriate places) were used in writing this book. Because of the introductory nature of this book we refer as a rule to monographs and reviews of the subject and only to those original papers whose results are used in the text.

Over the years my understanding of the theory and applications of the density matrix has benefited from many discussions with my colleagues at the Universities of Stirling and Münster. I am especially grateful to Prof. H. Kleinpoppen, who first aroused my interest in atomic physics, for his constant encouragement. I am indebted to Prof. J. Kessler for reading parts of the manuscript and making helpful suggestions for revisions in the first and second drafts. Dr. H. Jakubowicz has read the complete manuscript and made many improvements, and K. Bartschat has checked most equations. Finally, I wish to thank Mrs. Queen and Mrs. Raffin for their help in preparing the manuscript.

Karl Blum

## *Preface to the Second Edition*

Since publication of the first edition, many studies on oriented and aligned systems have been performed, ranging from atomic collision physics to molecular processes, and to interactions with surfaces. No attempt has been made in the present volume to cover all these developments. Rather, a few topics have been selected.

In Chapter 4 a section on the "natural system," popular in atomic collision physics, is included. In Section 4.6.5 a description of shape and spatial orientation of atomic charge distributions is given in order to obtain a deeper insight into the geometrical significance of state multipoles. Two new sections in Chapter 6 deal with the interactions of atomic charge clouds and external fields. Neither of these sections attempts to give a complete survey of the many experimental and theoretical results obtained in this field. Rather, the emphasis is on pointing out the essential features by studying simple cases.

The main addition is the new Chapter 7, in which the previously developed methods are extended to cover oriented and aligned molecules. The bulk of this chapter can be read after Section 4.5. The first sections contain a detailed treatment of angular momenta and axes distributions of linear rotors and symmetric tops. Since the angular momenta are often sufficiently high, semiclassical approximations apply and have been used throughout this chapter to illustrate quantum mechanical results. The techniques developed in these sections are then extended in order to include electronic orbital orientation and alignment, which are related, for example, to shape and spatial directions of electronic orbital lobes. A systematic treatment of these topics is attempted in Section 7.7. The basic definitions are introduced and illustrated with some simple examples, and the theory is then gradually developed. In Section 7.8 the formalism is applied to some topics in the rapidly expanding field of "dynamical stereochemistry." The main purpose of this chapter is to introduce methods which allow coverage of a broad range of phenomena in a systematic and coherent way.

Smaller additions have been made throughout the book in order to relate their material presented here to more recent experimental and theoretical results.