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Commentationes

Translations of Fields Represented by Spherical-Harmonic Expansions for Molecular Calculations

I. General Concepts and Methods

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In quantum chemistry one needs expansions of orbitals and operators, defined with respect to one origin, about another origin. Because there is no straightforward method of obtaining such expansions, it is helpful to interpret them as translations of fields. The connection between translations and rotations of fields with the transformations of functions is considered. Of special physical interest are expansions in spherical harmonics, which have the form of an addition theorem. General properties of such expansions and possible methods to derive them are discussed.

Key words: Fields, translations, rotations of ~ – Spherical harmonics, expansions in ~ – Addition theorems

1. Introduction

In molecular theory, many problems become soluble only if certain mathematical functions which occur can be expanded about various origins which are usually chosen to be the centers of atoms in molecules or crystals.

Since the wave functions used to describe a molecular system depend in a complicated manner on the coordinates of its electrons and nuclei, and since the energy and other quantities are determined by the structure of the system, the difficulty of a problem depends in a very sensitive way on the positions of the atomic centers and how they are mathematically taken into account. In order to make calculations feasible, one often wants to have expansions of the wave functions with respect to certain centers. For instance, such expansions are helpful or necessary for the calculation of matrix elements with a non-Gaussian basis set which has to be used if the exact behavior of the wave function near a nucleus or at long distances is important. These expansions are especially helpful for the evaluation of matrix elements which occur in the calculation of molecular properties such as electric multipole moments, diamagnetic susceptibilities, electron-proton hyperfine interaction, chemical shift, nuclear quadrupole coupling, and electron spin-spin and spin-orbit coupling. However, the expansions can also be applied to many other problems which one encounters, for instance, in the theory of phase transitions, in the theory of molecular interactions, and many other fields of chemical and mathematical physics.

In quantum chemistry, expansions in spherical harmonics are of special interest because the spherical harmonics, being solutions of the angular wave equation of the atomic Kepler problem, appear in many problems and quantities of quantum chemistry. For instance, they are contained in spherical Gaussian-type as well as Slater-type atomic orbitals. In addition, many operators may be expressed by or are closely connected to spherical harmonics. In fact, the operator (e^2/r_{12}) of the electrostatic interaction of two electrons provides the generating function of the Legendre polynomials. Hence, this important operator yields the most fundamental expansion in spherical harmonics. Furthermore, the spherical harmonics have the great advantage that their transformation properties under rotation are well known. This fact is helpful in many respects. For example, it enables one to use various atomic coordinate systems, which may be rotated with respect to each other, in order to simplify calculations.

It is clear why the spherical harmonics occur so often in quantum mechanical problems and why their behavior under rotational transformations has been well understood since the early days of quantum mechanics [1–3]. They are eigenfunctions of $\boldsymbol{L}^2$ and L_Z, where $\boldsymbol{L}$ is the angular momentum operator. The importance of central potentials and the conservation of angular momentum in many quantum mechanical problems prompted a thorough investigation of the mathematical tools needed to treat such problems [4–9]. It was fortunate that the solution of the differential equation which occurs was well known from potential theory.

In contrast, the conservation of linear momentum neither raised many questions nor could it be used extensively to simplify the problems. Usually, the only advantage was the fact that it allowed the separation of the wave equation of, say, a molecule into one which represents the translational motion of the molecule as a whole and another one which represents the relative motion of the particles, described by coordinates in the center-of-mass system. This may be the reason why the theory of angular momentum and, thereby, the theory of transformations of spherical harmonics under *rotations* has been much further developed than mathematical problems which are related to the *translation* of functions, for instance spherical harmonics.

The spherical harmonics are the basis functions of the irreducible representations of the three-dimensional rotation group. Plane waves are the basis functions of the irreducible representations of the pure translation group. Since the translation group is Abelian, it is simpler to translate a plane wave than it is to rotate a spherical harmonic. However, the equivalent transformation of functions which are not basis functions of the respective irreducible representations is much more difficult and still unsolved for many types of functions.

If the transformed function is expressed in terms of given functions which form a complete set, the expansion coefficients can in most cases be obtained in an explicit form only with great difficulty or not at all. But without knowing the exact expression of the expansion coefficients, an expansion is useless for practical purposes.

The translation of a function means, in fact, the expansion of a function about another origin. Because of the reasons mentioned above, it is desirable to have expansions of general functions about a new origin such that the

orientational dependencies of the expansion terms are expressed by spherical harmonics. Unfortunately, also in this case great difficulties must be surmounted in order to derive such expansions. If an expansion for a certain class of functions can be given, it provides a new relationship which can be used in many contexts.

Since Hobson's [10] pioneering work on "The Theory of Spherical and Ellipsoidal Harmonics", several investigations were concerned with the possibility of obtaining such expansions, as will be discussed later. It appears that the class of functions, which can be expanded with the least amount of difficulties, encompasses the regular and irregular solid spherical harmonics, which are defined by $r^L Y_L^M(\theta, \phi)$ or $r^{-L-1} Y_L^M(\theta, \phi)$, respectively, if r, θ, ϕ are the spherical coordinates of a field point and $Y_L^M(\theta, \phi)$ is a surface spherical harmonic. As has been shown recently [11a, 11b], for these functions not only translation formulas, but also multicenter expansions can be derived if certain conditions are obeyed. These relationships allow the expansion of a solid spherical harmonic, which is defined with respect to a given origin, in terms of other solid spherical harmonics, which are defined with respect to other centers.

It would be desirable to have such multicenter expansions for any function of interest in quantum mechanics. Since a general analytical function can be expanded in a series of functions $r^N Y_L^M(\theta, \phi)$, a step in this direction is to look for expansions of functions of this kind. It can be shown now, that for functions $r^N Y_L^M(\theta, \phi)$ with arbitrary N such multicenter expansions do exist [12]. Moreover, such multicenter expansions do also exist for several other functions which are products of a surface spherical harmonic and another function belonging to the class of special functions, e.g. a spherical Bessel function, a spherical Neumann function, or a spherical Hankel function. But also plane waves, spherical waves, Yukawa potentials etc. may be shown to fulfill equivalent relationships [13].

Some of the one- and two-center expansions mentioned above have been treated in the literature in the past, as will be discussed at the appropriate places. Even in these cases, however, new derivations and more compact results, more suitable for practical applications, can be given. In addition, we can show how all expansions are related to each other and that they can be described by a uniform theory. Only this makes it possible to derive the various multicenter expansions, which was not recognized until now.

In order to obtain these expansions, one must first clarify the problem of the one-center expansions in detail and provide the mathematical tools for the treatment of the two-center expansions as the next step. Previously it was not possible to derive two-center expansions of $r^N Y_L^M(\theta, \phi)$ for all values of N and for all regions of space, let alone multicenter expansions. It can be shown, however, that for each point in space one can arrive at two-center expansions, and that, for instance, a generalization of the bipolar expansion is possible [12]. This treatment finally leads to the multicenter expansions.

The present paper is the first in a series of articles which deal with new derivations and relationships describing the translation of fields. For this purpose it is important to clarify the general concepts of the translational transformation of functions, which will be done in the present article. Because it is helpful to consider some of the analogies between rotations and translations of functions, transformations under rotation will be discussed briefly in the next paragraph. On

this basis the general formalism of transformations under translation will be discussed in the following section. This finally allows the consideration of different methods for obtaining expansions in spherical harmonics which may be used or which were applied by various authors.

2. Transformations under Rotation

An orthogonal reference system may be defined by the unit vectors e_1, e_2, e_3 pointing along the x-, y-, or z-axis, respectively. The direction of the unit vector $\varrho = r/r$, which connects the origin of the reference system with a certain point on the unit sphere, is determined by the polar angle θ and the azimuthal angle ϕ, denoted by (θ, ϕ). If one wants to emphasize that the coordinates are defined with respect to e_1, e_2, e_3, one may write $(e; \varrho)$ instead of (θ, ϕ), where e represents e_1, e_2, e_3.

The original reference system e_1, e_2, e_3 may be rotated by Eulerian angles α, β, γ into a new reference system $\check{e}_1, \check{e}_2, \check{e}_3$ with the same origin. The unit vector ϱ, which had the spherical coordinates $(\theta, \phi) = (e; \varrho)$ in the original frame and did not move, has then the spherical coordinates $(\check{\theta}, \check{\phi}) = (\check{e}; \varrho)$ in the new frame.

The operator $\mathscr{R}$ rotates a vector or, as could be said, the entire coordinate space by the Eulerian angles α, β, γ. Hence, if $\mathscr{R}$ operates on the basis vectors, it is

$$\mathscr{R} e_i = \check{e}_i = \sum_{j=1}^{3} R_{ij}(\alpha, \beta, \gamma) e_j , \qquad i = 1, 2, 3 . \tag{2.1}$$

The operator $\mathscr{R}$ induces a rotation matrix with elements R_{ij} which, however, will not be used here.

A field in three-dimensional space is given by a function $f(r, \theta, \phi)$. Because the r-dependence is irrelevant to rotations, it is sufficient to consider a function which is defined on the unit sphere. This function may be written as $f(\theta, \phi)$ or $f(\varrho)$, if it is well understood which reference system is used. Here this notation refers to the system e_1, e_2, e_3. More clearly, one may write

$$f(\theta, \phi) = f(\varrho) = f(e; \varrho) . \tag{2.2}$$

Of course, a simultaneous rotation of the position vector ϱ and the basis vectors has no effect, i.e.

$$f(e; \varrho) = f(\mathscr{R} e; \mathscr{R} \varrho) . \tag{2.3}$$

The new coordinates $(\check{\theta}, \check{\phi})$ may be introduced into the function f, leading to $f(\check{\theta}, \check{\phi})$. If now the new coordinates are expressed by the old ones, a new function F will emerge, i.e.

$$f(\check{\theta}, \check{\phi}) = F(\theta, \phi) \tag{2.4}$$

or

$$f(\check{e}; \varrho) = F(e; \varrho) . \tag{2.5}$$

The new function will be denoted by $(\hat{P}_{\mathscr{R}} f)$. Hence

$$f(\mathscr{R} e; \varrho) = (\hat{P}_{\mathscr{R}} f)(e; \varrho) . \tag{2.6}$$

If one considers the vector $\mathscr{R}\varrho$ instead of ϱ, it follows with use of Eq. (2.3) that

$$f(\boldsymbol{e};\varrho)=\hat{P}_{\mathscr{R}}f(\boldsymbol{e};\mathscr{R}\varrho) \tag{2.7}$$

or with Eq. (2.2)

$$f(\varrho)=\hat{P}_{\mathscr{R}}f(\mathscr{R}\varrho)\,. \tag{2.8}$$

The "new function" has the same value at the point $\mathscr{R}\varrho$ as the "old function" has at the point ϱ. This means, the operator $\hat{P}_{\mathscr{R}}$ causes a positive rotation of the field. The transformation generated by $\mathscr{R}$ in coordinate space induces a transformation generated by $\hat{P}_{\mathscr{R}}$ in function space.

The most important functions defined on the unit sphere are the spherical harmonics. In Condon-Shortley phases [14] the surface spherical harmonics are defined by

$$Y_L^M(\theta,\phi)=\mathscr{P}_l^m(\zeta)\,e^{im\phi}(2\pi)^{-1/2} \tag{2.9}$$

with

$$\zeta=\cos\theta\,,\qquad -1\leqq\zeta\leqq 1\,, \tag{2.10}$$

$$l=0,1,2,3,\ldots,\qquad -l\leqq m\leqq l\,. \tag{2.11}$$

The $\mathscr{P}_l^m(\zeta)$ denote the normalized associated Legendre functions

$$\mathscr{P}_l^m(\zeta)=(-1)^m N_l^m P_l^m(\zeta) \tag{2.12}$$

with the normalization constant

$$N_l^m=\left[\frac{2l+1}{2}\,\frac{(l-m)!}{(l+m)!}\right]^{1/2}. \tag{2.13}$$

The unnormalized associated Legendre functions are given by

$$P_l^m(\zeta)=(1-\zeta^2)^{m/2}(d/d\zeta)^{l+m}(\zeta^2-1)^l/2^l l!\,. \tag{2.14}$$

Setting $m=0$ yields Rodrigues' formula for the Legendre polynomials

$$P_l(\zeta)=(2^l l!)^{-1}(d/d\zeta)^l(\zeta^2-1)^l\,. \tag{2.15}$$

The rotation operator $\hat{P}_{\mathscr{R}}$ should not be confused with these symbols.

The spherical harmonics are the basis functions of the irreducible representations of the three-dimensional rotation group. Under the rotation defined by the Eulerian angles α, β, γ, they transform according to

$$\hat{P}_{\mathscr{R}}Y_l^m(\theta,\phi)=Y_l^m(\check{\theta},\check{\phi})=\textstyle\sum_{m'=-l}^{l}Y_l^{m'}(\theta,\phi)\,D_{m'm}^{(l)}(\alpha,\beta,\gamma)\,, \tag{2.16}$$

see, e.g., Ref. [6]. This may be written as

$$\hat{P}_{\mathscr{R}}Y_l^m(\boldsymbol{e};\varrho)=Y_l^m(\boldsymbol{e};\mathscr{R}^{-1}\varrho)=\textstyle\sum_{m'=-l}^{l}Y_l^{m'}(\boldsymbol{e};\varrho)\,D_{m'm}^{(l)}(\mathscr{R})\,. \tag{2.17}$$

Hence, the rotated function $\hat{P}_{\mathscr{R}}Y_l^m$ is given by a linear combination of the unrotated functions $Y_l^{m'}$. The coefficients $D_{m'm}^{(l)}(\mathscr{R})$ of this finite expansion are the elements of the rotation matrices, which will not be given here.

Since the spherical harmonics define a complete set on the unit sphere [15], a function $f(\theta, \phi)$ may be expanded according to

$$f(\theta, \phi) = \sum_{l=0}^{\infty} \sum_{m=-l}^{l} C_l^m Y_l^m(\theta, \phi), \tag{2.18}$$

if one is able to determine the coefficients

$$C_l^m = \int_0^{2\pi} d\phi \int_0^{\pi} d\theta \sin\theta f(\theta, \phi) Y_l^{m*}(\theta, \phi). \tag{2.19}$$

A rotation of the function $f(\theta, \phi)$ may be accomplished by rotating each surface harmonic of the expansion. The equivalent procedure may be applied to functions $f(\boldsymbol{r})$. Then, the C_l^m become functions $C_l^m(r)$.

3. Transformations under Translation

3.1. The Translation Operator

A rotation can be defined by Eulerian angles which allow the final position of a rotated reference system to be determined with respect to its original position. The origin remains fixed.

A translation is defined by a vector $\boldsymbol{R}$ which connects the origin 0 of a reference system $\boldsymbol{e}_1, \boldsymbol{e}_2, \boldsymbol{e}_3$ to the origin 0′ of another reference system $\boldsymbol{e}'_1, \boldsymbol{e}'_2, \boldsymbol{e}'_3$. Each axis $\boldsymbol{e}'_i$ is chosen to be parallel to the corresponding axes $\boldsymbol{e}_i$, $i = 1, 2, 3$. Hence, the second reference system is obtained by shifting the first reference frame $\boldsymbol{e}_1, \boldsymbol{e}_2, \boldsymbol{e}_3$ along $\boldsymbol{R}$ and keeping the basis vectors unchanged. The two "parallel" systems differ by a "parallel displacement" only.

If a field point P has the coordinates x, y, z or r, θ, ϕ, respectively, with respect to the reference system $\boldsymbol{e}_1, \boldsymbol{e}_2, \boldsymbol{e}_3$, the same field point P will have the coordinates x', y', z' or r', θ', ϕ', respectively, with respect to the reference system $\boldsymbol{e}'_1, \boldsymbol{e}'_2, \boldsymbol{e}'_3$. In vector notation, this means (see Fig. 1)

$$\boldsymbol{r}' = \boldsymbol{r} - \boldsymbol{R}. \tag{3.1}$$

With these definitions, a function $f(r, \theta, \phi)$ defines a certain field. If the coordinates r', θ', ϕ' are formally introduced into the function f and subsequently expressed by the coordiantes r, θ, ϕ, a new function F will emerge:

$$f(r', \theta', \phi') = F(r, \theta, \phi). \tag{3.2}$$

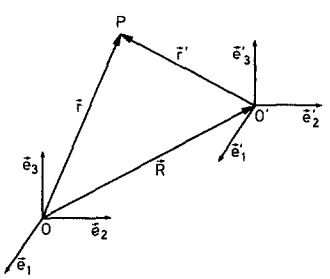

Fig. 1

Using Eq. (3.1) and denoting the new function F by $(\hat{P}_\tau f)$, this may be written as

$$f(\boldsymbol{r}-\boldsymbol{R})=\hat{P}_\tau f(\boldsymbol{r}) \tag{3.3}$$

or

$$f(\boldsymbol{r})=\hat{P}_\tau f(\boldsymbol{r}+\boldsymbol{R})\,. \tag{3.4}$$

The "new function" has the same value at the point defined by the local vector $(\boldsymbol{r}+\boldsymbol{R})$ as the "old function" has at the point P defined by $\boldsymbol{r}$. Hence, the operator $\hat{P}_\tau$ causes a *translation* of the field by $\boldsymbol{R}$. Defining an operator $\mathscr{T}$ such that

$$\mathscr{T}\boldsymbol{r}=\boldsymbol{r}+\boldsymbol{R}\,, \tag{3.5}$$

Eq. (3.4) may be written as

$$f(\boldsymbol{r})=\hat{P}_\tau f(\mathscr{T}\boldsymbol{r})\,. \tag{3.6}$$

which corresponds to Eq. (2.8). Since all functions are defined with respect to "parallel" reference systems, it is not necessary to specify the reference system in the argument as it was done, for instance, in Eqs. (2.2)–(2.7). In fact, any vector may be shifted arbitrarily in space if its length and direction remain unchanged. Therefore, one can assume that all vectors which occur originate at the origin 0 of reference system $\boldsymbol{e}_1, \boldsymbol{e}_2, \boldsymbol{e}_3$. This is also the reason why the operator $\mathscr{T}$ causes an *addition* of $\boldsymbol{R}$ to a given vector whose translation is arbitrary anyway. In this respect, $\mathscr{T}$ cannot be compared with $\mathscr{R}$, because $\mathscr{R}$ produces a rotation of a vector just as $\hat{P}_{\mathscr{R}}$ produces a rotation of the field.

The translation operator $\hat{P}_\tau$ can be specified with the help of the Taylor expansion

$$f(\boldsymbol{r}-\boldsymbol{R})=\sum_{t=0}^{\infty}(t!)^{-1}(-\boldsymbol{R}\cdot\partial/\partial\boldsymbol{r})^t f(\boldsymbol{r})\,. \tag{3.7}$$

If this relation is compared with Eq. (3.3), it follows

$$\hat{P}_\tau=\exp(-\boldsymbol{R}\cdot\partial/\partial\boldsymbol{r})\,. \tag{3.8}$$

It may be noted that application of this operator to a plane wave $\exp(i\boldsymbol{k}\cdot\boldsymbol{r})$ yields $\exp[i\boldsymbol{k}\cdot(\boldsymbol{r}-\boldsymbol{R})]$ because $i\boldsymbol{k}$ is the eigenvalue of $\partial/\partial\boldsymbol{r}$. The last two relations Eqs. (3.7) and (3.8) show that the mathematical representation of a translation defined by Eq. (3.3) can in fact be considered as an *expansion about another origin.*

3.2. Separation of Variables

For practical applications it is desirable to represent the translated function $\hat{P}_\tau f(\boldsymbol{r})$, which is equal to $f(\boldsymbol{r}-\boldsymbol{R})$, by an expansion of the form

$$f(\boldsymbol{r}-\boldsymbol{R})=\sum_\mu\sum_\nu C_{\mu\nu}g_\mu(\boldsymbol{r})\,h_\nu(\boldsymbol{R}) \tag{3.9}$$

with certain functions g_μ and h_ν, where each function in the expansion terms depends on one vector only. Then the variables $\boldsymbol{r}$ and $\boldsymbol{R}$ are separated.

For a given displacement vector $\boldsymbol{R}$ one may write the expansion Eq. (3.9) in the following form

$$f(\boldsymbol{r}-\boldsymbol{R})=\sum_\mu K_\mu(\boldsymbol{R})\,g_\mu(\boldsymbol{r})\,, \tag{3.10}$$

where

$$K_\mu(\boldsymbol{R}) = \sum_\nu C_{\mu\nu} h_\nu(\boldsymbol{R}) . \tag{3.11}$$

If the functions $g_\mu(\boldsymbol{r})$ form a complete orthonormal set, which means

$$\sum_\mu g_\mu^*(\boldsymbol{r}_1) g_\mu(\boldsymbol{r}_2) = \delta(\boldsymbol{r}_1 - \boldsymbol{r}_2) , \tag{3.12a}$$

$$\int d\boldsymbol{r} g_\lambda^*(\boldsymbol{r}) g_\mu(\boldsymbol{r}) = \delta_{\lambda\mu} , \tag{3.12b}$$

then $K_\mu(\boldsymbol{R})$ is given by

$$K_\mu(\boldsymbol{R}) = \int d\boldsymbol{r} g_\mu^*(\boldsymbol{r}) f(\boldsymbol{r} - \boldsymbol{R}) . \tag{3.13}$$

If also the functions $h_\nu(\boldsymbol{R})$ form a complete orthonormal set, the coefficients $C_{\mu\nu}$, which do not depend on any vector, are given by the two-center integral

$$C_{\mu\nu} = \int d\boldsymbol{R} \int d\boldsymbol{r} g_\mu(\boldsymbol{r}) h_\nu^*(\boldsymbol{R}) f(\boldsymbol{r} - \boldsymbol{R}) . \tag{3.14}$$

For practical purposes, one needs more than a separation of the argument vectors $\boldsymbol{r}$ and $\boldsymbol{R}$. In fact, it is important that the radial and angular dependencies also be separated. This can be achieved if an expansion in spherical harmonics can be given according to the following formula

$$f(\boldsymbol{r} - \boldsymbol{R}) = \sum_{k_1 l_1 m_1} \sum_{k_2 l_2 m_2} C_{l_1 m_1, l_2 m_2}^{k_1 k_2} u_{k_1}(r) Y_{l_1}^{m_1}(\boldsymbol{r}/r) v_{k_2}(R) Y_{l_2}^{m_2}(\boldsymbol{R}/R) . \tag{3.15}$$

Unfortunately, the functions $u_{k_1}(r)$ and $v_{k_2}(R)$ can be obtained in closed form only for a few special classes of functions $f(\boldsymbol{r} - \boldsymbol{R})$.

3.3. Translation of the Coulomb Field

The translation of the Coulomb field represented by an expansion in spherical harmonics will serve as a starting point for the following derivations. The field of a unit charge in the origin 0 of the reference system $\boldsymbol{e}_1, \boldsymbol{e}_2, \boldsymbol{e}_3$ (see Fig. 1), is rotationally invariant. The potential in the field point P is $1/r$. The translation of the unit charge causes a translation of its field. If the unit charge is shifted from 0 to 0′, its potential in P is $1/r'$. The potential $1/r'$ is the generating function for the Legendre polynomials according to

$$1/r' = (r^2 + R^2 - 2rR\cos\omega)^{-1/2} = \sum_{l=0}^{\infty} r_<^l r_>^{-l-1} P_l(\cos\omega) ; \tag{3.16}$$

$$r_< = \mathrm{Min}(r, R) , \quad r_> = \mathrm{Max}(r, R) , \tag{3.17}$$

where ω is the angle between $\boldsymbol{r}$ and $\boldsymbol{R}$,

$$rR\cos\omega = \boldsymbol{r} \cdot \boldsymbol{R} . \tag{3.18}$$

The finite expansion

$$P_l(\cos\omega) = 4\pi(2l+1)^{-1} \sum_{m=-l}^{l} Y_l^{m*}(\boldsymbol{r}/r) Y_l^m(\boldsymbol{R}/R) \tag{3.19}$$

is valid in any coordinate system with origin 0, for instance $\boldsymbol{e}_1, \boldsymbol{e}_2, \boldsymbol{e}_3$ of Fig. 1. Introducing it into Eq. (3.16), yields

$$1/|\boldsymbol{r} - \boldsymbol{R}| = 4\pi \sum_{l=0}^{\infty} \sum_{m=-l}^{l} (2l+1)^{-1} r_<^l r_>^{-l-1} Y_l^{m*}(\boldsymbol{r}/r) Y_l^m(\boldsymbol{R}/R) . \tag{3.20}$$

This relation, which is a special case of Eq. (3.15), illustrates not only the physical meaning of the translation of the field by $\boldsymbol{R}$, where $\boldsymbol{R}$ connects 0 to 0'. It also allows a physical interpretation of the "expansion about another origin" which stands for $1/r'$: The potential of the translated unit charge measured at the point P can be represented by the sum of the potentials of all multipoles in the origin 0.

This example shows also that the spherical harmonics, which are closely connected to rotations, are also connected to translations. Because the simplest harmonic P_l is generated by a translation of $1/r$, it is probable that translated functions of a more complicated form, e.g. r^N, can be represented by an expansion in spherical harmonics such that the radial functions u_{k_1} and v_{k_2} of Eq. (3.15) can be determined explicitly.

An *addition theorem* such as Eq. (3.19) allows a function which depends in an arbitrary way on two vectors to be expanded in terms of functions which depend on one vector only. Therefore, the translation formulas Eqs. (3.9) and (3.15) are special kinds of addition theorems, i.e. those for functions $f(\boldsymbol{r}-\boldsymbol{R})$ which depend on the *sum* of the two vectors only.

For a certain translation of a field by a vector $\boldsymbol{R}$, this vector $\boldsymbol{R}$ is a constant in the appropriate translation formulas as Eqs. (3.9) and (3.15). In these formulas, however, the vector $\boldsymbol{R}$ as well as the vector $\boldsymbol{r}$ can be considered as a variable, since any translation is possible. For symmetry reasons $\boldsymbol{r}$ can be called $\boldsymbol{r}_1$, and $\boldsymbol{R}$ can be called $\boldsymbol{r}_2$. Then a translation formula like Eq. (3.9) or Eq. (3.15), respectively, becomes in fact a *one-center expansion* because $f(\boldsymbol{r}_1-\boldsymbol{r}_2)$ is expressed by functions which are defined with respect to the same origin 0. If the renaming of the vectors $\boldsymbol{r}$ and $\boldsymbol{R}$ is done in Eq. (3.20), this formula becomes the Laplace expansion for the Coulomb energy $1/r_{12}$ of two unit point charges at the position $\boldsymbol{r}_1$ and $\boldsymbol{r}_2$, respectively. This is another interpretation of the formula Eq. (3.20).

3.4. *Translations of Scalar and Non-Scalar Functions*

Scalar functions $f(r)$ and general functions $f(\boldsymbol{r})$, which depend on the direction of $\boldsymbol{r}$, have different transformation properties under translations, which become apparent if the z-axis coincides with one of the vectors $\boldsymbol{r}_>$ or $\boldsymbol{r}_<$, respectively. Two cases are possible[1]: In case A the z-axis of a coordinate system $\boldsymbol{e}_1^A$ coincides with $\boldsymbol{r}_<$ and the z-axis of another reference system $\boldsymbol{e}_2^A$ coincides with $\boldsymbol{r}_>$. In case B the system $\boldsymbol{e}_1^B$ has its z-axis in the direction of $\boldsymbol{r}_>$, whereas the z-axis of system $\boldsymbol{e}_2^B$ coincides with $\boldsymbol{r}_<$, see Fig. 2a and b. Because of $Y_l^m(0,\phi)=[(2l+1)/4\pi]^{1/2}\delta_{m,0}$, the expansion given by Eq. (3.15) can be written in case A as

$$f(\boldsymbol{e}_i^A;\boldsymbol{r}')=\sum_{l,m} A_{l,m}^i(r_>,r_<)\,Y_l^m(\omega,\phi)\,, \tag{3.21a}$$

in case B as

$$f(\boldsymbol{e}_i^B;\boldsymbol{r}')=\sum_{l,m} B_{l,m}^i(r_>,r_<)\,Y_l^m(\omega,\phi) \tag{3.21b}$$

[1] In the foregoing, the lower index i of $\boldsymbol{e}_i$ was used to distinguish the three different axes of a reference system. However, in this Section 3.4 only z-axes are considered. Here the lower index i of $\boldsymbol{e}_i^K$ was redefined to specify two different coordinate systems with the same origin, but different z-axes: $i=1$ or 2. In addition, two cases are considered with $K=A$ or B as defined above.

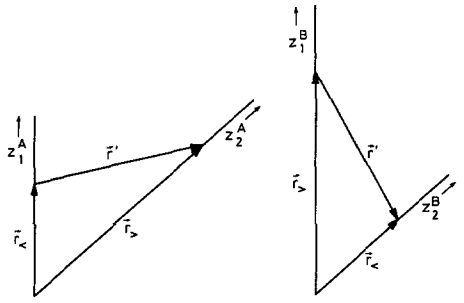

Fig. 2a and b

with $i=1,2$. Here, the notation of Eq. (2.2) is adopted. Of course, $\phi=\phi'$ and $(\omega, \phi)=(e_1^K; r_<)=(e_2^K; r_>)$ with $K=A, B$. The vectors $r_>$ and $r_<$ include the angle ω. With

$$(e_1^A; r')=(e_2^B; -r'), \quad (e_2^A; r')=(e_1^B; -r'), \tag{3.22}$$

it follows from Eqs. (3.21a) and (3.21b) that the radial functions obey the conditions $A_{l,m}^1=B_{l,m}^2$ and $A_{l,m}^2=B_{l,m}^1$. Because

$$(e_1^A; r')\neq(e_2^A; r'), \quad (e_1^B; r')\neq(e_2^B; r'), \tag{3.23}$$

one obtains $A_{l,m}^1\neq A_{l,m}^2$, $B_{l,m}^1\neq B_{l,m}^2$, $A_{l,m}^1\neq B_{l,m}^1$, and $A_{l,m}^2\neq B_{l,m}^2$.

Therefore, the transformation of a general function $f(\boldsymbol{r})$ under translations by arbitrary distances R in the direction of $\boldsymbol{R}$ is described by two different formulas. The z-axes of the reference systems e_1^A or e_1^B may be chosen to coincide with $\boldsymbol{R}$. If $R<r$, which means $R=r_<$ and $r=r_>$, the expansion Eq. (3.21a) is valid. If $R>r$, hence $R=r_>$ and $r=r_<$, the different expansion Eq. (3.21b) describes the translation.

For scalar functions one has $f(r')=f(e_i^K; r')$ for arbitrary i and K. Therefore, it follows from Eqs. (3.21a) and (3.21b) that $A_{l,m}^i=B_{l,m}^j$ for any $i,j=1,2$, which means that the two expansions are identical.

4. Methods for Obtaining Expansions in Spherical Harmonics

4.1. Fourier Transformation

Plane waves $\exp(i\boldsymbol{k}\cdot\boldsymbol{r})$, which are the basis functions of the irreducible representations of the pure translation group, transfer simply as

$$\hat{P}_\tau e^{i\boldsymbol{k}\cdot\boldsymbol{r}}=e^{i\boldsymbol{k}\cdot(\boldsymbol{r}-\boldsymbol{R})}. \tag{4.1}$$

In this case, the operator can be represented by

$$\hat{P}_\tau=e^{-i\boldsymbol{k}\cdot\boldsymbol{R}}. \tag{4.2}$$

There are, however, only a few classes of functions with well-known translational transformation properties.

A function may be represented by a Fourier integral

$$f(\boldsymbol{r})=(2\pi)^{-3/2}\int d\boldsymbol{k}\,\tilde{f}(\boldsymbol{k})\,e^{i\boldsymbol{k}\cdot\boldsymbol{r}}\,, \tag{4.3}$$

where

$$\tilde{f}(\boldsymbol{k})=(2\pi)^{-3/2}\int d\boldsymbol{r}\,f(\boldsymbol{r})\,e^{-i\boldsymbol{k}\cdot\boldsymbol{r}}\,. \tag{4.4}$$

In a sense, these two relationships correspond to the two expressions Eqs. (2.18) and (2.19), because both sets of equations define an expansion with respect to the basis functions of the irreducible representations of the respective symmetry groups. If the operator $\hat{P}_\tau$ is applied to Eq. (4.3), one obtains the following expression for the translated function at the point P, which is defined by $\boldsymbol{r}$ in the reference system $\boldsymbol{e}_1, \boldsymbol{e}_2, \boldsymbol{e}_3$,

$$\hat{P}_\tau f(\boldsymbol{r})=(2\pi)^{-3/2}\int d\boldsymbol{k}\,\tilde{f}(\boldsymbol{k})\,e^{i\boldsymbol{k}\cdot(\boldsymbol{r}-\boldsymbol{R})}\,. \tag{4.5}$$

For applications it is necessary to obtain expressions for the translated function where the variables represented by the argument vectors $\boldsymbol{r}$ or $\boldsymbol{R}$, respectively, are separated. This is the case for the integrand of Eq. (4.5). This is also the case for the whole integral if $\tilde{f}(\boldsymbol{k})$ is a delta function, i.e. if a plane wave is translated. Then Eq. (4.5) becomes Eq. (4.1). For more complicated cases, however, the evaluation of the integral, if it can be performed, will in general lead to infinite expansions. Therefore, instead of having the transformed function in form of an integral, it would be easier for possible applications to have an infinite expansion from the beginning. Then, this should be of the form Eq. (3.15).

The relationship Eq. (4.5) can be expressed in a form similar to Eq. (3.15) by introducing the plane wave expansion [16]

$$e^{i\boldsymbol{k}\cdot\boldsymbol{r}}=4\pi\sum_{l=0}^{\infty}\sum_{m=-l}^{l} i^l j_l(kr)\,Y_l^{m*}(\boldsymbol{k}/k)\,Y_l^m(\boldsymbol{r}/r) \tag{4.6}$$

into the integral. This yields the formula

$$f(\boldsymbol{r}-\boldsymbol{R})=4(2\pi)^{1/2}\sum_{l_1,l_2}\sum_{m_1,m_2}(-1)^{l_2}i^{l_1+l_2}Y_{l_1}^{m_1}(\boldsymbol{r}/r)\,Y_{l_2}^{m_2}(\boldsymbol{R}/R)\,I_{l_1,l_2}^{m_1,m_2}(r,R)\,. \tag{4.7}$$

The expansion terms contain the integral

$$I_{l_1,l_2}^{m_1,m_2}(r,R)=\int d\boldsymbol{k}\,\tilde{f}(\boldsymbol{k})j_{l_1}(kr)j_{l_2}(kR)\,Y_{l_1}^{m_1*}(\boldsymbol{k}/k)\,Y_{l_2}^{m_2*}(\boldsymbol{k}/k)\,. \tag{4.8}$$

The j_l are spherical Bessel functions. This expression was first obtained by Ruedenberg [17a] and independently by Silverstone [17b].

The Fourier transformation of a function in connection with Rayleigh's plane wave expansion Eq. (4.6) often fails to yield explicit coefficients because the integrals which occur cannot be evaluated analytically. If the Fourier transform does not exist in the usual function sense, one cannot even calculate the coefficients numerically. In such a case, one may apply the theory of distributions [18–20]. This was first done by Kay, Todd, and Silverstone [21], who also used this method for the evaluation of molecular integrals [22]. This method has the advantage that it allows the investigation of singularities. However, in most cases considered by Silverstone *et al.* [21], the integrals could only be transformed into new expressions which contained sequences of higher derivatives. Hence, they are not given

by explicit formulas, but instead by a prescription for obtaining them by executing all derivatives which occur.

It turns out that the transformation under translations is more difficult than the transformation under rotations, at least if the angular dependence of the transformed function is to be expressed in terms of spherical harmonics. The plane waves are the basis functions of the translation group just as the spherical harmonics are the basis functions of the rotation group. The Fourier transformation of a three-dimensional function, which can be interpreted as an expansion in plane waves, can therefore be compared with the expansion of a function on the unit sphere in spherical harmonics. If the coefficients of the last expansion are calculated, the problem of rotation is completely solved, i.e. the rotated function is also known as an expansion in spherical harmonics, which emerges from the application of $\hat{P}_{\mathcal{R}}$ on each term of the original series Eq. (2.18). If the Fourier transform of a function is calculated, one also knows the "expansion in plane waves" of the translated function. However, one still does not have the desired expansion in spherical harmonics for the translated function, because the coefficients $I_{l_1,l_2}^{m_1,m_2}$ of the expansion Eq. (4.7) remain to be calculated. The integrals $I_{l_1,l_2}^{m_1,m_2}$ can be evaluated only for certain classes of functions. There are other functions for which they diverge. Furthermore, even if the $I_{l_1,l_2}^{m_1,m_2}(r,R)$ can be determined in an explicit form, the variables r and R cannot be separated in many cases.

4.2. Derivations from the Differential Equation

If $F(\partial/\partial \boldsymbol{r}_1)$ is an even or odd function of the operator $\partial/\partial \boldsymbol{r}_1$, the identity

$$F(\partial/\partial \boldsymbol{r}_1) f(\boldsymbol{r}_1+\boldsymbol{r}_2)=F(\partial/\partial \boldsymbol{r}_2) f(\boldsymbol{r}_1+\boldsymbol{r}_2) \tag{4.9}$$

is valid, especially

$$(\partial/\partial \boldsymbol{r}_1)^2 f(\boldsymbol{r}_1+\boldsymbol{r}_2)=(\partial/\partial \boldsymbol{r}_2)^2 f(\boldsymbol{r}_1+\boldsymbol{r}_2)\,. \tag{4.10}$$

Sack [23, 24] used this property for the derivation of certain expansions of the type

$$f(\boldsymbol{r}_1+\boldsymbol{r}_2)=\sum_{l_1}\sum_{l_2}\sum_{m_1}\sum_{m_2} R_{l_1,l_2}^{m_1,m_2}(r_1,r_2)\, Y_{l_1}^{m_1}(\boldsymbol{r}_1/r_1)\, Y_{l_2}^{m_2}(\boldsymbol{r}_2/r_2)\,. \tag{4.11}$$

For this Ansatz, the relationship Eq. (4.10) yields

$$\left[\frac{\partial^2}{\partial r_1^2}+\frac{2}{r_1}\cdot\frac{\partial}{\partial r_1}-\frac{l_1(l_1+1)}{r_1^2}\right] R_{l_1,l_2}^{m_1,m_2}(r_1,r_2)$$
$$=\left[\frac{\partial^2}{\partial r_2^2}+\frac{2}{r_2}\cdot\frac{\partial}{\partial r_2}-\frac{l_2(l_2+1)}{r_2^2}\right] R_{l_1,l_2}^{m_1,m_2}(r_1,r_2)\,. \tag{4.12}$$

All radial functions $R_{l_1,l_2}^{m_1,m_2}(r_1,r_2)$ must satisfy this differential equation. In order to obtain an expansion Eq. (4.11) for a given function $f(\boldsymbol{r}_1+\boldsymbol{r}_2)$, it must be possible to specify the radial function $R_{l_1,l_2}^{m_1,m_2}(r_1,r_2)$ – for instance as a power series in r_1 and r_2 – in such a way that first it exhibits the necessary properties, and that second its coefficients can be found by solving the differential Eq. (4.12). A leading coefficient depending on l_1, l_2, m_1, m_2 remains to be determined. This may be

difficult. For doing it, it may be helpful to draw some new information from the differential equation which is satisfied by $f(\boldsymbol{r})$ itself.

Unfortunately, the radial functions $R^{m_1,m_2}_{l_1,l_2}(r_1, r_2)$ can be determined by the method described above only for a few classes of functions $f(\boldsymbol{r}_1+\boldsymbol{r}_2)$. Sack [24] developed and used this method for the derivation of translation formulas for functions $(r')^N$ and $(r')^N \cdot Y_L^M(\boldsymbol{r}'/r')$ with $\boldsymbol{r}'=\boldsymbol{r}-\boldsymbol{R}$.

Some addition theorems derived from solutions of the differential equations of mathematical physics are given in mathematical textbooks, for instance by Watson [25] in connection with Bessel functions.

4.3. Other Methods

There is no general formalism which allows the representation of the translation of a field by an expansion in a series of given functions which form a complete set, e.g. spherical harmonics, *if one insists upon obtaining explicit expressions for the expansion coefficients of any order*. Such explicit formulas are required for practical applications, for numerical calculations with any desired accuracy and for further analytical evaluations, for instance two- and multicenter expansions. In complicated cases, common procedures like Taylor or Fourier expansions often do not meet the requirements for practical applications. Since the Taylor expansion of a function is obtained by a repeated application of the operator $(-\boldsymbol{R}\cdot\partial/\partial\boldsymbol{r})$ on that function, one may arrive at any higher coefficient of the expansion in successive steps. However, the explicit form of the general coefficients may often not be recognized. Moreover, the expansion will usually be given as a series not of the desired, but of different functions.

If one tries to represent a translated field by an expansion in terms of given functions which form a complete, orthonormal set, see Section 3.4, one has to evaluate the integral Eq. (3.14) in order to obtain the expansion coefficients $C_{\mu\nu}$. Because this usually cannot be done analytically, this method cannot be applied in most cases.

Using a double Bessel integral transformation, which is closely related to the Fourier transformation, in connection with the differential Eq. (4.12), Rafiqullah [26] rederived Eq. (4.8) for scalar functions.

Unfortunately, most methods discussed so far are not suitable for general use. This may be the reason why for nearly every one of the few functions, whose transformation properties under translation were considered in the literature, a different method for obtaining the expansion Eq. (4.11) was used.

It is intended to give new expansion theorems for different classes of functions in forthcoming articles. Those special methods for obtaining expansions in spherical harmonics, which are not discussed above, will then be considered at the appropriate places. However, for the new derivations to be given, a "direct or analytical" method will be employed, which utilizes only properties of the special functions and common procedures of analysis. Although group theory or tensor algebra could be very helpful during the course of this investigation, it appears that a completely analytical approach to the problem of determining the functions $u_{k_1}(r)$ and $v_{k_2}(R)$ of the expansion Eq. (3.15) is advantageous. First it allows the application of the same formalism for the derivation of the various

relationships in order to make evident the connections between all the different expansion formulas that will be given. The physical meaning of the manipulations remains clear because properties of the surface spherical harmonics, which are eigenfunctions of L^2 and L_z, are widely used. Secondly, it allows the final relationships to be cast in a form which is immediately applicable to practical problems.

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