

*Hückel Molecular  
Orbital Theory*

KEITH YATES



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## PREFACE

As pointed out more than a decade ago by J. D. Roberts in his concise and valuable introduction to the simple LCAO method,<sup>1</sup> any organic chemist with no more than high school algebra can make useful calculations of semiempirical electronic energies and electron distributions for typical organic systems of interest. At that time Roberts stated, "there is no excuse for a modern organic chemist not to be able to use the LCAO method." With the passage of time, which has led to significant advances in our understanding of structure and reactivity, and particularly because of the development of powerful methods based on the principle of conservation of orbital symmetry, there is even less excuse today for such an inability on the part of organic chemists. The original development and continued use of the simple Hückel Molecular Orbital (HMO) method has provided organic chemists with a great many results that, although crude and approximate, have provided many significant insights into the properties and reactivities of organic molecules containing  $\pi$ -electron systems and increased our theoretical understanding of the nature of chemical bonding. Simple molecular orbital approaches of the HMO type have probably been more successful than many more advanced and sophisticated theoretical approaches in providing organic chemists with real predictions (and not *ex post facto* explanations or rationalizations of well-known properties) concerning the stabilities and reactivities of organic systems. One has only to consider the outstanding successes of Hückel's  $(4n + 2)$  rule and of the Woodward-Hoffman rules in this regard. It is also

clear that the simple HMO technique has given us a great deal of information and results, both of a qualitative and a semiquantitative nature, that could not have been obtained by use of valence-bond (resonance) theory. It is probably fair to say that the simple Hückel approach seldom, if ever, gives results or suggestions that are clearly at variance with experimental evidence.

This book is intended to be as simple, descriptive, and non-mathematical an introduction as possible to Hückel molecular orbital theory and its application to organic chemistry. It is suggested that the text could provide the basis for a one-semester or one-term course in theoretical organic chemistry, suitable either for juniors or seniors. The book is not intended to give an exhaustive or comprehensive treatment of the subject, but is meant to provide a simpler and more basic text that would complement available and more advanced works such as Streitwieser's "Molecular Orbital Theory for Organic Chemists"<sup>2</sup> and Woodward and Hoffmann's "The Conservation of Orbital Symmetry."<sup>3</sup> Each of these is an excellent and comprehensive treatment, replete with examples and illustrations from the current literature. Thus, specific examples have been included in the present work only to illustrate particular points. The reader is referred to these and other more comprehensive treatments for examples of the widespread application of simple molecular orbital concepts.

The emphasis in the present text is on basic concepts and methods. It is the author's feeling that many organic chemistry students, both undergraduate and graduate, frequently apply important ideas and approaches such as the Woodward-Hoffmann rules without a sufficiently sound understanding of their theoretical basis. Similarly, many students go on to make calculations of more sophisticated types such as the various CNDO methods or even the LCAO-SCF type in a very mechanical way, without ever having developed a feeling for the quantum mechanical concepts involved, or equally importantly, the nature of the approximations and limitations inherent in these methods.

One advantage of the simple LCAO approaches described in this book is that they can at the same time provide practicing organic students with a basic understanding of quantum mechanical ideas that they can profitably apply in many areas of experimental organic chemistry, and also provide a basis for further theoretical calculations if they become more deeply interested in the theoretical aspects of

the subject. The mathematics involved in these simple approaches need deter no organic student; in fact the mathematical simplicity of the HMO approach is one of its great advantages, in that basic quantum mechanical ideas are not obscured in a welter of complex equations and integrals. Numerous problems are included at the end of most chapters. These should be solved as they are approached in the text. (In many cases the answers are very easy to obtain and verify, and in other cases detailed numerical solutions are readily available in standard reference works.) In addition, supplementary texts and references are included at the end of every chapter. (No attempt has been made to include all pertinent references.) Those works indicated with an asterisk are strongly recommended as supplementary reading.

I hope that any organic students who work their way through this text and the problems will derive as much enjoyment from it as I have in writing it.

Finally I would like to thank Miss Helen Ohorodnyk, Professor I. G. Csizmadia, and Professor W. Forst for reading and commenting on various sections of the text and Mrs. Sue McClelland for her patience with the typing.

## REFERENCES

1. J. D. Roberts, "Molecular Orbital Calculations." Benjamin, Reading, Massachusetts, 1962.
2. A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists." Wiley, New York, 1961
3. R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry." Verlag Chemie, Weinheim, 1970; and references therein.

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# INTRODUCTION

## I

The problem of what constitutes the electronic structure of complex molecules is of fundamental importance to most of chemistry, and particularly to organic chemistry, since all of the experimental work in this field involves molecules and not atoms, and usually fairly large molecules. To obtain a satisfactory theoretical understanding of the molecular structure and properties of organic systems we must ultimately turn to quantum mechanics to answer questions concerning thermodynamic stabilities, spectroscopic properties, and chemical reactivities. These questions all resolve themselves finally into the question of the nature of the chemical bonding or electron distribution in the organic molecules. However, the fundamental wave equations that could be applied to the types of covalent bonding normally found in these molecules are impossible to solve exactly for any multibody problem such as that involved in a real molecular system. Even for the simplest molecular species  $H_2^+$ , which has only two nuclei and one electron, it is necessary to make a simplifying assumption (the Born-Oppenheimer approximation)<sup>1</sup> to arrive at any quantum mechanical solution. For more complex molecules, the situation becomes increasingly more difficult, and further simplifying assumptions or approximations must necessarily be made if we are to obtain even very

approximate answers to questions about molecular electronic structures and energies. This has led to the development of various quantum mechanical methods, whose results, albeit crude and approximate, have shed significant light on the nature of chemical bonding and reactivity, particularly in organic chemistry.

The simplest and most approximate of these approaches has come to be known as the *Hückel molecular orbital* (HMO) method,<sup>2</sup> on which most of this book is based. This approach, despite its theoretical naiveté, has several important advantages, particularly for practicing organic chemists. First, because of its simplicity, it is easy to understand and apply, even to fairly complex systems. Second, it does not differ fundamentally from other more sophisticated and less exact methods, and hence is very useful for developing a basic understanding of and feeling for quantum mechanical concepts, treatments, and results in a way that would not be possible using mathematically more sophisticated methods. Third, and perhaps most important, the results of this approximate theoretical treatment of organic molecules have contributed very significantly to the understanding of organic chemists, particularly in the last ten or fifteen years. As will be shown later, the results of HMO calculations have helped to correlate and explain a wide range of both physical and chemical properties, and have also in recent years helped to provide very significant predictive rules concerning the course of many organic reactions.

In order to provide a satisfactory conceptual basis for such approximate quantum mechanical methods, and to give some understanding of the necessity for and the nature of the simplifying assumptions and approximations that must be made, the remainder of this chapter will deal with basic concepts and definitions that underly all quantum chemical calculations.

## 1.1 THE BASIC POSTULATES OF QUANTUM MECHANICS

The quantum mechanical equations that are used to calculate molecular properties are based on a set of fundamental statements or postulates. These concern atomic and molecular properties and hence are outside everyday experience. They cannot be derived a priori or justified in any absolute sense, and the reader is thus asked at first to take these statements purely on faith. However, the main point is that these postulates *are* justified if and only if they are able to explain and

correlate experimentally observed data, to make predictions, and to be generally applicable to the chemical systems in which we are interested.

This set of postulates will serve to introduce the basic concepts and definitions we make frequent use of, either explicitly or implicitly, in all of the calculations and discussions in the rest of this book.

**Postulate I** (a) Any state of a system of  $n$  particles (such as a molecule) is described as fully as possible by a function  $\Psi$ , which is a function only of the spatial coordinates of the particles and the time, that is,

$$\Psi(q_1 q_2 q_3, q_1' q_2' q_3', \dots, q_1^n q_2^n q_3^n, t)$$

where  $q_1 q_2 q_3$  are the coordinates of the first particle, and so forth for each of the  $n$  particles.

(b) If we know that such a state is described by a particular  $\Psi$ , then the quantity  $\Psi\Psi^* d\tau$ ,<sup>†</sup> where  $d\tau$  is a volume element based on generalized spatial coordinates, gives the probability of finding  $q_1$  for the first particle between  $q_1$  and  $(q_1 + dq_1)$ ,  $q_2$  between  $q_2$  and  $(q_2 + dq_2)$ , and so on for each of the  $n$  particles at a specific time  $t$ .

Part (a) of this postulate tells us that all the information we need about the properties of any molecular system is contained in some mathematical function  $\Psi$ , a wave function, which is a function only of the spatial coordinates of the system and the time. If this  $\Psi$  includes  $t$  explicitly, it is called a time-dependent wave function. However, if the observable properties we are interested in do not change with time, the system is said to be in a stationary state. In this case, the time dependence can be separated out, and we are left with a time-independent or stationary-state wave function  $\Psi(q_1 q_2 q_3, \dots, q_1^n q_2^n q_3^n)$ . Since most properties of interest to organic chemists—such as energies, electron densities, dipole moments, bond orders, and bond lengths—are time independent (or time averaged, as far as experimental data are concerned), we will need to deal only with stationary states and their wave functions.

Part (b) of the postulate gives us a physical interpretation of  $\Psi$  in terms of its square, or more properly in terms of its  $\Psi\Psi^*$  product. However, in order that the  $\Psi$  are in accord with physical reality, these

<sup>†</sup> If  $\Psi$  is the wave function,  $\Psi^*$  is its complex conjugate. For example, if  $\Psi = f + ig$ ,  $\Psi^* = f - ig$ . The approximate wave functions used in this book do not contain complex parts, thus in general  $\psi\psi^*$  reduces to  $\Psi^2$ .

functions are subject to certain reasonable restrictions:

- (i)  $\Psi$  is everywhere finite, that is, the particles whose behavior  $\Psi$  describes must be bound to a nucleus or an assemblage of nuclei.
- (ii)  $\Psi$  is single-valued; that is, each particle in the system must be in one place at a time only.
- (iii)  $\Psi^2$  or  $\Psi\Psi^*$  must be an integrable function.

These restrictions arise mainly because  $\Psi^2 d\tau$  is a probability distribution function, and therefore its integral over a given region of space can have only one value under a given set of conditions, and this value must be finite. A special case of (iii) is when

$$\int_0^\infty \Psi^2 d\tau = 1$$

where  $\int_0^\infty$  is taken to mean integration over the limits of all coordinates over all space. When this is true, the function  $\Psi$  is said to be normalized. Thus the probability of finding each particle in *some* region of space, or the total probability of finding the system in some configuration or other, must be unity. All wave functions dealt with in this book will be normalized by multiplying them where necessary by an appropriate normalization factor.

**Postulate II** For every observable property of a system that is described by some  $\Psi$ , there exists a linear Hermitian operator. The physical properties we are interested in can be obtained from this operator and the wave function that describes the system.

An operator  $\hat{O}$  is linear if

$$\hat{O}(f + g) = \hat{O}f + \hat{O}g \quad \text{and} \quad \hat{O}(af) = a\hat{O}f$$

where  $f$  and  $g$  are functions and  $a$  is a constant. Frequent use will be made of the linearity property of certain operators in handling quantum mechanical equations.

The Hermitian property of the operators we will use ensures that we always obtain real solutions, since Hermitian operators are defined by the relation

$$\int_{\text{all space}} \Psi^* \hat{O} \Phi d\tau = \int_{\text{all space}} \Phi \hat{O}^* \Psi^* d\tau$$

where  $\Psi$  and  $\Phi$  are any two functions that satisfy the above conditions of acceptability and  $\hat{O}$  is the operator of interest (usually the Hamilto-

nian or total energy operator). Since we will only use real  $\Psi$  (or  $\Phi$ ), this means that in any quantum mechanical integral of the form

$$\int \Psi_i \hat{O} \Psi_j dt$$

the order of multiplication and operation with respect to  $\Psi_i$  and  $\Psi_j$  is immaterial, and the value of the integral will always be real. We will also make frequent use of this property of the operators of interest. It is sufficient for the purposes of this book to know that such a class of operators exists and that all operators to be used (particularly Hamiltonian operators) belong to this class.

**Postulate III.** To obtain the operator associated with a given observable, simply take the classical expression for that observable in terms of the coordinates, momenta, and time and make the following replacements:

(i) Each component of momentum  $p_q$  is replaced by the differential operator  $-i\hbar \partial/\partial q$ , where  $q$  is a generalized coordinate,  $i = \sqrt{-1}$ , and  $\hbar = h/2\pi$ . (Note that these operators are both linear and Hermitian, whereas  $\partial/\partial q$  alone is not Hermitian.)

(ii) Time  $t$  and all spatial coordinates  $q_i$  are left formally unchanged, and the corresponding operators are simply multiplication operators.

Although other operators will be considered later on, the operator that is of principal interest is the one associated with the energy values for the system under consideration. For example, the classical expression for the kinetic energy of a single particle, such as an electron, using Cartesian coordinates is

$$T = \frac{1}{2m}(p_x^2 + p_y^2 + p_z^2)$$

where  $p_q$  is the momentum component along the  $q$  direction. Using step (i) this becomes the kinetic energy operator

$$\begin{aligned} \hat{T} &= \frac{1}{2m} \left[ \left( -i\hbar \frac{\partial}{\partial x} \right)^2 + \left( -i\hbar \frac{\partial}{\partial y} \right)^2 + \left( -i\hbar \frac{\partial}{\partial z} \right)^2 \right] \\ &= -\frac{\hbar^2}{2m} \left( \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) = -\frac{\hbar^2}{2m} \nabla^2 \end{aligned}$$

where  $\nabla^2$  is the Laplacian operator and  $m$  is the mass of the particle at rest.



The potential energy  $V$  is a function only of the spatial coordinates of the particle, and contains physical constants such as the electronic and nuclear charge. For example, the classical expression for the potential energy of a single electron  $i$  of charge  $e$  in the field of a nucleus  $n$  of charge  $Ze$  is given by

$$V = -Ze^2/r_{ni}$$

where  $r_{ni}$  is the distance between the electron and the nucleus, which can be expressed in terms of coordinates  $x, y, z$ . This expression remains unchanged in quantum mechanics and hence  $V(x, y, z) \rightarrow \hat{V}(x, y, z)$ . Hence the operation involved under  $\hat{V}$  is simply multiplication of some function by  $\hat{V}$ .

The classical expression for the total energy  $E$  is Hamilton's function

$$E = T + V$$

and thus the associated quantum mechanical operator is

$$\hat{\mathcal{H}} = \hat{T} + \hat{V} = -\frac{\hbar^2}{2m}\nabla^2 + \hat{V}(x, y, z)$$

This is the Hamiltonian or total energy operator  $\hat{\mathcal{H}}$  for the system. (Examples of other Hamiltonian operators are given in Section I.2.)

**Postulate IV** If  $\hat{P}$  is an operator corresponding to some physical observable  $p$ , and there is a set of states each described by a function  $\Psi_s$ , which is an eigenfunction of  $\hat{P}$ , then a series of measurements of the physical quantity corresponding to  $p$  would always give the same result  $p_s$  for a given state  $s$ , which would be the eigenvalue of the operator  $P_s$ , where

$$\hat{P}\Psi_s = p_s\Psi_s$$

such that  $p_s$  is a real number.

For example, measurements of the energy of a series of identical systems in a state described by some wave function  $\Psi_n$  that is an eigenfunction of the total energy operator  $\hat{\mathcal{H}}$  will always give the same result  $E_n$ . Thus

$$\hat{\mathcal{H}}\Psi_n = E_n\Psi_n$$

and the eigenvalue is always exactly  $E_n$ . Therefore the problem of computing allowed energy states of a given system is reduced to the problem of finding the functions  $\Psi_n$  and energy values  $E_n$  that satisfy this