Integrals for Diatomic Molecular Calculations

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I. Introduction

IN THIS CHAPTER we wish to discuss a procedure for the computation of the integrals involving diatomic molecular wave functions composed of atomic orbitals. The most obvious use has been within the linear combination of atomic orbital-molecular orbital (LCAO-MO) scheme of theoretical calculations of molecular-energy levels of diatomic molecules. In this scheme one constructs a molecular wave function from a linear combination of simpler functions. One then finds the integral of the Hamiltonian operator between determinantal functions constructed from these molecular orbitals. This integral then gives an upper bound to the molecular energy. By variational procedures one can obtain a "best" molecular energy. This Hamiltonian integral in a diatomic molecule contains sums of integrals of the type which we wish to discuss. Rather than give a derivation of the LCAO-MO procedure which is adequately described eleswhere (Roothaan, 1951), we shall illustrate the type of problems to which the procedure has been applied. An

example of a quantum-mechanical energy calculation in a homonuclear diatomic molecules is the H_2 molecule (Aghajanian, 1957), in a heteronuclear diatomic molecule HF (Karo and Allen, 1958). These integrals also arise in more complicated molecules such as H_2O (Merrifield, 1962). The integrals have also been applied in the tight-binding method for energy bands in solids (Corbató, 1959), as well as in simple theories of magnetism (Watson and Freeman, 1961).

There are two fundamental techniques which can be used to compute two-center integrals. The first method is to express all functions in terms of spheroidal coordinates and perform analytic integrations to yield results dependent on the implicitly defined functions. These results have been extensively developed but from a computational view are quite complicated for functions with nontrivial quantum numbers (Ruedenberg, 1954). The second method, which will be the subject of this chapter, is to expand all functions in spherical coordinates about one atomic center, perform all angular integrations analytically, and do the final, double radial quadratures numerically. This method has been extensively used and partially described by Coolidge (1932), Coulson (1937), Barnett and Coulson (1951), Löwdin (1956), and Corbató (1956) and has the virtues of computational simplicity and generalization (although in a rapidly complicating way) to multicenter integrals. Multicenter integrals will not be considered here but it should be noted that for certain simple geometries, (such as the linear chain) and the planar molecules (such as the water molecule), the required multicenter integrals are particularly straightforward. For completeness, the Barnett-Coulson method, as it is often called, will be fully developed into a computational procedure without reference to earlier notations. The procedure forms the basis of programs that have been prepared by the authors for the IBM 704 and IBM 7090 computers and are generally available[1]. In particular, it is intended to give the reader sufficient information to allow him to alter, extend or reimplement the procedure on another computer.

II. Formulation

For the basic atomic orbitals, we restrict ourselves to linear combinations of analytic Slater atomic orbitals (AO's) with the same angular

[1] The IBM 704 program called MIDIAT is available from the SHARE Distribution Agency, Data Processing Division, 112 East Post Road, White Plains, N.Y. as Share Distribution No. 849, The IBM 790/90 version was adapted by Dr. Emmett Moore Jr. and Mr. Arnold Rom, of the Boeing Scientific Research Laboratories, Seattle, Washington.

quantum numbers l and m. By definition, we have for a normalized Slater AO (Slater, 1930):

$$\phi(n, l, m \mid \kappa \mid \mathbf{r}) = [N(n)]^{1/2} \cdot [L(l, m)]^{1/2} \cdot \kappa^{3/2}(\kappa r)^{n-1} e^{-\kappa r} P_l^m(\mu) \Phi_m(\varphi), \quad (1)$$

where n is the radial quantum number, l and m are angular quantum numbers, κ is the screening constant, $\mu = \cos\theta$, and

$$N(n) = \frac{2^{2n}}{(2n)!}, \quad (2)$$

$$L(l, m) = (2l + 1) \cdot \frac{(l - |m|)!}{(l + |m|)!}. \quad (3)$$

The associated Legendre functions are normalized in the usual way (where δ is the Kronecker delta function).

$$\int_{-1}^{1} P_l^m(\mu) P_j^m(\mu) \, d\mu = \delta_{lj} \cdot \frac{2}{L(l, m)}. \quad (4)$$

We also define for negative m,

$$P_l^{-m}(\mu) \equiv P_l^m(\mu). \quad (5)$$

Similarly the functions,

$$\Phi_m(\varphi) \equiv \frac{e^{im\varphi}}{\sqrt{2\pi}} \quad (6)$$

are normalized such that

$$\int_0^{2\pi} \Phi_m^*(\varphi) \Phi_j(\varphi) \, d\varphi = \delta_{mj}. \quad (7)$$

From Eqs. (2—7) the normalization of Eq. (1) immediately follows so that

$$\int \phi^*(n, l, m \mid \kappa \mid \mathbf{r}) \phi(n, l, m \mid \kappa \mid \mathbf{r}) \, d\tau = 1, \quad (8)$$

where the integral is over all space and $d\tau$ is the volume element

$$r^2 \, dr \, d\mu \, d\varphi.$$

Next we can form linear combinations of normalized Slater AO's for the kth orbital

$$\Psi_k(l_k, m_k \mid \mathbf{r}) = \sum_{i=1}^{c_k} w_{ki} \phi(n_{ki}, l_k, m_k \mid \kappa_{ki} \mid \mathbf{r}). \quad (9)$$

The expansion of a Slater AO about another center will be developed as a basic tool. We formally define the expansion of a Slater AO expressed in the primed coordinates of center O′ as a sum of functions expressed in the coordinates of center O, a distance a from center O′ as shown in Fig. 1.

$$\phi(n, l, m \mid \kappa \mid \mathbf{r}') = [L(l, m)]^{1/2} \cdot \sum_{j=|m|}^{\infty} \frac{\beta_j(n, l, m \mid \kappa \mid a \mid r)}{r} P_j^m(\mu)\, \Phi_m(\varphi)\,. \quad (10)$$

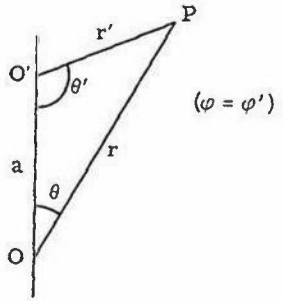

FIG. 1. Two-center coordinate system

Similarly, we define

$$\Psi(l, m \mid \mathbf{r}') = [L(l, m)]^{1/2} \cdot \sum_{j=|m|}^{\infty} \frac{\bar{\beta}_j(l, m \mid a \mid r)}{r} P_j^m(\mu)\, \Phi_m(\varphi)\,, \quad (11)$$

so that from Eq. (9) it follows that

$$\bar{\beta}_j(l_k, m_k \mid a \mid r) = \sum_{i=1}^{c_k} w_{ki}\, \beta_j(n_{ki}, l_k, m_k \mid \kappa_{ki} \mid a \mid r)\,. \quad (12)$$

For completeness, we can also write the required unexpanded functions of ϕ, ϕ/r, and $\frac{1}{2}\nabla^2\phi$ as single term sums of the form of Eq. (10) where the corresponding radial factors, β, ϵ, δ are of the form

$$\beta_i(n, l, m \mid \kappa \mid 0 \mid r)\,. \quad (13)$$

Even though the two functions ϕ/r and $\nabla^2\phi$ could be formally expanded, it is not desirable to do this since the functions are sometimes singular and, in any case, vary rapidly with r. Thus the expansions would require more significant terms and there would be increased numerical difficulties.

It is easy to confirm that

$$\beta_l(n, l, m \mid \kappa \mid 0 \mid r) = [N(n)]^{1/2} \cdot \kappa^{1/2}(\kappa r)^n e^{-\kappa r} \tag{14a}$$

$$\epsilon_l(n, l, m \mid \kappa \mid 0 \mid r) = \kappa \beta_l(n-1, l, m \mid \kappa \mid 0 \mid r) \tag{14b}$$

$$\delta_l(n, l, m \mid \kappa \mid 0 \mid r) = \kappa^2 [\beta_l(n, l, m \mid \kappa \mid 0 \mid r) - 2n \beta_l(n-1, l, m \mid \kappa \mid 0 \mid r) + (n+l)(n-l-1) \beta_l(n-2, l, m \mid \kappa \mid 0 \mid r)]. \tag{14c}$$

In general, the radial functions of the unexpanded orbitals, have the same form as Eq. (12).

In the case of Coulomb integrals and other integrals involving charge distributions, it is desirable to have expanded products of Slater AO's. We have (dropping parameters for brevity)

$$\phi_1^*(\mathbf{r}')\phi_2(\mathbf{r}') = [L(l_1, m_1) \cdot L(l_2, m_2)]^{1/2} \cdot \sum_{j=|m|}^{\infty} \frac{\gamma_j(n_1, l_1, m_1 \mid \kappa_1 \mid n_2, l_2, m_2 \mid \kappa_2 \mid a \mid r)}{r^2} P_j^m(\mu) \Phi_{m_1}^*(\varphi) \Phi_{m_2}(\varphi), \tag{15}$$

where $m = \mid m_1 - m_2 \mid$.

In a fashion analogous to the β functions for the orbital Ψ the $\bar{\gamma}$ expansion function can by Eq. (9) be written as a sum over the expansion functions for the components

$$\bar{\gamma}_j(l_1, m_1 \mid l_2, m_2 \mid a \mid r) = \sum_{k=1}^{c_1} \sum_{i=1}^{c_2} w_{1k} w_{2i} \gamma(n_{1k}, l_1, m_1 \mid \kappa_{1k} \mid n_{2i}, l_2, m_2 \mid \kappa_{2i} \mid a \mid r), \tag{16}$$

where the expansion of $\Psi_1^* \Psi_2$ is of the same form as Eq. (15).

We next introduce the expansion of a product of Legendre functions ($m_1, m_2 > 0$),

$$P_{l_1}^{m_1}(\mu) P_{l_2}^{m_2}(\mu) = \sum_{j=|l_1-l_2|}^{l_1+l_2} D(j, l_1, m_1, l_2, m_2) P_j^m(\mu), \tag{17}$$

where $m = \mid m_1 - m_2 \mid$.

The D coefficients are essentially Gaunt coefficients (Gaunt, 1929). The numerical generation techniques are developed at length in a later section. The important properties of the D coefficents are

1. They vanish unless the indices l_1, l_2, j obey the triangle rule;
2. They are zero for all j with opposite parity to $l_1 + l_2$;
3. They vanish if $j < \mid m \mid$, $l_1 < \mid m_1 \mid$, or $l_2 < \mid m_2 \mid$.

The above Eqs. (15) and (17) also allow us to write the unexpanded radial density function as

$$\bar{\gamma}_j(l_1, m_1 \mid l_2, m_2 \mid 0 \mid r) = D(j, l_1, m_1, l_2, m_2) \cdot \bar{\beta}_{l_1}(l_1, m_1 \mid 0 \mid r)\, \bar{\beta}_{l_2}(l_2, m_2 \mid 0 \mid r), \quad (18)$$

where it is noted that the j dependence is only in the coefficient D. A straightforward derivation for the γ functions used in Eq. (16) leads one to the expression,

$$\gamma_j(n_1, l_1, m_1 \mid \kappa_1 \mid n_2, l_2, m_2 \mid \kappa_2 \mid a \mid r) = \left[\frac{N(n_1)\, N(n_2)}{N(n_1 + n_2 - 1)}\right]^{1/2} \cdot \frac{{\kappa_1}^{n_1+1/2}\, {\kappa_2}^{n_2+1/2}}{(\kappa_1 + \kappa_2)^{n_1+n_2-1/2}} \cdot \sum_{p=|l_1-l_2|}^{l_1+l_2} D(p, l_1, m_1, l_2, m_2)\, \beta_j(n_1 + n_2 - 1, p, m \mid \kappa_1 + \kappa_2 \mid a \mid r), \quad (19)$$

where $m = |\, m_1 - m_2 \,|$.

The preceding forms allow us to proceed with the development of the necessary one- and two-electron integrals. We first illustrate the technique with the overlap integral,

$$S_{12} = \int \Psi_1^*(\mathbf{r})\, \Psi_2(\mathbf{r}')\, d\tau = [L(l_1, m_1) \cdot L(l_2, m_2)]^{1/2} \cdot \int_0^\infty dr \int_{-1}^1 d\mu \int_0^{2\pi} d\varphi\, \bar{\beta}_{l_1}(l_1, m_1 \mid 0 \mid r)\, P_{l_1}^{m_1}(\mu) \cdot \Phi_{m_1}^*(\varphi) \cdot \sum_{j=|m_2|}^{\infty} \bar{\beta}_j(l_2, m_2 \mid a \mid r)\, P_j^{m_2}(\mu)\, \Phi_{m_2}(\varphi), \quad (20)$$

performing the φ integration introduces a δ_{m_1,m_2}; performing the μ integration gives a factor of $\delta_{l_1,j}$ and normalization. Hence, if we introduce the notation

$$\langle \bar{\beta}_{l_1} \mid \bar{\beta}'_{l_1} \rangle \equiv \int_0^\infty \bar{\beta}_{l_1}(l_1, m_1 \mid 0 \mid r)\, \bar{\beta}_{l_1}(l_2, m_2 \mid a \mid r)\, dr, \quad (21)$$

where the prime indicates expansion of a function on the primed center, we have

$$S_{12} = 2\, \delta_{m_1,m_2} \left[\frac{L(l_2, m_2)}{L(l_1, m_1)}\right]^{1/2} \langle \bar{\beta}_{l_1} \mid \bar{\beta}'_{l_1} \rangle. \quad (22)$$

This closed expression result is characteristic of the method for all but

the two-center exchange integral. Similar relations hold for the kinetic energy, split nuclear attraction, and nuclear attraction integrals.

$$K_{12} = 2\,\delta_{m_1,m_2}\left[\frac{L(l_2, m_2)}{L(l_1, m_1)}\right]^{1/2} \langle \delta_{l_1} \mid \bar{\beta}'_{l_1} \rangle \tag{23}$$

$$N_{12} = 2\,\delta_{m_1,m_2}\left[\frac{L(l_2, m_2)}{L(l_1, m_1)}\right]^{1/2} \langle \bar{\epsilon}_{l_1} \mid \bar{\beta}'_{l_1} \rangle \tag{24}$$

$$A_{12} = 2\,\delta_{m_1,m_2}\left[\frac{L(l_1, m_1)\,L(l_2, m_2)}{L(0, 0)}\right]^{1/2} \langle r^{-1} \mid \bar{\gamma}'_0 \rangle \tag{25}$$

where

$$\langle r^{-1} \mid \bar{\gamma}'_0 \rangle = \int_0^\infty \frac{\bar{\gamma}_0(l_1, m_1 \mid l_2, m_2 \mid a \mid r)}{r}\, dr\,. \tag{26}$$

We note that the above forms are sufficient since interchanging the roles of the centers (that is, expanding the orbitals on the opposite center) allow us to compute all possible one-electron integrals.

In order to treat the two-electron cases, we note the expansion of $r_{12} = |\,\mathbf{r}_1 - \mathbf{r}_2\,|$ given by Condon and Shortley (1952).

$$\frac{1}{r_{12}} = \sum_{j=0}^{\infty} \sum_{m=-j}^{j} \frac{(r_<)^j}{(r_>)^{j+1}} \frac{L(j, m)}{(2j+1)} P_j^m(\mu_1)\, P_j^m(\mu_2) \exp im\,(\varphi_1 - \varphi_2)\,, \tag{27}$$

where $r_<$ and $r_>$ are the lesser and greater of r_1 and r_2, respectively.

As the first case, let us consider the two-center exchange integral,

$$\begin{aligned} I_{1234} &= \iint \Psi_1^*(\mathbf{r}_1)\, \Psi_2(\mathbf{r}_1')\left[\frac{1}{r_{12}}\right] \Psi_3^*(\mathbf{r}_2)\, \Psi_4(\mathbf{r}_2')\, d\tau_1\, d\tau_2 \\ &= [L(l_1, m_1)\,L(l_2, m_2)\,L(l_3, m_3)\,L(l_4, m_4)]^{1/2} \int_0^\infty dr_1 \int_0^\infty dr_2 \int_{-1}^{1} d\mu_1 \int_{-1}^{1} d\mu_2 \\ &\cdot \int_0^{2\pi} d\varphi_1 \int_0^{2\pi} d\varphi_2\, \bar{\beta}_{l_1}(l_1, m_1 \mid 0 \mid r_1)\, P_{l_1}^{m_1}(\mu_1)\, \Phi_{m_1}^*(\varphi_1) \cdot \sum_p \bar{\beta}_p(l_2, m_2 \mid a \mid r_1) \\ &\cdot P_p^{m_2}(\mu_1)\, \Phi_{m_2}(\varphi_1) \cdot \sum_{j=0}^{\infty} \sum_{m=-j}^{j} \frac{(r_<)^j}{(r_>)^{j+1}} \frac{L(j, m)}{(2j+1)} P_j^m(\mu_1)\, P_j^m(\mu_2) \exp im(\varphi_1 - \varphi_2) \\ &\cdot \bar{\beta}_{l_3}(l_3, m_3 \mid 0 \mid r_2)\, P_{l_3}^{m_3}(\mu_2)\, \Phi_{m_3}^*(\varphi_2) \\ &\cdot \sum_q \bar{\beta}_q(l_4, m_4 \mid a \mid r_2)\, P_q^{m_4}(\mu_2)\, \Phi_{m_4}(\varphi_2)\,. \end{aligned} \tag{28}$$

Performing the φ_1 and φ_2 integrations introduces $\delta_{m_1-m_2,\, m_4-m_3}$ so that if $m = |\, m_1 - m_2\,|$, we have, after expanding the products of Legendre functions,

$$I_{1234} = \delta_{m_1-m_2,m_4-m_3}\,[L(l_1, m_1)\,L(l_2, m_2)\,L(l_3, m_3)\,L(l_4, m_4)]^{1/2}$$

$$\cdot \sum_j \sum_p \sum_q \int_0^\infty dr_1 \int_0^\infty dr_2 \int_{-1}^1 d\mu_1 \int_{-1}^1 d\mu_2\, \bar{\beta}_{l_1}(l_1, m_1 \mid 0 \mid r_1)\, \bar{\beta}_p(l_2, m_2 \mid a \mid r_1)$$

$$\cdot\, \bar{\beta}_{l_3}(l_3, m_3 \mid 0 \mid r_2)\, \bar{\beta}_q(l_4, m_4 \mid a \mid r_2)\, \frac{L(j, m)}{(2j+1)} \sum_t D(t, l_1, m_1, p, m_2)$$

$$\cdot\, P_t^m(\mu_1)\, P_j^m(\mu_1) \sum_s D(s, l_3, m_3, q, m_4)\, P_s^m(\mu_2)\, P_j^m(\mu_2)\,. \tag{29}$$

Finally performing the μ_1 and μ_2 integrations, we have

$$I_{1234} = 4\,\delta_{m_1-m_2,m_4-m_3}\,[L(l_1, m_1)\,L(l_2, m_2)\,L(l_3, m_3)\,L(l_4, m_4)]^{1/2}$$

$$\cdot \sum_j \sum_p \sum_q \frac{(2j+1)\, D(j, l_1, m_1, p, m_2)\, D(j, l_3, m_3, q, m_4)}{L(j, m)}$$

$$\cdot\, \langle \bar{\beta}_{l_1}, \bar{\beta}_p' \mid j \mid \bar{\beta}_{l_3}, \bar{\beta}_q' \rangle\,, \tag{30}$$

where

$$\langle \bar{\beta}_{l_1}, \bar{\beta}_p' \mid j \mid \bar{\beta}_{l_3}, \bar{\beta}_q' \rangle = \int_0^\infty dr_1 \int_0^\infty dr_2 \bar{\beta}_{l_1}(l_1, m_1 \mid 0 \mid r_1)\, \bar{\beta}_p(l_2, m_2 \mid a \mid r_1)$$

$$\cdot\, \frac{r_<^{\,j}}{r_>^{\,j+1}}\, \bar{\beta}_{l_3}(l_3, m_3 \mid 0 \mid r_2)\, \bar{\beta}_q(l_4, m_4 \mid a \mid r_2)\,. \tag{31}$$

The satellite sums over p and q are finite as a result of the D coefficients with at most $(2\,l_1 + 1)\,(2\,l_3 + 1)$ terms.
The sum over j is from m to ∞, but by virtue of the convergence of the expansions, a moderate number of terms, $J_{\max}$, is usually sufficient.

To obtain the hybrid integrals we merely note that changing the second orbital of Eq. (28) to the unexpanded center causes the $\bar{\beta}_p$ to vanish except when p is l_2, thus eliminating the sum over p. By continuing this line of argument the one-center case is obtained where q takes on only the value l_4. In both the hybrid and one-center case the sum over j is finite as a result of the D coefficients.

The Coulomb case can be quickly derived from the hybrid result if $\bar{\beta}_q$ is replaced by $\bar{\gamma}_q$ and $\bar{\beta}_{l_3}$ is replaced by a unit function with effective $l_3 = 0$, $m_3 = 0$.

TABLE I

TWO-ELECTRON INTEGRAL SUMMATION LIMITS

Integral type	j min	j max	p min	p max	q min	q max
One-center	max ($\lvert l_1 - l_2 \rvert$, $\lvert l_3 - l_4 \rvert$, m)	min ($l_1 + l_2$, $l_3 + l_4$)	l_2	l_2	l_4	l_1
Hybrid	max ($\lvert l_1 - l_2 \rvert$, m)	$l_1 + l_2$	l_2	l_2	$\lvert j - l_3 \rvert$	$j + l_3$
Coulomb	max ($\lvert l_1 - l_2 \rvert$, m)	$l_1 + l_2$	l_2	l_2	j	j
Exchange	m	J_{max}	$\lvert j - l_1 \rvert$	$j + l_1$	$\lvert j - l_3 \rvert$	$j + l_3$

Since

$$D(j, 0, 0, q, m_4) = \delta_{j,q}\,, \tag{32}$$

it follows that the Coulomb integral is of the same form as the exchange except that the sum over p and q are of only one term and the radial integral is

$$\langle \bar{\beta}_{l_1}, \bar{\beta}_{l_2} \mid j \mid \bar{\gamma}_j' \rangle = \int_0^\infty dr_1 \int_0^\infty dr_2\, \bar{\beta}_{l_1}(l_1, m_1 \mid 0 \mid r_1)\, \bar{\beta}_{l_2}(l_2, m_2 \mid 0 \mid r_1)\, \frac{r_<^j}{r_>^{j+1}}$$
$$\cdot\, \bar{\gamma}_j(l_1, m_1 \mid l_2, m_2 \mid a \mid r_2)\,. \tag{33}$$

The above results are summarized in Table I.

The above Eqs. (22-25) and (30) for one- and two-electron integrals are the desired formulas which must be evaluated. Thus the integral problem has been reduced to one of generating the $\bar{\beta}$ and $\bar{\gamma}$ functions, generating the D coefficients, performing the indicated numerical quadratures, and the bookkeeping procedures for the cycling over all nonredundant orbital combinations. We will take up each of these processes in turn.

Before taking up the detailed, numerical techniques, we shall discuss the over-all philosophy and organization of the computer program designed to calculate all the required integrals between sets of orbitals located on the two atomic centers.

III. Organization

In designing the computer program that was written using the foregoing techniques for the computation of a collection of two-center integrals, certain properties were felt to be highly desirable. On one hand, the complete set of required integrals should be automatically calculated as soon as the physical orbitals and integral types were specified. On the other hand, whenever there was uncertainty in the method, such as in the accuracy of the numerical quadratures or in the number of terms in the infinite exchange series, an improved-meshand a last term descrepancy greater than a threshold value were offered as an attention signal for user inspection. No attempt was made to provide elaborate (but not rigorous) procedures for getting integrals automatically to a given accuracy; rather the user's judgment was retained. Similarly, in anticipation of future improvements and general ease of programming the program was kept carefully compartmentalized in separately translated subprograms with simplicity being the keynote throughout.

The bulk of the subprograms were written in the Fortran II language

of the IBM 704, 709, and 7090 computers with only a few of the subprograms and the library input-output subprograms being in machine language (SAP or FAP). To avoid excessively long, calling sequences between subprograms, all of the physical input values as well as several table areas were organized in the COMMON storage area known implicitly to all subprograms.

Because of the desire for simplicity, the calculation was organized into two major sections each of which contained several stages (a special loader for this purpose was written for the 704; CHAIN links were used in the 709/7090 version). The first section consisted of (1) reading in all input parameters and checking for absurdities, (2) generating and storing on magnetic tape all required $\bar{\beta}$ functions for the finest mesh required, (3) similarly generating all the $\bar{\gamma}$ functions required, (4) replicating the function tape several times to form a set of identical function tapes (for the purposes of time-efficient function retrieval and precaution against tape malfunctions as explained below) and (5) generating in core memory the frequently required tables of powers of r. (For time-efficiency when restarting a partially completed calculation, the user could if desired, supply a previously generated function tape and skip steps (2) and (3).)

The second section of the program proceeded to calculate selectively according to user specification the various types of integrals: overlap, nuclear attraction, split-nuclear attraction, kinetic energy, Coulomb, hybrid, and exchange. A principle feature of this section was the deliberate decoupling of computation from function retrieval. This was done for two reasons: (1) to minimize the amount of reprogramming required if the form of secondary storage changed (e.g. disk units for tape units) and (2) to allow the programming simplicity of an apparently random-access secondary memory.

The function retrieval subprogram GETFUN, upon being called for a function, looked up in the function directory (kept in core memory at all times) the location of the nearest copy on one of the multiple function tapes. By consulting its function-tape position-table, the subprogram selected the tape requiring the least time to position and read in the function. A very useful byproduct of this procedure was the ability to carry on the calculation in spite of faulty function tapes or tape drives since upon repeated reading trouble with a tape, the only step required is to make an entry in the tape-position-table indicating the tape to be grossly out-of-position for reading. However, because computational speed could be seriously affected, the user was kept of informed of these function-tape drop-outs.

The other major feature of the second section is the pattern for the

selection of the integrals to be calculated. Redundant calculation would be performed if no effort were made to use symmetry properly. This topic is taken up in a subsequent section.

To illustrate the program organization we give the list of important subroutines and their function, and the approximate sequence and hierarchy of operation.

DIATOM- Primary control sequence for integral program

READ— read in calculation parameters and orbital specifications

PRE— scan input for errors

PRER— generate radial mesh

GENBEU— generate and write on tape required unexpanded, $\bar{\beta}$ functions

GENBEX— generate and write on tape required expanded $\bar{\beta}$ functions

BETAFN— calculate β function

GENIN— calculate $i_N(x)$

GENKN— calculate $k_N(x)$

FNORM— calculate $[N(n)]^{1/2}$

FACTOR- calculate $L(l, m)$

GENGMX— generate and write on tape the required $\bar{\gamma}$ functions

DCOE— calculate $D(j, l_1, m_1, l_2, m_2)$

MID— duplicate function tape including function directories

RGEN— calculate r^j and dr/dt

CALC1E— calculate the desired one-electron integrals

CALC2E— calculate the desired two-electron integrals

GETFUN— retrieve desired function from tape

DOUBLE— form double integrand

SINGLE— form single integrand

INDEFI— perform indefinite integration

DEFINT— perform definite integration

PRINT— indentify and print integral

IV. Generation of β Functions

The basic attack on this aspect of the problem is to use an expansion given by Watson (Watson, 1952) in terms of the spherical Bessel functions

$$\frac{e^{-\kappa r'}}{\kappa r'} = \sum_{j=0}^{\infty} (2j+1)\, i_j\, k_j\, P_j(\mu)\,, \tag{34}$$

where $i_j = i_j(\sigma)$, $k_j = k_j(\rho)$ and σ and ρ are the lesser and greater, respectively, of κa and κr.

By differentiating with respect to κ, a second expression can be developed which we cast in the numerically accurate form

$$\epsilon^{-\kappa r'} = \sum_{j=0}^{\infty} (2j+1)\,[\rho\, i_j\, k_{j-1} - \sigma\, i_{j+1}\, k_j]\, P_j(\mu)\,. \tag{35}$$

From these expressions, the definition of Slater AO's and the $\beta(n, l, m)$ functions (where the arguments κ, a, and r have been dropped for brevity) it follows that

$$\beta_j(0, 0, 0) = \kappa^{1/2}(2j+1)\,(\kappa r)\, i_j\, k_j\,, \tag{36}$$

$$\beta_j(1, 0, 0) = \sqrt{2}\,\kappa^{1/2}(2j+1)\,(\kappa r)\,[\rho\, i_j\, k_{j-1} - \sigma\, i_{j+1}\, k_j]\,. \tag{37}$$

To build up β functions of higher quantum numbers, it is useful to develop a recursive procedure. We note the following geometric relationships from Fig. 1

$$(r')^2 = a^2 + r^2 - 2ar\cos\theta \tag{38}$$

$$r'\cos\theta' = a - r\cos\theta \tag{39}$$

$$r'\sin\theta' = r\sin\theta\,. \tag{40}$$

On defining the operators U_j and L_j as

$$U_j\beta_j(n, l, m) = \beta_{j+1}(n, l, m), \tag{41}$$

$$L_j\beta_j(n, l, m) = \beta_{j-1}(n, l, m), \tag{42}$$

and the operators X_j, Z_j, and R_j^2 as

$$X_j = \frac{\kappa r}{(2j+1)}\,[L_j - U_j] \tag{43}$$

$$Z_j = \kappa a - \frac{\kappa r}{(2j+1)}\,[(j - |m|)L_j + (j + |m| + 1)\,U_j] \tag{44}$$

$$R_j^2 = (\kappa a)^2 + (\kappa r)^2 - \frac{2(\kappa a)(\kappa r)}{(2j+1)}\,[(j - |m|)L_j + (j + |m| + 1)\,U_j], \tag{45}$$

then, by virtue of Eqs (38-40) and the properties of the $P_j^m(\mu)$,

$$\beta_j(n+2, l, m) = R_j^2\, \beta_j(n, l, m), \tag{46}$$

$$\beta_j(n+1, l+1, l+1) = (2l+1)\, X_j \beta_j(n, l, l), \tag{47}$$

$$\beta_j(n+1, l+1, m) = \left[\frac{2l+1}{l-|m|+1}\right] Z_j \beta_j(n, l, m) - \left[\frac{l+|m|}{l-|m|+1}\right] R_j^2 \beta_j(n-1, l-1, m). \tag{48}$$

In the last relation $\beta(n-1, l-1, l)$ is taken to be zero.

The recursion scheme is as follows. The set $\beta_j(0, 0, 0)$ or $\beta_j(1, 0, 0)$ is formed from tables of i_j and k_j depending on whether $(n-l)$ is even or odd, respectively, for the $J_{\max}$ required values plus $[(n+l)/2]$ extra values where brackets designate "the integral part of." We apply the operator, R_j^2, $[(n-l)/2]$ times until $\beta_j(n-l, 0, 0)$ is reached. We then apply the operator, $(2l+1)\ X_j$, $|m|$ times until $\beta_j(n-l+|m|, |m|, |m|)$ is reached. Finally we apply the last relation $(l-|m|)$ times until the desired $\beta_j(n, l, m)$ is reached. This scheme appears successful with the loss of about one binary digit per recursion. As a check on the recursion relations one can calculate normalization integrals the "hard-way," i.e., by expanding both orbitals. This procedure has been done for all orbitals up through $n = 4$, $l = 3$, $m = \pm 3$. In an eight-significant-figure machine, five-figure accuracy was obtained after numerical integration and summing 25 terms.

The two basic $\beta_j(0, 0, 0)$ and $\beta_j(1, 0, 0)$ functions are constructed from products of spherical Bessel functions of imaginary argument, $i_j(\sigma)$ and $k_j(\rho)$, where σ and ρ are the lesser and greater of κa and κr. We therefore need $i_j(x)$, $0 \leqslant x \leqslant \kappa a$ and $k_j(x)$, $\kappa a \leqslant x \leqslant \infty$ for j up to some $J_{\max}$ determined from Table I. The spherical Bessel functions of imaginary argument (Corbató and Uretsky, 1959) can be defined by the recurrence relations as

$$i_{n+1}(x) = i_{n-1}(x) - \left(\frac{2n+1}{x}\right) i_n(x) \tag{49}$$

$$k_{n+1}(x) = k_{n-1}(x) + \left(\frac{2n+1}{x}\right) k_n(x), \tag{50}$$

and have the values for order 0 and 1,

$$i_0(x) = \frac{\sinh(x)}{x}, \qquad i_1(x) = \frac{\cosh x}{x} - \frac{\sinh x}{x^2} \tag{51}$$

$$k_0(x) = \frac{e^{-x}}{x}, \qquad k_1(x) = \frac{e^{-x}}{x}\left[1 + \frac{1}{x}\right]. \tag{52}$$

For generation of functions of the second kind, k_n, it is clear from the recurrence relation that upward recursion will result in no major loss of accuracy. Since for our purposes the argument of $k_n(x)$ is ρ the greater of κr or the internuclear separation κa, for $x > 87.4$, in the IBM 7090 computer, the usual single-precision floating-point exponential subprogram underflows and yields a zero value for the function. In order to maintain greater accuracy the function $\hat{k}_n = e^x k_n$ is calculated using the above recurrence relations and the starting values of $\hat{k}_0(x) = x^{-1}$ and $\hat{k}_1(x) = [1 + x^{-1}]$.

For the functions i_n, upward recursion will also suffice in the region of $x > 4n + 2$ since $(2n + 1)x^{-1}i_n < \frac{1}{2} i_{n-1}$ and at most there will be a loss of one binary figure in each recurrence cycle, a result comparable to the truncation and round-off error. For $x < 4n + 2$ upward recursion will result in significant loss of accuracy and some other method must be used. An obvious approach would be to evaluate i_N and i_{N-1} for some large N and use downward recursion with no loss of numerical accuracy. Examination of the power series for i_N shows that for $x \cong 4N + 2$, for large N, convergence is very poor and this technique is unsatisfactory. An alternative procedure for generation of spherical Bessel functions is described by Miller (1952). This technique avoids the loss of significant figures with the function of the first kind, i_n, in the region $x < 4N + 2$. The method consists of assuming the unnormalized approximate values $i_\nu = 0$, $i_{\nu-1} = 1$ for ν sufficiently greater than N such that downward recursion of the ratios, $r_n = i_n/i_{n-1}$ yields the correct ratios of the i_n/i_{n-1} for $n \leqslant N$. From the Wronskian it can be shown that

$$i_0(x) = e^{|x|}/(1 + |x| + xr_0)\,. \tag{53}$$

With this normalization and the correct ratios the correct values of the i_n may be obtained. One expression for ν is

$$\nu = N' + \lambda(A + Bu')$$

where

$$\lambda = \text{binary significant figures desired for } n \leqslant N$$

$$u' = 2x/(2N' + 1)$$

$$N' = \text{greater of } N \text{ or } [\lambda Bx]^{1/2}$$

$$\text{and } A = 0.10,\ B = 0.35\,. \tag{54}$$

Again the actual functions calculated in a computer are

$$i_n(x) = e^{-x}\, i_n(x)\,, \tag{55}$$

so that the β functions can be calculated without underflow or overflow.

Following this procedure the required $i_n(\sigma)$ and $k_n(\rho)$ are generated for the required arguments. These are then used to form the initial β functions $\beta_j(000$, or $\beta_j(100)$. Then following the recursion scheme outlined above, the desired $\beta_j(n, l, m)$ are formed and from these the $\beta_j(l, m)$ representing the expansion of an orbital are written on the master function tape.

Similarly using the Eq. (19) the expansion function $\bar{\gamma}_j(l_1,m_1 \mid l_2, m_2)$ representing the expansion of a product of two orbitals, a charge density, are formed and stored on tape.

V. Generation of D Coefficients

Repeating the definition of the D coefficients, we have

$$P_i^m(\mu)\, P_j^n(\mu) = \sum_k D(k, i, m, j, n)\, P_k^{|m-n|}(\mu)\,. \tag{56}$$

The nonvanishing D are given as

$$D(k, i, m, j, n) = (-1)^{g+l+m'}\ (2k+1) \cdot \frac{(k - |\, m_1 - m_2\,|)!}{(k + |\, m_1 - m_2\,|)!}$$

$$\cdot \frac{g!\,(2g-2l')!\,(l'+m')!\,(l+m)!}{(g-l)!\,(g-l')!\,(g-l'')!\,(2g+1)!\,(l-m)!}$$

$$\cdot \sum_t (-1)^t \frac{(l''+m''+t)!\,(l+l'-m''-t)!}{(l''-m''-t)!\,(l'-m'-t)!\,(l-l'+m''+t)!\,t!}\,, \tag{57}$$

where $i, j > 0$; $g = 1/2(i+j+k)$ and an integer, and $|i-j| \leqslant k \leqslant i+j$. m'', m', m are such that m'' is the largest member of the triplet, $|\, m\,|$, $|\, n\,|$, and $|\, m-n\,|$ and l'', l', l are the corresponding members of the triplet i, j, k; the sum over t is to be taken over all terms involving nonnegative factorials.

Although recursion formulas exist, it is of great advantage in the organization of a computer program to be able to obtain coefficients in any arbitrary sequence. For that reason it is desirable to evaluate directly the above formula for the D coefficients.

Computation involving factorials in a digital computer has various hazards. Foremost of the hazards is the rapid build up with argument n, for example, $10! \sim 10^6$, $20! \sim 10^8$. Clearly a fixed-point representation will not suffice to avoid overflow except for trivial values of n; a floating-point representation will offer a short-lived reprieve from range overflow but will contain a limited number of significant figures.

For most purposes computing indirectly with a "compression function"

such as the logarithm will eliminate range-overflow problems; however the accuracy at best will be limited since the error produced by the $n - 2$ additions required to form log $(n!)$ will be the sum of the errors in the individual logarithms of the integers plus round-off error and will be transmitted through the exponential function to the result. These accuracy limitations are usually not a problem when the terms involving factorials all have like signs and no cancellations occur. Since the D coefficients contain terms involving rational fractions of factorials of like magnitude and alternating sign, unless full accuracy is preserved highly inaccurate answers may be obtained.

One may take recourse to multiple precision arithmetic with its consequent slowness but we will describe a technique which is well suited for the evaluation of the D coefficients (Corbató, 1961).

Specifically the technique consists of using a special representation for terms computed as rational fractions of factorials. Each term of value V is associated with an exponent table T of integer entries: $e(i)$, $i = 1, 2, \ldots, N$ where the location of the first entry $e(1)$, is the address T, and the value of the term is

$$V = \prod_{i=1}^{N} i^{e(i)} . \tag{58}$$

Multiplication (or division) of a term by an integer j in this representation is therefore just the addition (or subtraction) of a one from the entry $e(j)$. Because the modern digital computer has fast logic and fixed-point addition, multiplication or division by factorials in this representation is a relatively efficient process. To sum several terms, for example

$$S = \sum_{j=1}^{J} (-1)^j V_j , \tag{59}$$

the procedure is to make a preliminary exponent table T_j of each term to determine the highest common factor (HCF) of the J terms. Next each term divided by the HCF is computed directly as an exponent table with value V_j. Finally the necessary summation is made of the signed V_j, and the result multiplied and divided by the numerator and denominator, of the HCF, respectively.

The preceding computational process can be efficiently accomplished with six subprograms with names, program parameters, and specifications as follows: The symbol " $\rightarrow$ " means "replaces" and "N" when used as a program parameter designates "the address of the word containing N", etc. (Strictly speaking these two uses of N should be disting-

uished, but no ambiguity should arise from this convenient dual FORTRAN-like use of symbols.)

1. SET (N, T, s). Set Table T so that $s \to e(j)$ for $j = 1, 2, \ldots N$.

2. MULT (N, T, a, b). Multiply value of Table T by $(a!)/(b!)$ such that if $a = b$, Table T is unchanged; if $a > b$, $e(j) + 1 \to e(j), j = b + 1, b + 2, \ldots, a$; if $a < b$, $e(j) - 1 \to e(j), j = a + 1, a + 2, \ldots, b$. Give error procedure if max $(a, b) > N$, if a or b less than zero, or if an exponent exceeds integer capacity of a table entry.

3. HCF(N, T_1, T_2). Compare entries of table T_1 with corresponding entries of table T_2, setting the algebraically smaller entry in T_2, zero in T_1. Hence, min $(e_1(j), e_2(j)) \to e_2(j)$, $0 \to e_1(j), j = 1, 2, \ldots N$.

4. PRIME(N,T). Reduce nonprime entries of T to zero by successive factorization. Thus if j is prime, $e(j) \to e(j)$ or if j has factors i, k such that $j = ik$ then $e(i) + e(j) \to e(i)$, $e(k) + e(j) \to e(k)$, $0 \to e(j)$, for the sequence $j = N, N - 1, \ldots 1$. Use one (or two) auxiliary tables (which if two may be packed into one table in some computers) with entries i and/or k or a zero entry if j is prime for $j = 1, 2, \ldots M$. Give error procedure if $N > M$ or if any table entry capacities are exceeded.

5. COPYN(N, T_1, T_2). Copy negative of entries of table T_2 into table T_1 such that $-e_2(j) \to e_1(j), j = 1, 2, \ldots, N$.

6. VALUE(N, T, V, r). Evaluate numerator or denominator, V, of table T according to the sign of r. Thus

$$V = \prod_{j=1}^{N} i^{f(i)},$$

where $f(i) = \max(e(i), 0)$ if $r > 0$; or $f(i) = \min(e(i), 0)$ if $r < 0$. (60)

Give error procedure if V is too large to be represented exactly.

Finally one more subprogram can be written which allows results to be given as rational fractions of prime factors. This somewhat inefficient subprogram is

7. FACTR(N, T, V). Multiply table T by prime factors of V by the following procedure. Let $V \to W$; then $e(j) + k \to e(j)$ where k is the largest integer giving a zero remainder for $W/(j)^k$; make the replacement $W/(j)^k \to W$ for successive values $j = 1, 2, \ldots, N$ or as long as $W > 1$. For space efficiency use the same auxiliary table(s) as in the subprogram PRIME to determine primes, giving error procedure if $N > M$. Give error procedure if in factoring, any table entry capacities are exceeded. If the step for $j = N$ is completed and $W > 1$, an error procedure should also be given.

To illustrate the use of the above subprograms, the following set of steps evaluate the formula

$$s(a, b, c, d) = 10d! \sum_t (-1)^{a+b+c+t} \frac{(a-t)!\,(b-t)!}{(c+t)!}, \tag{61}$$

where a, b, c, d are positive integers and the sum is over all integral values of t yielding nonnegative factorials.

1. $0 \rightarrow S$.
2. $-c \rightarrow t_{\min}$, $\min(a, b) \rightarrow t_{\max}$.
3. $\max(a - t_{\min}, b - t_{\min}, c + t_{\max}, d, 10) \rightarrow N$.
4. If $t_{\min} \leqslant t_{\max}$, $t_{\min} \rightarrow t$; if not, go to step 25.
5. Use subprogram SET(N, T_2, q) where q is the largest positive integer which can be stored as a table entry. Use subprogram SET(N, T_1, 0).
6. Use subprogram MULT(N, T_1, $a - t$, $c + t$).
7. Use subprogram MULT(N, T_1, $b - t$, 1).
8. Use subprogram PRIME (N, T_1) to reduce table T_1 to prime entries.
9. Use subprogram HCF(N, T_1, T_2) to place current HCF in table T_2 and to clear table T_1.
10. $t + 1 \rightarrow t$; go to step 6 if $t \leqslant t_{\max}$; go to step 11 if $t > t_{\max}$.
11. $0 \rightarrow S$, $t_{\min} \rightarrow t$.
12. Use subprogram COPYN (N, T_1, T_2) to place reciprocal of HCF in table T_1.
13. Use subprogram MULT(N, T_1, $a - t$, $c + t$).
14. Use subprogram MULT(N, T_1, $b - t$, 1).
15. Use subprogram PRIME(N, T_1).
16. Use subprogram VALUE(N, T_1, V, + 1) to obtain V
17. $V - S \rightarrow S$.
18. $t + 1 \rightarrow t$; go to step 12 if $t \leqslant t_{\max}$; go to step 19, if $t > t_{\max}$.
19. Use subprogram MULT(N, T_2, 10, 1).
20. Use subprogram MULT(N, T_2, d, 1).
21. Use subprogram PRIME (N, T_2).
22. Use subprogram VALUE(N, T_2, A, + 1) to obtain A as numerator of 10 d! (HCF).
23. Use subprogram VALUE(N, T_2, B, -1) to obtain denominator.
24. $[(A)\ (S)/B]\ (-1)^h \rightarrow S$ where $h = a + b + c + t_{\max}$.
25. Return to main program.

If it were also desired to express the magnitude of the result S as a rational fraction of prime factors, in table T_2 it would be necessary to insert after step 24 the following steps:

24a. Use subprogram COPYN(N, T_1, T_2).
24b. Use subprogram SET($N_{\max}$, T_2, 0) where $N_{\max}$ is the maximum index of T_2.
24c. Use subprogram COPYN(N, T_2, T_1).
24d. Use subprogram FACTR($N_{\max}$, T_2, S).

It should be noted that the N set in step 3 could easily have been inadequate for factorization if used instead of $N_{\max}$ in step 24d. Additional remarks are that steps 6 through 8 and steps 13 through 15 could be more efficiently done with a single subroutine and that the exponent table convention can be generalized so that the contents of a special entry (e.g., $T(0)$) denotes the sign or a table value of zero (e.g., by $+1$, -1, or 0).

The D coefficients are also useful in problems of compling angular momentum. We give two useful formulas for relating the D coefficients to the Condon and Shortley (1952) coefficients $C^j(l_1, m_1, l_2, m_2)$ and the Wigner $3j$ symbols (Edmonds, 1957)

$$C^j(l_1, m_1, l_2, m_2) = (-1)^{m_1+1/2(|m_1|+|m_2|+|m_1-m_2|)} \cdot \left[\frac{(2l_1+1)(2l_2+1)(j+|m_1-m_2|)!\,(l_1-|m_1|)!\,(l_2-|m_2|)!}{(2j+1)^2\,(j-|m_1-m_2|)!\,(l_1+|m_1|)!\,(l_2+|m_2|)!}\right]^{1/2} \cdot D(j, l_1, m_1, l_2, m_2),$$

and

$$\begin{pmatrix} l_1 & l_2 & j \\ m_1 & -m_2 & m_2-m_1 \end{pmatrix} \begin{pmatrix} l_1 & l_2 & j \\ 0 & 0 & 0 \end{pmatrix} = (-1)^{1/2(|m_1|+|m_2|+|m_1-m_2|)} \cdot \left[\frac{(j+|m_1-m_2|)!\,(l_1-|m_1|)!\,(l_2-|m_2|)!}{(j-|m_1-m_2|)!\,(l_1+|m_1|)!\,(l_2+|m_2|)!\,(2j+1)^2}\right]^{1/2} \cdot D(j, l_1, m_1, l_2, m_2).$$

VI. Numerical Quadrature

From Eqs. (31) and (33) we see that once the unexpanded functions and expanded functions have been generated one is left with double integrals of the form

$$\int_0^\infty dr_1 \int_0^\infty dr_2 f(r_1)\, g(r_2) \frac{r_>{}^j}{r_<{}^{j+1}}, \tag{64}$$

where $r_<$, $r_>$ are the lesser or greater of, respectively, r_1 and r_2. This integral is to be done numerically. There are two places where the

derivative of the integrand is not continuous. The first point is at the internuclear separation a and arises from the functional definition involving $i_j(\sigma)\, k_j(\rho)$ which defines the behavior to be different for r less than a from that for r greater than a. Similarly there is a slope discontinuity as a result of definition of $r_<$ and $r_>$. Since integrating numerically over these points can introduce inaccuracies in the result, one should have all integration rules end on the points $r = a$ and $r_1 = r_2$. This divides our integral over the first quadrant into two integrals each over an octant. The first $0 \leqslant r_1 \leqslant r_2$, the second $r_2 < r_1 \leqslant \infty$. This gives a resulting sum of two integrals which we write in the symmetric form.

$$\int_0^\infty dr_1 \left[\frac{f(r_1)}{r_1^{j+1}} \int_0^{r_1} r_2^j\, g(r_2)\, dr_2 + \frac{g(r_1)}{r_1^{j+1}} \int_0^{r_1} r_2^j\, f(r_2)\, dr_2 \right]. \tag{65}$$

We now require the indefinite integral

$$\int_0^{r_1} h(r_2)\, dr_2 . \tag{66}$$

Since we wish to minimize the number of function entries we chose to generate the functions at equally spaced points and use a repeated Newton-Cotes form of integration rule. This allows us to use the same points for both the definite and indefinite integrations. It also allows us to conveniently end our integration rules at the point $r = a$. We can examine the error introduced by the numerical integration by doubling the mesh spacing and redoing the integral using every other value. If we do this by using every other value constructed for the original integrand, we can get a measure of the quadrature error with little additional effort.

Since the final value of the upper limit of our integrals is infinity and for various combinations of screening parameters κ the value of r at which the function goes effectively to zero may vary between 1 and 160, a mapping of the integration range from 0 to ∞ into some finite range of S is desirable. Since the slope is discontinous at a, it is desirable that this point should form an end point of the basic integration rules. A natural selection for a mapping would be $0 \to 0$, $a \to S/2$, $\infty \to S$. One finds that for functions which have molecular significance, maximums of the integrand occur between the two centers and the integrand is nonzero for a short distance beyond the other center. A division of the interval 0 to S into three parts was chosen with the center O′, $\frac{2}{3}$ of the distance along this line. A simple form of such a mapping and one used is

$$r = \frac{(0.5)\, at}{3 - t}, \qquad S = 3 . \tag{67}$$

This mapping requires the inclusion of the factor

$$\frac{dr}{dt} = \frac{(1.5)\,a}{(3-t)^2} \tag{68}$$

in all integrals.

Two integration routines are then needed, one for the indefinite integral

$$\int_0^t h(t)\,dt\,, \tag{69}$$

and the other for the definite integral

$$\int_0^3 g(t)\,dt\,. \tag{70}$$

In the program which was written Simpson's rule was used in the indefinite integration and a repeated 9-point Newton-Cotes rule was used in the definite integration The reason for the simplicity of the indefinite integration formula is the need for obtaining easily all the integrand points of the subsequent definite integration.

In any case since all functions were generated on a point-by-point basis one could easily change the integration mesh and even the integration rules, without changing the function routines.

VII. Exclusion of Redundant Integrals

One of the goals of a general two-center integral program is to produce all integrals between sets of orbitals located on the two centers. Since the total number of integrals goes like the total number of orbitals to the fourth power, one does not wish to calculate the same or equivalent integrals more than once. A great deal of difficulty arises from the fact that if one has an orbital with angular momentum component m, then the physical situation usually requires the inclusion of the orbital with $-m$. One could include this orbital explicitly as one of the basic set of orbitals, but if one considers the Eqs. (5) and (10) one sees that the expansion functions for $-m$ are trivially related to the expansion functions for m. For this reason the orbital with $-m$ is not included in the input set, but is implicitly included in the calculation of the integrals. We shall illustrate the procedure for eliminating vanishing and redundant integrals. This vanishing arises from the axial symmetry of the system and the redundancy from the specific form of the integrals. A further redundancy arises if there is a special symmetry in the problem, i.e., the same orbitals on both centers or a *one*-center problem.

If we symbolize an orbital with m value m_1 by $K1$ and its associated orbital with m value $-m_1$ by $-K1$ then we can denote the integral (28) by

$$(K1, K2 \mid K3, K4)$$

where $K1$, $K2$, $K3$, and $K4$ denote a specific selection of four orbitals of the total set. $K1$ and $K2$ have the coordinates of electron one and $K3$ and $K4$ have the coordinates of electron two. The m value associated with the pair $K1$, $K2$ is $M_{12} = m_2 - m_1$ because of our convention of taking the complex conjugate of the first and third orbitals. The m value associated with the second pair $K3$, $K4$ is $M_{34} = m_4 - m_3$. All of the two-electron integral vanish unless $M_{34} = -M_{12}$ or $m_1 - m_2 + m_3 - m_4 = 0$. This then allows the first reduction in the number of integrals. Of the integrals symbolized by

$$\begin{aligned}
&(K1, K2 \mid K3, K4)\\
&(K1, K2 \mid K3, -K4)\\
&(K1, K2 \mid -K3, K4)\\
&(K1, K2 \mid -K3, -K4)\\
&(K1, -K2 \mid K3, K4)\\
&(K1, -K2 \mid K3, -K4)\\
&(K1, -K2 \mid -K3, K4)\\
&(K1, -K2 \mid -K3, -K4)
\end{aligned} \tag{71}$$

associated with the various m values, *all having the same radial integration*, only those fulfilling the condition $M_{34} = -M_{12}$ are to be calculated. (The integrals with $-K1$ are just the complex conjugate of those in the above list and are also not calculated since all integrals have real values.) Similarly when an orbital has $m_i = 0$, integrals of the list (71) involving $-Ki$ should be excluded since they are obviously redundant.
For example the integrals to be calculated from four $\pi(l = 1, m = 1)$ orbitals are

$$\begin{aligned}
&(\pi, \pi \mid \pi, \pi)\\
&(\pi, \pi \mid -\pi, -\pi)\\
&(\pi, -\pi \mid -\pi, \pi)\,.
\end{aligned}$$

As an example of further redundant integrals, consider the exchange integral of orbitals on centers A and B,

$$(K1(A), K2(B) \mid K3(A), K4(B))\,.$$

In including all orbitals on center A and center B each pair need be included only once, for by the form of Eq. (28)

$$(K1(A), K2(B) \mid K3(A), K4(B)) = (K3(A), K4(B) \mid K1(A), K2(B))$$
$$= (K2(B), K1(A) \mid K4(B), K3(A)) = (K4(B), K3(A) \mid K2(B)\, K1(A))$$

We consider any pair of oribtals $K_i(A)$, $K_j(B)$ to be represented by the number $N_{ij} = i\, N_0 + j$ where N_0 is larger than the number of orbitals on either center. Then the redundancy of the exchange integrals is removed if we impose the condition that $N_{12} \geqslant N_{34}$.

Similar constraints can be developed for the Coulomb and hybrid integrals as well as for the homonuclear cases. For further details the reader is referred to the specific implementation done for the 704 computer.

Acknowledgments

The development of the present formulation of the Barnett-Coulson method and the various computer techniques was stimulated by George F. Koster and Harold Schweinler. For assistance in implementing early versions of the D coefficient subprogram for the IBM 704, we would like to express our appreciation to D. S. Villars, and V. Donlan. Much of the early development of the procedures presented here was done on the MIT Whirlwind I computer. The IBM 704 diatomic molecule integral program was prepared by the authors using the facilities of the MIT Computation Center. The IBM 7090 adaptation of this program has been prepared by Emmett Moore Jr. and Arnold Rom at the Boeing Aircraft Corporation.

We especially wish to express our appreciation to Professors John C. Slater and George F. Koster for their continued encouragement in this work. Valuable assistance was given by members of the Solid-State and Molecular Theory Group who have used our programs and techniques and confirmed the over-all validity of the approach.

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