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Dirac Delta Functions in the Laplace-Type Expansion of $r^n Y_l^m(\theta, \phi)$*

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The theory of generalized functions and Fourier transforms is used to derive the Laplace-type expansion for $r_{12}^n Y_l^m(\theta_{12}, \phi_{12})$. This approach leads naturally to a general formula for the Dirac delta-function terms which occur when $n \leq -3$ and $n-l$ is odd.

I. INTRODUCTION

Integrals involving $r^n Y_l^m(\theta, \phi)$, which occur in the calculation of molecular properties, often can be simplified by expansions similar to the Laplace expansion for $1/r_{12}$,

$$r_{12}^{-1} = 4\pi \sum_{l=0}^{\infty} r_<^l r_>^{-l-1}(2l+1)^{-1} \times \sum_{m=-l}^{l} Y_l^{m*}(\theta_1, \phi_1) Y_l^m(\theta_2, \phi_2). \quad (1)$$

Laplace-type expansions for solid harmonics, $r^l Y_l^m$ and $r^{-l-1} Y_l^m$, have been derived by Hobson[1] and others.[2–5] For arbitrary n, Chapman[6] treated r^n, and Sack[3] treated r^n and $r^n Y_l^m$. The remarkable discovery of delta functions in Laplace-type expansions of $r^{-l-1} Y_l^m$ was made in 1962 by Pitzer, Kern, and Lipscomb,[7] who gave explicit formulas for $l=2$ and 3. Since then the delta-function terms have not been treated in any more detail, and no delta-function formula has been given for the general case.

The purpose of this paper is to derive the delta-function terms in the Laplace-type expansion of $r^n Y_l^m$, where n is an arbitrary integer. We use the theory of generalized functions and Fourier transforms,[8] which greatly facilitate the derivation. Although the non-delta-function terms have already been obtained by Sack,[3] considerably simpler formulas are given here for certain cases.

II. NOTATION AND CONVENTIONS

Before proceeding, it is necessary to state what is meant by an integral involving $r^n Y_l^m$,

$$\int dV r^n Y_l^m(\theta, \phi) f(\mathbf{r}), \quad (2)$$

when n is ≤ -3, and $f(\mathbf{r})$ is any function analytic in x, y, and z at $\mathbf{r}=0$. The difficulty is that the integrand is singular at $r=0$. We adopt the convention that integrations over angle are to be carried out before integrations over r. Consequently the contribution to the integral (2) from the region about $\mathbf{r}=0$ is finite and well defined when

$$n+l+2 > -1. \quad (3)$$

Throughout this paper we assume the inequality (3) to hold.

Let $Y_l^m(\theta, \phi)$ denote the usual complex spherical harmonics, $\mathbf{r}_1$, $\mathbf{r}_2$, $\mathbf{r}_{12} = \mathbf{r}_1 - \mathbf{r}_2$, $\mathbf{k}$, etc., denote Cartesian coordinates, and let (r, θ_1, ϕ_1), (r_2, θ_2, ϕ_2), $(r_{12}, \theta_{12}, \phi_{12})$, (k, θ_k, ϕ_k), etc., denote the corresponding spherical polar coordinates. We use the Condon–Shortley coefficients,[9]

$$[(2l_2+1)/4\pi]^{1/2} c^{l_2}(lm; l_1, m_1) = \int d\Omega Y_l^{m*} Y_{l_1}^{m_1} Y_{l_2}^{m-m_1}, \quad (4)$$

the expansion,[10a]

$$\exp(i\mathbf{k}\cdot\mathbf{r}) = 4\pi \sum_{l=0}^{\infty} i^l j_l(kr) \sum_{m=-l}^{l} Y_l^{m*}(\theta_k, \phi_k) Y_l^m(\theta, \phi), \quad (5)$$

the spherical Bessel functions,[10b]

$$j_l(x) = (-x)^l (x^{-1} d/dx)^l x^{-1} \sin x \quad (6)$$

$$= \sum_{\nu=0}^{\infty} (-1)^\nu x^{l+2\nu} [(2\nu)!!(2l+2\nu+1)!!]^{-1}, \quad (7)$$

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[1] E. W. Hobson, *The Theory of Spherical and Ellipsoidal Harmonics* (Chelsea Publ. Co., New York, 1955), pp. 137–141. It appears that the essence of these formulas was known before 1900. Hobson's derivation is based on a theorem he gave in Proc. London Math. Soc. **24,** 55 (1892).

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[8] See, for instance, M. J. Lighthill, *Introduction to Fourier Analysis and Generalised Functions* (Cambridge University Press, New York, 1958).

[9] E. U. Condon and G. H. Shortley, *The Theory of Atomic Spectra* (Cambridge University Press, London, 1935).

[10] M. Abramowitz and I. A. Stegun (Eds.), Natl. Bur. Std. (U.S.), Appl. Math. Ser. **55** (1964): (a) Eq. (10.1.47), p. 440; (b) Eq. (10.1.25), p. 439.

the double factorial function,

$$(2N)!!=2^N N!, \tag{8}$$

$$(2N-1)!!=(2N)!/(2N)!! \tag{9}$$

$$=(-1)^N/(-2N-1)!!, \tag{10}$$

the function,

$$\operatorname{sgn}(x)=x/|x|, \tag{11}$$

and the nth derivative of the delta function,[8]

$$\delta^{(n)}(x)=(d/dx)^n\delta(x). \tag{12}$$

III. FORMULATION

Write $r_{12}^n Y_l^m(\theta_{12},\phi_{12})$ as an inverse Fourier transform,

$$r_{12}^n Y_l^m(\theta_{12},\phi_{12})=(2\pi)^{-3}\times\int d^3\mathbf{k}\exp[-i\mathbf{k}\cdot(\mathbf{r}_1-\mathbf{r}_2)]\,\text{F.T.}\{r^nY_l^m\}.$$

Then use Eqs. (4) and (5) to obtain[11]

$$r_{12}^n Y_l^m(\theta_{12},\phi_{12})=\sum_{l_1=0}^{\infty}\sum_{l_2=|l-l_1|}^{l+l_1} v_{l_1l_2l}^{(n)}(r_1,r_2)\times\sum_{m_1=-l_1}^{l_1}\left(\frac{2l_2+1}{4\pi}\right)^{1/2}c^{l_2}(lm;l_1m_1)\times Y_{l_1}^{m_1}(\theta_1,\phi_1)Y_{l_2}^{m-m_1}(\theta_2,\phi_2), \tag{13}$$

where

$$\text{F.T.}\{r^nY_l^m\}\equiv\int dV\exp(i\mathbf{k}\cdot\mathbf{r})r^nY_l^m(\theta,\phi) \tag{14}$$

$$=4\pi i^lY_l^m(\theta_k,\phi_k)\mathfrak{F}_{nl}(k), \tag{15}$$

$$\mathfrak{F}_{nl}(k)=\int_0^\infty dr r^{n+2}j_l(kr), \tag{16}$$

and

$$v_{l_1l_2l}^{(n)}(r_1,r_2)=4(-1)^{(l-l_1+l_2)/2}\times\int_{-\infty}^{\infty}dk k^2 j_{l_1}(kr_1)j_{l_2}(kr_2)\mathfrak{F}_{nl}(k). \tag{17}$$

IV. EVALUATION OF $\mathfrak{F}_{nl}$ AND $v_{l_1l_2l}^{(n)}$

To evaluate $\mathfrak{F}_{nl}(k)$ it is necessary to use the theory of generalized functions. With Eq. (6), $\mathfrak{F}_{nl}(k)$ becomes

$$\mathfrak{F}_{nl}(k)=-\tfrac{1}{2}(-k)^l(k^{-1}d/dk)^{l+1}\int_{-\infty}^{\infty}dr\,|r|^{n-l}\cos kr. \tag{18}$$

The integral in Eq. (18) is the Fourier transform of $|r|^{n-l}$ in the generalized function sense,[12] which is[8]

$$\int_{-\infty}^{\infty}dr\,|r|^{n-l}\cos kr=2\pi(-1)^{(n-l)/2}\delta^{(n-l)}(k),\qquad(n-l\text{ even};\,n-l\geq0) \tag{19}$$

$$=\pi(-1)^{(n-l)/2}k^{l-n-1}\operatorname{sgn}(k)/(l-n-1)!,\qquad(n-l\text{ even};\,l-n\geq2) \tag{20}$$

$$=2(-1)^{(n-l+1)/2}(n-l)!k^{l-n-1},\qquad(n-l\text{ odd};\,n-l\geq1) \tag{21}$$

$$=2(-1)^{(n-l-1)/2}k^{l-n-1}(\log|k|+C)/(l-n-1)!,\qquad(n-l\text{ odd},\,l-n-1\geq0), \tag{22}$$

where C is an irrelevant constant which doesn't survive the differentiations in Eq. (18). When Eqs. (19)–(22) are inserted into Eq. (18), and it is realized that $\mathfrak{F}_{nl}(k)$ will always appear in an integral multiplied by a function vanishing at $k=0$ at least as fast as k^{l+1}, we find that

$$\mathfrak{F}_{nl}(k)=[(n+l+1)!!/(l-n-2)!!]k^{-n-3},\qquad(n-l\text{ odd}), \tag{23}$$

$$k^{l+1}\mathfrak{F}_{nl}(k)=k^{l+1}(n+l+1)!!(n-l)!!(-1)^{(n+l)/2}\pi\delta^{(n+2)}(k)/(n+2)!,\qquad(n-l\text{ even},\,n-l\geq0), \tag{24}$$

$$=k^{l+1}\tfrac{1}{2}\pi\frac{(n+l+1)!!}{(l-n-2)!!}k^{-n-3}\operatorname{sgn}(k),\qquad(n-l\text{ even},\,l-n-2\geq0). \tag{25}$$

Substituting Eqs. (23)–(25) into Eq. (17), using Eqs. (6) and (7), and also using

$$j_{l_1}(kr_1)j_{l_2}(kr_2)=\tfrac{1}{2}(-1)^{l_1+l_2}r_1^{l_1}(r_1^{-1}d/dr_1)^{l_1}r_1^{-1}r_2^{l_2}(r_2^{-1}d/dr_2)^{l_2}r_2^{-1}k^{-l_1-l_2-2}[\cos k(r_1-r_2)-\cos k(r_1+r_2)], \tag{26}$$

[11] Equation (13) is identical with Eq. (20) of H. J. Silverstone, J. Chem. Phys. **47**, 537 (1967), which sets up this problem by an equivalent method.

[12] In the ordinary function sense

$$\int_{-\infty}^{\infty}dr\,|r|^{n-l}\cos kr$$

has no meaning.

we obtain the very simple expressions,[13]

$$v_{l_1 l_2 l}^{(n)}(r_1, r_2) = 4\pi(-1)^{l_2}(n+l+1)!!(n-l)!! \sum_{\substack{\mu_1+\mu_2=(n-l_1-l_2)/2 \\ \mu_1\geq 0,\, \mu_2\geq 0}} \frac{r_1^{l_1+2\mu_1} r_2^{l_2+2\mu_2}}{(2l_1+2\mu_1+1)!!(2\mu_1)!!(2l_2+2\mu_2+1)!!(2\mu_2)!!},$$

$$[n-l \text{ even};\ n-l\geq 0. \text{ N.B., } v_{l_1 l_2 l}^{(n)}=0 \text{ when } l_1+l_2>n], \quad (27)$$

$$= 2\pi(-1)^{l_2+(n-l)/2}(n+l+1)!![(l-n-2)!!(n+l_1+l_2+2)!]^{-1} r_1^{l_1}(r_1^{-1}d/dr_1)^{l_1} r_1^{-1}$$

$$\times r_2^{l_2}(r_2^{-1}d/dr_2)^{l_2} r_2^{-1}[(r_1-r_2)^{n+l_1+l_2+2}\log|r_1-r_2| - (r_1+r_2)^{n+l_1+l_2+2}\log(r_1+r_2)],$$

$$(n-l \text{ even};\ l-n-2\geq 0), \quad (28)$$

$$= 2\pi(-1)^{l_2+(n-l-1)/2}(n+l+1)!![(l-n-2)!!(n+l_1+l_2+2)!]^{-1} r_1^{l_1}\left(\frac{r_1^{-1}d}{dr_1}\right)^{l_1} r_1^{-1}$$

$$\times r_2^{l_2}\left(\frac{r_2^{-1}d}{dr_2}\right)^{l_2} r_2^{-1}[(r_1-r_2)^{n+l_1+l_2+2}\operatorname{sgn}(r_1-r_2) - (r_1+r_2)^{n+l_1+l_2+2}\operatorname{sgn}(r_1+r_2)], \qquad (n-l \text{ odd}). \quad (29)$$

One can also treat the case n is not an integer by the present approach. The corresponding formulas are

$$\mathfrak{F}_{nl}(k) = \cos[\tfrac{1}{2}(n+l+1)\pi]\Gamma(n-l+2)\frac{(l-n-3)!!}{(-l-n-3)!!}|k|^{-n-3}(\operatorname{sgn}k)^l, \quad (23')$$

$$v_{l_1 l_2 l}^{(n)}(r_1, r_2) = 2\pi(-1)^{l_1+1}\Gamma(n-l+2)\frac{(l-n-3)!!}{(-l-n-3)!!}[\Gamma(n+l_1+l_2+3)]^{-1} r_1^{l_1}\left(\frac{r_1^{-1}d}{dr_1}\right)^{l_1} r_1^{-1} r_2^{l_2}\left(\frac{r_2^{-1}d}{dr_2}\right)^{l_2} r_2^{-1}$$

$$\times(|r_1+r_2|^{n+l_1+l_2+2} - |r_1-r_2|^{n+l_1+l_2+2}), \quad (27')$$

in which Γ denotes the gamma function, the gamma-function reflection formula has been used, and the ratio of double factorials has an obvious meaning. This case was treated by Sack,[3] but the above formulas are more transparent than his.

V. REMARKS

That the series (13) terminates when $n-l$ is even and nonnegative is well known. The simple version of Eq. (28) for the case $n-l$ even and negative, although implicit in Sack's work,[3] seems not to have been given before in its general form. We have left the derivatives explicitly in this formula (28) because for $n\leq -3$, taking the derivatives would produce a pole at r_1-r_2 which would not be integrable in the ordinary sense. This nonintegrability remains if one expands in $(r_</r_>)$. The integrals do exist in the generalized function sense, which here would be equivalent to taking the derivatives after integration or (when appropriate) to integrating by parts. The formula (29) for $n-l$ odd contains delta functions implicitly when $n\leq -3$ via

$$(d/dx)\operatorname{sgn}(x) = 2\delta(x). \quad (30)$$

The δ terms are discussed in the next section. A rather extensive set of recursion formulas for the $v_{l_1 l_2 l}^{(n)}$ has been given by Sack.[3]

VI. DELTA-FUNCTION TERMS

We now separate the delta-function terms from Eq. (29). Write for the case $n-l$ odd, $n\leq -3$,

$$v_{l_1 l_2 l}^{(n)}(r_1, r_2) = v_{l_1 l_2 l}^{(n)(\text{no }\delta)}(r_1, r_2) + v_{l_1 l_2 l}^{(n)(\delta)}(r_1, r_2). \quad (31)$$

The part without δ functions is easily written in terms of $r_>$ and $r_<$, the larger and smaller of r_1 and r_2, and their

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[13] In some equations, $\operatorname{sgn}(r_1+r_2)$ appears. Since both $r_1, r_2\geq 0$, $\operatorname{sgn}(r_1+r_2)$ is essentially $=1$. Moreover, the delta functions generated by $(d/dr_1)\operatorname{sgn}(r_1+r_2) = 2\delta(r_1+r_2)$ do not contribute to integrals for the cases discussed in this paper, because the integrands vanish sufficiently fast as $(r_1+r_2)\to 0$.

corresponding l's, $l_>$ and $l_<$:

$$v_{l_1l_2l}^{(n)(\text{no }\delta)}(r_1,r_2)=4\pi(-1)^{l_1+(n+l+1)/2}(n+l+1)!![(l-n-2)!!]^{-1}\sum_{\nu=0}^{(n+l_>-l_<+1)/2}$$
$$\times\frac{r_>^n(r_</r_>)^{l_<+2\nu}}{(n-l_1-l_2-2\nu)!!(n+l_>-l_<+1-2\nu)!!(2l_<+2\nu+1)!!(2\nu)!!},$$
$$(n-l\text{ odd. N.B., }v_{l_1l_2l}^{(n)(\text{no }\delta)}=0\text{ when }n+l_>-l_<+1<0). \quad (32)$$

The δ terms come only from the derivatives of $\mathrm{sgn}(r_1-r_2)$ in Eq. (29). Terms like $\delta(r_1+r_2)$ cannot give a nonzero contribution to integrals under the conditions discussed here. After a few minor manipulations to change r_1's into r_2's, the δ-function terms are seen to be

$$v_{l_1l_2l}^{(n)(\delta)}(r_1,r_2)=4\pi(-1)^{(n+l-1)/2}\frac{(n+l+1)!!}{(l-n-2)!!}\sum_{\mu_1=0}^{l_1}\sum_{\substack{\mu_2=0\\(-n-3-\mu_1-\mu_2\geq0)}}^{l_2}(-1)^{\mu_2}\frac{(l_1+\mu_1)!}{(l_1-\mu_1)!(2\mu_1)!!}$$
$$\times\frac{(l_2+\mu_2)!}{(l_2-\mu_2)!(2\mu_2)!!}r_2^{-\mu_2-1}\left(\frac{d}{dr_2}\right)^{-n-3-\mu_1-\mu_2}r_2^{1-\mu_1}\frac{\delta(r_1-r_2)}{r_1^2}. \quad (33)$$

Equation (33) can be plugged into Eq. (13), and the summations over l_1 and l_2 can be carried out with the aid of

$$(\lambda+\mu)![(\lambda-\mu)!]^{-1}Y_\lambda^m(\theta,\phi)=1\cdot\hat{1}^2\cdot[\hat{1}^2-2]\cdots[\hat{1}^2-\mu(\mu-1)]Y_\lambda^m(\theta,\phi) \quad (34)$$
$$=\{\prod_{\nu=1}^{\mu}[\hat{1}^2-\nu(\nu-1)]\}Y_\lambda^m(\theta,\phi), \quad (35)$$

where $\hat{1}^2$ denotes the usual dimensionless orbital angular-momentum operator squared, and where the empty product (case $\mu=0$) is to be intepreted as unity, and with the aid of

$$\sum_{l_2=|l-l_1|}^{l+l_1}[(2l_2+1)/4\pi]^{1/2}c^{l_2}(lm;l_1m_1)Y_{l_2}^{m-m_1}(\theta_2,\phi_2)=Y_l^m(\theta_2,\phi_2)Y_{l_1}^{m_1*}(\theta_2,\phi_2), \quad (36)$$

$$\sum_{l_1=0}^{\infty}\sum_{m_1=-l_1}^{l_1}Y_{l_1}^{m_1*}(\theta_2,\phi_2)Y_{l_1}^{m_1}(\theta_1,\phi_1)=\delta(\Omega_{12}), \quad (37)$$

to obtain

$$r_1^{-2}\delta(r_1-r_2)\delta(\Omega_{12})=\delta(\mathbf{r}_1-\mathbf{r}_2), \quad (38)$$

$$[r_{12}^nY_l^m(\theta_{12},\phi_{12})]^{(\delta)}=\sum_{l_1=0}^{\infty}\sum_{l_2=|l-l_1|}^{l+l_1}v_{l_1l_2l}^{(n)(\delta)}(r_1,r_2)\sum_{m_1=-l_1}^{l_1}\left(\frac{2l_1+1}{4\pi}\right)^{1/2}c^{l_2}(lm;l_1m_1)Y_{l_1}^{m_1}(\theta_1,\phi_1)Y_{l_2}^{m-m_1}(\theta_2,\phi_2) \quad (39)$$
$$=4\pi(-1)^{(n+l-1)/2}(n+l+1)!![(l-n-2)!!]^{-1}\sum_{\mu_1\geq0}\sum_{\substack{\mu_2\geq0\\(-n-3-\mu_1-\mu_2\geq0)}}(-1)^{\mu_2}[(2\mu_1)!!(2\mu_2)!!]^{-1}$$
$$\times r_2^{-\mu_2-1}\left(\frac{d}{dr_2}\right)^{-n-3-\mu_1-\mu_2}r_2^{1-\mu_1}\prod_{\nu_2=1}^{\mu_2}[\hat{1}_2^2-\nu_2(\nu_2-1)]Y_l^m(\theta_2,\phi_2)\prod_{\nu_1=1}^{\mu_1}[\hat{1}_2^2-\nu_1(\nu_1-1)]\delta(\mathbf{r}_1-\mathbf{r}_2),$$
$$(n-l\text{ odd},\ -n-3\leq0). \quad (40)$$

The specific cases given by Pitzer, Kern, and Lipscomb[7] are readily obtained in an orientation-unrestricted form:

$$[r_{12}^{-3}Y_2^m(\theta_{12},\phi_{12})]^{(\delta)}=-(4\pi/3)Y_2^m(\theta_2,\phi_2)\delta(\mathbf{r}_1-\mathbf{r}_2), \quad (41)$$

$$[r_{12}^{-4}Y_3^m(\theta_{12},\phi_{12})]^{(\delta)}=-(4\pi/15)\{r_2^{-1}(d/dr_2)r_2Y_3^m(\theta_2,\phi_2)+\tfrac{1}{2}r_2^{-1}[Y_3^m(\theta_2,\phi_2)\hat{1}_2^2-\hat{1}_2^2Y_3^m(\theta_2,\phi_2)]\}\delta(\mathbf{r}_1-\mathbf{r}_2). \quad (42)$$

Note that to use Eqs. (33) and (40)–(42), first integrate over $\mathbf{r}_1$, then operate with the (d/dr_2) and $\hat{1}_2^2$.

It should be realized that when used in an integral whose integrand consists of radial functions times Y_l^m's, the form of the delta-function terms given in Eq. (40) does not necessarily provide a computational advantage over Eqs. (33) and (39). Should the integrand be a more general function of (x, y, z), however, then Eq. (40) is more advantageous, because it yields a finite number of terms. In this case $\hat{1}_2^2$ and (d/dr_2) can be evaluated in Cartesian coordinates.

VII. SUMMARY

The use of the theory of generalized functions and Fourier transforms yields a simple derivation of the Laplace-type expansion for $r_{12}^nY_l^m(\theta_{12},\phi_{12})$, Eqs. (13), (27)–(29), (31)–(33), and (40). When $n-l$ is odd and $n\leq-3$, the expansion contains Dirac delta functions, which are automatically obtained in this approach. A unified formula, Eq. (40), for the delta-function terms is given.