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Original Investigations

Gauss' Theorem Approach to Delta Function Terms in Solid Spherical Harmonic Expansions

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The nature of the Dirac delta-function singularity in the expansion theorem for an irregular solid spherical harmonic about another centre is discussed for the case $l=2$. An alternative derivation, motivated by Hobson's derivative expression for solid spherical harmonics and utilizing Gauss' Divergence Theorem, is presented. The orientation dependence is then simply derived from the rotational properties of spherical harmonics.

Key words: Spherical harmonics, expansions in ~ – Addition theorems – Delta functions

1. Introduction

An intriguing aspect of the expansion of the irregular solid spherical harmonics $r^{-l-1}Y_l^m(\theta, \phi)$ in terms of solid spherical harmonics about another centre [1–3] is the appearance for $l-m \geqslant 2$ of certain singular terms involving Dirac δ-functions, first observed by Pitzer, Kern and Lipscomb [4–6].

These authors considered integrals of the type

$$\int f(\boldsymbol{r}_A) r_B^{-l-1} Y_l^m(\theta_B, \phi_B)\, dV \tag{1.1}$$

where $f(\boldsymbol{r}_A)$ is some function expressed in terms of coordinates with origin at centre A, and (r_B, θ_B, ϕ_B) are the polar coordinates with respect to another origin at centre B. Their technique involved a very careful handling of the volume in the vicinity of the centre $r_B=0$.

A later, alternative, approach due to Kay, Todd and Silverstone [7] used Fourier transform techniques, and invoked the theory of generalized functions [8] to obtain the δ-function terms.

In this paper, we derive the δ-function term for the case $l=2$ by utilizing Gauss' divergence theorem. In doing so, we clarify its relation to the standard generalized function realization of the 3-dimensional Dirac δ-function

$$\nabla^2(r^{-1}) = -4\pi\,\delta(\boldsymbol{r}), \tag{1.2}$$

which may also be interpreted in terms of the Green's function for Laplace's equation [9]. This gives an immediate intuitive feel for the nature of this term.

The importance of this term can be gauged from the fact that early calculations of anisotropic proton hyperfine interactions failed to take account of this term and thus found expressions for some integrals differing by an algebraic term from the correct results, as described by Pitzer *et al.* [4]. Indeed, in some circumstances, the missing term could even give the dominant contribution.

2. Calculation of the Delta-Function Term

Our starting point is the formula [10, 11]

$$r^{-l-1}P_l^m(\cos\theta)\,e^{\pm im\phi} = (-1)^l[(l-m)!]^{-1}\left(\frac{\partial}{\partial x}\pm i\frac{\partial}{\partial y}\right)^m\left(\frac{\partial}{\partial z}\right)^{l-m}(r^{-1}) \tag{2.1}$$

where P_l^m are the standard associated Legendre functions [12][1].

The case of most interest is the dipolar-type operator with $l=2$, a practical application of which has recently been given by us [13]. From Eq. (2.1) we have

$$2r^{-3}P_2(\cos\theta) = \frac{\partial^2}{\partial z^2}(r^{-1}). \tag{2.2}$$

The right-hand side of Eq. (2.2) is so reminiscent of Eq. (1.2) that it should now come as no surprise that a δ-function term arises from the left-hand side of Eq. (2.2).

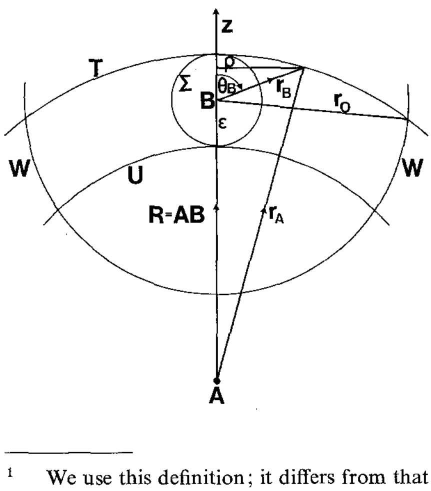

Fig. 1. The systems of coordinates

[1] We use this definition; it differs from that of Hobson [10] by a factor of $(-1)^m$.

Our method is based on that of Pitzer *et al.* [4], but we use Eq. (2.2) to convert the volume integral to a *surface* integral, part of which is trivially obtained by analogy with Eq. (1.2). Following Ref. [4], consider the expansion of the *function* $f(\boldsymbol{r}_A)$ as a Taylor series about the point $\boldsymbol{r}_B=\boldsymbol{r}_A-\boldsymbol{R}$, where $\boldsymbol{R}$ is the relative vector between the two centres, displaced along the z-axis, as in Fig. 1 (the case of arbitrary displacement direction is treated in Sect. 3). Then

$$f(\boldsymbol{r}_A)=f(\boldsymbol{R})+\boldsymbol{r}_B\cdot\nabla f(\boldsymbol{R})+\cdots. \tag{2.3}$$

Now power counting in the integral (1.1) shows that the second and higher terms in Eq. (2.3) cannot give any divergence problems for $l=2$ even near the surface of the sphere $r_A=R$. However, any non-zero contribution from the first term in Eq. (2.3) appearing in (1.1) through

$$f(\boldsymbol{R})\int_{\Delta} r_B^{-3}P_2(\cos\theta_B)\,dV, \tag{2.4}$$

where Δ is an infinitesimal region containing $r_B=0$, is equivalent to saying that there must be a term involving $\delta(\boldsymbol{r}_A-\boldsymbol{R})$ in the expansion of the *harmonic* $r_B^{-3}P_2(\cos\theta_B)$ in terms of r_A, θ_A, i.e. with respect to the centre at A.

For the cases $l=2$, $m=\pm 1$, the ϕ-integration will automatically give zero contribution.

Since the expansion formulae [1, 2] change their character according as $r_A \lesssim R$, we wish to evaluate the volume integral appearing in (2.4) in the spherical shell centred on A and bounded by $r_A=R\pm\varepsilon$, where ε is infinitesimal. As in Ref. [4], since the crucial point is clearly $r_B=0$, one excludes a small sphere of radius ε centred on B from the volume of integration $\hat{\Delta}$, and need only consider integration to some fixed finite distance $r_0(<R)$ from B (see Fig. 1), since later ε tends to zero.

Our method of evaluation hinges on Gauss' theorem and integral [14]. We recall Eq. (2.2) and convert the volume integral

$$I=\int_{\hat{\Delta}}\frac{\partial^2}{\partial z^2}(r_B^{-1})\,dV \tag{2.5}$$

(where the integrand is now free of singularities in the volume $\hat{\Delta}$) to a surface integral by Gauss' theorem:

$$I=\int_S\frac{\partial}{\partial z}(r_B^{-1})\hat{\boldsymbol{k}}\cdot d\boldsymbol{S}. \tag{2.6}$$

Here, $\hat{\boldsymbol{k}}$ is the unit vector in the z-direction and $d\boldsymbol{S}$ is the surface element with normal directed *outwards*. The surface S consists of the top shell surface T with $r_A=R+\varepsilon$ and the underneath shell surface U with $r_A=R-\varepsilon$, out as far as the surface of radius r_0 centred on B, the part W of this latter surface enclosed by the former shell, and the (inside) surface Σ of the small sphere with radius ε centred on B. (See Fig. 1.)

It follows immediately as for Gauss' integral formula [14] that

$$\int_{\Sigma} \frac{\partial}{\partial z}(r_B^{-1})\hat{\boldsymbol{k}}\cdot d\boldsymbol{S} = +4\pi/3 \tag{2.7}$$

independent of the value of ε. The plus sign occurs because the outward normal to our surface points into the sphere and the factor $\frac{1}{3}$ (by symmetry) because the differential operator in Eq. (2.5) is not the full ∇^2.

We also immediately deduce that

$$\mathrm{Lim}_{\varepsilon\to 0} \int_{W} \frac{\partial}{\partial z}(r_B^{-1})\hat{\boldsymbol{k}}\cdot d\boldsymbol{S} = 0 \tag{2.8}$$

because $r_B = r_0$ is a fixed finite radius and the surface width of order 2ε tends to zero.

It remains to evaluate over the relevant parts T and U of the top and underneath shell surfaces the integral

$$\int \frac{\partial}{\partial z}(r_B^{-1})\hat{\boldsymbol{k}}\cdot d\boldsymbol{S} = \mp \int\int z_B r_B^{-3} \rho \, d\rho \, d\phi \tag{2.9}$$

since $d\boldsymbol{S}\cdot\hat{\boldsymbol{k}}$ is just the signed projection of the curved surface element dS onto the x–y plane, which may then be expressed in cylindrical polar coordinates. Here, ϕ is the azimuthal angle measured around the z_B-axis, and ρ is the perpendicular distance from the z_B-axis to a point on the shell. The $\mp$ signs refer to T and U respectively. The ϕ integral immediately gives a factor 2π.

To evaluate Eq. (2.9) it is convenient to express the variables in terms of the polar angle $\theta \equiv \theta_B$:

$$z_B = r_B \cos\theta, \qquad \rho = r_B \sin\theta. \tag{2.10}$$

Thus

$$r_B^{-1}\, d\rho = \cos\theta \, d\theta + \sin\theta r_B^{-1}\, dr_B. \tag{2.11}$$

On the surfaces T and U, the cosine rule gives

$$r_B^2 + 2Rr_B\cos\theta = \pm 2R\varepsilon + \varepsilon^2 \tag{2.12}$$

where $\pm$ refers to T and U respectively. Thus

$$\cos\theta r_B^{-1}\, dr_B = \sin\theta \, d\theta - R^{-1}\, dr_B. \tag{2.13}$$

Combining (2.10), (2.11) and (2.13) we get

$$\begin{aligned} z_B r_B^{-3}\rho \, d\rho &= \cos\theta \sin\theta r_B^{-1}\, d\rho \\ &= \sin\theta \, d\theta - R^{-1}\sin^2\theta \, dr_B \end{aligned} \tag{2.14}$$

On the top surface T, (2.12) gives

$$r_B = -R\cos\theta + [R^2\cos^2\theta + 2R\varepsilon + \varepsilon^2]^{1/2} \tag{2.15}$$

so

$$r_B = R[-\cos\theta + |\cos\theta|] + \text{terms of order } \varepsilon. \tag{2.16}$$

One can of course use (2.15) in (2.14) to evaluate the integral (2.9). Much easier integrals are obtained by using (2.16) in (2.14) to evaluate (2.9), after noting that the right-hand sides of (2.14) and (2.16) are free of any possible singularity, no matter how small ε is. In either case we find, after splitting the range of θ integration into two parts about $\pi/2$ as implied by (2.16), that

$$\text{Lim}_{\varepsilon\to 0}\int_T z_B r_B^{-3}\rho\, d\rho = 1 + \cos\gamma - \tfrac{2}{3}\cos^3\gamma \tag{2.17}$$

where γ is the final limit as the shell width $2\varepsilon \to 0$ of the angle between the radius line r_0 and the positive z-axis. This is given from (2.12) by

$$\cos\gamma = -\tfrac{1}{2}R^{-1}r_0 \tag{2.18}$$

so $\gamma > \pi/2$.

On the underneath surface U,

$$r_B = -R\cos\theta \mp [R^2\cos^2\theta - 2R\varepsilon + \varepsilon^2]^{1/2} \tag{2.19}$$

where the $\mp$ signs correspond respectively to whether θ_B decreases (from π) or then increases as r_B increases and moves along U (see Fig. 1). The minimum value attained by θ clearly approaches $\pi/2$ for very small ε. Integration as above then gives

$$\text{Lim}_{\varepsilon\to 0}\int_U z_B r_B^{-3}\rho\, d\rho = -1 + \cos\gamma - \tfrac{2}{3}\cos^3\gamma. \tag{2.20}$$

Combining all these results, we have proved via surface integration that

$$\text{Lim}_{\varepsilon\to 0}\int_{\hat{A}} r_B^{-3}P_2(\cos\theta_B)\, dV = -4\pi/3 \tag{2.21}$$

as required. That is, the expansion of $r_B^{-3}P_2(\cos\theta_B)$ about the second centre A contains the singular term $-(4\pi/3)\,\delta(\boldsymbol{r}_A - \boldsymbol{R})$, when $\boldsymbol{R}$ is directed along the z-axis. This term must be included when evaluating integrals of the type (1.1) for $l=2$ when the point $r_B = 0$ is contained in the integration volume.

This is the approach, based on expansion theorems such as those of Chiu [2], which was used by us in analytically evaluating some integrals of the type (1.1) when $f(\boldsymbol{r}_A)$ is the square of a Slater wavefunction centred on A [13].

3. Orientation Dependence

We conclude by discussing the case when $\boldsymbol{R}$ is not necessarily directed along the z-axis.

The result obtained by the procedure of Pitzer *et al.* [4] might have appeared not to be orientation-dependent if one only had to consider a small *spherical* volume centred on B. However, it is the fact that the expansion nature changes [1] at $r_A = R$ which leads to the consideration of part of the thin *shell* about $r_A = R$ near $\boldsymbol{r}_A = \boldsymbol{R}$. This shell piece (see Fig. 1) clearly defines a direction (normal to its mid-point) and thus gives an orientation dependence in the general case.

We now recover the general orientation result [7] for $l=2$ directly from the preceding z-direction result by a straightforward application of the transformation properties of the surface spherical harmonics [15] Y_l^m under the rotation group [16].

Let $\theta_{R'}$, $\phi_{R'}$ be the polar coordinates of a general displacement vector $\boldsymbol{R}'$ relative to the $\boldsymbol{R}$ along the (old) z-axis considered above. Then if $\boldsymbol{r}_A = \boldsymbol{r}_B + \boldsymbol{R}'$, the Euler angles of the rotation about B from the direction of $\boldsymbol{R}'$ to the direction of $\boldsymbol{R}$ are, as described by Chiu [2], 0, $-\theta_{R'}$, $-\phi_{R'}$. Then from the transformation property of the surface spherical harmonics under rotations given by Rose [16]

$$Y_l^m(\theta_B, \phi_B) = \sum_{m'} D_{m'm}^{(l)}(0, -\theta_{R'}, -\phi_{R'}) Y_l^{m'}(\theta_B', \phi_B'). \tag{3.1}$$

Here θ_B', ϕ_B' are the polar angles of $\boldsymbol{r}_B$ relative to the direction $\boldsymbol{R}'$ and θ_B, ϕ_B are those relative to $\boldsymbol{R}$; $D_{m'm}^{(l)}$ is the matrix element of the $(2l+1)$-dimensional representation of the rotation group.

Denoting by $\{\ \}_\delta$ the δ-function term in the expansion, we therefore have for the case $l=2$, where only $m'=0$ is known to contribute,

$$\{r_B^{-3} Y_2^m(\theta_B, \phi_B)\}_\delta = D_{0m}^{(2)}(0, -\theta_{R'}, -\phi_{R'})\{r_B^{-3} Y_2^0(\theta_B', \phi_B')\}_\delta \tag{3.2}$$

$$= Y_2^m(\theta_{R'}, \phi_{R'})(-4\pi/3)\,\delta(\boldsymbol{r}_A - \boldsymbol{R}') \tag{3.3}$$

as desired. In deriving (3.3) from Eq. (3.2), we have used the standard relations [16] of the D_{0m}'s to the Y_l^m's, together with the result of our preceding calculation which in fact corresponded to polar angles (θ_B', ϕ_B') measured with respect to the displacement direction.

This completes our derivation of the orientation-dependence of the δ-function term in the expansion of the irregular solid spherical harmonic with $l=2$ relative to a second centre from which it is separated by an arbitrarily directed vector $\boldsymbol{R}'$.

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