PHILOSOPHICAL TRANSACTIONS OF THE ROYAL SOCIETY A MATHEMATICAL, PHYSICAL & ENGINEERING SCIENCES

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Phil. Trans. R. Soc. Lond. A 1951 **243**, 221-249
doi: 10.1098/rsta.1951.0003

THE EVALUATION OF INTEGRALS OCCURRING IN THE THEORY OF MOLECULAR STRUCTURE. PARTS I & II

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(*Received* 18 *May* 1950—*Revised* 14 *August* 1950)

CONTENTS

Part I: A new technique is developed for evaluating the integrals which occur in molecular theory. The method is based on the expansion of exponentials in terms of the so-called ζ functions. These involve modified Bessel functions. In this part we list the properties of these ζ functions needed for the two-centre integrals. A table is provided of the I's and K's used in their tabulation. An account is given of the properties of certain integrals of the ζ functions and some numerical examples are provided.

Part II: Methods are described for the evaluation of the two-centre, one-electron Coulomb, overlap and resonance integrals, for the two-electron Coulomb and hybrid (Coulomb-exchange) integrals, and for the penetration integrals. Formulae are listed for more than 180 distinct integrals.

PART I. BASIC FUNCTIONS

1. Introduction

The most serious technical difficulty in many calculations of molecular theory lies in the analytical complexity of the integrals which arise as soon as two or more centres of force become involved. Expressions for quantities as diverse as transition probabilities and dipole moments, energy levels and scattering coefficients can all be formulated, by use of wave mechanics, in terms of integrals of a few standard types. In many other branches of theoretical physics, there arise integrals which are formally identical with those of wave mechanics; thus examples are to be found both in nuclear theory and in astrophysics.

The calculations are sometimes extremely difficult when only two centres of force are involved, and the integration is to be carried out over the space of a single particle. An even worse situation arises when double space integration is necessary. For example, if the integration is over the space of two interacting electrons, we have the r_{12}-integrals mentioned

below. Multi-centre integrals, involving three or four centres of force, have hitherto been considered to be intractable except in a few isolated instances. New ways of calculating those molecular integrals which have previously been regarded as inaccessible, and better ways of calculating the others, are much needed. We are attempting to meet these needs, using a technique which involves certain ζ and $\mathbf{Z}$ functions introduced below.

The integrals with which we shall be concerned may be divided into two groups, according to whether they can be broken down to integrals of the form (1), which for convenience we shall call J integrals.

$$J = \int e^{-\alpha r_a - \beta r_b} r_a^u r_b^v Y_p(\theta_a, \phi)\, Y_q(\theta_b, \phi)\, dV. \tag{1}$$

In (1) (r_a, θ_a, ϕ) and (r_b, θ_b, ϕ) are the polar co-ordinates of a point, referred to two nuclei, A and B, as origins, and the lines AB and BA respectively as polar axes (figure 1). The Y's are surface spherical harmonics, and u, v, p, q are integers. The integration is over all space.

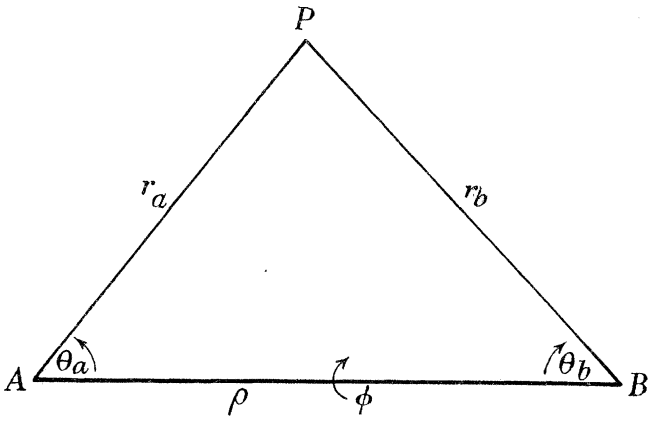

FIGURE 1

In the applications to molecular theory in its present state, the integrals which can be reduced to such J's include the one-electron overlap and resonance integrals, the two-electron Coulomb and hybrid (Coulomb-exchange) integrals, and also the 'penetration' integrals. These are all dealt with in part II. They comprise, in fact, all but one of the types of molecular integral which appear in systems involving only two nuclei. The one exception, the exchange integral, will be considered in a later part, together with the three- and four-centre integrals.

The immediate object of this first part is the description of the new method for evaluating the J's. Because the relevant properties of the ζ's and $\mathbf{Z}$'s suffice also for the evaluation of the multi-centre integrals, this part can be regarded as providing the mathematical basis for a systematic approach to the problem of evaluating all the conventional integrals of molecular theory.

2. Simplification of J integrals

Integrals such as (1) can always be simplified. For the integration over the co-ordinate ϕ is immediate, and by use of the relations (see figure 1)

$$r_a \sin\theta_a = r_b \sin\theta_b \tag{2a}$$

$$r_a \cos\theta_a = \rho - r_b \cos\theta_b \tag{2b}$$

we can subsequently remove θ_b from the integrand (ρ is the internuclear distance). This enables us to confine our attention when listing formulae, solely to the 'standard' J functions, defined in terms of three indices k, l, m by

$$J(k, l, m) = \int e^{-\alpha r_a - \beta r_b} \cos^k \theta_a r_a^{l-1} r_b^{m-1} dV. \tag{3}$$

When making this reduction we have to decide which nucleus shall be called A, and which B. For this purpose we need to consider the two differences $u-p$ and $v-q$ in (1). If both these differences are greater than or equal to -1, then the choice of A is irrelevant, and two distinct evaluations of the integrals are possible, thus providing a convenient check on our work. If $u-p<-1$, and $v-q\geqslant -1$, then θ_b should be eliminated, as in (3), and vice versa if $u-p\geqslant -1$, and $v-q<-1$. In these cases only one evaluation is possible. It transpires that the remaining possibility, in which both $u-p$ and $v-q$ are less than -1, seldom arises. In making the reduction to (3), we have eliminated $\sin\theta_a$ in favour of $\cos\theta_a$. No great difficulty arises in this latter step since one result of the ϕ integration, followed by application of $(2a)$, is that only even powers of $\sin\theta_a$ appear in the integrand.

The quantities which must first be constructed when using our method are certain **Z** functions to which reference has already been made. Any J integral of the form (1) can be expressed as a linear combination of a few such **Z**'s. To do this, the integral is first expressed as a sum of the 'standard' J's defined in (3). Expressions for these in terms of **Z**'s can then be obtained from equations (9), (11), (17) below, and combined algebraically. It may be pointed out that the standard J's are of use only for the purpose of listing formulae. For the purpose of systematic numerical tabulation, the most suitable quantities are the **Z** functions themselves.

It is important, at this point, to note that many simple cases of the original integral (1) can be readily evaluated by expressing the integrand in terms of confocal elliptic co-ordinates with foci at A and B. One of us (Coulson 1942) has already listed explicit expressions for about 50 of these integrals; this list is still the best source for such integrals as it contains. But when a J integral is not included in the list, or cannot immediately be obtained from one which is, some other procedure is necessary. Any extension of the list requires a very considerable amount of work, both algebraic and numerical; the later members of the list itself bear evidence of this growing complication. And we have found that for the purposes of part II, over 50 additional J's would be required. Expressions for these could be obtained by the same methods as were used previously, but, particularly when $u-p$ or $v-q$ is less than -1, they are too unwieldy for general use. This is still true even though we have shown, in some unpublished work, that such J's may be reduced in a systematic manner. We cannot, therefore, recommend this approach. Nor can we recommend a further alternative method, which we have studied carefully, in which the co-ordinates used are r_a, r_b and ϕ. Particularly when dealing with the two-electron integrals of II, this also is excessively laborious and unwieldy.

The technique that we have found most convenient consists of an expansion of $r_b^{m-1} e^{-\beta r_b}$ in (3) in terms of r_a and θ_a. The integration with respect to θ_a presents no great difficulty, but the final integration with respect to r_a is more troublesome. We shall return to this matter later.

3. Basis of the new method

The basis of our new method lies in the expansion of $r_b^{m-1}\,\mathrm{e}^{-\beta r_b}$ in terms of r_a and θ_a. Such expressions, which have already proved useful in certain three-centre integrals studied by one of us (Coulson 1937), take the form of infinite series. In general, let us write

$$r_b^{m-1}\,\mathrm{e}^{-\beta r_b} = \sum_{n=0}^{\infty} \frac{2n+1}{\sqrt{(r_a\rho)}} P_n(\cos\theta_a)\,\zeta_{m,n}(\beta, r_a;\ \rho) = \beta^{-m+1} \sum_{n=0}^{\infty} \frac{2n+1}{\sqrt{(t\tau)}} P_n(\cos\theta_a)\,\zeta_{m,n}(1, t; \tau), \tag{4}$$

where t and τ are the dimensionless variables

$$t = \beta r_a \tag{5a}$$

$$\tau = \beta\rho \tag{5b}$$

and P_n is the Legendre polynomial of order n. Each $\zeta_{m,n}(\beta, r_a;\ \rho)$ is a function of the variables β, r_a, ρ. Its form is defined by the two parameters m and n. When $m = 0, 1, 2$ the $\zeta_{m,n}$'s are the functions used previously (Coulson 1937), and denoted by $\gamma_n(\beta, r_a;\rho)$, $p_n(\beta, r_a;\rho)$ and $q_n(\beta, r_a;\rho)$ respectively. Of these the simplest is $\gamma_n(\beta, r_a;\ \rho)$ which may be expressed as:

$$\gamma_n(\beta, r_a;\ \rho) = I_{n+\frac{1}{2}}(\beta r_a)\,K_{n+\frac{1}{2}}(\beta\rho)\ ; \quad r_a \leqslant \rho. \tag{6}$$

When $r_a > \rho$, the positions of r_a and ρ on the right-hand side of (6) are interchanged. The I and K are standard Bessel functions of purely imaginary argument. It is obvious from the definition (4) that the $\zeta_{m,n}(\beta, r_a;\ \rho)$ functions of higher index m may be obtained from the γ_n's by partial differentiation with respect to β. They may all be expressed as linear combinations of γ functions. The expression for the p_n function is simply

$$p_n(1, t;\ \tau) = \frac{t\tau}{(2n+1)}\{\gamma_{n-1}(1, t;\ \tau) - \gamma_{n+1}(1, t;\ \tau)\}. \tag{7}$$

The $\zeta_{m,n}$ functions of higher index m can be reduced by repeated use of (8) to γ_n or p_n functions, depending on whether m is even or odd.

$$\zeta_{m+2,n} = (t^2+\tau^2)\,\zeta_{m,n} - \frac{2t\tau}{(2n+1)}\{n\zeta_{m,n-1} + (n+1)\,\zeta_{m,n+1}\}. \tag{8}$$

In equation (8), and elsewhere in this paper, when the symbols $\zeta_{m,n}$, γ_n, p_n or q_n are used without explicit reference to their arguments, these may be supposed to be $(1, t; \tau)$.

When the expansion (4) is substituted in the standard integral (3), the integration with respect to θ_a and ϕ is straightforward, and there remains a single integration, which can be written in the form

$$\beta^{(l+m+1)}\,J(k, l, m) = \frac{4\pi}{\sqrt{\tau}} \int_0^{\infty} \mathrm{e}^{-\kappa t}\, t^{l+\frac{1}{2}} f(m, k;\ t)\,dt, \tag{9}$$

where

$$\kappa = \alpha/\beta. \tag{10}$$

The f functions are linear combinations of the $\zeta_{m,n}$'s. In particular, we have

$$f(m, 0;\ t) = \zeta_{m,0} \tag{11a}$$

$$f(m, 1;\ t) = \zeta_{m,1} \tag{11b}$$

$$f(m, 2;\ t) = \zeta_{m,0} - \tfrac{2}{3}(\zeta_{m,0} - \zeta_{m,2}) \tag{11c}$$

$$f(m, 3;\ t) = \zeta_{m,1} - \tfrac{2}{5}(\zeta_{m,1} - \zeta_{m,3}) \tag{11d}$$

$$f(m, 4;\ t) = \zeta_{m,0} - \tfrac{4}{5}(\zeta_{m,0} - \zeta_{m,2}) - \tfrac{8}{35}(\zeta_{m,2} - \zeta_{m,4}). \tag{11e}$$

The expressions (11*c*) to (11*e*) are written in terms of differences in order that recursion formulae between the ζ's may be exploited. These formulae include (7) and (8) above, and also

$$p_{n-2}-p_n=(2n-1)\frac{t^2+\tau^2}{t\tau}\gamma_{n-1}-(2n-3)\gamma_{n-2}-(2n+1)\gamma_n \tag{12}$$

$$q_{n-2}-q_n=(2n-1)\frac{t^2+\tau^2}{t\tau}p_{n-1}-2(n-2)p_{n-2}-2(n+1)p_n. \tag{13}$$

For values of k greater than 4, the f functions can be found from the general expression

$$f(m,k;t)=\sum_{j=0}^{k}\frac{(2j+1)}{2}R_j^k\zeta_{m,j}(1,t;\tau), \tag{14}$$

where

$$R_j^k=\int_0^\pi P_j(\cos\theta)\cos^k\theta\sin\theta\,d\theta. \tag{15}$$

Values of the quantity R_j^k are listed by Rosen (1931), for j, k ranging from 1 to 10. In general, R_j^k has the value

$$R_j^k=\frac{2^{j+1}k!\left(\frac{k+j}{2}\right)!}{\left(\frac{k-j}{2}\right)!\,(k+j+1)!} \tag{16}$$

when $k-j$ is an even positive integer, including zero, but it is otherwise zero.

As a result of this, the function f in (9) may be supposed known, so that the final evaluation of the J integral is reduced to one single integration. This integration may either be performed numerically (see later), or it may be completed analytically as the sum of certain **Z** functions defined by

$$\mathbf{Z}_{m,n,l+\frac{1}{2}}(\kappa,\tau)=\int_0^\infty e^{-\kappa t}\zeta_{m,n}(1,t;\tau)\,t^{l+\frac{1}{2}}dt. \tag{17}$$

Particular cases of (17), corresponding to important low values for the parameter m, may be introduced as

$$\mathbf{G}_{n,l+\frac{1}{2}}(\kappa,\tau)=\int_0^\infty e^{-\kappa t}\gamma_n(1,t;\tau)\,t^{l+\frac{1}{2}}dt \tag{18a}$$

$$\mathbf{P}_{n,l+\frac{1}{2}}(\kappa,\tau)=\int_0^\infty e^{-\kappa t}p_n(1,t;\tau)\,t^{l+\frac{1}{2}}dt. \tag{18b}$$

Methods of dealing with the **Z**, **G** and **P** functions analytically are deferred to a later paragraph.

4. Numerical integration of the **Z** functions

Notwithstanding that these **Z** integrals can be reduced to standard mathematical functions, we have found that the alternative of numerical integration in (9) is often more convenient in practice. This arises from the fact that the geometrical dependence of the integrand upon the variable of integration is of the smoothly varying form shown in figure 2. Consequently, any of the standard integration rules (Bickley 1939) may be employed. It turns out that for large values of t (frequently as low as $t\geqslant 3\tau$), the integrand is effectively zero.

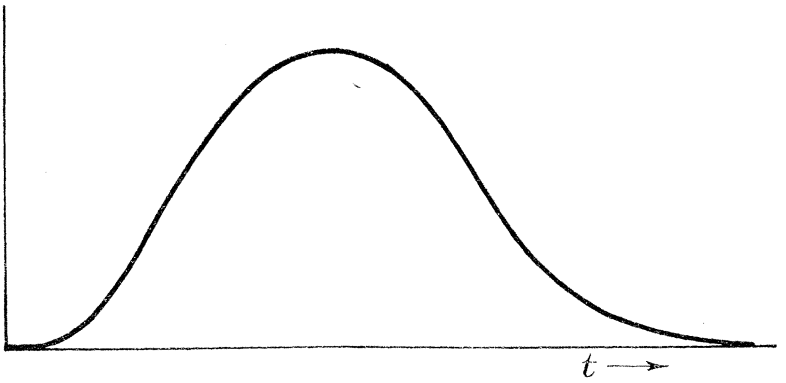

FIGURE 2

The procedure is then as follows. First the γ_n functions are listed, using tables of Bessel functions of half integral order. Equation (7) now gives the p_n functions, and equation (8) the $\zeta_{m,n}$ functions of higher order m. Alternatively differences $p_{n-2}-p_n$ can be found from (12), and $(q_{n-2}-q_n)$ from (13). If the tables of Bessel functions are not adequate, the γ_n's and p_n's can be developed by recurrence relations. This may be systematized most simply by a basic operation in which we use known values of $\gamma_{n-1}, \gamma_n, p_{n-1}$ and p_n to infer γ_{n+1} and p_{n+1}. The first of these $(\gamma_{n+1})$is found from (7), and the second (p_{n+1}) from (12). The cycle may now be repeated. It should be noted that

$$\left.\begin{aligned} p_{-1} &= (\tau+1)\,\gamma_{-1}-t\gamma_0 \\ p_0 &= (\tau+1)\,\gamma_0-t\gamma_{-1} \end{aligned}\right\} t\leqslant\tau, \qquad \left.\begin{aligned} p_{-1} &= (t+1)\,\gamma_{-1}-\tau\gamma_0 \\ p_0 &= (t+1)\,\gamma_0-\tau\gamma_{-1} \end{aligned}\right\} t\geqslant\tau, \tag{19}$$

in which

$$\gamma_{-1} = \frac{\mathrm{e}^{-|t-\tau|}+\mathrm{e}^{-(t+\tau)}}{2\sqrt{(t\tau)}} \qquad \gamma_0 = \frac{\mathrm{e}^{-|t-\tau|}-\mathrm{e}^{-(t+\tau)}}{2\sqrt{(t\tau)}}. \tag{20}$$

In this process, as in several other recursion techniques to be mentioned in this paper, a type of practical difficulty arises from what we shall term 'differencing effects'. It can be illustrated by reference to a recurrence formula

$$x_{n-1}-a_n x_n = \Delta_n$$

in which x_n and x_{n-1} are the functions of orders n and $n-1$; a_n is a coefficient and Δ_n some auxiliary function. Let these quantities all be positive. Then if

$$x_{n-1} \simeq \Delta_n$$

there is a loss of accuracy when x_n is found from x_{n-1}. If Δ_n is not only of the same order of magnitude as x_{n-1}, but has the same leading digits, then repeated use of the recurrence formula as a means of increasing the index n is not practicable. The formula could however be used to depress n without involving any loss of significant figures. It then becomes necessary to obtain x_n for certain maximum values of n by some independent route.

In connexion with the cycle just described, since $\gamma_{n-1}-\gamma_{n+1}>0$, $p_{n-1}-p_{n+1}>0$, repeated use of the process will result in serious loss of accuracy for certain ranges of the parameters. It is then expedient to calculate $\gamma_N, \gamma_{N-1}, \gamma_{N-2}, \gamma_{N-3}$ from values of the Bessel functions, with N equal to the maximum value needed for n. Then from γ_N and γ_{N-2} it is possible to find p_{N-1}; from p_{N-1}, γ_{N-1}, γ_{N-2}, γ_{N-3} a value is found for p_{N-3} and the cycle repeated, leading

ultimately to γ_0 which can be checked from the explicit expression. To obtain γ_N, γ_{N-1}, γ_{N-2} and γ_{N-3} values are needed of the Bessel functions. If these are not tabulated use can be made of (21 *a*) to get $I_{N+\frac{1}{2}}$ and $I_{N-\frac{1}{2}}$, and of (21 *b*) to get $K_{N-\frac{1}{2}}$ and $K_{N-\frac{3}{2}}$.

$$I_{n+\frac{1}{2}}(z) = \frac{1}{\sqrt{(2\pi z)}}\left\{e^z y_n\left(-\frac{1}{z}\right)+(-)^{n+1}e^{-z}y_n\left(\frac{1}{z}\right)\right\} \tag{21a}$$

$$K_{n+\frac{1}{2}}(z) = \sqrt{\left(\frac{\pi}{2z}\right)}e^{-z}y_n\left(\frac{1}{z}\right) \tag{21b}$$

$$y_n(z) = \sum_{j=0}^{n}\frac{(n+j)!}{j!(n-j)!\,2^j}z^j. \tag{21c}$$

If the argument is small, (21 *a*) cannot be used and the I's are then obtained from the infinite series (22)

$$I_{n+\frac{1}{2}}(z) = \pi^{-\frac{1}{2}}(2z)^{n+\frac{1}{2}}\sum_{j=0}^{\infty}\frac{(n+j)!}{j!(2n+2j+1)!}z^{2j}. \tag{22}$$

When $I_{N+\frac{1}{2}}$, $I_{N-\frac{1}{2}}$, $K_{N-\frac{1}{2}}$, $K_{N-\frac{3}{2}}$ have been found from these equations, they can be used to construct $I_{N-\frac{3}{2}}$, $I_{N-\frac{5}{2}}$ and $K_{N-\frac{1}{2}}$, $K_{N+\frac{1}{2}}$ by means of the well-known recurrence formulae for the modified Bessel functions.

For very small t and τ, and for large n, it is impracticable to use the cycle iteratively in either direction. The γ_n functions must then be obtained from Bessel functions, first calculating the latter by (21), (22) or recurrence formulae, if they are not already tabulated.

When (8) has been used to raise m, a check can be obtained by the use of the recurrence formulae between $\zeta_{m,n}$ functions whose m-values differ by 1. These formulae include, for example,

$$q_n = \frac{t\tau}{2n+1}\{p_{n-1}-p_{n+1}\}-p_n. \tag{23}$$

5. Analytical reduction of the Z functions

We now turn to the analytical method for evaluating the $\mathbf{Z}_{m,n,l+\frac{1}{2}}(\kappa,\tau)$ functions. Our previous analysis shows that for $J(k,l,m)$, values are needed of $\mathbf{Z}_{m,n,l+\frac{1}{2}}$ where n assumes integral values up to and including k, and with the same parity. On account of the relation (8), we can steadily lower the index m in this function. Thus

$$\mathbf{Z}_{m,n,l+\frac{1}{2}}(\kappa,\tau) = \tau^2\mathbf{Z}_{m-2,n,l+\frac{1}{2}}(\kappa,\tau)+\mathbf{Z}_{m-2,n,l+\frac{3}{2}}(\kappa,\tau) - \frac{2\tau}{(2n+1)}\{n\mathbf{Z}_{m-2,n-1,l+\frac{3}{2}}(\kappa,\tau)+(n+1)\mathbf{Z}_{m-2,n+1,l+\frac{3}{2}}(\kappa,\tau)\}. \tag{24a}$$

There are various other formulae of similar pattern. For example

$$\mathbf{Z}_{2,n,l+\frac{1}{2}}(\kappa,\tau) = \frac{\tau}{(2n+1)}\{\mathbf{P}_{n-1,l+\frac{3}{2}}(\kappa,\tau)-\mathbf{P}_{n+1,l+\frac{3}{2}}(\kappa,\tau)\}-\mathbf{P}_{n,l+\frac{1}{2}}(\kappa,\tau). \tag{24b}$$

This means that we need consider initially only values of $\mathbf{Z}_{m,n,l+\frac{1}{2}}$ for which $m = 0, 1$. According to (18), these are simply $\mathbf{G}_{n,l+\frac{1}{2}}$ and $\mathbf{P}_{n,l+\frac{1}{2}}$.

The calculation of any $\mathbf{Z}$ can now be split into three stages. First we imagine the $\mathbf{G}_{n,l+\frac{1}{2}}$ and $\mathbf{P}_{n,l+\frac{1}{2}}$ set out on two grids, in each of which n and l are measured along two perpendicular directions, and we determine values along the edges of these grids. Second, entries in the

body of the tables are found from those nearer the periphery by use of simple recursion formulae. Finally, the **Z**'s of higher m value are found from the **P**'s and **G**'s, using equations such as (24). The peripheral entries needed in the first stage of the evaluation of $\mathbf{Z}_{m,n,l+\frac{1}{2}}$ are

(*a*) the $\mathbf{G}_{\nu,\lambda+\frac{1}{2}}$ in which $\nu = 0, -1$ and $\lambda = 0, 1 \ldots, m+l$; the $\mathbf{P}_{\nu,\lambda+\frac{1}{2}}$ in which $\nu = 0, -1$ and $\lambda = 0, 1 \ldots, m+l-1$.

(*b*) the $\mathbf{G}_{\nu,\pm\frac{1}{2}}$. These are needed only if $n \geqslant l+1$ and then ν must assume the values $\nu = 0, 1 \ldots, n-l-1$, for $\mathbf{G}_{\nu,-\frac{1}{2}}$, and $\nu = 0, 1, \ldots, n-l$ for $\mathbf{G}_{\nu,\frac{1}{2}}$.

On account of the fact, mentioned in §2 that the analytical expressions for all the $\zeta_{m,n}$ functions change when $t = \tau$, the peripheral entries must be obtained by adding the corresponding integrals in (17) and (18), over the ranges $(0, \tau)$ and (τ, ∞). This is a very annoying, but inescapable, complication. We may conveniently represent the contributions from the lower and upper ranges by superscripts i and s, so that

$$\mathbf{G}_{n,l+\frac{1}{2}}(\kappa,\tau) = \mathbf{G}^i_{n,l+\frac{1}{2}}(\kappa,\tau) + \mathbf{G}^s_{n,l+\frac{1}{2}}(\kappa,\tau) \tag{25a}$$

$$\mathbf{P}_{n,l+\frac{1}{2}}(\kappa,\tau) = \mathbf{P}^i_{n,l+\frac{1}{2}}(\kappa,\tau) + \mathbf{P}^s_{n,l+\frac{1}{2}}(\kappa,\tau). \tag{25b}$$

The separate partial range integrals can be expressed quite simply in terms of certain integrals of the type introduced by Coulson (1937) and defined by

$$P_{l+\frac{1}{2},n+\frac{1}{2}}(\kappa,\tau) = \int_0^\tau \mathrm{e}^{-\kappa t} t^{l+\frac{1}{2}} I_{n+\frac{1}{2}}(t)\, dt \tag{26a}$$

$$S_{l+\frac{1}{2},n+\frac{1}{2}}(\kappa,\tau) = \int_\tau^\infty \mathrm{e}^{-\kappa t} t^{l+\frac{1}{2}} K_{n+\frac{1}{2}}(t)\, dt \tag{26b}$$

Evidently

$$\mathbf{G}^i_{n,l+\frac{1}{2}}(\kappa,\tau) = K_{n+\frac{1}{2}}(\tau)\, P_{l+\frac{1}{2},n+\frac{1}{2}}(\kappa,\tau) \tag{27a}$$

$$\mathbf{G}^s_{n,l+\frac{1}{2}}(\kappa,\tau) = I_{n+\frac{1}{2}}(\tau)\, S_{l+\frac{1}{2},n+\frac{1}{2}}(\kappa,\tau). \tag{27b}$$

As a result of equation (19) it follows that

$$\mathbf{P}^i_{-1,l+\frac{1}{2}}(\kappa,\tau) = (\tau+1)\, \mathbf{G}^i_{-1,l+\frac{1}{2}}(\kappa,\tau) - \mathbf{G}^i_{0,l+\frac{1}{2}}(\kappa,\tau) \tag{28a}$$

$$\mathbf{P}^i_{0,l+\frac{1}{2}}(\kappa,\tau) = (\tau+1)\, \mathbf{G}^i_{0,l+\frac{1}{2}}(\kappa,\tau) - \mathbf{G}^i_{-1,l+\frac{1}{2}}(\kappa,\tau) \tag{28b}$$

$$\mathbf{P}^s_{-1,l+\frac{1}{2}}(\kappa,\tau) = \mathbf{G}^s_{-1,l+\frac{1}{2}}(\kappa,\tau) + \mathbf{G}^s_{-1,l+\frac{1}{2}}(\kappa,\tau) - \tau \mathbf{G}^s_{0,l+\frac{1}{2}}(\kappa,\tau) \tag{29a}$$

$$\mathbf{P}^s_{0,l+\frac{1}{2}}(\kappa,\tau) = \mathbf{G}^s_{0,l+\frac{1}{2}}(\kappa,\tau) + \mathbf{G}^s_{0,l+\frac{1}{2}}(\kappa,\tau) - \tau \mathbf{G}^s_{-1,l+\frac{1}{2}}(\kappa,\tau). \tag{29b}$$

The $P_{l+\frac{1}{2},\pm\frac{1}{2}}(\kappa,\tau)$ and $S_{l+\frac{1}{2},\pm\frac{1}{2}}(\kappa,\tau)$ can be reduced to incomplete gamma functions $A^i_l(\xi,x)$ and $A^s_l(\xi,x)$ defined as in (30)

$$A^i_l(\xi,x) = \int_0^x \mathrm{e}^{-\xi t} t^l\, dt \tag{30a}$$

$$A^s_l(\xi,x) = \int_x^\infty \mathrm{e}^{-\xi t} t^l\, dt. \tag{30b}$$

In terms of these

$$P_{l+\frac{1}{2},-\frac{1}{2}}(\kappa,\tau) = \frac{1}{\sqrt{(2\pi)}}\{A^i_l(\kappa-1,\tau) + A^i_l(\kappa+1,\tau)\} \tag{31a}$$

$$P_{l+\frac{1}{2},+\frac{1}{2}}(\kappa,\tau) = \frac{1}{\sqrt{(2\pi)}}\{A^i_l(\kappa-1,\tau) - A^i_l(\kappa+1,\tau)\} \tag{31b}$$

$$S_{l+\frac{1}{2},\pm\frac{1}{2}}(\kappa,\tau) = \sqrt{\left(\frac{\pi}{2}\right)} A^s_l(\kappa+1,\tau). \tag{32}$$

The A's can be evaluated very rapidly, since

$$A_l^i(\xi, x) = \frac{l}{\xi} A_{l-1}^i(\xi, x) - \frac{e^{-\xi x} x^l}{\xi} \tag{33a}$$

$$A_0^i(\xi, x) = \frac{1 - e^{-\xi x}}{\xi} \tag{33b}$$

$$A_l^s(\xi, x) = \frac{l}{\xi} A_{l-1}^s(\xi, x) + \frac{e^{-\xi x} x^l}{\xi} \tag{33c}$$

$$A_0^s(\xi, x) = \frac{e^{-\xi x}}{\xi}. \tag{33d}$$

When $\xi = 0$, the A_l^i become merely

$$A_l^i(0, x) = \frac{x^{l+1}}{(l+1)}. \tag{33e}$$

The calculation of A_l^i for large values of l starting from A_0^i and repeatedly applying formula (33a) results in considerable differencing effects of the type described at the end of section 4. In such circumstances, it is more profitable to start from the value of A_l^i in which l has its maximum value, and to apply (33a) as a means of depressing the value of this index. To get this value of A_l^i directly, use can be made of the infinite series expansion (33f)

$$A_l^i(\xi, x) = x^{l+1} e^{-\xi x} \sum_{j=0}^{\infty} \frac{(\xi x)^j}{(l+1)(l+2)\ldots(l+j+1)}. \tag{33f}$$

The $P_{-\frac{1}{2}, n+\frac{1}{2}}(\kappa, \tau)$, $S_{-\frac{1}{2}, n+\frac{1}{2}}(\kappa, \tau)$ are constructed from $P_{-\frac{1}{2}, \frac{1}{2}}(\kappa, \tau), P_{-\frac{1}{2}, \frac{3}{2}}(\kappa, \tau)$ and from $S_{-\frac{1}{2}, \pm\frac{1}{2}}(\kappa, \tau)$ respectively, by use of the recursion formulae (34) and (35)

$$P_{-\frac{1}{2}, n+\frac{1}{2}}(\kappa, \tau) = \frac{1}{n}\left[(2n-1)\left\{\frac{e^{-\kappa\tau}}{\sqrt{\tau}} I_{n-\frac{1}{2}}(\tau) + \kappa P_{-\frac{1}{2}, n-\frac{1}{2}}(\kappa, \tau)\right\} - (n-1) P_{-\frac{1}{2}, n-\frac{3}{2}}(\kappa, \tau)\right] \tag{34}$$

$$S_{-\frac{1}{2}, n+\frac{1}{2}}(\kappa, \tau) = \frac{1}{n}\left[(2n-1)\left\{\frac{e^{-\kappa\tau}}{\sqrt{\tau}} K_{n-\frac{1}{2}}(\tau) - \kappa S_{-\frac{1}{2}, n-\frac{1}{2}}(\kappa, \tau)\right\} - (n-1) S_{-\frac{1}{2}, n-\frac{3}{2}}(\kappa, \tau)\right]. \tag{35}$$

The functions $P_{-\frac{1}{2}, \frac{1}{2}}, P_{-\frac{1}{2}, \frac{3}{2}}$, and $S_{-\frac{1}{2}, \pm\frac{1}{2}}$ can be expressed in terms of Legendre functions of the second kind, (Q's), and exponential integrals.

$$P_{-\frac{1}{2}, \frac{1}{2}}(\kappa, \tau) = \frac{1}{\sqrt{(2\pi)}}[2Q_0(\kappa) - E_1\{(\kappa-1)\tau\} + E_1\{(\kappa+1)\tau\}] \tag{36a}$$

$$P_{-\frac{1}{2}, \frac{3}{2}}(\kappa, \tau) = \frac{1}{\sqrt{(2\pi)}}\left[2Q_1(\kappa) - E_1\{(\kappa-1)\tau\} - E_1\{(\kappa+1)\tau\} + \frac{1}{\tau} E_2\{(\kappa-1)\tau\} - \frac{1}{\tau} E_2\{(\kappa+1)\tau\}\right] \tag{36b}$$

$$S_{-\frac{1}{2}, \pm\frac{1}{2}}(\kappa, \tau) = \sqrt{\left(\frac{\pi}{2}\right)} E_1\{(\kappa+1)\tau\}, \tag{37}$$

where $$Q_0(x) = \tfrac{1}{2}\log\left|\frac{x+1}{x-1}\right|; \quad Q_1(x) = xQ_0(x) - 1$$

and $$E_1(x) = -\mathrm{Ei}(-x); \quad E_2(x) = e^{-x} - xE_1(x).$$

The preceding equations suffice for the $P_{-\frac{1}{2}, n+\frac{1}{2}}$ and $S_{-\frac{1}{2}, n+\frac{1}{2}}$ when $\kappa \neq 1$. If, however, $\kappa = 1$, (36a) and (36b) become modified to

$$P_{-\frac{1}{2}, , \frac{1}{2}}(1, \tau) = \frac{1}{\sqrt{(2\pi)}}\{\gamma + \log 2\tau + E_1(2\tau)\} \tag{38a}$$

$$P_{-\frac{1}{2}, \frac{3}{2}}(1, \tau) = \frac{1}{\sqrt{(2\pi)}}\left\{\gamma + \log 2\tau - 2 + \frac{1}{\tau} - E_1(2\tau) - \frac{1}{\tau} E_2(2\tau)\right\}, \tag{38b}$$

where γ is Euler's constant.

In the calculation of the functions $P_{-\frac{1}{2},n+\frac{1}{2}}$ and $S_{-\frac{1}{2},n+\frac{1}{2}}$ for large values of n, the equations (34) and (35) must be applied repeatedly. It is useful, in these circumstances, to have an independent check on the final value of the $P_{-\frac{1}{2},n+\frac{1}{2}}$ and $S_{-\frac{1}{2},n+\frac{1}{2}}$ for the highest value of n needed. For the former, use can be made of the infinite series expansion (39) with $l=-1$.

$$P_{l+\frac{1}{2},n+\frac{1}{2}}(\kappa,\tau)=\frac{2^{n+1}}{\sqrt{(2\pi)}}\sum_{j=0}^{\infty}\frac{(j+n)!}{j!(2n+2j+1)!}A^{i}_{2j+l+n+1}(\kappa,\tau), \tag{39}$$

whilst for the latter, an expansion can be obtained from (40)

$$S_{l+\frac{1}{2},n+\frac{1}{2}}(\kappa,\tau)=\sqrt{\left(\frac{\pi}{2}\right)}\left[\sum_{j=0}^{l}\frac{(n+j)!}{j!(n-j)!\,2^{j}}A^{s}_{l-j}(\kappa+1,\tau)+\sum_{j=l+1}^{n}\frac{(n+j)!\,\tau^{l-j+1}}{j!(n-j)!\,2^{j}}E_{j-l}\{(\kappa+1)\tau\}\right]. \tag{40}$$

In (40), the second summation is ignored when $l\geqslant n$, and the first when $l<0$. The $E_j(x)$ are the generalized exponential integrals, needed also in (36) and (38):

$$E_j(x)=\int_1^{\infty}\mathrm{e}^{-xt}t^{-j}\,dt.$$

Equation (39) may also be used to generate $P_{-\frac{1}{2},n+\frac{1}{2}}(\kappa,\tau)$ for the highest n needed and the other $P_{-\frac{1}{2},n+\frac{1}{2}}$ can then be found by applying the recursion formula (34) as a method for depressing n. In this way differencing effects are overcome.

The $P_{\frac{1}{2},n+\frac{1}{2}}$ and $S_{\frac{1}{2},n+\frac{1}{2}}$ are obtained from the $P_{-\frac{1}{2},n+\frac{1}{2}}$ and $S_{-\frac{1}{2},n+\frac{1}{2}}$ by putting $l=0$ in the formulae (41) and (42). The 'starting values' of $P_{\frac{1}{2},\pm\frac{1}{2}}$ and $S_{\frac{1}{2},\pm\frac{1}{2}}$ are found from (31) and (32)

$$P_{l+\frac{1}{2},n+\frac{1}{2}}(\kappa,\tau)=P_{l+\frac{1}{2},n-\frac{3}{2}}(\kappa,\tau)-(2n-1)\,P_{l-\frac{1}{2},n-\frac{1}{2}}(\kappa,\tau) \tag{41}$$

$$S_{l+\frac{1}{2},n+\frac{1}{2}}(\kappa,\tau)=S_{l+\frac{1}{2},n-\frac{3}{2}}(\kappa,\tau)+(2n-1)\,S_{l-\frac{1}{2},n-\frac{1}{2}}(\kappa,\tau). \tag{42}$$

Again, with these $P_{\frac{1}{2},n+\frac{1}{2}}$ it may be advisable to obtain a value corresponding to the highest n from (39) and then to use (41) to depress this index.

The formulae which have been listed suffice for the evaluation of the peripheral **G** and **P**. The other **G**'s and **P**'s can now be tabulated, by use of the equations

$$\frac{2n-1}{\tau}\mathbf{P}_{n-1,l+\frac{1}{2}}(\kappa,\tau)=\mathbf{G}_{n-2,l+\frac{3}{2}}(\kappa,\tau)-\mathbf{G}_{n,l+\frac{3}{2}}(\kappa,\tau) \tag{43}$$

$$\mathbf{P}_{n-2,l+\frac{1}{2}}(\kappa,\tau)-\mathbf{P}_{n,l+\frac{1}{2}}(\kappa,\tau)=(2n-1)\left\{\frac{1}{\tau}\mathbf{G}_{n-1,l+\frac{3}{2}}(\kappa,\tau)+\tau\mathbf{G}_{n-1,l-\frac{1}{2}}(\kappa,\tau)\right\}$$
$$-(2n-3)\,\mathbf{G}_{n-2,l+\frac{1}{2}}(\kappa,\tau)-(2n+1)\,\mathbf{G}_{n,l+\frac{1}{2}}(\kappa,\tau). \tag{44}$$

The first step is to values of $\mathbf{G}_{1,l+\frac{1}{2}}$ using $\mathbf{G}_{-1,l+\frac{3}{2}}$ and $\mathbf{P}_{0,l+\frac{1}{2}}$, and equation (43). Next, the differences $\mathbf{P}_{-1,l+\frac{1}{2}}(\kappa,\tau)-\mathbf{P}_{1,l+\frac{1}{2}}(\kappa,\tau)$ are found from appropriate values of $\mathbf{G}_{-1,l+\frac{1}{2}}(\kappa,\tau)$, $\mathbf{G}_{0,l+\frac{1}{2}}(\kappa,\tau)$, $\mathbf{G}_{1,l+\frac{1}{2}}(\kappa,\tau)$, using (44). The $\mathbf{P}_{1,l+\frac{1}{2}}(\kappa,\tau)$ can then be found. The cycle can now be repeated indefinitely. In conclusion it may be added that for awkward ranges of the parameters and for large values n, 'differencing effects' occur. These can be overcome by constructing **G**'s of high n from equations (25a), (27), (39) and (40); from these **G**'s, the **P**'s of high n can be found, and the recursion cycle applied in reverse.

6. Numerical example

To illustrate the use of the method we have considered a single J integral which can actually be evaluated in several distinct ways. In addition we have considered the systematic evaluation of $\mathbf{Z}$ functions for a couple of pairs of values of the parameters κ, τ.

The J integral which has been considered is

$$\beta^3 \int e^{-\alpha r_a - \beta r_b} \sin^2 \theta_a \, dV.$$

In terms of the functions listed by Coulson (1942), this can be reduced to

$$\beta^3\{J_1(\alpha, \beta, \rho) - J_{41}(\alpha, \beta, \rho)\}, \quad \alpha \neq \beta$$
$$\beta^3\{K_1(\beta, \rho) - K_{48}(\beta, \rho)\}, \quad \alpha = \beta.$$

These expressions were evaluated using the formulae of Coulson's paper. In terms of the functions of this present paper, the integral reduces to

$$\frac{8\pi}{3\sqrt{\tau}} \int_0^\infty e^{-\kappa t} t^{\frac{3}{2}} \{p_0(1, t; \tau) - p_2(1, t; \tau)\} \, dt.$$

This was evaluated numerically, and also as

$$\frac{8\pi}{3\sqrt{\tau}} \{\mathbf{P}_{0,\frac{3}{2}}(\kappa, \tau) - \mathbf{P}_{2,\frac{3}{2}}(\kappa, \tau)\}.$$

For the numerical integration, 15 points spaced uniformly over the range $0 \leqslant t \leqslant 7$ were used. A value was obtained by use of Simpson's rule. An almost identical value was obtained by adding the contributions from the ranges $(0, 5)$ and $(5, 7)$, found respectively by use of the ten- and four-strip rules. For the values of the parameters $\kappa = 1; \tau = 3$, values obtained were

numerical integration	(Simpson's rule):	0·5078
	(accurate rules):	0·5077
expansion in $\mathbf{Z}$ functions:		0·5076
method of Coulson 1942:		0·5076

This shows that the method is correct and manageable. It also shows that for most purposes the method of numerical integration is entirely adequate. This method has the great advantage of not requiring any of the analysis from equation (24) onwards.

As regards the systematic tabulation of the $\mathbf{Z}$ functions, we found that no unforeseen difficulties arose during actual numerical computations when using several values for the parameters κ, τ. In this work it must be remembered that a peripheral $\mathbf{G}$ is obtained as the sum of $\mathbf{G}^i$ and $\mathbf{G}^s$. Now to get these $\mathbf{G}^i$ and $\mathbf{G}^s$ terms $P_{l+\frac{1}{2}, n+\frac{1}{2}}(\kappa, \tau)$ and $S_{l+\frac{1}{2}, n+\frac{1}{2}}(\kappa, \tau)$ are multiplied by $K_{n+\frac{1}{2}}(\tau)$ and $I_{n+\frac{1}{2}}(\tau)$ respectively. Since $K_{n+\frac{1}{2}}(\tau)$ decreases roughly as $e^{-\tau}$ and $I_{n+\frac{1}{2}}(\tau)$ increases roughly as e^{τ}, the S's must be evaluated to several decimal places more than the P's.

Although the need occasionally arises for the evaluation of one isolated J integral, we shall see in part II that much more frequently we require the compilation of blocks of related J's. These are J's such as (1) with the same α, β, ρ, but with different u, v, p, q. Such

blocks are most conveniently calculated from the **Z**'s, developing the latter by use of the explicit expressions given in this part; the larger the block the more economical of effort such calculations become.

7. Differentiation of the **Z** functions

This is an important consideration in variational calculations, when energy is to be minimized with respect to variable molecular parameters, such as the internuclear distance and the screening constants. The differentiation of the **Z**'s with respect to either of these quantities results merely in other **Z** functions.

Thus differentiation with respect to κ can be effected using

$$\frac{\partial}{\partial\kappa}\{\mathbf{Z}_{m,n,l+\frac{1}{2}}(\kappa,\tau)\} = -\mathbf{Z}_{m,n,l+\frac{3}{2}}(\kappa,\tau). \tag{45}$$

For differentiation with respect to τ we have

$$\frac{\partial}{\partial\tau}\{\mathbf{G}_{n,l+\frac{1}{2}}(\kappa,\tau)\} = K'_{n+\frac{1}{2}}(\tau)\,P_{l+\frac{1}{2},n+\frac{1}{2}}(\kappa,\tau) + I'_{n+\frac{1}{2}}(\tau)\,S_{l+\frac{1}{2},n+\frac{1}{2}}(\kappa,\tau), \tag{46a}$$

where I' and K' denote the first derivatives of the Bessel functions. There is also the recursion formula:

$$2\kappa\frac{\partial}{\partial\tau}\{\mathbf{G}_{n,l+\frac{1}{2}}(\kappa,\tau)\} = (2l+1)\frac{\partial}{\partial\tau}\{\mathbf{G}_{n,l-\frac{1}{2}}(\kappa,\tau)\} + 2\,\mathrm{e}^{-\kappa\tau}\tau^{l-\frac{1}{2}} - \mathbf{G}_{n-1,l+\frac{1}{2}}(\kappa,\tau) - \mathbf{G}_{n+1,l+\frac{1}{2}}(\kappa,\tau) - \frac{(2n+1)^2}{2\tau}\mathbf{G}_{n,l-\frac{1}{2}}(\kappa,\tau). \tag{46b}$$

Values of $I'_{n+\frac{1}{2}}(\tau)$ and $K'_{n+\frac{1}{2}}(\tau)$ can be found from I's and K's by use of the standard recursion formulae (Watson 1944).

8. Tabulation of necessary quantities

The general question of tables must now be considered more fully. First, we require Bessel functions of half integral order and imaginary argument. Some tables exist for functions of the first kind (Dinnick 1933) and of the second kind (Carsten & McKerrow 1944). However, these are inadequate for the calculations which we have described. Small tables are therefore provided (tables 1 and 2). The numerical values were obtained from the equations (21*a*), (21*b*), (21*c*), except for some half dozen entries in table 1 which were found by means of the infinite series (22). Our values for the K's are in complete agreement with those obtained by previous workers, where they overlap.

The construction of Q's for substitution in equation (36) presents no difficulty. Adequate tables are now available for most of the exponential integrals $-\mathrm{Ei}(-x)$. The generalized exponential integrals $E_n(x)$, needed in equation (40) have also been tabulated recently for orders up to 20 (Placzek 1946).

9. Comments on the derivation of the formulae

The various recursion formulae can all be obtained from the well-known recursion formulae between the I's and K's (Watson 1944). The formulae for the $\zeta_{m,n}$ are obtained first, and the formulae for the $\mathbf{Z}_{m,n,l+\frac{1}{2}}$ follow immediately from these.

TABLE 1. BESSEL FUNCTIONS OF THE FIRST KIND, OF IMAGINARY ARGUMENT, AND HALF INTEGRAL ORDER

$$I_{n+\frac{1}{2}}(x) = A(10)^p$$

	$I_{-\frac{1}{2}}(x)$		$I_{\frac{1}{2}}(x)$		$I_{\frac{3}{2}}(x)$		$I_{\frac{5}{2}}(x)$		$I_{\frac{7}{2}}(x)$		$I_{\frac{9}{2}}(x)$	
x	p	A	p	A	p	A	p	A	p	A	p	A
0·5	(0)	1·272 390	(−1)	5·879 931	(−2)	9·640 347	(−3)	9·572 244	(−4)	6·810 360	(−5)	3·774 019
1·0	(0)	1·231 200	(−1)	9·376 749	(−1)	2·935 253	(−2)	5·709 891	(−3)	8·030 780	(−4)	8·834 469
1·5	(0)	1·532 524	(0)	1·387 162	(−1)	6·077 498	(−1)	1·716 620	(−2)	3·554 311	(−3)	5·794 183
2·0	(0)	2·122 592	(0)	2·046 237	(0)	1·099 473	(−1)	3·970 271	(−1)	1·069 055	(−2)	2·285 787
2·5	(0)	3·094 516	(0)	3·053 094	(0)	1·873 278	(−1)	8·051 595	(−1)	2·629 594	(−2)	6·887 302
3·0	(0)	4·637 758	(0)	4·614 823	(0)	3·099 483	(0)	1·515 339	(−1)	5·739 177	(−1)	1·761 981
3·5	(0)	7·068 098	(0)	7·055 219	(0)	5·052 321	(0)	2·724 658	(0)	1·159 952	(−1)	4·047 541
4·0	(1)	1·089 441	(1)	1·088 710	(0)	8·172 633	(0)	4·757 627	(0)	2·225 600	(−1)	8·628 275
4·5	(1)	1·693 100	(1)	1·692 682	(1)	1·316 948	(0)	8·147 165	(0)	4·117 078	(0)	1·742 822
5·0	(1)	2·647 995	(1)	2·647 755	(1)	2·118 444	(1)	1·376 688	(0)	7·417 560	(0)	3·382 298
5·5	(1)	4·162 513	(1)	4·162 374	(1)	3·405 718	(1)	2·304 710	(1)	1·310 527	(0)	6·367 662
6·0	(1)	6·570 584	(1)	6·570 504	(1)	5·475 500	(1)	3·832 753	(1)	2·281 539	(1)	1·170 957
6·5	(2)	1·040 803	(2)	1·040 798	(1)	8·806 801	(1)	6·343 305	(1)	3·927 336	(1)	2·113 866
7·0	(2)	1·653 571	(2)	1·653 568	(2)	1·417 347	(2)	1·046 133	(1)	6·701 084	(1)	3·760 253
7·5	(2)	2·633 833	(2)	2·633 831	(2)	2·282 655	(2)	1·720 769	(2)	1·135 476	(1)	6·609 915
8·0	(2)	4·204 564	(2)	4·204 563	(2)	3·678 994	(2)	2·824 941	(2)	1·913 406	(2)	1·150 710
8·5	(2)	6·725 177	(2)	6·725 176	(2)	5·933 980	(2)	4·630 831	(2)	3·209 962	(2)	1·987 333
9·0	(3)	1·077 554	(3)	1·077 554	(2)	9·578 260	(2)	7·582 789	(2)	5·365 600	(2)	3·409 545
9·5	(3)	1·729 202	(3)	1·729 202	(3)	1·547 181	(3)	1·240 619	(2)	8·942 238	(2)	5·817 172
10·0	(3)	2·778 785	(3)	2·778 785	(3)	2·500 906	(3)	2·028 513	(3)	1·486 650	(2)	9·878 579

TABLE 2. BESSEL FUNCTIONS OF THE SECOND KIND, OF IMAGINARY ARGUMENT, AND HALF INTEGRAL ORDER

$$K_{n+\frac{1}{2}}(x) = A(10)^p$$

	$K_{\pm\frac{1}{2}}(x)$		$K_{\frac{3}{2}}(x)$		$K_{\frac{5}{2}}(x)$		$K_{\frac{7}{2}}(x)$		$K_{\frac{9}{2}}(x)$	
x	p	A	p	A	p	A	p	A	p	A
0·5	(0)	1·075 048	(0)	3·225 143	(1)	2·042 590	(2)	2·074 842	(3)	2·925 205
1·0	(−1)	4·610 685	(−1)	9·221 370	(0)	3·227 480	(1)	1·705 953	(2)	1·226 442
1·5	(−1)	2·283 351	(−1)	3·805 584	(−1)	9·894 519	(0)	3·678 731	(1)	1·815 687
2·0	(−1)	1·199 378	(−1)	1·799 067	(−1)	3·897 978	(0)	1·154 401	(0)	4·430 201
2·5	(−2)	6·506 594	(−2)	9·109 232	(−1)	1·743 767	(−1)	4·398 458	(0)	1·405 945
3·0	(−2)	3·602 599	(−2)	4·803 465	(−2)	8·406 063	(−1)	1·881 357	(−1)	5·230 439
3·5	(−2)	2·022 997	(−2)	2·600 996	(−2)	4·252 422	(−2)	8·675 885	(−1)	2·160 419
4·0	(−2)	1·147 762	(−2)	1·434 703	(−2)	2·223 790	(−2)	4·214 440	(−2)	9·599 060
4·5	(−3)	6·563 395	(−3)	8·021 927	(−2)	1·191 135	(−2)	2·125 676	(−2)	4·497 741
5·0	(−3)	3·776 613	(−3)	4·531 936	(−3)	6·495 775	(−2)	1·102 771	(−2)	2·193 457
5·5	(−3)	2·184 032	(−3)	2·581 128	(−3)	3·591 920	(−3)	5·846 510	(−2)	1·103 293
6·0	(−3)	1·268 287	(−3)	1·479 668	(−3)	2·008 121	(−3)	3·153 102	(−3)	5·686 739
6·5	(−4)	7·390 760	(−4)	8·527 801	(−3)	1·132 667	(−3)	1·724 062	(−3)	2·989 349
7·0	(−4)	4·319 660	(−4)	4·936 754	(−4)	6·435 412	(−4)	9·533 477	(−3)	1·596 889
7·5	(−4)	2·531 166	(−4)	2·868 655	(−4)	3·678 628	(−4)	5·321 074	(−4)	8·644 964
8·0	(−4)	1·486 480	(−4)	1·672 290	(−4)	2·113 589	(−4)	2·993 283	(−4)	4·732 712
8·5	(−5)	8·746 763	(−5)	9·775 794	(−4)	1·219 704	(−4)	1·695 053	(−4)	2·615 630
9·0	(−5)	5·155 708	(−5)	5·728 565	(−5)	7·065 230	(−5)	9·653 693	(−4)	1·457 366
9·5	(−5)	3·043 691	(−5)	3·364 080	(−5)	4·106 032	(−5)	5·525 149	(−5)	8·177 194
10·0	(−5)	1·799 348	(−5)	1·979 283	(−5)	2·393 133	(−5)	3·175 849	(−5)	4·616 227
11·0	(−6)	6·311 380	(−6)	6·885 141	(−6)	8·189 145	(−5)	1·060 748	(−5)	1·493 936
12·0	(−6)	2·222 980	(−6)	2·408 228	(−6)	2·825 037	(−6)	3·585 327	(−6)	4·916 478
13·0	(−7)	7·857 059	(−7)	8·461 448	(−7)	9·809 701	(−6)	1·223 441	(−6)	1·639 746
14·0	(−7)	2·785 308	(−7)	2·984 258	(−7)	3·424 792	(−7)	4·207 398	(−7)	5·528 491
15·0	(−8)	9·899 131	(−7)	1·055 907	(−7)	1·201 095	(−7)	1·456 272	(−7)	1·880 688
16·0	(−8)	3·526 048	(−8)	3·746 426	(−8)	4·228 503	(−8)	5·067 833	(−8)	6·445 680
17·0	(−8)	1·258 431	(−8)	1·332 456	(−8)	1·493 570	(−8)	1·771 741	(−8)	2·223 110
18·0	(−9)	4·499 073	(−9)	4·749 021	(−9)	5·290 576	(−9)	6·218 626	(−9)	7·708 931
19·0	(−9)	1·610 972	(−9)	1·695 760	(−9)	1·878 724	(−9)	2·190 161	(−9)	2·685 625
20·0	(−10)	5·776 374	(−10)	6·065 193	(−10)	6·686 153	(−10)	7·736 731	(−10)	9·394 009
21·0	(−10)	2·073 797	(−10)	2·172 549	(−10)	2·384 161	(−10)	2·740 206	(−10)	3·297 563
22·0	(−11)	7·453 667	(−11)	7·792 470	(−11)	8·516 277	(−11)	9·727 988	(−10)	1·161 155
23·0	(−11)	2·681 779	(−11)	2·798 378	(−11)	3·046 785	(−11)	3·460 722	(−11)	4·100 048
24·0	(−12)	9·657 990	(−11)	1·006 041	(−11)	1·091 554	(−11)	1·233 448	(−11)	1·451 310
25·0	(−12)	3·481 191	(−12)	3·620 439	(−12)	3·915 644	(−12)	4·403 568	(−12)	5·148 643

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The expressions (31), (32) and (36)–(40) for the P and S functions can be obtained from the explicit formulae (21), (22). To obtain expressions for the $P_{-\frac{1}{2},n+\frac{1}{2}}(\kappa,\tau)$ functions, it is necessary to use the result

$$\int_0^\infty \mathrm{e}^{-\kappa t} t^{-\frac{1}{2}} I_{n+\frac{1}{2}}(t)\,dt = \sqrt{\left(\frac{2}{\pi}\right)} Q_n(\kappa). \tag{47}$$

This infinite integral can be used only when $\kappa > 1$. By a long argument, which we shall not reproduce here, it can be shown that provided the definitions appropriate to the case $\kappa < 1$ are used for $Q_n(\kappa)$ and for $\mathrm{Ei}\{-(\kappa-1)\tau\}$, then the result (36) is still valid. Furthermore, as a by-product of this proof, the formulae (38a) and (38b), for the case $\kappa = 1$, are obtained, as a consequence of the result

$$\int_0^1 \frac{1-\mathrm{e}^{-t}}{t}\,dt - \int_1^\infty \frac{\mathrm{e}^{-t}}{t}\,dt = \gamma. \tag{48}$$

In conclusion, it may be mentioned that approximate formulae may be constructed for the **Z** functions, valid particularly at large internuclear distances, and large κ. These approximate expressions are rather clumsy, and several different cases have to be considered. For these reasons, we shall not describe them here.

PART II. OVERLAP, RESONANCE, COULOMB, HYBRID AND OTHER TWO-CENTRE INTEGRALS

10. Introduction

This part deals with certain integrals which result from the approximations now used in the theory of molecular structure. The relevant basic functions have already been discussed in part I, the results of which will be exploited.

The integrals which will be considered are the so-called Coulomb, overlap and resonance one-electron integrals, the two-electron Coulomb and hybrid (Coulomb-exchange) integrals, and the penetration integrals. These all arise in calculations which deal with systems of two nuclei and one or more electrons. Formal definitions are given in equations (49) to (51). These involve atomic wave functions, which are denoted by symbols of the form $\Psi'(X,i)$. The letters X and i define respectively the nucleus on which the wave function is based, and the electron on which it operates. The two nuclei are referred to by the letters A and B. When necessary, the electrons are specified by numerals 1 and 2. The distance from nucleus X to electron i is denoted by r_{xi}, and the distance between electrons 1 and 2 by r_{12}. The primes on the Ψ's show that they may be of different analytical form.

Resonance and overlap integrals involve just one electron; so also does the integral (49c) which is most conveniently termed a 'one-electron Coulomb' integral:

$$\text{overlap integral} \qquad \int \Psi'(A,1)\,\Psi''(B,1)\,dV_1 \tag{49a}$$

$$\text{resonance integral} \qquad \int \frac{1}{r_{b1}} \Psi'(A,1)\,\Psi''(B,1)\,dV_1 \tag{49b}$$

$$\text{Coulomb integral} \qquad \int \frac{1}{r_{b1}} \Psi'(A,1)\,\Psi''(A,1)\,dV_1. \tag{49c}$$

Coulomb integrals of another type (50*a*), and hybrid Coulomb-exchange integrals, (50*b*), occur in connexion with two-electron systems. Exchange integrals (50*c*) also appear in such calculations, but their evaluation will not be considered in this present paper.

$$\text{Coulomb integral} \qquad \iint \Psi(A,1)\,\Psi'(A,1)\,\frac{1}{r_{12}}\,\Psi''(B,2)\Psi'''(B,2)\,dV_1\,dV_2 \qquad (50a)$$

$$\text{hybrid integral} \qquad \iint \Psi(A,1)\,\Psi'(A,1)\,\frac{1}{r_{12}}\,\Psi''(A,2)\,\Psi'''(B,2)\,dV_1\,dV_2 \qquad (50b)$$

$$\text{exchange integral} \qquad \iint \Psi(A,1)\,\Psi'(B,1)\,\frac{1}{r_{12}}\,\Psi''(A,2)\,\Psi'''(B,2)\,dV_1\,dV_2. \qquad (50c)$$

The electrons in the hybrid integral display an allegiance intermediate between that found in the Coulomb integral and that found in the exchange integral. In (50*a*), each electron is controlled entirely by one or other nucleus. In (50*c*), both the electrons are shared between the two nuclei. In (50*b*), one electron is dominated by one nucleus and the other is shared. Mention may also be made of the mononuclear integral (50*d*):

$$\text{mononuclear integral} \qquad \iint \Psi(A,1)\,\Psi'(A,1)\,\frac{1}{r_{12}}\,\Psi''(A,2)\,\Psi'''(A,2)\,dV_1\,dV_2. \qquad (50d)$$

Although integrals of this type involve only one atom, their values are required in calculations dealing with two-atom systems. Furthermore, since they represent limiting cases of the integrals (50*a*) to (50*c*) they provide a check on the values found for these latter integrals at small internuclear distances.

Penetration integrals represent the energy of an electron in the field of an electrically neutral atom, X. The potential of an electron i due to this atom can be denoted by $H_x^*(i)$, and can be calculated by classical methods. The Coulomb-penetration and exchange-penetration integrals are then defined as in (51*a*) and (51*b*). We take nucleus A as belonging to the neutral atom.

$$\text{Coulomb-penetration integral} \qquad \int H_a^*(1)\,\Psi(B,1)\,\Psi''(B,1)\,dV_1, \qquad (51a)$$

$$\text{exchange-penetration integral} \qquad \int H_a^*(1)\,\Psi(A,1)\,\Psi''(B,1)\,dV_1. \qquad (51b)$$

The former measures the energy of an electron based on one atom, due to the field of a different, neutral atom. The latter measures the resonance energy between two atomic orbitals, one of which is based on the neutral atom.

The integrals of (49), (50) and (51) result from both the usual molecular orbital and valence-bond approximation. It is hoped later to generalize the method to deal with the integrals which result from more refined types of approximation (see for example, James & Coolidge 1933; Coulson & Duncanson 1938; Frost, Braunstein & Schwemer 1949).

By dealing with the three types of integral (49) to (51) in the same way, we reduce them to one single set of subsidiary quantities. Hitherto, integrals of different classes were treated separately, each with its own auxiliary functions. An additional advantage with our present treatment lies in the fact that no complications arise when the nuclei are of different elements.

11. Wave functions

The value of a molecular integral depends upon the analytical form and numerical parameters of its component wave functions. In what follows we shall be concerned with functions taken from table 3. This contains the familiar nodeless functions of Slater (1930). The more accurate 'orthogonalized' wave functions which contain nodes are, however, merely linear combinations of these nodeless ones, and need not be considered separately (Moffitt & Coulson 1947). It is also possible to obtain approximately self-consistent atomic orbitals as linear combinations of these nodeless functions.

Table 3. Wave-functions

$1s$	$(k^3/\pi)^{\frac{1}{2}}\,\mathrm{e}^{-kr}$
$2s$	$(k^5/3\pi)^{\frac{1}{2}}\,r\,\mathrm{e}^{-kr}$
$2p_x$, $2p_y$, $2p_z$	$(k^5/\pi)^{\frac{1}{2}}\begin{Bmatrix}(x)\\(y)\\(z)\end{Bmatrix}\mathrm{e}^{-kr}$
$3s$	$(2k^7/45\pi)^{\frac{1}{2}}\,r^2\,\mathrm{e}^{-kr}$
$3p_x$, $3p_y$, $3p_z$	$(2k^7/15\pi)^{\frac{1}{2}}\,r\begin{Bmatrix}(x)\\(y)\\(z)\end{Bmatrix}\mathrm{e}^{-kr}$
$3d_{z^2}$	$(k^7/18\pi)^{\frac{1}{2}}\,(3z^2-r^2)\,\mathrm{e}^{-kr}$
$3d_{xz}$, $3d_{yz}$, $3d_{xy}$	$(2k^7/3\pi)^{\frac{1}{2}}\begin{Bmatrix}(xz)\\(yz)\\(xy)\end{Bmatrix}\mathrm{e}^{-kr}$
$3d_{x^2-y^2}$	$(k^7/6\pi)^{\frac{1}{2}}\,(x^2-y^2)\,\mathrm{e}^{-kr}$

We may refer to any of these functions as $c_1, c_2, \ldots$. Where necessary the 'character' of the wave function will be indicated by modifying the symbol $\Psi(X,i)$, introduced earlier, to for example $\Psi(X,i;\,2p_x)$. The symbol $C(c_1,c_2)$ will be used to denote the one-electron Coulomb integral and the symbol $S(c_1,c_2)$ to denote the overlap integral derived from the two atomic orbitals, c_1 and c_2. Similarly, $R(c_1,c_2)$ will be used to denote the resonance integral involving orbitals c_1 and c_2. In this latter case, c_2 will always be taken as the orbital associated with the nucleus labelled B on which the radial operator is based (see equation (49b)). For example, if c_1 and c_2 denote $1s$ and $2p_z$ orbitals respectively, then

$$C(1s,2p_z) = \frac{1}{\pi}(k_1^3k_2^5)^{\frac{1}{2}}\int\exp\left[-(k_1+k_2)\,r_{a1}\right]\frac{r_{a1}}{r_{b1}}\cos\theta_{a1}\,dV_1$$

$$R(1s,2p_z) = \frac{1}{\pi}(k_1^3k_2^5)^{\frac{1}{2}}\int\exp\left[-(k_1r_{a1}+k_2r_{b1})\right]\cos\theta_{b1}\,dV_1$$

$$R(2p_z,1s) = \frac{1}{\pi}(k_1^5k_2^3)^{\frac{1}{2}}\int\exp\left[-(k_1r_{a1}+k_2r_{b1})\right]\frac{r_{a1}}{r_{b1}}\cos\theta_{a1}\,dV_1$$

$$S(1s,2p_z) = \frac{1}{\pi}(k_1^3k_2^5)^{\frac{1}{2}}\int\exp\left[-(k_1r_{a1}+k_2r_{b1})\right]r_{b1}\cos\theta_{b1}\,dV_1.$$

For the two-electron Coulomb integral the symbol $C(c_1,\ldots,c_4)$ will be used. In such a symbol, the c_1 and c_2 will be associated with nucleus A and electron 1, whilst the c_3 and c_4 will refer to nucleus B and electron 2. For example, if c_1, c_2, c_3 and c_4 denote respectively $1s$, $2s$, $2p_x$ and $2p_x$ orbitals

$$C(1s,2s;2p_x,2p_x) = \frac{1}{\pi^2}(k_1^3k_2^5k_3^5k_4^5/3)^{\frac{1}{2}}\iint\exp\left[-(k_1+k_2)\,r_{a1}-(k_3+k_4)\,r_{b2}\right]$$
$$\times\frac{r_{a1}r_{b2}^2}{r_{12}}\sin^2\theta_{b2}\cos^2\phi_2\,dV_1\,dV_2.$$

The symbol $I(c_1, c_2; c_3, c_4)$ will be used to denote a hybrid integral derived from the four atomic orbitals $c_1, \ldots, c_4$. In such a symbol, the functions c_1 and c_2 are associated with electron 1, and c_3 and c_4 with electron 2; also the first three atomic orbitals c_1, c_2, c_3 are centred around nucleus A, and the fourth one, c_4, around nucleus B. For example, if c_1, c_2, c_3, c_4 denote $1s$, $2s$, $2s$ and $2p_z$ orbitals respectively, then

$$I(1s, 2s; 2s, 2p_z) = \frac{1}{3\pi^2}(k_1^3 k_2^5 k_3^5 k_4^5)^{\frac{1}{2}} \iint \exp\left[-(k_1+k_2)\, r_{a1} - k_3 r_{a2} - k_4 r_{b2}\right] \times \frac{r_{a1} r_{a2} r_{b2}}{r_{12}} \cos\theta_{b2}\, dV_1\, dV_2.$$

Finally, the symbol $M(c_1, c_2; c_3, c_4)$ will be used to denote a mononuclear integral. The functions c_1, c_2 will be associated with electron 1, and c_3, c_4 with electron 2. Thus if c_1, c_2, c_3, c_4 denote $1s$, $2s$, $2p_x$ and $2p_x$ orbitals respectively, then

$$M(1s, 2s; 2p_x, 2p_x) = \frac{1}{\pi^2}(k_1^3 k_2^5 k_3^5 k_4^5/3)^{\frac{1}{2}} \iint \exp\left[-(k_1+k_2)\, r_{a1} - (k_3+k_4)\, r_{a2}\right] \frac{r_{a1} r_{a2}^2}{r_{12}} \sin^2\theta_{a2} \cos^2\phi_2\, dV_1\, dV_2.$$

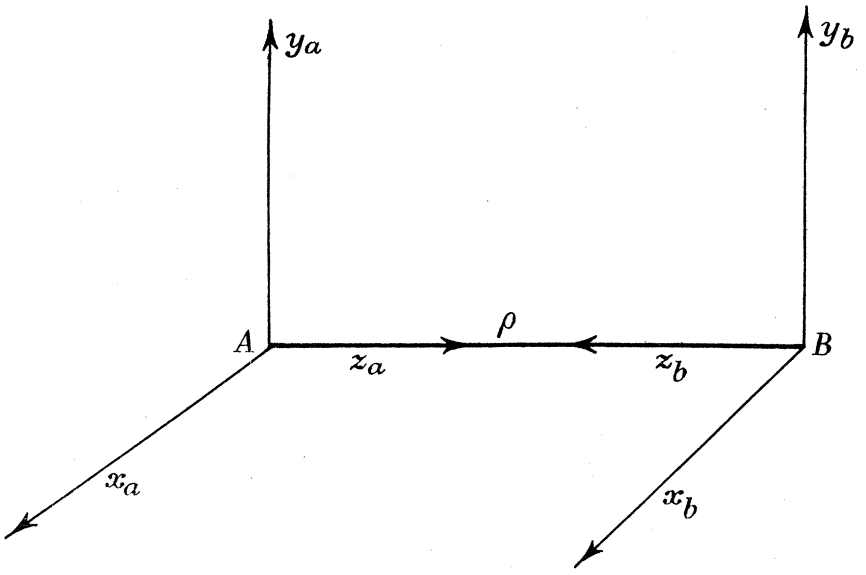

FIGURE 3

Co-ordinate axes x, y, z are required for complete definition of these functions. Each nucleus (figure 3) is taken as origin with its z axis directed towards the other nucleus. The distance between the two nuclei is ρ. The two x axes are parallel, but otherwise arbitrary, so that the two y axes are parallel: one system is right-handed, the other is left-handed. We use either Cartesian co-ordinates, or as in part I, polar co-ordinates (r_a, θ_a, ϕ), (r_b, θ_b, ϕ). This notation unambiguously describes all the integrals with which we are concerned.

We shall now deal with the integrals class by class, and show how in every case, their evaluation can be made to depend upon the basic **Z** functions of part I.

12. Reduction of one-electron integrals

The one-electron integrals (49) are of the form of the J integrals of part I. Their evaluation, either by a final numerical integration, or by the analytical method of part I, is immediate.

For certain of these integrals, explicit expressions are given by Coulson (1942). In addition, numerical values reliable to 2 or 3 significant figures, are listed for a few of the simpler overlap integrals by Mulliken, Rieke, Orloff & Orloff (1949), sometimes for quite wide ranges of the parameters involved. By a change of normalizing factor, these tables can be made to provide values for several resonance integrals.

Where necessary, all overlap integrals can be reduced to the form (52)

$$S(c_1, c_2) = N_s(c_1, c_2) \int_0^\infty \mathrm{e}^{-k_1 t/k_2}\, t^{\frac{3}{2}} f_s(c_1, c_2; t)\, dt. \tag{52}$$

Both the N_s's, which depend on the screening constants, and the f_s's which are functions of t, can be drawn from table 4. Here and elsewhere we use the subscripts s, r, c, and i for quantities relating to overlap, resonance, two-electron Coulomb and hybrid integrals

TABLE 4. OVERLAP INTEGRALS

$$S(c_1, c_2) = \int \Psi(A, 1; c_1)\, \Psi(B, 1; c_2)\, dV_1 = N_s(c_1, c_2) \int_0^\infty \mathrm{e}^{-k_1 t/k_2} t^{\frac{3}{2}} f_s(c_1, c_2; t)\, dt$$

$$p_n = p_n(1, t; k_2\rho), \quad q_n = q_n(1, t; k_2\rho), \quad \zeta_{3,n} = \zeta_{3,n}(1, t; k_2\rho)$$

c_1	c_2	$N_s(c_1, c_2)$	$f_s(c_1, c_2; t)$
$1s$	$1s$	$4(k_1^3/\rho)^{\frac{1}{2}} k_2^{-2}$	p_0
$2s$	$1s$	$4(k_1^5/3\rho)^{\frac{1}{2}} k_2^{-3}$	tp_0
	$2s$	$\frac{4}{3}(k_1^5/\rho)^{\frac{1}{2}} k_2^{-3}$	tq_0
$2p_x$	$2p_x$	$\frac{4}{3}(k_1^5/\rho)^{\frac{1}{2}} k_2^{-3}$	$t^2(p_0 - p_2)$
$2p_y$	$2p_y$		
$2p_z$	$1s$	$4(k_1^5/\rho)^{\frac{1}{2}} k_2^{-3}$	tp_1
	$2s$	$4(k_1^5/3\rho)^{\frac{1}{2}} k_2^{-3}$	tq_1
	$2p_z$	$4(k_1^5/\rho)^{\frac{1}{2}} k_2^{-3}$	$k_2\rho t p_1 - t^2\{p_0 - \frac{2}{3}(p_0 - p_2)\}$
$3s$	$1s$	$\frac{4}{3}(2k_1^7/5\rho)^{\frac{1}{2}} k_2^{-4}$	$t^2 p_0$
	$2s$	$\frac{4}{3}(2k_1^7/15\rho)^{\frac{1}{2}} k_2^{-4}$	$t^2 q_0$
	$2p_z$	$\frac{4}{3}(2k_1^7/5\rho)^{\frac{1}{2}} k_2^{-4}$	$t^2(k_2\rho p_0 - t p_1)$
	$3s$	$\frac{8}{45}(k_1^7/\rho)^{\frac{1}{2}} k_2^{-4}$	$t^2 \zeta_{3,0}$
$3p_x$	$2p_x$	$\frac{4}{3}(2k_1^7/15\rho)^{\frac{1}{2}} k_2^{-4}$	$t^3(p_0 - p_2)$
	$3p_x$	$\frac{8}{45}(k_1^7/\rho)^{\frac{1}{2}} k_2^{-4}$	$t^3(q_0 - q_2)$
$3p_y$	$2p_y$	as for $S(3p_x, 2p_x)$	
	$3p_y$	as for $S(3p_x, 3p_x)$	
$3p_z$	$1s$	$4(2k_1^7/15\rho)^{\frac{1}{2}} k_2^{-4}$	$t^2 p_1$
	$2s$	$\frac{4}{3}(2k_1^7/5\rho)^{\frac{1}{2}} k_2^{-4}$	$t^2 q_1$
	$2p_z$	$4(2k_1^7/15\rho)^{\frac{1}{2}} k_2^{-4}$	$t^2[k_2\rho p_1 - t\{p_0 - \frac{2}{3}(p_0 - p_2)\}]$
	$3s$	$\frac{8}{15}(k_1^7/3\rho)^{\frac{1}{2}} k_2^{-4}$	$t^2 \zeta_{3,1}$
	$3p_z$	$\frac{8}{15}(k_1^7/\rho)^{\frac{1}{2}} k_2^{-4}$	$t^2[k_2\rho q_1 - t\{q_0 - \frac{2}{3}(q_0 - q_2)\}]$
$3d_{z^2}$	$1s$	$\frac{8}{3}(k_1^7/2\rho)^{\frac{1}{2}} k_2^{-4}$	$t^2 p_2$
	$2s$	$\frac{8}{3}(k_1^7/6\rho)^{\frac{1}{2}} k_2^{-4}$	$t^2 q_2$
	$2p_z$	$\frac{8}{3}(k_1^7/2\rho)^{\frac{1}{2}} k_2^{-4}$	$t^2[k_2\rho p_2 - t\{p_1 - \frac{3}{5}(p_1 - p_3)\}]$
	$3s$	$\frac{8}{9}(k_1^7/5\rho)^{\frac{1}{2}} k_2^{-4}$	$t^2 \zeta_{3,2}$
	$3p_z$	$\frac{8}{3}(k_1^7/15\rho)^{\frac{1}{2}} k_2^{-4}$	$t^2[k_2\rho q_2 - t\{q_1 - \frac{3}{5}(q_1 - q_3)\}]$
	$3d_{z^2}$	$\frac{8}{9}(k_1^7/\rho)^{\frac{1}{2}} k_2^{-4}$	$t^2[k_2^2\rho^2 p_2 - \frac{2}{5}k_2\rho t(2p_1 + 3p_3) + t^2(\frac{1}{5}p_0 + \frac{2}{7}p_2 + \frac{18}{35}p_4)]$
$3d_{xz}$	$2p_x$	$\frac{4}{5}(2k_1^7/3\rho)^{\frac{1}{2}} k_2^{-4}$	$t^3(p_1 - p_3)$
	$3p_x$	$\frac{8}{15}(k_1^7/5\rho)^{\frac{1}{2}} k_2^{-4}$	$t^3(q_1 - q_3)$
	$3d_{xz}$	$\frac{8}{15}(k_1^7/\rho)^{\frac{1}{2}} k_2^{-4}$	$t^3[k_2\rho(p_1 - p_3) - t\{\frac{1}{3}(p_0 - p_2) + \frac{4}{7}(p_2 - p_4)\}]$
$3d_{yz}$	$2p_y$	as for $S(3d_{xz}, 2p_x)$	
	$3p_y$	as for $S(3d_{xz}, 3p_x)$	
	$3d_{yz}$	as for $S(3d_{xz}, 3d_{xz})$	
$3d_{x^2-y^2}$	$3d_{x^2-y^2}$	$\frac{8}{15}(k_1^7/\rho)^{\frac{1}{2}} k_2^{-4}$	$t^4\{\frac{1}{3}(p_0 - p_2) - \frac{1}{7}(p_2 - p_4)\}$
$3d_{xy}$	$3d_{xy}$		

respectively. The f_s's are expressed in terms of γ, p and other ζ functions of part I; these always have as arguments $(1, t; k_2\rho)$. The evaluation of such expressions is discussed exhaustively in part I. Except when c_1 and c_2 are identical, two different expressions can be obtained for $S(c_1, c_2)$ depending on which of the two wave functions is expanded about the distant origin. Thus for $S(3d_{z^2}, 1s)$ we have from table 4

$$S(3d_{z^2}, 1s) = \tfrac{8}{3}(k_1^7/2\rho)^{\frac{1}{2}} k_2^{-4} \int_0^\infty e^{-k_1 t/k_2} t^{\frac{7}{2}} p_2(1, t; k_2\rho)\, dt.$$

But another expression, equally valid, is

$$S(3d_{z^2}, 1s) = \tfrac{8}{3}(k_2^3/2\rho)^{\frac{1}{2}} k_1^{-2} \int_0^\infty e^{-k_2 t/k_1} t^{\frac{3}{2}} \{k_1^2\rho^2 p_0(1, t; k_1\rho) - 2k_1\rho t p_1(1, t; k_1\rho) + t^2 p_2(1, t; k_1\rho)\}\, dt.$$

This is much more complicated. The expressions actually quoted in table 4 are in every case the simpler of the two possible. The alternatives, if wanted, can be obtained without difficulty. They could be used to provide a check on numerical results.

In terms of the p and q functions, the resonance integrals can be put in the form (53). The N_r's and f_r's can be drawn from table 5. The p's and γ's still have as arguments $(1, t; k_2\rho)$.

$$R(c_1, c_2) = N_r(c_1, c_2) \int_0^\infty e^{-k_1 t/k_2} t^{\frac{3}{2}} f_r(c_1, c_2; t)\, dt. \tag{53}$$

TABLE 5. RESONANCE INTEGRALS

$$R(c_1, c_2) = \int \Psi(A, 1; c_1)\, \Psi(B, 2; c_2)\, r_{b1}^{-1} dV_1$$
$$= N_r(c_1, c_2) \int_0^\infty e^{-k_1 t/k_2} t^{\frac{3}{2}} f_r(c_1, c_2; t)\, dt$$

.....

$$\gamma_n = \gamma_n(1, t; k_2\rho), \quad p_n = p_n(1, t; k_2\rho)$$

.....

c_1	c_2	$N_r(c_1, c_2)$	$f_r(c_1, c_2; t)$
$1s$	$1s$	$4(k_1^3/\rho)^{\frac{1}{2}} k_2^{-1}$	γ_0
	$2s$	$4(k_1^3/3\rho)^{\frac{1}{2}} k_2^{-1}$	p_0
	$2p_z$	$4(k_1^3/\rho)^{\frac{1}{2}} k_2^{-1}$	$k_2\rho\gamma_0 - t\gamma_1$
$2s$	$1s$	$4(k_1^5/3\rho)^{\frac{1}{2}} k_2^{-2}$	$t\gamma_0$
	$2s$	$\frac{4}{3}(k_1^5/\rho)^{\frac{1}{2}} k_2^{-2}$	tp_0
	$2p_z$	$4(k_1^5/3\rho)^{\frac{1}{2}} k_2^{-2}$	$t(k_2\rho\gamma_0 - t\gamma_1)$
$2p_x$	$2p_x$	$4(k_1^5/\rho^3)^{\frac{1}{2}} k_2^{-3}$	tp_1
$2p_y$	$2p_y$		
$2p_z$	$1s$	$4(k_1^5/\rho)^{\frac{1}{2}} k_2^{-2}$	$t\gamma_1$
	$2s$	$4(k_1^5/3\rho)^{\frac{1}{2}} k_2^{-2}$	tp_1
	$2p_z$	$4(k_1^5/\rho^3)^{\frac{1}{2}} k_2^{-3}$	$t\{k_2^2\rho^2\gamma_1 - k_2\rho t\gamma_0 + 2p_1\}$

For the one-electron Coulomb integrals, it is possible to avoid the analysis of part I. These integrals could all be evaluated at once using the table of one-electron integrals of Coulson. Alternatively, $1/r_b$ can be expanded as an infinite series of spherical harmonics about nucleus A. On integrating, very few terms survive, and these are precisely the same as those obtained by the first method. In our present case, we have used the self-consistence of the pairs of expressions to check their reliability. These one-electron Coulomb integrals are listed in table 6, in terms of certain quantities which we denote by the symbol j_n. These j functions are of the form

$$j(r) = E(r) - F(r)\, e^{-r}$$

in which the $E(r)$ and $F(r)$ are simple polynomials. Explicit expressions for the necessary j's can be found in table 11. For these entries of table 6, the j's have as argument $\eta = (k_1+k_2)\rho$. For convenience we put $k_a = \frac{1}{2}(k_1+k_2)$.

TABLE 6. ONE-ELECTRON COULOMB INTEGRALS

$$C(c_1, c_2) = \int \Psi(A, 1; c_1)\, \Psi(A, 1; c_2)\, r_{b1}^{-1} dV_1$$

$$k_a = \tfrac{1}{2}(k_1+k_2), \quad \eta = 2k_a\rho$$

c_1	c_2	$C(c_1, c_2)$
$1s$	$1s$	$(k_1^3k_2^3)^{\frac{1}{2}}\, k_a^{-2}\eta^{-1}j_1(\eta)$
	$2s$	$\frac{1}{2}(k_1^3k_2^5/3)^{\frac{1}{2}}\, k_a^{-3}\eta^{-1}j_2(\eta)$
	$2p_z$	$\frac{1}{2}(k_1^3k_2^5)^{\frac{1}{2}}\, k_a^{-3}\eta^{-2}j_4(\eta)$
$2s$	$2s$	$\frac{1}{12}(k_1^5k_2^5)^{\frac{1}{2}}\, k_a^{-4}\eta^{-1}j_3(\eta)$
	$2p_z$	$\frac{1}{4}(k_1^5k_2^5/3)^{\frac{1}{2}}\, k_a^{-4}\eta^{-2}j_5(\eta)$
$2p_x$	$2p_x$	$\frac{1}{2}(k_1^5k_2^5)^{\frac{1}{2}}\, k_a^{-4}\eta^{-3}j_8(\eta)$
$2p_y$	$2p_y$	
$2p_z$	$2p_z$	$\frac{1}{4}(k_1^5k_2^5)^{\frac{1}{2}}\, k_a^{-4}\eta^{-3}j_6(\eta)$

13. TWO-ELECTRON COULOMB AND HYBRID INTEGRALS

The integration over the space of electron 1 is the same for both Coulomb and hybrid integrals (50a) and (50b) and the mononuclear integral (50d). We can denote it by the symbol $G(c_1, c_2;\, 2)$. Then we have

$$G(c_1, c_2;\, 2) = \int \frac{1}{r_{12}} \Psi(A, 1; c_1)\, \Psi(A, 1;\, c_2)\, dV_1. \tag{54}$$

These G functions are effectively identical with one-electron Coulomb integrals, electron 2 in the former corresponding to nucleus B in the latter. Their evaluation therefore requires no further explanation. The G's are obtained in terms of the j's of table 11, the j's argument is now $2k_a r_{a2}$. The G's are listed in table 7.

TABLE 7. $G(c_1, c_2;\, 2)$ INTEGRALS

$$G(c_1, c_2;\, 2) = \int \Psi(A, 1; c_1)\, \Psi(A, 1; c_2)\, r_{12}^{-1}\, dV_1$$

$$k_a = \tfrac{1}{2}(k_1+k_2), \quad j_n = j_n(2k_a r_{a2})$$

c_1	c_2	$G(c_1, c_2;\, 2)$
$1s$	$1s$	$\frac{1}{2}(k_1^3k_2^3)^{\frac{1}{2}}\, k_a^{-3} r_{a2}^{-1} j_1$
	$2s$	$\frac{1}{4}(k_1^3k_2^5/3)^{\frac{1}{2}}\, k_a^{-4} r_{a2}^{-1} j_2$
	$2p_x$, $2p_y$, $2p_z$	$\frac{1}{8}(k_1^3k_2^5)^{\frac{1}{2}}\, k_a^{-5}\, r_{a2}^{-3} \begin{Bmatrix} (x_{a2}) \\ (y_{a2}) \\ (z_{a2}) \end{Bmatrix} j_4$
$2s$	$2s$	$\frac{1}{24}(k_1^5k_2^5)^{\frac{1}{2}}\, k_a^{-5}\, r_{a2}^{-1} j_3$
	$2p_x$, $2p_y$, $2p_z$	$\frac{1}{16}(k_1^5k_2^5/3)^{\frac{1}{2}} k_a^{-6} r_{a2}^{-3} \begin{Bmatrix} (x_{a2}) \\ (y_{a2}) \\ (z_{a2}) \end{Bmatrix} j_5$
$2p_x$, $2p_y$, $2p_z$	$2p_x$, $2p_y$, $2p_z$	$\frac{1}{16}(k_1^5k_2^5)^{\frac{1}{2}}\, k_a^{-7}[r_{a2}^{-3}\, j_8 + \frac{1}{2} r_{a2}^{-5} \begin{Bmatrix} (x_{a2}^2) \\ (y_{a2}^2) \\ (z_{a2}^2) \end{Bmatrix} j_7]$
$2p_x$, $2p_x$, $2p_y$	$2p_y$, $2p_z$, $2p_z$	$\frac{1}{32}(k_1^5k_2^5)^{\frac{1}{2}}\, k_a^{-7}\, r_{a2}^{-5} \begin{Bmatrix} (x_{a2}y_{a2}) \\ (x_{a2}z_{a2}) \\ (y_{a2}z_{a2}) \end{Bmatrix} j_7$

The integration over the space of electron 1 thus provides a known function of the co-ordinates of electron 2. We can write

$$C(c_1, \ldots, c_4) = \int G(c_1, c_2;\ 2)\, \Psi(B, 2;\ c_3)\, \Psi(B, 2;\ c_4)\, dV_2 \qquad (55a)$$

$$I(c_1, \ldots, c_4) = \int G(c_1, c_2;\ 2)\, \Psi(A, 2;\ c_3)\, \Psi(B, 2;\ c_4)\, dV_2 \qquad (55b)$$

$$M(c_1, \ldots, c_4) = \int G(c_1, c_2;\ 2)\, \Psi(A, 2;\ c_3)\, \Psi(A, 2;\ c_4)\, dV_2. \qquad (55c)$$

The rest of the integration is now quite straightforward for the mononuclear integrals. Expressions are listed for these in table 8, in terms of the parameters

$$k_a = \tfrac{1}{2}(k_1 + k_2);\ k_b = \tfrac{1}{2}(k_3 + k_4);\ \chi = k_b/(k_a + k_b).$$

In the isolated atom, since $2p_x$, $2p_y$ and $2p_z$ orbitals are completely equivalent,

$$M(c_1, c_2;\ 2p_x, 2p_x) = M(c_1, c_2;\ 2p_y, 2p_y) = M(c_1, c_2;\ 2p_z, 2p_z)$$

when c_1 and c_2 are s orbitals. Similarly

$$M(2p_x, c_2;\ 2p_x, c_4) = M(2p_y, c_2;\ 2p_y, c_4) = M(2p_z, c_2;\ 2p_z, c_4)$$

when c_2 and c_4 are s orbitals. Furthermore

$$M(2p_x, 2p_x;\ 2p_x, 2p_x) = M(2p_y, 2p_y;\ 2p_y, 2p_y) = M(2p_z, 2p_z;\ 2p_z, 2p_z)$$
$$M(2p_x, 2p_x;\ 2p_y, 2p_y) = M(2p_x, 2p_x;\ 2p_z, 2p_z) = M(2p_y, 2p_y;\ 2p_z, 2p_z)$$
$$M(2p_x, 2p_y;\ 2p_x, 2p_y) = M(2p_x, 2p_z;\ 2p_x, 2p_z) = M(2p_y, 2p_z;\ 2p_y, 2p_z).$$

TABLE 8. MONONUCLEAR INTEGRALS

$$M(c_1, c_2;\ c_3, c_4) = \int \Psi(A, 1;\ c_1)\ \Psi(A, 1;\ c_2)\ r_{12}^{-1} \Psi(A, 2;\ c_3)\ \Psi(A, 2;\ c_4)\ dV_1 dV_2$$

$$k_a = \tfrac{1}{2}(k_1 + k_2);\quad k_b = \tfrac{1}{2}(k_3 + k_4);\quad \chi = k_b/(k_a + k_b)$$

c_1	c_2	c_3	c_4	$M(c_1, c_2;\ c_3\ c_4)$
$1s$	$1s$	$1s$	$1s$	$(k_1^3 k_2^3 k_3^3 k_4^3)^{\frac{1}{2}}\, k_a^{-3} k_b^{-2}(1 - 2\chi^2 + \chi^3)$
			$2s$	$\frac{1}{2}(k_1^3 k_2^3 k_3^3 k_4^5/3)^{\frac{1}{2}}\, k_a^{-3} k_b^{-3}(2 - 5\chi^3 + 3\chi^4)$
		$2s$	$2s$	$\frac{1}{2}(k_1^3 k_2^3 k_3^5 k_4^5)^{\frac{1}{2}}\, k_a^{-3} k_b^{-4}(1 - 3\chi^4 + 2\chi^5)$
		$2p_x$	$2p_x$	as for $M(1s, 1s;\ 2s, 2s)$
$1s$	$2s$	$1s$	$2s$	$\frac{1}{2}(k_1^3 k_2^5 k_3^3 k_4^5)^{\frac{1}{2}}\, k_a^{-4} k_b^{-3}(1 - 5\chi^3 + 6\chi^4 - 2\chi^5)$
		$2s$	$2s$	$\frac{1}{4}(k_1^3 k_2^5 k_3^5 k_4^5/3)^{\frac{1}{2}}\, k_a^{-4} k_b^{-4}(3 - 21\chi^4 + 28\chi^5 - 10\chi^6)$
		$2p_x$	$2p_x$	as for $M(1s, 2s;\ 2s, 2s)$
$1s$	$2p_x$	$1s$	$2p_x$	$\frac{1}{3}(k_1^3 k_2^5 k_3^3 k_4^5)^{\frac{1}{2}}\, k_a^{-5} k_b^{-2}(1 - 9\chi^2 + 17\chi^3 - 12\chi^4 + 3\chi^5)$
		$2s$	$2p_x$	$\frac{1}{6}(k_1^3 k_2^5 k_3^5 k_4^5/3)^{\frac{1}{2}}\, k_a^{-5} k_b^{-3}(2 - 35\chi^3 + 75\chi^4 - 57\chi^5 + 15\chi^6)$
$2s$	$2s$	$2s$	$2s$	$\frac{1}{2}(k_1^5 k_2^5 k_3^5 k_4^5)^{\frac{1}{2}}\, k_a^{-5} k_b^{-4}(1 - 14\chi^4 + 28\chi^5 - 20\chi^6 + 5\chi^7)$
		$2p_x$	$2p_x$	as for $M(2s, 2s;\ 2s, 2s)$
	$2p_x$	$2s$	$2p_x$	$\frac{5}{18}(k_1^5 k_2^5 k_3^5 k_4^5)^{\frac{1}{2}}\, k_a^{-6} k_b^{-3}(1 - 25\chi^3 + 69\chi^4 - 78\chi^5 + 42\chi^6 - 9\chi^7)$
$2p_x$	$2p_x$	$2p_x$	$2p_x$	$\frac{1}{10}(k_1^5 k_2^5 k_3^5 k_4^5)^{\frac{1}{2}}\, k_a^{-7}\, k_b^{-2}(5\chi^{-2} - 10\chi^{-1} + 9 - 150\chi^2 + 540\chi^3 - 830\chi^4 + 661\chi^5 - 270\chi^6 + 45\chi^7)$
		$2p_y$	$2p_y$	$\frac{1}{10}(k_1^5 k_2^5 k_3^5 k_4^5)^{\frac{1}{2}}\, k_a^{-7} k_b^{-2}(5\chi^{-2} - 10\chi^{-1} + 3 - 30\chi^2 + 150\chi^3 - 260\chi^4 + 217\chi^5 - 90\chi^6 + 15\chi^7)$
	$2p_y$	$2p_x$	$2p_y$	$\frac{3}{10}(k_1^5 k_2^5 k_3^5 k_4^5)^{\frac{1}{2}}\, k_a^{-7} k_b^{-2}(1 - 20\chi^2 + 65\chi^3 - 95\chi^4 + 74\chi^5 - 30\chi^6 + 5\chi^7)$

For the Coulomb and hybrid integrals the rest of the integration is now entirely similar to that for the one-electron integrals. For a few simple cases, the J's of Coulson's paper suffice, but in general it will be necessary to exploit the new methods developed in part I.

First, as regards the simple integrals which can be expressed in terms of known J's, an example is provided by the Coulomb integral

$$C(1s, 1s; 1s, 1s) = \{(k_1^3 k_2^3 k_3^3 k_4^3)^{\frac{1}{2}}/(\pi k_a^3)\}\{J_3(2k_b, 0, \rho) - J_3(2k_b, 2k_a, \rho) - k_a J_1(2k_a, 2k_b, \rho)\}.$$

A few of the hybrid integrals which can be reduced in a similar fashion are listed in table 12. As an example of the way in which the polynomials are combined to give explicit expressions for these molecular integrals, we may consider

$$I(1s, 1s; 1s, 1s) = \{(k_1^3 k_2^3 k_3^3 k_4^3)^{\frac{1}{2}}/(\pi k_a^3)\}\{J_3(k_4, k_3, \rho) - J_3(k_4, k_s, \rho) - k_a J_1(k_s, k_4, \rho)\},$$

where $k_s = k_1 + k_2 + k_3$. When $k_1 = k_2 = k_3 = k_4 = k$, the expression reduces to

$$k^{-1} I(1s, 1s; 1s, 1s) = \frac{1}{16k\rho}[e^{-k\rho}\{5 + 2k\rho + 16(k\rho)^2\} - e^{-3k\rho}\{5 + 2k\rho\}].$$

In all but the simplest cases it is necessary to put the integrals into a form similar to (52). Any Coulomb integral can be reduced to the form (56), and any hybrid integral to the form (57).

$$C(c_1, \ldots, c_4) = N_c(c_1, \ldots, c_4) \int_0^\infty t^{\frac{1}{2}} g_c(c_1, \ldots, c_4; t) dt \tag{56}$$

$$I(c_1, \ldots, c_4) = N_i(c_1, \ldots, c_4) \int_0^\infty t^{\frac{1}{2}} e^{-k_3 t/k_4} g_i(c_1, \ldots, c_4; t)\, dt. \tag{57}$$

The functions g_c and g_i are related to the ζ functions, involving products of the ζ's with the j's introduced in the previous section. The variable of integration, t, arises from the co-ordinate r_{a2} by a change of scale, as will be explained below. The N_c and N_i are numerical factors determined by the screening constants $k_1, \ldots, k_4$. The values of such N's and g's are listed in tables 9 and 10 for no less than 130 distinct integrals. These tables cover all the integrals of the two kinds which can arise from the various combinations of $1s$, $2s$ and $2p$ atomic orbitals. It is not difficult to extend these tables, if need arises, to deal with the more complicated wave functions. It will be noted that for many of the Coulomb integrals, two different expressions can be constructed, depending on which electron is selected as electron 1. The formulae listed in table 9 are in every case the simpler alternative.

As regards the arguments of the g functions, these are derived by the transformation $t = (k_3 + k_4) r_{a2}$ for the Coulomb integral, and $t = k_4 r_{a2}$ for the hybrid integral. It follows that the arguments of the γ, p and other ζ functions entering into the g's are $(1, t; 2k_b\rho)$ for the Coulomb integrals, and $(1, t; k_4\rho)$ for the hybrid integrals. The arguments of the j's are correspondingly $(k_a t/k_b)$ for the Coulomb integrals and $(2k_a t/k_4)$ for the hybrid integrals. It will be remembered that $k_a = \frac{1}{2}(k_1 + k_2)$ and that $k_b = \frac{1}{2}(k_3 + k_4)$. It will be noted that in this treatment no restriction is placed on the several screening constants which can all be distinct without in any way complicating the analysis. In this respect our present method is much more general than most others.

The expressions (56) and (57) can be evaluated by numerical integration or by expansion in **Z** functions. Either of these alternatives compares favourably with the methods previously

Table 9. Two-electron Coulomb integrals

$$C(c_1, c_2; c_3, c_4) = \int \Psi(A, 1; c_1)\, \Psi(A, 1; c_2)\, r_{12}^{-1} \Psi(B, 2; c_3)\, \Psi(B, 2; c_4)\, dV_1 dV_2$$

$$= N_c(c_1, c_2, c_3, c_4) \int_0^\infty t^{\frac{1}{2}} g_c(c_1, c_2, c_3, c_4; t)\, dt$$

.....

$$p_n = p_n(1, t; 2k_b\rho), \quad q_n = q_n(1, t; 2k_b\rho)$$

$$\zeta_{3,n} = \zeta_{3,n}(1, t; 2k_b\rho), \quad j_n = j_n(k_a t/k_b)$$

$$k_a = \tfrac{1}{2}(k_1 + k_2), \quad k_b = \tfrac{1}{2}(k_3 + k_4)$$

.....

c_1	c_2	c_3	c_4	$N_c(c_1, c_2, c_3, c_4)$	$g_c(c_1, c_2, c_3, c_4; t)$
$1s$	$1s$	$1s$	$1s$	$\frac{1}{2}(k_1^3 k_2^3 k_3^3 k_4^3/2k_b\rho)^{\frac{1}{2}}\, k_a^{-3} k_b^{-2}$	$j_1 p_0$
		$2p_x$	$2p_x$	$\frac{1}{24}(k_1^3 k_2^3 k_3^5 k_4^5/2k_b\rho)^{\frac{1}{2}}\, k_a^{-3} k_b^{-4}$	$t^2 j_1(p_0 - p_2)$
		$2p_y$	$2p_y$		
	$2s$	$1s$	$1s$	$\frac{1}{4}(k_1^3 k_2^5 k_3^3 k_4^3/6k_b\rho)^{\frac{1}{2}}\, k_a^{-4} k_b^{-2}$	$j_2 p_0$
			$2s$	$\frac{1}{24}(k_1^3 k_2^5 k_3^3 k_4^5/2k_b\rho)^{\frac{1}{2}}\, k_a^{-4} k_b^{-3}$	$j_2 q_0$
		$2p_x$	$2p_x$	$\frac{1}{48}(k_1^3 k_2^5 k_3^5 k_4^5/6k_b\rho)^{\frac{1}{2}}\, k_a^{-4} k_b^{-4}$	$t^2 j_2(p_0 - p_2)$
		$2p_y$	$2p_y$		
$1s$	$2p_x$	$1s$	$2p_x$	$\frac{1}{24}(k_1^3 k_2^5 k_3^3 k_4^5/2k_b\rho)^{\frac{1}{2}}\, k_a^{-5} k_b^{-2}$	$j_4(p_0 - p_2)$
$1s$	$2p_y$	$1s$	$2p_y$		
$1s$	$2p_z$	$1s$	$1s$	$\frac{1}{4}(k_1^3 k_2^5 k_3^3 k_4^3/2k_b\rho)^{\frac{1}{2}}\, k_a^{-5} k_b^{-1}$	$t^{-1} j_4 p_1$
			$2s$	$\frac{1}{8}(k_1^3 k_2^5 k_3^3 k_4^5/6k_b\rho)^{\frac{1}{2}}\, k_a^{-5} k_b^{-2}$	$t^{-1} j_4 q_1$
			$2p_z$	$\frac{1}{8}(k_1^3 k_2^5 k_3^3 k_4^5/2k_b\rho)^{\frac{1}{2}}\, k_a^{-5} k_b^{-2}$	$j_4\{2k_b\rho t^{-1} p_1 - p_0 + \frac{2}{3}(p_0 - p_2)\}$
		$2s$	$2s$	$\frac{1}{48}(k_1^3 k_2^5 k_3^5 k_4^5/2k_b\rho)^{\frac{1}{2}}\, k_a^{-5} k_b^{-3}$	$t^{-1} j_4 \zeta_{3,1}$
		$2p_x$	$2p_x$	$\frac{1}{80}(k_1^3 k_2^5 k_3^5 k_4^5/2k_b\rho)^{\frac{1}{2}}\, k_a^{-5} k_b^{-3}$	$t j_4(p_1 - p_3)$
		$2p_y$	$2p_y$		
$2s$	$2s$	$1s$	$1s$	$\frac{1}{24}(k_1^5 k_2^5 k_3^3 k_4^3/2k_b\rho)^{\frac{1}{2}}\, k_a^{-5} k_b^{-2}$	$j_3 p_0$
			$2s$	$\frac{1}{48}(k_1^5 k_2^5 k_3^3 k_4^5/6k_b\rho)^{\frac{1}{2}}\, k_a^{-5} k_b^{-3}$	$j_3 q_0$
		$2s$	$2s$	$\frac{1}{288}(k_1^5 k_2^5 k_3^5 k_4^5/2k_b\rho)^{\frac{1}{2}}\, k_a^{-5} k_b^{-4}$	$j_3 \zeta_{3,0}$
		$2p_x$	$2p_x$	$\frac{1}{288}(k_1^5 k_2^5 k_3^5 k_4^5/2k_b\rho)^{\frac{1}{2}}\, k_a^{-5} k_b^{-4}$	$t^2 j_3(p_0 - p_2)$
		$2p_y$	$2p_y$		
$2s$	$2p_x$	$1s$	$2p_x$	$\frac{1}{48}(k_1^5 k_2^5 k_3^3 k_4^5/6k_b\rho)^{\frac{1}{2}}\, k_a^{-6} k_b^{-2}$	$j_5(p_0 - p_2)$
$2s$	$2p_y$	$1s$	$2p_y$		
$2s$	$2p_x$	$2s$	$2p_x$	$\frac{1}{288}(k_1^5 k_2^5 k_3^5 k_4^5/2k_b\rho)^{\frac{1}{2}}\, k_a^{-6} k_b^{-3}$	$j_5(q_0 - q_2)$
$2s$	$2p_y$	$2s$	$2p_y$		
$2s$	$2p_z$	$1s$	$1s$	$\frac{1}{8}(k_1^5 k_2^5 k_3^3 k_4^3/6k_b\rho)^{\frac{1}{2}}\, k_a^{-6} k_b^{-1}$	$t^{-1} j_5 p_1$
			$2s$	$\frac{1}{48}(k_1^5 k_2^5 k_3^3 k_4^5/2k_b\rho)^{\frac{1}{2}}\, k_a^{-6} k_b^{-2}$	$t^{-1} j_5 q_1$
			$2p_z$	$\frac{1}{16}(k_1^5 k_2^5 k_3^3 k_4^5/6k_b\rho)^{\frac{1}{2}}\, k_a^{-6} k_b^{-2}$	$j_5\{2k_b\rho t^{-1} p_1 - p_0 + \frac{2}{3}(p_0 - p_2)\}$
		$2s$	$2s$	$\frac{1}{96}(k_1^5 k_2^5 k_3^5 k_4^5/6k_b\rho)^{\frac{1}{2}}\, k_a^{-6} k_b^{-3}$	$t^{-1} j_5 \zeta_{3,1}$
			$2p_z$	$\frac{1}{96}(k_1^5 k_2^5 k_3^5 k_4^5/2k_b\rho)^{\frac{1}{2}}\, k_a^{-6} k_b^{-3}$	$j_5\{2k_b\rho t^{-1} q_1 - q_0 + \frac{2}{3}(q_0 - q_2)\}$
		$2p_x$	$2p_x$	$\frac{1}{160}(k_1^5 k_2^5 k_3^5 k_4^5/6k_b\rho)^{\frac{1}{2}}\, k_a^{-6} k_b^{-3}$	$t j_5(p_1 - p_3)$
		$2p_y$	$2p_y$		
$2p_x$	$2p_x$	$2p_x$	$2p_x$	$\frac{1}{16}(k_1^5 k_2^5 k_3^5 k_4^5/2k_b\rho)^{\frac{1}{2}}\, k_a^{-7} k_b^{-2}$	$\frac{1}{3} j_8(p_0 - p_2) + \frac{1}{10} j_7\{(p_0 - p_2) - \frac{3}{7}(p_2 - p_4)\}$
$2p_y$	$2p_y$	$2p_y$	$2p_y$		
$2p_x$	$2p_x$	$2p_y$	$2p_y$	$\frac{1}{48}(k_1^5 k_2^5 k_3^5 k_4^5/2k_b\rho)^{\frac{1}{2}}\, k_a^{-7} k_b^{-2}$	$j_8(p_0 - p_2) + \frac{1}{10} j_7\{(p_0 - p_2) - \frac{3}{7}(p_2 - p_4)\}$
$2p_x$	$2p_y$	$2p_x$	$2p_y$	$\frac{1}{480}(k_1^5 k_2^5 k_3^5 k_4^5/2k_b\rho)^{\frac{1}{2}}\, k_a^{-7} k_b^{-2}$	$j_7\{(p_0 - p_2) - \frac{3}{7}(p_2 - p_4)\}$
$2p_x$	$2p_z$	$1s$	$2p_x$	$\frac{1}{80}(k_1^5 k_2^5 k_3^3 k_4^5/2k_b\rho)^{\frac{1}{2}}\, k_a^{-7} k_b^{-1}$	$t^{-1} j_7(p_1 - p_3)$
		$2s$	$2p_x$	$\frac{1}{160}(k_1^5 k_2^5 k_3^5 k_4^5/6k_b\rho)^{\frac{1}{2}}\, k_a^{-7} k_b^{-2}$	$t^{-1} j_7(q_1 - q_3)$
		$2p_x$	$2p_z$	$\frac{1}{80}(k_1^5 k_2^5 k_3^5 k_4^5/2k_b\rho)^{\frac{1}{2}}\, k_a^{-7} k_b^{-2}$	$j_7\{k_b\rho t^{-1}(p_1 - p_3) - \frac{1}{6}(p_0 - p_2) - \frac{2}{7}(p_2 - p_4)\}$
$2p_z$	$2p_z$	$1s$	$1s$	$\frac{1}{4}(k_1^5 k_2^5 k_3^3 k_4^3/2k_b\rho)^{\frac{1}{2}}\, k_a^{-7}$	$t^{-2}[j_8 p_0 + \frac{1}{2} j_7\{p_0 - \frac{2}{3}(p_0 - p_2)\}]$
			$2s$	$\frac{1}{8}(k_1^5 k_2^5 k_3^3 k_4^5/6k_b\rho)^{\frac{1}{2}}\, k_a^{-7} k_b^{-1}$	$t^{-2}[j_8 q_0 + \frac{1}{2} j_7\{q_0 - \frac{2}{3}(q_0 - q_2)\}]$
			$2p_z$	$\frac{1}{8}(k_1^5 k_2^5 k_3^3 k_4^5/2k_b\rho)^{\frac{1}{2}}\, k_a^{-7} k_b^{-1}$	$t^{-2}[2k_b\rho\{j_8 p_0 + \frac{1}{2} j_7(p_0 - \frac{2}{3}(p_0 - p_2))\}$ $- t\{j_8 p_1 + \frac{1}{2} j_7(p_1 - \frac{2}{5}(p_1 - p_3))\}]$
		$2s$	$2s$	$\frac{1}{48}(k_1^5 k_2^5 k_3^5 k_4^5/2k_b\rho)^{\frac{1}{2}}\, k_a^{-7} k_b^{-2}$	$t^{-2}[j_8 \zeta_{3,0} + \frac{1}{2} j_7\{\zeta_{3,0} - \frac{2}{3}(\zeta_{3,0} - \zeta_{3,2})\}]$
			$2p_z$	$\frac{1}{16}(k_1^5 k_2^5 k_3^5 k_4^5/6k_b\rho)^{\frac{1}{2}}\, k_a^{-7} k_b^{-2}$	$t^{-2}[2k_b\rho\{j_8 q_0 + \frac{1}{2} j_7(q_0 - \frac{2}{3}(q_0 - q_2))\}$ $- t\{j_8 q_1 + \frac{1}{2} j_7(q_1 - \frac{2}{5}(q_1 - q_3))\}]$
		$2p_x$	$2p_x$	$\frac{1}{16}(k_1^5 k_2^5 k_3^5 k_4^5/2k_b\rho)^{\frac{1}{2}}\, k_a^{-7} k_b^{-2}$	$\frac{1}{3} j_8(p_0 - p_2) + \frac{1}{10} j_7\{\frac{1}{3}(p_0 - p_2) + \frac{4}{7}(p_2 - p_4)\}$
		$2p_y$	$2p_y$		
		$2p_z$	$2p_z$	$\frac{1}{16}(k_1^5 k_2^5 k_3^5 k_4^5/2k_b\rho)^{\frac{1}{2}}\, k_a^{-7} k_b^{-2}$	$[4k_b^2\rho^2 t^{-2}\{j_8 p_0 + \frac{1}{2} j_7(p_0 - \frac{2}{3}(p_0 - p_2))\}$ $- 4k_b\rho t^{-1}\{j_8 p_1 + \frac{1}{2} j_7(p_1 - \frac{2}{5}(p_1 - p_3))\}$ $+ j_8\{p_0 - \frac{2}{3}(p_0 - p_2)\} + \frac{1}{2} j_7\{p_0 - \frac{4}{5}(p_0 - p_2)$ $- \frac{8}{35}(p_2 - p_4)\}]$

TABLE 10. HYBRID INTEGRALS

$$I(c_1, c_2; c_3, c_4) = \int \Psi(A, 1; c_1)\, \Psi(A, 1; c_2)\, r_{12}^{-1} \Psi(A, 2; c_3)\, \Psi(B, 2; c_4)\, dV_1\, dV_2$$

$$= N_i(c_1, c_2, c_3, c_4) \int_0^\infty t^{\frac{1}{2}}\, \mathrm{e}^{-k_3 t/k_4}\, g_i(c_1, c_2, c_3, c_4; t)\, dt$$

$$p_n = p_n(1, t; k_4\rho), \quad q_n = q_n(1, t; k_4\rho),$$

$$j_n = j_n(2k_a t/k_4), \qquad k_a = \tfrac{1}{2}(k_1 + k_2)$$

c_1	c_2	c_3	c_4	$N_i(c_1, c_2, c_3, c_4)$	$g_i(c_1, c_2, c_3, c_4; t)$
$1s$	$1s$	$1s$	$1s$	$2(k_1^3k_2^3k_3^3/\rho)^{\frac{1}{2}}\, k_a^{-3}k_4^{-1}$	j_1p_0
			$2s$	$2(k_1^3k_2^3k_3^3/3\rho)^{\frac{1}{2}}\, k_a^{-3}k_4^{-1}$	j_1q_0
			$2p_z$	$2(k_1^3k_2^3k_3^3/\rho)^{\frac{1}{2}}\, k_a^{-3}k_4^{-1}$	$j_1(k_4\rho p_0 - tp_1)$
		$2s$	$1s$	$2(k_1^3k_2^3k_3^3/3\rho)^{\frac{1}{2}}\, k_a^{-3}k_4^{-2}$	tj_1p_0
			$2s$	$\frac{2}{3}(k_1^3k_2^3k_3^5/\rho)^{\frac{1}{2}}\, k_a^{-3}k_4^{-2}$	tj_1q_0
			$2p_z$	$2(k_1^3k_2^3k_3^5/3\rho)^{\frac{1}{2}}\, k_a^{-3}k_4^{-2}$	$tj_1(k_4\rho p_0 - tp_1)$
		$2p_x$	$2p_x$	$\frac{2}{3}(k_1^3k_2^3k_3^5/\rho)^{\frac{1}{2}}\, k_a^{-3}k_4^{-2}$	$t^2j_1(p_0 - p_2)$
		$2p_y$	$2p_y$		
		$2p_z$	$1s$	$2(k_1^3k_2^3k_3^5/\rho)^{\frac{1}{2}}\, k_a^{-3}k_4^{-2}$	tj_1p_1
			$2s$	$2(k_1^3k_2^3k_3^5/3\rho)^{\frac{1}{2}}\, k_a^{-3}k_4^{-2}$	tj_1q_1
			$2p_z$	$2(k_1^3k_2^3k_3^5/\rho)^{\frac{1}{2}}\, k_a^{-3}k_4^{-2}$	$tj_1[k_4\rho p_1 - t\{p_0 - \frac{2}{3}(p_0 - p_2)\}]$
$1s$	$2s$	$1s$	$1s$	$(k_1^3k_2^5k_3^3/3\rho)^{\frac{1}{2}}\, k_a^{-4}k_4^{-1}$	j_2p_0
			$2s$	$\frac{1}{3}(k_1^3k_2^5k_3^3/\rho)^{\frac{1}{2}}\, k_a^{-4}k_4^{-1}$	j_2q_0
			$2p_z$	$(k_1^3k_2^5k_3^3/3\rho)^{\frac{1}{2}}\, k_a^{-4}k_4^{-1}$	$j_2(k_4\rho p_0 - tp_1)$
		$2s$	$1s$	$\frac{1}{3}(k_1^3k_2^5k_3^5/\rho)^{\frac{1}{2}}\, k_a^{-4}k_4^{-2}$	tj_2p_0
			$2s$	$\frac{1}{3}(k_1^3k_2^5k_3^5/3\rho)^{\frac{1}{2}}\, k_a^{-4}k_4^{-2}$	tj_2q_0
			$2p_z$	$\frac{1}{3}(k_1^3k_2^5k_3^5/\rho)^{\frac{1}{2}}\, k_a^{-4}k_4^{-2}$	$tj_2(k_4\rho p_0 - tp_1)$
		$2p_x$	$2p_x$	$\frac{1}{3}(k_1^3k_2^5k_3^5/3\rho)^{\frac{1}{2}}\, k_a^{-4}k_4^{-2}$	$t^2j_2(p_0 - p_2)$
		$2p_y$	$2p_y$		
		$2p_z$	$1s$	$(k_1^3k_2^5k_3^5/3\rho)^{\frac{1}{2}}\, k_a^{-4}k_4^{-2}$	tj_2p_1
			$2s$	$\frac{1}{3}(k_1^3k_2^5k_3^5/3\rho)^{\frac{1}{2}}\, k_a^{-4}k_4^{-2}$	tj_2q_1
			$2p_z$	$(k_1^3k_2^5k_3^5/3\rho)^{\frac{1}{2}}\, k_a^{-4}k_4^{-2}$	$tj_2[k_4\rho p_1 - t\{p_0 - \frac{2}{3}(p_0 - p_2)\}]$
$1s$	$2p_x$	$1s$	$2p_x$	$\frac{1}{6}(k_1^3k_2^5k_3^3/\rho)^{\frac{1}{2}}\, k_a^{-5}$	$j_4(p_0 - p_2)$
		$2s$	$2p_x$	$\frac{1}{6}(k_1^3k_2^5k_3^3/3\rho)^{\frac{1}{2}}\, k_a^{-5}k_4^{-1}$	$tj_4(p_0 - p_2$
		$2p_x$	$1s$	$\frac{1}{6}(k_1^3k_2^5k_3^3/\rho)^{\frac{1}{2}}\, k_a^{-5}k_4^{-1}$	$j_4(p_0 - p_2)$
			$2s$	$\frac{1}{6}(k_1^3k_2^5k_3^5/3\rho)^{\frac{1}{2}}\, k_a^{-5}k_4^{-1}$	$j_4(q_0 - q_2)$
			$2p_z$	$\frac{1}{2}(k_1^3k_2^5k_3^5/\rho)^{\frac{1}{2}}\, k_a^{-5}k_4^{-1}$	$j_4\{\frac{1}{3}k_4\rho(p_0 - p_2) - \frac{1}{5}t(p_1 - p_3)\}$
		$2p_z$	$2p_x$	$\frac{1}{10}(k_1^3k_2^5k_3^5/\rho)^{\frac{1}{2}}\, k_a^{-5}k_4^{-1}$	$tj_4(p_1 - p_3)$
$1s$	$2p_y$	c_3	$2p_y$	as for I $(1s, 2p_x; c_3, 2p_x)$	
		$2p_y$	c_4	as for I $(1s, 2p_x; 2p_x, c_4)$	
$1s$	$2p_z$	$1s$	$1s$	$\frac{1}{2}(k_1^3k_2^5k_3^3/\rho)^{\frac{1}{2}}\, k_a^{-5}$	$t^{-1}j_4p_1$
			$2s$	$\frac{1}{2}(k_1^3k_2^5k_3^3/3\rho)^{\frac{1}{2}}\, k_a^{-5}$	$t^{-1}j_4q_1$
			$2p_z$	$\frac{1}{2}(k_1^3k_2^5k_3^3/\rho)^{\frac{1}{2}}\, k_a^{-5}$	$j_4\{t^{-1}k_4\rho p_1 - p_0 + \frac{2}{3}(p_0 - p_2)\}$
		$2s$	$1s$	$\frac{1}{2}(k_1^3k_2^5k_3^5/3\rho)^{\frac{1}{2}}\, k_a^{-5}k_4^{-1}$	j_4p_1
			$2s$	$\frac{1}{6}(k_1^3k_2^5k_3^5/\rho)^{\frac{1}{2}}\, k_a^{-5}k_4^{-1}$	j_4q_1
			$2p_z$	$\frac{1}{2}(k_1^3k_2^5k_3^5/3\rho)^{\frac{1}{2}}\, k_a^{-5}k_4^{-1}$	$j_4[k_4\rho p_1 - t\{p_0 - \frac{2}{3}(p_0 - p_2)\}]$
		$2p_x$	$2p_x$	$\frac{1}{10}(k_1^3k_2^5k_3^5/\rho)^{\frac{1}{2}}\, k_a^{-5}k_4^{-1}$	$tj_4(p_1 - p_3)$
		$2p_y$	$2p_y$		
		$2p_z$	$1s$	$\frac{1}{2}(k_1^3k_2^5k_3^5/\rho^{\frac{1}{2}}\, k_a^{-5}k_4^{-1}$	$j_4\{p_0 - \frac{2}{5}(p_0 - p_2)\}$
			$2s$	$\frac{1}{2}(k_1^3k_2^5k_3^5/3\rho)^{\frac{1}{2}}\, k_a^{-5}k_4^{-1}$	$j_4\{q_0 - \frac{2}{5}(q_0 - q_2)\}$
			$2p_z$	$\frac{1}{2}(k_1^3k_2^5k_3^5/\rho)^{\frac{1}{2}}\, k_a^{-5}k_4^{-1}$	$j_4[k_4\rho\{p_0 - \frac{2}{3}(p_0 - p_2)\} - t\{p_1 - \frac{2}{5}(p_1 - p_3)\}]$
$2s$	$2s$	$1s$	$1s$	$\frac{1}{6}(k_1^5k_2^5k_3^3/\rho)^{\frac{1}{2}}\, k_a^{-5}k_4^{-1}$	j_3p_0
			$2s$	$\frac{1}{6}(k_1^5k_2^5k_3^3/3\rho)^{\frac{1}{2}}\, k_a^{-5}k_4^{-1}$	j_3q_0
			$2p_z$	$\frac{1}{6}(k_1^5k_2^5k_3^3/\rho)^{\frac{1}{2}}\, k_a^{-5}k_4^{-1}$	$j_3(k_4\rho p_0 - tp_1)$
		$2s$	$1s$	$\frac{1}{6}(k_1^5k_2^5k_3^5/3\rho)^{\frac{1}{2}}\, k_a^{-5}k_4^{-2}$	tj_3p_0
			$2s$	$\frac{1}{18}(k_1^5k_2^5k_3^5/\rho)^{\frac{1}{2}}\, k_a^{-5}k_4^{-2}$	tj_3q_0
			$2p_z$	$\frac{1}{6}(k_1^5k_2^5k_3^5/3\rho)^{\frac{1}{2}}\, k_a^{-5}k_4^{2}$	$tj_3(k_4\rho p_0 - tp_1)$
		$2p_x$	$2p_x$	$\frac{1}{18}(k_1^5k_2^5k_3^5/\rho)^{\frac{1}{2}}\, k_a^{-5}k_4^{-2}$	$t^2j_3(p_0 - p_2)$
		$2p_y$	$2p_y$		
		$2p_z$	$1s$	$\frac{1}{6}(k_1^5k_2^5k_3^5/\rho)^{\frac{1}{2}}\, k_a^{-5}k_4^{-2}$	tj_3p_1
			$2s$	$\frac{1}{6}(k_1^5k_2^5k_3^5/3\rho)^{\frac{1}{2}}\, k_a^{-5}k_4^{-2}$	tj_3q_1
			$2p_z$	$\frac{1}{6}(k_1^5k_2^5k_3^5/\rho)^{\frac{1}{2}}\, k_a^{-5}k_4^{-2}$	$tj_3[k_4\rho p_1 - t\{p_0 - \frac{2}{3}(p_0 - p_2)\}]$

TABLE 10 (*cont.*)

$2s$	$2p_x$	$1s$	$2p_x$	$\frac{1}{12}(k_1^5k_2^5k_3^3/3\rho)^{\frac{1}{2}}\,k_a^{-6}$	$j_5(p_0-p_2)$
		$2s$	$2p_x$	$\frac{1}{36}(k_1^5k_2^5k_3^5/\rho)^{\frac{1}{2}}\,k_a^{-6}k_4^{-1}$	$tj_5(q_0-q_2)$
		$2p_x$	$1s$	$\frac{1}{12}(k_1^5k_2^5k_3^5/3\rho)^{\frac{1}{2}}\,k_a^{-6}k_4^{-1}$	$j_5(p_0-p_2)$
			$2s$	$\frac{1}{36}(k_1^5k_2^5k_3^5/\rho)^{\frac{1}{2}}\,k_a^{-6}k_4^{-1}$	$j_5(q_0-q_2)$
			$2p_z$	$\frac{1}{4}(k_1^5k_2^5k_3^3/3\rho)^{\frac{1}{2}}\,k_a^{-6}k_4^{-1}$	$j_5[\frac{1}{3}k_4\rho(p_0-p_2)-\frac{1}{5}t(p_1-p_3)]$
		$2p_z$	$2p_x$	$\frac{1}{20}(k_1^5k_2^5k_3^5/3\rho)^{\frac{1}{2}}\,k_a^{-6}k_4^{-1}$	$tj_5(p_1-p_3)$
$2s$	$2p_y$	c_3	$2p_y$	as for I $(2s, 2p_x; c_3, 2p_x)$	
		$2p_y$	c_4	as for I $(2s, 2p_x; 2p_x, c_4)$	
$2s$	$2p_z$	$1s$	$1s$	$\frac{1}{4}((k_1^5k_2^5k_3^3/3\rho)^{\frac{1}{2}}\,k_a^{-6}$	$t^{-1}j_5p_1$
			$2s$	$\frac{1}{12}(k_1^5k_2^5k_3^3/\rho)^{\frac{1}{2}}\,k_a^{-6}$	$t^{-1}j_5q_1$
			$2p_z$	$\frac{1}{4}(k_1^5k_2^5k_3^3/3\rho)^{\frac{1}{2}}\,k_a^{-6}$	$j_5[t^{-1}k_4\rho p_1-p_0+\frac{2}{3}(p_0-p_2)]$
		$2s$	$1s$	$\frac{1}{12}(k_1^5k_2^5k_3^5/\rho)^{\frac{1}{2}}\,k_a^{-6}k_4^{-1}$	j_5p_1
			$2s$	$\frac{1}{12}(k_1^5k_2^5k_3^5/3\rho)^{\frac{1}{2}}\,k_a^{-6}k_4^{-1}$	j_5q_1
			$2p_z$	$\frac{1}{12}(k_1^5k_2^5k_3^5/\rho)^{\frac{1}{2}}\,k_a^{-6}k_4^{-1}$	$j_5[k_4\rho p_1-t\{p_0-\frac{2}{3}(p_0-p_2)\}]$
		$2p_x$	$2p_x$	$\frac{1}{20}(k_1^5k_2^5k_3^5/3\rho)^{\frac{1}{2}}\,k_a^{-6}k_4^{-1}$	$tj_5(p_1-p_3)$
		$2p_y$	$2p_y$		
		$2p_z$	$1s$	$\frac{1}{4}(k_1^5k_2^5k_3^5/3\rho)^{\frac{1}{2}}\,k_a^{-6}k_4^{-1}$	$j_5\{p_0-\frac{2}{3}(p_0-p_2)\}$
			$2s$	$\frac{1}{12}(k_1^5k_2^5k_3^5/\rho)^{\frac{1}{2}}\,k_a^{-6}k_4^{-1}$	$j_5\{q_0-\frac{2}{3}(q_0-q_2)\}$
			$2p_z$	$\frac{1}{4}(k_1^5k_2^5k_3^5/3\rho)^{\frac{1}{2}}\,k_a^{-6}k_4^{-1}$	$j_5[k_4\rho\{p_0-\frac{2}{3}(p_0-p_2)\}-t\{p_1-\frac{2}{5}(p_1-p_3)\}]$
$2p_x$ $2p_y$	$2p_x$ $2p_y$	$1s$	$1s$	$\frac{1}{4}(k_1^5k_2^5k_3^3/\rho)^{\frac{1}{2}}\,k_a^{-7}k_4$	$t^{-2}\{j_8p_0+\frac{1}{6}j_7(p_0-p_2)\}$
			$2s$	$\frac{1}{4}(k_1^5k_2^5k_3^3/3\rho)^{\frac{1}{2}}\,k_a^{-7}k_4$	$t^{-2}\{j_8q_0+\frac{1}{6}j_7(q_0-q_2)\}$
			$2p_z$	$\frac{1}{4}(k_1^5k_2^5k_3^3/\rho)^{\frac{1}{2}}\,k_a^{-7}k_4$	$k_4\rho t^{-2}\{j_8p_0+\frac{1}{6}j_7(p_0-p_2)\}-t^{-1}\{j_8p_1+\frac{1}{10}j_7(p_1-p_3)\}$
		$2s$	$1s$	$\frac{1}{4}(k_1^5k_2^5k_3^5/3\rho)^{\frac{1}{2}}\,k_a^{-7}$	$t^{-1}\{j_8p_0+\frac{1}{6}j_7(p_0-p_2)\}$
			$2s$	$\frac{1}{12}(k_1^5k_2^5k_3^5/\rho)^{\frac{1}{2}}\,k_a^{-7}$	$t^{-1}\{j_8q_0+\frac{1}{6}j_7(q_0-q_2)\}$
			$2p_z$	$\frac{1}{4}(k_1^5k_2^5k_3^5/3\rho)^{\frac{1}{2}}\,k_a^{-7}$	$k_4\rho t^{-1}\{j_8p_0+\frac{1}{6}j_7(p_0-p_2)\}-j_8p_1-\frac{1}{10}j_7(p_1-p_3)$
		$2p_z$	$1s$	$\frac{1}{4}(k_1^5k_2^5k_3^5/\rho)^{\frac{1}{2}}\,k_a^{-7}$	$t^{-1}\{j_8p_1+\frac{1}{10}j_7(p_1-p_3)\}$
			$2s$	$\frac{1}{4}(k_1^5k_2^5k_3^5/3\rho)^{\frac{1}{2}}\,k_a^{-7}$	$t^{-1}\{j_8q_1+\frac{1}{10}j_7(q_1-q_3)\}$
			$2p_z$	$\frac{1}{4}(k_1^5k_2^5k_3^5/\rho)^{\frac{1}{2}}\,k_a^{-7}$	$k_4\rho t^{-1}\{j_8p_1+\frac{1}{10}j_7(p_1-p_3)\}-j_8\{p_0-\frac{2}{3}(p_0-p_2)\}$ $-\frac{1}{5}j_7\{\frac{1}{6}(p_0-p_2)+\frac{2}{7}(p_2-p_4)\}$
$2p_x$ $2p_y$	$2p_x$ $2p_y$	$2p_x$	$2p_x$	$\frac{1}{4}(k_1^5k_2^5k_3^5/\rho)^{\frac{1}{2}}\,k_a^{-7}$	$\frac{1}{3}j_8(p_0-p_2)+\frac{1}{10}j_7\{(p_0-p_2)-\frac{3}{7}(p_2-p_4)\}$
		$2p_y$	$2p_y$		
$2p_x$	$2p_x$	$2p_y$	$2p_y$	$\frac{1}{12}(k_1^5k_2^5k_3^5/\rho)^{\frac{1}{2}}\,k_a^{-7}$	$j_8(p_0-p_2)+\frac{1}{10}j_7\{(p_0-p_2)-\frac{3}{7}(p_2-p_4)\}$
$2p_x$	$2p_y$	$2p_x$	$2p_y$	$\frac{1}{40}(k_1^5k_2^5k_3^5/\rho)^{\frac{1}{2}}\,k_a^{-7}$	$j_7\{\frac{1}{3}(p_0-p_2)-\frac{1}{7}(p_2-p_4)\}$
$2p_x$	$2p_z$	$1s$	$2p_x$	$\frac{1}{40}(k_1^5k_2^5k_3^3/\rho)^{\frac{1}{2}}\,k_a^{-7}k_4$	$t^{-1}j_7(p_1-p_3)$
		$2s$	$2p_x$	$\frac{1}{40}(k_1^5k_2^5k_3^5/3\rho)^{\frac{1}{2}}\,k_a^{-7}$	$j_7(p_1-p_3)$
		$2p_x$	$1s$	$\frac{1}{40}(k_1^5k_2^5k_3^5/\rho)^{\frac{1}{2}}\,k_a^{-7}$	$t^{-1}j_7(p_1-p_3)$
			$2s$	$\frac{1}{40}(k_1^5k_2^5k_3^5/3\rho)^{\frac{1}{2}}\,k_a^{-7}$	$t^{-1}j_7(q_1-q_3)$
			$2p_z$	$\frac{1}{40}(k_1^5k_2^5k_3^5/\rho)^{\frac{1}{2}}\,k_a^{-7}$	$j_7\{k_4\rho t^{-1}(p_1-p_3)-\frac{1}{3}(p_0-p_2)-\frac{4}{7}(p_2-p_4)\}$
		$2p_z$	$2p_x$	$\frac{1}{40}(k_1^5k_2^5k_3^5/\rho)^{\frac{1}{2}}\,k_a^{-7}$	$j_7\{\frac{1}{3}(p_0-p_2)+\frac{4}{7}(p_2-p_4)\}$
$2p_y$	$2p_z$	c_3	$2p_y$	as for $I(2p_x, 2p_z; c_3, 2p_x)$	
		$2p_y$	c_4	as for $I(2p_x, 2p_z; 2p_x, c_4)$	
$2p_z$	$2p_z$	$1s$	$1s$	$\frac{1}{4}(k_1^5k_2^5k_3^3/\rho)^{\frac{1}{2}}\,k_a^{-7}k_4$	$t^{-2}[j_8p_0+\frac{1}{2}j_7\{p_0-\frac{2}{3}(p_0-p_2)\}]$
			$2s$	$\frac{1}{4}(k_1^5k_2^5k_3^3/3\rho)^{\frac{1}{2}}\,k_a^{-7}k_4$	$t^{-2}[j_8q_0+\frac{1}{2}j_7\{q_0-\frac{2}{3}(q_0-q_2)\}]$
			$2p_z$	$\frac{1}{4}(k_1^5k_2^5k_3^3/\rho)^{\frac{1}{2}}\,k_a^{-7}k_4$	$k_4\rho t^{-2}[j_8p_0+\frac{1}{2}j_7\{p_0-\frac{2}{3}(p_0-p_2)\}]$ $-t^{-1}[j_8p_1+\frac{1}{2}j_7\{p_1-\frac{2}{5}(p_1-p_3)\}]$
		$2s$	$1s$	$\frac{1}{4}(k_1^5k_2^5k_3^5/3\rho)^{\frac{1}{2}}\,k_a^{-7}$	$t^{-1}[j_8p_0+\frac{1}{2}j_7\{p_0-\frac{2}{3}(p_0-p_2)\}]$
			$2s$	$\frac{1}{12}(k_1^5k_2^5k_3^5/\rho)^{\frac{1}{2}}\,k_a^{-7}$	$t^{-1}[j_8q_0+\frac{1}{2}j_7\{q_0-\frac{2}{3}(q_0-q_2)\}]$
			$2p_z$	$\frac{1}{4}(k_1^5k_2^5k_3^5/3\rho)^{\frac{1}{2}}\,k_a^{-7}$	$k_4\rho t^{-1}[j_8p_0+\frac{1}{2}j_7\{p_0-\frac{2}{3}(p_0-p_2)\}]-j_8p_1$ $-\frac{1}{2}j_7\{p_1-\frac{2}{5}(p_1-p_3)\}$
		$2p_x$	$2p_x$	$\frac{1}{4}(k_1^5k_2^5k_3^5/\rho)^{\frac{1}{2}}\,k_a^{-7}$	$\frac{1}{3}j_8(p_0-p_2)+\frac{1}{10}j_7\{\frac{1}{3}(p_0-p_2)+\frac{4}{7}(p_2-p_4)\}$
		$2p_y$	$2p_y$		
		$2p_z$	$1s$	$\frac{1}{4}(k_1^5k_2^5k_3^5/\rho)^{\frac{1}{2}}k_a^{-7}$	$t^{-1}[j_8p_1+\frac{1}{2}j_7\{p_1-\frac{2}{5}(p_1-p_3)\}]$
			$2s$	$\frac{1}{4}(k_1^5k_2^5k_3^5/3\rho)^{\frac{1}{2}}\,k_a^{-7}$	$t^{-1}[j_8q_1+\frac{1}{2}j_7\{q_1-\frac{2}{5}(q_1-q_3)\}]$
			$2p_z$	$\frac{1}{4}(k_1^5k_2^5k_3^5/\rho)^{\frac{1}{2}}\,k_a^{-7}$	$k_4\rho t^{-1}[j_8p_1+\frac{1}{2}j_7\{p_1-\frac{2}{5}(p_1-p_3)\}]-j_8\{p_0-\frac{2}{3}(p_0-p_2)\}$ $-\frac{1}{2}j_7\{p_0-\frac{4}{5}(p_0-p_2)-\frac{8}{35}(p_2-p_4)\}$

used. Most methods for evaluating these two-centre integrals begin, as we have done, by integrating with respect to electron 1. This provides explicit functions of the co-ordinates of electron 2. It is at this stage that the methods we have described for the Coulomb and hybrid integrals differ from those previously used.

TABLE 11. $j_n(r)$ FUNCTIONS

n	$j_n(r)$
1	$2-(2+r)\,e^{-r}$
2	$6-(6+4r+r^2)\,e^{-r}$
3	$24-(24+18r+6r^2+r^3)\,e^{-r}$
4	$8-(8+8r+4r^2+r^3)\,e^{-r}$
5	$40-(40+40r+20r^2+6r^3+r^4)\,e^{-r}$
6	$96+8r^2-(96+96r+56r^2+22r^3+6r^4+r^5)\,e^{-r}$
7	$144-(144+144r+72r^2+24r^3+6r^4+r^5)\,e^{-r}$
8	$-24+4r^2+(24+24r+8r^2+r^3)\,e^{-r}$

TABLE 12. SIMPLE HYBRID INTEGRALS

c_3	c_4	$\pi k_a^3(k_1^3k_2^3)^{-\frac{1}{2}}\,I(1s,\,1s;\,c_3,\,c_4)$
$1s$	$1s$	$(k_3^3k_4^3)^{\frac{1}{2}}\{J_3(k_4,k_3,\rho)-J_3(k_4,k_s,\rho)-k_aJ_1(k_s,k_4,\rho)\}$
	$2s$	$(k_3^3k_4^5/3)^{\frac{1}{2}}\{J_4(k_4,k_3,\rho)-J_4(k_4,k_s,\rho)-k_aJ_2(k_4,k_s,\rho)\}$
	$2p_z$	$(k_3^3k_4^5)^{\frac{1}{2}}\{J_9(k_4,k_3,\rho)-J_9(k_4,k_s,\rho)-k_aJ_7(k_4,k_s,\rho)\}$
$2s$	$1s$	$(k_3^5k_4^3/3)^{\frac{1}{2}}\{J_1(k_3,k_4,\rho)-J_1(k_s,k_4,\rho)-k_aJ_2(k_s,k_4,\rho)\}$
	$2s$	$\frac{1}{3}(k_3^5k_4^5)^{\frac{1}{2}}\{J_2(k_4,k_3,\rho)-J_2(k_4,k_s,\rho)-k_aJ_{13}(k_s,k_4,\rho)\}$
	$2p_z$	$(k_3^5k_4^5/3)^{\frac{1}{2}}\{J_7(k_4,k_3,\rho)-J_7(k_4,k_s,\rho)-k_aJ_{14}(k_4,k_s,\rho)\}$
$2p_x$	$2p_x$	$\frac{1}{2}(k_3^5k_4^5)^{\frac{1}{2}}\{J_{17}(k_3,k_4,\rho)-J_{17}(k_s,k_4,\rho)-k_aJ_{16}(k_s,k_4,\rho)\}$
$2p_y$	$2p_y$	
$2p_z$	$1s$	$(k_3^5k_4^3)^{\frac{1}{2}}\{J_6(k_3,k_4,\rho)-J_6(k_s,k_4,\rho)-k_aJ_7(k_s,k_4,\rho)\}$
$2s$	$2s$	$(k_3^5k_4^5/3)^{\frac{1}{2}}\{J_{15}(k_4,k_3,\rho)-J_{15}(k_4,k_s,\rho)-k_aJ_{14}(k_s,k_4,\rho)\}$
	$2p_z$	$(k_3^5k_4^3)^{\frac{1}{2}}\{J_{12}(k_3,k_4,\rho)-J_{12}(k_s,k_4,\rho)-k_aJ_{11}(k_s,k_4,\rho)\}$

$k_s=k_1+k_2+k_3;\quad k_a=\frac{1}{2}(k_1+k_2)$

.....

When $k_3=k_4$, the leading J integral in the above expressions is replaced by a K integral, $J_n\rightarrow K_m$ in which the n and m are related as follows:

n	1	2	3	4	6	7	9	12	15	17
m	1	2	3	4	6	7	10	13	23	25

.....

For the Coulomb integral, the standard practice hitherto has been to carry out the second step in elliptic co-ordinates, as with the one-electron integrals. Although this is quite satisfactory for the simplest cases, it suffers from the disadvantage that as the integrand becomes more complicated the final expressions become rather lengthy. An examination of these shows that they lack the economy provided by our method involving Bessel functions.

For the hybrid integral, there are three possible alternatives for the integration with respect to electron 2, after the integration has been carried out over the space of electron 1. If, in (55b), the integral over V_2 is expanded in elliptic co-ordinates, a finite number of terms results. But though we have carefully investigated this way of performing the integration, we do not recommend it, since many of the terms are exceedingly complex, and others have infinite values, the infinities finally cancelling on summation. Such a process is prone to many mistakes. If, on the other hand, the two radial distances r_a, r_b, and an azimuth ϕ are used (dipolar co-ordinates), we have the method employed by Sklar & Lyddane (1939), and Parr & Crawford (1948). This is also a very laborious process. Although it was not unreason-

able for the simpler hybrid integrals considered by early workers, extension to more complicated cases is really unsatisfactory. We shall return to this point shortly. The third method of integrating with respect to electron 2 is that which forms the basis of this part.

It should be mentioned that for these hybrid integrals, some workers followed Furry & Bartlett (1932), in carrying out the initial integration with respect to electron 2, having expanded $1/r_{12}$ by use of the Neumann formula. Both this step, and the final integration with respect to electron 1, were carried out using elliptic co-ordinates. Unless the screening constants k_3 and k_4 are identical, the final answer is obtained as an infinite series, and even when $k_3 = k_4$, the final expression is exceedingly complex.

TABLE 13. NUMERICAL EXAMPLE

					$k\rho = 3$		$k\rho = 5$	
c_1	c_2	c_3	c_4	$k^{-1}I(c_1, c_2; c_3, c_4)$	*	‡	†	‡
$2p_x$	$2p_x$	$2p_x$	$2p_x$	$2(k\rho)^{-\frac{1}{2}}\,(X/3+Y/5-3Z/35)$	0·1539	0·1538	0·0447	0·0448
$2p_x$	$2p_x$	$2p_y$	$2p_y$	$2(k\rho)^{-\frac{1}{2}}\,(X/3+Y/15-Z/35)$	0·1400	0·1399	0·0416	0·0415
$2p_x$	$2p_y$	$2p_x$	$2p_y$	$2(k\rho)^{-\frac{1}{2}}\,(Y/15-Z/35)$	0·0070	0·0069	0·0016	0·0016
$2p_x$	$2p_z$	$2p_z$	$2p_x$	$2(k\rho)^{-\frac{1}{2}}\,(Y/15+4Z/35)$	0·0160	—	0·0048	—
$2p_z$	$2p_z$	$2p_x$	$2p_x$	$2(k\rho)^{-\frac{1}{2}}\,(X/3+Y/15+4Z/35)$	0·1490	—	0·0447	—

The quantities X, Y, Z are defined in §13.

* Obtained by new method, using numerical integration.

† Obtained by new method, using **Z** functions.

‡ Obtained by Parr & Crawford.

Of the various possibilities previously available for the hybrid integral, the dipolar co-ordinate method was considered to be the least impracticable when occasion arose for evaluating cases which involved four $2p$ orbitals. These integrals were needed in the theory of the organic valence bond. This calculation featured in three papers before all the errors in the exceptionally tedious algebraic and arithmetic processes had been completely eliminated (Sklar & Lyddane, 1939; Griffing 1947, Parr & Crawford 1948). The necessity for an alternative method can be appreciated after a brief examination of the equations of the most recent of these papers, whose authors admit having found their work to be 'somewhat troublesome'. By way of contrast, our new method provided values of five hybrid integrals (which included those to which reference has just been made), in a calculation which was completed in a day. It may be stated that these are in agreement with the results of Parr & Crawford. In these integrals, the screening constants are all equal and written as k. Values are given of the quantities $k^{-1}I(c_1 \ldots, c_4)$ for two values of the parameter $k\rho$. By virtue of the formulae of table 10 all five integrals can be reduced to the three quantities X, Y, and Z, as shown in table 13. These X, Y, Z are defined as

$$X = \frac{1}{8}\int_0^\infty e^{-t} t^{\frac{1}{2}} j_8(2t)\,\{p_0(1,t;\,k_4\rho) - p_2(1,t;\,k_4\rho)\}\,dt$$

$$Y = \frac{1}{16}\int_0^\infty e^{-t} t^{\frac{1}{2}} j_7(2t)\,\{p_0(1,t;\,k_4\rho) - p_2(1,t;\,k_4\rho)\}\,dt$$

$$Z = \frac{1}{16}\int_0^\infty e^{-t} t^{\frac{1}{2}} j_7(2t)\,\{p_2(1,t;\,k_4\rho) - p_4(1,t;\,k_4\rho)\}\,dt.$$

These were evaluated numerically for $k\rho = 3$; for $k\rho = 5$ values were found by reduction to the **Z** functions. Values of the hybrid integrals are listed in table 13, in order that they may be compared with the previous published figures. The results of Parr & Crawford are also quoted in the table.

14. Exchange-penetration and Coulomb-penetration integrals

These are defined in equation (51). The reduction of these integrals resembles that of the Coulomb and hybrid integrals. In cases where the evaluation of the last mentioned type has proved difficult, these others have also given rise to tedious calculations.

The operator $H_x^*(i)$ (see equation (51)), can be shown to be of the form $\mathrm{e}^{-kr_{xi}}h(r_{xi})$, where k depends on the screening constants, and $h(r)$ is a simple polynomial in r (Goeppert-Mayer & Sklar 1938). From this stage the working is strictly analogous to that for the two-electron Coulomb and hybrid integrals, and either numerical integration or the analytical expansion in **Z** functions can be used. It is a matter of some convenience that many of the quantities needed for the Coulomb integrals are also required for the Coulomb-penetration integrals, and similarly with the hybrid and exchange-penetration integrals.

As an example we have considered the case discussed by earlier workers, in which the lone electron resonates between $2p_x$ orbitals on A and B, penetrating only the L shell of the neutral atom A. If this L shell is full, the integral is of the type denoted by $(A;\, ab)$. We let the screening constants for all the L orbitals on A be k; this will then also be the screening constant for $\Psi'(A, 1)$. The screening constant for $\Psi'(B, 1)$ is k_4. Then the exchange-penetration integral can be reduced to the form

$$(A;\, ab) = -\frac{(k^5k_4^5)^{\frac{1}{2}}}{\pi}\int H_a^*(1)\,\mathrm{e}^{-kr_{a1}-k_4r_{b1}}\,r_{a1}\,r_{b1}\sin\theta_{a1}\sin\theta_{b1}\cos^2\phi_1\,dV_1,$$

where

$$H_a^*(1) = -\frac{4}{r_{a1}}\mathrm{e}^{-2kr_{a1}}\{2+3kr_{a1}+2(kr_{a1})^2+(kr_{a1})^3\}.$$

This integral is readily reduced by the methods of this paper to

$$\tfrac{16}{3}(k^5/\rho)^{\frac{1}{2}}k_4^{-2}\int_0^\infty \mathrm{e}^{-3kt/k_4}\,t^{\frac{3}{2}}\{p_0(1,t;\,k_4\rho)-p_2(1,t;\,k_4\rho)\}\left\{2+3\left(\frac{kt}{k_4}\right)+2\left(\frac{kt}{k_4}\right)^2+\left(\frac{kt}{k_4}\right)^3\right\}dt.$$

We have evaluated this by writing it as a sum of **Z** functions, and choosing the special case $k_4 = k$; $k\rho = 5$. The value obtained was $k^{-1}(A;\, ab) = 0{\cdot}041848$, to be compared with the value 0·04180 obtained by Parr & Crawford.

The reduction of the Coulomb-penetration integrals is completely analogous to this.

As regards the relative merits of our method and those previously used, the same remarks apply to the Coulomb-penetration integrals as were made for the Coulomb integrals. Similarly the comments on the hybrid integrals apply also to integrals of the exchange-penetration type.

Acknowledgements

We are indebted to Dr Rado for advice in the extension of equation (36) to the case $\kappa < 1$. Thanks are also due to Dr Altmann and Dr van der Waals for pointing out some errors in the manuscript. One of us (M.P.B.) would like to acknowledge the receipt of a grant from the Board of the British Rayon Research Association, which has made possible this work.

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