THEORETICAL METHOD OF THE LIGAND FIELD THEORY

TANG AU-CHIN

SCIENCE PRESS

配位场理论方法

唐敖庆

THEORETICAL METHOD OF THE LIGAND FIELD THEORY

TANG AU-CHIN

SUN CHIA-CHUNG　KIANG YUAN-SUN
DENG ZUNG-HAU　LIU JO-CHUANG
CHANG CHAIN-ER　YAN GUO-SEN
COO ZIEN　TAI SHU-SAN

科学出版社
SCIENCE PRESS
BEIJING, 1979

THEORETICAL METHOD OF THE LIGAND FIELD THEORY

TANG AU-CHIN

配位场理论方法

唐敖庆

*

科学出版社出版
北京朝阳门内大街137号
Published by SCIENCE PRESS
No. 137, Chaoyangmennei Street,
Beijing, China
中国国际书店发行
Distributed by GUOZI SHUDIAN
P. O. Box 399, Beijing, China

*

1979年9月第一版　开本：850×1168 1/32
1979年9月第一次印刷　印张：11 1/2　插页：2
统一书号：13031·1048
本社书号：1470·13—4
13—E—1489 S
00530
Printed in the People's Republic of China

PREFACE

During 1963 and 1965, I had the opportunity of opening a seminar at Kirin University for the comrades who were engaged in the research work of quantum chemistry in universities and other institutes and for those who were desirous of making a deeper study in this field. The topics I selected for discussion in the group theory included the continuous, the symmetric, the point and the space groups as well as their applications in atoms, molecules and solids. I gave lectures to the participating members about twelve hours a week. I also invited Professors Chou Shiao-chein and Wu Shi-shou to give a few interesting topics on the nuclear shell model and the quantum field theories respectively. Besides, arrangements were made for several of the members to report some selected topics, such as the ligand field and the molecular orbital theories ... etc. Through the seminar, it was my purpose, on the one hand, to raise the academic level of the participants and, on the other hand, to provide them more skill in solving some important problems in quantum chemistry with the powerful tool of the group theory. Through the seminar I collaborated with my co-workers to do the research work, with the result that the manuscript of the present book was produced. The main contribution of this book may be ascribed to three aspects: to discuss the V-, W- and X- coefficients of the point group on the standardized irreducible representation bases; to define successfully the partition coupling coefficients from group $SO(3)$ to group O; to build up the molecular shell model. Other particulars about the content may be found in the introduction itself. It should be pointed out that although I took the initiative to offer the topics contained in this book and have solved some problems hitherto considered as unsolvable, the whole work was done through the collective efforts of my co-

workers and myself. But for their collaboration, the present book would not have been brought into existence.

Under the title *A Study of the Theory of Ligand Field*, the major part of this treatise had been presented to the 1966 Summer Physics Colloquium of the Peking Symposium. The authors will appreciate it very much if readers of the book would point out the short-comings or even errors in its content so that improvements will be made when it is re-printed.

I have to thank my collaborators, Sun Chia-chung, Yan Guo-sen and Tai Shu-san for their help in checking the manuscript and reading the proofs.

TANG AU-CHIN

CONTENTS

PART I

PART II TABLES

PART I

CHAPTER 1

INTRODUCTION

It has been more than forty years since the ligand field theory made its appearance. It was established in 1931, when Bethe's crystal field was proposed, although, of course, great contributions in this respect have been made by other authors later. The theory, up to now, found wider applications both in chemistry and in physics. The publication of Racah's four papers in the *Physical Review* under the title *Theory of Complex Spectra* had a great effect on the ligand field theory as it had affected the nuclear and elementary particle theories. As a result, Tanabe and Sugano, in their attempts to improve the original crystal field, proposed the strong field scheme and, later on, Griffith presented a particular version of the irreducible tensor method for molecular symmetry group. In recent years, there have been some more important and valuable works on the ligand field theory.

Since the point groups are not only of the finite groups but also of the subgroups of continuous groups. The continuous groups, as a consequence, may be introduced in the ligand field theory. Thus, we do not confine ourselves in this book to the applications to the point groups in the ligand field theory but will include the continuous groups in our discussions so as to present a systematic and unified treatment. The discussions will be carried out consecutively according to the kinds of the groups, namely, the point, the three-dimensional rotation and the continuous groups in the group chain. If we want to study the ligand field theory in a systematic and unified way, the question to be solved at the beginning is to find out the standardization of the irreducible representation bases of the

point groups for a better understanding of how the bases are to be transformed under the actions both of spatial transformation and of time reversal. Therefore, we can attain our aim of making a correct choice of phase factors, and this choice will have an important effect on our later discussions. This is the content we shall deal with in detail in Chapter 2, in which the irreducible representations of point groups are classified into the three different types of A, B and C. We shall find that the standardized irreducible bases are directly related to the symmetry properties of the V-, W- and X-coefficients of the point groups presented in Chapter 3. Moreover, it often happens that a certain irreducible representation Γ_1 of the point group may occur more than once in the reduction of the direct product of $\Gamma_2 \times \Gamma_3$, and, accordingly, the various kinds of coefficients mentioned above should be further modified. In Chapter 3, the V-, W- and X- coefficients defined will not be the same for different types of representations such as the types A, B and C. In the ligand field theory, the group chains, as is well known, proposed by Racah for studying the configurations d^n and f^n in atomic theory can be generalized into the following forms:

$$SU(5) \supset SO(5) \supset SO(3) \supset O \supset D_4 \text{ or } D_3 \qquad \text{(a)}$$

$$SU(7) \supset SO(7) \supset G_2 \supset SO(3) \supset O \supset D_4 \text{ or } D_3 \qquad \text{(b)}$$

For the purpose of applying the achievements of atomic theory to the ligand field theory, we have dealt with the partition coupling coefficient from $SO(3)$ to O so as to link up the continuous and the finite groups. This coefficient and that from O to D_4 or D_3 will be discussed in Chapter 4. In Chapter 5, the Wigner-Eckart theorem will be introduced in the evaluation of matrix elements in the ligand field theory rather than its most familiar application to atomic theory with respect to group $SO(3)$. The most interesting discussion will be the building up of the molecular shell model in Chapter 6, in which we shall analyze how many group chains are to be settled under the group $SU(10)$ or $SU(14)$ for proposing the calcula-

tion schemes such as the strong, the weak and the intermediate field schemes. Furthermore, we shall present a piece of evidence of how the molecular orbitals may constitute the irreducible bases for either group chain (a) or (b), and, as a consequence, of how the restriction of these group chains with the atomic orbitals as their irreducible bases are to be removed. Though we merely set forth some new concepts and their results, the readers may glance over this chapter, if they have already had the knowledge of the Lie algebra and its representations. In Chapter 7, we shall deal with the evaluation of various kinds of matrix elements of several important group chains. It is especially noteworthy that the partition coupling coefficients from $SO(3)$ to O will play an important role in the evaluations, since they bridge the gap between the results of the continuous and the finite groups.

For practical purposes, various kinds of tables are provided in Part II of this book.

CHAPTER 2

THE STANDARDIZATION OF IRREDUCIBLE BASES

As is well known, the eigenfunctions for a molecule are the bases for irreducible representations of the point group to which the molecule belongs. The question of how to standardize the irreducible bases is a matter of importance in the application of the irreducible tensor method. The question to be solved may be related, on one hand, to gaining an understanding of the spatail transformation property of irreducible bases under the action of group elements and, on the other hand, to dealing with how the same bases would be transformed under the time reversal. In this chapter, we shall give a systematic discussion of the standardization of irreducible bases of point groups whose representations are classified into three different types referred to as A, B and C. Since the standardization of irreducible bases of point groups may be in direct relation to those of group $SO(3)$, it will be appropriate to give, for the moment, a brief review of some properties of the irreducible bases for group $SO(3)$.

2.1 The Standardization of Irreducible Bases of Group $SO(3)$

Let us consider a physical system of spherical symmetry. It is clear that any rotation operator may commute with the Hamiltonian. We shall prove that the eigenfunctions for a given eigenvalue may constitute the bases for irreducible representations of group $SO(3)$.

Now let us start our discussion with the more general case. Suppose that a group $\{R\}$ consists of all spatial transformations

which commute with the Hamiltonian of a physical system, operation of the group element R upon the wave equation,

$$\mathbf{H}\phi_i^\mu = E^\mu \phi_i^\mu$$

gives

$$\mathbf{P}_R\mathbf{H}\phi_i^\mu = E^\mu \mathbf{P}_R\phi_i^\mu$$

The above expression can be written as

$$\mathbf{P}_R\mathbf{H}\mathbf{P}_R^{-1}(\mathbf{P}_R\phi_i^\mu) = E^\mu(\mathbf{P}_R\phi_i^\mu) \tag{2.1}$$

where $\mathbf{P}_R$ is an operator corresponding to the group element R. Since $\mathbf{P}_R$ commutes with the Hamiltonian $\mathbf{H}$,

$$\mathbf{P}_R\mathbf{H}\mathbf{P}_R^{-1} = \mathbf{H}$$

we have, from Eq. (2.1),

$$\mathbf{H}(\mathbf{P}_R\phi_i^\mu) = E^\mu(\mathbf{P}_R\phi_i^\mu) \tag{2.2}$$

This equation states that, if ψ_i^μ is a solution, the result of performing the operator indicated by $\mathbf{P}_R$ will yield a function $\mathbf{P}_R\psi_i^\mu$ which is also a solution of the wave equation. Up to the present, it has been more or less informed that for any eigenvalue E^μ, there is one appropriate eigenfunction ϕ_i^μ. This is often true, but there have been also many cases in which several eigenfunctions $\phi_1^\mu, \phi_2^\mu, \cdots, \phi_k^\mu$ give the same eigenvalue E^μ. It is clear that an eigenfunction $\mathbf{P}_R\psi_i^\mu$ belonging to eigenvalue E^μ is expressed as a linear combination of a set of eigenfunctions

$$\mathbf{P}_R\phi_i^\mu(\mathbf{r}_1, \mathbf{r}_2, \cdots, \mathbf{r}_n) = \sum_j D_{ji}^\mu(R)\phi_j^\mu(\mathbf{r}_1, \mathbf{r}_2, \cdots, \mathbf{r}_n) \tag{2.3}$$

where $D_{ji}^\mu(R)$ is dependent on E^μ, ϕ_i^μ, ϕ_j^μ and R, but not on the coordinates of particles. Eq. (2.3) states that the set of eigenfunctions $\{\phi_j^\mu\}$ spans an invariant subspace for the group $\{R\}$.

We shall show that the set of eigenfunctions $\{\phi_j^\mu\}$ may form the basis for a representation of group $\{R\}$. Let us consider a general vector with position $\mathbf{r}$. On applying a certain rotation R, this vector will be transformed to a new position $\mathbf{r}'$, i.e. $\mathbf{r}' = R\mathbf{r}$. It is clear that the value of the rotated function, $\mathbf{P}_R\psi_i^\mu$, at the point $(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_n)$ must be equal to that of the

unrotated function, ψ_i^μ, at the point $(R^{-1}\mathbf{r}_1, R^{-1}\mathbf{r}_2, \ldots, R^{-1}\mathbf{r}_n)$, i.e.

$$\mathbf{P}_R\phi_i^\mu(\mathbf{r}_1, \mathbf{r}_2, \cdots, \mathbf{r}_n) = \phi_i^\mu(R^{-1}\mathbf{r}_1, R^{-1}\mathbf{r}_2, \cdots, R^{-1}\mathbf{r}_n)$$

For some other operation, $\mathbf{P}_S$, acting on $\mathbf{P}_R\psi_i^\mu$, we have

$$\begin{aligned}
&\mathbf{P}_S\mathbf{P}_R\phi_i^\mu(\mathbf{r}_1, \mathbf{r}_2, \cdots, \mathbf{r}_n) \\
&\quad = \mathbf{P}_R\phi_i^\mu(S^{-1}\mathbf{r}_1, S^{-1}\mathbf{r}_2, \cdots, S^{-1}\mathbf{r}_n) \\
&\quad = \sum_j D_{ji}^\mu(R)\phi_j^\mu(S^{-1}\mathbf{r}_1, S^{-1}\mathbf{r}_2, \cdots, S^{-1}\mathbf{r}_n) \\
&\quad = \sum_{j,k} D_{ji}^\mu(R)D_{kj}^\mu(S)\phi_k^\mu(\mathbf{r}_1, \mathbf{r}_2, \cdots, \mathbf{r}_n) \\
&\quad = \sum_k (D^\mu(S)D^\mu(R))_{ki}\phi_k^\mu(\mathbf{r}_1, \mathbf{r}_2, \cdots, \mathbf{r}_n) \qquad (2.4)
\end{aligned}$$

Since R and S are members of $\{R\}$, there must be an element SR, the effect of which acting on one of the functions in the set can be expressed as follows

$$\begin{aligned}
&\mathbf{P}_{SR}\phi_i^\mu(\mathbf{r}_1, \mathbf{r}_2, \cdots, \mathbf{r}_n) \\
&\quad = \sum_k D^\mu(SR)_{ki}\phi_k^\mu(\mathbf{r}_1, \mathbf{r}_2, \cdots, \mathbf{r}_n) \\
&\quad = \sum_k (D^\mu(S)D^\mu(R))_{ki}\phi_k^\mu(\mathbf{r}_1, \mathbf{r}_2, \cdots, \mathbf{r}_n) \qquad (2.5)
\end{aligned}$$

Since ψ_k^μ are linearly independent, we know that if two symmetry operators of the group $\{R\}$, say S and R, combine to give product SR, the matrices corresponding to S and R must multiply together to give the matrix corresponding to SR

$$D^\mu(S)D^\mu(R) = D^\mu(SR) \qquad (2.6)$$

This expression indicates that $\{D^\mu(R)\}$ form a representation of group $\{R\}$ and the set of eigenfunctions $\{\phi_j^\mu\}$ with the same eigenvalue E^μ constitutes a basis for the representation $\{D^\mu(R)\}$. When there is no accidental-degeneration, the representation is irreducible.

It will be appropriate to give, at this stage, a brief discussion of the standardization of the basis for the group $SO(3)$. It is not necessary that the readers have a very extensive know-

ledge of group theory to follow the development in this section, but the information given here is essential.

1. The Standardization of Irreducible Bases under Spatial Transformation

As is well known, the $2j+1$ angular momentum eigenvectors form a basis for an irreducible representation j of $SO(3)$. Under the action of angular momentum operators $\mathbf{J}_z$ and $\mathbf{J}_x \pm i\mathbf{J}_y$, the eigen vectors $\{\phi_m^j\}$ can be transformed in the following manner

$$\mathbf{J}_z\phi_m^j = m\phi_m^j$$
$$(\mathbf{J}_x \pm i\mathbf{J}_y)\phi_m^j = \sqrt{(j \mp m)(j \pm m + 1)}\,\phi_{m\pm 1}^j \qquad (2.7)$$

where $h/2\pi$ is taken as the unit of angular momentum. Eq. (2.7) is referred to as the standardization condition for the irreducible bases of $SO(3)$.

Alternatively, when operating a rotation operator $\mathbf{P}_R$ on $\{\phi_m^j\}$, they may be transformed in the following way

$$\mathbf{P}_R\phi_m^j = \sum_{m'} D_{m'm}^j(R)\phi_{m'}^j \qquad (2.8)$$

where $R=(\alpha, \beta, \gamma)$ is used to denote the Euler angles which, in this chapter, describe the rotation of vector in a three-dimensional space. For any element $R=(\alpha, \beta, \gamma)$ of $SO(3)$ to which a rotation operator $\mathbf{P}_{(\alpha,\beta,\gamma)}$ may correspond, we may rewrite Eq. (2.8) in the form

$$\mathbf{P}_{(\alpha,\beta,\gamma)}\phi_m^j = \sum_{m'} D_{m'm}^j(\alpha, \beta, \gamma)\phi_{m'}^j \qquad (2.9)$$

Wigner has obtained the following standardized form of $D_{m'm}^j(\alpha, \beta, \gamma)$ by the use of the standardization condition (2.7)

$$D_{m'm}^j(\alpha, \beta, \gamma) = \sum_k (-1)^k \frac{\sqrt{(j-m)!(j+m)!(j-m')!(j+m')!}}{k!(j+m'-k)!(j-m-k)!(k-m'+m)!} \cdot e^{-im'\alpha}\left(\cos\frac{\beta}{2}\right)^{2j+m'-m-2k}\left(\sin\frac{\beta}{2}\right)^{2k+m-m'} e^{-im\gamma} \qquad (2.10)$$

If $D_{m'm}^j(\alpha, \beta, \gamma)$ in Eq. (2.9) takes the standardized form,