# THE JAHN–TELLER EFFECT
# IN PARAMAGNETIC RESONANCE

## 21.1. Introduction

PARAMAGNETIC resonance of transition elements is studied most conveniently in dilute samples. Given a crystal containing a regular array of diamagnetic ions such as, say, $Zn^{2+}$, a few of these are replaced by paramagnetic ions such as, say, $Cu^{2+}$ or $Mn^{2+}$, whose paramagnetic resonance is then observed. To interpret the results of the observations, the following simplifying assumptions are usually made.

(a) the influence of the environment on the electronic wave-function of the ion can be described by means of a *static* crystal field.

(b) if the paramagnetic ion has the same charge state as the diamagnetic ion which it has replaced, so that no charge compensation occurs, the symmetry (if not the magnitude) of the crystal field it 'sees', is unchanged.

There are, however, cases when these assumptions are invalid. Let us begin by neglecting spin-orbit coupling, a usual procedure in the iron group, and assume that the symmetry of the crystal potential is sufficiently high to leave some orbital degeneracy in the electronic ground state of the paramagnetic ion. In a cubic field this state will be a $\Gamma_3$ doublet or a $\Gamma_5$ triplet for a $D$-state of the free ion, and a $\Gamma_4$ triplet for an $F$-state. There exists a general theorem due to Jahn and Teller (1937) which predicts that such a degenerate state is unstable with respect to small displacements of the neighbouring atoms which lower the symmetry of the crystal field 'seen' by the ion. As a consequence of this theorem, whose precise meaning will be discussed in the following sections, either assumption (a) or (b) may be violated.

(a) The environment of the paramagnetic impurity ion may keep the same symmetry that it had for the diamagnetic ion but the description of this environment by the device of a static crystal field is invalid. This is the so-called dynamic Jahn–Teller effect.

(b) The approximation of using a static crystal field is still valid but this field has a lower symmetry than in the original crystal. This is the so-called static Jahn–Teller effect.

In either case, the consequences for the features of the paramagnetic

resonance spectrum are far-reaching. In the following sections we shall outline the general theoretical treatment of the Jahn–Teller effect, which will then be applied to situations that actually occur in paramagnetic ions.

Since the original work of Jahn and Teller (1937) and the pioneer work of Van Vleck (1939) a large number of articles, some of them of a highly sophisticated nature, have been published on the theory of static and dynamic Jahn–Teller effects. The reader will find in the detailed bibliography of the review article by Ham (1969) the references to the important work of Öpik and Pryce, Liehr, Moffitt and Thorson, Longuet-Higgins, Child, O'Brien, Bersuker, and many others, whose contributions have helped to clarify the various aspects of the theory. In spite of this theoretical effort and in contrast to it, experimental evidence of the existence of the Jahn–Teller effect had until recently been remarkably scarce, with the exception of the pioneer work of Bleaney and his colleagues on $Cu^{2+}$. Neither the reasons for the failure of the Jahn–Teller effect to materialize in the form in which it was expected nor its dependence on the temperature, when observed, were fully understood, in spite of the early work of Abragam and Pryce (1950), which has been considerably expanded, along different lines, by Bersuker (1962, 1963) and O'Brien (1964).

A major advance was achieved with the theoretical work of Ham (1965, 1968, 1969) who was the first to push to its logical consequences the idea, which somehow had escaped general attention, that the Jahn–Teller coupling between the nuclear and the electronic motion had necessarily the same high symmetry as the electronic Hamiltonian responsible for the degeneracy of the paramagnetic ion, and thus could not possibly lift that degeneracy. Ham pointed out that the Jahn–Teller effect whose influence had seemed to be mysteriously absent from certain paramagnetic spectra had been there all the time as large as life if one knew where to look for it. A second major advance has been the discovery by Coffman (1965) and Höchli (1966) of a new type of Jahn–Teller spectrum previously unobserved, which fitted beautifully into the general theory of the dynamic Jahn–Teller effect.

The treatment of this chapter owes much to the ideas and even the presentation of Ham in his two major papers (1965, 1968) and also to his review article (1969) which through his kindness was made available to the authors prior to its publication. This treatment, where the ion and its nearest neighbours are considered as an isolated molecule interacting only through relaxation mechanisms with the rest of the

crystal in which it is embedded, is undoubtedly a gross oversimplification. Its justification is twofold: first a rigorous theory of the Jahn–Teller coupling of the paramagnetic ion to the rest of the lattice simply does not exist at present; secondly, as elsewhere in this book, the most important features of the phenomenon are already determined by the symmetry of the problem, which is built into the approximate treatment to be given below.

We limit the discussion throughout to cubic symmetry. The changes needed when a field of lesser symmetry still leaves an orbital degeneracy, such as a trigonal field applied to a cubic $\Gamma_3$ doublet, are straightforward. Furthermore, we shall see that if these fields are much weaker than the cubic field, their effect is often appreciably quenched by the dynamic Jahn–Teller effect itself.

## 21.2. The Born–Oppenheimer approximation and the Jahn–Teller theorem

Let us make the simplifying assumption that for the electronic state of the paramagnetic ion under consideration we may disregard the influence of the positions (and motions) of all but its nearest neighbours in the crystal. We can then treat the complex $XY_n$ formed by the paramagnetic ion $X$ and its $n$ nearest neighbours $Y$ ($n = 6$ for octahedral and 4 for tetrahedral coordination) as a single molecule and we start by recalling the general method for finding its equilibrium configuration. The Hamiltonian $\mathscr{H}$ of the molecule can be written

$$\mathscr{H} = T + V = T_e + T_N + V_{ee} + V_{eN} + V_{NN}, \tag{21.1}$$

where the various terms of (21.1) are respectively the kinetic energy of the electrons and of the nuclei, together with the Coulomb interactions between the electrons, between electrons and nuclei, and between nuclei (smaller magnetic interactions are disregarded at this stage of approximation). Let the symbol $q$ represent the $3n$ coordinates of the $n$ electrons of the molecule and $Q$ the $3N$ coordinates of its $N$ nuclei. Equation (21.1) can then be rewritten as

$$\mathscr{H} = T + V = T_e(p) + T_N(P) + V_{ee}(q) + V_{eN}(q, Q) + V_{NN}(Q) \tag{21.1a}$$

where $p$ and $P$ are momenta conjugate to $q$ and $Q$. An eigenfunction $\Phi(q, Q)$ of (21.1a) satisfies the Schrödinger equation

$$\mathscr{H}\Phi(q, Q) = W\Phi(q, Q). \tag{21.1b}$$

These eigenfunctions are found by the following approximate

procedure due to Born and Oppenheimer (1927). The nuclear coordinates $Q$ are given some fixed numerical values $Q'$ (the nuclei are 'nailed down'), and the electronic Hamiltonian

$$\mathscr{H}_e(q, Q') = \mathscr{H} - T_N(P) = T_e(p) + V(q, Q'), \qquad (21.2)$$

where $Q'$ is a set of *numerical* parameters, is then diagonalized. Let $\varphi_{Q'}(q)$ be an eigenstate and $U(Q')$ the corresponding eigenvalue of (21.2) so that

$$\mathscr{H}_e(q, Q')\varphi_{Q'}(q) = U(Q')\varphi_{Q'}(q). \qquad (21.3)$$

This task is repeated for all values of $Q'$ in order to determine the function $U(Q')$. The complete wave-function of the molecule, the solution of (21.1b), is then sought in the so-called Born–Oppenheimer form

$$\Phi(q, Q) = \varphi_Q(q)\Psi(Q), \qquad (21.4)$$

where $\Psi(Q)$ is the nuclear part of the molecular wave-function. Introducing (21.4) into (21.1b) and making use of (21.2) and (21.3), one obtains the following equation for $\Psi(Q)$:

$$\{T_N(P) + U(Q)\}\Psi(Q) \approx W\Psi(Q). \qquad (21.5)$$

Equation (21.5) is only approximately correct: it is obtained by making the assumption

$$T_N\{\varphi_Q(q)\Psi(Q)\} \approx \varphi_Q(q)T_N\Psi(Q)$$

and implies that the electronic wave-function $\varphi_Q(q)$ is relatively insensitive to small nuclear displacements. A general discussion of the validity of this assumption, which relies on the smallness of the ratio of the electronic to nuclear masses, is outside the scope of this book. It is clear that it will in general become invalid in cases of degeneracy or near degeneracy when two eigenvalues of (21.3), $U_i(Q')$ and $U_j(Q')$, corresponding to two eigenstates $\varphi_{Q'}^i(q)$ and $\varphi_{Q'}^j(q)$ come very close to each other, because the kinetic energy terms neglected in (21.5) may appreciably mix these two states. This constitutes a failure of the Born–Oppenheimer approximation.

The Born–Oppenheimer procedure can now be summarized as follows. With the nuclei nailed down at positions $Q'$, the electronic eigenfunction $\varphi_{Q'}(q)$ and the electronic energy $U(Q')$ are found for all values of $Q'$. One then forgets completely about the electrons and solves a Schrödinger equation of motion for the nuclei, the inter-nuclear potential energy being precisely the electronic energy $U(Q)$ obtained previously by solving (21.3).

To find the equilibrium shape of the molecule (or of the paramagnetic complex $XY_n$, embedded in the crystal) one then seeks the minimum of the potential energy $U(Q)$, which requires a knowledge of the derivatives $\partial U/\partial Q_j$. Their calculation is facilitated by a remark due to Feynman (1939). From the relation

$$U(Q) = \langle \varphi_Q(q)| \ \mathscr{H}^e_Q(q) \ |\varphi_Q(q)\rangle, \qquad (21.6)$$

we find

$$\frac{\partial U}{\partial Q_j} = \langle \varphi_Q(q)| \frac{\partial \mathscr{H}^e_Q(q)}{\partial Q_j} |\varphi_Q(q)\rangle + U(Q)\frac{\partial}{\partial Q_j}\langle \varphi_Q \mid \varphi_Q \rangle. \qquad (21.6a)$$

The last term vanishes because $\varphi_Q(q)$ is normalized, so that

$$\frac{\partial U}{\partial Q_j} = \left\langle \frac{\partial \mathscr{H}^e_Q(q)}{\partial Q_j} \right\rangle = \left\langle \frac{\partial V}{\partial Q_j} \right\rangle, \qquad (21.7)$$

the expectation value being taken over an eigenstate $\varphi_Q(q)$ of (21.3). What the relation (21.7) means is this: suppose that for a set $Q_0$ of values of $Q$ the electronic wave-function $\varphi_{Q_0}(q)$ is either known or can be guessed from, say, symmetry considerations. In order to determine whether this set $Q_0$ corresponds to a minimum of $U(Q)$ it is *not* necessary to calculate $\partial U/\partial Q_j$ at $Q_0$, that is $U(Q)$ in the neighbourhood of $Q_0$. Rather, it is enough to calculate the expectation value, over $\varphi_{Q_0}(q)$, of the derivative $\partial V/\partial Q_j$ of the Coulomb energy whose expression, $V_{ee}(q)+V_{eN}(q, Q)+V_{NN}(Q)$, is naturally known. Formula (21.7) also follows directly from the well-known result of first-order perturbation theory whereby the first-order change in the energy is equal to the expectation value of the change in the potential, taken over the unperturbed wave-function.

Once the set of values $Q_0$ has been found which minimizes $U(Q)$, the latter is expanded as a quadratic form of the differences $Q_i - Q_{0i}$ and the vibrational motion of the nuclei around the equilibrium position $Q_0$ can be considered as harmonic. If one is not interested in nuclear vibrations one may solve the electronic equation (21.3) by giving to the nuclear coordinates $Q'$ the experimental values as found, for instance, from X-ray measurements of internuclear distances. This, however, is only an approximation, as will appear later in more detail.

If the central ion of the complex is a diamagnetic ion already non-degenerate when free, the minimum of $U(Q)$ will often occur for a set of values $Q_0$ such that the complex has a high symmetry, such as cubic. If the nucleus of the diamagnetic ion $X'$ has a spin $I > \frac{1}{2}$ this symmetry can be verified, for example, from the observation of its nuclear

resonance and the absence of any quadrupole splitting. What happens then if we replace the diamagnetic ion $X'$ by a paramagnetic ion $X$ which, when free, possesses an orbital degeneracy in its ground state? Let us nail down the nuclei at positions $Q_0$ in the paramagnetic complex $XY_n$ such that it has the same *symmetry* as the equilibrium position of the diamagnetic complex $X'Y_n$ (the overall *scale* may be different). The ground level $\Gamma$ of the ion $X$ in the environment created by its neighbours $Y$ may then still have some degeneracy left ($\Gamma_3$, $\Gamma_4$, or $\Gamma_5$). What the Jahn–Teller theorem says is that it is always possible, by shifting some of the nuclei, to lower the energy of at least one of the states that span the ground level.

In order to put the discussion on a quantitative basis some definitions are required. Let us consider as an example the octahedral complex $XY_6$ where the coordinates of the various atoms ($i = 1, \ldots, 6$) have in the cubic symmetry position $Q_0$ the following values $x_\alpha^{0i}$: $(a, 0, 0)$, $(0, a, 0)$, $(0, 0, a)$, $(-a, 0, 0)$, $(0, -a, 0)$, $(0, 0, -a)$. Any distortion or displacement of the complex is defined by the values of the 18 displacements $X_\alpha^i = x_\alpha^i - x_\alpha^{0i}$. Under symmetry operations of the cubic group the quantities $X_\alpha^i$ transform into themselves, providing a representation of the cubic group which is reducible. It is more convenient to introduce the so-called normal coordinates $Q_j$, linear combinations of the $X_\alpha^i$ which transform according to *irreducible* representations of the cubic group. These combinations are obtained by the standard methods of group theory. Three linear combinations of the $X_\alpha^i$ correspond to rotations without distortion of the octahedron $XY_6$ as a whole. They are of no interest to us in so far as we disregard interactions between the complex and the crystal wherein it is embedded. The fifteen remaining combinations transform according to a representation $\bar{\Gamma}$ which can be reduced as follows:

$$\bar{\Gamma} = \Gamma_1 + \Gamma_{3g} + \Gamma_{5g} + \Gamma_{5u} + \Gamma_{4u}^a + \Gamma_{4u}^b \qquad (21.8)$$

where the suffixes g and u mean even and odd. The indices a and b mean that $\Gamma_{4u}$ is contained twice in $\bar{\Gamma}$. As explained in § 14.6, only the even displacements are expected to change the potential energy of the complex in first order.

The explicit expressions of the $Q_i$ as functions of the $X_\alpha^i$ are given for the even representations in Table 26. Similar expressions can be written for $Q_7$ to $Q_{15}$ but we shall not require them. From now on when we write the Coulomb energy as $V(q, Q)$ and the potential energy as

$U(Q)$, where $Q$ stands for the set of normal coordinates defined above (suitably modified for groups other than $O_h$).

We now return to the ground manifold of the paramagnetic ion $X$ within the complex $XY_n$, a manifold spanned by the wave-functions $\varphi_Q^p(q)$ which obey the relations

$$\langle \varphi_Q^p(q)| \; \mathcal{H}_Q^e(q) \; |\varphi_Q^r(q)\rangle = \delta_p^r U_p(Q). \qquad (21.9)$$

We have made the assumption that this manifold is degenerate when the complex has a symmetrical shape invariant through a group $\mathcal{G}$. This occurs when all normal coordinates $Q_i$ are set equal to $Q_i^0 = 0$. Equation (21.9) then becomes

$$\langle \varphi_{Q_0}^p(q)| \; \mathcal{H}_{Q_0}^e(q) \; |\varphi_{Q_0}^r(q)\rangle = \langle p| \; \mathcal{H}_0^e(q) \; |r\rangle = \delta_r^p \, U(0) \qquad (21.10)$$

where we write for brevity $|\varphi_{Q_0}^r(q)\rangle = |r\rangle$ and $\mathcal{H}_{Q_0}^e(q) = \mathcal{H}_0^e$.

The functions $|r\rangle$ provide a basis for an irreducible representation $\Gamma$ of the group $\mathcal{G}$. If the normal coordinates are given small values $Q^j$, the potential $V(q, Q)$ will change in first approximation by an amount

$$\delta V \approx \sum_j V_j(q, 0)Q_j. \qquad (21.11)$$

Since $\delta V$ is clearly left unchanged by an operation of the group $\mathcal{G}$ acting simultaneously on the nuclear coordinates $Q$ *and* on the electronic coordinates $q$, the electronic operators $V_j(q, 0)$ must provide the same irreducible representations $\Gamma'$ of $\mathcal{G}$ as the $Q_j$. According to the rules of first-order perturbation theory, the changes in the energy $U(0)$ of the degenerate manifold caused by the term (21.11) are given by the eigenvalues of the matrix

$$\langle p| \; \delta V \; |r\rangle = \sum_j \langle p| \, V_j \, |r\rangle Q_j.$$

As shown in § 12.6 the degeneracy of the manifold $\Gamma$ will be lifted by the perturbation $V_j$ belonging to a representation $\Gamma'$ of $\mathcal{G}$ (different from the unit representation) if the direct product $\Gamma^* \times \Gamma \times \Gamma'$ contains the unit representation. The case where $\Gamma'$ is the unit representation corresponds to the totally symmetric (or breathing) mode, which simply changes the scale of the complex without altering its shape. The degenerate energy level of the complex is then shifted without being split.

The proof of the Jahn–Teller theorem consists in a systematic check, for all point-groups $\mathcal{G}$, that there always exists at least one representation $\Gamma'$, different from the unit representation, such that $\Gamma^* \times \Gamma \times \Gamma'$ contains the unit representation (excluding the case of a linear complex and

that of Kramers degeneracy). $\Gamma$ is an irreducible representation of $\mathscr{G}$ with more than one dimension, and $\Gamma'$ is one of the representations spanned by the normal coordinates of the complex which is left invariant through operations of $\mathscr{G}$.

The sum of the energy displacements induced by $V_j$ is equal to the trace $\sum_p \langle p| V_j |p \rangle$ which has been shown to vanish (eqn (12.40b)), (unless $V_j$ belongs to the unit representation $\Gamma_1$). It follows that for $|Q| \neq 0$ and sufficiently small there will always be at least one electronic energy level *lower* than the degenerate level for $Q = 0$.

We shall concern ourselves almost exclusively with cubic symmetry. The situation is very different depending on whether the degenerate multiplet is the doublet $\Gamma_3$ or the triplet $\Gamma_4$ or $\Gamma_5$ and we shall deal with them successively, starting with the doublet.

### 21.3. The magnetic properties of a $^2E$ level

It has already been stated (§ 14.2) that the doublet $\Gamma_3$ is non-magnetic. This statement, which means that inside the manifold $\Gamma_3$ a vector operator $\mathbf{V}$ has vanishing matrix elements, is a consequence of the reduction formula of the direct product (Table 2)

$$\Gamma_3 \times \Gamma_3 = \Gamma_3 + \Gamma_1 + \Gamma_2. \qquad (21.12)$$

Let $\theta$ and $\varepsilon$ be the two wave-functions that span the doublet $\Gamma_3$ and transform respectively like $(3z^2 - r^2)$ and $\sqrt{(3)}(x^2 - y^2)$ under the operation of the cubic group. Under a rotation $R$ of $2\pi/3$ or $R^2$ of $4\pi/3$ around the body diagonal [111] of the cube, these functions transform according to the formulae (14.4) which we reproduce here for convenience:

$$R\theta = -\frac{\theta}{2} + \frac{\sqrt{3}}{2}\varepsilon, \qquad R^2\theta = -\frac{\theta}{2} - \frac{\sqrt{3}}{2}\varepsilon;$$

$$R\varepsilon = -\frac{\sqrt{3}}{2}\theta - \frac{\varepsilon}{2}, \qquad R^2\varepsilon = \frac{\sqrt{3}}{2}\theta - \frac{\varepsilon}{2}. \qquad (21.13)$$

The normal coordinates $Q_3$ and $Q_2$ of Table 26 transform under the operation of the cubic group in the same way as $\theta$ and $\varepsilon$, and for this reason are often written as $Q_\theta$ and $Q_\varepsilon$.

Let $X = X_1 - X_4$, $Y = Y_2 - Y_5$, $Z = Z_3 - Z_6$ be the axial distortions of an octahedral complex $(XY_6)$. If the totally symmetrical (or 'breathing') coordinate $Q_1 = X + Y + Z$ is given the value zero, the quantities $X$, $Y$, and $Z$ are expressed by the following relations extracted from Table 26:

$$X = Q_2 - \frac{Q_3}{\sqrt{3}}, \qquad Y = -Q_2 - \frac{Q_3}{\sqrt{3}}, \qquad Z = \frac{2Q_3}{\sqrt{3}}. \qquad (21.14)$$

If we define two new variables $\varphi$ and $\rho$ by the formulae

$$Q_2 \equiv Q_\varepsilon = \rho \sin \varphi, \qquad Q_3 \equiv Q_\theta = \rho \cos \varphi, \qquad (21.15)$$

eqn (21.14) can be rewritten

$$Z = \frac{2\rho \cos \varphi}{\sqrt{3}}, \qquad X = \frac{2\rho}{\sqrt{3}} \cos\left(\varphi - \frac{2\pi}{3}\right), \qquad Y = \frac{2\rho}{\sqrt{3}} \cos\left(\varphi + \frac{2\pi}{3}\right).$$
$$(21.16)$$

We see that a cyclical permutation $X \to Y \to Z \to X$ can be described by successive changes $2\pi/3$ in the angle $\varphi$, which can thus be given the geometrical interpretation of a rotation through the angle $2\pi/3$ around the body diagonal [111]. For a given value of $\rho$, $\varphi = 0$ corresponds, according to (21.16), to an elongation of the octahedron along the $z$-axis, $\varphi = 2\pi/3$ along the $x$-axis, and $\varphi = -2\pi/3$ along the $y$-axis. Values of $\varphi = \pi$, $\pi + 2\pi/3$, and $\pi - 2\pi/3$ correspond to compressions of the octahedron along the same axes.

If two representations $\Gamma_3$ are spanned respectively by the two pairs $(\theta, \varepsilon)$ and $(\theta', \varepsilon')$ the direct product $\Gamma_3 \times \Gamma_3$ is spanned by the four products $\theta\theta'$, $\varepsilon\varepsilon'$, $\theta\varepsilon'$, $\varepsilon\theta'$. The linear combinations of these which span the irreducible representations, $\Gamma_1$, $\Gamma_2$, $\Gamma_3$ of the right hand of (21.12) are

$$(E)\Gamma_3 : \begin{cases} \theta'' = \varepsilon\varepsilon' - \theta\theta', \\ \varepsilon'' = \varepsilon\theta' + \theta\varepsilon', \end{cases}$$
$$(A_1)\Gamma_1 : \qquad \theta\theta' + \varepsilon\varepsilon', \qquad\qquad (21.17)$$
$$(A_2)\Gamma_2 : \qquad \theta\varepsilon' - \varepsilon\theta'.$$

The formulae (21.17) are easily obtained by standard methods of group theory or, in view of their simplicity, by direct inspection. It is clear from (21.15) and (21.17) that $\rho^2 = Q_\theta^2 + Q_\varepsilon^2$ is an invariant and that $\cos \varphi$ and $\sin \varphi$ transform like $\theta$ and $\varepsilon$; $\cos 2\varphi = \cos^2\varphi - \sin^2\varphi$ and $\sin 2\varphi = 2 \cos \varphi \sin \varphi$ transform like $-\theta$ and $\varepsilon$. The quantity

$$\cos 3\varphi = \cos 2\varphi \cos \varphi - \sin 2\varphi \sin \varphi$$

transforms like $-(\theta\theta' + \varepsilon\varepsilon')$ and is thus an invariant belonging to the unit representation $\Gamma_1$, whereas $\sin 3\varphi = \sin 2\varphi \cos \varphi + \sin \varphi \cos 2\varphi$ transforms like $\varepsilon'\theta - \theta'\varepsilon$ and belongs to the unidimensional representation $\Gamma_2(A_2)$.

Inside the manifold $\Gamma_3$ spanned by the functions $|\theta\rangle$ and $|\varepsilon\rangle$ all Hermitian operators can be expressed as a linear combination of the

four Pauli matrices

$$\sigma_1 = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} = |\theta\rangle\langle\varepsilon| + |\varepsilon\rangle\langle\theta|, \qquad \mathscr{I} = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} = |\theta\rangle\langle\theta| + |\varepsilon\rangle\langle\varepsilon|,$$

$$\sigma_2 = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} = i\{|\varepsilon\rangle\langle\theta| - |\theta\rangle\langle\varepsilon|\}, \quad \sigma_3 = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} = |\theta\rangle\langle\theta| - |\varepsilon\rangle\langle\varepsilon|.$$

(21.18)

A comparison of (21.18) with (21.17) shows that $\sigma_1$ and $\sigma_3$ transform respectively as $\varepsilon$ and $-\theta$ and for that reason, when they operate on the substates $|\theta\rangle$ and $|\varepsilon\rangle$ of a doublet $\Gamma_3$, they are usually written in the literature as: $\sigma_1 = U_\varepsilon$ and $\sigma_3 = -U_\theta$. Similarly $\sigma_2$, according to (21.17) and (21.18), belongs to the unidimensional representation $\Gamma_2$ and is usually written as $\sigma_2 = A_2$.

An alternative proof of the fact that $\sigma_3$, $\sigma_1$, $\sigma_2$ transform like $-\theta$, $\varepsilon$, and $A_2$, of which we shall make use very shortly, is as follows.

Consider the following Hermitian tensor operators

$$U'_\theta = \tfrac{1}{6}\{3L_z^2 - L(L+1)\}, \qquad U'_\varepsilon = \tfrac{1}{6}\sqrt{(3)}(L_x^2 - L_y^2),$$

$$A'_2 = -\frac{1}{\sqrt{3}}P(L_xL_yL_z),$$

(21.19)

where $L_x$, $L_y$, $L_z$ are the components of an orbital momentum in a $D$ state, $L = 2$, and $P(L_xL_yL_z)$ is the symmetrized product

$$\tfrac{1}{6}(L_xL_yL_z + L_yL_xL_z + \dots).$$

From their expressions (21.19) it is clear that the operators $U'_\theta$, $U'_\varepsilon$ transform respectively like $\theta$ and $\varepsilon$ of $\Gamma_3$ and that $A'_2$ belongs to the representation $\Gamma_2$.

Let us consider the particular doublet $\Gamma_3$, which is obtained from the splitting of a $D$ term and, according to Table 4, is spanned by the two functions

$$\theta = |0\rangle, \qquad \varepsilon = \frac{|2\rangle + |-2\rangle}{\sqrt{2}}.$$

(21.20)

An elementary calculation of the matrix elements of the operators (21.19) shows that inside this manifold the operators $U'_\theta$, $U'_\varepsilon$, and $A'_2$ are represented by the matrices $-\sigma_3$, $\sigma_1$, and $\sigma_2$, which shows that the latter do indeed transform like $\theta$, $\varepsilon$, and $A_2$. Being true for a particular manifold $\Gamma_3$ spanned by the functions (21.20), this result is clearly true whatever the nature of the manifold.

Although the existence of a $\Gamma_3$ doublet in a static crystal field is

not allowed by the Jahn–Teller theorem, it is interesting, and also very useful as we shall see shortly, to derive the spin Hamiltonian and the paramagnetic spectrum to be expected from a $^2\Gamma_3$ ground level, originating in the $^2D$ term of a paramagnetic ion, split by a cubic field. It turns out that our former treatment of the ions of type $A$ with a non-degenerate ground state $|O\rangle$ (in § 19.2) can be adapted with very little change to the present situation provided it is understood that the symbol $|O\rangle$ now means the twofold degenerate orbital ground manifold $\Gamma_3$. An expectation value such as say $\langle O|\,L_pL_q+L_qL_p\,|O\rangle$ now becomes an operator within this manifold represented by a $2\times 2$ matrix, that is by linear combination of the Pauli matrices $-U_\theta$, $U_\varepsilon$, $A_2$, and $\mathscr{I}$.

Let us consider, for instance, with this new interpretation where $|O\rangle$ is the ground manifold $\Gamma_3$, the expression given by formula (19.19),

$$\Lambda_{pq} = \sum_n{}' \frac{\langle O|\,L_p\,|n\rangle\langle n|\,L_q\,|O\rangle}{W_n-W_0}$$

or, since $\Lambda_{pq} = \Lambda_{qp}$,

$$\Lambda_{pq} = -\tfrac{1}{2}\langle O|\,L_pCL_q+L_qCL_p\,|O\rangle, \tag{21.21}$$

where $C$(eqn (19.17)) is the operator $-\sum_n{}' |n\rangle\langle n|/(W_n-W_0)$. The energy difference $W_n-W_0$ has the single value $\Delta = 10Dq$ equal to the distance between the ground doublet $\Gamma_3$ and the excited triplet $\Gamma_5$. We can thus write $C = -(1/\Delta)\{1-|O\rangle\langle O|\}$ where $1$ is the unit operator ($1$ is the unit operator inside the whole manifold $D$ rather than inside the more restricted manifold $\Gamma_3$ where it is represented by the unit $2\times 2$ matrix $\mathscr{I}$). Carrying this expression of $C$ into (21.21) and taking into account that $\langle O|\,L_p\,|O\rangle = 0$ for all $p$ (because the $\Gamma_3$ doublet is non-magnetic) we obtain

$$\Lambda_{pq} = \frac{1}{2\Delta}\langle O|\,L_pL_q+L_qL_p\,|O\rangle \tag{21.22}$$

or, since it is more convenient to deal with traceless tensors,

$$\left.\begin{array}{l}\Lambda_{pq} = \tilde{\Lambda}_{pq}+\delta_{pq}\Lambda_0 \text{ where } \Lambda_0 = \dfrac{L(L+1)\mathscr{I}}{3\Delta} = \dfrac{2\mathscr{I}}{\Delta}, \\[2mm] \tilde{\Lambda}_{pq} = \dfrac{1}{3\Delta}\langle O|\,\tfrac{3}{2}(L_pL_q+L_qL_p)-L(L+1)\,|O\rangle.\end{array}\right\} \tag{21.23}$$

Because of the reduction formula (21.12) the only components of the

tensor operator $\tilde{\Lambda}$ that do not vanish are

$$\tilde{\Lambda}_\theta = \frac{1}{6\Delta}\langle 0|\ 3L_z^2 - L(L+1)\ |0\rangle,$$

$$\tilde{\Lambda}_\varepsilon = \frac{1}{6\Delta}\sqrt{(3)}\langle 0|\ L_x^2 - L_y^2\ |0\rangle, \tag{21.24}$$

which we can identify, using (21.19), with $U_\theta/\Delta$ and $U_\varepsilon/\Delta$ and also $\Lambda_0 = 2\mathscr{I}/\Delta$. The Zeeman coupling given, according to (19.22) by the formula $Z = \beta H_p S_q(g_s\delta_{pq} - 2\lambda\Lambda_{pq})$, can now be written as

$$Z = \beta(\mathbf{H}\cdot\mathbf{S})(g_s\mathscr{I} - 2\lambda\Lambda_0) -$$
$$- 2\lambda\beta\{(3H_zS_z - \mathbf{H}\cdot\mathbf{S})\tilde{\Lambda}_\theta + (H_xS_x - H_yS_y)\sqrt{(3)}\tilde{\Lambda}_\varepsilon\}, \tag{21.25}$$

which we can rewrite as

$$Z = g_1\beta(\mathbf{H}\cdot\mathbf{S}) + \frac{g_2\beta}{2}\{(3H_zS_z - \mathbf{H}\cdot\mathbf{S})U_\theta + \sqrt{(3)}(H_xS_x - H_yS_y)U_\varepsilon\} \tag{21.26}$$

with, according to (21.24) and (21.25),

$$g_1 = g_s - \frac{4\lambda}{\Delta},$$

$$g_2 = -\frac{4\lambda}{\Delta}. \tag{21.27}$$

It should be noted that formula (21.26) is more general than (21.27). Indeed, once we had established through eqns (21.17) and (21.18) the transformation laws of the operators $U_\theta$ and $U_\varepsilon$, eqn (21.26) could have been written *a priori* as the only invariant Zeeman spin Hamiltonian for any $^2\Gamma_3$ level. On the other hand, eqn (21.27) assumes explicitly that the level $^2\Gamma_3$ originates in the splitting by a cubic field of a $^2D$ term.

Taking (21.26) as a starting point, the values (21.27) for $g_1$ and $g_2$ could have been derived directly by correlating them to the values of $g_\parallel(\theta)$ and $g_\parallel(\varepsilon)$ which are the values of $g_\parallel$ in tetragonal symmetry with either $\theta$ or $\varepsilon$ as the non-degenerate ground level. It is indeed sufficient to take the expectation value of (21.26) either in the state $\theta$ or $\varepsilon$ to see that

$$g_\parallel(\theta) = g_1 - g_2, \qquad g_\parallel(\varepsilon) = g_1 + g_2; \tag{21.28}$$

$g_\parallel(\theta)$ and $g_\parallel(\varepsilon)$ are given directly by the formulae (19.19) and (19.32) for ions of type $A$.

This remark will be helpful in writing down the hyperfine coupling with the nuclear spin. From invariance arguments this coupling is

necessarily of the form

$$A_1(\mathbf{I} . \mathbf{S}) + \frac{A_2}{2}\{(3I_zS_z - \mathbf{I} . \mathbf{S})U_\theta + \sqrt{(3)}(I_xS_x - I_yS_y)U_\varepsilon\} \quad (21.29)$$

where, as before, $A_1$ and $A_2$ can be correlated to $A_{\parallel}(\theta)$ and $A_{\parallel}(\varepsilon)$ obtained in tetragonal symmetry,

$$A_{\parallel}(\theta) = A_1 - A_2, \quad A_{\parallel}(\varepsilon) = A_1 + A_2. \quad (21.30)$$

Using the formula (19.32) for the hyperfine coupling where $\xi$ is given by (17.46) we find, writing $\mathscr{P}$ for $2\gamma_n\hbar\beta\langle r^{-3}\rangle = 2g_n\beta\beta_n\langle r^{-3}\rangle$ (see eqn (19.10)),

$$A_1 = -\mathscr{P}\left(\kappa + \frac{4\lambda}{\Delta}\right),$$

$$A_2 = -\mathscr{P}\left\{6\xi + \frac{4\lambda}{\Delta} + \left(\frac{9\lambda}{\Delta}\right)\xi\right\}. \quad (21.31)$$

For a $^2D$ term $\xi = \frac{2}{21}$.

The next problem is to find the resonance spectrum associated with the Zeeman Hamiltonian (21.26). Actually this problem has already been solved earlier in connection with the Zeeman effect of the $\Gamma_8$ quadruplet. When a spin $\frac{1}{2}$ is included the doublet $\Gamma_3$ becomes the fourfold level $D^{\frac{1}{2}} \times \Gamma_3 = \Gamma_6 \times \Gamma_3 = \Gamma_8$. The four states $|\theta, +\rangle$, $|\theta, -\rangle$, $|\varepsilon, +\rangle$, $|\varepsilon, -\rangle$ that span $\Gamma_3 \times \Gamma_6$ are linear combinations of the states $|\tilde{m}\rangle = |\frac{3}{2}\rangle, |\frac{1}{2}\rangle, |-\frac{1}{2}\rangle, |-\frac{3}{2}\rangle$ that span $\Gamma_8$ and were introduced in § 14.4. Actually the correspondence turns out to be very simple; it is

$$|\widetilde{\tfrac{3}{2}}\rangle = |\varepsilon, -\rangle; \ |\widetilde{\tfrac{1}{2}}\rangle = |\theta, +\rangle; \ |-\widetilde{\tfrac{1}{2}}\rangle = -|\theta, -\rangle; \ |-\widetilde{\tfrac{3}{2}}\rangle = -|\varepsilon, +\rangle. \quad (21.32)$$

To check the correspondence (21.32) we take again for $\theta$ and $\varepsilon$ the kets $|0\rangle$ and $(1/\sqrt{2})\{|2\rangle + |-2\rangle\}$ used previously. Under a rotation of $\pi/2$ around the axis $Oz$ the ket $|\widetilde{\tfrac{3}{2}}\rangle$ is multiplied by definition by $e^{3i\pi/4}$. The ket $\varepsilon = (1/\sqrt{2})\{|2\rangle + |-2\rangle\}$ is multiplied by $e^{i\pi}$ and the ket $|\varepsilon, -\rangle$ by $e^{3i\pi/4}$. It is easy to check that it is the only such one among the four kets $|\theta, \pm\rangle$, $|\varepsilon, \pm\rangle$. The first equality (21.32) is thus established and similarly for the others. The eigenvalues of the spin Hamiltonian (21.26) (divided by $\beta H$) are then given by the secular equation (18.30) where from (21.26) and (21.32) the coefficients $P$ and $Q$ are the expectation values,

$$P = \langle\varepsilon, -| \ g_1S_z\mathscr{I} + g_2S_zU_\theta \ |\varepsilon, -\rangle = -\frac{(g_1+g_2)}{2},$$

$$Q = \langle\theta, +| \ g_1S_z\mathscr{I} + g_2S_zU_\theta \ |\theta, +\rangle = \frac{g_1-g_2}{2}. \quad (21.33)$$

In practice we shall be concerned only with the case when $|g_2| \ll |g_1|$, that is $P \approx -Q$ or $|P+Q| \ll |P, Q|$. The roots of the secular equation (18.30) then take an approximate form that is rather simple. We shall not write them down, however, for in the case when $|g_2| \ll |g_1|$ it is more illuminating to write directly an approximate solution of (21.26).

Let $\xi$, $\eta$, $\zeta$ be the cosines of the direction $OZ$ of the magnetic field. The first term of (21.26) is $g_1 \beta H S_Z$ and the second term becomes, in first-order perturbation theory,

$$\frac{g_2 \beta H S_Z}{2}\{(3\zeta^2 - 1)U_\theta + \sqrt{(3)}(\xi^2 - \eta^2)U_\varepsilon\}.$$

The eigenvalues of (21.26) are then clearly (with $M = \pm \tfrac{1}{2}$)

$$g_1 \beta H M \pm g_2 \beta \frac{HM}{2}\{(3\zeta^2 - 1)^2 + 3(\xi^2 - \eta^2)^2\}^{\frac{1}{2}}$$
$$= \beta H M[g_1 \pm g_2\{1 - 3(\xi^2\eta^2 + \eta^2\zeta^2 + \zeta^2\xi^2)\}^{\frac{1}{2}}]. \quad (21.34)$$

There are two resonance frequencies,

$$h\nu = \beta H[g_1 \pm g_2\{1 - 3(\xi^2\eta^2 + \eta^2\zeta^2 + \zeta^2\xi^2)\}^{\frac{1}{2}}], \quad (21.34a)$$

and the four eigenstates are

$$|\pm\rangle\left\{\theta \cos\frac{\omega}{2} - \varepsilon \sin\frac{\omega}{2}\right\}, \; |\pm\rangle\left\{\theta \sin\frac{\omega}{2} + \varepsilon \cos\frac{\omega}{2}\right\}, \quad (21.35)$$

where $\omega$ is defined by

$$\cos\omega = \frac{(3\zeta^2 - 1)}{2}\{1 - 3(\xi^2\eta^2 + \eta^2\zeta^2 + \zeta^2\xi^2)\}^{-\frac{1}{2}},$$

$$\sin\omega = \frac{\sqrt{3}}{2}(\xi^2 - \eta^2)\{1 - 3(\xi^2\eta^2 + \eta^2\zeta^2 + \zeta^2\xi^2)\}^{-\frac{1}{2}}. \quad (21.36)$$

The spectrum is clearly anisotropic, and the two frequencies $\nu_1$ and $\nu_2$ become equal when the field is along a body diagonal of the cube where the cubic invariant in curly brackets vanishes.

Whereas the assumption $|g_1| \gg |g_2|$ is legitimate when $g_2$ is of the order $(\lambda/\Delta)$, a similar assumption $|A_1| \gg |A_2|$ is not warranted unless the coefficient $\kappa$, which represents the core polarization in (21.31), happens to be large. When $|A_1| \gg |A_2|$ the eigenvalues of the spin Hamiltonian, sum of (21.26) and (21.29), are given by

$$W_{M,m} = M[(g_1\beta H + A_1 m) \pm (g_2\beta H + A_2 m)\{1 - 3(\xi^2\eta^2 + \eta^2\zeta^2 + \zeta^2\xi^2)\}^{\frac{1}{2}}], \quad (21.37)$$

where $m = I_Z$ is the quantized projection of the nuclear spin along the applied field $H$. The resonance frequencies $\nu_m$, observed in an electronic spin transition $|\Delta M| = 1$ are given by

$$h\nu_m = (g_1\beta H + A_1 m) \pm (g_2\beta H + A_2 m)\{1 - 3(\xi^2\eta^2 + \eta^2\zeta^2 + \zeta^2\xi^2)\}^{\frac{1}{2}}. \quad (21.37\text{a})$$

The reader may well ask what is the point of calculating the shape of spectra such as (21.34a) or (21.37a) if the assumptions of cubic symmetry under which they are derived are made invalid by the Jahn–Teller theorem. The remarkable fact is that anisotropic spectra of this form *have* actually been observed. Furthermore, as will be shown later, their existence is by no means forbidden by the Jahn–Teller theorem but rather is a striking manifestation of a dynamic Jahn–Teller effect.

## 21.4. The static Jahn-Teller effect in a $^2E$ state

Using Table 26, which describes the various irreducible representations $\Gamma'$ spanned by the normal coordinates, and the reduction formula (21.12), we find that only the $\Gamma_3(E)$ mode of distortion $(Q_\theta, Q_\varepsilon)$ can lift the orbital degeneracy of a $\Gamma_3$ doublet. From what has been said about the transformation properties of the Pauli matrices $\sigma_1 = U_\varepsilon$ and $\sigma_3 = -U_\theta$ within the manifold $\Gamma_3$ it is clear that in first order the electron-nuclear coupling given by (21.11) is necessarily of the form

$$\delta V = V(Q_\theta U_\theta + Q_\varepsilon U_\varepsilon), \quad (21.38)$$

where $V$ is a constant. To it we must add the potential energy $\kappa(Q_\theta^2 + Q_\varepsilon^2)$ associated with the vibrations of the normal coordinates $(Q_\theta, Q_\varepsilon)$. We can write $\kappa = \mu\omega^2/2$ where $\omega$ is the harmonic frequency associated with the vibrational mode $E$ and where in first approximation we can equate the mass coefficient $\mu$ to the mass $M$ of each of the nuclei $Y$ of the complex $XY_6$.

The resultant potential energy operator

$$U = V(Q_\theta U_\theta + Q_\varepsilon U_\varepsilon) + \frac{M\omega^2}{2}(Q_\theta^2 + Q_\varepsilon^2)\mathscr{I} \quad (21.39)$$

can be rewritten as a function of the variables $\rho$ and $\varphi$ introduced in (21.15):

$$U = V\rho(U_\theta \cos\varphi + U_\varepsilon \sin\varphi) + \frac{M\omega^2\rho^2}{2}. \quad (21.39\text{a})$$

The two eigenfunctions of (21.39a) are

$$\psi_- = \theta \cos\frac{\varphi}{2} - \varepsilon \sin\frac{\varphi}{2}, \qquad \psi_+ = \theta \sin\frac{\varphi}{2} + \varepsilon \cos\frac{\varphi}{2}, \quad (21.40)$$

and the two eigenvalues are

$$U = \pm V\rho + \frac{M\omega^2\rho^2}{2} \qquad (21.41)$$

with the lower sign for $\psi_-$. It is clear that $\rho = 0$ is not a position of stable equilibrium for the complex and that a continuum of positions of minimum energy is obtained for $\rho_0 = |V|/M\omega^2$. The value of the minimum energy is

$$W_{\mathrm{JT}} = \frac{|V|\,\rho_0}{2} = \frac{V^2}{2M\omega^2} = \frac{M\omega^2\rho_0^2}{2}. \qquad (21.42)$$

The expression (21.41) for the potential energy suffers from a serious drawback: its symmetry far exceeds that of the cubic group since it is independent of $\varphi$ whereas, as we showed earlier, it need only be invariant when $\varphi$ is changed by $2\pi/3$. The picture can be made more realistic by what one calls warping of the potential energy surface, that is by adding higher-order terms either to the quasi-elastic second-order term $M\omega^2\rho^2/2$ or to the first-order Jahn–Teller coupling (21.39). The first term with cubic symmetry to be added to the potential energy will be of the form $V_3\rho^3\cos 3\varphi$ since, as we showed in § 21.3, $\cos 3\varphi$ is a cubic invariant. We can also add to the Jahn–Teller coupling a second-order term which, in order to be cubically invariant, must necessarily be of the form

$$V_2\rho^2(-U_\theta\cos 2\varphi + U_\varepsilon\sin 2\varphi) \qquad (21.43)$$

since, as we also showed in § 21.3, $\cos 2\varphi$ transforms like $-\theta$, and $\sin 2\varphi$ like $\varepsilon$. The electronic Hamiltonian becomes then

$$V\rho\left\{U_\theta\left(\cos\varphi - \frac{V_2\rho}{V}\cos 2\varphi\right) + U_\varepsilon\left(\sin\varphi + \frac{V_2\rho}{V}\sin 2\varphi\right)\right\} +$$
$$+ \left(\frac{M\omega^2\rho^2}{2} + V_3\rho^3\cos 3\varphi\right). \quad (21.44)$$

The eigenvalues of this Hamiltonian are

$$\pm V\rho\left\{\left(\cos\varphi - \frac{V_2\rho}{V}\cos 2\varphi\right)^2 + \left(\sin\varphi + \frac{V_2\rho}{V}\sin 2\varphi\right)^2\right\}^{\frac{1}{2}} +$$
$$+ \left(\frac{M\omega^2\rho^2}{2} + V_3\rho^3\cos 3\varphi\right)$$
$$= \pm V\rho\left(1 + \frac{V_2^2\rho^2}{V^2} - \frac{2V_2\rho}{V}\cos 3\varphi\right)^{\frac{1}{2}} + \frac{M\omega^2\rho^2}{2} + V_3\rho^3\cos 3\varphi, \quad (21.45)$$

which exhibit cubic symmetry by their dependence on $\varphi$ being solely

as $\cos 3\varphi$. The expression (21.45) shows that the minima of the potential energy no longer form a continuum but rather are obtained for discrete values of $\varphi$. These values are either $\varphi = 0$, $2\pi/3$, $4\pi/3$ or $\pi/3$, $\pi$, $5\pi/3$, depending on the relative signs and magnitudes of the coefficients $V_2$ and $V_3$. For simplicity we shall from now on, unless stated otherwise, take $V_2 = 0$. This has in particular the advantage of preserving for the eigenfunctions of (21.44) the simple form (21.40) whilst leaving intact all the qualitative features of the problem. If $V_3 < 0$ the minima occur for $\varphi = 0$, $2\pi/3$, $4\pi/3$ and correspond to an elongation of the octahedron along one of its three fourfold axes. If $V_3 > 0$ the minima are obtained for a compression along the same axes.

Consider in particular a distortion along the $z$-axis, that is $\varphi = 0$ or $\pi$. The ground state is given by Table 21.1. The electronic wave-functions that correspond to distortions along $Ox$ or $Oy$ can be obtained

<div align="center">

TABLE 21.1

</div>

| $V$ | $V_3$ | $\varphi$ | Ground state |
|-----|-------|-----------|--------------|
| $+$ | $+$ | $\pi$ | $\psi_-(\pi) = -\varepsilon$ |
| $+$ | $-$ | $0$ | $\psi_-(0) = \theta$ |
| $-$ | $+$ | $\pi$ | $\psi_+(\pi) = \theta$ |
| $-$ | $-$ | $0$ | $\psi_+(0) = \varepsilon$ |

from these by the formulae (21.13), which are equivalent to a cyclic permutation of the coordinates $x$, $y$, $z$ in the wave-functions $\theta$ and $\varepsilon$. In a simple-minded picture one is led to predict that since the three axes are equivalent, one-third of the octahedra present in the crystal will be distorted along each axis, and the observed paramagnetic spectrum should be a superposition of three normal tetragonal spectra in equal proportions. The parameters $g_\parallel$ and $g_\perp$ of these spectra are obtained by taking the expectation value of the coefficient of $S_z$ or $S_x$ in eqn (21.26) over the electronic wave-function of the appropriate ground state given in Table 21.1. For the parameters $A_\parallel$ and $A_\perp$ one takes similarly the expectation value of the coefficients of $I_z S_z$ or $I_x S_x$ in eqn (21.29). The results are given below (cf. Table 7.22):

$$g_\parallel^\pm = g_1 \pm g_2, \qquad g_\perp^\pm = g_1 \mp \frac{g_2}{2}; \qquad (21.46)$$

$$A_\parallel^\pm = A_1 \pm A_2, \qquad A_\perp^\pm = A_1 \mp \frac{A_2}{2}; \qquad (21.47)$$

where the sign $\pm$ in $g^\pm$ or $A^\pm$ is, according to Table 21.1, that of the

product $VV_3$, and $g_1$, $g_2$, $A_1$, $A_2$ are given by (21.27) and (21.31). Such a pattern is indeed observed in some copper salts at 20°K as discussed in detail in § 7.16. Experimentally it turns out that for $Cu^{2+}$, $3d^9$ it is the upper sign that is needed in (21.47).

## 21.5. Dynamic features of the static Jahn-Teller effect

In the foregoing we have implicitly assumed that at each minimum the nuclear parameters $\rho$ and $\varphi$ had fixed values, neglecting completely the zero-point motion of the nuclei; this is certainly incorrect. Actually for a distortion along $Oz$, assuming for the sake of definiteness that $V > 0$, $V_3 < 0$, the wave-function of the complex $XY_6$ should be written, if the Born–Oppenheimer approximation is valid, as

$$\Phi_Z = \psi_- \Psi_Z(\rho, \varphi), \tag{21.48}$$

where the nuclear wave-function $\Psi_Z(\rho, \varphi)$ is localized in the neighbourhood of $\rho = \rho_0$, $\varphi = 0$. For the Born–Oppenheimer approximation to be valid in the first place, we require that the distance between the two electronic energy levels that correspond to the wave-functions $\psi_-$ and $\psi_+$, which is of the order of $2 |V| \rho_0 = 4W_{JT}$, be much larger than the nuclear zero-point energy $\hbar\omega/2$. This is what is meant by strong Jahn–Teller coupling. Furthermore, for the nuclear wave-function $\Psi_Z$ to be strongly localized in the trough of the minimum corresponding to $\varphi = 0$, we require that the height $V_\varphi = |2V_3\rho^3|$ of the barrier that separates this minimum from the other two at $\varphi = \pm 2\pi/3$ be much greater than the zero-point energy $\hbar\omega'/2$ that corresponds to small oscillations of the coordinate $\varphi$.

The frequency $\omega'$ is of the order of

$$\omega' \approx \left(\frac{9V_\varphi}{2M\rho_0^2}\right)^{\frac{1}{2}} \approx \frac{3\omega}{2}\left(\frac{V_\varphi}{W_{JT}}\right)^{\frac{1}{2}}. \tag{21.49}$$

To obtain an order of magnitude for $Cu^{2+}$ surrounded by six water-molecules, we take an admittedly crude estimate of Öpik and Pryce (1957) that leads to

$$W_{JT} \approx 3000 \text{ cm}^{-1}, \qquad V_\varphi \sim 600 \text{ cm}^{-1},$$

$$\omega \sim 350 \text{ cm}^{-1}, \qquad \text{and from (21.49), } \omega' \approx \frac{2\omega}{3}.$$

Our calculation of the parameters (21.46), (21.47) of the paramagnetic spectra, using the wave-functions of Table 21.1, was tantamount to assuming that the nuclear wave-function $\Psi_Z(\rho, \varphi)$ of (21.48) had the form of a $\delta$-function $\delta(\varphi)$. A more realistic calculation should take into

account the finite extension of $\Psi_Z(\varphi)$. Making use of the relations

$$(\psi_{\pm}|\ U_{\theta}\ |\psi_{\pm}) = \pm\cos\varphi, \qquad (\psi_{\pm}|\ U_{\varepsilon}\ |\psi_{\pm}) = \pm\sin\varphi, \quad (21.50)$$

we find for the parameters $g$ and $A$,

$$g_{\parallel}^{\mp} = g_1 \pm ug_2, \qquad g_{\perp}^{\pm} = g_1 \mp \frac{ug_2}{2}$$

$$A_{\parallel}^{\mp} = A_1 \pm uA_2, \qquad A_{\perp}^{\pm} = A_1 \mp \frac{uA_2}{2} \tag{21.51}$$

where

$$u = \langle\cos\varphi\rangle = \iint\cos\varphi\ |\Psi_Z(Q)|^2\ dQ_\theta\ dQ_\varepsilon.$$

The point is that while at the precise position of the minimum, say $\varphi = 0$, the electronic wave-function $\psi_-$ is exactly $\theta$, because of the finite spatial extent of $\Psi_Z(\rho, \varphi)$ it is also partly $\varepsilon$, which gives a change in the values of $g$ and $A$ (O'Brien 1964). As discussed in § 7.16, it may also explain some features of the hyperfine structure on the ligands in the spectrum of $Ni^+$ in NaF.

The foregoing discussion has some very strong limitations. First, it applies only to the ground state of the complex, whereas there are many excited states connected with nuclear vibrations which may be appreciably populated at the temperature of the experiment. Second, by considering the complex $XY_6$ as an isolated system and neglecting the coupling with its surroundings in the crystal, one disregards the possibility of fast relaxation transitions from one configuration to another, which may drastically alter the observed patterns. Last, and this is really the main point, the dynamic features of the problem, caused by the existence of the kinetic nuclear energy, have far-reaching consequencies of which the finite extension of the nuclear wave-function in each trough, leading to the corrected formulae (21.51), is only one minor aspect.

We pass now to the study of the dynamic Jahn–Teller effect, at the end of which it will become clearer under what conditions a static effect such as the one described in the present section can be observed.

## 21.6. The dynamic Jahn–Teller effect in a $^2E$ state
*General*

In the last section we said that for a strong Jahn–Teller coupling, that is when the distance, $4W_{JT}$, between the two electronic energy states $\psi_+$ and $\psi_-$ was much greater than the nuclear zero-point energy

$\hbar\omega$, the Born–Oppenheimer approximation was valid and the wave-function of the system could be written as a single product of an electronic wave-function, say $\theta$, and a nuclear wave-function, say $\Psi_Z$. Actually a closer look shows that even in this case things are more complicated and electronic and nuclear motions are closely inter-twined. There are actually three potential minima with three wave-functions $\Phi_Z = \theta\Psi_Z$, $\Phi_X = R\theta\Psi_X$, $\Phi_Y = R^2\theta\Psi_Y$ and the total energy of the complex $XY_6$ is the same in all of these. This degeneracy, as will be discussed later in more detail, is lifted at least partially because of the finite overlap between the nuclear functions $\Psi_X, \Psi_Y, \Psi_Z$. The 'good' zero order wave-functions will then be suitable linear combinations of the three $\Phi$. States described by such linear combina-tions, where electronic and nuclear motions cannot be separated, are called vibronic states.

We take up now a study of these states in the general case, that is for an arbitrary strength of the Jahn–Teller coupling. The total vibronic Hamiltonian $\mathscr{H}_v$ is obtained by adding to the expression (21.44) the nuclear kinetic energy $(1/2M)(P_\theta^2+P_\varepsilon^2)$. This Hamiltonian operates on the two nuclear variables $Q_\theta$ and $Q_\varepsilon$ and on two electronic variables that are the amplitudes $C_\theta$ and $C_\varepsilon$ of the two electronic wave-functions $\theta$ and $\varepsilon$ which span the electronic doublet $\Gamma_3$. Under operations of the cubic group, $Q_\theta$ and $Q_\varepsilon$ on one hand, $C_\theta$ and $C_\varepsilon$ on the other, transform according to $\Gamma_3$ and the Hamiltonian $\mathscr{H}_v$ is invariant under a *simul-taneous* transformation

$$\begin{pmatrix} Q'_\theta \\ Q'_\varepsilon \end{pmatrix} = D^{\Gamma_3}\begin{pmatrix} Q_\theta \\ Q_\varepsilon \end{pmatrix}; \qquad \begin{pmatrix} C'_\theta \\ C'_\varepsilon \end{pmatrix} = D^{\Gamma_3}\begin{pmatrix} C_\theta \\ C_\varepsilon \end{pmatrix}$$

where $D^{\Gamma_3}$ is one of the $2 \times 2$ transformation matrices of $\Gamma_3$. $\mathscr{H}_v$ is thus invariant through a transformation of its *four* variables $Q_\theta, Q_\varepsilon, C_\theta, C_\varepsilon$ by $\Gamma_3 \times \Gamma_3 = \Gamma_3 + \Gamma_2 + \Gamma_1$.

The very important consequence of this fact is that all the vibronic eigenstates of $\mathscr{H}_v$ are either doublets of symmetry $\Gamma_3$ or singlets of symmetry $\Gamma_1$ or $\Gamma_2$. This result is quite general and would still be true if even higher-order terms, either for the Jahn–Teller coupling or the potential energy, were added to (21.44).

It is actually misleading to say that the Jahn–Teller effect lifts a degeneracy due to a high symmetry, since the Jahn–Teller coupling term itself has the same symmetry. What the Jahn–Teller coupling does is to replace a purely electronic degeneracy by a vibronic degeneracy of exactly the same symmetry. Consider in particular the ground vibronic

level of the complex $XY_6$. In the absence of Jahn–Teller coupling, the nuclear motion is that of a two-dimensional harmonic oscillator and *its* ground state $\Psi_0(Q)$ is *non-degenerate*. The overall degeneracy is then that of an electronic doublet $\Gamma_3$ spanned by the two Born–Oppenheimer functions $\Psi_0(Q)\theta$ and $\Psi_0(Q)\varepsilon$. A Jahn–Teller coupling will change the ground level into a *vibronic* $\Gamma_3$ doublet but a doublet it will remain.

We must now examine successively what must be the nature of the paramagnetic spectrum if the vibronic state is (a) a doublet, (b) a singlet, assuming in each case that the vibronic level under consideration is sufficiently removed from other vibronic levels for their mixing by the Zeeman Hamiltonian to be negligible. Finally, we shall have to explain the existence of a static Jahn–Teller effect whose occurrence in the form of three spectra of lower symmetry does not seem to fit at all into our picture of vibronic singlets and doublets.

### The vibronic doublet

A vibronic doublet is spanned by two wave-functions that we shall call $\Theta$ and $\mathscr{E}$. They contain both electronic and nuclear variables and transform like $\theta$ and $\varepsilon$, when *both* electronic and nuclear variables undergo a transformation of the cubic group. Following Ham (1968), we define the operators $U_{g\theta}$ and $U_{g\varepsilon}$, which are represented by the matrices $-\sigma_3$ and $\sigma_1$ when $\Theta$ and $\mathscr{E}$ are chosen as basis states and therefore can be written as

$$U_{g\theta} = |\mathscr{E}\rangle\langle\mathscr{E}| - |\Theta\rangle\langle\Theta|,$$
$$U_{g\varepsilon} = |\mathscr{E}\rangle\langle\Theta| + |\Theta\rangle\langle\mathscr{E}|.$$
(21.52)

Operators such as $U_\theta$ and $U_\varepsilon$, which were represented by the Pauli matrices $-\sigma_3$ and $\sigma_1$ when the purely electronic states $\theta$ and $\varepsilon$ were chosen as basic states, will have the following matrix elements inside the manifold of the vibronic doublet:

$$\langle\mathscr{E}|\, U_\theta \,|\mathscr{E}\rangle = -\langle\Theta|\, U_\theta \,|\Theta\rangle = \langle\Theta|\, U_\varepsilon \,|\mathscr{E}\rangle = \langle\mathscr{E}|\, U_\varepsilon \,|\Theta\rangle = q, \quad (21.53)$$

where $q$ is a number smaller than unity, whereas all the other matrix elements of $U_\theta$ and $U_\varepsilon$ vanish. This is a consequence of the Wigner–Eckart theorem since $(U_\theta, U_\varepsilon)$ have the same transformation properties as $(U_{g\theta}, U_{g\varepsilon})$. The unit operator $\mathscr{I}$ has naturally the same matrix elements within the vibronic doublet as within a purely electronic doublet. An electronic operator such as the Zeeman coupling (21.26), which in the absence of the Jahn–Teller effect could be written as

$$G_0\mathscr{I} + G_\varepsilon U_\varepsilon + G_\theta U_\theta,$$
(21.54)

can now be written

$$G_0\mathscr{I}+q(G_\varepsilon U_{g\varepsilon}+G_\theta U_{g\theta}), \qquad (21.54a)$$

where we repeat that, with our choice of $\Theta$ and $\mathscr{E}$ as the basic vibronic states, $U_{g\theta}$ and $U_{g\varepsilon}$ are simply the Pauli matrices $-\sigma_3$ and $\sigma_1$. Actually (21.54a) is not the most general operator acting inside the vibronic doublet and should be complemented by a term $G_2A_2$ proportional to the third Pauli matrix $A_2 = \sigma_2$. We define a coefficient $p = i\langle\Theta|\,A_2\,|\mathscr{E}\rangle$ and an operator $A_{\sigma_2} = i(|\mathscr{E}\rangle\langle\Theta| - |\Theta\rangle\langle\mathscr{E}|)$, and (21.54a) then becomes

$$G_0\mathscr{I}+q(G_\varepsilon U_{g\varepsilon}+G_\theta U_{g\theta})+pG_2A_{\sigma_2}. \qquad (21.55)$$

It is worth noting that $p$, the proportionality coefficient for the operator $A_2$, is different from that for $U_\varepsilon$ and $U_\theta$, because $A_2$ belongs to a different representation of the cubic group. Since the Zeeman coupling (21.26) does not contain the operator $A_2$, the resonance spectrum in the presence of the Jahn–Teller coupling must have exactly the same form as that calculated in § 21.3, provided that in the formulae (21.26) and (21.29) and also in (21.34) and (21.37) the splitting factor $g_2$ and the hyperfine constant $A_2$ (not to be confused with the operator $A_2$ proportional to $\sigma_2$) are replaced by $qg_2$ and $qA_2$.

One of the crucial problems of the theory is naturally the calculation of the coefficient $q$ for each vibronic doublet. It is a difficult problem that requires the knowledge of the eigenfunctions of a fairly complicated Hamiltonian $\mathscr{H}_v$.

If the Jahn–Teller coupling is weak (meaning thereby $W_{JT}/\hbar\omega \ll 1$) it is legitimate to simplify the problem by neglecting the warping terms, which can be expected to be small for values of $\rho \sim |V|/M\omega^2$. One of the undesirable features of this so-called linear approximation is the introduction of a spurious degeneracy. When the warping terms are neglected all states are doubly degenerate; not only the doublets $\Gamma_3$ but also the singlets belonging to the representations $\Gamma_1$ and $\Gamma_2$ which coincide in pairs. This can be seen as follows. The linear vibronic Hamiltonian $\mathscr{H}_v^L$, which has the form

$$\mathscr{H}_v^L(Q) = \frac{1}{2M}(P_\theta^2+P_\varepsilon^2)+\frac{M\omega^2}{2}(Q_\theta^2+Q_\varepsilon^2)+V(Q_\theta U_\theta+Q_\varepsilon U_\varepsilon), \quad (21.56)$$

is invariant under the transformation

$$\mathscr{H}_v^L(Q_\theta, Q_\varepsilon) = U_\theta^{-1}\mathscr{H}_v^L(Q_\theta, -Q_\varepsilon)U_\theta \qquad (21.56a)$$

which is a consequence of the commutation relations of $U_\theta$ and $U_\varepsilon$. It follows that if $\Phi(Q_\theta, Q_\varepsilon) = \theta\Psi_\theta(Q_\theta, Q_\varepsilon) + \varepsilon\Psi_\varepsilon(Q_\theta, Q_\varepsilon)$ is an

eigenstate of (21.56), so is $\tilde{\Phi}(Q_\theta, Q_\epsilon) = U_\theta \Phi(Q, -Q_\epsilon)$. It will shortly be shown explicitly (eqn (21.58a)) that $\tilde{\Phi} \neq \Phi$, thus demonstrating the twofold degeneracy. When the warping terms are introduced as a perturbation the singlets $A_1$ and $A_2$ separate, whereas the doublets $\Gamma_3$ naturally remain degenerate.

If we are interested in the ground doublet only, and if the first excited singlet is sufficiently removed from it, this spurious degeneracy is not very serious and the linear approximation is useful. To obtain the form of the wave-functions that span the ground doublet we take a trial function of the form $\Psi_\pm(Q)\psi_\pm$, where the electronic functions $\psi_\pm$ are given by (21.40). The vibronic Hamiltonian $\mathscr{H}_v^L$ acting on this function gives

$$\mathscr{H}_v^L\{\Psi_\pm(Q)\psi_\pm\} = \left(T + \frac{M\omega^2\rho^2}{2} \pm V\rho\right)\Psi_\pm(\rho, \varphi)\psi_\pm, \qquad (21.57)$$

where $T$ is the kinetic energy operator

$$T = -\frac{\hbar^2}{2M}\left\{\frac{1}{\rho}\frac{\partial}{\partial\rho}\left(\rho\frac{\partial}{\partial\rho}\right) + \frac{1}{\rho^2}\frac{\partial^2}{\partial\varphi^2}\right\}.$$

Since eqn (21.57) does not contain explicitly the variable $\varphi$ it is separable and we may seek a vibronic eigenfunction of the following form:

$$e^{in\varphi}\{f_n(\rho)\psi_- + ig_n(\rho)\psi_+\}. \qquad (21.58)$$

Here the two unknown functions $f_n(\rho)$ and $g_n(\rho)$ obey the following system of coupled equations, derived from (21.57),

$$-\frac{\hbar^2}{2M}\left\{\frac{1}{\rho}\frac{\partial}{\partial\rho}\left(\rho\frac{\partial}{\partial\rho}\right) - \frac{n^2+\frac{1}{4}}{\rho^2}\right\}\binom{f_n}{g_n} +$$
$$+ (\tfrac{1}{2}M\omega^2\rho^2 \mp V\rho - W_n)\binom{f_n}{g_n} = -\frac{\hbar^2 n}{2M\rho^2}\binom{g_n}{f_n}. \qquad (21.59)$$

Since (21.59) has real coefficients the complex conjugate of (21.58)

$$e^{-in\varphi}\{f_n(\rho)\psi_- - ig_n(\rho)\psi_+\} \qquad (21.58a)$$

is also a solution with the same energy. This corresponds to the twofold degeneracy of all eigenstates of $\mathscr{H}_v^L$, alluded to earlier. Instead of the two degenerate solutions (21.58) and (21.58a) it is often more convenient to use their real and imaginary parts. Since the electronic wave-functions $\psi_\pm$ of (21.40) are functions of $\varphi/2$, in order for the vibronic functions (21.58) and (21.58a) to be single-valued, the constant $n$ must be half-integer.

For $n = \frac{1}{2} + 3m$ or $n = \frac{5}{2} + 3m$ the doublets are bona fide $\Gamma_3$ doublets and remain such in the presence of warping, whereas for $n = \frac{3}{2} + 3m$ we have two states belonging to the unidimensional representations $A_1$ and $A_2$ which are split by the warping. In particular, the wave-functions $\Theta_{\frac{1}{2}}$ and $\mathscr{E}_{\frac{1}{2}}$, which span the ground vibronic doublet and are proportional to the real and imaginary part of (21.58), are given by

$$
\begin{aligned}
\sqrt{(2)}\Theta_{\frac{1}{2}} &= (f_{\frac{1}{2}} + g_{\frac{1}{2}})(-\theta \cos \varphi + \varepsilon \sin \varphi) + (g_{\frac{1}{2}} - f_{\frac{1}{2}})\theta, \\
\sqrt{(2)}\mathscr{E}_{\frac{1}{2}} &= (f_{\frac{1}{2}} + g_{\frac{1}{2}})(\theta \sin \varphi + \varepsilon \cos \varphi) + (g_{\frac{1}{2}} - f_{\frac{1}{2}})\varepsilon.
\end{aligned} \tag{21.60}
$$

Here we have written them in a way that displays explicitly their transformation character as $\theta$ and $\varepsilon$ in accordance with eqn (21.17).

If the Jahn–Teller energy $W_{JT}$ is small compared to $\hbar\omega$, the first excited state for $n = \frac{3}{2}$ will be approximately separated from the ground doublet by one vibrational quantum $\hbar\omega$ which is much greater than the Zeeman energy, and at helium or hydrogen temperatures it will not be populated. The coefficients $p$ and $q$ which are unity in the absence of Jahn–Teller coupling will be only slightly smaller than unity for a weak coupling. Within the linear approximation they have been computed numerically (Child and Longet-Higgins 1962) and their variation is represented in Fig. 21.1. Figure 21.2 gives the distance from the ground doublet to the first excited state.
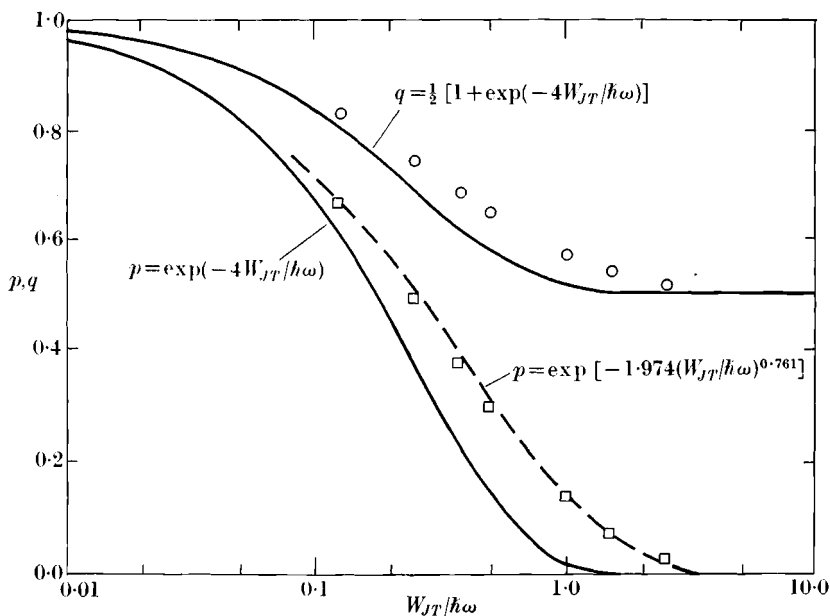


$$q = \frac{1}{2}[1 + \exp(-4W_{JT}/\hbar\omega)]$$

$$p = \exp(-4W_{JT}/\hbar\omega)$$

$$p = \exp[-1.974(W_{JT}/\hbar\omega)^{0.761}]$$

FIG. 21.1. Plot of the coefficients $p$ and $q$ against $W_{JT}/\hbar\omega$, together with approximate analytical expressions for these variations.
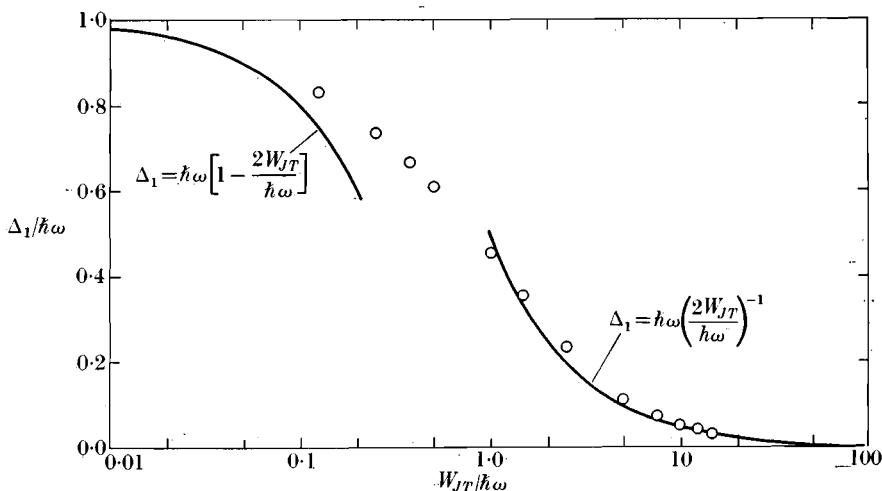
FIG. 21.2. Plot of the singlet-doublet splitting $\Delta_1$ against $W_{JT}/\hbar\omega$.

When the Jahn–Teller effect becomes large the Born–Oppenheimer approximation becomes valid, one of the components of the wavefunction (21.58), say $g_n$, vanishes and we may disregard the right-hand side of eqn (21.59). The energy gap $\Delta_1$ between the ground doublet and the first excited state then becomes approximately

$$\Delta_1 \approx \frac{\hbar^2}{2M}\left\{(\tfrac{3}{2})^2\langle f_{\frac{3}{2}}|\,\frac{1}{\rho^2}\,|f_{\frac{3}{2}}\rangle - (\tfrac{1}{2})^2\langle f_{\frac{1}{2}}|\,\frac{1}{\rho^2}\,|f_{\frac{1}{2}}\rangle\right\}.$$

Since $\rho$ is localized in the neighbourhood of the energy minimum $\rho_0 \sim |V|/M\omega^2$, we have $\langle f_{\frac{3}{2}}|\,1/\rho^2\,|f_{\frac{3}{2}}\rangle \approx \langle f_{\frac{1}{2}}|\,1/\rho^2\,|f_{\frac{1}{2}}\rangle \approx M^2\omega^4/V^2$ and

$$\Delta_1 \approx 2\frac{\hbar^2}{2M}\frac{M^2\omega^4}{V^2} \approx \hbar\omega\frac{\hbar\omega}{2W_{JT}}. \tag{21.60a}$$

If we take the values suggested by Öpik and Pryce (1957) for $Cu^{2+}$ we find $\Delta_1 \approx 20$ cm$^{-1}$. Unfortunately the linear approximation loses much of its significance when the Jahn–Teller effect becomes large. In particular, the energy of the first excited state depends very critically on the warping. A different approach, more suitable when the Jahn–Teller coupling *and* the warping terms are large, will be outlined shortly.

In view of the difficulty of the problem in the general case it is interesting to obtain the maximum of information from symmetry arguments only. Elementary group-theoretical considerations based on the relations (21.12) and (21.17) show that the most general expression

for two wave-functions that span a vibronic doublet $\Gamma_3$ is

$$\Theta = -b_\theta \theta + b_\varepsilon \varepsilon + a_1 \theta + a_2 \varepsilon,$$
$$\mathscr{E} = b_\varepsilon \theta + b_\theta \varepsilon + a_1 \varepsilon - a_2 \theta.$$
$$(21.61)$$

Here $\theta$ and $\varepsilon$ are two electronic wave-functions, whose coefficients $a\,b$ are functions of the nuclear variables $Q$ and transform as follows: $b_\theta(Q)$ and $b_\varepsilon(Q)$ belong to $\Gamma_3$ and transform like $\theta$ and $\varepsilon$; $a_1(Q)$ belongs to $\Gamma_1$ and $a_2(Q)$ to $\Gamma_2$. As a consequence the following orthogonality relations are evident:

$$\langle b_\theta^2 \rangle = \langle b_\varepsilon^2 \rangle = \langle b^2 \rangle; \langle b_\theta \cdot b_\varepsilon \rangle = \langle b_\theta \cdot a_{1,2} \rangle = \langle b_\varepsilon \cdot a_{1,2} \rangle = \langle a_1 \cdot a_2 \rangle = 0,$$
$$(21.62)$$

where the symbol $\langle \;\; \rangle$ means integration over the variables $Q$. We see that the wave-functions (21.60) obtained in the linear approximation for the ground doublet are of this form with $a_2(Q) = 0$.

From the normalization and orthogonality of $\Theta$ and $\mathscr{E}$ in (21.61) and making use of (21.62) we find

$$\langle a_1^2 \rangle + \langle a_2^2 \rangle + 2 \langle b^2 \rangle = 1. \tag{21.63}$$

For the coefficients $p$ and $q$ we get

$$p = \mathrm{i} \langle \Theta | \, A_2 \, | \mathscr{E} \rangle = \langle a_1^2 \rangle + \langle a_2^2 \rangle - 2 \langle b^2 \rangle,$$
$$q = \langle \Theta | \, U_\varepsilon \, | \mathscr{E} \rangle = \langle a_1^2 \rangle - \langle a_2^2 \rangle.$$
$$(21.64)$$

The relations (21.64), which are based on symmetry considerations only, are quite general and independent of the strength and the form of both the Jahn–Teller coupling and the warping terms. From (21.63) and (21.64) we get

$$q = \frac{1+p}{2} - 2 \langle a_2^2 \rangle. \tag{21.65}$$

For the ground doublet and in the linear approximation, since $a_2 = 0$, we have $q = \frac{1}{2}(1+p)$, a result due to Ham (1968).

If the Jahn–Teller coupling is very strong the two electronic wave-functions $\psi_\pm$ which make it diagonal (and which have the form (21.40) when this coupling is linear) differ in energy by a large amount, the Born–Oppenheimer approximation is valid and for the ground doublet only one of these, say $\psi_-$, multiplies both components of the doublet. This means that in (21.61) the coefficients of $\theta$ and $\varepsilon$ are in the same ratio for $\Theta$ and $\mathscr{E}$. Hence

$$\frac{a_1 - b_\theta}{a_2 + b_\varepsilon} = \frac{b_\varepsilon - a_2}{a_1 + b_\theta}$$

or

$$\langle a_1^2 \rangle + \langle a_2^2 \rangle = 2 \langle b^2 \rangle = \tfrac{1}{2}.$$
$$(21.66)$$

When (21.66) is valid we get from (21.64) and (21.65)

$$p = 0; \qquad q = \tfrac{1}{2} - 2\langle a_2^2 \rangle \leqslant \tfrac{1}{2}. \tag{21.67}$$

The results (21.67) for a strong Jahn–Teller effect with warping have been previously obtained by Ham (1968) for the ground doublet and with the assumption that the Jahn–Teller coupling contains first-order terms only.

### The vibronic singlets

These states can be dealt with very quickly. For singlet states, which belong to representations $A_1$ or $A_2$, it is clear that the expectation values of $U_\theta$ and $U_\varepsilon$, which transform like $\theta$ and $\varepsilon$ of $\Gamma_3$, vanish. The Zeeman spin-Hamiltonian and the hyperfine coupling then have necessarily the fully isotropic form

$$g_1\beta(\mathbf{H} . \mathbf{S}) + A_1(\mathbf{I} . \mathbf{S}). \tag{21.68}$$

Spectra corresponding to such a Hamiltonian have actually been observed. Indeed it was the first observation by Bleaney and Ingram in 1950 of an isotropic spectrum for $Cu^{2+}$ in copper fluosilicate, inexplicable in the framework of static crystal-field theory, which led Abragam and Pryce (1950) to postulate a dynamic Jahn–Teller effect as a possible explanation. However, as we shall see in a later section, fast relaxation may lead to a spectrum consistent with (21.68) even when the state of the system is a vibronic doublet and also when conditions are such that a static Jahn–Teller effect would be observable in the absence of relaxation. Thus an isotropic spectrum does not necessarily mean that the system is in a singlet state.

### The effects of strain

The paramount importance of the effects of strain in connection with the Jahn–Teller effect has been emphasized by Ham (1965, 1968). A uniform strain is best defined by its six components belonging respectively to

$$\Gamma_1 \ (e_{xx} + e_{yy} + e_{zz} = e_0),$$
$$\Gamma_5 \ (e_{xy}, e_{yz}, e_{zx}), \tag{21.69}$$
$$\Gamma_3 \left\{ e_\theta = \frac{3e_{zz} - e_0}{2}; \qquad e_\varepsilon = \frac{\surd(3)}{2}(e_{xx} - e_{yy}) \right\}.$$

Inside a cubic manifold $\Gamma_3$ the components $e_\theta$ and $e_\varepsilon$ are the only ones that split the energy level of the ion in first order. A trigonal strain $e_{xy}$ can affect it in second order only, via the spin-orbit coupling (Ham 1968).

The first-order change in energy can be rewritten in operator form as

$$V_{ES}(e_\theta U_\theta + e_\varepsilon U_\varepsilon), \tag{21.69a}$$

where $V_{ES}$ is a constant (the index $E$ stands for $E = \Gamma_3$ and $S$ for strain). Consider a distortion of the complex $XY_n$ described by the normal coordinates $Q_i$ and caused by a strain $e$. In order of magnitude we shall have $Q_i \sim eR$ where $R$ is the nearest neighbour distance. We are thus led to expect a relationship between the stress constant $V_{ES}$ and the Jahn–Teller coupling constant $V$ of the form $V \sim V_{ES}/R$. An elementary calculation based on the expressions of the $Q_i$ given in Table 26 leads to the following formulae (Ham 1968):

sixfold octahedral coordination, $\qquad V = \dfrac{\sqrt{3}}{2}(V_{ES}/R);$

eightfold cubic coordination, $\qquad V = \tfrac{3}{4}(V_{ES}/R);$ $\qquad$ (21.69b)

fourfold tetrahedral coordination, $\qquad V = \dfrac{3}{2\sqrt{2}}(V_{ES}/R).$

We see that ions with the largest Jahn–Teller effect will be the most sensitive to strain. In the numerical example of Öpik and Pryce for the $Cu^{2+}$ ion,

$$W_{JT} = 3000 \text{ cm}^{-1} = \frac{V\rho_0}{2} = V \times 0 \cdot 3 \times 10^{-8},$$

and if we take $R = 2 \times 10^{-8}$ cm for the distance to the nearest neighbour we find

$$V_{ES} = \frac{2VR}{\sqrt{3}} = \frac{V\rho_0}{2}\left(\frac{R}{\rho_0}\right)\frac{4}{\sqrt{3}} \approx 50000 \text{ cm}^{-1}.$$

A strain as small as $10^{-5}$ would in this particular case split the orbital doublet $\Gamma_3$ by an amount of the order of a wave-number, and even in the best crystals local random strains can be expected to influence the paramagnetic spectrum considerably.

Inside a vibronic doublet, the strain-induced energy change (21.69a) must naturally be multiplied by the same reduction factor $q$ defined in (21.53) as the anisotropy constants $g_2$ and $A_2$ of the Zeeman and hyperfine Hamiltonian (21.26) and (21.29). The total Hamiltonian, Zeeman plus hyperfine, plus strain, can then be written

$$\mathscr{H} = g_1\beta(\mathbf{S}\cdot\mathbf{H}) + A_1(\mathbf{I}\cdot\mathbf{S}) +$$

$$+ qU_\theta\left\{V_{ES}e_\theta + \frac{g_2\beta}{2}(3H_zS_z - \mathbf{S}\cdot\mathbf{H}) + \frac{A_2}{2}(3I_zS_z - \mathbf{I}\cdot\mathbf{S})\right\} +$$

$$+ qU_\varepsilon\left\{V_{ES}e_\varepsilon + \frac{g_2\beta\sqrt{3}}{2}(H_xS_x - H_yS_y) + \frac{A_2\sqrt{3}}{2}(I_xS_x - I_yS_y)\right\}. \tag{21.70}$$

To keep the problem simple we maintain the assumptions $|g_2| \ll |g_1|$, $|A_2| \ll |A_1|$, which enables us to rewrite (21.70) as

$$\mathcal{H} = g_1 \beta H M + A_1 M m +$$
$$+ q U_\theta \left\{ V_{ES} e_\theta + \frac{g_2 \beta H M}{2} (3\zeta^2 - 1) + \frac{A_2 M m}{2} (3\zeta^2 - 1) \right\} +$$
$$+ q U_\varepsilon \left\{ V_{ES} e_\varepsilon + \frac{g_2 \beta \surd(3) H M}{2} (\xi^2 - \eta^2) + \frac{\surd(3) A_2 M m}{2} (\xi^2 - \eta^2) \right\}. \quad (21.71)$$

With respect to the magnitude of the strain we consider two extreme cases

(a) *Very small strains*

These are defined by the inequality

$$V_{ES}(e_\theta^2 + e_\varepsilon^2)^{\frac{1}{2}} \ll \tfrac{1}{2} |g_2 \beta H + A_2 m| \{1 - 3(\xi^2 \eta^2 + \eta^2 \zeta^2 + \zeta^2 \xi^2)\}^{\frac{1}{2}}. \quad (21.72)$$

In this case the correct eigenfunctions of the Hamiltonian (21.71) are still given by formulae (21.35) and (21.36), provided the vibronic functions $\Theta$ and $\mathscr{E}$ replace the electronic functions $\theta$ and $\varepsilon$; the random strain affects the resonance frequencies and broadens the lines in second order in the strain by an amount of the order of

$$V_{ES}^2 (e_\theta^2 + e_\varepsilon^2)/|g_2 \beta H + A_2 m|.$$

The condition (21.72) may conceivably be fulfilled for certain hyperfine lines and certain orientations but not for others (and never with the field along a body diagonal). In view of the smallness of $g_2 \beta H$ (of the order of $0 \cdot 1$ cm$^{-1}$ in Cu$^{2+}$ for a field of 10 kG) an exceptionally strain-free crystal may be needed for (21.72) to be satisfied.

(b) *Large strains*

With the inequality (21.72) reversed, the correct wave-functions for the Hamiltonian (21.71), different from those given by eqn (21.35), are now

$$\Phi_a^M = |M\rangle \left( \Theta \cos \frac{\alpha}{2} - \mathscr{E} \sin \frac{\alpha}{2} \right),$$
$$\Phi_b^M = |M\rangle \left( \Theta \sin \frac{\alpha}{2} + \mathscr{E} \cos \frac{\alpha}{2} \right),$$
$$\quad (21.73)$$

where

$$\cos \alpha = e_\theta (e_\theta^2 + e_\varepsilon^2)^{-\frac{1}{2}},$$
$$\sin \alpha = e_\varepsilon (e_\theta^2 + e_\varepsilon^2)^{-\frac{1}{2}}.$$
$$\quad (21.73a)$$

The replacement in (21.71) of $U_\theta$ and $U_\varepsilon$ by their expectation values within the states $\Phi_{a,b}$, respectively $\pm\cos\alpha$ and $\pm\sin\alpha$, leads to the following formulae for the spectrum corresponding to (21.71):

$$h\nu_{a,b}(m) = (g_1\beta H + A_1 m)\pm$$

$$\pm q(g_2\beta H + A_2 m)\,\{1 - 3(\xi^2\eta^2 + \eta^2\zeta^2 + \zeta^2\xi^2)\}^{\frac{1}{2}}\cos(\omega - \alpha), \quad (21.74)$$

where $\cos\omega$ and $\sin\omega$ have been defined in eqn (21.36). Since the angle $\alpha$ related to the random strain by (21.73a) can be assumed to take all values between 0 and $2\pi$ it would seem that each line of the spectrum (21.74) should be broadened beyond recognition over a region

$$2q(g_2\beta H + A_2 m)\{1 - 3(\xi^2\eta^2 + \eta^2\zeta^2 + \zeta^2\xi^2)\}^{\frac{1}{2}}.$$

However, as pointed out by Ham (1969), each line of (21.74) so broadened has a singularity in its spectral density for

$$|\cos(\omega - \alpha)| = 1.$$

If all values of the random variable $\alpha$ are equally probable the spectral density is proportional to

$$d\nu \Big/ \left|\frac{d\nu}{d\alpha}\right| \propto \frac{1}{|\sin(\omega - \alpha)|} \propto \frac{1}{\sqrt{|\nu - \nu_0|}}, \quad (21.75)$$

where $\nu_0$ is the sharp frequency that would obtain in the absence of strain broadening. The quasi-continuous spectrum (21.74) exhibits sharp peaks at the same frequencies as in the absence of strain, namely

$$h\nu_{a,b}(m) = g_1\beta H + A_1 m \pm q(g_2\beta_2 H + A_2 m)\{1 - 3(\xi^2\eta^2 + \eta^2\zeta^2 + \zeta^2\xi^2)\}^{\frac{1}{2}}.$$

$$(21.76)$$

We have already stated, when establishing formula (21.37), that the assumption $|A_2| \ll A_1$ was often unwarranted. If we give up this assumption while keeping $|g_2| \ll |g_1|$ the formula (21.74) has to be replaced by the following,

$$h\nu_{a,b} = g_1\beta H \pm q g_2\beta H(1 - 3\bar{u})^{\frac{1}{2}}\cos(\omega - \alpha) + m\mathscr{A}, \quad (21.74a)$$

where we write for brevity $\xi^2\eta^2 + \eta^2\zeta^2 + \zeta^2\xi^2 = \bar{u}$, and

$$\mathscr{A}^2 = A_1^2 \pm 2q A_1 A_2 (1 - 3\bar{u})^{\frac{1}{2}}\cos(\omega - \alpha) + \frac{q^2 A_2^2}{2}\{1 + (1 - 3\bar{u})^{\frac{1}{2}}\cos(\omega + 2\alpha)\}.$$

Here $m$ is the projection of $\mathbf{I}$ along a direction whose cosines are given by

$$\mathscr{A}\xi' = \xi\left\{A_1 \pm \frac{qA_2}{2}(-\cos\alpha + \sqrt{(3)}\sin\alpha)\right\},$$

$$\mathscr{A}\eta' = \eta\left\{A_1 \pm \frac{qA_2}{2}(\cos\alpha + \sqrt{(3)}\sin\alpha)\right\}, \qquad (21.74\mathrm{b})$$

$$\mathscr{A}\zeta' = \zeta(A_1 \pm qA_2\cos\alpha).$$

These formulae are very easy to establish if one notices that for strong strain, $U_\theta$ and $U_\varepsilon$ can be replaced in (21.70) by their expectation values over the functions (21.73), namely $\pm\cos\alpha$ and $\pm\sin\alpha$. Strain also plays an important role in the passage from the static to the dynamic Jahn–Teller effect, a problem to be examined presently.

*The tunnelling model and the transition from the dynamic to the static Jahn–Teller effect*

In the foregoing studies of the effects of perturbations such as Zeeman and hyperfine couplings, and also strain, on the vibronic ground doublet, we have consistently assumed that the relevant Hamiltonians are very much smaller than the doublet-singlet distance and that their off-diagonal doublet-singlet matrix elements could therefore be disregarded. We saw, however, that even in the absence of warping, an increasingly strong Jahn–Teller coupling had a tendency to bring together the ground doublet and the first two excited (spuriously degenerate) singlet levels, the separation $\Delta_1$ or $3\Gamma$ as we shall call it henceforth, being, see (21.60a), approximately equal to $\hbar\omega(\hbar\omega/2W_{\mathrm{JT}})$. A numerical study (O'Brien 1964) has shown that the introduction of warping has two effects: first, it separates the singlets $A_1$ and $A_2$; second, it brings the lower of the two very much nearer to the ground doublet than predicted by the linear approximation.

We saw earlier (eqn (21.54a)) that any perturbation, such as caused by magnetic coupling or strain, whose action on a purely electronic $\Gamma_3$ doublet was expressed by an operator

$$G_0\mathscr{I} + G_\varepsilon U_\varepsilon + G_\theta U_\theta, \qquad (21.54)$$

could be written within a vibronic doublet spanned by two vibronic functions $\Theta$ and $\mathscr{E}$ as $G_0\mathscr{I} + q(G_\varepsilon U_{g\varepsilon} + G_\theta U_{g\theta})$ and within a vibronic singlet $A_1$ or $A_2$ as $G_0\mathscr{I}$. If the distance $3\Gamma$ between the singlet and the doublet is comparable to the interaction (21.54) we need the matrix elements of $U_\theta$ and $U_\varepsilon$ between the singlet and the doublet. They obey

the following relations, easily deduced using eqn (21.13):

$$\langle A_1 | U_\theta | \Theta \rangle = \langle A_1 | U_\varepsilon | \mathscr{E} \rangle = r,$$
$$\langle A_2 | U_\theta | \mathscr{E} \rangle = -\langle A_2 | U_\varepsilon | \Theta \rangle = r', \tag{21.77}$$

all other singlet-doublet matrix elements of $U_\theta$ and $U_\varepsilon$ being zero.

We now set up the secular matrix relative to the perturbation (21.54), which has a slightly different form depending on whether the singlet is $A_1$ or $A_2$. For $A_1$ it is given by (21.78),

$$
\begin{array}{cccc}
 & A_1 & \Theta & \mathscr{E} \\
A_1 & \begin{pmatrix} 3\Gamma + G_0 \\ \\ \\ \end{pmatrix} & \begin{matrix} rG_\theta \\ \\ \\ \end{matrix} & \begin{matrix} rG_\varepsilon \\ \\ \\ \end{matrix} \\
\Theta & \begin{matrix} rG_\theta \\ \end{matrix} & \begin{matrix} -qG_\theta + G_0 \\ \end{matrix} & \begin{matrix} qG_\varepsilon \\ \end{matrix} \\
\mathscr{E} & \begin{pmatrix} rG_\varepsilon \end{pmatrix} & qG_\varepsilon & qG_\theta + G_0 \end{pmatrix}
\end{array}
\tag{21.78}
$$

but if the excited singlet is $A_2$, $rG_\theta$ and $rG_\varepsilon$ are replaced in (21.78) respectively by $-r'G_\varepsilon$ and $r'G_\theta$. Since the quantities $G_\theta$, $G_\varepsilon$ are usually smaller than one wave-number, in order for $3\Gamma$ to be of the same order of magnitude both the Jahn–Teller coupling and the warping must be strong, an assumption we had made in the study of the static Jahn–Teller effect. This provides a basis for the so-called tunnelling model (Bersuker 1962).

Let us return to the static Jahn–Teller effect, assuming for the sake of definiteness that $V > 0$, $V_3 < 0$. We then found a potential minimum for $\varphi = 0$ and we described the complete wave-function of the system near that minimum by the Born–Oppenheimer product

$$\Phi_Z = \psi_z(\varphi) \Psi_Z(\rho, \varphi). \tag{21.79}$$

The nuclear wave-function $\Psi_Z(\rho, \varphi)$ is strongly localized in the neighbourhood of $\rho = \rho_0 \approx |V|/M\omega^2$. A reasonable approximation for $\Psi_Z(\rho, \varphi)$ would be a Gaussian function, the ground state of a two-dimensional harmonic oscillator,

$$\Psi_Z(\rho, \varphi) = \left(\frac{\alpha\alpha'}{\pi}\right)^{\frac{1}{2}} \exp -\tfrac{1}{2}\{\alpha^2(\rho - \rho_0)^2 + \alpha'^2\rho_0^2\varphi^2\}, \tag{21.80}$$

where $\alpha = (\hbar/M\omega)^{\frac{1}{2}}$, $\alpha' = (\hbar/M\omega')^{\frac{1}{2}}$. Here $\omega$ is the frequency for radial oscillation, which appears in the quadratic potential energy $\tfrac{1}{2}M\omega^2\rho^2$ and $\omega'$, given by eqn (21.49), is the frequency for azimuthal oscillation inside the potential trough at $\varphi = 0$, produced by the warping. Because of this strong localization of the nuclear wave-function one may in a first approximation replace the electronic wave-function $\psi_z(\varphi)$ by

$\psi_z(0)$. If one wishes to take into account the finite spread of the nuclear wave-function (21.80), one can replace $\psi_z(\varphi)$ in the neighbourhood of $\varphi = 0$ by

$$\psi_z(\varphi) = \theta \cos \frac{\varphi}{2} - \varepsilon \sin \frac{\varphi}{2}, \qquad (21.81)$$

which was used to obtain the corrected formulae (21.51) for $g_{\parallel}$ and $g_{\perp}$.

From the wave-function

$$\Phi_Z = \psi_z \Psi_Z \approx \theta \Psi_Z \propto (3z^2 - r^2)\Psi_Z \qquad (21.82)$$

we can deduce two other wave-functions, $\Phi_X$ and $\Phi_Y$, relative to the minima $\varphi = \pm 2\pi/3$, by the condition that $\Phi_X$, $\Phi_Y$, $\Phi_Z$ derive from each other by the cyclical permutation, $x \to y \to z \to x$,

$$\Phi_X \approx (3x^2 - r^2)\Psi_X(\rho, \varphi) = (3x^2 - r^2)\Psi_Z\left(\rho, \varphi - \frac{2\pi}{3}\right),$$
$$\Phi_Y \approx (3y^2 - r^2)\Psi_Y(\rho, \varphi) = (3y^2 - r^2)\Psi_Z\left(\rho, \varphi + \frac{2\pi}{3}\right). \qquad (21.82a)$$

A more accurate representation of $\Phi_X$ in the neighbourhood of $\varphi = 2\pi/3$, following (21.81), is

$$\left\{(3x^2 - r^2)\cos \tfrac{1}{2}\left(\varphi - \frac{2\pi}{3}\right) - \sqrt{3}(y^2 - z^2)\sin \tfrac{1}{2}\left(\varphi - \frac{2\pi}{3}\right)\right\}\Psi_Z\left(\rho, \varphi - \frac{2\pi}{3}\right), \qquad (21.82b)$$

with a similar expression for $\Phi_Y$.

The three wave-functions $\Phi_X$, $\Phi_Y$, $\Phi_Z$, which correspond to the same energy, provide a reducible representation of the cubic group. The combination

$$A_1 = \frac{1}{\sqrt{3}}\{\Phi_X + \Phi_Y + \Phi_Z\}, \qquad (21.83)$$

which is normalized if the small overlap between the functions is neglected, is clearly invariant under the operations of the cubic group and belongs to the representation $A_1$. The two combinations

$$\Theta = \frac{1}{\sqrt{6}}(2\Phi_Z - \Phi_X - \Phi_Y),$$
$$\mathscr{E} = \frac{1}{\sqrt{2}}(\Phi_X - \Phi_Y), \qquad (21.83a)$$

belong obviously to $\Gamma_3$ and transform like $\theta$ and $\varepsilon$. If we introduce the overlap $\delta = \langle \Phi_X \mid \Phi_Z \rangle$ between two functions $\Phi$, eqns (21.83),(21.83a)

are replaced by

$$A_1 = \frac{1}{\sqrt{(3+6\delta)}}(\Phi_X + \Phi_Y + \Phi_Z),$$

$$\Theta = \frac{1}{\sqrt{(6-6\delta)}}(2\Phi_Z - \Phi_X - \Phi_Y). \qquad (21.84)$$

It is sometimes stated (Bersuker 1962, Höchli 1967) that the overlap $\delta = \langle \Phi_X | \Phi_Z \rangle$ can be represented as the product of the overlap $\gamma = \langle \Psi_X | \Psi_Z \rangle$ of the nuclear wave-functions and the overlap $\langle 3x^2 - r^2 | 3z^2 - r^2 \rangle = -\frac{1}{2}$ (an immediate consequence of the relations (21.13)) of the electronic wave-functions. It should be remembered, however, that for $\psi_x$, for instance, the expression $\psi_x(2\pi/3) = 3x^2 - r^2$, and even the more accurate expression (21.82b), are only valid in the neighbourhood of $\varphi = 2\pi/3$, and the same is true for the expression (21.81) for $\psi_z(\varphi)$ in the neighbourhood of $\varphi = 0$. (Expressions such as (21.81) could not possibly be valid for all values of $\varphi$ since $\Phi_Z$ as given by (21.79),(21.80) would not be a single-valued function of $Q_\theta$, $Q_\varepsilon$.) The main contribution to the overlap between the two functions $\Phi_X$ and $\Phi_Y$ comes from regions of $\varphi$ distant from the minima. This means that the electronic scalar product $\langle \psi_x(\varphi) | \psi_z(\varphi) \rangle$ is an unknown function of $\varphi$ and a formula such as $\delta = -\gamma/2$ is unwarranted.

If we now assume that the product $VV_3$ of Table 21.1 is positive, the three wave-functions $\Phi_X$, $\Phi_Y$, $\Phi_Z$ become

$$\Phi_Z \approx \sqrt{(3)}(x^2 - y^2)\Psi_Z,$$

$$\Phi_X \approx \sqrt{(3)}(y^2 - z^2)\Psi_X, \qquad (21.85)$$

$$\Phi_Y \approx \sqrt{(3)}(z^2 - x^2)\Psi_Y,$$

where the nuclear wave-functions $\Psi$ are centered around $\varphi = \pi$ and $\varphi = \pi \pm 2\pi/3$. In contrast to eqn (21.83), the combination

$$A_2 = \frac{1}{\sqrt{(3)}}(\Phi_X + \Phi_Y + \Phi_Z) \qquad (21.86)$$

belongs this time to the unidimensional representation $A_2$ rather than to $A_1$. This can be checked by noticing that a rotation through $\pi/2$ around, say, $Oz$ changes $A_2$ as given by (21.86) into $-A_2$. The two combinations,

$$\Theta' = (\Phi_Y - \Phi_X)/\sqrt{2},$$

$$\mathscr{E}' = (2\Phi_Z - \Phi_X - \Phi_Y)/\sqrt{6}, \qquad (21.86a)$$

belong again to $\Gamma_3$ and transform like $\theta$ and $\varepsilon$ (we have neglected in (21.86) and (21.86a) the overlap $\delta$).

We have now, with eqns (21.83), (21.83a) or (21.86), (21.86a), constructed approximate expressions for the vibronic wave-functions that span the ground doublet and the first excited singlet, the latter being $A_1$ or $A_2$ depending on the sign of $VV_3$. The three wave-functions $\Phi_X$, $\Phi_Y$, $\Phi_Z$ are three degenerate eigenfunctions of an approximate Hamiltonian, the approximation being essentially that of an infinite barrier height between two neighbouring potential minima. We can take into account as a perturbation $\mathscr{H}_1$ the possibility of tunnelling through the barriers between the various minima. We need not concern ourselves with the actual form of this perturbation: the simple fact that it has cubic symmetry insures automatically that $A$, $\Theta$, $\mathscr{E}$ given by (21.83) etc. or (21.86) etc. are the 'good' zero-order wave-functions and that the triply degenerate level spanned by $\Phi_X$, $\Phi_Y$, $\Phi_Z$ will be split into a singlet $A$ and a doublet $(\Theta, \mathscr{E})$. This approximation should be good only when the barrier is very high and the overlap $3\Gamma$ very small. We expect the splitting to be positive by continuity, starting from no Jahn–Teller coupling when we know that the doublet is lower. We shall not discuss the approximate methods for calculating $\Gamma$, by the WKB approximation or otherwise (Bersuker 1962, Sturge 1967). This calculation, like that of the overlap $\delta$, is sensitive to the rather uncertain shape of the tails of the wave-functions $\Phi_X$, $\Phi_Y$, $\Phi_Z$ in between the minima.

Since in (21.83), (21.83a) or (21.86), (21.86a) we have explicit expressions for the vibronic functions $A$, $\Theta$, $\mathscr{E}$, we can calculate the coefficients $q$, $r$, and $r'$ (we have demonstrated in eqn (21.67) that $p = 0$ for strong Jahn–Teller coupling). We can obtain $q$ for instance from the relation $q = \langle \mathscr{E} | U_\theta | \mathscr{E} \rangle$ where $\mathscr{E}$ is given by (21.83a). Taking into account the expression (21.82b) for $\Phi_X$ (and a similar one for $\Phi_Y$) we obtain $q = \frac{1}{2} u$, where

$$u = \langle \cos \varphi \rangle = \int \Psi_Z^2(\rho, \varphi)\cos \varphi \, \mathrm{d}\varphi \qquad (21.87)$$

is the average value of $\cos \varphi$ in the trough $\varphi = 0$. In this calculation we have neglected the overlap between $\Psi_X$ and $\Psi_Y$. If the approximate form (21.82a) is used for $\Phi_X$ and $\Phi_Y$ in the calculation of the overlap this leads to a small correction to $q$, equal to $3\gamma/4$ (Höchli 1967). Actually, as we mentioned earlier, we do not know the form of the electronic wave-functions $\psi_x$ and $\psi_y$ in the regions where overlap is appreciable. While the correction to $q$ due to overlap must indeed be of the order of $\gamma$, there is no particular reason to believe it to be $3\gamma/4$. Disregarding this correction it is satisfactory to notice that the value

of $\frac{1}{2}u$ for $q$ is in accordance with the general inequality, $q \leqslant \frac{1}{2}$, derived in eqn (21.67). The reader may check that the same value is obtained for $q$ when the functions $\Phi$ are of the type (21.85) rather than (21.82), (21.82a).

A similar calculation of the matrix elements $\langle A_1 | U_\varepsilon | \mathscr{E} \rangle$ or $\langle A_2 | U_\varepsilon | \Theta \rangle$ yields

$$r = -\frac{u}{\sqrt{2}} = -q\sqrt{2}; \qquad r' = \frac{u}{\sqrt{2}} = q\sqrt{2}. \qquad (21.88)$$

In order to see what happens when the singlet-doublet splitting $3\Gamma$ is smaller than the Hamiltonian (21.54), it is illuminating to transcribe the matrix (21.78) for the representation $\Phi_X$, $\Phi_Y$, $\Phi_Z$ inverting the equations (21.82), (21.82a) or (21.86), (21.86a). We obtain

$$
\begin{array}{cccc}
 & \Phi_Z & \Phi_X & \Phi_Y \\
\Phi_Z & \begin{pmatrix} \Gamma + G_0 \mp 2qG_\theta \\ \Gamma \\ \Gamma \end{pmatrix} & \begin{matrix} \Gamma \\ \Gamma + G_0 \mp q(-G_\theta + \sqrt{3}G_\varepsilon) \\ \Gamma \end{matrix} & \begin{matrix} \Gamma \\ \Gamma \\ \Gamma + G_0 \mp q(-G_\theta - \sqrt{3}G_\varepsilon) \end{matrix} \end{array}
$$
$$(21.89)$$

where the upper sign corresponds to the situation (21.82), (21.82a) and the lower to (21.85), and where we have used the relations (21.88).

Let us temporarily assume that $G_\theta$ and $G_\varepsilon$ are much larger than $\Gamma$. It is then apparent in (21.89) that we may disregard the small off-diagonal matrix elements $\Gamma$ and that $\Phi_X$, $\Phi_Y$, $\Phi_Z$ become the good zero-order functions. They are precisely those we used for the static Jahn–Teller effect. If $G_0$, $G_\theta$, and $G_\varepsilon$ result from the Zeeman coupling (21.26) with

$$G_0 = g_1\beta(\mathbf{H} \cdot \mathbf{S}),$$

$$G_\theta = \frac{g_2\beta}{2}(3H_z S_z - \mathbf{H} \cdot \mathbf{S}),$$

$$G_\varepsilon = \frac{g_2\beta\sqrt{3}}{2}(H_x S_x - H_y S_y),$$

we find, as expected for the static Jahn–Teller effect, in the state $\Phi_Z$,

$$\langle \Phi_Z | Z | \Phi_Z \rangle = g_\parallel \beta H_z S_z + g_\perp \beta(H_x S_x + H_y S_y) \qquad (21.90)$$

and similar expressions for $\Phi_X$ and $\Phi_Y$ where, in accordance with (21.51)

$$g_\parallel = g_1 \mp 2qg_2 \approx g_1 \mp ug_2,$$
$$g_\perp = g_1 \pm qg_2 \approx g_1 \pm \frac{ug_2}{2}, \qquad (21.90a)$$

the upper sign corresponding to the case when $\Phi_Z$ is defined by (21.82).

We have already alluded to the smallness of $g_2\beta H$ ($\sim$0·1 cm$^{-1}$ for Cu$^{2+}$ in a field of 10 kG) which makes it unlikely that it will be larger than the tunnelling splitting $3\Gamma$. There is, however, a second origin for $G_\theta$ and $G_\varepsilon$, namely a strain-induced change in energy of the form (21.69a) $V_{ES}(e_\theta U_\theta + e_\varepsilon U_\varepsilon)$, whence $G_\theta = V_{ES}e_\theta$, $G_\varepsilon = V_{ES}e_\varepsilon$. From (21.89) and the definitions (21.69) of $e_\theta$ and $e_\varepsilon$, this gives for the state $\Phi_Z$ a change in energy $\mp qV_{ES}(2e_{zz}-e_{xx}-e_{yy})$ and similar expressions for $\Phi_X$, $\Phi_Y$.

These strain-induced energy changes may be much larger than $g_2\beta H$ and larger than $\Gamma$. We realize now the true origin of the static Jahn–Teller effect, as explained by Ham (1968). When, because of a strong Jahn–Teller coupling and a high warping barrier, the frequency $3\Gamma/\hbar$ for tunnelling between the three minima (which in the language of the dynamic Jahn–Teller effect is the distance between the ground doublet and the first excited singlet) becomes smaller than the strain energy, the latter 'locks' the system in one of the three potential minima corresponding to a static tetragonal distortion (with the possibility of small zero-point motion near each minimum). If the strain splitting is smaller than $kT$ all three states $\Phi_X$, $\Phi_Y$, $\Phi_Z$ will be equally populated but, even if $kT$ is very small, there will be an equal number of ions in the crystal in each state because of the random character of the local strain.

The intermediate situation where $\Gamma$ is neither large nor small compared to $g_2\beta H$ has been discussed in the literature by means of eqn (21.89) (Bersuker 1963, O'Brien 1964) before the importance of strain had been fully realized. We do not reproduce these discussions here since, especially for ions with strong Jahn–Teller coupling, the effect of strain is likely to be predominant.

### 21.7. Motional narrowing of the Jahn-Teller spectrum

*A survey of the various types of spectra*

In the foregoing we saw that three types of spectra could be expected from a $^2E$ level undergoing a Jahn–Teller effect:

(a) a superposition of three anisotropic spectra of tetragonal symmetry with parameters given by (21.46), (21.47) or better (21.51), characteristic of a static Jahn–Teller effect;

(b) a purely isotropic spectrum with isotropic $g$-factor and hyperfine structure constant, equal respectively to $g_1$ and $A_1$, characteristic of a vibronic singlet;

(c) an anisotropic spectrum described by parameters $g_1$, $qg_2$, $A_1$, $qA_2$, characteristic of a vibronic doublet. Actually this last spectrum can be subdivided into two types:

(c1) where the average local strain is larger than the anisotropic part of the magnetic interactions

$$V_{ES}(e_\theta^2 + e_\varepsilon^2)^{\frac{1}{2}} \gg |g_2\beta H + A_2 m| \qquad (21.91)$$

and where the resonance frequencies are given by eqn (21.74), and

(c2) where the inequality (21.91) is reversed and the spectrum is given again by (21.74) but with the factor $\cos(\omega - \alpha)$ missing in the anisotropic part.

The occurrence of these various spectra is determined by the relative magnitude of the following three quantities: the doublet-singlet splitting $3\Gamma$, the average strain $V_{ES}(e_\theta^2 + e_\varepsilon^2)^{\frac{1}{2}}$ henceforth called for brevity $\Delta_s$, and the anisotropic magnetic coupling $(g_2\beta H + A_2 m)$, called for brevity $\Delta_m$.

If $3\Gamma \gg \Delta_s$, $\Delta_m$, which will always occur for a weak or moderately strong Jahn–Teller coupling, the vibronic doublet, well separated from the first excited singlet, should exhibit either a spectrum (c1) or (c2) depending on the relative magnitude of $\Delta_s$ and $\Delta_m$. The isotropic spectrum (b) of the vibronic singlet will be observable if $kT/3\Gamma$ is sufficiently large for the singlet to be appreciably populated.

If the Jahn–Teller coupling and the warping are very strong, $3\Gamma$ becomes much smaller, while the strain splitting $\Delta_s$ is expected to be relatively large as suggested by eqn (21.69b). It is likely that in this case $\Delta_s \gg \Delta_m$, and the only question is the relative size of $3\Gamma$ and $\Delta_s$.

If $3\Gamma \gg \Delta_s$, a singlet spectrum (b), and a doublet spectrum (c1) should be observed.

If $3\Gamma \ll \Delta_s$, a static Jahn–Teller spectrum of type (a) should be observed as explained in the last section.

*Motional narrowing*

In our discussion we have hitherto considered the complex $XY_6$ as an isolated system, disregarding its coupling with the other degrees of freedom of the crystal in which the complex is embedded, such as lattice vibrations. If this coupling is switched on, fast transitions may occur between various states of the complex, with emission or absorption of one or more phonons resulting in an appreciable change in the observed pattern. The main change to be expected if these transitions are sufficiently fast is the transformation of the anisotropic spectra (a)

and (c) into an isotropic singlet-like spectrum (b). Thus the origin of the appearance of such a spectrum when the temperature is raised is not unambiguous: it may be due either to an increased population of an excited singlet or to an increase in relaxation rate that turns an anisotropic spectrum (a) or (c) into an isotropic spectrum (b) in ways now to be described.

Let us start with a static spectrum (a) and call $1/\tau$ the rate of change, due to thermal relaxation, of the population of anyone of the three distorted configurations described by the wave-functions $\Phi_X$, $\Phi_Y$, $\Phi_Z$. The following relation is easily established from the rate equations: $1/\tau = 3P_{XY}$, where on the right-hand side $P_{XY}$ represents the thermally induced transition probability from a configuration $\Phi_X$ to another configuration $\Phi_Y$. The total spread $\Delta\nu$ in the paramagnetic spectrum due to anisotropy is given by

$$h\Delta\nu = |(g_\parallel - g_\perp)\beta H + (A_\parallel - A_\perp)m| = \tfrac{3}{2}u\,|g_2\beta H + A_2 m|, \quad (21.92)$$

where we made use of (21.51). If $\tau$ is sufficiently short to satisfy the inequality $\Delta\nu \cdot \tau \ll 1$, then, according to the well-known theory of motional narrowing, only the average frequency of the three spectra will be observed, given by

$$h\nu(m) = (\tfrac{1}{3}g_\parallel + \tfrac{2}{3}g_\perp)\beta H + (\tfrac{1}{3}A_\parallel + \tfrac{2}{3}A_\perp)m = g_1\beta H + A_1 m, \quad (21.93)$$

which is identical with the spectrum of the singlet.

The reorientation from one configuration to another can occur through several processes among which we single out for a brief description, as in the theory of spin-lattice relaxation, the Orbach process, the direct process, and the Raman process, outlined in Chapter 10.

In the Orbach process a real transition to an excited vibronic state lying at a distance $W_0$ above the ground state will have a probability of the order of

$$\tau^{-1} \simeq \nu_0 \exp\left(-\frac{W_0}{kT_0}\right) \quad (21.94)$$

where, as explained in Chapter 10, $\nu_0$ is essentially the inverse lifetime of the excited state and $\exp(-W_0/kT_0)$ the relative probability of finding in the crystal an energetic phonon of frequency $W_0/h$ at the temperature of the experiment.

At the temperatures too low for the Orbach process to be appreciable the direct process corresponds to absorption or emission of a single phonon of energy equal to the energy difference $\Delta_{XY}$ induced by stress

between two distorted configurations $\Phi_X$ and $\Phi_Y$. We now consider this process.

As explained in § 21.6, the observability of a spectrum of type (a) characteristic of a static Jahn–Teller effect implies the assumption $|\Gamma| \ll |\Delta_{XY}, \Delta_{YZ}, \Delta_{ZX}|$. The calculation of the corresponding relaxation time, treating phonons as time-dependent strains, is standard except for one feature: only those phonons that have the symmetry properties of the strain components $e_\theta$ and $e_\varepsilon$ have non-vanishing matrix elements between various states of our system (unless higher-order terms involving spin-orbit coupling are brought in). On the other hand, the strain Hamiltonian $V_{ES}(e_\theta U_\theta + e_\varepsilon U_\varepsilon)$ does *not* have any off-diagonal matrix elements between the states $\Phi_X$, as can be seen from eqn (21.89). Such matrix elements can only appear because the states $\Phi_X$ are not exact eigenstates of the system, and because the off-diagonal matrix elements $\Gamma$ in (21.89) bring into, say $\Phi_Z$, admixtures of order $\Gamma/\Delta$ of $\Phi_X$ and $\Phi_Y$. It follows that the transition probability $P_{XY}$, instead of being proportional (as is usually the case) to the square of the energy difference $\Delta_{XY}$ (see chapter 10), is reduced by the square of the admixture coefficient $(\Gamma/\Delta)^2$ and thus is independent of $\Delta$.

Apart from these changes the transition rate due to the direct process has the usual form (Ham 1969)

$$P_{XY} = \frac{9\,\Gamma^2(qV_{ES})^2 kT_0}{5\pi\rho\hbar^4 v_t^{\,5}} \left\{1 + \frac{2}{3}\left(\frac{v_t}{v_l}\right)^5\right\}, \qquad (21.95)$$

where $\rho$ is the density of the crystal and $V_t$ and $V_l$ the transverse and longitudinal velocities of sound.

The Raman process, which has an unusual temperature-dependence with a transition rate proportional to $T^3$, is given by (Pirc, Zeks, and Gosar 1966)

$$P_{XY} = \frac{27\,\Gamma^2(qV_{ES})^4(kT_0)^3}{50\pi\hbar^7\rho^2 v_t^{\,10}} \left\{1 + \frac{2}{3}\left(\frac{v_t}{v_l}\right)^5\right\}^2. \qquad (21.96)$$

We consider also the transition from a spectrum of type (c1), a vibronic doublet with stress energy greater than the magnetic anisotropy but much smaller than the singlet-doublet splitting $3\Gamma$, to an isotropic singlet-like spectrum (b). The orbital eigenstates, given by eqns (21.73), (21.73a), are

$$\Psi_a = \Theta\cos\frac{\alpha}{2} - \mathscr{E}\sin\frac{\alpha}{2}, \qquad \cos\alpha = \frac{e_\theta}{\sqrt{(e_\theta^2 + e_\varepsilon^2)}}\,;$$

$$\Psi_b = \Theta\sin\frac{\alpha}{2} + \mathscr{E}\cos\frac{\alpha}{2}, \qquad \sin\alpha = \frac{e_\varepsilon}{\sqrt{(e_\theta^2 + e_\varepsilon^2)}}\,; \qquad (21.73a)$$

and are separated by an energy

$$\Delta = W_b - W_a = 2qV_{ES}\sqrt{(e_\theta^2 + e_\varepsilon^2)}.$$

The spread in frequency due to anisotropy is

$$h\Delta\nu(m) = 2q(g_2\beta H + A_2 m)\{1 - 3(\xi^2\eta^2 + \eta^2\zeta^2 + \zeta^2\xi^2)\}^{\frac{1}{2}}. \quad (21.97)$$

In order to be wiped out by fast transitions between $\Psi_a$ and $\Psi_b$, the relaxation rate $1/\tau$ must again be such that $\Delta\nu \, . \, \tau \ll 1$.

The calculation is standard and yields for the direct process:

$$\frac{1}{\tau} = \frac{3\,|\Delta|^3\,(qV_{ES})^2}{20\pi\hbar^4\rho v_t{}^5}\Big\{1 + \frac{2}{3}\Big(\frac{v_t}{v_l}\Big)^5\Big\}\coth\Big(\frac{\Delta}{2kT_0}\Big) \quad (21.98)$$

or, if $kT_0 \gg |\Delta|$,

$$\frac{1}{\tau} = \frac{3}{10}\frac{\Delta^2(qV_{ES})^2}{\pi\hbar^4\rho v_t{}^5}\Big\{1 + \frac{2}{3}\Big(\frac{v_t}{v_l}\Big)^5\Big\}kT_0. \quad (21.98')$$

For the Raman process a temperature-dependence of the rate on the fifth power is obtained (Ham 1968):

$$\frac{1}{\tau} = \frac{6\pi(qV_{ES})^4(kT_0)^5}{125\hbar^7\rho^2v_t{}^{10}}\Big\{1 + \frac{2}{3}\Big(\frac{v_t}{v_l}\Big)^5\Big\}^2. \quad (21.99)$$

All the transitions described so far are purely orbital with no spin flip involved. Spin flips can occur because the orbital parts of states of opposite spin belonging to different configurations are not strictly orthogonal. This lack of orthogonality is connected with paramagnetic anisotropy and leads to spin-lattice relaxation rates, $1/\tau_1$, smaller than the previously calculated purely orbital transition rates by reduction factors of the order of $(g_2/g_1)^2$ or $(A_2/g_1\beta H)^2$ as the case may be.

Even so, these rates may be much faster than those of ions in less symmetrical environments which are not subject to the Jahn–Teller effects. A detailed discussion of these and other spin-lattice relaxation processes characteristic of Jahn–Teller $^2E$ ions can be found elsewhere (Ham 1969, Williams et al. 1969).

## 21.8. Comparison with experiment

The anisotropic spectra of type (a) which correspond to a static Jahn–Teller effect, exhibited by the ion $Cu^{2+}$, $3d^9$ in cubic or nearly cubic environment, have already been discussed in § 7.16 and need not be considered again here. The review article of Ham (1969), which has provided the inspiration and the information for the writing of the present chapter, contains a thorough discussion of the experimental

evidence on the observation of the Jahn–Teller effect in EPR spectra of $^2E$ levels, to which the reader is referred. We shall be content to examine briefly, as an illustration of the theory, the measurements of Coffman on $Cu^{2+}$, $3d^9$ in MgO (Coffman 1965, 1966, 1968) and Höchli and Estle on $Sc^{2+}$ in $CaF_2$ and $SrF_2$ (Höchli and Estle 1967, Höchli 1967).

An anisotropic spectrum of type (c), characteristic of a vibronic doublet, was observed for $Cu^{2+}$ in MgO at $1\cdot2°K$ with the parameters

$$g_1 = 2\cdot195, \qquad qg_2 = 0\cdot108, \qquad q = \frac{qg_2}{g_1-g_s} \sim 0\cdot5.$$

This value of $q$ indicates a strong or moderately strong Jahn–Teller effect. It is not quite clear whether this spectrum is the no-strain spectrum (c2) or the strain broadened spectrum (c1) given by eqn (21.74). Using for the residual strain at the $Cu^{2+}$ site the same average value $\sim10^{-4}$ as found elsewhere for $Fe^{2+}$ in MgO, and for the strain coefficient $V_{ES}$ the same value as that estimated for $Ni^{3+}$ in $Al_2O_3$, Ham finds a value of the order of 1 cm$^{-1}$ for the strain splitting $\Delta_s \sim 2qV_{ES}(e_\theta^2+e_\varepsilon^2)^{\frac{1}{2}}$, which is much greater than the anisotropy energy $\Delta_m$. Unless this estimate turns out to be grossly incorrect the spectrum of $Cu^{2+}$ in MgO observed by Coffman at $1\cdot2°K$ should thus be of the strain-broadened type (c1). At $77°K$ this spectrum is replaced by an isotropic singlet spectrum (b), which is interpreted as a vibronic doublet spectrum (c1) narrowed by fast-relaxation transitions between the orbital states (21.73).

The resonance spectrum of $Sc^{2+}$, $3d^1$ in $CaF_2$ and $SrF_2$ provides an interesting example of a vibronic doublet spectrum (c) that corresponds to a rather weak Jahn–Teller effect. It should be noted that although $Sc^{2+}$ has one unpaired electron, rather than a hole as in $Cu^{2+}$, $3d^9$, the electronic ground multiplet is still a doublet $\Gamma_3$ because in $CaF_2$ the coordination is eightfold instead of sixfold as in MgO. Since the spin-orbit coupling is now positive, $g_1$ should be smaller than $g_s$ and $g_2$ should be negative. From the values, $g_1 = 1\cdot973$, $qg_2 = -0\cdot022$, one extracts for $q$ the value $q = qg_2/(g_1-g_s) = 0\cdot75$; according to the inequality (21.67) this precludes a strong Jahn–Teller effect and leads for $W_{JT}/\hbar\omega$ to an estimate (Ham 1968) of the order of $0\cdot25$. (In $SrF_2$ the value of $q$ is $0\cdot71$ and the estimate for $W_{JT}/\hbar\omega$ is $0\cdot34$.) For such weak couplings the linear theory based on the eqns (21.59) should be adequate. The assumption that here again the spectrum is of the strain-broadened type is supported by the fact that a stress of up to 250 kg/cm$^2$, applied

by Höchli to his sample, did not induce any observable change in the spectrum. This is to be expected if large random local strains exist already in the crystal.

When the temperature is raised to a few degrees K the (c) spectrum is replaced by an isotropic singlet-like spectrum. This spectrum was interpreted by Höchli as due to the increased population of the first excited singlet, and the singlet-doublet splitting was estimated from the temperature dependence of the intensity as 10 cm$^{-1}$ for Sc$^{2+}$ in CaF$_2$ and 8 cm$^{-1}$ in SrF$_2$. This is clearly incompatible with the assumption, made necessary by a coefficient $q \sim 0.75$, of a weak Jahn–Teller effect since the singlet-doublet distance is then of the order of $\hbar\omega \sim 200$ or 300 cm$^{-1}$. Ham therefore interprets the isotropic spectrum of Sc$^{2+}$ as due to the same motional narrowing of the low temperature spectrum as for Cu$^{2+}$ in MgO.

### 21.9. The Jahn–Teller effect in a triplet state

The problem of the Jahn–Teller effect in orbital triplets $\Gamma_4$ or $\Gamma_5$ differs from that of the orbital doublet in several respects that are all in some way connected with the reduction formula, which replaces eqn (21.12) applicable to $\Gamma_3$,

$$\Gamma_4 \times \Gamma_4 = \Gamma_5 \times \Gamma_5 = \Gamma_4 + \Gamma_5 + \Gamma_3 + \Gamma_1. \qquad (21.100)$$

Already in the absence of Jahn–Teller coupling this relation has important consequences for the ions with a degenerate triplet as ground state, classified as ions of type $B$ in § 19.3. For convenience, we summarize here some of the results.

The first far-reaching consequence of eqn (21.100) arises from the presence on its right-hand side of $\Gamma_4$, a tridimensional representation whose components transform like those of a vector. This means that, in contrast to $\Gamma_3$, the components of an orbital momentum will have non-vanishing components inside the triplets $\Gamma_4$ or $\Gamma_5$. We have shown in § 14.2 that it is convenient, using the Wigner–Eckart theorem, to introduce a pseudo-angular momentum whose components inside the manifold $\Gamma_4$ or $\Gamma_5$ have the same matrix elements as those of an orbital momentum $L = 1$ within a $p$-state. This is summed up by the relation

$$\langle \mathbf{L} \rangle = \alpha \tilde{\mathbf{l}}, \qquad (21.101)$$

where the coefficient $\alpha$ depends on the detailed structure of the orbital triplet $\Gamma_4$ or $\Gamma_5$ and the symbol $\langle \ \rangle$ means projection inside the triplet manifold. In particular, $\alpha$ has the value $-1$ for a $\Gamma_5$ triplet originating in a $D$-term, $\alpha = +\frac{1}{2}$ if $\Gamma_5$ comes from an $F$-term, and $\alpha = -\frac{3}{2}$ for the

triplet $\Gamma_4$ originating in an $F$-term. As basis states spanning $\Gamma_4$ or $\Gamma_5$ one can use either the eigenstates $|\pm\tilde{1}\rangle$, $|\tilde{0}\rangle$ of $l_z = \pm 1$, 0 or real wave-functions $\psi_X$, $\psi_Y$, $\psi_Z$ related to the former by

$$|\pm\tilde{1}\rangle = \mp \frac{\psi_X \pm i\psi_Y}{\sqrt{2}} \; ; \; |\tilde{0}\rangle = \psi_Z. \qquad (21.102)$$

The existence of a finite orbital momentum $\langle \mathbf{L} \rangle = \alpha\mathbf{l}$ entails also a finite spin-orbit coupling

$$\lambda\langle \mathbf{L} \rangle \cdot \mathbf{S} = \alpha\lambda(\tilde{\mathbf{l}} \cdot \mathbf{S}). \qquad (21.103)$$

If (in contrast to our treatment of $\Gamma_3$) we neglect second-order effects arising from the matrix elements of $\lambda(\mathbf{L} \cdot \mathbf{S})$ to the excited cubic multiplets, the total spin $\mathbf{S}$ and the pseudo-momentum $\tilde{\mathbf{l}}$ combine to yield the multiplets $\tilde{\mathscr{J}}$, where $\tilde{\mathscr{J}}$ takes all the values from $|S-1|$ to $S+1$. The spectroscopic splitting factor of the ion in a $\tilde{\mathscr{J}}$ multiplet is given by the Landé formula

$$g(\tilde{\mathscr{J}}) = \frac{1}{\tilde{\mathscr{J}}(\tilde{\mathscr{J}}+1)} \{\tilde{g}_l(\tilde{\mathbf{l}} \cdot \tilde{\mathscr{J}}) + g_s(\mathbf{S} \cdot \tilde{\mathscr{J}})\}$$

$$= \frac{1}{2\,\tilde{\mathscr{J}}(\tilde{\mathscr{J}}+1)} [\tilde{g}_l\{\tilde{\mathscr{J}}(\tilde{\mathscr{J}}+1) + 2 - S(S+1)\} +$$

$$+ g_s\{\tilde{\mathscr{J}}(\tilde{\mathscr{J}}+1) + S(S+1) - 2\}]. \qquad (21.104)$$

In (21.104) $\tilde{g}_l = \alpha g_L$, where $g_L$ is the *true* orbital gyromagnetic factor that may be smaller than unity because of covalency as explained in § 20.5.

The presence of $\Gamma_5$ and $\Gamma_3$ on the right-hand side of (21.100) means that the two even vibrational modes of Table 26 can both be coupled to the electronic states of the degenerate triplet with two coupling constants which we denote by $V_E$ and $V_T$ ($E$ and $T_2$ being alternative names for $\Gamma_3$ and $\Gamma_5$).

Our problem is to find, inside the degenerate triplet manifold, electronic operators transforming respectively like components of $\Gamma_3$ and $\Gamma_5$, thus taking the part played by $U_\theta$ and $U_\varepsilon$ for the degenerate doublet. These operators can be easily formed using the components of the pseudo-momentum $\tilde{\mathbf{l}}$. For $\Gamma_3$ they are

$$\mathscr{E}_\theta = \tfrac{1}{2}\{3\tilde{l}_z^2 - l(l+1)\} = \tfrac{1}{2}(3\tilde{l}_z^2 - 2),$$

$$\mathscr{E}_\varepsilon = \frac{\sqrt{3}}{2}(\tilde{l}_x^2 - \tilde{l}_y^2), \qquad (21.105)$$

and for $\Gamma_5$

$$T_{2X} = (\tilde{l}_y \tilde{l}_z + \tilde{l}_z \tilde{l}_y), \qquad T_{2Y} = (\tilde{l}_z \tilde{l}_x + \tilde{l}_x \tilde{l}_z), \qquad T_{2Z} = (\tilde{l}_x \tilde{l}_y + \tilde{l}_y \tilde{l}_x).$$

(21.105a)

It is easily checked, by writing them in the representation $\psi_X, \psi_Y, \psi_Z$, where they are diagonal (rather than in the representation $|\pm 1\rangle, |0\rangle$), that the operators $\mathscr{E}_\theta$ and $\mathscr{E}_\varepsilon$ commute with each other. (Naturally this is *not* a general property of tensor operators of the form (21.105) as we know very well from the example of the doublet where the non-commuting operators $U_\theta$ and $U_\varepsilon$ were, by eqn (21.19), of the form (21.105), with $L = 2$ rather than 1.) This makes the study of the Jahn–Teller coupling with the mode $\Gamma_3$ much simpler than that with the mode $\Gamma_5$ whose operators (21.105a) do not commute with each other. In the representation $\psi_X, \psi_Y, \psi_Z$ these operators are given by the following matrices:

$$\mathscr{E}_\theta = \begin{pmatrix} \tfrac{1}{2} & & \\ & \tfrac{1}{2} & \\ & & -1 \end{pmatrix}, \qquad \mathscr{E}_\varepsilon = \begin{pmatrix} -\surd(3)/2 & & \\ & \surd(3)/2 & \\ & & 0 \end{pmatrix},$$

$$T_{2X} = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & -1 \\ 0 & -1 & 0 \end{pmatrix}$$

(21.106)

with obvious changes for $T_{2Y}$ and $T_{2Z}$.

The vibronic Hamiltonian can be written as $\mathscr{H}_v = \mathscr{H}_v^E + \mathscr{H}_v^T$, where

$$\mathscr{H}_v^E = \frac{1}{2\mu}(P_\theta^2 + P_\varepsilon^2) + \frac{\mu\omega^2}{2}(Q_\theta^2 + Q_\varepsilon^2) + V_E(Q_\theta \mathscr{E}_\theta + Q_\varepsilon \mathscr{E}_\varepsilon), \quad (21.107)$$

$$\mathscr{H}_v^T = \frac{1}{2\mu'}(P_4^2 + P_5^2 + P_6^2) + \frac{\mu'\omega'^2}{2}(Q_4^2 + Q_5^2 + Q_6^2) +$$
$$+ V_T(Q_4 T_{2X} + Q_5 T_{2Y} + Q_6 T_{2Z}). \quad (21.107a)$$

We shall see in the next section that if the $\Gamma_3$ mode only is coupled to the triplet $(V_T = 0)$ the problem has an exact and rather simple solution. On the other hand, if the coupling is to the mode $\Gamma_5$ or to both, only qualitative statements can be made.

Before we discuss these two couplings we must make some assumptions about the magnitude of the spin-orbit coupling. As usual we shall consider the two cases when this coupling is either much stronger or

much weaker than the Jahn–Teller coupling, shirking the complicated intermediate situation. It has been shown (Öpik and Pryce 1957, Van Vleck 1960) that a spin-orbit coupling appreciably stronger than the Jahn–Teller coupling may quench the latter to a large extent. This can be seen as follows: consider a level $\tilde{\mathscr{J}}$ resulting from the spin-orbit coupling, represented as $\alpha\lambda(\tilde{\mathbf{l}} \cdot \mathbf{S})$. If $|\alpha\lambda| \gg V_E$, $V_T$ we may disregard off-diagonal matrix elements of the Jahn–Teller coupling between two different $\tilde{\mathscr{J}}$ multiplets and keep only those inside the multiplet $\tilde{\mathscr{J}}$ under consideration. Inside this multiplet the five operators (21.105), (21.105a) can be expressed by the Wigner–Eckart theorem as similar combinations of $\tilde{\mathscr{J}}_x$, $\tilde{\mathscr{J}}_y$, $\tilde{\mathscr{J}}_z$ multiplied by a constant $\sigma$ which is the same for all five tensor components:

$$\langle 3\tilde{l}_z^2 - \tilde{l}(\tilde{l}+1) \rangle_{\tilde{\mathscr{J}}} = \sigma\{3\tilde{\mathscr{J}}_z^2 - \tilde{\mathscr{J}}(\tilde{\mathscr{J}}+1)\}, \text{ etc.} \tag{21.108}$$

Here the constant $\sigma$ can be computed either by means of the Racah 6$j$- symbol (eqn (16.29)) or by a direct calculation. If the ground $\tilde{\mathscr{J}}$ multiplet is $\tilde{\mathscr{J}} = \frac{1}{2}$, the five operators (21.105; 21.105a) obviously vanish. This is to be expected, since otherwise the Jahn–Teller coupling would have been able to lift a Kramers-degeneracy which it cannot possibly do, being a time-even operator.

For values of $\tilde{\mathscr{J}}$ higher than $\frac{1}{2}$ the coefficient $\sigma$ often turns out to be small. Thus, for instance, for $Fe^{2+}, 3d^6$ in MgO, where the ground orbital triplet is $\Gamma_5(^5D)$, the ground $\tilde{\mathscr{J}}$ multiplet is also a triplet $\tilde{\mathscr{J}} = 1$. A direct calculation of the expectation value of $(\frac{1}{2})\{3\tilde{l}_z^2 - \tilde{l}(\tilde{l}+1)\}$ in the state $\tilde{\mathscr{J}} = \tilde{\mathscr{J}}_z = 1$ yields $\frac{1}{20}$, whence $\sigma = \frac{1}{10}$. The effective Jahn–Teller coupling is reduced in the ratio $\frac{1}{10}$ and the Jahn–Teller energy in the ratio $1/100$.

In the following sections we shall make the opposite assumption of a weak spin-orbit coupling, introduced as a perturbation once the Jahn–Teller coupling has been included, which implies that the spin-orbit coupling is also smaller than the vibrational quantum $\hbar\omega$.

## 21.10. The Jahn–Teller effect in an orbital triplet with $\Gamma_3$ coupling

*The vibronic wave-functions*

The eigenfunctions of the vibronic Hamiltonian $\mathscr{H}_v^E$ (eqn (21.107)) are Born–Oppenheimer products of the form

$$\Phi_X = \psi_X \Psi_X, \qquad \Phi_Y = \psi_Y \Psi_Y, \qquad \Phi_Z = \psi_Z \Psi_Z,$$

where $\psi_X$, $\psi_Y$, $\psi_Z$ are the electronic wave-functions that span the electronic triplet and $\Psi_X$, $\Psi_Y$, $\Psi_Z$ three nuclear functions of $Q_\theta$ and $Q_\varepsilon$. Applying $\mathscr{H}_v^E$ to $\psi_Z \Psi_Z$, we find for $\Psi_Z$ the equation

$$\left\{ \frac{1}{2\mu}(P_\theta^2 + P_\varepsilon^2) + \frac{\mu\omega^2}{2}(Q_\theta^2 + Q_\varepsilon^2) - V_E Q_\theta \right\} \Psi_Z = W\Psi_Z, \quad (21.109)$$

where use has been made of the form (21.106) of $\mathscr{E}_\theta$ and $\mathscr{E}_\varepsilon$; (21.109) is the equation of a two-dimensional harmonic oscillator in the plane $(Q_\theta, Q_\varepsilon)$ centred on the point

$$Q_\varepsilon^Z = 0, \qquad Q_\theta^Z = \frac{V_E}{\mu\omega^2}, \quad (21.110)$$

or in polar coordinates $\rho_0 = V_E/\mu\omega^2$, $\varphi = 0$, the point at which the potential energy in (21.109) is a minimum and has the Jahn–Teller value, $W_{JT} = V_E^2/2\mu\omega^2$. Because of cubic symmetry the two other functions $\Psi_X$ and $\Psi_Y$ must be similar oscillator functions but centred around the points $\rho = \rho_0$, $\varphi = \pm 2\pi/3$, which are the points

$$\begin{aligned} Q_\theta^X &= -\frac{1}{2}\frac{V_E}{\mu\omega^2}, \qquad Q_\varepsilon^X = \frac{\sqrt{3}}{2}\frac{V_E}{\mu\omega^2}, \\ Q_\theta^Y &= -\frac{1}{2}\frac{V_E}{\mu\omega^2}, \qquad Q_\varepsilon^Y = -\frac{\sqrt{3}}{2}\frac{V_E}{\mu\omega^2}, \end{aligned} \quad (21.110a)$$

in accordance with the form of $\mathscr{E}_\theta$ and $\mathscr{E}_\varepsilon$ given by (21.106). If, as is customary in the theory of the static Jahn–Teller effect, one neglects the nuclear motion, the three points in $Q$ space

$$\{Q_\varepsilon^X, Q_\theta^X; Q_\varepsilon^Y, Q_\theta^Y; Q_\varepsilon^Z, Q_\theta^Z\}$$

represent the stable equilibrium positions of the distorted complex with electronic functions $\psi_X$, $\psi_Y$, $\psi_Z$. At each of these points, say $(Q_\theta^Z, Q_\varepsilon^Z)$, the energy of the two other states $\psi_X$, $\psi_Y$ is greater by the amount $3W_{JT} = 3V_E^2/2\mu\omega^2$.

The potential energy surfaces relative to the three functions $\psi_X$, $\psi_Y$, $\psi_Z$ are three paraboloids shown in Fig. (21.3), which result from each other by a rotation of $2\pi/3$. This situation resembles to some extent the tunnelling model described in § 21.6 with the three potential minima depressed by the Jahn–Teller energy $W_{JT}$ and the three wave-functions (21.82, 21.82a) or (21.85). There is, however, an important difference: those three functions $\Phi$ were not orthogonal and their degeneracy was only approximate, due to the closeness of a singlet with a wave-function $A$ to the doublet $E$ spanned by two wave-functions $\Theta$ and $\mathscr{E}$. $A$, $\Theta$, and $\mathscr{E}$ were the 'good' wave-functions, linear combinations
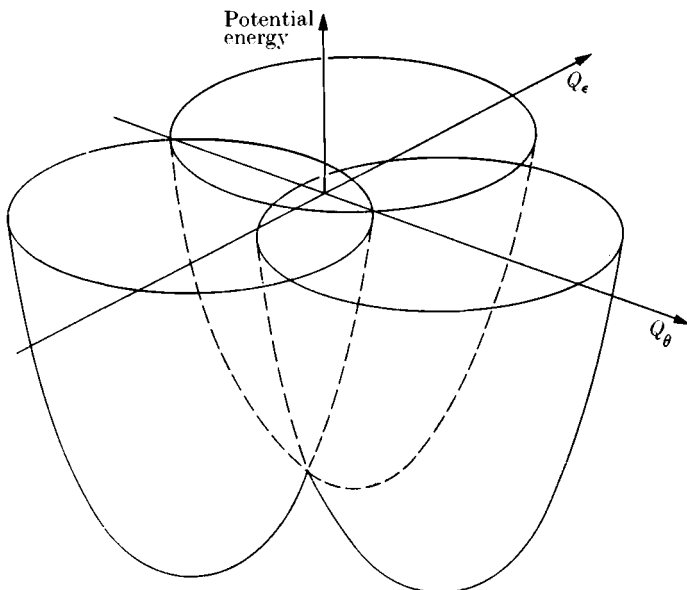
FIG. 21.3. Potential energy surfaces for a triplet with a $\Gamma_3$ Jahn–Teller coupling.

of $\Phi_X$, $\Phi_Y$, $\Phi_Z$, and the doublet and the singlet were split apart by an amount $3\Gamma$ when proper account was taken of the lack of orthogonality of $\Phi_X$, $\Phi_Y$, $\Phi_Z$.

In the present situation $\Phi_X$, $\Phi_Y$, $\Phi_Z$ are exactly orthogonal because their electronic parts $\psi_X$, $\psi_Y$, $\psi_Z$ are exactly orthogonal, and they span a bona fide triplet. It was already a degenerate triplet $\Gamma_4$ or $\Gamma_5$ before the Jahn–Teller coupling was switched on (the ground vibrational function is then the non-degenerate ground state of a two-dimensional harmonic oscillator and the overall degeneracy is that of the electronic triplet), and must stay a triplet of the same nature, $\Gamma_4$ or $\Gamma_5$, when the Jahn–Teller coupling is included.

The eigenstates of $\mathscr{H}_v^E$ (eqn (21.107)) can be written

$$\Phi_{i, n_\theta, n_\varepsilon}(q, Q) = \psi_i(q) F_{n_\theta}(Q_\theta - Q_\theta^i) F_{n_\varepsilon}(Q_\varepsilon - Q_\varepsilon^i). \qquad (21.111)$$

$i$ stands for $X$, $Y$, $Z$ in this formula; $Q_\theta^i$, $Q_\varepsilon^i$ are the equilibrium positions of the harmonic oscillators given by (21.110, 21.110a), $n_\theta$, $n_\varepsilon$ are integer quantum numbers, and $F_{n_\theta}(Q_\theta)$, $F_{n_\varepsilon}(Q_\varepsilon)$ the usual quantum states of one-dimensional harmonic oscillators. The energy of a state (21.111) is

$$W_{i, n_\theta, n_\varepsilon} = W_0 - \frac{V_E^2}{2\mu\omega^2} + (n_\theta + n_\varepsilon + 1)\hbar\omega. \qquad (21.112)$$

Here excited levels have a high and partly spurious degeneracy due to the linear character of the Hamiltonian $\mathscr{H}_v^E$ (21.107). We did not find it necessary to introduce into $\mathscr{H}_v^E$ higher-order warping terms, as we were forced to in the study of the electronic doublet, whose effect among other things was to split the spurious degeneracy of the singlets $A_1$, $A_2$. In the present case, from the relation (see Table 2)

$$\Gamma_3 \times \Gamma_4 = \Gamma_3 \times \Gamma_5 = \Gamma_4 + \Gamma_5,$$

using the same reasoning as in § 21.6, we see that the energy levels of the most general vibronic Hamiltonian, describing a $\Gamma_3$ Jahn–Teller coupling with an electronic triplet $\Gamma_4$ or $\Gamma_5$, are triplets $\Gamma_4$ *and* $\Gamma_5$, the ground level having the same symmetry as in the absence of Jahn Teller coupling.

*First-order effects*

Armed with the wave-functions (21.111) we can compute the matrix elements of the various electronic operators of interest for paramagnetic resonance, first and foremost being those of the orbital momentum $\tilde{l}$. From the form $\Phi_{in} = \psi_i \Psi_{in}$, where $n$ stands for $(n_\theta, n_\varepsilon)$, of the vibronic functions we see that for any electronic operator $O_d$ diagonal in the representation $\psi_i$ we have

$$\langle \Phi_{in} | O_d | \Phi_{jn'} \rangle = \delta_{nn'} \langle \psi_i | O_d | \psi_j \rangle. \tag{21.113}$$

Such operators are not affected by Jahn–Teller coupling. On the other hand, for an operator $O_{od}$ with off-diagonal matrix elements, such as the orbital momentum, we get

$$\langle \Phi_{in} | O_{od} | \Phi_{jn'} \rangle = \langle \psi_i | O_{od} | \psi_j \rangle \langle \Psi_{in} | \Psi_{jn'} \rangle, \tag{21.114}$$

in which

$$\langle \Psi_{in} | \Psi_{jn'} \rangle = \langle F_{in_\theta} | F_{jn'_\theta} \rangle \langle F_{in_\varepsilon} | F_{jn'_\varepsilon} \rangle$$
$$= \langle F_{n_\theta}(Q_\theta - Q_\theta^i) | F_{n'_\theta}(Q_\theta - Q_\theta^j) \rangle \langle F_{n_\varepsilon}(Q_\varepsilon - Q_\varepsilon^i) | F_{n'_\varepsilon}(Q_\varepsilon - Q_\varepsilon^j) \rangle, \tag{21.115}$$

where the scalar products $\langle F_{in_\theta} | F_{jn'_\theta} \rangle$ can be computed exactly from the known wave-functions of the harmonic oscillator (Ham 1965). In the ground triplet the relation (21.114) takes the form

$$\langle \Phi_{ioo} | O_{od} | \Phi_{joo} \rangle$$
$$= \langle \psi_i | O_{od} | \psi_j \rangle \langle F_o^i | F_o^j \rangle^2 = \langle \psi_i | O_{od} | \psi_j \rangle \exp(-3W_{JT}/2\hbar\omega). \tag{21.116}$$

This relation (21.116) means that in the ground triplet the orbital momentum, which in the representation $\psi_i$ has off-diagonal matrix elements only, is quenched by a factor $\exp(-3W_{\mathrm{JT}}/2\hbar\omega)$.

In the same way as we introduced for the vibronic doublet vibronic operators $U_{g\theta}$, $U_{g\varepsilon}$ (eqn (21.52)), we introduce here an operator $\mathbf{l}_g$ using the condition $\langle\Phi_{i0}|\,\mathbf{l}_g\,|\Phi_{j0}\rangle = \langle\psi_i|\,\tilde{\mathbf{l}}\,|\psi_j\rangle$. Within the ground triplet we can replace $\tilde{\mathbf{l}}$ by

$$\mathbf{l}_g \exp\left(-\frac{3W_{\mathrm{JT}}}{2\hbar\omega}\right).$$

It is easy to see that all electronic tensor components, with off-diagonal matrix elements only, which transform like $\Gamma_4$, that is as $\tilde{\mathbf{l}}_x$, $\tilde{\mathbf{l}}_y$, $\tilde{\mathbf{l}}_z$; or like $\Gamma_5$, that is as $T_{2X}$, $T_{2Y}$, $T_{2Z}$; will have the same reduction factors. On the other hand, tensor components that transform like $\mathscr{E}_\theta$ and $\mathscr{E}_\varepsilon$ are diagonal and unaffected by Jahn–Teller coupling. Following Ham (1969), we transcribe these results as

$$\kappa(T_1) = \kappa(T_2) = \exp\left(-\frac{3W_{\mathrm{JT}}}{\hbar\omega}\right), \qquad \kappa(E) = 1. \qquad (21.117)$$

Equation (21.117) shows in particular that a small static distortion of the cubic field will be partially quenched if it is trigonal (transforming as $T_2$), but unaffected if it is tetragonal (transforming as $E$).

The same reduction factor $\kappa(T_1) = \kappa_1$ applies naturally to the spin-orbit coupling $\lambda(\mathbf{L} . \mathbf{S}) = \alpha\lambda(\tilde{\mathbf{l}} . \mathbf{S})$, which now becomes in first order $\kappa_1\alpha\lambda(\mathbf{l}_g . \mathbf{S})$. We can still apply the method developed for ions of type $B$ in the absence of a Jahn–Teller effect and couple the vibronic operator $\mathbf{l}_g$ to $\mathbf{S}$ to obtain the multiplets $\tilde{\mathscr{J}}$, but the separation $\alpha\lambda\tilde{\mathscr{J}}$ between two multiplets $\tilde{\mathscr{J}}$ and $\tilde{\mathscr{J}}-1$ is also reduced by the factor $\kappa_1$.

### Second-order terms and the transition to the static effect

Obviously this procedure can only be valid as long as the reduced spin-orbit coupling $\kappa_1\alpha\lambda(\mathbf{l}_g . \mathbf{S})$ remains much larger than either the magnetic or strain perturbations whose expectation values we wish to calculate inside the multiplet $\tilde{\mathscr{J}}$. There is another limitation, which is the following: $\alpha\kappa_1\lambda(\mathbf{l}_g . \mathbf{S})$ represents only the first-order effect of the spin-orbit coupling inside the vibronic ground triplet. Second-order terms due to this coupling are small in a static crystal field because of the large energy denominators which are the cubic splittings. In the presence of Jahn–Teller coupling, however, matrix elements to excited vibronic states, such as $\langle\Phi_{i0}|\,\alpha\lambda(\tilde{\mathbf{l}} . \mathbf{S})\,|\Phi_{jn}\rangle$, which is equal to

$\langle \psi_i | \ \alpha\lambda(\tilde{\mathbf{l}} \cdot \mathbf{S}) \ | \psi_j \rangle \langle \Psi_{i0} | \Psi_{jn} \rangle$, do not vanish for $i \neq j$, and because the energy denominators $n\hbar\omega$ are much smaller than the cubic splittings, second-order terms may become appreciable especially in view of the quenching of the first-order terms. From symmetry arguments these second-order terms can be expressed as follows:

$$\mathscr{H}_{\mathrm{SO}}^{(2)} = -\frac{\lambda^2\alpha^2}{\hbar\omega}\{k_1(\mathbf{l}_g \cdot \mathbf{S})^2 + k_2(l_{gx}^2 S_x^2 + l_{gy}^2 S_y^2 + l_{gz}^2 S_z^2)\}. \quad (21.118)$$

The coefficients $k_1$ and $k_2$ can be computed exactly (Ham 1965).

If we write $x = 3W_{\mathrm{JT}}/\hbar\omega$, the coefficients $k_1(x)$ and $k_2(x)$ are given by

$$k_1(x) = \mathrm{e}^{-x}G(\tfrac{1}{2}x), \qquad k_2(x) = \mathrm{e}^{-x}\{G(x) - G(\tfrac{1}{2}x)\},$$
$$(21.119)$$

where

$$G(x) = \int_0^x \frac{1}{u}(\mathrm{e}^u - 1) \ \mathrm{d}u \underset{x \to \infty}{\sim} \frac{\mathrm{e}^x}{x}\left(1 + \frac{1}{x} + \dots\right). \quad (21.119a)$$

The coefficients $k_1$ and $k_2$ must naturally vanish in the absence of Jahn–Teller coupling, in accordance with (21.119). For $x$ relatively small, when the second-order spin-orbit term $\mathscr{H}_{\mathrm{SO}}^{(2)}$ is much smaller than the first-order term $\mathscr{H}_{\mathrm{SO}}^{(1)} = \alpha\lambda\mathrm{e}^{-x/2}(\mathbf{l}_g \cdot \mathbf{S})$, its only effect is to violate the Landé interval rule between the multiplets $\tilde{\mathscr{J}}$ and to split those for which $\tilde{\mathscr{J}} \geq 2$.

For very strong Jahn–Teller coupling $W_{\mathrm{JT}}/\hbar\omega \to \infty$ the orbital momentum and the spin-orbit coupling are quenched completely in first order by the reduction factor $\exp -(3W_{\mathrm{JT}}/2\hbar\omega)$. The second-order term (21.118) has the asymptotic form

$$-\frac{\lambda^2\alpha^2}{(\hbar\omega)x}(l_{gx}^2 S_x^2 + l_{gy}^2 S_y^2 + l_{gz}^2 S_z^2) = -\frac{\lambda^2\alpha^2}{3W_{\mathrm{JT}}}\{\dots\}. \quad (21.120)$$

In the ground state $\Phi_{ZO}$, (21.120) has the expectation value

$$-\frac{\lambda^2\alpha^2}{3W_{\mathrm{JT}}}(S_x^2 + S_y^2) = D\{S_z^2 - S(S+1)\} \text{ with } D = \frac{\lambda^2\alpha^2}{3W_{\mathrm{JT}}}. \quad (21.121)$$

This is the value predicted by static crystal-field theory for an ion of type $A$ in the non-degenerate electronic state $\psi_Z$ at the bottom $(Q_\theta^Z, Q_\varepsilon^Z)$ of the paraboloid $Z$, separated at that point by $3W_{\mathrm{JT}}$ from the paraboloids $X$ and $Y$ where the electronic wave-functions are $\psi_X$ and $\psi_Y$. This is exactly what one expects from a static Jahn–Teller effect.

The Zeeman energy $Z$ is expressed by the operator

$$Z = \beta g_L(\mathbf{L} \cdot \mathbf{H}) + g_s\beta(\mathbf{S} \cdot \mathbf{H}) = \beta\tilde{g}_l(\tilde{\mathbf{l}} \cdot \mathbf{H}) + g_s\beta(\mathbf{S} \cdot \mathbf{H}). \quad (21.122)$$

If second-order terms are negligible $Z$ can be rewritten as

$$Z^{(1)} = \beta\kappa_1\tilde{g}_l(\mathbf{l}_g \cdot \mathbf{H}) + g_S\beta(\mathbf{S} \cdot \mathbf{H}). \tag{21.122a}$$

The formula (21.104) can still be used for the gyromagnetic factor $g(\tilde{\mathscr{J}})$ provided $g_l = \alpha g_L$ is replaced by $\kappa_1 g_l = \alpha\kappa_1 g_L$, where $\kappa_1 = \kappa(T_1)$ in eqn (21.117). In second order, cross terms between the Zeeman Hamiltonian and the spin–orbit coupling yield an expression $Z^{(2)}$ very similar to (21.118),

$$Z^{(2)} = g_1\beta\{(\mathbf{l}_g \cdot \mathbf{S})(\mathbf{l}_g \cdot \mathbf{H}) + (\mathbf{l}_g \cdot \mathbf{H})(\mathbf{l}_g \cdot \mathbf{S})\} +$$
$$+ g_2\beta(l_{gx}^2 S_x H_x + l_{gy}^2 S_y H_y + l_{gz}^2 S_z H_z), \tag{21.123}$$

where

$$g_1 = -(\lambda\alpha^2/\hbar\omega)g_L k_1(x), \qquad g_2 = -(2\lambda\alpha^2/\hbar\omega)g_L k_2(x).$$

For a very strong Jahn–Teller effect when $x \to \infty$

$$g_1 \to 0, \qquad g_2 \to -\frac{2\lambda\alpha^2}{3W_{\mathrm{JT}}}g_L.$$

In the state $\Phi_{ZO} = \psi_Z \Psi_{ZO}$, $Z^{(2)}$ has a limiting expectation value

$$\langle\Phi_{ZO}|\, Z^{(2)}\, |\Phi_{ZO}\rangle = -\frac{2\lambda\alpha^2}{3W_{\mathrm{JT}}}g_L(S_x H_x + S_y H_y). \tag{21.124}$$

Again, this is what the theory of the static Jahn–Teller effect would predict.

This study of the orbital triplet coupled to the $\Gamma_3$ vibration mode can be summed up as follows. For moderate Jahn–Teller coupling, formally the system behaves very much as if the Jahn–Teller effect did not exist except for a reduction in some parameters such as the spin-orbit coupling, the orbital splitting factor, the trigonal distortion, and an increase in second-order terms such as (21.118). For a very strong Jahn–Teller coupling, the naïve theory of the static Jahn–Teller effect is valid, with orbital Zeeman energy and spin-orbit energy completely quenched in first order, and given in second order by the usual formulae for non-degenerate ions $A$, the excitation energy being $3W_{\mathrm{JT}}$, which at a point of stable equilibrium is the distance to the upper sheets of the potential energy surfaces.

## 21.11. The Jahn-Teller effect in an orbital triplet with $\Gamma_5$ coupling

We have already mentioned the fact that this problem is made difficult because the coupling operators $T_{2X}$, $T_{2Y}$, $T_{2Z}$ in the vibronic

Hamiltonian $\mathscr{H}_v^T$ (eqn (21.107a)) do not commute. It is easiest to approach from the limit of a very strong, nearly static, Jahn–Teller effect, when the tunnelling model can be used. We begin therefore by neglecting the nuclear kinetic energy and look for the points in $Q$ space where the potential energy is a minimum, using the method of Öpik and Pryce (1957). With the small change in notation, $Q_4 \rightarrow Q_X$, $Q_5 \rightarrow Q_Y$, $Q_6 \rightarrow Q_Z$, (and similarly for $P_4$, $P_5$, $P_6$), we can rewrite the vibronic Hamiltonian (21.107a) as

$$\mathscr{H}_v^T = T(P) + V + U_0(Q), \tag{21.125}$$

where the nuclear kinetic energy is

$$T(P) = \frac{1}{2\mu'}(P_X^2 + P_Y^2 + P_Z^2); \tag{21.125a}$$

the Jahn–Teller coupling operator is

$$V(Q) = V_T(Q_X T_{2X} + Q_Y T_{2Y} + Q_Z T_{2Z}); \tag{21.125b}$$

and the quasi-elastic potential energy is

$$U_0(Q) = \frac{\mu'\omega'^2}{2}(Q_X^2 + Q_Y^2 + Q_Z^2). \tag{21.125c}$$

Let $\psi = a_X \psi_X + a_Y \psi_Y + a_Z \psi_Z$ be an eigenstate of $V$ with the eigenvalue $\varepsilon'(Q)$, such that

$$V|a\rangle = \varepsilon'(Q)\,|a\rangle; \quad \varepsilon'(Q) = \langle a|\, V\, |a\rangle; \quad \langle a\,|\,a\rangle = 1, \tag{21.126}$$

where $|a\rangle$ is the set of amplitudes $(a_X, a_Y, a_Z)$. The points in $Q$ space where the potential energy $U(Q) = U_0(Q) + \varepsilon'(Q)$ is a minimum are given by

$$\frac{\partial U_0}{\partial Q_i} + \frac{\partial \varepsilon'}{\partial Q_i} = \mu'\omega'^2 Q_i + \langle a|\,\frac{\partial V}{\partial Q_i}\,|a\rangle = 0. \tag{21.127}$$

If we replace $T_{2X}$, $T_{2Y}$, $T_{2Z}$ by their matrix expression (21.106), eqns (21.126) become

$$\left. \begin{aligned} V_T(Q_Y a_Z + Q_Z a_Y) &= -\varepsilon' a_X, \\ V_T(Q_Z a_X + Q_X a_Z) &= -\varepsilon' a_Y, \\ V_T(Q_X a_Y + Q_Y a_X) &= -\varepsilon' a_Z, \end{aligned} \right\} \tag{21.126a}$$

in which

$$\varepsilon' = -2V_T(Q_X a_Y a_Z + Q_Y a_Z a_X + Q_Z a_X a_Y) \tag{21.126b}$$

and

$$a_X^2 + a_Y^2 + a_Z^2 = 1. \tag{21.126c}$$

Similarly eqns (21.127) become

$$Q_X = \frac{2V_T}{\mu'\omega'^2}a_Y a_Z, \quad Q_Y = \frac{2V_T}{\mu'\omega'^2}a_Z a_X, \quad Q_Z = \frac{2V_T}{\mu'\omega'^2}a_X a_Y.$$

$$(21.127a)$$

Carrying (21.127a) into (21.126a) and making use of (21.126b) and (21.126c) we find the following results:

$$a_X^2 = a_Y^2 = a_Z^2 = \tfrac{1}{3},$$

$$\varepsilon' = -\frac{4V_T^2}{3\mu'\omega'^2}, \qquad U_0 = \frac{2V_T^2}{3\mu'\omega'^2},$$

$$U = \varepsilon' + U_0 = -\frac{2V_T^2}{3\mu'\omega'^2}, \qquad Q_X = \frac{2V_T}{\mu'\omega'^2}a_Y a_Z.$$

$$(21.128)$$

The outcome of eqns (21.127) is that there are four equivalent equilibrium positions in $Q$ space, that is four equivalent distortions of the paramagnetic complex. The electronic wave-functions at these four points are given by

$$\psi_\nu = \frac{m_X\psi_X + m_Y\psi_Y + m_Z\psi_Z}{\sqrt{3}}, \qquad (21.128a)$$

where $m_X$, $m_Y$, $m_Z$ are $\pm 1$ and $\nu = 1, 2, 3, 4$. (A change of sign of all the $m$ naturally does not change the electronic state.) The equilibrium positions in $Q$ space are given by

$$(Q_X)_\nu = \frac{2V_T}{3\mu'\omega'^2}(m_Y m_Z)_\nu. \qquad (21.129)$$

The Jahn–Teller energy at each point, namely the depression with respect to the energy of the undistorted complex, is

$$W_{\mathrm{JT}} = -U(Q_0) = 2V_T^2/3\mu'\omega'^2. \qquad (21.130)$$

We have tacitly assumed that the condition (21.127) that is necessary for the positions (21.129) to be minima of energy in the $Q$ space was also a sufficient condition. This has been checked by Öpik and Pryce (1957) who have also shown that when $\Gamma_3$ and $\Gamma_5$ couplings are *both* present, the only relative minima are *still* those obtained when the two couplings are considered separately, a point which is by no means trivial. The position of the absolute minimum is determined by comparing the two Jahn–Teller energies,

$$(W_{\mathrm{JT}})_{\Gamma_3} = \frac{V_E^2}{2\mu\omega^2}, \qquad (W_{\mathrm{JT}})_{\Gamma_5} = \frac{2V_T^2}{3\mu'\omega'^2}.$$

The naive description of the static Jahn–Teller effect leads to the assumption that the system would be locked preferentially in the distortion that corresponds to the lowest minimum or minima, ignoring the higher ones. We know that because of the dynamic effects tunnelling will occur and the system will not sit in the lowest minima, unless helped by some external cause such as strain. The combined effects of $\Gamma_3$ and $\Gamma_5$ coupling simply cannot be predicted quantitatively on the basis of the existing theories.

Returning to $\Gamma_5$ coupling, we associate with each electronic function $\psi_\nu(m_X, m_Y, m_Z)$ a nuclear function $\Psi_\nu(Q-Q_\nu)$ localized around the minimum $Q_\nu$ and define four vibronic functions, $\Phi_\nu = \psi_\nu \Psi_\nu$. The index $\nu$ is associated with the values $m_X$, $m_Y$, $m_Z$ as follows:

$$\nu = 1, 2, 3, 4 \rightarrow (1, 1, 1), (-1, -1, 1), (1, -1, -1), (-1, 1, -1).$$

Having started with an orbital triplet in cubic symmetry we are faced here with an unexpected fourfold degeneracy. The situation is very similar to that described in § 21.6 where, starting with an orbital doublet, we had a threefold degeneracy. The answer is similar. Our present quadruplet, spanned by the functions $\Phi_\nu$, is not a true quadruplet but results from the merging of a singlet and a triplet. spanned by wave-functions which are 'good' linear combinations of the $\Phi_\nu$. The wave-function for the singlet is obviously

$$\Phi_S = (2\Lambda)^{-1}(\Phi_1+\Phi_2+\Phi_3+\Phi_4), \qquad (21.131)$$

where $\Lambda$ is a number of the order of unity that takes into account the small overlap of the $\Phi_\nu$. For the triplet the proper wave-functions are

$$\Phi_X = (2\Lambda')^{-1}(\Phi_1-\Phi_2+\Phi_3-\Phi_4),$$
$$\Phi_Y = (2\Lambda')^{-1}(\Phi_1-\Phi_2-\Phi_3+\Phi_4), \qquad (21.132)$$
$$\Phi_Z = (2\Lambda')^{-1}(\Phi_1+\Phi_2-\Phi_3-\Phi_4).$$

We can use the explicit expressions (21.132) to calculate the limiting values of the quenching factors $\kappa(T_1) = \kappa(\tilde{1})$, $\kappa(T_2)$ and $\kappa(E)$. Let us consider first the purely imaginary matrix element

$$\langle \Phi_X| \, l_z \, |\Phi_Y\rangle = -i\kappa(T_1).$$

If we use the expressions (21.132) for $\Phi_X$ and $\Phi_Y$ we find

$$\langle \Phi_X| \, l_z \, |\Phi_Y\rangle = 2(\Lambda')^{-2}\langle \Phi_3| \, l_z \, |\Phi_1\rangle. \qquad (21.133)$$

Notice that the diagonal terms $\langle \Phi_\nu| \, l_z \, |\Phi_\nu\rangle$ vanish since the $\Phi_\nu$ are real functions and $l_z$ is Hermitian and purely imaginary. As the strength of

the Jahn–Teller coupling increases, the overlap between the localized functions $\Phi_v$ goes to zero and so does $\kappa(T_1)$. In the same way we find

$$\langle\Phi_X|\,\mathscr{E}_\varepsilon\,|\Phi_X\rangle = 2(\Lambda')^{-2}\langle\Phi_3|\,\mathscr{E}_\varepsilon\,|\Phi_1\rangle, \qquad (21.134)$$

which also goes to zero with increasing Jahn–Teller coupling in contrast to what happened when this coupling was of the $\Gamma_3$ type and $\kappa(E)$ was equal to unity. Finally,

$$\langle\Phi_X|\,T_{2Z}\,|\Phi_Y\rangle = (\Lambda')^{-2}\{\langle\Phi_1|\,T_{2Z}\,|\Phi_1\rangle - \langle\Phi_1|\,T_{2Z}\,|\Phi_2\rangle\}. \qquad (21.135)$$

As the Jahn–Teller coupling increases, the limiting value of $\kappa(T_2)$ is $\frac{2}{3}$. This difference of behaviour between the $\mathscr{E}$ and $T_2$ tensors can be understood in simple terms (Ham 1965). A strain along the [100] axis, which is of the $\mathscr{E}$ type, cannot distinguish between the four distorted configurations that are equivalent with respect to that direction and causes no splitting, whilst a [111] strain of the $T_2$ type does distinguish between the four configurations.

The three quenching factors have been computed numerically by Caner and Englman (1966). Their variation with the strength of the Jahn–Teller coupling is shown in Fig. (21.4), together with the approximate expressions proposed by Ham (1965) as an extrapolation of a
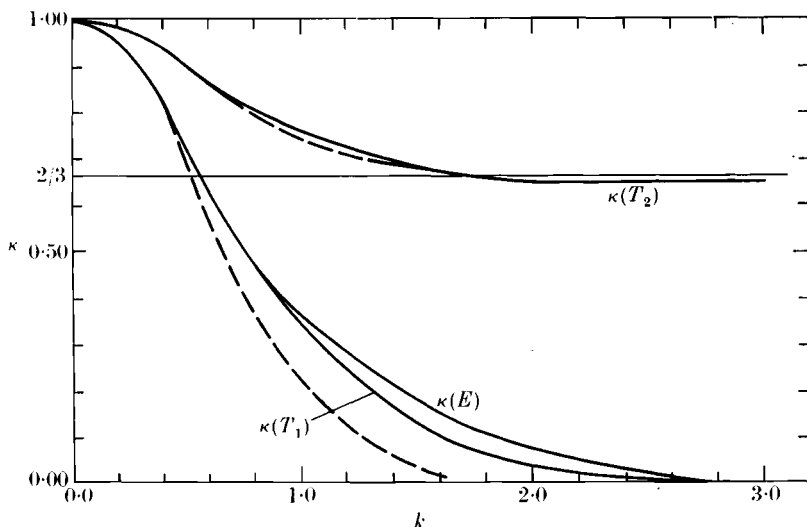


FIG. 21.4. Variation of the reduction factors $\kappa(T_1)$, $\kappa(T_2)$, $\kappa(E)$ against $k$, where $k^2 = \frac{3}{2}(W_{\mathrm{JT}}/\hbar\omega)$. The broken curves are the approximate expressions (21.136) (Ham 1965).

perturbation calculation of Moffitt and Thorson (1957). These are

$$\left.\begin{array}{l} \kappa(E) \approx \kappa(T_1) \approx \exp\{-\tfrac{9}{4}(W_{\mathrm{JT}}/\hbar\omega)\}, \\ \kappa(T_2) \approx \tfrac{1}{3}[2+\exp\{-\tfrac{9}{4}(W_{\mathrm{JT}}/\hbar\omega)\}]. \end{array}\right\} \qquad (21.136)$$

## 21.12. Comparison with experiment

The reader is again referred for a more detailed discussion of the experimental evidence to the review article by Ham (1969). There are several instances of anisotropic spectra in environments of apparently cubic symmetry which could be interpreted as due to a static Jahn–Teller distortion. A rather convincing example is that of $V^{2+}$ in $CaF_2$ (Höchli 1966; Zaripov, Kropotov, Lipanova, and Stepanov 1967). Since $V^{2+}$ has the same charge as $Ca^{2+}$, no charge compensation is expected and, in the absence of Jahn–Teller effect, the symmetry of the crystal potential should be cubic. Spectra having trigonal symmetry are observed, pointing, it would seem, to a predominant $\Gamma_5$ coupling.

Several remarkable examples of a dynamic Jahn–Teller effect are provided by the spectra of impurities belonging to the iron group, which occupy interstitial positions in silicon or substitutional positions in MgO and CaO (Ham 1965). They are summarized in Table 21.2 (Ham 1965).

For the ions $3d^6$, $^5T_2$ in the absence of orbital quenching the splitting factor $g$ should be given by (21.104) where $\tilde{\mathscr{J}} = 1$, $S = 2$, and $\alpha = -1$. This gives $g_{\tilde{\mathscr{J}}} = g_l = 1\cdot5g_s+0\cdot5g_L$, where $g_L$ is the true orbital gyromagnetic factor, possibly slightly reduced by covalency. A value $g_l \approx 3\cdot5$ is thus expected. It is clear from the values given in the table for $Mn^+$ and $Cr^0$ that there is a drastic reduction of the orbital momentum. On the other hand, in $Fe^{2+}$: MgO there is only a small quenching of the orbital momentum of the order of $0\cdot8$ which can be attributed to covalent bonding. This absence of Jahn–Teller quenching

TABLE 21.2

|  | Ion | $g$ |
|---|---|---|
| $3d^6$, $^5T_2$ | Fe²⁺:MgO | 3·428 |
|  | Fe²⁺:CaO | 3·30 |
|  | Mn⁺:Si | 3·01 |
|  | Cr⁰:Si | 2·97 |
| $3d^7$, $^4T_1$ | Co²⁺:MgO | 4·278 |
|  | Fe⁺:MgO | 4·15 |
|  | Mn⁰:Si | 3·362 |
|  | Fe⁺:Si | 3·524 |

can arise from the stabilizing effect of the spin-orbit coupling as explained in § 21.9. In $Fe^{2+}$: CaO, however, the experimental value $g = 3.30$ requires a reduction of the orbital momentum by a factor 0.60. One has the choice between greater covalency or stronger Jahn–Teller coupling than in $Fe^{2+}$:MgO. The former is unlikely since Mössbauer measurements of the isomer shift in the compounds would indicate *less* covalency for $Fe^{2+}$ in CaO than in MgO (Chappert, Frankel, and Blum 1967). The greater orbital quenching would thus imply a stronger Jahn–Teller coupling in CaO than in MgO.

For the $3d^7$, $^4T_1$ ions, eqn (21.104) with $S = \frac{3}{2}$, $\tilde{\mathscr{L}} = \frac{1}{2}$, $\alpha = -\frac{3}{2}$ predicts for a static field, $g_{\frac{1}{2}} = (\frac{5}{3})g_s + g_L \approx \frac{13}{3} \approx 4.33$ in the absence of all quenching. In fact the quenching factor is almost zero for $Mn^0$:Si and 0.2 for $Fe^+$:Si. It would appear that in these ions the spin-orbit coupling is probably smaller than the Jahn–Teller coupling and thus unable to stabilize it. The opposite situation must clearly prevail for $Co^{2+}$:MgO, where the $g$-factor is almost exactly that of the crystal-field theory, and to a lesser extent for $Fe^+$:MgO.

We refer the reader to the article by Ham (1969) for the discussion of a recent explanation by the Jahn–Teller effect of the puzzling spectrum of $Ti^{3+}$ in $Al_2O_3$ (see also the end of § 7.8).