Andrew Streitwieser

# MOLECULAR ORBITAL THEORY for ORGANIC CHEMISTS

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# Preface

This book concerns, principally, the simple molecular orbital methods and their application to organic chemistry. It is a commonplace that the chemical literature has grown apace in recent decades. The organic chemical molecular orbital literature dramatically exemplifies this trend. A mere handful of papers (approximately 20) in the thirties was followed by approximately 70 papers in the forties, whereas the decade of the fifties just completed has witnessed some 600 papers on this subject. This developing interest in the molecular orbital method is accented by the increased use of molecular orbital concepts in a number of recent elementary organic chemical courses and textbooks. Yet, despite this evidence of the popularity and importance of the molecular orbital method, few reviews and no adequate modern textbook for organic chemists exist in this vast body of literature.

The present book is a threefold attempt to annul this void. As a textbook, it offers instruction in the simple molecular orbital method with a minimum background in quantum mechanics. The introductory chapter is a review of elements of quantum chemistry which should be largely familiar to the experienced student but which are actually not necessary to an understanding of the simple molecular orbital methods described in the succeeding chapters. Exercises and examples are provided to help the student to learn enough to make his own calculations and applications. For the serious student the study of group theory, as described in Chapter 3, may be rewarding; however, such study is not essential to an understanding of the material that follows. A number of the applications involves topics not normally included in an organic chemical curriculum; for example, electron spin resonance, electronic transitions, electron affinity, and ionization potential. For such subjects an introductory exposition of the topic accompanies the molecular orbital treatment.

I have attempted in this book to provide an essentially complete review of the literature. It would be foolhardy to claim success in this attempt, and I shall simply apologize in advance for neglecting those contributions that I have undoubtedly, but inadvertently, overlooked. The literature citations should be relatively complete through mid-1960, although a few important references have been mentioned up to early 1961.

Finally, the present volume is in part a research paper. Established correlations between theory and experiment have been extended and new ones are documented. Some of the qualitative interpretations of chemistry in terms of theory are paraphrased from the literature; others are original.

In an effort to be all things to all chemists there is danger in not succeeding in any single phase; however, the present need for both a critical evaluation and a textbook is so great that the attempt had to be made.

In any work of this sort necessary innovations and uniformity of symbolism require apologia, particularly when reference is made to so many fields apart from my own areas of competency. Indeed, on rereading the manuscript, I am reminded of the story of the suspect, who, after long and diligent interrogation by experienced police officers, finally blurted out, "But fellows, I've told you more than I know already!" An explanation is demanded of my adoption of the term HMO, or Hückel molecular orbital. The foundations of molecular orbital theory were erected notably by Hund and Mulliken. The simple molecular orbital theory of organic chemistry was developed extensively by Lennard-Jones, Longuet-Higgins, Coulson, Wheland, and a host of others. Yet it remains that Hückel applied a certain set of approximations used previously in a simple theory of crystals to the $\pi$-electronic systems of conjugated compounds and showed how the results provided significant interpretations of the chemistry of such systems. These approximations, which are fully detailed in Chapter 2, are referred to frequently and are so important to the further development of the theory that they require a simple label; it seems singularly appropriate to call them the Hückel molecular orbital, or HMO method. Some of the approximations may be removed by the use of additional parameters within the framework of the basic theory. These methods constitute the "simple molecular orbital" methods. They, and their applications, make up the bulk of this book. Introduction of additional elaborations such as electronic repulsion integrals requires modification of the basic framework of the simple theory. Adaptation of these elaborations constitutes the "advanced molecular orbital methods" which are discussed in Chapter 16.

I must apologize also for the use of the "natural order" for the direction of arrows to represent absorption transitions in Chapter 8. The application of → for emission and ← for absorption transitions has been advocated. The extensive employment of absorption spectra by organic chemists would result in almost exclusive use of the "unnatural" sequence, $A^* \leftarrow A$,

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according to this convention. In considering this convention, I have been advised that I would be damned if I did and damned if I didn't. With such unhealthy alternatives, I have followed my instincts and have adopted the "natural order."

This book had its origin in a series of seminars that I presented in the spring of 1958 at the Shell Development Company at the suggestion of David P. Stevenson. The extensive transformation from lecture notes to manuscript was largely accomplished at Berkeley while I was on sabbatical leave as a National Science Foundation Science Faculty Fellow with additional assistance from the Alfred P. Sloan Foundation. The research and calculations described were supported in part by the Air Force Office of Scientific Research and in part by the National Science Foundation. I am indebted to George S. Hammond and John R. Platt for valued criticisms of the entire manuscript. Individual chapters were scrutinized by a number of persons, including W. H. Saunders, Jr., W. B. Schaap, K. S. Pitzer, W. D. Gwinn, J. Howe, R. L. Ward, and J. B. Bush. Last, but certainly not least, I am indebted to Miss Jayne Kravig for her superb typing of most of the manuscript and to my wife for her patience and her other specialized contributions.

ANDREW STREITWIESER, JR.

*Berkeley, California*
*August* 1961

# Table of symbols and abbreviations

| | |
|---|---|
| $a_{0r}$ | coefficient of $r$th AO in NBMO |
| $\boldsymbol{a}$ | a vector |
| $A_{rs}$ | cofactor of element $rs$ in a determinant |
| $A$ | electron affinity; annelation energy |
| $\mathscr{A}$ | a matrix |
| AH | alternant hydrocarbon |
| AIP | auxiliary inductive parameter |
| AO | atomic orbital |
| ASMO | antisymmetrized molecular orbital |
| $c_{ir}$ | coefficient of $r$th AO in $i$th MO |
| $C_j$ | $j$-fold rotation axis |
| $D$ | dissociation energy; units of dipole moment in Debye |
| $DE$ | delocalization energy |
| $E$ | total energy; identity operation |
| $E_\pi$ | $\pi$-Energy |
| EI | electron impact |
| ESR | electron spin resonance |
| $F$ | free energy |
| $\Delta F^\ddagger$ | free energy of activation |
| $F_r$ | free valence at position $r$ |
| FE | free electron |
| $h$ | order of a group |
| $h_r$ | Coulomb integral increment of $r$th AO in units of $\beta_0$ |

| | |
|---|---|
| $H_0$ | Hammett's acidity function |
| $\Delta H^{\ddagger}$ | enthalpy of activation |
| $H$ | magnetic field strength |
| $\mathbf{H}_{rs}$ | Hamiltonian integral between orbitals $r$ and $s$ |
| $\mathcal{H}$ | Hermitian matrix |
| $\boldsymbol{H}$ | Hamiltonian operator |
| hfs | hyperfine splitting |
| HMO | Hückel molecular orbital |
| $i$ | center of inversion |
| $i, j$ | indices of molecular orbitals |
| $I$ | ionization potential |
| $k_i$ | a rate constant |
| $k_{rs}$ | bond integral for r—s bond in units of $\beta_0$ |
| $K_i$ | an equilibrium constant |
| $l$ | angular momentum quantum number; dimension of a group representation |
| $L_b$ | bond localization energy |
| $L_p$ | para-localization energy |
| $L_r$ | localization energy of atom $r$ |
| $L_r^{\omega}$ | $\omega$-technique localization energy |
| LCAO | linear combination of atomic orbitals |
| $m$ | mass; magnetic quantum number; index of highest occupied MO |
| $m_i$ | bonding energy coefficient in $i$th MO |
| $M$ | bonding energy coefficient in total $\pi$-energy |
| MO | molecular orbital |
| $n$ | quantum number, principal quantum number; total number of AO's in MO |
| $n$ | index of MO of highest energy |
| $N_r$ | Dewar's reactivity number |
| NBMO | nonbonding molecular orbital |
| non-AH | nonalternant hydrocarbon |
| $p$ | atomic orbital with $l = 1$ |
| $p_{rs}$ | $\pi$-bond order between atoms $r$ and $s$ |
| PI | photoionization |

| | |
|---|---|
| $q_r$ | electron density at atom $r$ |
| $Q$ | hyperfine splitting proportionality constant |
| $r, s$ | indices of atoms or AO's |
| $R_{\mathrm{RS}}$ | conjugation energy between $\pi$-systems R and S |
| $RE$ | resonance energy |
| $s$ | atomic orbital with $l = 0$ |
| $S$ | overlap integral |
| $\Delta S^{\ddagger}$ | entropy of activation |
| $S_r$ | super-delocalizability at position $r$ |
| $\mathrm{S}_{rs}$ | overlap integral between AO's $r$ and $s$ |
| SCF | self-consistent field |
| $T$ | kinetic energy |
| $\mathcal{U}$ | unitary matrix |
| $V$ | potential energy |
| VB | valence-bond |
| $x$ | diagonal element in HMO determinant equivalent to $(\alpha - \epsilon)/\beta$ |
| $Z_r$ | Brown's reactivity index |
| $\alpha$ | Coulomb integral |
| $\alpha_0$ | standard Coulomb integral |
| $\alpha_r$ | Coulomb integral of $r$th AO or atom |
| $\beta$ | bond integral |
| $\beta_0$ | standard bond integral |
| $\beta_{rs}$ | bond integral between AO's $r$ and $s$ |
| $\gamma$ | bond integral with inclusion of overlap |
| $\Gamma$ | group representation |
| $\delta_{jk}$ | Kronecker delta |
| $\epsilon_i$ | energy of $i$th MO |
| $\epsilon_{1/2}$ | half-wave potential |
| $\zeta_r$ | charge density of position $r$ |
| $\mu$ | dipole moment |
| $\pi_{r,s}$ | atom-atom polarizability |
| $\pi_{rs,t}$ | bond-atom polarizability |
| $\pi_{t,rs}$ | atom-bond polarizability |

| | |
|---|---|
| $\pi_{rs,tu}$ | bond-bond polarizability |
| $\rho$ | reaction constant |
| $\rho_r$ | net spin density at atom *r* |
| $\sigma$ | plane of symmetry |
| $\sigma_r$ | substituent reactivity constant at position *r* |
| $\chi$ | character |
| $\psi$ | a wave function, molecular orbital |
| $\psi_j$ | *j*th molecular orbital |
| $\Psi$ | total product wave function |
| $\omega$ | parameter in $\omega$-technique |

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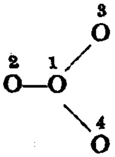
2.5 Trimethylenemethane.  43
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# I SIMPLE MOLECULAR ORBITAL THEORY

# 1

# Introduction

## 1.1 Quantum Mechanics

The development of the dual wave-particle concepts of light and matter only a few decades ago has altered along with much of the philosophical and intellectual world the thought and language of the organic chemist. The brilliant triumph of structure theory and the tetrahedral carbon was based virtually on a concept of bonds formed from miniscule hooks reminiscent of Lucretius' prickly atoms. The various intellectual constructions of ingenious but largely meaningless symbols for benzene represent an example of the frustration existent prior to the wave electron.

A major impetus for this change comes from Schrödinger's postulate, for the Schrödinger equation is a wave equation. With its development Dirac[1] was led to state, "The underlying physical laws necessary for the mathematical theory of a large part of physics and the whole of chemistry are thus completely known"—fortunately the quote does not end here, or we should miss the fun of doing an experiment—"and the difficulty is only that the application of these laws leads to equations much too complicated to be soluble."

In one dimension for one electron the Schrödinger equation for a conservative system, one which does not interact with its surroundings, may be written as

$$\frac{d^2\psi}{dx^2} + \frac{8\pi^2 m}{h^2}(E - V)\psi = 0 \qquad (1)$$

in which $E$ is the total energy, a constant, and $V$ is the potential energy, which in general is a function of $x$. Solution of this equation involves finding a *wave function*, $\psi$, a function of $x$, which will satisfy (1). This equation can be solved for some important simple cases such as the harmonic oscillator and the electron in a box (p. 27).

A simple and instructive case is that in which an electron is constrained to move in a circle of radius $r$. We let $V = 0$ at the circumference of the

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[1] P. A. M. Dirac, *Proc. Roy. Soc.*, A123, 714 (1929).

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