ON THE EXPANSION OF A COULOMB POTENTIAL IN SPHERICAL HARMONICS

BY B. C. CARLSON AND G. S. RUSHBROOKE

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1. Introduction and summary. The addition theorem for Legendre functions leads as is well known, to a useful expansion formula† of importance in the theory of electrostatic potentials,

\[ \frac{1}{r_{12}} = \sum_{l=0}^{\infty} \frac{r_{1}^{l}}{l^{2} + \frac{1}{2} (l + m)!} \sum_{m=-l}^{l} (2-\delta_{m}^{0}) P_{m}^{l}(\cos \theta_{1}) P_{m}^{l}(\cos \theta_{2}) \cos m(\phi_{1}-\phi_{2}) \]

(\delta_{m}^{0} = 0 \text{ when } m = 0; \delta_{m}^{0} = 1), \hspace{1cm} (1a)

or, in an alternative notation,

\[ \frac{1}{r_{12}} = \sum_{l=0}^{\infty} \frac{r_{1}^{l}}{l^{2} + \frac{1}{2} (l + m)!} \sum_{m=-l}^{l} (-1)^{m} Y_{l}^{m}(\theta_{1}, \phi_{1}) Y_{l}^{-m}(\theta_{2}, \phi_{2}). \] \hspace{1cm} (1b)

Fig. 1.

Here \( r_{12} \) is the distance between two points whose polar coordinates relative to a common origin, Fig. 1, are \((r_{1}, \theta_{1}, \phi_{1})\) and \((r_{2}, \theta_{2}, \phi_{2})\); \( r_{\geq} \) is the greater and \( r_{\leq} \) the lesser of \( r_{1} \) and \( r_{2} \). The associated Legendre function \( P_{m}^{l}(\cos \theta) \) is defined by‡

\[ P_{m}^{l}(\cos \theta) = (-1)^{m} \sin^{m} \theta \frac{d^{m} P_{l}(\cos \theta)}{d(\cos \theta)^{m}}, \]

\[ P_{l}^{-m}(\cos \theta) = (-1)^{m} \frac{(l-m)!}{(l+m)!} P_{l}^{m}(\cos \theta), \]

where \( m \geq 0 \) and \( P_{l} \) is the Legendre polynomial of degree \( l \). \( Y_{l}^{m}(\theta, \phi) \) is a spherical harmonic of degree \( l \) and order \( m \), defined for both positive and negative \( m \) by§

\[ Y_{l}^{m}(\theta, \phi) = \frac{(-1)^{m} (2l+1)!}{(l+m)! 4\pi} P_{l}^{m}(\cos \theta) e^{im\phi}. \]

§ Our \( Y_{l}^{m} \) is the same for all \( m \) as \( \Theta(\pm m) \sqrt{(2m)!} \) defined by E. U. Condon and G. H. Shortley, The theory of atomic spectra (Cambridge, 1935), p. 52.
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(4)

\[ [Y^m_l(\theta, \phi)]^* = (-1)^m Y^{-m}_l(\theta, \phi), \]

and that it is normalized to unity in the sense that

\[ \int_0^{2\pi} \int_0^\pi |Y^m_l(\theta, \phi)|^2 \sin \theta \, d\theta \, d\phi = 1. \]

Our primary purpose in this paper is to derive an analogous expansion for the case which \((r_1, \theta_1, \phi_1)\) and \((r_2, \theta_2, \phi_2)\) relate to different origins, at a distance \(R\) apart. The analysis for such an expansion is most evident in the theory of intermolecular forces, in which it is useful to be able to expand \(r^{-1}\) in successive powers of \(R^{-1}\), and \(R\) may be regarded as large compared with \(r_1\) and \(r_2\). The first few terms of the expansion are easily obtained, but we have failed to find in the literature any statement of the complete formula, which proves to have a remarkably simple form.

We shall first derive the expansion for the case illustrated in Fig. 2, in which \((r_1, \theta_1, \phi_1)\) and \((r_2, \theta_2, \phi_2)\) relate to mutually parallel axes at origins \(O_1\) and \(O_2\) and \(O_1O_2\) of length \(R\), lies along the common \(Z\)-axis. The resulting formulae, analogous to (Ia) and (Ib) above, are

\[ \sum_{l_1=0}^{\infty} \sum_{l_2=0}^{\infty} \frac{(-1)^{l_1} r_1^{l_1} r_2^{l_2}}{R^{l_1+l_2+1}} \sum_{m=0}^{m \leq 0} \frac{(l_1+l_2)!}{(l_1+m)!} \frac{(2-\delta_{l_10})}{(l_2+m)!} P_{l_1}^m(\cos \theta_1) P_{l_2}^m(\cos \theta_2) \cos m(\phi_1-\phi_2) \]

and

\[ \sum_{l_1=0}^{\infty} \sum_{l_2=0}^{\infty} \frac{(-1)^{l_1} r_1^{l_1} r_2^{l_2}}{R^{l_1+l_2+1}} \frac{4\pi(l_1+l_2)!}{((2l_1+1)(2l_2+1))^{3/2}} \sum_{m=0}^{m \leq 0} \frac{Y_{l_1}^m(\theta_1, \phi_1) Y_{l_2}^{-m}(\theta_2, \phi_2)}{(l_1+m)! (l_1-m)! (l_2+m)! (l_2-m)!} \]

respectively. We note, of course, that \(P_{l}^m(\cos \theta)\) and \(Y_{l}^m(\theta, \phi)\) vanish whenever \(m > l\).

It is then an easy matter to obtain the corresponding formulæ for the rather more general case, illustrated in Fig. 3, in which, whilst the two sets of axes are still mutually parallel, the line \(O_1O_2\) no longer lies along the \(Z\)-axis but has polar angles \((\Theta, \Phi)\) relative to the axes at \(O_1\).

† Terms up to an including \(R^{-4}\) are correctly given in Cartesian coordinates by R. Heller, J. Chem. Phys. 9 (1941), 156. Elsewhere the quadrupole term has often been written with one or more errors of sign.
The expansions in this case are

\[
\frac{1}{r_{12}} = \sum_{i=0}^{\infty} \sum_{l_{12}=-i}^{i} \frac{(-1)^{l_{12}} r_{12}^{l_{12}}}{R^{l_{12}+1}} \frac{(l_{1} + l_{2} - |m_{1} + m_{2}|)!}{(l_{1} + |m_{1}|)! (l_{2} + |m_{2}|)!} P_{l_{1}+l_{2}}^{m_{1}+m_{2}}(\cos \Theta) P_{l_{1}}^{m_{1}}(\cos \Theta_{1}) \times P_{l_{2}}^{m_{2}}(\cos \Theta_{2}) (-1)^{p_{1}^2} \cos ((m_{1} + m_{2}) \Phi - m_{1} \phi_{1} - m_{2} \phi_{2}),
\]

where \(2p = |m_{1}| + |m_{2}| - |m_{1} + m_{2}|\), and

\[
\frac{1}{r_{12}} = \sum_{i=0}^{\infty} \sum_{l_{12}=-i}^{i} \frac{(-1)^{l_{12}} r_{12}^{l_{12}}}{R^{l_{12}+1}} \frac{l_{1}}{m_{1}=-l_{1}} \frac{l_{2}}{m_{2}=-l_{2}} B_{l_{1}l_{2}m_{1}}^{m_{2}} Y_{l_{1}+l_{2}}^{m_{1}+m_{2}}(\Theta, \Phi) Y_{l_{1}}^{m_{1}}(\theta_{1}, \phi_{1}) Y_{l_{2}}^{m_{2}}(\theta_{2}, \phi_{2}),
\]

where

\[
B_{l_{1}l_{2}m_{1}}^{m_{2}} = \frac{(-1)^{m_{1}+m_{2}} (4\pi)^{l_{1}+l_{2}}}{(2l_{1}+1)(2l_{2}+1)(2l_{1}+2l_{2}+1)!} \left( \frac{l_{1}+l_{2}+m_{1}+m_{2}}{l_{1}+l_{2}-m_{1}-m_{2}} \right)! \left( \frac{l_{1}+l_{2}-m_{1}-m_{2}}{l_{1}+l_{2}+m_{1}+m_{2}} \right)! \left( \frac{l_{1}+m_{1}}{l_{1}-m_{1}} \right)! \left( \frac{l_{1}-m_{1}}{l_{1}+m_{1}} \right)! \left( \frac{l_{2}+m_{2}}{l_{2}-m_{2}} \right)! \left( \frac{l_{2}-m_{2}}{l_{2}+m_{2}} \right)!.
\]

Fig. 3.

In the following derivation of these formulae we shall make use of the Wigner coefficients, which arise in the reduction of the direct product of two irreducible representations of the rotation group†. We have obtained the expansion (II) by two other methods, using in one the generating function for the associated Legendre functions and Maxwell's theory of poles;‡ in the other. The expansion (III) has also been obtained directly by Maxwell's theory of poles. However, the most interesting aspect of these expansions is their simplicity when expressed in terms of Wigner functions (see below). The other derivations use more familiar methods of analysis, but give no hint of the simple symmetry properties of the result.

2. Derivation of formulae. With the choice of axes shown in Fig. 2,

\[
\frac{1}{r_{12}} = \left( (x_{1} - x_{2})^{2} + (y_{1} - y_{2})^{2} + (z_{1} - z_{2} - R^{2})^{2} \right)^{-1/2}
\]

\[
\frac{1}{r_{12}} = \frac{1}{R} \left( 1 - \frac{2(z_{1} - z_{2})}{R} + \frac{(x_{1} - x_{2})^{2} + (y_{1} - y_{2})^{2} + (z_{1} - z_{2})^{2}}{R^{2}} \right)^{-1/2}
\]

The power series in \(z_{1}, \ldots, z_{2}\) obtained by binomial expansion of (7) converges absolutely if

\[
2 \frac{|z_{1}| + |z_{2}|}{R} + \sum_{x, y, z} \frac{|x_{1}| + |x_{2}| + |y_{1}| + |y_{2}|}{R^{2}} < 1,
\]


‡ Hobson, E. W., loc. cit. §§ 83, 85, 88, 101 and 103.
and therefore if \( r_1 + r_2 < (\sqrt{2} - 1) R \). Under this condition, the terms can be so rearranged that

\[ \frac{1}{r_{12}} = \sum_{l_1=0}^{\infty} \sum_{l_2=0}^{\infty} \frac{1}{R(l_1,l_2 + 1) + f_{l_1,l_2}(x_1, y_1, z_1; x_2, y_2, z_2)}, \]

where \( f_{l_1,l_2} \) is a homogeneous polynomial in each of the two sets of variables

\[ f_{l_1,l_2}(\lambda x_1, \lambda y_1, \lambda z_1; \mu x_2, \mu y_2, \mu z_2) = \lambda^l \mu^l f_{l_1,l_2}(x_1, y_1, z_1; x_2, y_2, z_2). \]

We observe that \((r_{12})^{-1}\), as defined by (8), is a harmonic function in each of the two sets of variables. Since application of either Laplacian does not mix together terms with different degrees \( l_1 \) and \( l_2 \), the same statement must hold for \( f_{l_1,l_2} \), which can therefore be written as

\[ r_1^{l_1} r_2^{l_2} \sum_{\substack{m_1=-l_1 \cdots \sum \substack{m_2=-l_2 \cdots \alpha_{l_1,l_2}^{m_1,m_2} Y_{l_1}^{m_1}(\theta_1, \phi_1) Y_{l_2}^{m_2}(\theta_2, \phi_2).}}\]

The \( \alpha \)'s are constant coefficients which remain to be determined; the spherical polar coordinates are defined for each subscript by \( z = r \cos \theta \) and \( x + iy = r \sin \theta e^{i\phi} \).

If the \( X_1 Y_1 Z_1 \) axes are subjected to an arbitrary rotation, \( \mathcal{R} \), the set of \((2l_1 + 1)\) spherical harmonics \( Y_{l_1}^{m_1}(\theta_1, \phi_1) \) \((m_1 = -l_1, -l_1 + 1, \ldots, l_1)\) undergoes a homogeneous linear transformation, of which the matrix of coefficients, \( D^{(\phi)}(\mathcal{R}) \), belongs to an irreducible representation of the rotation group. This \((2l_1 + 1)\)-dimensional representation is symbolized by \( D^{(\phi)} \). If the same rotation is applied coherently to the \( X_2 Y_2 Z_2 \) axes, the set of \((2l_2 + 1)\) \((2l_2 + 1)\) 'product functions' \( F_{l_2}^{m_2}(\theta_1, \phi_1) Y_{l_2}^{m_2}(\theta_2, \phi_2) \) transforms according to the direct-product matrix \( D^{(\phi)}(\mathcal{R}) \times D^{(\phi)}(\mathcal{R}) \). However, the direct-product representation \( D^{(\phi)} \times D^{(\phi)} \) is reducible if neither \( l_1 \) nor \( l_2 \) is zero; there exists a unitary matrix which reduces it by similarity transformation to a block form symbolized by

\[ \sum_{L} D^{(L)} \quad (L = |l_1 - l_2|, \ldots, l_1 + l_2 - 1, l_1 + l_2). \]

The reduction amounts merely to choosing (as a new set of orthonormal basis functions) appropriate linear combinations of the original 'product functions'. The array of coefficients of these linear combinations determines the unitary matrix already mentioned. A formula for the coefficients \( S_{l_1,l_2}^{M} ; m_1, m_2 \) was derived by Wigner and the linear combinations

\[ W_{L,l_1,l_2}^{M}(\theta_1, \phi_1; \theta_2, \phi_2) = \sum_{(m_1,m_2) = M} S_{l_1,l_2}^{M} ; m_1, m_2 Y_{l_1}^{m_1}(\theta_1, \phi_1) Y_{l_2}^{m_2}(\theta_2, \phi_2), \]

\((M = -L, -L + 1, \ldots, L)\), \((L = |l_1 - l_2|, \ldots, l_1 + l_2 - 1, l_1 + l_2)\), will be referred to as Wigner functions. The set of \((2L + 1)\) functions with given \( L, l_1, l_2 \) transforms under proper rotation (applied coherently to both sets of axes) with exactly the same transformation coefficients as the corresponding set of \((2L + 1)\) spherical harmonics \( Y_{l_2}^{m_2}(\theta, \phi) \) in one set of variables.

Equations (10) permit a unique solution for the 'product functions' as linear combinations of Wigner functions, and (9) can consequently be rewritten in the form

\[ r_2^{l_2} \sum_{L=|l_1-l_2|}^{l_1+l_2} \sum_{M=-L}^{L} \beta_{l_1,l_2}^{L} W_{L,l_1,l_2}^{M}(\theta_1, \phi_1; \theta_2, \phi_2). \]

To determine the constant coefficients \( \beta \), we observe first that equation (6) is invariant under the group of axial rotations and reflexions (applied to both coordinate systems at once) associated with the common \( Z \)-axis. Both types of operation are represented
in Cartesian coordinates by homogeneous linear substitutions; hence \( f_{\lambda, \mu} \) must possess the same invariance. On the other hand, under a proper axial rotation through an arbitrary angle \( \alpha \), \( W_{\lambda, \mu}^{(M)} \) acquires a multiplicative factor \( e^{iM\alpha} \). From the linear independence of the Wigner functions it follows that the constants \( \beta \) vanish except when \( M = 0 \). Under axial reflexion as contrasted with a proper rotation, \( W_{\lambda, \mu}^{(0)} \) may not behave like \( Y_{\lambda} \). We note that any one of the three following operations is equivalent to the product of the other two, regardless of whether they are applied to a single set of axes or simultaneously to two sets: (a) reflexion in the \( XZ \) plane, (b) inversion in the origin of coordinates, (c) proper rotation through an angle \( \pi \) about the \( Y \)-axis. Now \( Y_{\lambda} \) (a Legendre polynomial normalized to unity) is invariant under (a) and acquires a factor \( (-1)^{L} \) under (b). It follows that both \( Y_{\lambda} \) and \( W_{\lambda, \mu}^{(0)} \) acquire a factor \( (-1)^{L} \) under the proper rotation (c). But by definition (10) the Wigner function has parity given by \( I_{1} + I_{2} \) and consequently acquires a factor \( (-1)^{L+I_{1}+I_{2}} \) under (a). We conclude that

\[
\frac{1}{r_{12}} = \sum_{L} \sum_{\lambda=0}^{\infty} \sum_{\mu=0}^{\infty} \frac{r_{1}^{L+1} r_{2}^{L+1}}{R^{L+4+1}} \sum_{\lambda_{1} \lambda_{2}} \ell_{\lambda_{1} \lambda_{2}} W_{\ell_{\lambda_{1} \lambda_{2}}}(\theta_{1}, \varphi_{1}; \theta_{2}, \varphi_{2}),
\]

where the summation now extends over \( L = |I_{1} - I_{2}|, |I_{1} + I_{2}| + 1, \ldots, I_{1} + I_{2} - 2, I_{1} + I_{2} \).

The remaining \( \beta \)'s may be evaluated by comparison with the special case in which \( r_{1} \) and \( r_{2} \) are parallel. In these circumstances, \( r_{1}^{2} = (r_{1} - r_{2})^{2} + R^{2} - 2(r_{1} - r_{2}) R \cos \theta_{1} \), and an elementary expansion in Legendre polynomials yields

\[
\frac{1}{r_{12}} = \sum_{k=0}^{\infty} \frac{(r_{1} - r_{2})^{k}}{R^{k+1}} \left[ \frac{4\pi}{2k+1} \right]^{1} Y_{k}^{0}(\theta_{1}).
\]

Since it represents a special case of the expansion of (7), this series is absolutely convergent if \( r_{1} + r_{2} < (\sqrt{2} - 1) R \). (The condition is sufficient though not necessary.) After rearrangement of terms,

\[
\frac{1}{r_{12}} = \sum_{L=0}^{\infty} \sum_{\lambda=0}^{\infty} \frac{(-1)^{L+1} r_{1}^{L+1} r_{2}^{L+1} (I_{1} + I_{2})!}{R^{L+4+1}} \frac{4\pi}{2L_{1} + 2L_{2} + 1} \left[ \frac{2L_{1} + 2L_{2} + 1}{2L_{1} + 2L_{2} + 1} \right]^{1} Y_{L_{1} + L_{2}}^{0}(\theta_{1}).
\]

To establish a comparison between (12) and (13), we must find out what happens to the Wigner functions when we set \( \theta_{1} = \theta_{2}, \varphi_{1} = \varphi_{2} \). These substitutions have no effect on the coefficients of the linear homogeneous equations describing the behaviour of the Wigner functions under rotations or reflexions (these operations being interpreted after the substitution as operations on a single set of axes). In particular,

\[
W_{\lambda_{1} \mu_{1}}^{(M)}(\theta_{1}, \varphi_{1}; \theta_{1}, \varphi_{1}) \text{ is a function of (a single set of variables) which transforms under proper rotations exactly like } Y_{L}^{M}(\theta_{1}, \varphi_{1}), \text{ and we suspect that the two are closely related. In fact, from (10) the former function is clearly well behaved and can be expanded in a (finite) series of spherical harmonics. But the only spherical harmonic which shares with it the property of belonging to the } M \text{th row of the irreducible representation } D^{(M)} \text{ of the rotation group is } Y_{L}^{M}(\theta_{1}, \varphi_{1}). \text{ Spherical harmonics of other degrees or orders must be orthogonal to it because of the orthogonality relations for functions belonging to different irreducible representations or to different rows of the same representation. The series thus reduces to a single term}
\]

\[
W_{\lambda_{1} \mu_{1}}^{(M)}(\theta_{1}, \varphi_{1}; \theta_{1}, \varphi_{1}) = C_{\lambda_{1} \mu_{1}}^{(M)} Y_{L}^{M}(\theta_{1}, \varphi_{1}).
\]

In order that a set of \( 2L + 1 \) \( W \)'s may transform under rotation exactly like the corresponding set of \( 2L + 1 \) \( Y \)'s, the coefficients \( C \) must fairly obviously be independent
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of $M$. And, in fact, a proof of this statement follows very easily from the theorem that only a constant multiple of the unit matrix can commute with all the matrices of an irreducible representation.

Equation (14) shows that when $l_1 + l_2 - L$ is odd, $C_{L,h_1}$ must be zero for reasons of parity. When $l_1 + l_2 - L$ is even, the value of $C_{L,h_1}$ may be determined in the following way. Since the matrix of the Wigner coefficients is real as well as unitary, the solution of equations (10) is

$$Y_{l_1}^m(\theta_1, \phi_1) Y_{l_2}^{m'}(\theta_2, \phi_2) = \sum_{L} \sum_{m_1, m_2} S^{l_1 l_2}_L (m_1 m_2; m_1, m_2) W_{L}^{m + m'}(\theta_1, \phi_1; \theta_2, \phi_2).$$  \hspace{1cm} (15)

The summation extends over $L' = |l_1 - l_2|, \ldots, l_1 + l_2 - 1, l_1 + l_2$. We set $\theta_1 = \theta_2 = \theta$, $\phi_1 = \phi_2 = \phi$, multiply by the complex conjugate of $Y_{L}^{m+m'}(\theta, \phi)$, and integrate, obtaining

$$\int\{Y_{L}^{m+m'}(\theta, \phi)\}^* Y_{L}^{m}(\theta, \phi) Y_{L}^{m}(\theta, \phi) \sin \theta d\theta d\phi = \delta_{(L_1, m_1; m_2, m_2)} C_{L, h_1, h_2}.$$ \hspace{1cm} (16)

A general formula for the integral of a product of three tesseral harmonics has been given by Gaunt. Neither Gaunt's formula nor the formula for the Wigner coefficients has been summed in the general case, but each reduces to a single term if $M = m_1 + m_2 = L$,

a condition which imposes no restriction upon $L$. Substitution of the two formulae in (16), with $m_1 + m_2 = L$, shows that

$$C_{L, h_1} = (-1)^{L - L_1} \frac{(2L + 1)(2L + 2)|^{L - g - L_2|^{L - g - L_2|^{L - g - L_2|^{L - g - L_2|^{L - g - L_2}}}}}{4\pi (2L + 1)!},$$ \hspace{1cm} (17)

when $l_1 + l_2 - L$ is even. $g$ is defined by $2g = l_1 + l_2 + L$. We are primarily concerned with the equation to which (17) reduces when $L = l_1 + l_2 = g$:

$$C_{g, h_1} = \frac{(l_1 + l_2)! (2l_1 + 1)!}{l_1! l_2!} \frac{4\pi (2l_1 + 2l_2 + 1)!}{4\pi (2l_1 + 2l_2 + 1)!}.$$

We can now return to the comparison of (12) and (13), setting $\theta_1 = \theta_2$ and $\phi_1 = \phi_2$ in the form. Then

$$\sum_{L} \sum_{h_1} Y_{L}^0(\theta_1) C_{L, h_1} \frac{(l_1 + l_2)!}{l_1! l_2!} (-1)^L \frac{4\pi}{(2l_1 + 2l_2 + 1)!} W_{L}^{0}(\theta_1).$$

$C$ is different from zero when $l_1 + l_2 - L$ is even, and it is precisely over such values of $L$ that the summation in (12) extends. It follows that $\beta$ is zero except when $L = l_1 + l_2$, and that

$$\beta_{l_1 + l_2, h_1} = (-1)^L 4\pi \frac{(2l_1 + 2l_2)!}{(2l_1 + 1)! (2l_2 + 1)!}.$$

Equation (12) now yields the expansion of $(r_{12})^{-1}$ in Wigner functions:

$$\frac{1}{r_{12}} = \sum_{l_1 = 0}^{\infty} \sum_{m_1 = 0}^{\infty} (-1)^{l_1} \frac{r_{12}^{l_1}}{R_{l_1 + 1}^{l_1 + 1} + 1} 4\pi \frac{(2l_1 + 2l_2)!}{(2l_1 + 1)! (2l_2 + 1)!} W_{l_1 + l_2, h_1}^{0}(\theta_1, \phi_1; \theta_2, \phi_2).$$ \hspace{1cm} (18)

Because of the simple rotational behaviour of the Wigner functions, the expansion in the form (18) is sometimes useful as it stands. Alternatively, if an expansion in ordinary

† J. A. Gaunt, Philos. Trans. A, 228 (1929), 151. Gaunt's formula is written in notation very similar to ours by Condon and Shortley, loc. cit. p. 175. Our $l_1, m_1, l_2, m_2, L$ are to be identified with their $l, m, l', m', L$, and the integral on the left side of (16) is $1/(2\pi)$ times the integral on the left side of their equation (11).
spherical harmonics is required, (10) can be substituted in (18). When \( L = l_1 + l_2 \), the Wigner coefficients reduce to the relatively simple form

\[
S_{(l_1, l_2)}^{(M, M, m, m)} = \delta_{m + m_3} \frac{(2l_1)! (2l_2)! (l_1 + l_2 + M)! (l_1 + l_2 - M)!}{(2l_1 + 2l_2)! (l_1 + m_3)! (l_1 - m_3)! (l_2 + m_3)! (l_2 - m_3)!}. \tag{19}
\]

Setting \( M = 0 \), we find equation (II b), which is repeated here for convenience in the following discussion:

\[
\frac{1}{r_{12}} = \sum_{l_1=0}^{\infty} \sum_{l_2=0}^{\infty} \frac{(-1)^{l_1} r_1 r_2}{R^{l_1 + l_2 + 1}} \frac{4\pi (l_1 + l_2)!}{(2l_1 + 1)(2l_2 + 1)!} \sum_{m=-(l_1 + l_2)}^{(l_1 + l_2)} \frac{Y_{l_1}^m(\theta_1, \phi_1) Y_{l_2}^{-m}(\theta_2, \phi_2)}{(l_1 + m)! (l_2 - m)!(l_2 + m)! (l_1 - m)!(l_1 + m)! (l_2 + m)! (l_2 - m)!}. \tag{II b}
\]

The summation extends over \( m = -l_1, -l_1 + 1, \ldots, l_1 \), where \( l_1 \) is the smaller of \( l_1 \) and \( l_2 \).

By use of Schwarz's inequality and of Unsöld's theorem, which becomes

\[
\sum_{m=-l}^l |Y_{l}^{m}(\theta, \phi)|^2 = \frac{2l + 1}{4\pi}
\]

in the present notation, it can readily be shown that the absolute value of the sum over \( m \) in equation (II b) is not greater than

\[
\frac{((2l_1 + 1)(2l_2 + 1))^{\frac{1}{4}}}{4\pi l_1! l_2!}.
\]

The series on the right side of (II b) is therefore absolutely convergent whenever the double series of positive terms

\[
\sum_{l_1=0}^{\infty} \sum_{l_2=0}^{\infty} \frac{r_1 r_2}{R^{l_1 + l_2 + 1}} \frac{(l_1 + l_2)!}{l_1! l_2!}
\]

is convergent. The latter series is obtainable as the binomial expansion of \((R - r_1 - r_2)^{-1}\) and consequently converges if \(r_1 + r_2 < R\).

Since the series on the right side of (II b) was derived essentially by rearranging the expansion of (7), it converges to \((r_{12})^{-1}\) as defined in (6), provided that \(r_1 + r_2 < \sqrt{(2 - 1)R}\). But we have just shown that the same series, considered on its own merits, is absolutely convergent in the wider range \(r_1 + r_2 < R\). By the principle of analytic continuation, it follows that the sum of the series is \((r_{12})^{-1}\) throughout the wider range \(r_1 + r_2 < R\) (for any \(\theta_1, \phi_1, \theta_2, \phi_2\)).

The form which the expansion takes in (18) provides an easy method of removing the restriction that the positive \(Z_1\)-axis must pass through \(O_2\). Keeping the two sets of axes parallel, we rotate them about their fixed origins to new positions, distinguished by primes, such that the vector \(\mathbf{R}\) has polar angles \((\Theta, \Phi)\) relative to \(X'_1' Y'_1' Z'_1\). The rotation of axes generates a linear transformation of spherical harmonics, with coefficients depending on \(\Theta\) and \(\Phi\) (as well as on a third Eulerian angle which is not of interest here):

\[
Y_{l}^{M}(\theta', \phi') = \sum_{M'=-L}^{L} D_{M}^{(l)}(\Theta, \Phi) Y_{l'}^{M'}(\theta_1, \phi_2). \tag{20}
\]

In particular, if \((\Theta_1, \Phi_1)\) are the polar coordinates of \(O_2\) relative to \(X_1 Y_1 Z_1\), then \(\theta'_1 = \Theta_1\) and \(\phi'_1 = \Phi_1\). But since \(\theta_1 = 0\), \(Y_{l'}^{M}(\theta_1, \phi_1)\) vanishes if \(M' \neq 0\); if \(M' = 0\), its value is \(((2L + 1)/4\pi)^{\frac{1}{4}}\). Consequently,

\[
D_{M}^{(l)}(\Theta, \Phi) = \left\{ \frac{4\pi}{(2L + 1)} \right\}^{\frac{1}{4}} Y_{l}^{M}(\Theta, \Phi).
\]
the transformation (20) is unitary, and its inverse is therefore given by

\[ Y_{M'}^L(\theta, \phi) = \sum_{M=-L}^{L} \{ D_{M'M}^{(Q)}(\Theta, \Phi) \}^* Y_{M'}^L(\theta', \phi'). \]

Letting \( M' = 0 \), we obtain

\[ Y_{L}^0(\theta, \phi) = \left( \frac{4\pi}{2L+1} \right)^{1/2} \sum_{M=-L}^{L} \{ Y_{M}^L(\Theta, \Phi) \}^* Y_{M}^L(\theta', \phi'). \]  

(21)

Because the Wigner functions transform, by their definition, exactly like spherical harmonics when the two sets of axes are rotated together, the addition theorem (21) permits (18) to be rewritten immediately in terms of primed coordinates:

\[ \frac{1}{r_{12}} = \sum_{i_1=0}^{\infty} \sum_{i_2=0}^{\infty} \frac{r_1^{i_1} r_2^{i_2}}{R_{i_1+i_2+1}} A_{i_1, i_2} \sum_{M=-i_1-i_2}^{i_1+i_2} \{ Y_{M}^{i_1+i_2}(\Theta, \Phi) \}^* W_{i_1+i_2}^M(\theta_1', \phi_1'; \theta_2', \phi_2'). \]

where

\[ A_{i_1, i_2} = (-1)^{i_1} (4\pi)^{1/2} \frac{2L_{i_1} + 2L_{i_2}}{(2L_{i_1} + 1)(2L_{i_2} + 1)} \]  

(22)

On using (10), (19) and (4), the expansion in spherical harmonics is found to be

\[ \frac{1}{r_{12}} = \sum_{i_1=0}^{\infty} \sum_{i_2=0}^{\infty} \frac{(-1)^{i_1} r_1^{i_1} r_2^{i_2}}{R_{i_1+i_2+1}} \sum_{m_{1}=-i_1}^{i_1} \sum_{m_{2}=-i_2}^{i_2} B_{i_1,i_2}^{m_{1}m_{2}} Y_{i_1}^{-m_{1}} Y_{i_2}^{-m_{2}}(\Theta, \Phi) Y_{i_1}^{m_{1}}(\theta_1', \phi_1') Y_{i_2}^{m_{2}}(\theta_2', \phi_2'). \]

(III b)

The constants \( B \) are given in the introduction, where the primes are dropped in writing (III b) and (III a).

If \( R \) is smaller than one or the other of \( r_1 \) and \( r_2 \) (for instance, if \( O_2 \) is separated from \( O_1 \) by a small displacement), analogous expansions can be obtained directly from (III b) by interchanging the roles of the variables, provided that either \( r_1 > r_2 + R \) or \( r_2 > r_1 + R \). If, say, \( R + r_2 < r_1 \) then

\[ r_{12} = |r_1 - r_2 - R| = |R - (-r_2) - r_1|. \]

Thus \((r_1, \theta_1, \phi_1)\) in (III b) are to be replaced by \((R, \Theta, \Phi)\), \((r_2, \theta_2, \phi_2)\) by \((r_2, \pi - \theta_2, \phi_2 + \pi)\), and \((R, \Theta, \Phi)\) by \((r_1, \theta_1, \phi_1)\). The correctness of the resulting formula can be partially checked by letting \( R \) vanish and comparing with expansion (I b).

We note for the sake of completeness that (I) also takes a simple form in terms of Wigner functions. If

\[ \cos \theta_{12} = \cos \theta_1 \cos \theta_2 + \sin \theta_1 \sin \theta_2 \cos (\phi_1 - \phi_2), \]

the addition theorem can be written as

\[ P_{\theta_{12}}(\cos \theta_{12}) = \left( \frac{(-1)^{i} 4\pi}{2L+1} \right)^{1/2} W_{0, L}^{0}(\theta_1, \phi_1; \theta_2, \phi_2). \]

The corresponding statement of (I) is

\[ \frac{1}{r_{12}} = \sum_{i=0}^{\infty} \frac{r_1^{i} r_2^{i}}{(2L+1)^{1/2}} W_{0, i}^{0}(\theta_1, \phi_1; \theta_2, \phi_2). \]

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