

Understanding Molecular Properties



CARL JOHAN BALLHAUSEN

Understanding Molecular Properties

*A Symposium in Honour of Professor Carl Johan Ballhausen,
held at The Royal Danish Academy of Sciences and Letters,
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"Today we realize that the whole of chemistry is one huge manifestation of quantum phenomena."

Carl Johan Ballhausen

INTRODUCTION

This book presents the proceedings of a symposium on "Understanding Molecular Properties" in honour of Professor Carl Johan Ballhausen. The symposium was held at the Royal Danish Academy of Sciences and Letters, Copenhagen, Denmark, April 4 and 5, 1986, in connection with Professor Ballhausen's 60th birthday, and in recognition of his important contributions to quantum chemistry.

The distinguished scientists from many parts of the world who have contributed to this book have all, at some time, been associated with Carl J. Ballhausen's laboratory at the University of Copenhagen. In fact, we prepared the list of invited speakers by going through the laboratory's guest book. The symposium was thus, in a sense, a "family reunion" as well as a scientific meeting.

Many of the contributions deal with a field in which Carl J. Ballhausen was a pioneer - the experimental and theoretical study of transition metal complexes. Experimental work in this field goes back to C.W. Blomstrand and S.M. Jørgensen, who called attention to seemingly anomalous compounds of chromium, cobalt and platinum, and to A. Werner, who correctly understood the stereochemistry of these compounds. More recently, experimental work on transition metal complexes has led to a renaissance of inorganic chemistry, through the work of Jannik Bjerrum, Sir Geoffrey Wilkinson, F. Albert Cotton, Harry B. Gray and others.

The theory of transition metal complexes is, of course, an application of quantum theory, for which Copenhagen has a long tradition going back to the pioneering work of Niels Bohr. By 1929, quantum theory was sufficiently developed to account for most of the details of the spectra of free atoms. In that year, Henri Bequerel put forward the idea that the central metal ion in a transition metal complex might be treated as a free ion except for the influence of the electric field due to the charges on the surrounding ligands. The presence of this "crystal field" meant that electrons on the central ion experienced a potential which had, typically, octahedral, tetrahedral or square-planar symmetry rather than spherical symmetry.

In the same year in which Bequerel proposed this model, the symmetry aspects of crystal field theory were treated in a classic paper by Hans Bethe. He had been reading Herman Weyl's book, "The Theory of Groups in Quantum Mechanics", and he took up the problem as an exercise in group theory to make sure that he understood Weyl's book!

Bethe's pioneering work was carried farther by Robert Schlapp, W.G. Penney and especially by J.H. Van Vleck. The applications of crystal field theory to magnetism were developed by Van Vleck in his important book, "The Theory of Electric and Magnetic Susceptibilities", which was published in 1932.

In 1935, E.U. Condon and G.H. Shortley published their classic work,

"The Theory of Atomic Spectra", summarizing all that was then known about the quantum theory of free atoms; and in 1961, J.S. Griffith published "The Theory of Transition Metal Ions", in which he combined the ideas in Condon and Shortley's book with those of Bethe, Schlapp, Penney and Van Vleck. All this work, however, was done by physicists, and the results were reported in a way which was more accessible to physicists than to chemists.

In the meantime, Carl J. Ballhausen had been studying quantum theory with W. Moffitt at Harvard; and in 1962 (almost simultaneously with Griffith) he published his extremely important book, "Introduction to Ligand Field Theory". This influential book was written from the standpoint of a chemist, and it became the standard work from which chemists learned the quantum theory of transition metal complexes.

While it treated in detail the group theoretical aspects of crystal field theory, Carl J. Ballhausen's book also emphasized the limitations of the theory. As he pointed out, it is often not sufficient to treat the central metal ion as free (apart from the influence of the charges on the surrounding ligands): - In many cases hybridization of metal and ligand orbitals is significant. Thus, in general, a molecular orbital treatment is needed to describe transition metal complexes. However, much of the group theory developed in connection with crystal field theory can also be used in the molecular orbital treatment.

The improved theory, which took metal-ligand hybridization into account, became known as "ligand field theory". It was applied to compound after compound by Carl J. Ballhausen and his coworkers, in more than 100 research papers. Carl J. Ballhausen's pedagogical activities (such as his three papers in the Journal of Chemical Education, Vol. 56, 1979) have also had an important effect in making ligand field theory known to chemists. Finally, we should mention his more recent books, "Molecular Orbital Theory" (with Harry B. Gray, 1964), "Molecular Electronic Structures of Transition Metal Complexes" (1979) and "Molecular Electronic Structures" (with Harry B. Gray, 1980). All of these works have had a great influence on theoretical chemistry.

Not all of the articles in this book are devoted to ligand field theory. Among the other topics treated are reaction rates, spectroscopy, floppy molecules and the liquid state, and computational quantum chemistry. However, in dealing with these varied topics, all of the authors have tried to deepen our understanding of molecular properties, and to show how the underlying and unifying quantum theory can be used to interpret and predict the varied experimentally observable characteristics of molecules. We feel that this is in the spirit of the quotation with which we began the introduction.

We take pleasure in dedicating this book to Professor Carl Johan Ballhausen on the occasion of his 60th birthday, as a tribute to his important contributions to theoretical chemistry. We would also like to thank the distinguished scientists from four continents who have contributed to this book, and who join us in this tribute.

John Avery, Jens Peder Dahl and Aage E. Hansen, Copenhagen, 1986