A General Formulation for the Evaluation of Two-center Moment Integrals

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The mathematical formulation necessary for the evaluation of two-center integrals for Slater-type orbitals has been presented. The formulation takes into consideration the arbitrary orientation of the two centers and presents a general expression involving the three quantum numbers, the effective charge of each of the two orbitals, the internuclear distance, and the usual A and B integrals. A flow chart for digital computer programming is also presented.

The present development is essentially a variation of the one presented by Kupperman, Karplus, and Isaacson [1] and recently commented by us [2]. However, unlike the one presented by the said authors, the present formulation considers the coincidence of the origin of the coordinates describing the position of the *i*th electron with one of the centers (see Fig. 1). This formulation was *originally* conceived for and is *particularly* useful in calculations involving inorganic complexes where the origin of the coordinate system which determines the molecular symmetry coincides with the central ion's.

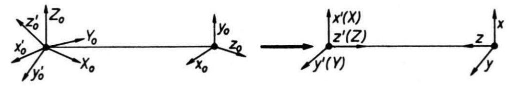

Fig. 1. Unorientied (1 a) and reorientied (1 b) cartesian coordinate systems.

In the present investigation we break down the problem at hand into three separate parts and investigate each in great depth. For simplicity, we deal with only one function on each center, although the extension of this is quite simple. The whole spirit of the paper has been to formulate general expressions useful particularly for those who study the magnetic and optical properties of the transition metal complexes, whether that be in the crystalline or ligand field approximations [3–7]. There is no doubt in our minds that, as it stands, the present formulation will be of great value to the inorganic chemist, and could be extremely useful to the organic chemist.

General Formulation

In the quantum mechanical calculation of the one-electron properties of atomic and molecular systems, one invariably ends up with integrals of the type

$$\langle \psi(R_0' \vartheta_0' \varphi_0') \mid X_{0i}^{\alpha} Y_{0i}^{\beta} Z_{0i}^{\gamma} \mid \psi(R_0 \vartheta_0 \varphi_0) \rangle \tag{1}$$

to evaluate [8].

Now, suppose that one considers the arbitrarily oriented coordinate systems depicted in Fig. 1 a. From purely mathematical considerations, the evaluation of an integral of the above from necessitates the transformation of *all* the coordinate systems into the final positions described in Fig. 1 b. This is, in essence, what we shall throughout this paper refer to as "reorientation". As is well known, the effect of this reorientation of axes is the breakdown of the functions, as well as the coordinates of the *i*th electron, into linear combinations of the bases describing these subspaces.

Therefore, what we shall attempt in this paper is to present a mathematical formulation to consider

(i) The position of the *i*th electron in the transformed coordinate system;

(ii) The effects of the reorientation of the coordinates on both functions;

(iii) The actual evaluation of integrals of the type

$$\langle \psi(R' \vartheta' \varphi') \mid X_i^{\alpha} Y_i^{\beta} Z_i^{\gamma} \mid \psi(R \vartheta \varphi) \rangle \tag{2}$$

which are the cross products emanating from the transformations of the functions in (ii).

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[1] A. Kupperman, M. Karplus, and L. M. Isaacson, Z. Naturforschg. **14 a**, 311 [1959].

[2] W. A. Yeranos and Nicholas W. Winter, Z. Naturforschg., submitted.

[3] C. J. Ballhausen, Ligand Field Theory, McGraw-Hill Book Co. Inc., New York 1962.

[4] C. J. Ballhausen and H. B. Gray, Molecular Orbital Theory, W. A. Benjamin, Inc., New York 1964.

[5] C. K. Jørgensen, Absorption Spectra and Chemical Bonding in Complexes, Addison-Wesley Publishing Co. Inc., Reading, Massachusetts 1962.

[6] J. S. Griffith, The Theory of Transition-Metal Ions, The University Press, Cambridge, Massachusetts 1961.

[7] M. Tinkham, Group Theory and Quantum Mechanics, McGraw-Hill Book Co. Inc., New York 1964.

[8] The functions involved may or may not be on the same center.

It is indeed important to bring to the readers's attention the fact that we have chosen coordinates of different handedness on the two centers. We have done this only because the majority of symmetry orbitals used in molecular orbital calculations of transition metal complexes have been reported within the framework of such a combination of coordinate systems [9]. Furthermore, we have used Synge and Griffith's definition of Eulerian angle transformations, as a consequence of which we have been compelled to use Rose's [11] expressions involving the matrix elements of the finite rotation operators.

1. Redescription of the Coordinates of the *i*-th Electron in the Rotated System

As is well known, one can carry out any transformation from a given cartesian coordinate system to another by means of successive rotations performed in a specific order. As mentioned earlier, we have adopted the sequence given by Synge and Griffith [10], such that the transformation $R(\varphi \vartheta \psi)$ is given by

$$R(\varphi \vartheta \psi) = R_{z'}(\psi)\, R_y(\vartheta)\, R_z(\varphi) \tag{3}$$

and as a consequence of which the coordinates X_{0i}, Y_{0i}, and Z_{0i} describing the position of the *i*-th electron in the unrotated system can be given by the unitary matrix U, such that

$$\begin{bmatrix} Y_{0i} \\ X_{0i} \\ Z_{0i} \end{bmatrix} = \begin{bmatrix} -\sin\varphi \sin\psi + \cos\vartheta \cos\varphi \cos\psi & -\sin\varphi \cos\psi - \cos\vartheta \cos\varphi \sin\psi & \sin\vartheta \cos\varphi \\ \cos\varphi \sin\psi + \cos\vartheta \sin\varphi \cos\psi & \cos\varphi \cos\psi - \cos\vartheta \sin\varphi \sin\psi & \sin\vartheta \sin\varphi \\ -\sin\vartheta \cos\psi & \sin\vartheta \sin\psi & \cos\vartheta \end{bmatrix} \begin{bmatrix} X_i \\ Y_i \\ Zi \end{bmatrix}. \tag{4}$$

Now, if we set $X_i \equiv X_i(1)$, $Y_i \equiv X_i(2)$, and $Z_i \equiv X_i(3)$, we then have the general relationship [12]

$$X_{0i}^{\alpha}\, Y_{0i}^{\beta}\, Z_{0i}^{\gamma} = [\sum_{j=1}^{3} U_{1j}\, X_i(j)\,]^{\alpha} \cdot [\sum_{k=1}^{3} U_{2k}\, X_i(k)\,]^{\beta} \cdot [\sum_{l=1}^{3} U_{3l}\, X_i(l)\,]^{\gamma}. \tag{5}$$

It is important to note that the position of the *i*-th electron is described in a right-handed coordinate system, and the rotations are considered positive if they are of the sense which would advance a right-handed screw in the positive direction along the axis. In fact, this is what we shall call anticlockwise rotation. Note also that the rotations are with respect to the rotated axes and in the $R_z(\varphi)$, $R_y(\vartheta)$, and $R_{z'}(\psi)$ sequence.

2. Redescription of the Functions in the Rotated Systems

As mentioned earlier, the functions $|\,\psi(R_0{}'\,\vartheta_0{}'\,\varphi_0{}') >$ and $|\,\psi(R_0\,\vartheta_0\,\varphi_0) >$ are described in different handed coordinate systems. The former is described in a right-handed coordinate system, and the latter in a left-handed one. The effect of a rotation on any Slater-type real wave function, which is itself a linear combination of several basic functions, can be given by [13]

$$\psi = \sum_m \varphi_m(j)\, \mathrm{C}_m = \Phi(j)\, \boldsymbol{C} \tag{6}$$

$$R(\alpha\beta\gamma)\, \psi = \sum_m C_m\, R(\alpha\beta\gamma)\, \varphi_m^{(j)} = \sum_m C_m \sum_{m'} \varphi_{m'}^{(j)} D_{m'm}^{(j)}(\alpha\beta\gamma) \qquad \text{(7 a) (7 b)}$$

where, following Rose's convention, we have

$$D_{m'm}^{(j)}(\alpha\beta\gamma) = e^{-im'\alpha}\, d_{m'm}^{(j)}(\beta)\, e^{-im\gamma} \qquad \text{(7 c)}$$

and where

$$d_{m'm}^{(j)}(\beta) = \sum_{k=0} \frac{(-1)^k \sqrt{(j+m)!\,(j-m)!\,(j+m')!\,(j-m')!}}{k!\,(j+m-k)!\,(j-m'-k)!\,(k+m'-m)!} \times (\cos\tfrac{1}{2}\beta)^{2j-2k-m'+m} \times (-\sin\tfrac{1}{2}\beta)^{2k+m'-m}. \qquad \text{(7 d)}$$

Note that the summation in Eq. (7 d) ends if any of the bracketed quantities in the denominator becomes negative, since $(-)! \equiv \infty$.

Hence, the final redescription of the wave functions considered can be given by

$$R(\alpha\beta\gamma)\, \psi = \sum_{m'} \varphi_{m'}^{(j)}\, [D^{(j)}(\alpha\beta\gamma)\, \boldsymbol{C}]_{m'} = \Phi^{(j)}\, \boldsymbol{C}' \qquad \text{(7 e)}$$

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[9] If same-handed coordinate systems are wished to be used, the development presented should culminate by $M_2{}' = (-1)^{l+m} M_2$.

[10] J. L. Synge and B. A. Griffith, Principles of Mechanics, McGraw-Hill Book Co. Inc., New York 1959.

[11] M. E. Rose, Elementary Theory of Angular Momentum, John Wiley & Sons, Inc., London 1957.

[12] Each summation may, in turn, be expressed as a binomial expansion.

[13] J. C. Slater, Phys. Rev. **36**, 57 [1930].

where $\boldsymbol{C}$ and $\boldsymbol{C}'$ are the column vectors composed of the coefficients in the linear combinations *before* and *after* the rotation.

It should be brought to the reader's attention that on *both* coordinate systems the sequence of the rotations is the same, mainly

$$R(\alpha \beta \gamma) = R_{z'}(\alpha)\, R_y(\beta)\, R_z(\gamma) \tag{8}$$

with the *important* difference that clockwise rotations in the right-handed coordinate system give positive angles, while in the left-handed coordinate system anticlockwise rotations give positive angles.

Finally, it should be mentioned that for computational purposes, it is best to represent Eq. (7 c) as

$$\begin{aligned} D^{(j)}_{m'm}(\alpha \beta \gamma) &= d^{(j)}_{m'm}(\beta) \cos(m' \alpha + m \gamma) \\ &\quad - i\, d^{(j)}_{m'm}(\beta) \sin(m' \alpha + m \gamma) \end{aligned} \tag{9}$$

since, as shall be seen later, for $m \leqq 0$ we shall have only the real part of Eq. (9), and for $m > 0$, the imaginary. See Ref. [7], page 112, for a worked-out example.

3. Evaluation of Two-Center Moment Integrals

As previously mentioned, any "reorientation" transformation of expression (1) invariably produces cross products of the type

$$\begin{aligned} M(n, l, m, \zeta, n', l', m', \zeta', a, \alpha, \beta, \gamma) &\equiv M_2 \\ &\equiv \langle \psi(R' \vartheta' \varphi') \mid X^\alpha Y^\beta Z^\gamma \mid \psi(R \vartheta \varphi) \rangle \end{aligned} \tag{10}$$

where the index i, specifying the coordinates of the ith electron, has now been dropped [14], and where α, β, and γ are *always* taken positive [15].

In the present section we shall develop a general formulation for the evaluation of integrals of the above type when the functions in question are taken to be *real* normalized SLATER-type orbitals [16]. That is

$$\mid \psi(R \vartheta \varphi) \rangle = \frac{(2\zeta)^{n+1/2}}{[(2n)!]^{1/2}} R^{n-1} e^{-\zeta R} S_{l,m}(\vartheta, \varphi) \tag{11}$$

where the angular part $S_{l,m}(\vartheta, \varphi)$ is defined [17] by

$$S_{l,m}(\vartheta, \varphi) = P_l^{|m|}(\cos \vartheta)\, C_m \frac{e^{im\varphi} + i^{1+|m|/m} e^{-im\varphi}}{2\, i^{(1+|m|/m)/2}}. \tag{12 a}$$

The coefficient C_m in Eq. (12 a) is given by

$$C_m = \pi^{-1/2}[1 - (1 - 2^{-1/2})\, \delta_{m,0}] \tag{12 b}$$

and whereby convention we set $|0|/0 \equiv -1$.

Unfortunately, however, the spherical coordinates are not the "natural" coordinates, so to speak, to be used in the evaluation of two-center integrals. Indeed, a substantial simplification in the algebra is obtained by the introduction of the prolate spherodial coordinates [18] ξ, η, and φ which are expressed by

$$\xi \equiv (R' + R)/2a; \quad \eta \equiv (R' - R)/2a; \quad \varphi \equiv \varphi' \tag{13}$$

and have the limits

$$1 \leqq \xi < +\infty, \quad -1 \leqq \eta \leqq +1, \quad \text{and} \quad 0 \leqq \varphi < 2\pi.$$

Furthermore, by using the above mentioned identities, we are able to obtain the following useful transformation relationship

$$\begin{aligned} R &= a(\xi - \eta), \\ R' &= a(\xi + \eta), \\ \cos \vartheta &= (1 - \xi \eta)/(\xi - \eta), \\ \cos \vartheta' &= (1 + \xi \eta)/(\xi + \eta), \\ d\tau &= a^3 (\xi^2 - \eta^2)\, d\xi\, d\eta\, d\varphi, \\ X &= a(\xi^2 - 1)^{1/2} (1 - \eta^2)^{1/2} \cos \varphi, \\ Y &= a(\xi^2 - 1)^{1/2} (1 - \eta^2)^{1/2} \sin \varphi, \\ Z &= a(1 + \xi \eta) \end{aligned} \tag{14}$$

where the coordinate system X, Y, and Z describing the electron is coincident with that of the atom centered on A as shown in Fig. 2. It should also be noted that, with respect to the relations given by Eq. (14), any SLATER-type orbital defined in the right-handed coordinate system can be expressed as

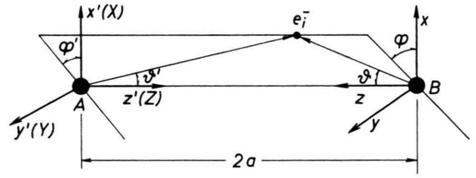

Fig. 2. Reoriented combination of coordinate systems used in the evaluation of the moment integrals formulated in this work. The internuclear distance is in atomic units i. e. the distance in Angstroms divided by 0.529.

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[14] The value of the integral does not depend on it.

[15] Their sum m denotes the order of the moment integral. In the event $\alpha = \beta = \gamma = 0$, then Eq. (10) reduces to a one- or two-center overlap integral.

[16] Complex normalized SLATER-type orbitals can be expressed as a linear combination of real orbitals by means of the DEMOIVRES relationship $e^{\pm im\varphi} = \cos m\varphi \pm i \sin m\varphi$.

[17] $m > 0$ for $\sin m\varphi$, and $m < 0$ for $\cos m\varphi$.

[18] L. PAULING and E. B. WILSON, Introduction to Quantum Mechanics, McGraw-Hill Book Co., Inc., New York 1935, p. 444.

$$|\psi(n'\,l'\,m')\rangle = \frac{(2\,\zeta')^{n'+1/2}}{[(2\,n')\,!]^{1/2}}\, a^{n'-1}(\xi+\eta)^{n'-1}\, e^{-a\zeta'(\xi+\eta)} \times P_{l'}^{|m'|}[(1+\xi)/(\xi+\eta)] \times \left[C_{m'}\, \frac{e^{im'\varphi}+i^{1+|m'|/m'}\, e^{-im'\varphi}}{2\, i^{(1+|m'|/m')/2}}\right] \tag{15 a}$$

and in the left-handed coordinate system as

$$|\psi(n\,l\,m)\rangle = \frac{(2\,\zeta)^{n+1/2}}{[(2\,n)\,!]^{1/2}}\, a^{n-1}(\xi-\eta)^{n-1}\, e^{-a\zeta(\xi-\eta)} \times P_{l}^{|m|}[(1-\xi)/(\xi-\eta)] \times \left[C_{m}\, \frac{e^{im\varphi}+i^{1+|m|/m}\, e^{-im\varphi}}{2\, i^{(1+|m|/m)/2}}\right]. \tag{15 b}$$

Substitution of wave functions of the above form in Eq. (10) and simplification [19] gives *for any two-center moment integral* the general expression [20]

$$M_2 = a^{\alpha+\beta+\gamma}(a\,\zeta)^{n+1/2}(a\,\zeta')^{n'+1/2}\, N\, N'\, M_\varphi \times \sum_{\sigma=n+n'-l-l'}^{2(\alpha+\beta+\gamma)+n+n'+l+l'}{}_{2} \;\; \sum_{\substack{s=\text{greater of}\\ 0 \text{ or } \sigma-(\alpha+\beta+\gamma+n+n')}}^{\substack{\text{smaller of}\\ \sigma \text{ or } \alpha+\beta+\gamma+n+n'}} \lambda_{s,\sigma-s}\cdot A_s[a(\zeta'+\zeta)]\, B_{\sigma-s}[a(\zeta'-\zeta)] \tag{16}$$

$$\text{where}\quad M_\varphi = \pi\, \frac{C_m\, C_{m'}}{2^{\alpha+\beta}} \cdot \frac{1+(-1)^{2\mu}}{2} \cdot \frac{1+(-1)^{\beta-(|m|/m-|m'|/m')/2}}{2\, i^{\beta-(|m|/m-|m'|/m')/2}} \times \sum_{k=0}^{\beta}(-1)^k \binom{\beta}{k}\left[\binom{\alpha}{v-k} + i^{1+|m'|/m'}\binom{\alpha}{\varepsilon-k}\right] \tag{17 a}$$

with μ, v, and ε being given by

$$\mu = (\alpha+\beta+|m|+|m'|)/2, \quad v = (\alpha+\beta-m+m')/2, \quad \text{and} \quad \varepsilon = (\alpha+\beta-m-m')/2 \tag{17 b}$$

and where the factor

$$\frac{1+(-1)^{2\mu}}{2} \cdot \frac{1+(-1)^{\beta-(|m|/m-|m'|/m')/2}}{2\, i^{\beta-(|m|/m-|m'|/m')/2}} \tag{17 c}$$

can have only values of -1, 0, and $+1$.

Furthermore, $\lambda_{s,\,\sigma-s}$ is given by the expression

$$\begin{aligned} \lambda_{s,\sigma-s} = (-1)^{n-l+\mu} & \sum_{\tau=0}^{\mu}\sum_{h=0}^{\mu}\sum_{g=0}^{\gamma}\sum_{j=0}^{\leq(l-|m|)/2}\sum_{j'=0}^{\leq(l'-|m'|)/2}\sum_{p=0}^{n-|m|}\sum_{k=0}^{l-|m|-2j}(-1)^{\tau+h+p+j+j'} \\ & \times \binom{\mu}{\tau}\binom{\mu}{h}\binom{l}{j}\binom{l'}{j'}\binom{\gamma}{g}\binom{2\,l-2\,j}{l-|m|-2\,j}\binom{2\,l'-2\,j'}{l'-|m'|-2\,j'}\binom{n-l+2\,j}{p-k}\binom{l-|m|-2\,j}{k} \\ & \times \binom{n'-l'+2\,j'}{-(\sigma-n-n'+l+l')/2+s-\tau+h-p+j+j'+k}\binom{l'-|m'|-2\,j'}{(\sigma-n-n'+l+l')/2-g-\tau-h-j-j'--k} \end{aligned} \tag{18}$$

and the constant factors N and N' have the general formula

$$N = \left[\frac{2\,l+1}{(2\,n)\,!}\, \frac{\binom{l+|m|}{l}}{\binom{l}{l-|m|}}\right]^{1/2} \times 2^{n-l}. \tag{19}$$

While the auxilliary integrals A and B [21] are given by

$$A\,s[t] = \int_{+1}^{+\infty} \xi^s\, e^{-t\xi}\, d\xi \quad s \geqq 0, \text{ integral; } t>0, \text{ real} \tag{20 a}$$

$$= \frac{e^{-t}}{t} \sum_{k=0}^{s} k!\binom{s}{k} t^{-k} \tag{20 b}$$

and

$$B\,s[t] = \int_{-1}^{+1} \eta^s\, e^{-t\eta}\, d\eta \quad s \geqq 0, \text{ integral; } t, \text{ real} \tag{21 a}$$

$$= 2(-1)^s \sum_{\varrho=0}^{\infty} \frac{t^{2\varrho+\varepsilon}}{(2\,\varrho+\varepsilon)\,!\,(s+2\,\varrho+\varepsilon+1)} \tag{21 b}$$

where $\varepsilon = 1$ if s is odd and $\varepsilon = 0$ if s is even [22].

In Fig. 3 we present a general scheme for coding the above mentioned formulation into computer programs. In it, it will be noticed, we have also included the computation of one-center moment integrals whose development in both schemes, KUPPERMAN et al.'s [1] and ours, is identically the same.

[19] This is done in a similar manner as in KUPPERMAN et al. [1] and, consequently, shall not be repeated here.

[20] The summation over σ is carried in steps of two.

[21] M. KOTANI, A. AMERNIYA, E. IOHIGURO, and N. KIMURA, Table of Molecular Integrals, Mauizen Co., Ltd., Tokyo 1955, p. 34.

[22] The factorial $(2\,\varrho+\varepsilon)\,!$ in the denominator of Eq. (21 b) restricts the upper limit of ϱ in any computer program. We have found it sufficient, but not necessary, to set $\varrho=10$ in our calculations, since the values of integrals, taking $\varrho=10$ and $\varrho=11$, were calculated without any change in the 8 decimal range of our computer (IBM 1620 Mark II).

Acknowledgement

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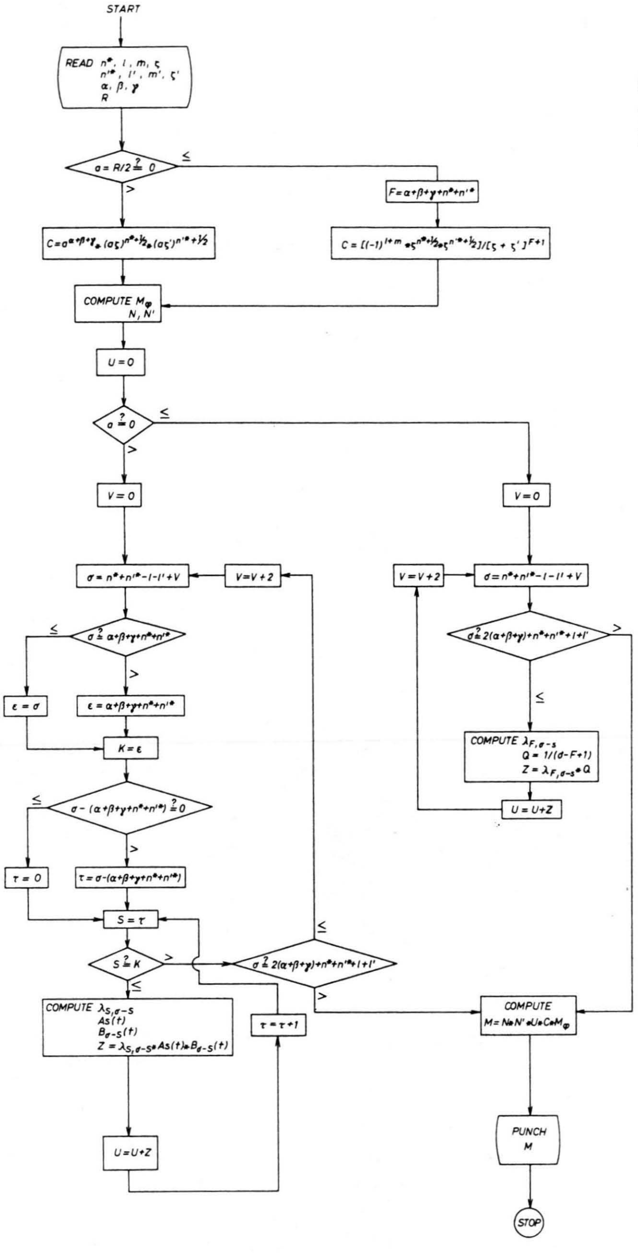

Fig. 3. The FORTRAN Program ($\zeta n'^{*}+{}^{1}/_{2}$ in C should actually read $\zeta'\, n'^{*}+{}^{1}/_{2}$).