John P. Lowe Kirk A. Peterson

THIRD EDITION

QUANTUM CHEMISTRY

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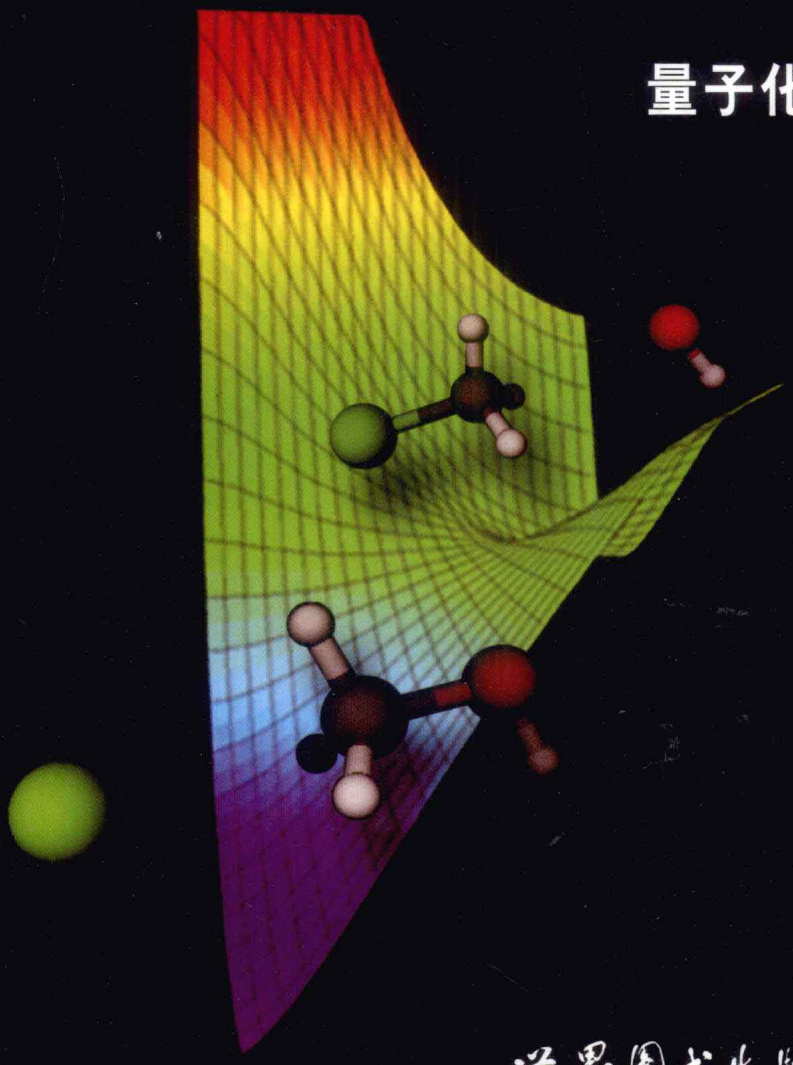

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Quantum Chemistry

Third Edition

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To
Nancy
-J. L.

THE MOLECULAR CHALLENGE

Sir Ethylene, to scientists fair prey,
(Who dig and delve and peek and push and pry,
And prove their findings with equations sly)
Smoothed out his ruffled orbitals, to say:
"I stand in symmetry. Mine is a way
Of mystery and magic. Ancient, I
Am also deemed immortal. Should I die,
Pi would be in the sky, and Judgement Day
Would be upon us. For all things must fail,
That hold our universe together, when
Bonds such as bind me fail, and fall asunder.
Hence, stand I firm against the endless hail
Of scientific blows. I yield not." Men
And their computers stand and stare and wonder.

W.G. LOWE

Preface to the Third Edition

We have attempted to improve and update this text while retaining the features that make it unique, namely, an emphasis on physical understanding, and the ability to estimate, evaluate, and predict results without blind reliance on computers, while still maintaining rigorous connection to the mathematical basis for quantum chemistry. We have inserted into most chapters examples that allow important points to be emphasized, clarified, or extended. This has enabled us to keep intact most of the conceptual development familiar to past users. In addition, many of the chapters now include multiple choice questions that students are invited to solve in their heads. This is not because we think that instructors will be using such questions. Rather it is because we find that such questions permit us to highlight some of the definitions or conclusions that students often find most confusing far more quickly and effectively than we can by using traditional problems. Of course, we have also sought to update material on computational methods, since these are changing rapidly as the field of quantum chemistry matures.

This book is written for courses taught at the first-year graduate/senior undergraduate levels, which accounts for its implicit assumption that many readers will be relatively unfamiliar with much of the mathematics and physics underlying the subject. Our experience over the years has supported this assumption; many chemistry majors are exposed to the requisite mathematics and physics, yet arrive at our courses with poor understanding or recall of those subjects. That makes this course an opportunity for such students to experience the satisfaction of finally seeing how mathematics, physics, and chemistry are intertwined in quantum chemistry. It is for this reason that treatments of the simple and extended Hückel methods continue to appear, even though these are no longer the methods of choice for serious computations. These topics nevertheless form the basis for the way most non-theoretical chemists understand chemical processes, just as we tend to think about gas behavior as "ideal, with corrections."

Preface to the Second Edition

The success of the first edition has warranted a second. The changes I have made reflect my perception that the book has mostly been used as a teaching text in introductory courses. Accordingly, I have removed some of the material in appendixes on mathematical details of solving matrix equations on a computer. Also I have removed computer listings for programs, since these are now commonly available through commercial channels. I have added a new chapter on MO theory of periodic systems—a subject of rapidly growing importance in theoretical chemistry and materials science and one for which chemists still have difficulty finding appropriate textbook treatments. I have augmented discussion in various chapters to give improved coverage of time-dependent phenomena and atomic term symbols and have provided better connection to scattering as well as to spectroscopy of molecular rotation and vibration. The discussion on degenerate-level perturbation theory is clearer, reflecting my own improved understanding since writing the first edition. There is also a new section on operator methods for treating angular momentum. Some teachers are strong adherents of this approach, while others prefer an approach that avoids the formalism of operator techniques. To permit both teaching methods, I have placed this material in an appendix. Because this edition is more overtly a text than a monograph, I have not attempted to replace older literature references with newer ones, except in cases where there was pedagogical benefit.

A strength of this book has been its emphasis on physical argument and analogy (as opposed to pure mathematical development). I continue to be a strong proponent of the view that true understanding comes with being able to "see" a situation so clearly that one can solve problems in one's head. There are significantly more end-of-chapter problems, a number of them of the "by inspection" type. There are also more questions inviting students to explain their answers. I believe that thinking about such questions, and then reading explanations from the answer section, significantly enhances learning.

It is the fashion today to focus on state-of-the-art methods for just about everything. The impact of this on education has, I feel, been disastrous. Simpler examples are often needed to develop the insight that enables understanding the complexities of the latest techniques, but too often these are abandoned in the rush to get to the "cutting edge." For this reason I continue to include a substantial treatment of simple Hückel theory. It permits students to recognize the connections between MOs and their energies and bonding properties, and it allows me to present examples and problems that have maximum transparency in later chapters on perturbation theory, group theory, qualitative MO theory, and periodic systems. I find simple Hückel theory to be educationally indispensable.

Much of the new material in this edition results from new insights I have developed in connection with research projects with graduate students. The work of all four of my students since the appearance of the first edition is represented, and I am delighted to thank Sherif Kafafi, John LaFemina, Maribel Soto, and Deb Camper for all I have learned from them. Special thanks are due to Professor Terry Carlton, of Oberlin College, who made many suggestions and corrections that have been adopted in the new edition.

Doubtless, there are new errors. I would be grateful to learn of them so that future printings of this edition can be made error-free. Students or teachers with comments, questions, or corrections are more than welcome to contact me, either by mail at the Department of Chemistry, 152 Davey Lab, The Pennsylvania State University, University Park, PA 16802, or by e-mail directed to JL3 at PSUVM.PSU.EDU.

Preface to the First Edition

My aim in this book is to present a reasonably rigorous treatment of molecular orbital theory, embracing subjects that are of practical interest to organic and inorganic as well as physical chemists. My approach here has been to rely on physical intuition as much as possible, first solving a number of specific problems in order to develop sufficient insight and familiarity to make the formal treatment of Chapter 6 more palatable. My own experience suggests that most chemists find this route the most natural.

I have assumed that the reader has at some time learned calculus and elementary physics, but I have not assumed that this material is fresh in his or her mind. Other mathematics is developed as it is needed. The book could be used as a text for undergraduate or graduate students in a half or full year course. The level of rigor of the book is somewhat adjustable. For example, Chapters 3 and 4, on the harmonic oscillator and hydrogen atom, can be truncated if one wishes to know the nature of the solutions, but not the mathematical details of how they are produced.

I have made use of appendixes for certain of the more complicated derivations or proofs. This is done in order to avoid having the development of major ideas in the text interrupted or obscured. Certain of the appendixes will interest only the more theoretically inclined student. Also, because I anticipate that some readers may wish to skip certain chapters or parts of chapters, I have occasionally repeated information so that a given chapter will be less dependent on its predecessors. This may seem inelegant at times, but most students will more readily forgive repetition of something they already know than an overly terse presentation.

I have avoided early usage of bra-ket notation. I believe that simultaneous introduction of new concepts and unfamiliar notation is poor pedagogy. Bra-ket notation is used only after the ideas have had a change to jell.

Problem solving is extremely important in acquiring an understanding of quantum chemistry. I have included a fair number of problems with hints for a few of them in Appendix 14 and answers for almost all of them in Appendix 15.[1]

It is inevitable that one be selective in choosing topics for a book such as this. This book emphasizes ground state MO theory of molecules more than do most introductory texts, with rather less emphasis on spectroscopy than is usual. Angular momentum is treated at a fairly elementary level at various appropriate places in the text, but it is never given a full-blown formal development using operator commutation relations. Time-dependent phenomena are not included. Thus, scattering theory is absent,

[1] In this Second Edition, these Appendices are numbered Appendix 12 and 13.

although selection rules and the transition dipole are discussed in the chapter on time-independent perturbation theory. Valence-bond theory is completely absent. If I have succeeded in my effort to provide a clear and meaningful treatment of topics relevant to modern molecular orbital theory, it should not be difficult for an instructor to provide for excursions into related topics not covered in the text.

Over the years, many colleagues have been kind enough to read sections of the evolving manuscript and provide corrections and advice. I especially thank L. P. Gold and O. H. Crawford, who cheerfully bore the brunt of this task.

Finally, I would like to thank my father, Wesley G. Lowe, for allowing me to include his sonnet, "The Molecular Challenge."

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