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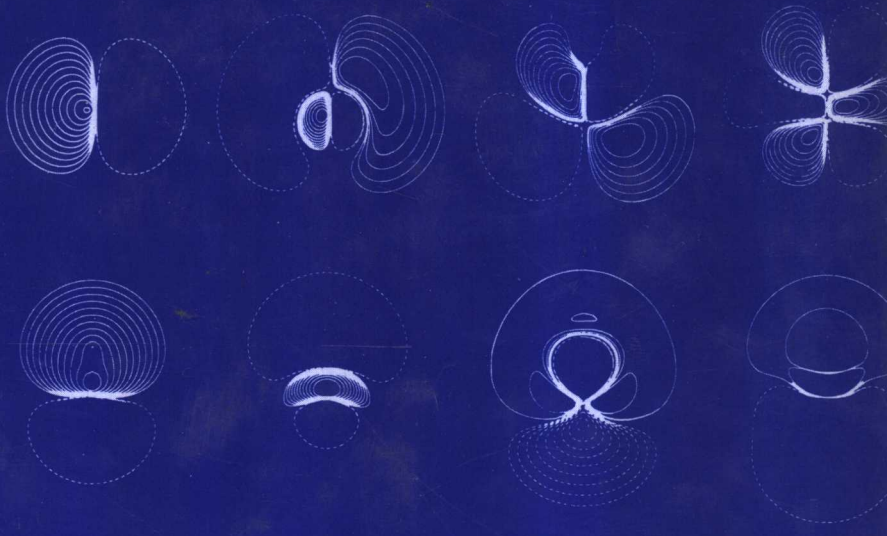

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Results of *ab Initio* Calculations

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PREFACE

This small book began as a set of notes for use by chemical physics students in a course that aimed to illustrate the *results* obtained from wave-mechanical calculations on the electronic structure of first diatomic, and hopefully, then polyatomic molecules. We hope that the book may serve as a reference for researchers interested in the electronic structure of diatomic molecules as well as provide background analyses of related concepts for undergraduate and graduate students.

In Chapters II–VI, the main outlines of needed theory are presented as simply as possible. It is assumed that the reader has a background in the elements of quantum chemistry. Detailed theoretical derivations are not given except very briefly in Chapter I, which may be regarded as a theoretical introduction to the later chapters. One might at first glance at Chapter I, then go on to Chapter II.

In later chapters, the emphasis is on *ab initio* calculations by SCF (self-consistent-field) and multiconfiguration SCF molecular orbital methods. The approach is in terms of linear combination of atomic orbitals (LCAO) methods, with considerable emphasis on basis sets and on some details of configuration mixing to secure electron correlation. The plethora of other methods that have been and are being developed is mentioned only very briefly. Semiempirical calculations are not discussed.

In Chapter II, on one-electron molecules, several topics are introduced that are also relevant to later chapters but which can be well illustrated for the one-electron case: LCAO and LCMAO approximations (MAO, modified atomic orbitals) and basis sets, electronic population analysis, spectroscopic transition probabilities, and the nature of chemical bonding. In each succeeding chapter, new features of theory that become prominent when two or more electrons are present, or are important in hydrides, in homopolar molecules, or in heteropolar molecules, are successively introduced. Hence for a given topic in the Index, reference may be needed to more than one chapter.

The discussion and references are based largely on relatively recent papers, but basic earlier work is first considered in each chapter. The aim is to emphasize the best up-to-date work, through 1976. We apologize for references we may have overlooked. For a much more complete bibliography covering older work through 1973, see Richards *et al.* (Ref. 49 in Chapter III). No systematic attempt has been made to discuss all molecules on which *ab initio* calculations have been made. Rather, what has been presented is intended to be illustrative, although perhaps more comprehensive for heteropolar than for homopolar molecules.

We have recently become aware of a small book (R. F. W. Bader, "An Introduction to the Electronic Structure of Atoms and Molecules," Clarke, Irwin, & Co., Toronto, Vancouver, 1970) that complements ours in its clear explanation and presentation of contour maps of molecular charge distributions and of the differences between these and corresponding atomic distributions.

ACKNOWLEDGMENTS

We greatly appreciate permission from several authors to reproduce figures from their papers, and permission from the relevant journals. We are also very grateful to Professor Klaus Ruedenberg for letting us reproduce an unpublished figure (Fig. II–3). The book includes a number of tables not attributed to other authors but which were computed in this laboratory. We are grateful to Mr. Michael D. Allison for carrying out the calculations on population analysis. With reference to the rather numerous population analysis tables, we should emphasize that while they are usefully illustrative they are based on formulas that must in general be "taken with some grains of salt."

LIST OF ACRONYMS

ANO	Approximate natural orbital
AO	Atomic orbital
APSG	Antisymmetrized product of strongly orthogonal geminals
CE	Correlation energy
CEPA	Coupled electron pair approximation
CI	Configuration interaction
CM	Configuration mixing
CSF	Configuration state function
GLF	Gaussian-lobe function
GTF	Gaussian-type function
GTO	Gaussian-type orbital
GVB	Generalized valence bond
HF	Hartree–Fock
IEPA	Independent electron pair approximation
INO	Iterative natural orbital
LCAO	Linear combination of atomic orbitals
LCGLF	Linear combination of Gaussian-lobe functions
LCGTF	Linear combination of Gaussian-type functions
LCMAO	Linear combination of modified atomic orbitals
LCSTF	Linear combination of Slater-type functions
MAO	Modified atomic orbital
MCSCF	Multiconfiguration self-consistent-field
MECE	Molecular extra correlation energy

MO	Molecular orbital
MSO	Molecular spin orbital
NO	Natural orbital
OVC	Optimized valence configurations
PNO	Pair (or pseudo) natural orbitals
POL-CI	Polarization configuration interaction
RHF	Restricted Hartree–Fock
SA	Separate atom
SAO	Separate-atom orbital
SASTF	Separate-atom Slater-type function
SCEP	Self-consistent electron pairs
SCF	Self-consistent field
SD	Slater determinant
STF	Slater-type function
STO	Slater-type orbital
UA	United atom
UAO	United-atom orbital
UASTF	United-atom Slater-type function
VCI	Valence configuration interaction

CONTENTS

CHAPTER I

INTRODUCTION

The main purpose of this book is to present a survey of the electronic structure of molecules as elucidated by means of *ab initio* quantum-mechanical calculations. New developments in the formal theory and the evolution of sophisticated computing facilities during the past two decades have led to innumerable important contributions to the basic understanding of molecular structure. The significance of these contributions will be exemplified in the discussion of results for representative molecules in the following chapters. We begin with a short review of the primary methods used in the computation of molecular wave functions and of related properties. The reader is referred to several representative sources for developments of the underlying quantum-mechanical theories [1]. Schaefer [2a, b] provides useful surveys of recent *ab initio* calculations, and has edited two volumes [2c] in a series on theoretical chemistry containing many excellent articles on methods of electronic structure theory. For an introductory discussion of diatomic spectra and structure, we suggest reference to Herzberg's well-known book [3].

The electronic structure of any molecule can be briefly characterized by giving an electronic configuration followed by a state symbol. The electron configuration consists of a listing of symbols for all the occupied molecular orbitals (MOs) in the order of decreasing strength of binding, with a super-

script denoting the number of electrons in the given MO. For example, the ground-state electron configuration of N_2 is $1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 2\sigma_u^2 1\pi_u^4 3\sigma_g^2$, while the state is $^1\Sigma_g^+$.

The MO symbols contain a serial number followed by a symbol for the *symmetry species*; each type of nuclear symmetry is represented by a different set of species symbols. For diatomic molecules, two types of symmetry exist—$D_{\infty h}$ for homopolar molecules and $C_{\infty v}$ for heteropolar molecules. The same symmetries occur for linear molecules in general.

For these molecules, the main species symbol indicates the value of the characteristic quantum number λ giving in units of $h/2\pi$ the magnitude $|m|$ of the orbital angular momentum $mh/2\pi$ around the symmetry axis; the symbols are σ, π, δ, φ, ... for $\lambda = 0, 1, 2, 3, \ldots$. For $D_{\infty h}$ molecules only, each symbol also contains a *parity* subscript which indicates the symmetry (g for even, u for odd) with respect to the operation of inversion of the wave function at the center of the molecule.

The state symbols are similar except that capital letters are used, which represent the *total* orbital angular momentum $\Lambda h/2\pi$ around the symmetry axis: Σ, Π, Δ, Φ, etc. However, there are two kinds of Σ states, Σ^+ and Σ^-, depending on whether the wave function does (Σ^-) or does not (Σ^+) change sign on reflection in a plane (any plane) passing through the nuclei. So we have Σ_g^+, Σ_g^-, Σ_u^+, Σ_u^-, Π_u, Π_g, Δ_g, Δ_u, and so on. The state symbols also are prefixed by a *multiplicity* superscript which indicates the quantum number of the resultant spin S (1, 2, 3, 4, ... for $S = 0, \frac{1}{2}, 1, \ldots$ respectively).

The detailed forms corresponding to the MO symbols are often given as LCAO (linear combination of atomic orbitals) expressions, or as linear combinations (LCSTF) of bits and pieces of AOs called STFs (Slater-type functions—see Section A). The AOs themselves have familiar symbols such as 1s, 2s, 2p, 3s, 3p, and 3d, but when used in building MOs, a symbol to indicate a particular value of λ must be added, as for example in $2p\sigma$, $2p\pi$, $3d\sigma$, $3d\pi$, and $3d\delta$. All s AOs are of type σ (or σ_g if the symmetry is $D_{\infty h}$) and one can write $1s\sigma$, $2s\sigma$, etc., but the σ can be understood without writing it explicitly. STFs can be symbolized in the same way as AOs, for example 1s, 2s, $2p\sigma$, $2p\pi$, 2s, $3p\sigma$, but it must then be understood that these symbols now refer in general to *pieces* of AOs, not to complete AOs. Instead of LCSTFs one can use LCGTFs or LCGLFs (see Section A). This can be done because each STF can be approximated by a linear combination of Gaussian-type functions (GTFs) or Gaussian-lobe functions (GLFs).

When one speaks of *the* electron configuration of a molecule, one is dealing with an approximation. For an exact wave function, other configurations must be mixed in.

The molecular wave functions from which the results here presented are obtained are of three general types:

(a) Hartree–Fock–Roothaan self-consistent-field (SCF) functions, each of which is an antisymmetrized product (Slater determinant) of one-electron functions called molecular spin orbitals (MSOs), each a product of a molecular orbital (MO) and a one-electron spin function; or in general a linear combination of such Slater determinants (SDs), called a configuration state function (CSF). Each CSF corresponds to a particular MO electron configuration, which means a specification of the number of electrons in each MO (here note that some MOs are degenerate); each MO is approximated as a linear combination of, usually, atomic basis functions;

(b) extensive linear combinations of CSFs corresponding to the superposition of different electronic configurations, commonly referred to as configuration interaction (CI) or, preferable, configuration mixing (CM)[1]; or

(c) more limited CM in the form of multiconfiguration self-consistent-field wave functions (MCSCF), which are obtained by the simultaneous optimization of the MOs of (a) and of CM coefficients corresponding to a selected (usually small) set of configurations. After an MCSCF function is obtained, it may be further improved by additional extensive CM.

A. BASIS SETS

The construction of good SCF MOs depends at present on having a well-chosen basis set.[2] Finite linear combinations of basis functions can then be used to approximate MOs to the desired level of accuracy within the limits of present-day computer technology. The two most commonly used kinds of basis functions are STFs and GTFs. The molecular basis set is usually formed by centering STFs or GTFs at each of the constituent atomic nuclei and/or sometimes at other points in regions near the nuclei. STFs are defined [6], in spherical polar coordinates, by

$$\chi_{nl}^{S} = N_S r^{n-1} \exp(-\zeta_{nl} r) Y_{lm}(\theta, \phi), \tag{1}$$

where n, l, and m are principal, azimuthal, and magnetic quantum numbers, ζ_{nl} an "orbital exponent," $Y_{lm}(\theta, \phi)$ a spherical harmonic, and N a normalization factor such that

$$\langle \chi_{nl} | \chi_{nl} \rangle = \int_0^{\infty} \int_0^{\pi} \int_0^{2\pi} \chi_{nl}^{*} \chi_{nl} r^2 \sin\theta \, d\phi \, d\theta \, dr = 1. \tag{2}$$

In Eq. (1) r is expressed in units of a_0 (atomic units). See Section II.C for further discussion.

[1] Hartree objected to the term "configuration interaction" and proposed "superposition of configurations" instead. We feel that Roothaan's term "configuration mixing" meets Hartree's objection but has the advantage of being much briefer.

[2] We should also mention recent investigations into the use of numerical methods for use in molecular calculations, see e.g. Refs. 4 and 5.

GTFs can be expressed [7] either in spherical polar coordinates as

$$\chi_{nl}^{\mathrm{Gs}} = N_{\mathrm{Gs}} r^{2n} \exp(-\zeta_{nl} r^2) Y_{lm}(\theta, \phi), \tag{3}$$

or in Cartesian coordinates as

$$\chi_{ijk}^{\mathrm{Gc}} = N_{\mathrm{Gc}} x^i y^j z^k \exp[-\zeta_{ijk}(x^2+y^2+z^2)]. \tag{4}$$

In Eqs. (1)–(4) the variables (r, θ, ϕ) or (x, y, z) measure the displacement of an electron from the point of reference of the basis function. GLFs are special cases of Eq. (3) where only the $\exp(-\zeta r^2)$ portion is used and several are centered at various positions in space in order to approximate the usual s, p, d, etc., atomic functions [8a]. When used in molecular wave functions GTFs are usually "contracted" [8], each of several GTFs being constrained to have fixed ratios of their coefficients, with the same ratios in each MO. The effective size of the basis set is thereby reduced, ideally with little loss of accuracy.

Experience has shown that extended basis sets used in the accurate computation of molecular wave functions are usually best set up by first adopting optimum basis sets previously obtained for the respective atoms [9], and adding "polarization functions," which are either functions having higher azimuthal quantum numbers than the occupied orbitals of the atoms [10] or are functions centered in regions of space other than at the atoms [11], or both. Calculations on Rydberg states of molecules in states with one or more MOs that are larger than in the ground state require additional basis functions with larger radial extents. For additional discussion on basis sets and on STFs, reference should be made to Section II.B.

B. HAMILTONIAN MATRIX ELEMENTS

A requirement common to both SCF–MO and CM procedures is the evaluation of integrals or matrix elements of the basis functions with respect to the terms in the nonrelativistic Hamiltonian. (Up to now, nearly all calculations have been nonrelativistic.) For a molecule having A nuclei of charge Z_a and N electrons, the Hamiltonian, in atomic units (electronic mass m_e, electronic charge e, and $h/2\pi$ set to unity), is

$$\mathscr{H} = -\frac{1}{2}\sum_{\mu}^{N} \nabla_\mu^2 - \sum_{\mu}^{N}\sum_{k}^{A} \frac{Z_k}{r_{\mu k}} + \sum_{\mu<\nu}^{N} \frac{1}{r_{\mu\nu}} + \sum_{a<b}^{A} \frac{Z_a Z_b}{r_{ab}}, \tag{5}$$

where we have assumed that the nuclei are fixed in space. The terms in Eq. (5) correspond, respectively, to the kinetic ($\hat{T}$), nuclear attraction ($\hat{V}^{\mathrm{na}}$), electronic repulsion ($\hat{G}$), and nuclear repulsion ($\hat{V}^{\mathrm{nr}}$), operators. The molecular wave function satisfying the Schrödinger equation

$$\hat{\mathscr{H}}\Psi = E\Psi, \tag{6}$$

being an eigenfunction of $\hat{\mathscr{H}}$, yields the total energy of the molecule as its eigenvalue. Assuming that Ψ is normalized, we have

$$E = \langle\Psi|\hat{\mathscr{H}}|\Psi\rangle = \langle\Psi|\hat{T}|\Psi\rangle + \langle\Psi|\hat{V}^{\mathrm{na}}|\Psi\rangle + \langle\Psi|\hat{G}|\Psi\rangle + V^{\mathrm{nr}}. \quad (7)$$

(The nuclear repulsion energy is a function only of internuclear distances, which are assumed to be fixed.)

The initial step in the SCF–MO and CM methods is the computation of integrals with respect to the basis functions and the $\hat{T}$, $\hat{V}^{\mathrm{na}}$, and $\hat{G}$ operators. It is well known that, because of certain permutational symmetries, a basis set comprised of m functions leads to $(m^2+m)/2$ $\hat{T}$ and $\hat{V}$ ("one-electron") matrix elements and to $(m^4+2m^3+3m^2+2m)/8$ $\hat{G}$ ("two-electron") matrix elements. These quantities are defined as

$$T_{pq} = \langle\chi_p|\hat{T}|\chi_q\rangle, \quad (8)$$

$$V^{\mathrm{na}}_{pq} = \langle\chi_p|\hat{V}^{\mathrm{na}}|\chi_q\rangle, \quad (9)$$

$$G_{pqrs} = \langle\chi_p\chi_q|\hat{G}|\chi_r\chi_s\rangle, \quad (10)$$

where the subscripts p, q, r, and s label the basis functions χ, which may be centered at one or more nuclei or at various points in space. A third set of one-electron integrals needed for the analysis comprise the overlap matrix

$$S_{pq} = \langle\chi_p|\chi_q\rangle. \quad (11)$$

The matrix elements defined in Eqs. (8)–(11) are machine-computed[3] and stored for use in the subsequent SCF–MO and CM procedures.

C. THE HARTREE–FOCK–ROOTHAAN EQUATIONS

MO theory was catapulted into extensive quantitative use with the development of the matrix Hartree–Fock self-consistent field equations by Roothaan in 1951 [12]. If it is assumed that the state of each electron in a molecule may be represented by an MSO, the total wave function for an N-electron molecular state which contains only closed shells of MOs is constructed as an antisymmetrized product, or Slater determinant, of MSOs,

$$\Psi = \mathscr{A}(\psi_1 \quad \psi_2 \quad \cdots \quad \psi_N) = (N!)^{-1/2} \begin{vmatrix} \psi_1(1) & \psi_2(1) & \cdots & \psi_N(1) \\ \psi_1(2) & \psi_2(2) & \cdots & \psi_N(2) \\ & \vdots & & \vdots \\ \psi_1(N) & \psi_2(N) & \cdots & \psi_N(N) \end{vmatrix} \quad (12)$$

[3] Several efficient integral evaluation programs are available from the Quantum Chemistry Program Exchange, Indiana University.

If we now assume that each MO ϕ may be approximated as a linear combination of m basis functions χ_p (STFs or GTFs) and that there are $n = N/2$ doubly occupied MOs, then

$$\phi_i = \sum_p^m \chi_p c_{pi} \tag{13}$$

or in matrix notation

$$\boldsymbol{\phi} = \boldsymbol{\chi}\mathbf{c}, \tag{14}$$

where $\boldsymbol{\phi}$ is a column vector of dimension n, $\boldsymbol{\chi}$ a row vector of dimension m, and $\mathbf{c}$ a matrix of m rows and n columns. It is also required that the MOs be orthonormal,

$$\langle \phi_i | \phi_j \rangle = \delta_{ij}, \tag{15}$$

or

$$\boldsymbol{\phi}^\dagger \boldsymbol{\phi} = \mathbf{c}^\dagger \mathbf{S} \mathbf{c} = \mathbf{1}, \tag{16}$$

where $\mathbf{S}$ is the overlap matrix [Eq. (11)], δ_{ij} the Kronecker delta, $\mathbf{1}$ the unit matrix, and † denotes the adjoint operation.

The total energy with respect to the MOs ϕ_i is now [Eq. (7)]

$$E^{\mathrm{SCF}} = 2\sum_i^n h_i + \sum_{i,j}^n (2J_{ij} - K_{ij}), \tag{17}$$

where

$$h_i = \langle \phi_i | \hat{T} + \hat{V}^{\mathrm{na}} | \phi_i \rangle, \tag{18}$$

$$J_{ij} = \langle \phi_i(1)\,\phi_j(2) | \frac{1}{r_{12}} | \phi_i(1)\,\phi_j(2) \rangle, \tag{19}$$

$$K_{ij} = \langle \phi_i(1)\,\phi_j(2) | \frac{1}{r_{12}} | \phi_j(1)\,\phi_i(2) \rangle. \tag{20}$$

In Eqs. (19) and (20) the J_{ij} are designated as Coulomb and K_{ij} as exchange repulsion integrals relative to electrons 1 and 2.

To form the SCF equations the J_{ij} and K_{ij} are first rewritten in terms of the one-electron Coulomb ($\hat{J}_i$) and exchange ($\hat{K}_i$) operators:

$$\hat{J}_i(2)\,\phi_j(2) = \langle \phi_i(1) | \frac{1}{r_{12}} | \phi_i(1) \rangle\, \phi_j(2), \tag{21}$$

$$\hat{K}_i(2)\,\phi_j(2) = \langle \phi_i(1) | \frac{1}{r_{12}} | \phi_j(1) \rangle\, \phi_i(2). \tag{22}$$

The first-order variation of the total energy combined with the orthonormality constraint imposed through the Lagrangian multipliers ε_{ij} leads to the Hartree–Fock–Roothaan SCF equations [12]

$$(\mathbf{F} - \boldsymbol{\varepsilon}\mathbf{S})\,\mathbf{c} = 0, \tag{23}$$