Irreducible Tensor Methods
AN INTRODUCTION FOR CHEMISTS

Brian L. Silver

内部交流

Irreducible Tensor Methods

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AN INTRODUCTION FOR CHEMISTS

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Preface

In this book I have attempted to give an introduction to the theory and use of irreducible tensor operators. The fact that the text is aimed at chemistry graduates has controlled both the mathematical level and the choice of illustrative examples. That part of the theory devoted to systems having spherical symmetry comes within the range of what physicists would call the theory of angular momentum, and has been summarized authoritatively by Fano and Racah (1959). The theory as applied to molecules is the subject of a monograph by Griffith (1962). Since the publication of these classic treatises there have been advances in technique most of which have not been incorporated into textbooks or treatises. The range of applications, especially in chemical physics, has increased rapidly in the last few years. I have included the developments in technique, in particular the use of second quantization, real Cartesian tensors, off-diagonal operator equivalents, and coupling and recoupling coefficients for spinor groups. In addition I have given an introduction to vector spherical harmonics and subsequently described the multipole expansion of light waves and the expression of the coherency matrix in terms of irreducible tensors. This material is used in the summary of the modern formalism for light scattering which concludes the book. The close relationship of the theories for spherical and lower symmetry has been stressed throughout the text.

The amount of mathematics required of the reader is modest. A little elementary group theory goes a long way. Physicists, mathematicians, or theoretical chemists may feel that depth has been sacrificed. Not as a concession to them, but as a pointer to the average chemist, there are, scattered in the text, brief–almost vanishing–paragraphs hinting at the delights of Lie groups, contragredience, time reversal, and other imaginary beings (Borges, 1974).

The examples are almost all taken from the recent research literature and have been worked through in considerable detail. I believe all the examples to be of interest in their own right, but their main purpose is to illustrate the practical application of the theoretical techniques.

The godfather of this book is Professor Ruben Pauncz, an invaluable colleague to have just down the corridor. My thanks are due to critical students at the Technion and the Weizmann Institute for forcing me, against the demands of entropy, to order my thoughts.

The manuscript was expertly and intelligently typed by Mrs. Norma Jacob.

I thank those at Academic Press involved in the production of this book. Their cooperation, care, and professionalism made it a pleasure to work with them.

Introduction

"Then the king's colour changed, and his thoughts alarmed him; his limbs gave way, and his knees knocked together. The king cried aloud to bring in the enchanters, the Chaldeans, and the astrologers. The king said to the wise men of Babylon, 'Whoever reads this writing, and shows me its interpretation, shall be clothed with purple, and have a chain of gold about his neck, and shall be third ruler in the kingdom.'"

Daniel 5:6,7

The use of symmetry to simplify problems in atomic and molecular quantum mechanics is familiar to those chemistry or physics undergraduates who have taken a course in elementary group theory and learned to classify wave functions and operators according to group representations. The almost trivial derivation of selection rules from this classification is the best known demonstration of the power of group theory to reveal generalizations without the need for computation. Roughly speaking the irreducible tensor method is designed to derive *all* those properties of a system which are consequences of its spatial symmetry. The method may be regarded as a branch of group theory, or, in its application to atomic systems, as a part of the theory of angular momentum.

The concept of irreducible tensors and the development of a formalism for making practical use of them are due mainly to Guilio Racah whose four classic papers (Racah,

1942a,b, 1943, 1949) are recognized as a breakthrough in atomic spectroscopy. Racah's methods for handling multielectron systems were soon seized upon by nuclear physicists, who realized the close mathematical relationship between two central field models: the electrons in an atom and the nucleons in the nuclear shell theory (cf. de-Shalit and Talmi, 1963).

Racah's work was not created in a vacuum, but was partially based on, and developed concurrently with advances in the theory of angular momentum made by Eugene Wigner. Two authoritative texts summarize their work: "Irreducible Tensorial Sets" by Fano and Racah (1959) and "Group Theory and Its Application to the Quantum Mechanics of Atomic Spectra" by Wigner (1959). In Part I of this book there is an account of those parts of the theory of angular momentum that are needed for an understanding of the irreducible tensor method. At the end of Part I, in Chapter 9, we derive the few basic expressions needed for a wide range of applications. Part II consists mainly of a variety of applications.

Wigner's work on angular momentum was largely couched in the language of group theory, and he pointed out that much of the theory was directly applicable to point groups (Wigner, 1940). This aspect was left untouched until the 1950s when the theory of irreducible tensors for point groups was developed, predominantly by Yukito Tanabe in Japan and subsequently by John Griffith in England whose monograph "The Irreducible Tensor Method for Molecular Symmetry Groups" (Griffith, 1962) is the most comprehensive summary of the theory. Part III is partly a presentation of Griffith's work. In addition there is an account of more recent work on spinor (double) groups. The techniques are again based on a correct classification of states and operators, but this time in terms of the transformations induced by a usually finite group of symmetry operations. The similarities between the methods for handing point group and spherical symmetries are many and pleasing and will be commented on frequently. Part IV includes applications of the theory given in Part III and also a short account of the use of second quantization.

In evaluating matrix elements in multielectron states it is convenient to make use of coefficients of fractional parentage (cfp). These coefficeints allow us to build up antisymmetric states of multielectron systems from states containing fewer electrons. The advantages of this procedure will, it is hoped, become apparent in Chapter 21. The use of cfp was developed almost entirely by Racah who was concerned with problems of atomic spectroscopy. The idea spread into nuclear shell theory and then into molecular electronic structure.

The basic and related concepts of symmetry and transformational properties can be applied to vector fields. Multipole expansions of fields have been used in physics for many years, for example, in connection with nuclear spectroscopy (Rose, 1955). The physical properties of molecules (e.g., polarizability, electric charge distribution) are frequently described by multipole expansions. In dealing with the interaction of static fields or radiation with molecules it seems natural to use multipole expansions of the relevant fields. In Part V an analysis is given of the transformations of vector fields under coordinate rotations.

The reader should not be discouraged by the occasionally forbidding formalism. The mathematical background of the average chemist is more than sufficient to overcome any difficulties. Some sections are marked (¤) to indicate that they are digressions and are temporarily or permanently dispensable. The form that these asides take is often that of a hint at the wider or deeper aspects of some part of the text, and in such cases the reader should not expect to find a substitute for serious discussion.

The text is a set of variations on a single simple theme—the behavior under coordinate transformations of scalar, spinor, and vector fields. We have limited ourselves to coordinate *rotations* and *inversions*. Even within these boundaries there are far more sophisticated developments which we do not touch, but which are primarily of importance to atomic and nuclear spectroscopists (cf. Judd, 1963, 1967). Further still, beyond these horizons, are the wide plains of general transformation theory, where roam the herds of exotic groups and transformations tamed by the physicists. The tensor methods which are our concern represent but a small domain within the empire of symmetry.

Although those pointing out the inevitable errors in the text will not be appointed third ruler in the kingdom, they will gain the author's gratitude.

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不可约张量法

这是 E. M. Loebl 编辑的"物理化学专论丛书"的第 36 卷。本书比较详细地叙述了不可约张量法，还讨论了点阵的不可约张量法，这两种方法是原子和分子结构量子力学计算中的重要数学方法。书中对点阵中双值不可约表示的不可约张量法的讨论较为详细，而且应用方面的举例也较为广泛。本书对量子化学工作者有参考价值。

目次如下：（一）：①旋转算符，②维格纳旋转矩阵，③两个角动量的耦合，④标量、向量、张量，⑤不可约张量算符，⑥维格纳-Eckart 定理，⑦ 6-j符号，⑧ 9-j符号，⑨不可约张量算符的矩阵元。（二）：⑩库仑作用，⑪旋轨耦合，⑫磁偶极-偶极作用，⑬自旋耦合，⑭电子的塞曼作用，⑮等价算符，⑯三维空间的实张量集——笛卡儿集，⑰一些多极展开式。（三）：⑱点群的 Racah 代数，⑲算符和矩阵元，⑳双值（旋子）群，（spinor groups），㉑多电子体系的矩阵元，㉒多电子体系的约化矩阵元。（四）：㉓ d^3 络离子的低自旋轨耦合，㉔旋轨耦合再举例，㉕四面体络合物中的电偶极跃迁，㉖二次量子化，㉗开壳层分子的光电子能谱。（五）：㉘矢量场，㉙光，㉚光散射。

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