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Reduced form for Coulomb-wave multicenter integrals

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In a previous paper [J. C. Straton, Phys. Rev. A **41**, 71 (1990)] an integro-differential transform was introduced and utilized to obtain the analytically reduced form for multicenter integrals composed of general-state hydrogenic orbitals, Yukawa or Coulomb potentials, and plane waves. The present paper extends this result to include Coulomb waves.

I. INTRODUCTION

Theories within atomic and molecular physics generally lead to multicenter integrals containing products of hydrogenic orbitals, Yukawa or Coulomb potentials, plane waves, and Coulomb waves. In a series of papers¹⁻⁵ the author has developed the analytically reduced form for the general case that excludes Coulomb

waves. The present paper removes this exclusion. Equations from Refs. 4 and 5 will be referred to by suffixing "I" and "II," respectively, to the equation numbers.

II. THE INCLUSION OF COULOMB WAVES

The general multicenter integral to be reduced is

$$S_{I_1 J_1 \dots I_M J_M}^{\eta_1 j_1 \dots \eta_M j_M}(\mathbf{p}_1, \dots, \mathbf{p}_M; \mathbf{y}_1, \dots, \mathbf{y}_M; \nu_K, \mathbf{Q}_K, \dots, \nu_M, \mathbf{Q}_M) \\ = \int d^3 x_1 \dots d^3 x_m e^{-i(\mathbf{p}_1 \cdot \mathbf{x}_1 + \dots + \mathbf{p}_m \cdot \mathbf{x}_m)} P_{I_1 J_1}^{\eta_1 j_1}(\mathbf{R}_1) \dots P_{I_{K-1} J_{K-1}}^{\eta_{K-1} j_{K-1}}(\mathbf{R}_{K-1}) \bar{P}_{I_K J_K}^{\eta_K j_K}(\mathbf{R}_K, \nu_K, \mathbf{Q}_K) \\ \times \dots \bar{P}_{I_M J_M}^{\eta_M j_M}(\mathbf{R}_M, \nu_M, \mathbf{Q}_M) \quad (1)$$

where

$$P_{IJ}^{\eta j}(\mathbf{R}) = u_I(\mathbf{R}) \dots u_J(\mathbf{R}) V^{\eta j}(\mathbf{R}) \quad (2)$$

and

$$\bar{P}_{IJ}^{\eta j}(\mathbf{R}, \nu, \mathbf{Q}) = P_{IJ}^{\eta j}(\mathbf{R}) {}_1F_1(i\nu, 1, i(QR + \mathbf{Q} \cdot \mathbf{R})) \quad (3)$$

in which the u 's are hydrogenic orbitals [(14-II)-(16-II)],

$$V^{\eta j}(\mathbf{R}) = R^{j-1} e^{-\eta R}, \quad (4)$$

and

$$\mathbf{R}_i = \sum_{j=1}^m t_{ij} \mathbf{x}_j + \sum_{j=1}^M u_{ij} \mathbf{y}_j. \quad (5)$$

For each confluent hypergeometric function, introduce the real-contoured integral transform⁶

$${}_1F_1(a, b, z) = \frac{1}{B(a, b-a)} \int_0^1 e^{z\tau} \tau^{a-1} (1-\tau)^{b-a-1} d\tau, \quad (6)$$

which is more amenable to numerical integration than the more commonly used⁷⁻⁹ complex-contoured transform (containing an identical integrand). It will be shown in Sec. III that the former choice gives the same result as the latter.

The final reduced form of the Coulomb-wave integral is

$$S_{I_1 J_1 \dots I_M J_M}^{\eta_1 j_1 \dots \eta_M j_M}(\mathbf{p}_1, \dots, \mathbf{p}_M; \mathbf{y}_1, \dots, \mathbf{y}_M; \nu_K, \mathbf{Q}_K, \dots, \nu_M, \mathbf{Q}_M) \\ = \pi^{3m/2} \int_0^\infty d\rho_1 \dots d\rho_M \int_0^1 d\tau_K \tau^{\nu_K-1} (1-\tau)^{-i\nu_K} \\ \times \dots \int_0^1 d\tau_M \tau^{\nu_M-1} (1-\tau)^{-i\nu_M} A_{I_1 J_1}^{\eta_1 j_1}(\rho_1, \mathbf{q}_1) \dots A_{I_{K-1} J_{K-1}}^{\eta_{K-1} j_{K-1}}(\rho_{K-1}, \mathbf{q}_{K-1}) \\ \times \frac{A_{I_K J_K}^{\eta_K j_K}(\rho_K, \mathbf{q}_K) \prod_{j'=1}^M e^{i u_{Kj'} \tau_K \mathbf{Q}_K \cdot \mathbf{y}_{j'}}}{B(i\nu_K, 1 - i\nu_K)} \\ \times \dots \frac{A_{I_M J_M}^{\eta_M j_M}(\rho_M, \mathbf{q}_M) \prod_{j'=1}^M e^{i u_{Mj'} \tau_M \mathbf{Q}_M \cdot \mathbf{y}_{j'}}}{B(i\nu_M, 1 - i\nu_M)} \frac{e^{-\Omega/\Lambda}}{\Lambda^{3/2}}. \quad (7)$$

The A 's are given by [(24-II)-(29-II)],

$$\begin{aligned}
 A_{IJ}^{\eta j}[\rho, i\mathbf{q}] = & \frac{e^{-\gamma^2/4\rho}}{2^j \sqrt{\pi}} \left(\sum_{s_I=0}^{n_I-\ell_I-1} \frac{(-1)^{s_I} (\lambda_I/n_I)^{s_I+\ell_I} \lambda_I^{3/2} N_{n_I \ell_I}}{(n_I - \ell_I - 1 - s_I)!(2\ell_I + 1 + s_I)!s_I!} \right. \\
 & \times \cdots \times \sum_{s_J=0}^{n_J-\ell_J-1} \frac{(-1)^{s_J} (\lambda_J/n_J)^{s_J+\ell_J} \lambda_J^{3/2} N_{n_J \ell_J}}{(n_J - \ell_J - 1 - s_J)!(2\ell_J + 1 + s_J)!s_J!} \Big) \\
 & \times \sum_{L_1=L_1 \min}^{L_1 \max} (2) (-1)^{M_{I+1}} \left(\frac{(2\ell_I + 1)(2\ell_{I+1} + 1)(2L_1 + 1)}{4\pi} \right)^{1/2} \begin{pmatrix} \ell_I & \ell_{I+1} & L_1 \\ 0 & 0 & 0 \end{pmatrix} \\
 & \times \begin{pmatrix} \ell_I & \ell_{I+1} & L_1 \\ m_I & m_{I+1} & -M_{I+1} \end{pmatrix} \\
 & \times \sum_{L_2=L_2 \min}^{L_2 \max} (2) (-1)^{M_{I+2}} \left(\frac{(2L_1 + 1)(2\ell_{I+2} + 1)(2L_2 + 1)}{4\pi} \right)^{1/2} \\
 & \times \begin{pmatrix} L_1 & \ell_{I+2} & L_2 \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} L_1 & \ell_{I+2} & L_2 \\ M_I & m_{I+2} & -M_{I+2} \end{pmatrix} \\
 & \times \cdots \times \sum_{L_J=L_J \min}^{L_J \max} (2) (-1)^{M_J} \left(\frac{(2L_{J-1} + 1)(2\ell_J + 1)(2L_J + 1)}{4\pi} \right)^{1/2} \\
 & \times \begin{pmatrix} L_{J-1} & \ell_J & L_J \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} L_{J-1} & \ell_J & L_J \\ M_{J-1} & m_J & -M_J \end{pmatrix} \\
 & \times \left(\frac{2^{L_J} H_{s_I+\ell_I+\cdots+s_J+\ell_J-L_J+j}(\gamma/2\sqrt{\rho})}{\rho^{(s_I+\ell_I+\cdots+s_J+\ell_J-L_J+1+j)/2}} \mathcal{Y}_{L_J M_J}(i\mathbf{q}) \right), \tag{8}
 \end{aligned}$$

where

$$M_j = m_I + m_{I+1} + \cdots + m_j, \tag{9}$$

$$L_j \max = L_{j-1} + \ell_j, \tag{10}$$

$$\mu_j = \max(|L_{j-1} - \ell_j|, |M_{j-1} + m_j|), \tag{11}$$

and

$$L_j \min = \begin{cases} \mu_j & \text{if } L_j \max + \mu_j \text{ is even} \\ \mu_j + 1 & \text{if } L_j \max + \mu_j \text{ is odd,} \end{cases} \tag{12}$$

and where the index "(2)" on the summation sign indicates that one is to sum in steps of 2.

To account for the Coulomb waves (30-II) must be modified to read

$$\begin{aligned}
 \gamma_j = & \lambda_{I_j}/n_{I_j} + \cdots + \lambda_{J_j}/n_{J_j} + \eta_j \\
 & + \begin{cases} 0, & j < K \\ -iQ_j \tau_j, & j \geq K. \end{cases} \tag{13}
 \end{aligned}$$

As in (36-II) and (34-II)

$$\Lambda = \begin{vmatrix} a_{11} & a_{12} & \cdots & a_{1m} \\ a_{21} & a_{22} & & a_{2m} \\ \vdots & & \ddots & \vdots \\ a_{m1} & a_{m2} & \cdots & a_{mm} \end{vmatrix}, \tag{14}$$

where

$$a_{ij} = \sum_{k=1}^M \rho_k t_{ki} t_{kj}. \tag{15}$$

From (38-II), (35-II), and (42-II)

$$\Omega = C\Lambda + \sum_{i=j}^m \sum_{j=1}^m \mathbf{b}_i \cdot \mathbf{b}_j (-1)^{i+j+1} \Lambda_{ij}, \tag{16}$$

where Λ_{ij} is Λ with the i th row and j th column deleted,

$$C = \sum_{k=1}^M \sum_{j=1}^M \sum_{j'=1}^M \rho_k u_{kj} u_{kj'} \mathbf{y}_j \cdot \mathbf{y}_{j'}, \tag{17}$$

and

$$\mathbf{q}_i = \frac{1}{\Lambda} \sum_{i'=1}^m \sum_{j'=1}^m (-1)^{i'+j'+1} \Lambda_{i'j'} t_{ii'} \mathbf{b}_{i'}, \tag{18}$$

in which the only modification for Coulomb waves is (33-II)

$$\mathbf{b}_{i'} = \frac{i\mathbf{p}_{i'}}{2} + \sum_{k=1}^M \rho_k t_{ki'} \sum_{j=1}^M u_{kj} \mathbf{y}_j - \frac{i}{2} \sum_{j=K}^M t_{ji'} Q_j \tau_j. \tag{19}$$

Finally, if the K th P in (1) contains two ${}_1F_1$ functions, depending on parameters $\nu, \mathbf{Q}$ and $\nu', \mathbf{Q}'$, one must insert

$$\int_0^1 d\tau'_K \frac{\tau'^{i\nu'_K-1}(1-\tau')^{-i\nu'_K}}{B(i\nu'_K, 1-i\nu'_K)} \quad (20)$$

in (7), set $\tau_K \mathbf{Q}_K \rightarrow \tau_K \mathbf{Q}_K + \tau'_K \mathbf{Q}'_K$ in the exponential

$$S^{\eta j}(\mathbf{p}; 0; \nu, \mathbf{Q}, \nu', \mathbf{Q}') = \int d^3x e^{-i\mathbf{p} \cdot \mathbf{x}} x^{j-1} e^{-\eta x} {}_1F_1[i\nu, 1, i(\mathbf{Q}x + \mathbf{Q} \cdot \mathbf{x})] {}_1F_1(i\nu', 1, i(\mathbf{Q}'x + \mathbf{Q}' \cdot \mathbf{x})) . \quad (21)$$

In this spherically symmetric case

$$A^{\gamma j}(\rho, \mathbf{q}) = \frac{e^{-\gamma^2/4\rho}}{2j\sqrt{\pi}} \frac{H_j(\gamma/2\sqrt{\rho})}{\rho^{(1+j)/2}} , \quad (22)$$

where

$$\gamma = \eta - i\tau\mathbf{Q} - i\tau'\mathbf{Q}' . \quad (23)$$

Also

$$\Lambda = \rho, \quad \Lambda_{11} \equiv 1 , \quad (24)$$

$$C = 0 , \quad (25)$$

and

$$\mathbf{b} = \frac{i}{2} (\mathbf{p} - \mathbf{Q}\tau - \mathbf{Q}'\tau') , \quad (26)$$

so that

$$\Omega = \frac{1}{4} (p^2 - 2\tau\mathbf{p} \cdot \mathbf{Q} - 2\tau'\mathbf{p} \cdot \mathbf{Q}' + Q^2\tau^2 + 2\tau\tau'\mathbf{Q} \cdot \mathbf{Q}' + Q'^2\tau'^2) . \quad (27)$$

For $j = 0$ the ρ integral gives

$$\begin{aligned} S^{\eta 0}(\mathbf{p}; 0; \nu, \mathbf{Q}, \nu', \mathbf{Q}') &= \frac{4\pi}{B(i\nu, 1-i\nu) B(i\nu', 1-i\nu')} \\ &\times \int_0^1 d\tau \tau^{i\nu-1} (1-\tau)^{-i\nu} \\ &\times \int_0^1 d\tau' \frac{\tau'^{i\nu'-1} (1-\tau')^{-i\nu'}}{(\gamma^2 + \Omega)} . \end{aligned} \quad (28)$$

The denominator is

$$\gamma^2 + \Omega = D + F\tau , \quad (29)$$

of (7), and in (19), and set $Q_K \tau_K \rightarrow Q_K \tau_K + Q'_K \tau'_K$ in (13).

III. EXAMPLES

Consider the integral

where

$$D = \eta^2 + p^2 + 2(-\mathbf{Q}' \cdot \mathbf{p} - i\eta\mathbf{Q}')\tau' \equiv 2\alpha + 2\beta\tau' \quad (30)$$

and

$$\begin{aligned} F &= -2(\mathbf{Q} \cdot \mathbf{p} + i\eta\mathbf{Q}) - 2(Q\mathbf{Q}' - \mathbf{Q} \cdot \mathbf{Q}')\tau' \\ &\equiv -2g - 2d\tau' . \end{aligned} \quad (31)$$

Then the τ integral gives¹⁰

$$\begin{aligned} S^{\eta 0}(\mathbf{p}; 0; \nu, \mathbf{Q}, \nu', \mathbf{Q}') &= \frac{4\pi}{B(i\nu, 1-i\nu')} \int_0^1 d\tau' \frac{\tau'^{i\nu'-1} (1-\tau')^{-i\nu'}}{(F+D)^{i\nu'} D^{1-i\nu'}} . \end{aligned} \quad (32)$$

Note that if $\nu = 0$, the τ' integral gives

$$S^{\eta 0}(\mathbf{p}; 0; 0, \mathbf{Q}, \nu', \mathbf{Q}') = \frac{4\pi}{(2\beta + 2\alpha)^{i\nu'} (2\alpha)^{1-i\nu'}} , \quad (33)$$

which is the known result¹¹ since ${}_1F_1(0, b, z) \equiv 1$.

For the general case define

$$\gamma = g - \alpha, \quad \delta = d - \beta . \quad (34)$$

Then

$$D = 2\alpha \left(1 + \frac{\beta}{\alpha} \tau' \right) \equiv 2\alpha(1 - b\tau') \quad (35)$$

and

$$F + D = -2\gamma \left(1 + \frac{\delta}{\gamma} \tau' \right) \equiv -2\gamma(1 - a\tau') . \quad (36)$$

Changing variables to

$$t = \tau' \left(\frac{1-a}{1-a\tau'} \right) , \quad (37)$$

$$\begin{aligned} S^{\eta 0}(\mathbf{p}; 0; \nu, \mathbf{Q}, \nu', \mathbf{Q}') &= \frac{4\pi(2\alpha)^{i\nu-1}(-2\gamma)^{-i\nu}}{B(i\nu', 1-i\nu')} (1-a)^{1-i\nu'-i\nu+i\nu-1} \\ &\times \int_0^1 dt t^{-2+i\nu'+1} (1-t)^{-i\nu'} (1-zt)^{i\nu-1} (1-a+at)^{-i\nu'-1+i\nu'+i\nu-i\nu+1} , \end{aligned} \quad (38)$$

where

$$z = \frac{b-a}{1-a} = \frac{\alpha\delta - \beta\gamma}{\alpha(\gamma + \delta)} . \quad (39)$$

The t integral may be evaluated¹² giving

$$S^{\eta 0}(\mathbf{p}; 0; \nu, \mathbf{Q}, \nu', \mathbf{Q}') = \frac{2\pi}{\alpha} e^{-\pi\nu} \left(\frac{\alpha}{\gamma}\right)^{i\nu} \left(\frac{\gamma + \delta}{\gamma}\right)^{-i\nu'} F(1 - i\nu, i\nu', 1, z), \quad (40)$$

where the factor $e^{-\pi\nu}$ arises from the identification $(1/-1)^{i\nu} = (-1/(-1)^2)^{i\nu} = (e^{i\pi}/1)^{i\nu}$. This is Nordsieck's result⁷ if one sets $\mathbf{Q} \rightarrow -\mathbf{p}_1$, $\mathbf{Q}' \rightarrow \mathbf{p}_2$, $\mathbf{p} \rightarrow -\mathbf{q}$, $\nu \rightarrow a_1$, $\nu' \rightarrow a_2$, and $\eta \rightarrow \lambda$.

Note that the limits of (33) and (40) are well defined for $\eta \rightarrow 0$ when factors of $(-1)^{i\nu}$ are properly accounted for.⁸ Thus the Gaussian transform¹³ leading to (8) is well defined in the limit $\text{Re}\gamma \rightarrow 0$ for integrals of this type.

IV. CONCLUSION

The analytically reduced form has been found for the general multicenter integral of products of hydrogenic orbitals, Yukawa or Coulomb potentials, plane waves, and Coulomb waves. It has been shown that the introduction of a real-contoured integral transform for the confluent hypergeometric function, which is more amenable to numerical evaluation than the more common complex-

contoured integral transform, gives the known analytical result for Nordsieck's integrals.

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¹J.C. Straton, Phys. Rev. A **35**, 2729 (1987); **37**, 4531 (1988).

²J.C. Straton, Phys. Rev. A **39**, 5062 (1989).

³J.C. Straton, Phys. Rev. A **39**, 5071 (1989).

⁴J.C. Straton, Phys. Rev. A **39**, 1676 (1989); **40**, 2819 (1989).

⁵J.C. Straton, Phys. Rev. A **41**, 71 (1990).

⁶*Handbook of Mathematical Functions with Formulas, Graphs, and Mathematical Tables*, Natl. Bur. Stand. Appl. Math. Ser. No. 55, edited by M. Abramowitz and I.A. Stegun (U.S. GPO, Washington, D.C., 1972), p. 505, No. 13.2.1.

⁷A. Nordsieck, Phys. Rev. **93**, 785 (1954).

⁸M.R.C. McDowell and J.P. Coleman, *Introduction to the Theory of Ion-Atom Collisions* (North-Holland, Amsterdam, 1970), pp. 364-370.

⁹M. Brauner, J.S. Briggs, and H. Klar, J. Phys. B **22**, 2265

(1989).

¹⁰I.S. Gradshteyn and I.M. Ryzhik, *Table of Integrals, Series, and Products* (Academic, New York, 1980), p. 287, No. 3.198; or W. Grobner and N. Hofreiter, *Integraltafel Zweiter Teil Bestimmte Integrale* (Springer-Verlag, Berlin, 1961), p. 175, No. 421.4.

¹¹J.P. Coleman, in *Case Studies in Atomic Collision Physics*, edited by M.R.C. McDowell and E.W. McDaniel (North-Holland, Amsterdam, 1969), Vol. 1, pp. 161-163.

¹²I.S. Gradshteyn and I.M. Ryzhik, *Table of Integrals, Series, and Products* (Academic, New York, 1980), p. 1040, No. 9.111.

¹³I.S. Gradshteyn and I.M. Ryzhik, *Table of Integrals, Series, and Products* (Academic, New York, 1980), p. 340, No. 3, 471(9); or derivatives with respect to b of W. Grobner and N. Hofreiter, *Integraltafel Zweiter Teil Bestimmte Integrale* (Springer-Verlag, Berlin, 1961), p. 66, No. 9c.