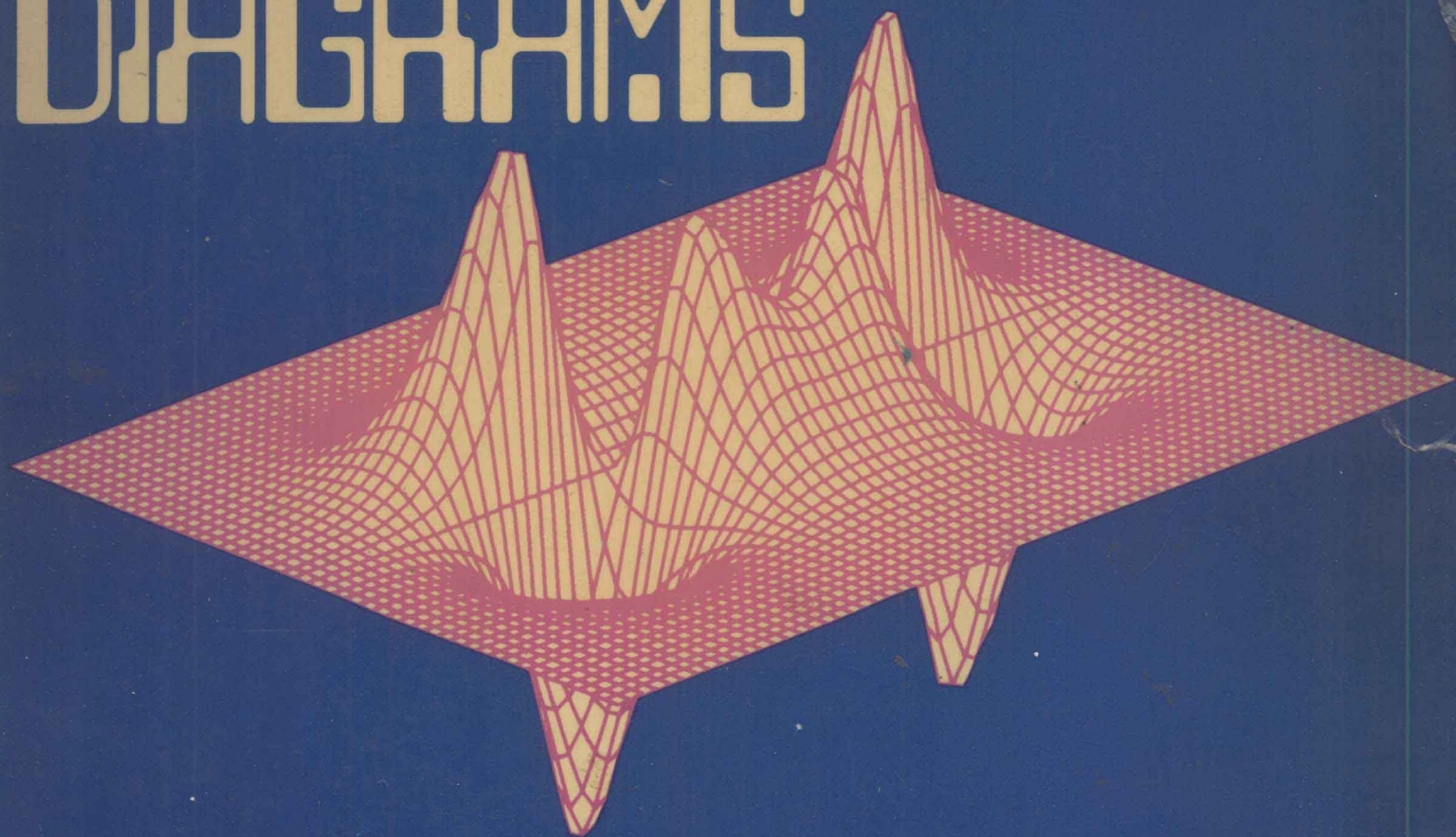
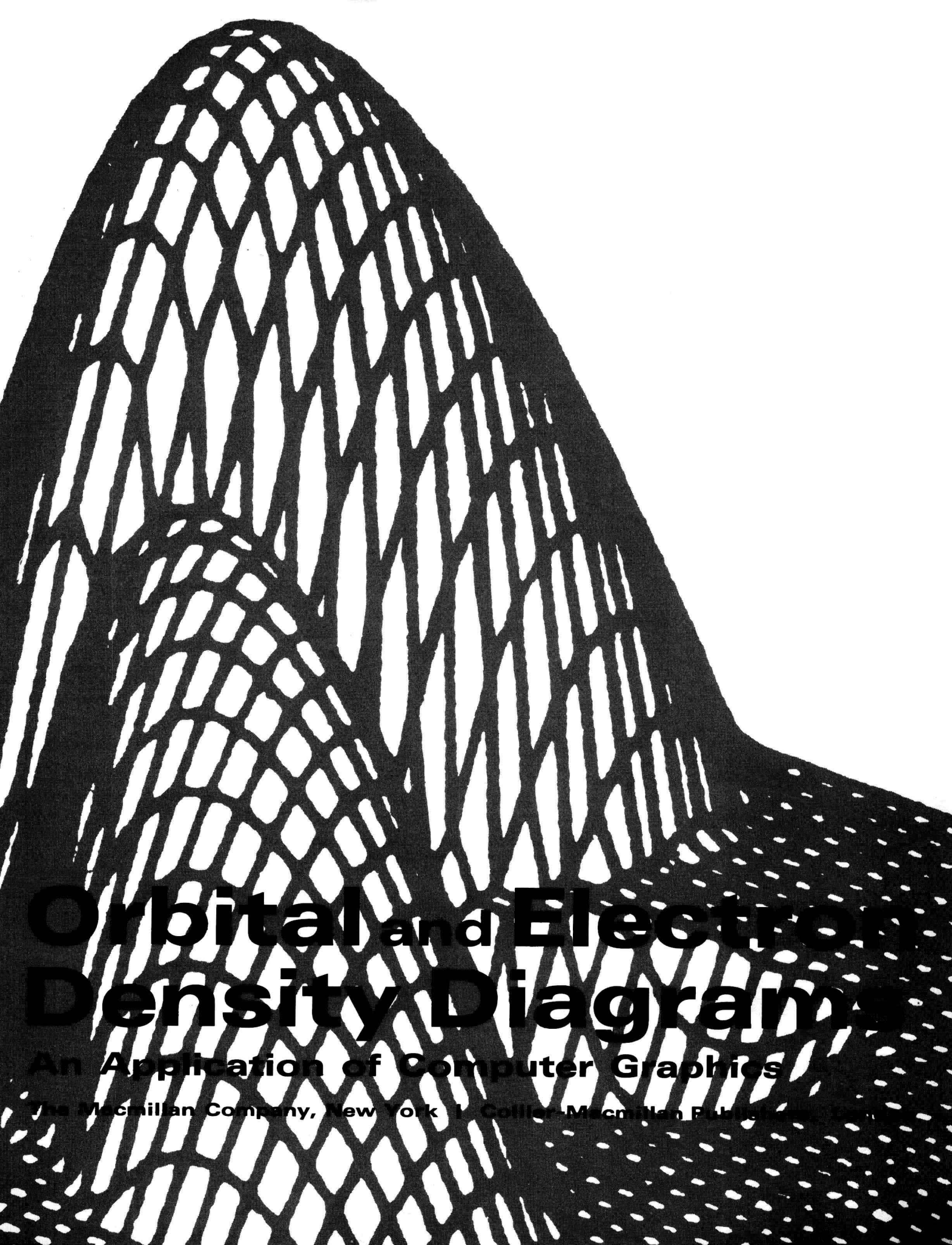


Andrew Streitwieser, Jr. and Peter H. Owens

ORBITAL AND ELECTRON DENSITY DIAGRAMS



An Application of Computer Graphics



Orbital and Electron Density Diagrams

An Application of Computer Graphics

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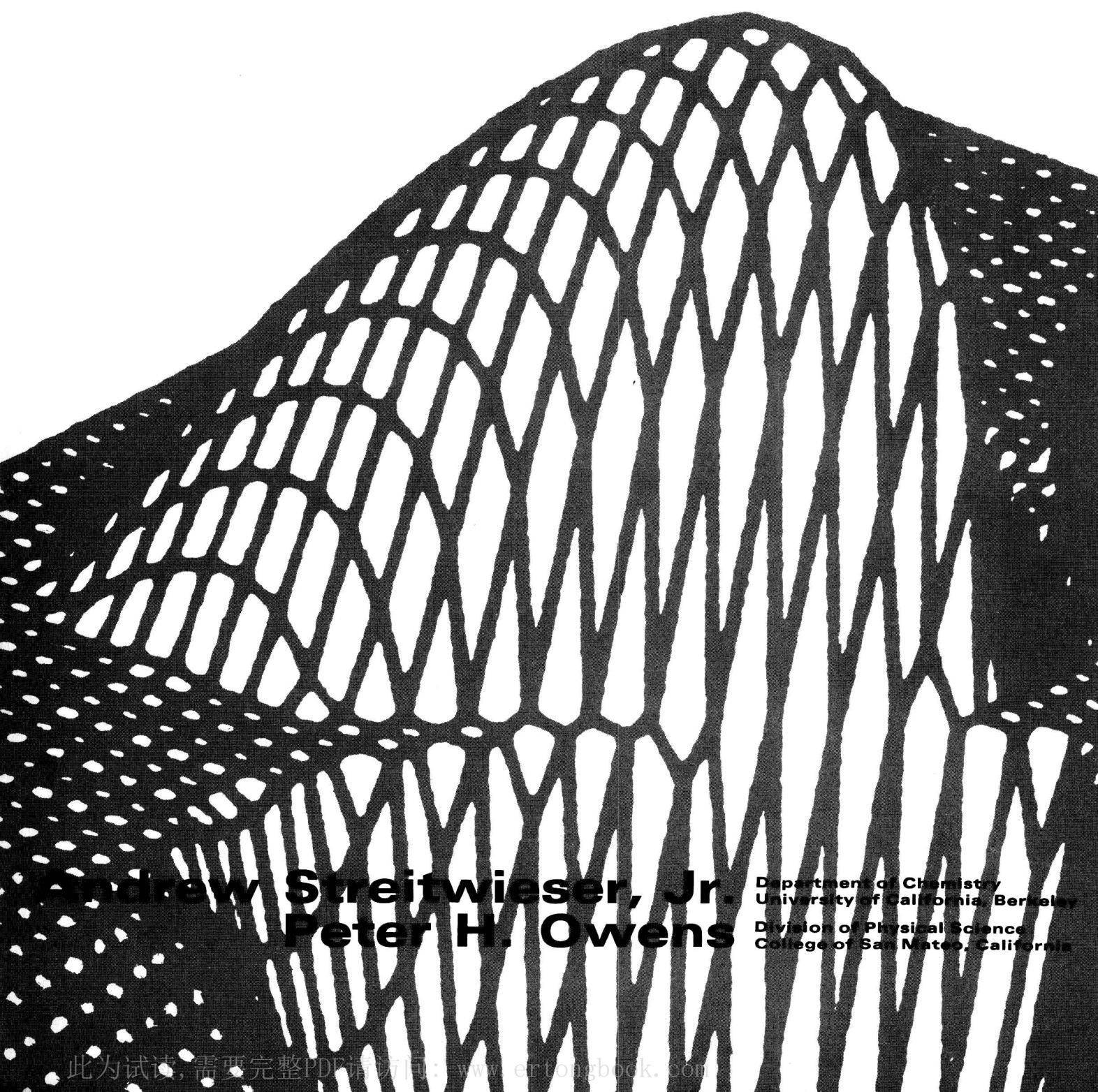
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An Application of Computer Graphics



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Preface

This book had its origin soon after we started our own research studies in *ab initio* quantum mechanical calculations of organic compounds. Our initial work in this field was made possible by a copy of the IBMOLIV program generously provided by Dr. Enrico Clementi of IBM. This program required extensive revision to function on the CDC-6400 computer of the Computer Center of the University of California, Berkeley. One of us, Peter Owens, brought the research program into being as part of his graduate research. Dr. Richard Wolf assisted greatly in this effort. We were able to incorporate additional features to make the calculations faster and more efficient, especially for use with Pople's STO-NG method. Mr. Julian Schaefer provided more efficiency by converting portions of the program into machine language.

To convert the results of the calculations to visual terms, we made early use of a three-dimensional plotting package written by Mr. Art Paradis of our campus Computer Center. His program efficiently takes care of the "hidden line problem" and is used in the plots shown in this book. We were immediately struck by the beauty of the results. However, in addition to the aesthetic qualities of the plots we saw their heuristic value and started examining a number of atomic and molecular orbitals, electron density distributions, and difference plots. As teachers, the use of such diagrams was soon apparent to us and we started plans for a book that would be useful for the entire chemistry curriculum, from freshman to organic, physical, and inorganic chemistry.

Similar plotting programs are available at many computer centers. During the summer of 1970, Professor Linnett of Cambridge University visited Berkeley and told us of his own three-dimensional plotting experiments which were subsequently published. Related plots of electron densities of orbitals and molecules have appeared in the literature, notably by Van Wazer. Some of our own research contributions have appeared as well. As is apparent in the plots in this book, the Paradis program gives results of exceptional quality. The results shown in this book represent the outcome of much additional experimentation but of a more esthetic type. We studied various grid sizes and spacings as well as perspective angles. We hope the results reflect the great effort that went into the determination of optimum representations.

In the representations of molecules we were faced with further decisions. Molecular orbital functions of near-Hartree-Fock limits are available for many compounds. We chose instead to represent the molecules in terms of minimum basis sets of Slater orbitals as approximated by the STO-4G method with optimized exponents. We are indebted to Professor John Pople for giving us the best least squares values for these functions before publication. By this minimum basis set type of representation, one sees more clearly the changes in a given atom from atom to molecule. If we had used the results of more extensive basis sets for molecules, one would generally see quantitative but not qualitative differences. In particular, the general appearances of the three-dimensional plots would still be the same.

Originally, we had planned to show just the diagrams with very little text. As the project developed, however, the text was found to be increasingly important as a teaching function. For example, many of the properties of orbitals, especially as concerns nodes and waves, are not to be found in most chemistry texts; therefore, more complete text material was added. We appreciate that the present work may, in part, tell students more about orbitals than they may want to know, but we hope that the pictures and text will underscore the unity of science and will introduce the concept that there is art in science and that science is beautiful.

The text material has been written primarily at a sophomore level, but the first two chapters were written with the alert freshman in mind. Some of the concepts discussed in the last chapter go beyond typical sophomore material but should suit junior and senior chemistry courses. Orbitals and bonds are taught repeatedly in successive chemistry courses at different levels of sophistication. Accordingly, the freshman who uses this book should be able to understand most of the early material, and we expect that he will refer to the text and pictures again and again during his chemical education, with increasing depth of understanding.

This book points up aspects of wave functions and bonds with a different emphasis from most current texts; our discussions are built around the three-dimensional perspective plots and are designed to be used as auxiliary material rather than as a complete textbook on valence theory.

Many people have looked at our pictures and commented on the text; we are indebted to many of our colleagues at the University of California as well as to Professor Heinz Koch, Ithaca College, Professor James Stoffer, University of Missouri at Rolla, and David R. Streitwieser, a U.C. student. We are especially indebted to the Computer Center of the University of California for extensive amounts of subsidized computer time, particularly to the director, Kenneth Hebert, for his continued help and encouragement, and to Jerry Golden and Marie Chenoweth for the CalComp operations. Last, but certainly not least, we owe thanks to Nancy Monroe for her drafting skills and to Lynne Anderson and Wendy Zucas for their secretarial and typing services.

A. S.
P. H. O.

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Atomic Orbitals

CHAPTER 1

1.1 Introduction

In earlier decades it was not uncommon for textbooks to represent an atom as a miniature solar system with electrons represented as planets revolving around the nucleus as a sun. With the advent of quantum or wave mechanics about a half century ago, this analogy was found to be virtually useless and without significant merit. The reason comes simply from the Heisenberg uncertainty principle, which states that it is impossible to determine simultaneously both the precise position and momentum of an electron; that is, the laws of nature are such that we cannot determine a trajectory for an electron. The best we can do is to describe a probability distribution that gives the probability of finding an electron in any region around a nucleus. The mathematical description that leads to this probability distribution is exactly the same as the mathematics of waves. Thus, when we talk of the motion of an electron around a nucleus as a “wave motion” or as a “wave function,” this does not mean that the electron moves up and down like a cork in a raging sea. It is only a convenient language that helps to characterize the mathematical equations that describe the electron probability distribution.

Wave motion is characterized by an **amplitude** which can be positive (a wave crest) or negative (a wave trough) and by **nodes**. A node is the region where a crest and a trough meet. These characteristics are embodied in the wave function, usually symbolized by the Greek letter ψ (psi, pronounced “sy”). This function contains the amplitude of the electron wave for any point in space. At a node, $\psi = 0$ and marks the transition of positive ψ to

negative ψ ; that is, ψ is a mathematical function of the spatial coordinates. Furthermore, waves generally change with time; hence, time is a fifth quantity in the wave function. However, all of the wave functions treated in this book will be those for **standing waves**, waves that do not change with time, and in such cases ψ is a function only of space coordinates. One physical significance of ψ is that the value of ψ^2 at a point describes the probability of finding an electron at that point; ψ^2 thus gives a probability distribution or an **electron density**.

In order to understand nature, we generally dissect complex phenomena into more simple parts and frequently represent the component parts in terms of symbols that we can “see” and manipulate. Symbolic representation of electron motion presents special problems. Since we have a wave function defined for each point in space, a complete description would require a four-dimensional figure. Our symbolic representations are generally confined to a two-dimensional page, and the actual symbolic representations that have been used approximate only a portion of the total ψ -function. These symbols have important limitations; thus, different types of symbols are used to emphasize different properties of wave functions. In this chapter we will review some of the conventional symbolic representations of electron waves in atoms and will then describe the relatively novel three-dimensional computer-drawn plots which constitute the bulk of this book.

1.2 Hydrogenic Orbitals

Wave functions, ψ , of electrons in atoms and molecules are solutions to the Schrödinger wave equation,¹ in which one considers explicitly all of the energy interactions in the system. That is, the wave equation contains the electrostatic attraction of each electron with each nucleus, the repulsions among electrons and among nuclei, and the kinetic energies of all electrons. The electrons are so small compared to nuclei and move so fast that the nuclei are usually considered to be at rest for setting up the wave equation; that is, the kinetic energies of the nuclei are generally neglected.

Actually, the only atomic system for which the wave equation can be solved exactly in closed form is that of the **hydrogenic atom**, an atom consisting of a nucleus having positive charge Ze and a single electron having

¹ The wave equation is frequently written as

$$\mathbf{H}\psi = E\psi$$

in which the Hamiltonian “operator” \mathbf{H} operating on ψ is equal to the product of the wave function and a scalar quantity E , the total energy of the system. The Hamiltonian operator is simply a concise mathematical symbolism that embodies the energy interactions summarized above.

negative charge of magnitude e at a distance r from the nucleus. Solutions of the resulting wave equation² give the corresponding ψ functions. ψ is an atomic orbital wave function, and orbitals are defined as one-electron wave functions. There are an infinite number of such wave functions that serve as solutions to the wave equation and each has an associated discrete energy. Each such orbital has the following general properties:

1. Single-valued and continuous
2. Exponential falloff with distance of the magnitude of the wave function, modified, however, by (1) and (3)
3. Nodal surfaces.

Recall that nodes are defined as those points in space for which $\psi = 0$. Nodes generally have one dimension less than the vibrating system. For a vibrating string, nodes are points along the string. For the vibrating surface of a drum, nodes are lines and circles. For the three-dimensional spatial system exemplified by electron motion in an atom, nodes are surfaces which may be spheres, planes, or cones. These nodal surfaces are characterized by **quantum numbers** that are summarized in Table 1.1. Because of this relationship of quantum numbers to the nodes inherent in wave motion,

Table 1.1
Quantum Numbers and Properties of Nodes

QUANTUM NUMBERS	POSSIBLE VALUES	NODAL CHARACTERISTICS
n , principal	$1 \leq n < \infty$	$n - 1$ nodal surfaces
l , azimuthal or angular momentum	$0 \leq l \leq n - 1$	l nonspherical nodal surfaces
m , magnetic	$-l \leq m \leq l$	character and orientation of nonspherical nodes
s , spin	$\pm \frac{1}{2}$	none

² For such a system the Schrödinger wave equation takes the form

$$\left(-\frac{1}{2} \cdot \frac{h^2}{4\pi^2 m} \nabla^2 - \frac{Ze^2}{r} \right) \psi = E\psi$$

The first term on the left is the kinetic energy term; m is the mass of the electron, h is Planck's constant and the Laplacian operator

$$\nabla^2 = \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right)$$

The second term is the potential energy of attraction (hence the negative sign of this term) of the electron having negative charge of magnitude e with the nucleus having positive charge of magnitude Ze . This term represents a simple Coulombic electrostatic attraction; r is the distance of the electron from the nucleus.

[1.2] Hydrogenic Orbitals