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Maxwell–Cartesian spherical harmonics in multipole potentials and atomic orbitals

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Abstract. The nature of the Maxwell–Cartesian spherical harmonics $S_K^{(n)}$ and their relation to tesseral harmonics Y_{nm} is examined with the help of "tricorn arrays" that display the components of a totally symmetric Cartesian tensor of any rank in a systematic way. The arrays show the symmetries of the Maxwell–Cartesian harmonic tensors with respect to permutation of axes, the traceless properties of the tensors, the linearly independent subsets, the nonorthogonal subsets, and the subsets whose linear combinations produce the tesseral harmonics. The two families of harmonics are related by their connection with the gradients of $1/r$, and explicit formulas for the transformation coefficients are derived. The rotational transformation of $S_K^{(n)}$ functions is described by a relatively simple Cartesian tensor method. The utility of the Maxwell–Cartesian harmonics in the theory of multipole potentials, where these functions originated in the work of Maxwell, is illustrated with some newer applications which employ a detracer exchange theorem and make use of the partial linear independence of the functions. The properties of atomic orbitals whose angular part is described by Maxwell–Cartesian harmonics are explored, including their angular momenta, adherence to an Unsöld-type spherical symmetry relation, and potential for eliminating an angular momentum "contamination" problem in Cartesian Gaussian basis sets.

Key words: Spherical harmonics – Tricorn – Multipole potential – Atomic orbitals

1 Introduction

There are two major families of spherical harmonic functions that are widely applied in physical problems: the Maxwell–Cartesian harmonics, which arise primarily in problems involving multipole expansions, and the tesseral harmonics, which are best known for their role in atomic orbitals and the general quantum mechanical problem of angular momentum, though they are widely used for multipole expansions and other problems as well.

The literature on this subject presents two different points of view on the definition of spherical harmonics. Major mathematical works [1–3] and some physics texts [4–7] adopt the classical definition of a spherical harmonic function as a homogeneous polynomial in x, y, z which satisfies the Laplace equation; however, modern physics works [8–14], limit spherical harmonics to the tesseral harmonics, sometimes basing this choice on a quantum mechanical definition whereby a surface spherical harmonic is an eigenfunction of both L^2, the square of the angular momentum operator, and L_z, the z-component of the angular momentum operator. The classical definition is the broader one, encompassing both families discussed here.

It is evident that certain functions in the two families are similar. Thus, the potential of a point charge has the same angular dependence as the s orbital of the hydrogen atom, the potential of a point dipole has the same angular dependence as a p orbital, the potential of a point quadrupole has the same angular dependence as a d orbital, and so on [15]. However, the relations between the two families are more generally in the form of linear transformations which combine the functions of one family to give any member of the other [11, 14, 16]. Apparently the fact is overlooked that most of the Maxwell–Cartesian harmonics are not eigenfunctions of L_z, and would not qualify as spherical harmonics by the quantum mechanical definition. Likewise any linear combination of tesseral harmonics of the same degree but with different eigenvalues of L_z would qualify as spherical harmonics under the classical, but not under the quantum mechanical, definition. Thus, while it is usually understood that the two families of functions apply to many of the same physical problems, there is a need for clarification of the properties of the Maxwell–Cartesian harmonics, particularly as these affect their

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application to problems usually cast in terms of tesseral harmonics.

The purpose of this work is to continue the systematic examination of the Maxwell–Cartesian harmonics which I began in an earlier paper [16], where their properties as components of totally symmetric and traceless Cartesian tensors were developed. The organization of the article is as follows. The major definitions are reviewed in Sect. 2. The "tricorn" array as a means of displaying important features of the Maxwell–Cartesian harmonics as tensor components is introduced in Sect. 3. Mathematical properties of the Maxwell–Cartesian harmonics and the relation of these functions to the tesseral harmonics are presented in Sects. 4–6. The unique properties of the Maxwell–Cartesian harmonics with some recent applications to the theory of multipole potentials are illustrated in Sect. 7. In Sect. 8 these functions are shown to be suitable descriptions of the angular part of atomic orbitals, and their properties are discussed.

2 Definitions

2.1 Cartesian tensors

A Cartesian tensor of rank n is denoted by a sans-serif symbol $\mathsf{A}^{(n)}$ or by the component index notation $A^{(n)}_{\alpha_1\cdots\alpha_n}$, where Greek subscripts denote Cartesian axes $1, 2, 3$, corresponding to axes x, y, z, respectively. The complete tensor is an array of 3^n components.

If $A^{(n)}_{\alpha_1\cdots\alpha_n}$ is invariant under any permuation of the sequence $\alpha_1\cdots\alpha_n$, the tensor is said to be totally symmetric. The compressed form of such a tensor is an array of the $(n+1)(n+2)/2$ distinct components of $\mathsf{A}^{(n)}$, and these are alternatively written $A^{(n)}_{n_1n_2n_3}$, where n_i is the number of times i occurs in the component index set $\alpha_1\cdots\alpha_n$. The n_i are called degree indices and satisfy $n_1+n_2+n_3=n$.

The components of $\mathsf{A}^{(n)}$ are also designated by the simpler notation $A^{(n)}_K$, where K is a running index which stands for a particular component index set or degree index set. The order of the K values is the canonical order [17]. The relations among the various index notations are illustrated in Table 1.

2.2 Tensor contractions

An n-fold contraction is denoted by $\cdot n\cdot$, as in

$$\mathsf{A}^{(n)}\cdot n\cdot\mathsf{B}^{(n)} = A^{(n)}_{\alpha_1\cdots\alpha_n}B^{(n)}_{\alpha_n\cdots\alpha_1}\ , \tag{1}$$

where the convention of implied summation over repeated Greek subscripts is followed. For totally symmetric tensors the contraction can be written [17]

$$\mathsf{A}^{(n)}\cdot n\cdot\mathsf{B}^{(n)} = \sum_{n_1n_2n_3} g(n;n_1n_2n_3)A^{(n)}_{n_1n_2n_3}B^{(n)}_{n_1n_2n_3}\ , \tag{2}$$

where $g(n;n_1n_2n_3) = n!/n_1!n_2!n_3!$, and the sum is over all degree index sets for rank n.

Table 1. Maxwell–Cartesian surface spherical harmonics

n	K	$\{\alpha\}$[a]	$\{n\}$[b]	$S^{(n)}_K(\hat{\mathbf{r}})$	N_{nK}
0	1	–	000	1	4π
1	1	1	100	$\hat{x}$	$4\pi/3$
	2	2	010	$\hat{y}$	$4\pi/3$
	3	3	001	$\hat{z}$	$4\pi/3$
2	1	11	200	$3\hat{x}^2-1$	$16\pi/5$
	2	21	110	$3\hat{x}\hat{y}$	$12\pi/5$
	4	22	020	$3\hat{y}^2-1$	$16\pi/5$
	5	32	011	$3\hat{y}\hat{z}$	$12\pi/5$
	6	33	002	$3\hat{z}^2-1$	$16\pi/5$
3	1	111	300	$15\hat{x}^3-9\hat{x}$	$144\pi/7$
	2	211	210	$15\hat{x}^2\hat{y}-3\hat{y}$	$96\pi/7$
	3	311	201	$15\hat{x}^2\hat{z}-3\hat{z}$	$96\pi/7$
	4	221	120	$15\hat{x}\hat{y}^2-3\hat{x}$	$96\pi/7$
	5	321	111	$15\hat{x}\hat{y}\hat{z}$	$60\pi/7$
	6	331	102	$15\hat{x}\hat{z}^2-3\hat{x}$	$96\pi/7$
	7	222	030	$15\hat{y}^3-9\hat{y}$	$144\pi/7$
	8	322	021	$15\hat{y}^2\hat{z}-3\hat{z}$	$96\pi/7$
	9	332	012	$15\hat{y}\hat{z}^2-3\hat{y}$	$96\pi/7$
	10	333	003	$15\hat{z}^3-9\hat{z}$	$144\pi/7$
4	1	1111	400	$105\hat{x}^4-90\hat{x}^2+9$	256π
	2	2111	310	$105\hat{x}^3\hat{y}-45\hat{x}\hat{y}$	160π
	3	3111	301	$105\hat{x}^3\hat{z}-45\hat{x}\hat{z}$	160π
	4	2211	220	$105\hat{x}^2\hat{y}^2-15\hat{x}^2-15\hat{y}^2+3$	144π
	5	3211	211	$105\hat{x}^2\hat{y}\hat{z}-15\hat{y}\hat{z}$	80π
	6	3311	202	$105\hat{x}^2\hat{z}^2-15\hat{x}^2-15\hat{z}^2+3$	144π
	7	2221	130	$105\hat{x}\hat{y}^3-45\hat{x}\hat{y}$	160π
	8	3221	121	$105\hat{x}\hat{y}^2\hat{z}-15\hat{x}\hat{z}$	80π
	9	3321	112	$105\hat{x}\hat{y}\hat{z}^2-15\hat{x}\hat{y}$	80π
	10	3331	103	$105\hat{x}\hat{z}^3-45\hat{x}\hat{z}$	160π
	11	2222	040	$105\hat{y}^4-90\hat{y}^2+9$	256π
	12	3222	031	$105\hat{y}^3\hat{z}-45\hat{y}\hat{z}$	160π
	13	3322	022	$105\hat{y}^2\hat{z}^2-15\hat{y}^2-15\hat{z}^2+3$	144π
	14	3332	013	$105\hat{y}\hat{z}^3-45\hat{y}\hat{z}$	160π
	15	3333	004	$105\hat{z}^4-90\hat{z}^2+9$	256π

[a] Set of component indices $\alpha_1\cdots\alpha_n$
[b] Set of degree indices $n_1n_2n_3$

2.3 Traces

The trace of $\mathsf{A}^{(n)}$ in one component index pair is formed by contraction of that pair, as in $A^{(n)}_{\nu\nu\alpha_3\ldots\alpha_n}$. For a totally symmetric tensor we can write

$$A^{(n)}_{\nu\nu\alpha_3\cdots\alpha_n} = A^{(n)}_{n_1+2,n_2,n_3} + A^{(n)}_{n_1,n_2+2,n_3} + A^{(n)}_{n_1,n_2,n_3+2}\ . \tag{3}$$

If the trace vanishes in all index pairs, the tensor is totally traceless. If a totally symmetric tensor is traceless in one index pair, it is totally traceless.

2.4 The detracer

A totally symmetric tensor $\mathsf{A}^{(n)}$ is rendered totally symmetric and traceless by the detracer operator $\mathscr{T}_n$, which forms a linear combination of the tensor with all its multiple traces [16] in the manner

$$\mathscr{T}_n A^{(n)}_{\alpha_1 \ldots \alpha_n} = \sum_{m=0}^{[n/2]} (-1)^m (2n-2m-1)!! \times \sum_{T\{\alpha\}} \delta_{\alpha_1\alpha_2} \cdots \delta_{\alpha_{2m-1}\alpha_{2m}} A^{(n)}_{v_1 v_1 \cdots v_m v_m \alpha_{2m+1} \cdots \alpha_n} \quad , \quad (4)$$

where $[n/2]$ denotes the integer part of $n/2$; $(2k-1)!! = 1 \cdot 3 \cdot 5 \cdot (2k-1)$ with $(-1)!! = 1$; $\delta_{\alpha\beta}$ is the Kronecker delta; and the sum over $T\{\alpha\}$ is the sum over all permutations of the symbols $\alpha_1 \cdots \alpha_n$ which give distinct terms.

2.5 Maxwell–Cartesian spherical harmonics

Let $\mathbf{r}$ designate a point with Cartesian coordinates $r_1 = x, r_2 = y, r_3 = z$. Let $\hat{\mathbf{r}} = \mathbf{r}/r$ represent a point on the unit sphere with coordinates $\hat{x} = x/r, \hat{y} = y/r, \hat{z} = z/r$.

A function $f(\mathbf{r})$ is called a solid spherical harmonic of degree n if f is homogeneous of degree n in x, y, z and satisfies the Laplace equation $\nabla^2 f = 0$. The function $f(\hat{\mathbf{r}})$ is called a surface spherical harmonic of degree n.

The Maxwell–Cartesian surface spherical harmonics $S^{(n)}_K$ arise in the following way. Maxwell [1, 18] related the potential of a general multipole of order n to an nth order gradient of r^{-1} with respect to a general set of axes, and he showed that a general surface spherical harmonic of degree n is simply related to the gradient so obtained. When all of the axes coincide with Cartesian axes, his formula reduces to [16]

$$S^{(n)}_{n_1 n_2 n_3}(\hat{\mathbf{r}}) \equiv (-1)^n r^{n+1} \nabla_1^{n_1} \nabla_2^{n_2} \nabla_3^{n_3} r^{-1} = \mathscr{T}_n \hat{\mathbf{r}}^n \quad (5)$$

where $\nabla_\alpha \equiv \partial/\partial r_\alpha$. See the Appendix for details. (I have previously [16] used the name "Cartesian basis spherical harmonics" for these functions, but "Maxwell–Cartesian spherical harmonics" seems preferable to avoid confusion with the infinite variety of spherical harmonics that can be expressed in terms of Cartesian coordinates.)

If we replace $\mathsf{A}^{(n)}$ in Eq. (4) with $\mathbf{r}^n$ and convert to degree index form, the result is the solid spherical harmonic [16]

$$S^{(n)}_{n_1 n_2 n_3}(\mathbf{r}) = \sum_{m_1=0}^{[n_1/2]} \sum_{m_2=0}^{[n_2/2]} \sum_{m_3=0}^{[n_3/2]} (-1)^m (2n-2m-1)!! \times \begin{bmatrix} n_1 \\ m_1 \end{bmatrix} \begin{bmatrix} n_2 \\ m_2 \end{bmatrix} \begin{bmatrix} n_3 \\ m_3 \end{bmatrix} r^{2m} x^{n_1-2m_1} y^{n_2-2m_2} z^{n_3-2m_3} \quad , \quad (6)$$

where $m = m_1 + m_2 + m_3$ and $\left[\begin{smallmatrix} n \\ m \end{smallmatrix}\right] = n!/2^m m!(n-2m)!$. The Maxwell–Cartesian surface spherical harmonics of nonnegative degree n are, in tensor form [1],

$$S^{(n)}(\hat{\mathbf{r}}) = r^{-n} \mathsf{S}^{(n)}(\mathbf{r}) \quad . \quad (7)$$

The particular formulas from Eqs. (6) and (7) for $n = 0$–4 are given in Table 1. The polynomials do not appear to be homogeneous in $\hat{x}, \hat{y}, \hat{z}$ because a factor r^{2m} in each term has been eliminated by virtue of the constraint $\hat{x}^2 + \hat{y}^2 + \hat{z}^2 = 1$.

Corresponding solid spherical harmonics of negative degree $-n-1$ are obtained by multiplying the surface spherical harmonic by r^{-n-1} [1]. Such harmonics are still components of a totally traceless and symmetric tensor of degree n, i.e., the rank of the tensor is no longer equal to the degree of the homogeneous function.

2.6 Tesseral harmonics

Let θ, ϕ be the polar angle and azimuth, respectively, of a spherical coordinate system. The unnormalized tesseral harmonics $Y^m_n(\theta, \phi)$ of degree n and order m are defined in terms of the associated Legendre functions $P^m_n(\cos\theta)$ according to

$$Y^m_n(\theta, \phi) = P^m_n(\cos\theta) \mathrm{e}^{\mathrm{i}m\phi} \quad (8)$$

for $m = 0, \pm 1, \ldots, \pm n$. The real and imaginary parts of Y^m_n are each surface spherical harmonics known as tesseral, sectoral, and zonal harmonics in much of the literature. The term "tesseral" harmonics is used here for any of the (generally complex) functions defined by Eq. (8).

Like the Maxwell–Cartesian harmonics, the tesseral harmonics can be derived from gradients of r^{-1} according to Hobson's formula [1] for $0 \le m \le n$:

$$Y^m_n(\hat{\mathbf{r}}) = \frac{(-1)^n r^{n+1}}{(n-m)!} (\nabla_1 + \mathrm{i}\nabla_2)^m \nabla_3^{n-m} r^{-1} \quad , \quad (9)$$

where the spherical coordinates θ, ϕ are replaced by the Cartesian unit vector $\hat{\mathbf{r}}$ corresponding to the same direction in space.

The normalized tesseral harmonics Y_{nm} are given by [8]

$$Y_{nm} = (-1)^m \left[\frac{(2n+1)(n-m)!}{4\pi(n+m)!} \right]^{1/2} Y^m_n \quad , \quad (10)$$

which obeys the useful relation [8]

$$Y_{n,-m} = (-1)^m Y^*_{nm} \quad , \quad (11)$$

where the asterisk denotes the complex conjugate. Explicit formulas for the lower order Y_{nm} in both spherical and Cartesian coordinates are available in various tables [8, 11, 14].

3 Tricorn arrays

A useful way to display the components of a totally symmetric Cartesian tensor of any rank n is the following. Consider the three-dimensional space of the degree indices, as shown in Fig. 1. A plane which intersects all axes at $n_i = n$ contains all the points whose coordinates are the degree indices satisfying $n_1 + n_2 + n_3 = n$. There are $(n+1)(n+2)/2$ such points within a triangular region of the plane. The array of points, which I will call a "tricorn", thus represents all the distinct components of a totally symmetric tensor of rank n. The full stack of tricorns extending from the origin to infinity comprises a polytensor [17].

A tricorn for $n = 3$ with the degree indices for each component is shown in Fig. 2. The tricorn will always be drawn here with n_3 increasing from bottom to top. Note

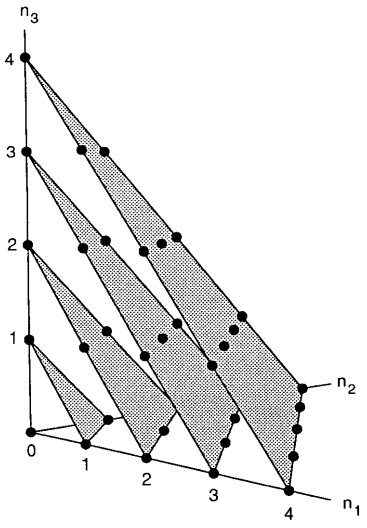

Fig. 1. The three-dimensional space of nonnegative integers. The *points* represent the degree indices of totally symmetric tensors. Each plane contains all points corresponding to the components of a compressed tensor of rank $n = n_1 + n_2 + n_3$

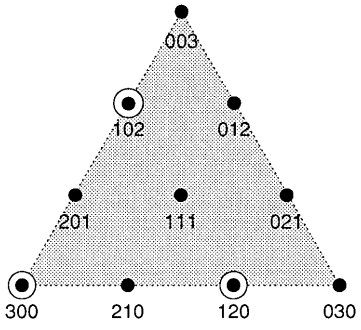

Fig. 2. Tricorn array of the degree indices of a tensor of rank 3. The *circled points* are an example of a set whose sum constitutes a trace of the tensor

the three circled points. These are the components whose sum is a trace of the tensor, according to Eq. (3). The sum of any three components which are located at the vertices of a "subtricorn" with sides of 2 integer units constitutes a trace of the tensor. In the case of a tensor of rank 2, there is only one such set of points, and these correspond to the diagonal elements of the conventional 3×3 matrix representation.

The canonical order of tensor components is shown by the dashed line in Fig. 3, starting with point $n00$ and proceeding in the direction of the arrow. The components are numbered in this order by index K in Table 1. The same order is followed in a proposed one-dimensional array of tensor components [17].

Tricorn arrays of the $\mathsf{S}^{(n)}$ tensors in graphical form based on the formulas of Table 1 are shown in Figs. 4, 5, 6, and 7. Each component function is shown as a surface whose distance from the origin in any direction is the absolute value of the function. Positive values are shown in dark gray and negative values in light gray. The origin for each function is centered in a cube whose edges are

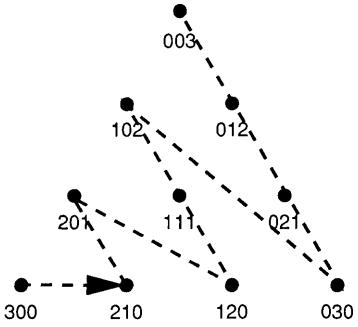

Fig. 3. Canonical order of tensor components in a tricorn array

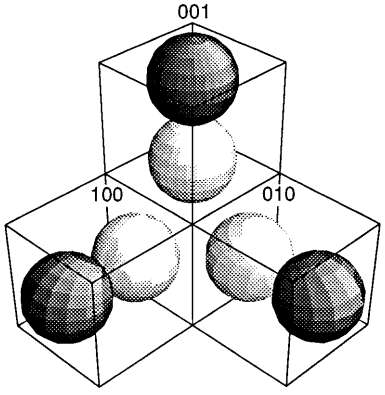

Fig. 4. Tricorn array for $\mathsf{S}^{(1)}$. In this and subsequent figures the *dark gray surfaces* correspond to positive values of the functions and the *light gray surfaces* to negative values, and all surfaces in the tricorn are drawn to the same scale. The figures were produced with the Mathematica package mentioned in Sect. 10

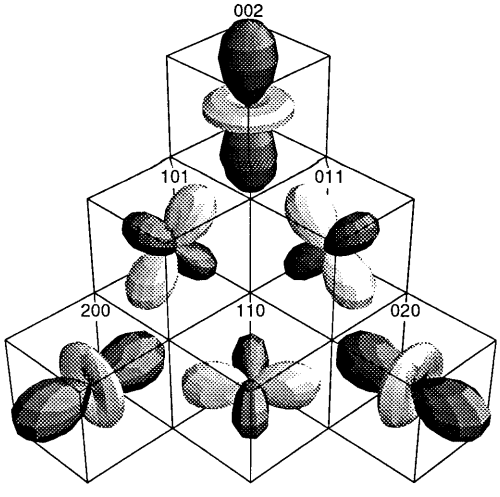

Fig. 5. Tricorn array for $\mathsf{S}^{(2)}$

parallel to the x-y-z-axes. The axes form a right-handed system with z toward the top.

There are several noteworthy features of the tricorns.

1. The functions show many similarities to the familiar angle-dependent parts of atomic orbital functions

found in textbooks. The latter are, however, tesseral harmonics, which differ in important ways from the Maxwell–Cartesian harmonics.

2. The arrays have a striking symmetry that is unfamiliar in the tesseral harmonics, i.e., the picture is unchanged on any permutation of the axes.
3. For $n \geq 2$ the number of functions in the array, $(n+1)(n+2)/2$, is greater than the number of tesseral harmonics, $2n+1$, of the same degree.
4. The traceless nature of $\mathsf{S}^{(n)}$ is evident from the tendency for positive and negative lobes to cancel for any three functions located on the vertices of a subtricorn as in Fig. 2. Where this is not obvious, one can prove it more easily by adding the corresponding functions in Table 1.

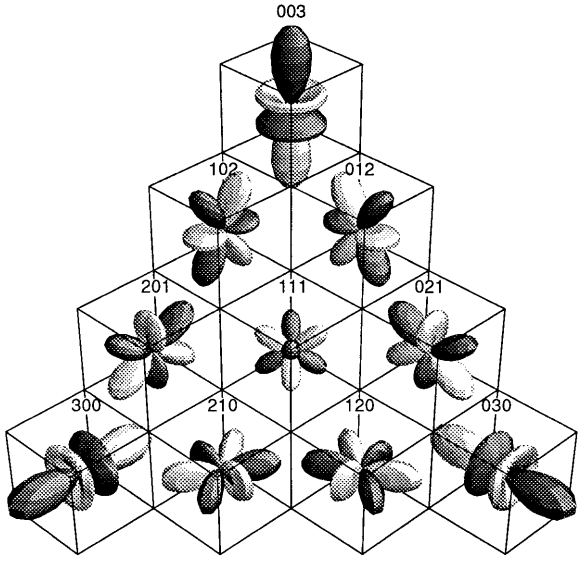

Fig. 6. Tricorn array for $\mathsf{S}^{(3)}$

The tricorn is also useful for displaying the relations among the coefficients of any particular harmonic function. Any solid spherical harmonic can be written in the form [16]

$$f(\mathbf{r}) = \mathsf{A}^{(n)} \cdot n \cdot \mathbf{r}^n = \sum_{n_1 n_2 n_3} g(n; n_1 n_2 n_3) A^{(n)}_{n_1 n_2 n_3} x^{n_1} y^{n_2} z^{n_3} \ , \tag{12}$$

where $\mathsf{A}^{(n)}$ is a totally symmetric and traceless tensor with constant components. For example, consider the function $S^{(4)}_{400}$ in Table 1. Let

$$\begin{aligned} f(\mathbf{r}) &= r^4 S^{(4)}_{400} = 105x^4 - 90x^2r^2 + 9r^4 \\ &= 24x^4 - 72x^2y^2 - 72x^2z^2 + 9y^4 + 18y^2z^2 + 9z^4 \ . \end{aligned} \tag{13}$$

The values of $A^{(4)}_K$ are obtained by dividing each coefficient in Eq. (13) by the appropriate g value. The resulting $\mathsf{A}^{(4)}$ tensor takes the tricorn form

$$\begin{array}{ccccccccc} & & & & 9 & & & & \\ & & & 0 & & 0 & & & \\ & & -12 & & 0 & & 3 & & \\ & 0 & & 0 & & 0 & & 0 & \\ 24 & & 0 & & -12 & & 0 & & 9 \ . \end{array}$$

Note that all traces vanish in this array. Such a "coefficient tricorn" of rank n uniquely defines each component of the spherical harmonic tricorn of rank n.

Illustrations of the tesseral harmonic surfaces are omitted here, as many excellent versions are available

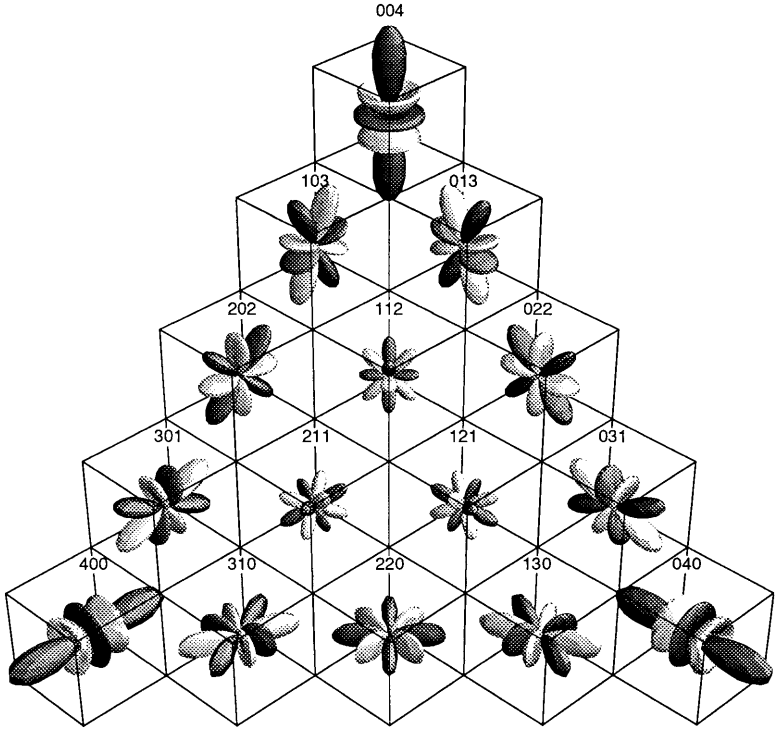

Fig. 7. Tricorn array for $\mathsf{S}^{(4)}$

[19–21]. They may also be generated with the Mathematica package mentioned in Sect. 10.

4 Properties of Maxwell–Cartesian harmonics

A number of properties of the Maxwell–Cartesian harmonics are listed here for use in the applications to follow. Some comparisons with tesseral harmonics are included to help in understanding the distinctions between the two families. The proofs have been given previously [16] for the Maxwell–Cartesian harmonics.

4.1 Independent subsets

Because of the vanishing of all traces, the components of $S^{(n)}_{n_1n_2n_3}$ are not linearly independent. A linearly independent subset is constituted by those components in which some n_i only has values 0 and 1. Such a subset is illustrated in Fig. 8, where the two bottom rows correspond to $n_3 = 0, 1$. Likewise, the row along any side of the tricorn along with the row next to it constitute a linearly independent subset. It is easily seen that there are $2n + 1$ components in such a subset and that there are no trace relations among them.

An interesting proof of the corresponding independent subsets has been given by Axler et al. [3] for spherical harmonics in N-dimensional space.

The number of independent components of $\mathsf{S}^{(n)}$ is the same as the number of components of Y_{nm}, i.e., $2n + 1$. The independent components are, however, different functions in the two families.

4.2 Spherical symmetry theorems

For Maxwell–Cartesian harmonics,

$$\mathsf{S}^{(n)}(\hat{\mathbf{r}}) \cdot n \cdot \mathsf{S}^{(n)}(\hat{\mathbf{r}}) = (2n)!/2^n \ . \tag{14}$$

The analogous equation due to Unsöld [22] applies to tesseral harmonics in the form

$$\sum_{m=-n}^{n} Y_{nm}(\hat{\mathbf{r}}) Y^*_{nm}(\hat{\mathbf{r}}) = (2n + 1)/4\pi \ . \tag{15}$$

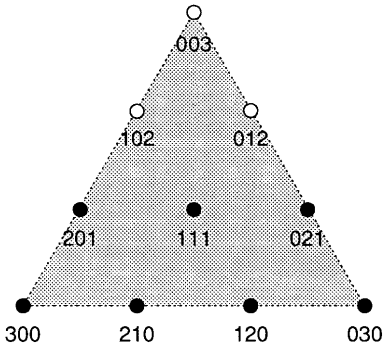

Fig. 8. A linearly independent subset of $\mathsf{S}^{(3)}$, shown by *filled circles*

Equations (14) and (15) both show that the sum of the squares of the magnitudes of the harmonics of degree n is independent of the direction in space.

4.3 Normalization integrals

The normalization factor N_{nK} for the Maxwell–Cartesian harmonics is the integral of the squared function over the surface of the unit sphere:

$$\begin{aligned} N_{n,n_1n_2n_3} &= \int_s [S^{(n)}_{n_1n_2n_3}(\hat{\mathbf{r}})]^2 \mathrm{d}s \\ &= \frac{4\pi n_1! n_2! n_3!}{2n+1} \sum_{m_1=0}^{[n_1/2]} \sum_{m_2=0}^{[n_2/2]} \sum_{m_3=0}^{[n_3/2]} (-1)^m (2n-2m-1)!! \\ &\quad \times \begin{bmatrix} n_1 \\ m_1 \end{bmatrix} \begin{bmatrix} n_2 \\ m_2 \end{bmatrix} \begin{bmatrix} n_3 \\ m_3 \end{bmatrix} g(m; m_1 m_2 m_3) \ , \end{aligned} \tag{16}$$

where $m = m_1 + m_2 + m_3$. Values of N_{nK} are listed for the low-order functions in Table 1. The analogous integral for the normalized tesseral harmonics is, of course [8],

$$\int_s Y_{nm}(\hat{\mathbf{r}}) Y^*_{nm}(\hat{\mathbf{r}}) \mathrm{d}s = 1 \ . \tag{17}$$

4.4 Orthogonalities

While the tesseral harmonics of differing degree n or different order m are all mutually orthogonal, the situation for the Maxwell–Cartesian harmonics is more complicated. If $n \neq l$ we have the orthogonality condition

$$\int_s S^{(n)}_{n_1n_2n_3} S^{(l)}_{l_1l_2l_3} \mathrm{d}s = 0 \ . \tag{18}$$

Likewise, if any degree index of function $S^{(n)}_K$ has parity opposite to that of the corresponding index of function $S^{(n)}_L$, the functions are orthogonal. If the corresponding degree indices have the same parity in both functions, the integral of their product is given by the nonvanishing expression

$$\begin{aligned} &\int_s S^{(n)}_{n_1n_2n_3} S^{(n)}_{l_1l_2l_3} \mathrm{d}s \\ &\quad = \frac{4\pi l_1! l_2! l_3!}{2n+1} \sum_{m_1=0}^{[n_1/2]} \sum_{m_2=0}^{[n_2/2]} \sum_{m_3=0}^{[n_3/2]} (-1)^m (2n-2m-1)!! \\ &\qquad \times \begin{bmatrix} n_1 \\ m_1 \end{bmatrix} \begin{bmatrix} n_2 \\ m_2 \end{bmatrix} \begin{bmatrix} n_3 \\ m_3 \end{bmatrix} g(m; k_1 k_2 k_3) \ , \end{aligned} \tag{19}$$

where $m = m_1 + m_2 + m_3$ and $k_i = (l_i - n_i)/2 + m_i$ and the g function is zero if any argument is negative. Thus, some of the component functions in $\mathsf{S}^{(n)}$ occur in nonorthogonal pairs, whose locations in the tricorn are shown in Fig. 9. A simple rule is that both members of such a pair are located on the same "trace network", i.e.,

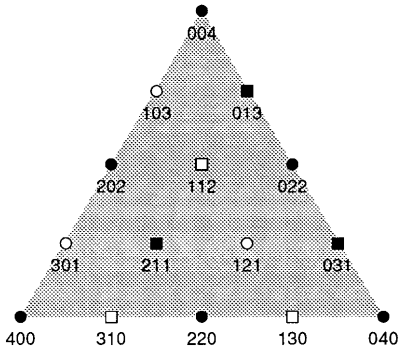

Fig. 9. Trace networks of nonorthogonal pairs of $S^{(4)}$ components, shown by points with like symbols

the network of contiguous subtricorns whose vertices comprise the traces of the tensor. A trace network thus constitutes a set of functions, any two of which are nonorthogonal.

A consequence of this result is that the independent subsets described previously contain nonorthogonal pairs of components. By contrast the Y_{nm} functions for given n are both independent and orthogonal.

5 Relations between $S_K^{(n)}$ and Y_{nm}

The Y_{nm} are related to the $S_K^{(n)}$ by way of their mutual connections with the gradients of r^{-1} in Eqs. (5) and (9). The result is, for $0 \le m \le n$, [16],

$$Y_{nm} = (-1)^m \left[\frac{2n+1}{4\pi(n+m)!(n-m)!}\right]^{1/2} \times \sum_{k=0}^{m} \mathrm{i}^{m-k} \binom{m}{k} S^{(n)}_{k,m-k,n-m} \quad , \tag{20}$$

where $\binom{m}{k} = m!/k!(m-k)!$. For negative orders Eq. (11) applies.

The following features of Eq. (20) are noteworthy:

1. The sum on the right side is a linear combination of the members of a single row in the $S^{(n)}$ tricorn. This is illustrated in Fig. 10, where the rows corresponding to each Y_{nm} are indicated. Some examples of the expansion for low n are shown in Table 2.
2. By inserting Eq. (6) into Eq. (20) one obtains a Cartesian polynomial for any Y_{nm}. This potentially useful formula is incorporated in the Mathematica package mentioned in Sect. 10. An alternative Cartesian polynomial form has been given by Thompson [13].
3. Y_{n0} is simply a constant times $S^{(n)}_{00n}$. Similarly, certain components in the second and third rows from the top of a tricorn are the same as the real or imaginary part of one of the Y_{nm}, aside from a constant factor. Otherwise the Y_{nm} are distinct from any of the $S_K^{(n)}$.

The inverse of this above transformation is accomplished as follows. We require an expansion of $S_K^{(n)}$ of the form

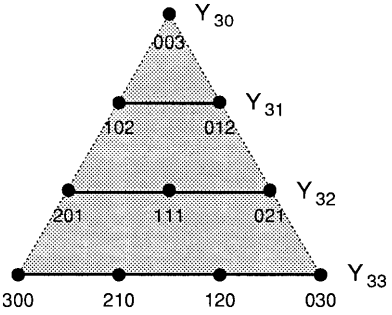

Fig. 10. Subsets of $S^{(3)}$ whose linear combinations give tesseral harmonics $Y_{3,\pm m}$

Table 2. Expansions of Y_{nm} in Maxwell–Cartesian harmonics

n	m	Y_{nm}
1	0	$(3/4\pi)^{1/2} S^{(1)}_{001}$
	± 1	$(3/4\pi)^{1/2}[\mp S^{(1)}_{100} - iS^{(1)}_{010}]$
2	0	$(5/16\pi)^{1/2} S^{(2)}_{002}$
	± 1	$(5/24\pi)^{1/2}[\mp S^{(2)}_{101} - iS^{(2)}_{011}]$
	± 2	$(5/96\pi)^{1/2}[-S^{(2)}_{020} + S^{(2)}_{200} \pm 2iS^{(2)}_{110}]$
3	0	$(7/144\pi)^{1/2} S^{(3)}_{003}$
	± 1	$(7/192\pi)^{1/2}[\mp S^{(3)}_{102} - iS^{(3)}_{012}]$
	± 2	$(7/480\pi)^{1/2}[-S^{(3)}_{021} + S^{(3)}_{201} \pm 2iS^{(3)}_{111}]$
	± 3	$(7/2880\pi)^{1/2}[\pm 3S^{(3)}_{120} \mp S^{(3)}_{300} + iS^{(3)}_{030} - 3iS^{(3)}_{210}]$

$$S_K^{(n)} = \sum_{m'=-n}^{n} c^{(n)}_{m'K} Y_{nm'} \quad , \tag{21}$$

where K, as usual, stands for an index set $n_1 n_2 n_3$. Since the Y_{nm} comprise an orthonormal set, we can find the coefficients by multiplying both sides by Y^*_{nm} and integrating. For $m \ge 0$ the result is

$$c^{(n)}_{mK} = \int_s S_K^{(n)} Y^*_{nm} \mathrm{d}s = (-1)^m \left[\frac{2n+1}{4\pi(n+m)!(n-m)!}\right]^{1/2} \sum_{k=0}^{m} (-\mathrm{i})^{m-k} \binom{m}{k} \times \int_s S_K^{(n)} S^{(n)}_{k,m-k,n-m} \mathrm{d}s \quad . \tag{22}$$

For negative order we have by virtue of Eq. (11)

$$c^{(n)}_{-m,K} = (-1)^m c^{(n)*}_{mK} \quad . \tag{23}$$

The integrals in Eq. (22) are evaluated by Eq. (19). An example of this transformation is given in Table 3. Note that all the expansions in the table are real, as required. Finally, by inserting Eq. (21) in Eq. (16) and using the orthonormality of the Y_{nm}, one obtains the sum rule

$$\sum_{m=-n}^{n} |c^{(n)}_{mK}|^2 = N_{nK} \quad . \tag{24}$$

Table 3. Expansion of $\mathsf{S}^{(2)}$ in tesseral harmonics

$n_1n_2n_3$	$S^{(2)}_{n_1n_2n_3}$
200	$-(4\pi/5)^{1/2}Y_{20}+(6\pi/5)^{1/2}(Y_{22}+Y_{2,-2})$
110	$i(6\pi/5)^{1/2}(-Y_{22}+Y_{2,-2})$
101	$(6\pi/5)^{1/2}(-Y_{21}+Y_{2,-1})$
020	$-(4\pi/5)^{1/2}Y_{20}-(6\pi/5)^{1/2}(Y_{22}+Y_{2,-2})$
011	$i(6\pi/5)^{1/2}(Y_{21}+Y_{2,-1})$
002	$(16\pi/5)^{1/2}Y_{20}$

6 Rotational transformations

The transformation of spherical harmonics under rotations is important in applications involving a number of systems with different orientations or the averaging of properties of a system over orientations.

We take the rotational transformation to have the following meaning. Let a point P on the unit sphere have coordinates $\hat{r}_\beta$ in a Cartesian system X. If we place in the same space a second Cartesian system X′, rotated with respect to X, then point P has coordinates $\hat{r}'_\alpha$ with respect to X′. The vector transformation is $\hat{r}'_\alpha=\lambda_{\alpha\beta}\hat{r}_\beta$, where $\lambda_{\alpha\beta}$ is the direction cosine of axis α in X′ with respect to axis β in X [23]. Then $S^{(n)}_K(\hat{\mathbf{r}}')$ is a function whose relation to X′ is the same as that of $S^{(n)}_K(\hat{\mathbf{r}})$ to X. We define the rotated function $S^{(n)\prime}_K(\hat{\mathbf{r}})\equiv S^{(n)}_K(\hat{\mathbf{r}}')$. The rotational transformation is

$$\mathsf{S}^{(n)'}(\hat{\mathbf{r}})=\mathbf{\Gamma}^{(n)}\mathsf{S}^{(n)}(\hat{\mathbf{r}})\ , \tag{25}$$

where $\mathbf{\Gamma}^{(n)}$ is the transformation matrix of order $(n+1)(n+2)/2$ and $\mathsf{S}^{(n)}$ is represented as a column vector with its components in canonical order. Let the rows and columns of $\mathbf{\Gamma}^{(n)}$ be indexed by the index sets $\alpha_1\cdots\alpha_n$ and $\beta_1\cdots\beta_n$, respectively, where both index sets span only the compressed arrays of order $(n+1)(n+2)/2$. Since $\mathsf{S}^{(n)}$ must transform like $\hat{\mathbf{r}}^n$, the matrix elements are [17]

$$\Gamma^{(n)}_{\alpha_1\cdots\alpha_n\beta_1\cdots\beta_n}=\sum_{N\{\beta\}}\lambda_{\alpha_1\beta_1}\cdots\lambda_{\alpha_n\beta_n}\ , \tag{26}$$

where the sum over $N\{\beta\}$ is the sum over all distinguishable permutations of $\beta_1\cdots\beta_n$ when numerical values are assigned. The $\lambda_{\alpha\beta}$ are known functions of the Eulerian angles [23], or they may be known directly from the geometry of the system.

As an example, consider the rotation of $S^{(2)}_{200}$ through 30° in the right-handed sense about the z-axis. Equation (25) gives

$$S^{(2)\prime}_{200}=(3/4)S^{(2)}_{200}+(\sqrt{3}/2)S^{(2)}_{110}+(1/4)S^{(2)}_{020}\ . \tag{27}$$

This case is shown graphically in Fig. 11, where the functions are scaled by their coefficients in Eq. (27). This example illustrates the basic feature of the rotational transformation of a tensor: the rotation of one component really is produced by a linear combination of the unrotated components.

The corresponding rotational transformation of tesseral harmonics is usually performed by the methods of spherical tensors, using spherical coordinates rather than Cartesian coordinates [11]. This procedure has the computational advantage of a tranformation matrix whose order is only $2n+1$, while the simple form of Eq. (26) gives the Cartesian method some programming advantage.

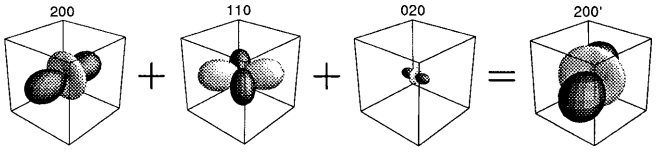

Fig. 11. Transformation of $S^{(2)}_{200}$ by 30° rotation about the z-axis

The Mathematica package mentioned in Sect. 10 includes programs for calculating the rotation matrix of Eq. (26) and carrying out the transformations.

7 Multipole potentials

Many problems related to the multipole expansion of the electrostatic potential have been worked out in terms of the Maxwell–Cartesian spherical harmonics using the formalism described here [16, 24, 25]. Two applications will be summarized here to bring out the importance of the Maxwell–Cartesian harmonics as components of traceless tensors.

7.1 The detracer exchange theorem

The detracer exchange theorem [16, 24] states that if $\mathsf{A}^{(n)}$ and $\mathsf{B}^{(n)}$ are totally symmetric tensors

$$\mathsf{A}^{(n)}\cdot n\cdot\mathscr{T}_n\mathsf{B}^{(n)}=\mathscr{T}_n\mathsf{A}^{(n)}\cdot n\cdot\mathsf{B}^{(n)}\ . \tag{28}$$

A useful application of this theorem is the following. Let $\rho(\mathbf{r})$ be the electric charge density at point $\mathbf{r}$ for an arbitrary charge distribution located within a finite circumsphere. Let the nth order multipole moment of the charge distribution about the origin be defined by [26]

$$\boldsymbol{\mu}^{(n)}=\frac{1}{n!}\int_v\rho(\mathbf{r})\mathbf{r}^n\,\mathrm{d}v\ , \tag{29}$$

where the integration is over the volume of the circumsphere. The potential of the charge distribution at a point $\mathbf{r}$ outside the circumsphere is [26]

$$\begin{aligned}\phi_c(\mathbf{r})&=\sum_{n=0}^{\infty}(-1)^n\boldsymbol{\mu}^{(n)}\cdot n\cdot\nabla^n r^{-1}\\&=\sum_{n=0}^{\infty}r^{-n-1}\boldsymbol{\mu}^{(n)}\cdot n\cdot\mathsf{S}^{(n)}(\hat{\mathbf{r}})\ ,\end{aligned} \tag{30}$$

where the last equality follows from Eq. (5). It is in the sense of Eq. (30) that $\mathsf{S}^{(n)}(\hat{\mathbf{r}})$ represents the angular dependence of the potential of a multipole moment of rank n. Now let $\mathsf{M}^{(n)}$ be the traceless multipole moment defined by $\mathsf{M}^{(n)}=\mathscr{T}_n\boldsymbol{\mu}^{(n)}$, a definition which is equivalent to the widely used multipole moments of Bucking-

ham [27]. Then, by the detracer exchange theorem, Eq. (30) becomes

$$\phi_c(\mathbf{r}) = \sum_{n=0}^{\infty} r^{-2n-1} \mathsf{M}^{(n)} \cdot n \cdot \mathbf{r}^n \ . \tag{31}$$

Thus, Eqs. (30) and (31) give the potential in equivalent forms, one of which is an expansion in spherical harmonics and the other a simple power series in $\mathbf{r}$. Certain electrostatic problems are greatly simplified by the latter form [16, 25]. This point is worth close attention, as it is widely overlooked in textbooks.

7.2 Linear independence

We have seen that the Maxwell–Cartesian harmonics are not all linearly independent, yet useful expansions with these functions as basis functions are possible using the limited independence that does exist. Suppose a physical problem reduces to the vanishing of an expansion in $\mathsf{S}^{(n)}$ of the form

$$\sum_{n=0}^{\infty} \mathsf{A}^{(n)} \cdot n \cdot \mathsf{S}^{(n)}(\mathbf{r}) = 0 \ , \tag{32}$$

where $\mathsf{A}^{(n)}$ is a totally symmetric tensor. If the $\mathsf{S}^{(n)}$ functions were all linearly independent, one could conclude that $\mathsf{A}^{(n)} = 0$ for all n, from which conclusions could be drawn regarding the physical quantities in the coefficient tensor. This is not the case here, but by the detracer exchange theorem we can transform Eq. (32) to

$$\sum_{n=0}^{\infty} \mathscr{T}_n \mathsf{A}^{(n)} \cdot n \cdot \mathbf{r}^n = 0 \ . \tag{33}$$

Since the functions $\mathbf{r}^n$ are entirely linearly independent, it follows that

$$\mathscr{T}_n \mathsf{A}^{(n)} = 0 \tag{34}$$

for all n. Hence, in spite of linear dependence among the spherical harmonics, one obtains an important relation regarding the traceless part of the coefficient tensor.

As an example of this type of problem, consider a conducting sphere of radius a placed in an arbitrary electrostatic field whose potential $\phi_0(\mathbf{r})$ is given by the Taylor series expanded about an origin at the center of the sphere:

$$\phi_0(\mathbf{r}) = -\sum_{n=0}^{\infty} (n!)^{-1} \mathsf{E}^{(n)}(0) \cdot n \cdot \mathbf{r}^n \ , \tag{35}$$

where $\mathsf{E}^{(n)}(0) = -\boldsymbol{\nabla}^n \phi_0(0)$. It may be noted that $\mathsf{E}^{(n)}(0)$ is totally symmetric and traceless for an electrostatic field, and hence Eq. (35) is equivalent to an expansion in $\mathsf{S}^{(n)}(\mathbf{r})$ by the detracer exchange theorem. The field induces a charge distribution in the sphere, giving rise to multipole moments whose potential is given by Eq. (30) or Eq. (31). The total potential must be equal to a constant (which we take to be 0) inside the sphere and equal to the sum $\phi_c + \phi_0$ outside the sphere. Continuity of the potential at the surface of the sphere then requires

$$\phi_c(a\hat{\mathbf{r}}) + \phi_0(a\hat{\mathbf{r}}) = 0 \ . \tag{36}$$

From Eqs. (32) and (33) the left side of Eq. (36) can be expressed as an expansion in either $\mathsf{S}^{(n)}$ or $\mathbf{r}^n$. The latter case is the more useful, since it has traceless coefficient tensors which must then vanish. Each vanishing tensor thus gives the relation

$$\mathsf{M}^{(n)} = (a^{2n+1}/n!)\mathsf{E}^{(n)}(0) \tag{37}$$

for all n. The coefficient $a^{2n+1}/n!$ is the multipole polarizability of a conducting sphere. The significance of this result for polarizabilities of atoms has been discussed elsewhere [25].

8 Atomic orbitals

8.1 Maxwell–Cartesian harmonics as angular functions for orbitals

The wave functions $\psi(\mathbf{r})$ for electron orbitals in the hydrogen atom are found by solving the Schrödinger equation under the assumption of separation of the coordinate variables [9]. A possible separation is

$$\psi(\mathbf{r}) = R(r)F(\hat{\mathbf{r}}) \ , \tag{38}$$

where $R(r)$ is a function only of the distance r from the nucleus and $F(\hat{\mathbf{r}})$ is a function only of the direction in space. It will be shown here that $S_K^{(l)}(\hat{\mathbf{r}})$ is a solution for $F(\hat{\mathbf{r}})$ and thus represents the angular part of a possible atomic orbital in a one-electron atom. The symbol l for the degree of the function is used in what follows to conform to universal usage in quantum mechanics.

The separation of variables results in a transformation of the Schrödinger equation into separate equations for $R(r)$ and $F(\hat{\mathbf{r}})$, the equation for the latter being [9]

$$L^2 F(\hat{\mathbf{r}}) = \beta F(\hat{\mathbf{r}}) \ , \tag{39}$$

where L^2 is the operator for the square of the angular momentum and β is an eigenvalue. The form of L^2 in terms of spherical polar coordinates is commonly used [9], but for the present purposes it is more useful to cast this operator in Cartesian form. Let $\hat{\mathbf{\nabla}} \equiv \partial/\partial\hat{\mathbf{r}}$, where the derivatives are to be taken before introducing the constraint $\hat{x}^2 + \hat{y}^2 + \hat{z}^2 = 1$. It is shown in the Appendix that

$$L^2 = -\hbar^2[\hat{\mathbf{\nabla}} \cdot \hat{\mathbf{\nabla}} - 2\hat{\mathbf{r}} \cdot \hat{\mathbf{\nabla}} - \hat{\mathbf{r}}\hat{\mathbf{r}} : \hat{\mathbf{\nabla}}\hat{\mathbf{\nabla}}] \ . \tag{40}$$

Since $S_K^{(l)}(\hat{\mathbf{r}})$ obeys the Laplace equation we have

$$\hat{\mathbf{\nabla}} \cdot \hat{\mathbf{\nabla}} S_K^{(l)}(\hat{\mathbf{r}}) = 0 \ . \tag{41}$$

Also, by Euler's theorem for homogeneous functions [16] we have

$$\hat{\mathbf{r}} \cdot \hat{\mathbf{\nabla}} S_K^{(l)}(\hat{\mathbf{r}}) = l S_K^{(l)}(\hat{\mathbf{r}}) \ , \tag{42}$$

$$\hat{\mathbf{r}}\hat{\mathbf{r}} : \hat{\mathbf{\nabla}}\hat{\mathbf{\nabla}} S_K^{(l)}(\hat{\mathbf{r}}) = l(l-1) S_K^{(l)}(\hat{\mathbf{r}}) \ ; \tag{43}$$

hence, from Eqs. (40), (41), (42), and (43),

$$L^2 S_K^{(l)}(\hat{\mathbf{r}}) = l(l+1)\hbar^2 S_K^{(l)}(\hat{\mathbf{r}}) \ . \tag{44}$$

Thus, $S_K^{(l)}$ satisfies Eq. (39) with $\beta = l(l+1)\ \hbar^2$. This means that $S_K^{(l)}$ defines an orbital with a definite value of the angular momentum. The above analysis shows that this is true for any homogeneous function of $\hat{\mathbf{r}}$ that obeys the Laplace equation, including, of course, the tesseral harmonics.

8.2 Components of angular momentum

The Cartesian operators for the components of angular momentum are, from the Appendix,

$$L_x = -\mathrm{i}\hbar(\hat{y}\hat{\nabla}_z - \hat{z}\hat{\nabla}_y) \ , \tag{45}$$

$$L_y = -\mathrm{i}\hbar(\hat{z}\hat{\nabla}_x - \hat{x}\hat{\nabla}_z) \ , \tag{46}$$

$$L_z = -\mathrm{i}\hbar(\hat{x}\hat{\nabla}_y - \hat{y}\hat{\nabla}_x) \ . \tag{47}$$

By straightforward application of these operators we find the following:

1. Application to $S_{l00}^{(l)}$, $S_{0l0}^{(l)}$, and $S_{00l}^{(l)}$ as given by Eqs. (6) and (7) gives

$$L_x S_{l00}^{(l)}(\hat{\mathbf{r}}) = 0 \ , \tag{48}$$

$$L_y S_{0l0}^{(l)}(\hat{\mathbf{r}}) = 0 \ , \tag{49}$$

$$L_z S_{00l}^{(l)}(\hat{\mathbf{r}}) = 0 \ . \tag{50}$$

   That is, each of these functions is an eigenfunction of one component operator, having eigenvalue 0. These are the only Maxwell–Cartesian harmonics which are eigenfunctions of the component operators. For these states the total angular momentum $[l(l+1)]^{1/2}\hbar$ lies in the plane perpendicular to the axis along which the angular momentum is zero.
2. More generally, $S_K^{(l)}$ is a linear combination of two or more Y_{lm} with different values of m. Since Y_{lm} is an eigenfunction of L_z with eigenvalue $m\hbar$, such an $S_K^{(l)}$ cannot be an eigenfunction of L_z. The same holds for L_x and L_y, since there is nothing unique about the z-axis.
3. Since $S_K^{(l)}$ is a linear combination of states with definite angular momentum components $m\hbar$ along a particular axis, the probability that an electron in that state has a particular value of m is $|c_{mK}^{(l)}|^2/N_{lK}$ [28]. The average angular momentum along the chosen axis is then

$$\langle L_\alpha \rangle = (\hbar/N_{lK}) \sum_{m=-l}^{l} m|c_{mK}^{(l)}|^2 \ ; \tag{51}$$

   however, from Eq. (23) the probability is the same for both m and $-m$. Hence $\langle L_\alpha \rangle = 0$. That is, the average angular momentum along any axis vanishes for any state $S_K^{(l)}$. (A referee of this work has kindly pointed out that this same conclusion follows from the fact that L_α is a pure imaginary Hermitian operator, while the $S_K^{(l)}$ are real, for the expectation values must be real and must therefore vanish.)

In properties 2 and 3 the $S_K^{(l)}$ are like the commonly used real orbital functions $C(Y_{lm} \pm Y_{l,-m})$, where C is a constant [29]. These functions are eigenfunctions of L_z only for $m = 0$, and $\langle L_z \rangle = 0$ owing to the equal probabilities of m and $-m$.

8.3 Spherical symmetry relations

Equation (15) for the Y_{lm} functions belonging to a given subshell l has been interpreted to mean that the electron density in a closed subshell is spherically symmetrical [29]. The remarkably similar Eq. (14) for $S_K^{(l)}$ evidently has a related signficance for electrons in orbitals described by these functions. We can get an insight into this significance by recasting Eq. (14) in terms of the components of the compressed tensor as in Eq. (2):

$$\sum_K g(l;K)[S_K^{(l)}(\hat{\mathbf{r}})]^2 = (2l)!/2^l \ , \tag{52}$$

where the index K spans the $(l+1)(l+2)/2$ component functions. Let the population of state lK be $g(l;K)N_{lK}$, the integral of the summand in Eq. (52) over the unit sphere. Then the equation says that the probability distribution of electrons is spherically symmetrical. An example for the case $l = 2$ shows the significance of this. From Eq. (15), the closed subshell for $l = 2$ obeys

$$Y_{20}^2 - 2Y_{21}Y_{2,-1} + 2Y_{22}Y_{2,-2} = 5/4\pi \tag{53}$$

and from Eq. (21)

$$\begin{aligned} &\sum_K g(2;K)[S_K^{(2)}]^2 \\ &= \sum_K g(2;K) \sum_{m=-2}^{2} \sum_{m'=-2}^{2} c_{mK}^{(2)} c_{m'K}^{(2)*} Y_{2m} Y_{2m'}^* \\ &= (24\pi/5)(Y_{20}^2 - 2Y_{21}Y_{2,-1} + 2Y_{22}Y_{2,-2}) \ , \end{aligned} \tag{54}$$

where the coefficients $c_{mK}^{(2)}$ are taken from Table 3. If we take the closed subshell sum $5/4\pi$ from Eq. (53), the sum in Eq. (54) is $(24\pi/5)(5/4\pi) = 6$, which is just the value $(2l)!/2^l$ required. That is, a distribution of electrons among $S_K^{(l)}$ states in proportion to $g(l;K)N_{lK}$ is equivalent to a uniform population of the Y_{lm} states, as in a closed subshell.

8.4 Basis functions for ab initio calculations

Electronic structures of molecules are calculated using various basis functions to represent atomic orbitals in modern ab initio computational methods [30, 31]. One of the most widely used "primitives" for creating basis functions is the Cartesian Gaussian function

$$\chi_{n_1 n_2 n_3} = r^l \mathrm{e}^{-\zeta r^2} c_{n_1 n_2 n_3} \hat{x}^{n_1} \hat{y}^{n_2} \hat{z}^{n_3} \ , \tag{55}$$

where $n_1 + n_2 + n_3 = l$, and ζ and $c_{n_1 n_2 n_3}$ are optimized to suit the particular problem. A typical basis function of degree l is taken as a linear combination of primitives,

which can be written in the notation of a tensor contraction:

$$\phi_l = r^l \mathrm{e}^{-\zeta r^2} \mathsf{C}^{(l)} \cdot l \cdot \hat{\mathbf{r}}^l \ , \tag{56}$$

where $\mathsf{C}^{(l)}$ is a totally symmetric Cartesian tensor whose components are the coefficients of the expansion. It is assumed that ζ is constant for all the Gaussian primitives in the contraction [32, 33]. The expression in Eq. (56) is a homogeneous polynomial of degree l, and is thus taken to represent, at least approximately, an electronic state with angular momentum quantum number l; however, a well-known problem that occurs when $l \geq 2$ is that the polynomial is, in general, "contaminated" by functions corresponding to lower angular momentum [30].

A method that has been used to eliminate, or at least separate, the contaminating functions is to combine the Cartesian monomials in linear combinations equivalent to the tesseral harmonics [32, 34]. A related but more general method that would completely eliminate contaminants suggests itself from the basic properties of spherical harmonics. A surface spherical harmonic $f_l(\hat{\mathbf{r}})$ can always be written [16]

$$f_l(\hat{\mathbf{r}}) = \mathscr{T}_l \mathsf{C}^{(l)} \cdot l \cdot \hat{\mathbf{r}}^l \ . \tag{57}$$

If we use this expression in place of the tensor contraction in Eq. (56), we obtain

$$\phi_l = r^l \mathrm{e}^{-\zeta r^2} \mathscr{T}_l \mathsf{C}^{(l)} \cdot l \cdot \hat{\mathbf{r}}^l \ . \tag{58}$$

Since $f_l(\hat{\mathbf{r}})$ is an eigenfunction of L^2 with eigenvalue $\hbar^2 l(l+1)$, ϕ_l is now a basis function with a definite angular momentum. The only additional constraint required in the optimization of the coefficients is that the traces of $\mathsf{C}^{(l)}$ given by Eq. (3) must all vanish.

It is worth noting that a basis function exactly equivalent to Eq. (58) can be written in terms of Maxwell–Cartesian harmonics. Equation (5) with the detracer exchange theorem gives

$$\mathscr{T}_l \mathsf{C}^{(l)} \cdot l \cdot \hat{\mathbf{r}}^l = \mathsf{C}^{(l)} \cdot l \cdot \mathsf{S}^{(l)}(\hat{\mathbf{r}}) \ . \tag{59}$$

The form on the right side is an expansion in pure harmonics of degree l with unconstrained coefficients. This form might be preferred for numerical computations if one wishes to trade the constraint of vanishing traces for the somewhat greater complexity of the harmonic functions.

9 Summary

This work presents a number of novel features of the Maxwell–Cartesian spherical harmonic functions $S_K^{(n)}(\hat{\mathbf{r}})$ and their relations to the more familiar tesseral harmonics $Y_{nm}(\hat{\mathbf{r}})$. A brief summary of the main results follows.

1. The tricorn array is introduced as a systematic means of displaying the components of higher-order, totally symmetric Cartesian tensors, such as those whose components are the $S_K^{(n)}$ functions. In addition to bringing out the symmetry of the components with respect to permutation of the axes, the tricorn conveniently displays the arrangement of functions constituting traces of the tensor on vertices of certain subtricorns, the location of linearly independent subsets on pairs of rows adjacent to the edges, the rows of functions whose linear combinations produce the tesseral harmonics, and the pattern of nonorthogonal pairs of functions on the trace networks.
2. The linear transformations between $S_K^{(n)}$ and Y_{nm} are accomplished with explicit formulas for the transformation coefficients.
3. The rotational transformation of the $S_K^{(n)}$ functions is described by the relatively simple method for a compressed Cartesian tensor.
4. Two applications of the $S_K^{(n)}$ functions in the theory of multipole potentials are reviewed to demonstrate the importance of the detracer exchange theorem and the use of expansions in basis functions that are partially linearly dependent.
5. It is shown that $S_K^{(l)}(\hat{\mathbf{r}})$ is a solution to the angular part of the Schrödinger equation for the hydrogen atom and represents an orbital with angular momentum $[l(l+1)]^{1/2}\hbar$. Such an orbital has no definite value of the angular momentum along any axis except in special cases where this component is zero. In general, the expectation value of the angular momentum along any axis is zero. The spherical symmetry of electron density in a closed shell expressed by the Unsöld relation is shown to be accomplished by an unequal population of the $S_K^{(l)}$ orbitals in proportion to appropriate weighting factors.
6. It is pointed out that the use of Cartesian spherical harmonics in Gaussian basis sets used in ab initio molecular structure calculations would provide basis functions with definite values of the angular momentum and thereby overcome the problem of "contamination" of angular momentum in commonly used basis functions.
7. Finally, the disparate definitions of spherical harmonics mentioned in the Introduction require some comment. We have seen that any function that fits the classical definition is also an eigenfunction of L^2. This is not surprising, since any "classical" spherical harmonic can be expressed as a linear combination of Y_{lm} functions of the same degree, and the linear form of the eigenvalue problem ensures that such combinations will be solutions. However, a curious consequence of the quantum mechanical definition is that such linear combinations are not, in general, spherical harmonics. The classical definition makes better sense for general usage, since it ensures that the general solution of any linear problem whose particular solutions are spherical harmonics will also be a spherical harmonic. This disparity would be easily resolved by omitting from the quantum mechanical definition the requirement that the function be an eigenfunction of L_z.

10 Mathematica package

A Mathematica [35] program package for generating formulas and graphics such as those shown here may be obtained at http://www.public.iastate.edu/~jba/ssh.

Appendix

Maxwell's harmonics. Here it will be shown how one obtains the Maxwell–Cartesian spherical harmonics from Maxwell's general harmonics. Maxwell defines a surface spherical harmonic H_n of degree n as a gradient of r^{-1} in the form [1, 18]

$$H_n = r^{n+1}\frac{(-1)^n}{n!}\frac{\partial^n}{\partial h_1 \partial h_2 \cdots \partial h_n}\frac{1}{r} \quad , \tag{A1}$$

where h_i denotes an arbitrary axis in the direction of unit vector $\hat{\mathbf{h}}_i$ and $\partial/\partial h_i = \hat{\mathbf{h}}_i \cdot \partial/\partial \mathbf{r}$. He obtained the following expression for the general gradient.

$$H_n = \sum_{m=0}^{[n/2]}(-1)^m \frac{(2n-2m)!}{2^{n-m}n!(n-m)!}\sum(\lambda^{n-2m}\mu^m) \quad , \tag{A2}$$

where $\sum(\lambda^{n-2m}\mu^m)$ represents the sum of products of m quantities $\mu_{ij} = \hat{\mathbf{h}}_i \cdot \hat{\mathbf{h}}_j$ and $n-2m$ quantities $\lambda_i = \hat{\mathbf{h}}_i \cdot \hat{\mathbf{r}}$, with each suffix i or j occurring only once in the product. If the h_i are all taken to be Cartesian axes α_i, then $\partial/\partial h_i = \partial/\partial r_{\alpha_i}$, $\lambda_i = \hat{r}_{\alpha_i}$, and $\mu_{ij} = \delta_{\alpha_i\alpha_j}$, so

$$\sum(\lambda^{n-2m}\mu^m) = \sum_{T\{\alpha\}} \delta_{\alpha_1\alpha_2}\cdots\delta_{\alpha_{2m-1}\alpha_{2m}}\hat{r}_{\alpha_{2m+1}}\cdots\hat{r}_{\alpha_n} \quad , \tag{A3}$$

where the sum over $T\{\alpha\}$ is the sum over all permutations of $\alpha_1 \cdots \alpha_n$ giving distinct terms. If we now use $(2n-2m-1)!! = (2n-2m)!/2^{n-m}(n-m)!$, Eqs. (A1) and (A2) give

$$\frac{\partial^n}{\partial h_1 \cdots \partial h_n}\frac{1}{r} = \frac{(-1)^n}{r^{n+1}}\sum_{m=0}^{[n/2]}(-1)^m(2n-2m-1)!! \times \sum_{T\{\alpha\}}\delta_{\alpha_1\alpha_2}\cdots\delta_{\alpha_{2m-1}\alpha_{2m}}\hat{r}_{\alpha_{2m+1}}\cdots\hat{r}_{\alpha_n} \quad . \tag{A4}$$

However, the right side is just $(-1)^n r^{-n-1}\mathscr{T}_n\hat{\mathbf{r}}^n$, according to Eq. (4). Thus, from Eqs. (A1) and (A4)

$$H_n = \frac{1}{n!}\mathscr{T}_n\hat{\mathbf{r}}^n \quad . \tag{A5}$$

That is, the surface spherical harmonics $\mathscr{T}_n\hat{\mathbf{r}}^n$ are special cases of Maxwell's spherical harmonics based on the Cartesian axes.

I find no indication in Maxwell's works [18, 36] that he ever reduced his spherical harmonics to the Cartesian form of Eq. (A4). Equivalent gradient formulas were obtained by Kielich [37], Burgos and Bonadeo [38], and Cipriani and Silvi [39] without reference to Maxwell's harmonics.

Angular Momentum. The angular momentum operators used in the text are presented in terms of the unit vector $\hat{\mathbf{r}}$ in place of the spherical coordinates θ, ϕ used in most of the literature. A proof is in order. We define $\mathbf{V} = \partial/\partial\mathbf{r}$ and start with the angular momentum operator in terms of $\mathbf{r}$ [9]

$$\mathbf{L} = -\mathrm{i}\hbar\mathbf{r}\times\mathbf{V} \quad . \tag{A6}$$

From the definition $\hat{\mathbf{r}} = \mathbf{r}/r$ one finds

$$\mathbf{V} = r^{-1}(\hat{\mathbf{V}} - \hat{\mathbf{r}}\hat{\mathbf{r}}\cdot\hat{\mathbf{V}}) \quad . \tag{A7}$$

Inserting Eq. (A7) into Eq. (A6) gives the desired vector operator:

$$\mathbf{L} = -\mathrm{i}\hbar\hat{\mathbf{r}}\times\hat{\mathbf{V}} \quad . \tag{A8}$$

Then,

$$L^2 = \mathbf{L}\cdot\mathbf{L} = -\hbar^2(\hat{\mathbf{r}}\times\hat{\mathbf{V}})\cdot(\hat{\mathbf{r}}\times\hat{\mathbf{V}}) \tag{A9}$$

Equation (A9) reduces to Eq. (40), with care to note that the left $\hat{\mathbf{r}}\times\hat{\mathbf{V}}$ operator acts on all that follows it, including the right $\hat{\mathbf{r}}\times\hat{\mathbf{V}}$ operator.

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