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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 papers\(^1-5\) 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

\[
S_{I_1J_1\cdots I_MJ_M}^{n_1j_1\cdots n_Mj_M}(p_1, \ldots, p_m; y_1, \ldots, y_M; \nu_K, Q_K, \ldots, \nu_M, Q_M) = \int d^3x_1 \cdots d^3x_m e^{-i(p_1 \cdot x_1 + \cdots + p_m \cdot x_m)} P_{I_1J_1}^{n_1j_1}(R_1) \cdots P_{I_KJ_K}^{n_Kj_K}(R_K) \frac{1}{B(i\nu_K, 1 - i\nu_K)} A_{I_KJ_K}^{n_Kj_K}(\rho_K, Q_K) \prod_{j=1}^M \frac{e^{i\nu_M, x_j} - e^{-\pi j/\Lambda}}{B(i\nu_M, 1 - i\nu_M)}
\]

where

\[
P_{I_1J_1}^{n_1j_1}(R) = u_I(R) \cdots u_J(R) \sqrt{v_{n_1j_1}(R)}
\]

and

\[
P_{I_1J_1}^{n_1j_1}(R, \nu, Q) = P_{I_1J_1}^{n_1j_1}(R) F_I(i\nu, 1, i(QR + Q \cdot R))
\]

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

\[
V_{n_1j_1}(R) = \frac{1}{R} e^{-\nu R}
\]

and

\[
R_i = \sum_{j=1}^m t_{ij} x_j + \sum_{j=1}^M u_{ij} y_j
\]

For each confluent hypergeometric function, introduce the real-contoured integral transform\(^6\)

\[
F_1(a, b, z) = \frac{1}{B(a, b - a)} \int_0^1 e^{(a - 1)(1 - \tau)b - a - 1} d\tau
\]

which is more amenable to numerical integration than the more commonly used\(^7-9\) 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

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.
The \( A \)'s are given by [(24-II)--(29-II)],
\[
A_{ij}^{pq}[\rho, iq] = \frac{e^{-\gamma^2/4\rho}}{2i\sqrt{\pi}} \left( \sum_{s_j=0}^{n_j-\ell_j-1} \frac{(-1)^s_j (\lambda_j/n_j)^{s_j+\ell_j} \lambda_j^{3/2} N_{n_j} \ell_j}{(n_j - \ell_j - 1 - s_j)(2\ell_j + 1 + s_j)!s_j!} \right)
\times \cdots \times \sum_{s_j=0}^{n_j-\ell_j-1} \frac{(-1)^s_j (\lambda_j/n_j)^{s_j+\ell_j} \lambda_j^{3/2} N_{n_j} \ell_j}{(n_j - \ell_j - 1 - s_j)(2\ell_j + 1 + s_j)!s_j!}
\times \frac{L_1_{\max}}{L_1_{\min}} \sum_{\ell_1=\ell_1_{\min}}^{L_1_{\max}} \frac{(2\ell_1 + 1)(2\ell_{I+1} + 1)(2L_1 + 1)}{4\pi} \left( \ell_1 \ell_{I+1} L_1 \right) \left( \ell_{I+1} \ell_{I+2} L_1 \right)
\times \cdots \times \frac{L_3_{\max}}{L_3_{\min}} \sum_{\ell_3=\ell_3_{\min}}^{L_3_{\max}} \frac{(2\ell_3 + 1)(2\ell_{I+2} + 1)(2L_2 + 1)}{4\pi} \left( \ell_3 \ell_{I+2} L_2 \right) \left( \ell_{I+2} \ell_{I+3} L_2 \right)
\times \cdots \times \frac{L_{J_{\max}}}{L_{J_{\min}} \sum_{\ell_{J=\ell_{J_{\min}}}^{J_{\max}}}} \frac{(2\ell_{J-1} + 1)(2\ell_{J} + 1)(2L_{J} + 1)}{4\pi} \left( \ell_{J-1} \ell_{J} L_{J-1} \right) \left( \ell_{J} \ell_{J+1} L_{J} \right)
\times \cdots \times \left( \frac{\gamma_j}{\rho(s_j+\ell_j+\cdots+s_j+\ell_j-L_{J-1}+1)}/2 \right) \mathbf{y}_{L_j,M_j}(iq),
\]

where
\[
M_j = m_I + m_{I+1} + \cdots + m_j,
\]
\[
L_j_{\max} = L_{j-1} + \ell_j,
\]
\[
\mu_j = \max(|L_{j-1} - \ell_j|, |M_{j-1} + m_j|),
\]
and
\[
L_j_{\min} = \begin{cases} 
\mu_j & \text{if } L_j_{\max} + \mu_j \text{ is even} \\
\mu_j + 1 & \text{if } L_j_{\max} + \mu_j \text{ is odd},
\end{cases}
\]
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
\[
\gamma_j = \lambda_j/n_j + \cdots + \lambda_j/n_j + \eta_j + \begin{cases} 
0, & j < K \\
-iQ_j\gamma_j, & j \geq K.
\end{cases}
\]
As in (36-II) and (34-II)
\[
\Lambda = \begin{bmatrix}
a_{11} & a_{12} & \cdots & a_{1m} \\
a_{21} & a_{22} & \cdots & a_{2m} \\
\vdots & \vdots & \ddots & \vdots \\
a_{m1} & a_{m2} & \cdots & a_{mm}
\end{bmatrix},
\]

where
\[
a_{ij} = \sum_{k=1}^{M} \rho_k t_{ki} t_{kj}.
\]
From (38-II), (35-II), and (42-II)
\[
\Omega = C\Lambda + \sum_{i=j}^{m} b_i \cdot b_j (-1)^{i+j+1} \Lambda_{ij},
\]
where \( \Lambda_{ij} \) is \( \Lambda \) with the \( i \)th row and \( j \)th column deleted,
\[
C = \sum_{k=1}^{M} \sum_{j=1}^{M} \sum_{j'=1}^{M} \rho_k u_{kj} u_{kj'} y_j \cdot y_j',
\]
and
\[
q_k = \frac{1}{\Lambda} \sum_{i'=1}^{m} (-1)^{i'+j'} \Lambda_{ij} t_{i'i} b_{i'},
\]
in which the only modification for Coulomb waves is (33-II)
\[
b_{i'} = \frac{ip_{i'}}{2} + \sum_{k=1}^{M} \sum_{j=1}^{M} u_{kj} y_j - \frac{i}{2} \sum_{j=K}^{M} t_{j'} Q_j \gamma_j.
\]
Finally, if the $K$th $P$ in (1) contains two $F_1$ functions, depending on parameters $\nu, Q$ and $\nu', Q'$, one must insert
\[
\int_0^1 d\tau_K \frac{\sin^{\nu'-1}(1-\tau')^{1-\nu} K}{B(\nu', K - 1)}
\]
in (7), set $\tau_K Q_K \rightarrow Q_K + \tau'_K Q'_K$ in the exponential of (7), and in (19), and set $Q_K \tau_K \rightarrow Q_K + \tau'_K Q'_K$ in (13).

### III. EXAMPLES

Consider the integral
\[
S^{ij}(p; 0; \nu, Q, \nu', Q') = \int d^3 x e^{-i\nu x} e^{i\nu' x} F_1[i(\nu Q + Q \cdot x), 1, i(Q' + Q' \cdot x)]
\]

In this spherically symmetric case
\[
A^{ij}(\rho, q) = \frac{e^{-\gamma/4\rho}}{2\sqrt{\pi}} H_j(\gamma/2\sqrt{\rho}) \rho^{(1+j)/2},
\]
where
\[
\gamma = n - i \nu Q - i \nu' Q'.
\]

Also
\[
\Lambda = \rho, \quad \Lambda_1 \equiv 1,
\]
\[
C = 0,
\]
and
\[
b = \frac{i}{2} (p - Qr - Q'r'),
\]
so that
\[
\Omega = \frac{1}{4} (p^2 - 2\nu p \cdot Q - 2\nu' p \cdot Q' + Q^2 \tau^2 + 2\tau \nu Q \cdot Q' + Q'^2 \tau'^2).
\]

For $j = 0$ the $\rho$ integral gives
\[
S^{ij}(p; 0; \nu, Q, \nu', Q') = \frac{4\pi}{B(\nu, 1 - i\nu')} \int d\tau \frac{\tau^{\nu'-1}(1-\tau')^{1-\nu'}}{1 + \frac{\nu}{\nu'}}
\]
The denominator is
\[
\gamma^2 + \Omega = D + F\tau,
\]
and
\[
S^{ij}(p; 0; \nu, Q, \nu', Q') = \frac{4\pi(2\tau)^{\nu'-1}(1-2\gamma)^{1-\nu'}}{B(\nu', 1 - i\nu')} (1 - a)^{1-\nu' - i\nu + i\nu - 1}
\]
\[
\times \int_0^1 dt t^{2+i\nu' + 1}(1-t)^{-\nu'} (1 - z)^{-1}(1-a + at)^{-i\nu' + i\nu + i\nu + 1},
\]
where
\[
z = \frac{b - a}{1 - a} = \frac{\alpha \delta - \beta \gamma}{\alpha(\gamma + \delta)}.
\]
The $t$ integral may be evaluated\textsuperscript{12} giving

$$S_{\eta}^{0}(p; 0; \nu, Q, \nu', Q') = \frac{2\pi}{\alpha} \int d\gamma \frac{\gamma}{\gamma} \left( \frac{\gamma + \delta}{\gamma} \right)^{-i\nu'} F(1 - i\nu, i\nu', 1, 2),$$

(40)

where the factor $e^{-x\nu}$ arises from the identification $(1/1)^{i\nu} = (-1/1)^{2i\nu} = (e^{i\pi}/1)^{i\nu}$. This is Nordsieck's result\textsuperscript{7} if one sets $Q \rightarrow -p_{1}$, $Q' \rightarrow -p_{2}$, $p \rightarrow -q$, $\nu \rightarrow a_{1}$, $\nu' \rightarrow a_{2}$, 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.\textsuperscript{8} Thus the Gaussian transform\textsuperscript{13} 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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