

# The Quantum-mechanical Calculation of One-electron Properties

## II. One- and two-center moment integrals\*

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Two-center moment integrals for SLATER-type atomic orbitals are explicitly expressed in terms of a general formula involving the three quantum numbers and the effective nuclear charge of each of the two orbitals, the internuclear distance, and the usual A and B functions. A corresponding expression for one-center moment integrals is also given. The use of the one- and two-center moment integral formulae in digital computer calculations is discussed.

In paper I of this series<sup>1</sup> a general formalism for the calculation of one-electron properties was developed. It was pointed out that for an  $N$ -electron system whose wave functions  $\psi_s(q_1, \dots, q_N)$  were expanded in terms of determinants of one-electron spin orbitals  $\psi_r(q_i)$ ,  $i = 1, 2, \dots, N$ , the evaluation of one-electron properties required the computation of integrals of the type

$$\int \psi_\mu^*(q_i) \mathbf{a}(q_i) \psi_r(q_i) dq_i \quad (1)$$

where  $q_i$  represents the space coordinate  $R_i$  and the spin coordinate  $s_i$  of electron  $i$  and  $\mathbf{a}(q_i)$  is a one-electron operator.

If the property under consideration is an  $m^{\text{th}}$  order moment of the electron charge distribution,  $\mathbf{a}(q_i)$  becomes

$$\mathbf{a}(q_i) = X_i^\alpha Y_i^\beta Z_i^\gamma, \quad \alpha + \beta + \gamma = m \quad (2)$$

where  $\alpha$ ,  $\beta$ ,  $\gamma$  and  $m$  are non-negative integers and  $X_i$ ,  $Y_i$ ,  $Z_i$  the coordinates of electron  $i$  with respect to a cartesian system  $XYZ$ . HARTREE atomic units<sup>2</sup> are used throughout this paper. The components of the  $2m$ -pole moment of the electron charge distribution are in general expressed as linear combinations of  $m^{\text{th}}$  order moments. For example, the quadrupole moment tensor of the electron charge distribution of a molecule that has an axis of symmetry of order three or greater is expressible in terms of the expectation value of a single scalar quantity<sup>3</sup> for which

the operator  $\mathbf{a}(q_i)$  is

$$\mathbf{a}(q_i) = Z_i^2 - \frac{1}{2}(X_i^2 + Y_i^2) \quad (3)$$

where the  $Z$  axis is the axis of symmetry.

In most approximate calculations<sup>4</sup> of atomic and molecular wave functions the  $\psi_r(q_i)$  have been expressed as linear combinations of SLATER-type<sup>5</sup> spin-orbitals. Introduction of these into eq. (1) followed by integration over the spin coordinate  $s_i$  yields  $m^{\text{th}}$  order moment integrals of the form

$$I = \int \psi_{n'l'm'}^*(R) X^\alpha Y^\beta Z^\gamma \psi_{n'l'm}(R) d\tau \quad (4)$$

where  $\psi_{nlm}$  and  $\psi_{n'l'm'}$  are SLATER-type atomic orbitals centered on nucleus  $M$  and  $M'$  respectively,  $R$  is a position vector for the electron and  $d\tau$  is the volume element in the configuration space. The dummy index  $i$  specifying the electron has been dropped since the value of the integral does not depend on it.

The SLATER-type atomic orbitals  $\psi_{nlm}$  and  $\psi_{n'l'm'}$  can be expressed in terms of cartesian systems  $x$ ,  $y$ ,  $z$  and  $x'$ ,  $y'$ ,  $z'$  centered on  $M$  and  $M'$  respectively. The three systems  $XYZ$ ,  $xyz$  and  $x'y'z'$  can have arbitrary orientations with respect to one another. It can be shown<sup>6</sup> that the general integral in eq. (4) is expressible as a linear combination of integrals of the same type, with the three coordinate systems having special relative orientations (see Section 1), which considerably simplify the integral evaluation.

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<sup>1</sup> M. KARPLUS, A. KUPPERMANN and L. M. ISAACSON, J. Chem. Phys. **29**, 1240 [1958].

<sup>2</sup> D. R. HARTREE, Proc. Camb. Phil. Soc. **24**, 89 [1928].

<sup>3</sup> J. O. HIRSCHFELDER, C. F. CURTISS and R. B. BIRD, Molecular

Theory of Gases and Liquids, John Wiley and Sons, Inc., New York 1954, pp. 839—841.

<sup>4</sup> J. C. SLATER, Electronic Structure of Atoms and Molecules, Technical Report No. 3, Solid-State and Molecular Theory Group, Massachusetts Institute of Technology, Cambridge, Mass., February 15, 1953.

<sup>5</sup> J. C. SLATER, Phys. Rev. **36**, 57 [1930]. — C. ZENER, Phys. Rev. **36**, 51 [1930].

<sup>6</sup> A. KUPPERMANN, L. M. ISAACSON and M. KARPLUS, forthcoming.



The present paper is concerned with the formulation of expressions for these specialized two-center ( $M \neq M'$ ) and one-center ( $M = M'$ ) moment integrals and with their calculation by means of digital computers<sup>7</sup>.

### 1. Definitions

The systems of reference<sup>8</sup> used in this paper for the two-center integrals are indicated in Fig. 1. The axes  $X$ ,  $x'$  and  $x$  are parallel to one another and oriented in the same direction. A similar statement is valid for  $Y$ ,  $y'$  and  $y$ . Axes  $Z$ ,  $z'$  and  $z$  are on the same straight line and oriented as shown in Fig. 1.  $X$ ,  $Y$ ,  $Z$  and  $x'$ ,  $y'$ ,  $z'$  are counterclockwise systems, whereas  $x$ ,  $y$ ,  $z$  is a clockwise one. Point C, the origin of systems  $XYZ$ , is the midpoint of the line segment  $MM'$  whose length is  $2a$ . The position of a general point  $P(X, Y, Z)$  is expressed in terms of the systems of spherical polar coordinates  $r$ ,  $\Theta$ ,  $\varphi$  and  $r'$ ,  $\Theta'$ ,  $\varphi'$  centered on nuclei  $M$  and  $M'$  respectively (note that  $\varphi = \varphi'$ ).

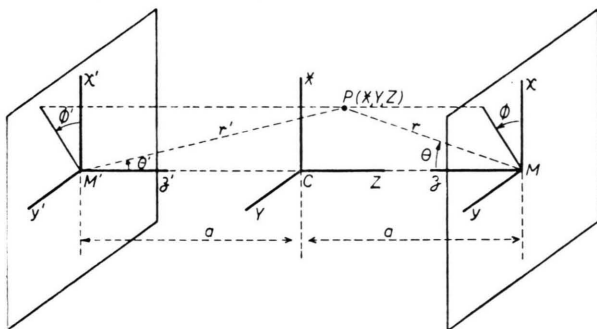


Fig. 1. Systems of reference.

In addition to these coordinate systems, it will be useful to introduce a set of confocal elliptic coordinates<sup>9</sup>  $\xi$ ,  $\eta$ ,  $\varphi$  where the angle  $\varphi$  is identical with that of the spherical polar coordinates and  $\xi$  and  $\eta$  are defined by the relations

$$\xi = \frac{r' + r}{2a}, \quad \eta = \frac{r' - r}{2a}. \quad (5)$$

The range of these variables is given by the expressions

$$1 \leq \xi < +\infty, \quad -1 \leq \eta \leq 1, \quad 0 \leq \varphi < 2\pi. \quad (6)$$

For the one-center integrals the three cartesian sys-

tems are chosen for convenience to be identical counterclockwise systems. Similarly, the spherical polar systems  $r$ ,  $\Theta$ ,  $\varphi$  and  $r'$ ,  $\Theta'$ ,  $\varphi'$  are identical to one another.

The real normalized SLATER-type orbitals  $\psi_{nlm}(r, \Theta, \varphi)$  used in this paper are defined by the expression

$$\psi_{nlm}(r, \Theta, \varphi) = \frac{(2\xi)^{n^*+1/2}}{[(2n^*)!]^{1/2}} r^{n^*-1} e^{-\xi r} P_l^m(\cos \Theta) \cdot \Phi_m(\varphi) \quad (7)$$

$$\text{where} \quad n^* = n - \delta^*, \quad (8)$$

$n$ ,  $l$  and  $m$  are integer quantum numbers subject to the conditions

$$n > 0, \quad 0 \leq l \leq n-1, \quad -l \leq m \leq l \quad (9)$$

and  $\delta^*$  is a parameter discussed below.

The function  $\Phi_m(\varphi)$  is defined by the equation

$$\Phi_m(\varphi) = \frac{1}{\sqrt{\pi}} \begin{cases} \sin m\varphi & \text{for } m > 0 \\ 1/\sqrt{2} & \text{for } m = 0 \\ \cos m\varphi & \text{for } m < 0 \end{cases} \quad (10)$$

$$= c_m \frac{e^{im\varphi + i1 + |m|/m} e^{-im\varphi}}{2 i^{1/2} (1 + |m|/m)} \quad (\text{see note ***})$$

where, by a convention used throughout this paper,

$$|0|/0 \equiv -1 \quad (11)$$

and  $c_m$  is the normalization coefficient,

$$c_m = \frac{1}{\sqrt{\pi}} \begin{cases} 1/\sqrt{2} & \text{for } m = 0 \\ 1 & \text{for } m \neq 0 \end{cases} \quad (12)$$

$$= \frac{1}{\sqrt{\pi}} \left[ 1 - \left( 1 - \frac{1}{\sqrt{2}} \right) \delta_{m,0} \right].$$

The function  $P_l^m(\cos \Theta)$  is the normalized associated LEGENDRE function defined by the expression

$$P_l^m(\cos \Theta) = \left[ \frac{2l+1}{2} \frac{(l-|m|)!}{(l+|m|)!} \right]^{1/2} (1 - \cos^2 \Theta)^{|m|/2} \cdot \frac{(-1)^l}{2^l l!} \frac{d^{l+|m|}}{[d(\cos \Theta)]^{l+|m|}} (1 - \cos^2 \Theta)^l. \quad (13)$$

The quantity  $\delta^*$ , an empirical parameter, depends on  $n$  alone and has the values given in the following table:

| $n$        | 1 | 2 | 3 | 4   | 5 | 6   |
|------------|---|---|---|-----|---|-----|
| $\delta$   | 0 | 0 | 0 | 0.3 | 1 | 1.8 |
| $\delta^*$ | 0 | 0 | 0 | 0   | 1 | 2   |

<sup>7</sup> M. KARPLUS, A. KUPPERMANN and L. M. ISAACSON, Bull. Amer. Phys. Soc., Ser. II, **2**, 133 [1957].

<sup>8</sup> K. RÜDENBERG, J. Chem. Phys. **19**, 1459 [1951].

<sup>9</sup> L. PAULING and E. B. WILSON, Introduction to Quantum Mechanics (McGraw-Hill Book Company, Inc., New York, 1935), p. 444.

\*\*\* The letter  $i$  here stands for  $\sqrt{-1}$ .

Instead of  $\delta^*$ , SLATER<sup>5</sup> used a quantity  $\delta$  whose values as a function of  $n$  are also included in the table. The  $\delta^*$  values, which are the integers closest to the corresponding  $\delta$ 's, are used here to simplify the integrals under consideration. The quantity  $\zeta$ , also an empirical parameter<sup>10</sup>, depends on  $n$  and the effective charge of the nucleus on which  $\psi_{nlm}$  is centered. For  $n=4$  and  $n=6$  values of  $\zeta$  slightly different from those obtained by applying the SLATER rules<sup>5</sup> should be used<sup>11</sup> to compensate for the substitution of  $\delta$  by  $\delta^*$ . As developed in this paper, the integral formulae require that  $n^*$  be an integer not smaller than  $l$ .

Complex normalized SLATER-type orbitals can be defined as the functions obtained by replacing  $\Phi_m(\varphi)$  in eq. (7) with  $(1/\sqrt{2\pi}) e^{im\varphi}$ . Since the complex orbitals can be expressed as linear combinations of the real orbitals by means of eq. (10), the discussion in this paper is restricted to real normalized SLATER-type orbitals.

In terms of the above definitions, the two-center and one-center integrals introduced in the paragraph of Section I can be written

$$I_2 = I_2(n, l, m, \zeta, n', l', m', \zeta', \alpha, \alpha, \beta, \gamma) \quad (14)$$

$$= \int \psi'_{n'l'm'}(r', \Theta', \varphi') X^\alpha Y^\beta Z^\gamma \psi_{nlm}(r, \Theta, \varphi) d\tau$$

Substitution of  $\cos \Theta$  in eq. (16) by eq. (17) yields

$$P_l^m\left(\frac{1-\xi\eta}{\xi+\eta}\right) = \frac{(l+|m|)!}{2^l l!} \left[ \frac{2l+1}{2} \frac{(l-|m|)!}{(l+|m|)!} \right]^{1/2} \frac{[(\xi^2-1)(1-\eta^2)]^{l/2}}{(\xi-\eta)^{|m|}} \quad (18)$$

$$\cdot \sum_{i=0}^{\leq 1/2(l-|m|)} (-1)^i \binom{l}{i} \binom{2l-2i}{l-|m|-2i} \frac{(1-\xi\eta)^{l-|m|-2i}}{(\xi-\eta)^{l-|m|}} (\xi-\eta)^{2i}.$$

From eqs. (20), (19) and (7) one obtains  $\psi_{nlm}$  in the form

$$\psi_{nlm}(\xi, \eta, \varphi) = \frac{(2\zeta)^{n^*+1/2}}{[(2n^*)!]^{1/2}} a^{n^*-1} (\xi-\eta)^{n^*-1} e^{-a\zeta(\xi-\eta)} \cdot \frac{(l+|m|)!}{2^l l!} \left[ \frac{2l+1}{2} \frac{(l-|m|)!}{(l+|m|)!} \right]^{1/2} \frac{[(\xi^2-1)(1-\eta^2)]^{l/2}}{(\xi-\eta)^l}$$

$$\cdot \sum_{i=0}^{\leq 1/2(l-|m|)} (-1)^i \binom{l}{i} \binom{2l-2i}{l-|m|-2i} (1-\xi\eta)^{l-|m|-2i} (\xi-\eta)^{2i} \Phi_m(\varphi). \quad (19)$$

Introduction of eq. (19) and a corresponding expression for  $\psi'_{n'l'm'}$  into eq. (14) furnishes, with the help of the relations of eqs. (17), the integral

$$I_2 = a^{\alpha+\beta+\gamma} (a\zeta)^{n^*+1/2} (a\zeta')^{n'^*+1/2} K K' \cdot \int_1^{+\infty} d\xi \int_{-1}^1 d\eta \int_0^{2\pi} d\varphi e^{-a(\zeta+\zeta')\xi+a(\zeta-\zeta')\eta} \quad (20)$$

$$\cdot \cos^\alpha \varphi \sin^\beta \varphi \Phi_m(\varphi) \Phi_{m'}(\varphi) p(\xi, \zeta).$$

<sup>10</sup> C. C. Roothaan, J. Chem. Phys. 19, 1445 [1951].

<sup>11</sup> W. H. Eberhardt, private communication.

and

$$I_1 = I_1(n, l, m, \zeta, n', l', m', \zeta', \alpha, \beta, \gamma) \quad (15)$$

$$= \int \psi'_{n'l'm'}(r', \Theta', \varphi') x^\alpha y^\beta z^\gamma \psi_{nlm}(r, \Theta, \varphi) d\tau$$

respectively.

## 2. Two-center integral expressions

### 2.1. Integrated expression for $I_2$

Performing the differentiation indicated in eq. (13), one obtains

$$P_l^m(\cos \Theta) \quad (16)$$

$$= \frac{(l+|m|)!}{2^l l!} \left[ \frac{2l+1}{2} \frac{(l-|m|)!}{(l+|m|)!} \right]^{1/2} (1-\cos^2 \Theta)^{|m|/2}$$

$$\cdot \sum_{i=0}^{\leq 1/2(l-|m|)} (-1)^i \binom{l}{i} \binom{2l-2i}{l-|m|-2i} (\cos \Theta)^{l-|m|-2i}$$

where the upper limit of the summation is the largest integer that does not exceed  $\frac{1}{2}(l-|m|)$ . It is now convenient to use the confocal elliptic coordinates defined in eq. (5). The pertinent transformation formulae are<sup>8</sup>

$$r = a(\xi - \eta), \quad r' = a(\xi + \eta),$$

$$\cos \Theta = \frac{1-\xi\eta}{\xi-\eta}, \quad \cos \Theta' = \frac{1+\xi\eta}{\xi+\eta},$$

$$d\tau = a^3 (\xi^2 - \eta^2) d\xi d\eta d\varphi,$$

$$X = a(\xi^2 - 1)^{1/2} (1 - \eta^2)^{1/2} \cos \varphi, \quad (17)$$

$$Y = a(\xi^2 - 1)^{1/2} (1 - \eta^2)^{1/2} \sin \varphi,$$

$$Z = a\xi\eta.$$

Here  $K$  is a constant factor defined by the equality

$$K = 2^{n^*-l} \left[ \frac{2l+1}{(2n^*)!} \left( \frac{l+|m|}{l} \right) \right]^{1/2}, \quad (21)$$

$K'$  is the corresponding constant arising from  $\psi'_{n'l'm'}$  and  $p(\xi, \eta)$  is a function of  $\xi$  and  $\eta$  given by the expression

$$p(\xi, \eta) = [(\xi^2 - 1)(1 - \eta^2)]^{1/2(\alpha + \beta + |m| + |m'|)} \xi^\gamma \eta^\gamma (\xi - \eta)^{n^*-l} (\xi + \eta)^{n^{**}-l'} \quad (22)$$

$$\cdot \sum_{i=0}^{\leq 1/2(l-|m|)} \sum_{i'=0}^{\leq 1/2(l'-|m'|)} (-1)^{i+i'} \binom{l}{i} \binom{l'}{i'} \binom{2l-2i}{l-|m|-2i}$$

$$\cdot \binom{2l'-2i'}{l'-|m'|-2i'} (1 - \xi \eta)^{l-|m|-2i} (1 + \xi \eta)^{l'-|m'|-2i'} (\xi - \eta)^{2i} (\xi + \eta)^{2i'}.$$

In eq. (20) the integral  $I_\varphi$

$$I_\varphi = \int_0^{2\pi} \cos^2 \varphi \sin^2 \varphi \Phi_m(\varphi) \Phi_{m'}(\varphi) d\varphi \quad (23)$$

involving the variable  $\varphi$  can be factored out and the integration performed separately. When this is done (see Section 2.2 for details) there results the expression

$$I_\varphi = \frac{c_m c_{m'}}{2^{\alpha+\beta}} \cdot \frac{1 + (-1)^{2\mu}}{2} \cdot \frac{1 + (-1)^{\beta-1/2[(|m|/m) - (|m'|/m')]} }{2 i^{\beta-1/2[(|m|/m) - (|m'|/m')]} } \sum_{k=0}^{\beta} (-1)^k \binom{\beta}{k} \left[ \binom{\alpha}{\nu-k} + i^{1+|m'|/m'} \binom{\alpha}{\varepsilon-k} \right] \quad (24)$$

where  $\mu \equiv \frac{1}{2}(\alpha + \beta + |m| + |m'|)$ ,  $\nu \equiv \frac{1}{2}(\alpha + \beta - m + m')$ ,  $\varepsilon \equiv (\alpha + \beta - m - m')$ . (25)

From its definition in eqs. (25) the quantity  $\mu$  is integral or half-integral. If it is half-integral  $I_\varphi$  and, therefore,  $I_2$  vanish because of the factor  $\frac{1 + (-1)^{2\mu}}{2}$ . This makes it possible to restrict  $\mu$  to integer values in eq. (22) without loss of generality insofar as  $I_2$  is concerned<sup>12</sup>. With this restriction, one sees from eq. (22), and from the fact that  $n^*$  and  $n^{**}$  are integers, that  $p(\xi, \eta)$  is simply a polynomial in  $\xi$  and  $\eta$  which can be written in the form

$$p(\xi, \eta) = \sum_{\substack{\sigma=2\gamma+n^* \\ -l+n^{**}-l'}}^{\substack{2(\alpha+\beta+\gamma)+n^* \\ +l+n^{**}+l'}} \sum_{\substack{\sigma=\text{smallest of } \sigma-\gamma, \\ \alpha+\beta+\gamma+n^*+n^{**}}}^{\substack{\text{Smallest of } \sigma-\gamma, \\ \alpha+\beta+\gamma+n^*+n^{**}}} b_{s, \sigma-s} \xi^s \eta^{\sigma-s} \quad (26)$$

with

$$b_{ij} = (-1)^{n^*-l} b_{ji}. \quad (27)$$

If  $n^*$  and  $n^{**}$  had not been made integers an infinite series expression for  $p(\xi, \eta)$  would have been obtained<sup>13</sup>.

The index 2 on the first summation sign of eq. (26) signifies, by convention, that  $\sigma$  is increased in steps of 2. An explicit expression for  $b_{s, \sigma-s}$  can be obtained (see Section 2.3 for details) and is given by

$$b_{s, \sigma-s} = (-1)^{n^*-l+\mu} \sum_{\tau=0}^{\mu} \sum_{\lambda=0}^{\mu} \sum_{i=0}^{\leq 1/2(l'-|m'|)} \sum_{i'=0}^{\leq 1/2(l-|m|)} \sum_{p=0}^{n^*-|m|} \sum_{k=0}^{l-|m|-2i} \quad (28)$$

$$(-1)^{\tau+\lambda+p+i+i'} \binom{\mu}{\tau} \binom{\mu}{\lambda} \binom{l}{i} \binom{l'}{i'} \binom{2l-2i}{l-|m|-2i} \binom{2l'-2i'}{l'-|m'|-2i} \binom{n^*-l+2i}{p-k} \binom{l-|m|-2i}{k}$$

$$\cdot \binom{n^{**}-l'+2i'}{-1/2[\sigma-n^*-n^{**}+l+l'] + s - \tau + \lambda - p + i + i' + k} \binom{l'-|m'|-2i'}{1/2[\sigma-n^*-n^{**}+l+l'] - \gamma - \tau - \lambda - i - i' - k}$$

<sup>12</sup> In eq. (24), the factor

$$\frac{1 + (-1)^{2\mu}}{2} \cdot \frac{1 + (-1)^{\beta-1/2[(|m|/m) - (|m'|/m')]} }{2 i^{\beta-1/2[(|m|/m) - (|m'|/m')]} }$$

which can have only the values  $-1, 0$  or  $+1$ , determines

the two-center moment integrals that are zero because of the symmetry of the wave functions and moment operator appearing in the integrand.

<sup>13</sup> L. LEIFER, F. A. COTTON and J. R. LETO, J. Chem. Phys. **28**, 364 [1958].

Substitution of eqs. (26) and (23) into the integral  $I_2$  (eq. 20) yields the formula

$$I_2 = a^{2+\beta+\gamma} (a\zeta)^{n^*+1/2} (a\zeta')^{n^*+1/2} K K' I_\varphi \sum_s \sum_s b_{s, \sigma-s} A_s(a\zeta' + a\zeta) B_{\sigma-s}(a\zeta' - a\zeta) \quad (29)$$

where the summation limits are the same as in eq. (26), and  $A$  and  $B$  are the standard functions<sup>14</sup> defined by the equations (30) and (31):

$$A_s(t) \equiv \int_1^{+\infty} \xi^s e^{-t\xi} d\xi \quad s \geq 0, \quad \text{integral} \quad t > 0, \quad \text{real}, \quad (30)$$

$$\text{and} \quad B_s(t) \equiv \int_{-1}^1 \eta^s e^{-t\eta} d\eta \quad s \geq 0, \quad \text{integral} \quad t \quad \text{real}. \quad (31)$$

Integrated expressions for  $A$  and  $B$  are given in eqs. (44) and (45) of Section 4.

Eq. (29) is the desired general integrated expression for the two-center moment integrals  $I_2$ . Its use in the digital computer computation of these integrals eqs. (44) and (45) of Section 3.

## 2.2. Integrated expression for $I_\varphi$

In order to perform the integration indicated in eq. (23) it is convenient to substitute  $\Phi_m(\varphi)$  and  $\Phi_{m'}(\varphi)$  by means of eq. (10) and to replace  $\sin \varphi$  and  $\cos \varphi$  by their usual exponential forms. This furnishes the expression

$$I_\varphi = \frac{c_m c_{m'}}{2^{\alpha+\beta+2} i^{\beta+1+1/2} [(|m|/m) + (|m'|/m')]} \int_0^{2\pi} (e^{i\varphi} + e^{-i\varphi})^\alpha \cdot (e^{i\varphi} - e^{-i\varphi})^\beta (e^{im\varphi} + i^{1+|m|/m} e^{-im\varphi}) (e^{im'\varphi} + i^{1+|m'|/m'} e^{-im'\varphi}) d\varphi. \quad (32)$$

If  $e^{i(\alpha+\beta)\varphi}$  is now factored out and the binomials are expanded there results the equation

$$I_\varphi = \frac{c_m c_{m'}}{2^{\alpha+\beta+2} i^{\beta+1+1/2} [(|m|/m) + (|m'|/m')]} \sum_{k=0}^{\beta} \sum_{j=0}^{\alpha} (-1)^{\beta-k} \binom{\alpha}{j} \binom{\beta}{k} \int_0^{2\pi} e^{-i(\alpha+\beta-2j-2k)\varphi} \cdot [e^{i(m+m')\varphi} + i^{(|m|/m) + (|m'|/m') + 2} e^{-i(m+m')\varphi} + i^{1+|m'|/m'} e^{i(m-m')\varphi} + i^{1+|m|/m} e^{-i(m-m')\varphi}] d\varphi \quad (33)$$

which can be simplified to give

$$I_\varphi = \frac{c_m c_{m'}}{2^{\alpha+\beta+1} i^{\beta+1+1/2} [(|m|/m) + (|m'|/m')]} \sum_{k=0}^{\beta} \sum_{j=0}^{\alpha} (-1)^{\beta-k} \binom{\alpha}{j} \binom{\beta}{k} \cdot [\delta_{2j+2k, \alpha+\beta-m-m'} + i^{2+(|m|/m) + (|m'|/m')} \delta_{2j+2k, \alpha+\beta+m+m'} + i^{1+|m'|/m'} \delta_{2j+2k, \alpha+\beta-m+m'} + i^{1+|m|/m} \delta_{2j+2k, \alpha+\beta+m-m'}]. \quad (34)$$

Eq. (34) can be expressed in terms of two convenient double sums

$$I_\varphi = \frac{c_m c_{m'}}{2^{\alpha+\beta+1} i^{\beta+1+1/2} [(|m|/m) + (|m'|/m')]} \cdot \left( \sum_{k=0}^{\beta} \sum_{j=0}^{\alpha} (-1)^{\beta-k} \binom{\alpha}{j} \binom{\beta}{k} \cdot [\delta_{2j+2k, \alpha+\beta-m-m'} + i^{1+|m'|/m'} \delta_{2j+2k, \alpha+\beta-m+m'}] + \sum_{k=0}^{\beta} \sum_{j=0}^{\alpha} (-1)^{\beta-k} \binom{\alpha}{j} \binom{\beta}{k} [i^{2+(|m|/m) + (|m'|/m')} \delta_{2j+2k, \alpha+\beta+m+m'} + i^{1+|m|/m} \delta_{2j+2k, \alpha+\beta+m-m'}] \right). \quad (35)$$

Change of summation indices  $j$  and  $k$  to  $\alpha-j$  and  $\beta-k$ , respectively, in the second of the double summations above furnishes the expression (36):

<sup>14</sup> M. KOTANI, A. AMERINIA, E. ISHIGURO and T. KIMURA, Table of Molecular Integrals, (Mauizen Co., Ltd., Tokyo 1955) p. 34.

$$I_{\varphi} = \frac{c_m c_{m'}}{2^{\alpha+\beta+1} i^{\beta+1+1/2} [(|m|/m) + (|m'|/m')]} \quad (36)$$

$$\cdot \left( \sum_{k=0}^{\beta} \sum_{j=0}^{\alpha} (-1)^{\beta-k} \binom{\alpha}{j} \binom{\beta}{k} [\delta_{2j+2k, \alpha+\beta-m-m'} + i^{1+|m'|/m'} \delta_{2j+2k, \alpha+\beta-m+m'}] \right.$$

$$\left. + \sum_{k=0}^{\beta} \sum_{j=0}^{\alpha} (-1)^k \binom{\alpha}{j} \binom{\beta}{k} [i^{2+(|m|/m) + (|m'|/m')} \delta_{2j+2k, \alpha+\beta-m-m'} + i^{1+|m|/m} \delta_{2j+2k, \alpha+\beta-m+m'}] \right).$$

Since  $j+k$  is a non-negative integer, a necessary condition for  $I_{\varphi}$  not to vanish is that  $\mu$ ,  $\varepsilon$ , and  $\nu$  defined by eq. (25) be integers. Using this fact and performing the summation over the variable  $j$ , one obtains

$$I_{\varphi} = \frac{1+(-1)^2 \mu}{2} \frac{c_m c_{m'}}{2^{\alpha+\beta+2} i^{\beta+1+1/2} [(|m|/m) + (|m'|/m')]} \quad (37)$$

$$\cdot \sum_{k=0}^{\beta} (-1)^k \binom{\beta}{k} \left( \binom{\alpha}{\nu-k} [(-1)^{\beta} i^{1+|m'|/m'} + i^{1+|m|/m}] + \binom{\alpha}{\varepsilon-k} [(-1)^{\beta} + i^{2+(|m|/m) + (|m'|/m')}] \right)$$

$$= \frac{1+(-1)^2 \mu}{2} \frac{c_m c_{m'}}{2^{\alpha+\beta+1}} \frac{i^{1+(|m|/m)} [1+(-1)^{\beta} i^{(|m'|/m') - (|m|/m)}]}{i^{\beta+1+1/2} [(|m|/m) + (|m'|/m')]} \sum_{k=0}^{\beta} (-1)^k \binom{\beta}{k} \left[ \binom{\alpha}{\nu-k} + i^{1+|m'|/m'} \binom{\alpha}{\varepsilon-k} \right].$$

In this expression, as in the rest of this paper, the usual convention according to which binomial coefficients with non-negative upper numbers and negative lower numbers are zero has been adopted. By means of the equality

$$i^{(|m'|/m') - (|m|/m)} = (-1)^{-1/2[(|m|/m) - (|m'|/m')]} \quad (38)$$

eq. (37) can be rewritten in the form

$$I_{\varphi} = \frac{c_m c_{m'}}{2^{\alpha+\beta}} \frac{1+(-1)^2 \mu}{2} \frac{1+(-1)^{\beta-1/2[(|m|/m) - (|m'|/m')]}]}{2 i^{\beta-1/2[(|m|/m) - (|m'|/m')}]}} \sum_{k=0}^{\beta} (-1)^k \binom{\beta}{k} \left[ \binom{\alpha}{\nu-k} + i^{1+|m'|/m'} \binom{\alpha}{\varepsilon-k} \right] \quad (26)$$

which is the integrated expression used in Section 2.1.

### 2.3. Explicit expression for $b_{s, \sigma-s}$

To derive an explicit expression for  $b_{s, \sigma-s}$  it is convenient to expand eq. (22) by means of the binomial theorem. There results the expression

$$p(\xi, \eta) = \sum_{i=0}^{\leq 1/2(l-|m|)} \sum_{i'=0}^{\leq 1/2(l'-|m'|)} \sum_{\tau=0}^{\mu} \sum_{\lambda=0}^{\mu} \sum_{j=0}^{n^*-l+2i} \sum_{j'=0}^{n^*-l'+2i'} \sum_{k=0}^{l-|m|-2i} \sum_{k'=0}^{l'-|m'|-2i'} \quad (39)$$

$$\xi^{2\tau+\gamma+j+j'+k+k'} \eta^{2\lambda+\gamma+n^*-l+2i-j+n^*-l'+2i'-j'+k+k'} \cdot (-1)^{\mu-\tau+\lambda+n^*-l-j+k+i+i'}$$

$$\cdot \binom{\mu}{\tau} \binom{\mu}{\lambda} \binom{n^*-l+2i}{j} \binom{n^*-l'+2i'}{j'} \binom{l-|m|-2i}{k} \binom{l'-|m'|-2i'}{k'} \binom{l}{i} \binom{2l-2i}{l-|m|-2i} \binom{l'}{i'} \binom{2l'-2i'}{l'-|m'|-2i'}$$

Substitution of the summation variables,  $k'$ ,  $j$  and  $j'$  by the variables  $s$ ,  $\sigma$  and  $p$  defined by the relations

$$s \equiv 2\tau + \gamma + j + j' + k + k', \quad p \equiv j + k;$$

$$\sigma - s \equiv 2\lambda + \gamma + n^* - l + 2i - j + n^* - l' + 2i' - j' + k + k', \quad (40)$$

and comparison of the resulting expression with eq. (26) shows that the  $b_{s, \sigma-s}$  are given by the equation

$$b_{s, \sigma-s} = (-1)^{n^*-l+\mu} \sum_{\tau=0}^{\mu} \sum_{\lambda=0}^{\mu} \sum_{i=0}^{\leq 1/2(l'-|m'|)} \sum_{i'=0}^{\leq 1/2(l-|m|)} \sum_{p=0}^{n^*-|m|} \sum_{k=0}^{l-|m|-2i} \quad (28)$$

$$(-1)^{\tau+\lambda+p+i+i'} \binom{\mu}{\tau} \binom{\mu}{\lambda} \binom{l}{i} \binom{l'}{i'} \binom{2l-2i}{l-|m|-2i} \binom{2l'-2i'}{l'-|m'|-2i'} \binom{n^*-l+2i}{p-k} \binom{l-|m|-2i}{k}$$

$$\cdot \binom{n^*-l'+2i'}{-1/2[\sigma-n^*-n^*+l+l'] + s - \tau + \lambda - p + i + i' + k} \binom{l'-|m'|-2i'}{1/2[\sigma-n^*-n^*+l+l'] - \gamma - \tau - \lambda - i - i' - k}.$$



### 3. One-center integral expression

An integrated expression for the one-center integral  $I_1$ , defined by eq. (15), can be obtained by use of eqs. (7), (16), and (24). However, for convenience in computer programming,  $I_1$  is here derived from the relation

$$I_1 = (n, l, m, \zeta, n', l', m', \zeta', \alpha, \beta, \gamma) = (-1)^{l+m} \lim_{\alpha \rightarrow 0} I_2(n, l, m, \zeta, n', l', m', \zeta', \alpha, \alpha, \beta, \gamma). \quad (41)$$

The  $(-1)^{l+m}$  factor arises from the fact that the system of reference on nucleus M (Fig. 1) must be reflected through the  $xy$  plane in order to make the three systems of reference coincide in the limit  $\alpha \rightarrow 0$ . Since this reflection is equivalent to replacing  $\Theta$  by  $\pi - \Theta$  in the orbital  $\psi_{nlm}$ , one finds with the equation

$$P_l^m[\cos(\pi - \Theta)] = P_l^m(-\cos \Theta) = (-1)^{l+m} P_l^m(\cos \Theta) \quad (42)$$

that eq. (41) is satisfied. From this result and eq. (29) it is seen that to obtain  $I_1$  the quantity

$$L = \lim_{\alpha \rightarrow 0} \alpha^{a+\beta+\gamma+n^*+n^{*'}+1} A_s(a\zeta' + \alpha\zeta) B_{s-s}(a\zeta' - \alpha\zeta) \quad (43)$$

must be evaluated.

Successive integration by parts of eq. (30) and eq. (31) for  $t \neq 0$  and direct integration of eq. (31) for  $B_s(0)$  yields the expressions

$$A_s(t) = \frac{e^{-t}}{t^{s+1}} \sum_{k=0}^s (s-k)! \binom{s}{k} t^k, \quad (44)$$

$$B_s(t) = \begin{cases} \frac{1}{t^{s+1}} \sum_{k=0}^s [(-1)^k e^t - e^{-t}] (s-k)! \binom{s}{k} t^k & \text{for } t \neq 0, \\ \frac{1}{s+1} [1 + (-1)^s] & \text{for } t = 0. \end{cases} \quad (45)$$

Substitution of eqs. (44) and (45) into eq. (43) gives the expression

$$L = \frac{1+(-1)^s}{s+1} \lim_{\alpha \rightarrow 0} e^{-\alpha(\zeta+\zeta')} \sum_{k=0}^s \frac{s! \alpha^{F-s+k}}{k! (\zeta+\zeta')^{s-k+1}} = \frac{F!}{(\zeta+\zeta')^{F+1}} \delta_{F,s} \quad (46)$$

$$\text{where} \quad F = \alpha + \beta + \gamma + n^* + n^{*'} \quad (47)$$

Introduction of eqs. (46) and (29) into eq. (41) furnishes the desired general integrated expression for the one-center moment integrals  $I_1$

$$I_1 = (-1)^{l+m} \frac{\zeta^{n^*+1/2} \zeta'^{n^{*'}+1/2}}{(\zeta+\zeta')^{F+1}} K K' I_\varphi [1 + (-1)^{\alpha+\beta+\gamma+l+l'}] (F!) \sum_{\sigma=F+\gamma+0,1}^{F+\alpha+\beta+\gamma+l+l'} \frac{b_{F,\sigma-F}}{\sigma-F+1} \quad (48)$$

where by convention  $F+\gamma+0, 1$  is equal to  $F+\gamma$  if  $\alpha+\beta+l+l'$  is even and  $F+\gamma+1$  if it is odd.

### 4. Digital computer calculation

The general moment integral formulae given in eqs. (29) and (48) are well suited for digital computer calculation. Their programming can be accomplished directly for obtaining the  $I_1$  and  $I_2$  integrals, once a suitable method for evaluation of the  $A_s(t)$  and  $B_s(t)$  functions (eq. 30 and 31) has been developed.  $A_s(t)$  can readily be obtained by use of the recursion formula

$$A_0(t) = e^{-t}/t, \quad A_s(t) = (1/t)[e^{-t} + s A_{s-1}(t)]; \quad s \geq 1. \quad (49)$$

Since for the  $B_s(t)$  the usual recursion relationship<sup>15</sup> leads to large errors for small values of  $t$ <sup>16</sup>, a power series expansion of the form

$$B_s(t) = (-1)^d \sum_{j=0}^{\infty} \frac{t^{2j+e}}{(2j+e)! (s+2j+1+e)!}, \quad (50)$$

$$e=0 \text{ for } s \text{ even, } e=1 \text{ for } s \text{ odd,}$$

$$d=s \text{ for } t>0, \quad d=0 \text{ for } t \leq 0$$

<sup>15</sup> Ref. 14, p. 56-57.

<sup>16</sup> F. J. CORBATO, J. Chem. Phys. **24**, 452 [1956]. — T. C. CHEN, *ibid.*, **24**, 1268 [1956].

can be used. For computational purposes the series can be cut off at a value of  $J$  such that

$$\frac{t^{2J+e}}{(2J+e)!(s+2J+1+e)!} < 10^{-n} \quad (51)$$

$$\sum_{j=0}^J \frac{t^{2j+e}}{(2j+e)!(s+2j+1+e)!}$$

where the choice of  $n$  is dictated by the accuracy required.

General programs for the  $I_1$  and  $I_2$  integrals have been prepared and tested on ILLIAC, the electronic digital computer of the University of Illinois. For this computer, which has a speed comparable to many

of the others in operation today, it was found that for 8 decimal digit accuracy and reasonable values of  $n$ ,  $n'$ , and  $m$  the calculation time is of the order of seconds (e. g.  $n=n'=m=2$ ,  $I_1 \sim 1-4$  seconds,  $I_2 \sim 2-12$  seconds). These results indicate that the formulae developed in this paper should be generally useful for the evaluation of one- and two-center moment integrals by means of high speed digital computers.

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## Zur Theorie der Transporterscheinungen in Entladungen sehr hoher Stromdichte

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Es wird die Theorie der Transporterscheinungen unter Berücksichtigung des Eigenmagnetfeldes — bei Anwesenheit eines longitudinalen Magnetfeldes — dargestellt. Die für ein LORENTZ-Gas gültigen Formelausdrücke lassen sich auf ein Plasma übertragen.

In Plasmen sehr hoher Stromdichte — neuerdings von verschiedenen Seiten untersucht — gewinnt das Eigenmagnetfeld für die Transporterscheinungen an Einfluß. Darüber hinaus wird zur Führung zylindrischer Entladungen häufig noch ein longitudinales Magnetfeld verwendet.

Im folgenden werden die Transporterscheinungen unter Berücksichtigung derartiger Magnetfelder untersucht. Die Überlegungen beziehen sich vorerst auf ein LORENTZ-Gas. Die Ausdrücke erscheinen daher in geschlossener leicht überschaubarer Form; der Übergang zum Plasma kann im Sinne einer Bemerkung in einer früheren Arbeit leicht bewerkstelligt werden (s. Abschnitt 4).

Für den Fall des Vorhandenseins eines Magnetfeldes hat schon GANS<sup>1</sup> — unter der Voraussetzung starrelastischer Kugeln als Streuzentren — ein Lösungsverfahren entwickelt, das sich jedoch durch einen geeigneten Ansatz (LORENTZ-Ansatz) vereinfachen läßt. Dabei wurde von GANS das Magnetfeld nur in der  $z$ -Richtung betrachtet. Die direkte Übertragung der GANSSchen Methodik durch Einführung einer geschwindigkeitsabhängigen freien Weglänge ermöglichte die Abschätzung des Einflusses des Eigenmagnetfeldes einer Entladung<sup>2</sup>.

Nun ist bekannt, daß sich die Transporterscheinungen in einem LORENTZ-Gas ohne Beschränkung auf starrelastische Kugeln durch die Einführung der geschwindigkeitsabhängigen „Transportquerschnitte“ der Atome und Ionen gegenüber Elektronen exakt erfassen lassen<sup>3,4</sup>. In der vorliegenden Arbeit wird in Erweiterung jener Ergebnisse gezeigt, daß dies auch für ein allgemein angesetztes Magnetfeld der Fall ist. Es werden die Komponenten der Stromdichte und des Wärmestroms einer zylindrischen Entladung vollständig bestimmt.

### 1. Die Lösung der Boltzmann-Gleichung eines Lorentz-Gases mit Magnetfeld für den Fall bestehender Zylindersymmetrie

Die BOLTZMANN-Gleichung eines LORENTZ-Gases mit Magnetfeld § lautet — unter der Voraussetzung der Stationarität — in Zylinderkoordinaten (mit den Komponenten  $H_x$ ,  $H_r$ ,  $H_\varphi$ )

<sup>1</sup> R. GANS, Ann. Phys., Lpz. (IV) 20, 293 [1906].

<sup>2</sup> H. SCHIRMER, Techn.-wiss. Abhandl. d. Osram-Ges. Bd. 7, S. 1, Berlin 1958.

<sup>3</sup> H. SCHIRMER, Z. Phys. 142, 1 [1955].

<sup>4</sup> H. SCHIRMER, Z. Phys. 142, 116 [1955].