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0521640628 - Group Theoretical Methods and Applications to Molecules and Crystals

Shoon K. Kim

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This book explains the basic aspects of symmetry groups as applied to problems in physics and chemistry using an approach pioneered and developed by the author. The symmetry groups and their representations are worked out explicitly, eliminating the unduly abstract nature of group theoretical methods.

The author has systematized the wealth of knowledge on symmetry groups that has accumulated during the century since Fedrov discovered the 230 space groups. All space groups, unitary as well as anti-unitary, are reconstructed from the algebraic defining relations of the point groups. The matrix representations are determined through the projective representations of the point groups. The representations of the point groups are subduced by the representations of the rotation group. The correspondence theorem on basis functions belonging to a representation is introduced to form the general expression for the symmetry-adapted linear combinations of equivalent basis functions with respect to a point group. This is then applied to form molecular orbitals and symmetry coordinates of vibration of a molecule or a crystal and the energy band eigenfunctions of the electrons in a crystal. The book assumes only an elementary knowledge of quantum mechanics. Numerous applications of the theorems are described to aid understanding.

This work will be of great interest to graduate students and professionals in solid state physics, chemistry, mathematics and geology and to those who are interested in magnetic crystal structures.

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SHOON K. KIM

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Preface

This book is written for graduate students and professionals in physics, chemistry and in particular for those who are interested in crystal and magnetic crystal symmetries. It is mostly based on the papers written by the author over the last 20 years and the lectures given at Temple University. The aim of the book is to systematize the wealth of knowledge on point groups and their extensions which has accumulated over a century since Schönflies and Fedrov discovered the 230 space groups in 1895. Simple, unambiguous methods of construction for the relevant groups and their representations introduced in the book may overcome the abstract nature of the group theoretical methods applied to physical chemical problems.

For example, a unified approach to the point groups and the space groups is proposed. Firstly, a point group of finite order is defined by a set of the algebraic defining relations (or presentation) through the generators in Chapter 5. Then, by incorporating the translational degree of freedom into the presentations of the 32 crystallographic point groups, I have determined the 32 minimum general generator sets (MGGs) which generate the 230 space groups in Chapter 13. Their representations follow from a set of five general expressions of the projective representations of the point groups given in Chapter 12. It is simply amazing to see that the simple algebraic defining relations of point groups are so very far-reaching.

In almost all other textbooks or monographs on solid-state physics, the space groups may be tabulated, but without their derivations, as if they were ‘god-given’. The main reason could have been the lack of a simple method for the derivations. As a result, the group theoretical methods have been unnecessarily abstract in an age when students are very familiar with non-commuting physical quantities in quantum mechanics.

The book is self-sufficient even though some elementary knowledge of quantum mechanics is assumed. No previous knowledge of group theory is required. In providing the basic essentials, introductory examples are given prior to the theorems. Effort has been made to provide the simplest and easiest but rigorous proofs for any theorem described in the book. Applications are fully developed. Each chapter contains something new or different in approach that cannot be found in any other monograph. For example, even in the basic theory on matrix transformation given in Chapter 2, I have introduced an involutorial transformation into the Dirac theory of the electron and arrived at the Dirac plane wave solution in one step. This transformation is used frequently in later chapters. The transformation is further extended to a new general theory of matrix diagonalization that provides the transformation matrix as a polynomial of the matrix to be diagonalized. This theory is included for its usefulness even though it is somewhat mathematical.

Some further typical features of the book are worth mentioning here. In Chapter 5, I have introduced a faithful representation for a point group using the unit basis vectors of the coordinate system. This allows one to construct the multiplication table of any point

group, e.g. the octahedral group, with ease. A new unified system of classifications for the improper point groups and anti-unitary (or magnetic) point groups is introduced, using the fact that both the inversion and the time-reversal operator commute with all the point operations. This system is quite effective for describing their isomorphisms, and thereby greatly simplifies the construction of their matrix representations and co-representations in its entirety. In Chapter 7, I have introduced a simple correspondence theorem on the basis functions of a point group G and thereby developed a general method of constructing the symmetry-adapted linear combinations (SALCs) of equivalent basis functions with respect to G . It is then applied to construct SALCs of equivalent atomic orbitals and the symmetry coordinates of vibration for molecules and later for crystals in Chapter 15. This theory requires only knowledge of the elementary basis functions of the irreducible representation and does not require the matrix representation. This is in quite a contrast to the conventional projection operator method. The correspondence theorem is further extended to form the energy band eigenfunctions of the electron in a solid in Chapter 15. By incorporating the time-reversal symmetry into point groups, anti-unitary (magnetic) point groups are formed in Chapter 16. Analogously, 38 assemblies of MGGs for 1421 anti-unitary space groups are formed from the 32 MGGs of space groups in Chapter 17. Their co-representations are introduced and applied to the selection rules under the anti-unitary groups.

Once a reader is familiar with the basic aspects of the group theoretical methods given in Chapters 3, 4 and 5, the reader can pick and choose to read any applications in later chapters using the rest of the book as the built-in references. This is possible because each chapter is as self-contained as possible and also an effective numbering system is introduced for referring to the theorems, equations and figures given in the book. Numerous examples of the applications of theorems are given as illustrations. In some chapters, I introduced a simplified special proof for a theorem to help understanding, even though its general proof had been given in an earlier chapter. In particular, those who are interested in the applications to inorganic chemistry may directly start from Chapter 7 with minimum knowledge of the group theoretical methods. One of my colleagues, Professor S. Jansen-Varnum, used the theory of symmetry-adapted linear combinations based on the correspondence theorem described in Chapter 7 of my manuscript for teaching both undergraduate and graduate courses in inorganic chemistry.

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I am very much indebted to many friends and colleagues for their help while I was writing this book. Firstly, I am very grateful to the chairpersons of the chemistry and physics departments, Dr G. Krow, Dr S. Wunder, Dr R. Salomon and E. Gawlinski. Special thanks are due to Dr D. J. Lee, the late Dr C. W. Pyun, Dr S. I. Choi, Dr S. Jansen-Varnum and Dr L. Mascavage for reviewing parts of the manuscript and to Dr K. S. Yun for valuable advice. I am also very grateful to Dr D. Titus for his help in scanning the figures into the manuscript. Whenever I had difficulty with a delicate sentence, Dr D. Dalton assisted me, so I express here my sincere gratitude for his help. Ms G. Basmajian typed the entire manuscript single-handedly. I am truly indebted to her patience and her typing skills in dealing with complicated mathematical equations.

Philadelphia, Pennsylvania

S. K. KIM

List of symbols

\in	belongs to, e.g. $g \in S$ means an element g belongs to a set S .
\forall	for all, e.g. $\forall g \in S$ means for all $g \in S$.
$*$	complex conjugate.
\sim	transpose, e.g. A^\sim is the transpose of the matrix A .
\dagger	adjoint or Hermitian adjoint, i.e. $A^\dagger = A^{*\sim}$.
\rightarrow	is mapped onto.
\leftrightarrow	one-to-one correspondence.
\otimes	direct product.
\oplus	direct sum.
\cap	set-theoretic intersection, e.g., $S_1 \cap S_2$ is the set common to the two sets S_1 and S_2 .
$\{ \}$	set of all elements.
$H < G$	H is a subgroup of a group G .
$H \triangleleft G$	H is an invariant subgroup of a group G .
$G_1 \times G_2$	the direct product group of two groups G_1 and G_2 .
$F \wedge H$	the semidirect product of two groups F and H , where F is invariant under H .
$F \simeq H$	Two groups F and H are isomorphic.