MAGNETISM AND LIGAND-FIELD ANALYSIS

M. GERLOCH

CAMBRIDGE UNIVERSITY PRESS
Cambridge
London New York New Rochelle
Melbourne Sydney

Published by the Press Syndicate of the University of Cambridge
The Pitt Building, Trumpington Street, Cambridge CB2 1RP
32 East 57th Street, New York, NY 10022, USA
296 Beaconsfield Parade, Middle Park, Melbourne 3206, Australia

© Cambridge University Press 1983

First published 1983

Printed in Great Britain at the University Press, Cambridge

Library of Congress catalogue card number: 83–1820

British Library cataloguing in publication data

Gerloch, M
Magnetism and ligand-field analysis.
1. Ligand field theory
I. Title
541.2'242 QD475

ISBN 0 521 24939 2

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Magnetism and Ligand-Field Analysis

For my wife, Annette
and daughters, Sarah and Joanna
who put up with it all.

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Preface

By ligand-field analysis, I mean the study of a variety of ligand-field properties of transition-metal and lanthanide complexes leading to a quantified *chemical* insight into the individual metal–ligand interactions in these molecular species. I take the view that we are engaged in chemistry, that our interest is ultimately focussed on molecules, individually and as types, and that we use magnetism, spectroscopy and ligand-field theories as parts of a technique. Earlier exploitation of magnetism and ligand-field theory was largely exemplary and full of promises: a mandate was established but for years the manifesto was not carried out. It now has been: and this book seeks to tell the story of how we start with real – rather than idealized – molecules and end up with answers which are useful and readily comprehensible to the mainstream inorganic chemist. In between are the nuts and bolts of the technique. The mathematical and technical nature of the bulk of this book arise out of a desire to review and firmly establish the foundations upon which the methods of magnetochemistry and ligand-field analysis rest. The book is not, therefore, about magnetism and also about ligand-field analysis – as two separate enterprises – although a fairly clean separation has been possible on purely technical grounds: rather is it about analysis, with magnetism playing one single but important role in it.

The notion of the functional group has long played a ubiquitous role in chemical thinking but, until very recently, has failed to enrich – and, one might argue, give purpose to – all that we call ligand-field theory. As chemists we are especially interested in the separate donor or acceptor functionality of individual ligands in their discrete σ- and π-bonding roles

within a complex. Inevitably, the parametrization schemes of traditional ligand-field models are unable to provide much valid insight into such properties for, being framed too strictly within a group-theoretical straightjacket, they refer only to global quantities. It is correlation with local regions of electron density in the molecule that we seek and in most cases that concept has more validity than an arid recourse to the Wigner–Eckart theorem alone. Our chemical goals are achieved here through the angular overlap model, but in the form of a cellular decomposition of ligand-field theory that resolves the spatially local, chemical functionality without taking on board the premises and approximations of semi-empirical molecular-orbital theory. A common practical objection to the AOM has been the high degree of parametrization required by this factorization of the ligand field. Our response is to argue that an increase in the number of variables must be matched by an increase in the experimental data base; an attitude directly contrary to some earlier views that more unknowns require more assumptions. All this leads to the position that the most successful ligand-field analyses are generally likely to be those based simultaneously upon a variety of experimental techniques – paramagnetic susceptibilities, electron spin resonance, and optical spectroscopy – preferably exploiting samples in the form of single crystals. While it can be more difficult to work with such systems rather than powders or solutions, observations of anisotropic properties adds enormously to the data base. However, anisotropy is manifested only in molecules with lower symmetry. Apparently there is a catch here, for lower molecular symmetry generally begets more independent system variables, so a compromise might be indicated. On the other hand, the lower numbers of independent variables defined by a more symmetrical molecule refer increasingly to overall, global molecular properties rather than to individual, local ligand interactions. Thus, studies of higher-symmetry systems are frequently rather bare of essentially chemical content: indeed, I would argue that such has been especially responsible for a decreasing interest in ligand-field studies at the research level. And the teaching of ligand-field theory relies almost exclusively upon the octahedron and tetrahedron because of the various group-theoretical rules that flow therefrom in a readily communicable way. Often, the mysteries of elementary group theory are allowed to obscure, and even totally replace, the essential reasons for developing the whole enterprise in the first place.

So this book begins with an introductory chapter, in Part I, which summarizes the position of magnetochemistry and ligand-field analysis as it was, say a decade ago; and it identifies the need for a fresh approach

to the whole subject. The last section of the book, Part IV, illustrates the results and significance of several recent ligand-field analyses. Both sections involve minimal mathematical technique, the last chapter in particular aiming to show how the conclusions, if not their attainment, are readily discussable by the non-specialist. In between are two large sections: Part II, describing the foundations of paramagnetism from both classical and quantum-mechanical viewpoints, and its exploitation with respect to anisotropic crystals; and Part III, dealing with technical, computational and theoretical aspects of ligand-field theory. The level of presentation varies across the fairly wide range of topics covered in these chapters, in a way which hopefully reflects the typical background of an honours student or young researcher with a chemist's training. Thus, while some of the quantum mechanics is treated with a modicum of briskness, a more elementary path is taken for much of the basic physics. It is, of course, impossible to please everyone and I do apologize to those who find the text either irritating here or baffling there. Some examples of the sorts of questions that are discussed and answered throughout the book are; How are crystal magnetic properties measured? What is the difference between the fields **B** and **H**? Why does the magnetic moment operator take the form $\mu = (\mathbf{l} + 2\mathbf{s})$? Why is spin-orbit coupling called a relativistic correction? How does an explanation for magnetism require both quantum theory and the special theory of relativity? All these points and many others arise in Part II. In Part III we consider questions like: What is the nature of the ligand-field approximation? What is the difference between molecular orbitals and ligand-field orbitals? Are the procedures of ligand-field theory legitimate and why should one doubt it? What is required to construct a complete, experimental, computational and theoretical framework for ligand-field analysis? And many more.

The bonding energies that ligand-field analysis probes are generally much greater than those involved in the processes of exchange coupling, even though these may give rise to dramatic magnetic consequences. It can be argued, but I do not do so here, that the purely chemical content of exchange studies is frequently, though not inevitably, meagre. Certainly, such reliable chemical insight as may be evinced from magnetically concentrated systems often comes only after very thorough and technically difficult analysis. In any case, the subject does not fall naturally into that chosen for the present book and so no attempt has been made to cover it here. Even diamagnetism is really only relevant as a correction so far as ligand-field analysis is concerned and therefore our review of this aspect of the subject is cursory. Electron spin resonance spectroscopy, on the

other hand, is only too relevant for our field. However, several splendid texts already exist in this area and so the subject is barely covered in the present book. I do include, nevertheless, discussions on how to calculate esr g values from our quantum models and also procedures for fitting such calculations to experimental results. For rather similar reasons, I present no detailed description of the methods of optical spectroscopy as applied to ligand-field systems: these are covered in many standard books and reviews or are of such a speciality as to require separate professional coverage. Of course, the fitting of spectral transition energies, and the assignment of bands by comparison with theory, *are* topics discussed here.

I consider myself fortunate to have worked with so many able and amiable colleagues and students over the years. In one way and another they have all contributed to this book and their work is cited throughout the text. Three have helped me here explicitly. Dr J.E. Davies provided the material for Appendix A and made many valuable suggestions concerning my approach to chapter 10. Dr R.F. McMeeking has not only checked several of my wilder follies but has also provided me with instruction on, and access to, his recent unpublished work: summaries of this appear, with explicit acknowledgement, in chapters 6 and 10. Finally, Dr R.G. Woolley has guided me on various theoretical matters throughout the preparation of the book and spent much time reading first drafts: above all, he was my co-author on the original material on which chapter 11 is based. Our collaboration, then and since, has afforded me a much greater understanding of both his and my own subjects and given me enormous pleasure. I sincerely thank them all.

Several chapters were written while on sabbatical leave in Australia and I would like to record my appreciation to Professor Hans Freeman in Sydney and to Professor Bruce West at Monash University in Melbourne for making those visits possible; and to them and their colleagues, and to all our many friends in Perth, Canberra, Brisbane, Townsville, Hobart and Adelaide for their company and hospitality. As promised, special thanks are also due to those at the University of Sydney for explaining that King's Cross is not a railway station.

Finally, I thank Mrs G. Neal-Freeman for preparing the lengthy typescript so accurately and quickly.

MG
October 1982

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PART I

CHEMICAL AIMS IN LIGAND-FIELD STUDIES

While ligand-field theory grew up in the physics literature, it is probably within the discipline of chemistry that the subject is more widely taught and applied. In large measure, the chemist's approach to ligand-field models has been to exploit the purely group-theoretical aspects of the subject in order to establish 'finger-printing' rules by which molecules may be classified according to structure and bonding. Used in conjunction with the wide range of other physical techniques available to chemistry over the years, this approach has enjoyed some measure of success and, in earlier days at least, inspired fresh appreciation of theories of chemical bonding. However, a marked decline of interest in the ligand-field properties of single-centre systems has taken place in the past 15 years. Lest it seem perverse, therefore, to present yet another book in this area, it must be said at the outset that many of the efforts of the past decade or so can now be seen as having paved the way towards a contemporary exploitation of ligand-field theory which begins at last, and almost for the first time, to fulfil the explicitly *chemical* promise, hoped and claimed for the subject as long ago as the 1930s. In order to appreciate the sea change brought about by the contemporary synthesis, it is necessary to understand the reasons for the chemists' disenchantment with ligand-field theory in the recent past. In chapter 1, therefore, we begin with a little history.

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