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Expansion about an Arbitrary Point of Three-Dimensional Functions Involving Spherical Harmonics by the Fourier-Transform Convolution Theorem*

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Expansion of $\Psi(\mathbf{r})=\psi(r)Y_L^M(\theta,\phi)$ in terms of spherical harmonics and radial functions, whose coordinates are measured from an arbitrary point in space, is obtained by use of the Fourier-transform convolution theorem. For a specific $\psi(r)$, two integrals most be evaluated to determine the expansion explicitly: (1) the radial part $\bar{\psi}(k)$ of the Fourier transform of $\psi(\mathbf{r})$; and (2) an integral of $\bar{\psi}(k)$ with spherical Bessel functions. The examples of noninteger-n and integer-n Slater-type orbitals are worked out by contour integration.

INTRODUCTION

Functions of the form

$$\Psi(\mathbf{r})=\psi(r)Y_L^M(\theta,\phi), \quad (1)$$

where $Y_L^M(\theta,\phi)$ is a spherical harmonic and (r,θ,ϕ) are the spherical polar coordinates of $\mathbf{r}$, pervade the quantum-theoretical treatments of atoms, molecules, and solids. Often one wishes to expand a $\Psi(\mathbf{r}-\mathbf{R})$ located at $\mathbf{R}$ (the spherical polar coordinates of $\mathbf{R}$ are denoted by R, θ_R, and ϕ_R) in terms of spherical harmonics whose coordinates are measured from the origin, i.e.,

$$\Psi(\mathbf{r}-\mathbf{R})=\sum_{l=0}^{\infty}\sum_{m=-l}^{l}\mathcal{V}(l,m;L,M;r,\mathbf{R})Y_l^m(\theta,\phi). \quad (2)$$

For instance, if $L=M=0$ and $\psi(r)=(4\pi)^{1/2}/r$, then Eq. (2) is the familiar Laplace expansion

$$\mathcal{V}(l,m;0,0;r,\mathbf{R})=(r_<^l/r_>^{l+1})(4\pi/2l+1)Y_l^{m*}(\theta_R,\phi_R). \quad (3)$$

In Eq. (3), $r_<$ is the smaller and $r_>$ the larger of r and R. If $L=M=0$ and $\psi(r)=(4\pi)^{1/2}\exp(-\zeta r)$, then Eq. (2) is the familiar Barnett–Coulson expansion[1]

$$\mathcal{V}(l,m;0,0;r,\mathbf{R})$$
$$=[-(d/d\zeta)\zeta\mathcal{I}_l(\zeta r_<)\mathcal{K}_l(\zeta r_>)]4\pi Y_l^{m*}(\theta_R,\phi_R). \quad (4)$$

The $\mathcal{I}_l$ and $\mathcal{K}_l$ are essentially modified spherical Bessel functions,[2]

$$\mathcal{I}_l(x)=x^l(x^{-1}d/dx)^l x^{-1}\sinh x, \quad (5)$$

$$\mathcal{K}_l(x)=(-x)^l(x^{-1}d/dx)^l x^{-1}\exp(-x). \quad (6)$$

Equations (3) and (4) have been used extensively in the evaluation of atomic and molecular integrals.[1,3,4]

In this work a general method for obtaining the "radial functions" $\mathcal{V}$ of Eq. (2) is derived from the Fourier-transform convolution theorem. Each $\mathcal{V}$ is expressed as an integral over the radial part of the Fourier transform of $\Psi(\mathbf{r})$. This method, when applied to integer-n Slater-type orbitals (STO), gives an extremely compact generalization of Eq. (4). The $\mathcal{V}$'s are also evaluated for noninteger-n STO's, thus making possible the evaluation of multicenter integrals with these basis functions by the methods[3,4] used for the integer-n ones.

Another approach to these expansions has been given by Sack.[5,6] In his first approach,[5] Sack derived expansions for $\psi(r)=r^n$, which in turn yield *series* expansions for the $\mathcal{V}$. Sack's second method[6] gives each $\mathcal{V}$ as an integral, but the kernal of the integral must first be found from $\psi(r)$ by solving an integral equation. In the present approach (1) all quantities are formulated as explicit one-dimensional integrals, no integral equation is involved; and (2) the $\mathcal{V}$ for a general ψ can often be obtained in closed form without going through a series expansion.

FORMULATION

First we obtain $\mathcal{V}$ as an overlap integral. Then we introduce the Fourier-transform convolution theorem for overlap integrals,[7–9] perform the angular integrations, and end up with $\mathcal{V}$ formulated as an integral over the radial part of the Fourier transform of $\Psi(\mathbf{r})$. In the next section we evaluate the $\mathcal{V}$'s explicitly for STO's.

By the orthogonality properties of spherical harmonics, the integral over angles of $Y_l^{m*}(\theta,\phi)$ times both sides of Eq. (2) gives

$$\mathcal{V}(l,m;L,M;r,\mathbf{R})=\iint \sin\theta d\theta d\phi Y_l^{m*}(\theta,\phi)\Psi(\mathbf{r}-\mathbf{R}). \quad (7)$$

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Introduction of the "radial function" $r^{-2}\delta(r'-r)$, and integration with respect to r' on the right-hand side of Eq. (7) casts $\mathcal{V}$ as an overlap integral

$$\mathcal{V}(l, m; L, M; r, \mathbf{R}) = \int dV' \Phi^*(\mathbf{r}') \Psi(\mathbf{r}'-\mathbf{R}), \quad (8)$$

where

$$\Phi(\mathbf{r}') = r^{-2}\delta(r-r') Y_l^m(\theta', \phi'). \quad (9)$$

With the aid of the Fourier-transform convolution theorem,[7–9] the $\mathbf{R}$ dependence of Eq. (8) is greatly simplified,

$$\mathcal{V}(l, m; L, M; r, \mathbf{R}) = (2\pi)^{-3} \int d^3\mathbf{k} \bar{\Phi}^*(\mathbf{k}) \bar{\Psi}(\mathbf{k}) \exp(i\mathbf{k}\cdot\mathbf{R}). \quad (10)$$

The transforms $\bar{\Phi}$ and $\bar{\Psi}$ are conveniently evaluated or simplified with the aid of the expansion[10]

$$\exp(i\mathbf{k}\cdot\mathbf{r}) = \sum_{l=0}^{\infty} \sum_{m=-l}^{l} 4\pi i^l j_l(kr) Y_l^m(\theta_k, \phi_k) Y_l^{m*}(\theta, \phi), \quad (11)$$

where the spherical polar coordinates of $\mathbf{k}$ are (k, θ_k, ϕ_k), and j_l is the spherical Bessel function of order l

$$j_l(x) = (-x)^l (x^{-1} d/dx)^l x^{-1} \sin x. \quad (12)$$

The results are

$$\bar{\Phi}(\mathbf{k}) \equiv \int dV' \exp(i\mathbf{k}\cdot\mathbf{r}') \Phi(\mathbf{r}') \quad (13)$$

$$= 4\pi i^l j_l(kr) Y_l^m(\theta_k, \phi_k), \quad (14)$$

$$\bar{\Psi}(\mathbf{k}) \equiv \int dV \exp(i\mathbf{k}\cdot\mathbf{r}) \Psi(\mathbf{r}) \quad (15)$$

$$= \bar{\psi}(k) Y_L^M(\theta_k, \phi_k), \quad (16)$$

$$\bar{\psi}(k) = 4\pi i^L \int_0^{\infty} dr r^2 \psi(r) j_L(kr). \quad (17)$$

Substituting Eqs. (14) and (16) into Eq. (10), using again Eq. (11), and introducing the Condon–Shortley coefficients[11]

$$\left(\frac{2\lambda+1}{4\pi}\right)^{1/2} c^{\lambda}(L, M; l, m) = \int d\Omega Y_{\lambda}^{M-m*}(\theta, \phi) Y_l^{m*}(\theta, \phi) Y_L^M(\theta, \phi), \quad (18)$$

we obtain for $\mathcal{V}(l, m; L, M; r, \mathbf{R})$

$$\mathcal{V}(l, m; L, M; r, \mathbf{R}) = \sum_{\lambda=|L-l|}^{L+l} \left(\frac{2}{\pi}\right) i^{\lambda-l} Y_{\lambda}^{M-m}(\theta_R, \phi_R) \left(\frac{2\lambda+1}{4\pi}\right)^{1/2} c^{\lambda}(L, M; l, m) \int_0^{\infty} dk k^2 j_{\lambda}(kR) j_l(kr) \bar{\psi}(k). \quad (19)$$

Finally, Eq. (19) can be substituted into Eq. (2) and $\mathcal{V}(l, m; L, M; r, \mathbf{R})$ can be replaced by a function independent of m, M, θ_R, and ϕ_R, to give

$$\Psi(\mathbf{r}-\mathbf{R}) = \sum_{l=0}^{\infty} \sum_{\lambda=|L-l|}^{L+l} v_{l,\lambda,L}(r, R) \sum_{m=-l}^{l} \left(\frac{2\lambda+1}{4\pi}\right)^{1/2} c^{\lambda}(L, M; l, m) Y_{\lambda}^{M-m}(\theta_R, \phi_R) Y_l^m(\theta, \phi), \quad (20)$$

where

$$v_{l,\lambda,L}(r, R) = \pi^{-1} i^{\lambda-l} \int_{-\infty}^{\infty} dk k^2 j_{\lambda}(kR) j_l(kr) \bar{\psi}(k). \quad (21)$$

The

$$2\int_0^{\infty} dk$$

has been replaced by

$$\int_{-\infty}^{\infty} dk.$$

The sum $\lambda+l+L$ must be even for $c^{\lambda}(L, M: l, m)$ to be nonzero, and

$$j_{\lambda}(-kR) j_l(-kr) \bar{\psi}(-k) = (-1)^{\lambda+l+K} j_{\lambda}(kR) j_l(kr) \bar{\psi}(k).$$

Equations (20), (21), and (17) constitute an explicit recipe for expanding $\Psi(\mathbf{r}-\mathbf{R})$ in terms of radial functions and $Y_l^m(\theta, \phi)$.

SLATER-TYPE ORBITALS

We now take $\Psi(\mathbf{r})$ to be a Slater-type orbital

$$\Psi(\mathbf{r}) = r^{n-1} \exp(-\zeta r) Y_L^M(\theta, \phi), \quad (22)$$

and evaluate the $v_{l\lambda L}$ explicitly. For a STO, $\bar{\psi}(k)$ is just the $f_{nl\zeta}(k)$ of Eq. (13) of Ref. 9:

$$\bar{\psi}(k) = 2\pi i^{L-1} \Gamma(n-L+1) (-k)^L (k^{-1} d/dk)^L k^{-1} [(\zeta-ik)^{L-n-1} - (\zeta+ik)^{L-n-1}]. \quad (23)$$

The $\Gamma(x)$ is the usual gamma function. From Eq. (21)

$$v_{l\lambda L}(r, R) = v_{l\lambda L}^{(n\zeta)}(r, R)$$
$$= 2i^{L+\lambda-l-1} \Gamma(n-L+1) \int_{-\infty}^{\infty} dk j_{\lambda}(kR) j_l(kr) (-k)^{L+2} \left(k^{-1} \frac{d}{dk}\right)^L k^{-1} [(\zeta-ik)^{L-n-1} - (\zeta+ik)^{L-n-1}]. \quad (24)$$

[10] Reference 2, p. 440, Eq. (10.1.47).
[11] E. U. Condon and G. H. Shortley, *The Theory of Atomic Spectra* (Cambridge University Press, London, 1935), p. 175, Eq. (6).

[In Eq. (24) the superscripts n and ζ which characterize the STO have been appended to v.] Make the substitution $k=ix$, and introduce $\mathcal{I}_m(x)$ [Eq. (5)] to obtain

$$v_{l\lambda L}^{(n\zeta)}(r,R)=2i(-1)^{L+\lambda}\Gamma(n-L+1)\int_{i\infty}^{-i\infty}dx\mathcal{I}_\lambda(xR)\mathcal{I}_l(xr)x^{L+2}\left(x^{-1}\frac{d}{dx}\right)^L x^{-1}[(\zeta+x)^{L-n-1}-(\zeta-x)^{L-n-1}]. \quad (25)$$

EVALUATION BY CONTOUR INTEGRATION

Equation (25) is readily evaluated by the technique of contour integration.[12] The well-known two-region form[1,3] of $v_{l\lambda L}(r,R)$ will emerge from "closure" of the contour at infinity.

First assume $R>r$. Use

$$\mathcal{I}_N(x)=-\tfrac{1}{2}[(-1)^N\mathcal{K}_N(x)+\mathcal{K}_N(-x)], \quad (26)$$

$$\mathcal{K}_N(x)=(-1)^N\mathcal{K}_N(-x), \quad (27)$$

and the evenness of the integrand of Eq. (25) to obtain

$$v_{l\lambda L}^{(n\zeta)}(r,R)=2i(-1)^{L+1}\Gamma(n-L+1)\int_{i\infty}^{-i\infty}dx\mathcal{K}_\lambda(xR)\mathcal{I}_l(xr)x^{L+2}\left(x^{-1}\frac{d}{dx}\right)^L x^{-1}[(\zeta+x)^{L-n-1}-(\zeta-x)^{L-n-1}]. \quad (28)$$

The only singularities of the integrand of (28) are poles or branch points at $x=\pm\zeta$. In the right-hand plane the integrand approaches zero exponentially fast at $|x|=\infty$, $|\arg x|<\frac{1}{2}\pi$. Thus, by Cauchy's theorem[12] the contour for Eq. (28) may be wrapped around the real $x(\geq\zeta)$ axis for the term with the factor $(\zeta-x)^{L-n-1}$. The term with $(\zeta+x)^{L-n-1}$ gives zero. The $v_{l\lambda L}$ becomes

$$v_{l\lambda L}^{(n\zeta)}(r,R)=2i(-1)^{L}\Gamma(n-L+1)\int_{\infty}^{(\zeta+)}dx\mathcal{K}_\lambda(xR)\mathcal{I}_l(xr)x^{L+2}\left(x^{-1}\frac{d}{dx}\right)^L x^{-1}(\zeta-x)^{L-n-1}, \qquad (r<R). \quad (29)$$

INTEGER n = STO

When n is an integer, Eq. (29) is trivial to evaluate by the residue theorem.[12] First integrate by parts L times so that the factor $(\zeta-x)^{L-n-1}$ is no longer differentiated, then take $2\pi i$ times the residue at $x=\zeta$:

$$v_{l\lambda L}^{(n\zeta)}(r,R)=4\pi(-1)^{n-L}(d/d\zeta)^{n-L}(\zeta^{-1}d/d\zeta)^L\zeta^{L+1}\mathcal{K}_\lambda(\zeta R)\mathcal{I}_l(\zeta r), \qquad (r<R). \quad (30)$$

The $r>R$ case works out to be

$$v_{l\lambda L}^{(n\zeta)}(r,R)=4\pi(-1)^{n}(d/d\zeta)^{n-L}(\zeta^{-1}d/d\zeta)^L\zeta^{L+1}\mathcal{I}_\lambda(\zeta R)\mathcal{K}_l(\zeta r), \qquad (R<r). \quad (31)$$

These formulas, (30) and (31), for $v_{l\lambda L}^{(n\zeta)}$ are exceedingly simple. By carrying out the differentiations and/or using power series for $\mathcal{I}$ and $\mathcal{K}$, one can obtain formulas already known. We anticipate using these expressions for analytical attacks on multicenter integrals[13] for which it is convenient to take the ζ derivatives after the further analysis.

RELATION TO BARNETT-COULSON ZETA FUNCTIONS, AND TO HARRIS AND MICHELS V FUNCTIONS

The Barnett–Coulson[1,3] zeta functions are the v functions for s orbitals. By setting $L=0$ and $\lambda=l$ in Eq. (20) and using the addition theorem for spherical harmonics, one finds the explicit connection,

$$\zeta_{n,l}(\zeta,r;R)=(4\pi)^{-1}(rR)^{1/2}v_{l,l,0}^{(n\zeta)}(r,R). \quad (32)$$

The V functions of Harris and Michels[4] correspond to the special case of translation along the negative z axis. They are essentially the coefficients of $Y_l^m(\theta,\phi)$ in Eq. (20), except for some constants, with θ_R set equal to $-\pi$:

$$V^M{}_{n,L,l}(\zeta r,\zeta R)=\zeta^{n-1}\left[\frac{(2l+1)(L+M)!(l-M)!}{(2L+1)(L-M)!(l+M)!}\right]^{1/2}\times\sum_{\lambda=|L-l|}^{L+l}\frac{2\lambda+1}{4\pi}(-1)^\lambda c^\lambda(L,M;l,M)v_{l,\lambda,L}^{(n\zeta)}(r,R). \quad (33)$$

NONINTEGER-n STO

When n is not an integer, $x=\zeta$ is a branch point, and Eq. (29) cannot be evaluated by the residue theorem. The v functions can be expressed in terms of the con-

[12] See, e.g., G. F. Carrier, M. Krook, and C. E. Pearson, *Functions of a Complex Variable* (McGraw-Hill Book Co., New York, 1966).
[13] H. J. Silverstone, "Analytical Evaluation of Three- and Four-Center Integrals of r_{12}^{-1} with Slater-Type Orbitals," Proc. Natl. Acad. Sci. U. S. (to be published).

fluent hypergeometric functions $U(a, b, z)$,[14]

$$\exp(-z)\,U(a,b,z)=(2\pi i)^{-1}\exp(-i\pi a)\,\Gamma(1-a)\int_{\infty}^{(1^+)}dt\,\exp(-zt)\,(t-1)^{a-1}t^{b-a-1}. \tag{34}$$

In Eq. (29), use Eqs. (5) and (6) for $\mathcal{K}_\lambda$ and $\mathcal{I}_l$, and use for $(x^{-1}d/dx)^L x^{-1}$ the expression

$$\left(x^{-1}\frac{d}{dx}\right)^L x^{-1}=\sum_{\mu=0}^{L}\frac{(L+\mu)!(-1)^\mu}{2^\mu(L-\mu)!\mu!}x^{-L-\mu-1}\left(\frac{d}{dx}\right)^{L-\mu}, \tag{35}$$

to obtain,

$$v_{l\lambda L}^{(n\zeta)}(r,R)=2i(-1)^L\Gamma(n-L+1)(-R)^\lambda\left(R^{-1}\frac{d}{dR}\right)^\lambda R^{-1}r^l\left(r^{-1}\frac{d}{dr}\right)^l r^{-1}\sum_{\mu=0}^{L}\frac{(L+\mu)!(-1)^\mu}{2^\mu(L-\mu)!\mu!}\frac{\Gamma(n-\mu+1)}{\Gamma(n-L+1)}$$
$$\times\int_{\infty}^{(\zeta^+)}dx\,\exp(-xR)\,\sinh xr\,x^{-\lambda-l-\mu-1}(\zeta-x)^{\mu-n-1}. \tag{36}$$

Making use of Eq. (34), we obtain

$$v_{l\lambda L}^{(n\zeta)}(r,R)=2\pi(-1)^{L+\lambda}R^\lambda\left(R^{-1}\frac{d}{dR}\right)^\lambda R^{-1}r^l\left(r^{-1}\frac{d}{dr}\right)^l r^{-1}\zeta^{-\lambda-l-n-1}\sum_{\mu=0}^{L}\frac{(L+\mu)!(-1)^\mu}{2^\mu(L-\mu)!\mu!}$$
$$\times\{\exp[-\zeta(R-r)]U[\mu-n,-\lambda-l-n,\zeta(R-r)]-\exp[-\zeta(R+r)]U[\mu-n,-\lambda-l-n,\zeta(R+r)]\},$$
$$(r<R). \tag{37}$$

The $r>R$ case gives a similar result. Both cases, $r<R$ and $r>R$, are covered by the formula

$$v_{l\lambda L}^{(n\zeta)}(r,R)=2\pi(-1)^{L+\lambda}\zeta^{-\lambda-l-n-1}R^\lambda\left(R^{-1}\frac{d}{dR}\right)^\lambda R^{-1}r^l\left(r^{-1}\frac{d}{dr}\right)^l r^{-1}\sum_{\mu=0}^{L}\frac{(L+\mu)!(-1)^\mu}{2^\mu(L-\mu)!\mu!}$$
$$\times\{\exp(-\zeta|R-r|)\,U(\mu-n,-\lambda-l-n,\zeta|R-r|)-\exp[-\zeta(R+r)]U[\mu-n,-\lambda-l-n,\zeta(R+r)]\}. \tag{38}$$

RECURRENCE FORMULAS

The integral form for $v_{l,\lambda,L}(r, R)$ [Eq. (21)] is convenient for deriving recurrence formulas. We give two examples. By use of recurrence relations[2] for the spherical Bessel functions one can easily derive

$$[(2\lambda+1)/R](v_{l-1,\lambda,L}-v_{l+1,\lambda,L})=[(2l+1)/r](v_{l,\lambda+1,L}-v_{l,\lambda-1,L}), \tag{39}$$

which is *independent* of $\psi(r)$. From the recurrence formula for the $v_{l,\lambda,L}$ for STO's [Eq. (22) of Ref. 9], one finds,

$$v^{(n\zeta)}{}_{l,\lambda,L}=[(n+L)/(n-L+1)]v^{(n\zeta)}{}_{l,\lambda,L-2}+[(2L-1)/(2l+1)][\zeta r/(n-L+1)]\times(v^{(n\zeta)}{}_{l-1,\lambda,L}-v^{(n\zeta)}{}_{l+1,\lambda,L-1}). \tag{40}$$

A number of other recurrence formulas derived by Barnett and Coulson[1,3] and by Harris and Michels[4] are applicable via Eqs. (32) and (33).

SUMMARY

The expansion in spherical harmonics and radial functions [$v_{l,\lambda,L}(r, R)$] of $\Psi(\mathbf{r})=\psi(r)\,Y_L^M(\theta,\phi)$ about an arbitrary point in space has been solved formally by applying the Fourier-transform convolution theorem. For a specific $\psi(r)$, two integrals must be evaluated: (1) the radial part $\bar{\psi}(k)$ of the Fourier transform of $\Psi(\mathbf{r})$ [Eq. (17)]; and (2) an integral involving $\bar{\psi}(k)$ and spherical Bessel functions [Eq. (21)]. Explicit solutions were found by contour integration for the $v_{l\lambda L}(r, R)$ for the case of integer-n and noninteger-n Slater-type orbitals [Eqs. (30), (31), and (38)].

[14] Reference 2, p. 505, Eq. (13.2.6).