

Reduced form for the general-state multicenter integral from an integro-differential transform

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In a previous paper Gaussian transforms were utilized to obtain the analytically reduced form for the class of multicenter integrals containing a product of hydrogenic orbitals for s -states, Yukawa or Coulomb potentials, and plane waves. In the present paper a related transformation is developed for nonspherical functions, leading to the reduced form for multicenter integrals that include hydrogenic orbitals representing states of arbitrary angular momentum.

I. INTRODUCTION

A central impediment to the evaluation of the merits of theories in atomic and molecular physics is the task of reducing the dimensionality of the multicenter integrals of a particular theory to a numerically tractable number. Direct spatial integration is not possible in general because the angular dependence in the coordinate-space functions appears sequestered in various square roots of quadratic forms. Researchers have commonly circumvented this problem by following the same general path.

(a) Introduce Fourier (three-dimensional integral) transforms¹ for each of the terms in the product of orbitals and potentials. After evaluating the original (coordinate) integrals, and using the resulting δ functions to evaluate one or more of the (introduced) momentum integrals, all of the angular dependence resides in simple quadratic forms in exponentials and in denominators.

(b) Feynman (one-dimensional integral) transforms² are then introduced for each term in the product of denominators to produce a quadratic form in a single denominator.

(c) One then completes the square in the denominator for each of the momentum integrals in turn, adjusting the exponentials accordingly, allowing that integral to be evaluated.

The author has attempted to make this generality of path explicit by carrying out these steps for a general multicenter integral. The Fourier transform has been found³ for a single-center product of hydrogenic orbitals representing arbitrary states and for a multicenter product of $1s$ orbitals and Coulomb or Yukawa potentials.⁴ For the latter, the iterative step c, was replaced by two steps.

(c') An additional one-dimensional integral transform was introduced to move the Feynman denominator into an exponential so that all momentum dependence was contained within a single quadratic form.

(d) Finally, a unitary operator,⁵ that does not need

to be explicitly found, was invoked to simultaneously diagonalize all momentum integrals so that they could be evaluated.

This approach was then used to find the reduced form for a multicenter integral (in any number of coordinates) of a product of $1s$ hydrogenic orbitals, Coulomb or Yukawa potentials, and plane waves.⁶

But a fundamental limitation of the Fourier transform prevents the development of a "final reduced form," one free of derivatives to be evaluated, for multicenter integrals involving excited states, even those with $\ell=0$. Consider the Fourier integral representation⁷ of the $2s$ hydrogenic orbital,

$$u_{2s}^\lambda(\mathbf{R}) = \left(\frac{\lambda}{\pi}\right)^{5/2} \frac{1}{2^{3/2}} \int \frac{d^3k e^{i\mathbf{k}\cdot\mathbf{R}} (k^2 - \lambda^2/4)}{\left(\frac{\lambda^2}{4} + k^2\right)^3}, \quad (1)$$

where

$$\lambda = \frac{Z}{a_0}. \quad (2)$$

The polynomial in k^2 that appears in the numerator, which is typical of excited states, prevents one from using the above methods unless (1) is rewritten using a polynomial of derivatives. Setting $\gamma = \lambda/2$,

$$u_{2s}^\lambda(\mathbf{R}) = \frac{\lambda^{3/2}}{2^{3/2}\sqrt{\pi}} \left(1 + \gamma \frac{\partial}{\partial \gamma}\right) e^{-\gamma R}, \quad (3)$$

which leads to

$$u_{2s}^\lambda(\mathbf{R}) = \left(\frac{\lambda}{\pi}\right)^{5/2} \frac{1}{2^{3/2}} \left(1 + \gamma \frac{\partial}{\partial \gamma}\right) \int d^3k \frac{e^{i\mathbf{k}\cdot\mathbf{R}}}{(\gamma^2 + k^2)^2} \quad (4)$$

One may then apply the general techniques outlined above, but the resulting expression contains derivatives of complicated functions left for the user to evaluate for his or her particular multicenter integral. Such an expression

cannot be considered to be in "final form" in the sense that a result free of derivatives to be evaluated is final.

Fortunately, in a previous paper⁸ it was shown that Gaussian transforms⁹⁻¹⁵ may be used, in place of steps (a), (b), and (c') above, to produce a quadratic form for step (d) to diagonalize.

Because the Gaussian transform is a one-dimensional integral, whereas the Fourier-Feynman transform is four-dimensional, one needs only to diagonalize with respect to the spatial variables. This gives a much simpler final reduced form than does the Fourier-Feynman transform in which both the spatial and the (introduced) momentum quadratic forms must be diagonalized.

However, the difference between these two transforms that is of a higher logical type than simple algebraic convenience is that the Gaussian transforms of ns orbitals do not have the "pathologies" of Fourier transforms of these orbitals. If one examines the Gaussian transform of the "seed function" from which excited states are built by derivatives,

$$\frac{e^{-\gamma R}}{R} = \frac{1}{\sqrt{\pi}} \int_0^\infty d\rho \frac{e^{-R^2\rho} e^{-\gamma^2/4\rho}}{\rho^{1/2}}, \quad (5)$$

it is seen that the parameter γ that is used for the derivatives in (3) is decoupled (in the sense of differentiation) from the quadratic form ρR^2 that will enter into the diagonalization. Then in the equivalent of (4),

$$\begin{aligned} u_{2s}^\lambda(\mathbf{R}) &= \frac{\lambda^{3/2}}{2^{3/2}\sqrt{\pi}} (R - \gamma R^2) \frac{e^{-\gamma R}}{R} \\ &= \frac{\lambda^{3/2}}{2^{3/2}\pi} \left(-\frac{\partial}{\partial\gamma} - \gamma \frac{\partial^2}{\partial\gamma^2} \right) \int_0^\infty d\rho \frac{e^{-\rho R^2} e^{-\gamma^2/4\rho}}{\rho^{1/2}}, \end{aligned} \quad (6)$$

one may evaluate the derivatives *before* diagonalizing and integrating over d^3R . Thus,

$$\begin{aligned} u_{2s}^\lambda(\mathbf{R}) &= \frac{\lambda^{5/2}}{2^{7/2}\pi} \int_0^\infty d\rho e^{-\rho R^2 - \lambda^2/16\rho} \\ &\quad \times \left(\frac{2}{\rho^{3/2}} - \frac{\lambda^2}{8\rho^{5/2}} \right). \end{aligned} \quad (7)$$

There is no such decoupling of the parameter γ , used in the derivatives, from the quadratic form in k^2 in the Fourier case (4).

In fact, the Gaussian transform for a spherically symmetric function

$$P(R) = \int_0^\infty d\rho e^{-R^2\rho} A(\rho) \quad (8)$$

is related to the Laplace transform^{9,14,15}

$$P(R) = G[A(\rho), R] = L[A(\rho); R^2], \quad (9)$$

so that one may find the shape function $A(\rho)$ that gives the correct integral transform of the object function $P(\mathbf{R})$ from tables of inverse Laplace transforms,¹⁶

$$A(\rho) = G^{-1}[P(R); \rho] = L^{-1}[P(s^{1/2}); \rho]. \quad (10)$$

In the previous paper,⁸ the shape function for products of s -state hydrogenic orbitals and Coulomb or Yukawa potentials was found, which gave the analytically reduced form for multicenter integrals of such products. In the present paper the properties of solid harmonics are folded into the Gaussian transform to create an integro-differential transform that places all coordinate dependence of an object function that may not be spherically symmetric into a single quadratic form in an exponential. This leads to the reduced form for a general multicenter integral that includes products of hydrogenic orbitals representing arbitrary states, Coulomb or Yukawa potentials, and plane waves.

II. THE EXTENDED TRANSFORM

The problem to be solved is the analytical reduction of the general class of integrals

$$\begin{aligned} S_{I_1 J_1 \dots I_M J_M}^{\eta_1 j_1 \dots \eta_M j_M}(\mathbf{P}_1, \dots, \mathbf{P}_M; \mathbf{Y}_1, \dots, \mathbf{Y}_M) \\ = \int d^3x_1 \dots d^3x_m e^{-i(\mathbf{P}_1 \cdot \mathbf{x}_1 + \dots + \mathbf{P}_m \cdot \mathbf{x}_m)} \\ \times P_{I_1 J_1}^{\eta_1 j_1}(\mathbf{R}_1) \dots P_{I_M J_M}^{\eta_M j_M}(\mathbf{R}_M), \end{aligned} \quad (11)$$

in which the arguments \mathbf{R} are linear functions of one or more of the variables of integration and coordinate vectors that are external to the integral,

$$\mathbf{R}_i = \sum_{j=1}^m t_{ij} \mathbf{x}_j + \sum_{j=1}^M u_{ij} \mathbf{y}_j. \quad (12)$$

In the object functions

$$P_{IJ}^{\eta j}(\mathbf{R}) = u_I(\mathbf{R}) \dots u_J(\mathbf{R}) V^{\eta j}(\mathbf{R}), \quad (13)$$

the u 's are hydrogenic orbitals,

$$u_{n\ell m}^\lambda(\mathbf{R}) = \lambda^{3/2} N_{n\ell} F_{n\ell}(2\lambda R/n) Y_{\ell m}(\hat{\mathbf{R}}), \quad (14)$$

where

$$N_{n\ell} = \frac{2}{n^2} \sqrt{(n-\ell-1)!(n+\ell)!}, \quad (15)$$

and

$$F_{n\ell}(2\lambda R/n) = \sum_{s=0}^{n-\ell-1} \frac{(-1)^s (2\lambda/n)^{s+\ell} R^{s+\ell} e^{-\lambda R/n}}{(n-\ell-1-s)!(2\ell+1+s)!s!}. \quad (16)$$

The function

$$V^{\eta j}(\mathbf{R}) = R^{j-1} e^{-\eta R} \quad (17)$$

is either a Coulomb potential ($j = 0, \eta = 0$), a Yukawa potential ($j = 0, \eta \neq 0$), or $\sqrt{\pi}/\eta^{3/2}$ times a $1s$ orbital ($j = 1, \eta \neq 0$). The usefulness of this j index will become apparent in Sec. IV. Note that integrals in which $j < 0$ require an independent derivation, from the

present development of the reduced form, because the inverse Laplace transform on which the derivation would be based¹⁷ cannot be obtained from the shape function in (5) by differentiation.

The central task is to find an integral transformation for object functions such as (13) that contain nonspherical functions. Any function $P(\mathbf{R})$ may be expanded in (the complete set of) spherical harmonics, so this task reduces to finding an integral transformation that includes these functions. Solid harmonics

$$\mathcal{Y}_{LM}(\mathbf{R}) \equiv R^L Y_{LM}(\hat{\mathbf{R}}) \quad (18)$$

have the property that¹⁸

$$\mathcal{Y}_{LM}(\mathbf{R}) e^{-i\mathbf{k}\cdot\mathbf{R}} = \mathcal{Y}_{LM}(i\nabla_{\mathbf{k}}) e^{-i\mathbf{k}\cdot\mathbf{R}} . \quad (19)$$

If

$$P(\mathbf{R}) = \sum_{L,M} P_{LM}(R) \mathcal{Y}_{LM}(\mathbf{R}) \quad (20)$$

and if one may find the Gaussian shape functions

$$A_{LM}(\rho) = G^{-1}[P_{LM}(R); \rho] = L^{-1}[P_{LM}(s^{1/2}); \rho] , \quad (21)$$

then one may define the shape functional

$$A[\rho, i\nabla_{\mathbf{k}}] = \sum_{L,M} A_{LM}(\rho) \mathcal{Y}_{LM}(i\nabla_{\mathbf{k}}) \quad (22)$$

such that

$$P(\mathbf{R}) = \int_0^\infty d\rho A[\rho, i\nabla_{\mathbf{k}}] e^{-(\rho R^2 + i\mathbf{k}\cdot\mathbf{R})} \Big|_{\mathbf{k}=0} . \quad (23)$$

This integro-differential transform has the desired form: All of the \mathbf{R} dependence lies within a quadratic form in an exponential so that products of P 's and plane waves may be written as an exponential of a single quadratic form to be diagonalized. In the present case it is found that after the diagonalization and integrating over the R 's, the derivatives in (23) may be evaluated, leaving a shape function $A(\rho, \mathbf{q})$.

III. THE REDUCED FORM OF THE MULTICENTER INTEGRAL

In the present case, (13) contains a product of spherical harmonics for which (19) will not be of help since the solid harmonic gradient operator is not a linear operator in general. The angular momentum coupling must first be carried out. Define the shorthand notation

$$\begin{aligned} \sum_{I,J} \circ Y_{L_J M_J}(\hat{\mathbf{R}}) &\equiv Y_{\ell_I m_I}(\hat{\mathbf{R}}) \cdots Y_{\ell_J m_J}(\hat{\mathbf{R}}) \\ &= \sum_{L_1=L_1 \min}^{L_1 \max} (2) (-1)^{M_{I+1}} \left(\frac{(2\ell_I + 1)(2\ell_{I+1} + 1)(2L_1 + 1)}{4\pi} \right)^{1/2} \begin{pmatrix} \ell_I & \ell_{I+1} & L_1 \\ 0 & 0 & 0 \end{pmatrix} \\ &\quad \times \begin{pmatrix} \ell_I & \ell_{I+1} & L_1 \\ m_I & m_{I+1} & -M_{I+1} \end{pmatrix} \\ &\quad \times \sum_{L_2=L_2 \min}^{L_2 \max} (2) (-1)^{M_{I+2}} \left(\frac{(2L_1 + 1)(2\ell_{I+2} + 1)(2L_2 + 1)}{4\pi} \right)^{1/2} \\ &\quad \times \begin{pmatrix} L_1 & \ell_{I+2} & L_2 \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} L_1 & \ell_{I+2} & L_2 \\ M_I & m_{I+2} & -M_{I+2} \end{pmatrix} \times \cdots \\ &\quad \times \sum_{L_J=L_J \min}^{L_J \max} (2) (-1)^{M_J} \left(\frac{(2L_{J-1} + 1)(2\ell_J + 1)(2L_J + 1)}{4\pi} \right)^{1/2} \\ &\quad \times \begin{pmatrix} L_{J-1} & \ell_J & L_J \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} L_{J-1} & \ell_J & L_J \\ M_{J-1} & m_J & -M_J \end{pmatrix} Y_{L_J M_J}(\hat{\mathbf{R}}) , \quad (24) \end{aligned}$$

where

$$M_j = m_I + m_{I+1} + \cdots + m_j , \quad (25)$$

$$L_j \max = L_{j-1} + \ell_j , \quad (26)$$

$$\mu_j = \max(|L_{j-1} - \ell_j|, |M_{j-1} + m_j|) , \quad (27)$$

and

$$L_j \min = \begin{cases} \mu_j & \text{if } L_j \max + \mu_j \text{ is even} \\ \mu_j + 1 & \text{if } L_j \max + \mu_j \text{ is odd} , \end{cases} \quad (28)$$

and where the index "(2)" on the summation sign indicates that one is to sum in steps of two.¹⁹ Then the shape functional corresponding to (13) is

$$A_{IJ}^{\eta_j}[\rho, i\nabla k] = \frac{e^{-\gamma^2/4\rho}}{2^j \sqrt{\pi}} \left(\sum_{s_I=0}^{n_I-\ell_I-1} \frac{(-1)^{s_I} (\lambda_I/n_I)^{s_I+\ell_I} \lambda_I^{3/2} N_{n_I \ell_I}}{(n_I-\ell_I-1-s_I)!(2\ell_I+1+s_I)!s_I!} \right. \\ \left. \times \cdots \times \sum_{s_J=0}^{n_J-\ell_J-1} \frac{(-1)^{s_J} (\lambda_J/n_J)^{s_J+\ell_J} \lambda_J^{3/2} N_{n_J \ell_J}}{(n_J-\ell_J-1-s_J)!(2\ell_J+1+s_J)!s_J!} \right) \\ \times \sum_{IJ} \circ \left(\frac{2^{L_J} H_{s_I+\ell_I+\cdots+s_J+\ell_J-L_J+j}(\gamma/2\sqrt{\rho})}{\rho^{(s_I+\ell_I+\cdots+s_J+\ell_J-L_J+1+j)/2}} \mathbf{y}_{L_J M_J}(i\nabla k) \right), \quad (29)$$

where

$$\gamma = \lambda_I/n_I + \cdots + \lambda_J/n_J + \eta \quad (30)$$

and H is a Hermite polynomial.

The reduced form of the multicenter integral, equation (67) of the previous paper, which will be referred to as (67-I), may be generalized to include the arbitrary hydrogenic states in (11),

$$S_{I_1 J_1 \cdots I_M J_M}^{\eta_1 j_1 \cdots \eta_M j_M}(\mathbf{p}_1, \dots, \mathbf{p}_M; \mathbf{y}_1, \dots, \mathbf{y}_M) = \pi^{3m/2} \int_0^\infty d\rho_1 \cdots d\rho_m A_{I_1 J_1}^{\eta_1 j_1}[\rho_1, i\nabla k_1] \cdots A_{I_M J_M}^{\eta_M j_M}[\rho_M, i\nabla k_M] \frac{e^{-\omega/\Lambda}}{\Lambda^{3/2}} \Big|_{\mathbf{k}_1=0}. \quad (31)$$

The only change is in the matrix W of (28-I) in which each $\mathbf{b}_{i'}$ is replaced by

$$\mathbf{B}_{i'} = \mathbf{b}_{i'} + \frac{i}{2} \sum_{j=1}^M t_{j i'} \mathbf{k}_j, \quad (32)$$

where \mathbf{b}_i (30-I), is

$$\mathbf{b}_{i'} = \frac{i p_{i'}}{2} + \sum_{k=1}^M \rho_k t_{k i'} \sum_{j=1}^M u_{k j} \mathbf{y}_j. \quad (33)$$

The other elements of W (28-I) remain the same, except that $N + M \rightarrow M$. Equation (29-I) is

$$a_{ij} = \sum_{k=1}^M \rho_k t_{k i} t_{k j} \quad (34)$$

and (31-I) is

$$C = \sum_{k=1}^M \sum_{j=1}^M \sum_{j'=1}^M \rho_k u_{k j} u_{k j'} \mathbf{y}_j \cdot \mathbf{y}_{j'}, \quad (35)$$

and the determinant (36-I) is

$$\Lambda = \begin{vmatrix} a_{11} & a_{12} & \cdots & a_{1m} \\ a_{21} & a_{22} & & a_{2m} \\ \vdots & & \ddots & \vdots \\ a_{m1} & a_{m2} & \cdots & a_{mm} \end{vmatrix}. \quad (36)$$

Then the determinant (36-I) of W is

$$\omega = \Omega - i \sum_{j=1}^M \mathbf{k}_j \cdot \mathbf{Q}_j, \quad (37)$$

where Ω (40-I) is as before,

$$\Omega = C\Lambda + \sum_{i=1}^m \sum_{j=1}^m \mathbf{b}_i \cdot \mathbf{b}_j (-1)^{i+j+1} \Lambda_{ij}, \quad (38)$$

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

$$\mathbf{Q}_j = - \sum_{i'=1}^m \sum_{j'=1}^m (-1)^{i'+j'+1} \Lambda_{i' j'} \\ \times \left(t_{j i'} \mathbf{b}_{i'} + \frac{i}{4} \sum_{\ell=1}^M t_{j i'} t_{\ell j'} \mathbf{k}_\ell \right). \quad (39)$$

Noting that

$$i \frac{\partial}{\partial k_j^s} \left(-\frac{\omega}{\Lambda} \right) = -\frac{1}{\Lambda} \left(Q_j^s + \sum_{i'=1}^M k_{i'}^r \frac{\partial}{\partial k_j^s} Q_{i' r} \right), \quad (40)$$

all of the derivatives in (31) may be evaluated and the k 's may be set to zero to give the final reduced form of the general multicenter integral,

$$S_{I_1 J_1 \cdots I_M J_M}^{\eta_1 j_1 \cdots \eta_M j_M}(\mathbf{p}_1, \dots, \mathbf{p}_M; \mathbf{y}_1, \dots, \mathbf{y}_M) \\ = \pi^{3m/2} \int_0^\infty d\rho_1 \cdots d\rho_M \\ \times A_{I_1 J_1}^{\eta_1 j_1}(\rho_1, \mathbf{q}_1) \cdots A_{I_M J_M}^{\eta_M j_M}(\rho_M, \mathbf{q}_M) \\ \times \frac{e^{-\Omega/\Lambda}}{\Lambda^{3/2}}, \quad (41)$$

where

$$\mathbf{q}_i = \frac{1}{\Lambda} \sum_{i'=1}^m \sum_{j'=1}^m (-1)^{i'+j'+1} \Lambda_{i'j'} t_{ii'} \mathbf{b}_{i'} \quad (42)$$

and the shape functions $A(\rho, \mathbf{q})$ are given by the shape functional $A[\rho, i\nabla_{\mathbf{k}}]$ (29) by replacing the operator $i\nabla_{\mathbf{k}}$ by the (c-number valued) vector $\mathbf{q}_{\mathbf{k}}$.

IV. EXAMPLES

In some cases (generally those in which no more than one \mathbf{y} or \mathbf{p} appears) the integrals in the "final" reduced form may be evaluated. Consider the easiest nontrivial case,

$$S_{21m\lambda}^{\eta j}(\mathbf{P}; 0) = \int d^3x e^{-i\mathbf{P}\cdot\mathbf{x}} u_{21m}^{\lambda}(\mathbf{x}) x^{j-1} e^{-\eta x} \quad (43)$$

In this case

$$A_{21m\lambda}^{\eta j}(\rho, \mathbf{q}) = \frac{e^{-\gamma^2/4\rho} \lambda^{3/2} 2\sqrt{3}!}{2^j \sqrt{\pi}} \frac{\lambda/2}{2^2} \frac{2^1 H_{1-1+j}(\gamma/2\sqrt{\rho})}{3!} \frac{\rho^{(1-1+1+j)/2}}{\rho^{(1-1+1+j)/2}} \times \mathcal{Y}_{1m}(\mathbf{q}) \quad (44)$$

where

$$\mathbf{q} = \frac{-i\mathbf{p}}{2\Lambda} \quad (45)$$

and

$$\gamma = \lambda/2 + \eta \quad (46)$$

The determinants are

$$\Lambda = \rho, \quad \Lambda_{11} \equiv 1 \quad (47)$$

and

$$\Omega = \frac{p^2}{4} \quad (48)$$

Then

$$S_{21m\lambda}^{\eta j}(\mathbf{P}; 0) = \frac{(2\pi)^{3/2} \lambda^{5/2}}{2^{3+j} \sqrt{3\pi}} \left(\frac{-ip}{2} \right) Y_{1m}(\hat{\mathbf{p}}) \times \int_0^{\infty} dp \frac{e^{-(\gamma^2+p^2)/4\rho}}{\rho^{(6+j)/2}} H_j \left(\frac{\gamma}{2\sqrt{\rho}} \right) \quad (49)$$

Setting $j = 1$,

$$S_{21m\lambda}^{\eta 1}(\mathbf{P}; 0) = -\frac{(2\pi)^{3/2} i\lambda^{7/2} 4\gamma p Y_{1m}(\hat{\mathbf{p}})}{\sqrt{3\pi} (\gamma^2 + p^2)^3} \quad (50)$$

If $\eta = 0$, (50) is the nonsymmetrically normalized Fourier transform of a $2p$ hydrogenic orbital,⁷

$$S_{21m\lambda}^{01}(\mathbf{P}; 0) = (2\pi)^{3/2} u_{21m}^{\lambda}(\mathbf{P}) = (2\pi)^{3/2} \left(\frac{-i2\lambda^{7/2} p Y_{1m}(\hat{\mathbf{p}})}{\sqrt{3\pi} \left(\frac{\lambda^2}{4} + p^2 \right)^3} \right) \quad (51)$$

Setting $\eta = \lambda$ yields $\sqrt{\pi}/\lambda^{3/2}$ times the nonsymmetrically normalized Fourier transform of the single center product of $1s$ and $2p$ orbitals³

$$S_{21m\lambda}^{\lambda 1}(\mathbf{P}; 0) = \frac{\sqrt{\pi}}{\lambda^{3/2}} I_{1s, 2p}(\mathbf{P}) = \frac{\sqrt{\pi}}{\lambda^{3/2}} \left(\frac{-i4\sqrt{6}\pi\lambda^5 p Y_{1m}(\hat{\mathbf{p}})}{(9\lambda^2/4 + p^2)^3} \right) \quad (52)$$

Finally, if $j = 0$, (49) gives

$$S_{21m\lambda}^{\eta 0}(\mathbf{P}; 0) = \frac{-(2\pi)^{3/2} i\lambda^{5/2} p Y_{1m}(\hat{\mathbf{p}})}{\sqrt{3\pi} (\gamma^2 + p^2)^2} \quad (53)$$

Now consider the more complicated integral

$$S_{21-m\lambda', 21m\lambda; \mathbf{1}}^{\eta_1 j_1, \eta_2 j_2}(0; 0, \mathbf{y}) = \int d^3x [u_{21-m}^{\lambda'}(\mathbf{x}) u_{21m}^{\lambda}(\mathbf{x}) x^{j_1-1} e^{-\eta_1 x}] \times (|\mathbf{x} - \mathbf{y}|^{j_2-1} e^{-\eta_2 |\mathbf{x} - \mathbf{y}|}) \quad (54)$$

The first shape function is

$$A_{21-m\lambda', 21m\lambda}^{\eta_1 j_1}(\rho_1, \mathbf{q}_1)$$

$$= \frac{e^{-\gamma_1^2/4\rho_1} (\lambda'\lambda)^{5/2}}{2^{j_1} \sqrt{\pi}} \frac{1}{4} \left(\frac{2\sqrt{3}!}{2^2} \right)^2 \frac{1}{3!^2} \sum_{L=0}^2 \binom{2}{L} 3 \left(\frac{2L+1}{4\pi} \right)^{1/2} \begin{pmatrix} 1 & 1 & L \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} 1 & 1 & L \\ -m & m & 0 \end{pmatrix} \times \frac{2^L H_{2-L+j_1}(\gamma_1/2\sqrt{\rho_1})}{\rho_1^{(2-L+1+j_1)/2}} \mathcal{Y}_{L0}(\mathbf{q}_1) \\ = \frac{(\lambda'\lambda)^{5/2}}{3 \times 2^{6+j_1} \pi} e^{-\gamma_1^2/4\rho_1} \left((-1)^m \mathcal{Y}_{00} \frac{H_{2+j_1}(\gamma_1/2\sqrt{\rho_1})}{\rho_1^{(3+j_1)/2}} + \frac{2^{2-|m|}}{\sqrt{5}} \mathcal{Y}_{20}(\mathbf{q}_1) \frac{H_{j_1}(\gamma_1/2\sqrt{\rho_1})}{\rho_1^{(1+j_1)/2}} \right) \quad (55)$$

and the second is

$$A_{\mathbf{1}}^{\eta_1 j_2}(\rho_2, \mathbf{q}_2) = \frac{e^{-\eta_2^2/4\rho_2} H_{j_2}(\eta_2/2\sqrt{\rho_2})}{2^{j_2}\sqrt{\pi} \rho_2^{(1+j_2)/2}}. \quad (56)$$

Also

$$a_{11} = \rho_1 + \rho_2 \equiv \Lambda, \quad (57)$$

$$\mathbf{b}_1 = -\rho_2 \mathbf{y}, \quad (58)$$

$$c = \rho_2 y^2, \quad (59)$$

$$\Omega = \rho_1 \rho_2 y^2, \quad (60)$$

and

$$\mathbf{q}_1 = \mathbf{q}_2 = -\frac{\mathbf{b}_1}{\Lambda} = \frac{\rho_2 \mathbf{y}}{\Lambda}. \quad (61)$$

Consider the case $j_1 = 1, j_2 = 0$, then

$$S_{21-m\lambda', 21m\lambda; \mathbf{1}}^{\eta_1 1; \eta_2 0}(0; 0, \mathbf{y}) = \frac{(\lambda'\lambda)^{5/2}}{3 \times 2^7} \int_0^\infty d\rho_1 \int_0^\infty d\rho_2 \left[\frac{(-1)^m \mathcal{Y}_{00} \gamma}{\rho_1^2} \left(\frac{\gamma^3}{\rho_1^{3/2}} - \frac{6\gamma}{\rho_1^{1/2}} \right) + \frac{2^{2-|m|}}{\sqrt{5}} \left(\frac{\rho_2}{\Lambda} \right)^2 \mathcal{Y}_{20}(\mathbf{y}) \frac{\gamma}{\rho_1^{3/2}} \right] \times e^{-\gamma^2/4\rho_1} e^{-\eta_2^2/4\rho_2} \frac{e^{-\rho_1 \rho_2 y^2/\Lambda}}{\Lambda^{3/2}}. \quad (62)$$

Changing variables from ρ_2 to

$$\sigma = \left(\frac{\rho_2}{\Lambda} \right)^{1/2} \quad (63)$$

and defining

$$\mu^2 = \gamma^2 + \frac{\eta_2^2(1-\sigma^2)}{\sigma^2} \quad (64)$$

one may reduce this to a one-dimensional integral²⁰

$$S_{21-m\lambda', 21m\lambda; \mathbf{1}}^{\eta_1 1; \eta_2 0}(0; 0, \mathbf{y}) = \frac{(\lambda'\lambda)^{5/2}\sqrt{\pi}}{3 \times 2^7} \int_0^1 d\sigma \left\{ (-1)^m \gamma \mathcal{Y}_{00} \left[\frac{2^7 \gamma^3}{\mu^{7/2}} \left(\frac{15}{4} + \frac{15}{4} \sigma y \mu + \frac{3}{2} \sigma^2 y^2 \mu^2 + \frac{\sigma^3 y^3 \mu^3}{4} \right) - \frac{3 \times 2^6 \gamma}{\mu^{5/2}} \left(\frac{3}{2} + \frac{3\sigma y \mu}{2} + \frac{\sigma^2 y^2 \mu^2}{2} \right) \right] + \frac{2^{2-|m|}}{\sqrt{5}} \gamma \mathcal{Y}_{20}(\mathbf{y}) \frac{2^3}{\mu^{3/2}} (\sigma^4 + y \sigma^5 \mu) \right\} e^{-\sigma y \mu}. \quad (65)$$

Finally, for the special case $\eta_2 = 0$ (the Coulomb integral) $\mu \equiv \gamma$ and the analytic result is

$$S_{21-m\lambda; 21m\lambda; \mathbf{1}}^{\eta_1 1; 00}(0; 0, \mathbf{y}) = \frac{(\lambda'\lambda)^{5/2}}{3 \times 2^3 \gamma^4} \sqrt{\pi} \left\{ (-1)^m Y_{00} \left[\frac{3 \times 2^4}{\gamma y} - \left(\frac{3 \times 2^4}{\gamma y} + 3^2 \times 2^2 + 3 \times 2^2 \gamma y + 2\gamma^2 y^2 \right) e^{-\gamma y} \right] + \frac{2^{2-|m|}}{\sqrt{5}} Y_{20}(\hat{\mathbf{R}}) \left[\frac{3^2 \times 2^4}{\gamma^3 y^3} - \left(\frac{3^2 \times 2^4}{\gamma^3 y^3} + \frac{3^2 2^4}{\gamma^2 y^2} + \frac{3^2 \times 2^3}{\gamma y} + 3 \times 2^3 + 3 \times 2\gamma y + \gamma^2 y^2 \right) e^{-\gamma y} \right] \right\}. \quad (66)$$

This is the same result obtained²¹ using Fourier techniques.³

V. CONCLUSION

An integro-differential transform has been developed for functions $P(\mathbf{R})$ that may not be spherically symmetrical, in which all \mathbf{R} dependence appears in a quadratic form in an exponential. This allows one to diagonalize the coordinate dependence of products of such functions and plane waves so that the \mathbf{R} integrals may be evaluated.

The angular momentum coupling has been explicitly

given for the case in which the P 's are products of hydrogenic orbitals representing arbitrary states and Coulomb or Yukawa potentials. This integro-differential transform is then used to find the analytically reduced form for the general class of multicenter integrals of products of such P 's with plane waves.

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