1971

Molecular integrals using the bipolar expansion and comments on localized orbitals in diatomic molecules

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by

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A Dissertation Submitted to the
Graduate Faculty in Partial Fulfillment of
The Requirements for the Degree of
DOCTOR OF PHILOSOPHY

Major Subject: Physical Chemistry

Approved:

Signature was redacted for privacy.

In Charge of Major Work

Signature was redacted for privacy.

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Signature was redacted for privacy.

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Iowa State University
Of Science and Technology
Ames, Iowa

1971

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ACKNOWLEDGEMENTS

The author would like to thank Professor Klaus Ruedenberg for his guidance, and for his suggestion of this work. She wishes to thank Hubert Kinser for collaborating with her on much of this work, for many useful discussions, and for providing her with his computer programs.

PART ONE. MOLECULAR MULTICENTER INTEGRALS BASED ON THE BIPOLAR EXPANSION

I. INTRODUCTION

The difficulty of calculating molecular multicenter integrals remains one of the major blocks to progress in quantum chemistry. The energy integrals for electronic interactions between orbitals on three or four different centers are especially troublesome. Two main types of orbitals have been used, Gaussian orbitals and Slater-type orbitals. The integrals over Gaussian orbitals are much easier to evaluate than those over Slater-type orbitals, but a much larger Gaussian basis set must be used to obtain the accuracy given by a smaller Slater-type basis set. Formulas have been found for integrals over several kinds of Gaussian orbitals: Gaussians multiplied by powers of the Cartesian coordinates (Boys, 1950; Wright, 1963); ellipsoidal Gaussians (Browne and Poshusta, 1962); and Gaussian radial functions multiplied by spherical harmonics (Harris, 1963; Krauss, 1964). A number of methods have been used to evaluate multicenter integrals over Slater-type orbitals: expansion of an orbital on one center in terms of another (Barnett and Coulson, 1951; Barnett, 1963; Harris and Michels, 1965, 1966; Ellis and Ros, 1966); various kinds of integral transforms (Shavitt, 1963; Shavitt and Karplus, 1965; Bonham, Peacher and Cox, 1964; Silverstone, 1968a, 1968b; Silverstone and Kay, 1968; Kay and Silverstone, 1969b); sophisticated numerical techniques (Wahl and Land, 1969; McLean, 1971); Taylor series methods (Kay and Silverstone,

1969a); and asymptotic expansions (Kay and Silverstone, 1970).

Many of these methods for evaluating molecular integrals are based on some kind of expansion for r_{12}^{-1}, the inverse interelectronic distance. For multicenter integrals, the bipolar expansion (Carlson and Rushbrooke, 1950; Buehler and Hirschfelder, 1951, 1952; Sack, 1964, 1967; Ellis and Palke, 1966; Kay, Todd and Silverstone, 1969) seems to be a suitable one, but few applications of it (Ellis and Ros, 1966; Kay and Silverstone, 1970) have been made.

The present work is concerned with further development of the bipolar expansion and its use to obtain new expressions for both kinds of integrals, those over Gaussian orbitals and those over Slater-type orbitals.

The analysis is based on a recent form of the bipolar expansion (Ruedenberg, 1967) derived by means of Fourier transforms. A new type of bipolar expansion is derived, in which the radial factor is expressed as a double infinite series with the same functional form for all values of its arguments. This series is shown to converge.

The new expansion for r_{12}^{-1} is used to obtain a formula, involving only finite sums, for integrals over products of Gaussian radial functions and spherical harmonics. Unlike previous expressions for such integrals (Harris, 1963; Krauss, 1964), our formula does not involve any rotation representation matrices, which are very time-consuming to calcu-

late. The integral expression has been put into a form suitable for efficient calculation of the large number of integrals needed in a molecular problem. This form has been used as the basis for computer programs by Hubert Kinser and the present author. Those written by the author are presented and discussed.

A "quadrupolar" expansion, involving four atomic centers, is derived from the new bipolar expansion. This expansion for r_{12}^{-1} is used to derive an asymptotic expansion for integrals over Slater-type orbitals on four different centers in terms of two-center charge distribution transforms. These have the nature of overlap integrals, and are finite sums over closed expressions. It is expected that this expression for the integral would be sufficiently accurate for cases in which either the orbital exponents or the internuclear distances are fairly large. In such cases only a few terms would be needed, so it is expected that an efficient calculational method could be based on the asymptotic expansion.

II. BIPOLAR EXPANSION AND GENERAL INTEGRAL

A. Formal Derivation

We wish to evaluate the integral

$$I = [u_{q_a} u_{q_b} | u_{q_c} u_{q_d}]$$

$$= \int dV_1 \int dV_2 \; u_{q_a}^*(\vec{r}_{A1}) u_{q_b}(\vec{r}_{B1}) r_{12}^{-1} u_{q_c}^*(\vec{r}_{C2}) u_{q_d}(\vec{r}_{D2}) \quad (1)$$

in which $u_q(\vec{r})$ is an atomic orbital whose functional form has not yet been specified. The subscript q denotes the set of three quantum numbers $\{n,\ell,m\}$, and the quantity r_{12} is the interelectronic distance.

The first step is to express r_{12}^{-1} by means of the bipolar expansion. For this purpose it is convenient to define the vectors,

$$\vec{x}_P, \; \vec{x}_Q = \text{positions of two arbitrary centers} \quad (2a)$$

$$\vec{x}_1, \; \vec{x}_2 = \text{positions of two electrons} \quad (2b)$$

$$\vec{r}_1 = \vec{x}_1 - \vec{x}_P, \quad \vec{r}_2 = \vec{x}_2 - \vec{x}_Q, \quad \vec{R} = \vec{x}_Q - \vec{x}_P \quad (3)$$

and introduce the corresponding polar coordinates

$$\{r_1,\theta_1,\phi_1\}, \quad \{r_2,\theta_2,\phi_2\}, \quad \{R,\Theta,\Phi\} \quad . \quad (4)$$

It is assumed here that the Cartesian coordinates on P and Q differ only by the translation $\vec{R}$, not by a rotation. More-

over, $\{R,\Theta,\Phi\}$ are the polar coordinates of center Q in the coordinate system on center P.

A bipolar expansion is defined as a series which expresses a function $f(r_{12})$ in terms of products of functions of θ_1, ϕ_1, θ_2, ϕ_2, Θ and Φ. This work is based on the bipolar expansion of r_{12}^{-1} derived by Ruedenberg (1967), which can be written in the form

$$r_{12}^{-1} = \sum_{\ell_1=0}^{\infty} \sum_{m_1=-\ell_1}^{+\ell_1} \sum_{\ell_2=0}^{\infty} \sum_{m_2=-\ell_2}^{+\ell_2}$$

$$\times(-1)^{\ell_1} Y_{\ell_1 m_1}(\theta_1,\phi_1) Y_{\ell_2 m_2}(\theta_2,\phi_2)$$

$$\times \sum_{L} Y_{LM}(\Theta,\Phi)\, \omega_L^{\ell_1\ell_2 m_1 m_2}\, J_{\ell_1\ell_2 L}(r_1,r_2,R) \qquad (5)$$

with the definitions

$$J_{\ell_1\ell_2 L}(r_1,r_2,R) = \left(\frac{2}{\sqrt{\pi}}\right) \int_0^{\infty} dk\; j_{\ell_1}(kr_1)\, j_{\ell_2}(kr_2)\, j_L(kR) \qquad (6)$$

$$\omega_L^{\ell_1\ell_2 m_1 m_2} = 8\pi(-1)^{(\ell_1+\ell_2+L)/2}$$

$$\times[(2\ell_1+1)(2\ell_2+1)(2L+1)]^{1/2}$$

$$\times \begin{pmatrix} \ell_1 & \ell_2 & L \\ m_1 & m_2 & M \end{pmatrix} \begin{pmatrix} \ell_1 & \ell_2 & L \\ 0 & 0 & 0 \end{pmatrix} \qquad (7)$$

$$M = -(m_1+m_2) \tag{8}$$

and the summation rules

$$\max\{|\ell_1-\ell_2|,\ |M|\} \le L \le \ell_1+\ell_2 \tag{9a}$$

$$\ell_1+\ell_2+L = \text{even}. \tag{9b}$$

The

$$\begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & m_3 \end{pmatrix}$$

are Wigner 3-j symbols, the $Y_{\ell m}$ are normalized spherical harmonics, and the j_ℓ are spherical Bessel functions, which are related to the Bessel functions of the first kind by

$$j_\ell(x) = (\pi/2x)^{1/2}\ J_{\ell+1/2}(x) \quad . \tag{10}$$

The integration over k is a result of the Fourier transform used in Ruedenberg's derivation (1967).

Substitution of this bipolar expansion (5) into the integral (1), followed by interchange of the summations with the volume integrations, leads to

$$I = \sum_{\ell_1=0}^{\infty} \sum_{m_1=-\ell_1}^{+\ell_1} \sum_{\ell_2=0}^{\infty} \sum_{m_2=-\ell_2}^{+\ell_2} I'_{\ell_1\ell_2 m_1 m_2} \tag{11}$$

in which

$$I'_{\ell_1\ell_2 m_1 m_2} = \int dV_1 \int dV_2 \; f_{\ell_1 m_1 q_a q_b}^{(1AB)} f_{\ell_2 m_2 q_c q_d}^{(2CD)}$$

$$\times (-1)^{\ell_1} \sum_L Y_{LM}(\Theta,\Phi)\, \omega_L^{\ell_1\ell_2 m_1 m_2}$$

$$\times J_{\ell_1\ell_2 L}(r_1, r_2, R) \qquad (12)$$

and

$$f_{\ell m q q'}(nPQ) = Y_{\ell m}(\theta_n, \phi_n)\, u_q^*(\vec{r}_{Pn})\, u_{q'}(\vec{r}_{Qn}) \quad . \qquad (13)$$

There are three different integrations in (12): two volume integrations and the integration contained in $J_{\ell\ell' L}$, the r-dependent factor of the bipolar expansion. We would like to be able to separate these integrations from each other, so that they can be performed independently. This can be done if the integrand in $J_{\ell\ell' L}$ can be expressed as a sum of functions, each of which is a product of a function of r_1, a function of r_2, and a function of both R and the integration variable k. To accomplish this we use the following expansion of spherical Bessel functions in terms of Laguerre polynomials (Abramowitz and Stegun, 1965, Item 22.9.16):

$$j_\ell(xy) = \exp(-x^2/4) \sum_{n=0}^{\infty} x^{2n+\ell}\, \mathcal{L}_{n\ell}(y) \qquad (14)$$

with

$$\mathcal{L}_{n\ell}(y) = y^{\ell} L_n^{\ell+1/2}(y^2)/2^n[2(n+\ell)+1]!! \quad , \tag{15}$$

where

$$\begin{aligned}(2p+1)!! &= 1\cdot 3\cdot 5\cdots(2p+1) \\ &= (2p+1)!/2^p p! \\ &= 2^{p+1}\,\Gamma(p+3/2)/\sqrt{\pi}\end{aligned} \tag{16}$$

and the functions

$$L_n^a(x) = e^x x^{-a}(d/dx)^n(e^{-x}x^{n+a})/n! \tag{17}$$

are the generalized Laguerre polynomials (Abramowitz and Stegun, 1965, Item 22.11.6). We write this expansion in the form

$$j_{\ell_p}(kr_p) = j_{\ell_p}(xy), \quad \text{with} \quad x = ka_p, \quad y = r_p/a_p \ , \tag{18}$$

where a_p is a scale factor, to be determined later, with the dimension of a length, and p=1 or 2. This expression is substituted for the spherical Bessel functions of kr_1 and kr_2 in the definition (6) of $J_{\ell_1\ell_2 L}$. The two summations are then interchanged with the integration over k. It will be proved in section III that this interchange is proper and that consequently the resulting series converges. Thus we have

$$J_{\ell_1\ell_2 L}(r_1,r_2,R) = \sum_{n_1=0}^{\infty}\sum_{n_2=0}^{\infty} \mathcal{R}_N^{\,L}(R,a_1,a_2) \times \mathcal{L}_{n_1\ell_1}(r_1/a_1)\mathcal{L}_{n_2\ell_2}(r_2/a_2) \quad , \quad (19)$$

where the function $\mathcal{L}_{n\ell}(r)$ is defined by (15) and the function $\mathcal{R}_N^{\,L}(R,a_1,a_2)$ is defined by

$$\mathcal{R}_N^{\,L}(R,a_1,a_2) = \left(\frac{2}{\sqrt{\pi}}\right) a_1^{\,2n_1+\ell_1}\, a_2^{\,2n_2+\ell_2} \times (a_1^{\,2}+a_2^{\,2})^{-(2N+L+1)/2} \times \int_0^{\infty} d\kappa\, \exp(-\kappa^2/4)\,\kappa^{2N+L}\, j_L(\kappa\rho) \quad . \quad (20)$$

($\mathcal{R}_N^{\,L}$ is the same as $\mathcal{R}_n'$ of Salmon, Birss and Ruedenberg (1968, Eq. 2.1).) Here

$$N = n_1+n_2+(\ell_1+\ell_2-L)/2 \quad (21)$$

$$\rho = R/(a_1^{\,2}+a_2^{\,2})^{1/2} \quad . \quad (22)$$

Note that the index N, by virtue of (9a) and (9b), is a non-negative integer. The integration variable in (20) is related to that in (6) by the substitution $\kappa = k(a_1^{\,2}+a_2^{\,2})^{1/2}$.

When this expression for the r-dependent factor, (19), is substituted into the bipolar expansion, (5), the result is a new form of the bipolar expansion

$$r_{12}^{-1} = \sum_{q_1} \sum_{q_2} W_{q_1 q_2}(\vec{R}, a_1, a_2) \Lambda_{q_1}(\vec{r}_1/a_1) \Lambda_{q_2}(\vec{r}_2/a_2) \quad , \tag{23}$$

in which

$$\sum_q = \sum_{\ell=0}^{\infty} \sum_{m=-\ell}^{+\ell} \sum_{n=0}^{\infty} \tag{24}$$

$$W_{q_1 q_2}(\vec{R}, a_1, a_2) = (-1)^{\ell_1} \sum_L Y_{LM}(\Theta, \Phi) \omega_L^{\ell_1 \ell_2 m_1 m_2}$$

$$\times \mathcal{R}_N^L(R, a_1, a_2) \tag{25}$$

$$\Lambda_q(\vec{r}) = Y_{\ell m}(\theta, \phi) \mathcal{L}_{n\ell}(r) \quad . \tag{26}$$

In (25) the summation over L is characterized by (9a) and (9b), the quantity $\omega_L^{\ell\ell' mm'}$ is defined by (7), and M is given by (8). ($W_{qq'}$ is the same as $R^{-1}\Omega_{qq'}$ of Salmon, Birss and Ruedenberg (1968, Eqs. 1.23 and 1.26).)

On the other hand, when (19) is substituted into (12) and the summations over n_1 and n_2 are <u>formally</u> interchanged with the volume integrations, a new formula for $I'_{\ell\ell' mm'}$ is obtained. We shall see that the validity of this interchange of summation and integration depends upon the form of the orbitals u. Supposing for the moment that it is valid, we substitute the new expression for $I'_{\ell\ell' mm'}$ into (11) and find a new formula for the integral defined by (1)

$$I \sim \sum_{q_1} \sum_{q_2} W_{q_1 q_2}(\vec{R}, a_1, a_2)$$

$$\times F_{q_1 q_a q_b}(1AB, a_1) F_{q_2 q_c q_d}(2CD, a_2) \quad , \qquad (27)$$

in which

$$F_{q_p q q'}(pPQ, a_p) = \int dV_p \; f_{\ell_p m_p q q'}(pPQ) \mathcal{L}_{n_p \ell_p}(r_p/a_p)$$

$$= \int dV_p \; u_q^*(\vec{r}_{Pp}) u_{q'}(\vec{r}_{Qp}) \Lambda_{q_p}(\vec{r}_p/a_p) \quad . \qquad (28)$$

Here the quantity f is defined by (13), the quantity $\mathcal{L}$ by (15) and the quantity Λ by (26); the functions u are the atomic orbitals. Of course, (27) could equally well be derived by substituting the new bipolar expansion, (23), into the definition of the electronic interaction integral (1).

It was possible to separate the volume integrations in (27) because of two properties of the r-dependent factor as given by (19): first, each term in the series is a product of a function of r_1, a function of r_2 , and a function of R; second, the expression has the same functional form for all values of r_1 , r_2 , and R . This second property contrasts with that of earlier expressions for the radial factor (Carlson and Rushbrooke, 1950; Buehler and Hirschfelder, 1951; Sack, 1964), which have different functional forms according to the relative values of r_1 , r_2 , and R ; there

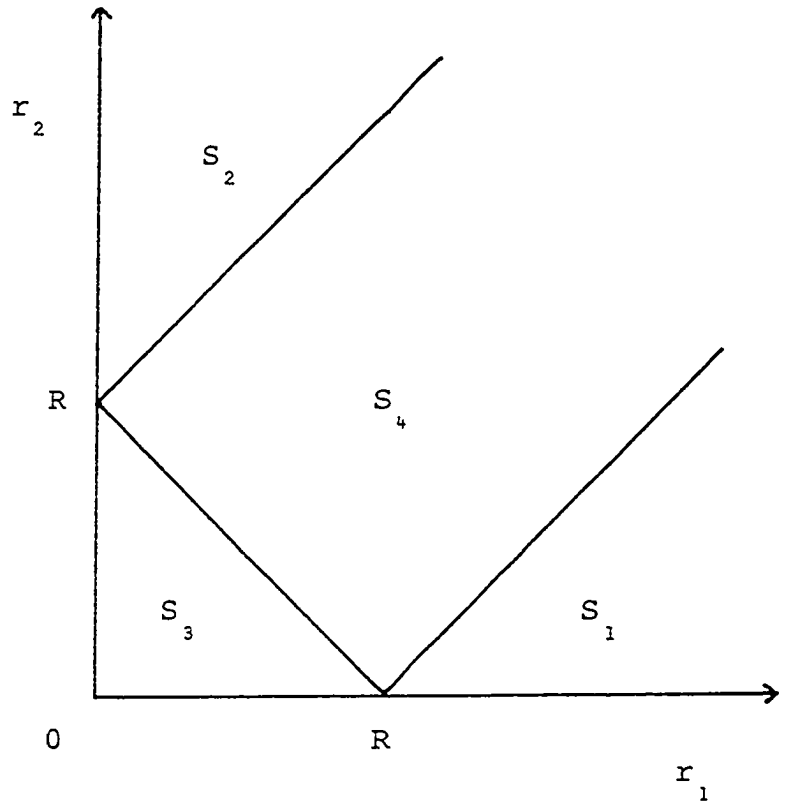


Figure 1. The four regions found by Carlson and Rushbrooke

are four forms, one for each of the four regions shown in Figure 1. However, these functions are all closed expressions, whereas (19) contains a double infinite series.

B. Evaluation of $\mathcal{R}_N^L$

The integral in (20) can be expressed (Abramowitz and Stegun, 1965, Item 11.4.28) in terms of the confluent hypergeometric function M(a,b,x) (Abramowitz and Stegun, 1965, Items 13.1.1-13.1.10). The result is

$$\mathcal{R}_N^L(R,a_1,a_2) = a_1^{2n_1+\ell_1}\, a_2^{2n_2+\ell_2}\, \Gamma(L+N+1/2)$$

$$\times[(a_1^2+a_2^2)^{(2N+L+1)/2}\, \Gamma(L+3/2)]^{-1}$$

$$\times 2^{2N+L}\, \rho^L\, M(L+N+1/2,L+3/2,-\rho^2) \quad . \qquad (29)$$

Now it is convenient to distinguish the cases N=0 and N>0. When N=0, which implies $n_1=n_2=0$ and $L=\ell_1+\ell_2$, we have (Abramowitz and Stegun, 1965, Item 13.6.10)

$$M(L+1/2,L+3/2,-\rho^2) = (L+1/2)\,\rho^{-2L-1}\, \gamma(L+1/2,\rho^2) \quad , \qquad (30)$$

where $\gamma(a,x)$ is the incomplete gamma function (Abramowitz and Stegun, 1965, Item 6.5.2). Consequently

$$\mathcal{R}_0^L(R,a_1,a_2) = a_1^{\ell_1}\, a_2^{\ell_2}\, R^{-L-1}\, 2^L\, \gamma(L+1/2,\rho^2) \quad . \qquad (31)$$

In the case N>0, we use the Kummer transformation (Abramowitz and Stegun, 1965, Item 13.1.27)

$$M(L+N+1/2,L+3/2,-\rho^2) = \exp(-\rho^2)M(-N+1,L+3/2,\rho^2) \quad , \qquad (32)$$

and since (-N+1) is a nonpositive integer, the righthand side is related to the Laguerre function of (17) by (Abramowitz and Stegun, 1965, Item 13.6.9)

$$M(-N+1,L+3/2,\rho^2)$$

$$= (N-1)![\Gamma(L+3/2)/\Gamma(L+N+1/2)]L_{N-1}^{L+1/2}(\rho^2) \quad . \qquad (33)$$

Substitution of (33) into (32) and then (32) into (29) yields

$$\mathcal{R}_{N>0}^{L}(R,a_1,a_2) = [a_1^{2n_1+\ell_1}\, a_2^{2n_2+\ell_2}/(a_1^2+a_2^2)^{L+N+1/2}]$$

$$\times 2^{L+2N}\,(N-1)!R^L\exp(-\rho^2)L_{N-1}^{L+1/2}(\rho^2) \quad . \qquad (34)$$

With $\mathcal{R}_N^L$ given by (31) and (34), the function $W_{qq'}$ of (25) has now been expressed in terms of known quantities.

C. Special Cases of $W_{qq'}$

1. $\underline{\theta = 0}$

Sometimes it is useful to define the coordinate systems on P and Q so that both z axes coincide with the vector $\vec{R} = \vec{x}_Q - \vec{x}_P$, which implies $\theta = 0$. This leads to the simplification

$$Y_{LM}(\theta=0,\Phi) = \delta_{M0}[(2L+1)/4\pi]^{1/2} \qquad (35a)$$

and, because of (8),

$$m_1+m_2 = 0 \quad . \qquad (35b)$$

Thus, the function $W_{q_1q_2}$ assumes the form

$$W_{q_1q_2}(\vec{R}||\vec{z}_P,a_1,a_2) = \delta_{-m_1,m_2}(-1)^{\ell_1}\sum_L [(2L+1)/4\pi]^{1/2}$$

$$\times\omega_L^{\ell_1\ell_2 m_1 m_2}\,\mathcal{R}_N^L(R,a_1,a_2) \quad . \quad (36)$$

Note that $m_1 = -m_2$ and $M = 0$ in the definition of $\omega_L^{\ell_1\ell_2 m_1 m_2}$, (7).

2. $\underline{R = 0}$

When the two points P and Q coincide, i.e. $R = 0$, the expression for W_{qq}, is considerably simplified. To find the new expression, one must investigate the behavior of $\mathcal{R}_N^L$ as $R \to 0$. We substitute the series expansion for $\gamma(a,x)$ (Abramowitz and Stegun, 1965, Items 6.5.4 and 6.5.29) into (31) to obtain

$$\mathcal{R}_0^L(R,a_1,a_2) = [a_1^{\ell_1}\, a_2^{\ell_2}/(a_1^2+a_2^2)^{L+1/2}]$$

$$\times[2^{L+1}/(2L+1)]R^L(1+cR^2+\cdots) \quad . \quad (37)$$

For $N>0$, we substitute the explicit polynomial expression for $L_n^a(x)$ (Abramowitz and Stegun, 1965, Item 22.3.9) into (34) to obtain

$$\mathcal{R}_{N>0}^{L}(R,a_1,a_2) = [a_1^{2n_1+\ell_1}\, a_2^{2n_2+\ell_2}/(a_1^2+a_2^2)^{L+N+1/2}]$$

$$\times 2^{L+N+1}[(2N+L-1)!!/(2L+1)!!]$$

$$\times \exp(-\rho^2)R^{L}(1+c'R^2+\cdots+c''R^{2N-2}) . \quad (38)$$

It is clear that $\mathcal{R}_N^{L}(R=0,a,a')$ vanishes in both cases unless L=0, which, according to (9a), is possible only if $\ell_1=\ell_2$. For L=0 we obtain

$$\mathcal{R}_N^{0}(0,a_1,a_2)$$

$$= 2^{N+1}(2N-1)!!a_1^{2n_1+\ell}\, a_2^{2n_2+\ell}/(a_1^2+a_2^2)^{N+1/2} , \quad (39)$$

where we have introduced $\ell=\ell_1=\ell_2$ and $(-1)!!=1$. The expression in (39) is valid not only for N>0, but also for N=0, because the simultaneous conditions L=0 and N=0 imply $n_1=n_2=\ell_1=\ell_2=0$.

When L=0 (9a) implies, in addition to $\ell_1=\ell_2=\ell$, that M=0 and $m_1=-m_2=m$. These conditions lead to great simplification in the expression for ω. The result is (Rotenberg et al., 1959, p. 12, Eq. 1.54)

$$\omega_0^{\ell\ell m,-m} = 8\pi(-1)^{\ell}\begin{pmatrix}\ell & \ell & 0\\ m & -m & 0\end{pmatrix}\begin{pmatrix}\ell & \ell & 0\\ 0 & 0 & 0\end{pmatrix}(2\ell+1)$$

$$= 8\pi(-1)^{m+\ell} . \quad (40)$$

These results, (39) and (40), along with the fact that

$$Y_{00}(\theta,\phi) = 1/2\sqrt{\pi} \quad , \tag{41}$$

are substituted into the definition of $W_{qq'}$, (25), to give

$$W_{q_1q_2}(\vec{0},a_1,a_2) = \delta_{-m_1,m_2}\delta_{\ell_1\ell_2}\, 2^{N+3}\sqrt{\pi}(-1)^m(2N-1)!! \times a_1^{2n_1+\ell}\, a_2^{2n_2+\ell}/(a_1^2+a_2^2)^{N+1/2}, \tag{42}$$

where $m=m_1$ and $\ell=\ell_1$. This is the one-center limit for $W_{qq'}$, that is, the limit when R=0 or P=Q.

D. Special Cases of the Bipolar Expansion

This section will deal with the forms to which the bipolar expansion reduces in certain cases, and some mathematical consequences of them. First the one-center limit will be considered, and then the multipole (large R) limit.

1. One-center limit (R=0)

We want to simplify the expansion (23) under the condition R=0. In the previous section an expression (42) was found for $W_{qq'}(\vec{0},a,a')$. That expression and the definition of Λ_q, (26), are substituted into (23); the result is

$$r_{12}^{-1} = \sum_{\ell=0}^{\infty} \sum_{m=-\ell}^{+\ell} Y_{\ell m}(\theta_1,\phi_1) Y_{\ell m}^{*}(\theta_2,\phi_2)$$

$$\times\sqrt{\pi} \sum_{n_1=0}^{\infty} \sum_{n_2=0}^{\infty} 2^{N+3}(2N-1)!!/(a_1^2+a_2^2)^{N+1/2}$$

$$\times a_1^{2n_1+\ell}\, a_2^{2n_2+\ell}\, \mathcal{L}_{n_1\ell}(r_1/a_1)\, \mathcal{L}_{n_2\ell}(r_2/a_2), \quad (43)$$

where $N = n_1+n_2+\ell$.

Now, since P and Q coincide, the positions of the two electrons are specified with respect to the same origin, and r_{12}^{-1} is given by the Laplace expansion (see, e.g., Eyring, Walter and Kimball (1944, p. 371, Eq. V17))

$$r_{12}^{-1} = \sum_{\ell=0}^{\infty} \sum_{m=-\ell}^{+\ell} Y_{\ell m}(\theta_1,\phi_1) Y_{\ell m}^{*}(\theta_2,\phi_2) \left(\frac{4\pi}{2\ell+1}\right) \left(\frac{r_<^{\ell}}{r_>^{\ell+1}}\right). \quad (44)$$

Then by comparing (43) and (44), we deduce the existence of the following series expansion for $r_<^{\ell}/r_>^{\ell+1}$:

$$\frac{r_<^{\ell}}{r_>^{\ell+1}} = \frac{(2\ell+1)}{\sqrt{\pi}} \sum_{n_1=0}^{\infty} \sum_{n_2=0}^{\infty} 2^{N+1}(2N-1)!!$$

$$\times a_1^{2n_1+\ell}\, a_2^{2n_2+\ell}/(a_1^2+a_2^2)^{N+1/2}$$

$$\times \mathcal{L}_{n_1\ell}(r_1/a_1)\, \mathcal{L}_{n_2\ell}(r_2/a_2) \quad , \quad (45)$$

which, for the choice $a_1=a_2=1$, reduces to

$$\frac{r_<^{\ell}}{r_>^{\ell+1}} = \left(\frac{2}{\pi}\right)^{1/2} (2\ell+1) \sum_{n_1=0}^{\infty} \sum_{n_2=0}^{\infty} (2n_1+2n_2+2\ell-1)!! \times \mathcal{L}_{n_1\ell}(r_1)\, \mathcal{L}_{n_2\ell}(r_2) \quad . \tag{46}$$

This series converges because, as will be shown, the series of (19) converges.

2. Multipole limit (large R)

In order to determine the form of the bipolar expansion (23) for large values of R, let us first examine the behavior of the function $\mathcal{R}_N^L$, which contains all of the R-dependence. It is clear from (34) that $\mathcal{R}_N^L$ decays exponentially for large R if N>0 , so only terms with N=0 make a significant contribution to r_{12}^{-1} when R is very large. These terms contain the incomplete gamma function, which can be expressed as the difference of a constant and a monotonically decreasing function of the argument (Abramowitz and Stegun, 1965, Item 6.5.3)

$$\gamma(L+1/2,\rho^2) = \Gamma(L+1/2) - \Gamma(L+1/2,\rho^2) \quad . \tag{47}$$

Here $\Gamma(a,x)$ is the complemented incomplete gamma function, and the quantity ρ was defined in (22). For large ρ, the asymptotic expansion (Abramowitz and Stegun, 1965, Item 6.5.32)

$$\Gamma(L+1/2,\rho^2) = \exp(-\rho^2)\rho^{2L-1}[1+(L-1/2)\rho^{-2}$$

$$+(L-1/2)(L-3/2)\rho^{-4}+\cdots] \qquad (48)$$

holds; thus, $\mathcal{R}_0^L$ also contains a term which decays exponentially. In fact, (47) shows that $\mathcal{R}_0^L$ can be expressed as a sum of a short range term, $\mathcal{R}_{0L}^{SR}$, and a long range term, $\mathcal{R}_{0L}^{LR}$:

$$\mathcal{R}_0^L(R,a_1,a_2) = \mathcal{R}_{0L}^{SR}(R,a_1,a_2) + \mathcal{R}_{0L}^{LR}(R,a_1,a_2) \qquad (49)$$

where

$$\mathcal{R}_{0L}^{LR}(R,a_1,a_2) = a_1^{\ell_1} a_2^{\ell_2} R^{-\ell_1-\ell_2-1} 2^{\ell_1+\ell_2}$$

$$\times\Gamma(\ell_1+\ell_2+1/2) \qquad (50)$$

and

$$\mathcal{R}_{0L}^{SR}(R,a_1,a_2) = -a_1^{\ell_1} a_2^{\ell_2} R^{-\ell_1-\ell_2-1} 2^{\ell_1+\ell_2}$$

$$\times\Gamma(\ell_1+\ell_2+1/2,\rho^2) \quad . \qquad (51)$$

Here we have used the fact that N=0 implies that $L=\ell_1+\ell_2$. This decomposition (49) enables us to decompose the expansion for r_{12}^{-1} in a similar way into the sum of a short range term, SR, comprising the terms which decay exponentially, and a long range or multipole term, LR, comprising the other

terms:

$$r_{12}^{-1} = (LR) + (SR) \quad . \tag{52}$$

(This separation is analogous to that given by O-ohata and Ruedenberg (1966, Eq. 4.4).)

As we have seen, the long range term contains only terms with N=0. This implies that $n_1=n_2=0$ and $L=\ell_1+\ell_2$, that is, that only one term from the summations over n_1 , n_2 , and L contributes to the long range term. To evaluate this term we shall use (50) and the relation

$$\mathcal{L}_{0\ell}(x) = x^{\ell}/(2\ell+1)!! \quad , \tag{53}$$

which is a consequence of the definition of $\mathcal{L}_{n\ell}$,(15), and the identity $L_0^{a}(x) = 1$. The resulting expression for the long range term is

$$(LR) = R^{-1} \sum_{\ell_1} \sum_{m_1} \sum_{\ell_2} \sum_{m_2} \mathcal{M}(\ell_1 m_1 \ell_2 m_2) Y_{\ell_1+\ell_2, M}(\Theta,\Phi)$$

$$\times (r_1/R)^{\ell_1} Y_{\ell_1 m_1}(\theta_1,\phi_1) \times (r_2/R)^{\ell_2} Y_{\ell_2 m_2}(\theta_2,\phi_2) \tag{54}$$

where

$$\mathcal{M}(\ell_1 m_1 \ell_2 m_2) = (-1)^{\ell_1} 2^{\ell_1+\ell_2} \Gamma(\ell_1+\ell_2+1/2)$$

$$\times \omega_{\ell_1+\ell_2}^{\ell_1 \ell_2 m_1 m_2} / [(2\ell_1+1)!!(2\ell_2+1)!!] \quad . \qquad (55)$$

Use of the properties of the 3-j symbols (Edmonds, 1957, p. 48, Eq. 3.7.10) and of the expression for $\Gamma(\ell+1/2)$ in terms of factorials (16) leads to

$$\mathcal{M}(\ell_1 m_1 \ell_2 m_2) = \frac{(-1)^{\ell_2+m_1+m_2} 8\pi^{3/2}}{[(2\ell_1+1)(2\ell_2+1)(2\ell_1+2\ell_2+1)]^{1/2}}$$

$$\times \left\{ \frac{(\ell_1+\ell_2+m_1+m_2)!(\ell_1+\ell_2-m_1-m_2)!}{(\ell_1+m_1)!(\ell_1-m_1)!(\ell_2+m_2)!(\ell_2-m_2)!} \right\}^{1/2} \quad . \qquad (56)$$

The expression for the long range term given by (54) and (56) can be used to obtain Silverstone's (1966) expression for the multipole term of a two-center Coulomb integral. Now if we make the particular choice $\Theta=0$, (35a) and (35b) hold, and, letting $m=m_1=-m_2$, we find

$$\mathcal{M}(\ell_1 m \ell_2, -m) Y_{\ell_1+\ell_2, 0}(0, \Phi) = 4\pi(-1)^{\ell_2} \delta_{-m_1, m_2}$$

$$\times (\ell_1+\ell_2)! [(2\ell_1+1)(2\ell_2+1)]^{-1/2}$$

$$\times [(\ell_1+m)!(\ell_1-m)!(\ell_2+m)!(\ell_2-m)!]^{-1/2} \quad . \qquad (57)$$

If this equation is substituted into (54), the result can be used to obtain the expression of O-ohata and Ruedenberg (1966).

The short range term is given by

$$(SR) = \sum_{\ell_1 m_1} \sum_{\ell_2 m_2} Y_{\ell_1 m_1}(\theta_1,\phi_1) Y_{\ell_2 m_2}(\theta_2,\phi_2)(-1)^{\ell_1}$$

$$\times \sum_{L} \omega_L^{\ell_1 \ell_2 m_1 m_2} Y_{LM}(\Theta,\Phi) \sum_{n_1=0}^{\infty} \sum_{n_2=0}^{\infty} \mathcal{R}_{NL}^{SR}(R,a_1,a_2)$$

$$\times \mathcal{L}_{n_1 \ell_1}(r_1/a_1)\, \mathcal{L}_{n_2 \ell_2}(r_2/a_2) \quad ; \tag{58}$$

the function $\mathcal{R}_{NL}^{SR}$ is defined by two equations, (51) and

$$\mathcal{R}_{N>0,L}^{SR}(R,a_1,a_2) = \mathcal{R}_{N>0}^{L}(R,a_1,a_2) \quad , \tag{59}$$

with $\mathcal{R}_{N>0}^{L}$ defined by (34). It is clear from (34), (51) and (48) that, for very large R, the short range term becomes negligible compared to the long range term. More than this can be said, however. The long range term given by (54) and (57) is identical with the multipole expansion which Carlson and Rushbrooke (1950) showed to be exact in the entire region $R > r_1+r_2$ (region S_3 of Figure 1). This implies that the short range term vanishes identically in this region. Since this is so for all values of the angles, the coefficient of each product

$$Y_{\ell_1 m_1}(\theta_1,\phi_1)Y_{\ell_2 m_2}(\theta_2,\phi_2)Y_{LM}(0,\phi)$$

in (SR) must vanish. That is, for each allowed combination of ℓ_1 , ℓ_2 , and L (see (9a) and (9b)), we have

$$0 = \sum_{n_1=0}^{\infty}\sum_{n_2=0}^{\infty} \mathcal{R}_{NL}^{SR}(R,a_1,a_2) \times \mathcal{L}_{n_1\ell_1}(r_1/a_1)\,\mathcal{L}_{n_2\ell_2}(r_2/a_2) \qquad (60)$$

<u>for $r_1+r_2 < R$</u> . When $L = \ell_1+\ell_2$, the first term of this identity has N=0 and , consequently, contains the complemented incomplete gamma function. Then (60) can be put in the form of an expression for that function; substitution of (51), (59), (34) and (15) yields

$$\Gamma(\ell_1+\ell_2+1/2,\rho^2) = \rho^{2\ell_1+2\ell_2+1}\exp(-\rho^2)\sum_{n_1 n_2}{}' T \quad , \qquad (61)$$

where

$$\sum_{n\nu}{}' = \sum_{n=0}^{\infty}\sum_{\nu=0}^{\infty} \quad \text{without the term with } n=\nu=0 \qquad (62)$$

$$T = A_{n_1 n_2 \ell_1 \ell_2}(a_1,a_2)\hat{\mathcal{L}}_{n_1 n_2 \ell_1 \ell_2}(\rho,r_1/a_1,r_2/a_2) \qquad (63)$$

$$A_{n\nu\ell\lambda}(a,b) = \frac{(2\ell+1)!!\,(2\lambda+1)!!\,2^{n+\nu}(n+\nu-1)!\,a^{2n}b^{2\nu}}{[2(n+\ell)+1]!!\,[2(\nu+\lambda)+1]!!\,(a^2+b^2)^{n+\nu}} \quad , \qquad (64)$$

and

$$\hat{\mathcal{L}}_{n\nu\ell\lambda}(\rho,r,s)$$

$$= L_{n+\nu-1}^{\ell+\lambda+1/2}(\rho^2)L_n^{\ell+1/2}(r^2)L_\nu^{\lambda+1/2}(s^2) \quad . \qquad (65)$$

When $L < \ell_1+\ell_2$, there is no term with N=0 , so that $\mathcal{R}_{NL}^{SR}$ in (60) can be replaced by $\mathcal{R}_N^L$. The series of (60) and (61) converge because that of (19) does.

III. PROOF OF CONVERGENCE

The derivation of the radial factor (19) involved two interchanges of summation and integration (i.e. term-by-term integrations). It must be shown that each of these is permissible. The main theorem to be used here is Theorem 1 of Appendix A. The proof for each interchange consists of two parts: first, to demonstrate that the interchange is valid for a finite interval of integration, and second, to show that one side of

$$\int_0^\infty dk \sum_{n=0}^{\infty} |I_n| = \sum_{n=0}^{\infty} \int_0^\infty dk \ |I_n| \tag{66}$$

converges, where I_n is the integrand in question. To facilitate the proof, we rewrite the series for the spherical Bessel function (14) in the following way:

$$j_\ell(kr) = \sum_{n=0}^{\infty} T_n{}^{\ell}(ka, r/a) \tag{67}$$

where

$$T_n{}^{\ell}(k,r) = \frac{(\sqrt{\pi}/2)\exp[-(k/2)^2](k/2)^{2n+\ell} r^{\ell} L_n{}^{\ell+1/2}(r^2)}{\Gamma(n+\ell+3/2)} . \tag{68}$$

The value of the scaling factor a does not affect the argument, and will be set equal to unity for simplicity.

A. Validity of First Interchange

From (6) and (67) we have

$$J_{\ell_1\ell_2 L}(r_1,r_2,R) = \frac{2}{\sqrt{\pi}} \int_0^\infty dk \sum_{n=0}^\infty U_n(k) \tag{69}$$

where

$$U_n(k) = T_n^{\ell_1}(k,r_1) j_{\ell_2}(kr_2) j_L(kR) \quad . \tag{70}$$

We need to show that

$$J_{\ell_1\ell_2 L}(r_1,r_2,R) = \frac{2}{\sqrt{\pi}} \sum_{n=0}^\infty \int_0^\infty dk\, U_n(k) \quad . \tag{71}$$

1. Interchange for finite interval

We shall use Theorem 2 of Appendix A to show that

$$\int_0^K dk \sum_{n=0}^\infty U_n(k) = \sum_{n=0}^\infty \int_0^K dk\, U_n(k) \quad , \tag{72}$$

for any positive K. It is clear from the definitions of U_n, (70), and T_n, (68), that $U_n(k)$ is integrable on the interval $0 \leq k < \infty$, or any subinterval thereof. It remains to show that the series

$$\sum_{n=0}^\infty U_n(k)$$

converges uniformly on the interval $0 \leq k \leq K$, for any posi-

tive K. In order to demonstrate this, we must first show that $\sum T_n$ converges uniformly on this interval. Because of the following inequality for generalized Laguerre polynomials (Erdélyi et al., 1953, p. 207, Eq. 14)

$$\left|L_n^a(x)\right| \leq e^{x/2}\Gamma(a+n+1)/[\Gamma(a+1)n!] \tag{73}$$

we have

$$\left|T_n^{\ell}(k,r)\right| \leq \mathcal{T}_n^{\ell}(k,r) \tag{74}$$

with

$$\mathcal{T}_n^{\ell} = \frac{(\sqrt{\pi}/2)\exp[-(k/2)^2](k/2)^{2n+\ell}r^{\ell}\exp(r^2/2)}{\Gamma(\ell+3/2)n!} \quad . \tag{75}$$

The series

$$\sum_{n=0}^{\infty} \mathcal{T}_n^{\ell}(k,r) = [(\sqrt{\pi}/2)r^{\ell}\exp(r^2/2)(k/2)^{\ell}/\Gamma(\ell+3/2)] \times \exp[-(k/2)^2] \sum_{n=0}^{\infty} (k/2)^{2n}/n!$$

$$= (\sqrt{\pi}/2)r^{\ell}\exp(r^2/2)(k/2)^{\ell}/\Gamma(\ell+3/2) \tag{76}$$

converges uniformly on $0 \leq k \leq K$ for any positive K, because it is a power series in k with an infinite radius of convergence. (See Theorem 5 of Appendix A.) Therefore, by the Cauchy condition for uniform convergence of series, Theorem 3

of Appendix A, for every $\varepsilon>0$, there exists an N such that $n>N$ implies

$$\left| \sum_{i=n+1}^{n+p} \mathcal{Y}_i \right| < \varepsilon \tag{77}$$

for each $p=1,2,\cdots$, and every k in $0 \le k \le K$. But (74) implies

$$\left| \sum_{i=n+1}^{n+p} T_i \right| \le \left| \sum_{i=n+1}^{n+p} |T_i| \right| \le \left| \sum_{i=n+1}^{n+p} \mathcal{Y}_i \right| , \tag{78}$$

so that

$$\sum_{n=0}^{\infty} T_n \quad \text{and} \quad \sum_{n=0}^{\infty} |T_n|$$

also fulfill the Cauchy condition. Therefore these series converge absolutely for any nonnegative k, and uniformly in $0 \le k \le K$ for any positive K. Now in view of the fact that

$$|j_n(x)| \le 1/(2n+1)^{1/2} \le 1 \qquad \text{for real } x, \quad n \ge 0, \tag{79}$$

which can be derived from (Abramowitz and Stegun, 1965, Item 10.1.50)

$$\sum_{n=0}^{\infty} (2n+1)[j_n(x)]^2 = 1 , \tag{80}$$

we have

$$|U_n| \leq |T_n| \quad , \tag{81}$$

and therefore

$$\left| \sum_{i=n+1}^{n+p} U_i \right| \leq \left| \sum_{i=n+1}^{n+p} |U_i| \right| \leq \left| \sum_{i=n+1}^{n+p} |T_i| \right| < \varepsilon \quad . \tag{82}$$

That is, the series for U_n and that for $|U_n|$ satisfy the Cauchy condition, which means that the series for U_n converges absolutely for all nonnegative k, and uniformly in $0 \leq k \leq K$ for any positive K. Thus the conditions of Theorem 2 are fulfilled, and (72) holds. Note that this argument holds for all values of $\{r_1, r_2, R\}$.

2. Interchange for infinite interval

In order to satisfy the remaining condition in Theorem 1, we shall show that

$$\sum_{n=0}^{\infty} \int_0^{\infty} dk \, |U_n(k)|$$

$$= \frac{\sqrt{\pi}}{2} \sum_{n=0}^{\infty} r_1^{\ell_1} \left| L_n^{\ell_1+1/2}(r_1^2) \right| / \Gamma(n+\ell_1+3/2)$$

$$\times \int_0^{\infty} dk \, \exp[-(k/2)^2] (k/2)^{2n+\ell_1} |j_{\ell_2}(kr_2) j_L(kR)| \tag{83}$$

converges. For this purpose, it is necessary to have an upper bound on $|x \cdot j_n(x)|$. We have seen, from (79), that

$|j_n(x)|$ is bounded, so that when $x=0$, $x \cdot j_n(x) = 0$. For all other values of x, it is clear from the relation (Abramowitz and Stegun, 1965, Item 10.1.8)

$$x \cdot j_n(x) = \sin(x-n\pi/2)P_n(x) + \cos(x-n\pi/2)Q_n(x)/x \quad , \tag{84}$$

where $P_n(x)$ and $Q_n(x)$ are polynomials in $(1/x^2)$, that $|x \cdot j_n(x)|$ is bounded. Thus, for nonnegative x,

$$|j_n(x)| \leq A(n)/x \quad , \tag{85}$$

where A(n) is a positive number which depends only on n. For example, since we have (Abramowitz and Stegun, 1965, Item 10.1.11)

$$j_0(x) = \sin(x)/x \quad , \tag{86}$$

it is clear that $A(0) = 1$.

a. <u>First term, for all values of $\{r_1,r_2,R\}$</u> For all values of $\{r_1,r_2,R\}$, we can obtain an upper bound for the first term in (83). Application of (79) to both spherical Bessel functions shows that

$$\int_0^\infty dk \; |U_0(k)| \leq C_{\ell_1}(r_1) \tag{87}$$

where

$$C_\ell(r) = \left(\frac{\sqrt{\pi}}{2}\right)[r^\ell/\Gamma(\ell+3/2)] \int_0^\infty dk\ \exp[-(k/2)^2](k/2)^\ell$$

$$= \left(\frac{\sqrt{\pi}}{2}\right) r^\ell \Gamma(\ell/2+1/2)/\Gamma(\ell+3/2) \quad . \tag{88}$$

Then

$$\sum_{n=0}^{\infty} \int_0^\infty dk\ |U_n(k)| \leq C_{\ell_1}(r_1) + \sum_{n=1}^{\infty} \int_0^\infty dk\ |U_n(k)| \quad , \tag{89}$$

and the left side converges if the right side converges. Thus we will consider only the terms with n>0 in the following.

b. Case when $r_2, R > 0$ In order to establish the convergence of the right side of (89), it is necessary to use somewhat different methods, depending on which, if any, of the quantities r_1, r_2, R are equal to zero. First, when r_2 and R are both greater than zero, (85) can be applied to both spherical Bessel functions in the integral of (83). The result, for n>0, is

$$\int_0^\infty dk\ |U_n(k)| \leq \left(\frac{\sqrt{\pi}}{2}\right)\left[\frac{A(\ell_2)A(L)}{4r_2R}\right] s_{n\ell_1}(r_1) \quad , \tag{90}$$

where

$$s_{n\ell}(r) = r^{\ell}\left|L_n^{\ell+1/2}(r^2)\right|/\Gamma(n+\ell+3/2)$$

$$\times\int_0^{\infty} dk\ \exp[-(k/2)^2](k/2)^{2n+\ell-2}$$

$$= r^{\ell}\left|L_n^{\ell+1/2}(r^2)\right|\Gamma(n+\ell/2-1/2)/\Gamma(n+\ell+3/2)\ . \qquad (91)$$

Thus the series of (89) converge if the series

$$\sum_{n=1}^{\infty} s_{n\ell}(r)$$

converges. To determine this, we must examine the behavior of the generalized Laguerre polynomial for large n.

i. Subcase when $r_1 > 0$ If $r_1 > 0$, Fejér's formula (Erdélyi et al., 1953, p. 199, Eq. 1) can be used:

$$L_n^a(x) = (1/\sqrt{\pi})e^{x/2}x^{-a/2-1/4}n^{a/2-1/4}\cos\theta$$

$$+ \mathcal{O}(n^{a/2-3/4}) \ , \qquad (92)$$

where θ is a function of x, n and a. Thus

$$\lim_{n\to\infty} s_{n\ell}(r) = [\exp(r^2/2)/\sqrt{\pi}r]\lim_{n\to\infty}|\cos\theta|a_{n\ell} \ , \qquad (93)$$

where

$$a_{n\ell} = n^{\ell/2}\Gamma(n+\ell/2-1/2)/\Gamma(n+\ell+3/2) \ . \qquad (94)$$

If ℓ is an even number, 2p, the argument of each of the gamma

functions is half an odd integer, so that one can cancel factors; hence

$$a_{n,2p} = n^p[(n+2p+1/2)(n+2p-1/2)\cdots(n+p-1/2)]^{-1} \quad . \qquad (95)$$

When p=0

$$a_{n0} = [(n+1/2)(n-1/2)]^{-1} = (n^2-1/4)^{-1} \qquad (96)$$

and

$$\lim_{n\to\infty} a_{n0}/n^{-2} = 1 \quad , \qquad (97)$$

so $\sum_{n=1}^{\infty} a_{n0}$ converges by Theorems 7 and 8. When p>0

$$a_{n,2p} < [(n+2p+1/2)(n+2p-1/2)]^{-1} < n^{-2} \quad , \qquad (98)$$

so

$$\sum_{n=1}^{\infty} a_{n,2p}$$

converges by Theorems 6 and 8. If ℓ is an odd number, 2p+1, the argument of the gamma function in the numerator of (94) is an integer, so

$$a_{n,2p+1} = n^{p+1/2}(n+p-1)!/\Gamma(n+2p+5/2) \qquad (99a)$$

$$a_{n+1,2p+1} = (n+1)^{p+1/2}(n+p)!/\Gamma(n+2p+7/2)$$

$$= [(1+\tfrac{1}{n})^{p+1/2}(n+p)/(n+2p+5/2)]a_{n,2p+1} \quad ; \qquad (99b)$$

thus

$$\frac{a_{n+1,2p+1}}{a_{n,2p+1}} = \left(1+\frac{1}{n}\right)^{p+1/2}(n+p)/(n+2p+5/2)$$

$$= 1 - 2/n + \mathcal{O}(1/n^2) \quad . \qquad (100)$$

Then, according to Theorem 9,

$$\sum_{n=1}^{\infty} a_{n,2p+1}$$

converges. It has now been shown that

$$\sum_{n=1}^{\infty} a_{n\ell}$$

converges for all values of ℓ. Therefore, since

$$|\cos\theta|a_{n\ell} \leq a_{n\ell} \quad , \qquad (101)$$

$\sum_{n=1}^{\infty} |\cos\theta|a_{n\ell}$ converges by Theorem 6, and, in view of (93),

$$\sum_{n=1}^{\infty} s_{n\ell}(r>0)$$

converges by Theorem 7.

ii. Subcase when $r_1=0$ If $r_1=0$, the only non-trivial case is that in which $\ell_1=0$. If $\ell_1>0$, all of the integrals on the left side of (89) are identically zero. Then we must test

$$\sum_{n=1}^{\infty} s_{n0}(0)$$

by using (Erdélyi et al., 1953, p. 189, Eq. 13)

$$L_n^a(0) = \Gamma(a+1+n)/\Gamma(a+1)n! \quad . \tag{102}$$

We have, substituting this identity into (91)

$$s_{n0}(0) = \Gamma(n-1/2)/\Gamma(3/2)n! \tag{103a}$$

$$s_{n+1,0}(0) = \Gamma(n+1/2)/\Gamma(3/2)(n+1)! \quad ; \tag{103b}$$

thus

$$\frac{s_{n+1,0}(0)}{s_{n0}(0)} = \frac{n-1/2}{n+1} = 1 - 3/2n + 3/2n(n+1) \quad . \tag{104}$$

Therefore $\sum_{n=1}^{\infty} s_{n0}(0)$ converges by Theorem 9. It has now been shown that $\sum_{n=1}^{\infty} s_{n\ell}(r)$ converges for all r and ℓ; this, together with (90) and Theorem 6, shows that (89) converges for all values of r_1 if r_2 and R are greater than zero.

c. Case when $r_1 > 0$, and r_2 or R, but not both, equals zero In this case, we need the value of $j_n(0)$, which is (Abramowitz and Stegun, 1965, Item 10.1.4)

$$j_n(0) = \delta_{n0} \quad . \tag{105}$$

This relationship shows that if $r_2=0$ and $\ell_2>0$, or $R=0$ and $L>0$, then both sides of (71) are identically zero. Hence we need consider only the case in which $r_2=0$ and $\ell_2=0$, or $R=0$ and $L=0$. Now since one of the ℓ's is zero, the other two must be equal, in view of (9a). Let r_g designate whichever of r_2 and R is greater than zero, and let ℓ designate $\ell_1=\ell_g$. Then we apply (85) to $j_\ell(r_g)$ and (105) to $j_0(0)$, to obtain for $n>0$

$$\int_0^\infty dk \; |U_n(k)| \leq (\sqrt{\pi}/2)[A(\ell)/2r_g]v_{n\ell}(r_1) \tag{106}$$

where

$$v_{n\ell}(r) = [r^\ell \left| L_n^{\ell+1/2}(r^2) \right| / \Gamma(n+\ell+3/2)] \times \int_0^\infty dk \; \exp[-(k/2)^2](k/2)^{2n+\ell-1}$$

$$= r^\ell \left| L_n^{\ell+1/2}(r^2) \right| \Gamma(n+\ell/2)/\Gamma(n+\ell+3/2) \quad . \tag{107}$$

Again we apply Fejér's formula (92) and find

$$\lim_{n\to\infty} v_{n\ell}(r) = [\exp(r^2/2)/r\sqrt{\pi}] \lim_{n\to\infty} |\cos\theta| b_{n\ell} \quad , \tag{108}$$

where

$$b_{n\ell} = n^{\ell/2}\Gamma(n+\ell/2)/\Gamma(n+\ell+3/2) \quad . \tag{109}$$

If ℓ is an even number, 2p, then the argument of the gamma function in the numerator is an integer, and

$$b_{n,2p} = n^p(n+p-1)!/\Gamma(n+2p+3/2) \tag{110a}$$

$$b_{n+1,2p} = (n+1)^p(n+p)!/\Gamma(n+2p+5/2) \quad . \tag{110b}$$

Therefore

$$\frac{b_{n+1,2p}}{b_{n,2p}} = \left(1+\frac{1}{n}\right)^p (n+p)/(n+2p+3/2)$$

$$= 1 - 3/2n + \mathcal{O}(1/n^2) \quad , \tag{111}$$

so $\sum_{n=1}^{\infty} b_{n,2p}$ converges by Theorem 9. If ℓ is an odd number, 2p+1, the argument of each of the gamma functions in (109) is half an odd integer, and cancellation occurs:

$$b_{n,2p+1} = n^{p+1/2}/(n+2p+3/2)(n+2p+1/2)\cdots(n+p+1/2)$$

$$< 1/n^{3/2} \quad . \tag{112}$$

Thus $\sum_{n=1}^{\infty} b_{n,2p+1}$ converges by Theorem 6, and we have shown that

$$\sum_{n=1}^{\infty} b_{n\ell}$$

converges for all ℓ. Then, since

$$|\cos\theta| b_{n\ell} \leq b_{n\ell} \quad , \tag{113}$$

$\sum_{n=1}^{\infty} |\cos\theta| b_{n\ell}$ converges by Theorem 6; and thus, because of (108), $\sum_{n=1}^{\infty} v_{n\ell}(r)$ converges by Theorem 7. Finally, because of (106), (89) converges by Theorem 6 when r_2 or R is zero. This result, together with that of the last section, demonstrates that the conditions of Theorem 1 are satisfied. Thus (71) is valid, and its right side converges absolutely, when no more than one of $\{r_1, r_2, R\}$ is zero.

3. Interchange when two of $\{r_1, r_2, R\}$ are zero

If two of the r's equal zero, then, because of (105) and (9a), both sides of (71) are identically zero unless $\ell_1 = \ell_2 = L = 0$. In this case

$$J_{000}(0,0,r) = \left(\frac{2}{\sqrt{\pi}}\right) \int_0^{\infty} dk \; j_0(0) j_0(0) j_0(r)$$

$$= \left(\frac{2}{\sqrt{\pi}}\right) \int_0^{\infty} dk \; [\sin(kr)]/kr = \sqrt{\pi}/r \quad , \tag{114}$$

where we have used (105) and (86). This integral converges conditionally (Apostol, 1957, p. 433, Ex. 4); that is, it converges but $\int_0^\infty dk\,|[\sin(kr)]/kr|$ does not. But

$$\int_0^\infty dk\,|[\sin(kr)]/kr| \leq \int_0^\infty dk \sum_{n=0}^\infty |U_n(k)| \quad , \tag{115}$$

so the right side does not converge, and the condition of Theorem 1 is not satisfied. Nevertheless, it can still be proved that (71) is valid in this case; one simply evaluates each of the two sides and shows that they are equal.

a. Case when $r_1 = 0$ When $r_1 = 0$

$$\frac{2}{\sqrt{\pi}} \sum_{n=0}^\infty \int_0^\infty dk\, U_n(k) = \frac{2}{\sqrt{\pi}} \sum_{n=0}^\infty \int_0^\infty dk\, T_n{}^0(k,0)\cdot 1 \cdot j_0(kr)$$

$$= \sum_{n=0}^\infty [L_n{}^{1/2}(0)/\Gamma(n+3/2)]$$

$$\times \int_0^\infty dk\, \exp[-(k/2)^2](k/2)^{2n} j_0(kr) \quad . \tag{116}$$

To evaluate this we substitute (102) for the generalized Laguerre polynomial, and use (20) and (29) to perform the integration. The result is

$$\frac{2}{\sqrt{\pi}} \sum_{n=0}^{\infty} \int_0^{\infty} dk\ U_n(k)$$

$$= \frac{2}{\sqrt{\pi}} \sum_{n=0}^{\infty} [\Gamma(n+1/2)/n!]M(n+1/2,3/2,-r^2)$$

$$= r^{-1}\gamma(1/2,r^2) + \sum_{n=1}^{\infty} \exp(-r^2)L_{n-1}^{1/2}(r^2)/n \ , \quad (117)$$

where we have used (30), (32) and (33) to express M(a,b,x). Now if we substitute n'=n-1 in the last series, we find (Erdélyi et al., 1953, p. 215, Eq. 19) that it has a known sum, namely

$$r^{-1}\exp(r^2)\Gamma(1/2,r^2) = \sum_{n'=0}^{\infty} L_{n'}^{1/2}(r^2)/(n'+1) \quad . \quad (118)$$

Therefore

$$\frac{2}{\sqrt{\pi}} \sum_{n=0}^{\infty} \int_0^{\infty} dk\ U_n(k) = r^{-1}[\gamma(1/2,r^2) + \Gamma(1/2,r^2)]$$

$$= r^{-1}\Gamma(1/2) = \sqrt{\pi}/r \quad . \quad (119)$$

Comparison of this with (114) shows that (71) is indeed satisfied in this case; however, since the series in (118) does not converge absolutely, neither does that in (71).

b. Case when $r_1 > 0$, $r_2 = R = 0$ When $r_1 = r > 0$

$$\frac{2}{\sqrt{\pi}} \sum_{n=0}^{\infty} \int_0^{\infty} dk\ U_n(k) = \frac{2}{\sqrt{\pi}} \sum_{n=0}^{\infty} \int_0^{\infty} dk\ T_n^{\,0}(k,r) \cdot 1 \cdot 1$$

$$= \sum_{n=0}^{\infty} L_n^{\,1/2}(r^2)/\Gamma(n+3/2)$$

$$\times \int_0^{\infty} dk\ \exp[-(k/2)^2](k/2)^{2n}$$

$$= \sum_{n=0}^{\infty} L_n^{\,1/2}(r^2)/(n+1/2) \quad . \tag{120}$$

The last series is a particular case of the Fourier-Laguerre series of a power (Erdélyi et al., 1953, p. 214, Eq. 16)

$$x^s = \Gamma(a+s+1) \sum_{n=0}^{\infty} \Gamma(n-s) L_n^{\,a}(x)/[\Gamma(-s)\Gamma(a+n+1)]$$

under the condition $-s < 1+\min\{a,a/2-1/4\}$, with parameters $s=-1/2$, $a=1/2$ and $x=r^2$. Then we have

$$\frac{2}{\sqrt{\pi}} \sum_{n=0}^{\infty} \int_0^{\infty} dk\ U_n(k) = \sqrt{\pi}/r \quad , \tag{121}$$

and comparison with (114) shows that (71) is again satisfied; but, as in the case when r_1 and one of the other two r's are zero, the series does not converge absolutely.

4. Conclusion for first interchange

It has been shown that (71) holds for all values of $\{r_1,r_2,R\}$ except $r_1 = r_2 = R = 0$. In that case $1/r_{12}$ is

infinite, and as one might expect, both sides of the equation diverge when $\ell_1 = \ell_2 = L = 0$. If any of the ℓ's is not zero, both sides of the equation are identically zero. Furthermore, it has been shown that the right side of (71) converges absolutely as long as no more than one of the r's is zero. In fact, when all of the r's are greater than zero, the convergence is like that of $\sum_{n=1} n^{-2}$; when any one of the r's is zero, the convergence is like that of $\sum_{n=1} n^{-3/2}$; but when two of the r's are zero, the terms go like n^{-1} , and the convergence is conditional (that is, not absolute). Here we write out (71) explicitly:

$$J_{\ell_1\ell_2L}(r_1,r_2,R) = \sum_{n=0}^{\infty} \left[r_1^{\ell_1} L_n^{\ell_1+1/2}(r_1^2)/\Gamma(n+\ell_1+3/2) \right] \times I_{2n+\ell_1,\ell_2,L}(r_2,R) \quad , \tag{122}$$

where

$$I_{N\ell L}(r,R) = \int_0^{\infty} dk \, \exp[-(k/2)^2](k/2)^N j_\ell(kr) j_L(kR) \quad . \tag{123}$$

B. Validity of Second Interchange

Now we substitute (67) into (123) and obtain

$$I_{N\ell L}(r,R) = \int_0^{\infty} dk \sum_{n=0}^{\infty} V_n(k) \tag{124}$$

where

$$V_n(k) = T_n^{\ell}(k,r)\exp[-(k/2)^2](k/2)^N j_L(kR) \quad . \tag{125}$$

We need to show that

$$I_{N\ell L}(r,R) = \sum_{n=0}^{\infty}\int_0^{\infty} dk\ V_n(k) \quad . \tag{126}$$

1. Interchange for finite interval

First, it is necessary to show, using Theorem 2, that

$$\int_0^K dk \sum_{n=0}^{\infty} V_n(k) = \sum_{n=0}^{\infty}\int_0^K dk\ V_n(k) \tag{127}$$

for any positive K. Certainly $V_n(k)$ is integrable on the interval $0 \le k \le K$, or any subinterval thereof. It must be shown that the series $\sum_{n=0}^{\infty} V_n(k)$ converges uniformly on the interval $0 \le k \le K$, for any positive K. In section III.A.1 it was proved that $\sum_{n=0}^{\infty}|T_n|$ converges uniformly in $0 \le k \le K$, for any finite K. Therefore it satisfies the Cauchy condition, Theorem 3; that is, for every $\varepsilon>0$, there exists an N such that n>N implies

$$\left| \sum_{i=n+1}^{n+p} |T_i| \right| < \varepsilon \tag{128}$$

for each p=1,2,$\cdots$ and every k in $0 \le k \le K$. Now the quantity $|\exp[-(k/2)^2](k/2)^N j_L(kR)|$ is bounded in $0 \le k \le K$; let its maximum value be denoted by B. Then

$$\left| \sum_{i=n+1}^{n+p} V_i \right| < \left| \sum_{i=n+1}^{n+p} |V_i| \right| < B\varepsilon = \varepsilon' \tag{129}$$

for each p and every k in $0 \le k \le K$ if $n>N$. That is, for every $\varepsilon'>0$, there exists an N such that $n>N$ implies (129) for each p and every k; thus the series $\sum_{n=0}^{\infty} V_n(k)$ and $\sum_{n=0}^{\infty} |V_n(k)|$ converge absolutely for any nonnegative k, and uniformly in $0 \le k \le K$ for any positive K. Therefore the conditions of Theorem 2 are satisfied, and so (127) holds. This argument is valid for all values of r and R.

2. Interchange for infinite interval

The last step consists of showing that

$$\int_0^{\infty} dk \sum_{n=0}^{\infty} |V_n(k)| = \int_0^{\infty} dk \exp[-(k/2)^2](k/2)^N |j_L(kR)| \times \sum_{n=0}^{\infty} |T_n{}^{\ell}(k,r)| \tag{130}$$

converges, in order to satisfy the hypothesis of Theorem 1. For this purpose we use (74) and (76) to obtain

$$\int_0^{\infty} dk \sum_{n=0}^{\infty} |V_n(k)| \le (\sqrt{\pi}/2) r^{\ell} \exp(r^2/2)/\Gamma(\ell+3/2) \times \int_0^{\infty} dk \exp[-(k/2)^2](k/2)^{N+\ell} |j_L(kR)| \; . \tag{131}$$

The integral on the right exists, so the left side must con-

verge. Then according to Theorem 1, (126) is valid, and, in fact, the convergence of the right side is absolute. Note that this proof holds for all values of r and R.

C. Validity of Bipolar Expansion

It has now been shown that both of the term-by-term integrations used in the derivation of (19) were permissible. This means that (19) and the new form of the bipolar expansion (23) are valid. The sums on the right side of (19) converge in all cases except when $r_1 = r_2 = R = 0$ and $\ell_1 = \ell_2 = L = 0$; in that case, both sides of the equation diverge.

The final result of this section can be obtained explicitly by substituting (126), (125) and (68) into (122); it is

$$J_{\ell_1\ell_2 L}(r_1,r_2,R) = \frac{\sqrt{\pi}}{2} \sum_{n_1=0}^{\infty} \frac{r_1^{\ell_1} L_{n_1}^{\ell_1+1/2}(r_1^2)}{\Gamma(n_1+\ell_1+3/2)} \times \sum_{n_2=0}^{\infty} \frac{r_2^{\ell_2} L_{n_2}^{\ell_2+1/2}(r_2^2)}{\Gamma(n_2+\ell_2+3/2)} \times \int_0^{\infty} dk \exp[-k^2/2](k/2)^{2N'+L} j_L(kR) \tag{132}$$

in which N' is the N of (21). This is the same as (19), with $a_1=a_2=1$.

IV. INTEGRALS OVER GAUSSIAN ATOMIC ORBITALS

A. Integrals over Complex Gaussians

1. Coulomb integrals over Gaussian charge distributions

The results of this section were obtained by Birss and Ruedenberg (Salmon, Birss and Ruedenberg, 1968); they are summarized here in order to make the discussion complete.

It was shown by Boys (1950) that all electron repulsion integrals with Gaussian atomic orbitals can be reduced to integrals of the type

$$[g_A|g_B] = \int dV_1 \int dV_2 \; r_{12}^{-1} \; g_{q_a}(\zeta_a \vec{r}_{A1}) g_{q_b}(\zeta_b \vec{r}_{B2}) \quad , \qquad (133)$$

where the g_q represent Gaussian "basic charge distributions" given by

$$g_q = g_{n\ell m}(\zeta\vec{r}) = \zeta^3(\zeta r)^{2n+\ell} \exp(-\zeta^2 r^2) Y_{\ell m}(\theta,\phi) \quad . \qquad (134)$$

As in section II, the coordinate axes on the centers A and B are parallel, but z_A and z_B do not necessarily coincide with the AB direction.

If in (1) and (28) the orbital product $u_q^* u_q$, is replaced by the Gaussian basic charge distribution g_q , then (27) becomes an expression for the integral $[g_A|g_B]$. Now, since the centers P and Q in the bipolar expansion are arbitrary, we can choose P=A and Q=B, so that the position of each electron is specified with respect to the same origin in both the expan-

sion and the charge distribution. This enables us to use the orthogonality properties of the spherical harmonics in (28) to obtain

$$F_{q_p q_a}(\zeta,a) = \int dV\, g_{q_a}(\zeta\vec{r})\Lambda_{q_p}(\vec{r}/a)$$

$$= \delta_{\ell_p \ell_a}\, \delta_{m_p,-m_a}\, G_{q_a}^{\,n_p} \quad , \tag{135}$$

where $G_q^{\,k}$ is defined by

$$G_q^{\,k} = (-1)^m \int_0^\infty r^2 dr\; \zeta^3 (\zeta r)^{2n+\ell} \exp(-\zeta^2 r^2)\, \mathcal{L}_{k\ell}(r/a) \quad . \tag{136}$$

Choosing $a=\zeta^{-1}$, using the definition of (15), and making the substitution $(\zeta r)^2 = t$, one finds

$$G_q^{\,k} = \left[(-1)^m / \{2^{k+1}[2(k+\ell)+1]!!\}\right]$$

$$\times \int_0^\infty dt\; t^{\ell+1/2}\, L_k^{\ell+1/2}(t) \exp(-t)\, t^n \quad . \tag{137}$$

The integral in this equation is essentially an expansion coefficient of t^n in terms of the Laguerre polynomials $L_k^{\ell+1/2}(t)$, and therefore vanishes for $k>n$. The nonvanishing $G_q^{\,k}$ can be written as (Rainville, 1960, pp. 206, 207)

$$G_q^{\,k} = \left[\frac{(-1)^{k+m}\sqrt{\pi}}{2^{2k+\ell+1}}\right]\left[\frac{n!}{k!(n-k)!}\right]\left[\frac{\Gamma(n+\ell+3/2)}{\Gamma(k+\ell+3/2)}\right] \quad . \tag{138}$$

Now, substitution of (135) into (27) yields the final formula for the Coulomb integral defined in (133)

$$[g_A|g_B] = \sum_{n_1=0}^{n_a} \sum_{n_2=0}^{n_b} W_{n_1,\ell_a,-m_a,n_2,\ell_b,-m_b}(\vec{R},\zeta_a^{-1},\zeta_b^{-1}) \times G_{n_a\ell_a m_a}^{n_1} G_{n_b\ell_b m_b}^{n_2} \quad . \tag{139}$$

It will be recalled that the derivation of (27) involved term-by-term integrations which have not been proved to be valid. Thus we must either prove their validity, or find an independent check on (139). There are, in fact, two such checks (Salmon, Birss and Ruedenberg, 1968, section IV). First, (139) can be derived from (11)-(13) by replacing $u_q^* u_{q'}$ by g_q, interchanging the order of integration, and using the polynomial representation for the Laguerre function which results from the volume integration. Second, (139) can be shown to be equivalent to the results obtained by Krauss (1964), by rotating the axis systems on the two centers so as to have z_A and z_B coincident with the AB direction. Thus (139) is verified; the infinite series not only converge, but they reduce to finite sums.

The nuclear attraction integral

$$[g_A|\delta(\vec{r}_{B2})] = \int dV\, g_{q_a}(\zeta_a \vec{r}_A)/|\vec{r}_B| \tag{140}$$

can be derived from (139) if the charge distribution $g_B(\zeta_b \vec{r}_{B2})$ is replaced by the three-dimensional delta function

$$\delta(\vec{r}_{B2}) = \lim_{\zeta_b \to \infty} [(\zeta_b{}^3/\pi^{3/2}) \exp(-\zeta_b{}^2 r_{B2}{}^2)]$$

$$= \lim_{\zeta_b \to \infty} [(2/\pi) g_{000}(\zeta_b \vec{r}_{B2})] \quad . \tag{141}$$

The final result is

$$[g_A | \delta(\vec{r}_{B2})] = 8\sqrt{\pi}(-1)^{m_a} Y_{\ell_a, -m_a}(\Theta, \Phi)$$

$$\times \sum_{n_1=0}^{n_a} \mathcal{R}_{n_1}{}^{\ell_a}(R, \zeta_a{}^{-1}, 0) G_{n_a \ell_a m_a}{}^{n_1} \tag{142}$$

The results of this section will be used in the evaluation of integrals over Gaussian orbital products.

2. Integrals with complex Gaussian orbitals

We now choose the orbitals u of section II to be unnormalized complex spherical Gaussian orbitals

$$\chi^C = \zeta^{3/2} (\zeta r)^{\ell} \exp(-\zeta^2 r^2) Y_{\ell m}(\theta, \phi) \quad , \tag{143}$$

so that the integral to be evaluated is

$$I = [\chi_A{}^C\chi_B{}^C|\chi_C{}^C\chi_D{}^C]$$

$$= \int dV_1 \int dV_2 \; \chi_A{}^C(1)\chi_B{}^C(1) r_{12}{}^{-1} \chi_C{}^C(2)\chi_D{}^C(2) \quad . \qquad (144)$$

The first step is to express the orbital product $\chi_A{}^C\chi_B{}^C$ as a linear combination of the Gaussian basic charge distributions defined by (134). To do this, we choose the point P such that

$$\vec{P} = (\zeta_A{}^2/\zeta_P{}^2)\vec{A} + (\zeta_B{}^2/\zeta_P{}^2)\vec{B} \quad , \qquad (145)$$

and consequently (Boys, 1950)

$$\exp(-\zeta_A{}^2 r_A{}^2)\exp(-\zeta_B{}^2 r_B{}^2)$$

$$= \exp[-(\zeta_A{}^2\zeta_B{}^2/\zeta_P{}^2)R_{AB}{}^2]\exp[-\zeta_P{}^2 r_P{}^2] \quad , \qquad (146)$$

where

$$\zeta_P{}^2 = \zeta_A{}^2 + \zeta_B{}^2 \quad . \qquad (147)$$

Observe that the point P always lies somewhere on the line AB.

Next, we translate the spherical harmonic in each orbital, without rotation, to the point P, using the relation (Steinborn, 1969)

$$r_A^{\ell} Y_{\ell m}(\theta_A, \phi_A) = \sum_{\varepsilon=0}^{\ell} \sum_{\eta} Q_{\ell\varepsilon}^{m\eta} r_P^{\varepsilon} Y_{\varepsilon\eta}(\theta_P, \phi_P)$$

$$\times R_{AP}^{\ell-\varepsilon} Y_{\ell-\varepsilon, m-\eta}(\Theta_{AP}, \Phi_{AP}) \quad , \qquad (148)$$

in which the summation on η is governed by

$$|\eta| \leq \varepsilon \qquad (149a)$$

$$|m-\eta| \leq \ell-\varepsilon \quad , \qquad (149b)$$

and the constant $Q_{\ell\varepsilon}^{m\eta}$ is defined by

$$Q_{\ell\varepsilon}^{m\eta} = \sqrt{2\pi}\, N_{\ell}^{m} / (N_{\ell-\varepsilon}^{m-\eta}\, N_{\varepsilon}^{\eta}) \qquad (150a)$$

and

$$N_{\ell}^{m} = N_{\ell}^{-m} = \{[(2\ell+1)/2](\ell+m)!(\ell-m)!\}^{1/2} \quad . \qquad (150b)$$

The coordinates are related by $\vec{r}_A = \vec{R}_{AP} + \vec{r}_P$. The result of this last operation contains products of two spherical harmonics with arguments θ_P, ϕ_P ; to each of these products we apply the identity (Edmonds, 1957, p. 63 , Eq. 4.6.5)

$$Y_{\varepsilon\eta}(\theta,\phi) Y_{\varepsilon'\eta'}(\theta,\phi) = (-1)^{m} \sum_{\ell} \left[\frac{(2\varepsilon+1)(2\varepsilon'+1)(2\ell+1)}{4\pi}\right]^{1/2}$$

$$\times \begin{pmatrix} \varepsilon & \varepsilon' & \ell \\ \eta & \eta' & m \end{pmatrix} \begin{pmatrix} \varepsilon & \varepsilon' & \ell \\ 0 & 0 & 0 \end{pmatrix} Y_{\ell,-m}(\theta,\phi) \qquad (151a)$$

with

$$m = -\eta-\eta' \quad . \tag{151b}$$

These manipulations lead to an expression for $\chi_A^C \chi_B^C$ which contains five summations; they are governed by

$$0 \le \varepsilon \le \ell_A \tag{152a}$$

$$0 \le \varepsilon' \le \ell_B \tag{152b}$$

$$\max\begin{Bmatrix} -\varepsilon \\ m_A-\ell_A+\varepsilon \end{Bmatrix} \le \eta \le \min\begin{Bmatrix} +\varepsilon \\ \ell_A+m_A-\varepsilon \end{Bmatrix} \tag{152c}$$

$$\max\begin{Bmatrix} -\varepsilon' \\ m_B-\ell_B+\varepsilon' \end{Bmatrix} \le \eta' \le \min\begin{Bmatrix} +\varepsilon' \\ \ell_B+m_B-\varepsilon' \end{Bmatrix} \tag{152d}$$

$$\max\begin{Bmatrix} |\varepsilon-\varepsilon'| \\ |m| \end{Bmatrix} \le \ell \le \varepsilon+\varepsilon' \quad , \quad \varepsilon+\varepsilon'+\ell = \text{even}. \tag{152e}$$

For computational convenience, we replace the first four of these indices by new ones, defined by (151b) and

$$\alpha = \ell_A-\ell_B-\varepsilon+\varepsilon' \tag{153a}$$

$$\beta = \ell_A+\ell_B-\varepsilon-\varepsilon' \tag{153b}$$

$$\delta = m_A-m_B-\eta+\eta' \quad . \tag{153c}$$

The summation on ℓ is interchanged with those on m and δ,

which leads to the final conditions on the summations

$$-\ell_B \le \alpha \le \ell_A \tag{154a}$$

$$|\alpha| \le \beta \le \ell_A+\ell_B-|\ell_A-\ell_B-\alpha| \quad , \quad \alpha+\beta = \text{even} \tag{154b}$$

$$\max\left\{\begin{matrix}|\ell_A-\ell_B-\alpha| \\ |m_A+m_B|-\beta\end{matrix}\right\} \le \ell \le \ell_A+\ell_B-\beta \quad , \quad \ell_A+\ell_B+\alpha+\ell = \text{even} \tag{154c}$$

$$\max\left\{\begin{matrix}-\ell \\ -m_A-m_B-\beta \\ -m_A-\ell_B-\alpha \\ -m_B-\ell_A+\alpha\end{matrix}\right\} \le m \le \min\left\{\begin{matrix}+\ell \\ -m_A-m_B+\beta \\ -m_A+\ell_B+\alpha \\ -m_B+\ell_A-\alpha\end{matrix}\right\} \tag{154d}$$

$$\max\left\{\begin{matrix}m_A-m_B+m-2\ell_B-\alpha+\beta \\ m_A+m_B+m+\alpha-\beta \\ m_A-m_B-m-2\ell_A+\alpha+\beta \\ -m_A-m_B-m-\alpha-\beta\end{matrix}\right\} \le \delta \le \min\left\{\begin{matrix}m_A-m_B+m+2\ell_B+\alpha-\beta \\ m_A+m_B+m-\alpha+\beta \\ m_A-m_B-m+2\ell_A-\alpha-\beta \\ -m_A-m_B-m+\alpha+\beta\end{matrix}\right\} \tag{154e}$$

The expression for the orbital product is

$$\chi_A^C \chi_B^C = B_{AB}(\rho,\tau) \sum_\alpha \sum_\beta \sum_\ell \sum_m \tau^\alpha \rho^\beta C_{\alpha\beta\ell m} g_{q_p}(\zeta_P \vec{r}_P) \quad , \tag{155}$$

where the following quantities have been introduced

$$B_{AB}(\rho,\tau) = \left[(\tau+\tau^{-1})^3 (1+\tau^2)^{\ell_A} (1+\tau^{-2})^{\ell_B}\right]^{-1/2} \exp(-\rho^2) \tag{156a}$$

$$\rho = \zeta_A \zeta_B R_{AB}/\zeta_P \tag{156b}$$

$$\tau = \zeta_B/\zeta_A \tag{156c}$$

$$q_p = \{(\ell_A+\ell_B-\beta-\ell)/2, \ell, -m\} \tag{157}$$

$$C_{\alpha\beta\ell m} = (-1)^m \sum_{\delta} Q_{\ell_A\varepsilon}{}^{m_A\eta} Y_{\ell_A-\varepsilon, m_A-\eta}(\Theta_{AB}, \Phi_{AB})$$

$$\times (-1)^{\ell_B-\varepsilon'} Q_{\ell_B\varepsilon'}{}^{m_B\eta'} Y_{\ell_B-\varepsilon', m_B-\eta'}(\Theta_{AB}, \Phi_{AB})$$

$$\times \left[\frac{(2\varepsilon+1)(2\varepsilon'+1)(2\ell+1)}{4\pi}\right]^{1/2} \begin{pmatrix} \varepsilon & \varepsilon' & \ell \\ \eta & \eta' & m \end{pmatrix} \begin{pmatrix} \varepsilon & \varepsilon' & \ell \\ 0 & 0 & 0 \end{pmatrix}. \tag{158}$$

The summations are governed by (154), and ζ_p is given by (147). The constant Q is defined by (150), and ε, ε', η, and η' can be obtained by inverting (151b) and (153).

Now, since the orbital product $\chi_A{}^C \chi_B{}^C$ has been expressed as a linear combination of the charge distributions g_p, the integral I of (144) must be a linear combination of the integrals $[g_p|g_Q]$ of (133) and (139). We have

$$I = B_{AB}(\rho_1, \tau_1) B_{CD}(\rho_2, \tau_2) \sum_{(\alpha\beta\ell mn)_1} \sum_{(\alpha\beta\ell mn)_2}$$

$$\times \tau_1^{\alpha_1} \rho_1^{\beta_1} C_{(\alpha\beta\ell m)_1} G_{q_p}^{n_1} \tau_2^{\alpha_2} \rho_2^{\beta_2} C_{(\alpha\beta\ell m)_2} G_{q_q}^{n_2}$$

$$\times W_{n_1\ell_1 m_1 n_2 \ell_2 m_2}(\vec{R}_{PQ}, \zeta_P^{-1}, \zeta_Q^{-1}) \quad , \tag{159}$$

where G is given by (138) and W by (25). This result was first obtained, in a slightly different form, by Kinser and Ruedenberg (1971). They have discussed the constant $C_{\alpha\beta\ell m}$. The index n has limits

$$0 \leq n \leq (\ell_A+\ell_B-\beta-\ell)/2 \quad . \tag{160}$$

A formula for the nuclear attraction integral can be found in an analogous manner by replacing $\chi_A{}^C\chi_B{}^C$ by the delta function of (141) and using (142) instead of (139).

B. Integrals over Real Gaussian Orbitals

For many purposes it is more convenient to use real Gaussian orbitals instead of complex ones. Then we would like to evaluate integrals of the type

$$I = [\chi_A{}^R\chi_B{}^R|\chi_C{}^R\chi_D{}^R]$$

$$= \int dV_1 \int dV_2 \; \chi_A{}^R(1)\chi_B{}^R(1)r_{12}{}^{-1}\chi_C{}^R(2)\chi_D{}^R(2) \quad , \tag{161}$$

in which the real Gaussian orbital χ^R is defined by

$$\chi_{\ell m}{}^R = \sum_{\mu=\pm|m|} M_{m\mu} \; \chi_{\ell\mu}{}^C \quad , \tag{162}$$

Here the complex Gaussian orbital $\chi_{\ell\mu}{}^C$ was defined by (143), and the constant $M_{m\mu}$ is given by

$$M_{00} = 1/2 \tag{163a}$$

and for $m \neq 0$,

$$\begin{pmatrix} M_{|m|,|m|} & M_{|m|,-|m|} \\ M_{-|m|,|m|} & M_{-|m|,-|m|} \end{pmatrix} = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 & (-1)^m \\ -i & i(-1)^m \end{pmatrix} \tag{163b}$$

1. Real orbital product

First we wish to express the product of two real orbitals $\chi_A^R \chi_B^R$ in terms of the Gaussian basic charge distributions. The definition (162) gives immediately

$$\chi_{\ell_A m_A}^R \chi_{\ell_B m_B}^R = \sum_{\mu_A} \sum_{\mu_B} M_{m_A \mu_A} M_{m_B \mu_B} \chi_{\ell_A \mu_A}^C \chi_{\ell_B \mu_B}^C \quad . \tag{164}$$

Substitution of the expression (155) for the product of complex orbitals into this equation yields

$$\chi_{\ell_A m_A}^R \chi_{\ell_B m_B}^R = B_{AB}(\rho,\tau) \sum_{\mu_A} \sum_{\mu_B} M_{m_A \mu_A} M_{m_B \mu_B} \times \sum_{\alpha} \sum_{\beta} \sum_{\ell} \sum_{m} \tau^{\alpha} \rho^{\beta} C_{\alpha\beta\ell m} g_{q_p} \quad . \tag{165}$$

The conditions on the summations are:

$$\mu_A = \pm |m_A| \tag{166a}$$

$$\mu_B = \pm |m_B| \tag{166b}$$

$$-\ell_B \leq \alpha \leq \ell_A \tag{166c}$$

$$|\alpha| \leq \beta \leq \ell_A+\ell_B-|\ell_A-\ell_B-\alpha| \qquad \alpha+\beta=\text{even} \tag{166d}$$

$$\max\left\{\begin{matrix}|\ell_A-\ell_B-\alpha| \\ |\mu_A+\mu_B|-\beta\end{matrix}\right\} \leq \ell \leq \ell_A+\ell_B-\beta \qquad \ell+\alpha+\ell_A+\ell_B=\text{even} \tag{166e}$$

$$\max\left\{\begin{matrix}-\ell \\ -\mu_A-\mu_B-\beta \\ -\mu_A-\ell_B-\alpha \\ -\mu_B-\ell_A+\alpha\end{matrix}\right\} \leq m \leq \min\left\{\begin{matrix}+\ell \\ -\mu_A-\mu_B+\beta \\ -\mu_A+\ell_B+\alpha \\ -\mu_B+\ell_A-\alpha\end{matrix}\right\} . \tag{166f}$$

On the right side of (165), only the constants M and C depend upon the indices μ_A and μ_B ; the other factors, containing the dependence on the orbital exponents and electronic coordinates, are independent of these indices. Thus it is desirable to rearrange the summations as follows:

$$\sum_{\mu_A}\sum_{\mu_B}\sum_{\alpha}\sum_{\beta}\sum_{\ell}\sum_{m} \rightarrow \sum_{\alpha}\sum_{\beta}\sum_{\ell}\sum_{m}\sum_{\mu_A}\sum_{\mu_B} . \tag{167}$$

After considerable algebraic manipulation, we find the new limits to be:

$$-\ell_B \leq \alpha \leq \ell_A \tag{168a}$$

$$|\alpha| \leq \beta \leq \ell_A+\ell_B-|\ell_A-\ell_B-\alpha| \qquad \alpha+\beta=\text{even} \tag{168b}$$

$$\ell_{\ell o} \leq \ell \leq \ell_A+\ell_B-\beta \qquad \ell+\alpha+\ell_A+\ell_B=\text{even} \tag{168c}$$

$$-\min\begin{Bmatrix} \ell \\ m_{hi} \end{Bmatrix} \le m \le \min\begin{Bmatrix} \ell \\ m_{hi} \end{Bmatrix} \qquad |m| \ge m_{\ell o} \tag{168d}$$

$$\mu_A = \pm|m_A| \tag{168e}$$

$$\mu_B = \pm|m_B| \quad , \tag{168f}$$

with the definitions

$$\ell_{\ell o} = \max\{|\ell_A - \ell_B - \alpha|, \; ||m_A| - |m_B|| - \beta\} \tag{169a}$$

$$m_{\ell o} = \max\begin{Bmatrix} 0 \\ |m_A| - \ell_B - \alpha \\ |m_B| - \ell_A + \alpha \\ ||m_A| - |m_B|| - \beta \end{Bmatrix} \tag{169b}$$

$$m_{hi} = \min\begin{Bmatrix} \ell_B + |m_A| + \alpha \\ \ell_A + |m_B| - \alpha \\ |m_A| + |m_B| + \beta \end{Bmatrix} \quad . \tag{169c}$$

Notice that (168d) implies that when $m_{\ell o}$ is positive the summation on m will split into two sums

$$\sum_{m=-m_{hi}}^{-m_{\ell o}} + \sum_{m=m_{\ell o}}^{m_{hi}} \quad ;$$

terms with m values in between these ranges do not occur. In addition to (168e) and (168f), there are the following re-

strictions on μ_A and μ_B :

$$|\mu_A+\mu_B| \leq \ell+\beta \tag{170a}$$

$$\max\begin{Bmatrix} -|m|+|m_B|-\beta \\ -m-|m_B|-\beta \\ -m-\ell_B-\alpha \end{Bmatrix} \leq \mu_A \leq \min\begin{Bmatrix} -m+|m_B|+\beta \\ -m+\ell_B+\alpha \end{Bmatrix} \tag{170b}$$

$$\max\begin{Bmatrix} -\mu_A-\beta-m \\ -\ell_A+\alpha-m \end{Bmatrix} \leq \mu_B \leq \min\begin{Bmatrix} -\mu_A+\beta-m \\ \ell_A-\alpha-m \end{Bmatrix} \quad . \tag{170c}$$

Thus, not all four combinations of μ_A and μ_B will occur for each m. In fact, Hubert Kinser (private communication on the summation conditions, 1970, Iowa State University, Ames, Iowa) has shown that for certain values of m none of the combinations are allowed, which implies that these values of m are not allowed.

With the summations restricted by (168)-(170), (165) becomes

$$\chi^R_{\ell_A m_A} \chi^R_{\ell_B m_B} = B_{AB}(\rho,\tau) \sum_\alpha \sum_\beta \tau^\alpha \rho^\beta \sum_\ell \sum_m g_{q_p}(\zeta_p \vec{r}_p) D_{\alpha\beta\ell m} \tag{171a}$$

with

$$D_{\alpha\beta\ell m} = \sum_{\mu_A \mu_B} M_{m_A \mu_A} M_{m_B \mu_B} C_{\alpha\beta\ell m} \quad . \tag{171b}$$

The quantities in these equations are defined by (156)-(158), (134) and (163). Since M and C depend only on the quantum

numbers, the positions of the centers A and B, and the summation indices, the sums over μ_A and μ_B can be performed immediately, before (171a) is substituted into the integral of (161).

Because the left side of (171a) is real, the right side is real, also. Furthermore, this is true for all values of τ and ρ. It is clear from (156) that B, τ, and ρ are real. Then the coefficient of each product of powers of τ and ρ must also be real; that is, the quantity

$$\sum_{\ell} \sum_{m} g_{q_p}(\zeta_p \vec{r}_p) D_{\alpha\beta\ell m}$$

is real for each combination of α and β.

2. Real form of the bipolar expansion

It would be possible to derive an expression for the integral of (161) by using (164) to express it as a linear combination of sixteen integrals over complex Gaussians, of the type given by (144) and (159). This approach would give an expression involving complex quantities. Since the integral of (161) contains only real quantities, it is itself real, and it should be possible to derive a formula for it which contains only real quantities. To accomplish this we need only express the bipolar expansion for r_{12}^{-1} in terms of real functions.

First we write down the bipolar expansion of (5) and put

it into a form with summations over only positive values of m_1 and m_2

$$r_{12}^{-1} = \sum_{\ell_1=0}^{\infty} \sum_{m_1=-\ell_1}^{+\ell_1} \sum_{\ell_2=0}^{\infty} \sum_{m_2=-\ell_2}^{+\ell_2} T_{q_1 q_2}$$

$$= \sum_{\ell_1=0}^{\infty} \sum_{m_1=0}^{\ell_1} \sum_{\ell_2=0}^{\infty} \sum_{m_2=0}^{\ell_2} [(1+\delta_{m_1 0})(1+\delta_{m_2 0})]^{-1}$$

$$\times [(T_{\ell_1 m_1 \ell_2 m_2} + T_{\ell_1,-m_1,\ell_2,-m_2})$$

$$+ (T_{\ell_1,m_1,\ell_2,-m_2} + T_{\ell_1,-m_1,\ell_2,m_2})] \quad . \tag{172}$$

Here the term T is given by

$$T_{\ell_1 m_1 \ell_2 m_2} = (-1)^{\ell_1} Y_{\ell_1 m_1}(\theta_1,\phi_1) Y_{\ell_2 m_2}(\theta_2,\phi_2)$$

$$\times \sum_L Y_{LM}(\Theta,\Phi) \omega_L^{\ell_1 \ell_2 m_1 m_2} J_{\ell_1 \ell_2 L}(r_1,r_2,R) \tag{173}$$

The summation on L is restricted by (9), and ω and M are given by (7) and (8), respectively. The function J is defined by (6); notice that it is real. In fact, the only complex quantities in (173) are the three spherical harmonics. Application of the identity (Edmonds, 1957, p. 21, Eq. 2.5.6)

$$Y_{\ell m}^{*}(\theta,\phi) = (-1)^m Y_{\ell,-m}(\theta,\phi) \tag{174}$$

to each of these spherical harmonics, followed by use of (8), yields

$$T_{\ell_1 m_1 \ell_2 m_2}^{*} = T_{\ell_1,-m_1,\ell_2,-m_2} \tag{175a}$$

and

$$T_{\ell_1,m_1,\ell_2,-m_2}^{*} = T_{\ell_1,-m_1,\ell_2,m_2} \quad . \tag{175b}$$

Then (172) can be written as

$$r_{12}^{-1} = \sum_{\ell_1=0}^{\infty} \sum_{m_1=0}^{\ell_1} \sum_{\ell_2=0}^{\infty} \sum_{m_2=0}^{\ell_2} [(1+\delta_{m_1 0})(1+\delta_{m_2 0})]^{-1}$$

$$\times 2\,\mathrm{Re}[T_{\ell_1 m_1 \ell_2 m_2} + T_{\ell_1,m_1,\ell_2,-m_2}] \quad , \tag{176}$$

where Re denotes the real part of the argument.

In order to evaluate the real part of T, we express each spherical harmonic in terms of its real and imaginary parts, and multiply the three expressions together. Then we make use of

$$\mathrm{Re}[Y_{\ell,-m}(\theta,\phi)] = (-1)^m \mathrm{Re}[Y_{\ell m}(\theta,\phi)] \tag{177a}$$

$$\mathrm{Im}[Y_{\ell,-m}(\theta,\phi)] = -(-1)^m \mathrm{Im}[Y_{\ell m}(\theta,\phi)] \quad , \tag{177b}$$

which is a consequence of (174). Finally, the notation

$$R_+(z) = \mathcal{R}e(z) = \text{real part of } z$$
$$R_-(z) = \mathcal{I}m(z) = \text{imaginary part of } z \tag{178}$$

and

$$\begin{pmatrix} S_{+|m|}(+,+) & S_{+|m|}(+,-) \\ S_{+|m|}(-,+) & S_{+|m|}(-,-) \end{pmatrix} = \begin{pmatrix} +1 & -1 \\ -1 & -1 \end{pmatrix} \tag{179a}$$

$$\begin{pmatrix} S_{-|m|}(+,+) & S_{-|m|}(+,-) \\ S_{-|m|}(-,+) & S_{-|m|}(-,-) \end{pmatrix} = (-1)^m \begin{pmatrix} +1 & +1 \\ -1 & +1 \end{pmatrix} \tag{179b}$$

is introduced. The result is

$$R_+(T_{\ell_1 m_1 \ell_2 m_2}) = (-1)^{\ell_1} \sum_L \omega_L^{\ell_1 \ell_2 m_1 m_2} J_{\ell_1 \ell_2 L}$$
$$\times \sum_{\varepsilon=\pm} \sum_{\eta=\pm} S_{m_2}(\varepsilon,\eta) R_{\varepsilon\eta}(Y_{LM}) R_\varepsilon(Y_{\ell_1 m_1}) R_\eta(Y_{\ell_2|m_2|}). \tag{180}$$

Here M is defined by (8), and the summation conditions for L are given by (9). Notice that the value of M, and hence of the lower limit on L, depends on the sign of m_2 ; m_1 is assumed to be nonnegative. The product $\varepsilon\eta$ is taken to be + if ε and η are the same, - if they are different. Because $\mathcal{I}m(Y_{\ell 0}) = 0$, terms in (180) with $m_1=0$ and $\varepsilon=-$, or $m_2=0$ and $\eta=-$, or M=0 and $\varepsilon\eta=-$ must vanish.

Now, to put this in its final form, we substitute (19) for J in (180), and put the result in (176). The function

$\mathcal{R}_N^L$ in (19), given by (31) and (34), is written in the following way:

$$\mathcal{R}_N^L(R,a_1,a_2) = (2a_1)^{2n_1+\ell_1}\ (2a_2)^{2n_2+\ell_2}$$

$$\times R^L\ f_{2N+L}^{\ L}(\rho^2, a_1^2+a_2^2) \quad , \tag{181}$$

with

$$f_L^{\ L}(x,a) = a^{-L-1/2}\ \Gamma(L+1/2)\,\gamma^*(L+1/2,x) \tag{182a}$$

$$f_{2N+L}^{\ L}(x,a) = a^{-N-L-1/2}\ (N-1)!e^{-x}\ L_{N-1}^{\ L+1/2}(x) \ . \tag{182b}$$

The index N is taken to be greater than zero in (182b), and in (182a), the function γ^* is related to the incomplete gamma function (Abramowitz and Stegun, 1965, Item 6.5.4). Next two new quantities are defined:

$$w_L^{\ \ell_1\ell_2 m_1 m_2} = N_L^{\ M}\ \omega_L^{\ \ell_1\ell_2 m_1 m_2} \quad , \tag{183}$$

and

$$\hat{\mathcal{Y}}_{LM}(\vec{R}) = R^L\ Y_{LM}(\Theta,\Phi)/N_L^{\ M} \quad , \tag{184}$$

which is related to the solid spherical harmonic

$$\mathcal{Y}_{LM}(\vec{R}) = R^L\ Y_{LM}(\Theta,\Phi) \quad . \tag{185}$$

The constant $N_L^{\ M}$ is defined by (150b). Then the real form of

the bipolar expansion is

$$r_{12}^{-1} = \sum_{q_1}' \sum_{q_2}' 2[(1+\delta_{m_1 0})(1+\delta_{m_2 0})]^{-1}$$

$$\times [\mathcal{Y}_{\ell_1 m_1 n_1 \ell_2 m_2 n_2} + \mathcal{Y}_{\ell_1, m_1, n_1, \ell_2, -m_2, n_2}] \quad (186)$$

with

$$\sum_{q}' = \sum_{\ell=0}^{\infty} \sum_{m=0}^{\ell} \sum_{n=0}^{\infty} \quad (187)$$

and

$$\mathcal{Y}_{\ell_1 m_1 n_1 \ell_2 m_2 n_2} = (-1)^{\ell_1} (2a_1)^{2n_1+\ell_1} (2a_2)^{2n_2+\ell_2}$$

$$\times \sum_{L} w_L^{\ell_1 \ell_2 m_1 m_2} f_{2N+L}^{L}(\rho^2, a_1^2+a_2^2)$$

$$\times \sum_{\varepsilon=\pm} \sum_{\eta=\pm} S_{m_2}(\varepsilon,\eta) R_{\varepsilon\eta}[\hat{\mathcal{Y}}_{LM}(\vec{R})]$$

$$\times R_{\varepsilon}[\Lambda_{\ell_1 m_1 n_1}(\vec{r}_1/a_1)] R_{\eta}[\Lambda_{\ell_2|m_2|n_2}(\vec{r}_2/a_2)] \; . \quad (188)$$

The function Λ is given by (26) and (15). Equations (186)-(188) represent a further development of a result obtained by Kinser and Ruedenberg (1971).

3. Integral formula

a. Preliminary formula Now we will combine the results of sections 1 and 2 to obtain a formula for the desired integral. First the expression for the product of real orbitals (171a) is substituted twice into the integral (161). The result is

$$I = B_{AB}(\rho_1,\tau_1)B_{CD}(\rho_2,\tau_2)$$

$$\times \sum_{\alpha_1}\sum_{\beta_1}\sum_{\alpha_2}\sum_{\beta_2} \tau_1^{\alpha_1}\rho_1^{\beta_1}\tau_2^{\alpha_2}\rho_2^{\beta_2} I'_{\alpha_1\beta_1\alpha_2\beta_2} \qquad (189)$$

with

$$I'_{\alpha_1\beta_1\alpha_2\beta_2} = \int dV_1 \int dV_2 \sum_{\ell_1'}\sum_{m_1'} g_{q_p'}(\zeta_P \vec{r}_{P1}) D_{(\alpha\beta\ell'm')_1}$$

$$\times r_{12}^{-1} \sum_{\ell_2'}\sum_{m_2'} g_{q_q'}(\zeta_Q \vec{r}_{Q2}) D_{(\alpha\beta\ell'm')_2} . \qquad (190)$$

Again we choose the origin points in the bipolar expansion to be the points P and Q defined by (145), and the scaling parameters a_1 and a_2 to be ζ_P^{-1} and ζ_Q^{-1}, respectively. Now the bipolar expansion of (186)-(188) is substituted into (190). The result contains products of two integrals of the form

$$G'_{q\alpha\beta\varepsilon} = \int dV\ R_\varepsilon\{\Lambda_{\ell mn}(\zeta\vec{r})\}\left[\sum_{\ell'}\sum_{m'} g_{n',\ell',-m'}(\zeta\vec{r}) D_{\alpha\beta\ell'm'}\right] , \qquad (191)$$

where

$$n' = (\ell_A+\ell_B-\beta-\ell')/2 \quad . \tag{192}$$

It was shown in section 1 that the quantity in brackets is real, which implies that the integral G' is real. It can be evaluated by using

$$R_\varepsilon(\Lambda_{\ell mn}) = (\Lambda_{\ell mn} + \varepsilon\Lambda^*_{\ell mn})/2\sqrt{\varepsilon}$$

$$= (\Lambda_{\ell mn} + \varepsilon(-1)^m \Lambda_{\ell,-m,n})/2\sqrt{\varepsilon} \quad , \tag{193}$$

(135), and the fact that $G_{q'}{}^n$ vanishes when $n>n'$. The result is

$$G'_{\ell mn\alpha\beta\varepsilon} = G_{n'\ell m}{}^n[D_{\alpha\beta\ell m} + \varepsilon(-1)^m D_{\alpha,\beta,\ell,-m}]/2\sqrt{\varepsilon} \tag{194}$$

provided that

$$\ell_{\ell o} \le \ell \le \ell_A+\ell_B-\beta \qquad \ell+\alpha+\ell_A+\ell_B=\text{even} \tag{195a}$$

$$m_{\ell o} \le m \le \min\{\ell,\ m_{hi}\} \tag{195b}$$

$$0 \le n \le n' \quad ; \tag{195c}$$

for all other values of $\{\ell mn\}$, G' vanishes. The quantities G and D in (194) are given by (138) and (171b). Now we have for I'

$$I'_{\alpha_1\beta_1\alpha_2\beta_2} = \sum_{\ell_1 m_1 n_1 \ell_2 m_2 n_2} \sum \sum \sum \sum \sum 2[(1+\delta_{m_1 0})(1+\delta_{m_2 0})]^{-1}$$

$$\times (2/\zeta_P)^{2n_1+\ell_1} (2/\zeta_Q)^{2n_2+\ell_2} (-1)^{\ell_1}$$

$$\times (\hat{T}_{\ell_1 m_1 n_1 \ell_2 m_2 n_2} + \hat{T}_{\ell_1, m_1, n_1, \ell_2, -m_2, n_2}), \quad (196)$$

with

$$\hat{T}_{\ell_1 m_1 n_1 \ell_2 m_2 n_2} = \sum_L w_L^{\ell_1 \ell_2 m_1 m_2} f_{2N+L}^{L}(\rho^2, \zeta_P^{-2}+\zeta_Q^{-2})$$

$$\times \sum_{\varepsilon=\pm} \sum_{\eta=\pm} S_{m_2}(\varepsilon,\eta) R_{\varepsilon\eta}[\hat{y}_{LM}(\vec{R})]$$

$$\times G'_{\ell_1 m_1 n_1 \alpha_1 \beta_1 \varepsilon} G'_{\ell_2 |m_2| n_2 \alpha_2 \beta_2 \eta} \quad . \quad (197)$$

The summation on L is governed by (8) and (9); the lower limit depends on the sign of m_2 . The other summations are restricted by (195).

b. Reordering of sums This formula can be put into a form which is more convenient for computation. First, the two indices n_1 and n_2 are replaced by new indices, σ_1 and σ_2, defined by

$$\sigma = 2n+\ell \quad , \quad (198a)$$

with limits

$$\ell \le \sigma \le \ell_A+\ell_B-\beta \quad . \tag{198b}$$

These new indices are the exponents on $(2/\zeta_P)$ and $(2/\zeta_Q)$, respectively. Notice that, in view of (21), the subscript on f_{2N+L}^{L} is equal to $\sigma_1+\sigma_2$. Next, the order of summation is changed from

$$\sum_{\ell}\sum_{m}\sum_{\sigma} \quad \text{to} \quad \sum_{\sigma}\sum_{\ell}\sum_{m} \quad ;$$

the consequent new limits are

$$\ell_{\ell o} \le \sigma \le \ell_A+\ell_B-\beta \qquad \sigma+\alpha+\ell_A+\ell_B=\text{even} \tag{199a}$$

$$\ell_{\ell o} \le \ell \le \sigma \qquad \sigma+\ell=\text{even} \tag{199b}$$

$$m_{\ell o} \le m \le \min\{\ell,\ m_{hi}\} \quad , \tag{199c}$$

with $\ell_{\ell o}$, $m_{\ell o}$ and m_{hi} defined by (169). At this point we can write (196) in the form

$$I'_{\alpha_1\beta_1\alpha_2\beta_2} = \sum_{\sigma_1} (2/\zeta_P)^{\sigma_1} \sum_{\sigma_2} (2/\zeta_Q)^{\sigma_2} V_{(\alpha\beta\sigma)_1(\alpha\beta\sigma)_2} \tag{200}$$

in which

$$V_{(\alpha\beta\sigma)_1(\alpha\beta\sigma)_2} = \sum_{\ell_1}\sum_{m_1}\sum_{\ell_2}\sum_{m_2} 2(-1)^{\ell_1} [(1+\delta_{m_1 0})(1+\delta_{m_2 0})]^{-1}$$

$$\times(\hat{T}_{\ell_1 m_1 n_1 \ell_2 m_2 n_2} + \hat{T}_{\ell_1,m_1,n_1,\ell_2,-m_2,n_2}) \quad , \tag{201}$$

with $n = (\sigma-\ell)/2$. All factors which depend on the orbital exponents, except those contained in $\hat{T}$, have been moved outside of the sums on $\ell_1 m_1 \ell_2 m_2$. The functions

$$f_{\sigma_1+\sigma_2}{}^{L}(\rho^2, \zeta_P^{-2}+\zeta_Q^{-2}) \quad \text{and} \quad R_{\varepsilon\eta}[\hat{\mathcal{Y}}_{LM}(\vec{R})] \quad ,$$

contained in $\hat{T}$, depend on the orbital exponents, because $R = R_{PQ}$ depends on the positions of the points P and Q, which in turn depend on the orbital exponents. We now move the function f outside of the sums on $\ell_1 m_1 \ell_2 m_2$ by making the following interchange of summations:

$$\sum_{\ell_1}\sum_{m_1}\sum_{\ell_2}\sum_{m_2}\sum_{L} \quad \rightarrow \quad \sum_{L}\sum_{\ell_1}\sum_{m_1}\sum_{\ell_2}\sum_{m_2} \quad . \tag{202}$$

Because the lower limit on L depends on the sign of m_2 , the new limits must be obtained separately for the term with $+m_2$ and that with $-m_2$. For $+m_2$ we have:

$$M = -m_1-m_2 \tag{203a}$$

$$\max\begin{Bmatrix} m_{1\ell o}+m_{2\ell o} \\ \ell_{1\ell o}-\sigma_2 \\ \ell_{2\ell o}-\sigma_1 \end{Bmatrix} \le L \le \sigma_1+\sigma_2 \qquad L+\sigma_1+\sigma_2=\text{even} \tag{203b}$$

$$\max\begin{Bmatrix} \ell_{1\ell o} \\ \ell_{2\ell o}-L \\ L-\sigma_2 \end{Bmatrix} \le \ell_1 \le \min\begin{Bmatrix} \sigma_1 \\ L+\sigma_2 \end{Bmatrix} \quad \ell_1+\sigma_1=\text{even} \tag{203c}$$

$$\max\begin{Bmatrix} \ell_{2\ell o} \\ |L-\ell_1| \end{Bmatrix} \le \ell_2 \le \min\begin{Bmatrix} \sigma_2 \\ L+\ell_1 \end{Bmatrix} \qquad \ell_2+\sigma_2=\text{even} \tag{203d}$$

$$m_{1\ell o} \le m_1 \le \min\begin{Bmatrix} \ell_1 \\ m_{1hi} \\ L-m_{2\ell o} \end{Bmatrix} \tag{203e}$$

$$m_{2\ell o} \le m_2 \le \min\begin{Bmatrix} \ell_2 \\ m_{2hi} \\ L-m_1 \end{Bmatrix} . \tag{203f}$$

For $-m_2$ the limits on ℓ_1 and ℓ_2 are the same as above, but the other limits are:

$$M = -m_1+m_2 \tag{203g}$$

$$\max\begin{Bmatrix} m_{1\ell o}-m_{2hi} \\ m_{2\ell o}-m_{1hi} \\ \ell_{1\ell o}-\sigma_2 \\ \ell_{2\ell o}-\sigma_1 \end{Bmatrix} \le L \le \sigma_1+\sigma_2 \qquad L+\sigma_1+\sigma_2=\text{even} \tag{203h}$$

$$\max\begin{Bmatrix} m_{1\ell o} \\ m_{2\ell o}-L \end{Bmatrix} \le m_1 \le \min\begin{Bmatrix} \ell_1 \\ m_{1hi} \\ L+m_{2hi} \end{Bmatrix} \tag{203i}$$

$$\max\begin{Bmatrix} m_{2\ell o} \\ m_1-L \end{Bmatrix} \le m_2 \le \min\begin{Bmatrix} \ell_2 \\ m_{2hi} \\ L+m_1 \end{Bmatrix} \quad . \tag{203j}$$

We can take (203h) to give the overall limits on L, but we must remember that there is no term with $M=-m_1-m_2$ if $L < m_{1\ell o}+m_{2\ell o}$.

This interchange of summations yields, for V of (201),

$$V_{(\alpha\beta\sigma)_1(\alpha\beta\sigma)_2} = \sum_L f_{\sigma_1+\sigma_2}{}^{L}(\rho^2, \zeta_P^{-2}+\zeta_Q^{-2})$$

$$\times \sum_{\ell_1\ell_2} \sum (-1)^{\ell_1} (U_{L\ell_1\ell_2}^{+} + U_{L\ell_1\ell_2}^{-}) \ , \tag{204}$$

with

$$U_{L\ell_1\ell_2}^{s} = \sum_{m_1m_2} \sum 2[(1+\delta_{m_1 0})(1+\delta_{m_2 0})]^{-1} w_L{}^{\ell_1\ell_2 m_1(sm_2)}$$

$$\times \sum_{\varepsilon=\pm} \sum_{\eta=\pm} S_{(sm_2)}(\varepsilon,\eta) R_{\varepsilon\eta}[\hat{\mathcal{Y}}_{LM}(\vec{R})]$$

$$\times \hat{G}_{(\alpha\beta\sigma\ell m)_1}^{\varepsilon}(k_{AB}, \vec{R}_{AB}) \hat{G}_{(\alpha\beta\sigma\ell m)_2}^{\eta}(k_{CD}, \vec{R}_{CD}) \ . \tag{205}$$

The following notation has been adopted:

$$\hat{G}_{\alpha\beta\sigma\ell m}^{\varepsilon}(k_{AB}, \vec{R}_{AB}) = G'_{\ell mn\alpha\beta\varepsilon} \tag{206}$$

$$k_{AB} = \{\ell_A, m_A, \ell_B, m_B\} \quad . \tag{207}$$

The limits on m_1 and m_2 are given by (203e) and (203f), M by (203a) when s=+ ; $U^+=0$ if $L<m_{1\ell o}+m_{2\ell o}$. The limits on m_1 and m_2 are given by (203i) and (203j), M by (203g) when s=- . The limits on L, ℓ_1 and ℓ_2 are given by (203h), (203c) and (203d).

c. Transformation of $\hat{\mathcal{Y}}_{LM}$ The last step is to transform the function $\hat{\mathcal{Y}}_{LM}(\vec{R})$ so as to separate the dependence on orbital exponents from the dependence on the geometry of the centers A, B, C and D. For this purpose we choose the point M to be the midpoint of the line AB, and the point N to be the midpoint of the line CD. Then we have

$$\vec{R}_{PQ} = \vec{R}_{PM} + \vec{R}_{MN} + \vec{R}_{NQ} \quad . \tag{208}$$

Two applications of Steinborn's (1969) result, (148)-(150), lead to

$$\hat{\mathcal{Y}}_{LM}(\vec{R}_{PQ}) = \sqrt{2\pi} \sum_{\lambda_1=0}^{L} \sum_{\mu_1} \hat{\mathcal{Y}}_{\lambda_1\mu_1}(\vec{R}_{PM})\, \hat{\mathcal{Y}}_{L-\lambda_1,M-\mu_1}(\vec{R}_{MQ})$$

$$= 2\pi \sum_{\lambda_1=0}^{L} \sum_{\lambda_2=0}^{L-\lambda_1} \sum_{\mu_1} \sum_{\mu_2} \hat{\mathcal{Y}}_{\lambda_1\mu_1}(\vec{R}_{PM})$$

$$\times \hat{\mathcal{Y}}_{\lambda_2\mu_2}(\vec{R}_{NQ})\, \hat{\mathcal{Y}}_{L-\lambda_1-\lambda_2,M-\mu_1-\mu_2}(\vec{R}_{MN}), \tag{209}$$

where the definition of (184) has been used. The summations on μ_1 and μ_2 are restricted by

$$|\mu_1| \leq \lambda_1 \tag{210a}$$

$$|M-\mu_1| \leq L-\lambda_1 \tag{210b}$$

$$|\mu_2| \leq \lambda_2 \tag{210c}$$

$$|M-\mu_1-\mu_2| \leq L-\lambda_1-\lambda_2 \quad . \tag{210d}$$

Substitution of the definitions of $\hat{\mathcal{G}}$ and τ, (184) and (156c), and use of the identity

$$Y_{\ell m}(\theta_{AB},\phi_{AB}) = (-1)^{\ell}\, Y_{\ell m}(\theta_{BA},\phi_{BA}) \tag{211}$$

transform (209) into

$$\hat{\mathcal{G}}_{LM}(\vec{R}_{PQ}) = \sum_{\lambda_1=0}^{L} \sum_{\lambda_2=0}^{L-\lambda_1} b_1{}^{\lambda_1}\, b_2{}^{\lambda_2}\, \mathcal{M}_{\lambda_1\lambda_2}{}^{LM}(ABCD) \quad , \tag{212}$$

with

$$\begin{aligned} b_1 &= (1-\tau_1{}^2)R_{AB}/2(1+\tau_1{}^2) \\ b_2 &= (1-\tau_2{}^2)R_{CD}/2(1+\tau_2{}^2) \end{aligned} \tag{213}$$

$$\mathcal{M}_{\lambda_1\lambda_2}{}^{LM}(ABCD) = 2\pi(-1)^{\lambda_2}\, R_{MN}{}^{L-\lambda_1-\lambda_2} \sum_{\mu_1}\sum_{\mu_2} \hat{Y}_{\lambda_1\mu_1}(\Theta_{AB},\Phi_{AB})$$

$$\times \hat{Y}_{\lambda_2\mu_2}(\Theta_{CD},\Phi_{CD})\, \hat{Y}_{L-\lambda_1-\lambda_2,M-\mu_1-\mu_2}(\Theta_{MN},\Phi_{MN}) \quad , \tag{214}$$

and

$$\hat{Y}_{\ell m}(\theta,\phi) = Y_{\ell m}(\theta,\phi)/N_\ell^m \quad . \tag{215}$$

The quantity $\mathcal{M}$ depends only on the geometry of the centers ABCD; the dependence on the orbital exponents is entirely contained in b_1 and b_2 . Thus it is desirable to move the sums on λ_1 and λ_2 as far out as possible. Since the limits depend only on L, the sums can immediately be moved outside of those on $\ell_1 m_1 \ell_2 m_2$, and then interchanged with that on L. The new summation conditions are

$$0 \le \lambda_1 \le \sigma_1+\sigma_2 \tag{216a}$$

$$0 \le \lambda_2 \le \sigma_1+\sigma_2-\lambda_1 \tag{216b}$$

$$\max\left\{\begin{matrix} \lambda_1+\lambda_2 \\ m_{1\ell o}-m_{2hi} \ , \ m_{2\ell o}-m_{1hi} \\ \ell_{1\ell o}-\sigma_2 \ , \ \ell_{2\ell o}-\sigma_1 \end{matrix}\right\} \le L \le \sigma_1+\sigma_2 \tag{216c}$$

$$L+\sigma_1+\sigma_2 = \text{even} \quad . \tag{216d}$$

Combining the results of this section, we have the final formula for the integral of (161)

$$I = B_{AB}(\rho_1,\tau_1)B_{CD}(\rho_2,\tau_2) \sum_{\alpha_1} \tau_1^{\alpha_1} \sum_{\beta_1} \rho_1^{\beta_1} \sum_{\sigma_1} \hat{a}_1^{\sigma_1}$$

$$\times \sum_{\alpha_2} \tau_2^{\alpha_2} \sum_{\beta_2} \rho_2^{\beta_2} \sum_{\sigma_2} \hat{a}_2^{\sigma_2} \sum_{\lambda_1} b_1^{\lambda_1} \sum_{\lambda_2} b_2^{\lambda_2}$$

$$\times \sum_{L} f_{\sigma_1+\sigma_2}^{L}[\rho^2,(\hat{a}_1^2+\hat{a}_2^2)/4] \, A_{(\alpha\beta\sigma\lambda)_1(\alpha\beta\sigma\lambda)_2}^{L} ; \quad (217)$$

here the quantities

$$\hat{a}_1 = 2/\zeta_P \qquad , \qquad \hat{a}_2 = 2/\zeta_Q \quad (218)$$

have been introduced, along with

$$A_{(\alpha\beta\sigma\lambda)_1(\alpha\beta\sigma\lambda)_2}^{L} = A_{(\alpha\beta\sigma\lambda)_1(\alpha\beta\sigma\lambda)_2}^{L}(k_{AB},k_{CD},ABCD)$$

$$= \sum_{\ell_1\ell_2} (-1)^{\ell_1} \sum_{s=\pm} \sum_{m_1m_2} 2[(1+\delta_{m_1 0})(1+\delta_{m_2 0})]^{-1}$$

$$\times w_L^{\ell_1\ell_2 m_1 (sm_2)} \sum_{\varepsilon=\pm} \sum_{\eta=\pm} S_{(sm_2)}(\varepsilon,\eta) R_{\varepsilon\eta}[\mathscr{M}_{\lambda_1\lambda_2}^{LM}(ABCD)]$$

$$\times \hat{G}_{(\alpha\beta\sigma\ell m)_1}^{\varepsilon}(k_{AB},\vec{R}_{AB}) \hat{G}_{(\alpha\beta\sigma\ell m)_2}^{\eta}(k_{CD},\vec{R}_{CD}) \quad . \quad (219)$$

The function B is defined by (156a); ρ_1 and ρ_2 by (156b), τ_1 and τ_2 by (156c), with subscript 1 associated with ABP, 2 with CDQ; b_1 and b_2 by (213); f by (182); w by (183); S by (179);

$\mathcal{M}$ by (214); and $\hat{G}$ by (206), (194), (138) and (171b). The summations on α_1, β_1, σ_1, α_2, β_2 and σ_2 are governed by (154a), (154b) and (199a), with subscript 1 associated with AB, and 2 with CD. The summations on L, λ_1, λ_2, ℓ_1 and ℓ_2 are governed by (216), (203c) and (203d). When s=+ , the summations on m_1 and m_2 are restricted by (203e) and (203f); if $L < m_{1\ell o}+m_{2\ell o}$, the value s=+ does not occur. When s=- , the summations on m_1 and m_2 are restricted by (203i) and (203j). In addition,

$$M = -m_1 - sm_2 \quad . \tag{220}$$

This formula is essentially that given by Kinser, Salmon and Ruedenberg (1971).

It should be recalled that the formula (217) is for unnormalized real Gaussian orbitals, defined by (162) and (143). All quantities contained in the formula are real. The factors depending on the orbital exponents have been separated from those depending only on the geometry of the centers and on the quantum numbers. The latter are all contained in the geometry factor A. The sums in (217) can be evaluated efficiently by a nesting procedure.

4. Simplifications when two or more centers coincide

a. A=B In this case, the real orbital product on the left side of (164) reduces to a product of orbitals on the same center, A, and so does the product of complex orbi-

tals on the right side. Furthermore, the point P of (145) coincides with A and B. Hence, the distance R_{AP} is zero, and all terms in (148) vanish except those with $\ell=\varepsilon$. This, together with (149b), implies that the only allowed value of η is $\eta=m$. This reasoning applies to both orbitals in the product, so the definitions of (151b) and (153) show that

$$\alpha = \beta = \delta = 0 \tag{221a}$$

$$m = -m_A - m_B \tag{221b}$$

for complex orbitals. In addition, the quantity ρ defined in (156b) vanishes. Then, for the real product, the summation conditions of (168) become

$$\alpha_1 = \beta_1 = 0 \tag{222a}$$

$$\ell_{1\ell o} \le \ell_1 \le \ell_A + \ell_B \qquad \ell_1+\ell_A+\ell_B=\text{even} \tag{222b}$$

$$\ell_{1\ell o} = \max\{|\ell_A-\ell_B|, ||m_A|-|m_B||\} \tag{222c}$$

$$\begin{aligned} m_1 = {} & +|m_A|-|m_B|, \quad -|m_A|+|m_B| \ ; \\ & -|m_A|-|m_B|, \quad +|m_A|+|m_B|, \text{ if } \ |m_A|+|m_B|\le\ell_1 \ . \end{aligned} \tag{222d}$$

The conditions on μ_A and μ_B are given by (168e), (168f) and (170). When the real form of the bipolar expansion, (186)-(188), is substituted into the integral of (161), we find that only one value of ε is needed, namely,

$$\varepsilon = \text{sign}(m_A)\cdot\text{sign}(m_B) \quad , \qquad \text{with sign}(0) = + \quad . \tag{223}$$

This is so because terms having the opposite value of ε include factors

$$\int_0^{2\pi} d\phi \, \sin(m\phi) \, \cos(m'\phi) \, \cos(m''\phi) = 0 \quad . \tag{224}$$

Instead of the range given by (195b), there are one or two possible values for m_1

$$m_1 = \{m_{1\ell o} \; ; \; m_{1hi} \text{ , if } m_{1hi} \leq \ell_1\} \quad , \tag{225}$$

with

$$m_{1\ell o} = \big||m_A|-|m_B|\big| \quad , \qquad m_{1hi} = |m_A|+|m_B| \quad . \tag{226}$$

When, in (219), s=+ , the value $m_1 = m_{1hi}$ does not occur if $m_{1hi} > L-m_{2\ell o}$. When s=- , the value $m_1 = m_{1\ell o}$ does not occur if $m_{1\ell o} < m_{2\ell o}-L$, and $m_1 = m_{1hi}$ does not occur if $m_{1hi} > L+m_{2hi}$. Finally, since $b_1 = 0$, we have

$$\lambda_1 = \mu_1 = 0 \quad . \tag{227}$$

The integral is given by (217), along with (222a), (223), (225) and (227). The remaining indices are restricted, as in the case of the four-center integral, by (199a), (216), (203c), (203d), (203f) and (203j), if (222a), (222c), (226) and (227) are used. Furthermore, $\rho_1=0$.

b. A=B and C=D In this case, the Coulomb integral, similar conditions apply to the second set of indices, also. We have, in (217),

$$\alpha_1 = \beta_1 = \lambda_1 = \alpha_2 = \beta_2 = \lambda_2 = 0 \quad . \tag{228}$$

Also, we have (223) and an analogous expression for η in terms of m_C and m_D, and (225) and the same expression with subscript 1 replaced by 2. Moreover, when s=+, $m_2 = m_{2hi}$ does not occur if $m_{2hi} > L-m_1$; when s=-, $m_2 = m_{2\ell o}$ does not occur if $m_{2\ell o} < m_1-L$, and $m_2 = m_{2hi}$ does not occur if $m_{2hi} > L+m_1$. If all four centers coincide, we also have $L = M = 0$, which implies $\ell_1 = \ell_2$ and $m_1 = m_2$.

c. A=C In this case, no simplifications occur in the two orbital products. However, we can simplify the expression for $\hat{\mathcal{Y}}_{LM}(\vec{R}_{PQ})$, (212), by taking advantage of the fact that the point A is one of the centers in each orbital product. Instead of using (208), we decompose $\vec{R}_{PQ}$ into only two vectors

$$\vec{R}_{PQ} = \vec{R}_{PA} + \vec{R}_{AQ} \quad . \tag{229}$$

The result is

$$\hat{\mathcal{Y}}_{LM}(\vec{R}_{PQ}) = \sum_{\lambda=0}^{L} \mathcal{B}_1^{\lambda}\, \mathcal{B}_2^{L-\lambda}\, \hat{\mathcal{M}}_{\lambda}^{LM}(ABAD) \quad , \tag{230}$$

where

$$\hat{b}_1 = R_{AB}/2 - b_1 \quad , \qquad \hat{b}_2 = R_{CD}/2 - b_2 \tag{231}$$

and

$$\hat{\mathcal{M}}_\lambda^{LM}(ABAD) = \sqrt{2\pi}\ (-1)^\lambda \sum_\mu \hat{Y}_{\lambda\mu}(\Theta_{AB},\Phi_{AB})\hat{Y}_{L-\lambda,M-\mu}(\Theta_{AD},\Phi_{AD}) \ . \tag{232}$$

Then, instead of (217), we have the integral formula

$$I = B_{AB}(\rho_1,\tau_1)B_{CD}(\rho_2,\tau_2) \sum_{\alpha_1} \tau_1^{\alpha_1} \sum_{\beta_1} \rho_1^{\beta_1} \sum_{\sigma_1} \hat{a}_1^{\sigma_1}$$

$$\times \sum_{\alpha_2} \tau_2^{\alpha_2} \sum_{\beta_2} \rho_2^{\beta_2} \sum_{\sigma_2} \hat{a}_2^{\sigma_2} \sum_\lambda \hat{b}_1^{\lambda} \sum_L \hat{b}_2^{L-\lambda}$$

$$\times f_{\sigma_1+\sigma_2}^{L}[\rho^2,(\hat{a}_1^2+\hat{a}_2^2)/4]\ A_{(\alpha\beta\sigma)_1 0 (\alpha\beta\sigma)_2 \lambda}^{L}, \tag{233}$$

and in the expression for A, (219), the quantity $\mathcal{M}_{\lambda_1\lambda_2}^{LM}$ is replaced by $\hat{\mathcal{M}}_\lambda^{LM}$.

d. <u>A=B=C</u> This case, the hybrid integral, combines the simplifications of sections a and c. We have

$$R_{PQ} = R_{AQ} \ , \qquad \hat{b}_1 = 0 \quad , \tag{234}$$

so (230) becomes simply

$$\hat{\mathcal{Y}}_{LM}(\vec{R}_{PQ}) = \hat{b}_2^{L}\ \hat{\mathcal{M}}_0^{LM}(AAAD) = \hat{b}_2^{L}\ \hat{Y}_{LM}(\Theta_{AD},\Phi_{AD}) \ . \tag{235}$$

The integral is given by (233), with

$$\alpha_1 = \beta_1 = \lambda = 0 \tag{236}$$

and (222c), (223), (225) and (226). In (219), the definition of A, the quantity $\mathcal{M}_{\lambda_1\lambda_2}^{LM}$ is replaced by $\mathcal{M}_0^{LM}$.

e. A=C and B=D In the case of the exchange integral, the points A, B, M, N, P and Q are all colinear. Therefore

$$\hat{\mathcal{Y}}_{LM}(\vec{R}_{PQ}) = (b_1-b_2)^L \hat{Y}_{LM}(\Theta_{AB},\Phi_{AB}) \quad , \tag{237}$$

and the integral is given by

$$I = B_{AB}(\rho_1,\tau_1)B_{CD}(\rho_2,\tau_2) \sum_{\alpha_1} \tau_1^{\alpha_1} \sum_{\beta_1} \rho_1^{\beta_1} \sum_{\sigma_1} \hat{a}_1^{\sigma_1}$$

$$\times \sum_{\alpha_2} \tau_2^{\alpha_2} \sum_{\beta_2} \rho_2^{\beta_2} \sum_{\sigma_2} \hat{a}_2^{\sigma_2} \sum_{L} (b_1-b_2)^L$$

$$\times f_{\sigma_1+\sigma_2}^{L}[\rho^2,(\hat{a}_1^2+\hat{a}_2^2)/4] \, A_{(\alpha\beta\sigma)_1 0 (\alpha\beta\sigma)_2 0}^{L} \, . \tag{238}$$

In the expression for A, (219), the quantity $\mathcal{M}_{\lambda_1\lambda_2}^{LM}$ is replaced by $\hat{Y}_{LM}(\Theta_{AB},\Phi_{AB})$.

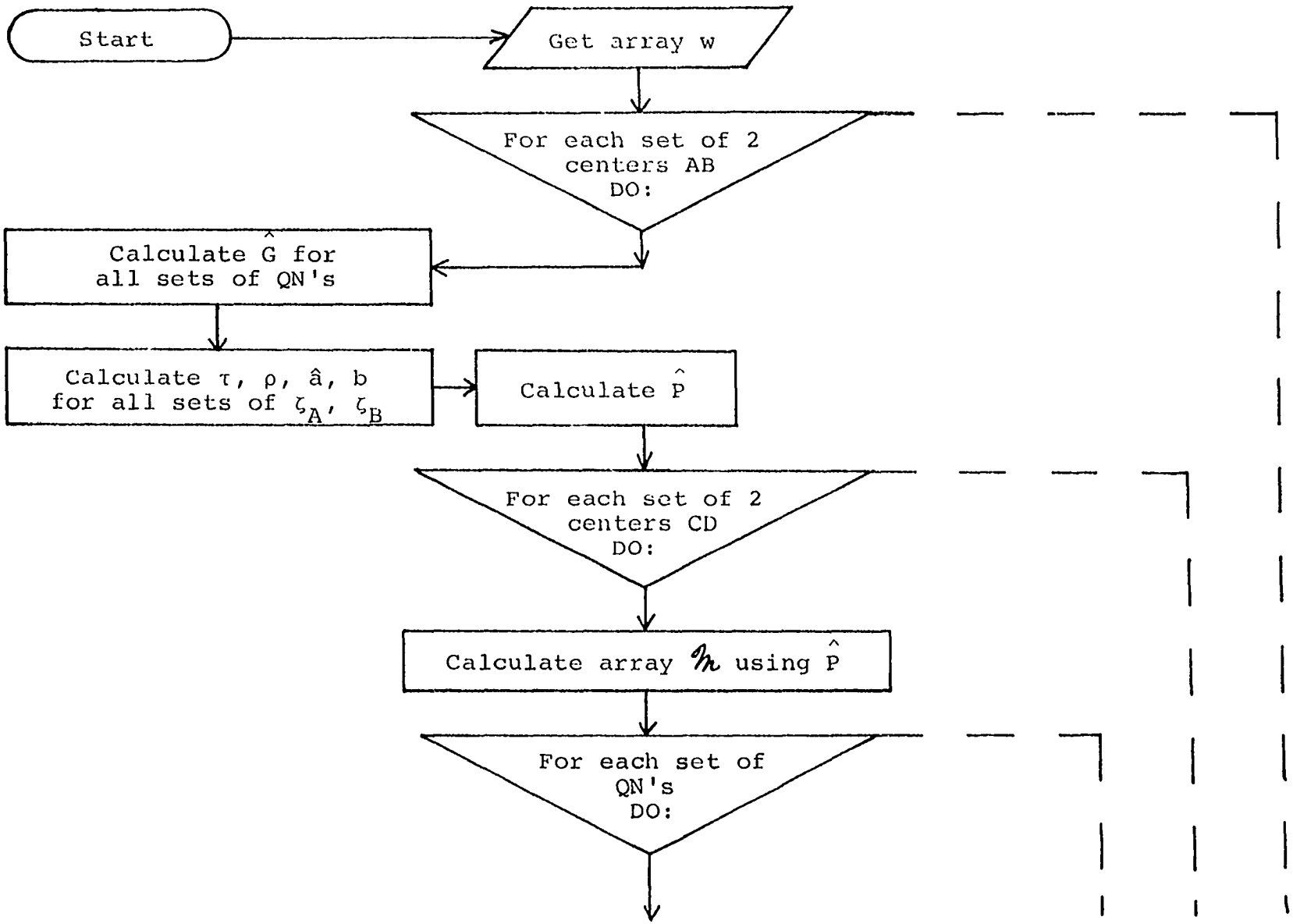
C. Discussion of Computational Methods

1. Method of calculating integrals

In any molecular calculation using a Gaussian basis set, it is necessary to use a number of Gaussians of each symmetry type (s, p, etc.) to obtain reasonable accuracy. Thus one must calculate many integrals with the same quantum numbers and centers, but different orbital exponents. Because of this, it is important to put the integral formula to be used in a form which permits as much of the calculation as possible to be done before the orbital exponents are specified. The results of these preliminary calculations can then be stored in some convenient way, and used repeatedly for different values of the orbital exponents.

One can easily see that (217) is an integral formula of the desired type. The geometry factor A depends only upon the quantum numbers, the indices, and the geometry of the centers. Thus, for given geometry and quantum numbers, an array of values of A for all possible combinations of the indices can be calculated and stored in the prescribed way.

The organization of the integral calculation is shown in Figure 2. First of all, the constant $w_L^{\ell\ell'mm'}$, defined by (183), (150b), (7) and (8), depends only on its indices, so it can be calculated for all desired combinations of these indices and stored permanently. Then the first step in the integral evaluation is to read in the stored array for w.


Start
Get array w
For each set of 2 centers AB DO:
Calculate $\hat{G}$ for all sets of QN's
Calculate τ, ρ, $\hat{a}$, b for all sets of ζ_A, ζ_B
Calculate $\hat{P}$
For each set of 2 centers CD DO:
Calculate array $\mathcal{H}$ using $\hat{P}$
For each set of QN's DO:

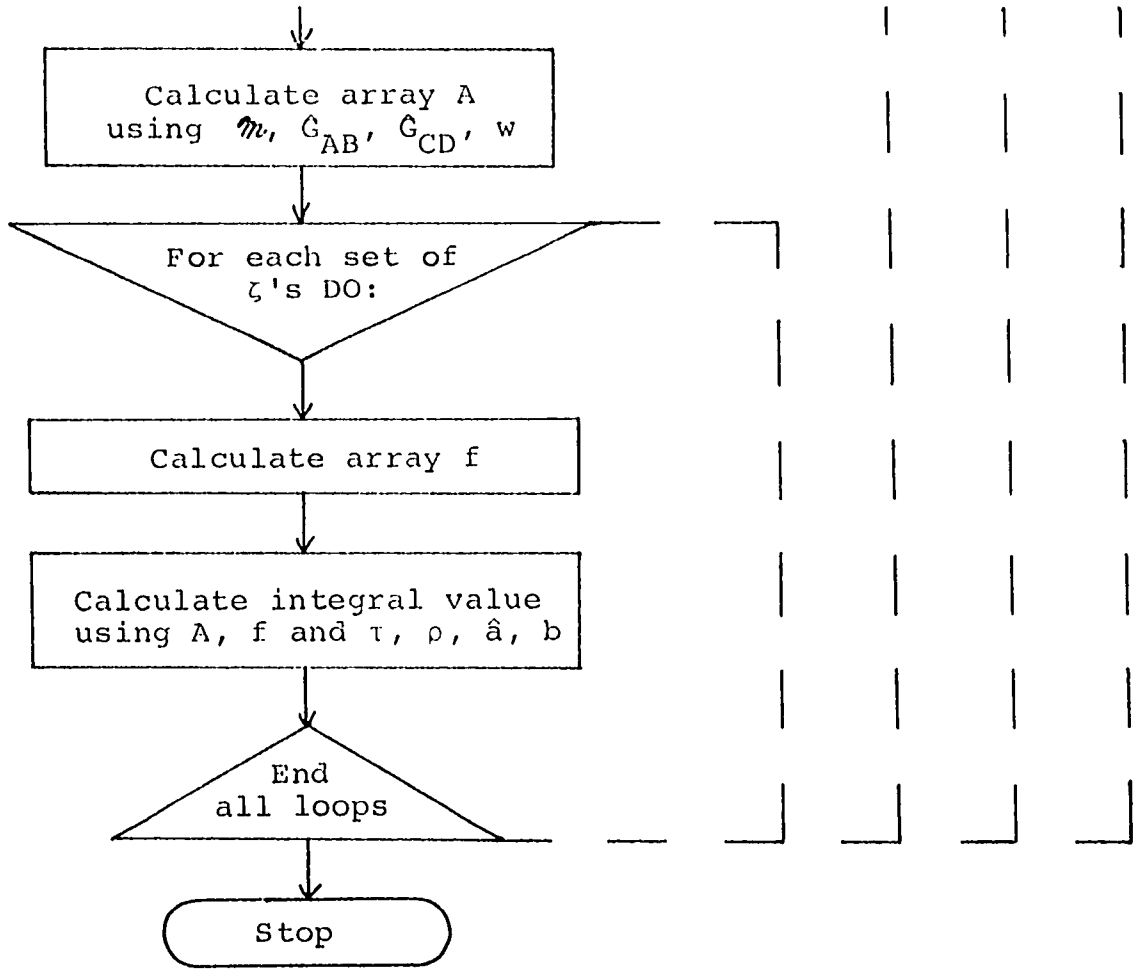


Figure 2. Flow chart of integral calculation. Triangles indicate the beginning and end of loops

A program to calculate such an array has been written by Hubert Kinser.

Now two of the atomic centers are defined, and an array of the quantities $\hat{G}$, defined by (206), (194), (138) and (171b), are calculated for all needed quantum numbers (QN's) and all values of the indices $\alpha\beta\sigma\ell m$. This array is stored on a disk or tape, along with another array containing the number of $\hat{G}$'s for each set of quantum numbers k_{AB}. Next the quantities ρ, τ, $\hat{a}$, and b, defined by (156b), (156c), (218) and (213), are calculated and stored for all pairs of orbital exponents. Kinser has written programs to calculate and store these arrays. Now the array $\hat{P}$, to be used in the evaluation of $\mathscr{m}$, is calculated. These programs are called each time one of the centers A or B is changed.

Next the other two centers, C and D, are defined, in such a way that CD is a pair of centers which has already occurred as AB; the quantities $\hat{G}$, ρ, τ, $\hat{a}$, b and $\hat{P}$ will thus be available. Now that all four centers have been specified, the quantity $\mathscr{m}$, defined by (214), or $\hat{\mathscr{m}}$, defined by (232), can be calculated and stored for all required values of its indices. (Since the dependence on the quantum numbers is contained only in the limits on the indices, one simply calculates the maximum number needed and uses them repeatedly.) Programs to calculate this array have been written by the author. These functions must be calculated each time any of the four centers is changed.

At this point the quantum numbers (QN's), k_{AB} and k_{CD}, are defined, and an array of the functions A, given by (219), is calculated for all values of the indices, using the arrays w, $\mathcal{M}$, and $\hat{G}$. The author has written programs to perform this calculation. It must be done each time any of the quantum numbers is changed.

After the geometry factor A has been computed, the orbital exponents ζ are defined. The functions f, defined by (182), are calculated for all values of the two indices; programs to do this have been written by the author. Note that each f will occur in several terms of the summations to be performed. Finally, the integral is calculated according to (217), using the stored values of ρ, τ, $\hat{a}$, b, f and A. A program for this has been written by Kinser. These two steps must be repeated each time one of the four orbital exponents is changed.

All programs were written in Fortran IV for the IBM 360-65 using double precision arithmetic.

2. Calculation of f_{ν}^{L}

The functions under consideration are defined by (182). There are two cases, which must be handled separately. The first case, $\nu = L$, is given by (182a), which is repeated here

$$f_L^L(\rho^2,a) = a^{-L-1/2}\,\Gamma(L+1/2)\gamma^*(L+1/2,\rho^2)$$

$$= a^{-L-1/2}\,\rho^{-2L-1}\,\gamma(L+1/2,\rho^2) \quad . \qquad (239)$$

The following recursion formula (Abramowitz and Stegun, 1965, Item 6.5.23) will be used:

$$\Gamma(L-1/2)\gamma^*(L-1/2,\rho^2)$$

$$= [\rho^2\,\Gamma(L+1/2)\gamma^*(L+1/2,\rho^2) + \exp(-\rho^2)]/(L-1/2) . \qquad (240)$$

Because both terms on the right side of this formula are always positive, there is no loss of significant figures if the recursion is done in the direction indicated, that is, downward. On the other hand, if upward recursion is used, significant figures will be lost; the severity of the loss depends upon the argument ρ^2 .

In order to recur downward, we must have an efficient way to calculate the function with the highest value of L which will be needed. To develop such a method, we will use the following series expansions(Abramowitz and Stegun, 1965, Item 6.5.29):

$$\Gamma(a)\gamma^*(a,z) = \sum_{n=0}^{\infty} (-z)^n/(a+n)n!$$

$$= \Gamma(a)e^{-z}\sum_{n=0}^{\infty} z^n/\Gamma(a+n+1) \quad . \qquad (241)$$

The first series is used to obtain the expression for the derivative

$$(d/dz)[\Gamma(a)\gamma^*(a,z)] = -\Gamma(a+1)\gamma^*(a+1,z) \quad , \tag{242}$$

which is substituted into the Taylor series expansion to give

$$\Gamma(L+1/2)\gamma^*(L+1/2,\rho^2)$$

$$= \sum_{n=0}^{\infty} [(-1)^n/n!](\rho^2-z)^n \, \Gamma(n+L+1/2)\gamma^*(n+L+1/2,z) . \tag{243}$$

To use this formula, one needs to have available a table of values of $\Gamma(L+1/2)\gamma^*(L+1/2,z)$ for as many values of L as required, and for values of z spaced closely enough so that only a few terms are needed. It was found that with an increment in z of 0.01, only three terms are needed to provide acceptable accuracy (at least eight significant figures). The table is generated by calculating the function for the largest L by means of the second series of (241), and then recurring downward with (240); this is done for each value of z up to some maximum value. The table is computed once and stored permanently by the program TABGAM (Program 1 of Appendix B). For very small values of ρ^2 (≤ 0.325), it is practical to use the second series of (241) to calculate the initial function for the recursion, rather than the Taylor series (243). The initial function for downward recursion is calculated by one of these two methods by the program GAMTØP

(Program 3).

It is not possible to store the table of $\Gamma(a)\gamma^*(a,z)$ for values of z up to the largest value of ρ^2 that would ever be needed. Therefore, some other method of calculating f must be used for large values of ρ^2 . If ρ is large enough, and if the maximum value of L is small enough, then one can recur upward using (240), without unacceptable loss of precision. For example, if $\rho > 4.0$, less than three significant figures will be lost in an upward recursion with maximum L less than 29. The initial function needed is (Abramowitz and Stegun, 1965, Item 6.5.16)

$$\Gamma(1/2)\gamma^*(1/2,\rho^2) = \sqrt{\pi}\ \mathrm{erf}(\rho)/\rho \quad , \tag{244}$$

where erf(x) is the error function (Abramowitz and Stegun, 1965, Item 7.1.1). For large values of ρ we can use the asymptotic expansion (Abramowitz and Stegun, 1965, Items 7.1.2 and 7.1.23)

$$\sqrt{\pi}\ \mathrm{erf}(x) \sim \sqrt{\pi} - [\exp(-x^2)/x] \sum_{m=0}^{\infty} (2m-1)!!(-1)^m/(2x^2)^m \ . \tag{245}$$

It was found that no more than four terms are required to get fifteen significant figures, when $\rho \geq 4.8$. The calculation of the function of (244), using (245), is done by the program GAMLØW (Program 4).

When $\rho = 0$, the only f's which are needed are those with $L = 0$; this is because the function $\hat{y}_{LM}(0)$ vanishes for all other cases. It is obvious from (241) that

$$\Gamma(1/2)\gamma^*(1/2,0) = 2 \quad . \tag{246}$$

Once $\Gamma(L+1/2)\gamma^*(L+1/2,\rho^2)$ has been computed for each needed L, it is multiplied by the necessary factor to get $f_L^{\ L}$ of (239).

The second case for $f_\nu^{\ L}$, $\nu = 2N+L$, with N a positive integer, is given by (182b), which is repeated here

$$f_{2N+L}^{\ L}(\rho^2,a) = a^{-N-L-1/2}\,(N-1)!\exp(-\rho^2)L_{N-1}^{\ L+1/2}(\rho^2) \quad . \tag{247}$$

These functions are computed by means of the recursion formula (Abramowitz and Stegun, 1965, Item 22.7.12)

$$(n+1)L_{n+1}^{\ a}(x) = (2n+a+1-x)L_n^{\ a}(x) - (n+a)L_{n-1}^{\ a}(x) \tag{248}$$

and the initial functions

$$L_0^{\ a}(x) = 1 \qquad \text{and} \qquad L_1^{\ a}(x) = 1+a-x \quad . \tag{249}$$

This recursion scheme is stable in spite of the occurrence of subtraction.

The possible combinations of the indices $\nu = \sigma_1+\sigma_2$ and

L are limited by (216c) and (216d). Thus the f's form a triangular matrix. However, to save both space and time, they are stored in the computer as a singly dimensioned array, in the order f_0^0 , f_1^1 , f_2^0 , f_2^2 , f_3^1 , etc. The number of f's depends on the maximum value of ν and L, which is

$$L_{max} = \ell_A+\ell_B+\ell_C+\ell_D \quad ; \tag{250}$$

we have for N_f , the number of f's,

$$N_f = \begin{cases} (L_{max}+1)(L_{max}+3)/4 & \text{for odd } L_{max} \\ (L_{max}+2)^2/4 & \text{for even } L_{max} \end{cases} . \tag{251}$$

The array of f's is computed by the program FLNRHØ (Program 2). This program calls GAMTØP and GAMLØW. Times for the computation of the array f_ν^L are given in Table 1.

3. Calculation of $\mathcal{m}_{\lambda_1\lambda_2}^{LM}$ and $\hat{\mathcal{m}}_\lambda^{LM}$

These functions are defined by (214), (232) and (215). In order to obtain a form more suitable for calculation, we substitute into (215) the definition of the spherical harmonic to get

$$\hat{Y}_{\ell m}(\theta,\phi) = \varepsilon_m \hat{P}_\ell^m(\theta) e^{im\phi} \quad , \tag{252}$$

with

$$\varepsilon_m = \begin{cases} (-1)^m , & \text{if } m \geq 0 \\ 1 , & \text{if } m \leq 0 \end{cases} \tag{253}$$

Table 1. Times for calculation of array f

L_{max}	Time in msec. ($\rho^2=0$)	Time in msec. ($0<\rho^2\leq 0.325$)	Time in msec. ($0.325<\rho^2\leq 23.044$)	Time in msec. ($\rho^2>23.044$)
0	0.16	0.66	0.51	0.66
1	0.35	0.66	0.66	0.82
2	0.35	0.82	0.82	0.82
3	0.35	0.82	0.82	0.82
4	0.35	1.02	1.02	1.17
5	0.35	1.17	1.17	1.17
6	0.35	1.52	1.52	1.52
7	0.51	1.68	1.33	1.84
8	0.51	1.99	1.99	1.99
9	0.51	2.34	2.34	2.34
10	0.66	2.85	2.85	2.85
11	0.66	3.52	3.52	3.32
12	0.82	3.67	3.82	3.82

and

$$\hat{P}_\ell^{\,m}(\theta) = P_\ell^{\,|m|}(\cos\theta)/\sqrt{2\pi}(\ell+m)! \quad , \tag{254}$$

where $P_\ell^{\,m}(x)$ is the associated Legendre function (see, e.g., (Edmonds, 1957, p. 22)). This expression for $\hat{Y}_{\ell m}$ is substituted into (214) three times; each term of the result contains a product

$$\exp(i\mu_1\Phi_{AB})\exp(i\mu_2\Phi_{CD})\exp[i(M-\mu_1-\mu_2)\Phi_{MN}]$$

$$= \cos(\Phi_{ABCD}) + i\sin(\Phi_{ABCD}) \quad , \tag{255}$$

where

$$\Phi_{ABCD} = \mu_1\Phi_{AB} + \mu_2\Phi_{CD} + (M-\mu_1-\mu_2)\Phi_{MN} \quad . \tag{256}$$

Then we have

$$\left.\begin{matrix}\mathcal{R}e\\ \mathcal{I}m\end{matrix}\right\}\mathcal{M}_{\lambda_1\lambda_2}^{\;\;LM}(ABCD) = 2\pi(-1)^{\lambda_2} R_{MN}^{\;\;L-\lambda_1-\lambda_2}$$

$$\times\sum_{\mu_1\mu_2}\sum\left\{\begin{matrix}\mathcal{R}e\\ \mathcal{I}m\end{matrix}\right\}T_{\mu_1\mu_2} \tag{257}$$

with

$$\left.\begin{matrix}\mathrm{Re}\\ \mathrm{Im}\end{matrix}\right\} T_{\mu_1\mu_2} = \varepsilon_{\mu_1}\,\varepsilon_{\mu_2}\,\varepsilon_{M-\mu_1-\mu_2}\,\hat{P}_{\lambda_1}^{|\mu_1|}(0_{AB})\,\hat{P}_{\lambda_2}^{|\mu_2|}(0_{CD})$$

$$\times \hat{P}_{L-\lambda_1-\lambda_2}^{|M-\mu_1-\mu_2|}(\Theta_{MN}) \left\{\begin{matrix}\cos(\Phi_{ABCD})\\ \sin(\Phi_{ABCD})\end{matrix}\right\} . \qquad (258)$$

The limits on the summations in (257) are given by (210).

When M=0, the result simplifies somewhat. In this case the limits of (210) become

$$-\mu_{1max} \le \mu_1 \le +\mu_{1max} \qquad (259a)$$

$$\mu_{1max} = \min\{\lambda_1 \ , \ L-\lambda_1\} \qquad (259b)$$

$$\mu_{2min}(\mu_1) \le \mu_2 \le \mu_{2max}(\mu_1) \qquad (259c)$$

$$\mu_{2min}(\mu_1) = \max\{-\lambda_2 \ , \ -\mu_1-L+\lambda_1+\lambda_2\} \qquad (259d)$$

$$\mu_{2max}(\mu_1) = \min\{+\lambda_2 \ , \ -\mu_1+L-\lambda_1-\lambda_2\} \ . \qquad (259e)$$

It is clear from the last two equations that

$$\mu_{2min}(\mu_1) = -\mu_{2max}(-\mu_1) \ . \qquad (260)$$

Now, defining $\mu_2' = -\mu_2$, using (260) and (253), and the properties of the sine and cosine functions, we obtain

$$\sum_{\mu_2}\left\{\begin{matrix}\mathrm{Re}\\ \mathrm{Im}\end{matrix}\right\} T_{\mu_1\mu_2} = \sum_{\mu_2'}\left\{\begin{matrix}\mathrm{Re}\\ \mathrm{Im}\end{matrix}\right\} T_{\mu_1,-\mu_2'} = \sum_{\mu_2}\left\{\begin{matrix}\mathrm{Re}\\ -\mathrm{Im}\end{matrix}\right\} T_{-\mu_1,\mu_2} \ , \qquad (261)$$

dropping primes in the last step. Hence we can sum over only nonnegative values of μ_1 . We find

$$\mathrm{Im}\left[\mathcal{M}_{\lambda_1\lambda_2}^{L0}(ABCD)\right] = 0 \quad , \tag{262}$$

as expected, and

$$\mathrm{Re}\left[\mathcal{M}_{\lambda_1\lambda_2}^{L0}(ABCD)\right] = 2\pi(-1)^{\lambda_2} R_{MN}^{L-\lambda_1-\lambda_2} \times \sum_{\mu_1=0}^{\mu_{1max}} \frac{2}{(1+\delta_{\mu_1 0})} \sum_{\mu_2} T_{-\mu_1,\mu_2} \quad , \tag{263}$$

in which the sum over μ_2 is governed by

$$\mu_{2min}(-\mu_1) \le \mu_2 \le \mu_{2max}(-\mu_1) \quad . \tag{264}$$

When $L = \lambda_1 = \lambda_2 = 0$, we have

$$\left.\begin{matrix}\mathrm{Re}\\ \mathrm{Im}\end{matrix}\right\}\mathcal{M}_{00}^{00}(ABCD) = \begin{cases} 1/\sqrt{2\pi} \\ 0 \end{cases} \quad . \tag{265}$$

Furthermore, when either $\lambda_2 = 0$ or $L = \lambda_1+\lambda_2$, the sum on μ_2 reduces to one term; when either $\lambda_1 = 0$ or $L = \lambda_1$, the sum on μ_1 reduces to one term.

For the four-center case (A, B, C, D all different), these results are used by the program MUSUM4 to calculate $\mathcal{M}_{\lambda_1\lambda_2}^{LM}$. It calls other programs TRIG3, which calculates

and stores all of the sines and cosines which will be needed, and PLMBAR, which calculates and stores the functions $\hat{P}$ of (254). These programs are given in Appendix B as Programs 5, 8 and 11, respectively. The $\mathscr{m}$'s are stored as a singly dimensioned array. The number of them depends upon the maximum value of L, L_{max} , which is given by (250). Using the fact that there are (2L+1) functions for each combination of L, λ_1 , λ_2 (one for M=0 and two, the real and imaginary parts, for all other M), we find for $N_{\mathscr{m}}$, the number of $\mathscr{m}$'s,

$$N_{\mathscr{m}} = (L_{max}+1)(L_{max}+2)(L_{max}+3)(3L_{max}+2)/12 \quad . \tag{266}$$

For example, if we have four d-orbitals the number is 2145.

The three-center cases are handled by the programs MUSUM3, TRIG2A and TRIG1, Programs 6, 9 and 10, respectively. For the case A=B, $\mathscr{m}_{0\lambda_2}^{LM}(AACD)$ is computed, using the results above. For the case A=C, $\hat{\mathscr{m}}_{\lambda}^{LM}(ABAD)$ is computed. This function was defined by (232), but, using the same reasoning as above, we can derive

$$\left.\begin{matrix}\mathscr{Re}\\ \mathscr{Im}\end{matrix}\right\}\hat{\mathscr{m}}_{\lambda}^{LM}(ABAD) = \sqrt{2\pi}\,(-1)^{\lambda}\sum_{\mu}\varepsilon_{\mu}\varepsilon_{M-\mu}\,\hat{P}_{\lambda}^{|\mu|}(\Theta_{AB})$$

$$\times\hat{P}_{L-\lambda}^{|M-\mu|}(\Theta_{AD})\left\{\begin{matrix}\cos(\Phi_{ABAD})\\ \sin(\Phi_{ABAD})\end{matrix}\right\} \quad , \tag{267}$$

where

$$\Phi_{ABAD} = \mu\Phi_{AB} + (M-\mu)\Phi_{AD} \quad . \tag{268}$$

Table 2. Real times for calculation of array $\mathcal{I}_n$

L_{max}	Time in sec. (2 centers)	Time in sec. (3 centers)	Time in sec. (4 centers)
0	0.001	0.009	0.002
1	0.012	0.014	0.002
2	0.005	0.036	0.012
3	0.011	0.044	0.041
4	0.010	0.135	0.104
5	0.014	0.116	0.222
6	0.017	0.169	0.423
7	0.025	0.227	0.632
8	0.030	0.467	1.053
10			2.793
12			5.613

The summation is governed by (210a) and (210b), without the subscripts.

The two-center cases are handled by TRIG1 and MUSUM2, Program 7. As we have seen, each of these three cases reduces to one spherical harmonic.

Times for computation of an array of $\mathcal{I}_n$'s are given in Table 2. These are real times obtained under multiprogramming, and thus represent upper bounds on the actual times.

4. Calculation of $\underline{\underline{A}}^{L}_{(\alpha\beta\sigma\lambda)_1(\alpha\beta\sigma\lambda)_2}$

The geometry factor, A, contains all quantities in the integral formula which do not depend on the orbital exponents. The definition of A, (219), will be put into a different form for computational efficiency. First, in view of (203c),

$$(-1)^{\ell_1} = (-1)^{\sigma_1} \quad . \tag{269}$$

The order of summations is changed from

$$\sum_{\ell_1}\sum_{\ell_2}\sum_{s}\sum_{m_1}\sum_{m_2}\sum_{\varepsilon}\sum_{\eta} \quad \text{to} \quad \sum_{\ell_1}\sum_{m_1}\sum_{\varepsilon}\sum_{\ell_2}\sum_{m_2}\sum_{s}\sum_{\eta} \quad .$$

The limits on ℓ_1 and ℓ_2 , given by (203c) and (203d), are not changed by this procedure. Those on m_1 and m_2 become

$$m_{1\ell o} \le m_1 \le \min\begin{Bmatrix} \ell_1 \\ m_{1hi} \\ L+m_{2hi} \end{Bmatrix} \tag{270a}$$

$$m_{2min} \le m_2 \le \min\begin{Bmatrix} \ell_2 \\ m_{2hi} \\ L+m_1 \end{Bmatrix} \quad , \tag{270b}$$

with

$$m_{2min} = \begin{Bmatrix} m_{2\ell o} & \text{if } m_1 \le L-m_{2\ell o} \\ \max\{m_{2\ell o} \ , \ m_1-L\} & \text{if } m_1 > L-m_{2\ell o} \end{Bmatrix} \tag{270c}$$

The other conditions of (203) give restrictions on which values of s (+ and -) may occur.

Terms with $m_1=0$, $m_2=0$, or both assume a much simpler form than the other terms, so they are treated separately. It has already been shown that when $m_1=0$, the index ε can only be + , and when $m_2=0$, η can only be + . By using (177)

and (179), together with the symmetry properties of the 3-j symbols contained in $w_L^{\ell_1\ell_2 m_1 m_2}$, it can be shown that if either $m_1=0$ or $m_2=0$ the terms with s=+ and s=- are equal.

These results are combined to give the following new form of the formula for A, in which the indices α, β, σ, λ and L have been omitted for brevity:

$$A = 2(-1)^{\sigma_1} \sum_{\ell_1} \Big[\delta_{m_1 \ell_o 0} \hat{G}_{\ell_1 0}^{+} \sum_{\ell_2} \mathrm{Sum}(0) + \sum_{m_1}{}' \sum_{\varepsilon} \hat{G}_{\ell_1 m_1}^{\varepsilon} \sum_{\ell_2} \mathrm{Sum}(m_1) \Big] \quad , \tag{271}$$

with

$$\mathrm{Sum}(0) = \delta_{m_2 \ell_o 0} \left(\tfrac{1}{2}\right) \hat{G}_{\ell_2 0}^{+} R_{+}(\mathcal{M}^{L0}) + \sum_{m_2}{}' w_L^{\ell_1 \ell_2 0 m_2} (-1)^{m_2} \sum_{\eta} \hat{G}_{\ell_2 m_2}^{\eta} R_{\eta}(\mathcal{M}^{Lm_2}) \tag{272}$$

and

$$\mathrm{Sum}(m_1) = \delta_{m_2 \ell_o 0} w_L^{\ell_1 \ell_2 m_1 0} (-1)^{m_1} \hat{G}_{\ell_2 0}^{+} R_{\varepsilon}(\mathcal{M}^{Lm_1}) + \sum_{m_2}{}' \sum_{s} w_L^{\ell_1 \ell_2 m_1 m_2} \sum_{\eta} S_{(sm_2)}(\varepsilon,\eta) \times \hat{G}_{\ell_2 m_2}^{\eta} R_{\varepsilon\eta}(\mathcal{M}^{LM}) \quad . \tag{273}$$

As before, M is given by (220); $\sum_m'$ is $\sum_m$ without the term with m=0.

In the derivation of the orbital product, certain restrictions were found on the indices μ_A and μ_B (170). The sums over these indices are included in the function $\hat{G}$. Hubert Kinser (private communication on the summation conditions, 1970, Iowa State University, Ames, Iowa) has shown that these restrictions lead to additional restrictions on the indices m_1 and ε; similar restrictions apply to m_2 and η. These restrictions will be expressed with the aid of the following definitions:

$$\delta_1 = \begin{cases} 1 \text{ if } |m_A|+|m_B|-\beta \le m_1 \\ 0 \text{ otherwise} \end{cases} \tag{274a}$$

$$\delta_2 = \begin{cases} 1 \text{ if } \begin{cases} \text{either } |m_A|>|m_B| \text{ and } m_1 \le \text{MINA} \\ \quad \text{or } |m_B|>|m_A| \text{ and } m_1 \le \text{MINB} \\ \quad \text{or } |m_A|=|m_B| \text{ and } m_1 \le (\text{MINA.OR.MINB}) \end{cases} \\ 0 \text{ otherwise} \end{cases} \tag{274b}$$

$$\delta_3 = \begin{cases} 1 \text{ if } \begin{cases} \text{either } |m_A|>|m_B| \text{ and } m_1 \le \text{MINB} \\ \quad \text{or } |m_B|>|m_A| \text{ and } m_1 \le \text{MINA} \\ \quad \text{or } |m_A|=|m_B| \text{ and } m_1 \le (\text{MINA.AND.MINB}) \end{cases} \\ 0 \text{ otherwise} \end{cases} \tag{274c}$$

$$\text{MINA} = \min\{\ell_A-|m_B|-\alpha_1 \ , \quad \beta_1+|m_A|-|m_B|\} \tag{274d}$$

$$\text{MINB} = \min\{\ell_B - |m_A| + \alpha_1 \ , \quad \beta_1 - |m_A| + |m_B|\} \quad . \tag{274e}$$

A particular value of m_1 will <u>not</u> occur if either

$$\delta_1 = \delta_2 = 1 \quad \text{and} \quad \min\{|m_A| \ , \ |m_B|\} > \beta_1 \quad , \tag{275a}$$

or

$$\delta_1 = \delta_2 = 0 \quad . \tag{275b}$$

In addition, the value $m_1=0$ will not occur if either

$$\beta_1 = 0 \quad \text{and} \quad \text{sign}(m_A)\cdot\text{sign}(m_B) = - \tag{275c}$$

or

$$\delta_1 = 0, \ \delta_3 = 1, \ |m_A| = |m_B|, \ \text{and} \ \text{sign}(m_A)\cdot\text{sign}(m_B) = - \tag{275d}$$

The restrictions on ε are as follows:

$$\begin{aligned} &\text{If} \quad \beta_1 = 0; \\ &\quad \text{or} \ \delta_2 = \delta_3 = 0 \ \text{and} \ m_1 = |m_A| + |m_B| \ ; \\ &\quad \text{or} \ \delta_1 = \delta_3 = 0 \ \text{and} \ m_1 = ||m_A| - |m_B|| \ ; \\ &\qquad\qquad \text{then} \quad \varepsilon = \text{sign}(m_A)\cdot\text{sign}(m_B) \ . \end{aligned} \tag{276a}$$

$$\text{If } \delta_2 = 1 \quad \text{and} \quad \delta_3 = 0$$

$$\text{and} \begin{cases} |m_A| = |m_B| = m_1 \quad \text{and} \begin{cases} m_1 \le \text{MINA}, & \varepsilon = \text{sign}(m_A) \\ m_1 \le \text{MINB}, & \varepsilon = \text{sign}(m_B) \end{cases} \\ |m_A| \ne |m_B| \quad \text{and} \quad m_1 = |\text{MMAX}|, & \varepsilon = \text{sign}(\text{MMAX}) \ . \end{cases} \tag{276b}$$

$$\text{If} \quad \delta_2 = 0, \quad \delta_3 = 1, \quad \text{and} \quad m_1 = |\text{MMIN}| > 0,$$

$$\text{then} \quad \varepsilon = \text{sign}(\text{MMIN}) \quad . \tag{276c}$$

Here MMIN is whichever of m_A and m_B has the smaller absolute value, and MMAX is whichever has the larger absolute value. We take sign(0) = + . These conditions, (275) and (276), are taken account of by the program DEL (Program 15), which decides whether a given value of m_1 occurs, and, if so, which of the two values of ε can occur.

There are three programs for calculating the array of A's. GEØM4C (Program 12) performs the calculation for all integrals having two two-center orbital products, that is, $[\chi_A\chi_B|\chi_C\chi_D] = [AB|CD]$, [AB|AD] and [AB|AB]. GEØM3C (Program 13) is for the integrals with a one-center orbital product and a two-center orbital product, [AA|CD] and [AA|AD]. GEØM2C (Program 14) is for the Coulomb integral, [AA|CC], with two one-center orbital products. These programs call DEL, mentioned above, and JØMG (Program 16), which determines the subscript for the constant w. The programs incorporate the simplifications of section IV.B.4 where appropriate.

The A's are stored as a singly dimensioned array in the order in which they are to be used in the integral calculation. The number of functions depends upon the quantum numbers; maximum values are given in Table 3 for certain combinations of ℓ quantum numbers. (Since the number also depends on the m's, the number will be somewhat smaller than the fig-

Table 3. Calculation of array A

ℓ_A	ℓ_B	ℓ_C	ℓ_D	Maximum array size	Time in sec. (GEØM2C)	Time in sec. (GEØM3C)	Time in sec. (GEØM4C)
0	0	0	0	1	<0.02	0.02	0.01[a]
1	0	0	0	4	<0.02	<0.02	0.02[a]
1	1	0	0	15	<0.02	0.02	0.03[a]
1	0	1	0	14	0.02	0.02	0.02[a]
2	0	0	0	10	<0.02	<0.02	0.02[a]
1	1	1	0	48	0.02	0.12	0.07[a]
2	1	0	0	37	0.02	0.02	0.05
2	0	1	0	33	0.02	0.05	0.05
1	1	1	1	158	0.02	0.23	0.29
2	0	1	1	108	0.02	0.13	0.20
2	2	0	0	89	0.02	0.02	0.15
2	1	1	0	112	0.04	0.12	0.22
2	0	2	0	74	0.02	0.04	0.10
2	2	2	2	3548	0.05	1.97	9.78

[a]Real time

ure given for certain combinations of m's.) Computation times for the three programs are also given in Table 3.

V. QUADRUPOLAR EXPANSION AND INTEGRALS OVER SLATER-TYPE ATOMIC ORBITALS

In section II a new bipolar expansion for r_{12}^{-1} was derived, which contains the coordinates of the first electron with respect to one center P and those of the second electron with respect to another center Q. This expansion was used in section IV to derive a formula for integrals over Gaussian atomic orbitals. Now we will transform this bipolar expansion into a "quadrupolar" expansion, containing the coordinates of the first electron with respect to two centers A and B, and those of the second electron with respect to two other centers C and D. The transformation is based on Steinborn's (1969) "multipolar" expansion of regular solid harmonics. The quadrupolar expansion will then be used to obtain an asymptotic expansion for integrals over Slater-type atomic orbitals.

A. Quadrupolar Expansion

1. Transformation of $\Lambda_q(\vec{r}_p/a)$

The quadrupolar expansion will be derived from the bipolar expansion (23) by a transformation of the quantity $\Lambda_q(\vec{r}_p/a)$ into a function of two vectors, $\vec{r}_A/a$ and $\vec{r}_B/a$. The definition of $\Lambda_q(\vec{r})$ was given by (26) and (15), but we shall now write it in a form more convenient for our present purpose:

$$\Lambda_q(\vec{r}) = \mathcal{Y}_{\ell m}(\vec{r}) L_n^{\ell+1/2}(r^2)/2^n[2(n+\ell)+1]!! \quad . \qquad (277)$$

Here $\mathcal{Y}_{\ell m}(\vec{r})$ is the solid spherical harmonic defined by (185), $(2p+1)!!$ is given by (16), and $L_n^a(x)$ is the generalized Laguerre polynomial, which is defined by (17) and has the explicit form (Abramowitz and Stegun, 1965, Item 22.3.9)

$$L_n^a(x) = \sum_{t=0}^{n} [(-1)^t/t!(n-t)!][\Gamma(n+a+1)/\Gamma(t+a+1)]x^t \qquad (278)$$

In order to perform the transformation on Λ, we must require P to lie on the line AB:

$$\overrightarrow{PB} = \varepsilon\overrightarrow{AB} , \qquad \overrightarrow{PA} = (1-\varepsilon)\overrightarrow{BA} , \qquad 0 \le \varepsilon \le 1 . \qquad (279)$$

No other restrictions will be imposed on the relative positions of A, B and P. The coordinates used are shown in Figure 3. The coordinate systems on A, B and P are parallel to each other. Note that the AB-direction does not necessarily coincide with any axis. In addition to the symbols introduced in Figure 3, we define R_{AB} as the distance between the points A and B, and we will use the ratio ε of (279). The point E denotes the position of the electron.

Consider first the Laguerre polynomial of (278). Application of the Law of Cosines to the triangles AEB and either AEP or BEP (see Figure 3) yields

$$r_p^2 = \varepsilon r_A^2 + (1-\varepsilon) r_B^2 - \varepsilon(1-\varepsilon) R_{AB}^2 \quad . \qquad (280)$$

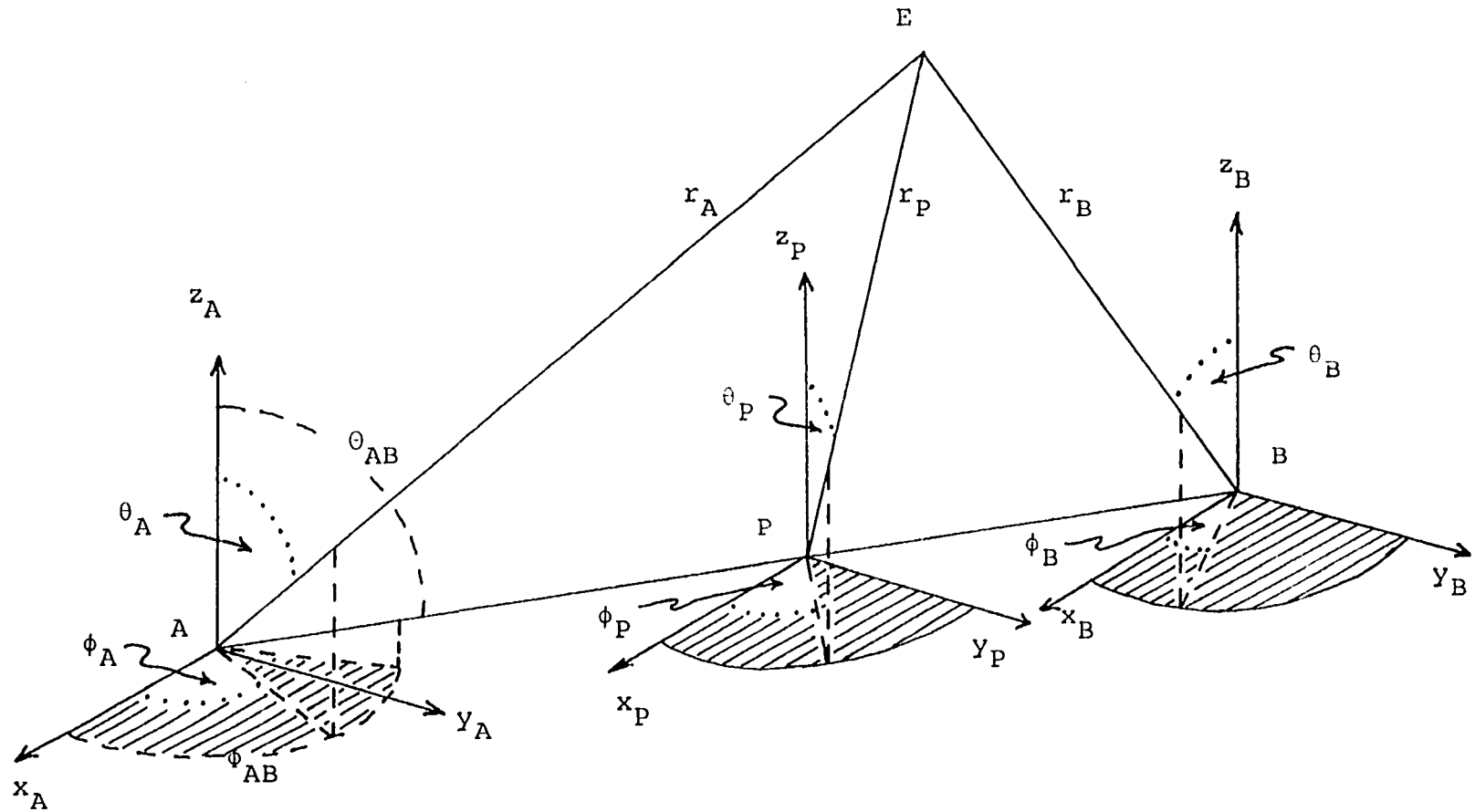


Figure 3. Coordinate systems on centers A, B and P. Axes are parallel to each other. Spherical coordinates R_{AB}, Θ_{AB}, Φ_{AB} are defined with respect to center A

Substitution of this identity into (278) [with x replaced by (r_P^2/a^2)] and two applications of the binomial expansion gives

$$L_n^{\ell+1/2}(r_P^2/a^2) = \sum_{t=0}^{n}\sum_{r=0}^{t}\sum_{s=0}^{r}\left[\frac{\Gamma(n+\ell+3/2)}{\Gamma(t+\ell+3/2)}\right]$$

$$\times\left[(-1)^r\binom{t}{r}\binom{r}{s}/t!(n-t)!\right]\left(\frac{r_A}{a}\right)^{2s}\left(\frac{r_B}{a}\right)^{2r-2s}$$

$$\times\ \varepsilon^s(1-\varepsilon)^{r-s}\left[\varepsilon(1-\varepsilon)\left(\frac{R_{AB}}{a}\right)^2\right]^{t-r} \quad . \qquad (281)$$

A rearrangement of the summations in this equation yields

$$L_n^{\ell+1/2}(r_P^2/a^2) = \sum_{r=0}^{n}\sum_{s=0}^{r}(r_A/a)^{2s}\ (r_B/a)^{2r-2s}$$

$$\times(-1)^r\binom{r}{s}\ \varepsilon^s(1-\varepsilon)^{r-s}\ G_r^{n\ell}[\varepsilon(1-\varepsilon)(R_{AB}/a)^2] \qquad (282)$$

where

$$G_r^{n\ell}(x) = (n!)^{-1}\binom{n}{r}\sum_{t=0}^{n-r}\binom{n-r}{t}\left[\frac{\Gamma(n+\ell+3/2)}{\Gamma(t+r+\ell+3/2)}\right]x^t \quad . \qquad (283)$$

Next, consider the solid spherical harmonic. Steinborn (1969) has shown that

$$\mathcal{Y}_{\ell m}(|\vec{AB}|\cdot\vec{r}_P)$$

$$= \sum_{\lambda=0}^{\ell}\sum_{\mu} Q_{\ell\lambda}^{\ m\mu}\ \mathcal{Y}_{\lambda\mu}(|\vec{AP}|\cdot\vec{r}_B)\,\mathcal{Y}_{\ell-\lambda,m-\mu}(|\vec{PB}|\cdot\vec{r}_A)\ , \quad (284)$$

where $Q_{\ell\lambda}^{\ m\mu}$ is defined by (150) and the limits for μ are

$$\max\{-\lambda,\ \lambda-\ell+m\} \le \mu \le \min\{\lambda,\ -\lambda+\ell+m\}\ . \quad (285)$$

This leads directly to

$$\mathcal{Y}_{\ell m}(\vec{r}_P/a)$$

$$= \sum_{\lambda=0}^{\ell}\sum_{\mu} \mathcal{Y}_{\ell-\lambda,m-\mu}(\vec{r}_A/a)\ \mathcal{Y}_{\lambda\mu}(\vec{r}_B/a)\ \varepsilon^{\ell-\lambda}(1-\varepsilon)^{\lambda}\ Q_{\ell\lambda}^{\ m\mu}\ . \quad (286)$$

By substituting the three expressions (282), (286) and (185) into (277) one obtains

$$\Lambda_q(\vec{r}_P/a) = \Lambda_q(\varepsilon,\ R_{AB}/a,\ \vec{r}_A/a,\ \vec{r}_B/a)$$

$$= \sum_{r=0}^{n}\sum_{s=0}^{r}\sum_{\lambda=0}^{\ell}\sum_{\mu} Q_{\ell\lambda}^{\ m\mu}\ C_{rs\lambda}^{\ n\ell}(\varepsilon,\ R_{AB}/a)$$

$$\times\ (r_A/a)^{2s+\ell-\lambda}\ Y_{\ell-\lambda,m-\mu}(\theta_A,\phi_A)$$

$$\times\ (r_B/a)^{2r-2s+\lambda}\ Y_{\lambda\mu}(\theta_B,\phi_B) \quad (287)$$

where

$$C_{rs\lambda}^{n\ell}(\varepsilon, R_{AB}/a) = (-1)^r \binom{r}{s} \{2^n [2(n+\ell)+1]!!\}^{-1}$$

$$\times G_r^{n\ell}[\varepsilon(1-\varepsilon)(R_{AB}/a)^2] \varepsilon^{s+\ell-\lambda}(1-\varepsilon)^{r-s+\lambda} \qquad (288)$$

and the limits on μ and the quantities ε, $Q_{\ell\lambda}^{m\mu}$ and $G_r^{n\ell}(x)$ are given by (285), (279), (150) and (283), respectively.

2. Expansion for r_{12}^{-1}

Now the expression for Λ_q is substituted into the bipolar expansion (23), and a quadrupolar expansion of r_{12}^{-1} is obtained:

$$r_{12}^{-1} = \sum_{q_1} \sum_{q_2} W_{q_1 q_2}(\vec{R}_{PQ}, a_1, a_2)$$

$$\times \Lambda_{q_1}(\varepsilon_1, R_{AB}/a_1, \vec{r}_{A1}/a_1, \vec{r}_{B1}/a_1)$$

$$\times \Lambda_{q_2}(\varepsilon_2, R_{CD}/a_2, \vec{r}_{C2}/a_2, \vec{r}_{D2}/a_2) \qquad (289)$$

with Λ_q given by (287) and (288) and W by (25), (7), (8), (181), (182) and (22). Notice that the position of the first electron is specified in terms of the centers A and B, and that of the second electron in terms of C and D, but the factor W, which is independent of the electronic coordinates, is still a function of the two points P and Q. There are four parameters in this expansion which one is free to specify in

some convenient way: a_1 and a_2 , the scaling parameters; and ε_1 and ε_2 , which fix the positions of P and Q on the lines AB and CD, respectively.

Since the quadrupolar expansion was obtained from the bipolar expansion by introducing a finite expansion for each term, the nature of the infinite series is not changed, so the new expansion converges because the bipolar expansion does.

B. Asymptotic Formula for Integrals over Slater-type Atomic Orbitals

1. Asymptotic expansion

Now we will use the quadrupolar expansion to obtain a formula for the integral

$$I = \int dV_1 \int dV_2 \; \chi_A^*(1)\chi_B(1) r_{12}^{-1} \chi_C^*(2)\chi_D(2) \quad , \qquad (290)$$

where

$$\chi_A(1) = \chi_{q_A}(\zeta_A \vec{r}_{A1})$$

is a Slater-type atomic orbital on center A defined by

$$\chi_q(\zeta\vec{r}) = 2^{n+1/2} \; \zeta^{3/2}[(2n)!]^{-1/2}(\zeta r)^{n-1} \; e^{-\zeta r} \; Y_{\ell m}(\theta,\phi) \; . \qquad (291)$$

The symbol q denotes the set $\{n,\ell,m\}$. As before, we take the Cartesian coordinate systems on the atomic centers A, B, C,

and D to be parallel to each other, but none of the coordinate axes is assumed to be parallel to any of the internuclear axes.

Substitution of either (289) (quadrupolar expansion) or (23) (bipolar expansion) into the integral (290) followed by interchange of summation and integration, leads to

$$I \sim \sum_{q_1} \sum_{q_2} W_{q_1 q_2}(\vec{R}_{PQ}, a_1, a_2)\, \mathcal{S}(q_A, q_B, q_1)\, \mathcal{S}(q_C, q_D, q_2) \quad . \tag{292}$$

The $\mathcal{S}$ are overlap-type integrals defined by

$$\mathcal{S}(q_A, q_B, q_1) = \int dV_1\, \chi_A^*(1)\chi_B(1)\Lambda_{q_1}(\vec{r}_{P1}/a_1) \quad , \tag{293}$$

and Λ is given either by (287) and (288), or by (277). As was pointed out by Silverstone and Kay (1969) and Ruedenberg and Salmon (1969), the interchange of summation and integration is not proper in the case of Slater-type orbitals, and the expansion of (292) is asymptotic (see, e.g. Whittaker and Watson, (1927, Ch. VIII)). This means that it is divergent, but the first few terms may be taken as an approximation to I. The accuracy of the approximation is greatest when the orbital exponents are all large, or equivalently, when the internuclear distances are large. Thus the expansion may be useful, especially for integrals involving relatively distant centers. Since only a few terms would be needed in such cases, it is expected that the method would be quite effi-

cient. In view of this, we present here a method for evaluating the terms of the expansion, (292). The results of the previous section will be used to evaluate the functions $\mathcal{S}$ explicitly.

2. Expression for $\mathcal{S}$ in terms of overlap integrals

Since, by virtue of (287), all factors occurring in $\mathcal{S}$ have been expressed in terms of coordinates centered at A and B, it is now possible to express $\mathcal{S}$ as a sum of standard overlap integrals. To this end, we substitute (287) and (291) into (293). The result contains products of the form

$$Y^*_{\ell_A m_A}(\theta_A,\phi_A)Y_{\ell-\lambda,m-\mu}(\theta_A,\phi_A) \quad \text{and} \quad Y_{\ell_B m_B}(\theta_B,\phi_B)Y_{\lambda\mu}(\theta_B,\phi_B),$$

which can be expanded by means of the formulas (Edmonds, 1957, p. 63, Eq. 4.6.5)

$$Y^*_{\ell_A m_A}(\theta_A,\phi_A)Y_{\ell-\lambda,m-\mu}(\theta_A,\phi_A)$$

$$= (-1)^{m_A} \sum_{\lambda_A} [(2\ell-2\lambda+1)(2\ell_A+1)(2\lambda_A+1)/4\pi]^{1/2}$$

$$\times \begin{pmatrix} \ell-\lambda & \ell_A & \lambda_A \\ m-\mu & -m_A & m_A+\mu-m \end{pmatrix} \begin{pmatrix} \ell-\lambda & \ell_A & \lambda_A \\ 0 & 0 & 0 \end{pmatrix} Y^*_{\lambda_A, m_A+\mu-m}(\theta_A,\phi_A) \tag{294a}$$

$$Y_{\ell_B,m_B}(\theta_B,\phi_B)Y_{\lambda\mu}(\theta_B,\phi_B)$$

$$= (-1)^{\mu+m_B}\sum_{\lambda_B}[(2\lambda+1)(2\ell_B+1)(2\lambda_B+1)/4\pi]^{1/2}$$

$$\times\begin{pmatrix}\lambda & \ell_B & \lambda_B\\ \mu & m_B & -\mu-m_B\end{pmatrix}\begin{pmatrix}\lambda & \ell_B & \lambda_B\\ 0 & 0 & 0\end{pmatrix}Y_{\lambda_B,\mu+m_B}(\theta_B,\phi_B) \quad , \qquad (294b)$$

with the summation conditions

$$|\ell-\lambda-\ell_A| \le \lambda_A \le \ell-\lambda+\ell_A \qquad \ell-\lambda+\ell_A+\lambda_A = \text{even} \qquad (295a)$$

$$|\lambda-\ell_B| \le \lambda_B \le \lambda+\ell_B \qquad \lambda+\ell_B+\lambda_B = \text{even} \qquad (295b)$$

By virtue of these equations and of (287), the definition (293) for $\mathscr{I}$ becomes

$$\mathscr{I}(q_A,q_B,q) = \sum_r\sum_s\sum_\lambda\sum_\mu[(-1)^{m_A+m_B+\mu}\,Q_{\ell\lambda}^{m\mu}/4\pi\cdot 2^{2r+\ell}]$$

$$\times\sum_{\lambda_A}\sum_{\lambda_B}[(2\ell-2\lambda+1)(2\lambda+1)(2\ell_A+1)(2\ell_B+1)(2\lambda_A+1)(2\lambda_B+1)]^{1/2}$$

$$\times\begin{pmatrix}\ell-\lambda & \ell_A & \lambda_A\\ m-\mu & -m_A & m_A+\mu-m\end{pmatrix}\begin{pmatrix}\ell-\lambda & \ell_A & \lambda_A\\ 0 & 0 & 0\end{pmatrix}\begin{pmatrix}\lambda & \ell_B & \lambda_B\\ \mu & m_B & -\mu-m_B\end{pmatrix}\begin{pmatrix}\lambda & \ell_B & \lambda_B\\ 0 & 0 & 0\end{pmatrix}$$

$$\times\mathscr{I}_{rs\lambda}^{n\ell n_A n_B}(\varepsilon,\rho_{AB})[\rho_A^{2s+\ell-\lambda}\,\rho_B^{2r-2s+\lambda}]^{-1}$$

$$\times\bar{S}_{n_A+2s+\ell-\lambda,n_B+2r-2s+\lambda}^{\lambda_A,\lambda_B,m_A+\mu-m,\mu+m_B} \quad , \qquad (296)$$

where

$$\rho_A = R_{AB}\zeta_A \qquad \rho_B = R_{AB}\zeta_B \qquad \rho_{AB} = R_{AB}/a \quad (297)$$

and

$$\mathscr{G}_{rs\lambda}^{n\ell n_A n_B}(\varepsilon,\rho) = \{[2(n_A+2s+\ell-\lambda)]![2(n_B+2r-2s+\lambda)]!\}^{1/2}$$

$$\times\{(2n_A)!(2n_B)!\}^{-1/2}\ \rho^{2r+\ell}\ C_{rs\lambda}^{n\ell}(\varepsilon,\rho)$$

$$= (-1)^r\binom{r}{s}\{2^n[2(n+\ell)+1]!!\}^{-1}$$

$$\times\{[2(n_A+2s+\ell-\lambda)]![2(n_B+2r-2s+\lambda)]!\}^{1/2}$$

$$\times\{(2n_A)!(2n_B)!\}^{-1/2}\ G_r^{n\ell}[\varepsilon(1-\varepsilon)\rho^2]$$

$$\times\varepsilon^{s+\ell-\lambda}(1-\varepsilon)^{r-s+\lambda}\ \rho^{2r+\ell} \quad . \quad (298)$$

The summation limits used in (296) are given in (295), (285) and (287). The functions $G_r^{n\ell}(x)$ are defined by (283), and

$$\bar{S}_{nn'}^{\ell\ell'mm'} = \int dV\ \chi_A^*(1)\chi_B(1)$$

denotes an overlap integral between the Slater-type atomic orbitals of (291) defined in terms of the A and B coordinates shown in Figure 3. It should be recalled again that, in general, the internuclear axis is not parallel to any of the coordinate axes. Consequently, $\bar{S}$ is not a <u>standard</u> overlap

integral.

However, since the coordinate axes on A and B are parallel to each other, it is possible to express $\bar{S}$ in terms of standard overlap integrals S by virtue of the following identity (Steinborn, 1969)

$$\bar{S}_{nn'}^{\ell\ell'mm'} = \sum_{M}\sum_{\Lambda}\begin{pmatrix}\ell & \ell' & \Lambda\\ -M & M & 0\end{pmatrix}\begin{pmatrix}\ell & \ell' & \Lambda\\ -m & m' & m-m'\end{pmatrix} Y^{*}_{\Lambda,m-m'}(\Theta_{AB},\Phi_{AB})$$

$$\times(-1)^{M+m}(2-\delta_{M0})\,[4\pi(2\Lambda+1)]^{1/2}\; S_{nn'}^{\ell\ell'M}(\rho_A,\rho_B)\ , \tag{299}$$

where the sums are given by

$$0 \le M \le \min\{\ell,\ \ell'\} \tag{300a}$$

$$\max\{|\ell-\ell'|,\ |m-m'|\} \le \Lambda \le \ell+\ell' \qquad \ell+\ell'+\Lambda = \text{even} \tag{300b}$$

The standard overlap integral $S_{nn'}^{\ell\ell'M}$ is defined as $\bar{S}_{nn'}^{\ell\ell'MM}$, but with the condition that $\vec{z}_A$, $\vec{z}_B$ and $\vec{R}_{AB}$ are all parallel to each other. Substitution of (299) into (296) yields the desired expression for $\mathcal{J}$ in terms of the standard overlap integrals

$$\mathcal{J}(q_A,q_B,q) = \sum_{r=0}^{n}\sum_{s=0}^{r}\sum_{\lambda=0}^{\ell}\sum_{\lambda_A}\sum_{\lambda_B}\sum_{M} \mathcal{G}_{rs\lambda}^{n\ell n_A n_B}(\varepsilon,\rho_{AB})$$

$$\times F_{\lambda\lambda_A\lambda_B M}^{\ell m\ell_A\ell_B m_A m_B}(\Theta_{AB},\Phi_{AB})\,[(2\rho_A)^{2s+\ell-\lambda}(2\rho_B)^{2r-2s+\lambda}]^{-1}$$

$$\times S_{n_A+2s+\ell-\lambda,\,n_B+2r-2s+\lambda}^{\lambda_A\lambda_B M}(\rho_A,\rho_B) \tag{301}$$

where the conditions on the summations over λ_A and λ_B are those given by (295) and the limits on the M-summation are

$$0 \le M \le \min\{\lambda_A, \lambda_B\} \quad . \tag{302}$$

Moreover, the following quantities have been used in (301)

$$F^{\ell m \ell_A \ell_B m_A m_B}_{\lambda \lambda_A \lambda_B M}(\theta,\phi) = (-1)^M (2-\delta_{M0}) \sum_{\Lambda} (-1)^{m+m_B}$$

$$\times [(2\Lambda+1)(2\ell+1)(2\ell_A+1)(2\ell_B+1)(2\lambda_A+1)(2\lambda_B+1)]^{1/2}$$

$$\times f^{\ell m \ell_A \ell_B m_A m_B}_{\Lambda \lambda \lambda_A \lambda_B M} \; Y^*_{\Lambda, m_A - m_B - m}(\theta,\phi) \tag{303}$$

$$f^{\ell m \ell_A \ell_B m_A m_B}_{\Lambda \lambda \lambda_A \lambda_B M} = \sum_{\mu} \binom{\ell+m}{\lambda-\mu} \left[\binom{\ell-m}{\lambda-\mu} \Big/ \binom{\ell+m}{\lambda+\mu} \right]^{1/2}$$

$$\times \begin{pmatrix} \ell-\lambda & \ell_A & \lambda_A \\ m-\mu & -m_A & m_A+\mu-m \end{pmatrix} \begin{pmatrix} \ell-\lambda & \ell_A & \lambda_A \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} \lambda & \ell_B & \lambda_B \\ \mu & m_B & -\mu-m_B \end{pmatrix} \begin{pmatrix} \lambda & \ell_B & \lambda_B \\ 0 & 0 & 0 \end{pmatrix}$$

$$\times \begin{pmatrix} \lambda_A & \lambda_B & \Lambda \\ m-\mu-m_A & \mu+m_B & m_A-m_B-m \end{pmatrix} \begin{pmatrix} \lambda_A & \lambda_B & \Lambda \\ -M & M & 0 \end{pmatrix} \quad , \tag{304}$$

where the summation over μ has limits given by (285), and that over Λ is limited by

$$\max\{|\lambda_A-\lambda_B|, \; |m-m_A+m_B|\} \le \Lambda \le \lambda_A+\lambda_B \tag{305a}$$

$$\lambda_A+\lambda_B+\Lambda = \text{even} \quad . \tag{305b}$$

3. Explicit dependence on ρ_A and ρ_B

Although (301) could be used as such, a more useful form can be obtained by applying the explicit expression obtained by Silver and Ruedenberg (1968, Eqs. 23-28) for the overlap integral, namely:

$$S^{\ell\ell'm}_{nn'}(\rho_A,\rho_B) = (-1)^{\ell'+m}(2\rho_A/\rho_A+\rho_B)^{n+1/2}(2\rho_B/\rho_A+\rho_B)^{n'+1/2}$$

$$\times\sum_{v=0}^{n+n'}(\rho_A-\rho_B)^v\, f_v(\rho_A,\rho_B)\sum_{w'}(\rho_A+\rho_B)^{w'}\, A_{vw',(nn'\ell\ell'm)} \tag{306}$$

where the limits on the summation over w' are

$$\max\begin{Bmatrix} 0 \\ |\ell-\ell'|-v \\ v-\ell-\ell' \end{Bmatrix} \le w' \le n+n'-m \quad .$$

The quantity f_v is defined by Eq. 24 of (Silver and Ruedenberg, 1968), and A is defined by

$$A_{vw',(nn'\ell\ell'm)} = (-1)^{\ell+\ell'}\left[\frac{(2\ell+1)(2\ell'+1)\binom{\ell+m}{m}\binom{\ell'+m}{m}}{\binom{\ell}{m}\binom{\ell'}{m}\binom{2n}{n}\binom{2n'}{n'}}\right]^{1/2}$$

$$\times\left[\frac{(n+n'-w')!}{n!n'!\binom{2v}{v}\Delta!}\right] B_{vw',(nn'\ell\ell'm)} \quad . \tag{307}$$

Note that Δ and B, defined by Eqs. 29ff of (Silver and Ruedenberg, 1968), depend only on the indices v and w' and on the arguments $nn'\ell\ell'$ and m. The formula of (306) differs from the expression of Silver and Ruedenberg (1968) by the factor $(-1)^{\ell'+m}$ because our z_B axis points in the direction opposite to that of their z_B axis. Insertion of (306) into (301) yields the following result:

$$\mathcal{S}(q_A,q_B,q) = (2\rho_A/\rho_A+\rho_B)^{n_A+1/2} \; (2\rho_B/\rho_A+\rho_B)^{n_B+1/2}$$

$$\times \sum \mathcal{G}_{rs\lambda}^{n\ell n_A n_B}(\varepsilon,\rho_{AB}) \; F_{\lambda\lambda_A\lambda_B M}^{\ell m \ell_A \ell_B m_A m_B}(\Theta_{AB},\Phi_{AB})$$

$$\times f_v(\rho_A,\rho_B) \; (\rho_A-\rho_B)^v (\rho_A+\rho_B)^{w'-2r-\ell} \; (-1)^{\lambda_B+M}$$

$$\times A_{vw'}(n_A+2s+\ell-\lambda, n_B+2r-2s+\lambda, \lambda_A, \lambda_B, M) \qquad (308)$$

where $\sum$ denotes the summations

$$\sum = \sum_{r=0}^{n} \sum_{s=0}^{r} \sum_{\lambda=0}^{\ell} \sum_{\lambda_A} \sum_{\lambda_B} \sum_{M} \sum_{v} \sum_{w'}$$

with the limits

$$0 \le v \le n_A+n_B+2r+\ell$$

$$\max \left\{ \begin{array}{c} 0 \\ |\lambda_A-\lambda_B|-v \\ v-\lambda_A-\lambda_B \end{array} \right\} \le w' \le n_A+n_B+2r+\ell-M \quad .$$

The limits on λ_A, λ_B and M are given by (295) and (302).

Interchanging summations, one can also write

$$\sum = \sum_{v} \sum_{r} \sum_{w'} \sum_{\lambda} \sum_{s=0}^{r} \sum_{\lambda_A} \sum_{\lambda_B} \sum_{M}$$

with the limits

$$0 \le v \le n_A+n_B+2n+\ell$$

$$\max\left\{\begin{matrix} 0 \\ [(v-n_A-n_B-\ell+1)/2] \end{matrix}\right\} \le r \le n$$

$$\max\left\{\begin{matrix} \mathrm{mod}(v+\ell+\ell_A+\ell_B,2) \\ |\ell_A-\ell_B|-\ell-v \\ v-\ell-\ell_A-\ell_B \end{matrix}\right\} \le w' \le n_A+n_B+2r+\ell$$

$$\max\{0,\ (\ell-k+\mathrm{Mod})/2\} \le \lambda \le \min\{\ell,\ (\ell+k-\mathrm{Mod})/2\}$$

$$\max\left\{\begin{matrix} |\ell-\lambda-\ell_A| \\ \lambda-\ell_B-v-w'+\mathrm{Mod} \\ \ell_B-\lambda-v-w'+\mathrm{Mod} \\ v-\ell_B-\lambda-w'+\mathrm{Mod} \end{matrix}\right\} \le \lambda_A \le \min\left\{\begin{matrix} \ell-\lambda+\ell_A \\ v+w'+\lambda+\ell_B-\mathrm{Mod} \end{matrix}\right\} \qquad (309a)$$

$$\max\left\{\begin{matrix} |\lambda-\ell_B| \\ \lambda_A-v-w'+\mathrm{Mod} \\ v-w'-\lambda_A+\mathrm{Mod} \end{matrix}\right\} \le \lambda_B \le \min\left\{\begin{matrix} \lambda+\ell_B \\ v+w'+\lambda_A-\mathrm{Mod} \end{matrix}\right\} \qquad (309b)$$

$$0 \le M \le \min\begin{Bmatrix} \lambda_A, & \lambda_B \\ n_A+n_B+2r+\ell-w' \end{Bmatrix} \tag{309c}$$

$$\ell-\lambda+\ell_A+\lambda_A = \text{even} \qquad \lambda+\ell_B+\lambda_B = \text{even} \quad . \tag{309d}$$

The following definitions have been used:

$$\text{mod}(n,2) = \begin{cases} 1 & \text{for } n=\text{odd} \\ 0 & \text{for } n=\text{even} \end{cases}$$

$$\text{Mod} = \text{mod}(v+w'+\ell+\ell_A+\ell_B,\ 2)$$

$$[x] = \text{largest integer} \le x$$

$$k = v+w'+\ell_A+\ell_B \quad .$$

Next the index w' is replaced by a new index

$$w = w'-2r-\ell \quad ,$$

which is the power of the quantity $(\rho_A+\rho_B)$ in (308), and the index s is replaced by a new index

$$\sigma = s+\ell-\lambda \quad ,$$

which is the power of ε in (298). The last step consists of rearranging the summations into the following order:

$$\sum = \sum_v \sum_w \sum_r \sum_\sigma \sum_\lambda \sum_{\lambda_A} \sum_{\lambda_B} \sum_M \quad .$$

The final result of these manipulations is the formula

$$\mathcal{S}(q_A,q_B,q) = (2\rho_A/\rho_A+\rho_B)^{n_A+1/2} \quad (2\rho_B/\rho_A+\rho_B)^{n_B+1/2}$$

$$\times \sum_v (\rho_A-\rho_B)^v f_v(\rho_A,\rho_B) \sum_w (\rho_A+\rho_B)^w$$

$$\times K_{vw}(\varepsilon,\rho_{AB},\Theta_{AB},\Phi_{AB}) \quad , \tag{310}$$

where the limits on v and w are given by

$$0 \le v \le n_A+n_B+2n+\ell \tag{311a}$$

$$\max \left\{ \begin{matrix} \mathrm{mod}(\ell+\ell_A+\ell_B+v,\ 2)-2n-\ell \\ |\ell_A-\ell_B|-2\ell-v-2n \\ v-\ell_A-\ell_B-2\ell-2n \end{matrix} \right\} \le w \le n_A+n_B \quad . \tag{311b}$$

The function K is discussed in the next section. Note that, since K does not depend on the orbital exponents, only two summations need be redone for each variation of the wave function.

4. Expression for K_{vw}

The transformations described in the preceding section yield the following definition for K

$$K_{vw}(\varepsilon,\rho,\theta,\phi) = \sum_r \sum_\sigma \sum_\lambda \sum_{\lambda_A} \sum_{\lambda_B} \sum_M \mathcal{G}^{n\ell n_A n_B}_{r,\sigma-\ell+\lambda,\lambda}(\varepsilon,\rho)$$

$$\times (-1)^{\lambda_B+M} F^{\ell m \ell_A \ell_B m_A m_B}_{\lambda\lambda_A\lambda_B M}(\theta,\phi)$$

$$\times A_{v,w+2r+\ell}(n_A+2\sigma-\ell+\lambda, n_B+2r-2\sigma+2\ell-\lambda, \lambda_A, \lambda_B, M) \qquad (312)$$

with the summation limits

$$\max\left\{\begin{array}{c} 0 \\ [(v-n_A-n_B-\ell+1)/2] \\ [-w-\ell+\mathrm{Mod}+\mathrm{mod}(v+\ell+\ell_A+\ell_B,2)]/2 \\ [|\ell_A-\ell_B|-2\ell-v-w+\mathrm{Mod}]/2 \\ [v-w-2\ell-\ell_A-\ell_B+\mathrm{Mod}]/2 \end{array}\right\} \le r \le n \qquad (313a)$$

$$\max\left\{\begin{array}{c} 0 \\ [-v-w-2r-\ell_A-\ell_B+\mathrm{Mod}]/2 \end{array}\right\} \le \sigma \le \min\left\{\begin{array}{c} \ell+r \\ \ell+2r+[v+w+\ell_A+\ell_B-\mathrm{Mod}]/2 \end{array}\right\} \qquad (313b)$$

$$\max\left\{\begin{array}{c} 0 \\ \ell-\sigma \\ [-v-w-2r-\ell_A-\ell_B+\mathrm{Mod}]/2 \end{array}\right\} \le \lambda \le \min\left\{\begin{array}{c} \ell \\ \ell+r-\sigma \\ r+\ell+[v+w+\ell_A+\ell_B-\mathrm{Mod}]/2 \end{array}\right\} \qquad (313c)$$

The limits on λ_A, λ_B and M are given by (309a)-(309d), but with $w' = w+2r+\ell$, and Mod now denotes $\mathrm{mod}(v+w+\ell_A+\ell_B, 2)$. The expressions of (298), (303) and (307) can now be introduced for $\mathcal{G}$, F and A. If the summation on Λ, which occurs

in (303), is brought outside of the summations over λ, λ_A, λ_B and M, one obtains the final form of K

$$K_{vw}(\varepsilon,\rho,\theta,\phi) = \sum_r (-1)^r G_r^{n\ell}[\varepsilon(1-\varepsilon)\rho^2]\rho^{2r+\ell}$$

$$\times \sum_\sigma \varepsilon^\sigma (1-\varepsilon)^{\ell+r-\sigma} \sum_\Lambda (-1)^{m+m_B} T_{vwr\sigma\Lambda}$$

$$\times Y^*_{\Lambda,m_A-m_B-m}(\theta,\phi) \quad , \tag{314}$$

where the limits on r and σ are those given by (313a) and (313b) and the limits on Λ are

$$\Lambda_1 \le \Lambda \le \Lambda_2 \tag{315a}$$

$$\Lambda_1 = \max \left\{ \begin{array}{c} |m-m_A+m_B| + \mathrm{mod}(m+m_A+m_B+\ell+\ell_A+\ell_B,\ 2) \\ |\ell_A-\ell_B|-\ell \\ \ell-\ell_A-\ell_B-2\sigma \\ \ell-\ell_A-\ell_B-2(\ell+r-\sigma) \\ v-w-2r-\ell-2(\ell_A+\sigma)+\mathrm{Mod} \\ v-w-2r-\ell-2(\ell_B+\ell+r-\sigma)+\mathrm{Mod} \end{array} \right\} \tag{315b}$$

$$\Lambda_2 = \min \left\{ \begin{array}{c} \ell+\ell_A+\ell_B \\ v+w+2r+\ell+2(\ell_A+\sigma)-\mathrm{Mod} \\ v+w+2r+\ell+2(\ell_B+\ell+r-\sigma)-\mathrm{Mod} \end{array} \right\} \tag{315c}$$

$$\ell+\ell_A+\ell_B+\Lambda = \text{even} \quad . \tag{315d}$$

The function $G_r^{n\ell}(x)$ was introduced in (283) and the constant T, which depends only on quantum numbers and summation indices, is defined by

$$T_{vwr\sigma\Lambda} = \left[\frac{(2\ell+1)(2\ell_A+1)(2\ell_B+1)(2\Lambda+1)}{(2n_A)!(2n_B)!}\right]^{1/2} \frac{1}{2^n[2(n+\ell)+1]!!}$$

$$\times \sum_{\lambda} \binom{r}{\sigma+\lambda-\ell} \sum_{\lambda_A}\sum_{\lambda_B} (-1)^{\lambda_A} (2\lambda_A+1)(2\lambda_B+1)$$

$$\times [(n_A+n_B-w)!/\binom{2v}{v}\Delta!] \sum_{M} (2-\delta_{M0}) f^{\ell m \ell_A \ell_B m_A m_B}_{\Lambda\lambda\lambda_A\lambda_B M}$$

$$\times \left[\binom{\lambda_A+M}{M}\binom{\lambda_B+M}{M}/\binom{\lambda_A}{M}\binom{\lambda_B}{M}\right]^{1/2}$$

$$\times B_{v,w+2r+\ell}(n_A+2\sigma-\ell+\lambda, n_B+2\ell+2r-2\sigma-\lambda, \lambda_A, \lambda_B, M) \tag{316}$$

with the limits

$$\lambda_1 \le \lambda \le \lambda_2 \tag{317a}$$

$$\lambda_1 = \max \left\{ \begin{array}{c} 0 \\ \ell-\sigma \\ [-v-w-2r-\ell_A-\ell_B+\mathrm{Mod}]/2 \\ [\ell-\ell_A-\ell_B-\Lambda]/2 \\ [|v-\Lambda|-w-2r-\ell-2\ell_B+\mathrm{Mod}]/2 \end{array} \right\} \tag{317b}$$

$$\lambda_2 = \min \left\{ \begin{array}{c} \ell \\ \ell+r-\sigma \\ \ell+[v+w+2r+\ell_A+\ell_B-\text{Mod}]/2 \\ [\Lambda+\ell+\ell_A+\ell_B]/2 \\ \{[|v-\Lambda|+w+2r+\ell-\text{Mod}]/2\}+\ell+\ell_A \end{array} \right\} \tag{317c}$$

$$\max \left\{ \begin{array}{c} |\ell-\lambda-\ell_A| \\ |\lambda-\ell_B|-v-w-2r-\ell+\text{Mod} \\ v-\lambda-\ell_B-w-2r-\ell+\text{Mod} \\ |\lambda-\ell_B|-\Lambda \\ \Lambda-\lambda-\ell_B \\ [|v-\Lambda|-w-2r-\ell+\text{Mod}]/2 \end{array} \right\} \leq \lambda_A \leq \min \left\{ \begin{array}{c} \ell-\lambda-\ell_A \\ v+w+2r+\ell+\lambda+\ell_B-\text{Mod} \\ \Lambda+\lambda+\ell_B \end{array} \right\} \tag{317d}$$

$$\max \left\{ \begin{array}{l} |\lambda-\ell_B| \\ |\Lambda-\lambda_A| \\ |v-\lambda_A|-w-2r-\ell+\text{Mod} \end{array} \right\} \leq \lambda_B \leq \min \left\{ \begin{array}{c} \lambda+\lambda_B \\ \Lambda+\lambda_A \\ v+w+2r+\ell+\lambda_A-\text{Mod} \end{array} \right\} \tag{317e}$$

$$0 \leq M \leq \min\{\lambda_A, \lambda_B, n_A+n_B-w\} \tag{317f}$$

Also, (309d) still holds. The constant f is given by (304) and the constants B and Δ are given by Eqs. 29ff of (Silver and Ruedenberg, 1968).

5. Discussion

The final asymptotic formula for the integral of (290) is given by (292), (310), (314), (283), (316) and (304). This formula has several desirable features. First, it contains no rotation representation matrices. Second, it makes maximum use of the charge distribution concept, which has proved essential for economy of computation time in diatomic calculations. Third, only two summations need to be performed in the calculation of $\mathcal{S}$ for each charge distribution, because the constants T can be calculated once for all and stored, and the set of constants K can be calculated once for each molecule and stored.

Since (292) is an asymptotic expansion, the series must be truncated at values of n_1 and n_2 less than those for which the terms begin to grow larger.

VI. APPENDIX A: MATHEMATICAL THEOREMS

Theorem 1:

Let $\{f_n\}$ be a sequence of functions defined on the infinite interval $x \geq a$ such that $f_n(x) \geq 0$ for each $x \geq a$ and each $n=1,2,\cdots$. If, for each $b \geq a$, it is known that

$$\int_a^b \sum_{n=1}^{\infty} f_n(x)\, dx = \sum_{n=1}^{\infty} \int_a^b f_n(x)\, dx \quad ,$$

then we also have that

$$\int_a^{\infty} \sum_{n=1}^{\infty} f_n(x)\, dx = \sum_{n=1}^{\infty} \int_a^{\infty} f_n(x)\, dx \quad ,$$

provided that either side of the last equation is convergent.

Note. We can omit the hypothesis $f_n(x) \geq 0$, if, instead, we assume that at least one side of the last equation is convergent when $f_n(x)$ is replaced by $|f_n(x)|$.

(Apostol, 1957, p. 451, Theorem 14-31)

Theorem 2:

Assume that $\sum f_n(x) = f(x)$ (uniformly on $a \leq x \leq b$), where each f_n is a real-valued function such that f_n is Riemann-integrable on $a \leq x \leq b$. Then we have

(a) f is Riemann-integrable on $a \leq x \leq b$.

(b) $\int_a^x \sum_{n=1}^{\infty} f_n(t)\,dt = \sum_{n=1}^{\infty} \int_a^x f_n(t)\,dt$ (uniformly on $a \le x \le b$).

(Apostol, 1957, p. 400, Theorem 13-11)

Definition: Uniform convergence of an infinite series

Given a sequence of functions $\{f_n\}$ defined on a set T. For each x in T, let

$$s_n(x) = \sum_{k=1}^{n} f_k(x) \qquad (n = 1,2,\cdots) .$$

If there exists a function f such that, for every $\varepsilon>0$, there exists an N (depending only on ε) such that $n > N$ implies

$$|s_n(x) - f(x)| < \varepsilon \quad , \quad \text{for every } x \text{ in } T,$$

we say the series $\sum f_n(x)$ converges uniformly on T and we write

$$\sum_{n=1}^{\infty} f_n(x) = f(x) \qquad \text{(uniformly on T)}.$$

(Apostol, 1957; p. 395, Definition 13-5 and p. 393, Definition 13-1)

Theorem 3: Cauchy condition for uniform convergence of series

The series $\sum f_n(x)$ converges uniformly on T if, and only if, for every $\varepsilon>0$ there is an N such that $n > N$ implies

$$\left| \sum_{k=n+1}^{n+p} f_k(x) \right| < \varepsilon \quad ,$$

for each $p=1,2,\cdots$, and every x in T.

(Apostol, 1957, p. 396, Theorem 13-6)

Theorem 4: Weierstrass' M-test

Let $\{M_n\}$ be a sequence of nonnegative numbers such that

$$0 \leq |f_n(x)| \leq M_n \quad ,$$

for $n=1,2,\cdots$, and for every x in T. Then $\sum f_n(x)$ converges uniformly on T if $\sum M_n$ converges.

(Apostol, 1957, p. 396, Theorem 13-7)

Theorem 5:

Given a power series $\sum_{n=0}^{\infty} a_n(z-z_0)^n$, let

$$\lambda = \lim_{n\to\infty} \sup[(|a_n|)^{(1/n)}] \quad , \qquad r = \frac{1}{\lambda} \quad ,$$

(where $r = 0$ if $\lambda = +\infty$ and $r = +\infty$ if $\lambda = 0$). Then the series converges absolutely if $|z-z_0| < r$ and diverges if

$|z-z_0| > r$. Furthermore, the series converges uniformly on every closed and bounded subset interior to the circle of convergence.

Note. If the limit

$$\lim_{n\to\infty} \left| \frac{a_n}{a_{n+1}} \right|$$

exists (or if this limit is $+\infty$), its value is also equal to the radius of convergence of the power series.

(Apostol, 1957; p. 409, Theorem 13-21 and p. 55, Theorem 340)

Theorem 6:

If $a_n > 0$ and $b_n > 0$ for $n=1,2,\cdots$, and if there exist positive constants c and N such that

$$a_n < cb_n \quad \text{for} \quad n \geq N ,$$

then convergence of $\sum b_n$ implies convergence of $\sum a_n$.

(Apostol, 1957, p. 360, Theorem 12-20)

Theorem 7:

Assume that $a_n > 0$ and $b_n > 0$ for $n=1,2,\cdots$, and suppose that

$$\lim_{n\to\infty} [a_n/b_n] = c > 0 .$$

Then $\sum a_n$ converges if, and only if, $\sum b_n$ converges.

(Apostol, 1957, p. 360, Theorem 12-21)

Theorem 8:

The series

$$\zeta(s) = \sum_{n=1}^{\infty} 1/n^s$$

converges if $s > 1$ and diverges if $s < 1$.

(Apostol, 1957, p. 363, Example 2)

Theorem 9:

If

$$|u_{n+1}/u_n| = 1 + A/n + \mathcal{O}(1/n^2) \quad ,$$

where A is independent of n, then the series $\sum u_n$ is absolutely convergent if $A < -1$.

(Whittaker and Watson, 1927, p. 24, Corollary to 2.37)

VII. APPENDIX B: COMPUTER PROGRAMS

PROGRAM 1: TABGAM

```
C TABGAM - CALCULATES TABLE GAMTAB AND STORES IT
C      IN A DIRECT ACCESS DATASET
C    GAMTAB(L,X)=GAMMA(L+1/2)*GAMMASTAR(L+1/2,X)
C         (SEE NBS APPL.MATH.SERIES 55,SECTION 6.5)
C    ARGUMENTS-LTGAM=MAXIMUM VALUE OF L=LA+LB+LC+LD
C
      SUBROUTINE TABGAM(LTGAM)
      IMPLICIT REAL*8(A-H,O-Z)
      REAL*4 RSQMAX
      DIMENSION GAMTAB(2272),EXPX(2272),X(2272)
      DEFINE FILE 10(45,1516,U,JDISK)
      IDISK=10
      LREC=758
C
C              LPMAX=NUMBER OF TERMS TO BE USED FOR
C                              INTERPOLATION
C
      LPMAX=3
      IMIN=LTGAM+LPMAX
      LTOP=IMIN-1
      J2LO=LREC+1
      J2HI=2*LREC
      J3LO=J2HI+1
C
C              RSQMAX=MAXIMUM VALUE OF ARG. OF GAMMA IN TABLE
C              DRHOSQ=INCREMENT IN ARG. OF GAMMA BETWEEN
C                              TABLE ENTRIES
C
      RSQMAX=23.044
      DRHOSQ=1.0D-02
C
C    THIS SECTION COMPUTES TOP ROW OF TABLE (HIGHEST L VALUE)
C    USING SERIES (NBS APPL.MATH.SERIES 55,ITEM 6.5.29)
C
      FACTO=1.D0/(LTOP+0.5D0)
      JMAX=INT(RSQMAX/SNGL(DRHOSQ))-32
      DO 110 J=1,JMAX
      X(J)=(J+32)*DRHOSQ
      EXPX(J)=DEXP(-X(J))
      FACT=FACTO
```

```
      SUM=FACT
      DO 100 I=IMIN,150
      FACT=FACT*X(J)/(I+0.5D0)
      SUM=SUM+FACT
      IF((FACT/SUM).LE.1.D-10) GO TO 110
  100 CONTINUE
  110 GAMTAB(J)=SUM*EXPX(J)
      WRITE(IDISK'3*IMIN-2) (GAMTAB(J),J=1,LREC)
      WRITE(IDISK'JDISK) (GAMTAB(J),J=J2LO,J2HI)
      WRITE(IDISK'JDISK) (GAMTAB(J),J=J3LO,2272)
C
C   THIS SECTION COMPUTES THE REST OF THE TABLE
C                              BY DOWNWARD RECURSION
C   (NBS APPL.MATH.SERIES 55,ITEM 6.5.23)
C
      DO 200 I=1,LTOP
      RALPH=1.0D0/(DFLOAT(LTOP-I)+0.5D0)
      L=IMIN-I
      DO 150 J=1,JMAX
  150 GAMTAB(J)=(X(J)*GAMTAB(J)+EXPX(J))*RALPH
      WRITE(IDISK'3*L-2) (GAMTAB(J),J=1,LREC)
      WRITE(IDISK'JDISK) (GAMTAB(J),J=J2LO,J2HI)
      IF(L.EQ.1) GO TO 160
      WRITE(IDISK'JDISK) (GAMTAB(J),J=J3LO,2272)
      GO TO 200
  160 WRITE(IDISK'JDISK) (GAMTAB(J),J=J3LO,2272),RSQMAX,
     1     LTGAM,DRHOSQ
  200 CONTINUE
      RETURN
      END
```

PROGRAM 2: FLNRHO

```
C FLNRHO    CREATES ARRAY EFFLN(J)=EFFLN(N,L) DEFINED BY
C    EFFLN(0,L)=ZETFAC**(L+1/2)*GAMMA(L+1/2)
C                              *GAMMASTAR(L+1/2,RHOSQ)
C    EFFLN(N,L)=ZETFAC**(N+L+1/2)*(N-1)FACTRL*EXROSQ
C                              *LAGUERRE(N-1,L+1/2)
C    J=(N+(L+1)/2)**2+(L+1)/2  = ((NU+1)/2)**2+(L+1)/2
C                                        IF L=ODD
C    J=(N+L/2)*(N+L/2+1)+L/2+1 = (NU/2)*(NU/2+1)+L/2+1
C                                        IF L=EVEN
C   ARGUMENTS
C    GAMTAB=TABLE OF GAMMA*GAMMASTAR FOR INTERPOLATION
C       (SEE NBS APPL.MATH.SERIES 55,SECTION 6.5)
C    LMAX=HIGHEST VALUE OF L=LA+LB+LC+LD
```

```
C     JFMAX=DIMENSION OF EFFLN=(LMAX/2+1)**2
C                                        IF LMAX IS EVEN
C                                 (LMAX/2+1)*(LMAX/2+2)
C                                        IF LMAX IS ODD
C
      SUBROUTINE FLNRHO(GAMTAB,LMAX,EFFLN,JFMAX)
      IMPLICIT REAL*8 (A-H,O-Z)
      REAL*4 RSQMAX
      COMMON/AF/ALPHAR(20),RSQMAX,LTGAM,DRHOSQ,AZ1,AZ2,PX1,
     1   PY1,PZ1,PX2,PY2,PZ2
C
C          ALPHAR(N)=1.0D0/(N-0.5D0)
C          RSQMAX=HIGHEST VALUE OF RHOSQ FOR WHICH GAMTAB
C                              IS TO BE USED
C          LTGAM=MAXIMUM VALUE OF L=LA+LB+LC+LD
C          DRHOSQ=INCREMENT IN ARG OF GAMTAB BETWEEN ENTRIES
C
      DIMENSION GAMTAB(2272,3)
      DIMENSION EFFLN(JFMAX)
      RHOSQ= (PX1-PX2)**2+(PY1-PY2)**2+(PZ1-PZ2)**2
      ZETFAC=1.0D0/(AZ1*AZ1+AZ2*AZ2)
      RHOSQ=RHOSQ*ZETFAC
C
C          RHOSQ=(DISTANCE BETWEEN POINTS P1 AND P2)**2
C                              DIVIDED BY (AZ1**2+AZ2**2)
C
      TEMPZF=DSQRT(ZETFAC)
      IF(SNGL(RHOSQ).LE.1.E-15) GO TO 400
      IF(LMAX.EQ.0) GO TO 70
      EXROSQ=DEXP(-RHOSQ)
C
C     CALC GAMMA*GAMMASTAR FOR ALL L BY RECURSION
C                                        (NBS ITEM 6.5.23)
C
      IF(SNGL(RHOSQ).GT.RSQMAX) GO TO 80
C
C          DOWNWARD RECURSION
C
      EFFLN(JFMAX)=GAMTOP(LMAX,RHOSQ,EXROSQ,GAMTAB)
      J=JFMAX
      JDIF=LMAX/2+1
      LMAX1=LMAX+1
      DO 60 LP=1,LMAX
      JNEW=J-JDIF
      L=LMAX1-LP
      EFFLN(JNEW)=ALPHAR(L)*(RHOSQ*EFFLN(J)+EXROSQ)
      J=JNEW
      IF(MOD(L,2).EQ.0) JDIF=JDIF-1
   60 CONTINUE
      GO TO 100
```

```
   7C IF(SNGL(RHOSQ).GT.RSQMAX) GO TO 76
      IF(SNGL(RHOSQ).LE.0.325) EXROSQ=DEXP(-RHOSQ)
      EFFLN(1)=TEMPZF*GAMTOP(0,RHOSQ,EXROSQ,GAMTAB)
      RETURN
   76 IF(SNGL(RHOSQ).LE.36.0) EXROSQ=DEXP(-RHOSQ)
      EFFLN(1)=TEMPZF*GAMLOW(RHOSQ,EXROSQ)
      RETURN
C
C         UPWARD RECURSION
C
   8C EFFLN(1)=GAMLOW(RHOSQ,EXROSQ)
      J=1
      JDIF=1
      RECIP=1.0D0/RHOSQ
      ALPHA=0.5D0
      DO 90 L=1,LMAX
      JNEW=J+JDIF
      EFFLN(JNEW)=RECIP*(ALPHA*EFFLN(J)-EXROSQ)
      ALPHA=ALPHA+1.0D0
      J=JNEW
      IF(MOD(L,2).EQ.1) JDIF=JDIF+1
   9C CONTINUE
C
C     CALC EFFLN FOR ALL L, N=0,1,2
C
  10C EFFLN(1)=TEMPZF*EFFLN(1)
      TEMPZF=TEMPZF*ZETFAC
      EFFLN(2)=TEMPZF*EFFLN(2)
      IF(LMAX/2-1) 350,110,150
  11C EFFLN(3)=TEMPZF*EXROSQ
      IF(LMAX.LT.3) GO TO 120
      TEMPZF=TEMPZF*ZETFAC
      EFFLN(4)=TEMPZF*EFFLN(4)
      EFFLN(5)=ZETFAC*EFFLN(3)
      EFFLN(6)=ZETFAC*TEMPZF*EFFLN(6)
      RETURN
  12C EFFLN(4)=ZETFAC*TEMPZF*EFFLN(4)
      RETURN
  15C EFFLN(3)=TEMPZF*EXROSQ
      TEMPZF=TEMPZF*ZETFAC
      EFFLN(4)=TEMPZF*EFFLN(4)
      SUM0=1.5D0-RHOSQ
      SUM=SUM0
      J=4
      J1=3
      JDIF=2
      LPMAX=LMAX-3
      LMAX5=LMAX-5
      DO 200 LP=1,LPMAX
      L=LP-1
```

```
      TEMPZF=ZETFAC*TEMPZF
      J=J+JDIF
      EFFLN(J)=TEMPZF*EFFLN(J)
      J1NEW=J-1
      EFFLN(J1NEW)=ZETFAC*EFFLN(J1)
      J1=J1NEW
      IF(MOD(L,2).EQ.0) JDIF=JDIF+1
      J2=J1+JDIF-1
      EFFLN(J2)=EFFLN(J1)*SUM
      IF(LMAX5-L) 200,190,170
C
C     CALC EFFLN FOR ALL L, N.GE.3 BY RECURSION
C                              (LAGUERRE POLYNOMIALS)
C
  170 NUMIN=6+L
      N=1
      J2OLD=J2-L-4
      DO 180 NU=NUMIN,LMAX,2
      J2NEW=J2+NU
      EFFLN(J2NEW)=ZETFAC*(((NU-4)+SUMO)*EFFLN(J2)-
     1    ZETFAC*N*((N+L)+0.5D0)*EFFLN(J2OLD))
      N=N+1
      J2OLD=J2
  180 J2=J2NEW
  190 SUM=SUM+1.0D0
  200 CONTINUE
      J=J+JDIF
      EFFLN(J)=ZETFAC*TEMPZF*EFFLN(J)
      EFFLN(J-1)=ZETFAC*EFFLN(J1)
  350 RETURN
C
C   ENTRY FOR ONE-CENTER CASE
C
      ENTRY FLN1C(LMAX,EFFLN,JFMAX)
      ZETFAC=1.0D0/(AZ1*AZ1+AZ2*AZ2)
      TEMPZF=DSQRT(ZETFAC)
C
C         RHOSQ=0.0,SO ONLY TERMS WITH L=0 APPEAR
C         GAMMA(1/2)*GAMMASTAR(1/2,0.0)=2.0
C
  400 EFFLN(1)=TEMPZF+TEMPZF
      IF(LMAX.EQ.0) RETURN
      DO 410 J=2,JFMAX
  410 EFFLN(J)=0.0D0
      IF(LMAX.EQ.1) RETURN
      TEMPZF=TEMPZF*ZETFAC
      EFFLN(3)=TEMPZF
      IF(LMAX.LE.3) RETURN
      TEMPZF=TEMPZF*ZETFAC
      EFFLN(7)=TEMPZF*1.5D0
```

```
      IF(LMAX.LE.5) RETURN
C
C     CALC EFFLN FOR L=0, N.GE.3 BY RECURSION
C                              (LAGUERRE POLYNOMIALS)
C
      J2=7
      N=1
      J2OLD=3
      DO 480 NU=6,LMAX,2
      J2NEW=J2+NU
      EFFLN(J2NEW)=ZETFAC*(((NU-4)+1.5D0)*EFFLN(J2)
     1   -ZETFAC*N*(N+0.5DC)*EFFLN(J2OLD))
      N=N+1
      J2OLD=J2
  480 J2=J2NEW
      RETURN
      END
```

PROGRAM 3: GAMTOP

```
C GAMTOP=GAMMA(LMAX+0.5)*INC.GAMMASTAR(LMAX+0.5,RHOSQ)
C    COMPUTED BY TAYLOR SERIES USING A GRID
C ASSUMES GAMTAB IS ALREADY IN CORE
C    GAMTAB=TABLE OF GAMMA*GAMMASTAR FOR INTERPOLATION
C   GAMTAB(L,X)=GAMMA(L+1/2)*GAMMASTAR(L+1/2,X)
C       (SEE NBS APPL.MATH.SERIES 55,SECTION 6.5)
C    EXROSQ=DEXP(-RHOSQ)
C
      FUNCTION GAMTOP(LMAX,RHOSQ,EXROSQ,GAMTAB)
      IMPLICIT REAL*8(A-H,O-Z)
      REAL*4 RSQMAX
      REAL*4 FJ
C
C  ALPHAR(L)=1.0D0/(L-0.5DC)
C         RSQMAX=HIGHEST VALUE OF RHOSQ FOR WHICH GAMTAB
C                              IS TO BE USED
C         LTGAM=MAXIMUM VALUE OF L=LA+LB+LC+LD
C         DRHOSQ=INCREMENT IN ARG OF GAMTAB BETWEEN ENTRIES
C
      COMMON/AF/ALPHAR(20),RSQMAX,LTGAM,DRHOSQ
      DIMENSION GAMTAB(2272,3)
      IF(SNGL(RHOSQ).LE.0.325) GO TO 350
C
C     CALC GAMTOP BY TAYLOR SERIES USING GAMTAB
C
   27 FJ=SNGL(RHOSQ)/SNGL(DRHOSQ)
```

```
      J=FJ
      FLOATJ=J
      J=J-32
      DELTA=RHOSQ-FLOATJ*DRHOSQ
      IF((FJ-SNGL(FLOATJ)).LE.0.5) GO TO 30
      J=J+1
      DELTA=DELTA-DRHOSQ
   30 CONTINUE
      SUM=GAMTAB(J,1)-DELTA*(GAMTAB(J,2)
     1                       -DELTA*0.5D0*GAMTAB(J,3))
  320 GAMTOP=SUM
      RETURN
C
C     CALC GAMTOP FOR SMALL RHOSQ BY SERIES(NBS ITEM 6.5.29)
C
  350 IF(LMAX.LT.5) GO TO 360
      SUM=1.D0
      GO TO 380
  360 IF(LMAX.LT.2) GO TO 370
      SUM=1.D0+RHOSQ*ALPHAR(LMAX+6)
      GO TO 380
  370 SUM=1.D0+RHOSQ*ALPHAR(LMAX+6)*(1.D0+RHOSQ*
     1                                ALPHAR(LMAX+7))
  380 SUM=ALPHAR(LMAX+1)*(1.D0+RHOSQ*ALPHAR(LMAX+2)
     1   *(1.D0+RHOSQ*ALPHAR(LMAX+3)*(1.D0+RHOSQ*ALPHAR(
     2   LMAX+4)*(1.D0+RHOSQ*ALPHAR(LMAX+5)*SUM))))
      GAMTOP=EXROSQ*SUM
      RETURN
      END
```

PROGRAM 4: GAMLOW

```
C GAMLOW=GAMMA(0.5)*INC.GAMMASTAR(0.5,RHOSQ)
C                          =SQRT(PI)*ERF(RHO)/RHO
C         (SEE NBS APPL.MATH.SERIES ITEM 6.5.16)
C  RHO=SQRT(RHOSQ)
C  ERF CALCULATED BY ASYMPTOTIC EXPANSION
C                          (NBS APPL.MATH.SERIES 7.1.23)
C  VALID FOR 4.8.LE.RHO (23.04.LE.RHOSQ)
C    EXROSQ=DEXP(-RHOSQ)
C
      FUNCTION GAMLOW(RHOSQ,EXROSQ)
      IMPLICIT REAL*8(A-H,O-R,T-Z)
      EQUIVALENCE(RHO,TERM1)
      RHO=DSQRT(RHOSQ)
      SNGRHO=SNGL(RHO)
```

```
      TERM1=1.772453850905516/RHO
      IF(SNGRHO.LT.6.0) GO TO 20
      GAMLOW=TERM1
      RETURN
   20 SRECIP=1.0/SNGL(RHOSQ)
      IF(SNGRHO.LT.5.2) GO TO 50
      IF(SNGRHO.LE.5.5) GO TO 30
      SSUM=1.0
      GO TO 100
   30 SSUM=1.0-0.5*SRECIP
      GO TO 100
   50 SFACTR=0.5*SRECIP
      IF(SNGRHO.LT.5.0) GO TO 60
      SSUM=1.0-SFACTR*(1.0-3.0*SFACTR)
      GO TO 100
   60 SSUM=1.0-SFACTR*(1.0-3.0*SFACTR*(1.0-5.0*SFACTR))
  100 GAMLOW=TERM1-SNGL(EXROSQ)*SRECIP*SSUM
      RETURN
      END
```

PROGRAM 5: MUSUM4

```
C MUSUM4  -  CALCULATES ARRAY SUMM AND PUTS IT IN CORE
C      SUMM DEPENDS ONLY ON THE LOCATION OF THE NUCLEI,
C                              NOT ON ORB. EXP'S
C      SUMM(J)=SUMM(M,L,LAMBD2,LAMBD1)
C      CALC INVOLVES SUMS ON MU1 AND MU2 IN STEINBORNS
C        FORMULA FOR A SOLID SPHERICAL HARMONIC OF ONE
C        VECTOR IN TERMS OF THOSE FOR THREE VECTORS
C      ARGUMENTS - NCENTR INDICATES WHICH NUCLEI CORRESPOND
C                                                    TO ABCD
C                  LMAX = MAX VALUE OF L,LAMBD1,LAMBD2
C    PAB,PHIAB REFER TO AB, PCD,PHICD REFER TO CD
C
      SUBROUTINE MUABCD(SUMM,NCENTR,LMAX,PAB,PHIAB,PCD,
     1                                              PHICD)
      IMPLICIT REAL*8(A-H,O-Z)
      COMMON/NUCLEI/CENTER(3,4),CHRG(4),LHI(4)
      COMMON/YS/RECIP(24),RRT2PI,PMN(45),PHIMN,COS00(4),
     1     COS0(26),COSM(386),SINM(386)
      DIMENSION PAB(45),PCD(45)
      DIMENSION RMIDPT(3),NCENTR(4),POWER(8)
      DIMENSION SUMM(1)
      DATA TWOPI/6.283185307179586/,RT2PI/2.506628274631001/
      SUMM(1)=RRT2PI
      IF(LMAX.EQ.0) RETURN
      LMAX1=LMAX+1
C
C    FIND COORDS OF VECTOR BETWEEN MIDPOINTS OF RAB AND RCD
C
      RMN=0.0D0
      DO 20 I=1,3
      RMIDPT(I)=0.5D0*(CENTER(I,NCENTR(3))+
     1   CENTER(I,NCENTR(4))-CENTER(I,NCENTR(1))
     2   -CENTER(I,NCENTR(2)))
   20 RMN=RMN+RMIDPT(I)*RMIDPT(I)
      RMN=DSQRT(RMN)
      JP=1
      IF(ABS(SNGL(RMIDPT(3))).NE.SNGL(RMN)) GO TO 200
C
C    TRIG2 CALCULATES AND STORES SINE AND COSINE OF ANG
C                                        FOR ALL M,MU1
C      ANG=MU1*PHIAB+(M-MU1)*PHICD  FOR CASE MU2=M-MU1,
C                                        PHIMN UNDEFINED
C
      CALL TRIG2(LMAX,LMAXD2,PHIAB,PHICD)
      IF(SNGL(RMN).NE.0.0) GO TO 100
      ASSIGN 320 TO KM0
      ASSIGN 395 TO KM
```

```
      GO TO 210
  100 IF(SNGL(RMIDPT(3)).LT.0.0) GO TO 105
      ASSIGN 120 TO KZ
      GO TO 110
  105 ASSIGN 115 TO KZ
C
C   CALCULATE PMN(L,0) FOR CASE COSTH=1 OR -1
C
  110 PMN(1)=RRT2PI
      JOLD=1
      DO 130 L=1,LMAX
      J=JOLD+L
      GO TO KZ,(115,120)
  115 PMN(J)=-RECIP(L)*PMN(JOLD)
      GO TO 130
  120 PMN(J)= RECIP(L)*PMN(JOLD)
  130 JOLD=J
      ASSIGN 345 TO K1
      ASSIGN 405 TO K2
      GO TO 205
  200 ASSIGN 355 TO K1
      ASSIGN 450 TO K2
      PHIMN=DATAN2(RMIDPT(2),RMIDPT(1))
      COSTH=RMIDPT(3)/RMN
C
C   PLMBAR CALCULATES PMN(L,M) FOR GENERAL CASE
      CALL PLMBAR(COSTH,LMAX,PMN)
C
C   TRIG3 CALCULATES AND STORES SINE AND COSINE OF ANG
C                                          FOR ALL M,MU1,MU2
C     ANG=MU1*PHIAB+MU2*PHICD+(M-MU1-MU2)*PHIMN
C
      CALL TRIG3(LMAX,LMAXD2,PHIAB,PHICD)
  205 ASSIGN 335 TO KPOW
      ASSIGN 330 TO KMO
      ASSIGN 400 TO KM
      POWER(1)=RMN
  210 ASSIGN 300 TO KLMIN
      JTO=LMAXD2+1
      JADDO=2*JTO
      DO 600 LAM1=1,LMAX1
      LAMBD1=LAM1-1
      JL1=LAMBD1*LAM1/2+1
      RPC=-1.0D0
      LAM2MX=LMAX1-LAMBD1
      DO 595 LAM2=1,LAM2MX
      LAMBD2=LAM2-1
      LAMSUM=LAMBD1+LAMBD2
      RPC=-RPC
C RPC=(-1)**LAMBD2
```

```
      JL2=LAMBD2*LAM2/2+1
      GO TO KLMIN,(220,300,215)
C 2ND TIME THRU LOOP ON L, POWER WAS CALCD 1ST TIME,
C     NEXT STMT PREVENTS RECALCULATION
  215 ASSIGN 340 TO KPOW
      ASSIGN 220 TO KLMIN
C 2ND AND SUBSEQUENT TIMES THRU LOOP ON L -
C CALC SUMM FOR L=LAMSUM.   THIS IS SKIPPED FOR LAMSUM = 0
C BECAUSE THAT CASE, SUMM(1), HAS BEEN DONE
  220 CONST=DSIGN(RT2PI,RPC)
      JM=JP
      JP=JP+LAMSUM+1
C
C M=0
      TM0=PAB(JL1)*PCD(JL2)
      MU1MAX=MIN0(LAMBD1,LAMBD2)
      IF(MU1MAX.EQ.0) GO TO 242
      SUMP=0.0D0
      ASSIGN 235 TO KMMOD
      JTRIG=JT0
      DO 240 MU1=1,MU1MAX
      IF(MU1.NE.1) JTRIG=JTRIG+JADD0-MU1
      TERM=PAB(JL1+MU1)*PCD(JL2+MU1)*COS0(JTRIG)
      GO TO KMMOD,(230,235)
C
C MU1 IS EVEN
  230 SUMP=SUMP+TERM
      ASSIGN 235 TO KMMOD
      GO TO 240
C
C MU1 IS ODD
  235 SUMP=SUMP-TERM
      ASSIGN 230 TO KMMOD
  240 CONTINUE
      SUMM(JP)=CONST*(TM0+2.0D0*SUMP)
      GO TO 244
  242 SUMM(JP)=CONST*TM0
C
C ALL M NOT 0
  244 SIGNM=1.0D0
      JTM=0
      DO 270 M=1,LAMSUM
      JM=JM+1
      JP=JP+1
      MU1MAX=MIN0( LAMBD1,M+LAMBD2)
      MU1MIN=MAX0(-LAMBD1,M-LAMBD2)
C SIGNM=(-1)**M
      SIGNM=-SIGNM
      LMAXMM=LMAX-M
      MDIF2=LMAXMM/2
```

```
      LMAXP=LMAX1-MOD(LMAXMM,2)
      JTRIG=JTM+MDIF2*LMAXP-MDIF2*(MDIF2-1)/2+1
      IF(MU1MIN.GT.0) GO TO 250
      JTRIGP=JTRIG+M
      TM0=PAB(JL1)*PCD(JL2+M)*SIGNM
      SUMP=TM0*COSM(JTRIGP)
      SUMN=TM0*SINM(JTRIGP)
      IF(MU1MIN.LT.0) GO TO 260
      IF(MU1MAX.EQ.0) GO TO 259
      MU1MIN=1
      GO TO 251
  250 SUMP=0.0D0
      SUMN=0.0D0
  251 SIGN=SIGNM
  252 DO 258 MU1=MU1MIN,MU1MAX
      MMMU1=M-MU1
      IF(MMMU1.LT.0) SIGN=-SIGN
C SIGN=EPSILON(MU1)*EPSILON(M-MU1)
      TM0=SIGN*PAB(JL1+MU1)*PCD(JL2+IABS(MMMU1))
      JTRIGP=JTRIG+MU1*LMAXP-MU1*(MU1-1)/2+MMMU1
      SUMP=SUMP+TM0*COSM(JTRIGP)
  258 SUMN=SUMN+TM0*SINM(JTRIGP)
  259 SUMM(JP)=CONST*SUMP
      SUMM(JM)=CONST*SUMN
      IF(M.NE.LAMSUM) JTM=LMAXP*LMAXP
     1                    -((LMAXP+1)*(LMAXP-1)+M*M)/4+JTM
      GO TO 270
  260 MU1MIN=-MU1MIN
      SIGN2=SIGNM
      SIGN=SIGNM
      DO 265 MU1=1,MU1MIN
C SIGN2=(-1)**(M-MU1)
      SIGN2=-SIGN2
      MPMU1=M+MU1
      MMMU1=M-MU1
      IF(MMMU1.LT.0) SIGN=-SIGN
C SIGN=EPSILON(MU1)*EPSILON(M-MU1)
      TM0=SIGN*PCD(JL2+IABS(MMMU1))
      TM1=SIGN2*PCD(JL2+MPMU1)
      JTERM=MU1*LMAXP-MU1*(MU1-1)/2
      JTRIGP=JTRIG+JTERM+MMMU1
      JTRIGM=JTRIG-JTERM+MPMU1
      J=JL1+MU1
      SUMP=SUMP+PAB(J)*(TM0*COSM(JTRIGP)+TM1*COSM(JTRIGM))
  265 SUMN=SUMN+PAB(J)*(TM0*SINM(JTRIGP)+TM1*SINM(JTRIGM))
      IF(MU1MIN.EQ.MU1MAX) GO TO 259
      MU1MIN=MU1MIN+1
      GO TO 252
  270 CONTINUE
      GO TO 310
```

```
C
C 1ST TIME THRU LOOP ON L
  300 ASSIGN 215 TO KLMIN
  310 IF(LAMSUM.EQ.LMAX) GO TO 600
C
C ALL L.GT.LAMSUM
      LMIN=LAMSUM+1
      CONSTA=DSIGN(TWOPI,RPC)
      DO 590 L=LMIN,LMAX
      JM=JP
      JP=JP+L+1
      GO TO KM0,(320,330)
C  RMN=0
  320 SUMM(JP)=0.0D0
      GO TO 390
C  RMN.NE.0
  330 GO TO KPOW,(335,340)
  335 IF(L.NE.1) POWER(L)=RMN*POWER(L-1)
  340 LAMBD3=L-LAMSUM
      LML1=L-LAMBD1
      JL3=LAMBD3*(LAMBD3+1)/2+1
      CONST=CONSTA*POWER(LAMBD3)
C  M=0
      SUMP=0.0D0
      SIGN=1.0D0
      GO TO K1,(345,355)
C  COSTH=1 OR -1
  345 TM0=PAB(JL1)*PCD(JL2)
      MU1MAX=MIN0(LAMBD1,LAMBD2)
      IF(MU1MAX.EQ.0) GO TO 352
      JTRIG=JT0
      DO 350 MU1=1,MU1MAX
C  SIGN=(-1)**MU1
      SIGN=-SIGN
      IF(MU1.NE.1) JTRIG=JTRIG+JADD0-MU1
  350 SUMP=SUMP+SIGN*PAB(JL1+MU1)*PCD(JL2+MU1)*COS0(JTRIG)
  352 SUMM(JP)=CONST*PMN(JL3)*(TM0+2.0D0*SUMP)
      GO TO 390
C
C  GENERAL VALUE OF COSTH
  355 TM0=PCD(JL2)*PMN(JL3)
      MU1MAX=MIN0(LAMBD1,LML1)
      MU2MAX=MIN0(LAMBD2,LAMBD3)
      IF(MU2MAX.EQ.0) GO TO 361
      DO 360 MU2=1,MU2MAX
C  SIGN=(-1)**MU2
      SIGN=-SIGN
  360 SUMP=SUMP+SIGN*PCD(JL2+MU2)*PMN(JL3+MU2)*COS00(MU2)
  361 TM0=PAB(JL1)*(TM0+2.0D0*SUMP)
      SUMP=0.0D0
```

```
      IF(MU1MAX.EQ.0) GO TO 385
      LMAXP=LMAX1-MOD(LMAX,2)
      SIGN=1.0D0
      DO 380 MU1=1,MU1MAX
C  SIGN=(-1)**MU1
      SIGN=-SIGN
      JTRIG=JT0+(MU1-1)*LMAXP-MU1*(MU1+1)/2
      MU2MAX=MIN0( LAMBD2,MU1+LAMBD3)
      MU2MIN=MAX0(-LAMBD2,MU1-LAMBD3)
      IF(MU2MIN.GT.0) GO TO 364
      SUM2=SIGN*PCD(JL2)*PMN(JL3+MU1)*COS0(JTRIG)
      IF(MU2MIN.LT.0) GO TO 370
      IF(MU2MAX.EQ.0) GO TO 368
      MU2MIN=1
      GO TO 365
  364 SUM2=0.0D0
  365 SIGN2=SIGN
      DO 367 MU2=MU2MIN,MU2MAX
      M1MM2=MU1-MU2
      IF(M1MM2.LT.0) SIGN2=-SIGN2
C  SIGN2=EPSILON(MU1)*EPSILON(MU1-MU2)
  367 SUM2=SUM2+SIGN2*PCD(JL2+MU2)*PMN(JL3+IABS(M1MM2))
     1                                  *COS0(JTRIG+MU2)
  368 SUMP=SUMP+PAB(JL1+MU1)*SUM2
      GO TO 380
  370 MU2MIN=-MU2MIN
      SIGN1=SIGN
      SIGN2=SIGN
      DO 375 MU2=1,MU2MIN
      M1PM2=MU1+MU2
      M1MM2=MU1-MU2
      SIGN1=-SIGN1
C SIGN1=(-1)**(MU1+MU2)
      IF(M1MM2.LT.0) SIGN2=-SIGN2
C  SIGN2=EPSILON(MU1)*EPSILON(MU1-MU2)
  375 SUM2=SUM2+PCD(JL2+MU2)*(SIGN1*PMN(JL3+M1PM2)
     1   *COS0(JTRIG-MU2)+SIGN2*PMN(JL3+IABS(M1MM2))
     2   *COS0(JTRIG+MU2))
      IF(MU2MIN.EQ.MU2MAX) GO TO 368
      MU2MIN=MU2MIN+1
      GO TO 365
  380 CONTINUE
  385 SUMM(JP)=CONST*(TMC+2.0D0*SUMP)
C
C  ALL M.GT.0
  390 SIGNM=1.0D0
      JTM=0
      DO 580 M=1,L
      JM=JM+1
      JP=JP+1
```

```
      GO TO KM,(395,400)
C  RMN=0
  395 SUMM(JM)=0.0D0
      SUMM(JP)=0.0D0
      GO TO 580
C
C  RMN.NE.0
  400 LMAXMM=LMAX-M
      MDIF2=LMAXMM/2
      LMAXP=LMAX1-MOD(LMAXMM,2)
      JTRIG=JTM+MDIF2*LMAXP-MDIF2*(MDIF2-1)/2+1
C  SIGNM=(-1)**M
      SIGNM=-SIGNM
      GO TO K2,(405,450)
C
C  COSTH= 1 OR -1
  405 MU1MAX=MIN0( LAMBD1,M+LAMBD2)
      MU1MIN=MAX0(-LAMBD1,M-LAMBD2)
      IF(MU1MIN.LE.MU1MAX) GO TO 410
      SUMM(JP)=0.0D0
      SUMM(JM)=0.0D0
      GO TO 575
  410 IF(MU1MIN.GT.0) GO TO 415
      JTRIGP=JTRIG+M
      TM0=SIGNM*PAB(JL1)*PCD(JL2+M)
      SUMP=TM0*COSM(JTRIGP)
      SUMN=TM0*SINM(JTRIGP)
      IF(MU1MIN.LT.0) GO TO 435
      IF(MU1MAX.EQ.0) GO TO 432
      MU1MIN=1
      GO TO 420
  415 SUMP=0.0D0
      SUMN=0.0D0
  420 SIGN=SIGNM
  422 DO 430 MU1=MU1MIN,MU1MAX
      MMMU1=M-MU1
      IF(MMMU1.LT.0) SIGN=-SIGN
C  SIGN=EPSILON(MU1)*EPSILON(M-MU1)
  424 TM0=SIGN*PAB(JL1+MU1)*PCD(JL2+IABS(MMMU1))
      JTRIGP=JTRIG+MU1*LMAXP-MU1*(MU1-1)/2+MMMU1
      SUMP=SUMP+TM0*COSM(JTRIGP)
  430 SUMN=SUMN+TM0*SINM(JTRIGP)
  432 TM0=CONST*PMN(JL3)
      SUMM(JP)=TM0*SUMP
      SUMM(JM)=TM0*SUMN
      GO TO 575
  435 MU1MIN=-MU1MIN
      SIGN2=SIGNM
      SIGN=SIGNM
      DO 445 MU1=1,MU1MIN
```

```
C  SIGN2=(-1)**(M-MU1)
       SIGN2=-SIGN2
       MPMU1=M+MU1
       MMMU1=M-MU1
       IF(MMMU1.LT.0) SIGN=-SIGN
C  SIGN=EPSILON(MU1)*EPSILON(M-MU1)
  438  TM0=SIGN*PCD(JL2+IABS(MMMU1))
       TM1=SIGN2*PCD(JL2+MPMU1)
       JTERM=MU1*LMAXP-MU1*(MU1-1)/2
       JTRIGP=JTRIG+JTERM+MMMU1
       JTRIGM=JTRIG-JTERM+MPMU1
       J=JL1+MU1
       SUMP=SUMP+PAB(J)*(TM0*COSM(JTRIGP)+TM1*COSM(JTRIGM))
  445  SUMN=SUMN+PAB(J)*(TM0*SINM(JTRIGP)+TM1*SINM(JTRIGM))
       IF(MU1MIN.EQ.MU1MAX) GO TO 432
       MU1MIN=MU1MIN+1
       GO TO 422
C
C  GENERAL VALUE OF COSTH
  450  SIGN1=1.0D0
       MU1MAX=MIN0( LAMBD1,M+LML1)
       MU1MIN=MAX0(-LAMBD1,M-LML1)
       IF(MU1MIN.GT.0) GO TO 468
C
C  MU1=0 FROM HERE TO STMNT 468
       MULOW=1
  456  MU2MIN=MAX0(-LAMBD2,M-LAMBD3)
       MU2MAX=MIN0( LAMBD2,M+LAMBD3)
       IF(MU2MIN.GT.0) GO TO 458
       TM0=SIGNM*PCD(JL2)*PMN(JL3+M)
       SUM1=TM0*COSM(JTRIG)
       SUM2=TM0*SINM(JTRIG)
       IF(MU2MIN.LT.0) GO TO 464
       IF(MU2MAX.EQ.0) GO TO 463
       MU2MIN=1
       GO TO 459
  458  SUM1=0.0D0
       SUM2=0.0D0
  459  SIGN=SIGNM
  460  DO 462 MU2=MU2MIN,MU2MAX
       MMMU2=M-MU2
C  SIGN=EPSILON(MU2)*EPSILON(M-MU2)
       IF(MMMU2.LT.0) SIGN=-SIGN
  461  TM0=SIGN*PCD(JL2+MU2)*PMN(JL3+IABS(MMMU2))
       JTRIGP=JTRIG+MU2
       SUM1=SUM1+TM0*COSM(JTRIGP)
  462  SUM2=SUM2+TM0*SINM(JTRIGP)
  463  SUMP=PAB(JL1)*SUM1
       SUMN=PAB(JL1)*SUM2
       IF(MU1MIN.LT.0) GO TO 560
```

```
      IF(MU1MAX.EQ.0) GO TO 570
      GO TO 469
  464 MU2MIN=-MU2MIN
      SIGN2=SIGNM
      SIGN=SIGNM
      DO 467 MU2=1,MU2MIN
C   SIGN2=(-1)**(M-MU2)
      SIGN2=-SIGN2
      MPMU2=M+MU2
      MMMU2=M-MU2
C   SIGN=EPSILON(MU2)*EPSILON(M-MU2)
      IF(MMMU2.LT.0) SIGN=-SIGN
      TM0=SIGN2*PMN(JL3+MPMU2)
      TM1=SIGN*PMN(JL3+IABS(MMMU2))
      J=JL2+MU2
      JTRIGP=JTRIG+MU2
      JTRIGM=JTRIG-MU2
      SUM1=SUM1+PCD(J)*(TM0*COSM(JTRIGM)+TM1*COSM(JTRIGP))
  467 SUM2=SUM2+PCD(J)*(TM0*SINM(JTRIGM)+TM1*SINM(JTRIGP))
      IF(MU2MIN.EQ.MU2MAX) GO TO 463
      MU2MIN=MU2MIN+1
      GO TO 460
C
  468 SUMP=0.0D0
      SUMN=0.0D0
      SIGNM1=SIGNM
      MULOW=MU1MIN
  469 MUHI =MU1MAX
      IND=1
  465 DO 550 MU1=MULOW,MUHI
      JTERM=MU1*LMAXP-MU1*(MU1-1)/2
      SIGN1=-SIGN1
C   SIGN1=(-1)**MU1
C
C SUMS OVER MU2 FOR +MU1
      JTERM3=JTRIG+JTERM
      MMMU1=M-MU1
      MU2MAX=MIN0( LAMBD2,MMMU1+LAMBD3)
      MU2MIN=MAX0(-LAMBD2,MMMU1-LAMBD3)
      IF(MMMU1) 483,470,472
  470 TM0=SIGNM*PCD(JL2)*PMN(JL3)
      SUM1=TM0*COSM(JTERM3)
      SUM2=TM0*SINM(JTERM3)
      IF(MU2MAX.EQ.0) GO TO 495
      SIGN=SIGNM
      DO 471 MU2=1,MU2MAX
C   SIGN=(-1)**(M-MU2)
      SIGN=-SIGN
      TM0=SIGN*PCD(JL2+MU2)*PMN(JL3+MU2)
      JTRIGP=JTERM3+MU2
```

```
      JTRIGM=JTERM3-MU2
      SUM1=SUM1+TM0*(COSM(JTRIGP    )+COSM(JTRIGM))
  471 SUM2=SUM2+TM0*(SINM(JTRIGP    )+SINM(JTRIGM))
      GO TO 495
  472 IF(MU2MIN.GT.0) GO TO 474
      TM0=SIGNM*PCD(JL2)*PMN(JL3+MMMU1)
      SUM1=TM0*COSM(JTERM3)
      SUM2=TM0*SINM(JTERM3)
      IF(MU2MIN.LT.0) GO TO 479
      IF(MU2MAX.EQ.0) GO TO 495
      MU2MIN=1
      GO TO 475
  474 SUM1=0.0D0
      SUM2=0.0D0
  475 SIGN=SIGNM
  476 DO 478 MU2=MU2MIN,MU2MAX
      MMM12=MMMU1-MU2
      IF(MMM12.LT.0) SIGN=-SIGN
C   SIGN=EPSILON(MU1)*EPSILON(MU2)*EPSILON(M-MU1-MU2)
      JTRIGP=JTERM3+MU2
      TM0=SIGN*PCD(JL2+MU2)*PMN(JL3+IABS(MMM12))
      SUM1=SUM1+TM0*COSM(JTRIGP)
  478 SUM2=SUM2+TM0*SINM(JTRIGP)
      GO TO 495
  479 MU2MIN=-MU2MIN
      SIGN =SIGNM
      SIGN2=SIGNM
      DO 482 MU2=1,MU2MIN
      MM1P2=MMMU1+MU2
      MMM12=MMMU1-MU2
      IF(MMM12.LT.0) SIGN=-SIGN
C   SIGN=EPSILON(MU1)*EPSILON(MU2)*EPSILON(M-MU1-MU2)
C   SIGN2=(-1)**(M-MU2)
      SIGN2=-SIGN2
      JTRIGP=JTERM3+MU2
      JTRIGM=JTERM3-MU2
      TM0=SIGN2*PMN(JL3+MM1P2)
      TM1=SIGN*PMN(JL3+IABS(MMM12))
      J=JL2+MU2
      SUM1=SUM1+PCD(J)*(TM0*COSM(JTRIGM)+TM1*COSM(JTRIGP))
  482 SUM2=SUM2+PCD(J)*(TM0*SINM(JTRIGM)+TM1*SINM(JTRIGP))
      IF(MU2MIN.EQ.MU2MAX) GO TO 495
      MU2MIN=MU2MIN+1
      GO TO 476
  483 MU2MIN=-MU2MIN
      SIGN=SIGN1
      IF(MU2MAX.LT.0) GO TO 485
      TM0=SIGN1*PCD(JL2)*PMN(JL3-MMMU1)
      SUM1=TM0*COSM(JTERM3)
      SUM2=TM0*SINM(JTERM3)
```

```
      IF(MU2MAX.GT.0) GO TO 488
      IF(MU2MIN.EQ.0) GO TO 495
      MU2MAX=1
      GO TO 486
  485 SUM1=0.0D0
      SUM2=0.0D0
      MU2MAX=-MU2MAX
  486 DO 487 MU2=MU2MAX,MU2MIN
      MM1P2=MMMU1+MU2
      JTRIGM=JTERM3-MU2
C   SIGN=EPSILON(  MU1)*EPSILON(M-MU1-MU2)
      IF(MM1P2.GT.0) SIGN=-SIGN
      TM0=PCD(JL2+MU2)*PMN(JL3+IABS(MM1P2))*SIGN
      SUM1=SUM1+TM0*COSM(JTRIGM)
  487 SUM2=SUM2+TM0*SINM(JTRIGM)
      GO TO 495
  488 SIGN2=SIGN1
      DO 489 MU2=1,MU2MAX
      MM1P2=MMMU1+MU2
      MMM12=MMMU1-MU2
      JTRIGP=JTERM3+MU2
      JTRIGM=JTERM3-MU2
C   SIGN2=(-1)**(  MU1+MU2)
      SIGN2=-SIGN2
C   SIGN=EPSILON(  MU1)*EPSILON(M-MU1-MU2)
      IF(MM1P2.GT.0) SIGN=-SIGN
      TM0=SIGN*PMN(JL3+IABS(MM1P2))
      TM1=SIGN2*PMN(JL3-MMM12)
      J=JL2+MU2
      SUM1=SUM1+PCD(J)*(TM0*COSM(JTRIGM)+TM1*COSM(JTRIGP))
  489 SUM2=SUM2+PCD(J)*(TM0*SINM(JTRIGM)+TM1*SINM(JTRIGP))
      IF(MU2MIN.EQ.MU2MAX) GO TO 495
      MU2MAX=MU2MAX+1
      GO TO 486
  495 IF(IND.GT.0) GO TO 520
C SUMS OVER MU2 FOR -MU1
      MPMU1=M+MU1
      JTERM3=JTRIG-JTERM
      MU2MAX=MIN0( LAMBD2,MPMU1+LAMBD3)
      MU2MIN=MAX0(-LAMBD2,MPMU1-LAMBD3)
C SIGNM1=(-1)*(M-MU1)
      SIGNM1=-SIGNM1
      IF (MU2MIN.GT.0) GO TO 500
      TM0=SIGNM1*PCD(JL2)*PMN(JL3+MPMU1)
      SUM1=TM0*COSM(JTERM3)+SUM1
      SUM2=TM0*SINM(JTERM3)+SUM2
      IF (MU2MIN.LT.0) GO TO 510
      IF(MU2MAX.EQ.0) GO TO 520
      MU2MIN=1
  500 SIGN=SIGNM1
```

```
  503 DO 505 MU2=MU2MIN,MU2MAX
      MP1M2=MPMU1-MU2
      IF(MP1M2.LT.0) SIGN=-SIGN
C   SIGN=EPSILON(MU2  )*EPSILON(M-MU1-MU2)
      JTRIGP=JTERM3+MU2
      TM0=SIGN*PCD(JL2+MU2)*PMN(JL3+IABS(MP1M2))
      SUM1=SUM1+TM0*COSM(JTRIGP)
  505 SUM2=SUM2+TM0*SINM(JTRIGP)
      GO TO 520
  510 MU2MIN=-MU2MIN
      SIGN =SIGNM1
      SIGN2=SIGNM1
      DO 515 MU2=1,MU2MIN
      MP1M2=MPMU1-MU2
      MPM12=MPMU1+MU2
C   SIGN=EPSILON(MU2  )*EPSILON(M-MU1-MU2)
      IF(MP1M2.LT.0) SIGN=-SIGN
C SIGN2=(-1)**(M-MU1-MU2)
      SIGN2=-SIGN2
      JTRIGP=JTERM3+MU2
      JTRIGM=JTERM3-MU2
      TM0=SIGN2*PMN(JL3+MPM12)
      TM1=SIGN*PMN(JL3+IABS(MP1M2))
      J=JL2+MU2
      SUM1=SUM1+PCD(J)*(TM0*COSM(JTRIGM)+TM1*COSM(JTRIGP))
  515 SUM2=SUM2+PCD(J)*(TM0*SINM(JTRIGM)+TM1*SINM(JTRIGP))
      IF(MU2MIN.EQ.MU2MAX) GO TO 520
      MU2MIN=MU2MIN+1
      GO TO 503
  520 J=JL1+MU1
      SUMP=SUMP+PAB(J)*SUM1
  550 SUMN=SUMN+PAB(J)*SUM2
      IF(MUHI.EQ.MU1MAX) GO TO 570
C   IF IND.GT.0, MUHI=MU1MAX ALWAYS
C
C NOW LOOP THRU MU1 FOR VALUES OF IABS(MU1) WHICH APPEAR
C                                          ONLY AS +MU1
      IND=1
      MULOW=MUHI+1
      GO TO 469
  560 IND=-1
      MUHI=-MU1MIN
      SIGNM1=SIGNM
      GO TO 465
  570 SUMM(JP)=CONST*SUMP
      SUMM(JM)=CONST*SUMN
  575 IF(M.NE.L)       JTM=LMAXP*LMAXP
     1                   -((LMAXP+1)*(LMAXP-1)+M*M)/4+JTM
  580 CONTINUE
  590 CONTINUE
```

```
  595 CONTINUE
  600 CONTINUE
      RETURN
      END
```

PROGRAM 6: MUSUM3

```
C MUSUM3 - FOR 3-CENTER INTEGRALS (AA|CD) AND (AB|AD)
C
C  ENTRY FOR (AA|CD)
C   PCD,PHICD REFER TO CD
C   PMN,PHIMN REFER TO AN
C
      SUBROUTINE MUAACD(SUMM,NCENTR,LMAX,PCD,PMN,PHICD,
     1       PHIMN)
      IMPLICIT REAL*8(A-H,O-Z)
      COMMON/NUCLEI/CENTER(3,4),CHRG(4),LHI(4)
      COMMON/SETUP/DUM(15),RECIP(16),RRT2PI,DUMM(138),
     1    COSOO(4),COSM(8),SINM(8),COSMMU(9,8),SINMMU(9,8)
      DIMENSION RMIDPT(3),NCENTR(4),POWER(8),PCD(45),PMN(45)
      DIMENSION SUMM(1)
      DATA RT2PI/2.506628274631001/
      SUMM(1)=RRT2PI
      IF(LMAX.EQ.0) RETURN
C
C  FIND COORDS OF VECTOR BETWEEN POINT A AND MIDPOINT OF RCD
C
      RMN=0.0D0
      DO 1020 I=1,3
      RMIDPT(I)=0.5D0*(CENTER(I,NCENTR(3))
     1           +CENTER(I,NCENTR(4))) - CENTER(I,NCENTR(1))
 1020 RMN=RMN+RMIDPT(I)*RMIDPT(I)
      RMN=DSQRT(RMN)
      ASSIGN 1316 TO KTYPE1
      ASSIGN 1342 TO KTYPE2
      JP=1
      IF(ABS(SNGL(RMIDPT(3))).NE.SNGL(RMN)) GO TO 1200
      CALL TRIG1(LMAX,PHICD)
C
C  TRIG1  CALCULATES AND STORES SINE AND COSINE OF ANG
C                                          FOR ALL M
C    ANG=  M*PHICD FOR CASE MU1=0,MU2=M,  PHIMN,PHIAB
C                                              UNDEFINED
C
      IF(SNGL(RMN).NE.0.0) GO TO 1100
      ASSIGN 1320 TO KM0
```

```
      ASSIGN 1395 TO KM
      GO TO 1210
 1100 IF(SNGL(RMIDPT(3)).LT.0.0) GO TO 1105
      ASSIGN 1120 TO KZ
      GO TO 1110
 1105 ASSIGN 1115 TO KZ
C
C   CALCULATE PMN(L,0) FOR CASE COSTH=1 OR -1
C
 1110 PMN(1)=RRT2PI
      JOLD=1
      DO 1130 L=1,LMAX
      J=JOLD+L
      GO TO KZ,(1115,1120)
 1115 PMN(J)=-RECIP(L)*PMN(JOLD)
      GO TO 1130
 1120 PMN(J)= RECIP(L)*PMN(JOLD)
 1130 JOLD=J
      ASSIGN 1345 TO K1
      ASSIGN 1405 TO K2
      GO TO 1205
 1200 ASSIGN 1355 TO K1
      ASSIGN 1450 TO K2
      PHIMN=DATAN2(RMIDPT(2),RMIDPT(1))
      COSTH=RMIDPT(3)/RMN
C
C   PLMBAR CALCULATES PMN(L,M) FOR GENERAL CASE
C
      CALL PLMBAR(COSTH,LMAX,PMN)
C
C  TRIG2A CALCULATES AND STORES SINE AND COSINE OF ANG
C                                          FOR ALL M,MU2
C    ANG=MU2*PHICD+(M-MU2)*PHIMN  FOR CASE MU1=C,PHIAB
C                                              UNDEFINED
C
      CALL TRIG2A(LMAX,PHICD,PHIMN)
 1205 ASSIGN 1335 TO KPOW
      POWER(1)=RMN
 1207 ASSIGN 1330 TO KM0
      ASSIGN 1400 TO KM
 1210 ASSIGN 1300 TO KLMIN
      RPC=-1.0D0
      LMAX1=LMAX+1
      DO 1595 LAM2=1,LMAX1
      LAMBD2=LAM2-1
      RPC=-RPC
C RPC=(-1)**LAMBD2
      JL2=LAMBD2*LAM2/2+1
      GO TO KLMIN,(1220,1300,1215)
C
```

```
C 2ND TIME THRU LOOP ON L. POWER WAS CALCD 1ST TIME,
C                    NEXT STMT PREVENTS RECALCULATION
 1215 ASSIGN 1340 TO KPOW
      ASSIGN 1220 TO KLMIN
C
C 2ND AND SUBSEQUENT TIMES THRU LOOP ON L -
C         CALC SUMM FOR L=LAMBD2.   THIS IS SKIPPED FOR
C         LAMBD2=0 BECAUSE THAT CASE, SUMM(1), HAS BEEN DONE
 1220 JM=JP
      JP=JP+LAM2
C
C M=0
      SUMM(JP)=RPC*PCD(JL2)
C
C ALL M NOT 0
      SIGN=RPC
      DO 1270 M=1,LAMBD2
      JM=JM+1
      JP=JP+1
C SIGN=(-1)**(M+LAMBD2)
      SIGN=-SIGN
      TMO=SIGN*PCD(JL2+M)
      SUMM(JP)=TMO*COSM(M)
      SUMM(JM)=TMO*SINM(M)
 1270 CONTINUE
      GO TO 1310
C
C 1ST TIME THRU LOOP ON L
 1300 ASSIGN 1215 TO KLMIN
 1310 IF(LAMBD2.EQ.LMAX) RETURN
C ALL L.GT.LAMBD2
      LMIN=LAMBD2+1
      CONSTA=DSIGN(RT2PI,RPC)
      GO TO KTYPE1,(1314,1316)
 1314 CONST=CONSTA
 1316 DO 1590 L=LMIN,LMAX
      JM=JP
      JP=JP+L+1
      GO TO KMO,(1320,1330)
C RMN=0
 1320 SUMM(JP)=0.0D0
      GO TO 1390
C RMN.NE.0
 1330 GO TO KPOW,(1335,1340)
 1335 IF(L.NE.1) POWER(L)=RMN*POWER(L-1)
 1340 LAMBD3=L-LAMBD2
      JL3=LAMBD3*(LAMBD3+1)/2+1
      GO TO KTYPE2,(1342,1355)
 1342 CONST=CONSTA*POWER(LAMBD3)
C
```

```
C M=0
      GO TO K1,(1345,1355)
C
C COSTH=1 OR -1
 1345 SUMM(JP)=CONST*PCD(JL2)*PMN(JL3)
      GO TO 1390
C
C GENERAL VALUE OF COSTH
 1355 TMO=PCD(JL2)*PMN(JL3)
      SUMP=0.0D0
      MU2MAX=MIN0(LAMBD2,LAMBD3)
      IF(MU2MAX.EQ.0) GO TO 1361
      SIGN=1.0D0
      DO 1360 MU2=1,MU2MAX
C  SIGN=(-1)**MU2
      SIGN=-SIGN
 1360 SUMP=SUMP+SIGN*PCD(JL2+MU2)*PMN(JL3+MU2)*COS00(MU2)
 1361 SUMM(JP)=CONST*(TMO+2.0D0*SUMP)
C
C ALL M.GT.0
 1390 SIGNM=1.0D0
      DO 1580 M=1,L
      JM=JM+1
      JP=JP+1
      GO TO KM,(1395,1400)
C RMN=0
 1395 SUMM(JM)=0.0D0
      SUMM(JP)=0.0D0
      GO TO 1580
C RMN.NE.0
C SIGNM=(-1)**M
 1400 SIGNM=-SIGNM
      GO TO K2,(1405,1450)
C COSTH=1 OR -1
 1405 IF(M.LE.LAMBD2) GO TO 1410
      SUMM(JP)=0.0D0
      SUMM(JM)=0.0D0
      GO TO 1580
 1410 TMO=CONST*SIGNM*PCD(JL2+M)*PMN(JL3)
      SUMM(JP)=TMO*COSM(M)
      SUMM(JM)=TMO*SINM(M)
      GO TO 1580
C
C GENERAL VALUE OF COSTH
 1450 MU2MIN=MAX0(-LAMBD2,M-LAMBD3)
      MU2MAX=MIN0( LAMBD2,M+LAMBD3)
      MULOW = (LMAX-M)/2+1
      IF(MU2MIN.GT.0) GO TO 1458
      TMO=SIGNM*PCD(JL2)*PMN(JL3+M)
      SUMP=TMO*COSMMU(MULOW,M)
```

```
      SUMN=TMO*SINMMU(MULOW,M)
      IF(MU2MIN.LT.0) GO TO 1464
      IF(MU2MAX.EQ.0) GO TO 1570
      MU2MIN=1
      GO TO 1459
 1458 SUMP=0.0D0
      SUMN=0.0D0
 1459 SIGN=SIGNM
 1460 DO 1462 MU2=MU2MIN,MU2MAX
      MMMU2=M-MU2
C   SIGN=EPSILON(MU2)*EPSILON(M-MU2)
      IF(MMMU2.LT.0) SIGN=-SIGN
 1461 TMO=SIGN*PCD(JL2+MU2)*PMN(JL3+IABS(MMMU2))
      JTRIGP=MULOW+MU2
      SUMP=SUMP+TMO*COSMMU(JTRIGP,M)
 1462 SUMN=SUMN+TMO*SINMMU(JTRIGP,M)
      GO TO 1570
 1464 MU2MIN=-MU2MIN
      SIGN2=SIGNM
      SIGN=SIGNM
      DO 1467 MU2=1,MU2MIN
C SIGN2=(-1)**(M-MU2)
      SIGN2=-SIGN2
      MPMU2=M+MU2
      MMMU2=M-MU2
C SIGN=EPSILON(MU2)*EPSILON(M-MU2)
      IF(MMMU2.LT.0) SIGN=-SIGN
      TMO=SIGN2*PMN(JL3+MPMU2)
      TM1=SIGN*PMN(JL3+IABS(MMMU2))
      J=JL2+MU2
      JTRIGP=MULOW+MU2
      JTRIGM=MULOW-MU2
      SUMP=SUMP+PCD(J)*(TMO*COSMMU(JTRIGM,M)
     1                          +TM1*COSMMU(JTRIGP,M))
 1467 SUMN=SUMN+PCD(J)*(TMO*SINMMU(JTRIGM,M)
     1                              +TM1*SINMMU(JTRIGP,M))
      IF(MU2MIN.EQ.MU2MAX) GO TO 1570
      MU2MIN=MU2MIN+1
      GO TO 1460
 1570 SUMM(JP)=CONST*SUMP
      SUMM(JM)=CONST*SUMN
 1580 CONTINUE
 1590 CONTINUE
 1595 CONTINUE
      RETURN
C
C  ENTRY FOR (AB|AD)
C    PCD,PHICD REFER TO AB
C    PMN,PHIMN REFER TO AD
C
```

```
      ENTRY MUABAD(SUMM,        LMAX,PCD,PMN,PHICD,PHIMN)
      SUMM(1)=RRT2PI
      IF(LMAX.EQ.0) RETURN
      ASSIGN 1314 TO KTYPE1
      ASSIGN 1355 TO KTYPE2
      ASSIGN 1340 TO KPOW
      ASSIGN 1450 TO K2
      JP=1
      CALL TRIG2A(LMAX,PHICD,PHIMN)
      GO TO 1207
      END
```

PROGRAM 7: MUSUM2

```
C MUSUM2 -
C   FOR 2-CENTER INTEGRALS (AA|CC),(AB|AB), AND (AA|AD)
C
C  ENTRY FOR (AA|CC)-COULOMB
C
      SUBROUTINE MUCOUL(SUMM,NCENTR, LMAX,PLM,PHI)
      IMPLICIT REAL*8(A-H,O-Z)
      COMMON/NUCLEI/CENTER(3,4),CHRG(4),LHI(4)
      COMMON/SETUP/DUM(15),RECIP(16),RRT2PI,DUMM(138),
     1    COSOO(4),COSM(8),SINM(8),COSMMU(9,8),SINMMU(9,8)
      DIMENSION RMIDPT(3),NCENTR(4),PLM(45)
      DIMENSION SUMM(1)
      SUMM(1)=RRT2PI
      IF(LMAX.EQ.0) RETURN
      ASSIGN 335 TO KPOW
C
C  FIND COORDS OF VECTOR BETWEEN POINTS A AND C
C
      RMN=0.0D0
      DO 20 I=1,3
      RMIDPT(I)=CENTER(I,NCENTR(3))-CENTER(I,NCENTR(1))
   20 RMN=RMN+RMIDPT(I)*RMIDPT(I)
      RMN=DSQRT(RMN)
      IF(ABS(SNGL(RMIDPT(3))).NE.SNGL(RMN)) GO TO 200
      IF(SNGL(RMN).EQ.0.0) RETURN
      ASSIGN 350 TO K
C
C   CALCULATE PMN(L,0) FOR CASE COSTH=1 OR -1
C
      IF(SNGL(RMIDPT(3)).LT.0.0) GO TO 105
      ASSIGN 120 TO KZ
      GO TO 110
```

```
  105 ASSIGN 115 TO KZ
  110 PLM(1)=RRT2PI
      JOLD=1
      DO 130 L=1,LMAX
      J=JOLD+L
      GO TO KZ,(115,120)
  115 PLM(J)=-RECIP(L)*PLM(JOLD)
      GO TO 130
  120 PLM(J)= RECIP(L)*PLM(JOLD)
  130 JOLD=J
      GO TO 300
  200 ASSIGN 380 TO K
      PHI=DATAN2(RMIDPT(2),RMIDPT(1))
      COSTH=RMIDPT(3)/RMN
C
C    PLMBAR CALCULATES PMN(L,M) FOR GENERAL CASE
C
      CALL PLMBAR(COSTH,LMAX,PLM)
      CALL TRIG1(LMAX,PHI)
      GO TO 300
C
C   ENTRY FOR (AB|AB)-EXCHANGE AND (AA|AB)-HYBRID
C
C    PLM,PHI REFER TO AB
C
      ENTRY MUEXHY(SUMM,LMAX,PLM,PHI)
      SUMM(1)=RRT2PI
      IF(LMAX.EQ.0) RETURN
      ASSIGN 340 TO KPOW
      ASSIGN 380 TO K
      CALL TRIG1(LMAX,PHI)
  300 JP=1
      POWER=1.0D0
      DO 500 L=1,LMAX
      JL=L*(L+1)/2+1
      GO TO KPOW, (335,340)
  335 POWER=POWER*RMN
C
C M=0
  340 JM=JP
      JP=JP+L+1
      SUMM(JP)=PLM(JL)*POWER
C
C ALL M.GT.0
      SIGNM=1.0D0
      DO 450 M=1,L
      JM=JM+1
      JP=JP+1
      GO TO K, (350,380)
  350 SUMM(JP)=0.0D0
```

```
      SUMM(JM)=0.0D0
      GO TO 450
  380 SIGNM=-SIGNM
      TMO=SIGNM*POWER*PLM(JL+M)
      SUMM(JP)=TMO*COSM(M)
      SUMM(JM)=TMO*SINM(M)
  450 CONTINUE
  500 CONTINUE
      RETURN
      END
```

PROGRAM 8: TRIG3

```
C TRIG
C       COMPUTES SINES AND COSINES NEEDED BY MUSUMS
C
      SUBROUTINE TRIG3(MMAX,MU1MAX,PHIAB,PHICD)
      IMPLICIT REAL*8(A-H,O-Z)
      COMMON/YS/RECIP(24),RRT2PI,PMN(45),PHIMN,COSOO(4),
     1     COSO(26),COSM(386),SINM(386)
      IF(MMAX.EQ.0) RETURN
      ANGLE1=PHIAB-PHIMN
      ANGLE2=PHICD-PHIMN
      IF(MMAX.EQ.1) GO TO 120
      MU1MAX=MMAX/2
      J=0
      DO 100 MU1=1,MU1MAX
      M2LOW=MU1-MU1MAX+8
      M2MAX=MU1MAX+8
      ANGLEA=MU1*ANGLE1
      COSOO(MU1)=DCOS(MU1*ANGLE2)
      DO 100 M2=M2LOW,M2MAX
      MU2=M2-8
      J=J+1
  100 COSO(J)=DCOS(ANGLEA-MU2*ANGLE2)
  120 J=0
      DO 200 M=1,MMAX
      ANGLEA=M*PHIMN
      M1LOW=(M-MMAX)/2+8
      M1MAX=(M+MMAX)/2+8
      DO 200 M1=M1LOW,M1MAX
      MU1=M1-8
      ANGLEB=MU1*ANGLE1+ANGLEA
      IF(MU1.LT.0) GO TO 150
      M2LOW=M1LOW
      M2MAX=M1MAX-MU1
```

```
      GO TO 160
  150 M2LOW=M1LOW-MU1
      M2MAX=M1MAX
  160 DO 200 M2=M2LOW,M2MAX
      J=J+1
      MU2=M2-8
      ANGLE=MU2*ANGLE2+ANGLEB
      COSM(J)=DCOS(ANGLE)
  200 SINM(J)=DSIN(ANGLE)
      RETURN
C
      ENTRY TRIG2(MMAX,MU1MAX,PHIAB,PHICD)
      IF(MMAX.EQ.0) RETURN
      ANGLEA=PHIAB-PHICD
      IF(MMAX.EQ.1) GO TO 320
      MU1MAX=MMAX/2
      J=MU1MAX+1
      DO 300 MU1=1,MU1MAX
      COS0(J)=DCOS(MU1*ANGLEA)
  300 J=J+2*MU1MAX+1-MU1
  320 J=(1+MMAX)/2+1
      DO 400 M=1,MMAX
      ANGLEB=M*PHICD
      M1LOW=(M-MMAX)/2+8
      MPMMAX=M+MMAX
      M1MAX=MPMMAX/2+8
      JDIF=MMAX-MOD(MPMMAX,2)
      DO 350 M1=M1LOW,M1MAX
      MU1=M1-8
      ANGLE=MU1*ANGLEA+ANGLEB
      COSM(J)=DCOS(ANGLE)
      SINM(J)=DSIN(ANGLE)
      IF(M1.EQ.M1MAX) GO TO 350
      IF(MU1.LT.0) GO TO 340
      J=J+JDIF-MU1
      GO TO 350
  340 J=J+JDIF+MU1+1
  350 CONTINUE
  400 J=J+MMAX+1
      RETURN
      END
```

PROGRAM 9: TRIG2A

```
C TRIG2A
C
      SUBROUTINE TRIG2A(MMAX,PHI1,PHI2)
      IMPLICIT REAL*8(A-H,O-Z)
      COMMON/SETUP/DUM(15),RECIP(16),RRT2PI,DUMM(138),
     1    COSOO(4),COSM(8),SINM(8),COSMMU(9,8),SINMMU(9,8)
      IF(MMAX.EQ.0) RETURN
      CALL TRIG1(MMAX,PHI1)
      ANGLEA=PHI1-PHI2
      IF(MMAX.EQ.1) GO TO 50
      MUMAX=MMAX/2
      DO 30 MU=1,MUMAX
   30 COSOO(MU)=DCOS(MU*ANGLEA)
   50 MMAX1=MMAX+1
      DO 100 M=1,MMAX
      ANGLEB=M*PHI2
      MMAXM=MMAX-M
      MUAMAX=MMAX1-MOD(MMAXM,2)
      MULOW=MMAXM/2+1
      DO 100 MUA=1,MUAMAX
      MU=MUA-MULOW
      ANGLE=MU*ANGLEA+ANGLEB
      COSMMU(MUA,M)=DCOS(ANGLE)
  100 SINMMU(MUA,M)=DSIN(ANGLE)
      RETURN
      END
```

PROGRAM 10: TRIG1

```
C TRIG1
C
      SUBROUTINE TRIG1(MMAX,PHI)
      IMPLICIT REAL*8(A-H,O-Z)
      COMMON/SETUP/DUM(15),RECIP(16),RRT2PI,DUMM(138),
     1    COSOO(4),COSM(8),SINM(8),COSMMU(9,8),SINMMU(9,8)
     1    SINM(8),COSMMU(9,8),SINMMU(9,8)
      IF(MMAX.EQ.0) RETURN
      DO 100 M=1,MMAX
      ANGLE=M*PHI
      COSM(M)=DCOS(ANGLE)
  100 SINM(M)=DSIN(ANGLE)
      RETURN
      END
```

PROGRAM 11: PLMBAR

```
C PLMBAR
C  PLM(J)=ASSOC.LEGENDRE FCN/SQRT(2*PI)*(L+M)FACTORIAL
C  J(L,M)=L*(L+1)/2+M+1
C
      SUBROUTINE PLMBAR(X,LMAX,PLM)
      IMPLICIT REAL*8(A-H,O-Z)
      COMMON/YS/RECIP(24),RRT2PI
      DIMENSION PLM(1)
C
C RRT2PI=1.0/SQRT(2*PI)
C
      PLM(1)=RRT2PI
      IF(LMAX.EQ.0) RETURN
      SINE=DSQRT(1.0D0-X*X)
      JOLD=1
      DO 10 L=1,LMAX
      JNEW=JOLD+L+1
      PLM(JNEW)=RECIP(2*L)*SINE*PLM(JOLD)
      PLM(JNEW-1)=X*PLM(JOLD)
   10 JOLD=JNEW
      IF(LMAX.LE.1) RETURN
      M1MAX=LMAX-1
      DO 20 M1=1,M1MAX
      M=M1-1
      M2=M1+1
      JOLD=M1*M2/2
      J=JOLD+M1
      DO 20 L=M2,LMAX
      JNEW=J+L
      PLM(JNEW)=RECIP(L+M)*RECIP(L-M)
     1              *((2*L-1)*X*PLM(J)-PLM(JOLD))
      JOLD=J
   20 J=JNEW
      RETURN
      END
```

PROGRAM 12: GEOM4C

```
C  GEOM4C CALCULATES ARRAY A,WHICH IS INDEPENDENT OF ZETAS,
C               FOR INTEGRALS (AB|CD),(AB|AD), AND (AB|AB)
C  ARGUMENTS    LAP,MAP,ETC. ARE ORBITAL QUANTUM NUMBERS
C               LTOP=LARGEST VALUE ATTAINED BY (LA+LB+LC+LD)
C               NTYPE=NUMBER OF CENTERS
C               NGAB=ONE LESS THAN THE SUBSCRIPT OF THE FIRST
C                         GAB FOR LA,LB,MA,MB
C               NGCD=ONE LESS THAN THE SUBSCRIPT OF THE FIRST
C                         GCD FOR LC,LD,MC,MD
C               NA=SIZE OF ARRAY A (CALCULATED BY GEOM)
C     INDICES RUN IN THIS ORDER, WITH LAST ONE CHANGING
C               FASTEST - ALPHA1,BETA1,SIGMA1,ALPHA2,BETA2,
C               SIGMA2,LAMBDA1,LAMBDA2,L
C
      SUBROUTINE GEOM4C(SUMM,OMEGA,LAP,MAP,LBP,MBP,LCP,MCP,
     1          LDP,MDP,LTOP,NA,NTYPE,NGAB,NGCD)
       IMPLICIT REAL*8(A-C,E-H,O-Z),LOGICAL*1(D)
       COMMON/AF/SHAM(30),GAB(340),GCD(340),A(3548)
       DIMENSION SUMM(1),OMEGA(1)
       IF(NTYPE-3) 1,2,3
C
C INTEGRAL IS TYPE (AB|AB) - LAMBDA1=LAMBDA2=0
    1  LAM1MX=1
       LAM2MX=1
       ASSIGN 46 TO KNTP
       ASSIGN 48 TO KNTYPE
       GO TO 4
C
C INTEGRAL IS TYPE (AB|AD) - LAMBDA1=0,
C               LAMBDA2 RUNS FROM 0 TO (SIGMA1+SIGMA2)
    2  LAM1MX=1
       ASSIGN 46 TO KNTP
       ASSIGN 47 TO KNTYPE
       GO TO 4
C
C INTEGRAL IS TYPE (AB|CD) -
C         LAMBDA1 RUNS FROM 0 TO (SIGMA1+SIGMA2),
C         LAMBDA2 RUNS FROM 0 TO (SIGMA1+SIGMA2-LAMBDA1)
    3  ASSIGN 47 TO KNTYPE
       ASSIGN 45 TO KNTP
C
    4  CONTINUE
       IT=LTOP+1
       LTPROD=2*IT*(IT+1)*(4*LTOP+3)
       LT1SQ6=6*IT*IT
       IF(LAP.LT.LBP) GO TO 5
       LA=LAP
```

```
      MA=MAP
      LB=LBP
      MB=MBP
      GO TO 6
    5 LA=LBP
      MA=MBP
      LB=LAP
      MB=MAP
C     NOW LA.GE.LB
C
    6 MAMMB =IABS(MA)-IABS(MB)
      IF(MAMMB) 7,8,9
    7 MABMAX=IABS(MB)
      MABMIN=IABS(MA)
      MABDIF=-MAMMB
      GO TO 10
    8 MABMAX=IABS(MA)
      MABMIN=MABMAX
      MABDIF=0
      GO TO 10
    9 MABMAX=IABS(MA)
      MABMIN=IABS(MB)
      MABDIF=MAMMB
C     MABMAX=MAXO(|MA|,|MB|)
C     MABMIN=MINO(|MA|,|MB|)
C     MABDIF=MABMAX-MABMIN
C
   10 IF(LCP.LT.LDP) GO TO 15
      LC=LCP
      MC=MCP
      LD=LDP
      MD=MDP
      GO TO 16
   15 LC=LDP
      MC=MDP
      LD=LCP
      MD=MCP
C     NOW LC.GE.LD
C
   16 MCMMD=IABS(MC)-IABS(MD)
      IF(MCMMD) 17,18,19
   17 MCDMAX=IABS(MD)
      MCDMIN=IABS(MC)
      MCDDIF=-MCMMD
      GO TO 20
   18 MCDMAX=IABS(MC)
      MCDMIN=MCDMAX
      MCDDIF=0
      GO TO 20
   19 MCDMAX=IABS(MC)
```

```
      MCDMIN=IABS(MD)
      MCDDIF=MCMMD
C    MCDMAX=MAXO(|MC|,|MD|)
C    MCDMIN=MINO(|MC|,|MD|)
C    MCDDIF=MCDMAX-MCDMIN
C
   20 LAMLB=LA-LB
      LCMLD=LC-LD
      LALB=LA+LB
      LCLD=LC+LD
      LBMA=LB+IABS(MA)
      LAMB=LA+IABS(MB)
      LDMC=LD+IABS(MC)
      LCMD=LC+IABS(MD)
      MMAB=IABS(MA)+IABS(MB)
      MMCD=IABS(MC)+IABS(MD)
      LBMMA=LB-IABS(MA)
      LAMMB=LA-IABS(MB)
      LDMMC=LD-IABS(MC)
      LCMMD=LC-IABS(MD)
      MOD1=MOD(LALB+MMAB,2)
      MOD2=MOD(LCLD+MMCD,2)
      IF(MA.LT.0) GO TO 507
      IF(MB.LT.0) GO TO 506
      DSGNAB=.TRUE.
      GO TO 510
  506 DSGNAB=.FALSE.
      GO TO 510
  507 IF(MB.LT.0) GO TO 508
      DSGNAB=.FALSE.
      GO TO 510
  508 DSGNAB=.TRUE.
C DSGNAB=.TRUE. IFF MA AND MB HAVE SAME SIGN (0 IS +)
C
  510 IF(MC.LT.0) GO TO 517
      IF(MD.LT.0) GO TO 516
      DSGNCD=.TRUE.
      GO TO 520
  516 DSGNCD=.FALSE.
      GO TO 520
  517 IF(MD.LT.0) GO TO 518
      DSGNCD=.FALSE.
      GO TO 520
  518 DSGNCD=.TRUE.
C DSGNCD=.TRUE. IFF MC AND MD HAVE SAME SIGN (0 IS +)
C
  520 CONTINUE
      JA=0
      JGABP=NGAB
      IA1MIN=8-LB
```

```
      IA1MAX=8+LA
      IA2MIN=8-LD
      IA2MAX=8+LC
      DO 480 IA1=IA1MIN,IA1MAX
      IALPH1=IA1-8
      LLAAB=IABS(LAMLB-IALPH1)
      MODAB=MOD(LLAAB,2)
      M1HIT=MINO(LBMA+IALPH1,LAMB-IALPH1)
      IF(IALPH1.EQ.0) GO TO 521
C
C  BETA1.NE.0
      IGAB=2
      DB1EQ0=.FALSE.
      IG1=1
      ASSIGN 540 TO KB1
      ASSIGN 240 TO KB01
      GO TO 524
C
C  FIRST VALUE OF BETA1=0
  521 IGAB=1
      DB1EQ0=.TRUE.
      IG1=0
      ASSIGN 530 TO KB1
      IF(DSGNAB) GO TO 522
      ASSIGN 251 TO KB01
      GO TO 524
  522 ASSIGN 240 TO KB01
C
  524 CONTINUE
      IB1MIN=IABS(IALPH1)+1
      IB1MAX=LALB-LLAAB+1
      DO 480 IB1=IB1MIN,IB1MAX,2
      IBETA1=IB1-1
      IS1MAX=LALB-IBETA1+1
      DBMIN1=.FALSE.
      IF(MABMIN.GT.IBETA1) DBMIN1=.TRUE.
      MDIFB1=MABDIF-IBETA1
      MSUMB1=MMAB-IBETA1
      MINA=MINO(LAMMB-IALPH1,IBETA1+MAMMB)
      MINB=MINO(LBMMA+IALPH1,IBETA1-MAMMB)
      L1LO=MAXO(LLAAB,MDIFB1+MOD1)
      IS1MIN=L1LO+1
      M1LO=MAXO(0,-LBMMA-IALPH1,-LAMMB+IALPH1,MDIFB1)
      DELAB=.TRUE.
      IF(M1LO.EQ.0) GO TO 527
      M1LOM1=M1LO-1
      M1MIN=M1LO
      DMODM1=.FALSE.
      IF(MOD(M1LO,2).EQ.0) DMODM1=.TRUE.
      GO TO 528
```

```
  527 M1LOM1=-1
      M1MIN=1
  528 M1HI=MINO(M1HIT,IBETA1+MMAB)
      IF(L1LO.LT.M1HI) GO TO 21
      ASSIGN 23 TO KG1
      ASSIGN 80 TO KJ1
      GO TO 22
   21 ASSIGN 24 TO KG1
      L1LOF=L1LO*(L1LO-2)
   22 GO TO KB1,(530,535,540)
C
C  BETA1=0
  530 IF(M1LO.EQ.0.AND..NOT.DSGNAB) DELAB=.FALSE.
      ASSIGN 535 TO KB1
      GO TO 540
C
C  BETA1 NO LONGER 0
  535 ASSIGN 240 TO KB01
      ASSIGN 540 TO KB1
      IGAB=2
      IG1=1
      DB1EQ0=.FALSE.
  540 DO 480 IS1=IS1MIN,IS1MAX,2
      JGCDP=NGCD
      ISIG1=IS1-1
      IS1P1=IS1+1
C
      JGABD=M1LOM1*(IS1P1-L1LO)
      GO TO KG1,(23,24)
   23 JT=M1HI*(IS1P1-L1LO)/2
      GO TO 28
   24 IF(ISIG1.GT.M1HI) GO TO 25
      JT=(ISIG1*IS1P1-L1LOF)/4
      ASSIGN 120 TO KJ1
      GO TO 28
   25 IF(MODAB.EQ.MOD(M1HI,2)) GO TO 26
      IT=1
      GO TO 27
   26 IT=0
   27 JGT1=IT+L1LOF+M1HI*(M1HI+2)
      JT=(2*IS1P1*M1HI-JGT1)/4
      ASSIGN 100 TO KJ1
   28 IF (DB1EQ0) GO TO 550
      IF(M1LO.EQ.0) JGABD=JGABD/2
      JGABD=2*JT-JGABD
      GO TO 560
  550 IF(DELAB) JT=JT-JGABD/2
      JGABD=JT
C JGABD=NUMBER OF FUNCTIONS GAB
C               FOR GIVEN SET (IALPH1,IBETA1,ISIG1)
```

```
C
  560 CONTINUE
      DO 470 IA2=IA2MIN,IA2MAX
      IALPH2=IA2-8
      LLACD=IABS(LCMLD-IALPH2)
      MODCD=MOD(LLACD,2)
      M2HIT=MINO(LDMC+IALPH2,LCMD-IALPH2)
      IF(IALPH2.EQ.0) GO TO 620
C
C  BETA2.NE.0
      IGCD=2
      IG2=1
      DB2EQO=.FALSE.
      ASSIGN 640 TO KB2
      ASSIGN 242 TO KBOO2
      ASSIGN 297 TO KBM02
      GO TO 624
C
C  FIRST VALUE OF BETA2=0
  620 IGCD=1
      IG2=0
      DB2EQO=.TRUE.
      ASSIGN 630 TO KB2
      IF(DSGNCD) GO TO 622
      ASSIGN 680 TO KBOO2
      ASSIGN 299 TO KBM02
      GO TO 624
  622 ASSIGN 242 TO KBOO2
      ASSIGN 297 TO KBM02
C
  624 CONTINUE
      IB2MIN=IABS(IALPH2)+1
      IB2MAX=LCLD-LLACD+1
      DO 470 IB2=IB2MIN,IB2MAX,2
      IBETA2=IB2-1
      IS2MAX=LCLD-IBETA2+1
      DBMIN2=.FALSE.
      IF(MCDMIN.GT.IBETA2) DBMIN2=.TRUE.
      MDIFB2=MCDDIF-IBETA2
      MSUMB2=MMCD-IBETA2
      MINC=MINO(LCMMD-IALPH2,IBETA2+MCMMD)
      MIND=MINO(LDMMC+IALPH2,IBETA2-MCMMD)
      L2LO=MAXO(LLACD,MDIFB2+MOD2)
      IS2MIN=L2LO+1
      M2LO=MAXO(0,-LDMMC-IALPH2,-LCMMD+IALPH2,MDIFB2)
      DELCD=.TRUE.
      IF(M2LO.EQ.0) GO TO 627
      M2LOM1=M2LO-1
      M2MINP=M2LO
      DMODM2=.FALSE.
```

```
      IF(MOD(M2LO,2).EQ.0) DMODM2=.TRUE.
      GO TO 628
  627 M2LOM1=-1
      M2MINP=1
  628 M2HI=MIN0(M2HIT,IBETA2+MMCD)
      LLOWP=MAX0(M1LO-M2HI,M2LO-M1HI)
      IF(MOD(IABS(LLOWP),2).NE.IABS(MODAB-MODCD))
     1          LLOWP=LLOWP+1
      IF(L2LO.LT.M2HI) GO TO 31
      ASSIGN 33 TO KG2
      ASSIGN 160 TO KJ2
      GO TO 32
   31 ASSIGN 34 TO KG2
      L2LOF=L2LO*(L2LO-2)
   32 GO TO KB2,(630,635,640)
C
C  BETA2=0
  630 IF(M2LO.EQ.0.AND..NOT.DSGNCD) DELCD=.FALSE.
      ASSIGN 635 TO KB2
      GO TO 640
C
C  BETA2 NO LONGER 0
  635 ASSIGN 242 TO KBCO2
      ASSIGN 297 TO KBMO2
      ASSIGN 640 TO KB2
      IGCD=2
      IG2=1
      D82EQC=.FALSE.
C
  640 DO 470 IS2=IS2MIN,IS2MAX,2
      ISIG2=IS2-1
      IS2P1=IS2+1
C
      JGCDD=M2LOM1*(IS2P1-L2LO)
      GO TO KG2, (33,34)
   33 JT=M2HI*(IS2P1-L2LO)/2
      GO TO 38
   34 IF(ISIG2.GT.M2HI) GO TO 35
      JT=(ISIG2*IS2P1-L2LOF)/4
      ASSIGN 200 TO KJ2
      GO TO 38
   35 IF(MODCD.EQ.MOD(M2HI,2)) GO TO 36
      IT=1
      GO TO 37
   36 IT=0
   37 JGT2=IT+L2LOF+M2HI*(M2HI+2)
      JT=(2*IS2P1*M2HI-JGT2)/4
      ASSIGN 180 TO KJ2
   38 IF(DB2EQ0) GO TO 650
      IF(M2LO.EQ.0) JGCDD=JGCDD/2
```

```
      JGCDD=2*JT-JGCDD
      GO TO 660
  650 IF(DELCD) JT=JT-JGCDD/2
      JGCDD=JT
C JGCDD=NUMBER OF FUNCTIONS GCD
C               FOR GIVEN SET (IALPH2,IBETA2,ISIG2)
C
  660 LLOW=MAXO(L1LO-ISIG2,L2LO-ISIG1,LLOWP)+1
      LMAX=ISIG1+IS2
      LMOD=MOD(LMAX,2)
      GO TO KNTP,(45,46)
   45 LAM1MX=LMAX
   46 DO 460 LAM1=1,LAM1MX
      LAMBD1=LAM1-1
      IT=LAM1-2
      JY1=(LTPROD-IT*(LT1SQ6-IT*(IT-1)))*LAMBD1/12
      GO TO KNTYPE,(47,48)
   47 LAM2MX=LMAX-LAMBD1
   48 DO 460 LAM2=1,LAM2MX
      LAMBD2=LAM2-1
      IT=LAMBD1+LAMBD2
      LAMSUM=IT+1
      JY12=JY1+(LT1SQ6-(LAM2-2)*(2*LAMBD2-1))*LAMBD2/6
     1       -LAMBD1*LAMBD2*(IT-1)-IT*IT
      IF(LLOW.LT.LAMSUM) GO TO 50
      LMIN=LLOW
      GO TO 70
   50 IF(MOD(LAMSUM,2).NE.LMOD) GO TO 60
      LMIN=LAMSUM
      GO TO 70
   60 LMIN=LAMSUM+1
C
C  LMIN=MAXO(LAMBDA1+LAMBDA2,M1LO-M2HI,M2LO-M1HI,
C        L1LO-SIGMA2,L2LO-SIGMA1)
C        (+1 IF NEEDED TO MAKE (LMIN+SIGMA1+SIGMA2) EVEN) +1
C
   70 DO 460 LP=LMIN,LMAX,2
      L=LP-1
      JY12L=JY12+L*L
C
C SUBSCRIPT FOR ARRAY SUMM = JY12L +M1 +OR- M2
C               (+L+1 IF REAL PART)
C
      L1MIN=MAXO(L1LO,L2LO-L,L-ISIG2)
      L1MAX=MINO(IS1,L+IS2)
      L1DIF=L1MIN-L1LO
C
      IF(L1DIF.NE.0) GO TO 75
      JGAB=JGABP
      GO TO 150
```

```
   75 JGAB=M1LOM1*L1DIF
      GO TO KJ1,(80,100,120)
   80 JT=M1HI*L1DIF/2
      GO TO 130
  100 IF(L1MIN-2.LE.M1HI) GO TO 120
      JT=(2*L1MIN*M1HI-JGT1)/4
      GO TO 130
  120 JT=(L1MIN*(L1MIN-2)-L1LOF)/4
  130 IF(DB1EQ0) GO TO 140
      IF(M1LO.EQ.0) JGAB=JGAB/2
      JGAB=JGABP+2*JT-JGAB
      GO TO 150
  140 IF(DELAB) JT=JT-JGAB/2
      JGAB=JGABP+JT
C  AT THIS POINT JGAB IS 1 LESS THAN THE INDEX FOR THE FIRST
C  GAB FUNCTION TO BE USED
C
  150 JA=JA+1
      SUM1=0.0D0
      L1MIN=L1MIN+1
      DO 450 L1P=L1MIN,L1MAX,2
      L1=L1P-1
      L2MIN=MAX0(L2LO,IABS(L-L1))
      L2MAX=MIN0(IS2,L+L1P)
      L2DIF=L2MIN-L2LO
C
      IF(L2DIF.NE.0) GO TO 155
      JGCDT=JGCDP
      GO TO 220
  155 JGCDT=M2LOM1*L2DIF
      GO TO KJ2,(160,180,200)
  160 JT=M2HI*L2DIF/2
      GO TO 205
  180 IF(L2MIN-2.LE.M2HI) GO TO 200
      JT=(2*L2MIN*M2HI-JGT2)/4
      GO TO 205
  200 JT=(L2MIN*(L2MIN-2)-L2LOF)/4
  205 IF(DB2EQ0) GO TO 210
      IF(M2LO.EQ.0) JGCDT=JGCDT/2
      JGCDT=JGCDP+2*JT-JGCDT
      GO TO 220
  210 IF(DELCD) JT=JT-JGCDT/2
      JGCDT=JGCDP+JT
C  AT THIS POINT JGCDT IS 1 LESS THAN THE INDEX FOR THE
C  FIRST GCD FUNCTION TO BE USED
C
  220 M1MAX=MIN0(L1 ,M1HI)
      M1MAXP=MIN0(M1MAX,L-M2LO)
      M1MAXM=MIN0(M1MAX,L+M2HI)
      IF(M1MAXP.EQ.M1MAXM) GO TO 230
```

```
      ASSIGN 255 TO KM1
      GO TO 235
  230 ASSIGN 262 TO KM1
      ASSIGN 290 TO KL2
      M2MIN=M2LO
  235 SUM2=0.0D0
      L2MIN=L2MIN+1
      IF(M1LO.EQ.0) GO TO KB01,(240,251)
      IF(M1MIN.GT.M1MAXM) GO TO 450
      IF(.NOT.DMODM1) GO TO 252
      ISIGN1=-1
      GO TO 253
C
C *   *   *   *   *   *   *   *   *   *   *   *   *   *   *
C
C M1=0, SO IMAG.PART OF GAB=0
C
  240 JGAB=JGAB+1
      CALL DELO(MSUMB1,MINA,MINB,MAMMB,DSGNAB,DBMIN1,NBR1)
      GO TO (241,251),NBR1
  241 JGCD=JGCDT
      DO 250 L2P=L2MIN,L2MAX,2
      L2=L2P-1
      M2MAX=MIN0(L2 ,M2HI)
      M2MAXM=MIN0(M2MAX,L)
C
C M2=0, SO IMAG. PART OF GCD=0
      IF(M2LO.EQ.0) GO TO KB002,(242,680)
      IF(M2MINP.GT.M2MAXM) GO TO 250
      IF(.NOT.DMODM2) GO TO 243
      ISIGN2=-1
      GO TO 244
  242 JGCD=JGCD+1
      CALL DELO(MSUMB2,MINC,MIND,MCMMD,DSGNCD,DBMIN2,NBR2)
      GO TO (675,680),NBR2
  675 SUM2=SUM2+OMEGA(JOMG(L,L1,0,L2,0))*SUMM(JY12L+LP)
     1          *GCD(JGCD)*C.5D0
  680 IF(M2MAXM.LT.1) GO TO 250
C
C LOOP OVER M2.NE.0,WITH M1.EQ.0
  243 ISIGN2=+1
  244 DO 245 M2=M2MINP,M2MAXM
      JGCD=JGCD+IGCD
C ISIGN2=(-1)**M2
      ISIGN2=-ISIGN2
      CALL DELM(M2,MSUMB2,MINC,MIND,MCMMD,MMCD,MC,MD,DSGNCD,
     1     DB2EQ0,DBMIN2,NBR2)
      GO TO (700,710,720,245),NBR2
C
C GCD HAS NONZERO REAL AND IMAG PARTS
```

```
  700 JYIMAG=JY12L+M2
      TEMP2=SUMM(JYIMAG+LP)*GCD(JGCD-1)
     1                      +SUMM(JYIMAG)*GCD(JGCD)
      GO TO 730
C
C GCD HAS ONLY REAL PART NONZERO
  710 TEMP2=SUMM(JY12L+M2+LP)*GCD(JGCD-IG2)
      GO TO 730
C
C GCD HAS ONLY IMAG PART NONZERO
  720 TEMP2=SUMM(JY12L+M2)*GCD(JGCD)
  730 IF(ISIGN2.LT.0) TEMP2=-TEMP2
      SUM2=SUM2+OMEGA(JOMG(L,L1,0,L2,M2))*TEMP2
  245 CONTINUE
  250 JGCD=JGCD+IGCD*(M2MAX-M2MAXM)
      SUM1=SUM1+GAB(JGAB)*SUM2
  251 IF(M1MAXM.LT.1) GO TO 450
C
C *   *   *   *   *   *   *   *   *   *   *   *   *   *   *
C
C LOOP OVER M1.NE.0
C
  252 ISIGN1=+1
  253 DO 430 M1=M1MIN,M1MAXM
      JGAB=JGAB+IGAB
C ISIGN1=(-1)**M1
      ISIGN1=-ISIGN1
      CALL DELM(M1,MSUMB1,MINA,MINB,MAMMB,MMAB,MA,MB,DSGNAB,
     1     DB1EQ0,DBMIN1,NBR1)
      GO TO (740,750,760,430),NBR1
C
C GAB HAS NONZERO REAL AND IMAG PARTS
  740 ASSIGN 770 TO KDELO
      ASSIGN 800 TO KDEL
      ASSIGN 320 TO KD
      ASSIGN 860 TO KDELMO
      ASSIGN 410 TO KDEL1
      GO TO 765
C
C GAB HAS ONLY REAL PART NONZERO
  750 ASSIGN 790 TO KDELO
      ASSIGN 820 TO KDEL
      ASSIGN 325 TO KD
      ASSIGN 865 TO KDELMO
      ASSIGN 420 TO KDEL1
      GO TO 765
C
C GAB HAS ONLY IMAG PART NONZERO
  760 ASSIGN 780 TO KDELO
      ASSIGN 840 TO KDEL
```

```
      ASSIGN 870 TO KDELMO
      ASSIGN 415 TO KDEL1
  765 GO TO KM1,(255,262)
  255 IF(M1.GT.M1MAXP) GO TO 260
      ASSIGN 290 TO KL2
      M2MIN=M2LO
      GO TO 262
  260 ASSIGN 295 TO KL2
      ASSIGN 330 TO KM2
      M2MIN=MAXO(M2LO,M1-L)
  262 IF(MOD(M2MIN,2).EQ.1) GO TO 265
      ASSIGN 301 TO KM2MIN
      GO TO 270
  265 ASSIGN 302 TO KM2MIN
  270 SUM2=0.0D0
      SUM3=0.0D0
  280 JGCD=JGCDT
      DO 400 L2P=L2MIN,L2MAX,2
      L2=L2P-1
      M2MAX=MINO(L2,M2HI)
      M2MAXM=MINO(M2MAX,L+M1)
      GO TO KL2,(290,295)
  290 M2MAXP=MINO(M2MAX,L-M1)
      IF(M2MAXM.EQ.M2MAXP) GO TO 292
      ASSIGN 305 TO KM2
      GO TO 295
  292 ASSIGN 310 TO KM2
  295 IF(M2MIN.EQ.0) GO TO 296
      IF(M2MIN.GT.M2MAXM) GO TO 400
      M2MINQ=M2MIN
      GO TO KM2MIN,(301,302)
  296 M2MINQ=1
      ISIGN2=+1
C
C M2=0, SO IMAG PART OF GCD=0
      GO TO KBM02,(297,299)
  297 JGCD=JGCD+1
      CALL DELO(MSUMB2,MINC,MIND,MCMMD,DSGNCD,DBMIN2,NBR2)
      GO TO (298,299),NBR2
  298 WTEMP=OMEGA(JOMG(L,L1,M1,L2,0))*GCD(JGCD)
      IF(ISIGN1.LT.0) WTEMP=-WTEMP
      JYIMAG=JY12L+M1
      GO TO KDELO,(770,790,780)
C
C GAB HAS NONZERO REAL AND IMAG PARTS
  770 SUM2=SUM2+WTEMP*SUMM(JYIMAG+LP)
C
C GAB HAS NONZERO IMAG PART
  780 SUM3=SUM3+WTEMP*SUMM(JYIMAG)
      GO TO 299
```

```
C
C  GAB HAS ONLY REAL PART NONZERO
   790 SUM2=SUM2+WTEMP*SUMM(JYIMAG+LP)
   299 IF(M2MAXM.LT.1) GO TO 400
       GO TO 304
   301 ISIGN2=-1
       GO TO 303
   302 ISIGN2=+1
   303 IF(M2MIN.EQ.M2LO) GO TO 304
       JGCD=JGCD+IGCD*(M2MIN-M2LO)
       IF(M2LO.EQ.0.AND.(.NOT.DB2EQ0.OR..NOT.DSGNCD))
      1          JGCD=JGCD-1
C
C  LOOP OVER M2.NE.0
   304 DO 390 M2=M2MINQ,M2MAXM
C  ISIGN2=(-1)**M2
       ISIGN2=-ISIGN2
       JGCD=JGCD+IGCD
       CALL DELM(M2,MSUMB2,MINC,MIND,MCMMD,MMCD,MC,MD,DSGNCD,
      1     DB2EQ0,DBMIN2,NBR2)
       IF(NBR2.EQ.4) GO TO 390
       GO TO KM2, (305,310,330)
   305 IF(M2.GT.M2MAXP) GO TO 330
C
C  SUM FOR +M2
   310 JYIMAG=JY12L+M1+M2
       JYREAL=JYIMAG+LP
       WTEMP=OMEGA(JOMG(L,L1,M1,L2,M2))
       IF(ISIGN1.NE.ISIGN2) WTEMP=-WTEMP
       DS1=.TRUE.
       DS2=.TRUE.
       DS3=.FALSE.
       ASSIGN 330 TO KBEEP
   795 TEMP2=0.0D0
       TEMP3=0.0D0
       GO TO KDEL,(800,820,840)
   800 GO TO (805,815,810),NBR2
C
C  GAB AND GCD HAVE NONZERO REAL AND IMAG PARTS
   805 TEMP2=SUMM(JYREAL)*GCD(JGCD-1)
       TEMP3=SUMM(JYIMAG)*GCD(JGCD-1)
       IF(.NOT.DS2) TEMP3=-TEMP3
C
C  GAB HAS NONZERO REAL AND IMAG PARTS,
C  GCD HAS NONZERO IMAG PART
   810 TERM=SUMM(JYIMAG)*GCD(JGCD)
       IF(.NOT.DS1) TERM=-TERM
       TEMP2=TEMP2+TERM
       TERM=SUMM(JYREAL)*GCD(JGCD)
       IF(.NOT.DS3) TERM=-TERM
```

```
      TEMP3=TEMP3+TERM
      GO TO 315
C
C GAB HAS NONZERO REAL AND IMAG PARTS,
C GCD HAS ONLY REAL PART NONZERO
  815 TEMP2=SUMM(JYREAL)*GCD(JGCD-IG2)
      TEMP3=SUMM(JYIMAG)*GCD(JGCD-IG2)
      IF(.NOT.DS2) TEMP3=-TEMP3
      GO TO 315
  820 GO TO (825,835,830),NBR2
C
C GAB HAS ONLY REAL PART NONZERO,
C GCD HAS NONZERO REAL AND IMAG PARTS
  825 TEMP2=SUMM(JYREAL)*GCD(JGCD-1)
C
C GAB HAS ONLY REAL PART NONZERO,
C GCD HAS NONZERO IMAG PART
  830 TERM=SUMM(JYIMAG)*GCD(JGCD)
      IF(.NOT.DS1) TERM=-TERM
      TEMP2=TEMP2+TERM
      GO TO 315
C
C GAB AND GCD HAVE ONLY REAL PARTS NONZERO
  835 TEMP2=SUMM(JYREAL)*GCD(JGCD-IG2)
      GO TO 315
  840 GO TO (845,855,850),NBR2
C
C GAB HAS ONLY IMAG PART NONZERO,
C GCD HAS NONZERO REAL AND IMAG PARTS
  845 TEMP3=SUMM(JYIMAG)*GCD(JGCD-1)
      IF(.NOT.DS2) TEMP3=-TEMP3
C
C GAB HAS ONLY IMAG PART NONZERO, GCD HAS NONZERO IMAG PART
  850 TERM=SUMM(JYREAL)*GCD(JGCD)
      IF(.NOT.DS3) TERM=-TERM
      TEMP3=TEMP3+TERM
      GO TO 320
C
C GAB HAS ONLY IMAG PART NONZERO,
C GCD HAS ONLY REAL PART NONZERO
  855 TEMP3=SUMM(JYIMAG)*GCD(JGCD-IG2)
      IF(.NOT.DS2) TEMP3=-TEMP3
      GO TO 320
  315 SUM2=SUM2+WTEMP*TEMP2
      GO TO KD,(320,325)
  320 SUM3=SUM3+WTEMP*TEMP3
  325 GO TO KBEEP,(330,390)
C
C SUM FOR -M2
  330 M2MM1=M2-M1
```

```
      JYIMAG=JY12L+IABS(M2MM1)
      JYREAL=JYIMAG+LP
      WTEMP=OMEGA(JOMG(L,L1,M1,L2,-M2))
      IF(M2MM1) 340,335,345
  335 WTEMP=WTEMP*SUMM(JYREAL)
      IF(ISIGN2.LT.0) WTEMP=-WTEMP
      GO TO KDELM0,(860,865,870)
  860 GO TO (337,339,338),NBR2
C
C GAB AND GCD HAVE NONZERO REAL AND IMAG PARTS
  337 SUM2=SUM2+WTEMP*GCD(JGCD-1)
C
C GAB AND GCD HAVE NONZERO IMAG PARTS
  338 SUM3=SUM3+WTEMP*GCD(JGCD)
      GO TO 390
  865 GO TO (339,339,390),NBR2
C
C GAB AND GCD HAVE NONZERO REAL PARTS
  339 SUM2=SUM2+WTEMP*GCD(JGCD-IG2)
      GO TO 390
  870 GO TO (338,390,338),NBR2
  340 IF(ISIGN1.LT.0) WTEMP=-WTEMP
      DS1=.FALSE.
      DS2=.TRUE.
      GO TO 350
  345 IF(ISIGN2.LT.0) WTEMP=-WTEMP
      DS1=.TRUE.
      DS2=.FALSE.
  350 DS3=.TRUE.
      ASSIGN 390 TO KBEEP
      GO TO 795
  390 CONTINUE
  400 JGCD=JGCD+IGCD*(M2MAX-M2MAXM)
C
C SUM2 IS MULTIPLIED BY THE REAL PART OF GAB
C SUM3 IS MULTIPLIED BY THE IMAG PART OF GAB
      GO TO KDEL1,(410,420,415)
  410 SUM1=SUM1+SUM2*GAB(JGAB-1)
  415 SUM1=SUM1+SUM3*GAB(JGAB)
      GO TO 430
  420 SUM1=SUM1+SUM2*GAB(JGAB-IG1)
  430 CONTINUE
C
C *   *   *   *   *   *   *   *   *   *   *   *   *   *   *
C
  450 JGAB=JGAB+IGAB*(M1MAX-M1MAXM)
      A(JA)=SUM1+SUM1
      IF(MOD(L1MIN,2).EQ.0) A(JA)=-A(JA)
C           INTRODUCE  FACTOR (-1)**L1
C
```

```
  460 CONTINUE
  470 JGCDP=JGCDP+JGCDD
  480 JGABP=JGABP+JGABD
      NA=JA
      RETURN
      END
```

PROGRAM 13: GEOM3C

```
C  GEOM3C CALCULATES ARRAY A, WHICH IS INDEPENDENT OF ZETAS,
C               FOR INTEGRALS (AA1CD) AND (AA1AD)
C  ARGUMENTS    LAP,MAP,ETC. ARE ORBITAL QUANTUM NUMBERS
C               LTOP=LARGEST VALUE ATTAINED BY (LA+LB+LC+LD)
C               NTYPE=NUMBER OF CENTERS
C               NGAB=ONE LESS THAN THE SUBSCRIPT OF THE FIRST
C                         GAB FOR LA,LB,MA,MB
C               NGCD=ONE LESS THAN THE SUBSCRIPT OF THE FIRST
C                         GCD FOR LC,LD,MC,MD
C               NA=SIZE OF ARRAY A (CALCULATED BY GEOM)
C     INDICES RUN IN THIS ORDER, WITH LAST ONE CHANGING
C               FASTEST - SIGMA1,ALPHA2,BETA2,SIGMA2,
C               LAMBDA2,L
C
      SUBROUTINE GEOM3C(SUMM,OMEGA,LAP,MAP,LBP,MBP,LCP,MCP,
     1          LDP,MDP,LTOP,NA,NTYPE,NGAB,NGCD)
      IMPLICIT REAL*8(A-C,E-H,O-Z),LOGICAL*1(D)
      COMMON/AF/SHAM(30),GAB(340),GCD(340),A(3548)
      DIMENSION SUMM(1),OMEGA(1)
      IF(NTYPE.LT.3) GO TO 2
      ASSIGN 47 TO KNTYPE
      GO TO 3
    2 ASSIGN 48 TO KNTYPE
      LAM2MX=1
    3 IT=LTOP+1
      LT1SQ6=6*IT*IT
      IF(LAP.LT.LBP) GO TO 5
      LA=LAP
      MA=MAP
      LB=LBP
      MB=MBP
      GO TO 6
    5 LA=LBP
      MA=MBP
      LB=LAP
      MB=MAP
C   NOW LA.GE.LB
```

```
C
     6 M1LO=IABS(IABS(MA)-IABS(MB))
       M1HI=IABS(MA)+IABS(MB)
       IF(MOD(M1LO,2).EQ.0) GO TO 7
       ISIGN1=-1
       GO TO 920
     7 ISIGN1=+1
   920 IF(M1LO.EQ.M1HI) GO TO 940
       DM1EQ=.FALSE.
       GO TO 10
   940 DM1EQ=.TRUE.
    10 IF(LCP.LT.LDP) GO TO 15
       LC=LCP
       MC=MCP
       LD=LDP
       MD=MDP
       GO TO 16
    15 LC=LDP
       MC=MDP
       LD=LCP
       MD=MCP
C    NOW LC.GE.LD
C
    16 MCMMD=IABS(MC)-IABS(MD)
       IF(MCMMD) 17,18,19
    17 MCDMAX=IABS(MD)
       MCDMIN=IABS(MC)
       MCDDIF=-MCMMD
       GO TO 20
    18 MCDMAX=IABS(MC)
       MCDMIN=MCDMAX
       MCDDIF=0
       GO TO 20
    19 MCDMAX=IABS(MC)
       MCDMIN=IABS(MD)
       MCDDIF=MCMMD
C    MCDMAX=MAXO(|MC|,|MD|)
C    MCDMIN=MINO(|MC|,|MD|)
C    MCDDIF=MCDMAX-MCDMIN
C
    20 LAMLB=LA-LB
       LCMLD=LC-LD
       LALB=LA+LB
       LCLD=LC+LD
       LDMC=LD+IABS(MC)
       LCMD=LC+IABS(MD)
       MMCD=IABS(MC)+IABS(MD)
       LDMMC=LD-IABS(MC)
       LCMMD=LC-IABS(MD)
       MOD1=MOD(LALB+M1LO,2)
```

```
      MOD2=MOD(LCLD+MMCD,2)
      IF(MA.LT.0) GO TO 507
      IF(MB.LT.0) GO TO 506
      GO TO 508
  506 DSGNAB=.FALSE.
      GO TO 510
  507 IF(MB.LT.0) GO TO 508
      GO TO 506
  508 DSGNAB=.TRUE.
C DSGNAB=.TRUE. IFF MA AND MB HAVE SAME SIGN (0 IS +)
C
  510 IF(MC.LT.0) GO TO 517
      IF(MD.LT.0) GO TO 516
      GO TO 518
  516 DSGNCD=.FALSE.
      GO TO 520
  517 IF(MD.LT.0) GO TO 518
      GO TO 516
  518 DSGNCD=.TRUE.
C DSGNCD=.TRUE. IFF MC AND MD HAVE SAME SIGN (0 IS +)
C
  520 IF(M1LO.EQ.0) GO TO 522
      ASSIGN 253 TO KAM1
      DM1ON=.FALSE.
      GO TO 525
  522 IF(DSGNAB) GO TO 523
      ASSIGN 430 TO KAM1
      DM1ON=.TRUE.
      GO TO 525
  523 ASSIGN 240 TO KAM1
      DM1ON=.FALSE.
C
C DM1ON=.TRUE. IFF MA.EQ.-MB.NE.0
C
  525 CONTINUE
      JA=0
      JGABP=NGAB
      IA2MIN=8-LD
      IA2MAX=8+LC
      MODAB=MOD(LALB,2)
      L1LO=MAXO(LAMLB,M1LO+MOD1)
      IF(L1LO.GE.M1HI) GO TO 530
      DL1GE=.FALSE.
      GO TO 535
  530 DL1GE=.TRUE.
  535 CONTINUE
C
C ALPHA1=BETA1=0 BECAUSE A=B
C
      IS1MIN=L1LO+1
```

```
      IS1MAX=LALB+1
      DO 480 IS1=IS1MIN,IS1MAX,2
      JGCDP=NGCD
      ISIG1=IS1-1
      IS1P1=IS1+1
C
      IF(DM1EQ.OR.ISIG1.LT.M1HI) GO TO 25
      IF(DL1GE) GO TO 23
      IF(DM1ON) GO TO 22
      ASSIGN 100 TO KJ1
      JGT1=(M1HI+MOD1+L1LO)/2
      JGABD=IS1P1-JGT1
      GO TO 28
   22 ASSIGN 110 TO KJ1
      JGABD=(ISIG1-M1HI-MOD1)/2+1
      GO TO 28
   23 IF(DM1ON) GO TO 26
      ASSIGN 120 TO KJ1
      JGABD=IS1P1-L1LO
      GO TO 28
   25 IF(DM1ON) GO TO 27
   26 ASSIGN 80 TO KJ1
      JGABD=(ISIG1-L1LO)/2+1
      GO TO 28
   27 ASSIGN 73 TO KJ1
      JGABD=0
   28 CONTINUE
C JGABD=NUMBER OF FUNCTIONS GAB FOR GIVEN ISIG1
C
      DO 470 IA2=IA2MIN,IA2MAX
      IALPH2=IA2-8
      LLACD=IABS(LCMLD-IALPH2)
      MODCD=MOD(LLACD,2)
      M2HIT=MINO(LDMC+IALPH2,LCMD-IALPH2)
      IF(IALPH2.EQ.0) GO TO 620
C
C  BETA2.NE.0
      IGCD=2
      IG2=1
      DB2EQ0=.FALSE.
      ASSIGN 640 TO KB2
      ASSIGN 242 TO KB002
      ASSIGN 297 TO KBM02
      GO TO 624
C
C  FIRST VALUE OF BETA2=0
  620 IGCD=1
      IG2=0
      DB2EQ0=.TRUE.
      ASSIGN 630 TO KB2
```

```
      IF(DSGNCD) GO TO 622
      ASSIGN 680 TO KB002
      ASSIGN 299 TO KBM02
      GO TO 624
  622 ASSIGN 242 TO KB002
      ASSIGN 297 TO KBM02
C
  624 CONTINUE
      IB2MIN=IABS(IALPH2)+1
      IB2MAX=LCLD-LLACD+1
      DO 470 IB2=IB2MIN,IB2MAX,2
      IBETA2=IB2-1
      IS2MAX=LCLD-IBETA2+1
      DBMIN2=.FALSE.
      IF(MCDMIN.GT.IBETA2) DBMIN2=.TRUE.
      MDIFB2=MCDDIF-IBETA2
      MSUMB2=MMCD-IBETA2
      MINC=MINO(LCMMD-IALPH2,IBETA2+MCMMD)
      MIND=MINO(LDMMC+IALPH2,IBETA2-MCMMD)
      L2LO=MAXO(LLACD,MDIFB2+MOD2)
      IS2MIN=L2LO+1
      M2LO=MAXO(0,-LDMMC-IALPH2,-LCMMD+IALPH2,MDIFB2)
      DELCD=.TRUE.
      IF(M2LO.EQ.0) GO TO 627
      M2LOM1=M2LO-1
      M2MINP=M2LO
      DMODM2=.FALSE.
      IF(MOD(M2LO,2).EQ.0) DMODM2=.TRUE.
      GO TO 628
  627 M2LOM1=-1
      M2MINP=1
  628 M2HI=MING(M2HIT,IBETA2+MMCD)
      LLOWP=MAXO(M1LO-M2HI,M2LO-M1HI)
      IF(MOD(IABS(LLOWP),2).NE.IABS(MODAB-MODCD))
     1          LLOWP=LLOWP+1
      IF(L2LO.LT.M2HI) GO TO 31
      ASSIGN 33 TO KG2
      ASSIGN 160 TO KJ2
      GO TO 32
   31 ASSIGN 34 TO KG2
      L2LOF=L2LO*(L2LO-2)
   32 GO TO KB2,(630,635,640)
C
C  BETA2=0
  630 IF(M2LO.EQ.0.AND..NOT.DSGNCD) DELCD=.FALSE.
      ASSIGN 635 TO KB2
      GO TO 640
C
C  BETA2 NO LONGER 0
  635 ASSIGN 242 TO KBC02
```

```
      ASSIGN 297 TO KBMO2
      ASSIGN 640 TO KB2
      IGCD=2
      IG2=1
      DB2EQ0=.FALSE.
C
  640 DO 470 IS2=IS2MIN,IS2MAX,2
      ISIG2=IS2-1
      IS2P1=IS2+1
C
      JGCDD=M2LOM1*(IS2P1-L2LO)
      GO TO KG2, (33,34)
   33 JT=M2HI*(IS2P1-L2LO)/2
      GO TO 38
   34 IF(ISIG2.GT.M2HI) GO TO 35
      JT=(ISIG2*IS2P1-L2LOF)/4
      ASSIGN 200 TO KJ2
      GO TO 38
   35 IF(MODCD.EQ.MOD(M2HI,2)) GO TO 36
      IT=1
      GO TO 37
   36 IT=0
   37 JGT2=IT+L2LOF+M2HI*(M2HI+2)
      JT=(2*IS2P1*M2HI-JGT2)/4
      ASSIGN 180 TO KJ2
   38 IF(DB2EQ0) GO TO 650
      IF(M2LO.EQ.0) JGCDD=JGCDD/2
      JGCDD=2*JT-JGCDD
      GO TO 660
  650 IF(DELCD) JT=JT-JGCDD/2
      JGCDD=JT
C JGCDD=NUMBER OF FUNCTIONS GCD
C               FOR GIVEN SET (IALPH2,IBETA2,ISIG2)
C
  660 LLOW=MAX0(L1LO-ISIG2,L2LO-ISIG1,LLOWP)+1
      LMAX=ISIG1+IS2
      LMOD=MOD(LMAX,2)
      GO TO KNTYPE,(47,48)
C
C INTEGRAL IS TYPE (AA|CD) -
C                   LAMBDA2 RUNS FROM 0 TO (SIGMA1+SIGMA2)
   47 LAM2MX=LMAX
C
C STMNT 47 IS SKIPPED IF INTEGRAL IS TYPE (AA|AD) -
C                   LAMBDA2=0
   48 DO 460 LAM2=1,LAM2MX
      LAMBD2=LAM2-1
      JY12=(LT1SQ6-(LAM2-2)*(2*LAMBD2-1))*LAMBD2/6
     1          -LAMBD2*LAMBD2
      IF(LLOW.LT.LAM2) GO TO 50
```

```
      LMIN=LLOW
      GO TO 70
   50 IF(MOD(LAM2,2).NE.LMOD) GO TO 60
      LMIN=LAM2
      GO TO 70
   60 LMIN=LAM2+1
C
C LMIN=MAX0(LAMBDA2,M1LO-M2HI,M2LO-M1HI,L1LO-SIGMA2,
C                                          L2LO-SIGMA1)
C        (+1 IF NEEDED TO MAKE (LMIN+SIGMA1+SIGMA2) EVEN) +1
C
   70 DO 460 LP=LMIN,LMAX,2
      L=LP-1
      JY12L=JY12+L*L
C
C SUBSCRIPT FOR ARRAY SUMM = JY12L +M1 +OR- M2
C               (+L+1 IF REAL PART)
C
      LMM2LO=L-M2LO
      LPM2HI=L+M2HI
      L1MIN=MAX0(L1LO,L2LO-L,L-ISIG2)
      L1MAX=MIN0(IS1,L+IS2)
      L1DIF=L1MIN-L1LO
C
      IF(L1DIF.NE.0) GO TO 75
   73 JGAB=JGABP
      GO TO 150
   75 GO TO KJ1,(73,80,100,110,120)
   80 JGAB=JGABP+L1DIF/2
      GO TO 150
  100 IF(L1MIN-2.LT.M1HI) GO TO 80
      JGAB=JGABP+L1MIN-JGT1
      GO TO 150
  110 IF (L1MIN-2.LT.M1HI) GO TO 73
      JGAB=JGABP+(L1MIN-M1HI-MOD1)/2
      GO TO 150
  120 JGAB=JGABP+L1DIF
C  AT THIS POINT JGAB IS 1 LESS THAN THE INDEX FOR THE FIRST
C  GAB FUNCTION TO BE USED
C
  150 JA=JA+1
      SUM1=0.0D0
      L1MIN=L1MIN+1
      DO 450 L1P=L1MIN,L1MAX,2
      L1=L1P-1
      L2MIN=MAX0(L2LO,IABS(L-L1))
      L2MAX=MIN0(IS2,L+L1P)
      L2DIF=L2MIN-L2LO
C
      IF(L2DIF.NE.0) GO TO 155
```

```
      JGCDT=JGCDP
      GO TO 235
  155 JGCDT=M2LOM1*L2DIF
      GO TO KJ2,(160,180,200)
  160 JT=M2HI*L2DIF/2
      GO TO 205
  180 IF(L2MIN-2.LE.M2HI) GO TO 200
      JT=(2*L2MIN*M2HI-JGT2)/4
      GO TO 205
  200 JT=(L2MIN*(L2MIN-2)-L2LOF)/4
  205 IF(DB2EQC) GO TO 210
      IF(M2LO.EQ.0) JGCDT=JGCDT/2
      JGCDT=JGCDP+2*JT-JGCDT
      GO TO 235
  210 IF(DELCD) JT=JT-JGCDT/2
      JGCDT=JGCDP+JT
C  AT THIS POINT JGCDT IS 1 LESS THAN THE INDEX FOR THE
C  FIRST GCD FUNCTION TO BE USED
C
  235 SUM2=0.0D0
      L2MIN=L2MIN+1
      GO TO KAM1,(240,253,430)
C
C *   *   *   *   *   *   *   *   *   *   *   *   *   *   *
C
C M1=0, SO IMAG.PART OF GAB=0
C
  240 JGAB=JGAB+1
  241 JGCD=JGCDT
      DO 250 L2P=L2MIN,L2MAX,2
      L2=L2P-1
      M2MAX=MINO(L2 ,M2HI)
      M2MAXM=MINO(M2MAX,L)
C
C M2=0, SO IMAG. PART OF GCD=0
      IF(M2LO.EQ.0) GO TO K8002,(242,680)
      IF(M2MINP.GT.M2MAXM) GO TO 250
      IF(.NOT.DMODM2) GO TO 243
      ISIGN2=-1
      GO TO 244
  242 JGCD=JGCD+1
      CALL DELO(MSUMB2,MINC,MIND,MCMMD,DSGNCD,DBMIN2,NBR2)
      GO TO (675,680),NBR2
  675 SUM2=SUM2+OMEGA(JOMG(L,L1,0,L2,0))*SUMM(JY12L+LP)
     1          *GCD(JGCD)*0.5D0
  680 IF(M2MAXM.LT.1) GO TO 250
C
C LOOP OVER M2.NE.0,WITH M1.EQ.0
  243 ISIGN2=+1
  244 DO 245 M2=M2MINP,M2MAXM
```

```
      JGCD=JGCD+IGCD
C ISIGN2=(-1)**M2
      ISIGN2=-ISIGN2
      CALL DELM(M2,MSUMB2,MINC,MIND,MCMMD,MMCD,MC,MD,DSGNCD,
     1     DB2EQC,DBMIN2,NBR2)
      GO TO (700,710,720,245),NBR2
C
C GCD HAS NONZERO REAL AND IMAG PARTS
  700 JYIMAG=JY12L+M2
      TEMP2=SUMM(JYIMAG+LP)*GCD(JGCD-1)
     1                      +SUMM(JYIMAG)*GCD(JGCD)
      GO TO 730
C
C GCD HAS ONLY REAL PART NONZERO
  710 TEMP2=SUMM(JY12L+M2+LP)*GCD(JGCD-IG2)
      GO TO 730
C
C GCD HAS ONLY IMAG PART NONZERO
  720 TEMP2=SUMM(JY12L+M2)*GCD(JGCD)
  730 IF(ISIGN2.LT.0) TEMP2=-TEMP2
      SUM2=SUM2+OMEGA(JOMG(L,L1,0,L2,M2))*TEMP2
  245 CONTINUE
  250 JGCD=JGCD+IGCD*(M2MAX-M2MAXM)
      SUM1=SUM1+GAB(JGAB)*SUM2
      GO TO 430
C
C *   *   *   *   *   *   *   *   *   *   *   *   *   *   *
C
C M1.NE.0
C
  253 M1=M1LO
C SUM FOR M1=M1LO=||MA|-|MB||
      ASSIGN 430 TO KM1
      JGAB=JGAB+1
  255 IF(M1.GT.LMM2LO) GO TO 260
      ASSIGN 290 TO KL2
      M2MIN=M2LO
      GO TO 262
  260 ASSIGN 295 TO KL2
      ASSIGN 330 TO KM2
      M2MIN=MAXO(M2LO,M1-L)
  262 IF(MOD(M2MIN,2).EQ.1) GO TO 265
      ASSIGN 301 TO KM2MIN
      GO TO 270
  265 ASSIGN 302 TO KM2MIN
  270 SUM2=0.0D0
      SUM3=0.0D0
  280 JGCD=JGCDT
      DO 400 L2P=L2MIN,L2MAX,2
      L2=L2P-1
```

```
      M2MAX=MINO(L2,M2HI)
      M2MAXM=MINO(M2MAX,L+M1)
      GO TO KL2,(290,295)
  290 M2MAXP=MINO(M2MAX,L-M1)
      IF(M2MAXM.EQ.M2MAXP) GO TO 292
      ASSIGN 305 TO KM2
      GO TO 295
  292 ASSIGN 310 TO KM2
  295 IF(M2MIN.EQ.0) GO TO 296
      IF(M2MIN.GT.M2MAXM) GO TO 400
      M2MINQ=M2MIN
      GO TO KM2MIN,(301,302)
  296 M2MINQ=1
      ISIGN2=+1
C
C M2=0, SO IMAG PART OF GCD=0
      GO TO KBM02,(297,299)
  297 JGCD=JGCD+1
      CALL DELO(MSUMB2,MINC,MIND,MCMMD,DSGNCD,DBMIN2,NBR2)
      GO TO (298,299),NBR2
  298 WTEMP=OMEGA(JOMG(L,L1,M1,L2,0))*GCD(JGCD)
      IF(ISIGN1.LT.0) WTEMP=-WTEMP
      JYIMAG=JY12L+M1
      IF(DSGNAB) GO TO 790
C
C GAB HAS ONLY IMAG PART NONZERO
      SUM3=SUM3+WTEMP*SUMM(JYIMAG)
      GO TO 299
C
C GAB HAS ONLY REAL PART NONZERO
  790 SUM2=SUM2+WTEMP*SUMM(JYIMAG+LP)
  299 IF(M2MAXM.LT.1) GO TO 400
      GO TO 304
  301 ISIGN2=-1
      GO TO 303
  302 ISIGN2=+1
  303 IF(M2MIN.EQ.M2LO) GO TO 304
      JGCD=JGCD+IGCD*(M2MIN-M2LO)
      IF(M2LO.EQ.0.AND.(.NOT.DB2EQ0.OR..NOT.DSGNCD))
     1          JGCD=JGCD-1
C
C LOOP OVER M2.NE.0
  304 DO 390 M2=M2MINQ,M2MAXM
C ISIGN2=(-1)**M2
      ISIGN2=-ISIGN2
      JGCD=JGCD+IGCD
      CALL DELM(M2,MSUMB2,MINC,MIND,MCMMD,MMCD,MC,MD,DSGNCD,
     1     DB2EQ0,DBMIN2,NBR2)
      IF(NBR2.EQ.4) GO TO 390
      GO TO KM2, (305,310,330)
```

```
  305 IF(M2.GT.M2MAXP) GO TO 330
C
C SUM FOR +M2
  310 JYIMAG=JY12L+M1+M2
      JYREAL=JYIMAG+LP
C ISIGN1=(-1)**M1
      WTEMP=OMEGA(JOMG(L,L1,M1,L2,M2))
      IF(ISIGN1.NE.ISIGN2) WTEMP=-WTEMP
      DS1=.TRUE.
      DS2=.TRUE.
      DS3=.FALSE.
      ASSIGN 330 TO KBEEP
  795 TEMP2=0.0D0
      TEMP3=0.0D0
      IF(.NOT.DSGNAB) GO TO 840
      GO TO (825,835,830),NBR2
C
C GAB HAS ONLY REAL PART NONZERO,
C GCD HAS NONZERO REAL AND IMAG PARTS
  825 TEMP2=SUMM(JYREAL)*GCD(JGCD-1)
C
C GAB HAS ONLY REAL PART NONZERO, GCD HAS NONZERO IMAG PART
  830 TERM=SUMM(JYIMAG)*GCD(JGCD)
      IF(.NOT.DS1) TERM=-TERM
      TEMP2=TEMP2+TERM
      GO TO 315
C
C GAB AND GCD HAVE ONLY REAL PARTS NONZERO
  835 TEMP2=SUMM(JYREAL)*GCD(JGCD-IG2)
  315 SUM2=SUM2+WTEMP*TEMP2
      GO TO 325
  840 GO TO (845,855,850),NBR2
C
C GAB HAS ONLY IMAG PART NONZERO,
C GCD HAS NONZERO REAL AND IMAG PARTS
  845 TEMP3=SUMM(JYIMAG)*GCD(JGCD-1)
      IF(.NOT.DS2) TEMP3=-TEMP3
C
C GAB HAS ONLY IMAG PART NONZERO,
C GCD HAS NONZERO IMAG PART
  850 TERM=SUMM(JYREAL)*GCD(JGCD)
      IF(.NOT.DS3) TERM=-TERM
      TEMP3=TEMP3+TERM
      GO TO 320
C
C GAB HAS ONLY IMAG PART NONZERO,
C GCD HAS ONLY REAL PART NONZERO
  855 TEMP3=SUMM(JYIMAG)*GCD(JGCD-IG2)
      IF(.NOT.DS2) TEMP3=-TEMP3
  320 SUM3=SUM3+WTEMP*TEMP3
```

```
  325 GO TO KREEP,(330,390)
C
C SUM FOR -M2
  330 M2MM1=M2-M1
      JYIMAG=JY12L+IABS(M2MM1)
      JYREAL=JYIMAG+LP
      WTEMP=OMEGA(JOMG(L,L1,M1,L2,-M2))
      IF(M2MM1) 340,335,345
  335 WTEMP=WTEMP*SUMM(JYREAL)
      IF(ISIGN2.LT.0) WTEMP=-WTEMP
      IF(.NOT.DSGNAB) GO TO 870
      GO TO (339,339,390), NBR2
C
C GAB AND GCD HAVE NONZERO REAL PARTS
  339 SUM2=SUM2+WTEMP*GCD(JGCD-IG2)
      GO TO 390
  870 GO TO (338,390,338),NBR2
C
C GAB AND GCD HAVE NONZERO IMAG PARTS
  338 SUM3=SUM3+WTEMP*GCD(JGCD)
      GO TO 390
  340 IF(ISIGN1.LT.0) WTEMP=-WTEMP
      DS1=.FALSE.
      DS2=.TRUE.
      GO TO 350
  345 IF(ISIGN2.LT.0) WTEMP=-WTEMP
      DS1=.TRUE.
      DS2=.FALSE.
  350 DS3=.TRUE.
      ASSIGN 390 TO KBEEP
      GO TO 795
  390 CONTINUE
  400 JGCD=JGCD+IGCD*(M2MAX-M2MAXM)
C
C SUM2 IS MULTIPLIED BY THE REAL PART OF GAB
C SUM3 IS MULTIPLIED BY THE IMAG PART OF GAB
      IF(DSGNAB) GO TO 420
      SUM1=SUM1+SUM3*GAB(JGAB)
      GO TO KM1,(430,450)
  420 SUM1=SUM1+SUM2*GAB(JGAB)
      GO TO KM1,(430,450)
  430 IF(DM1EQ.OR.L1.LT.M1HI) GO TO 450
      JGAB=JGAB+1
      IF(M1HI.GT.LPM2HI) GO TO 450
      M1=M1HI
      ASSIGN 450 TO KM1
C SUM FOR M1=M1HI=||MA|+|MB||
      GO TO 255
C
C *   *   *   *   *   *   *   *   *   *   *   *   *   *   *   *
```

```
C
  450 CONTINUE
      A(JA)=SUM1+SUM1
      IF(MOD(L1MIN,2).EQ.0) A(JA)=-A(JA)
C           INTRODUCE  FACTOR (-1)**L1
C
  460 CONTINUE
  470 JGCDP=JGCDP+JGCDD
  480 JGABP=JGABP+JGABD
      NA=JA
      RETURN
      END
```

PROGRAM 14: GEOM2C

```
C  GEOM2C CALCULATES ARRAY A, WHICH IS INDEPENDENT OF ZETAS,
C               FOR INTEGRAL  (AA|CC)
C  ARGUMENTS    LAP,MAP,ETC. ARE ORBITAL QUANTUM NUMBERS
C               NGAB=ONE LESS THAN THE SUBSCRIPT OF THE FIRST
C                           GAB FOR LA,LB,MA,MB
C               NGCD=ONE LESS THAN THE SUBSCRIPT OF THE FIRST
C                           GCD FOR LC,LD,MC,MD
C               NA=SIZE OF ARRAY A (CALCULATED BY GEOM)
C     INDICES RUN IN THIS ORDER, WITH LAST ONE CHANGING
C               FASTEST - SIGMA1,SIGMA2,L
C
      SUBROUTINE GEOM2C(SUMM,OMEGA,LAP,MAP,LBP,MBP,LCP,MCP,
     1          LDP,MDP,NA,NGAB,NGCD)
      IMPLICIT REAL*8(A-C,E-H,O-Z),LOGICAL*1(D)
      COMMON/AF/SHAM(30),GAB(340),GCD(340),A(3548)
      DIMENSION SUMM(1),OMEGA(1)
      IF(LAP.LT.LBP) GO TO 5
      LA=LAP
      MA=MAP
      LB=LBP
      MB=MBP
      GO TO 6
    5 LA=LBP
      MA=MBP
      LB=LAP
      MB=MAP
C   NOW LA.GE.LB
C
    6 M1LO=IABS(IABS(MA)-IABS(MB))
      M1HI=IABS(MA)+IABS(MB)
      IF(MOD(M1LO,2).EQ.0) GO TO 7
```

```
      ISIGN1=-1
      GO TO 920
    7 ISIGN1=+1
  920 IF(M1LO.EQ.M1HI) GO TO 940
      DM1EQ=.FALSE.
      GO TO 10
  940 DM1EQ=.TRUE.
   10 IF(LCP.LT.LDP) GO TO 15
      LC=LCP
      MC=MCP
      LD=LDP
      MD=MDP
      GO TO 16
   15 LC=LDP
      MC=MDP
      LD=LCP
      MD=MCP
C    NOW LC.GE.LD
C
   16 M2LO=IABS(IABS(MC)-IABS(MD))
      M2HI=IABS(MC)+IABS(MD)
      IF(MOD(M2LO,2).EQ.0) GO TO 17
      ISIGN2=-1
      GO TO 970
   17 ISIGN2=+1
  970 IF(M2LO.EQ.M2HI) GO TO 990
      DM2EQ=.FALSE.
      GO TO 20
  990 DM2EQ=.TRUE.
   20 LAMLB=LA-LB
      LCMLD=LC-LD
      LALB=LA+LB
      LCLD=LC+LD
      MOD1=MOD(LALB+M1LO,2)
      MOD2=MOD(LCLD+M2LO,2)
      IF(MA.LT.0) GO TO 507
      IF(MB.LT.0) GO TO 506
      GO TO 508
  506 DSGNAB=.FALSE.
      GO TO 510
  507 IF(MB.LT.0) GO TO 508
      GO TO 506
  508 DSGNAB=.TRUE.
C DSGNAB=.TRUE. IFF MA AND MB HAVE SAME SIGN (0 IS +)
C
  510 IF(MC.LT.0) GO TO 517
      IF(MD.LT.0) GO TO 516
      GO TO 518
  516 DSGNCD=.FALSE.
      GO TO 520
```

```
  517 IF(MD.LT.0) GO TO 518
      GO TO 516
  518 DSGNCD=.TRUE.
C DSGNCD=.TRUE. IFF MC AND MD HAVE SAME SIGN (0 IS +)
C
  520 IF(M1LO.EQ.0) GO TO 522
      ASSIGN 253 TO KAM1
      DM1ON=.FALSE.
      GO TO 525
  522 IF(DSGNAB) GO TO 523
      ASSIGN 430 TO KAM1
      DM1ON=.TRUE.
      GO TO 525
  523 ASSIGN 240 TO KAM1
      DM1ON=.FALSE.
C
C DM1ON=.TRUE. IFF MA.EQ.-MB.NE.C
C
  525 IF(M2LO.EQ.0) GO TO 527
      ASSIGN 244 TO KAOM2
      ASSIGN 300 TO KAMM2
      DM2ON=.FALSE.
      GO TO 529
  527 IF(DSGNCD) GO TO 528
      ASSIGN 248 TO KAOM2
      ASSIGN 390 TO KAMM2
      DM2ON=.TRUE.
      GO TO 529
  528 ASSIGN 242 TO KAOM2
      ASSIGN 296 TO KAMM2
      DM2ON=.FALSE.
C
C DM2ON=.TRUE. IFF MC.EQ.-MD.NE.0
C
  529 CONTINUE
      JA=0
      JGABP=NGAB
      MODAB=MOD(LALB,2)
      L1LO=MAXO(LAMLB,M1LO+MOD1)
      IF(L1LO.GE.M1HI) GO TO 530
      DL1GE=.FALSE.
      GO TO 535
  530 DL1GE=.TRUE.
  535 CONTINUE
C
C ALPHA1=BETA1=0 BECAUSE A=B
C
      IS1MIN=L1LO+1
      IS1MAX=LALB+1
      MODCD=MOD(LCLD,2)
```

```
      L2LO=MAXO(LCMLD,M2LO+MOD2)
      IF(L2LO.GE.M2HI) GO TO 630
      DL2GE=.FALSE.
      GO TO 635
  630 DL2GE=.TRUE.
  635 CONTINUE
      IS2MIN=L2LO+1
      IS2MAX=LCLD+1
      LLOWP=MAXO(M1LO-M2HI,M2LO-M1HI)
      IF(LLOWP.LT.0) GO TO 640
      IF(MOD(IABS(LLOWP),2).NE.IABS(MODA8-MODCD))
     1    LLOWP=LLOWP+1
      GO TO 540
  640 IF(MODA8.EQ.MODCD) GO TO 645
      LLOWP=1
      GO TO 540
  645 LLOWP=2*MOD(IABS(LLOWP),2)
  540 DO 480 IS1=IS1MIN,IS1MAX,2
      JGCDP=NGCD
      ISIG1=IS1-1
      IS1P1=IS1+1
C
      IF(DM1EQ.OR.ISIG1.LT.M1HI) GO TO 25
      IF(DL1GE) GO TO 23
      IF(DM10N) GO TO 22
      ASSIGN 100 TO KJ1
      JGT1=(M1HI+MOD1+L1LO)/2
      JGABD=IS1P1-JGT1
      GO TO 28
   22 ASSIGN 110 TO KJ1
      JGABD=(ISIG1-M1HI-MOD1)/2+1
      GO TO 28
   23 IF(DM10N) GO TO 26
      ASSIGN 120 TO KJ1
      JGABD=IS1P1-L1LO
      GO TO 28
   25 IF(DM10N) GO TO 27
   26 ASSIGN 80 TO KJ1
      JGABD=(ISIG1-L1LO)/2+1
      GO TO 28
   27 ASSIGN 73 TO KJ1
      JGABD=0
   28 CONTINUE
C  JGABD=NUMBER OF FUNCTIONS GAB FOR GIVEN ISIG1
C
C  ALPHA2=BETA2=0 BECAUSE C=D
C
      DO 470 IS2=IS2MIN,IS2MAX,2
      ISIG2=IS2-1
      IS2P1=IS2+1
```

```
C
      IF(DM2EQ.OR.ISIG2.LT.M2HI) GO TO 35
      IF(DL2GE) GO TO 33
      IF(DM2ON) GO TO 32
      ASSIGN 180 TO KJ2
      JGT2=(M2HI+MOD2+L2LO)/2
      JGCDD=IS2P1-JGT2
      GO TO 38
   32 ASSIGN 190 TO KJ2
      JGCDD=(ISIG2-M2HI-MOD2)/2+1
      GO TO 38
   33 IF(DM2ON) GO TO 36
      ASSIGN 200 TO KJ2
      JGCDD=IS2P1-L2LO
      GO TO 38
   35 IF(DM2ON) GO TO 37
   36 ASSIGN 160 TO KJ2
      JGCDD=(ISIG2-L2LO)/2+1
      GO TO 38
   37 ASSIGN 153 TO KJ2
      JGCDD=0
   38 CONTINUE
C JGCDD=NUMBER OF FUNCTIONS GCD FOR GIVEN ISIG2
C
  660 LLOW=MAXO(L1LO-ISIG2,L2LO-ISIG1,LLOWP)+1
C
C LLOW=MAXO(0,M1LO-M2HI,M2LO-M1HI,L1LO-SIGMA2,L2LO-SIGMA1)
C        (+1 IF NEEDED TO MAKE (LMIN+SIGMA1+SIGMA2) EVEN)+1
C
      LMAX=ISIG1+IS2
      DO 460 LP=LLOW,LMAX,2
      L=LP-1
      JY12L=L*L
C
C SUBSCRIPT FOR ARRAY SUMM = JY12L +M1 +OR- M2
C                                    (+L+1 IF REAL PART)
C
      LMM2LO=L-M2LO
      LPM2HI=L+M2HI
      L1MIN=MAXO(L1LO,L2LO-L,L-ISIG2)
      L1MAX=MINO(IS1,L+IS2)
      L1DIF=L1MIN-L1LO
C
      IF(L1DIF.NE.0) GO TO 75
   73 JGAB=JGABP
      GO TO 150
   75 GO TO KJ1,(73,80,100,110,120)
   80 JGAB=JGABP+L1DIF/2
      GO TO 150
  100 IF(L1MIN-2.LT.M1HI) GO TO 80
```

```
      JGAB=JGABP+L1MIN-JGT1
      GO TO 150
  110 IF (L1MIN-2.LT.M1HI) GO TO 73
      JGAB=JGABP+(L1MIN-M1HI-MOD1)/2
      GO TO 150
  120 JGAB=JGABP+L1DIF
C  AT THIS POINT JGAB IS 1 LESS THAN THE INDEX FOR THE FIRST
C          GAB FUNCTION TO BE USED
C
  150 JA=JA+1
      SUM1=0.0D0
      L1MIN=L1MIN+1
      DO 450 L1P=L1MIN,L1MAX,2
      L1=L1P-1
      L2MIN=MAX0(L2LO,IABS(L-L1))
      L2MAX=MIN0(IS2,L+L1P)
      L2DIF=L2MIN-L2LO
C
      IF(L2DIF.NE.0) GO TO 155
  153 JGCDT=JGCDP
      GO TO 235
  155 GO TO KJ2,(153,160,180,190,200)
  160 JGCDT=JGCDP+L2DIF/2
      GO TO 235
  180 IF(L2MIN-2.LT.M2HI) GO TO 160
      JGCDT=JGCDP+L2MIN-JGT2
      GO TO 235
  190 IF(L2MIN-2.LT.M2HI) GO TO 153
      JGCDT=JGCDP+(L2MIN-M2HI-MOD2)/2
      GO TO 235
  200 JGCDT=JGCDP+L2DIF
C  AT THIS POINT JGCDT IS 1 LESS THAN THE INDEX FOR THE
C        FIRST GCD FUNCTION TO BE USED
C
  235 SUM2=0.0D0
      L2MIN=L2MIN+1
      GO TO KAM1,(240,253,430)
C
C *   *   *   *   *   *   *   *   *   *   *   *   *   *   *
C
C M1=0, SO IMAG.PART OF GAB=0
C
  240 JGAB=JGAB+1
      IF(LMM2LO.LT.0) GO TO 430
  241 JGCD=JGCDT
      DO 250 L2P=L2MIN,L2MAX,2
      L2=L2P-1
      GO TO KAOM2,(242,244,248)
C
C M2=0, SO IMAG. PART OF GCD=0
```

```
  242 JGCD=JGCD+1
      SUM2=SUM2+OMEGA(JOMG(L,L1,0,L2,0))*SUMM(JY12L+LP)
     1       *GCD(JGCD)*0.5D0
      GO TO 248
C
C M2.NE.0,M1.EQ.0
  244 M2=M2LO
C TERM WITH M2=M2LO=||MC|-|MD||
      ASSIGN 248 TO KOM2
      JGCD=JGCD+1
  246 IF(.NOT.DSGNCD) GO TO 720
C
C GCD HAS ONLY REAL PART NONZERO
      TEMP2=SUMM(JY12L+M2+LP)*GCD(JGCD)
      GO TO 730
C
C GCD HAS ONLY IMAG PART NONZERO
  720 TEMP2=SUMM(JY12L+M2)*GCD(JGCD)
C ISIGN2=(-1)**M2
  730 SUM2=SUM2+OMEGA(JOMG(L,L1,0,L2,M2))*ISIGN2*TEMP2
      GO TO KOM2,(248,250)
  248 IF(DM2EQ.OR.L2.LT.M2HI) GO TO 250
      JGCD=JGCD+1
      IF(M2HI.GT.L) GO TO 250
      M2=M2HI
C TERM WITH M2=M2HI=||MC|+|MD||
      ASSIGN 250 TO KOM2
      GO TO 246
  250 CONTINUE
      SUM1=SUM1+GAB(JGAB)*SUM2
      GO TO 430
C
C *   *   *   *   *   *   *   *   *   *   *   *   *   *   *
C
C M1.NE.0
C
  253 M1=M1LO
C SUM FOR M1=M1LO=||MA|-|MB||
      ASSIGN 430 TO KM1
      JGAB=JGAB+1
  255 LMM1=L-M1
      LPM1=L+M1
      IF(M1.GT.LMM2LO) GO TO 260
      ASSIGN 290 TO KL2
      GO TO 262
  260 ASSIGN 295 TO KL2
      ASSIGN 330 TO KM2
  262 SUM2=0.0D0
      SUM3=0.0D0
  280 JGCD=JGCDT
```

```
      DO 400 L2P=L2MIN,L2MAX,2
      L2=L2P-1
      GO TO KL2,(290,295)
  290 IF(M2HI.LE.LMM1) GO TO 292
      ASSIGN 305 TO KM2
      GO TO 295
  292 ASSIGN 310 TO KM2
  295 GO TO KAMM2,(296,300,390)
C
C M2=0, SO IMAG PART OF GCD=0
  296 JGCD=JGCD+1
      IF(LMM1.LT.0) GO TO 390
  298 WTEMP=OMEGA(JOMG(L,L1,M1,L2,0))*GCD(JGCD)*ISIGN1
      JYIMAG=JY12L+M1
      IF(DSGNAB) GO TO 790
C
C GAB HAS ONLY IMAG PART NONZERO
      SUM3=SUM3+WTEMP*SUMM(JYIMAG)
      GO TO 390
C
C GAB HAS ONLY REAL PART NONZERO
  790 SUM2=SUM2+WTEMP*SUMM(JYIMAG+LP)
      GO TO 390
C
C M2.NE.0
  300 M2=M2LO
C TERM WITH M2=M2LO=||MC|-|MD||
      JGCD=JGCD+1
      IF(M2.LT.-LMM1) GO TO 390
      ASSIGN 390 TO KMM2
  302 GO TO KM2, (305,310,330)
  305 IF(M2.GT.LMM1) GO TO 330
C
C SUM FOR +M2
  310 JYIMAG=JY12L+M1+M2
      JYREAL=JYIMAG+LP
C ISIGN1=(-1)**M1
C ISIGN2=(-1)**M2
      WTEMP=OMEGA(JOMG(L,L1,M1,L2,M2))*(ISIGN1*ISIGN2)
      DS1=.TRUE.
      DS2=.TRUE.
      DS3=.FALSE.
      ASSIGN 330 TO KBEEP
  795 TEMP2=0.0D0
      TEMP3=0.0D0
      IF(.NOT.DSGNAB) GO TO 840
      IF(DSGNCD) GO TO 835
C
C GAB HAS ONLY REAL PART NONZERO,
C GCD HAS ONLY IMAG PART NONZERO
```

```
      TEMP2=SUMM(JYIMAG)*GCD(JGCD)
      IF(.NOT.DS1) TEMP2=-TEMP2
      GO TO 315
C
C GAB AND GCD HAVE ONLY REAL PARTS NONZERO
  835 TEMP2=SUMM(JYREAL)*GCD(JGCD)
  315 SUM2=SUM2+WTEMP*TEMP2
      GO TO 325
  840 IF(DSGNCD) GO TO 855
C
C GAB AND GCD HAVE ONLY IMAG PARTS NONZERO
      TEMP3=SUMM(JYREAL)*GCD(JGCD)
      IF(.NOT.DS3) TEMP3=-TEMP3
      GO TO 320
C
C GAB HAS ONLY IMAG PART NONZERO,
C GCD HAS ONLY REAL PART NONZERO
  855 TEMP3=SUMM(JYIMAG)*GCD(JGCD)
      IF(.NOT.DS2) TEMP3=-TEMP3
  320 SUM3=SUM3+WTEMP*TEMP3
  325 GO TO KBEEP,(330,380)
C
C SUM FOR -M2
  330 M2MM1=M2-M1
      JYIMAG=JY12L+IABS(M2MM1)
      JYREAL=JYIMAG+LP
      WTEMP=OMEGA(JOMG(L,L1,M1,L2,-M2))
      IF(M2MM1) 340,335,345
  335 WTEMP=WTEMP*ISIGN2*SUMM(JYREAL)
      IF(.NOT.DSGNAB) GO TO 870
      IF(.NOT.DSGNCD) GO TO 380
C
C GAB AND GCD HAVE ONLY REAL PARTS NONZERO
  339 SUM2=SUM2+WTEMP*GCD(JGCD)
      GO TO 380
  870 IF(DSGNCD) GO TO 380
C
C GAB AND GCD HAVE ONLY IMAG PARTS NONZERO
  338 SUM3=SUM3+WTEMP*GCD(JGCD)
      GO TO 380
  340 WTEMP=WTEMP*ISIGN1
      DS1=.FALSE.
      DS2=.TRUE.
      GO TO 350
  345 WTEMP=WTEMP*ISIGN2
      DS1=.TRUE.
      DS2=.FALSE.
  350 DS3=.TRUE.
      ASSIGN 380 TO KBEEP
      GO TO 795
```

```
  380 GO TO KMM2,(390,400)
  390 IF(DM2EQ.OR.L2.LT.M2HI) GO TO 400
      JGCD=JGCD+1
      IF(M2HI.GT.LPM1) GO TO 400
      M2=M2HI
C TERM WITH M2=M2HI=||MC|+|MD||
      ASSIGN 400 TO KMM2
      GO TO 302
  400 CONTINUE
C
C SUM2 IS MULTIPLIED BY THE REAL PART OF GAB
C SUM3 IS MULTIPLIED BY THE IMAG PART OF GAB
      IF(DSGNAB) GO TO 420
      SUM1=SUM1+SUM3*GAB(JGAB)
      GO TO KM1,(430,450)
  420 SUM1=SUM1+SUM2*GAB(JGAB)
      GO TO KM1,(430,450)
  430 IF(DM1EQ.OR.L1.LT.M1HI) GO TO 450
      JGAB=JGAB+1
      IF(M1HI.GT.LPM2HI) GO TO 450
      M1=M1HI
C SUM FOR M1=M1HI=||MA|+|MB||
      ASSIGN 450 TO KM1
      GO TO 255
C
C *   *   *   *   *   *   *   *   *   *   *   *   *   *   *
C
  450 CONTINUE
      A(JA)=SUM1+SUM1
  460 IF(MOD(L1MIN,2).EQ.0) A(JA)=-A(JA)
C STMNT 460 INTRODUCES FACTOR (-1)**L1
C
  470 JGCDP=JGCDP+JGCDD
  480 JGABP=JGABP+JGABD
      NA=JA
      RETURN
      END
```

PROGRAM 15: DEL

```
C DEL       CHECKS FOR G=0
C  NBRNCH=1 - REAL TERM ,=2 - NO TERM
      SUBROUTINE DELO(MSUMB,MINA,MINB,MAMMB,DSGN,DBMIN,
     1   NBRNCH)
      IMPLICIT LOGICAL*1(D)
      DMDIFO=.FALSE.
```

```
      D1=.FALSE.
      IF(MSUMB.LE.0) D1=.TRUE.
      D2=.FALSE.
      D3=.FALSE.
      IF(MAMMB) 20,25,30
   20 IF(MINB.GE.0) D2=.TRUE.
      IF(MINA.GE.0) D3=.TRUE.
      GO TO 35
   25 DMDIFO=.TRUE.
      IF(MINA.GE.0) GO TO 27
      IF(MINB.GE.0) D2=.TRUE.
      GO TO 35
   27 D2=.TRUE.
      IF(MINB.GE.0) D3=.TRUE.
      GO TO 35
   30 IF(MINA.GE.0) D2=.TRUE.
      IF(MINB.GE.0) D3=.TRUE.
   35 IF(D1) GO TO 40
      IF(.NOT.D2) GO TO 50
      IF(DMDIFO   .AND..NOT.DSGN) GO TO 60
      GO TO 50
   40 IF(D2.AND.DBMIN) GO TO 60
   50 NBRNCH=1
      RETURN
   60 NBRNCH=2
      RETURN
C  NBRNCH=1 - BOTH TERMS,=4 - NEITHER TERMS
C  NBRNCH=2 - REAL TERM ,=3 - IMAG TERM
      ENTRY DELM(M,MSUMB,MINA,MINB,MAMMB,MM   ,MA,MB,DSGN,
     1    DBEQO,DBMIN,NBRNCH)
      D1=.FALSE.
      IF(MSUMB.LE.M) D1=.TRUE.
      D2=.FALSE.
      D3=.FALSE.
      IF(MAMMB) 100,150,250
  100 ASSIGN 285 TO K5
      ASSIGN 290 TO K4
      IF(MINB.GE.M) D2=.TRUE.
      IF(MINA.GE.M) D3=.TRUE.
      GO TO 260
  150 IF(MINA.GE.M) GO TO 180
      IF(MINB.GE.M) GO TO 165
      IF(D1) GO TO 155
      NBRNCH=4
      RETURN
  155 IF(DBEQO.OR.M.EQ.MM) GO TO 160
      NBRNCH=1
      RETURN
  160 IF(DSGN) GO TO 162
      NBRNCH=3
```

```
      RETURN
  162 NBRNCH=2
      RETURN
C     D2=.TRUE.
  165 IF(.NOT.D1) GO TO 170
      IF(.NOT.DBMIN) GO TO 170
      NBRNCH=4
      RETURN
  170 IF(M.EQ.IABS(MB))GO TO 172
      NBRNCH=1
      RETURN
  172 IF(MB.GE.0) GO TO 175
      NBRNCH=3
      RETURN
  175 NBRNCH=2
      RETURN
C     D2=.TRUE.
  180 IF(.NOT.D1) GO TO 200
      IF(.NOT.DBMIN) GO TO 185
      NBRNCH=4
      RETURN
  185 IF(MINB.GE.M) GO TO 190
  186 IF(M.EQ.IABS(MA)) GO TO 187
      NBRNCH=1
      RETURN
  187 IF(MA.GE.0) GO TO 188
      NBRNCH=3
      RETURN
  188 NBRNCH=2
      RETURN
C     D3=.TRUE.
  190 NBRNCH=1
      RETURN
  200 IF(MINB.LT.M) GO TO 186
C     D3=.TRUE.
      NBRNCH=1
      RETURN
  250 ASSIGN 290 TO K5
      ASSIGN 285 TO K4
      IF(MINA.GE.M) D2=.TRUE.
      IF(MINB.GE.M) D3=.TRUE.
  260 IF(D1) GO TO 300
      IF(D2) GO TO 270
      NBRNCH=4
      RETURN
  270 IF(.NOT.D3) GO TO 280
      IF(DBEQC)  GO TO 160
      NBRNCH=1
      RETURN
  280 IF(DBEQ0.OR.M.EQ.IABS(MAMMB)) GO TO 160
```

```
      GO TO K4,(285,290)
  285 IF(M.EQ.IABS(MA)) GO TO 187
      NBRNCH=1
      RETURN
  290 IF(M.EQ.IABS(MB)) GO TO 172
      NBRNCH=1
      RETURN
  300 IF(.NOT.D2) GO TO 320
      IF(.NOT.DBMIN) GO TO 310
      NBRNCH=4
      RETURN
  310 IF(DBEQO) GO TO 160
      IF(.NOT.D3) GO TO K4,(285,290)
      NBRNCH=1
      RETURN
  320 IF(DBEQO) GO TO 160
      IF(D3) GO TO K5,(290,285)
      IF(M.EQ.MM) GO TO 160
      NBRNCH=1
      RETURN
      END
```

PROGRAM 16: JOMG

```
C JOMG=SUBSCRIPT FOR ARRAY OMEGA
      FUNCTION JOMG(L,L1,M1,L2,M2)
      INTEGER*2 JOMEGA
      DIMENSION JOMEGA(3,5,9)
      DATA JOMEGA/  1,  0,  0,  2,  0,  0,  0,  4,  0,  0,
     1     7,  0,  0,  0, 11,  0,  0,  0, 16,  0,  0, 18,  0,
     2     0,  0, 23,  0,  0, 31,  0,  0,  0,  0, 42,  0,  0,
     3    47, 50,  0, 60, 68,  0,  0, 83, 96,  0,  0,  0,  0,
     4     0,  0,116,  0,  0,124,128,  0,143,154,  0,  0,  0,
     5     0,  0,  0,  0,  0,176,  0,189,200,  0,222,227,247,
     6     0,  0,  0,  0,  0,  0,  0,  0,  0,  0,278,  0,296,
     7   310,  0,  0,  0,  0,  0,  0,  0,  0,  0,  0,  0,339,
     8     0,  0,364,387,  0,  0,  0,  0,  0,  0,  0,  0,  0,
     9     0,  0,  0,  0,425,  0,  0,  0,  0,  0,  0,  0,  0,
     1     0,  0,  0,  0,  0,  0,  0,457/
      IF(L1.GE.L2) GO TO 20
      LG=L2
      MG=ISIGN(M2,M1)
      LL=L1
      ML=ISIGN(M1,M2)
      GO TO 30
   20 LG=L1
```

```
      MG=M1
      LL=L2
      ML=M2
   30 J=JOMEGA(LL/2+1,LG+1,L+1)
      IF(MG-1) 33,36,40
   33 J=J+IABS(ML)
      GO TO 100
   36 J=J+MINO(L,LL)+MINO(LL,L+1)+ML+1
      GO TO 100
   40 IF(LL.GT.L-MG+1) GO TO 50
      J=J+MG*(2*LL+1)+ML
      GO TO 100
   50 IF(LL.LT.L+MG) GO TO 60
      J=J+2*MG*(L+1)+ML
      GO TO 100
   60 J=J+MG*(L+LL+1)-(MG*(MG-1)+(L-LL)*(L-LL+1))/2+ML
  100 JOMG=J
      RETURN
      END
```

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PART TWO. COMMENTS ON LOCALIZED ORBITALS IN DIATOMIC MOLECULES

I. INTRODUCTION

In his original paper on the Hartree-Fock equations, Fock (1930) pointed out that the same N-electron single determinant wave function can be expressed in terms of infinitely many sets of space orbitals. If two sets of orbitals $\{u_k\}$ and $\{v_k\}$ are related by a unitary transformation

$$v_k(\vec{x}) = \sum_{i=1}^{N} u_i(\vec{x}) T_{ik} \quad ,$$

in which $\underline{\underline{T}}$ is an orthogonal matrix, that is

$$\sum_i T_{ik} T_{ij} = \sum_i T_{ji} T_{ki} = \delta_{jk} \quad ,$$

then the N-electron wave function is

$$\Psi = \mathcal{A}[\prod_k u_k(2k-1)\alpha(2k-1)u_k(2k)\beta(2k)]$$

$$= \mathcal{A}[\prod_k v_k(2k-1)\alpha(2k-1)v_k(2k)\beta(2k)] \quad .$$

Since measurable properties depend only on the total wave function Ψ, no one of these sets of orbitals can be said to be more "correct" than any other. Thus, even after the total wave function has been determined by energy minimization, there still remains some freedom in choosing the orbitals.

Many investigators have made use of this freedom. Hund

(1931, 1932) used it in connection with H_2O, and Coulson (1937, 1942) in connection with CH_4. Sets of "equivalent" orbitals, for symmetric molecules, were constructed by Lennard-Jones and Hall (Lennard-Jones, 1949a, 1949b; Hall and Lennard-Jones, 1950): certain symmetry operations transform one of the equivalent orbitals into another. Lennard-Jones and Pople (1950) observed that the equivalent orbitals are "localized" in the sense that they minimize the electronic interactions between different orbitals. This property can be used to define localized orbitals for systems to which the concept of equivalent orbitals is inapplicable: atoms, and molecules having no symmetry. Edmiston and Ruedenberg (1963, 1965, 1966) have devised a method for determining such localized orbitals, and have calculated them for a large number of systems. (Other kinds of localized orbitals have been defined, for example by Boys (1960) and by Ruedenberg (1962), but we shall not be concerned with them here.)

The definition of these localized orbitals will now be stated precisely. The electronic interaction energy of a system with wave function Ψ can be written

$$EI = (\Psi | \sum_{i<j} r_{ij}^{-1} | \Psi) = C - X \quad ,$$

in which C is the Coulomb term

$$C = 2 \sum_n \sum_m [u_n^2 | u_m^2]$$

and X is the exchange term

$$X = \sum_n \sum_m [u_n u_m | u_n u_m] \quad .$$

The notation

$$[u_k u_\ell | u_m u_n] = \int dV_1 \int dV_2 \; u_k^*(1) u_\ell(1) r_{12}^{-1} u_m^*(2) u_n(2)$$

has been used. Since EI depends only on the wave function Ψ, it is invariant with respect to unitary transformations among the orbitals. But it is also true that C and X are invariant with respect to such transformations. (See, e.g. (Edmiston and Ruedenberg, 1963).) Now the Coulomb and exchange terms can each be split into a term which includes the orbital self-repulsions and a term which includes only interorbital interactions:

$$C = 2(C' + D) \qquad \text{and} \qquad X = X' + D \quad ,$$

with

$$D = \sum_n [u_n^2 | u_n^2]$$

$$C' = \sum_{n \neq m} [u_n^2 | u_m^2]$$

$$X' = \sum_{n \neq m} [u_n u_m | u_n u_m] \quad .$$

These quantities, C' , X' and D, are not invariant with re-

spect to orbital transformations. Thus the localized orbitals can be defined as that orthonormal basis in the space spanned by $\{u_k\}$ for which D, the sum of orbital self-repulsions, is maximum. It is clear from the invariance of C and X that maximization of D implies minimization of C' and X' . Thus the localized orbitals are indeed "localized", in the sense that they interact with each other to the least possible degree.

The method for determining the localized orbitals for a system, given some set of orbitals for that system, is based on the maximization of D. This method is described in detail by Edmiston and Ruedenberg (1963, 1965).

The localized orbitals have several useful characteristics. Localized molecular orbitals (LMO's) often turn out to be inner shells, lone pairs and bonding orbitals, which correspond quite well with traditional chemical concepts. Furthermore, the LMO's are often transferable with very little change between similar molecules. This property makes them particularly suitable for studying the similarities and differences between molecules. On the other hand, the canonical Hartree-Fock orbitals are particularly suited for the comparison of different electronic states of the same molecule. A thorough discussion of these points is given by England, Salmon and Ruedenberg (1971).

Edmiston and Ruedenberg (1965) have determined LMO's for a number of diatomic molecules containing atoms of the first row of the periodic table. They used as a starting point the

minimal basis set wave functions of Ransil (1960a, 1960b) and of Padgett (1958). Contour plots of these LMO's are presented here. These provide no information beyond that given by Edmiston and Ruedenberg (1965), but they present that information in a way which makes it easier to see certain interesting properties of the LMO's. In particular, they facilitate comparisons of different orbitals. We shall first discuss the orbitals molecule-by-molecule, and then compare similar orbitals in different molecules.

II. CONTOUR DIAGRAMS OF LMO'S

A. General Considerations

We present here contour diagrams of LMO's for certain diatomic molecules containing atoms of the first row of the periodic table. It should be emphasized that the function plotted is the orbital itself, not the electron density. The contours are lines of constant density, but the increments in density between them are not constant. The increment in the value of the orbital is constant for each contour plot. However, the same increment was not used for each plot, and this fact should be kept in mind when comparing them. The orbital increment will be given for each diagram.

The orbitals plotted are all minimum-basis-set functions. The most accurate of the functions found by Edmiston and Ruedenberg were used in all cases. In some cases wave functions in which the orbital exponents had been varied to minimize the energy of the molecule (best-molecule atomic orbitals or BMO's) were available; in others, Slater-orbitals (with orbital exponents determined by Slater's rules; abbreviated by SAO's) were used. We shall indicate in each case which kind of function is given.

In all cases the diagrams are drawn in a plane containing the internuclear axis. The positions of the nuclei are indicated by heavy dots. The scale is shown on the figures, and is the same throughout. Contours for which the orbital

has a positive value are shown as solid lines, those for which it has a negative value are shown as broken lines, and the nodes are shown as dotted lines. The sign of the wave function is shown whenever this is feasible.

The diagrams were produced in two steps. First, the value of the wave function was computed for each point on a rectangular grid. The resulting array of numbers was then used by a standard contour-plotting program to find lines of constant function value. The plots were made by an IBM 7074 computer and a CALCOMP plotter.

B. Orbitals in Various Molecules

1. Molecules having sigma bonds

Figures 4 and 5 exhibit contour diagrams of all localized molecular orbitals (BMO) in the molecules Li_2 and LiH, respectively. In Li_2 there are two inner shell orbitals and a bonding orbital. For LiH there are an inner shell orbital on lithium and a LiH bonding orbital. All of these orbitals are of sigma type, that is, they are symmetric with respect to rotation around the internuclear axis.

For the bonding orbital of Li_2 , the outermost contour line corresponds to an orbital value of 0.005, the next contour line to 0.015, the next to 0.025 as indicated. Thus the increment is 0.01 $Bohr^{-3/2}$ in this case. By contrast, the outermost contour in the bonding orbital of LiH corresponds to an orbital value of 0.025 $Bohr^{-3/2}$, and the increment of

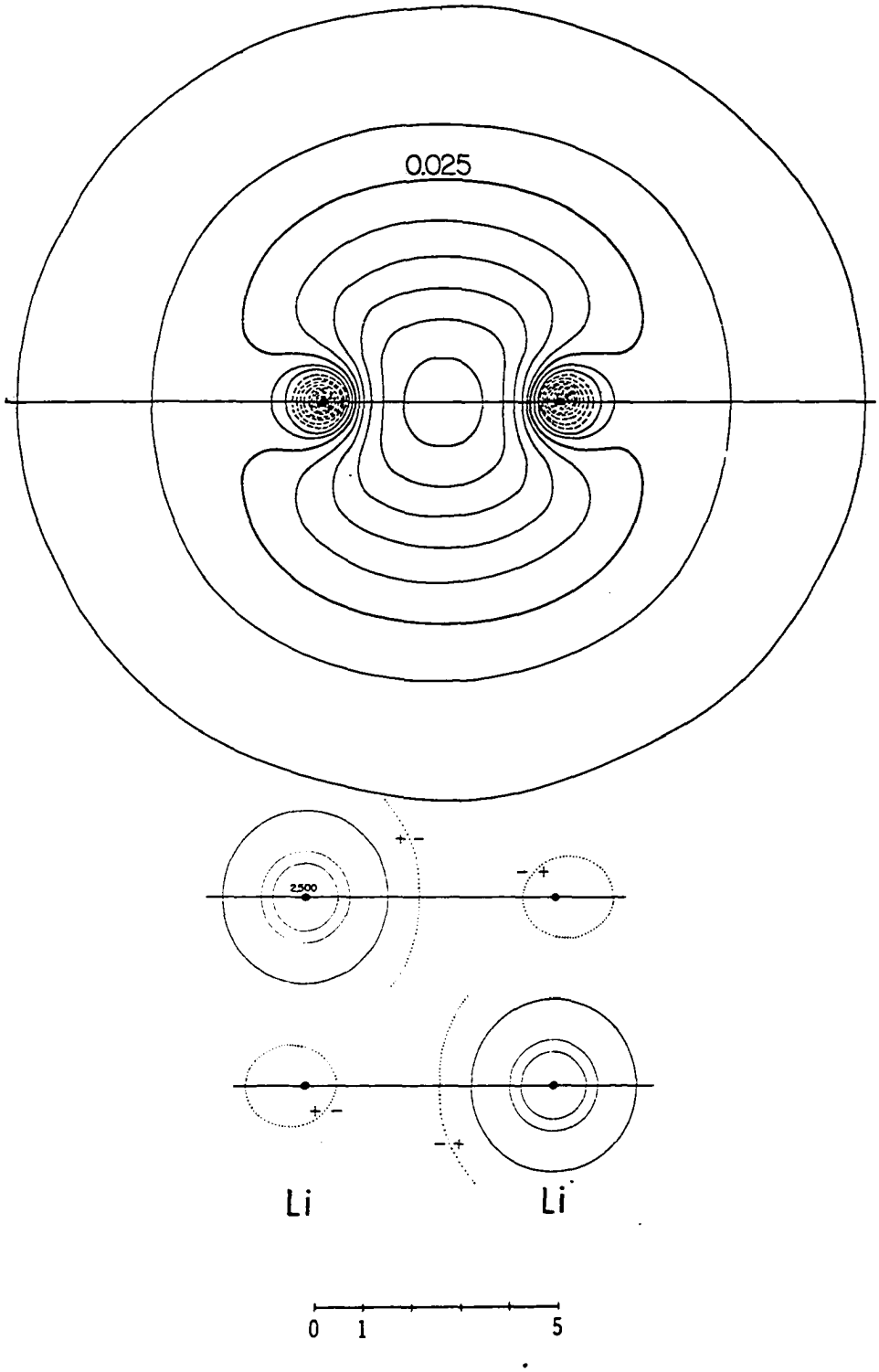


Figure 4. Localized MO's in Li_2

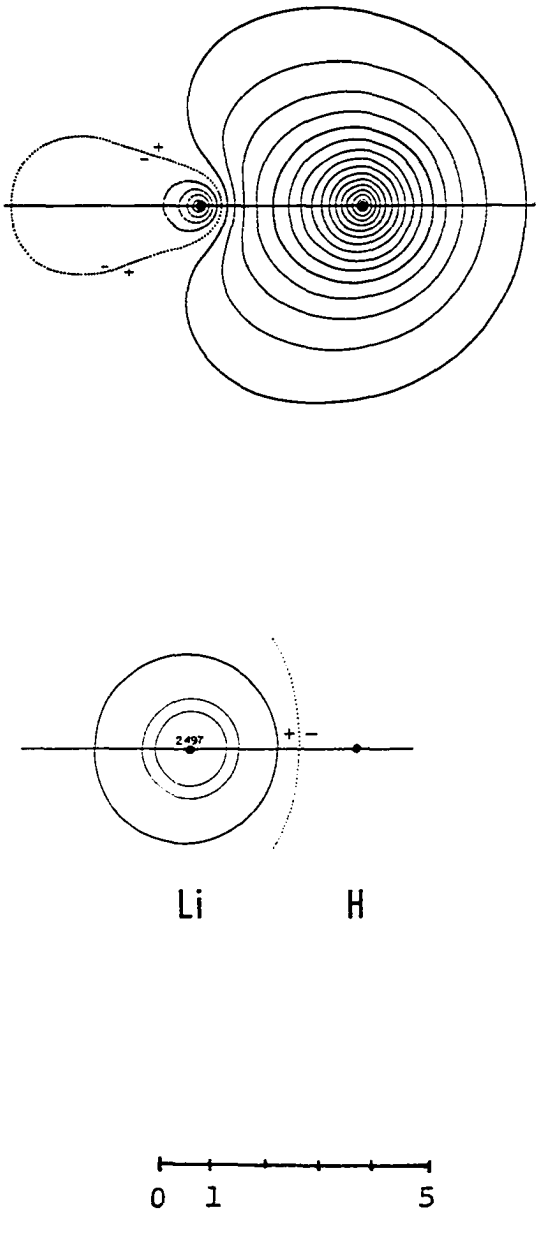


Figure 5. Localized MO's in LiH

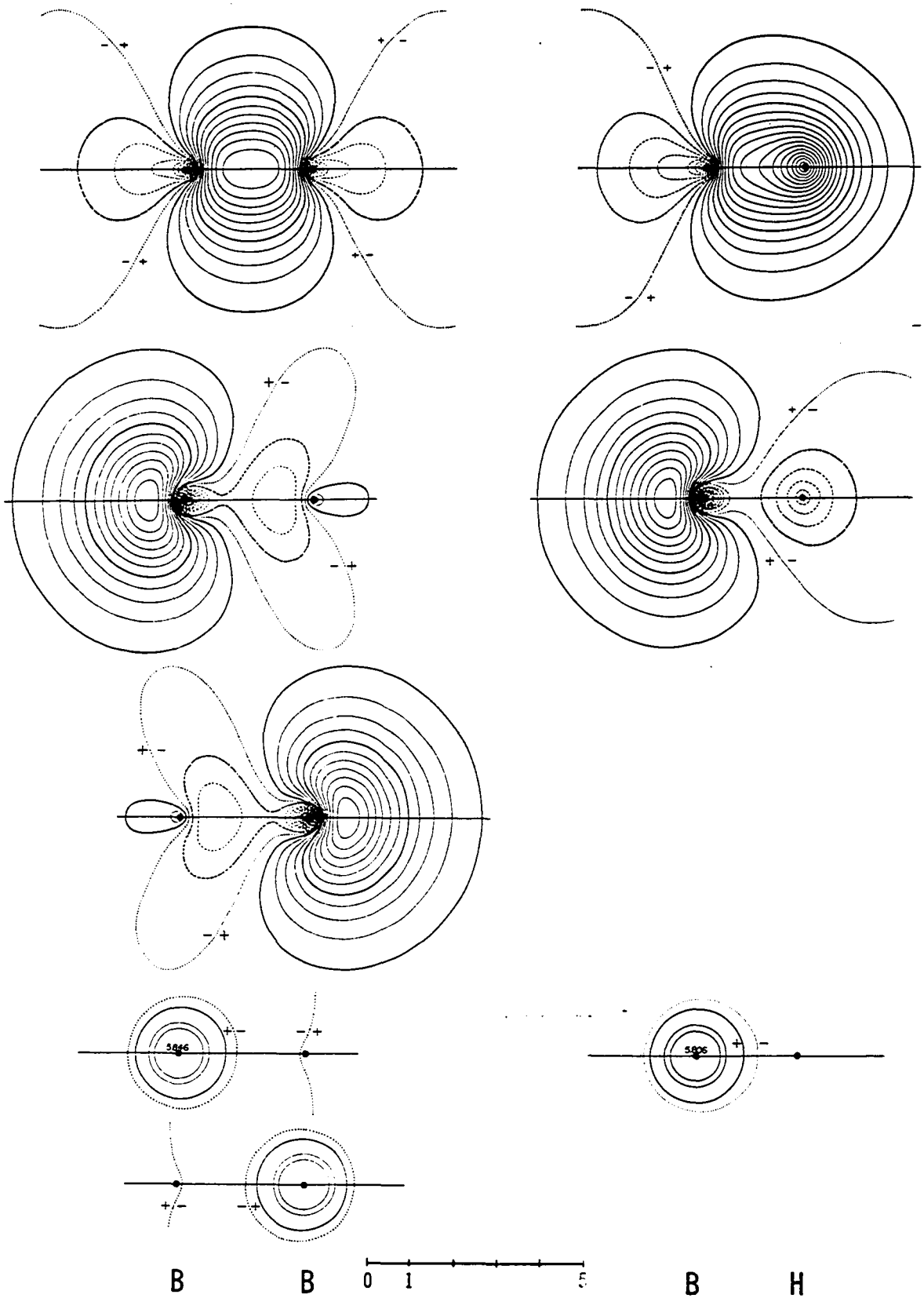
the wave function value from one contour line to another is also 0.025 $Bohr^{-3/2}$ in this case. Comparison of Li_2 and LiH shows that the Li_2 valence orbital is considerably larger than the LiH valence orbital and that its maximum is much lower. In short, it is a much less compact orbital. The bonding orbitals of Li_2 and LiH have a rather strong negative peak near the Li nucleus which establishes orthogonality to the inner shells.

For the inner shells the outermost contour is again 0.025 $Bohr^{-3/2}$. Because their value changes so rapidly, the increment for them is 0.2 $Bohr^{-3/2}$. Three of these inner shell contours are drawn. If the remaining inner shell contours were drawn, the inner part would be solid black. For this reason, the inner shell contours are not drawn beyond the third one and, instead, the value of the inner shell orbital at the position of the nucleus has been written into the diagram. From the figure, it is obvious that the inner shell of lithium is very similar in Li_2 and LiH and in a very practical sense transferable. However, note that the localized inner shell orbital of the lithium atom has a slight negative tail towards the other atom which yields a very small amount of antibinding.

2. Molecules having sigma bonds and sigma lone pairs

Figure 6 shows all localized orbitals for the ground state of the BH molecule (BMO) and the $^1\Sigma_g^+$ excited state of

Figure 6. Localized MO's in BH and the $(1\sigma_g)^2(1\sigma_u)^2(2\sigma_g)^2(2\sigma_u)^2(3\sigma_g)^2\ {}^1\Sigma_g^+$ state of B_2


B
B
0
1
5
B
H

B_2 (SAO). These are again rotationally symmetric orbitals, i.e., sigma type orbitals, and the complete contour surfaces can be obtained by spinning around the indicated axis. In all orbitals shown the outermost contour corresponds to a wave function value of 0.025 $Bohr^{-3/2}$. For all valence shell orbitals the increment from one contour to another is 0.025 $Bohr^{-3/2}$. For the inner shells the increment is again 0.2 $Bohr^{-3/2}$, but only three contours and the wave function values at the nuclear positions are shown.

The plots show clearly that the lone pair orbitals have almost all their density on that side of the atom which points away from the bond, whereas the bonding orbitals have almost all their density in between the two atoms. There is of course some local overlap between the orbitals; in particular, the bonding orbital has some negative contributions in the lone pair region and the lone pair orbital has some negative contribution in the bonding region, so that the resulting orbitals will be orthogonal to each other. It is evident that the positive contours of the lone pair orbital have very similar distributions in B_2 and BH, as one would like to see them have. It is gratifying that the negative sides are only somewhat different even though rather different atoms are involved.

For the inner shell orbitals, too, one finds near-perfect transferability as was the case for lithium.

3. Molecules having sigma bonds and triple lone pairs

Figure 7 exhibits the localized orbital structure of the F_2 and HF molecules (BMO). The wave function for the F_2 molecule is made up from one localized orbital representing a single sigma bond and six lone pair orbitals, three on each atom, which accommodate the twelve lone pair electrons. All orbitals are much more contracted than those of boron, because of the higher nuclear charge of fluorine (note that the scale of all figures is the same). The outermost contour corresponds again to 0.025 $Bohr^{-3/2}$, but the increment between adjacent contours in the valence shell is now 0.05 $Bohr^{-3/2}$. The contour surfaces of the bonding orbital can be obtained by spinning the contours around the nuclear axis.

For the lone pair orbitals the situation is somewhat more complicated. There are three trigonally equivalent lone pair orbitals at each end of the molecule which are arranged at 120° to each other; only one of these is shown on each atom. It can be observed that the lone pair orbital looks very much like an (s-p) hybrid on that particular atom, except for the slight build-up of charge near the other atom. By connecting the position of the nucleus with the maximum of the lone pair orbital one can define an approximate axis of the lone pair orbital. The three-dimensional contours of this lone pair are approximated by spinning the orbital around this axis, except in the region near the other atom. It is of interest that this axis of the lone pair orbital is not very

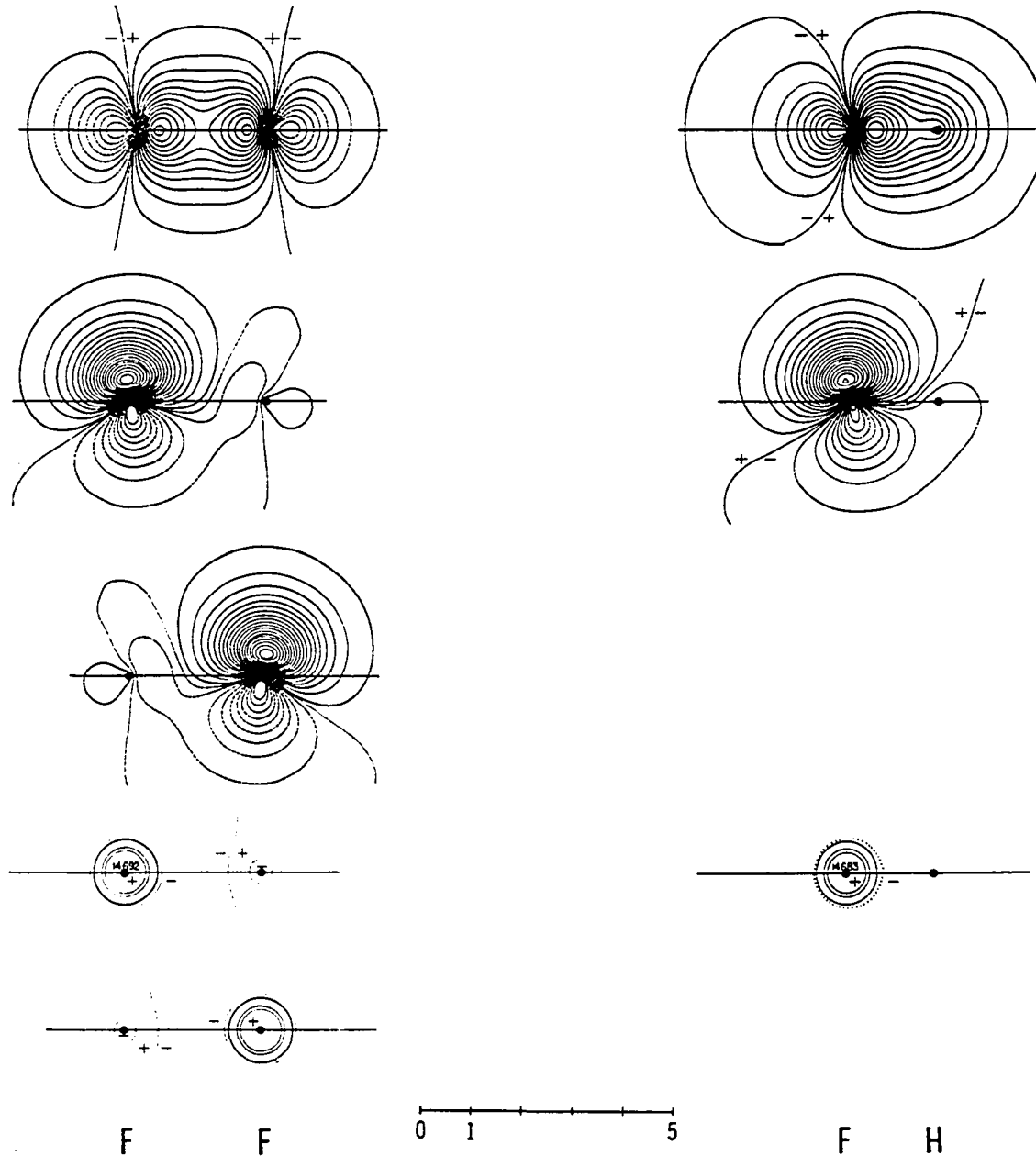


Figure 7. Localized MO's in F_2 and HF

far from being perpendicular to the internuclear axis. It is much less inclined toward the back of the molecule than it would be in the case of tetrahedral hybridization. This shows that the electrostatic repulsion between the three lone pair orbitals is stronger in its effect than the repulsion between any one lone pair and the bonding orbital.

The relation between F_2 and HF is similar to that observed between B_2 and BH. The HF molecule has a sigma bonding orbital and has three trigonally equivalent lone pairs, which are almost identical in character and shape to the corresponding lone pairs of F_2 . These contracted lone pairs are less sensitive to the other atom than those on B. We also find nearly complete transferability between the inner shells. Here again the outermost contour is 0.025 $Bohr^{-3/2}$ and the increment of those contours which are shown is 0.2 $Bohr^{-3/2}$.

The main difference between the two molecules lies in the bonding orbital, although the part of the bonding orbital near the fluorine nucleus is rather similar in the two systems. In both molecules the bonding orbital exhibits a maximum close to the fluorine atom, which arises from the increased ($2p\sigma$) admixture to the bonding orbital. Thus, proceeding from F along the internuclear axis, the orbital rises from the value zero, at the atom, to the maximum, and then begins to drop in the bond region. This is different from what was seen in B_2 and BH.

4. Molecules having a triple bond and sigma lone pairs

The left side of Figure 8 shows the localized orbital structure of the N_2 molecule (BMO). There are one lone pair on each nitrogen atom and three trigonally equivalent "banana" bonds between the two atoms. The outermost contour in each orbital shown in this figure represents an orbital value of 0.025 $Bohr^{-3/2}$. The increment is 0.05 $Bohr^{-3/2}$ for the valence orbitals and 0.2 $Bohr^{-3/2}$ for the inner shell orbitals. There are three bonding orbitals arranged in a trigonally symmetric fashion around the internuclear axis; only one of them is shown in the figure. For this one, the contour lines in the plane containing the orbital maximum and the internuclear axis are exhibited. The three-dimensional contours can be expected to form a three-dimensional cloud essentially above the internuclear axis. The cross section in a plane perpendicular to the axis should be roughly that of a (p)-type distribution. A distinct maximum is observed near each nucleus, but it is less pronounced than those seen in the sigma bonding orbitals of F_2 and HF.

The right side of the figure shows the localized structure of the CO molecule (SAO). The quantitative meanings of the contours are the same as in N_2. CO is isoelectronic with N_2, and the localized orbital structure brings this out very clearly. One can imagine the CO structure as obtained from the N_2 structure by transferring one proton charge from the left nucleus to the right nucleus. This results in the

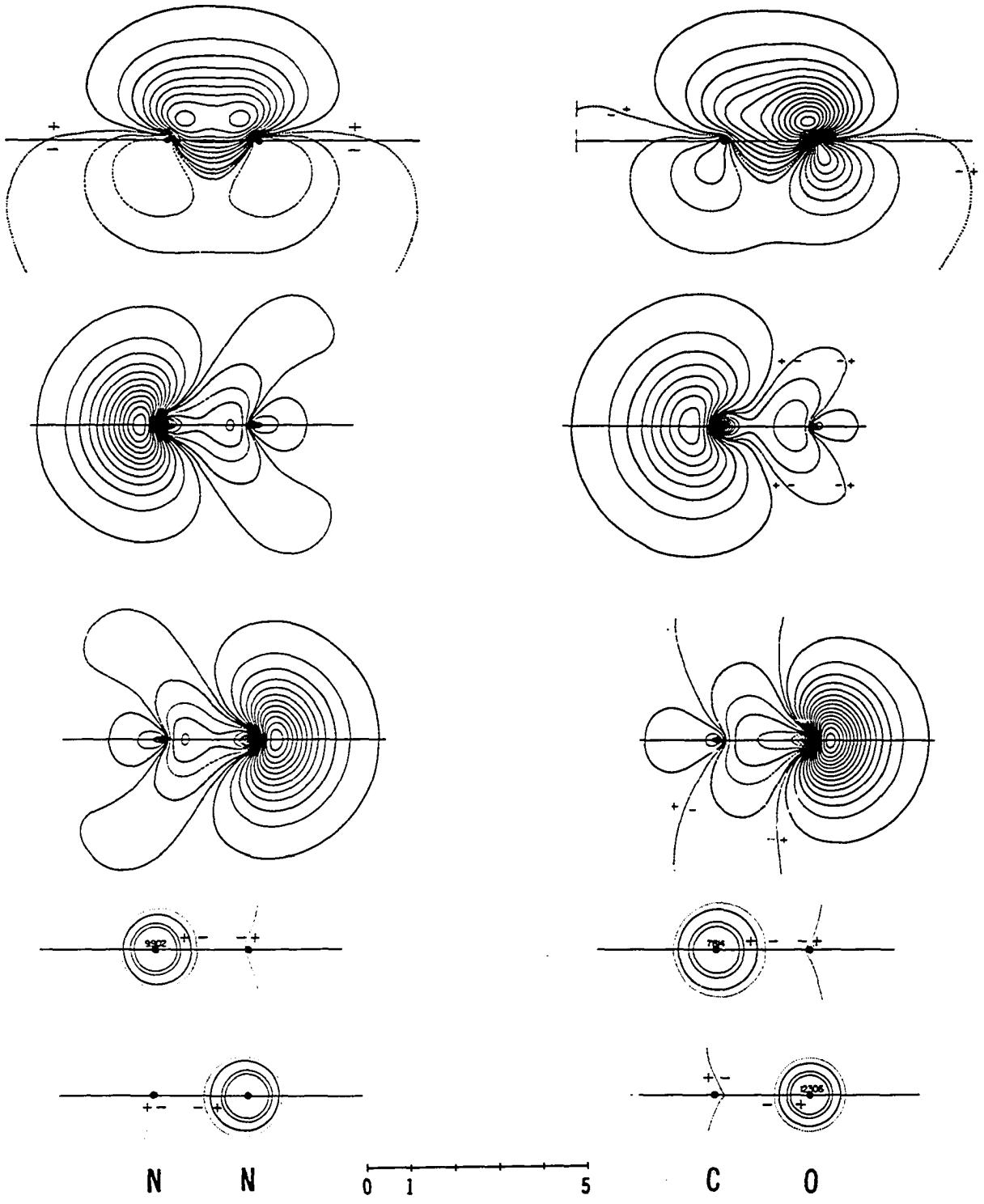


Figure 8. Localized MO's in N_2 and CO

contraction of the lone pair near the O nucleus and the expansion of the lone pair near the C nucleus, as compared to the nitrogen lone pairs. Due to the orthogonality requirement, the negative contours of the carbon lone pair are less spread toward oxygen than are the negative contours of the oxygen lone pair toward carbon. The negative contours of the N_2 lone pairs are intermediate in spread. Moreover, each of the three bonding orbitals is polarized towards the oxygen atom. Finally, the inner shell of oxygen is smaller than that of nitrogen, whereas that of carbon is larger.

The third molecule in this isoelectronic series, BF, is shown on the left side of Figure 9. The localized orbitals (SAO) are completely analogous to N_2 and CO, except that the charge difference between B and F is even greater than that between C and O. Hence the lone pair of fluorine is even more contracted near the F nucleus and more diffuse toward the B nucleus, whereas the lone pair of boron is more expanded near the B nucleus and less spread toward the F nucleus. The inner shell of fluorine is also contracted; the inner shell of boron is expanded. The three trigonal bonding orbitals are even more polarized towards the heavy atom than they were in CO and concomitantly acquire more fluorine character. In fact, near the fluorine atom the trigonal bonding orbitals look similar to the trigonal lone pairs of fluorine found in F_2 and HF, except that the axis is, of course, tilted towards the bond. Since the boron lone pair orbital is considerably

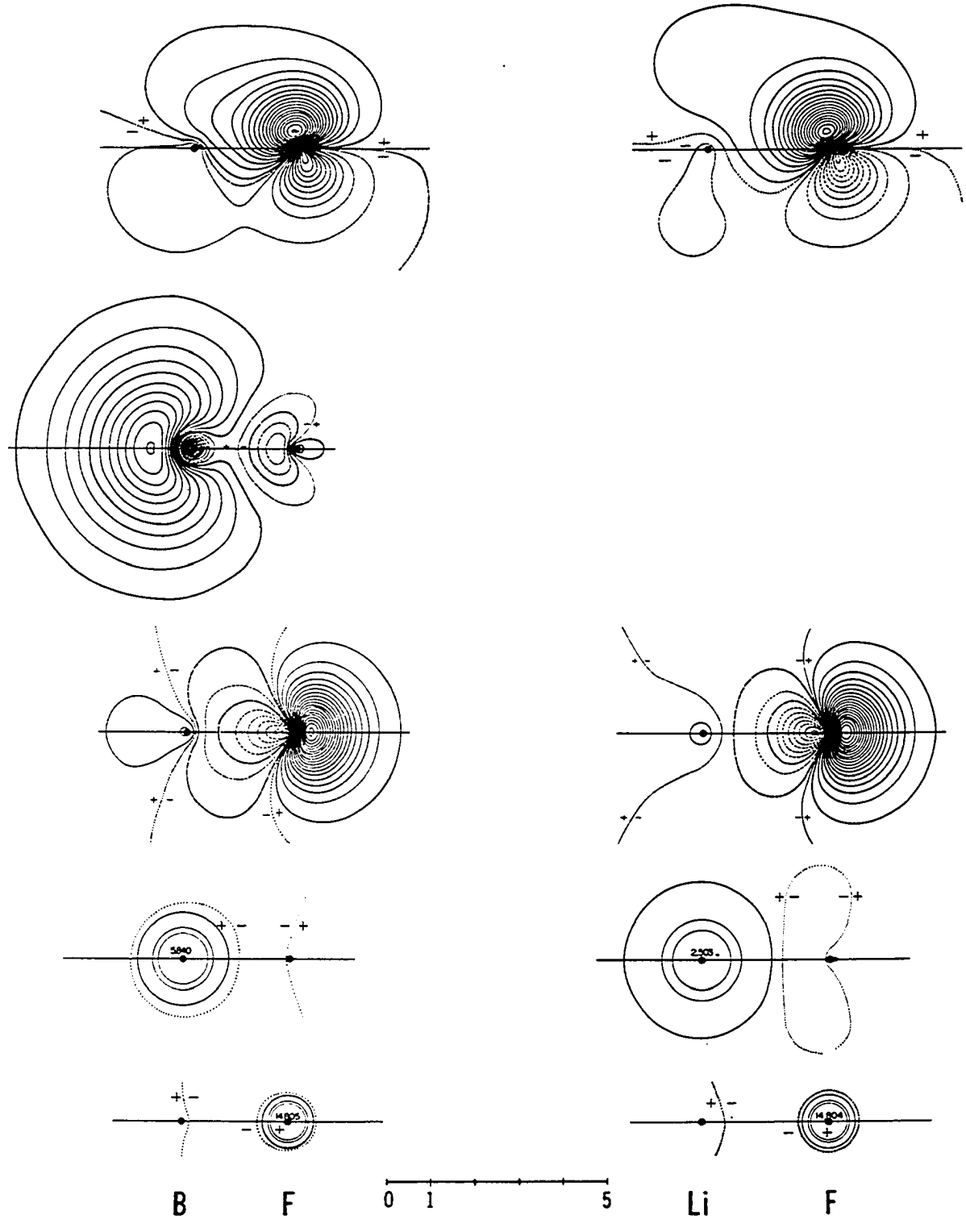


Figure 9. Localized MO's in BF and LiF

more extended, the increment between adjacent contours is chosen to be 0.025 $Bohr^{-3/2}$; that is, a step by two contours in the B lone pair corresponds to a step by one contour in the F lone pair or in the bonding orbital in this figure.

The right side of Figure 9 shows the LiF molecule (SAO). Although it is not isoelectronic with BF, its localized structure is not so different, because it can be thought of as being obtained from the BF molecule by removing two positive nuclear charges and the two lone pair electrons from the boron atom. There remain then the fluorine lone pair and inner shell orbitals, all of which are similar to those found in BF, and the trigonal bonding orbitals which, although they are even more polarized towards the fluorine atom, still show some similarity to those found in BF. The inner shell in lithium is, of course, considerably larger, and similar to that found in Li_2 and in LiH.

5. A molecule having a triple bond and no lone pair

The ground state of the NH molecule has the electron configuration $^3\Sigma\ (1\sigma)^2(2\sigma)^2(3\sigma)^2(\pi x)(\pi y)$. When the πx, πy orbitals are excluded from the localization procedure, the localized structure consists of an inner shell on nitrogen, a lone pair on nitrogen and a sigma bonding orbital. A visualization of this can be obtained from the oxygen atom in the electron configuration $(1s)^2(2s)^2(2p\sigma)^2(2p\pi)(2p\bar{\pi})$. First, we hybridize the (2s) and (2pσ) orbitals to obtain

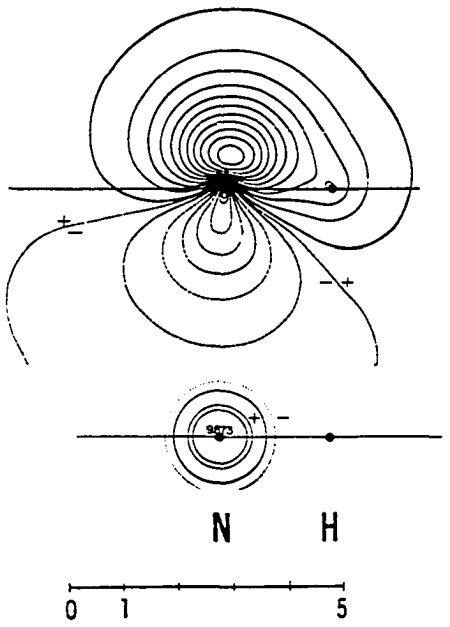


Figure 10. Localized MO's in the $^{1}\Sigma\ (1\sigma)^{2}(2\sigma)^{2}(1\pi)^{4}$ excited state of NH

digonal hybrids. Then, we imagine removing a proton from inside the O nucleus to obtain N and H nuclei. The digonal hybrids on O then become a lone pair on N and a σ bonding orbital.

In Figure 10, there is shown the localized orbital (SAO) structure of the $^{1}\Sigma\ (1\sigma)^{2}(2\sigma)^{2}(1\pi)^{4}$ excited state, which can be thought to result from promoting two electrons from the σ lone pair into the nonbonding orbitals (πx) and (πy), which are essentially atomic (p) orbitals. When this structure is localized, the sigma bonding orbital combines with

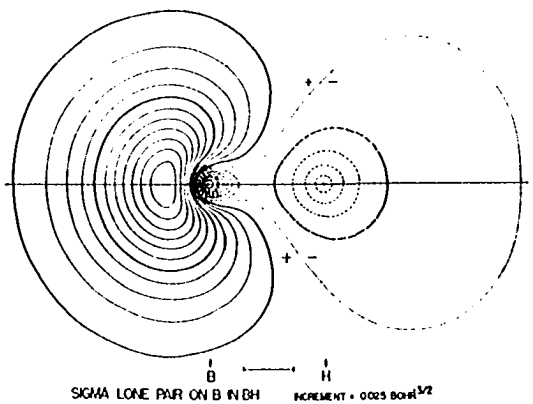
the π orbitals to form three trigonally arranged banana bonds between the nitrogen and the hydrogen, only one of which is shown in the figure. The quantitative meanings of the contours are the same as for N_2 and LiF. Unlike other cases involving a common atom in different molecules (e.g. B_2 , BH, BF), the inner shell in NH is more nearly spherically symmetric about N than are the inner shells on N_2 ; i.e., the atomic (1s) orbitals in N_2 are mixed with the valence atomic orbitals to a slightly greater extent than the nitrogen (1s) orbital in NH. Perhaps this is due to the fact that there is no longer a sigma lone pair. The resulting structure of bonding orbitals is analogous to that found in LiF. This example shows how localization can lead to different localized orbitals in different states of a molecule.

C. Similar Orbitals in Different Molecules

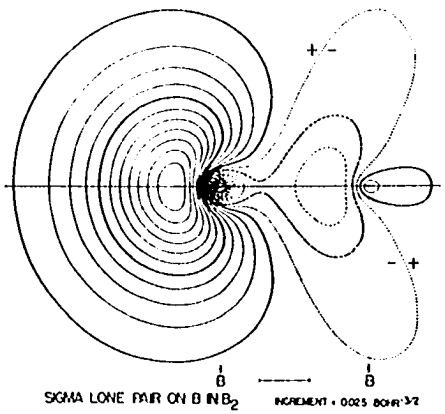
1. Comparison of sigma lone pair orbitals in different molecules

In Figure 11 we have collected all sigma lone pairs for the molecules discussed in the previous section. They are arranged according to increasing nuclear charge. The overall impression is that of a great similarity in the geometrical shapes of the lone pair orbitals. In all cases the density is concentrated on the side of the atom away from the bond, and in all cases the shape is that of an (s-p) hybrid with considerable (s) character. Except for F, the latter is

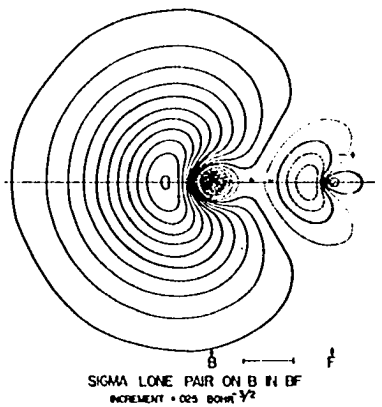
Figure 11. Sigma lone pair MO's for diatomic molecules



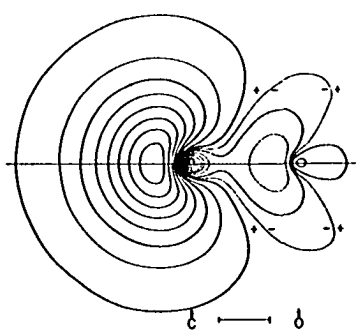
SIGMA LONE PAIR ON B IN BH INCREMENT = 0.025 BOHR$^{-3/2}$



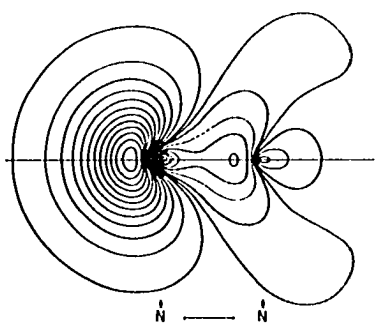
SIGMA LONE PAIR ON B IN B_2 INCREMENT = 0.025 BOHR$^{-3/2}$



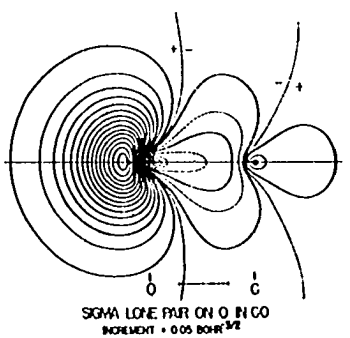
SIGMA LONE PAIR ON B IN BF INCREMENT = 025 BOHR$^{-3/2}$



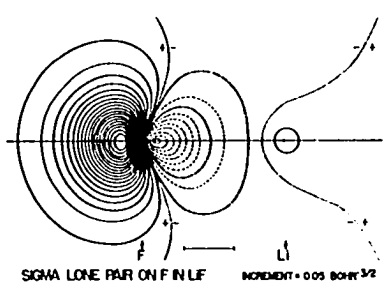
SIGMA LONE PAIR ON C IN CO INCREMENT = 0.05 BOHR$^{-3/2}$



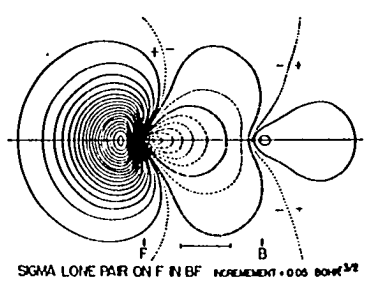
SIGMA LONE PAIR ON N IN N_2 INCREMENT = 0.05 BOHR$^{-3/2}$



SIGMA LONE PAIR ON O IN CO INCREMENT = 0.05 BOHR$^{-3/2}$



SIGMA LONE PAIR ON F IN LiF INCREMENT = 0.05 BOHR$^{-3/2}$



SIGMA LONE PAIR ON F IN BF INCREMENT = 0.05 BOHR$^{-3/2}$

always larger than 50%. The larger the fraction of the valence orbitals which are lone pairs, the larger the (2s) character of the lone pair orbitals (Edmiston and Ruedenberg, 1963, 1965). In all cases, there is a smaller negative contribution towards the second atom. Even though different atoms are involved, the general shape of this usually weak antibonding contribution is fairly uniform. The general lone pair shape is preserved throughout the whole series, even though the overall size of the lone pair orbital decreases progressively as one proceeds from lighter to heavier nuclei.

All lone pair orbitals have a node between the two atoms and, hence, have a slightly antibonding character. This destabilizing effect of the lone pair localized molecular orbitals corresponds to the nonbonded repulsions between lone pair atomic orbitals in the valence bond theory. In the MO theory all bonding and antibonding resonance effects can be described as sums of contributions from orthogonal molecular orbitals. Hence, the "nonbonded repulsions" appear here as "intra-orbital" antibonding effects in contrast to the valence bond description.

Very close transferability can be observed between the three boron and the two fluorine lone pair orbitals. From these results, it appears virtually certain that if one has a localized orbital in a larger molecule, and if one changes some of the atoms which the orbital itself does not reach, then almost absolute transferability can be expected.

2. Comparison of sigma bonding orbitals in different molecules

All sigma bonding orbitals in the molecules considered are collected in Figure 12. To save space, the two outer contours of the Li_2 molecule have been removed (c.f. Figure 4). The bonding orbitals show the overall contraction going from light atoms to heavy atoms. Also observe that in B_2 and F_2, the bonding orbital has negative parts in the lone pair regions, because it has to be orthogonal to the lone pairs; this is not the case in Li_2.

As regards the hydrides, it is of interest to compare the bonding orbitals of BH and HF with the corresponding lone pairs on B and F shown in Figure 11. The similarity in the overall size of the bonding and the lone pair orbitals is quite remarkable. This indicates that there must be a large degree of overlap between the H orbital and the (sp) hybrid of the heavy atom contributing to the bonding orbital. However, it is apparent that this hybrid has more (p) character than the lone pair. In going from LiH to BH to HF the bonding orbital acquires an increasingly greater ($p\sigma$) character because of an increasing amount of nonbonded repulsion from lone pair electrons. This is manifest in the bonding orbital as an elongation and an increased number of negative contours outside the bond region from LiH to BH to HF.

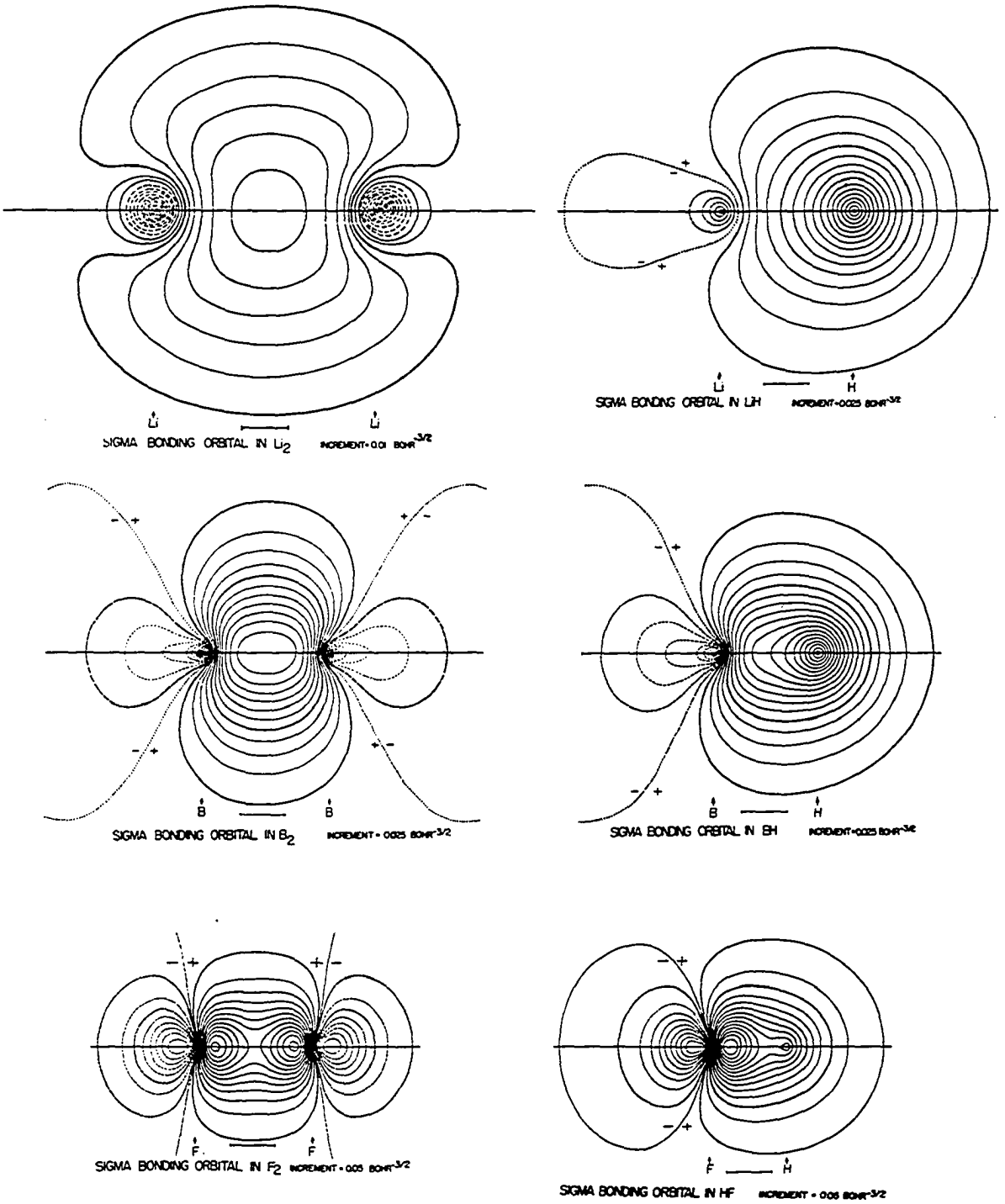


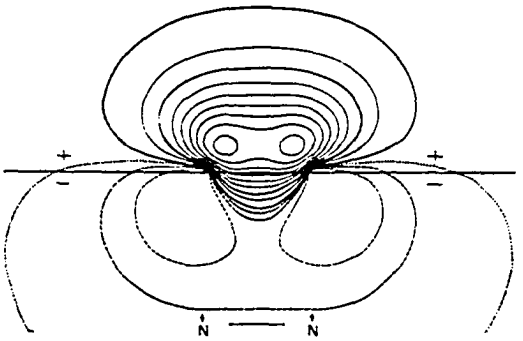
Figure 12. Sigma bonding MO's for diatomic molecules

3. Comparison of trigonal orbitals in different molecules

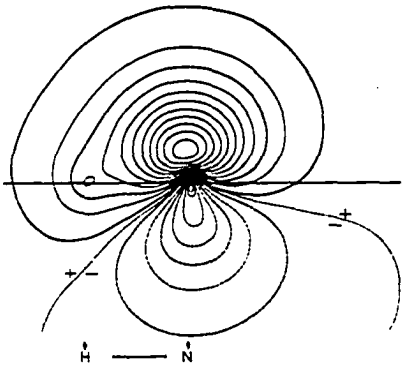
Figure 13 contains all trigonal orbitals in the molecules considered. The bonding orbitals in the left column exhibit the increasing polarization from N_2 to LiF. Moreover, the inclination of the contributing (s-p) hybrid of the right atom into the bond region diminishes as the polarization increases, i.e., the axis of this hybrid is much closer to being perpendicular to the internuclear axis in LiF than in N_2. Clearly, an increase in (p) character accompanies the diminished inclination.

The lone pairs in F_2 are even more nearly perpendicular to the internuclear axis. They are very similar, but the one in HF is slightly more inclined away from the bond; i.e., it has a slightly lower (p) character. This is so, presumably, because the HF bonding orbital puts more charge in the immediate neighborhood of the F atom.

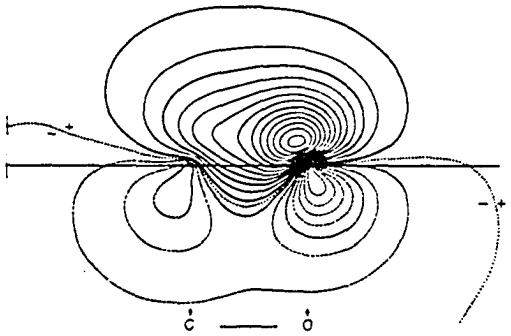
Figure 13. Trigonal bonding and lone pair MO's for diatomic molecules



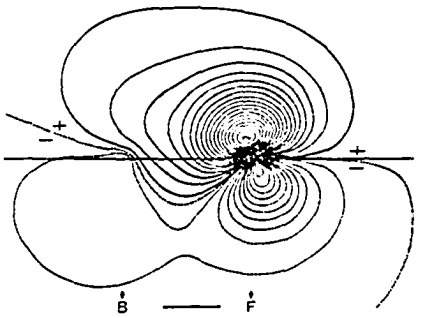
TRIGONAL BONDING ORBITAL IN N_2 INCREMENT=0.05 BOHR$^{-3/2}$



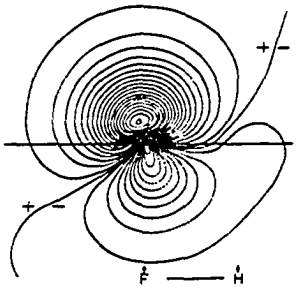
TRIGONAL BONDING ORBITAL IN NH INCREMENT=0.05 BOHR$^{-3/2}$



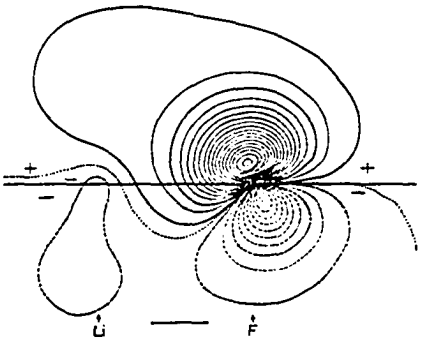
TRIGONAL BONDING ORBITAL IN CO INCREMENT=0.05 BOHR$^{-3/2}$



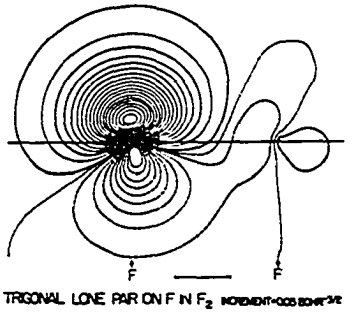
TRIGONAL BONDING ORBITAL IN BF INCREMENT=0.05 BOHR$^{-3/2}$



TRIGONAL LONE PAIR ON F IN HF
INCREMENT=0.05 BOHR$^{-3/2}$



TRIGONAL BONDING ORBITAL IN LiF INCREMENT=.05 BOHR$^{-3/2}$



TRIGONAL LONE PAIR ON F IN F_2 INCREMENT=0.05 BOHR$^{-3/2}$

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