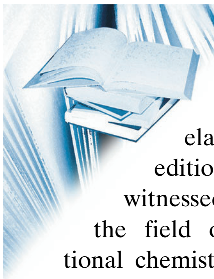
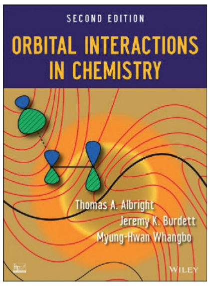


Orbital Interactions in Chemistry



Orbital Interactions in Chemistry
2nd Edition. By Thomas A. Albright, Jeremy K. Burdett and Myung Hwan Whangbo. John Wiley & Sons, Hoboken, 2013. 834 pp., hardcover, € 135.60.—ISBN 978-0471080398

The thirty years that have elapsed since the acclaimed first edition of this book have witnessed a spectacular evolution of the field of theoretical and computational chemistry. Luckily, the authors have decided to preserve the original orbital approach to bonding, stereochemistry, and reactivity that was the landmark of the original version, and readers who are familiar with the first edition will find essentially all the useful descriptions of fragment orbitals and orbital interaction diagrams, and should therefore feel comfortable in switching to the new expanded edition. At the same time, a wealth of new literature references has been added, and the structure of the book has been partially reshaped. In the first edition, the book's orbital perspective was complemented by a chapter dealing with the theoretical foundations of two-electron terms. Now, added to that, there are two sections that consider post-Hartree–Fock and density functional methods. The cover also keeps the original look, only with a different orbital depicted, as a subtle homage to one of the authors, Jeremy Burdett, who passed away in 1997.

With twice as many pages and a larger format than its predecessor, this new edition has become unsuitable for reading while riding the subway. What do we get in exchange? The most relevant changes are the addition of two new chapters on surfaces and on magnetism, and three appendices that provide a detailed formulation of perturbation MO (molecular orbital) theory, a set of character tables, and a pictographic collection of normal vibration modes. The latter two appendices are expected to be of help when reading some parts of the book, although the character tables lack the usual column that would indicate the representation to which some simple functions belong (x, y, z, xy …), so useful for classifying atomic orbitals and normal modes by their symmetry. It is no coincidence that the chapter that has been most extensively restructured and expanded is the one devoted to symmetry. Another most welcome addition is a short section on photoelectron spectra as the experimental counterpart to the MO diagrams, which is included in the chapter devoted to diatomic molecules. Consistently, there are many such spectra throughout the book to accompany the discussion of the electronic structures of a variety of representative molecules. Another systematic improvement is the inclusion of contour plots of the frontier orbitals of the most important fragments, reminiscent of a rare unpublished pamphlet written by one of the authors in 1977 under the title *A Holiday Coloring Book of Fragment Molecular Orbitals*. Wisely enough, the authors have decided to keep, side-by-side, the schematic drawings that, although less accurate, give a better visual representation of the topology of a molecular orbital than is given by a cross-section of the isodensity surfaces. Along the same lines, a few dozen of the schematic drawings of molecular structures that were present in the previous edition are now supplemented (not replaced) by three-dimensional representations.

The aim of providing qualitative theoretical explanations for the experimental behavior of the compounds discussed is a trademark of this book. In most cases this is done by showing the stereochemistry or bonding parameters of specific molecules that are considered to be representative of important families of compounds. Only occasionally are there attempts to present larger collections of data in the form of plots or statistical parameters, as is done in the discussion of the bridging and semi-bridging nature of the carbonyl ligand, or of the ionization potentials of the group 15 hydrides.

The book is organized in 24 chapters. Molecular orbital concepts and theory are introduced in the first eight chapters, which show how to build MOs from fragment orbitals using the simplest examples, consisting only of hydrogen atoms or a main-group element surrounded by two or three hydrogen atoms. Two further chapters deal with molecules that are still small and are composed of one or two main-group element atoms and hydrogen atoms. Then two chapters discuss simple organic molecules such as cyclopropane, cyclobutane, and polyenes, including the concepts of through-space and through-bond interaction, as well as the Hückel theory.

The next chapter introduces the reader to the formalism and the tools of band theory for chains and solids, significantly expanded in this edition, with a more detailed discussion of the dispersion and density-of-states diagrams. Also two- and three-dimensional systems are introduced more gradually in this edition, and one finds newly added discussions on the shape of Fermi surfaces, nesting vectors, and charge density waves. A section devoted to the Zintl–Klemm concept is also a welcome addition to this chapter. Subsequent chapters include sections on extended systems as a follow-up to molecular compounds made from a particular fragment, thus encompassing molecules, chains, and solids within the same conceptual framework. This is a bonus of this book, and differentiates it from other excellent texts devoted only to solids that have been published in recent years by Dronskowski and by Canadell, Doublet, and Iung (not to mention the pedagogical view of a classic booklet by Hoffmann). A chapter centered on hypervalent molecules is structured in three broad sections, the first and third ones of which are devoted to molecules, without further subdivision, which makes it difficult to follow an argumental thread or to find the specific cases discussed. The second section is devoted to hypervalency in solid state compounds, which is indeed a good reason for considering hypervalent molecules after the general introduction to solid state theory.

The parts of the book that deal with transition metal complexes are organized according to two different classification criteria: first by coordination number (chapters for six-, four-, and five-coordinate complexes), then by molecular fragments (one chapter for the planar ML_3 fragment, another for ML_2 and ML_4 fragments, and one for pyramidal ML_3 together with MCp and MCp_2 fragments). The section of the chapter on four-coordinate complexes that is devoted to solid state compounds includes a thorough discussion of the copper-based high-temperature superconductors, although that topic is not indicated in either the section title or the subject index. With all the fragment orbitals toolbox now at hand, two elegant chapters follow naturally, focusing on the isolobal analogy and cluster compounds. Clusters are now treated in more detail, including the ML_n fragment orbitals that participate in skeletal bonding, extensions to capped deltahedra, and a new section on known violations of Wade's rules.

The last two chapters are new additions in the second edition. One of those chapters presents an introduction to different surface types and surface coverage, and discusses the adsorption of diatomic molecules on a surface as well as the surfaces of semiconductors and their reconstruction. The final chapter, on magnetic properties, presents a personal view of the field, focused essentially on solid state compounds, and practically disregarding the subject of molecular magnetism, which contains such important topics as spin crossover complexes and single-molecule magnets. Thus, for example, the topic of spin polarization and the low/high dichotomy of spin states for paramagnetic molecules is only discussed in the chapter devoted to organic molecules and free radicals.

Unlike its predecessor, this book provides a collection of exercises at the end of each chapter. The solutions to those exercises can, in principle, be obtained from the publisher's website. Unfortunately, access to that content requires one to be a registered user provided with a password, and this reviewer has been unable to register and gain access to the solutions to the exercises, even after an exchange of several e-mails with the publisher.

Even a high-density book as this one cannot be comprehensive, and the authors must make some choices. One of the topics that is scarcely covered at all is multiple metal–metal bonding, which is only mentioned briefly in a section under the generic title "Olefin ML_4 Complexes and M_2L_8 Dimers" and in the section entitled "Derivation of Orbitals for a C_{3v} ML_3 Fragment". In the subject index the term "metal–metal bonding" refers only to the page where single bonds are taken into account for electron counting purposes. Some topics that are covered are not easy to locate, and one would have expected a more detailed subject index. Some examples of topics not found in the index are: quintuple/pentuple, quadruple, or multiple bonds, soft or hard acids and bases, spin crossover, hydrogen bonding, intermolecular or van der Waals interactions, Zeise's salt, Magnus green salt, trigonal prism, Bailar twist, and Berry pseudorotation. Some other named compounds appear only through their formulas, not under their common names, as in the cases of Wolfram red salt (found as Pt^{2+}/Pt^{4+} mixed valence) or the Hogeveen dication (found as $C_6H_6^{2+}$). Some readers may also be surprised to see that the formulas of coordination compounds are not enclosed in square brackets in accordance with the IUPAC recommendations for chemical nomenclature.

The many interesting aspects of this book largely outweigh the few shortcomings mentioned. On the positive side, we can count the large collection of examples and topics that are covered under a unifying orbital view, the excellent layout and the high quality graphics, the pedagogical writing style, the practical exercises at the end of each chapter, the updated bibliography, and the inclusion of experimental photoelectron spectra to compare with the molecular orbital diagrams. In summary, this new edition fully deserves to replace, or better to accompany, the earlier edition in our bookshelves and libraries.

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