Orbitals in Chemistry

Modern chemistry owes a great deal to two fundamental concepts, energy and probability, usually coupled to each other. One of the main examples of such a fruitful convergence is the field of quantum chemistry and orbital theory. The orbital concept provides the basic preparation in atomic and molecular structure theory needed for the understanding and interpretation of organic chemistry, inorganic chemistry and spectroscopy.

This text presents a unified and up-to-date discussion of the role of atomic and molecular orbitals in chemistry, from the quantum mechanical foundations to the recent developments (brief discussion of special systems such as solids and C_{60}, density-functional theory and Kohn–Sham orbitals) and applications (physical properties, reactivity, spectroscopy). The discussion is mainly qualitative, largely based on symmetry arguments. It is felt that a sound mastering of the concepts and qualitative interpretations is needed especially when students are becoming more and more familiar with numerical calculations based on atomic and molecular orbitals. The text is mathematically less demanding than most traditional quantum chemistry books but still retains clarity and rigour. The physical insight is maximized and abundant illustrations are used. The relationships between the more formal quantum-mechanical formalisms and the traditional descriptions of chemical bonding are critically established.

This book is of primary interest to undergraduate chemistry students and others taking courses of which chemistry is a significant part.

VICTOR M. S. GIL was born in Portugal on 13 March 1939. His Ph.D. was in NMR spectroscopy at the University of Sheffield in 1965. He is past Chairman of the Installation Committee and was first Rector of the University of Aveiro (Portugal) from 1973 to 1977. He is currently Professor of Chemistry at the University of Coimbra, Portugal, and Director of Explorations, the interactive science centre of Coimbra. His active area of research is NMR spectroscopy, in particular spectral parameters and molecular structure, conformational analysis, sugar chemistry and coordination compounds (vanadium, molybdenum, tungsten and uranium). He is author of over 100 scientific papers, co-author of a book on NMR spectroscopy and has written several papers on the teaching and learning of chemistry. He has also co-authored the current chemistry syllabus for Portuguese schools (from 8th grade to 12th grade) and is co-author of several books and software products for chemistry teaching in schools. He has taught more than 10 000 undergraduate students and has supervised 10 Ph.D. and M.Sc. theses along his career.

Orbitals in Chemistry
A Modern Guide for Students

VICTOR M. S. GIL
University of Coimbra, Portugal

CAMBRIDGE
UNIVERSITY PRESS

CAMBRIDGE UNIVERSITY PRESS
Cambridge, New York, Melbourne, Madrid, Cape Town, Singapore,
São Paulo, Delhi, Dubai, Tokyo

Cambridge University Press
The Edinburgh Building, Cambridge CB2 8RU, UK

Published in the United States of America by Cambridge University Press, New York

www.cambridge.org
Information on this title: www.cambridge.org/9780521666497

First published 2000

A catalogue record for this publication is available from the British Library

Library of Congress Cataloguing in Publication data

Gil, Victor M. S., 1939–
Orbitals in chemistry: modern guide for students/Victor M. S. Gil.
p. cm.
Includes bibliographical references.
ISBN 0-521-66167-6 (hb)
1. Molecular orbitals. I. Title.

QD461 G52 2000
541.2′8–dc21 99-461968

ISBN 978-0-521-66167-6 Hardback
ISBN 978-0-521-66649-7 Paperback

Transferred to digital printing 2009

Contents

Preface

Modern chemistry owes a great deal to two fundamental concepts, energy and probability, which appear frequently coupled to each other. Main examples of such a fruitful convergence are the second law of thermodynamics and entropy (in the field of chemical transformations) and quantum chemistry and orbitals (in the field of structure of atoms and their groupings and properties). Orbitals are the central subject of this book, presented in a unified and updated review. The discussion is mainly qualitative, largely based on symmetry arguments. It is felt that a sound mastering of the concepts and qualitative interpretations is needed especially when students are becoming more and more familiar with numerical calculations based on atomic and molecular orbitals. The text is mathematically less demanding than most traditional quantum chemistry books, but still retains clarity and rigour.

This is thus a chemically oriented, not too advanced book, written in an easy-going style. Without loss of correctness, the physical insight is maximized and abundant graphical illustrations are used. A large number of figures (127) and many diagrams help to make the book less dense and more instructive. The relationships between the more formally based quantum-mechanical formalisms and the traditional chemical descriptions of atomic and molecular structure are established and discussed in a critical manner.

A selected collection of problems (120) is included. Instead of listing the problems at the end of each chapter, they are presented at the right moment in the text and totally integrated with it; the reader is, thus, strongly encouraged to solve the problems in the appropriate context (and compare his or her answers to those given at the end of the book), but it is not compulsory to do that in order to continue the reading and learning process.

The bibliography includes 85 papers on the teaching of Chemistry and Physics (73 of which are from the *Journal of Chemical Education*). Accordingly, the book reflects the up-dated views conveyed by the numerous publications especially in the *Journal of Chemical Education* related to the subject. It was the critical use of all this information together with his own experience and discussions with colleagues that enabled the author to avoid the enigma and the misinterpretations frequently encountered in introductions to quantum theory in many chemistry books and to produce a simple, yet correct, text. Examples of topics which deserved detailed attention because they are often objects of misinterpretation are the wave–particle duality and the Heisenberg principle, the question of the electronic energy in terms of the orbital contributions, the use (and misuse) of hybrid orbitals and localized descriptions of the chemical bonding and the widely used qualitative models of molecular geometry.

Here is a brief description of the contents. Setting the stage for the main chapters, two short introductory chapters are devoted to the fundamentals of quantum mechanics: energy quantization; wave–particle duality in relation to observations, wavefunctions and the indeterminacy principle; the main operators and their properties, the Schrödinger equation for simple systems and, briefly, spin and relativity. Atomic and molecular orbitals for one-electron systems are introduced in Chapters 3 and 4; molecular orbitals are approximated by linear combinations of atomic orbitals; total electron angular momentum is analyzed. The adaptation of the orbital concept to many-electron atoms is dealt with in Chapter 5: Hartree–Fock orbitals, Kohn–Sham orbitals and electron correlation; electron configurations, terms and levels for open-shell atoms are discussed; some attention is also paid to relativistic effects. Molecular orbitals and chemical bonding in diatomic and polyatomic molecules are presented in Chapters 6 and 7, respectively, taking advantage of symmetry; electronegativity scales are compared; an introduction is made to the quantitative determination of molecular orbitals for any molecule, at different levels of approximation. Chapter 8 establishes the bridge between molecular orbitals, which are by definition delocalized functions, and the classical language used by chemists in their discussion of bonding and other electronic properties, namely the concepts of electron pair bonding and structural formulae: an introduction to Bader's theory of atoms in molecules, a discussion of canonical molecular orbitals and localized (or quasi-localized) functions, an introduction to electron pairing in valence-bond theory, a critical analysis of the VSEPR method in the interpretation of molecular geometry, a thorough discussion of the uses and misuses of hybrid orbitals. The theme of structural formulae is resumed in

Chapter 10, in relation to classical bond orders and bond energies. In the meantime, Chapter 9 deals with the σ–π molecular orbital separation, conjugated systems, non-localizable π molecular orbitals and resonance. In Chapter 11 a brief extension of molecular orbital theory is made to include three categories of systems: fullerenes, transition metal complexes, solid aggregates (and band theory). Finally, Chapter 12 mainly illustrates the direct relations between orbitals and chemical reactivity and between orbitals and spectroscopy, with emphasis on electronic transitions and on spectral parameters in NMR spectroscopy.

It is hoped that the present book, which is of primary interest to undergraduate chemistry students, will provide, in an economic way, the basic preparation in atomic and molecular structure and chemical bonding theory needed for the interpretation of organic chemistry, inorganic chemistry and spectroscopy.

Victor M. S. Gil
Coimbra (Portugal), September 1999

Acknowledgements

My first thoughts of gratitude go to (the late) Professor F. Pinto-Coelho of the University of Coimbra (Portugal), for teaching me about orbitals when I was an undergraduate student, and to Professor John N. Murrell of the University of Sussex, (U.K.), for making me use the concept in a critical manner when I was a Ph.D student of his at the University of Sheffield (U.K.) and for his guidance and collaboration ever since.

Thanks are also due to many of my colleagues and students who directly or indirectly contributed to my education in this field. The more recent help of many is gratefully acknowledged, especially the theoretical physicists Helena Caldeira and Carlos Fiolhais (for discussions on the wave–particle duality and the Heisenberg principle and on density-functional theory, respectively), the Ph.D. students Jorge Trindade and Sérgio Rodrigues (for help with the numerical calculations and the graphical displays of molecular orbitals), the chemist Paula Catarro (for the molecular orbital diagrams), the chemists Christoffer Brett, Hugh Burrows, Brian Goodfellow and Ana Gil (for criticizing the text and correcting the language mistakes). Thanks are also extended to the reviewers of Cambridge University Press.

Finally, I am thankful to those periodicals and authors who permitted the reproduction of figures and to the Gulbenkian Foundation (Lisbon) for allowing the use of much of the material which I have included in a Portuguese book previously edited by them.