VALENCY AND BONDING

This graduate-level text presents the first comprehensive overview of modern chemical valency and bonding theory, written by internationally recognized experts in the field. The authors build on the foundation of Lewis- and Pauling-like localized structural and hybridization concepts to present a book that is directly based on current *ab initio* computational technology.

The presentation is highly visual and intuitive throughout, being based on the recognizable and transferable graphical forms of natural bond orbitals (NBOs) and their spatial overlaps in the molecular environment. The book shows applications to a broad range of molecular and supramolecular species of organic, inorganic, and bioorganic interest. Hundreds of orbital illustrations help to convey the essence of modern NBO concepts in a facile manner for those with no extensive background in the mathematical machinery of the Schrödinger equation. This book will appeal to those studying chemical bonding in relation to chemistry, chemical engineering, biochemistry, and physics.

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VALENCY AND BONDING

A Natural Bond Orbital Donor–Acceptor Perspective

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Preface

Two daunting questions face the authors of prospective textbooks. (1) For whom is the book intended? (2) What makes it different from other books intended for the same audience? We first address these questions.

One might think from counting the mathematical equations that the book is intended for a theoretical physicist. This is partially true, for indeed we hope the subject is presented in a way that will satisfy a rigorously inclined mathematical physicist that "valency and bonding" is not just murky chemical voodoo, but authentic science grounded in the deepest tenets of theoretical physics.

Beyond Chapter 1 the reader may be relieved to find few if any equations that would challenge even a moderately gifted high-school student. The emphasis on orbital diagrams and "doing quantum mechanics with pictures" might then suggest that the book is intended for undergraduate chemistry students. This is also partially true. For example, we believe that our treatment of homonuclear diatomic molecules (Section 3.2.9) should be accessible to undergraduates who commonly encounter the topic in introductory chemistry courses.

Our principal goal has been to translate the deepest truths of the Schrödinger equation into a visualizable, intuitive form that "makes sense" even for beginning students, and can help chemistry teachers to present bonding and valency concepts in a manner more consistent with modern chemical research. Chemistry teachers will find here a rather wide selection of elementary topics discussed from a high-level viewpoint. The book includes a considerable amount of previously unpublished material that we believe to be of broad pedagogical interest, such as the novel Lewis-like picture of transition-metal bonding presented in Chapter 4.

Because we are both computational chemistry researchers, we have naturally directed the book also to specialists in this field, particularly those wishing to incorporate natural bond orbital (NBO) and natural resonance theory (NRT) analysis into their methodological and conceptual toolbox. Researchers will find here a

rather broad sampling of NBO/NRT applications to representative chemical problems throughout the periodic table, touching on many areas of modern chemical, biochemical, and materials research.

But, we expect that the majority of readers will be those with only a rudimentary command of quantum chemistry and chemical bonding theory (e.g., at the level of junior-year physical chemistry course) who wish to learn more about the emerging *ab initio* and density-functional view of molecular and supramolecular interactions. While this is not a "textbook in quantum chemistry" per se, we believe that the book can serve as a supplement both in upper-level undergraduate courses and in graduate courses on modern computational chemistry and bonding theory.

In identifying the features that distinguish this book from many predecessors, we do not attempt to conceal the enormous debt of inspiration owed to such classics as Pauling's *Nature of the Chemical Bond* and Coulson's *Valence*. We aspire neither to supplant these classics nor to alter substantially the concepts they expounded. Rather, our goal is to take a similarly global view, but develop a more current and quantitative perspective on valency and bonding concepts such as hybridization, electronegativity, and resonance, capitalizing on the many advances in wavefunction calculation and analysis that have subsequently occurred. We hope thereby to sharpen, revitalize, and enhance the usefulness of qualitative bonding concepts by presenting a "twenty-first-century view" of the nature of chemical bonding.

Readers who are accustomed to seeing chemical theorizing buttressed by comparisons with experiments may be surprised to find little of the latter here. Throughout this book, computer solutions of Schrödinger's equation (rather than experiments) are regarded as the primary "oracle" of chemical information. We specifically assume that high-level calculations (e.g., at the hybrid density-functional B3LYP/6-311++G** level) can be relied upon to describe molecular electronic distributions, geometries, and energetics to a sufficient degree of chemical accuracy for our purposes. (In fact, the accuracy is often comparable to that of the best available experimental data, more than adequate for qualitative pedagogical purposes.) The viewpoint of this book is that modern *ab initio* theory no longer requires extensive experimental comparisons in order for it to be considered seriously, and indeed, theory can be expected to supplant traditional experimental methods in an increasing number of chemical investigations. In the deepest sense, this is a "theory book."

Dual authorship naturally brings a distinctive blend of perspectives. The book reflects the influence of a "donor–acceptor" perspective based on NBO/NRT wavefunction analysis methods developed in the research group of F. W. (a physical chemist). While NBO analyses are now rather common in the chemical literature, the present work provides the first broad overview of organic and inorganic chemical phenomena from this general viewpoint. The book also incorporates key insights gained from constructing valence-bond-based (VALBOND) molecular-mechanics

potentials for transition metals and hypervalent main-group species, as carried out in the research group of C. R. L. (an inorganic chemist). We both recognize how the constructive synergism of our distinct cultures has added breadth and dimension to this work.

Uppermost in our minds has been a strong concern for chemical pedagogy, which is manifested in several ways. Because we were often prompted by such questions ourselves, we have tended to organize the presentation around "frequently asked questions," with the emphasis being on individual species that hold special fascination for students of bonding theory. Although leading references for further study are provided, in few if any cases do we attempt a comprehensive survey of the literature; indeed, such a survey would be quite impractical for many of the evergreen bonding topics. Our treatment therefore resembles a textbook rather than a specialist research monograph or review article. We have also taken the opportunity to include numerous examples, including worked-out problems, derivations, and illustrative applications to chemical problems. These often serve as a parallel presentation of important concepts, giving the student a helping hand through rough spots and putting "some flesh on those bones" of abstract text equations.

We are grateful to numerous colleagues who contributed encouragement, advice, criticism, and topics for study. Special thanks are due to Christine Morales for performing the numerical applications of Chapter 4 at higher triple-zeta level, to Mark Wendt for assistance with *NBOView* orbital imagery, and to Bill Jensen for providing photographic portraits from the Oesper Collection at the University of Cincinnati. We benefited from the excellent computing facilities at the University of Wisconsin-Madison under the long-time direction of Brad Spencer. We also wish to acknowledge the patience and support of our families and the kind cooperation of our Cambridge University Press editors, who confronted the many production challenges of the manuscript with skill and good cheer.