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ELECTRONIC STRUCTURE OF MOLECULES

ABSTRACT

This paper, following a brief introduction, is divided into five parts. Part I outlines the theory of the molecular orbital method for the ground, ionized and excited states of molecules. Part II gives a brief summary of the interaction integrals and their tabulation. Part III outlines an automatic program designed for the computation of various states of molecules. Part IV gives examples of the study of ground, ionized and excited states of CO, BH and N_2 where the programs of automatic computation and molecular integrals have been utilized. Part V enlists some special problems of Molecular Quantum Mechanics which are being tackled at New York University.

Ψ total state function

Ψ_i single electron function

ϵ_i energy of the ith electron

υ_i the potential energy of the ith electron in the field of nuclei alone

$d\upsilon_j$ the integration over the entire space for the jth electron

$\sum\limits_{j}'$ summation over all values of $j = 1,2 \ldots n$ except $j = i$

$-\dfrac{\hbar^2}{m}\Delta_i$ the kinetic energy operator of the ith electron

M O   molecular orbitals

L C A O   linear combination of atomic orbitals

P   permutation operator

$\mathcal{H}$ the complete many electron Hamiltonian

H   bare nuclear field Hamiltonian operator

J   Coulomb operator

K   exchange operator

α electron   electron with α spin

β electron   electron with β spin

A,B   origins or centers of atoms a and b, respectively

a,b   atoms

C,C'   abbreviated notations for auxiliary functions C and C'

$C_{\alpha\beta}^{\gamma\delta\epsilon}$, $C_{\alpha\beta}'^{\gamma\delta\epsilon}$ auxiliary functions used in expressing overlap, Coulomb, and hybrid integrals

$D_{TV} = (-1)^V 2(2T+1)\left[\dfrac{(T-V)!}{(T+V)!}\right]^2$ where $V \geq 1$; $D_{TV} = 2T+1$ where $V = 0$

$G_T{}^V$, $W_T{}^V$ auxiliary functions for expressing exchange integrals

i   integer

K   defined by equation (49)

k   index of summation

ℓ,m   secondary quantum numbers

$N = n_a + n_a' + n_b + n_b'$

$N_a = n_a + n_a'$

$N_b = n_b + n_b'$

n, n' principal quantum numbers of atomic orbitals X and X' on center denoted by subscript

P_T^V, Q_T^V associated Legendre functions of Vth order and first and second kind, respectively

R internuclear distance, atomic units

r, θ, ϕ spherical polar coordinates of an electron with respect to origin denoted by subscript

r_{12} distance between electrons 1 and 2

$1s, 2s, 2p$ atomic orbitals

T integer assuming values 0, 1, 2, . . .

V order of Legendre polynomials

$v = (1 + \gamma)/(1 - \gamma)$

α, β orbital exponents of atomic orbitals on center A with $n = 1$ and 2, respectively

α, β orbital exponents of atomic orbitals on center B with $n = 1$ and 2, respectively

$\triangle$ Laplacian operator

μ, μ', μ'' orbital exponents or screening constants for X, X', and X'' atomic orbitals, respectively

$\bar{\mu} = 1/2 (\mu + \mu')$

ξ, η, ϕ elliptical coordinates of electron denoted by subscript

ξ_+, ξ_- larger and smaller of ξ_1 and ξ_2, respectively

ρ variable going from 0 to ∞

ρ', τ' variables used in expressing C'

τ variable going from 0 to 1

X, X', X'' different atomic orbitals on atom denoted by subscript

$X(i)$ atomic orbital for ith electron of atom denoted by subscript

$(\ )', (\ )''$ different orbitals on same center

X an atomic orbital

a_{ip}	undetermined coefficients, a's
$\underline{a}_i^\times$	Hermitian conjugate of the vector $\underline{a}_i$
$\underline{F}^\alpha$ and $\underline{F}^\beta$	matrices defined by equation (63)
$\underline{I}$	unit matrix
$^3\pi_g, ^3\pi_u, ^3\Sigma_u^+ \; ^3\Sigma_u^-$	excited states of N_2
$^2\Sigma_u^+ \quad ^2\Sigma_g^+$	ionized states of N_2
$v\sigma \quad \wedge\sigma \quad t\sigma \quad \sigma^\times$	molecular orbitals of σ symmetry for the ground state of CO molecule
$\pi_x, \; \pi_x^\times$	molecular orbitals of π symmetry
$\sigma_1 \; \sigma_2 \; \sigma_3, \; \sigma^\times$	molecular orbitals of σ symmetry of BH molecule
$\sigma_g 1s, \; \sigma_g 2s, \; \sigma_g 2p$	
$\sigma_u 1s, \; \sigma_u 2s, \; \sigma_u 2p$	symmetry orbitals of N_2 molecule
$\pi_u 2p, \; \pi_g 2p$	defined in Table 7
$\pi_u^\times 2p, \; \pi_g^\times 2p$	
LCAO SCF MO theory	abbreviation for "Linear combination of atomic orbital self-consistent field molecular orbital theory"

I. INTRODUCTION

Since molecules are built from two or more atoms, it is obvious that an understanding of the electronic states of molecules must be built upon a prior knowledge of the electronic states of atoms.

Just as each energy level of an atom corresponds to a certain electronic configuration, similarly molecular spectra are analysed into levels, each of which is analogous to an electronic level in an atom. With each electronic level is associated a group of neighbouring levels which are attributed to the quantized vibration of the molecule. Again each vibration level has associated with it a group of levels due to the quantized rotation of the molecule with the same electronic configuration and the same energy of vibration. Theory[1] shows that the electronic, vibrational, and rotational levels may, to a first approximation, be considered separately and their respective contributions to the energy are to this approximation additive, thus:

$$E = E_{elec} + E_{vib} + E_{rot}$$

Since the knowledge of electronic levels forms the basis for understanding of spectra and the structure of molecules, we shall, therefore, in this review discuss the electronic levels (states or wave functions) of molecules and will outline a procedure for their automatic computation on the electronic machine.

PART I.   MOLECULAR ORBITAL METHOD

THE ONE-ELECTRON APPROXIMATION.

The calculation of the electronic wave functions of atoms and molecules with more than two electrons, is based on the Hartree Model of the atom, which gives an approximate value of the total state function Ψ obtained by the product of n one-electron functions Ψ's. Thus

$$\Psi(x_1 y_1 z_1, \ldots x_n y_n z_n) = \Psi_1(x_1 y_1 z_1) \; \Psi_2(x_2 y_2 z_2) \ldots \Psi_n(x_n y_n z_n) \qquad (1)$$

Hartree[2] suggested on the basis of plausibility that each one-electron function Ψ in equation (1) should satisfy a one-electron Schrödinger equation, in which the potential includes a term that takes into account the coulomb field of the other electrons as well as the field arising from nuclei. He chose this term as the classical electrostatic potential of the n-1 normalised charge distributions $|\Psi_j|^2 e^2$.

Hence his equations for Ψ_1 are

$$\frac{-\hbar^2}{2m} \triangle_1 \Psi_1(r_1) + \left[v_i(r_1) + \sum_j' e^2 \int \frac{\Psi_j(r_2)^2}{r_{12}} \; dT_j \right] \Psi_1(r_1) = \epsilon_1 \Psi(r_1) \qquad (2)$$

where

r_1 denotes the space co-ordinates (x_1, y_1, z_1) of the ith electron,

ϵ_1 is the energy value of the ith electron,

v_i is the potential energy of the ith electron in the field of nuclei alone,

dT_j is the integration over the entire space for the jth electron,

$\sum_j'$ is the summation over all values of j = 1, 2...n except when j = i

and $\dfrac{-\hbar^2}{2m} \triangle_1$ is the kinetic energy operator of the ith electron.

Equations (2) have been further modified by Fock[3] so as to include exchange terms, and are now known as Hartree-Fock equations

$$-\frac{\hbar^2}{2m}\Delta \Psi_i(r_1) + \left[V(r_1) + \sum_j e^2 \int \frac{\Psi_j(r_2)^2}{r_{12}} d\tau_2'\right]\Psi_i(r_1)$$

$$-\sum_j \left[e^2 \int \frac{\Psi_j^*(r_2)\Psi_i(r_2)}{r_{12}} d\tau_2'\right]\Psi_j(r_1) = \sum_j \lambda_{ij}\Psi_j(r_1) \tag{3}$$

in which $\lambda_{ii} = \epsilon_i$

The general procedure for solving Hartree-Fock equations is one of trial and error. One assumes a set of Ψ's, solves the equations for the required ϵ's and Ψ's and compares the resulting Ψ's with the assumed ones. Guided by this comparison a new set of Ψ's is chosen and the procedure is repeated. This process is then continued until the assumed and calculated Ψ's agree. This iterative method of solving equations (3) is called the Hartree-Fock self-consistent field method.

For atoms, the problem of solving Hartree-Fock equations is greatly simplified by the central symmetry. For molecules because of the absence of central symmetry the numerical solution of these equations is a very difficult problem. This difficulty is overcome by using the molecular orbital approximation, described in the next section.

MOLECULAR ORBITAL METHOD

The molecular orbital method is essentially an extension of the Bohr theory of electron configurations from atoms to molecules. Each electron is assigned to a one-electron wave function, or molecular orbital, which is the quantum mechanical analogue of an electron orbit. Molecular orbitals (MO) are generally built up as linear combinations of atomic orbitals (LCAO).

The molecular orbital theory, based on a single-determinantal wave function for the ground state of molecules having doubly occupied orbitals, has been applied to molecules, on the lines similar to Hartree-Fock treatment for atoms, by a number of workers [4,5,6]. Lennard-Jones[7] has also considered a determinantal wave function in which molecular orbitals

Ψ_1, Ψ_2 ... Ψ_p are associated with two electrons of opposite (α and β) spins and Ψ_{p+1}, Ψ_{p+2} ... Ψ_{n+q} with only one electron (of α or β spin). Such a wave function can be written

$$\Psi = \left[(2p+q)!\right]^{-\frac{1}{2}} \sum_p (-1)^p P\left[\Psi_1(1)\alpha(1)\cdots\Psi_p(2p)\beta(2p)\Psi_{p+1}(2p+1)\alpha(2p+1)\right.$$
$$\left.\cdots \Psi_{p+q}(2p+q)\beta(2p+q)\right] \quad (4)$$

where P runs over the (2p+q)! permutations of the (2n+q) variables and $(-1)^p$ is the parity of the pth permutation. Considering all the functions as orthogonal, he has also deduced a set of differential equations for their optimum forms. These equations for the paired spins can be written

$$(H + J - K)\ \Psi_n = \sum_m \varepsilon_{i,m}\Psi_m \quad (5)$$

where H, J and K are the bare-nuclear field Hamiltonian operator, Coulomb operator and Exchange operator respectively. E_{mn} is defined by

$$E_{m,n} = \int \overline{\Psi}_m (H + J - K)\ \Psi_n\ dT \quad (6)$$

and the Coulomb operator J_i and the Exchange operator K_i are defined by

$$J_i(1)\Psi(1) = \left(\int \overline{\Psi}_i(2)\ \frac{1}{r_{12}}\ \Psi_i(2)dT_2\right)\Psi(1)$$

and

$$K_i(1)\Psi(1) = \left(\int \overline{\Psi}_i(2)\ \frac{1}{r_{12}}\ \Psi(2)dT_2\right)\Psi_i(1) \quad (7)$$

so that they can be expressed as one-electron integrals involving the operators J_i and K_i.

Equations (5) do not define the orbitals uniquely so that the motion of the electrons can be described with equal accuracy using several types of orbitals. One possible type is the molecular orbital description which is defined by the condition that

$$E_{m,n} = 0, \qquad m \neq n \quad (8)$$

From this definition it can be proved that each molecular orbital belongs to one or other of the irreducible representations of the symmetry group of the molecule. This means that they cannot be localized in a certain part of the molecule, but are spread throughout it.

SINGLE DETERMINANT WAVE FUNCTION

The wave function (4) is not the most general form of a single deter-
minant wave function. If the number of α electrons (N_α) is not equal to
the number of β electrons (N_β), it can be shown[8,9] that there is no
a priori reason why any of the orbitals containing α electrons should be
identical with any of the rest. In the most general form we may introduce
$N_\alpha + N_\beta$ molecular orbitals, all of which may be varied independently in
the Ritz variational process. This wave function can be written as

$$\Psi = \left[(N_\alpha + N_\beta)! \right]^{-\frac{1}{2}} \sum_P (-1)^P P \left[\psi_1(1)\,\alpha(1)\,\psi_2(2)\,\alpha(2)\cdots \psi_{N_\alpha}(N_\alpha)\,\alpha(N_\alpha) \right.$$

$$\left. \cdots\cdots \psi_{N_\alpha+N_\beta}(N_\alpha+N_\beta)\,\beta(N_\alpha+N_\beta) \right] \quad (9)$$

In addition to being more general than (4), the wave equation (9) has
the additional advantage of simplifying the variational problem. By carry-
ing out linear transofrmation within the determinant, we may take the α
orbitals to be an orthogonal set; the same applies to the β orbitals.
However, there is no need for any of the α orbitals to be orthogonal to any
of the β orbitals, since the complete one-electron functions are orthogonal
on account of spin.

The total electronic energy for such a wave function is given by the
formula

$$E = \int \bar{\Psi}\, H\, \Psi\, dT \quad (10)$$

where H, the complete many electron Hamiltonian is

$$H = \sum_i H_i + \sum_{i>j} \frac{1}{r_{ij}} \quad (11)$$

H_i is the Hamiltonian operator for the ith electron in the field of the
nuclei alone.

For the wave function of equation (9) we have, therefore,

$$E = \left[(N_\alpha + N_\beta)!\right]^{-1} \int \sum_P (-1)^P P\left[\psi_1(1)\,\alpha(1)\cdots\right] H \sum_{P'} (-1)^{P'} P'\left[\psi_1(1)\,\alpha(1)\cdots\right] d\tau \quad 6$$

$$= \int \left[\psi_1(1)\,\alpha(1)\cdots\right] H \sum_{P'} (-1)^{P'} P'\left[\psi_1(1)\,\alpha(1)\cdots\right] d\tau$$

<div align="right">(12)</div>

where H is totally symmetrical in all its variables. Most of the permutations in (12) lead to vanishing terms on account of orthogonality. The only ones that do not vanish are the identical permutation and all single permutations of the same spin. These lead to the following expression for the energy E

$$E = \sum_i^{\alpha+\beta} H_i + \frac{1}{2} \sum_i^{\alpha+\beta} \sum_j^{\alpha+\beta} J_{ij} - \frac{1}{2}\left(\sum_i^{\alpha} \sum_j^{\beta}\right) K_{ij} \quad (13)$$

Here $\sum_i^{\alpha}$ and $\sum_i^{\beta}$ indicate summation over suffixes corresponding to molecular orbitals ψ_i that are occupied by α and β electrons respectively. $\sum_i^{\alpha+\beta}$ is used for summation over all orbitals.

If we are dealing with a close shell ground state in which the two sets of orbitals are identical, the energy expression (13) reduces to the usual form

$$E = 2\sum_i H_i + \sum_{i,j}(2J_{ij} - K_{ij}) \quad (14)$$

LCAO SELF-CONSISTENT FIELD ORBITALS

In the LCAO MO method all the electrons of the molecule are represented by linear combinations of atomic orbitals.

$$\psi_i = \sum_p a_{ip} \chi_p \quad (15)$$

where i specifies the MO's, ψ,

p specifies the atomic orbitals, χ,

and a_{ip} specifies the undetermined coefficients, a's.

Equation (15) can be written in the matrix notation as

$$\psi_i = \underline{a_i}\,\underline{\chi} \quad (16)$$

The condition that the MO's be orthogonal then reduces to

$$\int \psi_i \psi_j \, dT = \underline{a}_i^* \underline{S} \, a_j = \delta_{ij} \tag{17}$$

where the elements of the overlap matrix $\underline{S}$ are defined by

$$S_{pq} = \overline{S}_{qp} = \int \overline{\chi}_p \chi_q \, dT \tag{18}$$

and $\underline{a}_1^*$ is the Hermitian conjugate of the vector $\underline{a}_1$.

If we write the terms in the energy expression of equation (13) in the matrix form

$$H_1 = \underline{a}_1^* \, \underline{H} \, \underline{a}_1,$$

$$J_{ij} = \underline{a}_i^* \, \underline{J}_j \, \underline{a}_i = \underline{a}_j^* \, \underline{J}_i \, \underline{a}_j,$$

$$K_{ij} = \underline{a}_i^* \, \underline{K}_j \, \underline{a}_i = \underline{a}_j^* \, \underline{K}_i \, \underline{a}_j, \tag{19}$$

and vary the coefficients $\underline{a}_1$ by an amount $\delta \underline{a}_1$, the resulting variation in E is found to be

$$\delta E = \sum_i^{\alpha+\beta} \delta a_i^* \, H a_i + \sum_i^{\alpha+\beta} \sum_j^{\alpha+\beta} \delta a_i^* \, J_j a_i - \left(\sum_i^{\alpha} \sum_j^{\alpha} + \sum_i^{\beta} \sum_j^{\beta} \right) \delta a_i^* K a_j + \text{Complex Conjugate}$$

$$= \sum_i^{\alpha+\beta} \delta \underline{a}_i^* (H + J) a_i - \sum_i^{\alpha} \delta \underline{a}_i^* K \underline{a}_i - \sum_i^{\beta} \delta a_i^* K \, \underline{a}_i + \text{Complex Conjugate} \tag{20}$$

Where $\underline{J}, \underline{K}^{\alpha}, \underline{K}^{\beta}$, the total coulomb and exchange matrices are defined as

$$\underline{J} = \sum_i^{\alpha+\beta} \underline{J}_i$$

$$\underline{K}^{\alpha} = \sum_i^{\alpha} \underline{K}_i \; ; \; \underline{K}^{\beta} = \sum_i^{\beta} \underline{K}_i \tag{21}$$

$\delta \underline{a}_1$ is subject to the orthonormality restriction (17)

$$\delta a_i^* \underline{S} \, a_j + a_i^* \underline{S} \delta a_j = 0 \qquad \text{(i, j in same set)} \tag{22}$$

Multiplying equation (22) by Lagrangian multipliers $-\epsilon_{ji}$ and adding to equation (20) we obtain the minimization condition

$$\sum_i^{\alpha} \delta a_i^* (H + J - K^{\alpha}) \underline{a}_i - \sum_j^{\alpha} \underline{S} \, \underline{a}_j \epsilon_{ji}) + \sum_i^{\beta} \delta a_i^* ((H + J - K^{\beta}) \underline{a}_i - \sum_j^{\beta} \underline{S} \underline{a}_j \epsilon_{ji})$$

$$+ \text{complex conjugate} = 0 \tag{23}$$

From (23) we conclude that the coefficients $\underline{a}_i$ must satisfy

either $\qquad (\underline{H} + \underline{J} - \overset{\alpha}{\underline{K}})\underline{a}_i = \overset{\alpha}{\underset{j}{\sum}} \underline{S} \, \underline{a}_j \, \epsilon_{ji}$ $\hfill$ (24)

or $\qquad (\underline{H} + \underline{J} - \overset{\beta}{\underline{K}})\underline{a}_i = \overset{\beta}{\underset{j}{\sum}} \underline{S} \, \underline{a}_j \, \epsilon_{ji}$ $\hfill$ (25)

according as Ψ_i' be associated with α or β electrons. We can further

diagonalise the matrices ϵ_{ji} by the orthonormal transofrmation of the

orbitals reducing equations (24) and (25) respectively to

$$(\underline{H} + \underline{J} - \overset{\alpha}{\underline{K}}) \, \overset{\alpha}{\underline{a}_i} = \overset{\alpha}{\epsilon_i} \underline{S} \, \overset{\alpha}{\underline{a}_i} \qquad (26)$$

and $\qquad (\underline{H} + \underline{J} - \overset{\beta}{\underline{K}}) \, \overset{\beta}{\underline{a}_i} = \overset{\beta}{\epsilon_i} \underline{S} \, \overset{\beta}{\underline{a}_i}$ $\hfill$ (27)

The elements of the matrices $\underline{H}$, $\underline{J}$ and $\underline{K}^{\alpha \, or \, \beta}$ are defined by

$$H_{pq} = \int \overline{\chi}_p \, H \, \chi_q \, dT$$

$$J_{pq} = \underset{\tau \upsilon}{\sum} \left(\overset{\alpha}{\underset{i}{\sum}} \overline{a}_{\tau i} a_{\upsilon i} + \overset{\beta}{\underset{i}{\sum}} \overline{a}_{\tau i} a_{\upsilon i} \right) \iint \overline{\chi}_p{}^{(1)} \overline{\chi}_\tau{}^{(2)} \frac{1}{r_{12}} \chi_q{}^{(1)} \chi_\upsilon{}^{(2)} dT_1 dT_2 \qquad (28a)$$

and $\underset{pq}{\overset{\alpha \, or \, \beta}{K}} = \underset{\tau \upsilon}{\sum} \left(\overset{\alpha \, or \, \beta}{\underset{i}{\sum}} \overline{a}_{\tau i} a_{\upsilon i} \right) \iint \overline{\chi}_p{}^{(1)} \overline{\chi}_\tau{}^{(2)} \frac{1}{r_{12}} \chi_q{}^{(2)} \chi_\upsilon{}^{(1)} dT_1 dT_2$ $\hfill$ (28b)

Though equations (26) and (27) describe two straightforward eigen-value

problems, the calculation of the elements of matrix J, which is common to

both, involves the $\underline{a}_i$ coefficients which are assumed for the first cycle

but for the subsequent cycles they have to be obtained from the solution of

both the eigen-value problems. The equations are, therefore, best solved

by a cyclic process:

1.   to begin with, values of $\underline{a}_i$ are assumed consistent with the

orthonormality condition of equation (17),

2.   these $\underline{a}_i$ are used to calculate the matrices $\underline{J}$, $\underline{K}^{\alpha}$ and $\underline{K}^{\beta}$,

3.   the determinants (equation 29) of secular equations (26) and (27) are

solved for n lowest roots ϵ_i and for their coefficients $\overset{\alpha}{\underline{a}_i}$ and $\overset{\beta}{\underline{a}_i}$,

$$|F^{\alpha} - \epsilon S| = 0 \; ; \qquad |F^{\beta} - \epsilon S| = 0 \; ; \qquad (29)$$

$\underline{F}^{\alpha}$ and $\underline{F}^{\beta}$ are defined by

$$\underline{F}^{\alpha} = \underline{H} + \underline{J} - \underline{K}^{\alpha}$$

and $\quad \underline{F}^{\beta} = \underline{H} + \underline{J} - \underline{K}^{\beta} \qquad (30)$

4. the new coefficients $\underline{a}_i^{\alpha}$ and $\underline{a}_i^{\beta}$, thus obtained, are used to calculate matrices $\underline{J}$, $\underline{K}^{\alpha}$, $\underline{K}^{\beta}$ and the process is repeated till self-consistency is attained; that is, the coefficients $\underline{a}_i^{\alpha}$ and $\underline{a}_i^{\beta}$ obtained from the nth cycle are in agreement with those obtained from the $(n-1)^{th}$ cycle, within predetermined limits.

After the self-consistency is obtained, the eigenvectors $\underline{a}_i$ of the secular equations give the LCAO MO's and the eigen-values ϵ_i the vertical ionization potentials.

We shall describe in the following section the computation of atomic and molecular integrals required in the calculation of $\underline{S}$, $\underline{H}$, $\underline{J}$ and $\underline{K}$ matrices.

PART II. ATOMIC AND MOLECULAR INTEGRALS

TABLES OF MOLECULAR INTEGRALS

A variety of physical properties of molecules such as energies, polarize-
bilities, susceptibilities, and transition moments can be calculated by use
of quantum mechanics from the knowledge of molecular wave functions. The
calculation of these functions by any of the standard methods, such as valence
bond or molecular orbital, involves the calculation of molecular integrals
which is extremely tedious and requires considerable mathematical understand-
ing. Until recently only approximate methods were used to evaluate these
integrals; however, progress has been made in the past few years in the
evaluation of the basic integrals. Numerical values of some of these integrals
have been tabulated by some investigators;$^{(10)---(13)}$ however, the available values
are not sufficient to provide all the integrals required in the calculation
of molecular wave functions.

It has therefore been considered worth-while to study a number of these
integrals and tabulate their values. In carrying out these computations a
number of factors were considered and material tabulated for:

(1) Integrals which contain all the interaction integrals arising in the
calculation of the properties of diatomic molecules containing electrons of
1s, 2s, and 2p atomic orbitals.

(2) Integrals or their auxiliary functions as functions of one or two
variables over wide ranges of internuclear distance.

(3) Integrals which are functions of more than two variables which have
been expressed as a linear combination of auxiliary functions of two variables
ρ and τ. The values of τ may range from 0 to 1, and all the required
values at suitable intervals are tabulated, while the values of ρ may range
from 0 to ∞. The upper limit of the values of ρ is chosen to have integrals
for values of the internuclear distance even beyond the dissociation distance.

Tables which contain one-center one-electron and two-center two-electron

integrals have been prepared automatically on an electronic computer. The monocenter integrals involving 1s, 2s, and 2p atomic orbitals are special cases of two-center integrals for $\rho = 0$ and can also be obtained from these tables.

The tables of integrals[*] are divided into four parts and will appear in six volumes.

Volume 1 (designated as Part I) contains two-center two-electron and monocenter one-electron-integrals.

Volume 2 (designated as Part II) contains two-center two-electron and monocenter two-electron Coulomb integrals.

Volumes 3, 4 and 5 (designated as Parts III (a), III (b) and III (c) contain $C_{\alpha\beta}^{\gamma\delta\epsilon}(\rho,\tau)$, $C_{-\alpha\beta}^{\gamma\delta\epsilon}(\rho,\tau)$ and $C_{-\alpha\beta}^{\gamma\delta\epsilon}(\rho,-\tau)$ auxilliary functions of the hybrid integrals.

Volume 6 (designated as Part IV) contains exchange integrals and the auxilliary functions, W and G, required for the computation of some exchange integrals.

CHOICE OF ATOMIC ORBITALS

For the Computation of the different types of integrals given below, Slater-type atomic orbitals (AO's) were used for the computations. For quantum numbers n=1 and 2 the normalized Slater AO's are

$$1s = \left(\frac{\mu^3}{\pi}\right)^{\frac{1}{2}} e^{-\mu r}$$

$$2s = \left(\frac{\mu^5}{3\pi}\right)^{\frac{1}{2}} r\, e^{-\mu r}$$

$$\left.\begin{array}{c} 2p_z \\ 2p_x \\ 2p_y \end{array}\right\} = \left(\frac{\mu^5}{\pi}\right)^{\frac{1}{2}} r\, e^{-\mu r} \times \left\{\begin{array}{l} \cos\theta \\ \sin\theta\cos\varphi \\ \sin\theta\sin\varphi \end{array}\right. \tag{31}$$

where the effective charge μ is arbitrary.

TYPES OF INTEGRALS

The following types of integrals or their auxiliary functions are tabulated in Parts 1, II, III And IV. The notations χ_a, χ_a', χ_a'' are used for the various atomic orbitals on atom a and, similarly, the notations χ_ℓ, χ_ℓ', χ_ℓ'' are used for the various atomic orbitals on atom b.

Overlap integrals:

$$\int \chi_a(1)\, \chi_\ell(1)\, dv_1 \tag{32}$$

Nuclear-attraction integrals

$$\int \chi_a(1)\, \frac{1}{r_\ell}\, \chi_a'(1)\, dv_1 \tag{33}$$

$$\int \chi_\ell(1)\, \frac{1}{r_a}\, \chi_\ell'(1)\, dv_1$$

Potential-energy integrals:

$$\int \chi_a(1)\, \frac{1}{r_a}\, \chi_\ell(1)\, dv_1 \tag{34}$$

$$\int \chi_a(1)\, \frac{1}{r_\ell}\, \chi_\ell(1)\, dv_1$$

Kinetic-energy integrals:

$$-\frac{1}{2} \int \chi_a(1)\, \Delta\, \chi_\ell(1)\, dv_1 \tag{35}$$

Coulomb integrals:

$$\iint \chi_a(1)\, \chi_a'(1)\, \frac{1}{r_{12}}\, \chi_\ell(2)\, \chi_\ell'(2)\, dv_1\, dv_2 \tag{36}$$

Hybrid integrals:

$$\iint \chi_a(1)\, \chi_a'(1)\, \frac{1}{r_{12}}\, \chi_a''(2)\, \chi_\ell(2)\, dv_1\, dv_2 \tag{37}$$

Exchange integrals:

$$\iint \chi_a(1)\, \chi_\ell(1)\, \frac{1}{r_{12}}\, \chi_a'(2)\, \chi_\ell'(2)\, dv_1\, dv_2 \tag{38}$$

Tables of Molecular Integrals (Part 1)

TWO-CENTER ONE-ELECTRON NUCLEAR-ATTRACTION, OVERLAP,

AND POTENTIAL- AND KINETIC-ENERGY INTEGRALS[*]

The tables in Part I deal with the two-center one-electron and monocenter one-electron integrals and are presented in two parts. The first part, table 1(a), contains nuclear-attraction integrals and the second part, table 1(b), contains all the functions necessary for two-center one-electron overlap and potential- and kinetic-energy integrals.

NUCLEAR-ATTRACTION INTEGRALS

The nuclear-attraction integrals are

$$\left(\chi_a \left| \frac{1}{r_b} \right| \chi_a' \right) = \int \chi_a(1) \frac{1}{r_b} \chi_a'(1) \, dv_1 \tag{39}$$

$$\left(\chi_b \left| \frac{1}{r_a} \right| \chi_b' \right) = \int \chi_b(1) \frac{1}{r_a} \chi_b'(1) \, dv_1$$

These integrals can be expressed in the form

$$\frac{\mu^{n+\frac{1}{2}} \mu'^{n'+\frac{1}{2}}}{\bar{\mu}^{n+n'}} \cdot f(\rho) \tag{40}$$

where $\bar{\mu} = \frac{1}{2}(\mu + \mu')$. The function $f(\rho)$ is a function of the single parameter.

$$\rho = R\bar{\mu} \tag{41}$$

and is given for each atomic-orbital pair in table 1(a) for values of ρ from 0 to 14.95 in 0.05 steps.

For sufficiently high values of ρ, the numerical entries are given by the following expressions:

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[*] An expanded version of the information presented in this section is included in "Part 1 - Tables for Two-Center One-Electron Nuclear-Attraction, Overlap, and Potential- and Kinetic-Energy Integrals."

$$(1s_a \mid \tfrac{1}{r_a} \mid 1s_e) \approx \tfrac{1}{\rho} \qquad\qquad (2s_e \mid \tfrac{1}{r_a} \mid 2p_{z_e}) \approx \frac{5}{2\sqrt{3}\,\rho^2}$$

$$(1s_e \mid \tfrac{1}{r_a} \mid 2s_e) \approx \tfrac{13}{2\rho} \qquad\qquad (2p_z \mid \tfrac{1}{r_a} \mid 2p_{z_e}) = \tfrac{1}{\rho} + \tfrac{3}{\rho^3} \qquad (42)$$

$$(1s_e \mid \tfrac{1}{r_a} \mid 2p_{z_e}) = \tfrac{1}{\rho^2}$$

$$(2s_e \mid \tfrac{1}{r_a} \mid 2s_e) \approx \tfrac{1}{\rho} \qquad\qquad (2p_{x_e} \mid \tfrac{1}{r_a} \mid 2p_{x_e}) = \tfrac{1}{\rho} - \tfrac{3}{2\rho^3}$$

In every case, formulas (42) yield better than 7-digit accuracy for values
of ρ beyond the range of the tables.

OVERLAP and POTENTIAL- and KINETIC-ENERGY INTEGRALS

The numerical values for overlap integrals

$$(\chi_a \mid \chi_e) = \int \chi_a(1)\, \chi_e(1)\, dv_1 \qquad (43)$$

are contained in table 1(b) along with some additional functions necessary for
two-center one-electron potential-energy integrals

$$(\chi_a \mid \tfrac{1}{r_a} \mid \chi_e) = \int \chi_a(1)\, \tfrac{1}{r_a}\, \chi_e(1)\, dv_1$$

$$(\chi_a \mid \tfrac{1}{r_e} \mid \chi_e) = \int \chi_a(1)\, \tfrac{1}{r_e}\, \chi_e(1)\, dv_1 \qquad (44)$$

and kinetic-energy integrals

$$(\chi_a \mid -\tfrac{1}{2}\Delta \mid \chi_e) = -\tfrac{1}{2} \int \chi_a(1)\, \Delta\, \chi_e(1)\, dv_1 \qquad (45)$$

These additional functions are the overlap integrals of the fictitious
orbitals given by the following equations:

$$0s = \left(\tfrac{\mu}{\pi}\right)^{\tfrac{1}{2}} r^{-1}\, e^{-\mu r}$$

$$\left. \begin{array}{c} 1p_z \\ 1p_x \\ 1p_y \end{array} \right\} = \left(\tfrac{\mu^3}{\pi}\right)^{\tfrac{1}{2}} e^{-\mu r} \left\{ \begin{array}{l} \cos\theta \\ \sin\theta\cos\varphi \\ \sin\theta\sin\varphi \end{array} \right. \qquad (46)$$

The 0s and 1p orbitals used here are actually $\sqrt{2}$ and $1/\sqrt{3}$, respectively,
times those given by Slater's general formula.

All the overlap integrals including those of the fictitious orbitals are given in table 1(b) as functions of two parameters.

$$\rho = \frac{R}{2} \left(\mu_a + \mu_b \right)$$

$$\tau' = \frac{\mu_a - \mu_b}{\mu_a + \mu_b} \tag{47}$$

The ranges and intervals of the overlap integrals are such that all integrals can be obtained for

$$\tau' = 0.0(p.02)0.94^*$$

and for

$\rho = 0.0(0.1)50.0(0.2)60.0(0.4)79.6$ if $n_a = n_b = 1$

$\rho = 0.0(0.1)30.0(0.2)40.0(0.4)59.6$ if $n_a = 1, n_b = 2$ or $n_a = 2, n_b = 1$

$\rho = 0.0(0.1)20.0(0.2)30.0(0.4)49.6$ if $n_a = n_b = 2$

The numerical values of these overlap integrals are given in the form of 7-digit mantissas (between -1 and 1) followed by an exponent giving the power of 10 by which the mantissas are to be multiplied.

For example, the value of $(1s|1s)$ for $\rho = 25.0$ and $\tau = 0.70$ is given in the table as

$$3.434471,-4$$

(see sample page bound). This value is to be interpreted as

$$3.434471 \times 10^{-4}$$

The overlap integrals $(\chi|\chi)$ listed in the tables are defined so that the first atomic orbital in the parentheses is on atom a and the second is on atom b. Only positive values of τ are listed so that if an integral with a negative value of τ' is needed one must interchange the a and b orbital functions and then obtain the value from the appropriate table; that is, for $(0s|1s)$ for $\tau = -0.8$ one should use $(1s|0s)$ for $\tau' = 0.8$.

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* This notation indicates "values of from 0.0 to 0.94 in 0.02 steps." Likewise the notation for ρ indicates "values of ρ from 0.0 to 50.0 in 0.1 steps, values from 50.0 to 60.0 in 0.2 steps, and values from 60.0 to 79.6 in 0.4 steps," and so forth.

Tables of Molecular Integrals (Part II)

TWO-CENTER TWO-ELECTRON COULOMB INTEGRALS[*]

The general expression for two-center two-electron Coulomb integrals is given by

$$\iint \chi_a(1)\, \chi_a'(1)\, \frac{1}{r_{12}}\, \chi_b(2)\, \chi_b'(2)\, dv_1\, dv_2 \tag{48}$$

where X_a, X_a' and X_b, X_b' are atomic orbitals on centers A and B, respectively, and where 1 and 2 refer to coordinates of electrons 1 and 2.

The Coulomb integrals are obviously functions of five parameters, namely, the four orbital exponents μ_a, μ_a', μ_b, and μ_b' and the internuclear distance R. However, a product of two atomic orbitals on the same center is equal to a radial function times the product of two spherical harmonics. The exponent $\bar{\mu}$ of the radial function is the average orbital exponent of the two constituting atomic orbitals. It is thus clear that these Coulomb integrals can be expressed as a function of three variables

$\bar{\mu}_a = 1/2\,(\mu_a + \mu_a')$, $\bar{\mu}_b = 1/2(\mu_b + \mu_b')$ and R. Replacing these parameters by

$$\rho = \frac{R}{2}\,(\bar{\mu}_a + \bar{\mu}_b)$$

$$\tau = \frac{\bar{\mu}_a - \bar{\mu}_b}{\bar{\mu}_a + \bar{\mu}_b}$$

these integrals can be represented as functions of ρ and τ. The complete integral (11) is then

$$\iint \chi_a(1)\, \chi_a'(1)\, \frac{1}{r_{12}}\, \chi_b(2)\, \chi_b'(2)\, dv_1\, dv_2 = K f(\rho\tau)$$

where

$$K = \frac{\mu_a^{n_a+\frac{1}{2}}\ \mu_a'^{n_a'+\frac{1}{2}}\ \mu_b^{n_b+\frac{1}{2}}\ \mu_b'^{n_b'+\frac{1}{2}}}{\bar{\mu}_a^{n_a+n_a'+1}\ \bar{\mu}_b^{n_b+n_b'+1}} \cdot \frac{\bar{\mu}_a + \bar{\mu}_b}{2} \tag{49}$$

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[*] An expanded version of the information contained in this section is included in Supplement 11 - Tables for Two-Center Two-Electron Coulomb Integrals.

For a given set of orbitals, $f(\rho, \tau')$ is listed in the tables in Supplement 11 headed by the four orbital functions χ_a, χ_a', χ_b, χ_b'.

The principal quantum numbers of the four orbitals are n_a, n_a', n_b, and n_b' where $n = 1$ for 1s and $n = 2$ for 2s and 2 p.

The range and spacing of ρ depend upon the value of $N = n_a + n_a' + n_b + n_b'$. They are as follows in the same notation as that used previously:

$$N = 4: \quad p = 0(0.1)50(0.2)60(0.4)79.6$$

$$N = 5: \quad p = 0(0.1)40(0.2)50(0.4)69.6$$

$$N = 6: \quad p = 0(0.1)30(0.2)40(0.4)59.6$$

$$N = 7: \quad p = 0(0.1)\ 25(0.2)35(0.4)54.6$$

$$N = 8: \quad p = 0(0.1)20(0.2)30(0.4)49.6$$

The range and spacing of τ' depend upon $N_a = n_a + n_a'$ and $N_b = n_b + n_b'$ as follows:

$$N_a \leq N_b \qquad \tau' = 0(0.02)0.94$$

$$N_a = N_b + 1 \qquad \tau' = 0(0.02)0.78$$

$$N_a = N_b + 2 \qquad \tau' = 0(0.2)0.62$$

Some integrals for the orbitals involving p_x and p_y are not listed since these can be obtained by using the relation

$$\left(\chi_a \chi_a' \mid 2p_{x_\ell} 2p_{x_\ell}' \right) = \tfrac{1}{2}\left[3\left(\chi_a \chi_a' \mid 2\sigma_\ell 2\sigma_\ell' \right) - \left(\chi_a \chi_a' \mid 2p_{z_\ell} 2p_{z_\ell}' \right) \right] \tag{50}$$

which holds except when $x_a x_a'$ involve p_x or p_y orbitals. In the latter case

$$\left(2p_x 2p_x' \mid 2p_x 2p_x' \right) = \tfrac{1}{4}\left[\left(2\sigma 2\sigma' \mid 2\sigma 2\sigma' \right) - 3\left(2\sigma 2\sigma' \mid 2p_z 2p_z' \right) \right.$$
$$\left. - 3\left(2p_z 2p_z' \mid 2\sigma 2\sigma' \right) + \left(2p_z 2p_z' \mid 2p_z 2p_z' \right) \right] \tag{51}$$
$$+ \left(2p_x 2p_y' \mid 2p_x 2p_y' \right)$$

and

$$\left(2p_y 2p_y' \mid 2p_x 2p_x' \right) = \tfrac{1}{4}\left[9\left(2\sigma 2\sigma' \mid 2\sigma 2\sigma' \right) - 3\left(2\sigma 2\sigma' \mid 2p_z 2p_z' \right) \right.$$
$$\left. - 3\left(2p_z 2p_z' \mid 2\sigma 2\sigma' \right) + 2p_z 2p_z' \mid 2p_z 2p_z' \right) \right] \tag{52}$$
$$- \left(2p_x 2p_y' \mid 2p_x 2p_y' \right)$$

Table of Molecular Integrals (part III (a), Part III (b), and
Part III (c)

TWO- CENTER TWO-ELECTRON HYBRID INTEGRALS[*]

The general expression for two-center two-electron hybrid integrals is given by

$$\iint \chi_a(1) \; \chi_a{}'(1) \; \frac{1}{r_{12}} \; \chi_a{}''(2) \; \chi_b(2) \; dv_1 \, dv_2 \tag{53}$$

where χ_a, $\chi_a{}'$, $\chi_a{}''$ and χ_b are AO's on centers A and B, respectively, and
when 1 and 2 refer to coordinates of electrons 1 and 2.

For the hybrid integrals, electron 1 belongs wholly to atom a while
electron 2 is exchanged between atoms a and b. The same method as that
for the Coulomb integrals can be applied, that is, integration over the
coordinates of the second electron in the potential field of the first. This
gives a finite series of the overlap integrals discussed earlier when the
potential due to electron 1 is spherically symmetrical, that is, due to
(1s) (1s), (1s) (2s), or (2s) (2s). For the electron 1 with 2p AO's the
same treatment as for the Coulomb integrals can be carried out.

Unlike Coulomb integrals these hybrid integrals are not generally functions
of two variables. They can, however, be expressed as a linear combination of
auxiliary functions C and C'[(14)]. These functions are functions of two
variables. For the C function these variables are

$$\rho = (\mu_a + \mu_a{}' + \mu_a{}'' + \mu_b) R/2$$

$$\tau = \frac{\mu_a + \mu_a{}' + \mu_a{}'' - \mu_b}{\mu_a + \mu_a{}' + \mu_a{}'' + \mu_b} \tag{54}$$

and C' is a function of the two variables

$$\rho' = (\mu_a{}'' + \mu_b) R/2$$

$$\tau' = \frac{\mu_a{}'' - \mu_b}{\mu_a{}'' + \mu_b} \tag{55}$$

The C and C are tabulated as functions of two variables for intervals and ranges such that all hybris integrals between 1s, 2s, and 2p orbitals can be obtained from the tables of supplement III.

Tables of Molecular Integrals (Part IV)
TWO— CENTER TWO—ELECTRON EXCHANGE INTEGRALS

In the two-center two-electron exchange integrals each of the electrons is exchanged between two atoms. They are represented by the formula:

$$\iint \chi_a(1)\, \chi_b(1)\, \frac{1}{r_{12}}\, \chi'_a(2)\, \chi'_b(2)\, dv_1\, dv_2 \qquad \cdots (56)$$

These integrals can be evaluated by using the elliptical coordinates and expanding $\frac{1}{r_{12}}$ in the Neumann series

$$\frac{1}{r_{12}} = \frac{2}{R} \sum_{T=0}^{\infty} \sum_{V=0}^{T} D_{TV} \left[Q_T^V(\xi_+)\, P_T^V(\xi_-)\, P_T^V(\eta_1)\, P_T^V(\eta_2)\, \cos V(\varphi_1 - \varphi_2) \right] \cdot (57)$$

where

$$D_{TO} = 2T+1$$

$$D_{TV} = (-1)^V\, 2\, (2T+1) \left[\frac{(T-V)!}{(T+V)!} \right]^2 \qquad (V \geqslant 1) \cdots (58)$$

and ξ_+ is the larger and ξ_-, the smaller of ξ_1, and ξ_2. Integration with respect to ξ_1, and ξ_2 gives the integral

$$W_T^V(m, n, \rho, \rho') = \int_1^{\infty}\int_1^{\infty} Q_T^V(\xi_+)\, P_T^V(\xi_-)\, e^{-\rho\xi_1 - \rho'\xi_2}\, \xi_1^m\, \xi_2^n\, (\xi_1^2 - 1)^{1/2} (\xi_2^2 - 1)^{1/2}\, d\xi_1\, d\xi_2 \cdot (59)$$

while the integrations with respect to η_1 and η_2 give

$$\left. \begin{array}{l} G_T^V(m\,\sigma) = \int_{-1}^{1} e^{-\sigma}\, P_T^V(\eta_1)\, \eta_1^m\, (1 - \eta_1^2)^{1/2}\, d\eta_1 \\[8pt] G_T^V(m\,\sigma') = \int_{-1}^{1} e^{-\sigma'}\, P_T^V(\eta_2)\, \eta_2^m\, (1 - \eta_2^2)^{1/2}\, d\eta_2 \end{array} \right\} \cdots \cdots (60)$$

where ρ, ρ', σ and σ' of equations (59) and (60) are given as

---

* An expanded version of the information contained in this section will be included in "Supplement IV — Tables for Two-Center Two--Electron Exchange Integrals.")

$$P = \frac{R}{2}(\mu_a + \mu_\ell) \qquad\qquad \sigma = \frac{R}{2}(\mu_a - \mu_\ell)$$

$$P' = \frac{R}{2}(\mu_a' + \mu_\ell') \qquad\qquad \sigma' = \frac{R}{2}(\mu_a' - \mu_\ell') \tag{61}$$

where R is the internuclear distance and μ_a, μ_ℓ, μ_a' and μ_ℓ' are the screening constants of the atomic orbitals χ_a, χ_ℓ, χ_a' and χ_ℓ'

In case $P = P'$, these integrals are functions of two variables and can be easily tabulated. When $P \neq P'$, these integrals are functions of more than two variables and cannot be easily tabulated. However, these integrals can be expressed as a linear combination of the auxiliary integrals W and G given in equations (59) and (60). These auxiliary integrals can be expressed as functions of two variables.

Still another method of computing these integrals has been developed which is an extension of the Coulson and Barnett method for Coulomb and hybrid integrals.$^{(15)}$ This method can also be extended to three- and four-center integrals.

The tables in Part IV contain the numerical values of exchange integrals of $P = P'$ along with W and G functions for the exchange integrals of $P \neq P'$ for intervals and ranges such that all exchange integrals between 1s, 2s, and 2p orbitals can be obtained for diatomic molecules even beyond the dissociation limit.

A photographic copy of a page from table 1(b) is attached along with this proposal to acquaint the reader with the type of information contained in each table.

PART III.   PROGRAM FOR COMPUTING WAVE FUNCTIONS USING MOLECULAR INTEGRALS

The two essential stages[9] in the calculation of LCAO MO's and their ionization potentials are the calculation of the F^{α} and F^{β} matrices, and the calculation of the LCAO MO's from these matrices.

It was not found possible to construct a programme, which could cover both these stages of computation in a single run, because of the limitation of the available storage capacity of the computer. However, it was found possible to construct two master programmes, A and B, prepared in the usual manner punched on I.B.M. cards, requiring less than the available storage space of the machine. The programme A was so constructed as to carry out the following:

1. to normalize the vectors $\underline{a}_i$ according to the equation

$$\underline{a}_i \, \underline{S} \, \underline{a}_j = \delta_{ij} \tag{62}$$

2. to multiply $\underline{a}_i$ with integrals J_{ij} and K_{ij} to give matrices $\underline{J}$, $\underline{K}^{\alpha}$, and $\underline{K}^{\beta}$

3. to evaluate matrices $\underline{F}^{\alpha}$ and $\underline{F}^{\alpha}$ according to the equations

$$\underline{H} + \underline{J} - \underline{K}^{\alpha} = \underline{F}^{\alpha}$$

and

$$\underline{H} + \underline{J} - \underline{K}^{\beta} = \underline{F}^{\beta} \tag{63}$$

4. to punch out matrices F^{α} and F^{β} in the binary form on I.B.M. cards which serve as the input data for programme B.

The programme B uses the matrices $\underline{F}$ and $\underline{S}$ as the input data together with a card which contains some instructions in the form of constants, which depend on the order of the matrices. The programme solves the eigenvector equations

$$(\underline{F}^{\alpha} - \epsilon_i \underline{S})\underline{a}_i = 0$$

and

$$(\underline{F}^{\beta} - \epsilon_i \underline{S})\underline{a}_i = 0 \tag{64}$$

both for the LCAO coefficients and ϵ_i values in a single run by the iteration-rotation process described in appendices I and II.

The programme B, at the end of every run, punches out the coefficients $\underline{a}_i$ and $\in_i$, both in the decimal form, for comparison with the values of the previous run, and also in the binary form. The $\underline{a}_i$ coefficients, punched out in the binary form, serve as the input data for the second run of the programme A. Programme A in return punches out matrices $\underline{F}^\alpha$ and $\underline{F}^\beta$ which are used as the input data for programme B. This is continued till the required self-consistency is obtained. In all about 15-20 cycles, requiring about $\frac{1}{2}$ hour of computation on the machine, are generally needed for the self-consistent calculation of an electronic state of a molecule.

THE SCOPE AND USE OF THE PROGRAMME

The programme for the calculation of molecular orbitals is naturally divided into two parts:

(a) evaluation of the matrices $\underline{F}^\alpha$ and $\underline{F}^\beta$ from the molecular integrals of Part II.

(b) calculation of the LCAO MO's and their energy values.

The programme for part A has been so constructed that it can be used for the calculation of the matrices for the ground state as well as those for the excited and ionic states. In fact, it can be used even for doubly and triply ionized states of molecules; a card has been made in the programme with the necessary instructions punched out in certain locations, which can be modified so as to exclude the contributions to the energy value from those orbitals, which remain unoccupied in any state of the molecule.

Both the programmes, A and B, are constructed, at the present stage, to cope with the $\underline{F}^\alpha$ and $\underline{F}^\beta$ matrices up to the order 10. This is due to the fact that nearly every calculation in the molecular orbital theory can be carried out with a matrix of the order less than 10, if group representation is taken into consideration (see appendix III). However, if it becomes necessary

to use matrices of the order higher than 10, the programmes can be easily modified.

The programmes are also useful in the more accurate treatments of the wave functions of atoms and molecules; such as the configuration interaction, and the use of codetors (linear combinations of determinants), which involve the use of equations of the type

$$(\underline{F} - \epsilon \underline{I}) \; \underline{a}_j = 0 \tag{65}$$

containing the unitary matrix $\underline{I}$. The equations (65) are a special case of equations (64), in which the diagonal elements of the overlap matrix $\underline{S}$ are unity and the off-diagonal elements are zero.

The above programmes have been applied to calculate the electronic wave functions and some of the properties of the following molecules:

1. Co   molecule   (ground state)

2. BH   molecule   (ground state)

3. $^3\Pi_g$, $^3\Pi_u$, $^3\Sigma_u^+$ and $^3\Sigma_u^-$ states of N_2 molecule (excited states)

4. $B\,^2\Sigma_u^+$ and $X\,^2\Sigma_g^+$ of N_2^+ molecule (ionized states)

The calculations are now being extended to the ground, excited and ionized states of a number of other molecules and, at the same time, techniques are being developed to improve these wave functions. It is hoped that these calculations, a brief summary of them will be given in the following sections, will form the basis of further work in the field and its application to other problems of molecular physics and spectroscopy.

THE STRUCTURE OF CARBON MONOXIDE[6]

THE MOLECULAR ORBITALS OF CARBON MONOXIDE.

The most practical form of expression of molecular orbitals at present is to use linear combinations of atomic orbitals. This method is adopted here for carbon monoxide, atomic orbitals of the Slater type being used for carbon and oxygen, the only modification of the original Slater functions being to form orthogonal functions from the 1s and 2s orbitals. This ensures that all orbitals on the same atom are orthogonal to each other. All the orbitals will be taken in their normalized form. The convention to be adopted for the sign of the $2p_z$ orbitals is to use the oxygen nucleus as origin, to denote the OC axis as the positive direction and to make the p-orbitals positive on the side of increasing z. The atomic orbitals of oxygen and carbon are distinguished by the suffixes o and c.

Table 1. MOLECULAR ORBITALS OF σ SYMMETRY FOR THE GROUND STATE OF CARBON MONOXIDE

Molecular orbital	$(2s)_O$	$(2s)_C$	$(2p_z)_O$	$(2p_z)_C$	energy (eV)	observed energy(eV)
$\cup\sigma$	0.187	0.6145	−0.189	0.7626	-13.373	-14.009
$\curvearrowright\sigma$	0.7176	-0.4926	-0.6065	0.168	-20.011	-19.695
$t\sigma$	0.675	0.270	0.231	-0.227	-43.369	
σ^{*}	0.973	-0.971	1.0	1.055	15.613	

The two most tightly bound molecular orbitals are taken to be the same as the atomic orbitals $(1s)_O$ and the $(1s)_C$, their computed energies (negative) being 562.76 eV and 308.52 eV. From the four atomic orbitals of σ symmetry, viz. $(2s)_O$, $(2p_z)_O$, $(2s)_C$ and $(2p_x)_C$, four orthogonal molecular orbitals can be constructed. Those that satisfy most nearly the equations for the molecular orbitals and give self-consistent results have the linear coefficients given in table 1, the nomenclature being that used by Mulliken.
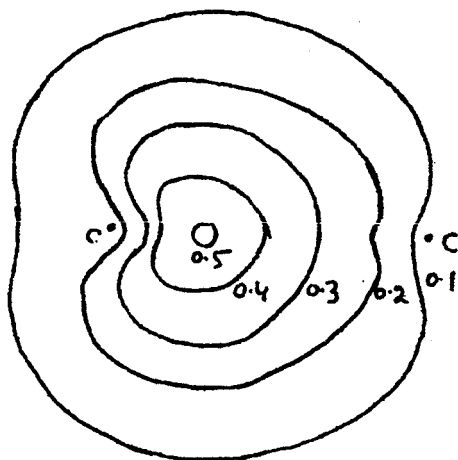
Fig. 1. $t\sigma$ bonding molecular orbital of CO

It is instructive to examine the distribution of the three occupied molecular orbitals, which are given in fig. 1, 2 and 3. The most tightly bound one, $t\sigma$, is concentrated mainly between the two nuclei where the potential field is strong. The energy of bonding is accordingly large. It is evident from the countours of equal density, plotted in the figure, that the greater

field of the oxygen pulls the electron distribution towards it. This represents a form of polarization, or induction. If the two nuclei were equal, as in the nitrogen molecule, the distribution would be symmetrical about the midplane. The asymmetry in the CO molecule produces a shift towards the oxygen and at the same time there is a distortion of the pattern near the oxygen nucleus corresponding to a contraction of the distribution; there is a corresponding expansion of the distribution round the carbon nucleus.
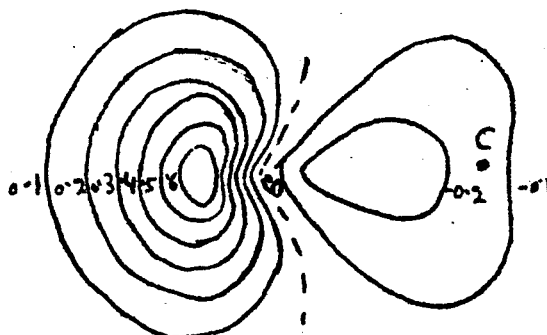

Fig. 2. $(\rho\sigma)$ non-bonding molecular orbital of CO

The next orbital in order of energy is the $\rho\sigma$ one and this is distributed mainly on the reverse side of the oxygen. This is like a localized oxygen atomic orbital, made up of $(2s)_O$ and $(2p_z)_O$, directed away from the carbon, though polarised to some extent towards it. This distribution, which puts a pair of electrons away from the carbon and so in a region where the field is not so strong, is due to the powerful influence of the exclusion principle, for the orbital must be orthogonal to the $t\sigma$ orbital . This important effect is illustrated also in the next orbital, $\upsilon\sigma$, which is mainly concentrated on the side of the carbon remote from the oxygen, for it must be orthogonal to both $t\sigma$ and $\rho\sigma$

We thus see that when electrons are assigned in pairs to the σ orbitals in accordance with the exclusion principle, they are distributed mainly in three regions, viz. between the nuclei, on the outer side of the oxygen and on the outer side of the carbon respectively.

field of the oxygen pulls the electron distribution towards it. This represents a form of polarisation, or induction. If the two nuclei were equal, as in the nitrogen molecule, the distribution would be symmetrical about the midplane. The asymmetry in the CO molecule produces a shift towards the oxygen and at the same time there is a distortion of the pattern near the oxygen nucleus corresponding to a contraction of the distribution; there is a corresponding expansion of the distribution round the carbon nucleus.

Fig. 2. $(\rho\sigma)$ non-bonding molecular orbital of CO

The next orbital in order of energy is the $\rho\sigma$ one and this is distributed mainly on the reverse side of the oxygen. This is like a localized oxygen atomic orbital, made up of $(2s)_0$ and $(2p_z)_0$, directed away from the carbon, though polarised to some extent towards it. This distribution, which puts a pair of electrons away from the carbon and so in a region where the field is not so strong, is due to the powerful influence of the exclusion principle, for the orbital must be orthogonal to the $t\sigma$ orbital . This important effect is illustrated also in the next orbital, $\upsilon\sigma$, which is mainly concentrated on the side of the carbon remote from the oxygen, for it must be orthogonal to both $t\sigma$ and $\rho\sigma$

We thus see that when electrons are assigned in pairs to the σ orbitals in accordance with the exclusion principle, they are distributed mainly in three regions, viz. between the nuclei, on the outer side of the oxygen and on the outer side of the carbon respectively.
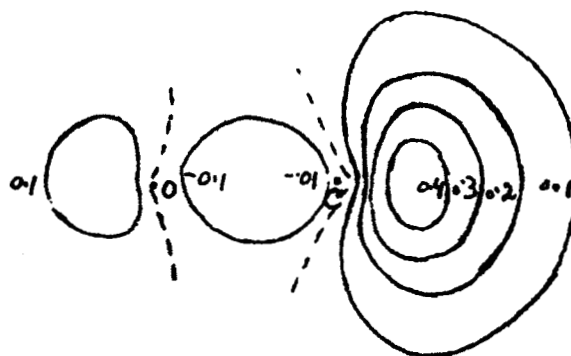
Fig. 3. ($\cup\sigma$) non-bonding molecular orbital of CO.

There are two atomic orbitals each of $2p_x$ and $2p_y$ symmetry and from them two molecular orbitals each of π_x and π_y symmetry are derived. Those for π_x are given in table 2, and the coefficients for π_y are the same. The bonding π_x molecular orbital is shown in fig. 4. The distribution is seen to be mainly concentrated in the neighbourhood of the oxygen nucleus but with some extension of the pattern in the direction of the carbon. If, as suggested by Mulliken, the electrons to be associated with each nucleus are calculated from the squares of the coefficients given in table 2, allowing half the overlap contribution to each, the four electrons assigned to the π_x and π_y orbitals may be regarded as distributed between the oxygen and the carbon in the ratio of approximately three to one.
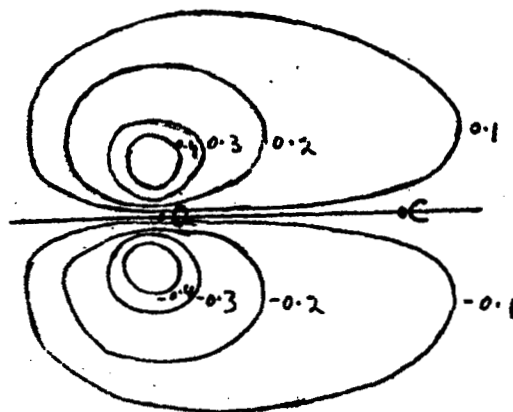

Fig. 4. A π-bonding molecular orbital of CO.

THE ELECTRON DISTRIBUTION IN CO and CO_2. - The contours of the total electron density in CO are shown in fig. 5, these being obtained by summing the squares of the occupied orbitals $\upsilon\sigma$, $\smallfrown\sigma$, $t\sigma$, π_x and π_y. A similar diagram was constructed for CO_2, based on Mulligan's calculations[5] of the occupied orbitals, in order to find out what modification was made in the CO distribution by the removal of an oxygen atom. A comparison of the electron density for CO and CO_2 as integrated over planes through points on the nuclear axis is given in fig. 6. It appears that the main effect is on the lone pair side of the carbon atom, the distribution between the carbon and oxygen not being greatly changed. Whereas the distribution round the carbon in carbon dioxide is, of course, symmetrical, that in carbon monoxide projects out slightly on the remote side from the bond.

Table 2. MOLECULAR ORBITALS OF π_x SYMMETRY

Molecular orbital	$(2p_x)_o$	$(2p_x)_c$	energy (eV)	observed energy (eV)
π_x	0.8145	0.4162	-15.969	-16.578
π_x^*	0.631	-0.9425	7.245	

This no doubt is the major factor in contributing to the dipole moment of the molecule. It means also that the molecule is electron-rich in that region and so is likely to be attracted to electrophilic groups. This may facilitate attachment to other molecules and be a primary step in the formation of complexes as in the carbonyl compounds.
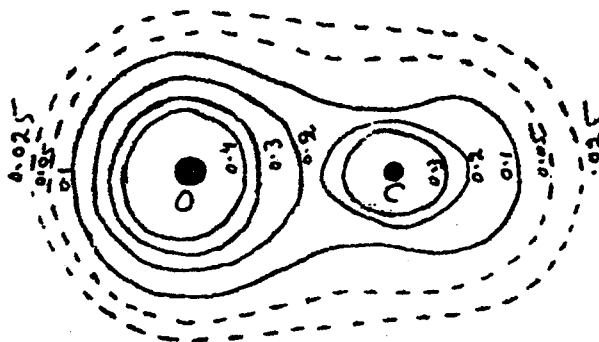
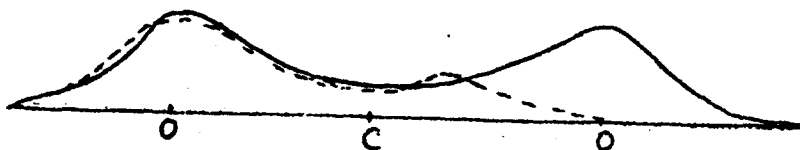Fig. 5.   The charge density contours of CO.

Fig. 6.   The charge density at points along the nuclear axes for CO and CO_2. (The full line curve shows the charge distribution of the outer valence shell electrons of CO_2; the dotted line curve shows the charge distribution of the outer valence shell electrons of CO.)

ELECTRONIC STRUCTURE OF BH[16]

This calculation presents the SCF LCAO MO treatment of the BH molecule in which no approximations excepting those inherent in the theory have been applied. Two different treatments, A and B, have been carried out to compute the wave function, ionization potentials, total energy, binding energy, and the dipole moment of BH. In one of the treatments, called A, the interactions of all the electrons have been included explicitly. In the second treatment, called B, the inner shell -- outer shell mixing is neglected but all the orbitals are made orthogonal to one another and to the inner shells. This is done to find how far

the neglect of inner shell — outer shell mixing affects the results of the calculation. For if this mixing can be neglected, the eigenvector problem becomes simpler and the evaluation of some of the integrals is also not required.

The wave functions of the BH molecule, calculated by both the treatments, are further utilized to calculate the total energy, binding energy, dipole moment, and ionization potentials of the molecule. All the integrals used in these calculations have been computed at the observed equilibrium internuclear separation, 1.2325 A (or 2.329 atomic units), of BH.

The electron distribution analysis, suggested by Mulliken, has also been carried out to get intimate insight into the distribution of charges around and between the nuclei, and to get such information as the degree of hybridization, and the bonding or antibonding nature of MO's.

ATOMIC ORBITALS AND LCAO MO'S OF BH

The molecular orbitals are built up from the Slater AO's. The notation b, s, and z is adopted for the 1s, 2s, and $2p_z$ AO's of boron; h denotes the 1s AO of hydrogen. The $2p_z$ AO is directed along the internuclear axis having the boron nucleus as the origin, and the positive z direction pointing toward the hydrogen nucleus.

The atomic orbitals on each atom are normalized and mutually orthogonal except that the nodeless 2s AO is not orthogonal to 1s. The orthogonal 2s AO is therefore formed from the 1s and 2s AO's of boron. These normalized AO's are then orthogonal to all the orbitals of the same atom.

On inserting the necessary integrals the matrices $\underline{S}$ and $\underline{H}$ were determined for both the treatments, A and B. The elements of the $\underline{G}$ matrix depend on the undetermined coefficients $\underline{a}_i$ and contain contributions from all the occupied orbitals of the closed-shell ground state. For BH, these orbitals are here denoted by σ_1 , σ_2 and σ_3 .

The self-consistent calculations, A and B, were performed using programs of Part III. After the self-consistency was obtained the eigenvectors $\underline{a}_i$ and the

eigenvalues ϵ_i gave the LCAO coefficients and LCAO orbital energies which are given in Table 3 (a) for treatment A and in Table 3 (b) for treatment B.

Table 3.[*] (a)

LCAO MO's		Energy values in atomic units
σ_1	1.000 4(b) + 0.017 7(s) + 0.006 2(z) − 0.007 1(h)	−7.699 7
σ_2	−0.048 3(b) + 0.558 3(s) + 0.217 1(z) + 0.481 4(h)	−0.646 6
σ_3	−0.027 6(b) − 0.799 9(s) + 0.552 9(z) + 0.446 6(h)	−0.346 8
	Unoccupied orbitals	
σ^*	−0.103 0(b) − 0.906 4(s) − 1.145 9(z) + 1.422 2(h)	0.467 1

(b)

σ_1	1.0	−7.696 3
σ_2	−0.037 0(b) + 0.560 6(s) + 0.216 9(z) + 0.479 5(h)	−0.647 7
σ_3	−0.034 6(b) − 0.799 5(s) + 0.552 5(z) + 0.448 5(h)	−0.346 8
	Unoccupied orbitals	
σ^*	−0.109 6(b) − 0.905 5(s) − 1.146 1(z) + 1.422 3(h)	0.466 7

[*]All the MO's in Table 3 (a) and (b) satisfy the orthonormality condition.

THE CALCULATION OF THE DIPOLE MOMENT OF BH

The dipole moment was determined by finding the center of the charge for each molecular orbital using the well-known formula

$$\bar{z} = \int \psi_i \, z \, \psi_i \, d\tau \Big/ \psi_i^2 \, d\tau \tag{66}$$

The integrals were evaluated by using the formulas given by Sahni[6]. The moment was actually computed from both the origins. The value of the moment was found to be 0.389 au (0.989 D) for each of the treatments, A and B.

Table 4. Comparison of calculated and observed total energies.

	Total energy	Ratio of computed to observed molecular energy	% Error
Calculation A	-681.8 ev	0.9924	0.76
Calculation B	-681.7 ev	0.9923	0.77
Observed value*	-687.0 ev		

THE TOTAL ENERGY OF THE BH MOLECULE

The total energy was calculated by using the formula

$$E = \sum_n \left(E_{nn} + H_{nn} \right) + \sum \frac{Z_\alpha^2 Z_\beta^2}{r_{\alpha\beta}} \tag{67}$$

where E_{nn} is the sum of the orbital energies of the occupied orbitals, and

$$H_{nn} = \int \Psi_n \left(-\frac{1}{2}\Delta - \frac{Z_{boron}}{r_{boron}} - \frac{Z_{hydrogen}}{r_{hydrogen}} \right) \Psi_n \, dT \tag{68}$$

The total energies for both the treatments, A and B, are compared in Table 4.

THE BINDING ENERGY OF THE BH MOLECULE

For the comparison of the observed binding energy with the calculated one, we have calculated the energy of the boron atom, using the same Slater AO's as used for the calculation of the energy value of BH. The total energy for boron was found to be

E = -666.4 electron volts.

The calculated binding energy of the BH molecule is given for both the calculations A and B, together with the experimental value, in Table 5.

TABLE 5. Calculated and observed binding energies in
electron volts

Energy	Calculation A	Calculation B	Experimental
BH	-681.8 ev	-681.7 ev	
B	-666.4 ev	-666.4 ev	
H	-13.6 ev	-13.6 ev	
BH-B-H = binding energy	-1.8 ev	-1.7 ev	-2.6 ev

ELECTRON DISTRIBUTION ANALYSIS

If a normalized MO Ψ of a diatomic molecule is written as a linear combination of normalized AO's χ_r and χ_s of the two respective atoms k and l,

$$\Psi = C_r \chi_r + C_s \chi_s \tag{69}$$

then the atomic population for atoms k and l is given by the following equations respectively:

$$N C_r^2 + N C_r C_s S_{rs} \tag{70}$$

and

$$N C_s^2 + N C_r C_s S_{rs} \tag{71}$$

where S_{rs} is the overlap integral $\int \chi_r \chi_s \, dT$, N is the number of electrons in each MO, C_r and C_s are the LCAO coefficients. The overlap population is given by $2NC_rC_sS_{rs}$.

The atomic population $N(i,\chi)$ thus calculated is given in Table 6.

TABLE 6. AO population N (i,χ) in BH

	N(i,b)	N(i,s)	N(i,z)	N(i,h)	N(i)
σ_1	2.0006	0.0005	0.0000	-0.0011	2.0000
σ_2	0.0010	0.9252	0.2032	0.8706	2.0000
σ_3	-0.0004	0.8786	0.8686	0.2532	2.0000
subtotals	2.0012	1.8043	1.0718	1.1227	6.0000

S - p hybridization is 9.78%

IONIZED AND EXCITED STATES OF N_2 MOLECULE [17]

ATOMIC ORBITALS AND LCAO MO's

For the construction of LCAO MO's of different states of N_2 the following set of Slater AO's was adopted.

$$1s = \left(\frac{Z_1^3}{\pi}\right)^{\frac{1}{2}} e^{-Z_1 r}$$

$$2s = \left(Z_2^5/3\pi\right)^{\frac{1}{2}} r\, e^{-Z_2 r}$$

$$\left.\begin{array}{l} 2p_z = \\ 2p_x = \\ 2p_y = \end{array}\right\} \left(\frac{Z_2^5}{\pi}\right)^{\frac{1}{2}} r\, e^{-Z_2 r} \left[\begin{array}{l} \cos\theta \\ \sin\theta \cos\varphi \\ \sin\theta \sin\varphi \end{array}\right. \qquad (72)$$

for nitrogen $Z_1 = 6.7,\ Z_2 = 1.95$

The atomic orbitals of each atom are normalized and mutually orthogonal to all the orbitals of the same atom. The notation n, s, z, x, y is adopted for the nitrogen 1s, 2s, $2p_z$, $2p_x$, and $2p_y$ orbitals with n′, s′, z′, x′, y′ for the corresponding orbitals of the second nitrogen atom. The $2p_z$ orbitals are directed along the internuclear axis with the positive Z-directions towards each other.

SYMMETRY ORBITALS

From the 10 atomic orbitals 10 molecular orbitals were formed according to equation (76). These LCAO MO's were chosen so that they belonged in sets to irreducible representations of the symmetry group of N_2. To obtain the proper symmetry for these MO's, it was convenient to introduce symmetry orbitals.

The symmetry orbitals of N_2 were obtained from the atomic orbitals by the following transformation

$$\underline{\sigma} = \underline{U} \, \underline{\chi}$$

(73)

where

$\underline{\sigma}$ represents symmetry orbitals

$\underline{\chi}$ represents atomic orbitals

and $\underline{U}$ is a real orthogonal matrix.

The resulting symmetry orbitals and the irreducible representations of the symmetry group $D_{\infty h}$ to which they belong are given in Table 7. It should be noted that the symmetry orbitals are not normalized.

Table 7.
Symmetry Orbitals of N_2

Symmetry species	σ_g	σ_u	π_u	π_g
	σ_g 1s $= 1/2(n+n')$	σ_u 1s $= 1/2(n-n')$	π_u 2p$=1/2(x+x')$	π_g 2p$=1/2(x-x')$
	σ_g 2s $= 1/2(s+s')$	σ_u 2s $= 1/2(s-s')$	π_u 2p $= 1/2(y+y')$	π_g 2p$=1/2(y-y')$
	σ_g 2p $= 1/2(z+z')$	σ_u 2p $= 1/2(z-z')$		

There are three σ_g, three σ_u, two π_u and two π_g symmetry orbitals. By taking linear combinations of these orbitals, a like number of molecular orbitals of the same symmetry was formed. These MO's were related to the symmetry orbitals σ_n by the transformation

$$\psi_i = \sum_n \ell_{in} \sigma_n$$

(76)

which reduces to

$$1\sigma_g = b_{11} \, \sigma_g \, 1s + b_{12} \, \sigma_g \, 2s + b_{13} \, \sigma_g \, 2p_z$$

$$2\sigma_g = b_{21} \, \sigma_g \, 1s + b_{22} \, \sigma_g \, 2s + b_{23} \, \sigma_g \, 2p_z$$

$$3\sigma_g = b_{31} \, \sigma_g \, 1s + b_{32} \, \sigma_g \, 2s + b_{33} \, \sigma_g \, 2p_z$$

and

$$1\sigma_u = b_{44}\,\sigma_u\,1s + b_{45}\,\sigma_u\,2s + b_{46}\,\sigma_u\,2p_z$$

$$2\sigma_u = b_{54}\,\sigma_u\,1s + b_{55}\,\sigma_u\,2s + b_{56}\,\sigma_u\,2p_z$$

$$3\sigma_u = b_{64}\,\sigma_u\,1s + b_{65}\,\sigma_u\,2s + b_{66}\,\sigma_u\,2p_z$$

π_u and π_g each belong to a one-membered class. The LCAO coefficients for such a class are completely determined by the normalization condition; thus in the present case the π MO's are uniquely determined.

DETERMINATION OF LCAO MO's

The LCAO MO's of the following states of N_2 were constructed by assigning the electrons to the orbitals in the manner given in Table 8. Using Tables of Molecular Integrals $\underline{S}$, $\underline{H}$, and $\underline{G}$ matrices were constructed. Two different treatments were carried out to obtain the $G^{\alpha\,or\,\beta}$ matrix. In one of the treatments called the generalized treatment, the J_{pq} and $K_{pq}^{\alpha\,or\,\beta}$ elements of the matrix were calculated using equations (28a) and (28b). In the second treatment called the restricted treatment, the a_i for the β orbitals were taken to be the same as those for the α orbitals to calculate the $J_{pq}^{\alpha\,or\,\beta}$ and $K_{pq}^{\alpha\,or\,\beta}$ for $G^{\alpha\,or\,\beta}$ matrix. The LCAO MO's and orbitals energies were then calculated using program described in Part III.

	Observed equilibrium Internuclear distances
1. <u>Ground State</u>	
$X^1\Sigma_g^+$	1.094 A
2. <u>Ionized States (N_2^+)</u>	
$X\ ^2\Sigma_g^+$	1.116 A
$B\ ^2\Sigma_u^+$	1.075 A
3. <u>Excited States</u>	
$B\ ^3\pi_g$	1.2123 A
$C\ ^3\pi_u$	1.1482 A
4. <u>Excited States</u>	
$A\ ^3\Sigma_u^+$	1.293 A
$^{1,3}\Sigma_u^-$	(1.28 A)

TABLE 8

OCCUPIED LCAO MO's OF DIFFERENT STATES OF N_2

(Generalized Treatment)

		$1\sigma_g$	$2\sigma_g$	$3\sigma_g$	$1\sigma_u$	$2\sigma_u$	$1\pi_u$	$1\bar{\pi}_u$	$1\pi_g$	$1\bar{\pi}_g$	$3\sigma_u$
$^2\Sigma_g^+$	α	x	x	x	x	x	x	x			
	β	x	x	---	x	x	x	x			
$^2\Sigma_u^+$	α	x	x	x	x	x	x	x			
	β	x	x	x	x	---	x	x			
$^3\pi_g$	α	x	x	x	x	x	x	x	x		
	β	x	x	---	x	x	x	x			
$^3\pi_u$	α	x	x	x	x	x	x	x	x		
	β	x	x	x	x	---	x	x			
$^3\Sigma_u^+$	α	x	x	x	x	x	x	x	x		
	β	x	x	x	x	x	---	x			
$^{1,3}\Sigma_u^-$	α	x	x	x	x	x	x	x	x		
	β	x	x	x	x	x	x	---			
$^1\Sigma_g^+$	α	x	x	x	x	x	x	x			
	β	x	x	x	x	x	x	x			

THE TOTAL ENERGY OF DIFFERENT STATES OF N_2

The total energy for each of the states was calculated by using the equation

$$E = 1/2 \sum_n (E_{nn} + H_{nn}) + 1/2 \sum_m (E_{mm} + H_{mm}) + \sum_{\alpha \neq \beta} \frac{Z_\alpha Z_\beta}{r_{\alpha\beta}} \qquad (75)$$

where $\sum_{\alpha \neq \beta} \frac{Z_\alpha Z_\beta}{r_{\alpha\beta}}$ represents the internuclear repulsion.

E_{nn} is the sum of the orbital energies of the orbitals occupied by α

electrons, and

$$H_{nn} = \int \Psi_n \left(-\tfrac{1}{2} \nabla^2 - \frac{2}{r_n} - \frac{2}{r_{\tilde{n}}} \right) \Psi_n \, dT$$

$$= \sum_{ij} a_{ni} a_{nj} h_{ij}$$

or

$$\sum_n H_{nn} = \sum_{ij} h_{ij} \left(\sum_n a_{ni} a_{nj} \right) \qquad (76)$$

E_{mm} and H_{mm} have the same meaning for the orbitals occupied by β electrons, as E_{nn} and H_{nn} for the orbitals occupied by α electrons.

The calculated total energies for the $X^2\Sigma_g$ and $B^2\Sigma_u$ ionized states of N_2^+ are given in Table 9A. The difference between the calculated energies of the ionized states and that of the ground state $X'\Sigma_g$ of N_2 are given in Table 9b along with the experimental ionization potentials (reference 18) and the ionization energies obtained from the calculation of the ground state $(X'\Sigma_g{}^+)$ of N_2 Molecule.

The energy of an excited state is calculated by finding the difference between the energy of the excited orbitals and the energy of the original orbital, from which the electron is excited, of the ground state. The energies of the excited states $C^3\pi_u$, $B^3\pi_g$ thus calculated, are given in Table 10 along with the experimental values (reference 18) and the energies of $A^3\pi_u{}^+$ and $^{1,3}\pi_u{}^-$ are given in Table 11, along with the experimental values (reference 18).

TOTAL ENERGIES* OF X $\frac{1}{2}\Sigma_g^+$ $X^2\Sigma_g^+$ AND B $^2\Sigma_u^+$ STATES OF N$_2$

	$^1\Sigma_g$	$^2\Sigma_u^+$	$^2\Sigma_g^+$
Restricted Treatment	-108.571	-108.8261	-108.0416
Generalised Treatment	-108.571	-107.8262	-108.0507

* In atomic units (1 atomic unit = 27.204 e.v.)

Table 9b

IONIZATION POTENTIALS

	$E_{ground} - E_{ionic}$		Calculation from the ground state wave function	Experimental values
	Restricted Treatment	Generalised Treatment		
$2\Sigma_u^+$	-20.267 e.v.	-20.267 e.v.	-19.868 e.v.	-18.72 e.v.
$2\Sigma_g^+$	-14.399 e.v.	-14.154 e.v.	-14.807 e.v.	-15.602 e.v.

Table 10
EXCITATION ENERGIES OF $C^3\pi_u$ and $B^3\pi_g$ STATES OF N$_2$

	Calculations from the wave function of $C^3\pi_u$ and $B^3\pi_g$ States		Experimental values
	(Generalised)	(Restricted)	
$^3\pi_u$	10.958 e.v.	10.976 e.v.	11.049 e.v.
$^3\pi_g$	7.306 e.v.	7.131 e.v.	7.390 e.v.

Table 11

EXCITATION ENERGIES

	Calculations from the wave function of $A\ ^3\Sigma_u^+$ and $^{1,3}\Sigma_u^-$ states		Experimental values
	Generalised	Restricted	
$^3\Sigma_u^+$	6.953 e.v.	7.056 e.v.	6.223 e.v.
$^{1,3}\Sigma_u^-$	8.150 e.v.	8.255 e.v.	7.437 e.v.

DISCUSSION OF THE RESULTS

The results of the above calculation of the different states of N_2 show
that the LCAO MO method gives the results of the same order of accuracy for
the excited and ionised states as that for the ground state of molecules.
It is further apparent from the calculations that both the generalised and
restricted treatments give nearly the same results for both the ionised and
excited states. Since the calculations have been carried out for both
g and u states, it appears the method holds for the states (ground, ionised and
excited states) of molecules which can be represented by a single determinant.
This is the first calculation where the quantum mechanical treatment of ionised
and excited states has been carried out without using any approximations, within
the rigorous framework of the LCAO SCF MO theory. It is hoped that this calcula-
tion will form the basis of the much needed work on the ionised and excited
states of molecules.

(Of particular interest is the rate at which the NO β -bands are filled.)

        e. Dissociation rates: rates of transfer of rotational, vibrational, and electronic energies.

3. **Electron-Molecule Reactions**

    a. Elastic scattering - scattering from ground, excited, and ionic molecular states.

    b. Inelastic scattering.

    c. Ionization reactions.

    d. Coulomb scattering.

    e. The reaction $NO^+ + e = N+O$ is of importance in determining whether the electrons are in equilibrium with the rest of the plasma.

4. **Radiation**. Of primary interest is radiation from β , γ and δ bands of NO and from excited states of N_2. To estimate the transition probabilities accurately the potential curves for the various excited and ground states are needed.

5. **Non-air Molecules**. Some of these are C_2, CN, CH, OH, and various metallic oxides.

6. **Computation of Potential energy curve**.

The potential energy curves of different states of a number of molecules will be computed by calculating electronic wave functions and their energy values at a number of internuclear distances (R) and drawing the curve with the electronic energy E(R) as the ordinate and internuclear distance (R) as the abscissa.

APPENDIX I

THE DIAGONALISATION OF MATRICES

The iteration-rotation method for the diagonalisation of a matrix is based on the fact, that by an orthogonal transformation from variables x, y to variables x', y', which can be described in the forms

$$\begin{vmatrix} x' \\ y' \end{vmatrix} = \begin{bmatrix} \cos\theta & \sin\theta \\ -\sin\theta & \cos\theta \end{bmatrix} \begin{vmatrix} x \\ y \end{vmatrix} \tag{77}$$

One can express the quadratic form

$$ax^2 + 2hxy + by^2 = 0 \tag{78}$$

as a sum of squares

$$Ax'^2 + by'^2 = 0 \tag{79}$$

θ is chosen such that

$$\tan 2\theta = 2h\,(a-b)^{-1} \tag{80}$$

where h is the largest off-diagonal element, a and b being the corresponding diagonal elements.

For example, if one takes the matrix,

$$A = \begin{bmatrix} 2.879 & -0.841 & -0.148 & 0.506 \\ -0.841 & 3.369 & -0.111 & 0.380 \\ -0.148 & -0.111 & 1.216 & -0.740 \\ 0.506 & 0.380 & -0.740 & 3.536 \end{bmatrix}$$

$h = -0.841$,

$$\tan 2\theta = \frac{-2 \times 0.841}{2.879 - 3.369},$$

$$\text{and } T_\theta = \begin{bmatrix} \cos\theta & \sin\theta & 0 & 0 \\ -\sin\theta & \cos\theta & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{bmatrix}$$

then the element in $T_\theta^{-1} A \, T_\theta \; (=A_1)$ corresponding to -0.841 will be zero.

The matrix, A_1, thus obtained, is again subjected to a similar operation $T_\varphi^{-1} A_1 T_\varphi$ for its largest off-diagonal element h.

When all the off-diagonal elements are reduced to zero, or to negligibly small values, the final matrix will take the following form

$$T_\psi^{-1} A_{n-1} T_\psi = \begin{bmatrix} 4.005 & 0.0 & 0.0 & 0.0 \\ 0.0 & 4.000 & 0.0 & 0.0 \\ 0.0 & 0.0 & 1.005 & 0.0 \\ 0.0 & 0.0 & 0.0 & 1.990 \end{bmatrix}$$

suggesting that the characteristic roots, which are invariant under the above orthogonal transformations are approximately 4.005, 4.000, 1.005 and 1.990.

APPENDIX II

EQUIVALENT FORMS OF MO EQUATIONS

The molecular orbital equations

$$(\underline{F} - \epsilon \underline{S})\, \underline{a}_i = 0 \tag{81}$$

can be obtained in the following equivalent forms,

$$(\underline{F} - \epsilon \underline{S})\, \underline{a}_i \tag{82}$$

$$= (\underline{F} - \epsilon T^{-1} \underline{L} T)\, \underline{a}_i \tag{83}$$

$$= T^{-1}(T \underline{F} T^{-1} - \epsilon \underline{L}) T \tag{84}$$

$$= T^{-1} L^{\frac{1}{2}} (L^{-\frac{1}{2}} T \underline{F} T^{-1} L^{-\frac{1}{2}} - \epsilon \underline{I}) L^{+\frac{1}{2}} T \tag{85}$$

where $\underline{L}$ and $\underline{I}$ are the diagonal and unitary matrices.

Equations (83) are obtained from equations (82) by replacing $\underline{S}$ by its equivalent

$$\underline{S} \equiv T^{-1} \underline{L} T \tag{86}$$

where $\underline{L}$ is the diagonal matrix obtained from $\underline{S}$ by the iteration-rotation process described in appendix I.

The matrix $\overset{!}{B}$ ($= L^{-\frac{1}{2}} T F T^{-1} L^{-\frac{1}{2}} - \epsilon \underline{I}$) of equations (85) is also diagonalized by the iteration-rotation process using the transformation

$$y^{-1} \overset{!}{\underline{B}} y = \underline{B} \tag{87}$$

The elements of the diagonal matrix B, thus obtained, will give the ionization potentials (refer to appendix I) while the vectors

$$L^{-\frac{1}{2}} T Y$$

give the coefficients for the LCAO MO's.

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