

1520

PHYSICAL CHEMISTRY — A Series of Monographs

# Electron Densities in Molecules and Molecular Orbitals



John R. Van Wazer  
Ilyas Absar

ACADEMIC PRESS, INC.

A Subsidiary of Harcourt Brace Jovanovich, Publishers

# Electron Densities in Molecules and Molecular Orbitals

*John R. Van Wazer*  
*Ilyas Absar*

Department of Chemistry  
Vanderbilt University  
Nashville, Tennessee

COPYRIGHT © 1975, BY ACADEMIC PRESS, INC.  
ALL RIGHTS RESERVED.  
NO PART OF THIS PUBLICATION MAY BE REPRODUCED OR  
TRANSMITTED IN ANY FORM OR BY ANY MEANS, ELECTRONIC  
OR MECHANICAL, INCLUDING PHOTOCOPY, RECORDING, OR ANY  
INFORMATION STORAGE AND RETRIEVAL SYSTEM, WITHOUT  
PERMISSION IN WRITING FROM THE PUBLISHER.

ACADEMIC PRESS, INC.  
111 Fifth Avenue, New York, New York 10003

*United Kingdom Edition published by*  
ACADEMIC PRESS, INC. (LONDON) LTD.  
24/28 Oval Road, London NW1

Library of Congress Cataloging in Publication Data

Van Wazer, John R

Electron densities in molecules and molecular  
orbitals.

(Physical chemistry, a series of monographs ; vol. 35)

Bibliography: p.

Includes index.

1. Molecular structure. 2. Molecular orbitals.

I. Absar, Ilyas, joint author. II. Title.

III. Series.

QD461.V32 539'.6 74-30809

ISBN 0-12-714550-8

PRINTED IN THE UNITED STATES OF AMERICA



This is Volume 35 of  
PHYSICAL CHEMISTRY  
A Series of Monographs

Editor: ERNEST M. LOEBL, *Polytechnic Institute of New York*

A complete list of titles in this series appears at the end of this volume.

## Preface

Unlike physics, chemistry has attracted many persons who are not particularly adept or interested in mathematics. To these people, most of the literature dealing with molecular orbitals is distasteful, if not actually repulsive. Yet the concept of spin-paired canonical molecular orbitals obtained from self-consistent-field (SCF) calculations offers considerable insight into the electronic structure of matter, particularly molecular structures. When we first started to make plots in which the electron density in a cross-sectional plane passing through a molecule is plotted at right angles to that plane, we became enamored with the relatively high information content of this method of representing not only total electron densities but the densities of the various molecular orbitals. The Confucian maxim that "one picture is worth ten-thousand words" seems to us to be indeed true concerning cross-sectional electron-density plots. Therefore this book is primarily a picture book, with just enough text to alert the reader to some of the items he should be looking for in these plots.

In this book, we have attempted to address everyone interested in the electronic structure of molecules. We feel that the omission of all mathematics is really an advantage since this information is readily available elsewhere (e.g., see the books by Schaefer and by Pilar referenced on p. 11) and would not be of value to either the neophyte or initiate in quantum chemistry. We believe that the illustrations included in this book will be of service in explaining electronic structure to college undergraduates even at the freshman level. We have found this to be true in our own teaching, and believe that SCF molecular orbitals as depicted in this book are no more difficult for the rank beginner to understand than are the rather shopworn but basically equally valid concepts of atomic hybridization and chemical bonds now being purveyed. The molecular orbitals have the advantage of emphasizing the diffuse nature of the electrons as well as the role of this diffuseness in the bonding process.

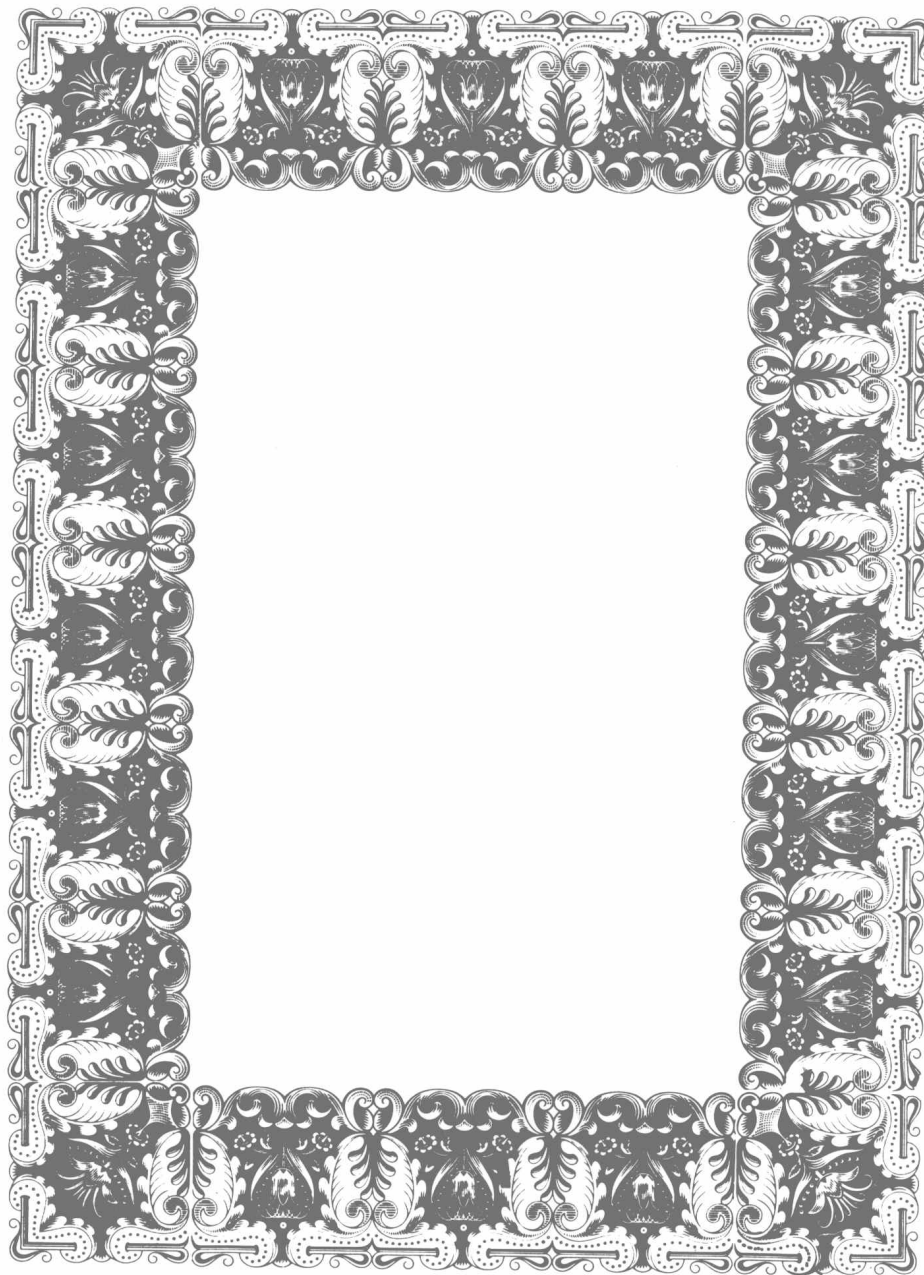
Throughout much of Chapters 2 and 3 we have tried in words to relate each valence-shell molecular orbital to its dominant chemical-bonding contribution in order that experienced chemists (in both industry and academia) who think in terms of qualitative bonding concepts might become readily familiar with the SCF molecular orbitals and their significance within a familiar frame of reference. It seems to us that anyone who invokes atomic orbitals and their hybrids in considerations concerning chemical phenomena should at least be aware of SCF molecular orbitals other than the  $\sigma$  and  $\pi$  orbitals of diatomic and other linear molecules since the molecular orbitals result for molecular structures in exactly the same way that atomic orbitals follow from atomic structures.

This volume should also be of some value to the theoretician who is well versed in quantum chemistry. To him we commend the examples of Chapter 2 which demon-

strate the effects of varying the basis set on the electron distribution within an orbital. The pictorial treatment of internal rotation at the end of Chapter 3 may also be of some interest. Our experience in dealing with a number of theoreticians is that they too sometimes have trouble in obtaining a spatial concept of electronic behavior from the usual mathematical format of their art. Spatial conceptualizing has historically been proved to be of great value in both physics and chemistry.

For those of you whose minds are spatially oriented, this book should be fun to peruse. We both hope that you will find some of the pleasure we have experienced in interrelating molecular orbitals among different molecules and among various configurations of the same molecule by means of cross-sectional electron-density plots.

*Ilyas Absar*  
*John R. Van Wazer*



Full-view of an electron enlarged 10,000-fold. Note that the electron extends beyond edge of frame in all directions.

# Contents

Preface.....	ix
--------------	----

## 1 Orbitals in Quantum-Chemical Calculations

A. Introduction.....	1
B. Polyelectronic Atoms.....	2
C. Molecular Calculations.....	3
D. Basis Sets.....	7
E. Semiempirical Calculations.....	9
F. Electronic Ionizations and Transitions.....	10
G. Molecular-Orbital Charge Distributions.....	10
H. Orbital Transformations and Calculations Not Involving Orbitals.....	11
<i>References</i> .....	11

## 2 Electron Densities and Shapes in Atoms and Molecules

A. Some Typical Atoms.....	12
B. Some Typical Molecules.....	16
C. Representation of Orbital Shapes in Molecules.....	20
D. Effect of Poor Basis Sets on Electron-Density Distributions.....	24
<i>References</i> .....	27

## 3 Cross-Sectional Plots of Electron Densities

A. Introduction.....	28
B. Methane, Ethane, and Ethylene.....	28
C. Methyl Fluoride, Methyl Chloride, Methyl Isocyanide, and Acetonitrile.....	34
D. Methyl Mercaptan, Methyl Alcohol, and Dimethyl Ether.....	40
E. Monomeric Lithium Fluoride and Monomeric Methyl Lithium.....	45
F. Hydrogen Cyanide and Its Analog, Methinophosphide.....	46
G. Ammonia, Phosphine, and Arsine.....	49



H. Methylamine, Methylphosphine, and Its Isomeric Phosphorus Ylide.....	51
I. Cyclopropane, Phosphirane, and Thiirane.....	54
J. Hydrogen Sulfide and Its Two Hypothetical Derivatives: $\text{H}_2\text{SO}$ and $\text{H}_2\text{SO}_2$ .....	57
K. Phosphorus Trifluoride and Phosphoryl Trifluoride, as well as Difluorophosphine and Difluorophosphine Oxide.....	68
L. Orbital Interrelationships among Water, Formaldehyde, and Ketene.....	69
M. Monomeric Borane and Diborane.....	74
N. Chlorosilane and the Role of d Orbitals in Charge Transfer to Third-Period Atoms...	76
O. Phosphorus Pentafluoride.....	80
P. Internal Rotation in Molecules, with Emphasis on Diphosphine.....	88
<i>References</i> .....	98
INDEX.....	99

# 1 Orbitals in Quantum-Chemical Calculations

## A. Introduction

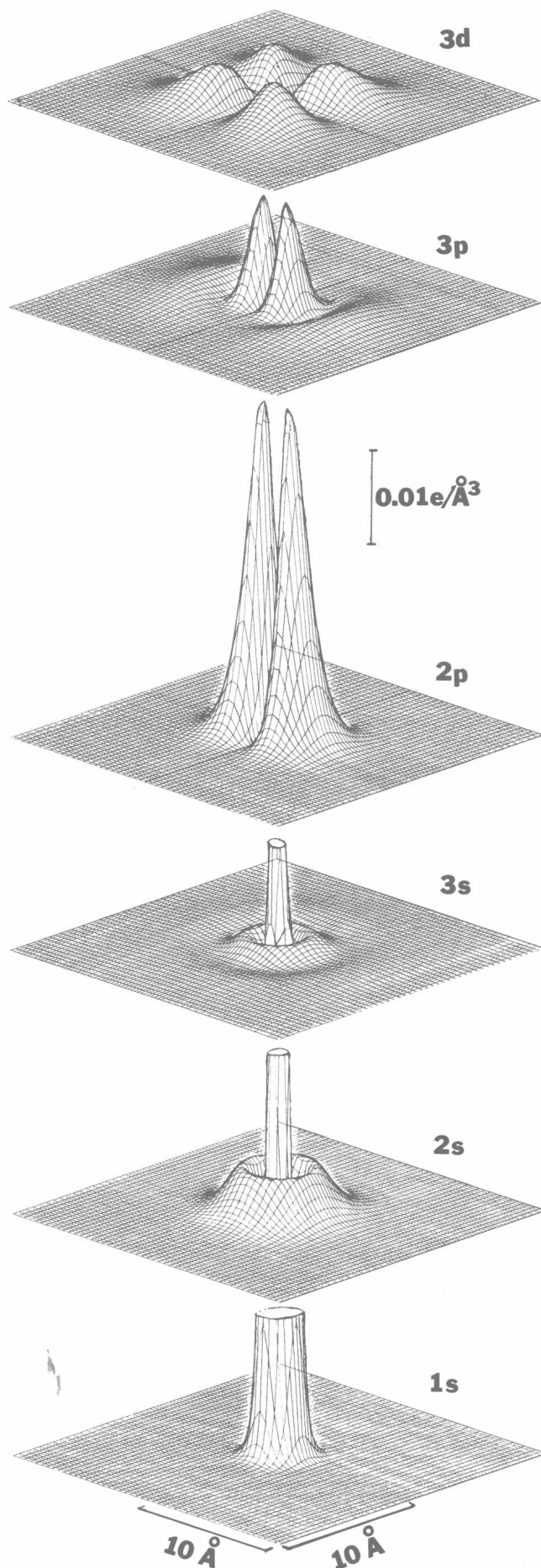
In the study of the electronic structure of matter, it is assumed that chemical systems such as atoms and molecules and, in turn, fundamental species such as electrons, neutrons, and protons can be represented by mathematical functions. The purpose of quantum-mechanical calculations as applied to chemistry is to find these functions, which are called the "eigenfunctions" or "wave functions" of the atom, molecule, or assemblage of atoms and/or molecules being investigated.

A theory of physical science must be able to predict as well as to explain natural phenomena and the laws that govern them. These predictive and explanative abilities are embodied in the mathematics of the Schrödinger equation [1, 2], which relates the energy of an atomic or molecular system (or their assemblages) to its wave function. Accurate wave functions may be used to calculate the energetics of chemical processes, with due allowance being made for the statistical behavior [3] of collections of atoms and/or molecules at temperatures above absolute zero. In addition, the proper arrangement of atoms necessary to make a stable molecule can be calculated without recourse in any way to experiment (i.e., on an *ab initio* basis), since the wave function corresponding to this particular arrangement will correspond to an energy minimum. Similar calculations can be used to obtain the energies associated with changes in molecular configurations [2]. Furthermore, a number of physical properties [2], such as dipole moment and diamagnetic susceptibility, may be obtained from a good *ab initio* wave function. Thus, in one sense, the long-term purpose of quantum-mechanical calculations is progressively to make experiments obsolete.

Unfortunately, the Schrödinger equation, which is a partial differential equation, cannot be solved exactly for any system containing more than one electron so that a precise analytic solution for a neutral atom can be obtained only for hydrogen. There are certain natural restrictions on these solutions which are embodied in the quantum numbers. For the one-electron problem of the hydrogen atom, there are four such quantum numbers three of which are a consequence of the three degrees of freedom in space. These three quantum numbers, which are derived from the usual solution in spherical polar coordinates, are designated  $n$ ,  $l$ , and  $m$ , with  $n$  taking integer values starting with 1. For each  $n$ , there are  $n$  values of  $l$  starting with 0 and going up to  $(n - 1)$ ; and, furthermore, for each  $l$  there are  $(2l + 1)$  values of  $m$  starting with  $-l$  and increasing in integral steps up to  $+l$ . The fourth quantum number,  $s$ , is introduced to account for electron spin, and  $s$  may have the values  $+\frac{1}{2}$  or  $-\frac{1}{2}$ .

The values of  $l = 0, 1, 2, 3, 4$ , etc., are generally represented by the lower case letters  $s, p, d, f, g$ , etc. The various states of the hydrogen atom are designated by  $nl_m$ , e.g.,  $1s_0$ ,  $2p_{-1}$ ,  $2p_0$ ,  $2p_{+1}$ ,  $3d_{-2}$ ,  $3d_{-1}$ ,  $3d_0$ ,  $3d_{+1}$ ,  $3d_{+2}$ . An alternative, closely related designation uses the subscripts  $x, y$ , and  $z$  for  $p$  and  $xy, xz, yz, z^2$ , and  $x^2 - y^2$  for  $d$  to define a similar set of  $m$  quantum numbers with respect to the spatial geometry of the resulting functions according to the Cartesian coordinate axes  $x, y$ , and  $z$ . These various notations are simply formalities to describe the electronic states of hydrogen.

Each of the states of the hydrogen atom corresponds to a certain spatial distribution of electronic charge. This distribution may be considered



as the probability of finding the electron at any given spot or, with equal veracity, as the fraction at that position of the charge of a spatially distributed electron. This electron density is evaluated [1, 2] from the square of the wave function (or more precisely from the wave function multiplied by its complex conjugate, i.e.,  $\psi\psi^*$ ). The wave function is calibrated (by a process called "normalization") so that the summation of the electron density over all space equals unity for the single electron of the hydrogen atom.

The spatial distributions of the electron corresponding to several states of the hydrogen atom (each one of which may be called an orbital) are shown in Fig. 1.1. Each of the plots of this figure corresponds to a cut through the hydrogen atom passing through its nucleus, with the geometry of the cut being represented by the basal plane and the electron density at any point on this plane being plotted perpendicular to it. If the basal plane of these diagrams is the  $xy$  plane with the  $x$  axis running from the upper left to the lower right of each diagram, the p-type orbitals are shown as the  $2p_x$  and  $3p_x$  and the d-type orbital is the  $3d_{xy}$ . Note in the figure that the s-type orbitals are truncated in order to display them on the same scale as those of p and d symmetry. The electron density of any s orbital is a maximum at the position of the nucleus. For the 1s orbital of the hydrogen atom, the density at the nucleus is  $2.148 \text{ e}/\text{\AA}^3$ ; for the 2s it is  $0.2685 \text{ e}/\text{\AA}^3$ , and for the 3s it is  $0.0796 \text{ e}/\text{\AA}^3$ .

It is seen in Fig. 1.1 that, whereas the s orbitals exhibit their highest electron density at the nucleus, the p and d orbitals have no electron density at this point, but instead exhibit nodal planes (i.e., planes of zero electron density) passing through the nucleus. The differences in the energies corresponding to these various states,  $nl_m$ , of hydrogen are found to agree to good accuracy with the respective values obtained from spectroscopic measurements. The major correction is called "spin-orbit coupling," and it is necessitated by neglect of the fact that the moving electron is spinning.

## B. Polyelectronic Atoms

In order to obtain meaningful solutions for polyelectronic atoms, it is necessary to use approximations in addition to those employed for

Fig. 1.1. A cross-sectional electron-density plot of the various atomic orbitals corresponding to the ground and some excited states of the hydrogen atom.

the hydrogen atom. One of these approaches, called the "Hartree-Fock approximation," involves the assumption of mutually independent one-electron wave functions that are used to build up the many-electron wave function, which can be expressed as a product of these one-electron orbitals. Moreover, since all electrons are identical, it is possible to switch any pair of them and the Pauli principle implies that the resulting many-electron wave function should be antisymmetric with respect to interchange of any two electrons. Therefore, it may be appropriately handled in the form of a determinant [2] of the one-electron wave functions, and this is called a "Slater determinant." Since it appears that a good fit to reality (i.e., a wealth of experimental data) is obtained when the one-electron wave functions used in constructing a polyelectronic atom are set up in analogy to hydrogen, this mathematical description allows the various atomic orbitals of a polyelectronic atom to be closely similar to the various states of hydrogen, so that these atomic orbitals may be described by the same set of quantum numbers.

A second common approximation, which is mathematically consistent with the previous one and which is employed in conjunction with it, is called the "self-consistent field" (SCF) approach [1, 2]. This approximation consists of a mathematical treatment in which the spatially distributed electron is considered to lie in the average potential field of all the other electrons and a series of iterations is employed to make the fields mutually consistent within the framework of the Schrödinger equation. In the above approximations, the best mathematical description of each atomic orbital leads to what is called the "limiting Hartree-Fock solution."

The energy of an atomic state obtained from a Hartree-Fock solution is never as low as the experimental energy, primarily because of the neglect of electronic correlation. Furthermore, there are relativistic effects. Although these corrections together seldom amount to more than ca. 1% of the total energy,  $E$ , of forming the atom from the isolated electrons and the isolated nucleus, the magnitude of the difference,  $\Delta E$ , between the experimental and the Hartree-Fock energies is extremely large in chemical terms, especially for the heavier atoms. For the ground-state lithium atom, it has been estimated [4] that  $\Delta E = 28.8$  kcal/mole, of which only 1.2% is due to relativistic effects, with  $\Delta E/E = 0.61\%$ ; likewise, for the fluorine atom,  $\Delta E = 250$  kcal/mole, of which 20.8% is relativistic, with  $\Delta E/E =$

0.40%. For the sodium atom,  $\Delta E = 368$  kcal/mole, of which 34.1% is relativistic, with  $\Delta E/E = 0.36\%$ ; for the chlorine atom,  $\Delta E = 1279$  kcal/mole, of which 67.3% is relativistic, with  $\Delta E/E = 0.44\%$ .

The correction for electron correlation accounts for details of electronic motion that are not covered by the SCF approximation (in which each electron is considered to move in the average field of the all of other electrons). In particular, this assumption of an average potential field allows electrons with antiparallel (i.e., opposite) spins to avoid each other less assiduously than is the case in reality. Various approximations [2] have been employed for estimating the contribution of electron correlation to the total energy. Such estimates generally deal only with interactions between pairs of electrons. A rough rule of thumb for atoms and ions with six or more electrons is that the correlation energy is around  $-50$  kcal/mole per doubly filled orbital.

The relativistic correction [2] is also attributable to electron dynamics and is primarily assignable to the innermost orbitals of the larger atoms (exhibiting the larger nuclear charges). The mechanical analogy to the situation of a negative charge lying close to a large positive point charge is for the negative charge to move at an excessively high speed so that the centrifugal force will counterbalance the Coulombic attraction between the opposite charges. For electrons, this speed of revolution about the nucleus is rapid enough to lead to relativistic effects.

### C. Molecular Calculations

The SCF technique can be applied to molecules in just the same way as it is applied to atoms, if we consider the molecule in the fixed-nucleus approximation [2] (which corresponds to a zero-order Born-Oppenheimer wave function). This approximation assumes that electronic motion is sufficiently faster than nuclear motion so that the nuclei may be regarded as fixed particles. Thus, the effects of small relative motions of the nuclei may be omitted from the wave function. Both theoretical and experimental evidence has amply justified the use of this approach. The functions resulting from the solution of the molecular Schrödinger wave equation are a natural extension of the atomic-orbital approach. Again, the one-electron wave functions are called "orbitals," but in this case they are molecular rather than atomic orbitals. It is important to note that except for the chemically insignificant effects

introduced by the fixed-nucleus approximation, Hartree-Fock SCF molecular orbitals have exactly the same degree of significance and meaningfulness as do the Hartree-Fock SCF atomic orbitals.

For historical reasons, chemists have been at ease in thinking of atoms in terms of orbitals, even for large atoms for which wave functions could not be obtained until the last few years, when large-scale computers became generally available. In part, this touching confidence is due to the fact that the one-electron wave functions (i.e., atomic orbitals) used to describe a polyelectronic atom are similar in form to the various states (ground and excited) of the hydrogen atom for which each state is in itself a one-electron wave function. This similarity to hydrogen allowed chemists to discuss semiquantitatively the electronic structure of the heavier atoms long before it was practicable to calculate the respective wave functions.

Because there is more than one nuclear center in a molecule, the straightforward analogy to the hydrogen atom is lost and such matters as the spatial distribution of electrons in molecular orbitals have not been adequately considered until quite recently. As a result of this and because the notions of chemical bonds as electronic charge concentration entered chemistry in pre-quantum-chemical days, the molecular orbitals have seemed forbidding and cumbersome to most chemists, because it is not uncommon for the electronic charge in a single molecular orbital to be distributed around several of the nuclear centers of the molecule. Furthermore, for closed-shell systems (the usual case for stable molecules), the symmetry inherent in the arrangement of the nuclear centers carries over into the molecular orbitals which are usually described in terms of point-group notation.

Linear molecules (naturally, including all diatomics) have cylindrical symmetry and therefore may be specified by a notation which is a straightforward extension of the one used for atoms, which all have spherical symmetry. Thus, in parallel to the s, p, d, f, g, etc., atomic orbitals, the molecular orbitals of these linear structures are designated as  $\sigma$ ,  $\pi$ ,  $\delta$ ,  $\phi$ ,  $\gamma$ , etc. Just as the s atomic orbital has spherical symmetry, so the  $\sigma$  molecular orbital exhibits cylindrical symmetry. Likewise, just as each of the p, d, f, g, etc., atomic orbitals can be considered as resulting from the introduction of one, two, three, four, etc., nodal planes of symmetry to an s atomic orbital, similarly, the  $\pi$ ,  $\delta$ ,  $\phi$ ,  $\gamma$ , etc., molecular orbitals in linear molecules exhibit one, two, three, four, etc.,

planes of symmetry, each containing the cylindrical axis of the molecule.

As a pedagogic exercise to demonstrate how molecular orbitals are formed from a combination of atomic orbitals, three-dimensional electron-density plots for any plane running through the linear axis of typical  $\sigma$ ,  $\pi$ , and  $\delta$  orbitals are shown in Fig. 1.2. These plots represent the electronic structures obtained by bringing two hydrogen atoms together at a distance essentially that at which maximum overlap is achieved between the participating atomic orbitals. For example, the pseudomolecular orbital marked  $(\sigma_{1s})_g$  is constructed as follows:  $\psi_{(\sigma_{1s})_g} = (1/\sqrt{2})(\psi_{1s}^H + \psi_{1s}^{H'})$ ; similarly  $\psi_{(\sigma_{1s})_u} = (1/\sqrt{2})(\psi_{1s}^H - \psi_{1s}^{H'})$  and  $\psi_{(\pi_{2p})_u} = (1/\sqrt{2})(\psi_{2p}^H + \psi_{2p}^{H'})$ , where g stands for *gerade* (i.e., straightforward) and u for *ungerade*. Although these constructed pseudomolecular orbitals were not optimized by any SCF procedure or its equivalent, it is interesting to note that they are closely related to the symmetry states of the hydrogen molecular ion,  $H_2^+$ . For this  $H_2^+$  ion [5], only three stable states,  $(\sigma_{1s})_g$ ,  $(\pi_{2p})_u$ , and  $(\sigma_{3d})_g$ , were found; and these exhibit bond distances of 1.06, 4.8, and 4.2 Å, respectively. In the diagrams of Fig. 1.2 the related distance for the pseudomolecular orbitals involving the 1s atomic orbitals was also 1.06 Å, whereas a distance of 5.3 Å was employed for the pseudomolecular orbitals based on 2s or 2p atomic functions. For the pseudomolecular orbitals of Fig. 1.2 involving 3s, 3p, or 3d atomic orbitals, the interatomic distance chosen to correspond to maximum overlap was 10.6 Å.

If we consider that the plots of Fig. 1.2 approximate the probability of finding the single electron of the pseudomolecular orbital at a given position with respect to the two protons, we see that the  $(\sigma_{1s})_g$  orbital corresponds to the electron lying close to the vicinity of the two nuclei and also between them. The deleted top portion of the diagram of orbital  $(\sigma_{1s})_g$  in Fig. 1.2 shows individual peaks above each hydrogen nucleus with a valley between them, not unlike the uppermost part of the central portion of orbital  $(\sigma_{2p})_g$ . Orbitals  $(\sigma_{2s})_g$  and  $(\sigma_{3s})_g$  exhibit the same general form of orbital  $(\sigma_{1s})_g$ , except for the introduction of a spherical nodal surface around each hydrogen for  $(\sigma_{2s})_g$  and two such nodal surfaces around each hydrogen for  $(\sigma_{3s})_g$ . These, of course, correspond to the inner nodes of the participating atomic orbitals. Note that the bonding is achieved by overlap of the outer antinodes, whereas the inner antinodes act simply as reservoirs for some of the



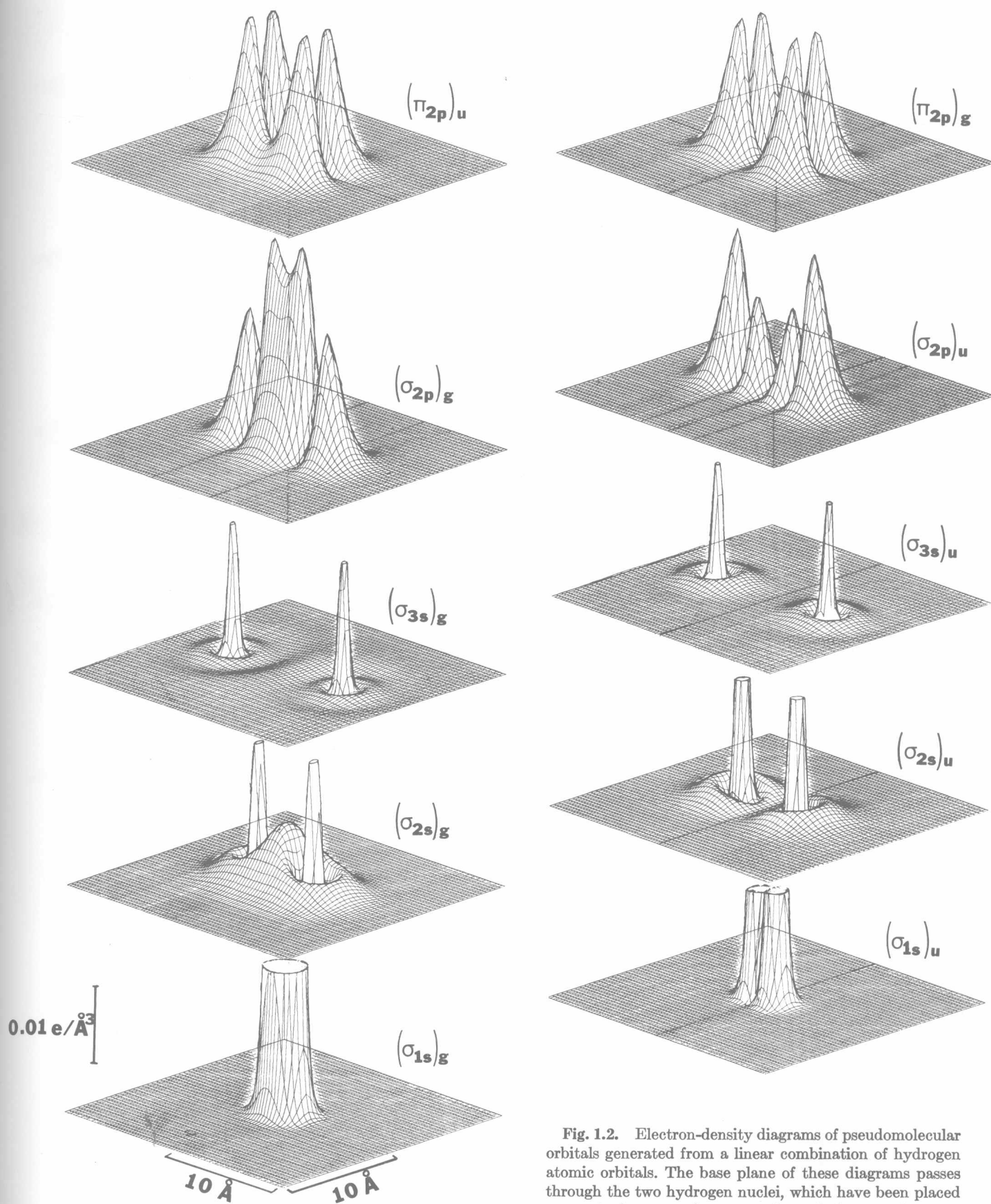


Fig. 1.2. Electron-density diagrams of pseudomolecular orbitals generated from a linear combination of hydrogen atomic orbitals. The base plane of these diagrams passes through the two hydrogen nuclei, which have been placed so as to have maximum overlap of the atomic wave functions. (Fig. 1.2 continued p. 6.)

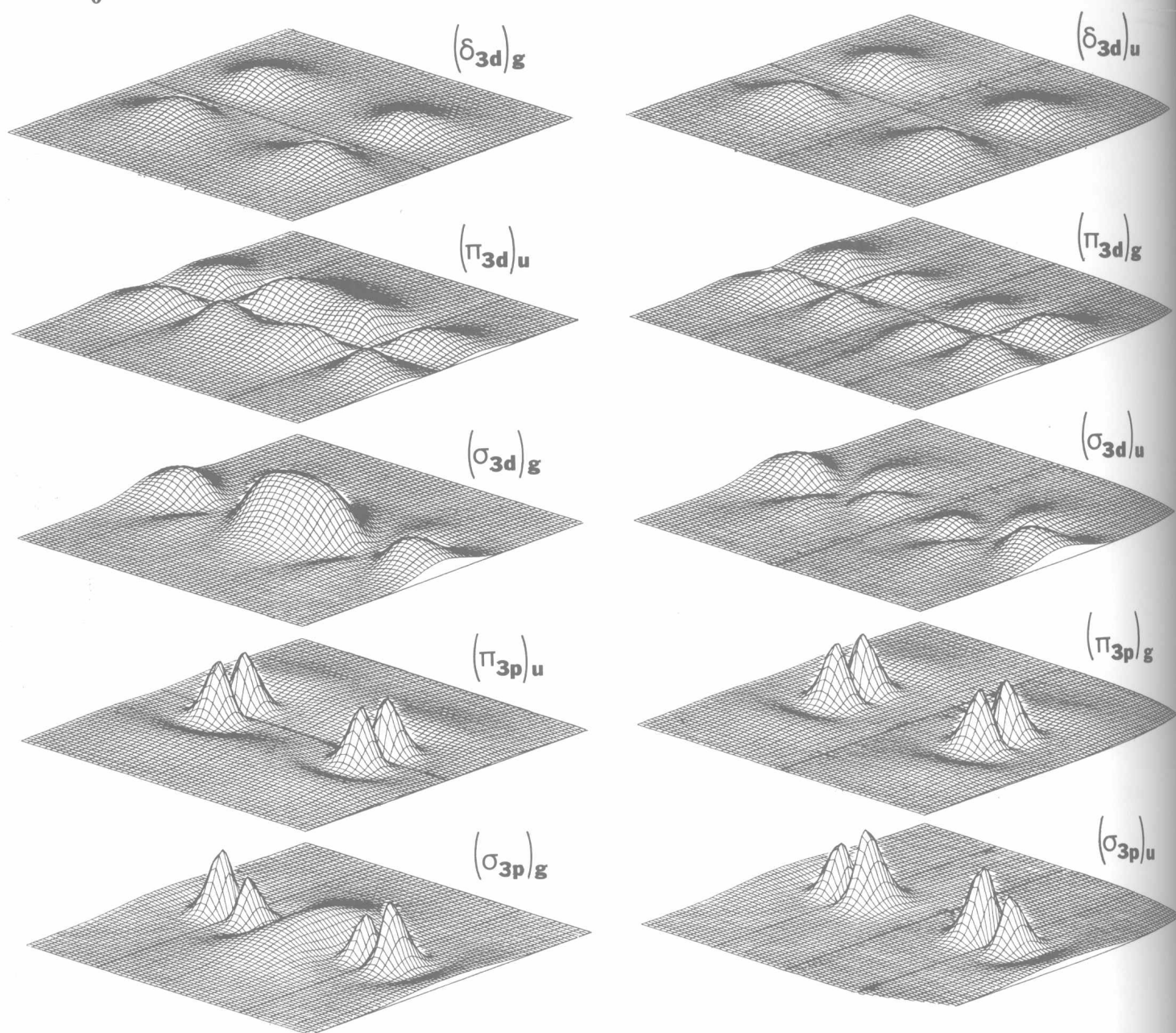


Fig. 1.2. (continued)

electron density. Orbitals  $(\sigma_{1s})_u$ ,  $(\sigma_{2s})_u$ , and  $(\sigma_{3s})_u$  have the same spherical nodal surfaces as orbitals  $(\sigma_{1s})_g$ ,  $(\sigma_{2s})_g$ , and  $(\sigma_{3s})_g$ ; but, in addition, each of them exhibits a nodal plane which bisects the internuclear axis. The intersection of these planes with the basal plane of the diagram is shown by the heavy line on the latter.

Pseudomolecular orbital  $(\sigma_{2p})_g$  consists of the end-on interaction of a 2p lobe on one hydrogen with that on the other. Naturally, this orbital exhibits the two nodal planes corresponding to those of the participating 2p functions. However, orbital  $(\sigma_{2p})_u$  has an additional nodal plane lying exactly between these two. Note that the outer

lobes of the participating 2p functions of orbital  $(\sigma_{2p})_g$  and  $(\sigma_{2p})_u$  act as reservoirs of electron density, with the density being transferred into the bonding region for the bonding orbital  $(\sigma_{2p})_g$  and out of this region for the antibonding orbital  $(\sigma_{2p})_u$ . The  $(\pi_{2p})_u$  pseudomolecular orbital involves the sidewise interaction of the 2p lobes on each of the hydrogen atoms so that it exhibits only one nodal plane, which passes through the internuclear axis. Likewise, orbital  $(\pi_{2p})_g$  exhibits not only this plane but a plane at right angles to it, which bisects the internuclear axis. These arguments may be extended to the other orbitals shown in Fig. 1.2.

## D. Basis Sets

SCF calculations may be carried out in various ways. A common procedure is to use an exponential function or a linear combination of such functions to describe each orbital, with the exponents being optimized by SCF procedures to find the set of exponents giving minimum energy. The exponential function of the form  $r^{m-1}e^{-\zeta r}$ , where  $r$  is the radial distance from the nucleus and  $\zeta$  (zeta) is a variational parameter called the "orbital exponent," makes up the radial contribution to what is called a "Slater-type function." The exponential function of the form  $r^{m-1}e^{-\alpha r^2}$ , where  $\alpha$  is another variational parameter (orbital exponent), is the radial contribution to what is called a "Gaussian-type function," with each atomic orbital being represented by a linear combination of several such functions. The various functions used to describe an atomic orbital are called "basis functions," and the number of these functions designates the size of the basis set. Although the Slater-type orbitals exhibit the same exponential form as do the analytical solutions for the various states of the single-electron hydrogen atom, it turns out that the evaluation of the various multicenter integrals involved in a molecular SCF calculation may be carried out more easily using Gaussian rather than Slater functions. At the present time, therefore, a Gaussian representation is usually preferred for *ab initio* molecular calculations.

When only one Slater-type function is used to describe each atomic orbital, the representation is called a "minimum-Slater basis set." However, even at convergence with atom optimization of the value of each orbital exponent, this basis set gives only a moderately good description of the atom. This description is considerably improved when two or more Slater-type functions are used to represent each atomic orbital. Thus, we have a minimum-Slater set as well as various extended-Slater basis sets, such as a double-zeta, triple-zeta, etc., set corresponding to the use of two, three, etc., Slater functions to describe each atomic orbital. If, say, a different number of Slater functions is employed to describe the various orbitals (e.g., a double zeta for a 1s and a triple zeta for a 2s), the overall description is simply included in the generic class of extended-Slater basis sets. Since the exponential form of Gaussian functions is different from that of analytical solutions for the hydrogen atom, two to four Gaussian orbitals are required as replacements

for each Slater orbital to get about the same total energy of the atom or molecule. Quite large Gaussian basis sets are generally employed in modern calculations, with optimization of all of the exponents in the respective atoms, as well as the usual optimization of the coefficients that weight the contributions of each Gaussian function in the linear combination employed. It is the exponent that determines the "orbital radius" for each atomic orbital, with a larger exponent corresponding to a smaller radius. If several exponents are employed to describe a given atomic orbital, the orbital radius then results from a weighting by the respective coefficients of the contributing exponential functions.

In dealing with Gaussian basis sets, it is common practice to employ the full set of exponents of a given symmetry (i.e.,  $l$  quantum number) for each atomic orbital of that symmetry (i.e., the same set of exponents are used for the 1s, 2s, and 3s orbitals of a given third-period atom). Under these conditions, the members of an atom-optimized set of Gaussian exponents used for each symmetry are spaced approximately evenly on a log scale, with some bunching up of the larger exponents because they predominate in the description of the higher-energy inner orbitals and because the optimization is carried out through minimization of the total atomic energy. Furthermore, it is found [6] that the values of the atom-optimized exponents obtained for a selected number of Gaussian functions of a given symmetry are practically unaffected by the number of Gaussian functions employed to describe the orbitals of different symmetry. Thus, for carbon, essentially the same individual values were obtained for a set of, say, nine s-type functions when optimized with anywhere from one to six p-type functions.

Of course, calculations on molecules may be carried out just as they are on atoms, with full optimization of all coefficients and exponents of appropriately chosen exponential functions. However, it is found to be computationally expeditious to use a linear combination of atomic orbitals (LCAO) in the SCF calculation [1, 2]. Just as an atomic orbital can be described in a Gaussian or a multiple-zeta Slater basis set in terms of a linear combination of orbital functions, a molecular orbital may be treated as a linear combination of atomic orbitals. These, in turn, are often linear combinations themselves. Since the chemical bonding in molecules really represents only a small perturbation of the constituent atoms, it is quite common to optimize the exponents of the

filled atomic orbitals in the ground-state atom and to use these "atom-optimized" exponents in the molecular calculation. This may lead to some error in the description of an atom within a molecule when a minimum-Slater basis set is employed. However, when several atom-optimized exponents are used for each atomic orbital without contraction (see below), the molecular optimization of the coefficients of the individual functions used to describe a given atomic orbital can make allowance for an effective change in radius of this orbital when going from the atom to the molecule in question. This method of indirectly achieving molecular optimization of atomic-orbital radii is particularly effective when the entire range of Gaussian exponents for a given orbital symmetry contributes to each individual atomic orbital of that symmetry.

Two common ways of lowering the cost of an LCAO-MO-SCF calculation are the use of orbital contraction and symmetry adaption. In orbital contraction, the original linear combination of basis functions used to describe each atom in a molecule is reduced by bunching several basis functions together through the use of linear combinations, with the integrals being evaluated for the overall basis set and the SCF optimization being carried out on the contracted set. This procedure has the disadvantage of reducing the capability of adjusting atomic-orbital radii to fit the requirements of various molecules, as described for uncontracted orbitals above. Symmetry adaption merely means that the individual functions of a complete basis set (or the combinations of these functions) which are unneeded for a particular molecular symmetry are deleted so that computer time is not wasted in calculating large numbers of zero-valued integrals and the full Hartree-Fock matrix may be replaced by smaller matrices, one for each pertinent symmetry type, to reduce the cost of matrix diagonalization.

When the SCF procedure is used for energy optimization, the total energy corresponding to the mathematical description afforded by a given basis may be obtained to a high degree of accuracy. Thus, for a given choice of say, Slater or Gaussian exponents, the final SCF energy after a sufficient number of iterations will always be the same, and this basis-set-dependent value is called the "convergence limit." However, if increasingly larger basis sets are used, it is found that the convergence limit approaches a limiting value of the total energy and this limiting energy, corresponding to an infinitely large basis set, is called the "energy

at the Hartree-Fock or SCF limit" [2]. This Hartree-Fock energy is always the same for any given atom or molecule and is independent of the choice of the basis set, as well as of the type of function used to describe the orbitals making up the basis set. In the study of molecules, various odd combinations [2] of orbitals have been tried in order to minimize calculational expenses. From these studies it is clear that the LCAO approximation may be extended in peculiar ways. Thus, the Hartree-Fock limit might possibly be obtained by using only s-type orbitals, which are scattered around in space and not necessarily centered on any nuclei. In the extreme, it may well be that one can use an infinitely large basis set consisting of practically any or many kinds of orbital functions expressed in any convenient mathematical form scattered around or located at an arbitrary or optimized point in space. Although the application of this approach to atoms has not received much attention, there is no basic reason that it cannot be generally employed. If these ideas seem hard to visualize, note that a properly chosen s orbital (described by, say, several Gaussian functions), when centered at the appropriate distance from the selected nucleus along the positive  $x$  axis with another of opposite sign similarly located along the negative  $x$  direction, gives a good description of a  $p_x$  orbital. (This particular type of representation is sometimes called a "Gaussian lobe function" [2].)

A commonly used formality in chemistry is the discussion of molecules and molecular orbitals in terms of the atomic orbitals making up the LCAO basis set. If the atomic orbitals are properly chosen (as in a minimum-Slater basis set) and are each centered on their respective atoms, the formality of discussing the molecule in terms of atomic orbitals can be useful and edifying. However, in such discussions it is important that the basis set be "balanced" [7] so that the choice of the atomic orbitals does not lead to bookkeeping errors in the atomic charges, as analyzed either per atom or per atomic orbital. Except for the case of the minimum-Slater basis set, it is difficult to judge when a combination of atomic orbitals is well balanced and the literature is full of examples of extremely poorly balanced basis sets. When too many atomic orbitals are assigned to one atom as compared to one or more of the others in a limited basis set, these atomic orbitals may effectively represent the starved atom(s), although being formally assigned to the other atom. An extreme case of this situation is found for the one-center