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978-0-521-10567-5 - The Determination and Interpretation of Molecular Wave Functions

Erich Steiner

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Cambridge University Press

CAMBRIDGE

LONDON · NEW YORK · MELBOURNE

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CAMBRIDGE UNIVERSITY PRESS

Cambridge, New York, Melbourne, Madrid, Cape Town, Singapore, São Paulo, Delhi

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/9780521105675

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First published 1976

This digitally printed version 2009

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

Library of Congress Catalogue Card Number: 75-18120

ISBN 978-0-521-21037-9 hardback

ISBN 978-0-521-10567-5 paperback

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Preface

It is a fact of some historical interest that although a comprehensive and detailed theory of the electronic structure and bonding in molecules had been developed by the year 1960 (Pauling 1960; Coulson 1961), very few non-empirical ('*ab initio*') quantum-mechanical calculations for polyatomic molecules were performed before that date. The theory was built up almost wholly intuitively and empirically from an experimental knowledge of the physical and chemical properties of molecules, coupled with an extrapolation to polyatomic molecules of the results of (i) accurate solutions of the Schrödinger equation for the hydrogen molecule and molecular ion, (ii) highly approximate non-empirical calculations for small, and mainly diatomic, molecules, and (iii) semi-empirical calculations, mainly of the Hückel molecular-orbital type, for some larger molecules. It was not until the late 1950s that the advent of the electronic computer brought with it the possibility of performing accurate non-empirical calculations for polyatomic molecules of chemical interest. Much of the subsequent evolution of the theory of molecular structure has paralleled, and has to a certain extent depended on, the development of computing machines and techniques.

The advent of the computer has led to the creation of a new branch of theoretical chemistry, computational quantum chemistry, with its own specialized language, and with concepts that are increasingly influenced by questions of mathematical tractability and computational expedience. One consequence has been the creation of new problems of communication between theoretical chemist and experimental chemist, and this book can be regarded as an attempt to bridge the widening gap between the two. The primary concern of the book is the exposition of some of the more important theoretical and computational techniques that have been developed in recent years for the determination and interpretation of molecular wave functions, with particular emphasis on the non-empirical molecular-orbital approach. A feature of the evolution of the theory since 1960 has been the declining importance of the valence-bond approach as a practical tool of the computational quantum chemist. Although valence-bond theory is as valid as molecular-orbital theory, and merely represents an alternative method of constructing molecular wave functions, molecular-orbital theory has been found to be the more con-

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venient for computational purposes and, to a lesser extent, for interpretative purposes.

It has been assumed that the reader is a graduate or advanced undergraduate in chemistry, with the appropriate knowledge of mathematics and of the applications of quantum mechanics in chemistry. Chapter 1 is devoted to a brief discussion of the non-relativistic time-independent Schrödinger equation for the motion of electrons in molecules, and of the general techniques available for its solution. Chapter 2 deals with the symmetry properties of electronic wave functions. Nearly all of the material in these first two chapters can be found discussed at greater length in standard undergraduate texts, but it has been included both to make the book more or less self-contained and to introduce the notation, units, and those general concepts that are used in the subsequent discussion. Chapter 3 is devoted to the Hartree–Fock model of electronic structure, and to its relation to what is commonly known as molecular-orbital theory. Methods of proceeding beyond the orbital approximation towards the exact solution of the Schrödinger equation are considered in chapter 4, which also includes a brief discussion of relativistic effects. Chapter 5 is concerned with some of the computational techniques that have been developed for the practical implementation of the theory developed in the previous chapters. The analysis and interpretation of molecular wave functions is discussed in the final two chapters. Chapter 6 is concerned with the electron distribution and chapter 7 with the nature of the chemical bond.

I wish to acknowledge with gratitude the encouragement and advice given to me by several of my colleagues in the Chemistry Department. Particularly I would like to thank Dr B. J. Skillerne de Bristowe for reading much of the manuscript during the earlier stages of preparation, and for many helpful suggestions.

E. S.

University of Exeter

May 1975