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

II. Translations of Powers of the Length of the Local Vector

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For an arbitrary integer N, the expansion theorem

$|\boldsymbol{r}_> - \boldsymbol{r}_<|^N = r_>^N \sum_l \sum_k (2l+1) T_{l,k}^N (r_</r_>)^k P_l(\cos\theta)$

is derived by an induction method, which yields explicit expressions for the expansion coefficient $T_{l,k}^N$. Such expansions are useful in molecular theory because functions $(r')^N$ with $r' = |\boldsymbol{r}_> - \boldsymbol{r}_<|$ are contained in many operators. This investigation provides also a basis for the derivations of expansion theorems for more complicated functions which will be dealt with in later articles of this series.

Key words: Spherical harmonics, expansions of functions r^N in ~

1. Introduction

In the first paper of this series [1], hereafter referred to as Paper I, general concepts and methods for deriving addition theorems for functions of physical interest were discussed. It turned out that most methods encounter great difficulties, and that there is no straightforward way how to obtain the desired expansion theorems. This series of articles deals with derivations of such expansion theorems for certain classes of functions. In order to emphasize the relations between different formulas, a uniform "analytical" approach will be employed. This allows to derive explicit expressions for the expansion coefficients by relying only on common procedures of analysis.

For molecular calculations, the transformational behavior of quantum mechanical *operators* as well as that of *wave functions* is of great interest. Especially for the handling of operators not only translations or one-center expansions, but also multicenter expansions are useful. They, however, can only be obtained by studying the tranformations under translations first. The function r^N represents many operators and is part of many wave functions as well. Therefore, in the present article, the translation of r^N is considered, i.e. the translation of (positive or negative integer) powers N of the length r of the local vector $\boldsymbol{r}$. This investigation provides also a basis for the derivations of expansion theorems for more complicated functions as, for instance, $(kr)^{-N} j_N(kr)$, $r^N e^{-\zeta r}$, $r^N Y_L^M(\theta, \phi)$, $j_L(kr) Y_L^M(\theta, \phi)$, and other functions, which will be given in future work. Here, the j_l denote spherical Bessel functions, the $Y_L^M(\theta, \phi)$ are surface spherical harmonics.

If a field is defined by the function $f(\boldsymbol{r})$, the same field translated by the vector $\boldsymbol{R}$ is given by $\hat{P}_\tau f(\boldsymbol{r}) = f(\boldsymbol{r}')$ with $\boldsymbol{r}' = \boldsymbol{r} - \boldsymbol{R}$, where the translation operator $\hat{P}_\tau$ is defined by $\exp(-\boldsymbol{R} \cdot \partial/\partial \boldsymbol{r})$. As was discussed in I, the translation of a certain field should be represented by an expansion which has the form of an addition theorem, cf. Eq. (I.3.9). Furthermore, it is desirable for physical applications that in the addition theorem the radial and angular dependencies be separated according to Eq. (I.3.15), which corresponds to an expansion in spherical harmonics. This *expansion of* $f(\boldsymbol{r}')$ may then be referred to as a "translation formula", which describes the *translation of* $f(\boldsymbol{r})$. In the following, translation formulas for $(r')^N$ will be derived; the next section deals with special, the third section with general powers N.

2. Translations of r^N for $N = \pm 1, \pm 2, -3, -5$

The derivation of the formula for the translation of general powers r^N of the length r of the local vector $\boldsymbol{r}$ will be based on an induction method. Therefore, the translation of some special powers r^N must be considered first, which will be done for $N = \pm 1, \pm 2, -3$, and -5. For these special powers it is sufficient to consider translations along the z-axis. Therefore, in this section the vector $\boldsymbol{R}$ is assumed to coincide with the z-axis. Then, the angle ω between $\boldsymbol{r}$ and $\boldsymbol{R}$ as defined by Eq. (I.3.18) becomes the polar angle θ of the local vector $\boldsymbol{r}$ with respect to the z-axis. Of course, one still has $\boldsymbol{r}' = \boldsymbol{r} - \boldsymbol{R}$ and $r_< = \mathrm{Min}(r, R)$, $r_> = \mathrm{Max}(r, R)$ as defined by Eqs. (I.3.1) and (I.3.17). The generalization of the translation formulas to translations in arbitrary directions can easily be obtained and will be given for arbitrary exponents N in the next section.

The *translation of* r^2 is determined by the cosine theorem itself, because

$$(r')^2 = r_<^2 + r_>^2 - 2r_< r_> P_1(\cos\theta) . \tag{2.1}$$

The *translation of* r can be described by multiplying Eq. (2.1) with the Laplace expansion Eq. (I.3.16). Using Bonnet's formula [2–4]

$$(2l+1)\zeta P_l(\zeta) = (l+1)P_{l+1}(\zeta) + lP_{l-1}(\zeta) \tag{2.2}$$

with $P_1(\zeta) = \zeta = \cos\theta$ and renaming certain summation indices, one obtains

$$r' = r_> \sum_{l=0}^{\infty} [(2l+3)^{-1}(r_</r_>)^{l+2} - (2l-1)^{-1}(r_</r_>)^l] P_l(\cos\theta) . \tag{2.3}$$

The *translation of* r^{-1} along the z-axis is given by Eqs. (I.3.16) and (I.3.17), if ω is replaced by θ.

The *translation of* r^{-2} is obtained by applying Cauchy's double series theorem to the product of two Laplace-type expansions of $(r')^{-1}$. Due to this theorem [5, 6], the product of two infinite series, which are absolutely convergent, is unchanged if the terms are rearranged in order to form the "Cauchy product" according to

$$\sum_{k=0}^{\infty} q_k \sum_{l=0}^{\infty} q_l = \sum_{j=0}^{\infty} \sum_{k=0}^{j} q_k q_{j-k} . \tag{2.4}$$

As Mertens has shown [7, 8], it is sufficient that at least one of the two infinite series of the product is absolutely convergent. This property will be used later.

With

$$q_k = (r_</r_>)^k P_k(\cos\theta)\,, \tag{2.5}$$

applying the coupling rule for spherical harmonics with the same arguments as given by Rose [9], the product of two Laplace expansions as defined by Eq. (I.3.16) yields

$$(r')^{-2} = (r_>)^{-2} \sum_{j=0}^{\infty} (r_</r_>)^j \sum_{k=0}^{j} \sum_l P_l(\cos\theta) C^2(k, j-k, l; 0, 0)\,. \tag{2.6}$$

The summation over l is restricted by the condition

$$|l_1 - l_2| \leqq l_3 \leqq l_1 + l_2\,, \qquad l_1 + l_2 + l_3 \quad \text{even}, \tag{2.7}$$

with $l_1 = k$, $l_2 = j-k$, and $l_3 = l$. It is advantageous to express the square of the Clebsch-Gordan coefficient [10], which here is defined in Rose's notation [11], by double factorial functions. Using the definitions

$$(2n)!! = 2 \cdot 4 \cdot 6 \cdots (2n) = 2^n n!\,, \tag{2.8a}$$

$$(2n+1)!! = 1 \cdot 3 \cdot 5 \cdots (2n+1) = (2^n n!)^{-1} (2n+1)!\,, \tag{2.8b}$$

$$0!! = (-1)!! = 1!! = 1\,, \tag{2.8c}$$

$$\alpha(n) = \frac{(n-1)!!}{n!!}\,, \tag{2.8d}$$

for natural numbers n, one obtains

$$\begin{aligned} C^2(l_1, l_2, l_3; 0, 0) = {} & (2l_3+1)\alpha(l_1+l_2+l_3+1)\alpha(l_1+l_2-l_3) \\ & \alpha(l_2+l_3-l_1)\alpha(l_3+l_1-l_2)\delta(l_1, l_2; l_3)\,. \end{aligned} \tag{2.9}$$

The symbol $\delta(l_1, l_2; l_3)$ equals one if the condition Eq. (2.7) is fulfilled, but is zero otherwise. This ensures that the double factorial functions have no negative arguments.

If in Eq. (2.6) the summations over k and l are interchanged, the condition Eq. (2.7) requires that the new l values run over

$$l = j, j-2, j-4, \ldots \begin{cases} 0 & (j \text{ even}) \\ 1 & (j \text{ odd}), \end{cases} \tag{2.10}$$

whereas k runs in steps of one between the limits

$$(j-l)/2 \leqq k \leqq (j+l)/2\,. \tag{2.11}$$

The k-summation yields the interesting result

$$\sum_k C^2(k, j-k, l; 0, 0) = (2l+1)\alpha(j-l)\alpha(j+l+1)\,, \tag{2.12}$$

which does not seem to have been given before. A comparison with Eq. (2.9) shows that a remaining factor

$$S_l = \sum_k \alpha(l+j-2k)\alpha(l-j+2k) \tag{2.13}$$

is suppressed because, strangely enough, it is equal to one for any l and j. The factor $\delta(k, j-k; l)$ has been omitted in Eq. (2.13) because it equals one within the range of the index k and zero outside this range. Substituting $\lambda=(l+j-2k)/2$ yields

$$S_l=\sum_{\lambda=0}^{l}\alpha(2\lambda)\alpha(2l-2\lambda). \tag{2.14}$$

For $|x|<1$ the binomial theorem gives

$$(1+x)^{-1/2}=\sum_{\lambda=0}^{\infty}(-1)^{\lambda}\alpha(2\lambda)x^{\lambda}. \tag{2.15}$$

The Cauchy product of this series with itself yields

$$(1+x)^{-1}=\sum_{l=0}^{\infty}(-1)^{l}x^{l}S_l. \tag{2.16}$$

It is obvious from the power series expansion of $(1+x)^{-1}$ that $S_l=1$. Therefore, from Eq. (2.14) one obtains the formula

$$\sum_{\lambda=0}^{l}\binom{2\lambda}{\lambda}\binom{2l-2\lambda}{l-\lambda}=2^{2l}, \tag{2.17}$$

if the functions α are expressed by binomial coefficients.

If the summations over j and l are interchanged, Eq. (2.6) becomes finally with the help of Eq. (2.12)

$$(r')^{-2}=(r_>)^{-2}\sum_{l=0}^{\infty}\sum_{j=l}^{\infty}{}^{(2)}(2l+1)\alpha(j-l)\alpha(j+l+1)(r_</r_>)^{j}P_l(\cos\theta). \tag{2.18}$$

At the second summation symbol it is indicated that the summation over j proceeds in steps of two.

The formula for the *translation of* r^{-3} may be interpreted as a one-center expansion of r_{12}^{-3}, which is needed, for instance, for the calculation of magnetic spin-spin interactions. The expansion of $(r')^{-3}$ may be obtained by differentiating the expansion of $(r')^{-1}$, which is given by Eq. (I.3.16) with respect to $\cos\omega$ and applying the recursion relation [2, 3]

$$P'_{l+1}(\zeta)=(2l+1)P_l(\zeta)+P'_{l-1}(\zeta) \tag{2.19}$$

repeatedly [12]. By differentiating the relationships obtained by this method, one can derive the translation formulas for the higher odd inverse powers of r in a successive way. However, it is advantageous to use another approach in order to emphasize certain geometric aspects of the problem, which become apparent in the translation of r^{-3} and are of importance in other formulas later.

Because in this section it is assumed that $\boldsymbol{R}$ coincides with the z-axis, the cosine theorem for the triangle defined by $\boldsymbol{r}'=\boldsymbol{r}-\boldsymbol{R}$ requires that

$$\cos\theta'=(r^2/2r'R)-(r'/2R)-(R/2r'). \tag{2.20}$$

From the expression for $(\cos\theta')^n$ one can obtain the expansion of $(r')^{-2n-1}$ in an iterative way. Using $\cos\theta'=P_1(\cos\theta')$, it follows

$$(r')^{-3}=R(R^2-r^2)^{-1}[-2(r')^{-2}P_1(\cos\theta')-R^{-1}(r')^{-1}]. \tag{2.21}$$

The functions in the last bracket are special irregular solid spherical harmonics which can be translated along the z-axis according to the following formulas:

Using $P_l^m[\cos(\pi-\theta')]=(-1)^{l+m}P_l^m(\cos\theta')$, one has [13] for $R<r$

$$\frac{P_l^m(\cos\theta')}{(r')^{l+1}}=\sum_{k=0}^{\infty}\binom{l+k-m}{l-m}\frac{R^k}{r^{l+k+1}}P_{l+k}^m(\cos\theta)\,. \tag{2.22a}$$

However, one has [14] for $R>r$

$$\frac{P_l^m(\cos\theta')}{(r')^{l+1}}=\sum_{k=|m|}^{\infty}(-1)^{l+m}\binom{l+k}{l-m}\frac{r^k}{R^{l+k+1}}P_k^m(\cos\theta)\,, \tag{2.22b}$$

where the polar angle of $\boldsymbol{r}$ is θ and that of $\boldsymbol{r}'$ is θ'. These two relationships are examples of the translation of non-scalar functions and correspond to Eqs. (I.3.21a) and (I.3.21b) and, therefore, to the two cases discussed at the end of Section 3 of I. For each case the appropriate expansion for $(r')^{-2}P_1(\cos\theta')$ and $(r')^{-1}$ must be inserted into Eq. (2.21). After some manipulations, one obtains

$$(r')^{-3}=[r_>(r_>^2-r_<^2)]^{-1}\sum_{l=0}^{\infty}(2l+1)(r_</r_>)^l P_l(\cos\theta)\,. \tag{2.23}$$

This formula is valid for both cases because $(r')^{-3}$ is a scalar function. The separation of the variables $r_>$ and $r_<$ can be achieved by expanding the first factor in a power series. This yields

$$(r')^{-3}=(r_>)^{-3}\sum_{l=0}^{\infty}\sum_{j=l}^{\infty}{}^{(2)}(2l+1)(r_</r_>)^j P_l(\cos\theta)\,. \tag{2.24}$$

Squaring Eq. (2.20) and using $(\cos\theta')^2=[2P_2(\cos\theta')+1]/3$, one can express $(r')^{-5}$ as a sum of terms $(r')^{-3}P_2(\cos\theta')$, $(r')^{-3}$, and $(r')^{-1}$, multiplied by some functions of r and R. Using the expansion of $(r')^{-3}$ as given in Eq. (2.24) and the translation theorems Eqs. (2.22a) and (2.22b), one arrives at the formula for the *translation of* r^{-5}:

$$(r')^{-5}=(r_>)^{-5}\sum_{l=0}^{\infty}\sum_{j=l}^{\infty}{}^{(2)}(3!)^{-1}(2l+1)(j-l+2)(j+l+3)(r_</r_>)^j P_l(\cos\theta)\,. \tag{2.25}$$

There are many applications of these expansions. The last one is especially needed for calculations of spin-spin interactions, because the Hamiltonian representing the coupling of two magnetic moments contains r_{12}^{-5} in addition to r_{12}^{-3}.

3. Translations of r^N for an Arbitrary Integer N

The formulas for *translations of* r^N for an arbitrary integer N can be derived by using the geometry of the vectors which occur and the results of the last section. Assuming again that the vector $\boldsymbol{R}$ of the triangle defined by $\boldsymbol{r}'=\boldsymbol{r}-\boldsymbol{R}$ coincides with the z-axis, the cosine theorem gives

$$(r')^N=(r^2+R^2)^{N/2}[1-\varrho(r,R)\zeta]^{N/2} \tag{3.1}$$

with the abbreviations

$$\varrho(r,R)=2rR(r^2+R^2)^{-1}\,,\qquad \zeta=\cos\theta\,. \tag{3.2}$$

Because $|\varrho(r,R)|<1$ unless $r=R$, it holds that $|\varrho(r,R)\zeta|<1$ except for $\boldsymbol{r}'=0$ and $\boldsymbol{r}'=-2\boldsymbol{R}$. If these points are excluded, the binomial theorem allows the expansion of the square bracket raised to the power $N/2$ in a series in terms of powers of $\varrho(r, R)\zeta$. If this is done, the powers of ζ can be expressed by Legendre polynomials according to the formula [15, 16]

$$\zeta^n = a_n^n P_n(\zeta) + a_{n-2}^n P_{n-2}(\zeta) + \ldots + \begin{cases} a_0^n & \text{for even } l \\ a_1^n P_1(\zeta) & \text{for odd } l, \end{cases} \tag{3.3}$$

which may be written as

$$\zeta^n = \sum_{\nu=[0,1]}^{n}{}^{(2)} a_\nu^n P_\nu(\zeta), \tag{3.4}$$

introducing a new summation symbol for later use. The coefficients

$$a_\nu^n = n!(2\nu+1)[(n-\nu)!!(n+\nu+1)!!]^{-1} \tag{3.5}$$

play an important role in all following formulas. Therefore, it is advantageous to define for integers p and q the functions

$$\beta_q^p = [(p-q)!!(p+q+1)!!]^{-1}, \tag{3.6a}$$

$$\gamma_q^p = (p-q)!!(p+q+1)!!, \qquad \gamma_q^p = (\beta_q^p)^{-1}, \tag{3.6b}$$

using the double factorial functions as defined by Eqs. (2.8a)–(2.8d).

If the aforementioned expansions are introduced into Eq. (3.1) one obtains after a change of summations according to

$$\sum_{t=0}^{\infty} \sum_{l=[0,1]}^{t}{}^{(2)} = \sum_{l=0}^{\infty} \sum_{t=l}^{\infty}{}^{(2)} \tag{3.7}$$

the following expansion:

$$(r')^N = (r^2+R^2)^{N/2} \sum_{l=0}^{\infty} \sum_{t=l}^{\infty}{}^{(2)} (-1)^l (2l+1)\beta_l^t \\ N(N-2)\ldots(N-2t+2)2^{-t}\varrho^t(r, R)P_l(\zeta). \tag{3.8}$$

Because this expression is symmetric in r and R, one can utilize the fact that $(r^2+R^2) = (r_<^2 + r_>^2)$ and $rR = r_< r_>$. With $x = r_</r_>$ it holds that

$$(r^2+R^2)^{N/2}\varrho^t(r, R) = r_>^N 2^t x^t (1+x^2)^{(N/2)-t}. \tag{3.9}$$

For $r \neq R$, which means $x < 1$, the last factor can be expanded in a power series as

$$(1+x^2)^{(N/2)-t} = \sum_{j=0}^{\infty}{}^{(2)} (j!!)^{-1}(N-2t)(N-2t-2)\ldots(N-2t-j+2)x^j, \tag{3.10}$$

where Eq. (2.8a) has been used.

It is economical to define

$$\Pi_{2n}^a = a(a-2)\ldots(a-2n+2) \quad \text{for} \quad n = 1, 2, 3, \ldots, \tag{3.11a}$$

$$\Pi_{2n}^a = 0 \quad \text{for} \quad n = -1, -2, -3, \ldots, \tag{3.11b}$$

$$\Pi_0^a = 1 \tag{3.11c}$$

for an arbitrary a. If the constant a is an even positive integer, one has

$$\Pi_{2n}^{2m}=0 \quad \text{for} \quad n \geqq m+1\,, \qquad n, m=1,2,3,\ldots\,. \tag{3.11d}$$

For even positive N, the series in Eq. (3.10) becomes a finite sum, because the coefficient Π_j^{N-2t} vanishes for $j>N-2t$. In this context the products Π_{2n}^a of factors, which descend in steps of two, are of greater advantage than Pochhammer's symbols [17, 18], which are defined by products of factors which ascend in steps of one:

$$(a)_m=a(a+1)\ldots(a+n-1)\,, \qquad (a)_0=1\,. \tag{3.11e}$$

Inserting Eqs. (3.9) and (3.10) into Eq. (3.8) and using

$$\sum_{t=l}^{\infty}{}^{(2)} \sum_{j=0}^{\infty}{}^{(2)} f_{t,j}=\sum_{\sigma=0}^{\infty}{}^{(2)} \sum_{j=0}^{\sigma}{}^{(2)} f_{\sigma-j+l,j} \tag{3.12}$$

one obtains

$$(r')^N=r_>^N \sum_{l=0}^{\infty} \sum_{\sigma=0}^{\infty}{}^{(2)} (2l+1) S_{l,\sigma}^N x^{\sigma+l} P_l(\zeta)\,. \tag{3.13}$$

Now the coefficients $S_{l,\sigma}^N$ are determined by

$$S_{l,\sigma}^N=(-1)^l \sum_{j=0}^{\sigma}{}^{(2)} (j!!)^{-1} \Pi_{2l+2\sigma-j}^N \beta_l^{l+\sigma-j}\,. \tag{3.14}$$

Inserting the complete expressions for Π and β, one sees that this sum can be split into two sums according to

$$S_{l,\sigma}^N=(N+2)^{-1}(N+2-2l-2\sigma) S_{l,\sigma}^{N+2}+S_{l,\sigma-2}^N\,. \tag{3.15}$$

The second term is obtained by substituting $j-2=\tau$ and considering

$$\begin{aligned}&\sum_{j=0}^{\sigma}{}^{(2)} j(j!!)^{-1} \Pi_{2l+2\sigma-j-2}^N \beta_l^{l+\sigma-j}\\ &\quad=\sum_{\tau=0}^{\sigma-2}{}^{(2)} (\tau!!)^{-1} \Pi_{2l+2(\sigma-2)-\tau}^N \beta_l^{l+(\sigma-2)-\tau}\,.\end{aligned} \tag{3.16}$$

At this point it is convenient to substitute $\sigma=k-l$ and

$$S_{l,k-l}^N=T_{l,k}^N\,. \tag{3.17}$$

Then, Eq. (3.15) may be written as

$$(N+2-2k) T_{l,k}^{N+2}=(N+2)[T_{l,k}^N-T_{l,k-2}^N]\,. \tag{3.18}$$

The *expansion of* $(r')^N$ finally becomes

$$(r')^N=r_>^N \sum_{l=0}^{\infty} \sum_{k=l}^{\infty}{}^{(2)} (2l+1) T_{l,k}^N (r_</r_>)^k P_l(\cos\theta) \tag{3.19}$$

with different expressions for the coefficients $T_{l,k}^N$ for the following cases:

I) *N is a positive even integer* ($N=2, 4, 6, \ldots$), $k=l, l+2, \ldots, N-l$

$$T_{l,k}^N=(-1)^l \beta_l^k \beta_l^{N-k} \gamma_0^N\,, \qquad l+k \leqq N\,; \tag{3.20}$$

II) *N is a positive odd integer* ($N=1, 3, 5, \ldots$), $k=l, l+2, \ldots, N+l+1$

$$T_{l,k}^N=(-1)^{(3l+k-N-1)/2} \frac{(l+k-N-2)!!}{(l-k+N+1)!!} \beta_l^k \gamma_0^N\,, \qquad l+k \geqq N+1\,; \tag{3.21a}$$

$$T_{l,k}^N=(-1)^l \beta_l^k \beta_l^{N-k} \gamma_0^N\,, \qquad l+k \leqq N-1\,; \tag{3.21b}$$

III) *N is a negative integer* ($N=-2, -3, -4, -5, \ldots$), $k=l, l+2, \ldots$

$$T_{l,k}^N=\beta_l^k \beta_0^{-N-3} \gamma_l^{-N+k-3}\,, \qquad T_{l,k}^{-1}=(2l+1)^{-1}\delta_{l,k} \tag{3.22}$$

The functions β_q^p and γ_q^p are defined by Eqs. (3.6a) and (3.6b). The coefficients $T_{l,k}^N$ vanish if the indices k and l assume values outside the given ranges. This terminates the summations defined in Eq. (3.19) in cases I and II such that the summation indices run only within the limits

$$0 \leqq l \leqq N/2\,, \qquad l \leqq k \leqq N-l \qquad \text{for case I,} \tag{3.23a}$$

$$0 \leqq l < \infty\,, \qquad l \leqq k \leqq N+l+1 \quad \text{for case II.} \tag{3.23b}$$

The k values proceed in steps of 2.

The recursion relation Eq. (3.18) allows one to prove that in fact the expansion Eq. (3.19) is valid if the coefficients $T_{l,k}^N$ are given by Eqs. (3.20)–(3.22). This is possible because the coefficients $T_{l,k}^N$ of an expansion $(r')^N$ with an arbitrary integer N can be connected with those of the expansions $(r')^N$ with $N=\pm 1, \pm 2, -3$, which are given in Section 2. One may assume for a moment that the expansion coefficients in Eq. (3.19) are denoted by $\hat{T}_{l,k}^N$, whereas the expressions given by Eqs, (3.20)–(3.22) are still denoted by $T_{l,k}^N$. If $\hat{T}_{l,k}^N$ would differ from $T_{l,k}^N$, one could measure the deviation by $\theta_{l,k}^N$, putting

$$\hat{T}_{l,k}^N=T_{l,k}^N+\theta_{l,k}^N\,. \tag{3.24}$$

Then, the recursion relation of Eq. (3.18) holds also for $\theta_{l,k}^N$. In the following it will be shown that the quantities $\theta_{l,k}^N$ vanish in all cases.

In case I a comparison of Eq. (2.1) with Eqs. (3.19) and (3.20) shows that $\theta_{l,k}^2=0$ for *all* l, k. Because of Eq. (3.18) all $\theta_{l,k}^N$ with $N=2, 4, 6, \ldots$ vanish if $2k \neq N+2$. If $2k=N+2$ one has $\theta_{l,(N/2)+1}^N=\theta_{l,(N/2)-1}^N=0$.

In case II it follows from a comparison of Eq. (2.3) with Eqs. (3.19), (3.21a), and (3.21b) that $\theta_{l,k}^1=0$ for *all* l, k. Therefore, one has $\theta_{l,k}^N=0$ for $N=1, 3, 5, \ldots$ due to Eq. (3.18).

In case III the recursion relation Eq. (3.18) will be used in the form

$$N_0[\theta_{l,k}^{N_0-2}-\theta_{l,k-2}^{N_0-2}]=(N_0-2k)\theta_{l,k}^{N_0}\,. \tag{3.25}$$

If $\theta_{l,k}^{N_0}=0$ for a certain $N_0<0$, it follows, because $N_0 \neq 2k$, that

$$\theta_{l,k}^{N_0-2}=\theta_{l,k-2}^{N_0-2}=\ldots=\theta_{l,l}^{N_0-2}\,. \tag{3.26}$$

However, $\theta_{l,l}^{N}=0$ as can be seen from Eqs. (3.14), (3.17), and (3.22). The expansions of $(r')^{-2}$ and $(r')^{-3}$, given by Eq. (2.18) and Eq. (2.21), respectively, yield $\theta_{l,k}^{-2}=\theta_{l,k}^{-3}=0$ for *all* l, k. Putting $N_0=-2, -4, \ldots$ and $N_0=-3, -5, \ldots$, respectively, it follows from Eq. (3.26) that $\theta_{l,k}^{N_0}=0$ for any N_0, q.e.d.

It may be noted that in the cases I and II the correctness of Eqs. (3.19), (3.20), (3.21a), and (3.21b) can also be shown by a complete induction. The general formulas for the coefficients $T_{l,k}^{N+2}$ can be obtained from those for $T_{l,k}^{N}$ by multiplying the expansion of $(r')^N$ as given by Eq. (3.19) with the expression for $(r')^2$ as given by Eq. (2.1) and applying the coupling rule for spherical harmonics [9]. In case III the induction requires the multiplication of the expansion of $(r')^N$ with that of $(r')^{-2}$. Because $(r')^{-2}$ is given by a complicated infinite series [see Eq. (2.18)], the induction procedure seems to be too difficult.

So far, it has been shown that the coefficients $T_{l,k}^{N}$ as given by Eqs. (3.20)–(3.22) are correct. In the first place, the formulas for these coefficients are found by inspection of the expressions which are obtained by successive application of Eq. (3.18). This is similar to the procedure which is necessary for the complete induction. For negative N, the successive procedures as described in Section 2 have been used.

The two summations, which determine the expansion of $(r')^N$, are both finite in case I, because then the coefficients $T_{l,k}^{N}$ vanish for $l+k>N$ and $l>N/2$ as is seen from Eqs. (3.14) and (3.11d). In case II, one summation is infinite, the other one is restricted, since $T_{l,k}^{N}=0$ for $k \geqq N+l+3$. This follows from the recursion relation Eq. (3.18) and the fact that $T_{l,N+l+3}^{N}=0$, because the sum given by Eq. (3.14) reduces to the binomial expansion of $(1-1)^{(N+3)/2}$. In case III the summation over l as well as that over k is infinite.

Of course, the expansion Eq. (3.19) holds for *arbitrary* parallel coordinate systems if $P_l(\cos\theta)$ is expressed by the addition theorem Eq. (I.3.19) because θ denotes the angle between $\boldsymbol{r}_<$ and $\boldsymbol{r}_>$.

4. Discussion and Relation to Previous Work

In Eq. (3.19) together with Eqs. (3.6a), (3.6b), and (3.20)–(3.22), a spherical-harmonic expansion of the function $(r')^N$ is given for arbitrary integer N. This expansion represents a translation of the field defined by the function r^N. The coefficients $T_{l,k}^{N}$ as given by Eqs. (3.20)–(3.22) are closely related to the coefficients contained in expansions of other functions, as will be shown later. Therefore, the present investigation is a first step in the direction of expanding more complicated functions to be considered in future work. Furthermore, the functions r^N have the advantage that they can be used as expansion bases for other scalar functions.

Functions r^N play an important role in many physical problems. For instance, because interatomic potentials contain terms r^N, expansions of r^N are needed in the theory of molecular interactions. Therefore, the interest of a number of research workers has focused on that function.

In 1956, Balescu [19] tried to reexpand a series of Gegenbauer polynomials into one of Legendre polynomials but could not give the coefficients in closed form. He arrived at an expansion of an integer power of r, but gave the expansion coefficients only as finite sums. This may be the reason why his result was erroneously considered as being not correct [20]. Already in 1916 Chapman [21] evaluated these sums, but his work remained widely unknown. In 1961, Fontana [22] gave a formula for the translation of r^{-2} in which the variables were not completely separated. In 1964, Sack [23] started a series of very fruitful investigations in this field by giving, among others, expansions in spherical harmonics of functions r^N with arbitrary N, approaching the problem as discussed in Section 4.2 of I. Utilizing the dimensionality of the function r^N and its continuity properties as $r_< \to 0$, Sack was able to specify for this function the radial dependency of its expansion in form of a power series and to determine the coefficients by solving the radial differential equation given by Eq. (I.4.12). This approach may be very difficult or even impossible for other types of functions which are to be expanded. Sack expressed his expansion theorems in terms of hypergeometric functions of the radial variables. Due to the inherent complexity of these functions, these expressions are less suitable for practical applications than the formulas containing coefficients $T_{l,k}^N$. Furthermore, it seems difficult to use Sack's formulas as a starting point for the derivation of factorless multicenter expansions [24].

There are several papers which contain translation formulas for special powers of r. Some of them have been applied in textbooks of the theory of atomic spectra [25]. Judd [12] treated r^{-3} and r^{-5} showing that by successive differentiation one can arrive at expansions for higher negative odd powers of r. Perkins [26] derived by complete induction the addition theorem for r^N, where N is a positive integer. In 1971, Yasuda and Yamamoto [20] derived a bipolar expansion of r^N in the non-overlapping, not spherically connected region [27], which contains the translation formula as a special case, by making extensive use of tensor algebra. For negative integer values of N they used this expansion in the theory of phase transitions in solid methane. However, for positive odd integer values of N they gave a finite series which obviously does not hold. A new aspect of the expansion of r_{12} and r_{12}^{-1} in terms of spherical harmonics was considered by Cressy and Ruedenberg [28], who expressed the *non-analytic* factors $(r_<^l/r_>^{l+1})$ by further expansions in terms of *analytic* functions of r_1 and r_2.

Some authors applied methods different from those discussed so far. Matcha and Daiker [29] gave expansions of r^N in spherical polar and confocal elliptical coordinates without performing the inner summations, utilizing solutions of separable differential operators which annihilate the functions which are to be expanded. In 1967, Ruedenberg [30] investigated the problem of bipolar expansions by means of the Fourier transformation method representing the radial expansion coefficients by integrals over spherical Bessel functions. Of course, his results may be specialized to describe translations. This method was discussed in Section 4.1 of I. Using the method of Fourier transformation, Salmon, Birss, and Ruedenberg [31] gave a spherical-harmonic expansion of the Coulomb potential. Expanding the spherical Bessel functions in terms of Laguerre polynomials, the radial integrals could be evaluated and gave the expansion coefficients as infinite series of Laguerre functions. Several authors [32–34] discussed the translation of solid spherical harmonics, because they are of great physical interest. These functions are special cases of $r^N Y_L^M(\theta, \phi)$ which was first expanded by Sack [35]. An expansion theorem for this function was also obtained by Kay, Todd, and Silverstone [36] by application of Ruedenberg's Fourier transformation method. The evaluation of the radial integrals was possible by utilizing the theory of generalized functions. However, this method fails to yield explicit formulas for r^N with $N = -2, -4, \ldots$. Based on the derivations given in the present paper, one-, two-, and multicenter expansions for those and other functions can be obtained, as will be shown later.

References

1. Steinborn, E. O., Filter, E.: Theoret. Chim. Acta (Berl.) **38**, 247 (1975)
2. Lense, J.: Kugelfunktionen, S. 16, 17. Leipzig: Akademische Verlagsgesellschaft 1950
3. Bethe, H. A., Salpeter, E. E.: In: Flügge, S. (Hrsg.): Handbuch der Physik, Bd. 35, S. 430. Berlin: Springer Verlag 1957
4. Abramowitz, M., Stegun, I. A.: Handbook of mathematical functions, pp. 782, 783. New York: Dover Publications 1965
5. Knopp, K.: Theorie und Anwendung der unendlichen Reihen, S. 147. Berlin: Springer Verlag 1964
6. Bromwich, T. J.: An introduction to the theory of infinite series, p. 72. London: Macmillan 1965
7. Reference [5], S. 330
8. Reference [6], p. 92
9. Rose, M. E.: Elementary theory of angular momentum, p. 241. New York: Wiley 1957
10. Racah, G.: Phys. Rev. **62**, 438 (1942)
11. Reference [9], pp. 47, 222
12. Judd, B. R.: Operator techniques in atomic spectroscopy, p. 88. New York: McGraw-Hill 1963
13. Steinborn, E. O., Ruedenberg, K.: Advan. Quantum Chem. **7**, 1 (1973), p. 53, Eq. (240)
14. Reference [13], p. 54, Eq. (247)
15. Reference [2], S. 45
16. Reference [13], p. 11, Eqs. (22)–(26)
17. Bateman, H.: Higher transcendental functions, Vol. 2, p. 236. New York: McGraw-Hill 1953
18. Magnus, W., Oberhettinger, F., Soni, R. P.: Formulas and theorems for the special functions of mathematical physics, pp. 1–3. Berlin: Springer 1966
19. Balescu, R.: Physica **22**, 224 (1956)
20. Yasuda, H. Y., Yamamoto, T.: Progr. Theoret. Phys. **45**, 1485 (1971)
21. Chapman, S.: Quart. J. Pure Appl. Math. **185**, 16 (1916)
22. Fontana, P. R.: J. Math. Phys. **2**, 825 (1961)
23. Sack, R. A.: J. Math. Phys. **5**, 245 (1964)
24. Steinborn, E. O., Filter, E.: To be published
25. Shore, B. W., Menzel, D. H.: Principles of atomic spectra, p. 176. New York: Wiley 1968
26. Perkins, J. F.: J. Chem. Phys. **50**, 2819 (1969)
27. Löwdin, P.-O.: Advan. Phys. (Phil. Mag. Suppl.) **5**, 1 (1956), pp. 15, 95, 110
28. Cressy, N., Ruedenberg, K.: Int. J. Quantum Chem. **3**, 493 (1969)
29. Matcha, R. L., Daiker, K. C.: J. Math. Phys. **15**, 114 (1974)
30. Ruedenberg, K.: Theoret. Chim. Acta (Berl.) **7**, 359 (1967)
31. Salmon, L. S., Birss, F. W., Ruedenberg, K.: J. Chem. Phys. **49**, 4293 (1968)
32. Chiu, Y. N.: J. Math. Phys. **5**, 283 (1964)
33. Dahl, J. P., Barnett, M. P.: Mol. Phys. **9**, 175 (1965)
34. Steinborn, O.: Chem. Phys. Letters **3**, 671 (1969)
35. Sack, R. A.: J. Math. Phys. **5**, 252 (1964)
36. Kay, K. G., Todd, H. D., Silverstone, H. J.: J. Chem. Phys. **51**, 2359 (1969)

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