15

TIME REVERSAL AND KRAMERS DEGENERACY

15.1. Operations involving the time

In the previous sections we have considered the effects of certain purely spatial operations, namely proper and improper rotations, on the eigenstates of a Hamiltonian invariant with respect to these transformations. We consider now two new operations that involve the time.

The first is the displacement in time D_t which relates the wave-function Ψ at time 0 to the wave-function $\Psi(t)$ at time t. For a time-independent Hamiltonian $\mathscr{H}$, $D_t = \exp(-i\mathscr{H}t/\hbar)$ which, applied to an eigenstate of $\mathscr{H}$ of energy W, yields

$$D_t\Psi = \exp\left(-\frac{iW}{\hbar}t\right)\Psi. \tag{15.1}$$

The second operation, usually called time reversal but which would be better called reversal of direction of motion, is an operation where all velocities (including those associated with the spinning of the electrons) are reversed. If this operation, which we shall denote by the letter θ, leaves the Hamiltonian $\mathscr{H}$ invariant and if Ψ is an eigenstate of $\mathscr{H}$ with an energy W, $\theta\Psi$ is obviously also an eigenstate with the same energy. The invariance of the Hamiltonian of a system by time reversal has far-reaching consequences for its magnetic properties. The formalism involved is rather different from the usual calculations of quantum mechanics and as it is sometimes misunderstood it warrants a rather detailed discussion.

The following relation is a straightforward consequence of the definitions of θ and D_t:

$$D_t(\theta\varphi) = \theta D_{-t}(\varphi). \tag{15.2}$$

This equation states in effect that if two states of a system have opposite velocities at time zero they have opposite velocities at opposite times.

Since time reversal, as we shall continue to call it, is a symmetry operator it follows from general principles of quantum mechanics that it cannot change the transition probability between two states Ψ and Φ so that we have

$$|(\Psi \mid \Phi)| = |(\theta\Psi \mid \theta\Phi)|. \tag{15.3}$$

It can be shown (Wigner, *Group theory*, Chap. 26) that if a physical relationship expressed by an operator θ is such that (15.3) holds, it is always possible to re-define the phases of all wave-functions in such a way that θ is either a linear unitary operator or an antilinear anti-unitary one.

For convenience we re-state here that under a unitary transformation we have for a linear unitary operator A

$$A(C\Psi) = C(A\Psi), \tag{15.4}$$

whereas for an antilinear operator we have

$$A(C\Psi) = C^*(A\Psi). \tag{15.5}$$

An antilinear operator that satisfies (15.3) is further said to be anti-unitary. The first alternative (15.4) implies

$$\begin{cases} \theta(C_1\Psi_1+C_2\Psi_2) = C_1\theta\Psi_1+C_2\theta\Psi_2, \\ (\theta\Psi \mid \theta\Phi) = (\Psi \mid \Phi). \end{cases} \tag{15.6}$$

The second (15.5) implies that

$$\begin{cases} \theta(C_1\Psi_1+C_2\Psi_2) = C_1^*\theta\Psi_1+C_2^*\theta\Psi, \\ (\theta\Psi \mid \theta\Phi) = (\Psi \mid \Phi)^* = (\Phi \mid \Psi). \end{cases} \tag{15.7}$$

To establish the category to which θ belongs, consider the relation (15.2) where we expand φ into a sum of eigenstates $\varphi = \sum a_k\Psi_k$ of a Hamiltonian $\mathscr{H}$. If θ is linear and (15.6) holds, the left-hand side of (15.2) can be written $\sum_k a_k e^{-iW_kt/\hbar}(\theta\varphi_k)$, while the right-hand side becomes $\sum_k a_k e^{+iW_kt/\hbar}(\theta\varphi_k)$, which is contradictory. On the other hand, if θ is anti-linear, both sides of (15.2) yield $\sum a_k^* e^{-iW_kt/\hbar}(\theta\varphi_k)$. The time-reversal operator must thus be antilinear and antiunitary. Some caution must be exercised in the manipulation of antilinear operators. In particular, the customary notation $(\Phi| A |\Psi)$ for the matrix element of an operator A between two states Φ and Ψ is ambiguous if A is antilinear. We shall write instead $(A\Phi, \Psi)$ or $(\Phi, A\Psi)$, as the case may be.

15.2. Complex conjugation

One of the simplest antilinear operators is that which converts a wave-function Ψ into its complex conjugate Ψ^*. We denote this operator by K_0 and we use here the word wave-function in a rather general sense. For instance, dealing with angular momenta, if a state

$|\xi\rangle$ can be expanded into a sum of state vectors

$$|\xi\rangle = \sum_{J,M} C_{J,M} |J, M\rangle, \tag{15.8}$$

what we call the wave-function of $|\xi\rangle$ is the set of numbers $C_{J,M}$; the state vector $K_0 |\xi\rangle$ will then have as wave-function the set of numbers $C^*_{J,M}$,

$$K_0 |\xi\rangle = \sum_{J,M} C^*_{J,M} |J,M\rangle. \tag{15.9}$$

Clearly K_0 is an antiunitary operator since

$$(K_0\Psi, K_0\Phi) = (\Psi, \Phi)^* = (\Phi, \Psi);$$

and it obeys the obvious relation

$$K_0^2 = 1. \tag{15.10}$$

An operator $K_0^{-1}AK_0$, the complex conjugate of an operator A, is by definition an operator whose matrix elements are the complex conjugates of those of A. It is clear that the definition of K_0 depends on the basis states chosen to define the representation. For instance, in the representation $\mathbf{r}$, the complex conjugate of the operator

$$L_z = \frac{1}{\mathrm{i}}\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right)$$

is $-L_z$, but it is $+L_z$ in the representation $|L, M_L\rangle$. In the representation $\mathbf{r}$ the operator $p_x = (\hbar/\mathrm{i})\,\partial/\partial x$ changes its sign under conjugation, but not in the representation $\mathbf{p}$ where it is diagonal. We cannot therefore identify θ with K_0 in all representations since θ should be independent of the representation chosen, while K_0 clearly is not. There is, however, a relationship between θ and K_0 that we establish now, by introducing the operator $U = \theta K_0$ or, since $K_0^2 = 1$, $\theta = UK_0$.

We can show immediately that $U = \theta K_0$ is unitary; since θ and K_0 are both antilinear, $U = \theta K_0$ is linear, and since both θ and K_0 leave invariant the absolute value of the scalar product $|(\Phi, \Psi)|$ so does U. Hence it is unitary. We can also show that $\theta^2 = \pm 1$. The operator θ applied twice leaves the system in its original state and one must have

$$\theta^2 = UK_0 \,.\, UK_0 = UK_0^{-1}UK_0 = UU^* = c \,.\, 1, \tag{15.11}$$

where c is a number of modulus unity and 1 the unit operator. From

(15.11) we find:

$$U = cU^{*-1} \text{ or, since } U \text{ and } U^* \text{ are unitary,}$$

$$U = c(U^*)^\dagger = c\tilde{U}, \text{ the transposed of which is}$$

$$\tilde{U} = cU \text{ whence } U = c^2U \text{ and}$$

$$c^2 = 1, \qquad c = \pm 1.$$

It follows that the square of the time-reversal operator is

$$\theta^2 = \pm 1. \tag{15.12}$$

15.3. Determination of the time-reversal operator

We begin by disregarding the spin. The dynamical variables are then the coordinates x and momenta p_x, which under time reversal should transform as

$$\theta^{-1}x\theta = x; \qquad \theta^{-1}p_x\theta = -p_x,$$

or

$$x\theta = \theta x, \qquad p_x\theta = -\theta p_x. \tag{15.13}$$

Hence, on writing $\theta = UK_0$, we have

$$\begin{aligned} xUK_0 &= UK_0x, \qquad p_xUK_0 = -UK_0p_x, \\ xU &= UK_0xK_0^{-1}, \qquad p_xU = -UK_0p_xK_0^{-1}. \end{aligned} \tag{15.14}$$

Let us choose the **r** representation where x is real; i.e., $x = K_0xK_0^{-1}$ and p_x is purely imaginary so that $p_x = -K_0p_xK_0^{-1}$. Then (15.14) yields

$$xU = Ux, \qquad p_xU = Up_x. \tag{15.15}$$

Thus the operator U commutes with all the dynamical variables x and p_x and must therefore be a constant that we can choose equal to unity. In the absence of spin and in the **r** representation (but not in the **p** representation !) the time-reversal operator θ is represented by the complex conjugation operator K_0.

We now include the spin and consider first a single electron. The three components s_q of the spin operator change their sign under time-reversal and must satisfy the relations

$$s_q = -\theta s_q\theta^{-1}, \qquad s_q\theta = -\theta s_q, \tag{15.16}$$

giving

$$s_qUK_0 = -UK_0s_q,$$

or

$$s_qU = -UK_0s_qK_0^{-1}, \tag{15.17}$$

so that

$$s_qU = -Us_q^*. \tag{15.18}$$

In the usual representation where s_x and s_z are real matrices and s_y is a purely imaginary one, U must anticommute with s_x and s_z and commute with s_y. We may take for U the matrix $\sigma_y = 2s_y$ which is unitary and answers our requirements, or better still $i\sigma_y$ which has the advantage of being a real matrix so that it commutes with K_0. The latter will be our choice. To recapitulate, in a representation where $\mathbf{r}$ is diagonal (the $\mathbf{r}$ representation) and s_x and s_z real, the time-reversal operator for a single electron can be represented by

$$\theta = i\sigma_y K_0. \tag{15.19}$$

Its square is given by

$$\theta^2 = (i\sigma_y)K_0(i\sigma_y)K_0 = (i\sigma_y)^2K_0^2 = -1. \tag{15.20}$$

For n electrons $1, 2, \ldots, n$ the time-reversal operator θ will be the product

$$\theta = \prod_1^n \theta_p. \tag{15.21}$$

Its square will be ± 1 depending on whether the number n of electrons is even or odd, a particularly important result.

15.4. Kramers degeneracy

Consider a system with an odd number of electrons for which $\theta^2 = -1$ and assume that its Hamiltonian commutes with θ. This will be the case in the absence of a magnetic field for then the kinetic and potential energy as well as spin-spin and spin-orbit interactions are invariant through time reversal. Let Ψ be an eigenstate of the system with energy W; then the function $\Phi = \theta\Psi$ is also an eigenstate with the same energy. Consider the scalar product $(\Psi, \Phi) = (\Psi, \theta\Psi)$. Since θ is antilinear,

$$(\Psi, \Phi) = (\Psi, \theta\Psi) = (\theta\Psi, \theta^2\Psi)^* = (\theta^2\Psi, \theta\Psi) = -(\Psi, \theta\Psi) = 0,$$

showing that Φ is orthogonal to Ψ and is naturally distinct from it. It follows that the eigenvalue W is at least twofold degenerate. This is Kramers theorem. We shall call the state $\Phi = \theta\Psi$ the Kramers-conjugate of Ψ and represent it by the symbol $\overline{\Psi}$.

A few useful relations are connected with the properties of θ. We shall call an operator O time-odd if $\theta O\theta^{-1} = -O^\dagger$ and similarly an operator time-even if $\theta O\theta^{-1} = +O^\dagger$. If O is Hermitian, $O^\dagger = O$ but it is sometimes convenient to use non-Hermitian operators such as $L_\pm$ or $J_\pm$.

It should be noticed in this connection that the product of two non-commuting Hermitian operators A and B of well-defined time-parity (say for instance both even) does not have a well-defined time-parity but is the sum of a time-even and a time-odd operator:

$$AB = \tfrac{1}{2}(AB+BA)+\tfrac{1}{2}(AB-BA) = C+D$$

where C is Hermitian and D anti-Hermitian, and

$$\theta AB\theta^{-1} = \theta C\theta^{-1}+\theta D\theta^{-1} = C+D = C^{\dagger}-D^{\dagger}.$$

Hence C is time-even but D is time-odd!

Spin-spin and spin-orbit interactions, which are *Hermitian* products of time-odd operators, are time-even.

If $\theta^2 = -1$, the following theorems hold.

(a) A time-even operator has no matrix elements between two Kramers conjugate states, since

$$\begin{aligned}(\Psi|\, O\,|\overline{\Psi}) &= (\Psi, O\theta\Psi) = (\theta O\theta\Psi, \theta\Psi) = -(\theta O\theta^{-1}\Psi, \theta\Psi)\\ &= -(O^{\dagger}\Psi, \theta\Psi) = -(\Psi|\, O\,|\overline{\Psi}) = 0. \qquad (15.22a)\end{aligned}$$

(b) A time-even operator has the same expectation value in two Kramers conjugate states since

$$\begin{aligned}(\Psi|\, O\,|\Psi) &= (\Psi, O\Psi) = (\theta O\Psi, \theta\Psi) = (\theta O\theta^{-1}\theta\Psi, \theta\Psi)\\ &= (O^{\dagger}\theta\Psi, \theta\Psi) = (\theta\Psi, O\theta\Psi) = (\overline{\Psi}|\, O\,|\overline{\Psi}). \qquad (15.22b)\end{aligned}$$

(c) A time-odd operator has opposite expectation values in two Kramers conjugate states. The proof is similar to that in (b).

If $\theta^2 = +1$, time reversal plays a much less important role because a state Ψ can now coincide with its time-reversed state $\overline{\Psi} = \theta\Psi$. The analogues of the previous results (a), (b), (c) are the following:

(a′) A time-odd operator has no matrix elements between two Kramers conjugate states. The proof is the same as for (a).

(b′), (c′) The theorems (b), (c) do not depend on the value of θ^2 and are therefore also valid for $\theta^2 = +1$.

The result (a′) leads to a generalization of Van Vleck's theorem on the quenching of the orbital momentum proved in § 11.7. Consider a time-even Hamiltonian $\mathscr{H}$ with a *non-degenerate* eigenstate Ψ, which necessarily implies $\theta^2 = +1$. The state $\overline{\Psi} = \theta\Psi$ is an eigenstate of $\mathscr{H}$ with the same energy and since Ψ is non degenerate $\overline{\Psi}$ must coincide with Ψ within a phase-factor. The matrix elements of time-odd operators between Ψ and $\overline{\Psi}$ which vanish according to (a′) are just the expectation values in the state Ψ. It follows that all components of the

magnetic moment, being time-odd operators have vanishing expectation values in non-degenerate states of time-even Hamiltonians, which is a generalization of Van Vleck's theorem on the quenching of the orbital momentum.

Invariance through time reversal is also connected with the so-called Van Vleck cancellation that is responsible for the T^9 temperature variation of the Raman relaxation rate for Kramers ions (see Chapter 10). What is meant by the Van Vleck cancellation is the *near* cancellation of two second-order probability amplitudes, caused by the *exact* cancellation

$$\langle \bar{a}| V' |c\rangle\langle c| V |a\rangle + \langle \bar{a}| V |\bar{c}\rangle\langle \bar{c}| V' |a\rangle = 0, \qquad (15.23a)$$

where V and V' are two time-even non-Hermitian operators (actually lattice-orbit coupling operators for emission or absorption of a phonon) and $|\bar{a}\rangle$, $|a\rangle$ and $|\bar{c}\rangle$, $|c\rangle$ are two pairs of Kramers conjugate states (see Chapter 10). The proof of (15.23a) is as follows (most of the proofs given in the literature, except that of Van Vleck, are incomplete or incorrect). The first term of (15.23a) can be written

$$\begin{aligned}(\theta a, V'c)(c, Va) &= (\theta V'c, \theta^2 a)(\theta Va, \theta c) = (\theta V'\theta^{-1}\theta c, \theta^2 a)(\theta V\theta^{-1}\theta a, \theta c)\\ &= -(V'^{+}\bar{c}, a)(V^{+}\bar{a}, \bar{c}) = -(\bar{c}| V' |a)(\bar{a}| V |\bar{c}), \qquad (15.23b)\end{aligned}$$

which proves (15.23a).

Since Kramers degeneracy is directly related to invariance with respect to time reversal one may ask whether this is or is not a new degeneracy superimposed on that connected with the spatial symmetry of the environment. There is no single answer to that question since examples of either situation can be found. Thus, for instance, in an environment of cubic symmetry, for an odd number of electrons all representations are at least two-dimensional and no extra degeneracy is brought about by the invariance of the Hamiltonian with respect to time reversal. On the other hand, the double trigonal group (§ 14.5) has two unidimensional representations, Γ_4^T and Γ_5^T, which must correspond to the same energy if Kramers' theorem is to be obeyed. The mathematical criteria for the occurrence of either situation are discussed in Wigner's book but we shall have no occasion to make use of them.

15.5. Time-reversal operator in the $|J, M\rangle$ representation

Since, as has already been stated, eigenstates $|J, M\rangle$ of the angular momentum provide a convenient basis for expanding eigenstates of the bound ion, it is useful to be able to write directly the effect of time

reversal on a state vector

$$|\xi\rangle = \sum_{J,M} C_{J,M} |J, M\rangle. \tag{15.24}$$

Since **J** is a time-odd operator, we must have

$$\begin{aligned} \theta \mathbf{J} \theta^{-1} &= -\mathbf{J} \\ \theta \mathbf{J} &= -\mathbf{J}\theta \\ U K_0 \mathbf{J} &= -\mathbf{J} U K_0 \\ U K_0 \mathbf{J} K_0^{-1} &= -\mathbf{J} U \end{aligned}$$

or

$$U\mathbf{J}^* = -\mathbf{J}U. \tag{15.25}$$

With the usual choice of phases, J_z and J_x are real operators, in the sense that all their matrix elements are real, whereas J_y is purely imaginary. According to (15.25) we need for U a unitary operator that commutes with J_y and anticommutes with J_x and J_z. The operator $e^{i\pi J_y}$ satisfies these requirements. This is obvious for J_y. For J_x, $e^{i\pi J_y} J_x = -J_x e^{i\pi J_y}$ implies $e^{-i\pi J_y} J_x e^{i\pi J_y} = -J_x$ which is satisfied since, as we saw in § 13.1, $e^{-i\pi J_y}$ expresses a rotation by an angle π around Oy which must change J_x into $-J_x$. The same is true for J_z. We can thus take for θ the form

$$\theta = e^{i\pi J_y} K_0 = K_0 e^{i\pi J_y}. \tag{15.26}$$

For $J = \frac{1}{2}$

$$e^{i\pi J_y} = e^{(i\pi/2)\sigma_y} = \cos\frac{\pi}{2} + i\sigma_y \sin\frac{\pi}{2} = i\sigma_y, \tag{15.27}$$

which is consistent with (15.19).

The only non-vanishing matrix elements of $e^{i\pi J_y}$ can be shown to be

$$\langle -M| e^{i\pi J_y} |M\rangle = (-1)^{J-M}, \tag{15.28}$$

which gives for $\bar{\xi} = \theta\xi$ the expression

$$|\bar{\xi}\rangle = \theta |\xi\rangle = \sum_{J,M} C^*_{J,M} (-1)^{J-M} |J, -M\rangle. \tag{15.29}$$

The reader may verify that this sign rule is consistent with the expansion of the various kets in Tables 4 and 9.

15.6. The 'Spin Hamiltonian' for a Kramers doublet

Consider a paramagnetic ion with an odd number of electrons in an environment of symmetry sufficiently low for the ground level to have only Kramers degeneracy. This will be the case for any symmetry lower than cubic, and also for the cubic levels Γ_6 and Γ_7.

This degenerate Kramers doublet is spanned by two kets $|\xi\rangle$ and $|\bar{\xi}\rangle = \theta\,|\xi\rangle$. There is an arbitrariness in the choice of these basis states. We can always choose two other states by a substitution of the form

$$\begin{cases} |\xi'\rangle = a\,|\xi\rangle + b\,|\bar{\xi}\rangle \\ |\bar{\xi}'\rangle = \theta\,|\xi'\rangle = -b^*\,|\xi\rangle + a^*\,|\bar{\xi}\rangle, \end{cases} \tag{15.30}$$

with $aa^* + bb^* = 1$. The substitution (15.30) is not only unitary but also unimodular and, as we saw in Chapter 13 in considering the rotation group, we can associate with it a certain rotation R by means of eqn (13.14) and the formulae following it in § 13.2.

The degeneracy of the Kramers doublet can only be lifted by a magnetic field, which may be either an applied external field or the field produced by the magnetic moment $\boldsymbol{\mu}_I = -\gamma_n \hbar \mathbf{I}$ of the nucleus if it is not zero. The corresponding energies can be written $-\boldsymbol{\mu}_e \cdot \mathbf{H}$ and $-\boldsymbol{\mu}_I \cdot \mathbf{H}_e$ where vector operators $\boldsymbol{\mu}_e$ and $\mathbf{H}_e$ represent respectively the magnetic moment of the ion and the magnetic field produced by its electrons at the position of the nucleus. If we assume that either interaction is much smaller than the distance between the doublet and excited levels, we need only their matrix elements within the ground manifold. It is well known that any Hermitian two-by-two matrix can be expressed as a linear combination with real coefficients of the three Pauli matrices and of the unit matrix. Since all components of $\boldsymbol{\mu}$ and $\mathbf{H}_e$ are time-odd operators, their expectation values in the states $|\xi\rangle$ and $|\bar{\xi}\rangle$ have opposite values (theorem (c) of § 15.4) and we can write for the components μ_q and H_{eq}

$$\begin{cases} \mu_q = -\dfrac{\beta}{2} \sum\limits_{\alpha} g_{q\alpha} \sigma_\alpha \\ H_{eq} = \sum\limits_{\alpha} a_{q\alpha} \sigma_\alpha, \end{cases} \tag{15.31}$$

with no contribution from the unit matrix. The index q refers to the components x, y, z of the vectors $\boldsymbol{\mu}$ and $\mathbf{H}_e$ and α to the Pauli matrices σ_1, σ_2, σ_3. The set of matrices $\sigma_1/2$, $\sigma_2/2$, $\sigma_3/2$ is often referred to as the components of the fictitious spin $\mathbf{s}$ and the sets of real numbers $g_{q\alpha}$ and $a_{q\alpha}$ are called the magnetogyric tensor and the hyperfine structure tensor. The deeply ingrained habit of calling the $g_{q\alpha}$ and the $a_{q\alpha}$ tensors, proceeds from a confusion between the fictitious spin $\boldsymbol{\sigma}/2$ of the Kramers doublet and a real electronic spin and is a serious misnomer in general as will now appear.

There are two operations that can modify the set of numbers $g_{q\alpha}$ (and $a_{q\alpha}$). The first is a spatial rotation S of coordinate axes whereby the components μ_q are replaced by another set

$$\mu'_q = \sum_p S_{qp}\mu_p \tag{15.32}$$

and consequently

$$g'_{q\alpha} = \sum_p S_{qp}g_{p\alpha}. \tag{15.33}$$

The second is the substitution (15.30) of the basis states $|\xi\rangle$ and $|\bar{\xi}\rangle$ which, because of the *mathematical* connection between a matrix u of the unitary group U and a real orthogonal matrix R of the rotation group, results in the substitution

$$\sigma'_\gamma = \sum_\alpha R_{\gamma\alpha}\sigma_\alpha \quad \text{or} \quad \sigma_\alpha = \sum (R^{-1})_{\alpha\gamma}\sigma'_\gamma = \sum R_{\gamma\alpha}\sigma'_\gamma, \tag{15.34}$$

which leads to the substitution

$$g''_{p\gamma} = \sum R_{\gamma\alpha}g_{p\alpha}. \tag{15.35}$$

If we decided, quite arbitrarily, always to associate with a rotation S of the coordinate axes, expressed by (15.32), a substitution (15.30) of the basis states, such that the corresponding substitution R for the σ_α, expressed by (15.34), would coincide with the spatial rotation S, then and only then would the $g_{q\alpha}$ (and $a_{q\alpha}$) transform as the components of a tensor. A true tensor G_{pq} does, however, appear when we look for the eigenvalues of the Zeeman Hamiltonian $-\boldsymbol{\mu}\,.\,\mathbf{H}$. Let λ_x, λ_y, λ_z be the cosines of the direction of $\mathbf{H}$. Then from (15.31)

$$-\boldsymbol{\mu}\,.\,\mathbf{H} = \sum_{q,\alpha}\frac{\beta}{2}H_q g_{q\alpha}\sigma_\alpha = \sum_{q,\alpha}\frac{\beta H}{2}\lambda_q g_{q\alpha}\sigma_\alpha = \frac{\beta H}{2}\sum_\alpha \sigma_\alpha f_\alpha \tag{15.36}$$

where $f_\alpha = \sum_q \lambda_q g_{q\alpha}$.

The eigenvalues of (15.36) result from the well known properties of the Pauli matrices,

$$\begin{aligned} W_\pm &= \pm\frac{\beta H}{2}\left(\sum_\alpha f_\alpha^2\right)^{\frac{1}{2}} = \pm\frac{\beta H}{2}\left(\sum_{p,q}\lambda_p\lambda_q\sum_\alpha g_{p\alpha}g_{q\alpha}\right)^{\frac{1}{2}} \\ &= \pm\frac{\beta H}{2}\left(\sum_{p,q}\lambda_p\lambda_q G_{pq}\right)^{\frac{1}{2}}. \end{aligned} \tag{15.37}$$

The set of numbers

$$G_{pq} = \sum_\alpha g_{p\alpha}g_{q\alpha} \tag{15.38}$$

is indeed a symmetric tensor that has the correct transformation properties under spatial rotations and can always be made diagonal by a proper choice of coordinate axes. Its eigenvalues are all positive and their square roots give the three principal values of the Larmor frequency of the electron spin in the applied field **H**. A tensor $A_{pq} = \sum_{\alpha} a_{p\alpha} a_{q\alpha}$ can be similarly defined.

From what has been said about the 'tensor' $g_{q\alpha}$ it follows that the question of whether it is symmetric is of little importance. Since we have six parameters at our disposal, three for the spatial rotation S in (15.33), and three for the fictitious rotation R in (15.35), we have enough freedom to make the 'tensor' $g_{q\alpha}$ diagonal. Once the 'tensor' g has been reduced to a diagonal form g_1, g_2, g_3 it is always possible to reverse the sign of two of the components, say g_1 and g_3, by a rotation of π around the y-axis (or by a change of σ_1 and σ_3 into $-\sigma_1$ and $-\sigma_3$ by an interchange of the basic states). On the other hand, the product $g_1 g_2 g_3$ which is the determinant of the $g_{q\alpha}$, is an invariant.

When $g_{p\alpha}$ is diagonal, so naturally is G_{pq} according to (15.38), since

$$G_{xx} = g_{x1}^2, \qquad G_{yy} = g_{y2}^2, \qquad G_{zz} = g_{z3}^2. \tag{15.38'}$$

In the same manner, with two other rotations R' and S' we can make the hyperfine 'tensor' $a_{p\alpha}$ diagonal. The relevant question is then whether both 'tensors' $g_{q\alpha}$ and $a_{q\alpha}$ be made diagonal simultaneously with the same choice of rotations R and S, that is with the same choice of coordinate axes and basis states.

We have so far said nothing about the spatial environment of our ion. If we make some restrictive assumptions on its symmetry we shall find situations where the 'tensors' $g_{q\alpha}$ and $a_{q\alpha}$ can be diagonalized simultaneously. For example, if the strength of the interactions due to the environment is small compared to the distance between two J multiplets of the free ion, we may assume that the wave-functions of our Kramers doublet can be constructed from the wave-functions of a single J level of the free ion (this may occur in the rare-earth group but not in general in the iron group). Then, according to the Wigner–Eckart theorem, all matrix elements within the doublet of the components of any vector, and in particular of $\boldsymbol{\mu}$ and $\mathbf{H}_e$, will be proportional to the corresponding matrix elements of the vector **J**. The 'tensors' $g_{q\alpha}$ and $a_{q\alpha}$ will be proportional to each other and can be diagonalized simultaneously.

15.7. The rhombic group

Suppose that the environment of the ion has two twofold symmetry axes, the z- and y-axes (it then has necessarily a third, the x-axis). We now show that in this case $g_{q\alpha}$ and $a_{q\alpha}$ can simultaneously be made diagonal.

We can expand one of the kets spanning the Kramers doublet into eigenstates $|J, M\rangle$ of the free ion (where $i \equiv \alpha, J, M$)

$$|\xi\rangle = \sum_{\alpha,J,M} C_i \, |\alpha, J, M\rangle, \tag{15.39}$$

where $J_z = M$ is quantized along the binary z-axis. The values of M in (15.39) are half integer and differ by at least two units because of binary symmetry. This prevents the values M and $-M$ from being simultaneously present in the expansion (15.39).

The matrix elements $\langle\xi| \, \mu_x \, |\xi\rangle = g_{x3}$ and $\langle\xi| \, \mu_y \, |\xi\rangle = g_{y3}$ vanish because μ_x and μ_y obey the selection rule $|\Delta M| = 1$. To find the other matrix elements let R be the rotation $R = \mathrm{e}^{\mathrm{i}\pi J_y}$. Then from eqns (15.26), (15.29) the Kramers conjugate $|\bar{\xi}\rangle$ is given by

$$|\bar{\xi}\rangle = \theta \, |\xi\rangle = RK_0 \, |\xi\rangle = \sum_{\alpha,J,M} C_i^*(-1)^{J-M} \, |\alpha, J, -M\rangle. \tag{15.40}$$

It is clear that $\langle\xi| \, \mu_z \, |\bar{\xi}\rangle = g_{z1} - \mathrm{i}g_{z2}$ vanishes since μ_z obeys the selection rule $|\Delta M| = 0$. Since the y-axis is a binary axis, $R \, |\xi\rangle$ is also an eigenstate with the same energy as $|\xi\rangle$ and clearly orthogonal to it. It must therefore coincide with $|\bar{\xi}\rangle = RK_0 \, |\xi\rangle$ within a phase factor and all the C_i in (15.39) can be chosen to be real. We then have the relations

$$R \, |\xi\rangle = \theta \, |\xi\rangle = |\bar{\xi}\rangle, \qquad \langle\bar{\xi}| = \langle\xi| \, R^\dagger$$

and hence

$$\langle\xi| \, \mu_x \, |\bar{\xi}\rangle = -\langle\xi| \, R^{-1}\mu_x R \, |\bar{\xi}\rangle = -\langle\xi| \, R^\dagger \mu_x R^2 \, |\xi\rangle = \langle\bar{\xi}| \, \mu_x \, |\xi\rangle$$

since $R^2 = -1$. Hence $\langle\xi| \, \mu_x \, |\bar{\xi}\rangle$ must be real and since it is equal to $g_{x1} - \mathrm{i}g_{x2}$, it follows that g_{x2} vanishes. Similarly it is found that

$$g_{y1} - \mathrm{i}g_{y2} = \langle\xi| \, \mu_y \, |\bar{\xi}\rangle = -\langle\bar{\xi}| \, \mu_y \, |\xi\rangle.$$

$\langle\xi| \, \mu_y \, |\bar{\xi}\rangle$ is imaginary and g_{y1} vanishes. The 'tensor' $g_{q\alpha}$ is thus diagonal with our choice of eigenstates and coordinate axes. Since we made no assumptions about $\boldsymbol{\mu}$ apart from its being a time-odd vector, this is clearly also true for the 'tensor' $a_{q\alpha}$ associated with $\mathbf{H}_e$.

15.8. Threefold symmetry

The trigonal symmetry C_3 provides an example of a situation where it may be impossible to diagonalize $g_{q\alpha}$ and $a_{q\alpha}$ simultaneously.

Consider a system that possesses no symmetry beyond a threefold z-axis and assume that the expansion (15.39) of $|\xi\rangle$ contains the value $M = +\frac{1}{2}$. The other values of M in the expansion will be $+\frac{1}{2}+3p$ with p integer. Similarly the expansion of $|\bar{\xi}\rangle$ will contain the values $M = -\frac{1}{2}+3p'$. This has the following consequences for the 'tensor' g.

$$\begin{cases} \langle\xi|\,\mu_x\,|\xi\rangle = g_{x3} = 0, \\ \langle\xi|\,\mu_y\,|\xi\rangle = g_{y3} = 0, \\ \langle\xi|\,\mu_z\,|\xi\rangle = g_{z3} = g_{\parallel}, \end{cases} \tag{15.41}$$

and

$$\begin{cases} \langle\xi|\,\mu_z\,|\bar{\xi}\rangle = g_{z1}-\mathrm{i}g_{z2} = 0, \\ \langle\xi|\,\mu_-\,|\bar{\xi}\rangle = \langle\xi|\,(\mu_x-\mathrm{i}\mu_y)\,|\bar{\xi}\rangle, \\ \qquad\qquad = g_{x1}-\mathrm{i}g_{x2}-\mathrm{i}(g_{y1}-\mathrm{i}g_{y2}) = 0. \end{cases} \tag{15.42}$$

From these last equations (15.42) we have

$$\begin{aligned} g_{z1} &= g_{z2} = 0, \\ g_{x1} &= g_{y2} = g', \\ g_{x2} &= -g_{y1} = g''. \end{aligned} \tag{15.43}$$

Thus the 'tensor' g has the form

$$\begin{pmatrix} g' & g'' & 0 \\ -g'' & g' & 0 \\ 0 & 0 & g_{\parallel} \end{pmatrix}, \tag{15.44}$$

which can be brought into diagonal form by a rotation S of the coordinate axes around Oz through an angle Φ such that $\tan\Phi = -g''/g'$, giving

$$\begin{pmatrix} g_{\perp} & 0 & 0 \\ 0 & g_{\perp} & 0 \\ 0 & 0 & g_{\parallel} \end{pmatrix}, \tag{15.45}$$

where $g_{\perp}^2 = g'^2+g''^2$.

Similarly the hyperfine structure 'tensor' will initially have the form

$$\begin{pmatrix} a' & a'' & 0 \\ -a'' & a' & 0 \\ 0 & 0 & a_{\parallel} \end{pmatrix}, \tag{15.46}$$

which can be reduced by a rotation of the coordinates about the axis

Oz through an angle Ψ such that $\tan\Psi = -a''/a'$ to a diagonal form

$$\begin{pmatrix} a_\perp & 0 & 0 \\ 0 & a_\perp & 0 \\ 0 & 0 & a_\parallel \end{pmatrix}. \tag{15.47}$$

However there is no *a priori* reason why $\tan\Psi$ should be equal to $\tan\Phi$, and this implies that we have to use two different sets of axes: Z, x, y for the components of the external magnetic field $\mathbf{H}$ and Z, X, Y for the components of the nuclear magnetic moment $\boldsymbol{\mu}_I = \gamma_n\hbar\mathbf{I}$. The spin Hamiltonian can then be written as

$$\tfrac{1}{2}\beta g_\parallel H_Z\sigma_3 + \tfrac{1}{2}\beta g_\perp(H_x\sigma_1 + H_y\sigma_2) - \gamma_n\hbar a_\parallel I_Z\sigma_3 - \gamma_n\hbar a_\perp(I_X\sigma_1 + I_Y\sigma_2). \tag{15.48}$$

The fact that the components of $\mathbf{I}$ are not measured along the same axes as those of $\mathbf{H}$ would not be observable if there did not exist another term in the Hamiltonian, the direct coupling of the nuclear moment with the applied field $\mathbf{H}$, which is

$$-\gamma_n\hbar(\mathbf{I}\,.\,\mathbf{H}) = -\gamma_n\hbar(I_xH_x + I_yH_y + I_ZH_Z). \tag{15.49}$$

Although this term is very small, it can be measured with reasonable precision in Endor experiments (cf. Chapter 4). In general the hyperfine term will be much larger, so that we should use the (X, Y, Z) axes for the components of $\mathbf{I}$. Then if $\mathbf{H}$ is, for example, along the x-axis, the diagonal term in (15.49) becomes $-\gamma_n\hbar I_X H_X \cos(\Psi - \Phi)$. Thus in principle the difference in orientation that may occur in C_3 symmetry for the axes OX, OY and Ox, Oy could be detected, although it does not appear to have been observed in practice.

15.9. Selection rules related to time reversal

Let us consider a system S with a Hamiltonian $\mathscr{H}_0$ invariant through the transformations of a spatial group G, for instance, a paramagnetic ion whose environment has a symmetry describable by that group. As we have seen in § 12.6, a perturbation expressed by an operator V_β belonging to a representation Γ' of G cannot lift the p-fold degeneracy of an energy level of S, spanned by the wave-functions Ψ_α that belong to a p-dimensional representation Γ of G, unless the direct product $\Gamma^* \times \Gamma \times \Gamma'$ contains the unit representation of G. If this condition is not satisfied all the matrix elements $(\Psi_\alpha|\, V_\beta\, |\Psi_\gamma)$ vanish. It was shown in § 12.6 that if the representations Γ and Γ' are equivalent to their

complex conjugates, respectively Γ^* and Γ'^*, that is if all their characters are real (an assumption that we retain in the following discussion), this condition is equivalent to the requirement that $(\Gamma \times \Gamma)$ contains Γ'. Furthermore, we shall show that if the Hamiltonian $\mathscr{H}_0$ is invariant through the time-reversal operation θ, the condition for the lifting of the degeneracy is more restrictive than the one stated above.

Let us define two symbols ε_V and ε_θ equal to ± 1: ε_V is equal to $+1$ if the operator V_β is time-even, and -1 if it is time-odd; ε_θ is equal to the square θ^2 of the time-reversal operator: it is $+1$ if the number of electrons is even and -1 if the number of electrons is odd (eqn (15.21)). The result that we shall establish can be stated as follows. In order for the operator V_β, belonging to Γ', to have non-vanishing matrix elements inside the manifold Γ the following are necessary conditions: if $\varepsilon_V \varepsilon_\theta > 0$, Γ' must be contained in the symmetric direct product $[\Gamma \times \Gamma]_S$; if $\varepsilon_V \varepsilon_\theta < 0$, Γ' must be contained in the antisymmetric direct product $[\Gamma \times \Gamma]_A$. The characters of these products are given in eqn (12.43). These conditions are more restrictive than the requirement obtained in § 12.6 prior to the introduction of time reversal, namely that Γ' must be contained in the direct product $\Gamma \times \Gamma$.

The proof is as follows. Under an operation R belonging to G the functions Ψ_α transform according to the law

$$R\Psi_\alpha = \sum_\gamma \Psi_\gamma D_\Gamma(R)_{\gamma\alpha}. \tag{15.50}$$

Let us introduce the set of functions

$$\bar{\Psi}_\alpha = \theta \Psi_\alpha, \tag{15.51}$$

which are generated from the Ψ_α through time reversal. Under an operation R the functions $\bar{\Psi}_\alpha$ transform as

$$\begin{aligned} R\bar{\Psi}_\alpha &= R\theta\Psi_\alpha = \theta R\Psi_\alpha = \theta \sum_\gamma D_\Gamma(R)_{\gamma\alpha}\Psi_\gamma \\ &= \sum_\gamma D^*_\Gamma(R)_{\gamma\alpha}\theta\Psi_\gamma = \sum_\gamma D^*_\Gamma(R)_{\gamma\alpha}\bar{\Psi}_\gamma, \end{aligned} \tag{15.52}$$

where we have used the facts that the time-reversal operator θ commutes with the operations R of the group G and that it is antilinear. Equation (15.52) shows that the functions $\bar{\Psi}_\alpha$ afford for the group G a representation D^*_Γ which, according to our assumption of real characters, is equivalent to D_Γ; hence there must exist a unitary matrix U

relating the two representations D_Γ and D_Γ^* through the equations

$$D_\Gamma^*(R) = UD_\Gamma(R)U^{-1}. \tag{15.53}$$

The fact that the two representations D_Γ^* and D_Γ are equivalent does not necessarily mean that they can be made to coincide, that is in the present case made real, by a similarity transformation as described by eqn (12.5). In fact it can be shown that the matrices D_Γ can always be made real by a similarity transformation if the square θ^2 of the time-reversal operation is $+1$; on the other hand, D_Γ and D_Γ^*, although equivalent, are always different if $\theta^2 = -1$ (see, for instance, Fano and Racah 1959, Griffith 1961) but we shall not make use of these results in the following.

Instead of the set of matrix elements $(\Psi_\alpha| V_\beta |\Psi_\gamma) = Y_{\alpha\gamma,\beta}$ it is convenient to introduce the mixed matrix elements $(\bar{\Psi}_\alpha| V_\beta |\Psi_\gamma) = Z_{\alpha\gamma,\beta}$. Since the $\bar{\Psi}_\alpha$ form a set of normalized orthogonal functions, spanning the same manifold as the Ψ_α, it is clear that the vanishing of all the $Y_{\alpha\gamma,\beta}$ implies that of the $Z_{\alpha\gamma,\beta}$ and vice versa. Let us then transform the expression $Z_{\alpha\gamma,\beta}$ as follows:

$$\begin{aligned} Z_{\alpha\gamma,\beta} &= (\bar{\Psi}_\alpha| V_\beta |\Psi_\gamma) = (\theta\Psi_\alpha, V_\beta\Psi_\gamma) = (\theta V_\beta\Psi_\gamma, \theta^2\Psi_\alpha) \\ &= (\theta V_\beta\theta^{-1}\theta\Psi_\gamma, \theta^2\Psi_\alpha) = \epsilon_\theta\varepsilon_V(V_\beta^\dagger\bar{\Psi}_\gamma, \Psi_\alpha) \\ &= \epsilon_\theta\varepsilon_V(\bar{\Psi}_\gamma, V_\beta\Psi_\alpha) = \epsilon_\theta\varepsilon_V(\bar{\Psi}_\gamma| V_\beta |\Psi_\alpha) = \varepsilon_\theta\varepsilon_V Z_{\gamma\alpha,\beta}. \end{aligned} \tag{15.54}$$

We can write now:

$$Z_{\alpha\gamma,\beta} = \tfrac{1}{2}(Z_{\alpha\gamma,\beta} + \varepsilon_V\varepsilon_\theta Z_{\gamma\alpha,\beta}). \tag{15.55}$$

It is clear from (15.55) that, depending on the sign of $\varepsilon_V\varepsilon_\theta = \pm 1$, $Z_{\alpha\gamma,\beta}$ belongs to the representation $[\Gamma\times\Gamma]_S\times\Gamma'$ or $[\Gamma\times\Gamma]_A\times\Gamma'$.

In order for this set and therefore also for the set $Y_{\alpha\gamma,\beta} = (\Psi_\alpha| V_\beta |\Psi_\gamma)$ not to vanish identically the unit representation must be contained either in the product $[\Gamma\times\Gamma]_S\times\Gamma'$ or $[\Gamma\times\Gamma]_A\times\Gamma'$ (depending on the sign of $\varepsilon_\theta\varepsilon_V$), rather than simply in the product $(\Gamma\times\Gamma)\times\Gamma'$ as proved in § 12.6. This in turn implies that Γ' must be contained either in $[\Gamma\times\Gamma]_S$ or $[\Gamma\times\Gamma]_A$ depending on the sign of $\varepsilon_\theta\varepsilon_V$.

Let us illustrate these results with a few examples. In § 13.5 we used the Wigner–Eckart theorem to prove that inside a manifold J every vector $\mathbf{V}$ is proportional to the angular momentum $\mathbf{J}$:

$$\mathbf{V} = \alpha\mathbf{J}, \tag{15.56}$$

where the constant α must be real if $\mathbf{V}$ is Hermitian. As the vector $\mathbf{J}$ is time-odd, $\mathbf{V}$ must also be time-odd and $\varepsilon_V = -1$. Since $\mathbf{V}$ transforms according to the representation D^1 of the rotation group, the condition

for a matrix element $(JM|\, V_\beta \,|JM')$ to be different from zero is that $D^J \times D^J$ must contain D^1, which of course it does, if $J \neq 0$, as shown by the relation (13.17). However, our theorem tells us something more: if J is half integer, $\varepsilon_\theta = -1$, $\varepsilon_V \varepsilon_\theta = +1$ and D^1 belongs to $[D^J \times D^J]_S$; if J is an integer, $\varepsilon_\theta = +1$, $\varepsilon_V \varepsilon_\theta = -1$ and D^1 belongs to $[D^J \times D^J]_A$.

A less trivial example is that of the fictitious angular momentum introduced in § 14.2. There again the Wigner–Eckart theorem predicts that, inside a cubic triplet Γ_4 or Γ_5, the matrix elements of the components of a vector **V** are determined within a proportionality constant, because (see Table 2) the direct product $\Gamma_4 \times \Gamma_4$ or $\Gamma_5 \times \Gamma_5$ contains the vector representation Γ_4 only once. Moreover, as shown in this Table, it is the antisymmetric product $[\Gamma_4 \times \Gamma_4]_A$ or $[\Gamma_5 \times \Gamma_5]_A$ that contains Γ_4 and the product $\varepsilon_V \varepsilon_\theta$ must be equal to -1. Since the representations Γ_4 and Γ_5 arise only for an even number of electrons, $\varepsilon_\theta = +1$ and ε_V must be -1. Therefore only time-odd vectors have non-vanishing matrix elements inside the triplet Γ_4 or Γ_5. We anticipated this result when we introduced the fictitious angular momentum (necessarily time-odd) to which every vector must be proportional within the triplets Γ_4 or Γ_5.

15.10. The effect of an applied electric field on a paramagnetic ion

The potential energy of an ion, due to the presence of a homogeneous electric field **E** can be written:

$$V_E = -(-e)\mathbf{E} \cdot \sum_p \mathbf{r}_p = -\mathbf{E} \cdot \mathbf{p}_e, \tag{15.57}$$

where $\sum_p \mathbf{r}_p$ is a summation over the positions of the electrons of the ion and $\mathbf{p}_e = -e \sum_p \mathbf{r}_p$ is here the operator for the electric dipole moment of the ion.

The energy changes induced by the electric perturbation (15.57) can be separated into first-order effects that are linear in **E** and higher-order effects, predominantly quadratic in the field strength, known as polarization effects. The quadratic polarization effects give rise to a change in energy expressed by the usual second-order perturbation formula:

$$\Delta_2 W_E = \sum_n{}' \frac{\langle O|\, \mathbf{E} \cdot \mathbf{p}_e \,|n\rangle\langle n|\, \mathbf{E} \cdot \mathbf{p}_e \,|O\rangle}{W_0 - W_n}. \tag{15.58}$$

The electric fields E that can be conveniently obtained in laboratories are at most of the order of a few thousand volts per millimeter and the

corresponding matrix elements $\langle O|\, \mathbf{p}_e \cdot \mathbf{E}\, |n\rangle$ expressed in wavenumbers turn out to be of the order of one cm^{-1} or so, that is, very much less than the energy separations $W_n - W_0$. The first-order effect of (15.57)

$$\Delta_1 W_E = -\mathbf{E} \cdot \langle \mathbf{p}_e \rangle, \tag{15.59}$$

where the expectation value $\langle \mathbf{p}_e \rangle$ is to be taken over the ground state, or more generally inside the ground manifold if the latter is degenerate, will thus be very much greater than $\Delta_2 W_E$ given by (15.58), unless it vanishes because of selection rules. It is these selection rules that we wish to investigate using a few specific examples.

If the environment and therefore also the Hamiltonian of the paramagnetic ion is invariant through inversion, the ground manifold of the ion has a definite parity positive or negative and in either case $\langle \mathbf{p}_e \rangle$ vanishes because $\mathbf{p}_e$ is a polar (or space-odd) vector which is changed into $-\mathbf{p}_e$ through inversion. On the other hand, if the Hamiltonian of the ion is *not* invariant through inversion, $\langle \mathbf{p}_e \rangle$ *may* be different from zero.

If the starting point of our description of the ion is the free ion placed in a crystal potential $V(\mathbf{r})$, the lack of a centre of symmetry in the environment implies the existence in $V(\mathbf{r})$ of a part V_{odd} that changes its sign through inversion. The energy change linear in $\mathbf{E}$ appears then as a second-order term, cross product between $-(\mathbf{p} \cdot \mathbf{E})$ and V_{odd}. Writing c.c. for the complex conjugate, we have

$$\Delta_1 W_E = -\sum_n{}' \frac{\langle O|\, \mathbf{p} \cdot \mathbf{E}\, |n\rangle\langle n|\, V_{\text{odd}}\, |O\rangle + \text{c . c.}}{W_0 - W_n}, \tag{15.60}$$

where the states $|O\rangle$, $|n\rangle$ and the energies W_0, W_n are those of a free ion. Internal crystal electric fields are usually very much stronger than applied electric fields; the matrix element $\langle n|\, V_{\text{odd}}\, |O\rangle$ is therefore very much larger than $\langle n|\, \mathbf{p} \cdot \mathbf{E}\, |O\rangle$, and correspondingly $\Delta_1 W_E$ as given by (15.60), is very much larger than the polarization term $\Delta_2 W_E$ given by (15.58).

A different approach is first to diagonalize the Hamiltonian of the ion embedded in the crystal and then to calculate the expectation value

$$\Delta_1 W_E = -\langle O|\, \mathbf{p} \cdot \mathbf{E}\, |O\rangle. \tag{15.61}$$

The state $|O\rangle$ in (15.61) is the ground state of the *bound* ion which contains both odd and even admixtures. This approach is more convenient

when covalent rather ionic bonding exists between the ion and its surroundings (see Chapter 20).

We shall now show that the absence of a centre of inversion is only a necessary condition for a change of energy linear with **E** and that selection rules connected with time reversal may also forbid such an effect. The first and very general example is that of a system, whose Hamiltonian is invariant through rotation without being necessarily invariant through inversion (as for instance that of a free molecule). Its energy eigenstates are degenerate manifolds spanned by eigenstates of $\mathcal{J}$. Inside each manifold $\mathcal{J}$, according to eqn (15.56), only time-odd vectors have non-vanishing matrix elements and the expectation value of the dipole moment $\mathbf{p}_e$, which is a time-even vector, vanishes (barring accidental degeneracy).

A second example is an environment of cubic symmetry *without* inversion symmetry that is invariant through the group O (but not O_h!). We have already shown in § 15.9 that only time-odd vectors have non-vanishing matrix elements inside the triplets Γ_4 or Γ_5, and this again precludes a finite expectation value for $\mathbf{p}_e$. It is easy to show that the same is true if the ion has an odd number of electrons, for which the specific representations are Γ_6, Γ_7, Γ_8. In that case, for the time-even vector **p** the product $\varepsilon_V \varepsilon_\theta$ defined in § 15.9 is equal to -1, which means that the vector representation Γ_4 should be contained in one of the antisymmetric products $[\Gamma_6 \times \Gamma_6]_A$, $[\Gamma_7 \times \Gamma_7]_A$, $[\Gamma_8 \times \Gamma_8]_A$ for the matrix elements of $\mathbf{p}_e$ to be non-zero.

We see, however, in Table 8, that none of these products contain Γ_4, and we can state the result that in a cubic environment an electric field cannot produce a first-order change in energy. To dispel a possible misunderstanding, let us emphasize again that it is invariance through time reversal rather than through space inversion which is responsible for this selection rule. This misunderstanding arises sometimes because a cubic environment is usually represented by drawing a cube or an octahedron, a figure that does possess a centre of symmetry, and this may create the mistaken impression that cubic symmetry does imply inversion symmetry. As a counter example one can think, for instance, of a cube with a left hand at each apex; such a figure is invariant through the cubic group of rotations but not through inversion.

At the risk of increasing the confusion a little further we shall show that if the environment of the ion has tetrahedral symmetry and therefore is invariant through the group of improper rotations T_d, which is isomorphic to O, and does not possess a centre of inversion,

an applied electric field *does* produce a linear change in the energy of the ion. The temptation to associate the absence of a linear effect in O and its presence in T_d which is isomorphic to O, with the mistaken notion that O has a centre of inversion, must be resisted.

The gist of the proof for T_d is as follows. The components of a polar vector, which transform like the functions x, y, z under proper or improper rotations and which therefore in the group O span the representation Γ_4, in the group T_d span the representation Γ_5. This can be checked as follows. We have already stated respectively in §§ 14.1 and 14.6 that O and T_d are isomorphic to the group of permutations S_4; now the rotations of O permute among themselves the four body-diagonals of the cube, while the improper rotations of T_d permute the four apexes of the tetrahedron. Let us then consider for instance the permutation (12): for O it means a permutation of the body diagonals 1 and 2, that is a rotation C_2' around one of the six twofold axes passing through the centre points of opposite edges; for T_d it means a reflection in a plane passing through the edge 34 and the centre point of the edge 12. It is easy to check that the matrix for the transformation of (x, y, z) through the transformation (12) has a trace equal to -1 for O and $+1$ for T_d. From the characters in Table 1 (which is the same for isomorphic operations of O and T_d) we conclude that the components x, y, z of a polar vector must span the representation Γ_5 of T_d rather than Γ_4.

We see in Table 8 that Γ_5 is contained once in $[\Gamma_4 \times \Gamma_4]_S$, $[\Gamma_5 \times \Gamma_5]_S$, $[\Gamma_8 \times \Gamma_8]_A$. Therefore in all these multiplets a linear splitting is induced by an applied electric field. In the same way as we replaced a vector inside a multiplet Γ_4 or Γ_5 by a fictitious angular momentum $\tilde{\mathbf{l}}$, within the multiplets Γ_4, Γ_5 and Γ_8 of T_d we can replace the three components of a polar vector, which transform through T_d according to the representation Γ_5, by the three operators

$$\tilde{\mathcal{J}}_y\tilde{\mathcal{J}}_z+\tilde{\mathcal{J}}_z\tilde{\mathcal{J}}_y, \qquad \tilde{\mathcal{J}}_z\tilde{\mathcal{J}}_x+\tilde{\mathcal{J}}_x\tilde{\mathcal{J}}_z, \qquad \tilde{\mathcal{J}}_x\tilde{\mathcal{J}}_y+\tilde{\mathcal{J}}_y\tilde{\mathcal{J}}_x. \quad (15.62)$$

In (15.62) $\tilde{\mathcal{J}}$ is an axial (or space-even) time-odd vector whose components are transformed by T_d according to the representation Γ_4 (in contrast to a polar vector whose components are transformed by T_d as Γ_5). Inside Γ_4 and Γ_5, $\tilde{\mathcal{J}}$ coincides with the fictitious angular momentum $\mathbf{l}$ introduced in § 14.2. Inside Γ_8, as will be explained in more detail in § 18.3, the matrix elements of $\tilde{\mathcal{J}}$ are those of a fictitious angular momentum $\tilde{\mathcal{J}} = \frac{3}{2}$. The splitting of each of the multiplets Γ_4, Γ_5, Γ_8

of T_d by an electric field $\mathbf{E}$ can thus be expressed by a spin Hamiltonian:

$$\mathscr{H}_E = a\{E_x(\tilde{\mathscr{J}}_y\tilde{\mathscr{J}}_z+\tilde{\mathscr{J}}_z\tilde{\mathscr{J}}_y)+E_y(\tilde{\mathscr{J}}_z\tilde{\mathscr{J}}_x+\tilde{\mathscr{J}}_x\tilde{\mathscr{J}}_z)+E_z(\tilde{\mathscr{J}}_x\tilde{\mathscr{J}}_y+\tilde{\mathscr{J}}_y\tilde{\mathscr{J}}_x)\}. \tag{15.63}$$

The combined effect of an electric and a magnetic field

Finally we investigate changes in the energy of the ion which are bilinear in the components of an applied electric field $\mathbf{E}$ and an applied magnetic field $\mathbf{H}$, that is changes in the 'g- tensor'.

For brevity we limit ourselves to the triplets Γ_4 and Γ_5 of the groups T_d and O. (For Γ_8 the situation becomes rather complicated.) The general expression for an operator responsible for such a change should be of the form

$$V_{EH} = \sum_{p,q} H^p E^q \mu_e'^p p_e'^q. \tag{15.64}$$

Here H^p, etc., are components of $\mathbf{H}$, etc., and the vectors $\boldsymbol{\mu}_e'$ and $\mathbf{p}_e'$, which depend on the electronic variables of the ion, have respectively the time and space properties of the magnetic moment $\boldsymbol{\mu}_e$ and of the electric dipole moment $\mathbf{p}_e$; namely, $\boldsymbol{\mu}_e$ is time-odd and space-even, whereas $\mathbf{p}_e$ is time-even and space-odd.

We begin with the group O, within which μ_e' and p_e' each transform as Γ_4. V_{EH} is a time-odd operator that transforms through the group O (see Table 2) according to

$$\Gamma_4\times\Gamma_4 = \Gamma_1+\Gamma_3+\Gamma_4+\Gamma_5. \tag{15.65}$$

Since the operator V_{EH} is time-odd, it will have non-vanishing matrix elements inside the triplets Γ_4 or Γ_5 of the group O only if at least one of the representations on the right-hand side of (15.65) is contained in the antisymmetric products $[\Gamma_4\times\Gamma_4]_A$ or $[\Gamma_5\times\Gamma_5]_A$, $(\varepsilon_\theta\varepsilon_V = -1)$. We see in Table 2 that $[\Gamma_4\times\Gamma_4]_A = [\Gamma_5\times\Gamma_5]_A = \Gamma_4$. Therefore the only part of the operator V_{EH} given by (15.64) which has non-vanishing matrix elements both in Γ_4 and Γ_5 is that which contains the three combinations of the bilinear products $\mu_e'^p p_e'^q$ which transform according to Γ_4. It can be shown that these three combinations are

$$\mu_e'^y p_e'^z - \mu_e'^z p_e'^y, \qquad \mu_e'^z p_e'^x - \mu_e'^x p_e'^z, \qquad \mu_e'^x p_e'^y - \mu_e'^y p_e'^x. \tag{15.66}$$

Within the manifolds Γ_4 or Γ_5 of O they are proportional respectively to $\tilde{\mathscr{J}}_x$, $\tilde{\mathscr{J}}_y$, $\tilde{\mathscr{J}}_z$ and V_{EH} can be represented within Γ_4 or Γ_5 of O as

$$V_{EH} = a\{(H_yE_z-H_zE_y)\tilde{\mathscr{J}}_x+(H_zE_x-H_xE_z)\tilde{\mathscr{J}}_y+(H_xE_y-H_yE_x)\tilde{\mathscr{J}}_z\} \tag{15.67}$$

or in a vector notation as

$$V_{EH} = a(\mathbf{H} \wedge \mathbf{E}) \cdot \tilde{\mathscr{J}}.$$

We see from eqn (15.67) that for the group O, an electric field gives rise to a skew-symmetric contribution to the g-tensor.

We consider now the tetrahedral group T_d: here the space-even vector $\boldsymbol{\mu}'_e$ transforms like Γ_4, that is in the same way as through O, but the polar vector $\mathbf{p}'_e$ transforms like Γ_5 and the operator V_{EH} given by (15.64) transforms like

$$\Gamma_4 \times \Gamma_5 = \Gamma_2 + \Gamma_3 + \Gamma_4 + \Gamma_5. \tag{15.68}$$

For T_d, as for O, only the representation Γ_4 on the right-hand side of (15.68) is contained in $[\Gamma_4 \times \Gamma_4]_A$ and $[\Gamma_5 \times \Gamma_5]_A$. However, the three combinations of $\mu'^{p}_e p'^{q}_e$, which transform like Γ_4 through T_d and which inside the manifold Γ_4 or Γ_5 of T_d can be taken as proportional to $\tilde{\mathscr{J}}_x$, $\tilde{\mathscr{J}}_y$, $\tilde{\mathscr{J}}_z$, are different from (15.66). In this case they are

$$\mu'^{y}_e p'^{z}_e + \mu'^{z}_e p'^{y}_e, \qquad \mu'^{z}_e p'^{x}_e + \mu'^{x}_e p'^{z}_e, \qquad \mu'^{x}_e p'^{y}_e + \mu'^{y}_e p'^{x}_e. \tag{15.69}$$

Within the manifolds Γ_4 or Γ_5 of T_d the operator V_{EH} can therefore be represented as

$$V_{EH} = a\{(H_y E_z + H_z E_y)\tilde{\mathscr{J}}_x + (H_z E_x + H_x E_z)\tilde{\mathscr{J}}_y + (H_x E_y + H_y E_x)\tilde{\mathscr{J}}_z\} \tag{15.70}$$

and we see that the contribution to the g-tensor is symmetrical.

The present discussion is entirely based on symmetry considerations and no attempt is made to investigate the actual physical mechanism responsible for the g-shifts induced by an electric field. (It leans heavily on a set of unpublished lectures given by F. S. Ham in 1967 at the Nato School in Ghent.) Let us say only that an expression such as (15.64) for V_{EH} results in second order from the perturbing electric and magnetic Hamiltonians $-(\boldsymbol{\mu}_e \cdot \mathbf{H})$ and $-(\mathbf{p}_e \cdot \mathbf{E})$ and clearly cannot arise unless the system has states of mixed parity and therefore lacks an inversion centre.

Both of the effects studied above, namely a linear splitting of the energy levels and a linear g-shift, induced by an applied electric field, have been observed on transition ions of the iron group embedded in tetrahedral coordination in silicon (Ludwig and Woodbury 1961, Ham 1961, Ludwig and Ham 1962).