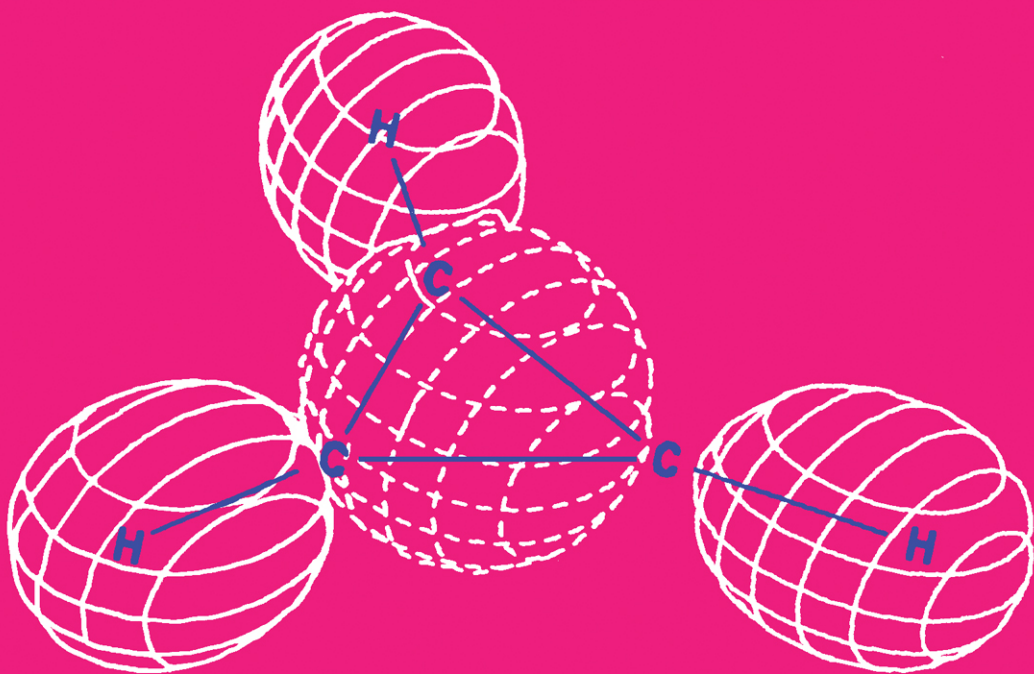


THE ORGANIC CHEMIST'S BOOK OF ORBITALS

WILLIAM L. JORGENSEN
LIONEL SALEM



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WILLIAM L. JORGENSEN

*Department of Chemistry
Harvard University
Cambridge, Massachusetts*

LIONEL SALEM

*Université de Paris-Sud
Centre d'Orsay
Orsay, France*

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To Alice and Axel

To Catherine

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To the people of Vietnam

December 25, 1972

Science sans conscience n'est que ruine de l'âme

RABELAIS, Pantagruel, 1532

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Preface

The last decade has witnessed an unprecedented strengthening of the bond between theory and experiment in organic chemistry. Much of this success may be credited to the development of widely applicable, unifying concepts, such as the symmetry rules of Woodward and Hoffmann, and the frontier orbital theory of Fukui. Whereas the theoretical emphasis had historically been on detailed structure and spectroscopy, the new methods are designed to solve problems of special importance to organic chemists: reactivity, stereochemistry, and mechanisms.

These theories are inevitably based upon analyses of the interactions and transformations of molecular orbitals, and consequently the accurate construction and representation of molecular orbitals has become essential. Furthermore, although the forms of molecular orbitals in diatomics and of delocalized π orbitals in conjugated systems are familiar, a general, non-computational method for determining the qualitative nature of σ and π orbitals in arbitrary molecules has been lacking.

In the present work a theory for the facile construction of complex molecular orbitals from bond and group orbitals is presented and complemented by accurate drawings of the valence molecular orbitals for over one hundred molecules representing a wide range of connectivities and functional groupings. Direct applications to phenomena in organic chemistry are also discussed.

This book is addressed to all those for whom orbitals have ceased to be an abstract concept, but have instead become concrete and useful in the daily practice of chemistry. It is especially directed to the new generation of chemists eager to understand molecular structure at the electronic level.

We are greatly indebted to Professor E. J. Corey for much stimulating advice and for the unswerving encouragement which he gave us. We wish to thank Dr. Donald Barth for consultation on the graphic aspects of the project, and also many friends for their advice. Receipt of numerous unpublished results from Dr. Warren J. Hehre, Prof. J. M. Lehn, and Dr. Georges Wipff was greatly appreciated.

The greater part of the book was written while L. S. was Visiting Professor at Harvard University. He sincerely thanks the Chemistry Department for their kind hospitality.

William L. Jorgensen
Lionel Salem

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I. How Molecular Orbitals Are Built by Delocalization

A Unified Approach Based on Bond Orbitals and Group Orbitals

1. Bond Orbitals and Group Orbitals

The delocalization of molecular orbitals lies at the heart of modern chemistry. The concept that the π orbitals of benzene or naphthalene cover the entire carbon skeleton promoted the successful understanding of conjugated molecules. The work of R. Hoffmann and others has proven that in saturated molecules σ orbitals are also delocalized over several bonds, often reaching opposite ends of a sizable molecule. The purpose of this chapter is to provide some enlightenment as to the mechanism by which delocalization of orbitals occurs in organic molecules.

By far the most obvious, but also the most significant characteristic of the molecular orbitals which are pictured in Chapter III is that they are composed almost exclusively of a very small number of typical *group* and *bond* orbitals which recur endlessly from molecular orbital to molecular orbital and from molecule to molecule. Generally, in a given molecular orbital only a given type of group or bond orbital occurs, from which the label of the molecular orbital is derived (see also Chapter II). The reader will soon become proficient at recognizing the basic types of localized orbitals. The following sections are aimed at helping him in this exercise, and at allowing him to go one step further to construct, qualitatively, the delocalized molecular orbitals from the localized group orbitals. The concept which we use is an old one: localized bond orbitals were first introduced by Lennard-Jones and Hall, and the wave-mechanical properties of localized electron pairs have been widely discussed. How-