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PREFACE

Most books on ligand-field theory are concerned with the symmetry-determined aspects of the subject. The assignment of *d–d* spectra and the construction of crystal-field correlation diagrams form the stuff of most conventional texts, whilst the differences between various books in this area usually reflect only different degrees of mathematical sophistication. In the main, the discipline and rigour such books describe refer only to quantities which depend on the angular properties of wavefunctions, radial properties being sequestered into 'proportionality constants'. From an heuristic point of view, such approaches are obviously sensible in that a qualitative understanding of phenomena must always precede a quantitative one. On being confronted with a succession of transition-metal electronic spectra, for example, it is clearly desirable to establish qualitative relationships between them and to assign electronic transitions to experimental bands before commenting upon 'crystal-field strengths'. All this is to say that the usual approach to ligand-field theory is *via* symmetry and group theory. However mathematical, such an approach is essentially qualitative; although a semi-quantitative understanding of spectra and magnetism readily follows.

The principles of crystal-field theory are usually illustrated by reference to systems with cubic symmetry, and Dq as the only scaling parameter: but few transition-metal complexes are exactly octahedral or tetrahedral. In general such distorted molecules display anisotropy in their electronic, or other, properties as evidenced, for example, by magnetic anisotropy and spectral polarization studies of single crystals. Molecules involving coordination numbers other than four or six may be anisotropic without there being distortion from some ideal symmetry: five-coordinate trigonal bipyramidal complexes typify such cases. Less tractable are molecules with rhombic or lower symmetry, though many may be described as axially distorted from an appropriate cubic symmetry precursor. In all cases, departure from cubic symmetry means less information can be had from group theory alone. Crystal-field parameters proliferate in these circumstances, $Dq, Ds, Dt, Cp, D\sigma, D\tau, \rho_2, \rho_4$, being some of the symbols used to label them throughout the literature. The parameters used vary from coordination number to coordination number, from symmetry to symmetry and from author to author. It is not always clear whether any or all of these parameters are, or can be, related to one another. Nor is it clear how the parameter values deduced from the spectra or magnetism of 'distorted' systems reflect geometrical distortions as opposed to some radial properties which may be related to bonding in some way analogous to the behaviour of $10\,Dq$.

The present book has been written to describe and explore the nature of the purely non-symmetry-determined part of ligand-field theory. Discussion of symmetry properties is only made to introduce and define ligand-field parameters. Accordingly an elementary knowledge of the usual approaches to ligand-field theory is assumed, together with a similar acquaintance with elementary group theory. It is hoped that the subject matter of this book will draw the attention of those already expert in the general area of ligand-field theory. However, the detailed presentation of the material has also been made with final year honours students and young researchers in mind. Some of the ideas described are well-established and some are new. The subject of ligand-field parameters is not closed and to some extent this book presents a progress report which includes commentary of some current areas of disagreement in the literature.

The plan of the book is roughly as follows. The introductory chapter outlines the role of symmetry in ligand-field theory and contrasts it with the function of splitting parameters. Interpretations and predictions of the simplest crystal-field and molecular-orbital approaches to the Spectrochemical Series are reviewed to focus attention on those aspects of ligand-field theory which are not determined by symmetry. Chapter 2 describes the crystal-field formalism, introducing potentials, angular and radial integrals and the multipole expansion. The expansion of the $1/r_{ij}$ operator in terms of spherical harmonics is written in various different ways in order to clarify its use. The significance of $1/r_{ij}$ as a two-electron operator, and hence the fundamental character of the crystal-field model, is elaborated in the third chapter where it is discussed in the more general context of interelectron repulsion parameters. This chapter also presents a simple discussion of interelectron repulsion parameters as determined by group theory and describes some of the approximations involved in their definition. A brief resumé of Trees' correction is included here.

Radial parameters which arise in angularly-distorted systems are described in chapter 4 and the second-order radial parameter Cp is introduced. Separation of angular distortion from radial parameters is emphasized here and several recent results of magnetic and spectral studies of single crystals are reviewed in this spirit. A similar treatment of D_{4h} symmetry molecules is made in chapter 5 where Ds and Dt parameters are defined. It is shown how values for these parameters may be recast in terms of Cp and Dq, thus possibly leading to interesting, and apparently general, trends in the ratio Cp/Dq. Throughout both chapters, the philosophy of crystal-field parameterization is discussed and the dangers of a too-literal interpretation of the definitions of Ds, Dt, Cp and Dq are emphasized.

Interpretations of radial parameters begin in chapter 6 which reviews the nature and calculation of $10\,Dq$, ranging from the most elementary point-charge model to the latest all-electron, *ab initio*, molecular-orbital calculations. The chapter aims to identify the assumptions and problems of the various methods which have been employed to calculate $10\,Dq$ and so give an insight into the various factors which really determine this quantity. No attempt is made to provide a basis for actual computation. The difficulties of *ab initio* calculations are such that simpler models must generally be used for understanding splitting parameters for a wide range of compounds and in chapter 7, a fresh appraisal of the unrealistic point-change model is described, largely in a spirit of exploration. Simple trends in the relative behaviour of Cp and Dq as functions of bond length, effective nuclear charge and ligand charge are deduced which indicate an, albeit temporary, utility for the approach described. Semi-empirical molecular-orbital models, especially the angular overlap method, are alternatives favoured by some authors and these are reviewed in chapter 8. The chapter ends with a comparison of the parameterized point-charge model and the angular overlap method applied to low-symmetry ligand-field parameters.

The Nephelauxetic effect is discussed in chapter 9. The various formalisms used to describe the effect are outlined and the apparently opposing views about evidence for differential orbital expansion are reviewed. The discussion thus centres round parameters conventionally symbolized by $B, C, F_2, F_4, \beta_{33}, \beta_{35}, \beta_{55}$. As in the discussion of the low-symmetry crystal-field parameters, some of the current areas of ignorance and the need for further research are pointed out.

To some extent each chapter may be read independently and in this form may commend itself as a 'teaching review'. All but one chapter end with a listing of particularly relevant and useful texts which are cited by a lower case letter. All other references are cited numerically and listed numerically and alphabetically at the end of the book.

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