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EXPANSIONS IN SPHERICAL HARMONICS. IV

INTEGRAL FORM OF THE RADIAL DEPENDENCE

by

R. A. Sack

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ERRATA

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Page 12, Eqn. (26)	:	The expression preceding the first integral sign should be put in parentheses.
Page 16, Eqn. (34)	:	Write "ℓ_2" for "ℓ"
Following line	:	Insert "resulting from the substitution of (34)" before "in (32b)"
Page 26, Eqn. (53) and line 13.		Put "G" for "g".
Page 27, line 3	:	Read: "If ϑ_3 is kept fixed", not "ℓ_3"
line 10	:	Read: "three indices" for "two indices"
line 12	:	Insert "Legendre and" before "Bessel functions
Page 29, line 1	:	Insert "ℓ_3" after "m_2"
Page 35, Eqn. (A6)	:	The last "ℓ" in the top line should be "ℓ'".

EXPANSIONS IN SPHERICAL HARMONICS. IV

INTEGRAL FORM OF THE RADIAL DEPENDENCE *

by

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ABSTRACT

A function $f(r_{AB})\, Y_L^M(\vartheta_{AB}, \varphi_{AB})$ of a vector $\underset{\sim}{r}_{AB} = \sum \underset{\sim}{r}_i$ can be expanded in spherical harmonics $Y_\ell^m(\vartheta, \varphi)$ of the directions of the individual vectors. The radial coefficients satisfy simple differential equations which in three previous papers[1] were solved in terms of series in r_i^2/r_j^2 ; these were different in various regions depending on the relative magnitudes of the r_i . In this paper the solutions are found as multiple integrals over the product of Legendre polynomials and of a function $G(w)$ where w depends linearly on the r_i . The kernel $G(w)$ is independent of the number of constituent vectors, their relative sizes and the orders of their harmonics; it contains the Heaviside step function $H(w)$ as a factor which takes care of the various regions. The precise form of G can be found from f and L by an integral equation which for $L = 0, 1$ is solved for arbitrary f , and for $L > 1$ for sufficiently large positive powers. The explicit expressions of Milleur, Twerdochlib and Hirschfelder for the angle average can be obtained simply by repeated integration of $G(w)$ or directly from the differential equations. For the inverse distance between two points $G(w)$ becomes Dirac's delta function; the number of integrations is thereby reduced by one. Possible applications of the new approach to the evaluation of molecular many-center integrals are outlined. Some corrections are given for the results of the previous papers in the series.

AUTHOR

I. Introduction

In a series of three papers[1] the writer has presented a number of expansions for a function of the distance r_{12} between two points Q_1 and Q_2, which are specified by $\underset{\sim}{r}_1$ $(r_1, \vartheta_1, \varphi_1)$ and $\underset{\sim}{r}_2$ $(r_2, \vartheta_2, \varphi_2)$ about a common origin $\mathcal{O}$ or two distinct origins $\mathcal{O}_1$ and $\mathcal{O}_2$; the directions of the polar axes and of the planes defining $\varphi = 0$ are parallel throughout (cf. Figure 1). The dependence on each angle, including ϑ_3 and φ_3 where $\underset{\sim}{r}_3$ $(r_3 = a, \vartheta_3, \varphi_3)$ is the vector $\mathcal{O}_1\mathcal{O}_2$, is given by surface spherical harmonics, expressed either in their unnormalized

$$\Omega_\ell^m(\vartheta,\varphi) = e^{im\varphi}\,\mathcal{P}_\ell^m(\cos\vartheta) \qquad (1a)$$

or normalized forms

$$Y_\ell^m(\vartheta,\varphi) = \left[\frac{(2\ell+1)\,(\ell-m)!}{4\pi\,(\ell+m)!}\right]^{1/2} e^{im\varphi}\,\mathcal{P}_\ell^m(\cos\vartheta), \qquad (1b)$$

where the associated Legendre functions $\mathcal{P}_\ell^m(u)$ are defined by the standard Rodrigues formula,

$$\mathcal{P}_\ell^m(u) = (-)^m \frac{(1-u^2)^{m/2}}{2^\ell\,\ell!}\left(\frac{d}{du}\right)^{\ell+m}(u^2-1)^\ell . \qquad (1c)$$

The expansion for a function

$$V = f(\underset{\sim}{r}_{AB}) = f(\underset{\sim}{r}_1 + \underset{\sim}{r}_2 + \cdots + \underset{\sim}{r}_\nu) \qquad (2a)$$

and more particularly for an isotropic function

$$V = f(r_{AB}) = f(|\underset{\sim}{r}_1 + \underset{\sim}{r}_2 + \cdots + \underset{\sim}{r}_\nu|) \tag{2b}$$

can always be written as[2]

$$V = \sum_{\underset{\sim}{\ell}\,\underset{\sim}{m}} \left[\prod_{i=1}^{\nu} \Omega_{\ell_i}^{m_i}(\vartheta_i, \varphi_i) \right] \cdot \mathcal{R}(f; \underset{\sim}{\ell}, \underset{\sim}{m}; \underset{\sim}{r}). \tag{3}$$

Here the vectors $\underset{\sim}{\ell}$, $\underset{\sim}{m}$ and $\underset{\sim}{r}$ denote the sets of ν values ℓ_i, m_i and r_i respectively; they are not geometric vectors in the 3-dimensional space such as $\underset{\sim}{r}_{AB}$. The summation in (3) in general is to be taken over each ℓ_i from 0 to ∞ and each m_i from $-\ell_i$ to ℓ_i. The only cases hitherto considered in detail have been $\nu = 2$ and $\nu = 3$ which are relevant for the one-center and two-center expansions respectively.

The basis of the theory developed in I–III was that since V depends on each x_i only through the linear combination $\sum x_i$, the derivatives $\partial/\partial x_i$ are the same for all i and correspondingly for $\partial/\partial y_i$ and $\partial/\partial z_i$. In particular

$$\nabla_1^2 V = \nabla_2^2 V = \cdots \nabla_\nu^2 V \tag{4}$$

which when substituted in (3) yields for each individual $R(\underset{\sim}{\ell}, \underset{\sim}{m}; \underset{\sim}{r})$

$$\left(\partial^2/\partial r_i^2 + (2/r)\partial/\partial r - \ell_i(\ell_i+1)/r^2\right) \mathcal{R} = \textit{invariant} \quad (i = 1, 2 \ldots \nu). \tag{5}$$

By solving (5) together with the appropriate boundary conditions for

$$V = r_{AB}^{\ N} \quad \text{and} \quad V = r_{AB}^{\ N}\, \Omega_L^{\ M}(\vartheta_{AB}, \varphi_{AB}) \tag{6a,b}$$

the writer was able to derive explicit expressions for R in terms of hypergeometric functions (Appell functions for $\nu=3$)[3]; some of the one-center expansions for isotropic V had already been found by Chapman[4] using a different approach. The explicit forms of the radial functions differ according to the relative sizes of the r_i ; for $\nu=2$ there are two regions

$$S_1 : r_1 > r_2 \quad , \quad S_2 : r_2 > r_1 \quad ; \tag{7a}$$

for $\nu=3$ there are four regions as first shown by Buehler and Hirschfelder[5]

$$\begin{aligned} &S_1 : r_1 > r_2 + r_3 \ , \quad S_3 : r_3 > r_1 + r_2 \ , \\ &S_2 : r_2 > r_1 + r_3 \ , \quad S_4 : |r_1 - r_2| < r_3 < r_1 + r_2 \ , \end{aligned} \tag{7b}$$

(see Figure 2). Whereas in the case (6a) the series expressions for R are convergent and reasonably simple in the outer regions S_1, S_2 and S_3 , the corresponding series in the overlap region S_0 are in general divergent, and the only explicit series obtained in III were for integer N = -1,0,1,2...; even these were not likely to be of great practical use, e.g. for numerical integrations, for large ℓ_i because of the partial cancellation of large terms with a small algebraic sum. In the one-center expansion of isotropic functions of the type (2b) quadratic transformations applied to the hypergeometric functions led in I to expressions for R which were symmetric in r_1 and r_2 ; some of these had already been derived by Chapman[4] and by Fontana[6], but the appearance of powers of (r_1+r_2) or $(r_1^2+r_2^2)$ in the denominator seems to preclude their usefulness for most practical purposes. Fontana[6] has also outlined an approach to an analogous symmetric two-center expansion, but for reasons to be given in a later paper, these expansions would not be absolutely convergent everywhere, quite apart from the complicated analytic form they would take.

A rather different approach to the two-center expansion has been taken independently by Nozawa[7] and Chiu[8]. Both these authors are essentially concerned with the solution of the wave equation $\nabla^2 V = \pm k^2 V$, but their method can be directly applied to any function V . They first break up the vector $\tilde{r}_{12}$ into $\tilde{r}_1$ and $\tilde{r}_2'$ where $\tilde{r}_2' = 0_1Q_2$ and employ the usual one-center expansion, and then similarly re-expand the dependence on $\tilde{r}_2'$ in terms of r_2 and r_3 . As a result they obtain different expressions for R in three regions only

$$\begin{aligned} &S_1' : r_1 > r_2' , \\ &S_2' : r_1 < r_2' , \; r_2 > r_3 , \\ &S_3' : r_1 < r_2' , \; r_3 > r_2 , \end{aligned} \tag{8}$$

(there is no subdivision of S_1') . The regions S_1, S_2 and S_3 of (7b) are completely contained in their primed counterparts and the expressions obtained are obviously pairwise identical, and in addition the overlap region S_o is split up between the three regions of (8). But as the magnitude of r_2' depends on the angle ω_{23} between $\tilde{r}_2$ and $\tilde{r}_3$, the boundary between S_1' on the one hand and S_2' or S_3'

on the other depends on ϑ_2, φ_2, ϑ_3 and φ_3, and in the expansion (3) the variables are no longer strictly separated as the radial coefficients R involve the angles. In consequence it is no longer possible to use the orthogonality relations for the surface harmonics to carry out the integration over the angles. And any attempt to extend the validity of the expressions for the outer regions into S_o in such a way that the boundaries are independent of the angles, e.g. by using the formulas for S_i whenever r_i is the largest of the three vectors will make the expansion (3) diverge as was already implicit in the work of Carlson and Rushbrooke[9] on r_{12}^{-1} ; though these authors avoid any explicit mention of the overlap region, they specify in which regions the other formulas converge, and these exclude S_o . If additional factors multiplying V enforce convergence after integration over angles, the results obtained in S_o from formulas valid in S_i are likely to be erroneous. For these reasons the writer considers any expansion of the form (3) which ignores the distinct form of the radial coefficient R in S_o , while not necessarily incorrect, at any rate not very useful for most practical purposes.

Recently a new approach to the two-center expansion has been made by Milleur, Twerdochlib and Hirschfelder[10]. For an isotropic function $f(r_{12})$ they obtained simple expressions for the angle average $\langle f \rangle = R(f;\, \underset{\sim}{0}\, \underset{\sim}{0};\, \underset{\sim}{r})$ by explicit integration over angles. The results involve the r_i only as linear combinations $(\pm r_1 \pm r_2 \pm r_3)$, and the functions appearing are obtained from f by integration so that the method is applicable to fractional powers and to piece-wise continuous functions to which the series expansions for R derived in III cannot be applied. Two questions posed themselves immediately:

(a) Could the closed form expressions for the angle average be obtained more simply as solutions of the differential equations (5) with the appropriate boundary conditions?

(b) Could the general solution of the equations (5) with arbitrary ℓ_i be given in a form which preserved the linearity in the r_i ?

Both these problems were quickly resolved, and the new derivations are presented in sections 2 and 3 respectively. It was too much to expect closed expressions for the solutions of (b), hence attempts in this direction were quickly abandoned. Instead solutions were successfully sought in terms of an integral over a function $G(w)$ where w is a linear function of the r_i . This function was found to be independent of the ℓ_i and of the regions S_i , its exact form is determined by a Volterra-type integral equation involving $V(\underset{\sim}{r})$ and the Heaviside function

$$\begin{aligned} H(w) &= 1 \qquad w \geqslant 1 \\ H(w) &= 0 \qquad w < 1 \end{aligned} \tag{9}$$

the derivative of which is Dirac's delta function $\delta(w)$. The explicit solution of this equation was obtained for functions V given by (2b) or (6), in the latter case only for sufficiently large N .

The intervention of the factor $H(w)$ automatically takes care of the different analytic forms of the integrals in the various regions; its influence on the solution and special forms of the results are discussed in Section 4, and in Section 5 some applications of the new approach for the evaluation of 2, 3 and 4 center integrals are outlined.

2. The Angle Average

The formula derived by Milleur, Twerdochlib and Hirschfelder[10] for the angle average $\langle f \rangle$, i.e. for the radial coefficient $R(\underset{\sim}{0}, \underset{\sim}{0}; r)$, of a spherically symmetric function $f(r_{AB})$ or $f(r_{12})$ is

$$\text{In } S_o: \quad \langle f \rangle = \frac{1}{4 r_1 r_2 r_3}\Big[h(r_1+r_2+r_3) - h(r_1+r_2-r_3) - h(r_1-r_2+r_3) - h(r_2-r_1+r_3)\Big], \tag{10a}$$

$$\text{In } S_1: \quad \langle f \rangle = \frac{1}{4 r_1 r_2 r_3}\Big[h(r_1+r_2+r_3) - h(r_1+r_2-r_3) - h(r_1-r_2+r_3) + h(r_1-r_2-r_3)\Big] \tag{10b}$$

where

$$h(w) = \int_0^w v(w-v)\, f(v)\, dv \ ; \tag{11}$$

the expressions valid in S_2 and S_3 are obtained from (10b) by permutation of the indices. Substitution of this integral in (10) shows that the lower limit of integration is immaterial in S_1, though not in S_o; in consequence a singularity of $f(r_{12})$ at $r_{12} = 0$ will not show up in $\langle f \rangle$ in the outer regions, but may crucially affect the result in the overlap region. Thus for $f(r_{12}) = r_{12}^N$ (10b) remains meaningful for all N, provided the lower limit in (11) is taken to be $\epsilon > 0$; on the other hand convergence of the individual terms in (10a) requires $N > -3$. The formulas (10) and (11) have a well-defined meaning for any function $f(r_{12})$ which is integrable for all non-negative r_{12}; no analyticity of f need be assumed as was required in III.

The expressions (10) and (11) were obtained by Milleur, Twerdochlib and Hirschfelder[10] by integrations over the geometric angles. To derive the same results as solutions of differential equations, we must put all the ℓ_i equal to zero in (5). Consider first the one-center case $\nu = 2$ and put

$$T = r_1 r_2 \langle f \rangle \quad . \tag{12}$$

For this function (5) becomes

$$\partial^2 T / \partial r_1^2 = \partial^2 T / \partial r_2^2 \, , \tag{13}$$

which is d'Alembert's equation with the well-known general solution

$$T = g_1(r_1 + r_2) + g_2(r_1 - r_2) \, . \tag{14a}$$

Hence $\langle f \rangle$ must be of the form

$$\langle f \rangle = (r_1 r_2)^{-1} \left[g_1(r_1 + r_2) + g_2(r_1 - r_2) \right] . \tag{14b}$$

However as r_2 tends to zero in the region S_1 , $\langle f \rangle$ tends to $f(r_1)$; hence by L'Hôpital's rule

$$g_1(r_1) \equiv -g_2(r_1) = \tfrac{1}{2} g(r_1) \, , \tag{15a}$$

$$r_1^{-1} \, dg(r_1)/dr_1 = f(r_1) \tag{15b}$$

or

$$g(w) = \int_0^w v\, f(v)\, dv\ , \tag{16}$$

although again the lower limit of integration is essentially arbitrary. The angle average is thus

$$\text{In } S_1 : \quad \langle f \rangle = \left[g(r_1 + r_2) - g(r_1 - r_2) \right] (2 r_1 r_2)^{-1}\ , \tag{17a}$$

$$\text{In } S_2 : \quad \langle f \rangle = \left[g(r_1 + r_2) - g(r_2 - r_1) \right] (2 r_1 r_2)^{-1}\ , \tag{17b}$$

with $g(w)$ defined in (16); the second formula follows from the first by symmetry. For the two-center case ($\nu = 3$) we put

$$T = r_1\, r_2\, r_3\, \langle f \rangle\ , \tag{18}$$

for which (5) becomes

$$\partial^2 T / \partial r_1^2 = \partial^2 T / \partial r_2^2 = \partial^2 T / \partial r_3^2\ . \tag{19}$$

Considering the three sides of this equation in pairs we see that each r_i is coupled to the others by addition or subtraction as in (14a), hence $\langle f \rangle$ is of the form

$$\langle f \rangle = (r_1 r_2 r_3)^{-1} \left[h_1(r_1 + r_2 + r_3) + h_2(r_1 + r_2 - r_3) + h_3(r_1 - r_2 + r_3) + h_4(r_1 - r_2 - r_3) \right]. \tag{20}$$

As r_3 tends to zero in S_1, (20) must tend to (17a) and a renewed application of L'Hôpital's rule yields the solution (11) and (10b). The formulas valid in S_2 and S_3 follow from symmetry, and (10a) can be deduced as the only function of the form (20) which smoothly links the known solutions in the outer regions.

Both (16), (17) and (10), (11) can be written in a form independent of the region in which they apply by making use of the Heaviside function $H(w)$:

$$\langle f \rangle = (2r_1 r_2)^{-1} \sum_{\underset{\sim}{\sigma}} (-)^{\sigma_1+\sigma_2} g(\sigma_1 r_1 + \sigma_2 r_2)\, H(\sigma_1 r_1 + \sigma_2 r_2) \tag{21a}$$

$$\langle f \rangle = (4r_1 r_2 r_3)^{-1} \sum_{\underset{\sim}{\sigma}} (-)^{\sigma_1+\sigma_2+\sigma_3} h(\sigma_1 r_1 + \sigma_2 r_2 + \sigma_3 r_3)\, H(\sigma_1 r_1 + \sigma_2 r_2 + \sigma_3 r_3) \tag{21b}$$

where each σ_i can take the values ± 1 independently. The step function thus takes care of the various regions by eliminating terms of negative argument; there should be no ambiguity on the boundaries of the regions as long as g(0) or h(0) vanish, i.e. as long as $v\, f(v)$ (or its integral) is integrable at $v = 0$.

The generalization of (10), (11) for the angle average of a function $f(r_{AB})$ where $\underset{\sim}{r}_{AB}$ is composed of an arbitrary number ν of vectors (cf. 2b) follows easily by induction

$$R(\underset{\sim}{0}, \underset{\sim}{0}; \underset{\sim}{r}) = 2^{1-\nu} \left(\prod r_i\right)^{-1} \sum_{\underset{\sim}{\sigma}} (-)^{\Sigma \sigma_i} g_\nu \left(\sum_1^\nu \sigma_i r_i\right), \tag{22a}$$

where

$$g_1(w) = w\, f(w)\, H(w) \quad ; \quad g_\nu(w) = \int_0^w g_{\nu-1}(v)\, dv. \tag{22b}$$

3. Integral Solutions for Arbitrary l_i.

(i) General form of the solutions.

The differential equations (5) for the radial coefficients R do not involve the azimuthal quantum numbers m_i , which can therefore affect the solution only in the form of a constant factor; hence the functions R can always be decomposed into two factors, one depending on $\underset{\sim}{l}$ and $\underset{\sim}{m}$ only, the other on $\underset{\sim}{l}$ and $\underset{\sim}{r}$ as well as on the nature of the functions V to be expanded:

$$R\left(V; \underset{\sim}{l}, \underset{\sim}{m}; \underset{\sim}{r}\right) = K''(\underset{\sim}{l}, \underset{\sim}{m}) \times R''\left(V; \underset{\sim}{l}; \underset{\sim}{r}\right). \tag{23}$$

As already pointed out in II and III, this partitioning is not unique, as any dependence on the $\underset{\sim}{l}$ only may be drawn into either factor.

As mentioned in the introduction the chief aim of the present investigation was to establish solutions of (5) involving the r_i only in linear combinations, i.e. in the form

$$G(w) = G\left(r_1 u_1 + r_2 u_2 + \ldots + r_\nu u_\nu\right) \tag{24}$$

summed or integrated over various values of u_i . As the solution was bound to involve the rotational quantum numbers ℓ_i in some way the most obvious trial solution was

$$\mathcal{R}''(\underset{\sim}{\ell}, \underset{\sim}{r}) = \int_{-1}^{1} \cdots \int_{-1}^{1} du_1\, du_2 \cdots du_\nu$$

$$\times\ G(w)\, P_{\ell_1}(u_1) P_{\ell_2}(u_2) \cdots P_{\ell_\nu}(u_\nu)\ . \qquad (25)$$

Assuming that $G(w)$ has a second derivative everywhere and applying the r_1-operator of (5) to the first integral in (25) only we obtain:

$$\frac{\partial^2}{\partial r_1^2} + \frac{2}{r_1}\frac{\partial}{\partial r_1} - \frac{\ell_1(\ell_1+1)}{r_1^2} \int_{-1}^{1} G(w)\, P_{\ell_1}(u_1)\, du_1 =$$

$$= \int_{-1}^{1} \left[u_1^2\, G''(w) + \frac{2u_1}{r_1^2}\, G'(w) - \frac{\ell_1(\ell_1+1)}{r_1^2}\, G(w)\right] P_{\ell_1}(u_1)\, du_1$$

$$= \int_{-1}^{1} G''(w)\, P_{\ell_1}(u_1)\, du_1$$

$$+ \int_{-1}^{1} \left[\frac{d}{du_1} \frac{(u_1^2-1)\, G'(w)}{r_1} - \frac{\ell_1(\ell_1+1)\, G(w)}{r_1^2}\right] P_{\ell_1}(u_1)\, du_1\ ) \qquad (26)$$

where the last integral vanishes on integration by parts. The r_1-operator in (5) applied to the trial function R'' of (25) yields thus a similar ν-fold integral, with $G''(w)$ replacing $G(w)$; the resulting expression is thus invariant whichever particular operator in (5) is chosen, and (25) is indeed a solution of (5). The general nature of G makes it likely that (25) represents the general solution of (5) except possibly for some singular solutions. Although for the purposes of the proof it has been assumed that $G(w)$ possesses second derivatives everywhere, this is not a necessary condition as even a discontinuous $G(w)$ can be treated as the limit of a sequence of functions with second derivatives.

Having thus established the general nature of the solution of (5) we next have to show that for the expansion of a function

$$V = f(r_{AB}) \; \Omega_L^M (\vartheta_{AB}, \varphi_{AB}) \tag{27}$$

(which includes (2b) as a special case) with a suitable choice of the factor K'' the function $G(w)$ is independent of the number of component vectors ν and the rotational quantum numbers ℓ_i. Once this has been established it remains to determine the dependence of G on f and L.

(ii) Invariance of G.

The transformation properties of the spherical harmonics Ω_ℓ^m or Y_ℓ^m of (1) under rotation require that the coefficients of each individual term in (3) involve the azimuthal quantum numbers m only through the integrals (generalized Gaunt's coefficients)

$$I_\Omega \begin{pmatrix} \ell_1 & \ell_2 \cdots & \ell_s \\ m_1 & m_2 \cdots & m_s \end{pmatrix} = \int_{-1}^{1} \prod_{1}^{s} P_{\ell_j}^{m_j}(u) \cdot du \tag{28}$$

or

$$I_Y'\begin{pmatrix} l_1 & l_2 \dots & l_s \\ m_1 & m_2 \dots & m_s \end{pmatrix} = \int_0^{\pi}\int_0^{2\pi} \prod_1^s Y_{l_j}^{m_j}(\vartheta,\varphi)\cdot \sin\vartheta\, d\vartheta\, d\varphi. \quad (29)$$

The latter integral vanishes unless

$$\sum_1^s m_j = 0\,, \quad (30a)$$

$$\sum_1^s l_j = \text{even} = 2\Lambda\,, \quad (30b)$$

$$\Lambda - l_j \geq 0 \qquad (j = 1, 2 \dots s)\,. \quad (30c)$$

Here (30b) follows from parity considerations and (30a) and (30c) from the orthogonality relations of the spherical harmonics. The integral I_Ω in (28) does not necessarily vanish if (30a) is violated, but as the only integrals of importance are those for which (30a) is valid, we assume the relation must hold. In view of the writers personal preference for unnormalized harmonics, the derivation will be given in terms of these functions; some of the formulas required in this section are derived in Appendix A if their presentation here would interrupt the flow of the argument.

If in the expansion of (27) we put for the $\underset{\sim}{m}$-dependent coefficient K'' of R (cf. (3) and (23)):

$$K''(\underset{\sim}{l}, \underset{\sim}{m}) = (-)^M \prod_1^\nu (l_i + \tfrac{1}{2}) \times I_\Omega \begin{pmatrix} L & l_1 & l_2 \dots & l_\nu \\ M & -m_1 & -m_2 \dots & -m_\nu \end{pmatrix}, \quad (31)$$

the I_Ω is a consequence of the transformation properties, the additional factors have been chosen for convenience. To show that with this choice of K'' the function $G(\boldsymbol{w})$ in (24) and (25) is indeed independent of ν and $\underset{\sim}{\ell}$ we note that by making $r_\nu = 0$, the only dependence of the integrand of (25) on u_ν is through the Legendre polynomial; hence by orthogonality all the integrals (25) vanish, unless $\ell_\nu = 0$, in which case the integral is just twice that obtained with r_ν and u_ν missing; at the same time (31) has exactly half the value it would have in the absence of $\ell_\nu + \frac{1}{2}$. Hence for the expansion (3) to be invariant under the addition of an arbitrary number of zero vectors, $G(\boldsymbol{w})$ must be invariant under the accretion or deletion of an arbitrary number of u_j terms with $\ell_j = 0$.

More generally we can show that the invariance of G in (25) ensures the identity of the expansion (3) whether we take two radii (say $\underset{\sim}{r}_1$ and $\underset{\sim}{r}_2$) in the same direction or take a single vector of magnitude $r_1 + r_2$. Collecting only those factors in (3), (25) and (31) which depend on $(\vartheta_1, \varphi_1) = (\vartheta_2, \varphi_2)$, ℓ_1 and ℓ_2 and summing over these, we obtain in the one case the contribution

$$J_1 = \sum_{\ell_1 m_1} \sum_{\ell_2 m_2} \iint \Omega_{\ell_1}^{m_1}(\vartheta, \varphi)\, \Omega_{\ell_2}^{m_2}(\vartheta, \varphi)$$

$$\times (\ell_1 + \tfrac{1}{2})(\ell_2 + \tfrac{1}{2})\, I_\Omega \begin{pmatrix} L & \ell_1 & \ell_2 & \cdots & \ell_\nu \\ M & -m_1 & -m_2 & \cdots & -m_\nu \end{pmatrix} \qquad (32a)$$

$$\times\, P_{\ell_1}(u_1) P_{\ell_2}(u_2)\, G(r_1 u_1 + r_2 u_2 + \cdots)\, du_1\, du_2$$

and in the other

$$J_2 = \sum_{\ell m} \int \Omega_\ell^m(\vartheta,\varphi) \left(\ell+\tfrac{1}{2}\right) I_\Omega \begin{pmatrix} L & \ell & \dots & \ell_\nu \\ M & -m & \dots & -m_\nu \end{pmatrix}$$

$$\times P_\ell(u_1)\, G\left[(r_1+r_2)u_1 + \dots\right] du_1 \quad . \tag{32b}$$

The products of two spherical harmonics in (32a) can be expanded in the usual way as sums of single harmonics

$$\Omega_{\ell_1}^{m_1}(\vartheta,\varphi)\, \Omega_{\ell_2}^{m_2}(\vartheta,\varphi) = \sum_\ell (-)^m I_\Omega \begin{pmatrix} \ell & \ell_1 & \ell_2 \\ -m & m_1 & m_2 \end{pmatrix} \left(\ell+\tfrac{1}{2}\right) \Omega_\ell^m(\vartheta,\varphi), \tag{33}$$

$$m = m_1 + m_2 \quad ,$$

whereas the single integral in (32b) can be converted into a double one with the same argument for G as in (32a) by multiplying with the delta function

$$\delta(u_1 - u_2) = \sum \left(\ell+\tfrac{1}{2}\right) P_\ell(u_1)\, P_\ell(u_2) \quad . \tag{34}$$

On expanding the products of Legendre functions of u_1 in (32b) the same way as in (33) we obtain as the factor of

$$\left(\ell+\tfrac{1}{2}\right)\left(\ell_1+\tfrac{1}{2}\right)\left(\ell_2+\tfrac{1}{2}\right) \Omega_\ell^m(\vartheta,\varphi)\, P_{\ell_1}(u_1)\, P_{\ell_2}(u_2)\, G(w) \tag{35a}$$

from (32b) and (34)

$$\bar{I}_{\Omega}\begin{pmatrix} L & \ell \ldots & \ell_\nu \\ M & -m \ldots & -m_\nu \end{pmatrix} \bar{I}_{\Omega}\begin{pmatrix} \ell_1 & \ell_2 & \ell \\ 0 & 0 & 0 \end{pmatrix}, \tag{35b}$$

and from (32a) and (33)

$$(-)^m \sum_{m_1} \bar{I}_{\Omega}\begin{pmatrix} \ell & \ell_1 & \ell_2 \\ -m & m_1 & m_2 \end{pmatrix} \bar{I}_{\Omega}\begin{pmatrix} L & \ell_1 & \ell_2 \ldots \\ M & -m_1 & m_1 - m \ldots \end{pmatrix} \tag{35c}$$

$$= \sum_{m_1, \lambda} \bar{I}_{\Omega}\begin{pmatrix} \ell & \ell_1 & \ell_2 \\ -m & m_1 & m-m_1 \end{pmatrix} (\lambda + \tfrac{1}{2}) \bar{I}_{\Omega}\begin{pmatrix} L & \lambda & \ldots \\ M & -m & \ldots \end{pmatrix} \bar{I}_{\Omega}\begin{pmatrix} \lambda & \ell_1 & \ell_2 \\ m & -m_1 & m_1 - m \end{pmatrix} \tag{35d}$$

$$= \sum_{\lambda} \delta_{\ell\lambda} \bar{I}_{\Omega}\begin{pmatrix} L & \lambda & \ldots \\ M & -m & \ldots \end{pmatrix} \bar{I}_{\Omega}\begin{pmatrix} \ell & \ell_1 & \ell_2 \\ 0 & 0 & 0 \end{pmatrix} \tag{35e}$$

in view of (A3) and (A6). The expressions (32a) and (32b) are thus identical provided $G(\omega)$ does not depend on ν or the $\underset{\sim}{\ell}$. While this is not a rigorous proof that $G(\omega)$ <u>must</u> be independent of these quantities, it makes it more than plausible. A complete proof would have to show that the reduction for ν to ν -1 vectors gives identical results even when $(\vartheta_1, \varphi_1) \neq (\vartheta_2, \varphi_2)$; the writer has been able to derive such a proof, but as it involves quite a number of intermediary lemmas, it will be omitted here.

If the spherical harmonics in both (3) and (27) are given in normalized form, we obtain for the factor K''_γ from (1), (29) and (31)

$$K_\gamma''(\underset{\sim}{l}, \underset{\sim}{m}) = (-)^M (2\pi)^{\nu-1} I_\gamma' \begin{pmatrix} L & l_1 & l_2 \ldots l_\nu \\ M & -m_1 & -m_2 \ldots -m_\nu \end{pmatrix}. \quad (36)$$

(iii) Relation of f and G .

Having established the invariance of $G(w)$ with ν and $\underset{\sim}{l}$, it is an easy matter to find the exact relation of $G(w)$ to f and L in (27). One simply has to put $\nu = 1$, in which case only one term in the expansion (3) survives in view of the orthogonality relations, and the equation to be solved becomes

$$f(r) = \int_{-1}^{1} G(ru)\, P_L(u)\, du \,. \quad (37)$$

Here it should be noticed that r can by definition take only real non-negative values and $f(r)$ can to some extent be chosen arbitrarily for $r < 0$. The easiest way to achieve this is by multiplying $f(r)$ by the Heaviside function H(r) ; any ambiguities arising from branch points of f(r) at r=0 are thereby automatically eliminated. Correspondingly we may choose $G(w) \equiv 0$ for $w < 0$ so that (37) becomes

$$f(r)\, H(r) = \int_0^1 G_L(ru)\, P_L(u)\, du \,, \quad (38)$$

where the suffix L has been added to G to indicate which Legendre polynomial enters into the transform. For L = 0 we obtain

$$f(r)\ H(r) = \int_0^r G_0(w)\,(dw/r) \tag{39}$$

with the solution

$$G_0(w) = (d/dw)\left[w\, f(w)\ H(w)\right]. \tag{40}$$

For L = 1 the corresponding equation and solution are

$$f(r)\ H(r) = \int_0^r G_1(w)\,(w/r)\,(dw/r)\ , \tag{41}$$

$$G_1(w) = w^{-1}\,(d/dw)\left[w^2 f(w)\,H(w)\right]. \tag{42}$$

The solutions for the transforms in (38) with $L > 1$ are less straightforward in general, and the only case discussed in the present paper is that of a real power $f(r) = r^N$. It is obvious from (38) that $G_L(w)$ must also be proportional to the same power

$$G_L(w) = C_{LN}\ w^N\ H(w)\ , \tag{43}$$

where C_{LN} is the reciprocal of the integral

$$\int_0^1 P_L(u)\,u^N du = \frac{\pi^{1/2}\,\Gamma(1+N)\ 2^{-1-N}}{\Gamma(1+\frac{1}{2}N-\frac{1}{2}L)\,\Gamma(\frac{3}{2}+\frac{1}{2}N+\frac{1}{2}L)} \tag{44}$$

(cf. (3.12.23) of Ref.[3]). Hence we get

$$C_{LN} = \frac{(1+N)(3+N)\ldots(L+N+1)}{(2+N-L)(4+N-L)\ldots N}, \qquad L \text{ even} \tag{45a}$$

$$= \frac{(2+N)(4+N)\ldots(L+N+1)}{(2+N-L)(4+N-L)\ldots(N-1)}, \qquad L \text{ odd} \tag{45b}$$

valid for

$$N > L-2 \ . \tag{45c}$$

The exceptions are $L = 0$ and $L = 1$ for which the products in the denominators of (45 a,b) become empty with the value unity, and hence these formulas remain valid provided

$$N > -1 \quad , \; L = 0 \; , \tag{45d}$$

$$N > -2 \quad , \; L = 1 \; , \tag{45e}$$

in agreement with (40) and (52). A more detailed discussion of the solution of (38) in the general case with $L > 1$ will be given in a subsequent paper.

4. Discussion of Results

The integral expressions (23)-(25) with (31) and (40), (42) or (38) provide a general solution for the radial factors $R(\underset{\sim}{\ell}, \underset{\sim}{m}; \underset{\sim}{r})$ in the expansion (3) of V as defined in (2); to the writer's knowledge this form of the solution is completely new, apart from one special case mentioned after (48) below. The form of the function (25) is such that the factors R'' can be interpreted as weighted averages of another function G, not of r_{AB} itself, but of its component along a prescribed z-direction. However, it should be borne in mind that the quantities u_i occurring in (25) do not represent physical direction cosines, but are simply integration variables; all the dependence on the geometric angles is contained in the spherical harmonics in (3). It is interesting to note that the partitioning of R according to (23) with the object of keeping $G(\omega)$ invariant leads to factors K'', and hence R'', which agree with the singly primed factors derived in III (29), (34) for the two-center expansion for $L = 0$ and only differ from those in II (33), (37) for the one-center expansion by the factor $(-)^{\Lambda+L}$; yet the precise partitioning in II had no stronger motivation than keeping the recurrence relations between the R' as simple as possible.

The occurrence of the Heaviside function $H(\omega)$ as a factor in $G(\omega)$ in (24), (25) and (38) means that in general the integration is effectively carried out over only half the ν-dimensional hypercube $-1 \leq u_i \leq 1$, the domain on one side of the hyperplane $\omega = 0$ (which passes through the origin) having zero integrand. If for a particular index i

$$\nu_i > \sum_{j \neq i} \nu_j \qquad (46)$$

the surface $u_i = 1$ is everywhere a boundary of the integrated domain, and $u_i = -1$ lies wholly outside it. Thus if the first integration is carried out over u_i the lower limit is a function of the other u_j's, but the limits of all subsequent integrations are independently -1 and $+1$. If however none of the radii satisfies (46), no face of the cube lies entirely on one side of the separating plane, and the upper limit of the first integration as well as the lower limit of at least one further integration are also variable. The Heaviside function thus automatically sorts out the various regions S ; a passage of the separating plane through a corner of the cube corresponds to the passage to another region. This is illustrated in Figure 3 for the case $\nu = 3$.

If the integrand in (25), apart from the factor $H(\mathcal{W})$ of (38), is regular everywhere in the hypercube and is invariant under simultaneous change of sign of all the u_i (an even function), then the integrals over the domains $\mathcal{W} \gtrless 0$ are identical. We may therefore drop the factor $H(\mathcal{W})$ and take instead half the integral over the whole hypercube; from this point of view there is no separating plane and the expansion (3) is the same in all regions. Thus if V is a sum of terms of the form (6b) it follows from (30b), (31) and (45) that for

$$N = L + 2k \quad , \quad k = 0, 1, 2 \ldots \tag{47}$$

the same analytic expressions for the $R(\underset{\sim}{\ell}, \underset{\sim}{m}; \underset{\sim}{r})$ are valid for all $\underset{\sim}{r}$; this is in agreement with the fact that both the solid harmonics $r_{AB}^{\ L} Y_L^{\ M}(\theta_{AB}, \varphi_{AB})$ and all positive integral powers of $r_{AB}^{\ 2}$ have universally valid expansion coefficients R [1,6,11].

The evenness of the integrand without analyticity throughout the cube does not ensure the uniformity of the integral through all regions.

Thus we obtain from (40) for

$$V = r_{AB}^{-1} \quad , \quad G_o(w) = \delta(w) \; , \tag{48a,b}$$

which is an even function even after multiplication by the $P_{\ell_i}(u_i)$ compatible with (31); yet this was the case for which the existence of different regions was first established by Laplace. The identity of the coefficients $r_<^{\ell}/r_>^{\ell+1}$ with the double integral (25) using (23) (31) and (48b) has already been established by Nozawa and Linderberg[7].

Whenever one of the indices ℓ_i vanishes, the integration over the corresponding u_i can be carried out explicitly. In particular the expressions (21) and (22), and hence the form (10) given by Milleur et al[10] for the angle average $\langle f \rangle$, follow from a repeated integration of (23)-(25) and (40) with all $\ell_i = 0$ since in view of (31)

$$K''\begin{pmatrix} 0 \dots 0 \\ 0 \dots 0 \end{pmatrix} = 2^{1-\nu} \; ; \tag{49}$$

the function $G_o(w)$ is thus identical with $g_o(w)$ which would precede g_1 in the recurrence relations (22b).

The integral form of the radial coefficients R as opposed to the series derived in I-III makes possible the expansion of non-analytic, even discontinuous functions $f(\underset{\sim}{r}_{AB})$ in (2). A discontinuity in f will produce a delta function in $G(w)$ in view of (38)-(42). If $f(\underset{\sim}{r}_{AB})$ diverges at $r_{AB} = 0$, but it is known from other considerations that a required integral over $\underset{\sim}{r}_{AB}$ is convergent, one can introduce a cut-off at $r_{AB} = \epsilon > 0$ and let ϵ tend to zero later;

this merely means replacing $H(w)$ by $H(w-\epsilon)$ in (38)-(42). An interesting application of this arises in the expansion of the first order irregular solid spherical harmonic $\mathcal{Y}_1$

$$V = \cos\vartheta_{AB}/r_{AB}^{2}\ , \qquad G_1(w) = w^{-1}\,\delta(w)\ , \tag{50a,b}$$

if the formula (42) were applied uncritically, but this expression is meaningless. On introducing a cut-off, we can put from (42) and (50)

$$G_1(w) = \lim\left[\epsilon^{-1}\ \delta(w-\epsilon)\right] \tag{50c}$$

again the expression has no limit as $\epsilon \to 0$, but we can add any even function $\gamma(w)$ to $G_1(w)$ without affecting the integral (25) as the product of the $P_\ell(u)$ is odd in view of (30b) and (31). The delta function $\delta(w)$ is an even function of w , thus we can put

$$G_1(w) = \lim\ \epsilon^{-1}\left[\delta(w-\epsilon) - \delta(w)\right] = -\,\delta'(\epsilon) \tag{50d}$$

by L'Hôpital's rule. Even more elaborate tricks are required in the expansion of the higher $\mathcal{Y}_L^M$; except for $L = 2$, ϵ cannot be made to tend to zero, at least not for values of the r_i corresponding to the region S_o . Similarly a cut-off must be introduced in the expansion for $V = r_{AB}^{\ n}$ where $n < -1$; after performing the integrations ϵ

may be reduced to zero for $-1 > n > -3$, but not in general for $n \leq -3$ (cf. Milleur et al[10]).

Another possible operation on $G(w)$ follows from (26)

$$V \to G(w) \quad \subset \quad \nabla^2 V \to G''(w) . \tag{51}$$

Applying this to (48) we obtain

$$V = \delta^3(r_{AB}) = -\frac{1}{4\pi} \nabla^2 \frac{1}{r_{AB}} ; \quad G = -\frac{1}{4\pi} \delta''(w) . \tag{52}$$

For the angle average this leads to the expression (22) of Milleur, Twerdochlib and Hirschfelder[10]; for general ℓ_i (23)-(25) integrate to the formulas given by Tanabe[11] and in III (40); as first pointed out by Milleur et al. the latter formula should be divided by (-8), not only for the angle average, but for all $\underset{\sim}{\ell}$.

One aspect which awaits fuller investigation is the convergence of the expressions. Two main types of convergence have to be considered:

(a) of the individual integrals (25) for all fixed sets r_i ;

(b) of the sum (3) for all fixed sets $(r_i, \vartheta_i, \varphi_i)$, the radial functions R being given (23)-(25) and (31).

With regard to (a) it is clear that the integrals converge whenever $G(w)$ considered as a function of a single variable is everywhere integrable. Difficulties may arise through singularities at the origin and through the introduction of generalized function; some practical aspects of this have been described in the preceding paragraphs. The point (b) has not been investigated at all, and I can only express my personal opinion (or hope) that the expansion will converge in most practical cases.

Another point arising in this context is the possible interchange of the order of performing the summations in (3) and the integrations in (25). It is easily shown that a summation over all $\underset{\sim}{\ell}$, $\underset{\sim}{m}$ at fixed $\underset{\sim}{r}$, $\underset{\sim}{\vartheta}$, $\underset{\sim}{\varphi}$, $\underset{\sim}{u}$ may diverge; one only has to put $\nu = 2$, $L = 0$, $\vartheta_1 = 0$, $u_1 = u_2 = 1$, in which case the sum becomes

$$g(r_1 + r_2) \cdot \sum (\ell + \tfrac{1}{2}) P_\ell(\cos\vartheta_2). \qquad (53)$$

On the other hand when integrations over the angles with specific weight factors are carried out, the resulting series at constant u may easily converge; the advantage* of this approach is that the integrations over the radii and the angles are thereby completely separate (which they are anyway in the expansion (3)), but in addition the linearity of $g(w)$ of (24), (25) in the r_i remains preserved; an application of this will be outlined in the next section.

5. Application to two-center expansions and further research

The main applications of the theory developed in this paper are likely to concern two-center expansions, corresponding to the case $\nu = 3$ (cf. Figure 1). This raises the question whether any advantage is gained by identifying the axis $0_1 0_2$ with the Z-axis from the start, i.e. by putting $\vartheta_3 = 0$. Such an approach must be emphatically rejected in the development of the theory. The different radial coefficients R corresponding to given ℓ_1 and ℓ_2 in (3) now depend on m_1 instead of ℓ_3, but their number remains the same; for instance in the isotropic case $L = 0$ in (27) $|m_1| = |m_2|$ can take all values between 0 and $\ell_<$, whereas ℓ_3 runs from $|\ell_1 - \ell_2|$ to

$\ell_1 + \ell_2$ in steps of 2, the number of different values being $\ell_< + 1$ in either case. On the other hand one of the sides of the differential equations (5) is lost if ℓ_3 is kept fixed, and the expressions derived for R are bound to be more complicated than those for fixed ℓ_3. This is borne out by the greater regularity of the coefficients in the expansions for $1/r_{12}$ derived in III than in the formulation by Buehler and Hirschfelder[5]; a generating function which these authors give in their second paper is too cumbersome to be of practical use. Similarly Nozawa, who fixes the direction of $0_1 0_2$,[7] is obliged to define generalized Bessel functions carrying two indices when expanding regular solutions of the wave equation; in the analogous expansion given in II for variable ϑ_3 the corresponding expressions are merely products of Bessel functions which have to be added with the appropriate angular integrals as coefficients.

Once the theory has been established there are fewer objections to fixing $\vartheta_3 = 0$. If in the expansion of (27) the radial coefficients corresponding to given values of ℓ_1, m_1, ℓ_2, m_2 and $m_3 = 0$ are summed over all ℓ_3 including those for which R vanishes in view of the conditions (30b,c), the relevant factor becomes in view of (28) and (34)

$$\sum_{\ell_3} (\ell_3 + \tfrac{1}{2})\, I_\Omega \begin{pmatrix} L & \ell_1 & \ell_2 & \ell_3 \\ M & -m_1 & -m_2 & 0 \end{pmatrix} P_{\ell_3}(u)$$

$$= \int \sum_{\ell_3} (\ell_3 + \tfrac{1}{2})\, P_L^M(v)\, P_{\ell_1}^{-m_1}(v)\, P_{\ell_2}^{-m_2}(v)\, P_{\ell_3}(v) P_{\ell_3}(u)\, dv$$

$$= \int P_L^M(v)\, P_{\ell_1}^{-m_1}(v)\, P_{\ell_2}^{-m_2}(v)\, \delta(u_3 - v)\, dv. \tag{54}$$

The complete radial factor R is thus obtained as

$$\mathcal{R}(\ell_1, \ell_2, \underset{\sim}{m}; \underset{\sim}{r}) = (-)^M (\ell_1 + \tfrac{1}{2})(\ell_2 + \tfrac{1}{2}) \; \delta_{M, m_1+m_2} \int_{-1}^{1} G_L(r_1 u_1 + r_2 u_2 + r_3 u_3)$$
$$\times P_{\ell_1}(u_1) P_{\ell_2}(u_2) P_L^M(u_3) P_{\ell_1}^{-m_1}(u_3) P_{\ell_2}^{-m_2}(u_3)\, du_1\, du_2\, du_3 \,, \quad (55)$$

with possibly an additional sign change[2]. From a theoretical point of view it is very doubtful if such a formula could have been derived without going through the procedure of section 3. The expression (55) itself is not too unwieldy especially for L = 0 ; its main drawback is that the upper indices now appear inside the integral, instead of merely through the constants I_Ω in (28).

The integrals I_Ω in the two-center expansion of an isotropic interaction V involve three factors; in their normalized form (29) they are most easily expressed in terms of Wigner 3j-symbols, on which there exists an extensive literature regarding both theory and tabulation (cf.[13] or Refs.[3,4,10,16] of II); an approach to the theory in terms of unnormalized 3j-symbols, which are integers, was outlined in II and will be further developed in a subsequent paper in this series. Even ~~if~~ $L \neq 0$, the integrals are easily calculated from those with three factors by means of (A3).

The evaluation of integrals over all positions of two particles with interaction

$$\int d^3\underset{\sim}{r}_1 \int d^3\underset{\sim}{r}_2 \quad \rho_1(\underset{\sim}{r}_1)\; \rho_2(\underset{\sim}{r}_2)\; V(\underset{\sim}{r}_{12}) \qquad (56)$$

can be turned, in view of (3), into a summation over ℓ_1, m_1, ℓ_2, m_2 of integrals over the radii r_1 and r_2, but involving the radial coefficients R, the separation of origins $r_3 = a$ being kept fixed. As these coefficients themselves are expressed as triple integrals in (23)-(25), the method would involve replacing the 6-fold integral (56) by a multiple sum of 5-dimensional integrals of the form

$$\int_{-1}^{1}\int_{-1}^{1}\int_{-1}^{1}\int_{0}^{\infty}\int_{0}^{\infty} d^3\underset{\sim}{u}\, dr_1\, dr_2\; G(r_1 u_1 + r_2 u_2 + r_3 u_3) \times \chi_1(r_1)\,\chi_2(r_2)\, P_{\ell_1}(u_1)\, P_{\ell_2}(u_2)\, P_{\ell_3}(u_3)\,, \tag{57}$$

which appears a most uneconomic procedure. However, if the functions $\chi_1(r_1)$ and $\chi_2(r_2)$ either are independent of ℓ_1 and ℓ_2, or else can be broken up into terms which possess this independence, the integrations over r_1 and r_2 could be done first for each point of the cube in $\underset{\sim}{u}$-space, and the remaining three integrations could then be carried out numerically; such an approach would be all the more practicable when the r-integrations can be performed analytically.

Fortunately the situation is more favorable in the most important case $V = 1/r_{12}$. In view of (48) the function $G(\omega)$ in (57) is the delta function $\delta(\omega)$, and the number of integrations is thereby effectively reduced by one, e.g. any variation of r_1 at constant $\underset{\sim}{u}$ implies a definite linear dependence of r_2 on r_1. However a further property of the delta function

$$\delta(k\omega) = \delta(\omega)/|k| \tag{58}$$

reduces the number of integrations yet further. If the integration over the radii has been carried out at a particular point (u_1, u_2, u_3) in $\underset{\sim}{u}$-space, the corresponding integral at (ku_1, ku_2, ku_3) is simply the original one divided by $|k|$. (This argument cannot be applied if the first integration is over one of the u_i because of the finite limits.) It is therefore sufficient to evaluate the r-integrals for points on the surface of the $\underset{\sim}{u}$-cube, and the volume integrals with weight factors $\prod P_{\ell_i}(u_i)$ can be expressed as surface integrals with correspondingly adjusted weights. These surface integrals would have to be evaluated numerically; a Gaussian quadrature scheme could be set up in which the points on the surface of the $\underset{\sim}{u}$-cube are tabulated for which the r-integration is to be performed, together with their weights appropriate to each triple (ℓ_1, ℓ_2, ℓ_3), or (ℓ_1, ℓ_2, m) if the approach of (55) is used.

The most delicate part of such a scheme would be the integration over the radii; it depends on the nature of the functions $\chi(r_1)$ and $\chi(r_2)$ whether these are best performed analytically or numerically. If they are Slater functions or products thereof, analytic methods are appropriate. We may define

$$\begin{aligned} I_{st} &= \iint_0^\infty \exp(-\alpha r_1 - \beta r_2)\, r_1^s r_2^t\, \delta(r_1 u_1 + r_2 u_2 + a u_3)\, dr_1\, dr_2 \\ &= (-\partial/\partial\alpha)^s (-\partial/\partial\beta)^t I_{00} \end{aligned} \tag{59}$$

where I_{00} can be easily calculated

$$I_{00} = 0 \qquad u_1, u_2, u_3 > 0 \tag{60a}$$

$$= \frac{\exp(-|u_3| a\beta/u_2) - \exp(-|u_3| a\alpha/u_1)}{\alpha u_2 - \beta u_1} \qquad u_1, u_2 > 0, \; u_3 < 0, \tag{60b}$$

$$= \frac{\exp(-\beta a u_3/|u_2|)}{\alpha|u_2| + \beta u_1} \qquad u_1, u_3 > 0, \; u_2 < 0, \tag{60c}$$

$$= \frac{\exp(-\alpha a u_3/|u_1|)}{\alpha u_2 + \beta|u_1|} \qquad u_2, u_3 > 0, \; u_1 < 0. \tag{60d}$$

The derivatives (59) can then be calculated by recurrence relations,[14,15] though care has to be taken to avoid instabilities in the derivatives of (60b), which can be expressed in terms of confluent hypergeometric functions[14,3].

The situation is more involved if the functions χ_1 and χ_2 are not just products of powers and exponentials, especially if they contain a factor arising out of the expansion of a Slater orbital about a center other than 0_1 or 0_2, as in the Barnett-Coulson approach to the evaluation of 3 and 4 center integrals[16,17]. An increment in r_1 will correspond to various increments in r_2, depending on the ratio u_1/u_2. Unless therefore χ_1 and χ_2 can be evaluated rapidly for arbitrary values of their arguments, numerical quadrature would be too time-consuming. It may be that in this case the expansion of an orbital about one center in a complete orthonormal set about another center would be more efficient; with the basis set of Löwdin-Shull functions[18] recently proposed by Smeyers[19] each integral would be a sum of terms (59), which could be evaluated on the basis of (60). It appears however from the applications quoted by Smeyers that the convergence is rather slow.

The foregoing discussion is of necessity rather sketchy as no actual calculations have been carried out along these lines; in consequence the writer has no idea how well the new approach would compare with other methods. In view of the importance and the difficulty of calculating 3 and 4 center integrals, no avenue should be left unexplored, and the ideas have therefore been presented as far as they have been thought out to date.

Two other directions for further research are mentioned in conclusion. One concerns the generalization of the expansion (3) to vectors in an arbitrary number of dimensions. The form of the function G depending on the projection of the vector $\underset{\sim}{r}_{AB}$ onto a fictitious polar axis can be adapted to these cases without difficulty; the further factors in the integral (25) and in the definition (38) of G would be cosines in the plane and Gegenbauer functions in more than 3 dimensions (cf. section 3.15 of Ref. 3).

An interesting problem in pure mathematics may be approached from a new direction on the basis of the present research. The solutions for R when V is a power were presented in III in terms of Appell functions F_4 and here in terms of the integrals (25) where G is still a power. This suggests the possibility of expressing F_4 in terms of 3-dimensional integrals; so far it has not been possible to express this function in terms of simple single or double Euler integrals.[3]

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Appendix A. Some relevant properties of the Legendre functions and their integrals.

The associated Legendre functions $\mathcal{P}_\ell^m$ satisfy the well-known orthogonality condition

$$\int_{-1}^{1} \mathcal{P}_\ell^{m}(u)\, \mathcal{P}_n^{-m}(u)\, du = (-)^m\, \delta_{\ell n}\, (\ell+\tfrac{1}{2})^{-1} . \tag{A1}$$

From this relation and the completeness of the functions follows the expansion for the delta function

$$\delta(u-u') = (-)^m \sum_{0}^{\infty} (\ell+\tfrac{1}{2})\, \mathcal{P}_\ell^{m}(u)\, \mathcal{P}_\ell^{-m}(u') \tag{A2}$$

valid for arbitrary m ; equation (34) represents the special case m = 0 . Similarly with the definition for the integrals (28) and (A1) and (A2), the expression (33) is an identity. The integrals (28) are invariant under permutation of the columns, and the single integral over u can always be turned into a double integral by the insertion of the factor (A2). Carrying out both integrations and summing we obtain the identity

$$\begin{aligned} \overline{I}_\Omega \begin{pmatrix} \ell_1 \cdots \ell_q & \ell_{q+1} \cdots & \ell_s \\ m_1 \cdots m_q & m_{q+1} \cdots & m_s \end{pmatrix} &= (-)^m \sum_\ell (\ell+\tfrac{1}{2})\, \overline{I}_\Omega \begin{pmatrix} \ell_1 \cdots \ell_q & \ell \\ m_1 \cdots m_q & -m \end{pmatrix} \\ &\times \overline{I}_\Omega \begin{pmatrix} \ell & \ell_{q+1} \cdots & \ell_s \\ m & m_{q+1} \cdots & m_s \end{pmatrix} ; \qquad m = m_1 + \ldots + m_q . \end{aligned} \tag{A3}$$

For the last result we make use temporarily of the normalized harmonics (1b) and their integrals (29). For products of three harmonics these integrals are given in terms of the Wigner 3j-symbols

$$\underline{I}_Y{}'\begin{pmatrix} l_1 & l_2 & l_3 \\ m_1 & m_2 & m_3 \end{pmatrix} = \left[\frac{\prod(2l_i+1)}{4\pi}\right]^{1/2}\begin{pmatrix} l_1 & l_2 & l_3 \\ m_1 & m_2 & m_3 \end{pmatrix}\begin{pmatrix} l_1 & l_2 & l_3 \\ 0 & 0 & 0 \end{pmatrix} . \qquad \text{(A4)}$$

The Wigner symbols satisfy the orthogonality relation (cf.(3.7.8) and (4.6.3) of Reference 13)

$$\sum_{m_1} \begin{pmatrix} l_1 & l_2 & l \\ m_1 & m-m_1 & -m \end{pmatrix}\begin{pmatrix} l_1 & l_2 & l' \\ m_1 & m-m_1 & -m \end{pmatrix} = \frac{\delta_{ll'}}{2l+1}\ \delta(l_1\, l_2\, l)$$

(A5)

where $\delta(l_1\ l_2\ l_3)$ is unity provided the triangle conditions (30c) are valid and zero otherwise (though in this case the sum (30b) may be even or odd). Re-expressing (1b) and (29) by their unnormalized counterparts (1a) and (28) we obtain from (A4) and (A5)

$$\sum_{m_1} \underline{I}_\Omega\begin{pmatrix} l_1 & l_2 & l \\ m_1 & m-m_1 & -m \end{pmatrix}\ \underline{I}_\Omega\begin{pmatrix} l_1 & l_2 & l \\ -m_1 & m_1-m & m \end{pmatrix}$$

$$= \frac{\delta_{ll'}}{l+1/2}\ \underline{I}_\Omega\begin{pmatrix} l_1 & l_2 & l \\ 0 & 0 & 0 \end{pmatrix} . \qquad \text{(A6)}$$

It is intended in a future publication to establish an exhaustive theory of the integrals $\underline{I}_\Omega$ by analytical methods only, so that no group-theoretical arguments are required to derive results such as (A6).

Appendix B. Errata to Parts I, II and III

Part I: J. Math. Phys. 5, 245 (1964).

Abstract: Delete "for $n = -1$ and $n = -2$".

Abstract: In the last line read "or of" for "of of".

(27a): The second line should begin

$$\times F\left[\tfrac{1}{2}\ell - \tfrac{1}{4}n,\ \tfrac{1}{2} - \tfrac{1}{4}n + \tfrac{1}{2}, \cdots\right.$$

(36b): The first line should read

$$-\frac{(\ell-1)!}{(3/2)_{\ell-1}}\frac{r_<^{\ell}(r_>^2 - r_<^2)^2}{r_>^{\ell+4}}$$

(49) : Read $(2s+2\ell+1)!!$ for $(2s+2^{\ell}+1)!!$

Part II : J. Math. Phys. 5, 252 (1964).

Line following (47) should begin:

"the value of L at constant N"

(57a): Read "r_2^2" for "dr_2^2" in last fraction.

Part III: J. Math. Phys. 5, 260 (1964).

(40b): This should be multiplied by a factor: $-\frac{1}{8}$ to read:

$${}_{\ell}\mathcal{R}_0{}'(\delta, \underset{\sim}{\ell}) = \frac{(-)^{\ell_3}(2\ell_1-1)!!\,(2\ell_2-1)!!}{\pi(2\lambda_3-1)!!\,2^{\Lambda+1}\,\Lambda!} \cdots$$

p. 266, 2nd line of § (a): read "charge" for "change".

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1. R. A. Sack, J. Math. Phys., 5, 246, 252, 260 (1964). (Though these papers do not carry the same global title, they are to be considered as Parts I, II and III of the present series and hereafter referred to as such).

2. The change of $\tilde{r}_1$ in $\tilde{r}_{AB}$ to $-\tilde{r}_1$ in $\tilde{r}_{12}$ simply introduces a factor ± 1 in the terms in (3) depending on the parity of ℓ_1.

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Text to Figures

Figure 1. Polar coordinates for two-center expansion.

The angles φ_i are not shown to avoid cluttering up the diagram.

Figure 2. The various regions:

a. The one-center case.

b. The two-center case.

Figure 3. Position of the plane $w = 0$ in the u-cube.

a. $r_i > r_j + r_k$,

b. $|r_1 - r_2| < r_3 < r_1 + r_2$.

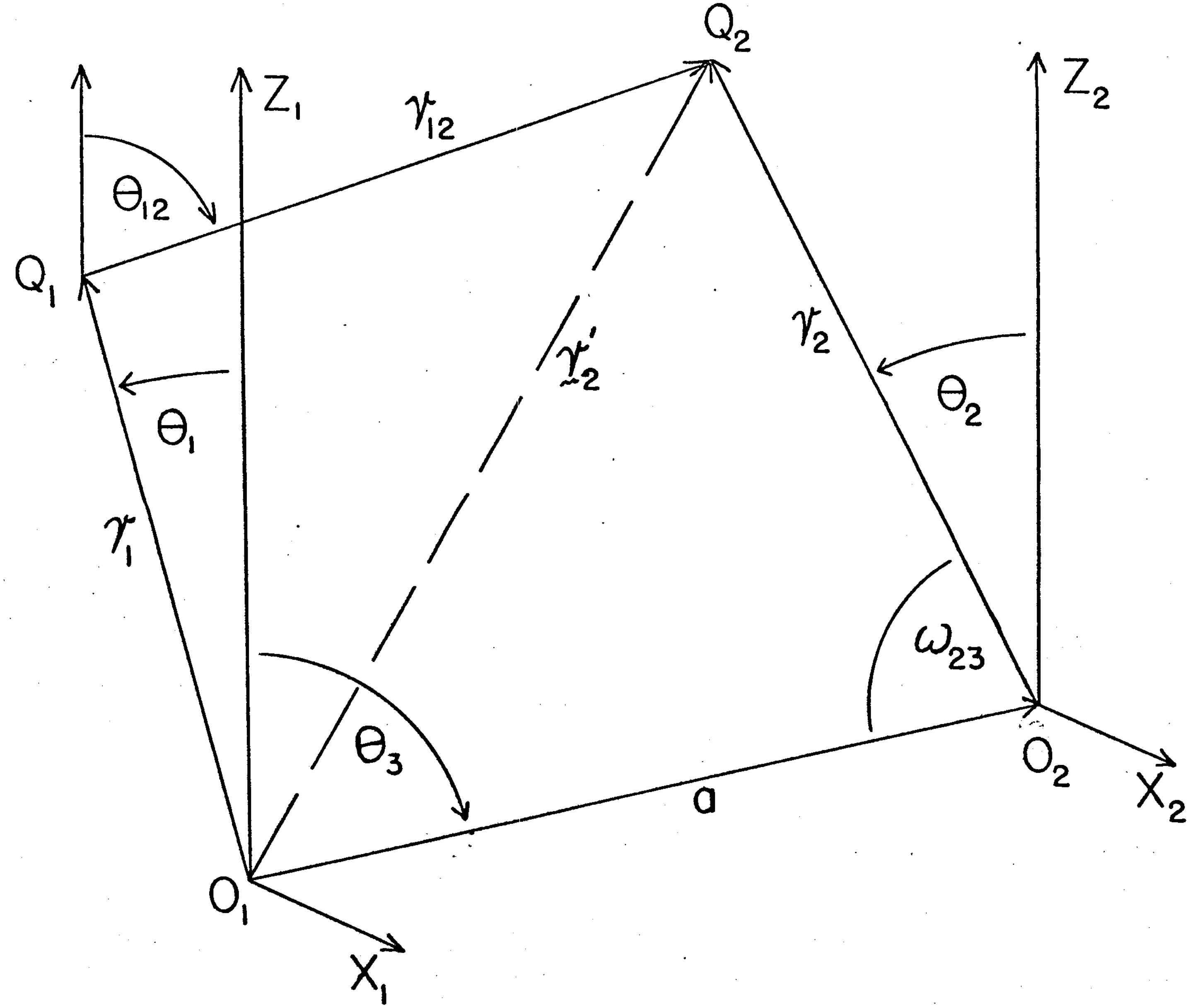

Figure 1

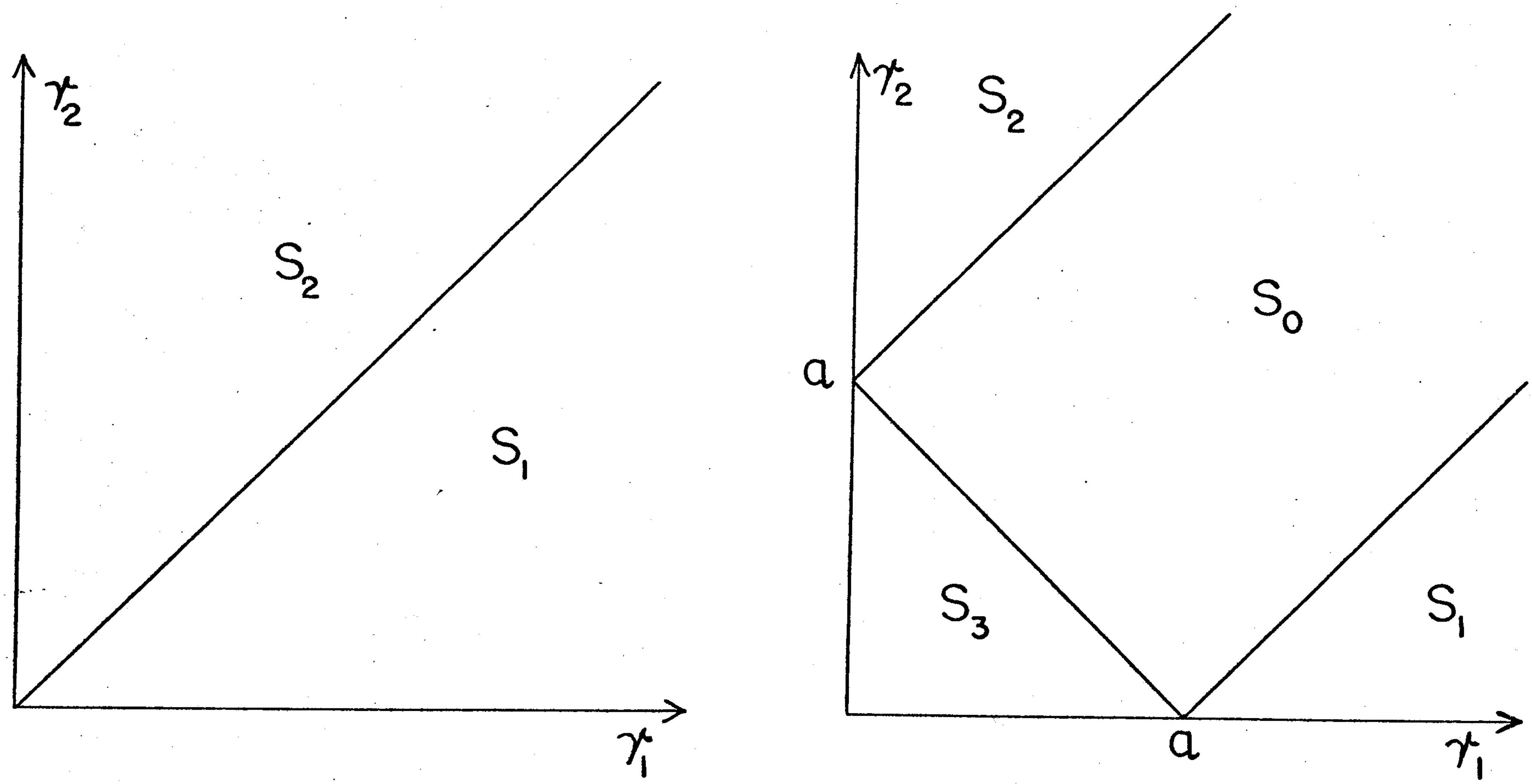

Figure 2

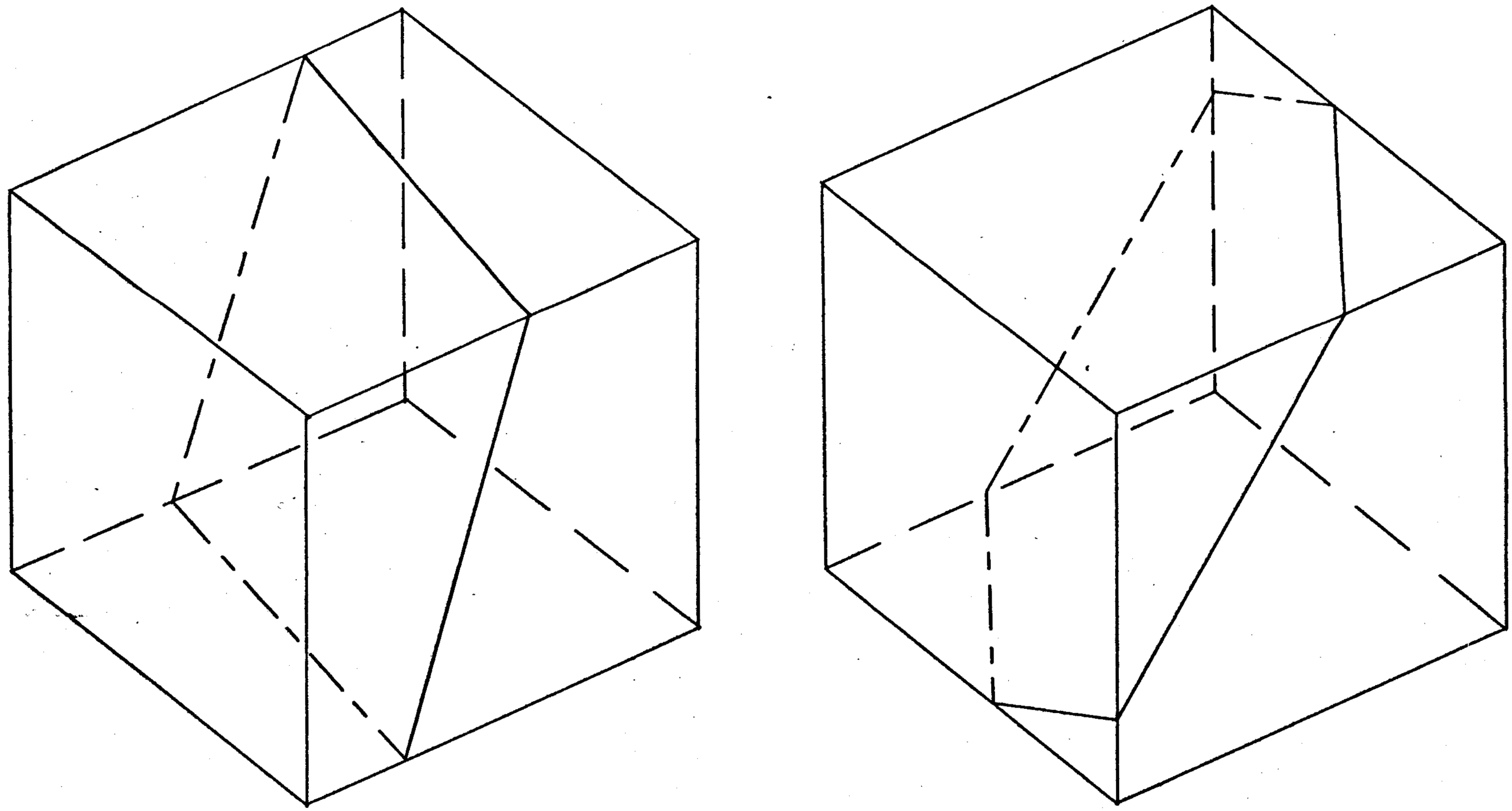

Figure 3