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Molecular symmetry with quaternions

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Abstract

A new and relatively simple version of the quaternion calculus is offered which is especially suitable for applications in molecular symmetry and structure. After introducing the real quaternion algebra and its classical matrix representation in the group SO(4) the relations with vectors in 3-space and the connection with the rotation group SO(3) through automorphism properties of the algebra are discussed. The correlation of the unit quaternions with both the Cayley–Klein and the Euler parameters through the group SU(2) is presented. Besides rotations the extension of quaternions to other important symmetry operations, reflections and the spatial inversion, is given. Finally, the power of the quaternion calculus for molecular symmetry problems is revealed by treating some examples applied to icosahedral symmetry. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

In certain applications of symmetry and group theory to molecular and solid state problems in spectroscopy and magnetism it is advantageous to use tools from vector spaces and fields beyond conventional algebra over the real and complex numbers, $\mathbb{R}$ and $\mathbb{C}$. This is especially true for compounds and clusters important in materials science as, for example, metallic and spin glasses showing icosahedral symmetry and beyond, quasicrystals, buckminster fullerenes and their derivatives, respectively. In this context an algebra, i.e. a vector space over $\mathbf{R}_4$, whose elements are the so-called real quaternions, plays an important role in diverse areas such as mechanics and kinematics on one side, and group representations in quantum mechanics and chemistry related to spin transformations in orthogonal and unitary symmetry groups on the other side.

The structure of the paper is as follows: in Section 2 we present some tools from the quaternion algebra and one of its matrix realisations. Sections 3 and 4 deal with the role of quaternions in 4-space for vectors and geometrical symmetry in our 3-space. Section 5 is devoted to group theoretical aspects with special emphasis on the automorphism properties and their consequences for the quaternion calculus. Here, another matrix realisation is presented. Furthermore, we intro-

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duce the symmetry operations of reflections and the spatial inversion that are scarcely treated in the literature in this context. Finally, in Section 6 applications of these matters to certain symmetry properties of the regular icosahedron are presented that show the elegance and relative simplicity of the quaternion tools for the geometrical molecular symmetry.

2. Quaternions

We deal here with the algebra of rank 4 of quaternions $\mathbb{H}$ which can be closely related in applications to the symmetry operations of rotations in conventional 3-space. However, it is less known that $\mathbb{H}$ can also be related to reflections (involutions) and the spatial inversion in this space in an elegant manner. (For a detailed treatment and the historical side of quaternions see [1] and [2].) We endow — according to brilliant work by Euler, Gauss, Hamilton, and others — $\mathbb{H}$ with the canonical basis,

$$\underline{\vec{e}} = (e_0,e_1,e_2,e_3), \tag{2.1}$$

having the (Hamilton) multiplication rules in tabular form,

$$\begin{array}{cccc} e_0 & e_1 & e_2 & e_3 \\ e_1 & -e_0 & e_3 & -e_2 \\ e_2 & -e_3 & -e_0 & e_1 \\ e_3 & e_2 & -e_1 & -e_0 \end{array} \tag{2.2}$$

to be read $e_1\,e_3 = -e_2$, etc.

From Eq. (2.2) we learn that the algebra is associative but not commutative. Furthermore, we note that the basis element e_0 acts like the number 1 (therefore, some authors use the number symbol or leave it out completely in calculations). A general element of $\mathbb{H}$, a say, is the *quaternion*, which often is also called a *hypercomplex number*,

$$a = e_0a_0 + e_1a_1 + e_2a_2 + e_3a_3 = \sum_{k=0}^{3} e_ka_k, \quad \text{with} \quad a_0,a_1,a_2,a_3 \in \mathbb{R}. \tag{2.3}$$

With Eqs. (2.2) and (2.3) we can now calculate the quaternion product of a and b, say,

$$\begin{aligned} ab &= (e_0a_0 + e_1a_1 + e_2a_2 + e_3a_3) \\ &\quad (e_0b_0 + e_1b_1 + e_2b_2 + e_3b_3) = \sum_{k=0}^{3}\sum_{t=0}^{3} e_ke_ta_kb_t \\ &= e_0(a_0b_0 - a_1b_1 - a_2b_2 - a_3b_3) \\ &\quad + e_1(a_1b_0 + a_0b_1 + a_2b_3 - a_3b_2) \\ &\quad + e_2(a_0b_2 + a_2b_0 - a_1b_3 + a_3b_1) \\ &\quad + e_3(a_0b_3 + a_3b_0 + a_1b_2 - a_2b_1), \end{aligned} \tag{2.4}$$

where the (expected) result is again a quaternion, c say. For all what follows it is crucial to realise that Eq. (2.4) can be written in matrix form, i.e.

$$\begin{aligned} ab &= (e_0,e_1,e_2,e_3) \begin{pmatrix} a_0 & -a_1 & -a_2 & -a_3 \\ a_1 & a_0 & -a_3 & a_2 \\ a_2 & a_3 & a_0 & -a_1 \\ a_3 & -a_2 & a_1 & a_0 \end{pmatrix} \begin{pmatrix} b_0 \\ b_1 \\ b_2 \\ b_3 \end{pmatrix} \\ &= (e_0,e_1,e_2,e_3) \begin{pmatrix} c_0 \\ c_1 \\ c_2 \\ c_3 \end{pmatrix}, \end{aligned} \tag{2.5}$$

or in compact notation,

$$ab = \underline{\vec{e}}\underline{A}\underline{b} = \underline{\vec{e}}\underline{c}, \tag{2.6}$$

where the (4,4) representation matrix $\underline{A}$ belongs to SO(4), the special orthogonal group in four dimensions.

It is interesting to observe that quaternions appear as special types of matrices depending upon their position in Eqs. (2.5) and (2.6). Thus, we find that $ba = \underline{\vec{e}}\underline{B}\underline{a} = \underline{\vec{e}}\underline{d}$, and in general, $ab \neq ba$.

Furthermore, we learn that each *quaternion matrix* is determined by the first column (or row) alone which simplifies the construction of the corresponding (4,4)-matrix algebra considerably.

Looking again at Eq. (2.4) which reads in rewritten form,

$$\begin{aligned} ab &= e_0(a_0b_0) + e_0(-a_1b_1 - a_2b_2 - a_3b_3) \\ &\quad + (e_1a_1 + e_2a_2 + e_3a_3)b_0 \\ &\quad + (e_1b_1 + e_2b_2 + e_3b_3)a_0 + e_1(a_2b_3 - a_3b_2) \end{aligned}$$

$$- e_2(a_1b_3 - a_3b_1) + e_3(a_1b_2 - a_2b_1) = e_0(a_0b_0) + e_0[-(a_v,b_v)] + a_vb_0 + b_va_0 + a_v \times b_v. \quad (2.7)$$

This suggests the 'splitting' of a general element $a \in \mathbb{H}$ into two parts, $e_0a_0 = a_s$ and $e_1\,a_1 + e_2\,a_2 + e_3\,a_3 = a_v$ say, which have the quality of a *scalar part* (subscript s) and a *vector part* (subscript v). For $a = a_s + a_v$ and $b = b_s + b_v$, their quaternion product then reads,

$$ab = (a_s + a_v)(b_s + b_v): = a_sb_s + a_vb_s + b_va_s + a_vb_v. \quad (2.8)$$

The comparison of Eq. (2.8) with Eq. (2.7) yields two important correspondences in the a_vb_v term,

$$a_vb_v = e_0[-(a_v,b_v)] + a_v \times b_v, \quad \text{with} \quad (a_v,b_v) = a_1b_1 + a_2b_2 + a_3b_3, \quad \text{and} \quad a_v \times b_v = e_1(a_2b_3 - a_3b_2) - e_2(a_1b_3 - a_3b_1) + e_3(a_1b_2 - a_2b_1), \quad (2.9)$$

where, respectively, a_v, b_v and $a_v \times b_v$ point at the well known *scalar product* and *vector product* of the vector parts of a and b.

Due to the frequent appearance of a_v and b_v in applications one denotes them as either *pure* or (purely) *imaginary quaternions*, where, e.g.

$$a_v = (e_1,e_2,e_3)(a_1,a_2,a_3)^{\mathrm{T}}. \quad (2.10)$$

Here we use the matrix transposition symbol T with a row vector to indicate a column vector.

Now we introduce to each quaternion $a = a_s + a_v$, its *conjugate* one, $a^* = a_s - a_v$, i.e.

$$a^* = (e_0,e_1,e_2,e_3)(a_0, -a_1, -a_2, -a_3)^{\mathrm{T}}. \quad (2.11)$$

The quaternion product aa^*, applying either Eq. (2.4) or Eq. (2.5), gives a real non-negative number,

$$aa^* = (e_0,e_1,e_2,e_3)(a_0^2 + a_1^2 + a_2^2 + a_3^2,0,0,0)^{\mathrm{T}} = \sum_{k=0}^{3} a_k^2 = |a|^2 \equiv a^*a, \quad (2.12)$$

called the *norm* of a. The (positive) number $|a| = (aa^*)^{1/2}$, the modulus of $a \neq 0$, is the *length* of the quaternion. If $|a| = 1$, a is normalised to unity and called a *normed* or *unit quaternion*.

Finally, we define the *inverse quaternion* a^{-1} of a,

$$a^{-1} = (1/|a|^2)a^*, \quad \text{with} \quad aa^{-1} = a^{-1}a = e_0, \quad (2.13)$$

where $e_0 = 1$ denotes the *identity quaternion* $\in \mathbb{H}$.

In the next step we can extend without problems Eqs. (2.4), (2.5) and (2.6) to the quaternion products of three and more partners; for example,

$$abc = (e_0,e_1,e_2,e_3)\begin{pmatrix} a_0 & -a_1 & -a_2 & -a_3 \\ a_1 & a_0 & -a_3 & a_2 \\ a_2 & a_3 & a_0 & -a_1 \\ a_3 & -a_2 & a_1 & a_0 \end{pmatrix} \begin{pmatrix} b_0 & -b_1 & -b_2 & -b_3 \\ b_1 & b_0 & -b_3 & b_2 \\ b_2 & b_3 & b_0 & -b_1 \\ b_3 & -b_2 & b_1 & b_0 \end{pmatrix} \begin{pmatrix} c_0 \\ c_1 \\ c_2 \\ c_3 \end{pmatrix} = (e_0,e_1,e_2,e_3)\begin{pmatrix} d_0 \\ d_1 \\ d_2 \\ d_3 \end{pmatrix},$$

or

$$abc = \underline{\vec{e}}\,\underline{A}\,\underline{B}\,\underline{c} = \underline{\vec{e}}\,\underline{d} \equiv (ab)c = a(bc), \quad (2.14)$$

which also confirms the associative properties of $\mathbb{H}$.

Technically speaking, all these properties together qualify $\mathbb{H}$ as a division algebra or a skew-field over the reals since all group axioms for the mathematical structure 'field' are fulfilled, with the exception of the commutative axiom of quaternion multiplication.

3. Quaternions and vectors

On our approach to use quaternions for symmetry problems we establish a 1-1 correspondence of the following kind: Given a *polar vector* in the space $V_3(\mathbb{R})$,

$$\bar{r} = \underline{\vec{e}}_x x + \underline{\vec{e}}_y y + \underline{\vec{e}}_z z, \quad \text{with} \quad x,y,z \in \mathbb{R}, \quad (3.1)$$

where $\vec{e}_x$,$\vec{e}_y$,$\vec{e}_z$ indicate three unit vectors along the Cartesian axes, we define a bijection ϕ,

$$\phi:\vec{e}_x \leftrightarrow e_1 \vec{e}_y \leftrightarrow e_2, \vec{e}_z \leftrightarrow e_3, \tag{3.2}$$

onto the quaternion units. Thereby we map the vector $\vec{r}$ onto the pure quaternion r_v,

$$\phi:\vec{r} = \vec{e}_x x + \vec{e}_y y + \vec{e}_z z \leftrightarrow r_v = e_1 x + e_2 y + e_3 z, \tag{3.3}$$

and call r_v a quaternion vector or *q-vector*. For the product of two (or more) such q-vectors, Eq. (2.9) reveals even more mutual relations on which we will put important properties using the well-known scalar and vector product relations, but now formulated in quaternion language! Encouraged by the correspondences (3.2) and (3.3), we go one step further and correlate other vector properties in 3-space, as for example their lengths, directions and, respectively, direction cosines, with properties of q-vectors.

To give the reader some flavour of these aspects we start with Eqs. (2.3) and (2.11) for a *unit* quaternion a, i.e.

$$aa^* = 1 = \frac{a_0^2}{|a|^2} + \frac{a_1^2 + a_2^2 + a_3^2}{|a|^2} := \cos^2\varphi + \sin^2\varphi. \tag{3.4}$$

Therefore, since $|a| = 1$, a can be written,

$$a \equiv \frac{a}{|a|} = e_0 \frac{a_0}{|a|} + \frac{1}{|a|}(e_1 a_1 + e_2 a_2 + e_3 a_3)$$
$$= e_0 \cos\varphi + (e_1 \cos\chi_x + e_2 \cos\chi_y + e_3 \cos\chi_z)\sin\varphi,$$

or

$$a := e_0 \cos\varphi + q_a \sin\varphi. \tag{3.5}$$

The introduction of trigonometric functions and the pure unit quaternion q_a in terms of the directional angles χ_x, χ_y, χ_z with respect to a right-handed Cartesian coordinate system may seem artificial at this stage. However, it will turn out soon that Eq. (3.5) is of foremost importance for symmetry applications. At present we recognise that the *directional pure quaternion* q_a, with $q_a q_a^* = q_a^* q_a = 1$, defines an axis in the three-dimensional subspace of $\mathbb{H}$ in 1-1 correspondence with the ordinary vectors in 3-space.

If we work out the special quaternion product $a r_v a^{-1}$; then we obtain with Eqs. (2.8) and (2.9),

$$a r_v a^{-1} = (e_0 \cos\varphi + q_a \sin\varphi)(e_1 x + e_2 y + e_3 z)$$
$$(e_0 \cos\varphi - q_a \sin\varphi), \tag{3.6}$$

and it turns out that the q-vector r_v is transformed into the q-vector, $r'_v = e_1 x' + e_2 y' + e_3 z'$ say, in the passive viewpoint. With Eqs. (2.3) and (3.5) we find for the new vector components in terms of the original ones,

$$\begin{pmatrix} x' \\ y' \\ z' \end{pmatrix}$$

$$\begin{pmatrix} a_0^2 + a_1^2 - a_2^2 - a_3^2 & -2a_0a_3 + 2a_1a_2 & 2a_0a_2 + 2a_1a_3 \\ 2a_0a_3 + 2a_1a_2 & a_0^2 - a_1^2 + a_2^2 - a_3^2 & -2a_0a_1 + 2a_2a_3 \\ -2a_0a_2 + 2a_1a_3 & 2a_0a_1 + 2a_2a_3 & a_0^2 - a_1^2 - a_2^2 + a_3^2 \end{pmatrix}$$

$$\begin{pmatrix} x \\ y \\ z \end{pmatrix} = \underline{R}(a) \begin{pmatrix} x \\ y \\ z \end{pmatrix}, \tag{3.7}$$

The matrix $\underline{R}(a)$ is orthogonal with $\det \underline{R}(a) = 1$ since all real(!) matrix elements are continuous functions of the quaternion components of Eq. (2.3). Therefore, Eq. (3.7) describes a rotation operation.

A final word in this context: doing calculations with Eqs. (3.6) and (3.7) it might well be that some readers feel unhappy using quaternions in this form. Therefore, we will, respectively, must look for the possibility of simplifications in certain cases of practical interest as exploited in the next section.

4. Quaternions and geometrical symmetry

For quaternion products, like ab, $a r_v a^{-1}$ and others, the bijective or 1-1 correspondence with ordinary vectors immediately suggests that, e.g. the *rotation quaternion a* and the vector b_v generate a plane. If a is given by Eq. (3.5) we can represent the *polar vector* b_v, for example, by

$$b_v = q_a b + q'_a b', \tag{4.1}$$

where q_a and q'_a are defined as orthogonal unit q-vectors spanning the plane of a_v and b_v. In order not to be limited to a plane in 2-space for the sequel of observations, we extend these two basis vectors with a third unit q-vector q''_a such that they form an orthogonal triad in 3-space. Furthermore, we define their (right-handed) multiplication table similar to that in Eq. (2.2), i.e.

$$\begin{matrix} e_0 & q_a & q'_a & q''_a \\ q_a & -e_0 & q''_a & q'_a \\ q'_a & -q''_a & -e_0 & q_a \\ q''_a & q'_a & -q_a & -e_0 \end{matrix},$$

to be read $q_a q''_a = -q'_a$, etc. (4.2)

This situation is depicted in Fig. 1.

With these definitions and with Eqs. (3.5), (4.1) and (4.2), we work out Eq. (3.6) and obtain,

$$\begin{aligned} ab_v a^{-1} &= (e_0\cos\varphi_a + q_a\sin\varphi_a)(q_a b + q'_a b') \\ &\quad (e_0\cos\varphi_a - q_a\sin\varphi_a) \\ &= q_a b + q'_a b'\cos 2\varphi_a + q''_a b'\sin 2\varphi_a := d_v. \end{aligned} \quad (4.3)$$

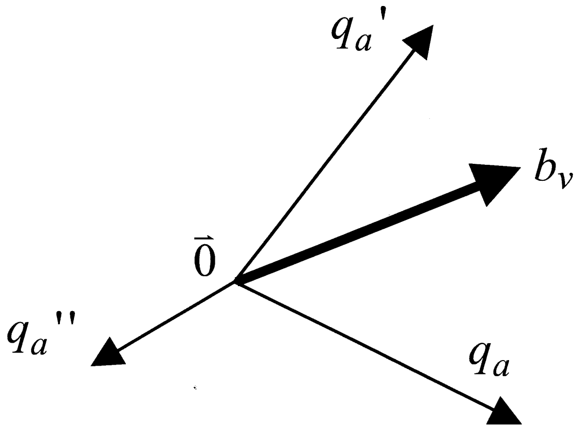

Fig. 1. The vector b_v represented by the orthogonal triad of pure unit quaternions q_a, q'_a, q''_a. b_v is defined to be in the plane of q_a and q'_a, whereas q''_a is orthogonally oriented in the three-dimensional subspace of the quaternion 4-space $\mathbb{H}$.

The result is remarkable in various ways: Firstly, d_v and b_v have the same component in the direction of a. Secondly, the new vector d_v is — in general — out of the plane of a_v and b_v, and thirdly, the norms and moduli are identical under this transformation, i.e. $|d_v| = |b_v|$, such that we have applied an orthogonal transformation in the form of a *rotation* of b_v around the axis of a.

Finally, notice in Eq. (4.3) the appearance of twice the angle φ_a. In this context we point out that this fact is often considered in the literature by redefining Eq. (3.5) as

$$a := e_0\cos(\varphi_a/2) + q_a\sin(\varphi_a/2). \quad (4.4)$$

For example, for $a = e_0\cos(\varphi_a/2) + e_2\sin(\varphi_a/2)$. and the vector $r_v = e_1 x + e_2 y + e_3 z$ we have,

$$\begin{aligned} ar_v a^{-1} &= [e_0\cos(\varphi_a/2) + e_2\sin(\varphi_a/2)] \\ &\quad (e_1 x + e_2 y + e_3 z)[e_0\cos(\varphi_a/2)\text{-}e_2\sin(\varphi_a/2)] \\ &= e_1(x\cos\varphi_a + z\sin\varphi_a) + e_2 y \\ &\quad + e_3(-x\sin\varphi_a + z\cos\varphi_a) = r'_v \end{aligned} \quad (4.5)$$

Basically, however, this angular behaviour is a consequence of the automorphism group of the quaternion algebra; see below for details.

5. Some group theory with quaternions

5.1. Motivation

In his remarkable book, *Symmetry* [3], Hermann Weyl, one of the giants of symmetry and group theory in mathematics and physics, writes on pages 144 and 145,...... 'Whenever you have to do with a structure-endowed entity Σ, try to determine its group of automorphisms, the group of those element-wise transformations which leave all structural relations undisturbed'........ and....'Symmetry is a vast subject, significant in art and nature'........

Clearly, we would add today to the last sentence..'significant in....physics and chemistry, too'.

Suppose we have an *automorphism* of the quaternion algebra A ($\mathbb{H}$) in form of a basis transformation ρ basis $\underline{e}\rightarrow$ basis $\underline{d}$, such that

$$(d_0,d_1,d_2,d_3)=(e_0,e_1,e_2,e_3)\left(\begin{array}{c|ccc} t_{00} & t_{01} & t_{02} & t_{03} \\ \hline t_{10} & t_{11} & t_{12} & t_{13} \\ t_{20} & t_{21} & t_{22} & t_{23} \\ t_{30} & t_{31} & t_{32} & t_{33} \end{array}\right) \tag{5.1}$$

What can be said about the structure and properties of the (4,4)-transformation matrix, $\underline{T}$ say, according to the multiplication rules given in Eq. (2.2)? Firstly, due to the period-preserving property of each automorphism we have, $t_{1\,0}=t_{2\,0}=t_{3\,0}=0$ and $t_{0\,0}=1$.

Next we investigate the equation $d_1\,d_1=-1$, i.e. with Eq. (5.1) we find

$$d_1d_1=-1=t_{01}^2-(t_{11}^2+t_{21}^2+t_{31}^2)+2t_{01}(e_1t_{11}+e_2t_{21}+e_3t_{31}). \tag{5.2}$$

Since the term in the bracket of the last term in Eq. (5.2) is different from zero, we must have,

$$t_{01}=0, \quad \text{and} \quad t_{11}^2+t_{21}^2+t_{31}^2=1. \tag{5.3}$$

In analogy we obtain,

$$t_{02}=t_{03}=0, \text{ together with } t_{12}^2+t_{22}^2+t_{32}^2=1, \text{ and } t_{13}^2+t_{23}^2+t_{33}^2=1. \tag{5.4}$$

Looking at the equation $d_1\,d_2=d_3$, i.e.

$$d_1d_2=e_1(t_{21}t_{32}-t_{22}t_{31})+e_2(t_{31}t_{12}-t_{11}t_{32})+e_3(t_{22}t_{11}-t_{21}t_{12})=d_3=e_1t_{13}+e_2t_{23}+e_3t_{33}, \tag{5.5}$$

we find for the (3,3)-submatrix, $\underline{M}$ say, indicated by the broken lines in Eq. (5.1), that its determinantal value based upon Eq. (5.4) equals 1.

Finally, we work out the anti-commutator $[d_1,d_2]_+=0$, i.e.

$$[d_1,d_2]_+:=d_1d_2+d_2d_1=0=-2(t_{11}t_{12}+t_{21}t_{22}+t_{31}t_{32}). \tag{5.6}$$

In addition, we have from the two analogous equations the information,

$$t_{11}t_{13}+t_{21}t_{23}+t_{31}t_{33}=0, \quad \text{and} \quad t_{12}t_{13}+t_{22}t_{23}+t_{32}t_{33}=0. \tag{5.7}$$

Discussion. Concerning the properties of the matrices $\underline{T}$ and especially $\underline{M}$ we learn from Eq. (5.3) through Eq. (5.7) that the rows and columns of $\underline{M}$ are, respectively, normalised to one and orthogonal to each other. Furthermore, det $\underline{M}=1$ such that $\underline{M}$ is an *orthogonal matrix* representing a *rotation* in ordinary 3-space. Thus we have proved, tracing Hamilton's work of around 1850, that the automorphism group A ($\mathbb{H}$) of the real unit quaternions is *homomorphic* to the rotation group SO(3), also called the special orthogonal group in three dimensions.

In reverse, given a (3,3) orthogonal or rotation matrix, we can always work out the corresponding automorphisms of the quaternion algebra.

To learn more about the connection of real unit quaternions with rotations in 3-space we look at a subgroup of A($\mathbb{H}$), denoted the inner automorphism group I ($\mathbb{H}$), where the action of the multiplicative quaternion group in 4-space is by conjugation on vector quaternions in 3-space, as already worked out in Section 4, e.g. in Eqs. (4.4) and (4.5).

In this context it is of importance to realise that we have for Eq. (4.5) the equality,

$$ar_va^{-1}=(-a)r_v(-a^{-1}), \tag{5.8}$$

which means that the multiplicative group $\mathbb{H}$ is not isomorphic, but 2:1-epimorphic to the group SO(3). The same relation is valid for the corresponding subgroups of them. Without exaggeration one can consider Eq. (5.8) as the entrance gate to the 2:1-epimorphism: SU(2)→SO(3), where SU(2) is the special unitary group in two dimensions that acts as the *covering* or *double group* for SO(3). About the situation for the finite subgroups (i.e. point groups) of physical and chemical importance with respect to these compact groups, see elsewhere [6].

Let us now look at a further example of an *inner automorphism* using for the unit quaternion a the ansatz

$$a=e_0\cos(\varphi_a/2)+e_3\sin(\varphi_a/2)\equiv e_0c_a+e_3s_a. \tag{5.9}$$

In the sense of Eqs. (4.5) and (4.3) we find,

$$ar_va^{-1}=e_1(x\cos\varphi_a-y\sin\varphi_a)+e_2(x\sin\varphi_a+y\cos\varphi_a)+e_3z\equiv e_1x'+e_2y'+e_3z'. \tag{5.10}$$

The result for the components of the two q-vectors, r_v and its transformed one r'_v, reads in matrix form,

$$\begin{pmatrix} x' \\ y' \\ z' \end{pmatrix} = \begin{pmatrix} \cos\varphi_a & -\sin\varphi_a & 0 \\ \sin\varphi_a & \cos\varphi_a & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} x \\ y \\ z \end{pmatrix} \qquad (5.11)$$

which clearly reveals that the quaternion a in 4-space induces a rotation about the z-axis with the angle φ_a in the ordinary 3-space.

At this stage we mention again the important correlation of the multiplicative group of the quaternion algebra A ($\mathbb{H}$) with the group SO(4). In Section 2 we based the quaternion products ab and abc in Eqs. (2.5) and (2.14) upon the action of a (4,4)-matrix $\underline{A}$ on the column vector $\underline{b}$. Therefore, for our example in Eq. (5.10) this means,

$$ar_v a^{-1} = \underline{e} \begin{pmatrix} c_a & 0 & 0 & -s_a \\ 0 & c_a & -s_a & 0 \\ 0 & s_a & c_a & 0 \\ s_a & 0 & 0 & c_a \end{pmatrix}$$

$$\begin{pmatrix} 0 & -x & -y & -z \\ x & 0 & -z & y \\ y & z & 0 & -x \\ z & -y & x & 0 \end{pmatrix} \begin{pmatrix} c_a \\ 0 \\ 0 \\ -s_a \end{pmatrix}$$

$$= \underline{e} \begin{pmatrix} 0 \\ x\cos\varphi_a - y\sin\varphi_a \\ x\sin\varphi_a + y\cos\varphi_a \\ z \end{pmatrix}, \qquad (5.12)$$

where $\underline{e}$ denotes the quaternion matric basis. Note that the real (4,4)-representation matrix $\underline{A}$ for a on the right hand side of Eq. (5.12) is unimodular and an element $\in$SO(4). The mapping: $a \to \underline{A}$ is an *isomorphism*.

In addition another important matrix representation for unit quaternions in the group SU(2) should be pointed out, the special unitary group in two dimensions. Looking at the connection of a with a complex (2,2)-representation matrix $\underline{U}(a) \in SU(2)$, one can show that an isomorphism is operative here too, if one defines a bijective mapping: $a \to \underline{U}(a)$, such that

$$\underline{U}(a) = \begin{pmatrix} k_a & l_a \\ -l_a^* & k_a^* \end{pmatrix} = \begin{pmatrix} a_0 - ia_3 & ia_1 + a_2 \\ ia_1 - a_2 & a_0 + ia_3 \end{pmatrix}, \qquad (5.13)$$

where k_a and l_a are complex numbers often denoted as *Cayley–Klein parameters*. For our example in Eq. (5.9) this reads,

$$\underline{U}(a;z) = \begin{pmatrix} \cos(\varphi_a/2) - i\sin(\varphi_a/2) & 0 \\ 0 & \cos(\varphi_a/2) + i\sin(\varphi_a/2) \end{pmatrix}$$

$$\equiv \begin{pmatrix} \exp(-i\varphi_a/2) & 0 \\ 0 & \exp(i\varphi_a/2) \end{pmatrix}. \qquad (5.14)$$

On the other hand, we find for the inner automorphisms in analogy to Eqs. (5.9) and (5.10),

$$a = e_0\cos(\varphi_a/2) + e_1\sin(\varphi_a/2) \equiv e_0 c_a + e_1 s_a, \text{ and}$$
$$a = e_0\cos(\varphi_a/2) + e_2\sin(\varphi_a/2) \equiv e_0 c_a + e_2 s_a, \qquad (5.15)$$

the corresponding matrix forms,

$$\begin{pmatrix} x' \\ y' \\ z' \end{pmatrix} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & \cos\varphi_a & -\sin\varphi_a \\ 0 & \sin\varphi_a & \cos\varphi_a \end{pmatrix} \begin{pmatrix} x \\ y \\ z \end{pmatrix}, \quad \text{and}$$

$$\begin{pmatrix} x' \\ y' \\ z' \end{pmatrix} = \begin{pmatrix} \cos\varphi_a & 0 & \sin\varphi_a \\ 0 & 1 & 0 \\ -\sin\varphi_a & 0 & \cos\varphi_a \end{pmatrix} \begin{pmatrix} x \\ y \\ z \end{pmatrix}, \qquad (5.16)$$

which point at ordinary 3-space rotations around the x- and the y-axis, respectively. The corresponding complex representation matrices $\underline{U}(a) \in$SU(2) reads,

$$\underline{U}(a;x) = \begin{pmatrix} c_a & is_a \\ is_a & c_a \end{pmatrix}, \quad \text{and}$$

$$\underline{U}(a;y) = \begin{pmatrix} c_a & s_a \\ -s_a & c_a \end{pmatrix}. \qquad (5.17)$$

Discussion. For applications in molecular and solid state symmetry we recall that since the fundamental work of Euler on the kinematics of rigid body motion a general rotation in our 3-space can be formulated, for example, as a product of three rotations about (at least) two non-coinciding and space-fixed axes containing the origin [5]. Here we define this product as follows: first a rotation about the z-axis through the angle α is performed, followed by a rotation about the y-axis through an angle β, and, finally, a rotation, again about the z-axis through an angle λ is applied.

With Eqs. (5.14) and (5.17) we obtain for this definition

$$\underline{U}(\alpha,\beta,\lambda) = \underline{U}(\lambda;z)\underline{U}(\beta;y)\underline{U}(\alpha;z) = \begin{pmatrix} \exp(-i(\alpha+\gamma)/2)\cos\beta/2, & \exp(i(\alpha-\gamma)/2)\sin\beta/2 \\ -\exp(-i(\alpha-\gamma)/2)\sin\beta/2, & \exp(i(\alpha+\gamma)/2)\cos\beta/2 \end{pmatrix}. \quad (5.18)$$

In this and other equations containing α, β and γ the term Euler angles is often used for them.

Their angular domains are defined as follows:

$$0° \leq \alpha < 360°, \quad 0° \leq \beta \leq 180°, \quad 0° \leq \gamma < 360°. \quad (5.19)$$

Because of many different conventions in the literature [5], the term *Euler parameters* is preferred instead. For more information on these aspects and examples from molecular symmetry groups the reader is referred to the literature [6]. The correlation of the Euler and Cayley–Klein parameters with the components of the corresponding quaternion is obvious from Eqs. (5.13) and (5.18).

5.2. A digression from rotations to other symmetry operations

Let us go back to Eqs. (4.1) and (4.4) and Fig. 1 for the case of a *twofold rotation* of the polar vector b_v about q_a, i.e.

$$q_a b_v q_a^{-1} = q_a(q_a b + q'_a b')(-q_a) = q_a b - q'_a b' \quad (5.20)$$

Note that in this case the rotational quaternion (4.4) contains no scalar part and its vector part equals the unit q-vector.

For a twofold rotation of b_v about q'_a, we find,

$$q'_a b_v (q'_a)^{-1} = q'_a(q_a b + q'_a b')(-q'_a) = -q_a b + q'_a b'. \quad (5.21)$$

Furthermore, if we apply q''_a, we obtain,

$$q''_a b_v (q''_a)^{-1} = q''_a(q_a b + q'_a b')(-q''_a) = -q_a b - q'_a b' = -b_v, \quad (5.22)$$

Eqs. (5.20), (5.21) and (5.22) contain important results for applications in molecular symmetry, since we can now go beyond rotations with the quaternion calculus: Although Eq. (5.22) was obtained by the action of a rotational operator on a polar vector, the result also points at the action of the spatial inversion operator on this vector. Is something wrong here? To find a way out of this apparent contradiction we proceed as follows: let the action of the spatial inversion operator $\hat{i}$ in $V_3(\mathrm{R})$, i.e. $\hat{i}\vec{b} = -\vec{b}$, be operative in the quaternion space,

$$q_\alpha b_v q_\beta := -b_v, \quad (5.23)$$

without knowing the precise form of q_α and q_β at this stage. Then, for the action of the following twofold rotation, $\hat{C}_{2x}$ say, and its quaternionic image, q_a say, we obtain,

$$q_a(-b_v)q_a^{-1} = q_a(-b_v)(-q_a) = -q_a b + q'_a b'. \quad (5.24)$$

For $\hat{C}_{2y}$ and $\hat{C}_{2z}$ and their images, q'_α and q_α'' say, we find,

$$q'_a(-b_v)(q'_a)^{-1} = q'_a b_v q'_a = q_a b - q'_a b', \quad (5.25)$$

and

$$q''_a(-b_v)(q''_a)^{-1} = q''_a b_v q''_a = q_a b + q'_a b' = b_v(!). \quad (5.26)$$

Next we calculate q_α and q_β: for example, from Eqs. (5.23) and (5.24) we get,

$$q_a(q_\alpha b_v q_\beta)q_a^{-1} = q_a b_v q_a \Rightarrow q_\alpha b_v q_\beta = q_\alpha^{-1}(q_a b_v q_a)q_a = e_0 b_v(-e_0), \quad (5.27)$$

which means that $q_\alpha = e_0$ and $q_\beta = -e_0$. From Eq. (5.23) with Eqs. (5.25) and (5.26) we get the same results for q_α and q_β. Thus the action of the *spatial inversion* can be written,

$$q_a b_v q_\beta = e_0 b_v(-e_0) = -b_v. \quad (5.28)$$

This information can be used to work out the action of the *reflection* operators. It is well known that in our 3-space the (commutative) product of the inversion through the origin with a twofold rotation is a reflection in a plane perpendicular to the rotational axis. To better understand the role of a reflection in quaternion space we start from the observation that any(!) pure (unit or not) quaternion can always be composed as the product of two (or more, clearly, in general) vector quaternions. For example, with Eq. (2.9) we can put,

$$c = d_1 d_2 = d_{v1} d_{v2} = c_s + c_v. \tag{5.29}$$

For the pure unit quaternions (see Fig. 1) this behaviour is laid down in Eq. (4.2): for example, in the case, $q_{\rm a} = q'_a q''_a$, the constituent partners q'_a and q''_a define a plane that contains the origin and is perpendicular to the (resultant) $q_{\rm a}$. This plane is defined as *the plane of the quaternion* q_a.

The action of q_a on the polar vector b_v is then equivalent to a reflection of b_v in the plane spanned by q'_a and q''_a, with similar interpretations for the other two reflections induced by the actions of q'_a and q''_a, respectively.

Thus, the results of these quaternionic *reflections* are as follows,

$$q_a b_v q_a = -q_a b + q'_a b', \quad q'_a b_v q'_a = q_a b - q'_a b',$$
$$\text{and} \quad q''_a b_v q''_a = q_a b + q'_a b' = b_v, \tag{5.30}$$

where the last case reveals the invariance of b_v under the reflection q''_a because this polar vector has been defined to lie in the plane of q''_a [see Eq. (4.1)].

Furthermore, it is worth observing that the *inversion* through the origin can also be generated by three successive reflections with respect to perpendicular planes. In quaternion language this reads with Eq. (4.2),

$$(q''_a q'_a q_a) b_v (q_a q'_a q''_a) = e_0 b_v (-e_0) = -b_v. \tag{5.31}$$

6. Quaternions and molecular symmetry — an example

We are now in a position to perform symmetry calculations on the regular polyhedra including the Platonic solids using our *quaternion calculus* of the previous sections. We select as an example a regular icosahedron which recently has gained great importance for various applications in chemistry and physics. For this model, shown in Fig. 2, we also provide in Table 1 the Cartesian coordinates of the 12 numbered vertices. Using my convention, the midpoints of all 30 edges are

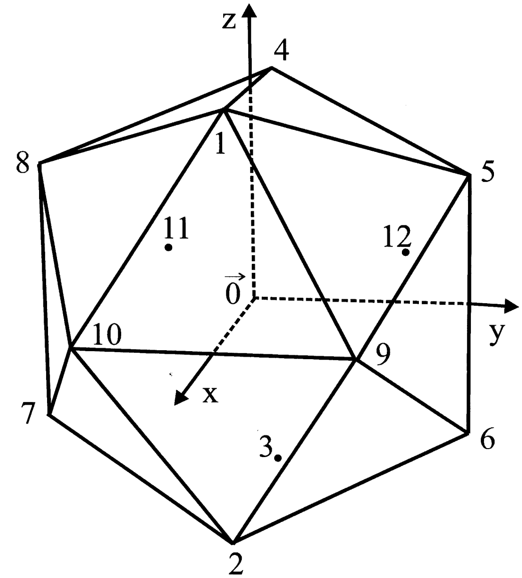

Fig. 2. A regular icosahedron whose vertices are indexed as Cartesian coordinates in Table 1.

Table 1
For the model shown in Fig. 2 we present the Cartesian coordinates of the 12 numbered vertices

No.	x	y	z
1	d	0	1
2	d	0	−1
3	−d	0	−1
4	−d	0	1
5	0	1	d
6	0	1	−d
7	0	−1	−d
8	0	−1	d
9	1	d	0
10	1	−d	0
11	−1	−d	0
12	−1	d	0

The coordinate d equals 2 cos 72°.

normalised to a unit distance from the origin $\vec{0}$ of this Platonic solid.

The coordinates d and $-d$ are related to the *golden ratio*, $\tau = (1/2)(\sqrt{5}+1)$, i.e..

$d = \tau - 1 = (1/2)(\sqrt{5}-1) = 2\cos 72°$.

Although the properties of the icosahedral rotation group I of order 60 are well known [7], we will use this point group to show the power and simplicity of the quaternion calculus in this context. Suppose we are interested in the fivefold rotations about the symmetry axis containing the origin $\vec{0}$ and vertex 1. The corresponding unit quaternion, a_1 say, is represented by

$$a_1 = e_0\cos(72°/2) + q_1\sin(72°/2), \tag{6.1}$$

where q_1 denotes a pure unit quaternion that describes the direction of the rotation axis,

$$q_1 = e_0\cos\chi_{1x} + e_2\cos\chi_{1y} + e_3\cos\chi_{1z}, \tag{6.2}$$

in terms of the direction cosines with the Cartesian axes. With the coordinates of the vertex or 'pole' 1 [see Table 1, Eqs. (3.5) and (4.4)] we calculate the quaternion components a_{01}, a_{11}, a_{21}, a_{31} and map them onto the (4,4)-matrix in Eq. (2.5) which is denoted here by $\underline{A}_1$ [refer to Eq. (2.6)]. To study the symmetry action of the quaternion a_1 and its matrix representative $\underline{A}_1 \in SO(4)$, we use Eqs. (2.14) and (3.6) to establish an inner automorphism,

$$(\pm a_1)r_k(\pm a_1^{-1}) = r_k' \overset{2:1}{\leftrightarrow} (\pm \underline{A}_1)\underline{R}_k(\pm \underline{a}_1^*) = \underline{R}_k'. \tag{6.3}$$

Here, * denotes the complex conjugation operator of Eq. (2.11) to construct the (4,1)-column matrix $\underline{a}_1^*$ which is equal to the first row of the matrix $\underline{A}_1$. The (4,4)-matrix $\underline{R}_k$ represents the unit vector quaternion r_k corresponding to the position vector $\vec{r}_k$ which is directed from the origin $\vec{0}$ to the vertex or pole no. k (see Fig. 2). As an example we take the vector $\vec{r}_4$, i.e. applying Eq. (6.3), which gives as a result the vector $\vec{r}_8$,

$$\underline{A}_1\underline{R}_4\underline{a}_1^* = \begin{pmatrix} 0.809 & -0.309 & 0.000 & -0.500 \\ 0.309 & 0.809 & -0.500 & 0.000 \\ 0.000 & 0.500 & 0.809 & -0.309 \\ 0.500 & 0.000 & 0.309 & 0.809 \end{pmatrix} \frac{1}{|\vec{r}_k|} \begin{pmatrix} 0 & d & 0 & -1 \\ -d & 0 & -1 & 0 \\ 0 & 1 & 0 & d \\ 1 & 0 & -d & 0 \end{pmatrix} \begin{pmatrix} 0.809 \\ -0.309 \\ 0.000 \\ -0.500 \end{pmatrix} = \frac{1}{|\vec{r}_k|} \begin{pmatrix} 0 \\ 0 \\ -1 \\ d \end{pmatrix}, \tag{6.4}$$

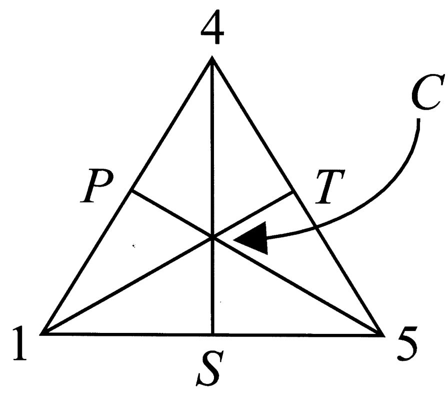

Fig. 3. One of the equilateral triangular faces of the regular icosahedron. The special point C is the centroid of the triangle and is on a threefold rotation axis, whereas the special points P, S, and T at the medial intersections of the sides are on twofold rotation axes. Finally, the vertices 1, 4 and 5 are on fivefold rotation axes of this solid figure.

where $|\vec{r}_k| = |\vec{r}_1| = \ldots = |\vec{r}_4| = |\vec{r}_5| = \ldots = 1.1756$ units for all 12 vertices of the solid figure in my normalisation convention (see above). Looking at Fig. 2 we interpret Eq. (6.4) as an anti-clockwise fivefold rotation (as viewed from the positive hemisphere onto the origin of the figure) such that $\vec{r}_4$ is transformed into $\vec{r}_8$.

At this stage it is both interesting and important to realise that the period p of the quaternion matrix $\underline{A}_1$ in SO(4) equals 10. This is one example for the appearance of both a *finite double group* and the corresponding *period-splitting rules* worked out by the author [4][1]. Here, they are needed for the transformation from the 3-space into the quaternion 4-space $\mathbb{H}$.

[1] I take this occasion to mention an uncorrected misprint in the published version. On page 479 in the fifth line of the section on Dihedral symmetry it should read: "…when n is even whereas when n is odd there……".

A characteristic feature of the regular icosahedron is the occurrence of 20 equilateral triangular faces. One of these, containing the vertices 1, 4 and 5, is presented in Fig. 3.

This information will now be used in the next example. We ask which symmetry operation (SOP) is equivalent to the product of the two twofold rotations, C_{2P} and C_{2S} say, containing the points P and S? Since group I is *non-Abelian* we have to be careful about the sequence of the two SOPs. To apply the quaternion calculus we must know the coordinates of these points. From the figures and the table we find the following Cartesian coordinates using tools of analytical geometry,

$$P \to (0;0;1),\quad S \to (d/2;1/2;(1+d)/2),\ \text{and}\ C \to (0;1/3;(2+d)/3). \tag{6.5}$$

The requested unit quaternions representing the SOPs follow from Eqs. (3.5) and (4.4),

$$a_P = e_0\cos(180°/2) + (\sin(180°/2))(e_1\cos 90° + e_2\cos 90° + e_3\cos 0°) = q_P = e_3,\ \text{and}$$

$$a_S = (e_1\cos 72° + e_2\cos 60° + e_3\cos 36°) = q_S. \tag{6.6}$$

In addition we point out that the corresponding periods of $\underline{A}_P$ and $\underline{A}_S$ in SO(4) are both $p = 4$, *but* they induce twofold rotations in the real 3-space.

Thus we have for one of the two possibilities the combined operation,

$$a_P a_S = e_3 q_S = e_0(-\cos 36°) + e_1(-\cos 60°) + e_2\cos 72° \equiv e_0(\cos\varphi_a/2) + q_a(\sin\varphi_a/2). \tag{6.7}$$

By comparison of the corresponding terms we find for the resulting quaternion,

rotational angle: $\varphi_a/2 = 144°$; directional angles of the rotation axis:

$$\chi_x = 148.2825°;\quad \chi_y = 58.2825°,\quad \text{and}\quad \chi_z = 90°. \tag{6.8}$$

(For the directional angles we use the convention: $0 \le \chi_x,\chi_y,\chi_z \le 180°$). Since the rotation axis has no z-component we find with Eq. (6.8) and Table 1 that it is equal to the position vector $\vec{r}_{1\,2}$, i.e.

$$a_P a_S = a_{12} = e_0\cos(288°/2) + q_{12}\sin(288°/2), \tag{6.9}$$

which in the 3-space of group I corresponds to the SOP of a *clockwise* fivefold rotation about $\vec{r}_{1\,2}$ with the angle $\varphi_a = 4 \times 72°$ or, alternatively, to an *anti-clockwise* rotation about the same axis with the angle 72°. By a similar treatment we find for the other possibility,

$$a_S a_P = a_{10} = e_0\cos(288°/2) + q_{10}\sin(288°/2), \tag{6.10}$$

which leads to an equivalent interpretation with $\vec{r}_{1\,0}$ as rotation axis.

For the periods of the corresponding rotation matrices with their rotational angles, $\underline{A}_{1\,2}(144°)$ and $\underline{A}_{1\,0}(144°)$, we find $p = 5$ for both.

The extension of the quaternion calculus to the *full icosahedral group* of order 120, i.e. the direct product $I_h = I \times C_i$, is straightforward. The consideration of the improper rotations follows the strategy described in the course of Eqs. (5.20), (5.21), (5.22), (5.23), (5.24), (5.25), (5.26), (5.27), (5.28), (5.29), (5.30) and (5.31) of the last section. For example, one of the 15 reflections of I_h has a mirror plane generated by the position vectors $\vec{r}_2$ and $\vec{r}_5$. This then is the plane of the reflection quaternion, q_v say, which is constructed via $q_v = r_2 \times r_5$. In normalised form we find, $q_v = e_1\cos 36° + e_2\cos 108° + e_3\cos 60°$. The action, $q_v r_k q_v = r'_k$, gives, $r_1 \to r_{12}$, $r_2 \to r_2$, $r_3 \to r_{10}$, etc., which is typical for a reflection in the plane of q_v.

With these tools and the given numerical examples the interested reader should have no difficulties in studying the symmetry properties of the icosahedron (and of other complex polyhedra) in a consistent manner with the bonus of having immediate access to the corresponding representation matrices and irreducible representations of the solid figure(s) in both the single and the double group modes, almost without any extra effort!

7. Conclusions

The most important issues of this paper are: the multiplicative group of the non-zero, unit quaternions in the 4-space $\mathbb{H}$ *induces* rotations of vectors in our 3-space, whereas the unit pure quaternions in a three-dimensional subspace of $\mathbb{H}$ induce either twofold rotations, or reflections and the spatial inversion in the 3-space. Furthermore, we can easily find the defining representations of the corresponding *double groups* of SO(3) and its subgroups by working out the inner automorphism group I($\mathbb{H}$). Furthermore, from experience with the icosahedral example it turns out that molecular symmetry properties of the more complex chemical coordination polyhedra can be found by using the corresponding quaternion calculus in a relatively simple manner.

Furthermore, in the icosahedral case it was shown clearly that the quaternion calculus is much simpler to apply than the conventional methods of geometrical molecular symmetry and group theory. Finally, my primary objective in this paper was to make difficult symmetry aspects more transparent.

Acknowledgements

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