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ANALYTIC SELF-CONSISTENT FIELD WAVE FUNCTIONS AND COMPUTED PROPERTIES FOR HOMONUCLEAR DIATOMIC MOLECULES

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ABSTRACT

The analytic and computational framework on homonuclear diatomic molecules for Hartree-Fock-Roothaan calculations is presented. Several approaches to calculating the wave function are sketched, as well as methods of computing molecular properties from the wave function. The efficient organization of these calculations for existing digital computers is emphasized. Typical results obtained through the application of the programs and techniques developed are presented for the fluorine molecule.

INTRODUCTION

Although many calculations have been performed on diatomic molecules, few have been of sufficient depth and scope to establish the usefulness of the mathematical model. This work presents the analytic and inescapable, computational framework for Hartree-Fock-Roothaan calculations on diatomic molecules. Once the necessary one- and two-center, one- and two-electron integrals are available,[1] different types of wave functions can be constructed for diatomic molecules. Among these types of calculations are straight LCAO (Linear Combination of Atomic Orbitals), valence bond, atoms in molecules, limited configuration mixing, and self-consistent field molecular orbital calculations. The methods discussed in this paper apply to the calculations of analytic, self-consistent, field-wave functions for homonuclear diatomic molecules by the Roothaan method. The analysis for the self-consistent field equations is well documented,

and the programs available for atoms[2-4] remain virtually intact when
linked to the calculation of the diatomic matrix and supermatrix elements.
The methods employed to evaluate these elements were presented
recently.[1]

Even with the present, large-memory, high-speed, digital computers,
the calculations presented in this paper would be intractable unless con-
siderable attention was given to possible economies in the analysis and
organization of the matrix and supermatrix computations. What follows
will present such an organization for the calculation of self-consistent,
field-wave functions and properties for homonuclear, diatomic molecules,
and the specific application of these programs to the fluorine molecule.

I. CHOICE OF UNITS, COORDINATE SYSTEMS, AND ATOMIC BASIS FUNCTIONS

Atomic units will be used through this paper. In this system, the unit of length is the Bohr (0.52917 Å), the unit of energy the Hartree ($2R_\infty hc$ = 27.20974 eV), and the unit of charge that of the electron, e⁻. In these units, the electronic Hamiltonian for a diatomic molecule is

$$H = \sum_{\mu} (-\frac{1}{2}\Delta_\mu) - Z_a/r_{a\mu} - Z_b/r_{b\mu}) + \sum_{\mu < \nu} 1/r_{\mu\nu}. \tag{1}$$

The sums are over the electrons of the molecule. The two centers will be designated by subscripts a and b, and their mutual separation by R. The quantities $r_{a\mu}$ and $r_{b\mu}$ are the distances from nuclei a and b respectively. Z_a and Z_b are the charges on the two nuclei.

The position of the electrons with reference to the two centers will be described in terms of the following three[1] coordinate systems:

1. Cartesian coordinate systems, centered on nuclei a and b and on the midpoint between a and b, respectively. The z_a and z_b axes are chosen to lie along the internuclear axis pointing toward one another.

2. Spherical coordinates, centered on nuclei a and b. The atomic orbitals are usually defined in terms of these coordinates.

3. Prolate spheroidal coordinates, with foci on nuclei a and b. These coordinates are defined in terms of the spherical coordinates by

$$\xi = (r_a + r_b)/R; \quad \eta = (r_a - r_b)/R; \quad \phi = \phi_a = \phi_b. \tag{2}$$

The normalized complex STO's (Slater Type Orbitals) are used throughout this paper. The STO's designated by $\chi_{ap\lambda\alpha}$ or $\chi_{bp\lambda\alpha}$ indicate the triple n, ℓ, m and are given by

$$(n, \ell, m) = (2\zeta)^{n+1/2} [(2n)!]^{-1/2} r^{n-1} e^{-\zeta r} Y_{\ell m}(\theta, \phi), \tag{3}$$

where the spherical coordinate system is centered on nucleus a or b, and the $Y_{\ell m}(\theta,\phi)$ are the normalized, complex, spherical harmonics defined by

$$Y_{\ell m}(\theta,\phi) = \mathscr{P}_{\ell m}(\cos\theta)\Phi_m(\phi),$$

and

$$\Phi_m(\phi) = (2\pi)^{-1/2} e^{im\phi}; \tag{4}$$

and the normalized associated Legendre functions are defined by

$$\mathscr{P}_{\ell m}(\cos\theta) = \frac{1}{2^\ell \ell!} \left[\frac{2\ell+1}{2} \cdot \frac{(\ell-m)!}{(\ell+m)!} \right]^{1/2}$$

$$\times (-\sin\theta)^m \left[\frac{d}{d\cos\theta} \right]^{\ell+m} (\cos^2\theta - 1)^\ell, \qquad (5)$$

where $-\ell \le m \le \ell$.

In Eq. (3), n is taken as being a positive integer and ζ is completely flexible.

The normalized, associated Legendre functions are related to the unnormalized, associated Legendre functions by

$$\mathscr{P}_{\ell m}(x) = \left[\frac{(2\ell+1)}{2} \cdot \frac{(\ell-m)!}{(\ell+m)!} \right]^{1/2} P_{\ell m}(x).$$

The $P_{\ell m}(x)$ functions are defined by

$$P_{\ell m}(x) = \frac{(-)^m}{2^\ell \ell!} (1-x^2)^{1/2m} \frac{d^{\ell+m}}{dx^{\ell+m}} (x^2-1)^\ell. \qquad (6)$$

For the calculation of the exchange integrals, we make use of similar functions defined for $1 \le x \le \infty$ by

$$\hat{P}_\ell^m(x) = \frac{(-)^m}{2^\ell \ell!} (x^2-1)^{1/2m} \frac{d^{\ell+m}}{dx^{\ell+m}} (x^2-1)^\ell. \qquad (7)$$

Details of these considerations are presented elsewhere.[1]

II. REVIEW OF GENERAL THEORY

The total N-electron wave function is put forth as an antisymmetrized product of MSO's (Molecular Spin Orbitals),[2]

$$\Phi = (N!)^{1/2} \, \psi_1^{[1,2,\,\ldots\,,\,N]} \psi_N, \tag{8}$$

where $[1,2,\ldots,N]$ indicates the operation of "alternation" and

$$\psi_\kappa^\mu = \phi_{i(\kappa)}^\mu \eta_\kappa^\mu, \tag{9}$$

where the superscript μ stands for the space and spin coordinates of the μth electron, and the subscripts κ and i label the different MSO's and MO's (Molecular Orbitals), respectively. In the following, the superscript μ and subscript κ are dropped in order to simplify salient features of the MO $\phi_{i(\kappa)}^\mu$ for the homonuclear diatomic molecule. In the expansion form of the self-consistent field method, the molecular orbital ϕ_i is expanded in terms of a set of suitable functions called basis functions χ_p,

$$\phi_i = \sum_p \chi_p C_{ip}, \tag{10}$$

where the C_{ip} are the expansion coefficients which are determined by the variational procedure. It is convenient to group the basis functions χ_p according to the symmetry of the molecular orbital

$$\chi_p \to \chi_{p\lambda\alpha}, \tag{11}$$

so that

$$\phi_{i\lambda\alpha} = \sum_p \chi_{p\lambda\alpha} C_{i\lambda p}, \tag{12}$$

where λ is the symmetry species and α is the subspecies of symmetry λ.

The total electronic energy of the system is expressed in terms of matrices and supermatrices, whose elements are one- and two-electron integrals over the basis functions $\chi_{p\lambda\alpha}$, and suitably-defined density matrices built from the coefficients $C_{i\lambda p}$.[2-4] The variational principle is applied to minimize the energy with respect to the linear parameters $C_{i\lambda p}$. By proper manipulation, the variational equations determining the coefficients $C_{i\lambda p}$ can be written in the form of pseudo-eigenvalue equations. These equations are customarily solved by the iterative SCF (Self-consistent Field) procedure. A complete and authoritative discussion of the SCF equations and process for atoms has been given by Roothaan and Bagus.[4] The reader is encouraged to refer to this work for details since the formalism for atoms is virtually the same as that for molecules.

III. APPLICATION TO THE HOMONUCLEAR DIATOMIC MOLECULE

For the homonuclear diatomic molecule, two-center symmetry basis functions belonging to the rotation-reflection group $D_{\infty h}$ are introduced by

$$\chi_{p\lambda\alpha} = (1/\sqrt{2})(\chi_{ap\lambda\alpha} + \sigma_\lambda \chi_{bp\lambda\alpha}), \tag{13}$$

where the subscripts a and b refer to the two atoms. For $\chi_{p\lambda\alpha}$ to have proper symmetry, $\chi_{ap\lambda\alpha}$ must be the mirror image of $\chi_{bp\lambda\alpha}$ when reflected through a plane midway between atoms a and b and perpendicular to the internuclear axis. The parameter σ_λ is determined by the gerade or ungerade symmetry of the basis function $\chi_{p\lambda\alpha}$ and is given by $\sigma_\lambda = (-)^{m_\lambda}$ for g symmetry and $\sigma_\lambda = (-)^{m_\lambda + 1}$ for μ symmetry.

For a given symmetry λ, the subspecies α permits two values, namely, $\alpha = \pm m_\lambda$, where m_λ is the value of the projection of orbital angular momentum on the internuclear axis. Henceforth the notation $\overline{m}_\lambda$ in lieu of $-m_\lambda$ will be used. The introduction of symmetry basis functions permits considerable computational economies.

The variational principle is applied to minimize the total energy of the molecule yielding the Roothaan equations determining the linear coefficients $C_{i\lambda p}$. The expression for the total energy of the molecule is given by[3,4]

$$E = H^\dagger D_T + \frac{1}{2} D_T^\dagger \mathcal{P} D_T - \frac{1}{2} D_O^\dagger \mathcal{Q} D_O + \frac{Z^2}{R}. \tag{14}$$

In the above expression, the elements of the H matrix (which is a collection of all one-electron integrals between basis functions and is considered as a supervector) and the $\mathcal{P}$ and $\mathcal{Q}$ supermatrices (which are ordered collections of all two-electron integrals between basis functions) are only dependent upon the set of basis functions $\chi_{p\lambda\alpha}$ employed. The total density matrix D_T and the open-shell density matrix D_O, however, are constructed from the expansion coefficients $C_{i\lambda p}$, which are determined by the self-consistent field process.[3]

The bulk of the diatomic SCF calculation is the evaluation of the matrix elements $H_{\lambda pq}$ and the supermatrix elements $\mathcal{P}_{\lambda pq, \mu rs}$ and $\mathcal{Q}_{\lambda pq, \mu rs}$, where λ and μ designate the symmetry of the basis functions, and p, q, r, and s label the functions within a given symmetry. For the homonuclear diatomic molecule,

$$H_{\lambda pq} = d_\lambda^{-1} \int \chi_{p\lambda\alpha}^* \left[-\frac{1}{2}\Delta - Z\left(r_a^{-1} + r_b^{-1}\right) \right] \chi_{q\lambda\alpha} dV, \tag{15}$$

$$\mathcal{I}_{\lambda pq,\mu rs} = (d_\lambda d_\mu)^{-1} \sum_{\alpha\beta} \iint \chi^*_{p\lambda\alpha}(1)\chi^*_{r\mu\beta}(2)(1/r_{12})$$

$$\times \chi_{q\lambda\alpha}(1)\chi_{s\mu\beta}(2)dV_1 dV_2, \tag{16}$$

$$\mathcal{K}_{\lambda pq,\mu rs} = (d_\lambda d_\mu)^{-1} \sum_{\alpha\beta} \iint \chi^*_{p\lambda\alpha}(1)\chi^*_{s\mu\beta}(2)(1/r_{12})$$

$$\times \chi_{r\mu\beta}(1)\chi_{q\lambda\alpha}(2)dV_1 dV_2, \tag{17}$$

and

$$\mathcal{P}_{\lambda pq,\mu rs} = \mathcal{I}_{\lambda pq,\mu rs} - \frac{1}{2}\mathcal{K}_{\lambda pq,\mu rs},$$

$$\mathcal{Q}_{\lambda pq,\mu rs} = \alpha\mathcal{I}_{\lambda pq,\mu rs} - \frac{1}{2}\beta\mathcal{K}_{\lambda pq,\mu rs}, \tag{18}$$

where d_λ and d_μ are the dimensions of the representation λ, and the basis functions are given in terms of atomic functions by Eq. (13). In Eqs. (18) the parameter α and β are the vector coupling coefficients appropriate to the open-shell structure of the molecule.

Equation (13) indicates that $H_{\lambda pq}$ reduces to a sum of one- and two-center one-electron integrals, which can be evaluated in a straightforward manner. However, the evaluation of the supermatrix elements, $\mathcal{I}_{\lambda pq,\mu rs}$ and $\mathcal{K}_{\lambda pq,\mu rs}$, presents a formidable computational problem for any large molecular calculation. One economy that makes these calculations feasible in practice is that no single, two-electron integral is ever computed as such. Instead, the scalar product of a total symmetrized charge distribution with a one-center potential yields all coulomb[5,6] and hybrid[5,6] integrals contributing to a given supermatrix element. Similarly, all exchange[7] contributions are evaluated as the scalar product of a pair of two-center exchange functions, symmetrized for the homonuclear diatomic molecule. Another important principle that leads to considerable economy is to confine all numerical work to a manifold of points characteristic of the molecule being studied and chosen to be physically significant. Finally, the saving and interlacing of reusable information during a lengthy calculation leads to a significant extension of computer capacity (particularly during the variation of orbital exponents).

IV. CALCULATION OF THE MATRIX ELEMENTS

We write down the explicit expressions used for the evaluation of matrix elements, $H_{\lambda pq}$ and $S_{\lambda pq}$, for the homonuclear diatomic molecule, although the methods employed may be easily used to evaluate matrix elements for other operators. The formulas are

$$S_{\lambda pq} = d_\lambda^{-1} \sum_\alpha \int \chi_{p\lambda\alpha}^* \chi_{q\lambda\alpha} dV; \tag{19}$$

$$U_{\lambda pq} = d_\lambda^{-1} \sum_\alpha \int \chi_{p\lambda\alpha}^* (r_a^{-1} + r_b^{-1}) \chi_{q\lambda\alpha} dV; \tag{20}$$

$$T_{\lambda pq} = -\frac{1}{2} d_\lambda^{-1} \sum_\alpha \int \chi_{p\lambda\alpha}^* \Delta \chi_{q\lambda\alpha} dV; \tag{21}$$

$$H_{\lambda pq} = T_{\lambda pq} - Z U_{\lambda pq}. \tag{22}$$

If we now introduce the explicit form of the symmetry basis function given by Eq. (13) and carry out the summation over α, we obtain

$$S_{\lambda pq} = \int \chi_{ap\lambda\alpha}^* \chi_{aq\lambda\alpha} dV + \sigma_\lambda \int \chi_{ap\lambda\alpha}^* \chi_{bq\lambda\alpha} dV; \tag{23}$$

$$U_{\lambda pq} = \int \chi_{ap\lambda\alpha}^* r_a^{-1} \chi_{aq\lambda\alpha} dV + \sigma_\lambda \int \chi_{ap\lambda\alpha}^* r_a^{-1} \chi_{bq\lambda\alpha} dV$$

$$+ \sigma_\lambda \int \chi_{ap\lambda\alpha}^* r_b^{-1} \chi_{bq\lambda\alpha} dV + \int \chi_{ap\lambda\alpha}^* r_b^{-1} \chi_{aq\lambda\alpha} dV; \tag{24}$$

$$T_{\lambda pq} = -\frac{1}{2} \int \chi_{ap\lambda\alpha}^* \Delta \chi_{aq\lambda\alpha} dV - \frac{1}{2} \sigma_\lambda \int \chi_{ap\lambda\alpha}^* \Delta \chi_{bq\lambda\alpha} dV. \tag{25}$$

The one-center integrals occurring in Eqs. (23-25) are easily computed by using the functions[4]

$$V_i(x) = x^{-i-1} i! = \int_0^\infty dr\, r^i e^{-xr}. \tag{26}$$

The two-center coulomb integral $\int \chi^*_{ap\lambda\alpha} r_b^{-1} \chi_{aq\lambda\alpha} dV$ can be computed by applying the Laplace expansion[1] to r_b^{-1}.

The remaining two-center integrals are of the type $\int \chi^*_{ap\lambda\alpha} M \chi_{bq\lambda\alpha} dV$, where M is a one-electron operator. They are computed via the auxiliary functions $L_{\alpha\beta}^{\gamma\delta\epsilon} (\tau,\rho)$.[1,8]

The various one-electron programs were amalgamated into the di-atomic matrix program in a straightforward manner. Note that all integrals reduce to analytical expressions. The main programming consideration was to avoid any redundant computation. In any event, the evaluation of the one-electron matrix elements constitutes only a small fraction of the total computation time.

V. REDUCTION OF THE SUPERMATRIX ELEMENTS TO INTEGRALS OVER CHARGE DISTRIBUTIONS

After the explicit form for $\chi_{p\lambda\alpha}$ given by Eq. (13) is introduced into Eqs. (16-17), it is clear that the general supermatrix element may be considered to be the sum of electrostatic interactions of charge distributions built from products of atomic basis functions. A given charge distribution occurs in many supermatrix elements, and these distributions will be used to achieve great computational economy in the evaluation of the supermatrices. The charge distributions that are particularly useful for the homonuclear molecule are

$$\Omega^a_{p\lambda\alpha,r\mu\beta} = \frac{1}{2}\chi^*_{ap\lambda\alpha}\chi_{ar\mu\beta},$$

$$\Omega^{ab}_{p\lambda\alpha,r\mu\beta} = \sigma_\mu \chi^*_{ap\lambda\alpha}\chi_{br\mu\beta} + \sigma_\lambda \chi^*_{bp\lambda\alpha}\chi_{ar\mu\beta}. \tag{27}$$

It is easily established that

$$\Omega_{p\lambda\alpha,r\mu\beta} = (-)^{\alpha+\beta}\Omega^*_{p\lambda-\alpha,r\mu-\beta}, \tag{28}$$

which holds for charge distributions with the superscript a or ab.

If we recast the expressions for the supermatrices $\mathscr{J}$ and $\mathscr{K}$ as given by Eqs. (16-17) in terms of the above charge distributions (27), we obtain

$$\left.\begin{aligned}
\mathscr{J}_{\lambda pq,\mu rs} &= \mathscr{J}^c_{\lambda pq,\mu rs} + \mathscr{J}^x_{\lambda pq,\mu rs}; \\
\mathscr{K}_{\lambda pq,\mu rs} &= \mathscr{K}^c_{\lambda pq,\mu rs} + \mathscr{K}^x_{\lambda pq,\mu rs},
\end{aligned}\right\} \tag{29}$$

where

$$\left.\begin{aligned}
\mathscr{J}^c_{\lambda pq,\mu rs} &= \left[\Omega^a_{p\lambda\alpha,q\lambda\alpha}(1)\,\big|\,\Omega^{*a}_{r\mu\beta,s\mu\beta}(2) + \Omega^{*ab}_{r\mu\beta,s\mu\beta}(2) + \Omega^{*b}_{r\mu\beta,s\mu\beta}(2)\right] \\
&\quad + \left[\Omega^a_{r\mu\beta,s\mu\beta}(1)\,\big|\,\Omega^{*a}_{p\lambda\alpha,q\lambda\alpha}(2) + \Omega^{*ab}_{p\lambda\alpha,q\lambda\alpha}(2) + \Omega^{*b}_{p\lambda\alpha,q\lambda\alpha}(2)\right]; \\
\mathscr{K}^c_{\lambda pq,\mu rs} &= d_\mu^{-1}\sum_\beta\left\{\left[\Omega^a_{p\lambda\alpha,r\mu\beta}(1)\,\big|\,\Omega^{*a}_{q\lambda\alpha,s\mu\beta}(2) + \Omega^{*ab}_{q\lambda\alpha,s\mu\beta}(2)\right.\right. \\
&\quad \left.+ \sigma_\lambda\sigma_\mu\Omega^{*b}_{q\lambda\alpha,s\mu\beta}(2)\right] + \left[\Omega^a_{q\lambda\alpha,s\mu\beta}(1)\,\big|\,\Omega^{*a}_{p\lambda\alpha,r\mu\beta}(2)\right. \\
&\quad \left.\left.+ \Omega^{*ab}_{p\lambda\alpha,r\mu\beta}(2) + \sigma_\lambda\sigma_\mu\Omega^{*b}_{p\lambda\alpha,r\mu\beta}(2)\right]\right\},
\end{aligned}\right\} \tag{30}$$

and

$$\mathscr{J}^{x}_{\lambda pq,\mu rs} = \frac{1}{4}\left[\Omega^{ab}_{p\lambda\alpha,q\lambda\alpha}(1) \mid \Omega^{*ab}_{r\mu\beta,s\mu\beta}(2)\right];$$

$$\mathscr{K}^{x}_{\lambda pq,\mu rs} = \frac{1}{4}\,d_{\mu}^{-1}\sum_{\beta}\left[\Omega^{ab}_{p\lambda\alpha,r\mu\beta}(1) \mid \Omega^{*ab}_{q\lambda\alpha,s\mu\beta}(2)\right].$$

$$\left.\right\} \tag{31}$$

The methods that will be used to evaluate these supermatrix elements divide them naturally into two classes. The first class, Eqs. (30), consisting of the coulomb and hybrid integrals, will be evaluated as scalar products between two vectors - one having as its components the values of a reduced charge distribution, the other having as its components the weighted values of the electrostatic potential arising from a one-center charge distribution. Both of these vectors occur over a two-dimensional manifold of points used for numerical integration. The second class, Eqs. (31), consisting of the exchange integrals, will also be evaluated as scalar products between two vectors; however, for this class the components of each vector are the values of a weighted exchange function over a one-dimensional manifold of points. This exchange function is obtained through the analysis[1] recently presented, organized specifically for distributions of the form $\Omega^{ab}_{p\lambda\alpha,r\mu\beta}$.

VI. THE COULOMB AND HYBRID INTEGRALS

For the evaluation of the supermatrix contributions $\mathscr{J}^c_{\lambda pq, \mu rs}$, and $\mathcal{K}^c_{\lambda pq, \mu rs}$, the analysis given recently[1] was organized for the computation of large batches of integrals and for the symmetry $D_{\infty h}$. Since the integration over the angle ϕ is done analytically, the functions necessary for the numerical evaluation of the coulomb and hybrid integrals need to be tabulated only over a two-dimensional manifold of points. The selection of this manifold is strongly influenced by the particular two-dimensional integration scheme used. In principle, this integration can be performed over any two-dimensional coordinate system; in practice, however, the accuracy and reliability obtained depends strongly on the specific choice of the manifold. After various attempts, it was found that a grid constructed as the direct product of two gaussian grids over the prolate spheroidal coordinates ξ and η was the most satisfactory of those grids tried.

Since all numerical work for the evaluation of the coulomb and hybrid integrals is confined to the chosen manifold, which will be referred to by P, it is useful to define the reduced atomic basis functions $\chi_{ap\lambda\alpha}(P)$ by means of

$$\chi_{ap\lambda\alpha}(P, \phi) = \underset{\sim}{\chi}_{ap\lambda\alpha}(P) e^{i\alpha\phi} / \sqrt{2\pi} . \tag{32}$$

From these reduced atomic basis functions, we can build the reduced, one-center, charge distributions,

$$\underset{\sim}{\Omega}^a_{p\lambda\alpha, r\mu\beta}(P) = \frac{1}{2} \underset{\sim}{\chi}_{ap\lambda\alpha}(P) \underset{\sim}{\chi}_{ar\mu\beta}(P);$$

and a reduced, symmetrized, two-center, charge distribution,

$$\underset{\sim}{\Omega}^{ab}_{p\lambda\alpha, r\mu\beta}(P) = \sigma_\mu \underset{\sim}{\chi}_{ap\lambda\alpha}(P) \underset{\sim}{\chi}_{br\mu\beta}(P) + \sigma_\lambda \underset{\sim}{\chi}_{bp\lambda\alpha}(P) \underset{\sim}{\chi}_{ar\mu\beta}(P). \tag{33}$$

At this point it is convenient to limit considerations to the use of $\alpha = m_\lambda$ and $\beta = \pm m_\mu$, and to the only combination of the reduced distributions of Eqs. (33) that will appear in the working formulas for the supermatrices of the homonuclear diatomic molecule. We accordingly define reduced homonuclear distributions by

$$\underset{\sim}{\Omega}'^+_{p\lambda r\mu}(P) = \underset{\sim}{\Omega}^a_{p\lambda m_\lambda, r\mu m_\mu}(P) + \underset{\sim}{\Omega}^{ab}_{p\lambda m_\lambda, r\mu m_\mu}(P) + \sigma_\lambda \sigma_\mu \underset{\sim}{\Omega}^b_{p\lambda m_\lambda, r\mu m_\mu}(P);$$

$$\underset{\sim}{\Omega}'^-_{p\lambda r\mu}(P) = \underset{\sim}{\Omega}^a_{p\lambda m_\lambda, r\mu \overline{m}_\mu}(P) + \underset{\sim}{\Omega}^{ab}_{p\lambda m_\lambda, r\mu \overline{m}_\mu}(P) + \sigma_\lambda \sigma_\mu \underset{\sim}{\Omega}^b_{p\lambda m_\lambda, r\mu \overline{m}_\mu}(P). \tag{34}$$

It is easily shown from the properties of the spherical harmonics[1,9] that

$$\underset{\sim}{\Omega}^{-}_{P\lambda r\mu}(P) = (-)^{m\mu}\underset{\sim}{\Omega}'^{+}_{P\lambda r\mu}(P). \tag{35}$$

The second quantity necessary for evaluating the coulomb and hybrid integrals as scalar products over the manifold P is the weighted potential arising from a one-center distribution. These weighted potentials may be developed from the familiar[1] one-center potentials obtained by the integration over the coordinates of one electron,

$$\left.\begin{array}{l} U^{+}_{P\lambda r\mu}(2) = \int \Omega^{a}_{P\lambda m_{\lambda}, r\mu m_{\mu}}(1)(1/r_{12})dV_1; \\[2mm] U^{-}_{P\lambda r\mu}(2) = \int \Omega^{a}_{P\lambda m_{\lambda}, r\mu \bar{m}_{\mu}}(1)(1/r_{12})dV_1, \end{array}\right\} \tag{36}$$

where the above integration is performed <u>analytically</u> in a <u>spherical</u> coordinate system centered on nucleus a. The definition of the potential, Eqs. (36), has been limited to center a, since reference to only one center is necessary for the final evaluation of the integrals due to the $D_{\infty h}$ symmetry of the distributions, Eqs. (34). The specific reference to electrons 1 and 2 in Eqs. (36) is only necessary to define these potentials formally. Once defined, they may be considered as functions of three dimensions and the reference to the coordinates of electron 2 dropped. Since we will need only the dependence of this function over the manifold P, we define the <u>reduced</u> <u>potentials</u> $\underset{\sim}{U}^{\pm}_{P\lambda r\mu}(P)$ by

$$U^{\pm}_{P\lambda r\mu}(P,\phi) = \underset{\sim}{U}^{\pm}_{P\lambda r\mu}(P)e^{-i(m_{\lambda}\mp m_{\mu})\phi}. \tag{37}$$

From this reduced potential, we construct the <u>reduced</u> <u>weighted</u> <u>potentials</u> over the manifold P defined by

$$\underset{\sim}{V}^{\pm}_{P\lambda r\mu}(P) = W(P)\underset{\sim}{U}^{\pm}_{P\lambda r\mu}(P), \tag{38}$$

where $W(P)$ is the weight factor necessary for the numerical integration over the manifold P. It arises from the gaussian weight factors and the volume element in the prolate, spherical coordinate system.

For the $\mathscr{J}$ supermatrix, only the limited class of distributions $\underset{\sim}{\Omega}'^{+}_{P\lambda q_{\lambda}}$ and potentials $\underset{\sim}{V}^{+}_{P\lambda q_{\lambda}}$ are needed. We therefore introduce the abbreviated notation defined by

$$\underset{\sim}{\Omega}'_{\lambda pq}(P) = \underset{\sim}{\Omega}'^{+}_{P\lambda q_{\lambda}}(P); \quad \underset{\sim}{V}_{\lambda pq}(P) = \underset{\sim}{V}^{+}_{P\lambda q_{\lambda}}(P). \tag{39}$$

The working expressions for the coulomb and hybrid integral contributions then become

$$
\left.
\begin{aligned}
\mathscr{J}^{c}_{\lambda pq,\mu rs} &= \underset{\sim}{V}_{\lambda pq} \cdot \underset{\sim}{\Omega}'_{\mu rs} + \underset{\sim}{V}_{\mu rs} \cdot \underset{\sim}{\Omega}'_{\lambda pq}; \\[2mm]
\mathscr{K}^{c}_{\lambda pq,\mu rs} &= \tfrac{1}{2}(\underset{\sim}{V}^{+}_{\lambda p\mu r} + (-)^{m_\mu}\, \underset{\sim}{V}^{-}_{\lambda p\mu r}) \cdot \underset{\sim}{\Omega}'^{+}_{\lambda q\mu s} \\[2mm]
&\quad + \tfrac{1}{2}(\underset{\sim}{V}^{+}_{\lambda q\mu s} + (-)^{m_\mu}\, \underset{\sim}{V}^{-}_{\lambda q\mu s}) \cdot \underset{\sim}{\Omega}'^{+}_{\lambda p\mu r}.
\end{aligned}
\right\}
\qquad (40)
$$

VII. THE EXCHANGE INTEGRALS

The exchange supermatrix contributions, $\mathscr{J}^{x}_{\lambda pq,\mu rs}$ and $\mathscr{K}^{x}_{\lambda pq,\mu rs}$, were evaluated by a straightforward application of the methods presented recently.[1] Again the incorporation of the $D_{\infty h}$ symmetry of the charge distributions $\Omega^{ab}_{p\lambda\alpha,r\mu\beta}$ into the analysis leads to significant computational economies. Both $\mathscr{J}^{x}_{\lambda pq,\mu rs}$ and $\mathscr{K}^{x}_{\lambda pq,\mu rs}$ can be considered as special cases of the general integral

$$X_{p\lambda\alpha,r\mu\beta;m\nu\gamma,n\kappa\delta} = \left[\Omega^{ab}_{p\lambda\alpha,r\mu\beta}(1) \mid \Omega^{*ab}_{m\nu\gamma;n\kappa\delta}(2) \right], \tag{41}$$

where ν and κ indicate symmetry species, and γ and δ subspecies. It is computationally convenient to formulate this integral as the scalar product of two vectors over a one-dimensional manifold of points, where the manifold is defined by the numerical aspects of the exchange integral analysis. Each of these vectors arises from an <u>exchange function</u> determined by a charge distribution.

It is easily shown[1,7] that the basis function product $\chi_{ap\lambda\alpha}\chi^{*}_{br\mu\beta}$ may be expanded in prolate spheroidal coordinates by

$$(-)^{\beta}(\tfrac{1}{2}R)^{3}(\xi^{2}-\eta^{2})\chi_{ap\lambda\alpha}\chi_{br\mu-\beta} = (-)^{\beta}K_{ab}\omega(\xi,\eta)e^{-\rho\xi-\tau\rho\eta}$$

$$\times \; [(\xi^{2}-1)(\eta^{2}-1)]^{\tfrac{1}{2}M} \Phi_{\alpha}(\phi)\Phi_{-\beta}(\phi), \tag{42}$$

where

$$\omega(\xi,\eta) = \sum_{n}\sum_{j} a_{nj}\xi^{n}\eta^{j},$$

and

$$M = \alpha - \beta.$$

The normalization factor K_{ab}, the parameters ρ and τ, and the expansion coefficients a_{nj} are determined by the product $\chi_{ap\lambda\alpha}\chi_{br\mu-\beta}$. Since the distribution $\Omega^{ab}_{p\lambda\alpha,r\mu\beta}$ is a linear combination of two basis function products which differ only by the inversion of the centers a and b, it may be expanded by

$$(\tfrac{1}{2}R)^{3}(\xi^{2}-\eta^{2})\Omega^{*ab}_{p\lambda\alpha,r\mu\beta} = (-)^{\beta}K_{ab}[(\xi^{2}-1)(\eta^{2}-1)]^{\tfrac{1}{2}M}$$

$$\times \; \Phi_{\alpha}(\phi)\Phi_{-\beta}(\phi)e^{-\rho\xi} \times [\sigma_{\lambda}\,\omega(\xi,\eta)e^{-\tau\rho\eta} + \sigma_{\mu}\omega(\xi,-\eta)e^{\tau\rho\eta}]. \tag{43}$$

The introduction of these expanded distributions into expression (41) is followed by familiar steps.[1,7] First the Neuman expansion for $1/r_{12}$ is introduced and the trivial integration over the angles ϕ_1 and ϕ_2 performed. Then, the results of the analytic integrations over η_1 and η_2 are expressed in terms of the auxiliary functions[1,7] defined by

$$B_j^{M\ell}(\rho\tau) = \int_{-1}^{1} d\eta \; \eta^j (1-\eta^2)^{\frac{1}{2}M} \mathscr{P}_{\ell}^{M}(\eta),$$

for which it is verified that

$$B_j^{M\ell}(-\rho\tau) = (-)^{\ell+M+j} B_j^{M\ell}(\rho\tau). \tag{44}$$

Finally, several partial integrations over the variables ξ_1 and ξ_2 lead to the following expression:

$$X_{p\lambda\alpha,r\mu\beta;m\nu\gamma,n\kappa\delta} = (-)^{\beta+\delta} \sum_{\ell=\ell\min}^{\infty} I_{p\lambda\alpha,r\mu\beta;m\nu\gamma,n\kappa\delta}^{\ell}, \tag{45}$$

where

$$\left. \begin{aligned} I_{p\lambda\alpha,r\mu\beta;m\nu\gamma,n\kappa\delta}^{\ell} &= 4R^{-1}\Big[\sigma_\lambda + \sigma_\mu(-)^{\ell+M}\Big]\Big[\sigma_\nu + \sigma_\kappa(-)^{\ell+M}\Big] \\ &\quad \times \int_1^\infty \frac{d\xi}{(\xi^2-1)\Big[\hat{P}_\ell^M(\xi)\Big]^2} F_{\ell;p\lambda\alpha,r\mu\beta}^M(\xi;\rho,\tau) \; F_{\ell;m\nu\gamma,n\kappa\delta}^M(\xi;\rho,\tau), \\[2ex] F_{\ell;p\lambda\alpha,r\mu\beta}^M(\xi;\rho,\tau) &= K_{ab} \int_1^\xi dx \hat{P}_\ell^M(x)(x^2-1)^{\frac{1}{2}M} \\ &\quad \times \sum_j B_j^{M\ell}(\rho\tau) \sum_n a_{nj} x^n e^{-\rho x}. \end{aligned} \right\} \tag{46}$$

Note that the $I_{p\lambda\alpha,r\mu\beta,m\nu\gamma,n\kappa\delta}^{\ell}$ integral vanishes identically unless $\sigma_\lambda \sigma_\mu = \sigma_\nu \sigma_\kappa$ and $\alpha - \beta = \gamma - \delta$. The parameters ρ and τ, the indices n and j, and the coefficients a_{nj} entering into this auxiliary function are determined by the charge distribution $\Omega_{p\lambda\alpha,r\mu\beta}^{ab}$ through Eqs. (42-43).

The numerical scheme presented recently[1] was used to evaluate the integrals $I_{p\lambda\alpha,r\mu\beta;m\nu\gamma,n\kappa\delta}^{\ell}$, namely Simpson's-rule integrations over the variables ξ and x. This numerical procedure was used to avoid many complications[7] that arise in the analytic evaluation of these integrals over the numerous orbital products appearing as integrands. The Simpson's-rule

integration introduces in a natural way the manifold S as the selection of points used for the numerical integrations. (See Appendix A.) To organize the numerical work in the simplest possible terms, it is useful to define the <u>weighted exchange function</u> over this manifold S by

$$
\left.
\begin{aligned}
\mathcal{G}^{+}_{\ell\,;p\lambda\,r\mu}(S) &= (-)^{m_\mu}\,2R^{-\frac{1}{2}}\sqrt{W(S)}\left[(S^2-1)^{\frac{1}{2}}\,\hat{P}^{m\lambda-m\mu}_{\ell}(S)\right]^{-1} \\
&\quad \times F^{m\lambda-m\mu}_{\ell\,;p\lambda m_\lambda,\,r\mu\overline{m}_\mu}(S;\rho,\tau) \\[2mm]
\mathcal{G}^{-}_{\ell\,;p\lambda r\mu}(S) &= (-)^{m_\mu}\,2R^{-\frac{1}{2}}\sqrt{W(S)}\left[(S^2-1)^{\frac{1}{2}}\,\hat{P}^{m\lambda+m\mu}_{\ell}(S)\right]^{-1} \\
&\quad \times F^{m\lambda+m\mu}_{\ell\,;p\lambda m_\lambda,\,r\mu m_\mu}(S;\rho,\tau),
\end{aligned}
\right\} \tag{47}
$$

where $W(S)$ is the necessary weight factor for the Simpson's-rule integration over the manifold.

For the exchange contribution to the supermatrix $\mathscr{J}$, only the limited class of exchange functions, namely $\mathcal{G}^{+}_{\ell\,;p\lambda q\lambda}$, will be needed. As was done for the coulomb hybrid contribution, we introduce the abbreviated notation

$$
\mathcal{G}_{\ell\,;\lambda pq}(S) = \mathcal{G}^{+}_{\ell\,;p\lambda q\lambda}(S). \tag{48}
$$

The final working expressions for the exchange integral contribution to the supermatrices in terms of scalar products are

$$
\left.
\begin{aligned}
\mathscr{J}^{x}_{\lambda pq,\,\mu rs} &= 2\sum_{\ell=0}^{\infty}\mathcal{G}_{\ell\,;\lambda pq}\cdot\mathcal{G}_{\ell\,;\mu rs}; \\[3mm]
\mathcal{K}^{x}_{\lambda pq,\,\mu rs} &= 2\sum_{\ell=\left[\begin{smallmatrix}m\lambda-m\mu\\ m\lambda-m\mu+1\end{smallmatrix}\right]}^{\infty}\mathcal{G}^{+}_{\ell\,;p\lambda r\mu}\cdot\mathcal{G}^{+}_{\ell\,;q\lambda s\mu} \\[3mm]
&\quad + 2\sum_{\ell=\left[\begin{smallmatrix}m\lambda+m\mu\\ m\lambda+m\mu+1\end{smallmatrix}\right]}^{\infty}\mathcal{G}^{-}_{\ell\,;p\lambda r\mu}\cdot\mathcal{G}^{-}_{\ell\,;q\lambda s\mu},
\end{aligned}
\right\} \tag{49}
$$

where in the summations over ℓ, the smaller lower limit is used if $\sigma_\lambda\sigma_\mu(-)^{m\lambda+m\mu}=1$ and the larger lower limit if $\sigma_\lambda\sigma_\mu(-)^{m\lambda+m\mu}=-1$. Also note that the summation over ℓ proceeds in steps of two. This economy results from the inversion symmetry of the distributions, as expressed by Eq. (43).

VIII. CALCULATION OF THE WAVE FUNCTION

Fully automatic computer programs were built that incorporated the analysis and organization discussed in Sections I-VII of this paper. These programs, which computed the H matrix and the supermatrices, $\mathcal{P}$ and $\mathcal{Q}$, were linked to a modified version of the atomic SCF program written at The University of Chicago and Argonne National Laboratory.[4] The modifications that had to be made in the atomic SCF program were, of course, complete replacement of the atomic integral computation, new closed- and open-shell weight factors, and extensive changing of the "screening" of input data and printing of results to fit the diatomic molecule. The specifications for the preparation of input and use of the molecular program[10] are given in Appendix B.

Once such a program exists, it can be used in a variety of ways ranging from the calculation of crude SCF wave functions[11,12] to an attempt to reach the molecular Hartree-Fock function for the ground and excited states of diatomic molecules.[13-16] An infinite number of crude functions may be calculated, depending upon the use for which they are desired, and in many cases personal taste. There is within the framework of the analysis, however, only one molecular Hartree-Fock function. It has been the goal of this work to make it possible to approach very closely the molecular Hartree-Fock function with a truncated expansion. This function may be represented by several choices of basis sets, and currently the path to the "final" function depends on computer economics, program capacity, intuition, and previous data. A brief discussion of the approaches used in this work is therefore in order.

The gradual improvement of the molecular wave function depends upon the judicious addition of basis functions $\chi_{p\lambda\alpha}$ and the optimization of the orbital exponents of the added functions to make them most effective. This improvement process may be done in many different ways. Two methods were employed in this work.

The first method was to start with a minimal basis set, optimize the basis function exponents in a coupled way (using chemical intuition and computer experimentation to determine which functions should influence each other), gradually add new basis functions, and optimize the new exponents. This process was continued until the total molecular energy showed little further improvement upon the addition of new functions or until program capacity was exhausted. The second method was to start the molecular calculation with a large basis set that was obtained independently for the constituent atoms, singly optimize each basis function exponent, and add functions with higher quantum numbers to each molecular symmetry with optimization of the new exponents. Ideally these two methods would lead to the same result. However, computer economics

makes extensive coupled optimization of the molecular basis function exponents intractable. The <u>exhaustively</u> optimized <u>atomic basis sets</u>[17] therefore appear to be an energetically better representation of the molecular wave function after the exponents are singly optimized and functions with higher ℓ values are added to each molecular symmetry. These considerations will be elaborated in forthcoming work.[13-16] It is sufficient to say here that the atomic Hartree-Fock function is a dominant contributor to the molecular Hartree-Fock function and forms a good starting point for the further development of the molecular wave function. Currently attempts are being made to develop some wave function "prescription" which, by starting with atomic basis sets, will efficiently lead to the molecular Hartree-Fock function with a minimum of effort.

IX. CALCULATION OF MOLECULAR PROPERTIES

To evaluate any molecular property characterized by an operator M that has cylindrical symmetry, the matrix elements defined by

$$M_{\lambda pq} = \int \chi^*_{p\lambda\alpha} M \chi_{q\lambda\alpha} \, dV \tag{50}$$

are necessary. The matrix element $M_{\lambda pq}$ may be conveniently evaluated as the scalar product of two vectors over the manifold P. For this purpose, we introduce still another reduced homonuclear distribution, defined by

$$\underset{\sim}{\Omega}_{\lambda pq}(P) = \underset{\sim}{\Omega}^a_{p\lambda\alpha,q\lambda\alpha}(P) + \frac{1}{2}\underset{\sim}{\Omega}^{ab}_{p\lambda\alpha,q\lambda\alpha}(P) + \underset{\sim}{\Omega}^b_{p\lambda\alpha,q\lambda\alpha}(P),$$

and the weighted property operator, defined by

$$\underset{\sim}{M}(P) = W(P)M(P), \tag{51}$$

where $M(P)$ is the value of the property operator over the manifold P and, as before, $W(P)$ is the weight factor necessary for the numerical integration over the manifold. We may integrate analytically over the angle ϕ. The general expression for the property matrix elements is then

$$M_{\lambda pq} = \underset{\sim}{M} \cdot \underset{\sim}{\Omega}_{\lambda pq}. \tag{52}$$

The molecular property is given as the inner product of the density matrix with the property matrix (52), where both are considered as supervectors, by

$$M = D_T \cdot M. \tag{53}$$

A quantity often of interest, the contribution of a given orbital to this property, may be defined in terms of the contribution of the ith orbital to the density matrix,

$$M_i = D_i \cdot M, \tag{54}$$

where D_i contains only coefficients from orbital i. This numerical scheme is conceptually simple, and a large class of properties can be evaluated in this way, particularly since most differential operators can be expressed as multiplicative ones.[1] An important feature of this method is its generality and easy extendability. The basic quantities needed are only the charge distributions $\underset{\sim}{\Omega}_{\lambda pq}$ and the weighted property operator $\underset{\sim}{M}$ over the manifold of points P. Properties characterized by operators that have

strong singular behavior at one of the nuclei can be evaluated by this method if a suitable manifold P is designed; however, better methods exist for the calculation of this type of operator.

For the evaluation of spectroscopic constants, the computed SCF potential curve for the molecule must be used. This computed potential curve has two serious shortcomings. The first is that the molecular orbital wave function dissociates properly only for a limited class of systems. For all others, it dissociates into a sum of neutral and ionic atomic states. Although this error is largest at $R = \infty$, it probably also tends to increase the molecular energy, even at the equilibrium internuclear distance. Even if the proper dissociation took place, there is the second error which tends to increase the molecular energy. This is the increased correlation energy in the molecule. Both of these factors decrease the computed dissociation energy, which in this work is defined as

$$D_e = E_{molecule} - 2E_{atom}, \tag{55}$$

where E_{atom} is the Hartree-Fock atomic energy. Often the sum of these two errors is sufficient to overshadow completely the comparatively small binding energy of many diatomic systems. However, the failure of the molecular wave function to show binding on this basis (55) does not completely obviate the significance of the SCF potential energy curve. We may say that

$$E_{exact} = E_{Hartree-Fock} + \Delta E, \tag{56}$$

where ΔE is the correction energy. It is not <u>unreasonable</u> to expect that over <u>any small</u> range of R, for instance, near the computed potential minimum ($R_e - \Delta R < R < R_e + \Delta R$, where $\Delta R \sim 0.25$ bohrs), ΔE is roughly constant, so that

$$\frac{dE_{exact}}{dR} \sim \frac{dE_{Hartree-Fock}}{dR}. \tag{57}$$

This should allow the equilibrium internuclear distance and the <u>first</u>-order spectroscopic constants to be predicted fairly well. In this work, a Dunham analysis was used over the region near the equilibrium internuclear distance, and the first-order spectroscopic constants thus obtained show fair agreement with experiment.

Total electronic charge densities for the molecule are defined by

$$\Omega = \sum_{\lambda} \sum_{p} \sum_{q} D_{\lambda pq} \Omega_{\lambda pq}. \tag{58}$$

Normally these densities are visualized by being plotted as contour lines in the x,z plane. These lines are defined by

$$\Omega(x,z) = C, \tag{59}$$

where C is the value of the density for which a contour is desired. Although the total charge density is significant, orbital densities, obtained by including only the contributions of a given orbital to the density matrix, should be of even greater interest. These orbital densities should prove useful in studying the visual aspect of molecular and atomic orbital comparisons, concepts like S-P hybridization, and the difference between bonding and antibonding orbitals. These contours are currently produced and plotted automatically by the computer.

X. DETAILS OF THE COMPUTATION

The following general computational considerations made possible the calculations with existing computing facilities of Section XI.

1. The reliability and accuracy of the methods used to evaluate the supermatrices depend upon the proper selection of the manifolds P and S. This selection is discussed in Appendix A. The three basic working functions $\underline{V}^{\pm}_{\tilde{p}\lambda r\mu}$, $\underline{\Omega}'^{\pm}_{\tilde{p}\lambda r\mu}$, and $G^{\pm}_{\tilde{\ell};p\lambda r\mu}$ depend only upon a single pair of basis functions. This retains the computational identity of electrons 1 and 2. Thus, the most arduous part of the supermatrix evaluation (namely the evaluation of these three types of functions) need be done for approximately

$$\sum_{\mu} \sum_{\lambda} n_{\lambda} n_{\mu}$$ basis function pairs, as opposed to the square of the dependence

that would arise if this identity were sacrificed (n_{λ} is the number of basis functions in symmetry λ). In addition, the conceptual simplicity of this formulation makes it easily extendable to polyatomic systems. The principal further developments necessary are the selection of the manifolds, characteristic of the molecule under study, over which numerical work will be done, and a general reorganization for the multicenter geometry.

2. To avoid extensive redundant computation in the evaluation of the supermatrices, <u>all</u> vectors $\underline{V}^{\pm}_{\tilde{p}\lambda r\mu}$ must be available when a single vector $\underline{\Omega}'^{\pm}_{\tilde{p}\lambda r\mu}$ is constructed. The size of existing computer memories makes this impossible for a moderately large basis set. Therefore the manifold P was divided into regions determined by values of the prolate spheroidal coordinate ξ. The vector tabulations were then made only over a region in the manifold, and the total supermatrix contribution was evaluated as the sum of the regional integrations.

3. The convergence of the coulomb and hybrid integrals as a function of the number of points in the manifold P was a matter of experimentation and depended upon the molecule under investigation. It was found that the ξ integration should be truncated at $\xi < 50/(\zeta_{min}R)$, where ζ_{min} is the minimum exponent in the basis set, and that a grid of 20 points on each of the variables ξ and η was sufficient for studies of first-row diatomic systems. For investigations of second-row molecules, however, grids of 36 points were necessary.

The convergence of the exchange integrals as a function of ℓ in the Neumann expansion is controlled by a single threshold. When all contributions arising from a given vector $G^{\pm}_{\tilde{\ell};p\lambda r\mu}$ are below this threshold in absolute value, the calculation of this vector is terminated. The iteration on ℓ is terminated when the contributions for all vectors $G^{\pm}_{\tilde{\ell};p\lambda r\mu}$ lie below this threshold <u>or</u> when $\ell = 30$. Should the latter occur, a record is made of the largest last contribution, and the calculations are continued. In

practice, the exchange contributions have converged well before $\ell = 30$. It was found that 40 points in the manifold S were sufficient for all exchange integrals occurring in studies of first- and second-row molecules.

4. Because of the numerical characteristics of the exchange integral analysis, the functions $P_\ell^M(x)$, e^{-x}, and $B_j^{\ell m}(x)$ had to be scaled.

5. During the variation of orbital exponents, considerable machine time may be saved by saving and reusing the vectors $\underset{\sim}{V}_{\bar{p}\lambda\eta\mu}^{\pm}$ and $\underset{\sim}{G}_{\bar{\ell},p\lambda r\mu}^{\pm}$ that are not built from a basis function being varied. Therefore the program was designed to save and reuse those vectors during the variation of exponents.

6. Because of the large amount of computer time needed for any sizable molecular computation, a true interrupt procedure and an emergency feature were built into the molecular program. The interrupt procedure allows the calculations to be interrupted and restarted when scheduling permits, with virtually no backtracking necessary. The emergency procedure periodically saves sufficient information to restart the computation. Thus, should some catastrophe occur, calculations may be continued with the loss of only a small fraction of the computing done before the disaster.

XI. RESULTS FOR THE FLUORINE MOLECULE

The fluorine molecule was selected as a prototype system for investigation through the use of the techniques developed in the preceding sections. The reasons for this choice were several: (1) there is a comparative lack of experimental and theoretical information on this system; (2) if fluorine could be successfully studied with these programs, it should clear the way for studies of smaller systems and provide a guidepost for the investigation of larger systems; and (3) the fluorine molecule was estimated to be the largest system for which extensive optimization of basis function exponents would be economically feasible and for which the molecular Hartree-Fock function might be attainable.

Previous calculations of the fluorine molecule consist of SCF calculations by Ransil[11] and Eve[12] yielding total energies of -197.87694 and -197.87017 hartrees, respectively. Eve[12] also performed a limited configuration-mixing calculation yielding a total energy of -197.95036 hartrees. The best wave function presented in this work yields an energy of -198.76825 hartrees.

The above F_2 function is presented in Table I along with the orbital energies. Table II presents additional properties computed from this function. The ionization potential (IP) was evaluated by Koopman's Theorem. No experimental comparisons are available for the molecular quadrupole moment (Q), the field gradient at the nucleus (q), or the average molecular size $\langle r_a + r_b \rangle_{av}$.

Table I

NEAR HARTREE-FOCK WAVE FUNCTION FOR GROUND STATE OF FLUORINE MOLECULE

Internuclear Distance = 2.68 bohrs						
Basis Functions (Quantum Numbers, Orbital Exponents)						

Molecular Symmetry Species	σ_g	σ_u	π_u	π_g		
	1S 8.27336	1S 8.28062	2P 1.67164	2P 1.58741		
	1S 13.17191	1S 13.16925	2P 3.20350	2P 3.18020		
	3S 4.90649	3S 5.03602	2P 6.11692	2P 6.15863		
	2S 2.26251	2S 2.23962	3D 2.49433	3D 2.43222		
	2P 1.84915	2P 1.44746	4F 2.85001	4F 2.56431		
	2P 3.26935	2P 3.00518				
	2P 5.85912	2P 6.35647				
	3D 2.44269	3D 3.60759				
	4F 2.83176	4F 1.52251				

Total Energy −198.76825		Potential Energy −397.35489		Kinetic Energy +198.58664		Virial Theorem −2.0009145	

Molecular Orbital	$1\sigma_g$	$2\sigma_g$	$3\sigma_g$	$1\sigma_u$	$2\sigma_u$	$1\pi_u$	$1\pi_g$
Orbital Energy (hartrees)	−26.42269	−1.75654	−0.74604	−26.42244	−1.49499	−0.80523	−0.66290
Vector Components	+0.92243	−0.23113	+0.04801	+0.92318	−0.24801	+0.50684	+0.57948
	+0.08175	−0.00452	+0.00260	+0.08074	−0.00368	+0.45168	+0.51156
	+0.00560	+0.29092	−0.05578	+0.00618	+0.29569	+0.07153	+0.07716
	−0.00037	+0.67105	−0.25752	−0.00098	+0.82366	+0.02122	−0.00102
	+0.00032	+0.06396	+0.58162	−0.00036	−0.02437	+0.00992	+0.00352
	−0.00066	+0.05373	+0.30716	−0.00033	−0.08330		
	+0.00145	+0.00749	+0.08509	+0.00120	−0.00927		
	−0.00025	+0.02017	+0.04571	−0.00043	−0.00633		
	−0.00000	+0.00931	+0.01416	+0.00005	+0.00264		

Table II

COMPUTED PROPERTIES FOR NEAR HARTREE-FOCK
GROUND STATE WAVE FUNCTION* OF FLUORINE MOLECULE

Molecular Property	R bohrs	E hartrees	μ	Q $e(bohrs)^2$	q $e/(bohrs)^3$	Ip eV	De eV	$\langle r_a + r_b \rangle_{av}$ bohrs	$\langle X^2 \rangle_{av}$ $(bohrs)^2$
Computed	2.68	-198.7683	0	0.659	6.868	18.04	-1.370	3.689	0.7772
Experiment	2.68	-199.670	0	.	..	16.3	1.68	..	..

	Spectroscopic Constants via Dunham Analysis				
	$\omega_e(cm^{-1})$	$\omega_e X_e(cm^{-1})$	B_e	α_e	$R_e(\text{Å})$
Computed	1257	9.85	1.003	0.0108	1.33
Experiment	919.0	13.6	0.8901	0.0146	1.42

*The basis set was constructed by starting with the nominal atomic set of Bagus
and Gilbert: (1) singly optimizing all zetas, (2) adding 3d functions with single
optimization, (3) adding 4f functions with single optimization.

Table III compares the function (atomic start) obtained by starting
with the atomic Hartree-Fock results with the molecular wave function
which was built up gradually (arduous). The <u>atomic start</u> function is ener-
getically superior and represents far less computation.

Table III

COMPARISON OF ARDUOUSLY* BUILT-UP MOLECULAR BASIS SET WITH SET
OBTAINED STARTING FROM ATOMIC** FUNCTIONS FOR FLUORINE MOLECULE

Basis Set				R bohrs	E hartrees	μ	Q $e(bohrs)^2$	Ip hartrees	De hartrees	$\langle r_a + r_b \rangle_{av}$ bohrs	$\langle X^2 \rangle_{av}$ $(bohrs)^2$
σ_g	σ_u	π_u	π_g								
Atomic Start											
1s	1s	2p	2p	2.68	-198.7683	0	0.6589	0.66290	-0.048	3.689	0.7772
1s'	1s'	2p'	2p'								
2s	2s	2p''	2p''								
3s	3s	3d	3d								
2p	2p	4f	4f								
2p'	2p'										
2p''	2p''										
3d	3d										
4f	4f										
Arduously Built											
1s	1s	2p	2p	2.68	-198.7563	0	0.5753	0.66894	-0.060	3.695	0.7874
1s'	1s'	2p'	2p'								
2s	2s	2p''	2p''								
2s	2s	3d	3d								
2p	2p	4f	4f								
2p	2p										
2p	3d										
3d	4f										
4f											

*"Arduous" refers to starting with a small basis set and gradually adding functions with
coupled optimization of zetas at each addition.
**Starting point was the "nominal" atomic set: the result of a very careful investigation
of first-row atoms of Bagus and Gilbert.[17]

Table IV presents a hierarchy of functions ending with the final function. Note the convergence of the energy as contrasted to the wide variation of several of the properties when basis set size is increased.

Table IV

SUMMARY OF BASIS SET (EXPANSION) BUILDUP FOR FLUORINE MOLECULE

| Basis Set | | | | Functions Added | | | | R bohrs | E hartrees | Q e(bohrs)^2 | q e/(bohrs)^3 | Ip hartrees | $\langle r_a + r_b \rangle_{av}$ bohrs | $\langle x^2 \rangle_{av}$ (bohrs)^2 |
σ_g	σ_u	π_u	π_g	σ_g	σ_u	π_u	π_g							
3 x 3 x 1 x 1														
1s	1s	2p	2p											
2s	2s							2.68	-197.8865	0.2379	5.349	0.47497	3.618	0.6411
2p	2p													
5 x 5 x 2 x 2														
1s	1s	2p	2p	2s	2s	2p	2p							
2s	2s	2p'	2p'	2p	2p			2.68	-198.7075	0.3474		0.66496	3.694	0.7717
2s'	2s'													
2p	2p													
2p'	2p'													
Nominal Atom Buildup														
7 x 7 x 3 x 3														
1s	1s	2p	2p	3s	3s	2p	2p	*2.68	-198.7364	0.2622	7.107	0.68199	3.704	0.7906
1s'	1s'	2p'	2p'	2p	2p			**2.68	-198.7418	0.3235	7.042	0.67562	3.699	0.7832
2s	2s	2p''	2p''	-2s	-2s									
3s	3s													
2p	2p													
2p'	2p'													
2p''	2p''													
8 x 8 x 4 x 4														
1s	1s	2p	2p	3d	3d	3d	3d							
2s	2s	2p'	2p'											
2s'	2s'	2p''	2p''					2.68	-198.7639	0.7843	6.950	0.66402	3.689	0.7817
3s	3s	3d	3d											
2p	2p													
2p'	2p'													
2p''	2p''													
3d	3d													
9 x 9 x 5 x 5														
1s	1s	2p	2p	4f	4f	4f	4f							
2s	2s	2p'	2p'											
2s'	2s'	2p''	2p''					2.68	-198.7683	0.6589	6.868	0.66290	3.689	0.7772
3s	3s	3d	3d											
2p	2p	4f	4f											
2p'	2p'													
2p''	2p''													
3d	3d													
4f	4f													
Experimental Values								2.68	-199.670	..	..	0.5990	..	..

*Straight nominal atom function (from atomic studies of Bagus and Gilbert).[17]
**Single optimization of all nominal atom zetas.

Figure 1 is a contour diagram of the total electronic charge density in the x,z plane, where the wave-function normalization is $\int \psi \psi^* dV = 2\pi N$ (where N is the number of electrons).
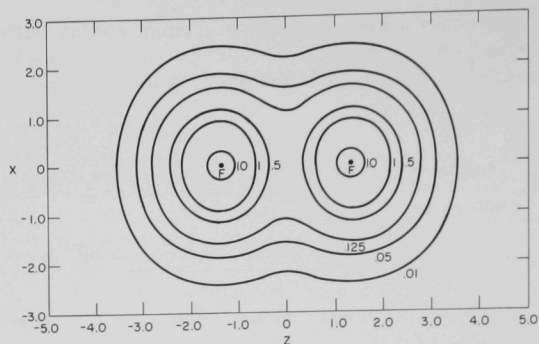
120-8254

Fig. 1. Total Molecular Charge
Density Contours for
the Fluorine Molecule

     The computed dissociation energy (D_e) is poor (in fact, of the wrong sign). Evidently the two shortcomings of the molecular wave function discussed in Section IX (namely, the increased correlation energy in the molecule and the improper description of molecular dissociation) are serious enough to mask completely the relatively small binding energy for this molecule. This failure to yield energetic binding, however, should not be considered a total condemnation of the wave function. The calculated ionization potential, internuclear distance, and the first-order spectroscopic constants show fair agreement with experiment. In addition, the binding energy is a very subtle quantity and the definition of it used in this work is a particularly hard test of the theory. Less rigorous definitions would yield almost any binding energy desired.

     In conclusion, the results obtained for the fluorine molecule are encouraging, but only through a consistent study of the Hartree-Fock-Roothaan wave function for a large series of molecules will the ultimate usefulness of this function become established. Such a study is now possible with existing "computing machinery" and is, in fact, under way. The molecular Hartree-Fock function is lower in energy than any limited configuration-mixing wave function currently available. This suggests that a next logical step is to add the one additional configuration that would lead to the proper description of the dissociation of the molecule. Significant improvement of the potential curve would then be expected, resulting in the more reliable computation of the spectroscopic constants. Hopefully studies of this sort for a series of molecules will aid in developing a set of consistent rules which will allow us to use the Hartree-Fock function more effectively without enormous computational effort. The atomic Hartree-Fock functions are necessary to evaluate efficiently the molecular Hartree-Fock function, as diatomic Hartree-Fock functions may prove to be the dominant contributors to polyatomic and ultimately solid-wave functions.

APPENDIX A

THE MANIFOLDS P AND S

The existence of a series of manifolds P, which will yield increasingly accurate results by numerical integration, is basic to the very definition of the Riemann integral. In practice, the problem is to find an optimal, small set of points that will yield results of a desired accuracy. The development of this set is a matter of experimentation guided by a knowledge of the spatial behavior of the charge distributions which appear as integrands. These distributions show their steepest variation in the region near the nuclei, thus requiring a manifold that concentrates points about the two nuclei and distributes points more diffusely as the distance in every direction from the internuclear axis increases. After experimentation with several coordinate systems, it was found that the manifold P obtained by a crossed-gaussian numerical integration over the prolate spheroidal coordinates ξ and η yielded the most satisfactory results where the inverse transformation $\xi = (1 + \beta)/(1 - \beta t)$ was employed. The parameter β was chosen to confine the manifold P inside an ellipsoid of revolution outside of which the wave function of the molecule under study is no longer computationally significant.

The manifold S, used for the numerical integration necessary for the evaluation of the exchange integrals, must concentrate points near the internuclear axis ($\xi = 1$). The inverse transformation, $\xi = 1/T$, where a Simpson-rule integration is performed over the variable T, was satisfactory. An equal-interval numerical integration procedure must be used so that the inner integrations over the variables x may be performed efficiently.[1] If the selection of the manifold S does not extend to infinity, a correction term is added to the formula, Eqs. (46), given for the $I^\ell_{p\lambda\alpha,r\mu\beta;m\nu\gamma,n\kappa\delta}$ integral. This truncation correction term is defined by

$$
T^\ell_{p\lambda\alpha,r\mu\beta;m\nu\gamma,n\kappa\delta} = 4R^{-1}\left[\sigma_\lambda + \sigma_\mu(-)^{M+\ell}\right]\left[\sigma_\nu + \sigma_\kappa(-)^{M+\ell}\right]
$$

$$
\times \frac{(\ell - M)!}{(\ell + M)!} \times (-)^M
$$

$$
\times \left[Q^M_\ell(\xi_{max})/\hat{P}^M_\ell(\xi_{max})\right] F^M_{\ell;p\lambda\alpha,r\mu\beta}(\xi_{max};\tau,\rho)
$$

$$
\times F^M_{\ell;m\nu\gamma,n\kappa\delta}(\xi_{max};\tau,\rho), \tag{60}
$$

where ξ_{max} is the finite upper limit of the ξ integration, and $Q^M_\ell(x)$ is the associated Legendre function of the second kind.[1] The analysis in Section VII was presented for the infinite upper limit of the ξ integration since the above correction complicates formulas unnecessarily while representing no real computational difficulty.

APPENDIX B

THE COMPUTER PROGRAM

1. General Considerations

A fully automatic program that computes the SCF wave function for homonuclear diatomic molecules was constructed for the IBM 7094 computer. It incorporates the features discussed previously in this paper. An SCF run using the first basis set presented in Table IV requires about 40 sec; the "final" basis set requires about 45 minutes.

The orbital exponents are varied automatically by an essentially brute-force technique, which is the same as that presented for atoms.[4] The program handles a limited number of open shell cases, among which are $\sigma_{g,u}$, $\pi_{g,u}$, $\delta_{g,u}$, $\pi_{g,u}^2$, $\delta_{g,u}^2$, $\pi_{g,u}^3$, $\delta_{g,u}^3$. The necessary α and β coefficients are presented in Table V. The homonuclear diatomic SCF program is designed to include certain open-shell configuration cases. Table V lists the vector coupling coefficients for the open-shell configuration cases now acceptable by the program. The number of basis functions permissible is determined by

$$\sum_{\lambda}\left(\frac{1}{2}\right)(N_\lambda)(N_\lambda + 1) \leq 144,$$

where N_λ is the total number of <u>symmetry</u> <u>basis</u> <u>functions</u>, Eq. (13), of symmetry λ. The restrictions on basis function quantum numbers are $1 \leq N \leq 6$, $0 \leq \ell \leq 3$, and $-\ell \leq m \leq \ell$. Experience has shown that this program is useful for obtaining near Hartree-Foch wave functions for molecular systems ranging in size from H_2 through Cl_2.

Table V

VECTOR COUPLING COEFFICIENTS FOR
HOMONUCLEAR OPEN-SHELL CONFIGURATIONS

Open-shell Case(s)	State(s)		
$\sigma_{g,u}$	$^2\Sigma_{g,u}^+$	1	$-1/2$
$\pi_{g,u}$, $\delta_{g,u}$	$^2\Pi_{g,u}$, $^2\Delta_{g,u}$	1	$-1/2$
$\pi_{g,u}^2$, $\delta_{g,u}^2$	$^3\Sigma_g^-$, $^3\Sigma_g^-$	0	$1/2$
	$^1\Delta_g$, $^1\Gamma_g$	$1/2$	$-1/2$
	$^1\Sigma_g^+$, $^1\Sigma_g^+$	1	$-3/2$
$\pi_{g,u}^3$, $\delta_{g,u}^3$	$^2\Pi_{g,u}$, $^2\Delta_{g,u}$	$1/9$	$-1/18$

2. Loading Conventions

The input to the program is specified as follows on FAP (Fortran Assembly Program) cards:

Location	Operation	Contents
10	BCD	Heading sentence. Inserted in first line of input and final output page. Also inserted in heading of each interrupt page.
20	DEC	Nuclear charge. Floating or fixed point number.
21	DEC	Internuclear separation, R. Floating point number. Up to nine R values permitted to be run consecutively.
30	DEC	Number of <u>symmetry-orbitals</u> basis functions, according to symmetry. Order is $\#\sigma_g$, $\#\sigma_u$, $\#\pi_u$, $\#\pi_g$, $\#\delta_g$, $\#\delta_u$, $\#\gamma_u$, $\#\gamma_g$. The total number of symmetry-orbitals basis functions is limited by $$\sum_\lambda \left(\frac{1}{2}\right) N_\lambda (N_\lambda + 1) \le 144,$$ where N_λ is the total number of symmetry-orbital basis functions of λ symmetry.
40	DEC	Number of closed-shell molecular <u>orbitals</u>, according to symmetry. Order is $\#\sigma_g$, $\#\sigma_u$, $\#\pi_u$, $\#\pi_g$, $\#\delta_g$, $\#\delta_u$, $\#\gamma_u$, and $\#\gamma_g$ closed shells.
50	DEC	Number of open-shell <u>electrons</u>, according to symmetry. Order is $\#\sigma_g$, $\#\sigma_u$, $\#\pi_u$, $\#\pi_g$, $\#\delta_g$, $\#\delta_u$, $\#\gamma_u$, and $\#\gamma_g$ open-shell electrons. No more than one open shell per symmetry is permitted.
60	DEC	Open-shell alpha coefficients. Listed in Table V.
80	DEC	Open-shell beta coefficients. Listed in Table V.
100	DEC	Quantum number N for symmetry-orbitals basis functions given above. Order is σ_g, σ_g', ..., σ_u, σ_u', ..., π_u, π_u', ..., π_g, π_g', ..., δ_g, δ_g', ..., δ_u, δ_u', ..., γ_u, γ_u', ..., γ_g, γ_g', ... Limit is $N \le 6$.
133	DEC	Quantum number L for symmetry-orbitals basis functions given above. Order is same as for quantum numbers N order. $L \le 3$.

Location	Operation	Contents
166	DEC	Orbital exponents for the symmetry-orbitals basis functions given above. The order coincides with that of N and L just preceding. All orbital exponents must exceed the input threshold (normally 0.100). In addition, the difference between orbital exponents for symmetry-orbitals basis functions with the same N and L value must be greater in absolute magnitude than a given threshold (also normally 0.100).
200	DEC	SCF input vectors. No more than 200 total vector components are permitted.
400	DEC	Indices of symmetry-orbitals basis functions whose orbital exponents are to be varied and mutually optimized. One, two, or three orbital exponents may be simultaneously optimized. Each set of indices must be separated by a zero. The basis functions are numbered in the order given above where the N, L, and orbital exponent values are listed. A typical variational chain might be 1, 2, 0, 3. This would specify that the orbital exponents of symmetry-orbital functions 1 and 2 are simultaneously optimized, and then the orbital exponents of symmetry-orbital function 3 is singly optimized. In preparing the coupling chains, always put the most energy-sensitive orbital exponent first in the indices.
420	DEC	Increment for the variation of the symmetry-orbitals basis functions orbital exponents. Loaded in the same manner and sequence as the indices immediately preceding, except that the increments replace the indices. If any particular increment or all the increments are not explicitly given, or if any are less than 0.001, 10% of the orbital exponent involved is employed in the variation. The set of increments is called the mesh of the variation.

SCF Convergence Control

Location	Operation	Contents
440	DEC	N Diagonalization SCF Threshold Bias. $1 \leq N \leq 5$, and normally program is set to $N = 1$.
441	DEC	N Number of SCF Extrapolations. $5 \leq N \leq 25$, and normally program is set to $N = 5$.
442	DEC	N Number of Prior SCF Extrapolations. $0 \leq N \leq 25$, and normally program is set to $N = 0$.

Location	Operation	Contents
443	DEC	N Number of Diagonalization Iterations. $5 \le N \le 25$, and normally program is set to $N = 5$.
444	DEC	Number of Locked Passes Prior to SCF. $0 \le N \le 9$, and normally program is set to $N = 0$.
445	DEC	N Maximum Number of Extrapolations. $5 \le N \le 100$, and normally program is set to $N = 50$.
446	DEC	N Extrapolation Method. $N = 1$ for Hartree-Roothaan Method, $N = 2$ for Sack Method. Normally program is set to $N = 1$.
447	DEC	N Diagonalization Method. $N = 1$ for SVDG (Single Vector Diagonalization), and $N = 2$ for Jacobi. Normally program is set to $N = 1$.
448	DEC	25 Computes expectation values of 1, $(\sin^2\theta_a)/r_a$ $(\cos^2\theta_a)/r_a$, $3z_a^2 - r_a^2$, $1/r_a$, ξ, r_a^2, z_a^2, and $x_a^2 + y_a^2$.
449	DEC	Quadratic one-dimensional exponent variation employed.

Intermediate Output Requests

Location	Operation	Contents
460	DEC	*Intermediate matrices printout. S, U, T, , and matrices are printed in format*.
461	DEC	*S-Matrix, its eigenvalues, and vectors are printed in format*.
462	DEC	*Final matrices S,H,P,Q, D-Open, D-Total, F-Open, F-Closed, R-Open, and R-Closed are printed in format*.
463	DEC	*Integrals between final orbitals, H-integrals, P-integrals. Q-integrals, and La Grangian multipliers are printed in format*.
464	DEC	*F Matrix, its eigenvalues, and vectors are printed in format*.
465	DEC	1 SCF iterations are printed.
		*Gives the printout format (always off line): If * equals 1, the output will be eight-column floating point decimal.
		If * equals 2, the output will be eight-column fixed point decimal.
466	DEC	Print final vectors of intermediate results during variation run.

Location	Operation	Contents
470	DEC	Integration truncation cutoff value in floating decimal. If omitted, a standard value is used: RTRUN = 60. This assumes no STO's are more diffuse than a hydrogen IS function.
476	DEC	Only used in <u>variation</u> runs. Number of Neumann expansion terms to be included in exchange integral calculations. The maximum number of terms permitted is $(30 - M_{max})$, after which record is kept of any exchange integral that does not meet the threshold of 10^{-6}, and computations are continued.
477	DEC	1 Save current input flag. Current input will be re-used with any modifications as read in for the next case; it does not save itself.
480	OCT	NSIMP000001. Number of Simpson's-rule points in octal. The maximum number of points is 70.
481	OCT	NPETA0000NPXI. Number of Gaussian points in octal used in the double Gaussian numerical integrations. NPETA and NPXI may take any of the values 12, 16, 20, 24, 30, or 36 points (in decimal). If no grid is specified, a 30 x 30 grid is employed.
482	DEC	1 Output flag to call for eight-column floating point decimal print-out (off line) to addends to J and K supermatrix elements for exchange and coulomb passes.
500	BCD	Symmetry symbol list, only if order of molecular orbitals departs from the order $1\,\sigma_g,\ 2\,\sigma_g,\ \dots,$ $1\,\sigma_u,\ 2\,\sigma_u,\ \dots,\ 1\,\pi_u,\ 2\,\pi_u,\ \dots,\ 1\,\pi_g,\ 2\,\pi_g,\ \dots,$ $1\,\delta_g,\ 2\,\delta_g,\ \dots,\ 1\,\delta_u,\ 2\,\delta_u,\ \dots,\ 1\,\gamma_u,\ 2\,\gamma_u,\ \dots,\ 1\,\gamma_g,$ $2\,\gamma_g,\ \dots$

3. Operating Instructions

a. To Start Any Run

1. Mount LMSS-AA-SCF No. 1 tape on B7.
2. Mount blanks on B3, B4, B5, A5, A6, and A7.
3. Mount output tape on A3.
4. Place deck in card reader headed by molecule card.
5. Clear, put SSW 1, 4, and 5 down.
6. Load cards.

Program will load cards and proceed with computation.

b. To Interrupt

1. Place SSW 3 down.
2. Within 1-60 minutes, run will stop and print out on-line interrupt sentence.
3. Unload tapes B7 and B5, and save these tapes for subsequent continuation of computation.

c. To Restart Interrupted Run

1. Mount tapes B7, and B5 saved in interrupt procedure.
2. Place blanks on B3, B4, and A3, A5, A6, and A7.
3. Place INTERRUPT-RESTART card in card reader.
4. Clear, put SSW 1, 4, and 5 down.
5. Load INTERRUPT-RESTART card.
6. Computations will be continued from interrupted point.

d. Also Note

1. Description of emergency procedure on page 40.
2. Details of interrupt output option on pages 39 and 40.
3. Channel a tape option on page 40.
4. Program STOP with END in IR 4, 5, 6, 7 lights is normal conclusion.

e. Sense Switch Controls

SSW	Function
1.	If down, program considers current input to be last case.
2.	If down, exponent variation will be terminated at current iteration, and final output page printed.
3.	If down, computation will be interrupted and tapes written for subsequent continuence of computation at point of interruption. See following paragraphs for output option at this point.
4.	If down, input is called from cards. If up, input is called from tape A2.
5.	If down, tapes A5 and A6 are used for saving and editing of two electron potentials during exponent variation. If up, tapes A5 and A6 are not used at the expense of computer time.
6.	If down, current internuclear distance in a series of values is considered as last one.

f. Interrupt

The depression of SSW 3 interrupts the current molecular computation. The computer will come to a program stop after printing an interrupt message on the one-line printer.* The stop will occur within 1-60 minutes of the time SSW 3 is pressed. Tape B5 must be saved for restarting of computations.

---

*If a full requested output at the time of interruption is desired, push SSW 3 up after the stop has occurred, and press the START button. The output will be written on tape A3, and the computer will come to a second program stop.

For restarting of interrupted computation, tape B5 should be re-mounted with program tape on B7. Blanks on B3, B4, A5, A6, and A7. Machine is cleared and interrupt restart card loaded. Computations will restart at point of interruption.*

g. Emergency Procedure

Should computations stop at an unexpected point, or should the tapes give trouble, provide new tapes as follows:**

1. Ready EMERGENCY RESTART AND RECOVERY card in reader.

2. Clear machine; load cards.

USE OF EMERGENCY PROCEDURE WILL LEAD TO A LOSS OF NO MORE THAN 60 MINUTES OF COMPUTATION.

h. Channel A Tape Option

If the heavy use of tapes A5 and A6 leads to continued difficulty after new tapes have been provided, computations may be continued less efficiently without the use of these tapes as follows:

1. Clear machine at any time other than when tape B3 is being referenced.

2. Put SSW 5 up.

3. Load EMERGENCY RESTART AND RECOVERY CARD.

ACKNOWLEDGMENT

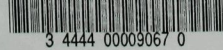*If the restart fails (very unlikely), use the emergency procedure.

**Directions will appear on on-line printer.

REFERENCES

1. A. C. Wahl, P. E. Cade, and C. C. J. Roothaan, A Study of Two Center Integrals Useful in Calculations on Molecular Structure, to be published in J. C. P.

2. C. C. J. Roothaan, Revs. Modern Phys. 23, 69 (1951).

3. C. C. J. Roothaan, Revs. Modern Phys. 32, 179 (1960).

4. C. C. J. Roothaan and P. S. Bagus, Atomic Self-Consistent Field Calculations by the Expansion Method, to be published.

5. C. C. J. Roothaan, J. Chem. Phys. 19, 1445 (1951).

6. K. Ruedenberg, C. C. J. Roothaan, and W. Jaunzemis, J. Chem. Phys. 24, 201 (1956).

7. K. Ruedenberg, J. Chem. Phys. 19, 1449 (1951).

8. C. C. J. Roothaan, J. Chem. Phys. 24, 947 (1956).

9. M. E. Rose, Elementary Theory of Angular Momentum (John Wiley and Sons, Inc., New York, 1957), Chapter III.

10. Laboratory of Molecular Structure and Spectra, The University of Chicago.

11. B. J. Ransil, Revs. Modern Phys. 32, 245 (1960).

12. J. Eve, Proc. Roy. Soc. (London), 246, 582 (1958).

13. P. E. Cade, K. D. Sales, and A. C. Wahl, The Electronic Structure of the Nitrogen Molecule, to be published.

14. W. Huo, SCF Wave Function and Computed Properties for CO and BF, Ph.D. Thesis, The University of Chicago.

15. A. C. Wahl, SCF Wave Function and Properties for Cl_2, to be published.

16. A. C. Wahl and T. L. Gilbert, A Theoretical Study of the Cl_2^- Molecule-Ion, to be published.

17. P. Bagus and T. L. Gilbert, Accurate SCF Wave Functions for First Row Atoms and Ions, to be published.