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The analysis of spin and spin–orbit coupling in quantum and classical physics by quaternions

W Gough

Department of Physics, University College, Cardiff, Wales

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Abstract It is shown that quaternions offer a simple elegant description of spin of a single particle, perhaps superior to that of conventional quantum mechanics. The spin operators are $S_x = \frac{1}{2}i$, $S_y = \frac{1}{2}j$ and $S_z = \frac{1}{2}k$ (in units where $\hbar = 1$). Quaternion angular functions $Z_j^{\pm}, m_j$ are given, which are explicit expressions for $|l, s, j, m_j\rangle$ in terms of the states $|l, s, m_l, m_s\rangle$. Use of these $Z^{\pm}$ functions offer an elegant analysis of: (i) the relativistic hydrogen atom; (ii) problems in classical physics, such as the wave equation (in which 'spin' emerges as a feature of the mathematics).

Consideration is given to a speculation that there is simultaneous 'reality' of all three components of spin.

The quaternion quantum mechanical arguments developed here are not incompatible with the results of a recent experiment on phase change commutivity by Kaiser, George and Werner.

Resumé Il est montré que les quaternions offrent une description simple et élègante du spin d'une seule particule, peut être supérieure à celle de la mécanique quantique conventionnelle. Ces operateurs de spin sont $S_x = \frac{1}{2}i$, $S_y = \frac{1}{2}j$ et $S_z = \frac{1}{2}k$ (en unités de $\hbar = 1$). Les fonctions angulaires des quaternions $Z_j^{\pm}, m_j$ sont données, qui sont expressions explicites pour $|l, s, j, m_j\rangle$ en fonctions des états $|l, s, m_l, m_s\rangle$. L'utilisation de ces fonctions $Z^{\pm}$ offre une analyse élègante de: (i) l'atome d'hydrogene en relativité; (ii) des problèmes de physique classique, telle que l'èquation d'onde dans laquelle le 'spin' emerge comme une caracteristique mathématique.

On considère la spéculation qui considère que toutes les trois composantes du spin ont simultanement un sens physique.

Les arguments de quaternions en mécanique quantique developpés ici ne sont pas incompatibles avec les résultats d'une expérience récente de Kaiser, George et Werner sur la commutativité des changements de phase.

1. Introduction

The quaternion was invented in the last century by Hamilton, who considered it to be of profound importance in mathematics, comparable with that of calculus. However, with the emergence of vector analysis, and after a long controversy concerning the relative merits of vectors and quaternions (Bork 1966, Stephenson 1966), the quaternion vanished into comparative obscurity, and became regarded as an inferior rival to the vector. In this century, and particularly in recent years, mathematicians and physicists have come to realise that the quaternion has much to offer, and its relegation to a backwater of scientific lore may have been a regrettable instance of wrongful neglect.

In a previous paper (Gough 1984, hereafter denoted G84), the elements of quaternion algebra were expounded for the benefit of a newcomer to the subject. It was then shown that the quaternion (more so than the vector) is a natural tool for formulating angular functions in problems where there is a centre of symmetry. Quaternion functions $U_{lm}^{\prime}$ and $V_{lm}^{\prime}$ (hereafter called $U_{lm_l}^{\prime}$ and $V_{lm_l}^{\prime}$) were derived, which are alternatives to the familiar spherical harmonics, and have some remarkably simple properties.

In this paper we shall develop the analysis. One interesting thing which will emerge is that 'particle spin' should not be regarded as quantum mechanical in essence! Rather, it is a feature which emerges quite

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simply and logically out of the mathematics of quaternions. This is not as surprising as it might appear, since a quaternion theory can be developed for the electron, which is equivalent to the well known Dirac theory. In the latter, spin emerges as an integral feature of the theory. It will be shown too that the notion of 'spin' (and even spin–orbit coupling!) is relevant in some problems of *classical* physics, for example, that of a spherical acoustic wave emitted by a point source.

2. Angular momentum in quaternion theory

2.1. The operators ∇_q, r_q and L_q

In quaternion theory, there are three anticommuting 'values' of $\sqrt{-1}$, namely $\imath, \jmath$ and k, i.e.

$$\imath^2 = \jmath^2 = k^2 = -1, \tag{1}$$

$$\imath\jmath = -\jmath\imath \qquad \jmath k = -k\jmath \qquad k\imath = -\imath k \tag{2}$$

where

$$\imath\jmath = k \qquad \jmath k = \imath \qquad k\imath = \jmath .$$

Quaternion algebra is non-commutative, but associative, i.e. $(q_1q_2)q_3 = q_1(q_2q_3) = q_1q_2q_3$.

Any quaternion (or 'hypercomplex' number) is expressible as

$$a_0 + a_1\imath + a_2\jmath + a_3k$$

where $a_0, \ldots, a_3$ are real. Likewise, as a logical extension of conventional quantum mechanics, we represent a single particle by a quaternion wave-function with spatial part expressible in the form

$$\psi = \psi_0 + \psi_1\imath + \psi_2\jmath + \psi_3k ,$$

where $\psi_0, \ldots, \psi_3$ are real functions of the spatial coordinates.

The quaternion equivalents of the vector operator $\mathbf{\nabla}$ and the displacement vector $\boldsymbol{r}$ are

$$\nabla_q = \imath\frac{\partial}{\partial x} + \jmath\frac{\partial}{\partial y} + k\frac{\partial}{\partial z} \tag{3}$$

$$r_q = \imath x + \jmath y + k z. \tag{4}$$

From equations (1), (2) and (3),

$$\nabla_q^2 = -\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right) = -\nabla^2. \tag{5}$$

In G84, we introduced the operator L, but, for consistency, we shall here denote it L_q,

$$L_q = \imath\left(z\frac{\partial}{\partial y} - y\frac{\partial}{\partial z}\right) + \jmath\left(x\frac{\partial}{\partial z} - z\frac{\partial}{\partial x}\right) + k\left(y\frac{\partial}{\partial x} - x\frac{\partial}{\partial y}\right) \tag{6}$$

which is expressible† as

$$L_q = \imath L_x + \jmath L_y + k L_z \tag{7}$$

where

$$L_x = z\frac{\partial}{\partial y} - y\frac{\partial}{\partial z}, \qquad L_y = x\frac{\partial}{\partial z} - z\frac{\partial}{\partial x}, \qquad L_z = y\frac{\partial}{\partial x} - x\frac{\partial}{\partial y} \tag{8}$$

For convenience, we repeat some of the relations given in G84

$$r_q\nabla_q = -r\frac{\partial}{\partial r} - L_q$$

$$r_q\nabla_q - \nabla_q r_q = 3 - 2L_q$$

$$r_q\nabla_q + \nabla_q r_q = -2r\frac{\partial}{\partial r} - 3$$

$$r_q(L_q - 1) + (L_q - 1)r_q = 0$$

$$\nabla_q(L_q - 1) + (L_q - 1)\nabla_q = 0.$$

2.2. Operators involving post-multiplication

The operators normally involved in mathematical physics are of the form 'operator A acting on a function'. In the following analysis, we shall need to consider operators which also involve post-multiplication by a quaternion q. For example, the operation $\partial/\partial z$ on a function ψ, and of post-multiplication by q would result in $(\partial/\partial z)\psi q$, and the appropriate operator would be designated $(\partial/\partial z)(\ )q$, the operand being the quantity in the second pair of brackets. So long as q is a constant quaternion (in all cases which concern us, q is $\imath$, $\jmath$ or k), there is no ambiguity in this nomenclature. (Of course, $(\partial/\partial z)(\ )q$ is not in general the same as $q(\partial/\partial z)(\ )$ or $(\partial/\partial z)q(\ )$ since quaternion operation is not commutative.)

In this example, the eigenvalue equation $A\psi =$ constant $\times\ \psi$ takes the form $(\partial\psi/\partial z)q =$ constant $\times\ \psi$.

We here make the general point that if a function ψ is an eigenfunction of an operator A which acts 'only from the left', then ψ, *post*-multiplied by any constant quaternion, is also an eigenfunction. This result, however, is not true for an operator which also involves post-multiplication. In the example above, $(\partial/\partial z)(\psi q')q \neq \text{constant}(\psi q')$ in general.

2.3. Observable values of angular momentum components

The form of equations (7) and (8) implies that L_z $(= y\partial/\partial x - x\partial/\partial y = -\partial/\partial\phi)$ is to be identified with the

† The form of equation (7) is in keeping with that of equations (3) and (4), and is therefore preferable to that used in G84, namely $L_q = L_x + L_y + L_z$, where $L_x = \imath(z\partial/\partial y - y\partial/\partial z)$, etc. L_q is not to be interpreted as the sum of the angular momentum components as stated in G84; its correct significance is given in § 2.4.

operator for the z component of angular momentum, in units such that $\hbar = 1$. However, it does not satisfy the requirement of conventional quantum mechanics that

$$L_z Y_{lm_l}(\theta, \phi) = m_l Y_{lm_l}(\theta, \phi)$$

where $Y_{lm_l}(\theta, \phi)$ is a spherical harmonic given in the usual notation, by constant $P_l^{m_l}(\cos\theta)\exp(k m_l \phi)$. (As explained in G84, the exponent is $k m_l \phi$, not $i m_l \phi$, since the coordinate ϕ refers to a rotation about the z, not the x, axis.)

We proceed by insisting that the eigenfunctions of L_z are indeed $Y_{lm_l}(\theta, \phi)$, but accepting that it has non-real eigenvalues. This represents a departure from the postulate of conventional quantum mechanics that all operators have real eigenvalues, which are the observable values of the corresponding physical quantities. We must therefore distinguish between L_z and the operator whose eigenvalues give the observable values of m_l.

What will be the form of this latter operator? It could be taken to be $k L_z (= -k\, \partial/\partial\phi)$ as in conventional quantum mechanics, but an alternative choice, which will be shown to be preferable, is the operator $L_z(\ )k$. So we have

$$L_z Y_{lm_l}(\theta, \phi)k = -(\partial/\partial\phi) Y_{lm_l}(\theta, \phi)k = m_l Y_{lm_l}(\theta, \phi).$$

We therefore take $L_x(\ )i$, $L_y(\ )j$ and $L_z(\ )k$ as the operators which will give the observable values of the orbital angular momentum components. This is in the nature of an *ad hoc* postulate for the development of a quaternion quantum mechanical theory of angular momentum.

Again, the observable values of the (total orbital angular momentum)^2 are the eigenvalues of the operator $L_x^2(\ )i^2 + L_y^2(\ )j^2 + L_z^2(\ )k^2$, which equals $-(L_x^2 + L_y^2 + L_z^2)$.

2.4. *Spin in quaternion theory*

We now draw attention to the operator (cf Edmonds 1972) $y\partial/\partial x - x\partial/\partial y + \frac{1}{2}k (= -\partial/\partial\phi + \frac{1}{2}k)$. A straightforward calculation reveals that this operator has the remarkable property of commuting with ∇_q, r_q and L_q; it is therefore of considerable importance. It is readily seen that $(y\partial/\partial x - x\partial/\partial y + \frac{1}{2}k)(\ )k$ also has this property (but not $k(y\partial/\partial x - x\partial/\partial y + \frac{1}{2}k)$, which is of no obvious importance). We are led, in anticipation of its significance, to denote $y\partial/\partial x - x\partial/\partial y + \frac{1}{2}k$ by J_z, and decompose it into two terms (Edmonds 1972)

$$J_z = L_z + S_z \tag{9}$$

where

$$S_z = \tfrac{1}{2}k. \tag{10}$$

Also, of course, $J_x = L_x + S_x$, $J_y = L_y + S_y$, $S_x = \frac{1}{2}i$ and $S_y = \frac{1}{2}j$.

We can now interpret the operator L_q, since from equation (7),

$$L_q = 2(L_x S_x + L_y S_y + L_z S_z).$$

The observable values (cf § 2.3) of $2(L_x S_x + L_y S_y + L_z S_z)$ are the eigenvalues of $2L_x S_x(\ )ii + 2L_y S_y(\ )jj + 2L_z S_z(\ )kk$, which are minus the eigenvalues of L_q. These are therefore (G84) l and $-(l+1)$, as is well established (see, for example, Atkin 1956).

By analogy with equation (7), we write

$$S_q = i S_x + j S_y + k S_z = -\tfrac{3}{2}$$

and

$$J_q = i J_x + j J_y + k J_z = L_q + S_q = L_q - \tfrac{3}{2}.$$

These operators are of course those for orbital and spin angular momentum and their components in quaternion quantum mechanics; it is noteworthy that the spin component operators are simply imaginary multiplying factors.

The commutation relations are, from equations (8), (9) and (10)

$$[L_x, L_y] = L_z \tag{11}$$

$[S_x, S_y] = S_z$, $[L_x, S_x] = [L_x, S_y] = 0$, etc whence

$$[J_x, J_y] = J_z, \text{ etc.} \tag{12}$$

From equations (6) to (12), it is readily shown too that

$$(L_x^2 + L_y^2 + L_z^2) = -L_q^2 + L_q$$
$$(S_x^2 + S_y^2 + S_z^2) = -S_q^2 - S_q = -\tfrac{3}{4}$$
$$(J_x^2 + J_y^2 + J_z^2) = -J_q^2 - J_q$$
$$[L_q, L_z^2 + k L_z] = 0.$$

2.5. *Observable values for spin components, and the corresponding eigenfunctions*

By analogy with the postulate given in § 2.3, the observable values m_s of the spin orientation are the solutions of the equation

$$S_z(\psi)k = m_s \psi$$

that is,

$$\tfrac{1}{2}k(\psi)k = m_s \psi.$$

This leads us to a very interesting conclusion. Suppose a quaternion wavefunction ψ is expanded as $\psi_0 + \psi_1 i + \psi_2 j + \psi_3 k$, where $\psi_0, \ldots, \psi_3$ are real. Then if $\psi_1 = \psi_2 = 0$, it follows that $m_s = -\frac{1}{2}$; and if $\psi_0 = \psi_3 = 0$, then $m_s = \frac{1}{2}$. In particular, it follows that *implicit in the spherical harmonic* Y_{l,m_l} *itself* is that *the spin is 'down'* ($m_s = -\frac{1}{2}$), whereas $i Y_{l,m_l}$ and $j Y_{l,m_l}$ imply that *the spin is 'up'* ($m_s = \frac{1}{2}$). Spin will also be 'up' for $Y_{l,m_l} i$ and $Y_{l,m_l} j$.

3. Quaternion angular functions in the j, m_j representation

In G84, we derived the eigenfunctions of L_q, showing them to be mixtures of spherical harmonics with quaternion coefficients, and deducing some of their simple properties. From equations (23) and (30) of that reference, they are expressible in the forms

$$U'_{lm_l} = -\left(\frac{l-m_l}{2l+1}\right)^{1/2} \mathbf{j}\, Y_{l,-m_l-1} + \left(\frac{l+m_l+1}{2l+1}\right)^{1/2} Y_{l,-m_l} \qquad (m_l = 0, \ldots, l) \qquad (13a)$$

$$V'_{lm_l} = \left(\frac{l+m_l+1}{2l+1}\right)^{1/2} \mathbf{j}\, Y_{l,-m_l-1} + \left(\frac{l-m_l}{2l+1}\right)^{1/2} Y_{l,-m_l} \qquad (m_l = 0, \ldots, l-1). \qquad (13b)$$

Written in this form, the functions U'_{lm_l} and V'_{lm_l} are to be regarded as mixtures of the states $|-m_l-1\rangle$ and $|-m_l\rangle$, not $|m_l+1\rangle$ and $|-m_l\rangle$ as stated in G84.

Now the quantities in brackets are all expressible as Clebsch–Gordon coefficients (see, for example, Rose 1957) appropriate to the coupling of orbital angular momentum quantum number l with a spin $s=\frac{1}{2}$, whence

$$U'_{lm_l} = -C(l, \tfrac12, l+\tfrac12; -m_l-1, \tfrac12, -m_l-\tfrac12)\mathbf{j}\, Y_{l,-m_l-1} + C(l, \tfrac12, l+\tfrac12; -m_l, -\tfrac12, -m_l-\tfrac12) Y_{l,-m_l}$$

$$V'_{lm_l} = -C(l, \tfrac12, l-\tfrac12; -m_l-1, \tfrac12, -m_l-\tfrac12)\mathbf{j}\, Y_{l,-m_l-1} + C(l, \tfrac12, l-\tfrac12; -m_l, -\tfrac12, -m_l-\tfrac12) Y_{l,-m_l}$$

Now compare these with the expression for ψ_{jm_j} (Rose 1957) in terms of the orbital and spin wavefunctions ψ_{lm_l} and ψ_{sm_s} respectively, (with $m_j = m_l + m_s$), namely

$$\psi_{l,s,j,m_j} = \sum_{m_l} C(l, \tfrac12, j; m_l, m_s, m_j) \times \psi_{sm_s}\psi_{lm_l}\delta_{m_l+m_s, m_j}. \qquad (14)$$

An exact comparison is inappropriate, since this equation is derived for conventional, as opposed to quaternion, quantum mechanics: in the former, the multiplication of ψ_{sm_s} with ψ_{lm_l} is commutative. Nevertheless, it is clear that U'_{lm_l} corresponds to $j=l+\frac12$, and V'_{l,m_l} to $j=l-\frac12$, with $m_j=-m_l-\frac12$ in both cases. Furthermore, we have confirmation of the conclusion reached in § 2.5, that $\mathbf{j}Y_{l,m_l}$ and Y_{l,m_l} signify 'spin up' and 'spin down' respectively.

We are therefore led to adopt the more suitable nomenclature $Z^{\pm}_{l,s,j,m_j}$ (where $j=l\pm s=l\pm\frac12$). This may be written in the more compact form without ambiguity as $Z^{\pm}_{j,m_j}$. Specifically, $Z^{+}_{l+1/2,-m_l-1/2} = U'_{lm_l}$ and $Z^{-}_{l-1/2,-m_l-1/2} = V'_{lm_l}\mathbf{k}$. (The inclusion of the phase factor $\mathbf{k}$ in the latter avoids $\mathbf{k}$ s appearing in some of the equations (17) to (22) below.) Explicitly then equations (13) give

$$Z^{+}_{l+1/2, m_l+1/2} = -\left(\frac{l+m_l+1}{2l+1}\right)^{1/2} \mathbf{j}\, Y_{l,m_l} + \left(\frac{l-m_l}{2l+1}\right)^{1/2} Y_{l,m_l+1} \qquad (m_l = -l-1, \ldots, l) \qquad (15a)$$

$$Z^{-}_{l-1/2, m_l+1/2} = \left(\frac{l-m_l}{2l+1}\right)^{1/2} \mathbf{i}\, Y_{l,m_l} + \left(\frac{l+m_l+1}{2l+1}\right)^{1/2} \mathbf{k}\, Y_{l,m_l+1} \qquad (m_l = -l, \ldots, l-1). \qquad (15b)$$

In terms of the Clebsch–Gordon coefficients,

$$Z^{+}_{l+1/2, m_l+1/2} = -C(l, \tfrac12, l+\tfrac12; m_l, \tfrac12, m_l+\tfrac12)\mathbf{j}\, Y_{lm_l} + C(l, \tfrac12, l+\tfrac12; m_l+1, -\tfrac12, m_l+\tfrac12) Y_{l,m_l+1} \qquad (16a)$$

$$Z^{-}_{l-1/2, m_l+1/2} = -C(l, \tfrac12, l-\tfrac12; m_l, \tfrac12, m_l+\tfrac12)\mathbf{i}\, Y_{lm_l} + C(l, \tfrac12, l-\tfrac12; m_l+1, -\tfrac12, m_l+\tfrac12)\mathbf{k}\, Y_{l,m_l+1}. \qquad (16b)$$

It should be noted that m_l is allowed to range over positive *and* negative values. In G84 it was argued that the functions for negative m_l could be disregarded, since they were related to those for non-negative m_l by post-multiplicative quaternion phase factors. But we have now abandoned (§ 2.2) the idea that post-multiplication by $\mathbf{j}$ gives the same state, therefore we allow the whole range of m_l. For a given l, there is a total of $2(2l+1)$ functions.

These equations (16) show that Z^+ and Z^- are the angular functions appropriate to the $|j, m_j\rangle$ representation in spin–orbit coupling. It is evident that quaternions are very powerful in this context, and that equations (15) and (16) are preferable to the conventional equation (14), since we have *explicit expressions* for the $|j, m_j\rangle$ angular functions, which entirely dispense with the need for concepts like 'spin wavefunctions' and 'spin space' which are as vague as they are unsatisfactory.

The angular functions for m_j are related very simply to those for $-m_j$ by

$$Z^{\pm}_{j,m_j} = (-1)^{m_j+1/2} Z^{\pm}_{j,-m_j}\mathbf{j}.$$

A number of properties of the $Z^{\pm}$ functions can be derived from equations (31) to (36) in G84 which now take the following forms:

$$L_q Z^{+}_{j,m_j} = -(j-\tfrac12) Z^{+}_{j,m_j} \qquad (17a)$$

$$L_q Z^{-}_{j,m_j} = (j+\tfrac32) Z^{-}_{j,m_j} \qquad (17b)$$

$$\frac{r_q}{r} Z^{+}_{j,m_j} = Z^{-}_{j,m_j} \qquad (18a)$$

$$\frac{r_q}{r} Z^{-}_{j,m_j} = -Z^{+}_{j,m_j} \qquad (18b)$$

$$r_q \nabla_q Z^{+}_{j,m_j} = (j-\tfrac12) Z^{+}_{j,m_j} \qquad (19a)$$

$$r_q \nabla_q Z^{-}_{j,m_j} = -(j+\tfrac32) Z^{-}_{j,m_j} \qquad (19b)$$

Table 1 The functions $Z^{+}_{l,s,j,m}$ for $l=0$, 1 and 2, $s=\frac{1}{2}$.

l	Z^{+}_{l,s,j,m_j}	Z_{l,s,j,m_j}
0	$Z^{+}_{0,1/2,1/2,1/2}=-\left(\frac{1}{4\pi}\right)^{1/2}\mathbf{j}$	
	$Z^{+}_{0,1/2,1/2,-1/2}=\left(\frac{1}{4\pi}\right)^{1/2}$	
1	$Z^{+}_{1,1/2,3/2,3/2}=\frac{1}{r}\left(\frac{3}{8\pi}\right)^{1/2}(x\mathbf{j}+y\mathbf{i})$	
	$Z^{+}_{1,1/2,3/2,1/2}=\frac{1}{r}\left(\frac{1}{8\pi}\right)^{1/2}(-x-y\mathbf{k}-2z\mathbf{j})$	$Z_{1,1/2,1/2,1/2}=\frac{1}{r}\left(\frac{1}{4\pi}\right)^{1/2}(-x\mathbf{k}+y+z\mathbf{i})$
	$Z^{+}_{1,1/2,3/2,-1/2}=\frac{1}{r}\left(\frac{1}{8\pi}\right)^{1/2}(-x\mathbf{j}+y\mathbf{i}+2z)$	$Z_{1,1/2,1/2,-1/2}=\frac{1}{r}\left(\frac{1}{4\pi}\right)^{1/2}(x\mathbf{i}+y\mathbf{j}+z\mathbf{k})$
	$Z^{+}_{1,1/2,3/2,-3/2}=\frac{1}{r}\left(\frac{3}{8\pi}\right)^{1/2}(x-y\mathbf{k})$	
2	$Z^{+}_{2,1/2,5/2,5/2}=\frac{1}{r^2}\left(\frac{15}{32\pi}\right)^{1/2}(-x^2\mathbf{j}+y^2\mathbf{j}-2xy\mathbf{i})$	
	$Z^{+}_{2,1/2,5/2,3/2}=\frac{1}{r^2}\left(\frac{3}{32\pi}\right)^{1/2}(x^2-y^2+2xy\mathbf{k}+4xz\mathbf{j}+4yz\mathbf{i})$	$Z_{2,1/2,3/2,3/2}=\frac{1}{r^2}\left(\frac{3}{8\pi}\right)^{1/2}(x^2\mathbf{k}-y^2\mathbf{k}-2xy-xz\mathbf{i}+yz\mathbf{j})$
	$Z^{+}_{2,1/2,5/2,1/2}=\frac{1}{r^2}\left(\frac{3}{16\pi}\right)^{1/2}(x^2\mathbf{j}+y^2\mathbf{j}-2z^2\mathbf{j}-2xz-2yz\mathbf{k})$	$Z_{2,1/2,3/2,1/2}=\frac{1}{r^2}\left(\frac{1}{8\pi}\right)^{1/2}(-x^2\mathbf{i}-y^2\mathbf{i}+2z^2\mathbf{i}-3xz\mathbf{k}+3yz)$
	$Z^{+}_{2,1/2,5/2,-1/2}=\frac{1}{r^2}\left(\frac{3}{16\pi}\right)^{1/2}(-x^2-y^2+2z^2-2xz\mathbf{j}+2yz\mathbf{i})$	$Z_{2,1/2,3/2,-1/2}=\frac{1}{r^2}\left(\frac{1}{8\pi}\right)^{1/2}(-x^2\mathbf{k}-y^2\mathbf{k}+2z^2\mathbf{k}+3xz\mathbf{i}+3yz\mathbf{j})$
	$Z^{+}_{2,1/2,5/2,-3/2}=\frac{1}{r^2}\left(\frac{3}{32\pi}\right)^{1/2}(-x^2\mathbf{j}+y^2\mathbf{j}+2xy\mathbf{i}+4xz-4yz\mathbf{k})$	$Z_{2,1/2,3/2,-3/2}=\frac{1}{r^2}\left(\frac{3}{8\pi}\right)^{1/2}(x^2\mathbf{i}-y^2\mathbf{i}+2xy\mathbf{j}+xz\mathbf{k}+yz)$
	$Z^{+}_{2,1/2,5/2,-5/2}=\frac{1}{r^2}\left(\frac{15}{32\pi}\right)^{1/2}(x^2-y^2-2xy\mathbf{k})$	

$$\nabla_q Z^{+}_{j,m_j} = -\frac{j-\frac{1}{2}}{r} Z^{-}_{j,m_j} \tag{20a}$$

$$\nabla_q Z^{-}_{j,m_j} = -\frac{j+\frac{3}{2}}{r} Z^{+}_{j,m_j} \tag{20b}$$

to which we append

$$J_z(Z^{\pm}_{j,m_j})\mathcal{k} = m_j Z^{\pm}_{j,m_j} \tag{21}$$

$$\nabla_q(RZ^{+}_{j,m_j}) = \left(\frac{\mathrm{d}R}{\mathrm{d}r} - \frac{j-\frac{1}{2}}{r}R\right) Z^{-}_{j,m_j} \tag{22a}$$

$$\nabla_q(RZ^{-}_{j,m_j}) = -\left(\frac{\mathrm{d}R}{\mathrm{d}r} + \frac{j+\frac{3}{2}}{r}R\right) Z^{+}_{j,m_j} \tag{22b}$$

where R is any real function of r only.

It should be noted that if equations (18) are written out fully,

$$\frac{r_q}{r} Z^{\pm}_{l,1/2,l\pm 1/2,m_j} = \pm Z^{\mp}_{l\pm 1,1/2,l\pm 1/2,m_j}$$

the operator r_q/r is seen to couple states with l values differing by ± 1. The same is true for the operator ∇_q.

In table 1, the functions $Z^{\pm}_{j,m_j}$ have been tabulated for $l=0$, 1 and 2. The use of cartesian, rather than polar, coordinates facilitates calculation and manipulation.

4. Simultaneous observability of spin components?

It has long been established in conventional quantum mechanics that if two operators do not commute, the corresponding observables cannot be simultaneously observed with perfect accuracy, since they have no common eigenfunction. This is certainly true for the orbital angular momentum components L_x and L_y, for instance (unless $L_z = 0$).

But is this so for spin components? It is true that the operators S_x and S_y do not commute. But consider a wavefunction of the form $R(r)Y_{00}(\theta, \phi)$, i.e. real and spherically symmetric. From the discussion in § 2.5, $m_s^{(z)}$ for this state is $-\frac{1}{2}$, and therefore by symmetry, $m_s^{(x)}$ and $m_s^{(y)}$ must also be $-\frac{1}{2}$. Again, if the wavefunction is $R(r)Y_{00}\mathcal{k}$, then $m_s^{(z)} = -\frac{1}{2}$, and $m_s^{(x)} = m_s^{(y)} = \frac{1}{2}$. Likewise, for $R(r)Y_{00}\mathcal{i}$, $m_s^{(x)} = -\frac{1}{2}$, $m_s^{(y)} = \frac{1}{2}$, $m_s^{(z)} = \frac{1}{2}$, and for $R(r)Y_{00}\mathcal{j}$, $m_s^{(x)} = \frac{1}{2}$, $m_s^{(y)} = -\frac{1}{2}$, $m_s^{(z)} = \frac{1}{2}$.

It therefore behoves the scientific world to be cautious in asserting that only one component of spin angular momentum is well defined, or that a particle can be regarded as having a spin orientation which is fixed in space. We do not assert, however, that it is possible to have simultaneous *knowledge* of more than one component of spin angular momentum. If, for instance, $m_s^{(z)}$ is known to be $+\frac{1}{2}$, then ψ will be of the form $\psi_1\mathcal{i} + \psi_2\mathcal{j}$, where ψ_1 and ψ_2 are real. It may, however, be impossible to devise any thought experiment in which ψ is of the form (say) $\psi_1\mathcal{i}$, in which all three spin components are well defined.

While these points are very pertinent in discussions of the Einstein–Podolsky–Rosen paradox (see, for example, d'Espagnat 1979), it is in no way intended to offer a simple explanation of the results of recent experiments (Aspect *et al* 1982). Even if a particle has simultaneous 'reality' in all of its spin components, the results of the above mentioned experiment cannot be explained by local realistic theories.

5. Commutivity of phase changes

For a wavefunction ψ in conventional quantum mechanics, there are two components (real and pure imaginary) which are of course related to the amplitude and phase of ψ. But in quaternion quantum mechanics, a wavefunction $\psi_0 + \psi_1\mathcal{i} + \psi_2\mathcal{j} + \psi_3\mathcal{k}$ can be decomposed into four components $\psi_0, \ldots, \psi_3$ which are all real.

Peres (1979) has given consideration to the problem of interference of two quaternion wavefunctions, pointing out that this can be regarded as the addition of vectors in four-dimensional space. According to this interpretation, a phase change can be represented by a rotation in this space. Now since spatial rotations are not commutative, phase changes corresponding to successive rotations are not additive. Peres suggested that if a particle passes through two successive dissimilar absorbers, the total phase change Δ_{12} is not in general equal to the sum of the phase changes Δ_1 and Δ_2 produced by each individually. Moreover, if the absorbers are interchanged, it would be expected that the phase change Δ_{21} may not be equal to Δ_{12}. A recent experiment (Kaiser *et al* 1984) has not confirmed this speculation; Δ_{12} was shown to equal Δ_{21} to within 1 part in 30 000.

It might appear that this experiment would indicate that quaternion quantum mechanics is not correct, at least when describing the rectilinear motion of a particle. However, no such problems arise when quaternions are used to describe angular functions, since as was seen in § 2.5, the latter contain information not only on the amplitude and phase, but also on the spin orientation. Suppose for simplicity that the angular part of the quaternion wavefunction of a particle is $Y_{lm_l}(a_0 + a_1\mathcal{i} + a_2\mathcal{j} + a_3\mathcal{k})$, where $a_0, \ldots, a_3$ are real. Then the two constants a_0 and a_3 will give the amplitude and phase of the $m_s = -\frac{1}{2}$ component, while a_1 and a_2 give that information for $m_s = \frac{1}{2}$. So instead of regarding this function as a vector in four-dimensional space, it is more logical to decompose it into two vectors each in two-dimensional space, each having a conventional amplitude and phase. Phase is a scalar, and described by only one component.

6. The Dirac theory of the electron in the hydrogen atom

With the results of § 3, we will see that the functions $Z^{\pm}_{j,m_j}$ are instrumental in a very satisfactory relativistic treatment of the hydrogen atom. The quaternion approach is equivalent to the Dirac theory (an excellent elementary account of which is given by Atkin 1956), but the former has the advantage of avoiding the awkward 4×4 matrices, Pauli spin matrices, and the concept of spin space. It has long been established that quaternions can be used in the relativistic theory of the electron (see, for example, Conway 1937). In his treatment, *complex* quaternions were used ($i\sigma_1$, $i\sigma_2$, $i\sigma_3$, where $\sigma_1^2 = -1$ etc, and $\sigma_1\sigma_2 = \sigma_3$, etc); here, where we are not concerned with time development, these are unnecessary.

The relativistic energy E of a free particle with momentum p and rest mass m is given by

$$E^2 = p^2 + m^2$$

in units where $c = 1$. The corresponding Klein–Gordon wave equation is obtained with the substitution $p^2 = -\nabla^2 = \nabla_q^2$,

$$\nabla_q^2 \psi = (E^2 - m^2)\psi = (E + m)(E - m)\psi \tag{23}$$

which is expressible as two coupled equations

$$\nabla_q \psi = (E + m)\phi, \qquad \nabla_q \phi = (E - m)\psi.$$

In the case of the hydrogen electron, where the potential energy is $-e^2/r$ (in units where $4\pi\varepsilon_0 = 1$), E is replaced by $E + e^2/r$. Let us try solutions for ψ and ϕ of the form $R_1 Z_{jm_j}^+$ and $R_2 Z_{jm_j}^-$ respectively, where R_1 and R_2 are real functions of r only. The coupled equations are

$$\nabla_q R_1 Z_{j,m_j}^+ = (E + m + e^2/r) R_2 Z_{j,m_j}^-$$
$$\nabla_q R_2 Z_{j,m_j}^- = (E - m + e^2/r) R_1 Z_{j,m_j}^+.$$

From equations (22), these reduce to

$$R_1' - \frac{j - \frac{1}{2}}{r} R_1 = (E + m + e^2/r) R_2 \tag{24a}$$

$$R_2' + \frac{j + \frac{3}{2}}{r} R_2 = -(E - m + e^2/r) R_1 \tag{24b}$$

as given by the Dirac theory (Dirac 1935, Atkin 1956). The solution $\psi = R_1 Z_{j,m_j}^+$ implies that the wavefunction ψ is appropriate to $j = l + \frac{1}{2}$. It should be noted that the angular part of $\nabla_q \psi$ is Z_{j,m_j}^-, or more fully written $Z_{l+1,1/2,l+1/2,m_j}^-$, and is appropriate to an orbital quantum number of $l + 1$.

The same coupled equations are also valid for the case where the wavefunction ψ corresponds to $j = l - \frac{1}{2}$, but here it is $R_2 Z_{j,m_j}^-$ which is to be interpreted as ψ. The distribution of $\nabla_q \psi$ has angular dependence appropriate to orbital quantum number $l - 1$.

Since equations (24) contain j, but not l, it follows that the energy eigenvalues E will be coincident for the cases $l = j + \frac{1}{2}$ and $l = j - \frac{1}{2}$, as is well known.

7. Quaternions applied to the wave equation

Finally we analyse an example to illustrate that the quaternion angular functions $Z_{j,m_j}^{\pm}$ relate not merely to quantum mechanics, but also to pure mathematics and *classical* physics. Consider a monochromatic sound wave in air, with circular wavenumber K, emanating from the origin of polar coordinates (r, θ, ϕ). The wave equation is

$$\nabla^2 u = -K^2 u$$

where u is the acoustic pressure.

From equation (5),

$$\nabla_q^2 u = K^2 u$$

which is expressible as two coupled equations

$$\nabla_q u = Kv \qquad \text{and} \qquad \nabla_q v = Ku. \tag{25}$$

Following § 6, we write

$$u = R_1 Z_{j,m_j}^+ \qquad v = R_2 Z_{j,m_j}^- \tag{26}$$

where R_1 and R_2 are real functions of r only. Then from equations (22),

$$R_1' - \frac{j - \frac{1}{2}}{r} R_1 = KR_2$$

$$R_2' + \frac{j + \frac{3}{2}}{r} R_2 = -KR_1.$$

Elimination of R_2, then R_1, from these equations gives

$$R_1'' + \frac{2}{r} R_1' + \left(K^2 - \frac{(j - \frac{1}{2})(j + \frac{1}{2})}{r^2}\right) R_1 = 0$$

$$R_2'' + \frac{2}{r} R_2' + \left(K^2 - \frac{(j + \frac{1}{2})(j + \frac{3}{2})}{r^2}\right) R_2 = 0.$$

Comparing these with the radial part of the wave equation (see, for example, Margenau and Murphy 1956),

$$R'' + \frac{2}{r} R' + \left(K^2 - \frac{l(l+1)}{r^2}\right) R = 0,$$

we see that our choice in equations (26) is appropriate to $j = l + \frac{1}{2}$ for the pressure wave u. From equations (25) and (26), the v wave is the grad of the pressure (which is proportional to the displacement) and has an angular dependence appropriate to $l + 1$, since j is the same for both waves. Conversely, the same coupled equations apply if v is the pressure, and u its gradient. In this case, the acoustic pressure wave corresponds to $j = l - \frac{1}{2}$, and the displacement wave to $l - 1$.

8. Conclusion

It has been shown that the set of quaternion functions $Z_{j,m_j}^{\pm}$ form an alternative to the set of spherical harmonics in problems where there is a centre of symmetry. Implicit in these functions is the idea of 'spin' which, although normally associated with quantum mechanics, is also applicable in classical physics. The functions $Z_{j,m_j}^{\pm}$ have been expressed in terms of those appropriate to a well defined m_l and m_s, drawing parallels with results familiar in elementary angular momentum theory. Although the expressions are simple, they are thought by the author to be original (or buried very deep in the abundance of scientific literature). With the use of quaternions, it may be possible to re-write large sections of standard texts on the theory of atomic physics (see, for example, Condon and Shortley 1964), with no need for some of the awkward concepts, particularly that of the 'spin wavefunction'.

References

Aspect A, Dalibard J and Roger G 1982 *Phys. Rev. Lett.* **49** 1084–7

Atkin R H 1956 *Mathematics and Wave Mechanics* (London: Heinemann)

Bork A M 1966 *Am. J. Phys.* **34** 202–11

Condon E U and Shortley G H 1964 *The Theory of Atomic Spectra* (Cambridge: Cambridge University Press)

Conway A W 1937 *Proc. R. Soc.* A **162** 145–54

Dirac P A M 1935 *Quantum Mechanics* (Oxford: Oxford University Press)

Edmonds J D 1972 *Int. J. Theor. Phys.* **6** 205–24

d'Espagnat B 1979 *Sci. Am.* **241** (11) 128–40

Gough W 1984 *Eur. J. Phys.* **5** 163–71

Kaiser H, George E A and Werner S A 1984 *Phys. Rev.* A **29** 2276–9

Margenau H and Murphy G M 1956 *The Mathematics of Physics and Chemistry* 2nd edn (Princeton, NJ: van Nostrand)

Peres A 1979 *Phys. Rev. Lett.* **42** 683–6

Rose M E 1957 *Elementary Theory of Angular Momentum* (New York: Wiley)

Stephenson R J 1966 *Am. J. Phys.* **34** 194–201