# Chapter 7
# Spherical Symmetry and Spins

**Abstract** A brief excursion is made into the concept of continuous groups, with an example of the rotation groups. The purpose is to familiarize the reader with the concept of electron spin. The coupling of spins is discussed. Applications are taken from Crystal-Field Theory and Electron Spin Resonance.

**Contents**



## 7.1 The Spherical-Symmetry Group

Consider the row vector of coordinate functions $(|x\rangle\ |y\rangle\ |z\rangle)$ in 3D space. A rotation must conserve the norm of this function space. As we have seen in Chap. 2, this can be realized by a unitary matrix transformation. For real functions, the unitary transformation is reduced to an orthogonal one. A matrix is orthogonal if the following condition is fulfilled (where $T$ denotes transposition):

$$\mathbb{D}^T\mathbb{D} = \mathbb{I} = \mathbb{D}\mathbb{D}^T \tag{7.1}$$

The set of all ortho-gonal $3 \times 3$ matrices forms a group, which is called the orthogonal group in three dimensions, $O(3)$. The order of this group is infinite. It can be shown that this group is isomorphic with the complete group of all proper and improper rotations in three dimensions. The structure that embodies this symmetry is the sphere. Hence, $O(3)$ is the symmetry group of the sphere. The determinants of the matrices must be real with modulus one, which means that they can

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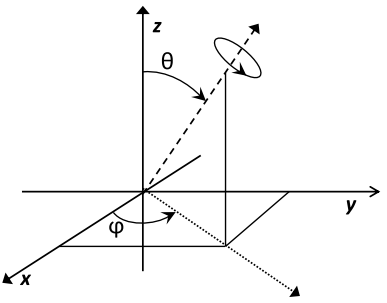


**Fig. 7.1** *The dashed line* represents an axis of rotation at an angle $\theta$ from the positive $z$-axis and an angle $\phi$ in the $(x, y)$-plane, measured counterclockwise from the positive $x$-direction

only be $\pm 1$. Improper symmetry elements are represented by matrices with determinant $-1$, while the proper symmetry elements have determinant $+1$. The latter matrices form a halving subgroup, which is called the *special orthogonal group* in three dimensions, $SO(3)$. This subgroup describes the rotational subgroup of the sphere. A convenient representation of an arbitrary rotation is described by four parameters: the rotation angle, $\alpha$, and three direction cosines, $n_x, n_y, n_z$, indicating the orientation of the pole of the rotation axis in the Cartesian frame. The latter are normalized as $n_x^2 + n_y^2 + n_z^2 = 1$. This means that only three angles are required to describe a rotation: the rotational angle $\alpha$ and two angular coordinates of the rotational pole (see Fig. 7.1), a result which was obtained by Euler [1]:

$$\begin{aligned} n_x &= \sin\theta\cos\phi \\ n_y &= \sin\theta\sin\phi \\ n_z &= \cos\theta \end{aligned} \tag{7.2}$$

This $SO(3)$ matrix for the row vector $(|x\rangle|y\rangle|z\rangle)$ under a rotation $\hat{R}(\alpha, n_x, n_y, n_z)$ reads:

$$\mathbb{O}(R) = \begin{pmatrix} 1-2(n_y^2+n_z^2)\gamma & -n_z\sin\alpha + 2n_x n_y\gamma & n_y\sin\alpha + 2n_z n_x\gamma \\ n_z\sin\alpha + 2n_x n_y\gamma & 1-2(n_z^2+n_x^2)\gamma & -n_x\sin\alpha + 2n_y n_z\gamma \\ -n_y\sin\alpha + 2n_z n_x\gamma & n_x\sin\alpha + 2n_y n_z\gamma & 1-2(n_x^2+n_y^2)\gamma \end{pmatrix} \tag{7.3}$$

with $\gamma = \sin^2(\alpha/2)$.

The determinant of this matrix is $+1$, as expected. In $(n_x, n_y, n_z)$ space any rotation $\hat{R} \in G$ has two poles. These are the points on the unit sphere that are invariant under the rotation. These points are at $\pm\mathbf{n}$ and thus are mutual antipodes. We recall that a rotation over a positive angle is viewed from the pole as counterclockwise. In the antipodal pole this rotation is observed as clockwise. Rotations about antipodal poles and over opposite angles thus produce the same effect. Hence, a sign change of all parameters leaves the matrix invariant. Moreover, since a rotation through an angle of $2\pi$ is equivalent to the unit element, the rotation angle can also be specified as $\alpha - 2\pi$. In total in the range $[-2\pi, +2\pi]$, there are thus four equivalent sets of

parameters that give rise to the same matrix $\mathbb{O}(R)$:

$$\begin{aligned}&\hat{R}(\alpha, n_x, n_y, n_z)\\ &\hat{R}(-\alpha, -n_x, -n_y, -n_z)\\ &\hat{R}(-2\pi+\alpha, n_x, n_y, n_z)\\ &\hat{R}(2\pi-\alpha, -n_x, -n_y, -n_z)\end{aligned} \tag{7.4}$$

The transformations of the standard vector form the fundamental irrep of spherical symmetry. All other irreps can be constructed by taking direct products of this vector. In particular, the *spherical harmonic functions* can be constructed by taking fully symmetrized powers of the vector. The symmetrized direct square of the $p$-functions yields a six-dimensional function space with components: $\{z^2, x^2, y^2, yz, xz, xy\}$. This space is not orthonormal: the components are not normalized, and the first three components do overlap. In fact, the space is reducible since the sum of the squares $z^2 + x^2 + y^2$ is a radial function, which is totally symmetric under rotations. Taking out this root leaves five components, which are irreducible and correspond to the five $d$ orbitals, shown in Table 7.1. This result parallels the cubic $[T_{1u}]^2 = A_{1g} + E_g + T_{2g}$ coupling [2].

When extending these results to the $n$th power of the $p$-irrep, symmetrization will be governed by the irreducible representations of the corresponding $S_n$ permutation group. The $f$-orbitals may be generated by the third power of the $p$-irrep. Full symmetrization of the three components generates 10 functions, $\{z^3, x^3, y^3, z^2x, z^2y, x^2z, x^2y, y^2z, y^2x, xyz\}$, which in cubic symmetry transform as $A_{2u} + 2T_{1u} + T_{2u}$. Again, this space is reducible and contains a $p$- and an $f$-subspace. The reduction is based on the removal of the totally symmetric trace. Indeed, the combination $z(x^2 + y^2 + z^2)$ and its cyclic permutations reduce to the fundamental $p$-vector. The remainder of the space is irreducible and corresponds to the seven $f$-functions listed in Table 7.1. Further explorations of the spherical symmetry group opens the book of angular momentum arithmetic and the underlying theory of Lie groups.[1] This is outside the present scope. We shall restrict the treatment to indicating the subduction rules, which describe the decomposition of the spherical irreps in point-group symmetries. To obtain these rules, we have to derive the character of function space of the spherical harmonics, $\{Y_{\ell m_\ell}\}$, for $m_\ell = -\ell, -\ell+1, \ldots, \ell-1, \ell$, under the proper and improper rotations of the point group. We shall start by considering the proper ones first. It is sufficient to limit the treatment to rotations around the $z$-axis since on a sphere all directions are equivalent. Rotations around $z$ will affect only the angular coordinate, $\phi$, in the equatorial plane and leave the azimuthal coordinate, $\theta$, unchanged. The $\phi$-dependence of the

[1] See, e.g., [3, 4].

**Table 7.1** Complex and cubic real forms of the spherical harmonics for $\ell = 0, 1, 2, 3$. The constants $N_\ell$ are the common normalizing factors over the $\theta$ and $\phi$ coordinates

| $\ell$ | $N_\ell$ | $\lvert LM\rangle$ | $\lvert \Gamma\gamma\rangle$ |
|---|---|---|---|
| $s$ | $\sqrt{\frac{1}{4\pi}}$ | $\lvert 00\rangle = 1$ | $\lvert A_{1g}\rangle = 1$ |
| $p$ | $\sqrt{\frac{3}{4\pi}}r^{-1}$ | $\lvert 1+1\rangle = -\frac{1}{\sqrt{2}}(x+iy)$ | $\lvert T_{1u}x\rangle = x$ |
| | | $\lvert 1-1\rangle = \frac{1}{\sqrt{2}}(x-iy)$ | $\lvert T_{1u}y\rangle = y$ |
| | | $\lvert 10\rangle = z$ | $\lvert T_{1u}z\rangle = z$ |
| $d$ | $\sqrt{\frac{15}{8\pi}}r^{-2}$ | $\lvert 2+2\rangle = \frac{1}{2}(x+iy)^2$ | $\lvert E_g\theta\rangle = \frac{1}{\sqrt{6}}(3z^2-r^2)$ |
| | | $\lvert 2-2\rangle = \frac{1}{2}(x-iy)^2$ | $\lvert E_g\epsilon\rangle = \frac{1}{\sqrt{2}}(x^2-y^2)$ |
| | | $\lvert 2+1\rangle = -(x+iy)z$ | $\lvert T_{2g}\xi\rangle = \sqrt{2}yz$ |
| | | $\lvert 2-1\rangle = (x-iy)z$ | $\lvert T_{2g}\eta\rangle = \sqrt{2}xz$ |
| | | $\lvert 20\rangle = \frac{1}{\sqrt{6}}(3z^2-r^2)$ | $\lvert T_{2g}\zeta\rangle = \sqrt{2}xy$ |
| $f$ | $\sqrt{\frac{35}{8\pi}}r^{-3}$ | $\lvert 3+3\rangle = -\frac{1}{2\sqrt{2}}(x+iy)^3$ | $\lvert A_{2u}\rangle = \sqrt{\frac{3}{2}}xyz$ |
| | | $\lvert 3-3\rangle = \frac{1}{2\sqrt{2}}(x-iy)^3$ | $\lvert T_{1u}x\rangle = \frac{1}{\sqrt{10}}x(5x^2-3r^2)$ |
| | | $\lvert 3+2\rangle = \frac{\sqrt{3}}{2}z(x+iy)^2$ | $\lvert T_{1u}y\rangle = \frac{1}{\sqrt{10}}y(5y^2-3r^2)$ |
| | | $\lvert 3-2\rangle = \frac{\sqrt{3}}{2}z(x-iy)^2$ | $\lvert T_{1u}z\rangle = \frac{1}{\sqrt{10}}z(5z^2-3r^2)$ |
| | | $\lvert 3+1\rangle = -\frac{\sqrt{3}}{2\sqrt{10}}(x+iy)(5z^2-3r^2)$ | $\lvert T_{2u}\xi\rangle = \sqrt{\frac{3}{2}}x(z^2-y^2)$ |
| | | $\lvert 3-1\rangle = \frac{\sqrt{3}}{2\sqrt{10}}(x-iy)(5z^2-3r^2)$ | $\lvert T_{2u}\eta\rangle = \sqrt{\frac{3}{2}}y(x^2-z^2)$ |
| | | $\lvert 30\rangle = \frac{1}{\sqrt{10}}z(5z^2-3r^2)$ | $\lvert T_{2u}\zeta\rangle = \sqrt{\frac{3}{2}}z(y^2-x^2)$ |

spherical harmonics is given by

$$\Phi_{m_\ell}(\phi) = \frac{1}{\sqrt{2\pi}}\exp(im_\ell\phi) \tag{7.5}$$

A rotation $\hat{C}_\alpha$ about the $z$-direction affects this function in the following way:

$$\hat{C}_\alpha\Phi_{m_\ell}(\phi) = \Phi_{m_\ell}(\phi-\alpha) = \exp(-im_\ell\alpha)\Phi_{m_\ell}(\phi) \tag{7.6}$$

The trace over the entire function space is then given by

$$\chi^\ell(C_\alpha) = \sum_{m_\ell=-\ell}^{\ell}\exp(-im_\ell\alpha) = \frac{\sin(\ell+1/2)\alpha}{\sin(\alpha/2)} \tag{7.7}$$

To obtain this result, the following sum-rule was used, which is obtained by carrying out a straightforward division:

$$\sum_{n=0}^{N} r^n = \frac{1 - r^N}{1 - r} \tag{7.8}$$

As an example, for $\ell = 1$, the rotation matrix corresponds to the matrix $\mathbb{O}(R)$ in Eq. (7.3). Its trace is given by

$$\chi^p(C_\alpha) = 3 - 4\sin^2(\alpha/2) = \frac{\sin(3\alpha/2)}{\sin(\alpha/2)} \tag{7.9}$$

Improper rotations can always be written as the products of a proper rotation and the inversion operation. The resulting character is then given by the product of the rotational character in Eq. (7.7), times the parity of the spherical harmonics, which is given by

$$\hat{\imath} Y_{\ell m_\ell} = (-1)^\ell Y_{\ell m_\ell} \tag{7.10}$$

Finally, we also remind that the definition of the spherical harmonics in the standard phase convention implies complex conjugation, as

$$\bar{Y}_{\ell m_\ell} = (-1)^{m_\ell} Y_{\ell -m_\ell} \tag{7.11}$$

In Sect. A.2 the character tables for the groups $O(3)$ and $SO(3)$ are given. The subduction relations are listed in Sect. C.1.

## 7.2 Application: Crystal-Field Potentials

Model treatments of transition-metal and lanthanide complexes are essentially based on the $d^n$ or $f^n$ open-shell states of the central metal atom, which are perturbed by the electrostatic field of the surrounding ligating groups:

$$\mathcal{V}_{CF} = \sum_L \frac{\mathrm{e}^2 Z_L}{4\pi\epsilon_0 |\mathbf{R}_L - \mathbf{r}|} \tag{7.12}$$

This term describes the electrostatic repulsion between an electron residing in the metal orbital at a position $\mathbf{r}$ and a negatively charged ligand, with charge $-\mathrm{e}Z_L$ at a position $\mathbf{R}_L$. In crystal-field theory the electrostatic field of the surroundings is written as an expansion in spherical harmonic operators, as these elements will be evaluated in the $d$ or $f$ function space of the central metal atom. Series expansion for distances $r < R_L$ yields

$$\mathcal{V}_{CF} = \sum_L \frac{\mathrm{e}^2 Z_L}{4\pi\epsilon_0} \sum_{\ell=0}^{\infty} \sum_{m_\ell=-\ell}^{m_\ell=+\ell} \frac{4\pi}{2\ell+1} \frac{r^\ell}{R^{\ell+1}} Y_{\ell m_\ell}(\theta,\phi) \bar{Y}_{\ell m_\ell}(\theta_L,\phi_L) \tag{7.13}$$

This potential is invariant under the symmetry properties of the metal complex. As a result, the operator part reduces to the totally symmetric components of the spherical harmonics. Moreover, interactions with $d$ electrons imply that $\ell$ must be limited to four, and to six for $f$ electrons. In the case of an octahedral field, the subduction relations for spherical harmonics (see Sect. C.1) indicate that a totally symmetric $A_{1g}$ component can be subduced only from $\ell = 4$ and $\ell = 6$. Filling in the angular positions of the ligands in an octahedron then yields

$$\mathcal{V}_{O_h} = \frac{6\mathrm{e}^2 Z_L}{\sqrt{4\pi}\epsilon_0 R_L} Y_{00} + \frac{\mathrm{e}^2 Z_L r^4}{\sqrt{4\pi}\epsilon_0 R_L^5} \frac{\sqrt{35}}{6\sqrt{2}} \left( Y_{44} + Y_{4-4} + \frac{\sqrt{14}}{\sqrt{5}} Y_{40} \right) \tag{7.14}$$

This is the famous crystal-field operator for an octahedron, which splits the $d$-shell into $e_g$ and $t_{2g}$ subshells. The crystal-field interaction is usually parameterized by the crystal-field parameter, $10Dq$, which corresponds to the splitting of the $e_g$ and $t_{2g}$ orbitals. The term in brackets here is the octahedral invariant of rank 4. In the multipole expansion this corresponds to a *hexadecapole* operator. In normalized form it reads

$$|4A_{1g}| = \frac{1}{2\sqrt{3}} \left( \frac{\sqrt{5}}{\sqrt{2}} (Y_{44} + Y_{4-4}) + \sqrt{7} Y_{40} \right) \tag{7.15}$$

Here the notation between vertical bars indicates that this is an operator. We shall now derive this expression with the aid of the coupling coefficients. Since the $d$ orbitals transform as $e_g + t_{2g}$, the squares of the $d$-orbitals yield two totally symmetric results, which may be abbreviated as follows:

$$\begin{aligned} \big|A_{1g}(e \times e)\big| &= \frac{1}{\sqrt{2}} \big(\theta^2 + \epsilon^2\big) \\ \big|A_{1g}(t_2 \times t_2)\big| &= \frac{1}{\sqrt{3}} \big(\xi^2 + \eta^2 + \zeta^2\big) \end{aligned} \tag{7.16}$$

These two invariants are at the origin of two spherical operators: one corresponds to the constant scalar $|0A_{1g}|$, and the other to $|4A_{1g}|$. The former invariant may be obtained by taking the norm of the entire $d$-manifold, which can be expressed in the $A_{1g}$ functions of Eq. (7.16) as follows:

$$\begin{aligned} |0A_{1g}| &= \frac{1}{\sqrt{5}} \big(\theta^2 + \epsilon^2 + \xi^2 + \eta^2 + \zeta^2\big) \\ &= \frac{1}{\sqrt{5}} \big(\sqrt{2}\big|A_{1g}(e \times e)\big| + \sqrt{3}\big|A_{1g}(t_2 \times t_2)\big|\big) \end{aligned} \tag{7.17}$$

The $|4A_{1g}|$ invariant must be orthonormal to this result and thus will be given by

$$|4A_{1g}| = \frac{1}{\sqrt{5}} \big(\sqrt{3}\big|A_{1g}(e \times e)\big| - \sqrt{2}\big|A_{1g}(t_2 \times t_2)\big|\big) \tag{7.18}$$

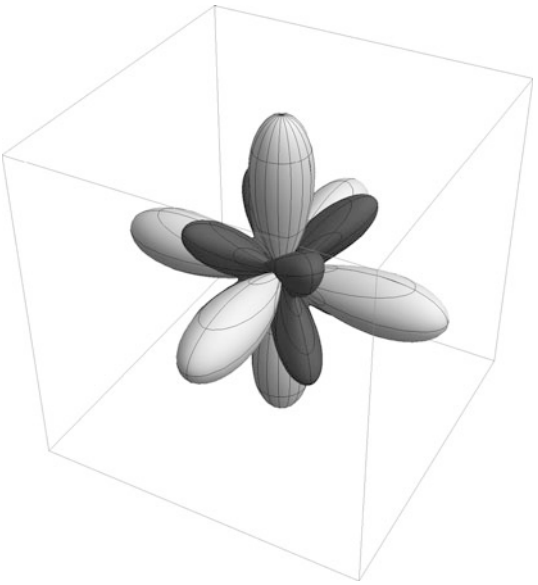

**Fig. 7.2** The octahedral crystal-field potential corresponding to the $|4A_1|$ hexadecapole. *Grey* and *black* refer to positive and negative values, respectively

We can use this result to write the functional form of the hexadecapolar invariant by combining the squares of the $d$-functions:

$$\begin{aligned} |4A_{1g}| &= \frac{1}{\sqrt{5}}\left[\frac{\sqrt{3}}{\sqrt{2}}\left(\theta^2+\epsilon^2\right)-\frac{\sqrt{2}}{\sqrt{3}}\left(\xi^2+\eta^2+\zeta^2\right)\right] \\ &\sim \left[z^4+x^4+y^4-3\left(x^2y^2+x^2z^2+y^2z^2\right)\right] \end{aligned} \tag{7.19}$$

This function corresponds precisely to the crystal-field operator of Eq. (7.14). Figure 7.2 shows this invariant. It is clearly a function that mimics the octahedral symmetry. Moreover, it reflects the multipole character of the crystal-field potential. The potential is repulsive along the coordinate axes where the ligands are and of opposite sign along the threefold directions, in between the ligands, corresponding to the vertices of the cube. In fact, Eq. (7.19) provides a direct route to the crystal-field splitting. The coefficient in front of $\theta^2$ and $\epsilon^2$ in this equation is proportional to the interaction of these $e_g$-orbitals with the crystal-field operator, and similarly for the coefficient in front of the $t_{2g}$ orbitals. The ratio of these coefficients can be reduced to

$$\frac{\frac{\sqrt{3}}{\sqrt{2}}}{-\frac{\sqrt{2}}{\sqrt{3}}}=\frac{3}{-2} \tag{7.20}$$

which reflects the crystal-field splitting of the $d$-shell, where the $e_g$ level is raised by $6Dq$, while the $t_{2g}$ level is lowered by $4Dq$, so that the barycentre is conserved and that the total splitting remains $10Dq$.

Typically, the first invariant multipole corresponds to the charge distribution of the Platonic solids of the given symmetry: hence, the $L = 4$ term describes the octahedron, and its dual the cube, while the next invariant, belonging to the $L = 6$ multipoles, represents the dominant term for the charge distribution in the 12-vertex Archimedean solid, known as the cuboctahedron, with a ligand in every edge of the octahedron. Entirely similar relations exist for the icosahedral group. The first icosahedral invariant, with $L = 6$, is the dominant term for the icosahedron and its dual dodecahedron. The next term, with $L = 10$, is the leading multipole for the truncated dodecahedron, alias the "buckyball" [5, 6].

## 7.3 Interactions of a Two-Component Spinor

The standard vector space in spherical symmetry has three components. We now explore the possibility of a function space with only two components. Such a space will correspond to a spinor. The strategy is to set up a general Hamiltonian matrix in a space with two components and verify that it has spherical symmetry. In order to describe the general interaction Hamiltonian in a space of only two components, a $2 \times 2$ Hermitian matrix, $\mathbb{H}$, is required. We can take this matrix to be traceless since the trace will not introduce an interaction inside the spin space but will simply shift the barycentre of the two levels with respect to an external reference. In its most general form, such a traceless Hermitian matrix will thus contain three independent real parameters, which we shall label as $x, y, z$:

$$\mathbb{H} = \begin{pmatrix} z & x - iy \\ x + iy & -z \end{pmatrix} \tag{7.21}$$

We have purposely chosen the Cartesian labels for the three independent parameters since, later on, a connection will be established between the 2D complex interaction space and the real 3D vector space. An example of such a Hamiltonian is the Zeeman interaction of an isolated spin in a magnetic field:

$$\mathcal{H} = 2.0023 \frac{\mu_B}{\hbar} \mathbf{B} \cdot \mathbf{S} \tag{7.22}$$

Here, $\mathbf{S}$ is the operator for the spin momentum, expressed in units of $\hbar$. The $x, y, z$ parameters in this case are proportional to the magnitude of the magnetic field, $\mathbf{B}$, in the three Cartesian directions.

However, for now, we shall not yet make use of this spatial connotation and just continue to consider $x, y, z$ as the general variables of the Hamiltonian matrix. The two components of the space will be denoted as the spin functions $|\alpha\rangle, |\beta\rangle$, which together form a spinor. The corresponding interaction operator can then be expressed as

$$\begin{aligned} \mathcal{H} = z\big(|\alpha\rangle\langle\alpha| - |\beta\rangle\langle\beta|\big) + x\big(|\alpha\rangle\langle\beta| + |\beta\rangle\langle\alpha|\big) \\ - iy\big(|\alpha\rangle\langle\beta| - |\beta\rangle\langle\alpha|\big) \end{aligned} \tag{7.23}$$

This result can also be recast in matrix form as

$$\mathcal{H} = \begin{pmatrix} |\alpha\rangle & |\beta\rangle \end{pmatrix} \mathbb{H} \begin{pmatrix} \langle\alpha| \\ \langle\beta| \end{pmatrix} \tag{7.24}$$

or, inversely, as

$$\mathbb{H} = \begin{pmatrix} \langle\alpha| \\ \langle\beta| \end{pmatrix} \mathcal{H} \begin{pmatrix} |\alpha\rangle & |\beta\rangle \end{pmatrix} \tag{7.25}$$

To establish the connection between the spinor and the vector, we now need to verify how transformations in the spinor are manifested as transformations in the vector. Consider a finite unitary transformation of the spinor. The transformation belongs to the unitary group, $U(2)$, and, as we have seen, the determinant of this matrix is unimodular. We consider the special case, however, where the determinant is $+1$. Such matrices form the special unitary group, $SU(2)$. The most general form of an $SU(2)$ matrix involves two complex parameters, say $a$ and $b$, subject to the condition that their squared norm, $|a|^2 + |b|^2$, equals unity. These parameters are also known as the Cayley–Klein parameters. (Cf. Problem 2.1.) One has

$$\mathbb{U} = \begin{pmatrix} a & b \\ -\bar{b} & \bar{a} \end{pmatrix} \tag{7.26}$$

The operation $\hat{R}$ transforms the spinor as follows:

$$\begin{pmatrix} |\alpha'\rangle & |\beta'\rangle \end{pmatrix} = \hat{R} \begin{pmatrix} |\alpha\rangle & |\beta\rangle \end{pmatrix} = \begin{pmatrix} |\alpha\rangle & |\beta\rangle \end{pmatrix} \mathbb{U}(R) \tag{7.27}$$

In order to apply the transformation to the interaction operator, we must also consider the effect of $\hat{R}$ on the column of bra-functions. This simply requires the inverse of the matrix, which, for a unitary matrix, is nothing but its complex conjugate transposed:

$$\begin{pmatrix} \langle\alpha'| \\ \langle\beta'| \end{pmatrix} = \hat{R} \begin{pmatrix} \langle\alpha| \\ \langle\beta| \end{pmatrix} = \bar{\mathbb{U}}^T(R) \begin{pmatrix} \langle\alpha| \\ \langle\beta| \end{pmatrix} \tag{7.28}$$

The transformation of the spinor thus changes the interaction matrix as follows:

$$\begin{aligned} \mathbb{H}' &= \begin{pmatrix} \langle\alpha'| \\ \langle\beta'| \end{pmatrix} \mathcal{H} \begin{pmatrix} |\alpha'\rangle & |\beta'\rangle \end{pmatrix} \\ &= \bar{\mathbb{U}}^T \begin{pmatrix} \langle\alpha| \\ \langle\beta| \end{pmatrix} \mathcal{H} \begin{pmatrix} |\alpha\rangle & |\beta\rangle \end{pmatrix} \mathbb{U} \\ &= \bar{\mathbb{U}}^T \times \mathbb{H} \times \mathbb{U} \end{aligned} \tag{7.29}$$

The transformed Hamiltonian matrix is defined by a new set of parameters $(x', y', z')$:

$$\mathbb{H}' = \begin{pmatrix} z' & x' - iy' \\ x' + iy' & -z' \end{pmatrix} \tag{7.30}$$

In this way, the transformation of the spinor $(|\alpha\rangle\ |\beta\rangle) \rightarrow (|\alpha'\rangle\ |\beta'\rangle)$ *induces* a transformation of the vector $(x\ y\ z) \rightarrow (x'\ y'\ z')$. In the vector space this transformation is described by a matrix $\mathbb{O}(R)$. This matrix may easily be constructed by combining the previous two equations. One has

$$\begin{pmatrix} x' & y' & z' \end{pmatrix} = \hat{R}(x \quad y \quad z) = (x \quad y \quad z)\mathbb{O}(R) \tag{7.31}$$

where the transformation matrix is given by

$$\mathbb{O}(R) = \begin{pmatrix} \frac{1}{2}(a^2 + \bar{a}^2 - b^2 - \bar{b}^2) & -\frac{i}{2}(a^2 - \bar{a}^2 + b^2 - \bar{b}^2) & -ab - \overline{ab} \\ \frac{i}{2}(a^2 - \bar{a}^2 - b^2 + \bar{b}^2) & \frac{1}{2}(a^2 + \bar{a}^2 + b^2 + \bar{b}^2) & -i(ab - \overline{ab}) \\ a\bar{b} + \bar{a}b & -i(a\bar{b} - \bar{a}b) & |a|^2 - |b|^2 \end{pmatrix} \tag{7.32}$$

It can easily be shown that this matrix is an orthogonal transformation with determinant equal to unity. Hence, it belongs to the $SO(3)$ group. As a result, it will leave the squared length of the vector invariant:

$$x^2 + y^2 + z^2 = x'^2 + y'^2 + z'^2 \tag{7.33}$$

This conservation of length is the property that confirms the previous identification of the interaction matrix elements with a 3-vector and relates it to ordinary space. In fact, by identifying the rotation matrices in Eqs. (7.3) and (7.32), we may determine the Cayley–Klein parameters. Two solutions with opposite signs are possible:

$$\begin{aligned} a &= \left(\cos\frac{\alpha}{2} - in_z \sin\frac{\alpha}{2}\right) \\ b &= \left(-n_y \sin\frac{\alpha}{2} - in_x \sin\frac{\alpha}{2}\right) \end{aligned} \tag{7.34}$$

or

$$\begin{aligned} a &= -\left(\cos\frac{\alpha}{2} - in_z \sin\frac{\alpha}{2}\right) \\ b &= -\left(-n_y \sin\frac{\alpha}{2} - in_x \sin\frac{\alpha}{2}\right) \end{aligned} \tag{7.35}$$

As this equation shows, the mapping $\mathbb{O}(R)$ is not an isomorphism but a homomorphism (see Fig. 7.3). Indeed, the elements of the matrix $\mathbb{O}$ are bilinear in the $a$ and $b$ parameters; hence, an overall sign change of the two Cayley–Klein parameters will give the same rotational matrix. The mapping between $SU(2)$ and $SO(3)$ is a two-to-one mapping. Each element of the rotation group in 3D space is the image of two elements in $SU(2)$. For this reason, $SU(2)$ is also called a covering group of $SO(3)$. The unit element in $SO(3)$ is the image of the identity matrix in $SU(2)$ and minus the identity matrix. This homomorphism also appears when we check the parameter list of Eq. (7.4), which leaves the rotation matrix of the vector unchanged. The overall sign change of the rotation angle and the directional cosines to

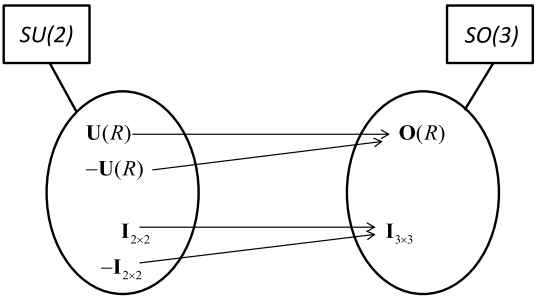


**Fig. 7.3** Homomorphism between $SU(2)$ and $SO(3)$

$\hat{R}(-\alpha, -\mathbf{n})$ leaves the Cayley–Klein parameters unchanged. By contrast, the combinations $\hat{R}(2\pi - \alpha, -\mathbf{n})$ and $\hat{R}(-2\pi + \alpha, \mathbf{n})$ change the signs of both Cayley–Klein parameters.

## 7.4 The Coupling of Spins

The entries in the Hamiltonian provide us with coupling coefficients between vector and spinor. Applying the Wigner–Eckart theorem to the matrix elements of the Zeeman spin Hamiltonian and separating out the constant parameters for the magnetic field yield the following nonzero coupling coefficients in the spin operator $\mathbf{S}$, where $K$ is the reduced matrix element:

$$\begin{aligned}
\langle\alpha|\hat{S}_z|\alpha\rangle &= K\langle\alpha|z\alpha\rangle = 1/2 \\
\langle\beta|\hat{S}_z|\beta\rangle &= K\langle\beta|z\beta\rangle = -1/2 \\
\langle\alpha|\hat{S}_x|\beta\rangle &= K\langle\alpha|x\beta\rangle = 1/2 \\
\langle\beta|\hat{S}_x|\alpha\rangle &= K\langle\beta|x\alpha\rangle = 1/2 \\
\langle\alpha|\hat{S}_y|\beta\rangle &= K\langle\alpha|y\beta\rangle = -i/2 \\
\langle\beta|\hat{S}_y|\alpha\rangle &= K\langle\beta|z\alpha\rangle = i/2
\end{aligned} \tag{7.36}$$

These coefficients can also be reversed to describe the coupling between two spinors to yield a vector. This requires that the ket spin in the coefficients is relocated to the bra part. In Sect. 6.3 we indicated that, for real functions, such a shift does not change the coupling, except for a renormalization factor. The transposition of the spin functions is more delicate since the bra functions transform as the complex conjugate of the ket functions, as indicated in Eq. (7.28). In order to establish the equivalences between transformations of bra and ket spins, one must identify the basis transformation that turns the matrix $\mathbb{U}$ into its complex conjugate. This transformation is readily achieved by replacing $|\alpha\rangle$ by $|\beta\rangle$, and $|\beta\rangle$ by $-|\alpha\rangle$. The

**Table 7.2** The coupling coefficients for the direct product of two spins

| | $S=0$ | $S=1$ | | | | | |
|---|---|---|---|---|---|---|---|
| | | $\|+1\rangle$ | $\|0\rangle$ | $\|-1\rangle$ | $\|x\rangle$ | $\|y\rangle$ | $\|z\rangle$ |
| $\|\alpha\rangle\|\alpha\rangle$ | 0 | 1 | 0 | 0 | $-1/\sqrt{2}$ | $i/\sqrt{2}$ | 0 |
| $\|\alpha\rangle\|\beta\rangle$ | $1/\sqrt{2}$ | 0 | $1/\sqrt{2}$ | 0 | 0 | 0 | $1/\sqrt{2}$ |
| $\|\beta\rangle\|\alpha\rangle$ | $-1/\sqrt{2}$ | 0 | $1/\sqrt{2}$ | 0 | 0 | 0 | $1/\sqrt{2}$ |
| $\|\beta\rangle\|\beta\rangle$ | 0 | 0 | 0 | 1 | $1/\sqrt{2}$ | $i/\sqrt{2}$ | 0 |

interchange corresponds to the following matrix transformation:

$$\begin{pmatrix} |\alpha\rangle & |\beta\rangle \end{pmatrix} \begin{pmatrix} 0 & -1 \\ 1 & 0 \end{pmatrix} \tag{7.37}$$

This matrix gives rise to the mapping of $\mathbb{U}$ onto its complex conjugate:

$$\begin{pmatrix} 0 & -1 \\ 1 & 0 \end{pmatrix} \begin{pmatrix} a & b \\ -\bar{b} & \bar{a} \end{pmatrix} \begin{pmatrix} 0 & 1 \\ -1 & 0 \end{pmatrix} = \begin{pmatrix} \bar{a} & \bar{b} \\ -b & a \end{pmatrix} \tag{7.38}$$

For this reason, the matrix in Eq. (7.37) is also called the *conjugating matrix*. The conjugating matrix is defined up to an arbitrary phase. We have taken here the standard phase choice. The conjugating relationships between the two spins can now be used to transfer the spin functions in the coupling coefficients from the ket to the bra part. An $\alpha$ spin in the ket part becomes a $\beta$ spin in the bra part, while a $\beta$ spin in the ket becomes a $-\alpha$ spin in the bra part.

The corresponding coupling coefficients are summarized in Table 7.2. They indicate how two spins can be coupled to a vector. Here, we also express the vector in complex form, as

$$\begin{aligned} |+1\rangle &= -\frac{1}{\sqrt{2}}\big(|x\rangle + i|y\rangle\big) \\ |0\rangle &= |z\rangle \\ |-1\rangle &= \frac{1}{\sqrt{2}}\big(|x\rangle - i|y\rangle\big) \end{aligned} \tag{7.39}$$

This transformation is in accordance with the Condon–Shortley phase conventions for the spherical basis functions [7]. In fact, our initial Hamiltonian matrix in Eq. (7.21) was constructed in this way. The resulting vector corresponds to the triplet spin functions, which we used in Sect. 6.4. The total spinor product space has dimension 4. The remainder after extraction of the three triplet functions corresponds to the spin singlet, which is invariant and transforms as a scalar. Spinors are thus the fundamental building blocks of 3D space. Their transformation properties were known to Rodrigues as early as 1840. It was some ninety years before Pauli realized that elementary particles, such as electrons, had properties that could be described

as internal spin states. In spin-orbit coupling the internal spin degrees of the electron are coupled to its external momentum, and this can be based on the embedding of $SO(3)$ in $SU(2)$.

## 7.5 Double Groups

The spinor basis enables us to obtain a two-dimensional matrix representation of the point-group operations. Let us first limit ourselves to the relationships for the proper rotations. The counterclockwise rotation of the vector over an angle $\alpha$ with the pole at the positive $z$-axis is given by the matrix:

$$\hat{R}\left(|x\rangle \quad |y\rangle \quad |z\rangle\right) = \left(|x\rangle \quad |y\rangle \quad |z\rangle\right) \begin{pmatrix} \cos\alpha & -\sin\alpha & 0 \\ \sin\alpha & \cos\alpha & 0 \\ 0 & 0 & 1 \end{pmatrix} \tag{7.40}$$

According to Eqs. (7.34) and (7.35), the corresponding rotation matrix in the spinor basis is determined up to a sign by

$$\hat{R}\left(|\alpha\rangle \quad |\beta\rangle\right) = \pm\left(|\alpha\rangle \quad |\beta\rangle\right) \begin{pmatrix} \exp(\frac{-i\alpha}{2}) & 0 \\ & \exp(\frac{i\alpha}{2}) \end{pmatrix} \tag{7.41}$$

How does one deal with this ambiguity of sign? A plausible way is to use a continuity argument [8]. If we approach the neighborhood of the unit element for both spinor and vector by letting $\alpha$ decrease to zero, we should converge to the unit matrix and, hence, take the $+$ sign in Eq. (7.41) with $\alpha = 0$. Now let the rotation angle increase continuously from 0 to $2\pi$. While the matrix $\mathbb{O}(R)$ is periodic in $\alpha$ and passes again to the unit matrix, the spinor matrix becomes minus the unit matrix. Continuing the path in parameter space and increasing the angle to $4\pi$ drive the vector rotation once again over the same interval, while the spinor rotation finally completes its path and reaches the unit element again. So, the difference between $\mathbb{U}$ and $-\mathbb{U}$ can be interpreted as a rotation over a full angle of $2\pi$. From the topological point of view, the path that we have described corresponds to a full circle in the 4-parameter space of $SU(2)$, and the rotation over $2\pi$ connects a point in this space to its antipode. In this space the $SO(3)$ operations may be identified as the set of straight lines connecting antipodal points.

Our real interest at present is molecular Hamiltonians that are characterized by a point group $G$. However, as compared with the Hamiltonian considered in Chap. 5, we should also include *spin-orbit coupling* operators. These will be invariant only under concerted transformations of the orbital and spin parts. The homomorphism between $SO(3)$ and $SU(2)$ provides a straightforward *algebraic* way to construct the spinor group associated with the point group. For each operation, $\hat{R} \in G$, a matrix $\mathbb{O}(R)$ is defined, which offers a faithful representation of $G$ and, in turn, gives rise to two spinor matrices, $\pm\mathbb{U}(R)$, which describe the spinor transformation. The set of these matrices forms a group, which contains twice as many elements as $G$ and thus

**Table 7.3** Representation matrices for the spinor basis in $D_2^*$

| | |
|---|---|
| $\mathbb{D}(E) = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$ | $\mathbb{D}(\aleph) = \begin{pmatrix} -1 & 0 \\ 0 & -1 \end{pmatrix}$ |
| $\mathbb{D}(C_2^x) = \begin{pmatrix} 0 & -i \\ -i & 0 \end{pmatrix}$ | $\mathbb{D}(\aleph C_2^x) = \begin{pmatrix} 0 & i \\ i & 0 \end{pmatrix}$ |
| $\mathbb{D}(C_2^y) = \begin{pmatrix} 0 & -1 \\ 1 & 0 \end{pmatrix}$ | $\mathbb{D}(\aleph C_2^y) = \begin{pmatrix} 0 & 1 \\ -1 & 0 \end{pmatrix}$ |
| $\mathbb{D}(C_2^z) = \begin{pmatrix} -i & 0 \\ 0 & i \end{pmatrix}$ | $\mathbb{D}(\aleph C_2^z) = \begin{pmatrix} i & 0 \\ 0 & -i \end{pmatrix}$ |

is called the *double group*, denoted by $G^*$. While this construction is algebraic, the definition of a *geometrical* link between both groups is much less straightforward and unavoidably involves the introduction of phase conventions. Bethe introduced a formal symmetry operation, $R$, which corresponds to a rotation over $2\pi$. Subsequently, we shall replace this by the symbol $\aleph$, in order to avoid confusion. This operation is fictitious to the extent that the poles of this rotation are left undefined. It can be multiplied with every operator in the group and thus leads to an actual doubling of the number of symmetry elements. Nonetheless, the double group is not the direct product of $G$ with the group $\{\hat{E}, \aleph\}$. The reason is that $G$ is not a subgroup of $G^*$ because it is no longer closed. Indeed, applying a $\hat{C}_n$ axis in $G$ $n$ times will not lead to the unit element but to $\aleph$.

For the actual construction of the double group as a group of operators, we need a convention to connect the spatial operators to the spinor matrices. As we have seen in Sect. 7.2, the four possible parametric descriptions of a given rotation yield two different choices for the Cayley–Klein parameters. Hence, our convention should define how to characterize unequivocally the parameters of a rotation. It will consist of two criteria: the rotation angle must be positive, and the pole from which the rotation is seen as counterclockwise must belong to the *positive hemisphere* in the $n_x, n_y, n_z$ parameter space. This is the hemisphere above the equatorial plane, i.e., with $n_z > 0$. In the $(n_x, n_y)$-plane, we include the half-circle of points with positive $n_x$-value, i.e., with $n_z = 0, n_x > 0$, and also the point with $n_y = 1, n_x = 0$, and $n_z = 0$. The rotational parameters $(\alpha, \mathbf{n})$ are thus chosen in such a way that $\alpha$ is positive, i.e., counterclockwise, and that the vector $\mathbf{n}$ points to the positive hemisphere. This eliminates three of the four equivalent parameter choices of Eq. (7.4). The only remaining description is then inserted into Eq. (7.34) to determine the Cayley–Klein parameters.

As a straightforward example, we take the double group of $D_2$. The standard drawing puts the twofold rotational axes in the positive hemisphere, and the corresponding spinor matrices are easily obtained from Eq. (7.34). The results are given in Table 7.3. For each operation of $G$, there are two operations in the double group, $\hat{R}$ and $\aleph\hat{R}$. Note that the Bethe operation, $\aleph$, commutes with every element of the group. Armed with this set of matrices, one can easily construct the multiplication

**Table 7.4** Character table for the double group $D_2^*$

| | $\hat{E}$ | $\aleph$ | $\begin{pmatrix}\hat{C}_2^z\\ \aleph\hat{C}_2^z\end{pmatrix}$ | $\begin{pmatrix}\hat{C}_2^y\\ \aleph\hat{C}_2^y\end{pmatrix}$ | $\begin{pmatrix}\hat{C}_2^x\\ \aleph\hat{C}_2^x\end{pmatrix}$ |
|---|---|---|---|---|---|
| $A$ | 1 | 1 | 1 | 1 | 1 |
| $B_1$ | 1 | 1 | 1 | −1 | −1 |
| $B_2$ | 1 | 1 | −1 | 1 | −1 |
| $B_3$ | 1 | 1 | −1 | −1 | 1 |
| $E_{1/2}$ | 2 | −2 | 0 | 0 | 0 |

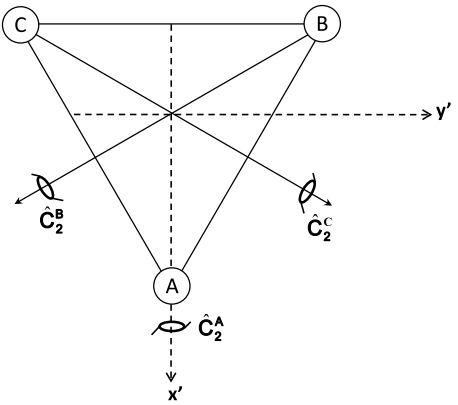


**Fig. 7.4** $D_3$ trischelate complex: orientation of the twofold axes on the positive hemicircle in the $(x', y')$ plane

table; as an example,

$$\mathbb{D}(C_{2x}) \times \mathbb{D}(C_{2y}) = \mathbb{D}(\aleph C_{2z}) \tag{7.42}$$

From the multiplication table one can obtain the conjugacy classes. The double group, $D_2^*$, has five classes; hence, it will contain one extra irrep, as compared with the parent group. The character table is shown in Table 7.4. The irreps are of two different kinds. The *orbital* irreps are not changed under $\aleph$ and thus retain the characters of the single group. The other kind is the *spin* irreps, which are anti-symmetric under $\aleph$. Direct product tables may also be constructed. Note that the totally symmetric component in this case belongs to the anti-symmetrized part of the direct square of the spinor irreps. Relevant tabular information concerning the double groups and spinor irreps is gathered in Appendix G.

As a further example, in the $D_3$ symmetry group, the three $\hat{C}_2$ operators, which bisect the chelating ligand (cf. Fig. 6.5), all lie in the $(x', y')$ plane. In order to obey the conventions, we have to take the poles of these axes in the positive semicircle with $x' > 0$ (see Fig. 7.4). The $(\alpha, n_{x'}, n_{y'}, n_{z'})$ labeling in the primed coordinate

**Table 7.5** Representation matrices for the spinor basis in $D_3^*$. $\omega = \exp\frac{i\pi}{6}$

$$\mathbb{D}(E) = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \qquad \mathbb{D}(C_2^A) = \begin{pmatrix} 0 & -i \\ -i & 0 \end{pmatrix}$$

$$\mathbb{D}(C_3) = \begin{pmatrix} \bar{\omega}^2 & 0 \\ 0 & \omega^2 \end{pmatrix} \qquad \mathbb{D}(C_2^B) = \begin{pmatrix} 0 & \bar{\omega} \\ -\omega & 0 \end{pmatrix}$$

$$\mathbb{D}(C_3^2) = \begin{pmatrix} -\omega^2 & 0 \\ 0 & -\bar{\omega}^2 \end{pmatrix} \qquad \mathbb{D}(C_2^C) = \begin{pmatrix} 0 & -\omega \\ \bar{\omega} & 0 \end{pmatrix}$$

**Table 7.6** Character table for the double group $D_3^*$

| | | $\hat{E}$ | $\aleph$ | $\begin{pmatrix} \hat{C}_3 \\ \aleph\hat{C}_3^2 \end{pmatrix}$ | $\begin{pmatrix} \aleph\hat{C}_3 \\ \hat{C}_3^2 \end{pmatrix}$ | $\begin{pmatrix} \hat{C}_2^A \\ \aleph\hat{C}_2^B \\ \aleph\hat{C}_2^C \end{pmatrix}$ | $\begin{pmatrix} \aleph\hat{C}_2^A \\ \hat{C}_2^B \\ \hat{C}_2^C \end{pmatrix}$ |
|---|---|---|---|---|---|---|---|
| $E_{1/2}$ | | 2 | $-2$ | 1 | $-1$ | 0 | 0 |
| $E_{3/2}$ | $\rho_1$ | 1 | $-1$ | $-1$ | 1 | $i$ | $-i$ |
| | $\rho_2$ | 1 | $-1$ | $-1$ | 1 | $-i$ | $i$ |

system is thus as follows:

$$\begin{aligned} \hat{C_2^A} &\quad (180^\circ, \quad 1, \quad 0, \quad 0) \\ \hat{C_2^B} &\quad \left(180^\circ, \quad \frac{1}{2}, \quad -\frac{\sqrt{3}}{2}, \quad 0\right) \\ \hat{C_2^C} &\quad \left(180^\circ, \quad \frac{1}{2}, \quad \frac{\sqrt{3}}{2}, \quad 0\right) \end{aligned} \tag{7.43}$$

The corresponding Cayley–Klein parameters are then determined as

$$\begin{aligned} \hat{C_2^A} &\quad (a = 0, b = -i) \\ \hat{C_2^B} &\quad \left(a = 0, b = \frac{\sqrt{3}}{2} - \frac{i}{2}\right) \\ \hat{C_2^C} &\quad \left(a = 0, b = -\frac{\sqrt{3}}{2} - \frac{i}{2}\right) \end{aligned} \tag{7.44}$$

In Tables 7.5 and 7.6 we provide the corresponding matrices and the character table. The $\rho$ designations in the latter table refer to Kramers doublets and will be explained in the subsequent section. The class structure of the double group in connection to the point group is determined by the Opechowski theorem [9].

**Theorem 17** *If a set of proper rotations, $\hat{C}_n$, forms a class in the single group $G$, then it gives rise to two separate classes in the double group, corresponding to conjugacy classes $\{\hat{C}_n\}$ and $\{\aleph\hat{C}_n\}$. The case of $n = 2$ is exceptional: when $n = 2$*

*and there is another twofold axis in G perpendicular to this* $\hat{C}_2$*, both this* $\hat{C}_2$ *and* $\aleph\hat{C}_2$ *belong to the same class.*

The theorem can easily be demonstrated in an algebraic way. If a symmetry element $\hat{A}$ is conjugate to $\hat{B}$, then element $\aleph\hat{A}$ is conjugate to $\aleph\hat{B}$, since the Bethe operation commutes with all symmetry elements:

$$\hat{A} = \hat{X}\hat{B}\hat{X}^{-1} \rightarrow \aleph\hat{A} = \hat{X}\aleph\hat{B}\hat{X}^{-1} \tag{7.45}$$

Since multiplication by $\aleph$ corresponds to multiplication by $-\mathbb{I}$, a symmetry element $\hat{A}$ and its double-group partner $\aleph\hat{A}$ have characters that differ by sign. Unless their characters are zero, they cannot belong to the same class since symmetry elements in the same class must have the same character. This explains the first rule of the theorem.[2]

Exceptions can exist when the character is zero. The character of the spinor irrep is given by

$$\chi^{\text{spin}} = a + \bar{a} = \pm 2\cos\frac{\alpha}{2} \tag{7.46}$$

This character can be zero only for $\alpha = \pm\pi$ and, hence, for binary rotations with $n = 2$. To examine whether or not the matrix for a binary rotation can be class-conjugated to minus itself, we may limit ourselves to the study of one orientation of the rotation axis, say $\hat{C}_2^z$. Indeed, in $SU(2)$ any orientation can always be transformed backward to this standard choice by a unitary transformation. The problem thus reduces to finding a spinor operation $\hat{X}$ represented by a matrix $\mathbb{X}$ with Cayley–Klein parameters $a_x, b_x$, which transforms $\mathbb{D}(C_2^z)$ into minus itself:

$$\hat{X}\hat{C}_2^z\hat{X}^{-1} = \aleph\hat{C}_2^z \tag{7.47}$$

or, in terms of the spinor matrices,

$$\begin{pmatrix} a_x & b_x \\ -\bar{b}_x & \bar{a}_x \end{pmatrix}\begin{pmatrix} -i & 0 \\ 0 & i \end{pmatrix}\begin{pmatrix} \bar{a}_x & -b_x \\ \bar{b}_x & a_x \end{pmatrix} = \begin{pmatrix} i & 0 \\ 0 & -i \end{pmatrix} \tag{7.48}$$

This expression reduces to a set of two equations:

$$\begin{aligned} |a_x|^2 - |b_x|^2 &= -1 \\ a_x b_x &= 0 \end{aligned} \tag{7.49}$$

These equations can be solved only when $a_x$ is equal to zero. This implies that both the real and complex parts of this parameter must be equal to zero; hence,

$$\begin{aligned} \alpha &= \pi \mod 2\pi \\ n_z &= 0 \end{aligned} \tag{7.50}$$

[2]Note that not all elements in the same class will be oriented in the positive hemisphere, as is clear from Tables 7.4 and 7.6.

This result identifies the $\hat{X}$ operator as a twofold rotation in a plane perpendicular to the $z$-direction. Hence, a twofold rotation axis, $\hat{C}_2$, and its double group extension $\aleph\hat{C}_2$ belong to the same class only if the group contains additional binary elements in a plane perpendicular to this axis. Otherwise, the first rule will apply. The exception referred to in this theorem is illustrated by the $D_2^*$ class structure as shown in Table 7.4.

So far, we have been concerned only with proper rotations because in the spinor basis improper rotations are not defined. Since the electron spin is associated with an internal "spinning" of the electron around its axis, the electron spin is assigned an intrinsic positive parity. As we have seen before in Sect. 3.8, every improper rotation can be written as the product of a proper rotation and an inversion; therefore, whenever an improper rotation acts on a spinor, we simply take the matrix representation for the proper factor in this improper rotation.

## 7.6 Kramers Degeneracy

In 1930, Kramers showed that in the presence of an arbitrary electrostatic field all states with an odd number of spins must still have even degeneracy.[3]

**Theorem 18** *The energy levels of a system that contains an odd number of spin-$\frac{1}{2}$ particles are at least doubly degenerate in the absence of an external magnetic field.*

This theorem reflects the influence of time-reversal symmetry. Already in Chap. 2, we showed that the time-reversal operator is an anti-linear operator. It will turn any spatial wavefunction into its complex conjugate. Applying it twice in succession will return the original wavefunction, and, hence, we may write for spatial functions:

$$\text{vectors}: \quad \vartheta^2 = +1 \tag{7.51}$$

However, the time-reversal properties of a spinor are different. Here we can use the same argument as in Sect. 7.4, viz. in Eq. (7.38), by requiring that the time reversal of the spinor components would lead to complex conjugation of their transformation properties. This implies that time reversal must turn $|\alpha\rangle$ into $|\beta\rangle$, and vice versa, but with a sign difference:

$$\begin{aligned} \vartheta\,|\alpha\rangle &= |\beta\rangle \\ \vartheta\,|\beta\rangle &= -|\alpha\rangle \end{aligned} \tag{7.52}$$

Hence, for spinors, applying time reversal twice leads to a sign change:

$$\text{spinors}: \quad \vartheta^2 = -1 \tag{7.53}$$

[3] Adapted from [10].

Note that the action of time reversal on the spin functions precisely corresponds to the $\hat{C}_2^y$ operator and thus is represented by $\mathbb{D}(C_2^y)$. This result may be generalized, in the sense that time reversal can be represented as the product of complex conjugation, denoted as $K$, and a unitary operator acting on the components of a function space, which we shall denote by the unitary matrix $\mathbb{U}$. We thus write $\vartheta = \mathbb{U}K$. When this operator is applied twice, it must return the same state, except possibly for a phase factor, say $\exp(i\kappa)$. Following Wigner, we now show that the two cases $\vartheta^2 = \pm 1$ are in fact the only possibilities. Hence, the phase factor can be only either $+1$ (time-even state) or $-1$ (time-odd state) [11, Chap. 26]. Taking time reversal twice, we have

$$\vartheta^2 = \mathbb{U}K\mathbb{U}K = \mathbb{U} \times \bar{\mathbb{U}} = \exp(i\kappa)\mathbb{I} \tag{7.54}$$

Since $\mathbb{U}$ is unitary, we have $\mathbb{U} \times \bar{\mathbb{U}}^T = \mathbb{I}$. Comparing this result with the previous expression, it follows that

$$\bar{\mathbb{U}} = \exp(i\kappa)\bar{\mathbb{U}}^T \tag{7.55}$$

Taking the transpose of both matrices in this equation will not affect the phase factor:

$$\bar{\mathbb{U}}^T = \exp(i\kappa)\bar{\mathbb{U}} \tag{7.56}$$

Combining Eqs. (7.55) and (7.56) yields

$$\bar{\mathbb{U}} = \exp(2i\kappa)\bar{\mathbb{U}} \tag{7.57}$$

which implies that $\exp(i\kappa) = \pm 1$.

We shall now examine the effects of these two kinds of time-reversal symmetry on quantum systems under time-even Hamiltonians, i.e., in the absence of external magnetic fields.

- $\vartheta^2 = +1$. In the case of a positive sign, it is always possible to write states that are time invariant. Consider a state that is described by a complex wavefunction, $|\Psi\rangle$, which is an eigenfunction of a time-even Hamiltonian. The time-reversed function, $\vartheta|\Psi\rangle$, will thus also be an eigenfunction with the same eigenenergy. The two functions will either coincide or be linearly independent. The latter case leads to a state that is at least twofold-degenerate. Both components of this degeneracy may transform as the complex-conjugate irreps of point groups such as the cyclic groups or the $T_h$ group. When $\vartheta^2 = +1$, it is always possible to recombine these two degenerate states into two linear combinations that are invariant under time reversal. It is indeed sufficient to project the real and imaginary parts of these functions:

$$\begin{aligned} |\phi\rangle &= \frac{1}{\sqrt{2}}\big(|\Psi\rangle + \vartheta|\Psi\rangle\big) \\ |\chi\rangle &= \frac{-i}{\sqrt{2}}\big(|\Psi\rangle - \vartheta|\Psi\rangle\big) \end{aligned} \tag{7.58}$$

It can easily be demonstrated that the Hamiltonian in this new basis is real:

$$\langle\phi|\mathcal{H}|\chi\rangle = \overline{\langle\vartheta\phi|\vartheta(\mathcal{H}\chi)\rangle} = \overline{\langle\vartheta\phi|\vartheta\mathcal{H}\vartheta|\vartheta\chi\rangle} = \overline{\langle\phi|\mathcal{H}|\chi\rangle} \tag{7.59}$$

Hence, in this case, it is always possible to rewrite the basis in such a way that the Hamiltonian matrix is completely real, and the states behave in all respects as a real twofold-degenerate irrep, which can be split by symmetry-lowering electrostatic fields. In particular, such states will be subject to Jahn–Teller distortions.

- $\vartheta^2 = -1$. In the case of a negative sign, it is impossible to obtain states that are time invariant. This can be shown as follows. We start again with two states that are each other's time inverse ($|\Psi\rangle$ and $\vartheta|\Psi\rangle$) and first show that these states must be linearly independent:

$$\langle\Psi|\vartheta\Psi\rangle = \overline{\langle\vartheta\Psi|\vartheta^2\Psi\rangle} = -\overline{\langle\vartheta\Psi|\Psi\rangle} = -\langle\Psi|\vartheta\Psi\rangle = 0 \tag{7.60}$$

In contrast to the previous case, all attempts to construct a linear combination of these basis states that is invariant under time reversal, fail. Indeed, suppose that $|X\rangle$ is a linear combination with coefficients $a$ and $b$, such that $\vartheta|X\rangle = |X\rangle$. Then we have:

$$\begin{aligned} |X\rangle &= a|\Psi\rangle + b\vartheta|\Psi\rangle \\ \vartheta|X\rangle &= \bar{a}\vartheta|\Psi\rangle - \bar{b}|\Psi\rangle \equiv a|\Psi\rangle + b\vartheta|\Psi\rangle \end{aligned} \tag{7.61}$$

Since the two kets are linearly independent, their respective coefficients must coincide, and this is possible only for $a = b = 0$. Hence, it is not possible to remove the degeneracy by time-even external fields. In particular, these states will not be subject to the JT effect.

### *Time-Reversal Selection Rules*

The argument used in Eq. (7.59) can be generalized to describe selection rules that depend on time reversal [12]. We first introduce two parities, $\tau$ and $\eta$, which describe the time-dependence of the state and of the Hamiltonian:

$$\begin{aligned} \vartheta^2 &= (-1)^\tau \hat{E} \\ \vartheta\mathcal{H}\vartheta^{-1} &= (-1)^\eta \mathcal{H} \end{aligned} \tag{7.62}$$

The first label, $\tau$, indicates the parity of the state functions, as we have just introduced in this section. The second label, $\eta$, indicates whether the Hamiltonian is time-even or time-odd. Time-even interactions are typically interactions associated with the electrostatic potential, such as the Jahn–Teller and Stark effects. Time-odd interactions are electrodynamic in nature, the most common one being the Zeeman interaction. We shall now study a function space that is invariant under time reversal

and transforms according to a degenerate irrep $\Gamma$ with all characters real. As we have seen, this can be either an orbital or a spinor irrep. If $|\phi\rangle$ is an element of this space, so is $\vartheta|\phi\rangle$. Now, instead of considering matrix elements of type $\langle\phi|\mathcal{H}|\chi\rangle$, we shall replace the bra-functions by their time-reversed partners. The interaction element will then be of type $\langle\vartheta\phi|\mathcal{H}|\chi\rangle$. This may seem awkward, but in fact it does not lead to inconsistencies. In the case of orbital irreps, basis functions will either be real or may be arranged in complex-conjugate pairs, which are mutually time inverses. For spinor irreps, we can always write the basis functions in time-reversal pairs, such as the $\alpha$ and $\beta$ spins.

The Hamiltonian for physical interactions must be Hermitian; hence, the bracket will be equal to the complex-conjugate inverted bracket:

$$\langle\vartheta\phi|\mathcal{H}|\chi\rangle = \overline{\langle\chi|\mathcal{H}|\vartheta\phi\rangle} \tag{7.63}$$

Complex conjugation of the bracket can also be achieved by time reversal. But, as an operator, time reversal can also enter into the bracket and operate on the components:

$$\overline{\langle\chi|\mathcal{H}|\vartheta\phi\rangle} = \big\langle\vartheta\chi\big|\vartheta\big(\mathcal{H}\vartheta\phi\big)\big\rangle = \big\langle\vartheta\chi\big|\vartheta\mathcal{H}\vartheta^{-1}\big|\vartheta^2\phi\big\rangle = (-1)^{\tau+\eta}\langle\vartheta\chi|\mathcal{H}|\phi\rangle \tag{7.64}$$

By combining these results we may thus write

$$\langle\vartheta\phi|\mathcal{H}|\chi\rangle = \frac{1}{2}\big[\langle\vartheta\phi|\mathcal{H}|\chi\rangle + (-1)^{\tau+\eta}\langle\vartheta\chi|\mathcal{H}|\phi\rangle\big] \tag{7.65}$$

The transformations of a time-reversed bra, $\langle\vartheta f_i|$, and its original ket, $|f_i\rangle$, are described by exactly the same matrices because complex conjugation is applied twice:

$$\begin{aligned}\hat{R}\langle\vartheta f_i| &= \sum_j D^{\Gamma}_{ji}(R)\langle\vartheta f_j| \\ \hat{R}|f_i\rangle &= \sum_j D^{\Gamma}_{ji}(R)f_j\rangle\end{aligned} \tag{7.66}$$

This implies that the matrix elements in Eq. (7.65) are described by CG coupling coefficients, which are symmetric with respect to exchange of the bra and ket parts. This result leads to the following selection rules:

1. If the Hamiltonian and the system have the same parity under time reversal, interaction can take place only with the symmetrized square of the irrep, $[\Gamma]^2$.
2. If the Hamiltonian and the system have opposite parity under time reversal, the only allowed interaction elements must belong to the anti-symmetrized square of the irrep, $\{\Gamma\}^2$.

As a case in point, the JT Hamiltonian for orbital systems is limited to the symmetrized square, whereas the Zeeman Hamiltonian only arises if the anti-symmetrized square contains the symmetries of an axial field. For systems with an odd number of electrons, which therefore transform according to spinor representations, the selection rules are exactly opposite.

## 7.7 Application: Spin Hamiltonian for the Octahedral Quartet State

The octahedral double group contains a four-dimensional spin representation, which is commonly denoted as the $\Gamma_8$ quartet, or $U'$ in Griffith's notation. The direct square of this irrep is given by

$$\Gamma_8 \times \Gamma_8 = [A_2 + 2T_1 + T_2] + \{A_1 + E + T_2\} \tag{7.67}$$

According to the time-reversal selection rules, time-odd interactions with a magnetic field will be based on the symmetrized square. The spin-operator of the Zeeman Hamiltonian transforms as $T_{1g}$, which is indeed included in the symmetrized square. The present case is, however, special since the $T_{1g}$ irrep occurs twice in the product. The multiplicity separation cannot be achieved on the basis of symmetrization since both $T_{1g}$ irreps appear in the symmetrized part. One way to distinguish the two products is through the subduction process from spherical symmetry. The addition rules of angular momenta give rise to

$$3/2 \times 3/2 = [p + f] + \{s + d\} \tag{7.68}$$

On these grounds the two $T_{1g}$ interactions can be distinguished on the basis of a different spherical parentage corresponding to $p$ or $f$ coupling. We shall return to this point in a moment. For a systematic treatment of this problem, we start by setting up a suitable function space. The spherical $S = 3/2$ spin-quartet level subduces directly the octahedral $\Gamma_8$. We can thus use the quartet spin functions as symmetry bases. The components of $S = 3/2$ can be obtained by a fully symmetrized product of the basic spinor:

$$\begin{aligned}
|3/2 + 3/2\rangle &= \alpha_1\alpha_2\alpha_3 \\
|3/2 + 1/2\rangle &= \frac{1}{\sqrt{3}}(\alpha_1\alpha_2\beta_3 + \alpha_1\beta_2\alpha_3 + \beta_1\alpha_2\alpha_3) \\
|3/2 - 1/2\rangle &= \frac{1}{\sqrt{3}}(\alpha_1\beta_2\beta_3 + \beta_1\alpha_2\beta_3 + \beta_1\beta_2\alpha_3) \\
|3/2 - 3/2\rangle &= \beta_1\beta_2\beta_3
\end{aligned} \tag{7.69}$$

In this expression the fundamental $\{|\alpha\rangle, |\beta\rangle\}$ spinor resembles a quark state: three quarks are coupled together to form the quartet result. The use of the quartet spin bases does not mean that our $\Gamma_8$ really corresponds to a quartet spin. It only means that we can introduce a fictitious spin operator, $\tilde{\mathbf{S}}$, which acts on the $\Gamma_8$ components in the same way as the real spin momentum would act on the components of a spin quartet. The transformations of the $\Gamma_8$ spinor under the elements of the group $O^*$ may be obtained by combining the transformation matrices for the fundamental $(|\alpha\rangle|\beta\rangle)$ spins with the quartet coupling scheme in Eq. (7.69). In the group $O^*$, this irrep is denoted as $\Gamma_6$. In Table 7.7 the results are shown for two generators of the octahedral group. These matrices can be taken as the canonical basis relationships

**Table 7.7** Representation matrices for the spinor basis in $O^*$

$$\mathbb{D}^{\Gamma_6}(C_4^z) = \frac{1}{\sqrt{2}}\begin{pmatrix} 1-i & 0 \\ 0 & 1+i \end{pmatrix} \quad \mathbb{D}^{\Gamma_6}(C_3^{xyz}) = \frac{1}{2}\begin{pmatrix} 1-i & -1-i \\ 1-i & 1+i \end{pmatrix}$$

$$\mathbb{D}^{\Gamma_8}(\hat{C}_4^z) = \frac{1}{\sqrt{2}}\begin{pmatrix} -1-i & 0 & 0 & 0 \\ 0 & 1-i & 0 & 0 \\ 0 & 0 & 1+i & 0 \\ 0 & 0 & 0 & -1+i \end{pmatrix}$$

$$\mathbb{D}^{\Gamma_8}(\hat{C}_3^{xyz}) = \frac{1}{4}\begin{pmatrix} -1-i & \sqrt{3}(-1+i) & \sqrt{3}(1+i) & 1-i \\ \sqrt{3}(-1-i) & -1+i & -1-i & \sqrt{3}(-1+i) \\ \sqrt{3}(-1-i) & 1-i & -1-i & \sqrt{3}(1-i) \\ -1-i & \sqrt{3}(1-i) & \sqrt{3}(1+i) & -1+i \end{pmatrix}$$

that define the components of the $\Gamma_8$. In Griffith's notation, these four components are defined in the following way:

$$\begin{aligned} |U'\kappa\rangle &\sim \left|\frac{3}{2}+\frac{3}{2}\right\rangle \\ |U'\lambda\rangle &\sim \left|\frac{3}{2}+\frac{1}{2}\right\rangle \\ |U'\mu\rangle &\sim \left|\frac{3}{2}-\frac{1}{2}\right\rangle \\ |U'\nu\rangle &\sim \left|\frac{3}{2}-\frac{3}{2}\right\rangle \end{aligned} \tag{7.70}$$

Knowing the symmetries of the components, we can now turn to the coupling coefficients that describe their interactions. The coupling coefficients that we need are determined by the Zeeman Hamiltonian, which can be written as

$$\mathcal{H}_{Ze} = \frac{\mu_B}{\hbar}\mathbf{B}\cdot(\mathbf{L}+2.0023\mathbf{S}) \tag{7.71}$$

The electronic part of this operator contains the orbital angular momentum and the spin operator. In octahedral symmetry the overall electronic operator transforms as $T_{1g}$. Applying the Wigner–Eckart theorem to the interaction elements in this operator yields

$$\begin{aligned} \frac{\mu_B}{\hbar}\langle \Gamma_8 i|(\mathbf{L}+2.0023\mathbf{S})|\Gamma_8 j\rangle = {} & \langle \Gamma_8||T_1||\Gamma_8\rangle_a \langle \Gamma_8 i|T_1 j\,\Gamma_8 k\rangle_a \\ & + \langle \Gamma_8||T_1||\Gamma_8\rangle_b \langle \Gamma_8 i|T_1 j\,\Gamma_8 k\rangle_b \end{aligned} \tag{7.72}$$

Here, we have introduced the extra labels $a$ and $b$ in order to distinguish that there are two coupling channels. The coupling coefficients that are required are of type $\langle \Gamma_{8k}|\Gamma_{8i}T_{1j}\rangle$, while the coefficients, as given in Appendix G, are of type

$\langle \Gamma_{8i} T_{1j} | \Gamma_{8k} \rangle$ and describe the spin-orbit coupling coefficients for the spin-orbit levels of a ${}^4T_1$ state. However, since all coefficients in the table are real, turning them around does not make any difference. Hence, we can directly use the spin-orbit tables to obtain the Zeeman matrix. Only one of the coupling channels is seen to link the $\kappa$ and $\nu$ levels. In spherical symmetry this requires a jump of 3 spin units, which can be bridged only by an $\ell = 3$ operator. The coupling coefficients of this channel are thus of spherical octupole parentage ($\ell = 3$), while the other set is of dipole parentage ($\ell = 1$). We shall parameterize the corresponding reduced matrix elements as $J_f$ and $J_p$, respectively. The constant $\mu_B/\hbar$, as well as a common factor of $1/\sqrt{15}$, is also absorbed into these parameters. The electronic operator will be represented as $|T_i|$, and the Zeeman Hamiltonian is then recast in complex form as

$$\begin{aligned} \mathcal{H}_{Ze} &= B_x|T_x| + B_y|T_y| + B_z|T_z| \\ &= B_z|T_0| - \frac{1}{\sqrt{2}}(B_x - iB_y)|T_{+1}| + \frac{1}{\sqrt{2}}(B_x + iB_y)|T_{-1}| \end{aligned} \tag{7.73}$$

This expression follows the convention of Eq. (7.39). The operator part is defined by

$$\begin{aligned} |T_0| &= |T_z| \\ |T_{+1}| &= -\frac{1}{\sqrt{2}}\big(|T_x| + i|T_y|\big) \\ |T_{-1}| &= \frac{1}{\sqrt{2}}\big(|T_x| - i|T_y|\big) \end{aligned} \tag{7.74}$$

The elements of the interaction matrix are then given by

$$\begin{aligned} H_{ij} = B_z\big(J_p\langle \Gamma_8 i|T_0\Gamma_8 j\rangle_p + J_f\langle \Gamma_8 i|T_0\Gamma_8 j\rangle_f\big) \\ - \frac{1}{\sqrt{2}}(B_x - iB_y)\big(J_p\langle \Gamma_8 i|T_{+1}\Gamma_8 j\rangle_p + J_f\langle \Gamma_8 i|T_{+1}\Gamma_8 j\rangle_f\big) \\ + \frac{1}{\sqrt{2}}(B_x + iB_y)\big(J_p\langle \Gamma_8 i|T_{-1}\Gamma_8 j\rangle_p + J_f\langle \Gamma_8 i|T_{-1}\Gamma_8 j\rangle_f\big) \end{aligned} \tag{7.75}$$

The resulting interaction matrix is given in Table 7.8. Since the Zeeman interaction leads to a splitting of the levels that conserves the barycentre, the secular equation does not contain odd powers in the energy:

$$aE^4 + bE^2 + c = 0 \tag{7.76}$$

**Table 7.8** Spin Hamiltonian matrix for the octahedral quartet irrep. A common factor of $1/\sqrt{15}$ is absorbed into the $J$-parameters

| $B_z$ | $\|\Gamma_8\kappa\rangle$ | $\|\Gamma_8\lambda\rangle$ | $\|\Gamma_8\mu\rangle$ | $\|\Gamma_8\nu\rangle$ |
|---|---|---|---|---|
| $\langle\Gamma_8\kappa\|$ | $(3J_p - J_f)$ | | | |
| $\langle\Gamma_8\lambda\|$ | | $(J_p + 3J_f)$ | | |
| $\langle\Gamma_8\mu\|$ | | | $-(J_p + 3J_f)$ | |
| $\langle\Gamma_8\nu\|$ | | | | $-(3J_p - J_f)$ |

| $B_x - iB_y$ | $\|\Gamma_8\kappa\rangle$ | $\|\Gamma_8\lambda\rangle$ | $\|\Gamma_8\mu\rangle$ | $\|\Gamma_8\nu\rangle$ |
|---|---|---|---|---|
| $\langle\Gamma_8\kappa\|$ | | $\sqrt{3}(J_p + \frac{1}{2}J_f)$ | | |
| $\langle\Gamma_8\lambda\|$ | | | $(2J_p - \frac{3}{2}J_f)$ | |
| $\langle\Gamma_8\mu\|$ | | | | $\sqrt{3}(J_p + \frac{1}{2}J_f)$ |
| $\langle\Gamma_8\nu\|$ | $-\frac{5}{2}J_f$ | | | |

| $B_x + iB_y$ | $\|\Gamma_8\kappa\rangle$ | $\|\Gamma_8\lambda\rangle$ | $\|\Gamma_8\mu\rangle$ | $\|\Gamma_8\nu\rangle$ |
|---|---|---|---|---|
| $\langle\Gamma_8\kappa\|$ | | | | $-\frac{5}{2}J_f$ |
| $\langle\Gamma_8\lambda\|$ | $\sqrt{3}(J_p + \frac{1}{2}J_f)$ | | | |
| $\langle\Gamma_8\mu\|$ | | $(2J_p - \frac{3}{2}J_f)$ | | |
| $\langle\Gamma_8\nu\|$ | | | $\sqrt{3}(J_p + \frac{1}{2}J_f)$ | |

The parameters are identified as

$$
\begin{aligned}
a &= 1 \\
b &= -10\big(B_x^2 + B_y^2 + B_z^2\big)\big(J_p^2 + J_f^2\big) \\
c &= \big(B_x^4 + B_y^4 + B_z^4\big)\big(9J_p^4 + 48J_p^3J_f + 46J_p^2J_f^2 - 48J_pJ_f^3 + 9J_f^4\big) \\
&\quad + \big(B_x^2B_y^2 + B_x^2B_z^2 + B_y^2B_z^2\big) \\
&\quad \times \big(18J_p^4 - 144J_p^3J_f + 32J_p^2J_f^2 + 24J_pJ_f^3 + 63J_f^4\big)
\end{aligned}
\tag{7.77}
$$

The parameter $b$ in this expression is isotropic, i.e., it does not depend on the orientation of the magnetic field in the octahedron. On the other hand, the parameter $c$ contains an anisotropic contribution. It depends on the orientation of the magnetic field in the octahedron, but symmetry-equivalent orientations must, of course, yield the same splitting. This means that $c$ is certainly an octahedral invariant and may thus be written as the sum of the familiar scalar $L = 0$ and hexadecapolar $L = 4$ cubic invariants that we derived in Sect. 7.2. We thus write

$$
\begin{aligned}
c &= c_1\big(B_x^2 + B_y^2 + B_z^2\big)^2 \\
&\quad + c_2\big(B_x^4 + B_y^4 + B_z^4 - 3B_x^2B_y^2 - 3B_x^2B_z^2 - 3B_y^2B_z^2\big)
\end{aligned}
\tag{7.78}
$$

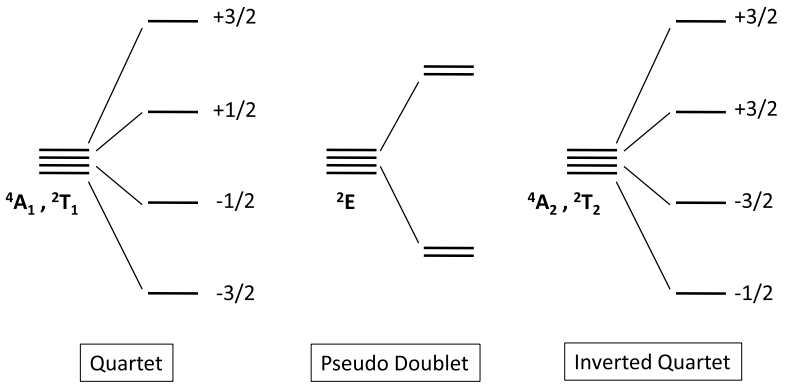


**Fig. 7.5** Possible isotropic Zeeman splittings of the octahedral $\Gamma_8$ spinor irrep

The coefficients in this equation are identified as

$$\begin{aligned} c_1 &= 9J_p^4 + 34J_p^2J_f^2 - 24J_pJ_f^3 + 18J_f^4 \\ c_2 &= J_f(4J_p + 2J_f)^2(3J_p - 9/4J_f) \end{aligned} \tag{7.79}$$

The $c_2$ coefficient is of special interest since it controls the only octahedral term in the linear Zeeman effect. If this coefficient vanishes, the splitting will be completely isotropic and does not depend on the orientation of the magnetic field in the octahedron. There are three possible isotropies [13].

- For $J_f = 0$, the spin operator is strictly dipolar, and the Zeeman Hamiltonian will induce a regular splitting of the quartet level, which is proportional to the spin quantum number, $M_S$. This case is illustrated in the left-hand panel of Fig. 7.5. Such cases will arise for an octahedral ${}^4A_1$ state and also for the quartet spin-orbit level of a ${}^2T_1$ state.
- For $4J_p + 2J_f = 0$, the matrix splits into two separate $2 \times 2$ blocks, which have the same eigenvalues. The splitting pattern is thus as in the central panel of Fig. 7.5. Such a case can occur for a ${}^2E$ state. The orbital part of this state has no angular momentum, since the corresponding operator is not included in the direct square: $T_1 \notin E \times E$. As a result, the magnetic moment of such a state is due only to the doublet spin part. Such a state behaves as a *pseudo-doublet*.
- Finally, for $3J_p - 9/4J_f = 0$, the splitting again resembles the Zeeman splitting of a regular spherical quartet, but the spin labels are interchanged, as compared with the standard quartet splitting: the $\pm 3/2$ levels become the inner levels of the split manifold, while the $\pm 1/2$ levels form the outer levels. This *inverted quartet* behavior is observed for ${}^2A_2$ and ${}^2T_2$ states. The orbital part in these states reverses the assignment of the fictitious spin levels, as can be seen, for instance, from the $A_2 \times \Gamma_8$ coupling table in Appendix G.

To conclude, we present the eigenenergies in the notation of Satten [14], who used parameters $g_1$ and $g_2$. The reduced matrix elements are expressed as

$$\begin{aligned} J_p &= \frac{\mu_B}{2\hbar}\frac{g_1 + 9g_2}{10} \\ J_f &= \frac{\mu_B}{2\hbar}\frac{3(g_1 - g_2)}{10} \end{aligned} \tag{7.80}$$

Furthermore, the magnetic field is represented by directional cosines as $B_z = Bn_z$, $B_x = Bn_x$, $B_y = Bn_y$. The four eigenvalues then become

$$\begin{aligned} E = \pm\frac{\mu_B}{2\hbar}B\Big[\frac{1}{2}\big(g_1^2 + 9g_2^2\big) \pm \frac{1}{4\sqrt{2}}(g_1 + 3g_2)\big(9(g_1 - 9g_2)(g_1 - g_2)\mathcal{F} \\ - \big(g_1^2 - 42g_1g_2 + 9g_2^2\big)\big)^{1/2}\Big]^{1/2} \end{aligned} \tag{7.81}$$

The three isotropic cases are reflected by the zeroes of the three factors preceding the function $\mathcal{F} = (n_x^4 + n_y^4 + n_z^4)$.

## 7.8 Problems

7.1 Find a relationship between the crystal-field potentials of an octahedron and a cube.

7.2 The product of two rotations is a rotation. Obtain an expression for the Cayley–Klein parameters of the product as a function of the parameters of its factors. Is the product commutative? The $SU(2)$ matrices may also be identified as normalized *quaternions*.

7.3 Work out the group multiplication table for the $D_3^*$ double group and derive the class structure.

7.4 Consider a set of three eigenlevels transforming as $A_1 + E$ in $D_3$ symmetry. A general matrix for the interaction between the states can be written as

| $\mathcal{H}$ | $\lvert A_1\rangle$ | $\lvert E_x\rangle$ | $\lvert E_y\rangle$ |
|---|---|---|---|
| $\langle A_1\rvert$ | $-2\Delta$ | a + ib | c + id |
| $\langle E_x\rvert$ | a − ib | $\Delta$ | e − if |
| $\langle E_y\rvert$ | c − id | e + if | $\Delta$ |

Introduce a fictitious spin operator $\tilde{\mathbf{S}}$ that recognizes these states as the components of a triplet spin, $\tilde{S} = 1$, and consider the spin Hamiltonian

$$\mathcal{H}_{Ze} = \frac{\mu_B}{\hbar}\big[g_\parallel B_z\tilde{S}_z + g_\perp(B_x\tilde{S}_x + B_y\tilde{S}_y)\big] \tag{7.82}$$

Express the $a, \ldots, f$ parameters as functions of the two $g$-parameters.

7.5 In octahedral symmetry the fictitious $\tilde{\mathbf{S}}$ operator follows the $T_1$ irrep. Its third symmetrized power transforms as the components of the $f$-harmonics and also subduces a $T_1$ irrep, as indicated in Table 7.1. Rewrite the $p$- and $f$-parts of the $|T_i|$ operators for the $\Gamma_8$ quartet state as a spin Hamiltonian of the fictitious spin.

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