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## A combined Jahn–Teller and pseudo-Jahn–Teller effect: an exactly solvable model

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**Abstract.** The problem of an  $(ns)^2$  ion in an isolated regular octahedron of ligands with an  $A_{1g}$  ground state and a  $T_{1u}$  excited state is solved exactly for the case of the linear vibronic coupling approximation and a harmonic potential energy. The excited state is susceptible to a  $T \otimes (\tau_{2g} + \epsilon_g)$  Jahn–Teller effect (JTE). Three regimes can be found: (i) The difference in energy between the ground and excited states exceeds a certain threshold, so that the interaction does not result in instability. The  $A_{1g}$  level is the ground state. (ii) The excited state has a very strong JTE, so that its energy is lowered far below the  $A_{1g}$  state. (iii) There is strong interaction between the two levels, a pseudo-Jahn–Teller effect (PJTE) mixes the excited state into the ground state and a dipole moment arises. Through the mixing-in of the excited state, the  $\tau_{2g}$  or  $\epsilon_g$  deformations are also present in the ground state. Only trigonally or tetragonally deformed octahedra with an additional dipolar distortion in the case of a PJTE are expected. A condition for strong PJTE is derived, which is shown to be reached more easily for two electrons than for one electron in the ground state.

### 1. Introduction

Cations from the post-transition elements occur in compounds in two oxidation states. Examples are In(I, III), Tl(I, III), Pb(II, IV), Sb(III, V), etc. (e.g. Wells 1984, Huheey 1972). The ions with the lower oxidation state have an outer electronic configuration  $(ns)^2$ , where  $n = 4, 5$  or  $6$ . In complex ions such as  $SbBr_6^{3-}$  and  $TeCl_6^{2-}$ , for example, the  $(ns)^2$  does not lead to a distortion ('inert electron pair'). However, stereochemical activity is often encountered as in deformed Sn(II) halides or in the  $InCl_6^{2-}$  octahedra in yellow and red InCl, where even and odd distortion modes can be distinguished from the crystal structures. The connection of these latter distortions with a pseudo-Jahn–Teller effect (PJTE) has been noted by Van der Vorst and Maaskant (1980).

An important contribution from the Jahn–Teller (JT) viewpoint was made by Öpik and Pryce (1957), in which static deformation for the case of one electron in a  $T_1$  or  $T_2$  degenerate state of a metal ion in an octahedral environment was extensively studied by treating a  $T \otimes (\tau + \epsilon)$  coupling scheme. It follows, depending on the magnitude of certain constants, that either trigonal or tetragonal deformations can be found.

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The case of a combined PJTE and JTE has also been mentioned by Öpik and Pryce (1957), but has not been worked out in detail. They give as an example an excited F-centre, where a 2p state interacts with a 2s ground state. The coupling scheme here is  $(A_{1g} + T_{1u}) \otimes (\alpha_{1g} + \epsilon_g + \tau_{1u}^1 + \tau_{1u}^2 + \tau_{2g})$ .

A combined JTE and PJTE has also been studied on off-centre impurities like the  $\text{Li}^+:\text{KCl}$  system by G I Bersuker and Polinger (1984). They use perturbation theory, which is therefore approximate.

In this paper a combined JTE–PJTE is described, in line with what has been called the method of Öpik and Pryce (1957). An  $A_{1g}$  ground state can, depending on certain conditions, interact with an excited  $T_{1u}$  state. When this occurs, odd distortion modes ( $\tau_{1u}$ ) are introduced, but since the excited state is Jahn–Teller-active even distortion modes also occur and can be observed, for example from the crystal structure. Only linear vibronic coupling and a harmonic potential energy are assumed. Also, an isolated octahedron is considered. There are no molecular fields working on this polyhedron. Exact solutions can be found when only one type of  $\tau_{1u}$  mode is considered. The coupling scheme is therefore  $(A_{1g} + T_{1u}) \otimes (\alpha_{1g} + \epsilon_g + \tau_{1u} + \tau_{2g})$ . The model will be shown to incorporate the JTE of Öpik and Pryce (1957).

Although in practice there are often disturbance factors, which render the problem too complicated to be solved exactly (e.g. quadratic vibronic coupling, anharmonicity or a multimode problem), we think it useful to have an exact prototype in order to discuss the underlying physics.

In section 2 a complete set of stationary points of the adiabatic potential surface corresponding to the linear vibronic interaction is derived, by using the method of Öpik and Pryce (1957). However, unlike their case, the diagonalization of a  $2 \times 2$  matrix is needed in order to find the energies and the values of the normal coordinates.

In section 3 the complete theory is described for one electron as well as for two electrons, although in the latter case the repulsion between the two electrons is neglected. The conditions necessary for the occurrence of a PJTE are derived and also those which determine whether a trigonal or a tetragonal distortion will take place.

Section 4 gives the discussion.

Part of the motivation for this study is the observation that  $\text{InCl}$  (Van den Berg 1964, 1966, Van der Vorst *et al* 1978) exists in two forms: a yellow crystal below 390 K, containing trigonally distorted octahedra with an extra dipole moment, and a red form above this transition temperature, having dipolar and tetragonal deformations. The discussion of these different structures is interesting in relation to the presently developed theory, but is postponed for reasons of clarity to another paper.

## 2. The method of Öpik and Pryce applied to a four-level system

In this section the exact conditions for a PJTE for the case of one electron are derived, according to the method of Öpik and Pryce (1957).

The ground state  ${}^2A_{1g}$  is assumed to be at  $-3\Delta$ . Its wavefunction is denoted by  $|s\rangle$ . The electronic excited state  ${}^2T_{1u}$  is at  $\Delta$ . Its electronic wavefunctions are denoted as  $|x\rangle$ ,  $|y\rangle$  and  $|z\rangle$ .

The Hamiltonian to be used is essentially a vibrational Hamiltonian with a vibronic coupling term:

$$H = T + V + \mathbf{W} \quad (1)$$

where  $T$  is the kinetic energy of the vibrational modes.  $T$  will not be needed in the

following and will henceforth be ignored.  $V$  is the potential energy, for which we consider only the harmonic part

$$V = \frac{1}{2}k_0 S^2 + \frac{1}{2}k_1 P^2 + \frac{1}{2}k_2 R^2 + \frac{1}{2}k_3 U^2. \quad (2)$$

$S$  is the breathing normal coordinate of symmetry  $\alpha_{1g}$ ,  $P^2 = P_x^2 + P_y^2 + P_z^2$  by definition, where the components of  $P$  are dipolar  $\tau_{1u}$  coordinates. By definition  $R^2 = Q_{yz}^2 + Q_{zx}^2 + Q_{xy}^2$ , consisting of the  $\tau_{2g}$  normal coordinates. Similarly by definition  $U = Q_\theta^2 + Q_\epsilon^2$  ( $\epsilon_g$  coordinates). All force constants are assumed to be positive (Bersuker 1988).

The matrix  $\mathbf{W}$  describes the electron–vibration coupling between the different electronic levels. It contains the vibronic coupling constants  $t$ ,  $v$ ,  $e$  and  $b$ . Here  $t = \langle s | \partial H_e / \partial P_x | x \rangle$ ,  $v = \langle x | \partial H_e / \partial Q_{xy} | y \rangle$ ,  $e = \frac{1}{2} \langle z | \partial H_e / \partial Q_\theta | z \rangle$  and  $b = \langle z | \partial H_e / \partial S | z \rangle$ , where  $H_e$  is the electronic Hamiltonian at the equilibrium configuration (e.g. Bersuker 1984, I B Bersuker and Polinger 1989). Use is made of the Wigner–Eckart theorem.

It is convenient to take energy units of  $\Delta$  and transformed normal coordinates:

$$\begin{aligned} S' &= bS/\Delta & P'_\alpha &= tP_\alpha/\Delta \quad (\alpha = x, y, z) & Q'_\alpha &= vQ_\alpha/\Delta \quad (\alpha = xy, yz, zx) \\ Q'_\alpha &= eQ_\alpha/\Delta \quad (\alpha = \theta, \epsilon) & R' &= vR/\Delta & U' &= eU/\Delta & P' &= tP/\Delta \end{aligned} \quad (3)$$

and

$$h = b^2/(k_0\Delta) \quad f = t^2/(k_1\Delta) \quad c = v^2/(k_2\Delta) \quad g = e^2/(k_3\Delta). \quad (4)$$

Note that the constants  $h$ ,  $f$ ,  $c$  and  $g$  are all positive.

Then  $\mathbf{W}$  and  $V$  become respectively:

$$\mathbf{W} = \begin{bmatrix} |s\rangle & |x\rangle & & |y\rangle & & |z\rangle \\ -3 & P'_x & & P'_y & & P'_z \\ P'_x & 1 - Q'_\theta + \sqrt{3}Q'_\epsilon + S' & & Q'_{xy} & & Q'_{zx} \\ P'_y & Q'_{xy} & & 1 - Q'_\theta - \sqrt{3}Q'_\epsilon + S' & & Q'_{yz} \\ P'_z & Q'_{zx} & & Q'_{yz} & & 1 + 2Q'_\theta + S' \end{bmatrix} \quad (5)$$

and

$$V = S'^2/2h + P'^2/2f + R'^2/2c + U'^2/2g. \quad (6)$$

Let  $\mathbf{a} = \{a_0, a_1, a_2, a_3\}$  be a normalized column eigenvector of  $H$ , of the coefficients of the electronic functions  $|s\rangle$ ,  $|x\rangle$ ,  $|y\rangle$  and  $|z\rangle$ , respectively. For an extremum it is required (Öpik and Pryce 1957) that the corresponding eigenvalue  $\epsilon$  of  $H$

$$H\mathbf{a} = \epsilon\mathbf{a} \quad (7)$$

is non-degenerate, and that the variation with respect to all mentioned normal coordinates ( $Q_s$ ) is zero:

$$\mathbf{a}'(\partial\mathbf{W}/\partial Q_s)\mathbf{a} + \partial V/\partial Q_s = 0. \quad (8)$$

It follows that

$$S' = -h(a_1^2 + a_2^2 + a_3^2) \quad (9)$$

$$Q'_{xy} = -2ca_1a_2 \quad Q'_{yz} = -2ca_2a_3 \quad Q'_{zx} = -2ca_3a_1 \quad (10)$$

$$Q'_\theta = -g(2a_3^2 - a_1^2 - a_2^2) \quad Q'_\epsilon = -g\sqrt{3}(a_1^2 - a_2^2) \quad (11)$$

$$P'_x = -2fa_0a_1 \quad P'_y = -2fa_0a_2 \quad P'_z = -2fa_0a_3. \quad (12)$$

A related eigenvalue problem is:

$$\mathbf{W}\mathbf{a} = \varepsilon'\mathbf{a} \quad (13)$$

$$\varepsilon = \varepsilon' + V \quad (14)$$

which leads to four equations cubic in the coefficients.

It is easy to derive the solutions of these equations, almost by inspection.

(A)  $a_1 = a_2 = a_3 = 0, a_0 = 1; \varepsilon' = \varepsilon = -3$ . This is the case of no PJTE and/or JTE. We will refer to it as the isotropic case.

(B)  $a_0 = 0$ . This case has been solved by Öpik and Pryce (1957). Three possibilities arise:

(B1)  $a_0 = 0$ , one of the coefficients of the excited states is one and the others are zero;  $\varepsilon' = 1 - 4g - h, \varepsilon = 1 - 2g - \frac{1}{2}h$ . This is the tetragonal JT case. It has three possible orientations.

(B2)  $a_0 = 0$  and two of the three remaining coefficients are non-zero, e.g.  $a_1 = \pm a_2 = \pm 1/\sqrt{2}, a_3 = 0; \varepsilon' = 1 - g - h - c, \varepsilon = 1 - \frac{1}{2}g - \frac{1}{2}h - \frac{1}{2}c$ . This is the intermediate JT case. It has six possible orientations.

(B3)  $a_0 = 0$  and the three remaining coefficients are non-zero,  $a_1 = \pm a_2 = \pm a_3 = \pm 1/\sqrt{3}; \varepsilon' = 1 - \frac{2}{3}c - h, \varepsilon = 1 - \frac{2}{3}c - \frac{1}{2}h$ . This is the trigonal JT case. There are four possible orientations.

(C) There are further solutions where  $a_0$  and at least one other coefficient are non-zero:

(C1)  $a_0$  and  $a_3$  are non-zero,  $a_1 = a_2 = 0$ . This is the tetragonal PJT case. There are six possible orientations.

(C2)  $a_0, a_1$  and  $a_2$  are non-zero,  $a_3 = 0, a_1 = \pm a_2 = \pm a/\sqrt{2}$ , with  $a = (1 - a_0^2)^{1/2}$ . This is referred to as the 'intermediate' PJT case. There are 12 possible orientations.

(C3) All coefficients are non-zero,  $a_1 = \pm a_2 = \pm a_3 = \pm a/\sqrt{3}$ , with  $a = (1 - a_0^2)^{1/2}$ . This is the trigonal PJT case. There are eight orientations.

The contribution from this paper concerns the pseudo-Jahn-Teller cases arranged under (C). In all three cases, the  $4 \times 4$  matrix  $\mathbf{W}$  can be transformed to a  $2 \times 2$  matrix and two  $1 \times 1$  matrices. The eigenvalues of  $\mathbf{W}$  can therefore be derived exactly.

The seven mentioned solutions of equation (6) form a complete set of stationary points. However, they can be minima, maxima or saddlepoints. In the next section we will find the conditions for the minima to arise. Also we have to check whether these give non-degenerate solutions to  $\varepsilon$  (equation (7)).

### 3. The conditions for a pseudo-Jahn-Teller effect

We discuss first the cases (C1) and (C3), which give rise to tetragonal and trigonal solutions, respectively. By substitution of equations (9)–(12) in equation (5) it is found

that in the tetragonal case the matrix  $\mathbf{W}$  is already block-diagonalized into two  $1 \times 1$  matrices and one  $2 \times 2$  matrix. In particular, the  $2 \times 2$  matrix is important, since this can lead to a mixture of the ground and excited states and therefore to a PJTE. In the trigonal case an orthogonal transformation of the type  $\mathbf{T}^{-1}\mathbf{W}\mathbf{T}$  has to be applied. For the choice of coefficients  $a_1 = a_2 = a_3 = a/\sqrt{3}$ ,  $\mathbf{T}$  is

$$\mathbf{T} = \begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & -1/\sqrt{6} & -1/\sqrt{2} & 1/\sqrt{3} \\ 0 & -1/\sqrt{6} & 1/\sqrt{2} & 1/\sqrt{3} \\ 0 & 2/\sqrt{6} & 0 & 1/\sqrt{3} \end{bmatrix}. \quad (15)$$

The  $2 \times 2$  matrix  $\mathbf{W}'$ , which has to be diagonalized, has the same form in both cases (C1) and (C3), and leads to the determinant

$$\begin{vmatrix} -3 - \epsilon' & P' \\ P' & 1 + 2Q' + S' - \epsilon' \end{vmatrix} = 0. \quad (16)$$

$P' = P_z$  and  $Q' = Q_\theta$  for the tetragonal case and  $P' = P'_z\sqrt{3}$  and  $Q' = Q'_{xy}$  in the trigonal case for the chosen settings. For the other settings a form similar to equation (16) can be derived, although  $P'$  and  $Q'$  then refer to other components. For other trigonal orientations a change of sign of some coefficients of  $\mathbf{T}$  is necessary to rederive equation (16).

The solutions of equation (16) are

$$\epsilon'_\pm = -1 + Q' + \frac{1}{2}S' \pm [(-2 - Q' - \frac{1}{2}S')^2 + P'^2]^{1/2}. \quad (17)$$

For the total energy  $\epsilon$  (equation (14)) the potential energy has to be incorporated as well, but this differs for the tetragonal and the trigonal case.

In addition the case of two electrons is incorporated, where the electronic repulsion energy between these electrons is not taken into account. Let  $j = 1$  for one and  $j = 2$  for two electrons. The electronic wavefunctions  $|s\rangle$ ,  $|x\rangle$ ,  $|y\rangle$  and  $|z\rangle$  refer for  $j = 2$  to a  ${}^1A_{1g}$  and a  ${}^1T_{1u}$  state, where for example

$$|x\rangle = [(ns)_1(np_x)_2 + (ns)_2(np_x)_1](\alpha_1\beta_2 - \alpha_2\beta_1).$$

For the chosen tetragonal setting:

$$\epsilon_\pm = S'^2/2h + P'_z{}^2/2f + Q'_\theta{}^2/2g + j(-1 + Q'_\theta + \frac{1}{2}S') \pm j[(2 + Q'_\theta + \frac{1}{2}S')^2 + P'_z{}^2]^{1/2}. \quad (18)$$

Although we study the PJTE (case (C1),  $a_0, a_3$  non-zero), this has as adjacent stationary points, the case (A) ( $a_3 = 0$ ) and the pure JT case (B1) ( $a_0 = 0$ ) of the corresponding orientation. A minimum requires that the first derivatives of  $\epsilon_\pm$  with respect to the normal coordinates in equation (18) vanish:

$$\partial\epsilon_\pm/\partial P'_z = P'_z/f + P'_z j/[2 + Q'_\theta + \frac{1}{2}S')^2 + P'_z{}^2]^{1/2} = 0 \quad (19)$$

$$\partial\epsilon_\pm/\partial S' = S'/h + \frac{1}{2}j \pm \frac{1}{2}j(2 + Q'_\theta + \frac{1}{2}S')/[(2 + Q'_\theta + \frac{1}{2}S')^2 + P'_z{}^2]^{1/2} = 0 \quad (20)$$

$$\partial\epsilon_\pm/\partial Q'_\theta = Q'_\theta/g + j \pm j(2 + Q'_\theta + \frac{1}{2}S')/[(2 + Q'_\theta + \frac{1}{2}S')^2 + P'_z{}^2]^{1/2} = 0. \quad (21)$$

There are two solutions for equation (19):

$$P'_z = 0 \quad (22)$$

or

$$P_z'^2 = j^2 f^2 - (2 + Q'_\theta + \frac{1}{2} S')^2. \quad (23)$$

For condition (22) either the + or the - solutions of (20) and (21) apply. For the minus sign,  $S' = Q'_\theta = 0$  and from (18) this solution has the energy

$$E_1 = -3j. \quad (24)$$

For the plus sign,  $S' = -jh$  and  $Q'_\theta = -2jg$ , from which

$$E_2 = j - 2j^2 g' \quad \text{with } g' = g + \frac{1}{2} h. \quad (25)$$

Equations (24) and (25) are respectively the isotropic and the tetragonal JT cases (A) and (B1).

If the solution of equation (23) applies, use has been made of the - sign in (19). Working out equations (20) and (21) also for the - sign gives

$$Q'_\theta = -g(jf - 2)/(f - g') \quad (26)$$

$$S' = -\frac{1}{2} h(jf - 2)/(f - g') \quad (27)$$

$$P_z'^2 = f^2(jf - 2)(jf + 2 - 2jg')/(f - g')^2 \quad (28)$$

and the PJT solution (C1)

$$E_3 = \frac{1}{2}(jf + 2 - 2jg')(jf - 2)/(f - g') - j(jf + 1). \quad (29)$$

It is possible to relate  $E_3$  with  $E_1$  and  $E_2$ :

$$E_3 = E_1 - \frac{1}{2}(jf - 2)^2/(f - g') \quad (30)$$

$$E_3 = E_2 - \frac{1}{2}(jf + 2 - 2jg')^2/(f - g'). \quad (31)$$

Also  $P_z'$  has to be real so that  $P_z'^2$  is positive in (28). This means that either

$$jf > 2 \quad \text{and} \quad (jf + 2) > 2jg' \quad \text{which implies } (f - g') > 0 \quad (32)$$

or

$$jf < 2 \quad \text{and} \quad (jf + 2) < 2jg' \quad \text{which implies } (f - g') < 0. \quad (33)$$

From (30) and (31) it is clear that the solution (C1) is only stable with respect to (A) or (B1) when  $f > g'$ , so that (32) gives the conditions for a tetragonal PJTE.

For the trigonal case the reasoning is similar, but different constants apply, since the  $\tau_{2g}$  normal coordinates have to be used instead of the  $\varepsilon_g$  coordinates. One finds ( $c' = c/3 + h/4$ ):

$$Q' = -c(jf - 2)/3(f - c') \quad (34)$$

$$S' = -\frac{1}{2} h(jf - 2)/(f - c') \quad (35)$$

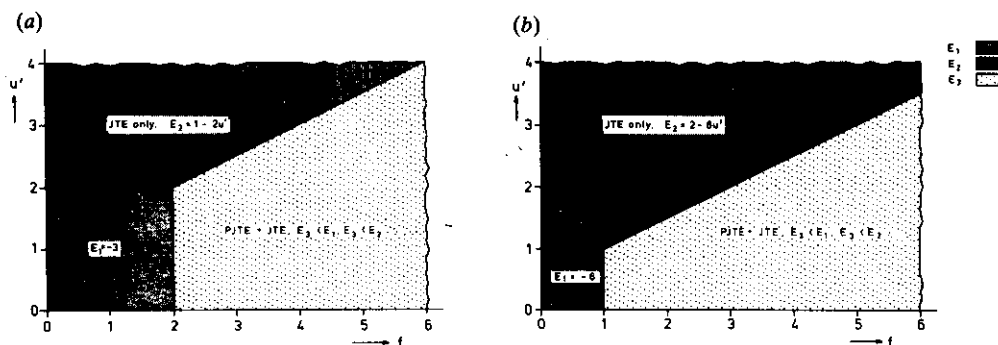
$$P'^2 = f^2(jf - 2)(jf + 2 - 2jc')/(f - c')^2 \quad (36)$$

$$E_1 = -3j \quad (37)$$

$$E_2 = j - 2j^2 c' \quad (38)$$

$$E_3 = \frac{1}{2}(jf + 2 - 2jc')(jf - 2)/(f - c') - j(jf + 1) \quad (39)$$

$$E_3 = E_1 - (jf - 2)^2/2(f - c') \quad (40)$$



**Figure 1.** (a) Domains for the case of *one* electron as a function of  $u'$  and  $f$ . Three regions are possible: no JTE, only JTE and PJTE + JTE. For the tetragonal case  $u' = g'$ . For the trigonal case  $u' = c'$ . The energy is given in units of  $\Delta$ . (b) As (a) but for *two* electrons.

$$E_3 = E_2 - (jf + 2 - 2c')^2 / (f - c'). \quad (41)$$

The conditions for a trigonal PJTE with respect to case (A) and (B3) are

$$f > c' \quad jf > 2 \quad (jf + 2) > 2jc'. \quad (42)$$

In figure 1 the regions of the three different ground states (A), (B) or (C)) are designated for the case of one electron or of two electrons. This figure applies for the tetragonal case as well as for the trigonal case.

In order to compare the tetragonal PJTE and the trigonal PJTE, from equations (30) and (40), it is clear that when  $c' > g'$  (or  $c/3 > g$ ) a trigonal solution and when  $g' > c'$  (or  $g > c/3$ ) a tetragonal solution has the lowest energy. These are the same results as found for the JT cases (equations (25) and (38)) and which have been found by Öpik and Pryce (1957):

$$c/3 > g \quad \rightarrow \quad \text{trigonal minima} \quad (43)$$

$$c/3 < g \quad \rightarrow \quad \text{tetragonal minima.} \quad (44)$$

Moreover, it is easily checked that in both cases the eigenvalues are non-degenerate, in agreement with the text after equation (7).

Öpik and Pryce (1957) also found that the so-called ‘intermediate’ states (our case (B2)) always have an energy in between the trigonal and tetragonal solutions, so that these states are never expected to be a minimum under the given assumptions. In the appendix this is also shown to be true for the ‘intermediate’ PJTE states. An exception arises for  $g = c/3$ . Then the cases (C1), (C2) and (C3) have the same energy. For the dynamic JT case ( $T \otimes (\tau + \epsilon)$ ), this situation has been described by O’Brien (1969).

Öpik and Pryce (1957) used a more general perturbational approach in order to find the minima by studying a Taylor expansion in the deviations of the normal coordinates from the stationary points (their equation (17)). When the second derivatives of  $(V + \mathbf{W})$  (equation (1)) with respect to the different normal coordinates are appropriately arranged in a matrix, this matrix has to be positive definite in the case of a minimum. This is true when all principal minors are positive (e.g. Born and Huang 1954). This procedure is straightforward, since the eigenvalues and eigenvectors of the excited states are known exactly. We have checked the previously found minima and conditions, and



found them to be correct. Since no new conditions appear and since the derivation given in this section is simpler, we omit the description of this perturbational treatment.

#### 4. Discussion

A model of an isolated octahedral complex with a central ion having a  $(ns)^1$  or a  $(ns)^2$  electron configuration has been solved exactly under the assumptions of a linear vibronic coupling, a three-fold degenerate odd excited state and a harmonic potential energy. In section 2 a complete set of stationary points has been derived, from which the minima have been derived in sections 3 and 4. There are three classes of stationary points, a tetragonal, an intermediate and a trigonal one. In the case of the PJTE there are twice as many different settings, compared to the  $T \otimes (\tau + \epsilon)$  JTE (Öpik and Pryce 1957, I B Bersuker and Polinger 1989). This is due to an extra dipole moment in the case of the PJTE with an undetermined sign.

The possibility of solving the problem exactly has been facilitated by the introduction of only four parameter:  $g$ ,  $c$ ,  $h$  and  $f$ . Also the restriction to one type of  $\tau_{1u}$  mode is essential, since this leads to the diagonalization of at most  $2 \times 2$  matrices. Although a large number of normal coordinates have been considered, they all differ in symmetry. This problem is therefore not a multimode but an ideal one (I B Bersuker and Polinger 1989).

In the case of no distortion (A), the ground state is the original  $A_{1g}$  state. However, the frequencies of vibration near these minima as well as other characteristics (I B Bersuker and Polinger 1989) are essentially changed. When a tetragonal minimum is present, equation (26) shows with condition (32) and the fact that  $g > 0$ , that  $Q'_\theta < 0$ . Since the untransformed normal coordinate  $Q_\theta = \Delta Q'_\theta / e$  (section 2) an elongation or shortening of the octahedron depends on the sign of the coupling constant  $e$ . Similarly the signs of the coupling constants  $v$  and  $b$  have to be known in order to know the signs of the  $\tau_{2g}$  and the  $\alpha_{1g}$  distortions.

Since there are no external fields or coupling terms between  $P$  and  $Q$  and since the ground state is totally symmetric, the choice between a tetragonal and a trigonal minimum is entirely decided within the excited state. It is possible, therefore, to give an alternative derivation starting with a particular solution of the excited state and coupling this with the ground state.

A certain threshold has to be reached before a distortion connected with the PJTE occurs (figure 1) (Bersuker 1984, I B Bersuker and Polinger 1989). Explicitly this means that  $f > 1$  ( $j = 2$ ) or  $f > 2$  ( $j = 1$ ), where  $f = t^2/k_1\Delta$ . Therefore a larger  $t$ , a smaller  $k_1$  or a smaller  $\Delta$  can help to overcome the barrier. There are many examples of  $(ns)^2$  ions, which show a dipolar moment (stereochemically activity). But very often undistorted environments occur as well. The reason for these undeformed structures might very well be that  $f < 1$ , although for specific cases other reasons have to be considered as well.

Interesting and instructive is the special case for vanishing (or almost vanishing) JTE (G I Bersuker and Polinger 1984). Let  $e = v = b = 0$ . Then only the  $P'$  coordinates survive. Under the condition  $jf > 2$  a PJTE occurs, with  $P'^2 = (j^2f^2 - 4)$  and  $E_3 = j - \frac{1}{2}(jf + 2)^2/f$ . The adiabatic potential surface forms a spherical trough in the space of the three  $P'$  components, with a minimum at a radius corresponding with the absolute value of  $P'$ . When the constants  $e$ ,  $v$  and  $b$  are no longer zero, but still small with respect

to  $f$ , the symmetry reduces from spherical to cubic. From equations (29), (39) and (A9) one can derive to first order:

$$E_3(\text{tetr}) = -\frac{1}{2}(jf + 2)^2/f + j - \frac{1}{2}g'(jf - 2)^2/f^2 \quad (45)$$

$$E_3(\text{trig}) = -\frac{1}{2}(jf + 2)^2/f + j - \frac{1}{2}c'(jf - 2)^2/f^2 \quad (46)$$

$$E_3(\text{inter}) = -\frac{1}{2}(jf + 2)^2/f + j - \frac{1}{2}g''(jf - 2)^2/f^2 \quad (47)$$

from which it follows that

$$E_3(\text{inter}) = \frac{1}{4}E_3(\text{tetr}) + \frac{3}{4}E_3(\text{trig}). \quad (48)$$

Our model predicts trigonal or tetragonal distortions of octahedra for the PJTE, depending on whether  $c' > g'$  or  $c' < g'$  respectively. The 'intermediate' solutions never form a minimum under the accepted conditions. However, this is not necessarily the case when quadratic vibronic coupling is also considered (I B Bersuker and Polinger 1989). An experimental example of an 'intermediate' PJTE in yellow InCl is under investigation.

As a new result the model gives the possibility that only a JTE arises. The conditions for this to occur have been described in section 3 and have been sketched in figure 1. Examples of this behaviour are not known to us.

A number of simplifications have been made:

(1) Only one set of  $\tau_{1u}$  modes has been assumed, whereas for an isolated octahedron with a central particle there are at least two such modes (e.g. Herzberg 1945, I B Bersuker and Polinger 1989).

(2) The interelectronic repulsion energy has been neglected. It is conceivable that for comparing two types of distortion of one kind of octahedron this is allowed. Since the second electron to be placed has the advantage that the first electron has distorted the octahedron already, the final energy lowering for two electrons is more than twice the amount for one electron.

(3) The problem is limited to four electronic levels. Other electronic levels are always present and might interfere with the predicted results.

(4) In experiments, very often these octahedra are imbedded in a crystal and solid-state effects are expected.

(5) Non-linear vibronic and anharmonic interactions not incorporated in this model may be essential in changing the kind of JT minima in the excited state, e.g. making the 'intermediate' saddlepoints become minima, resulting in the coexistence of different minima, etc (I B Bersuker and Polinger 1989). In addition third-order anharmonic terms of the type  $(2P_z^2 - P_x^2 - P_y^2)Q_\theta$  and  $Q_\theta^3 - 3Q_\theta Q_\epsilon^2$  for the tetragonal case are expected. For the trigonally distorted PJTE similar anharmonic contributions can be of influence.

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## Appendix

We want to show that the 'intermediate' PJTE solutions (C2) have a higher energy than either the tetragonal (C1) or the trigonal (C3) for one or two electrons. One of these

'intermediate' settings can be represented by  $\mathbf{a} = \{(1 - a^2)^{1/2}, a/\sqrt{2}, a/\sqrt{2}, 0\}$ . Substituting in equations (9) to (12) gives a  $\mathbf{W}$  matrix, which by the orthogonal transformation

$$\mathbf{T} = \begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & 1/\sqrt{2} & 1/\sqrt{2} & 0 \\ 0 & 1/\sqrt{2} & -1/\sqrt{2} & 0 \\ 0 & 0 & 0 & 1 \end{bmatrix} \quad (\text{A1})$$

is block diagonalized into a  $2 \times 2$  matrix and two  $1 \times 1$  matrices. As before the  $2 \times 2$  matrix is relevant for the PJTE and leads to the determinant

$$\begin{vmatrix} -3 - \varepsilon' & P' \\ P' & 1 - Q'_\theta + S' + Q'_{xy} - \varepsilon' \end{vmatrix} = 0. \quad (\text{A2})$$

This determinant contains three normal coordinates instead of two as in (16). Similarly to section 3 the lowest solutions are determined. When  $P' = 0$  either case (A) or (B2) applies:

$$E_1 = -3j \quad (\text{A3})$$

$$E_2 = j - 2j^2g'' \quad \text{where } g'' = \frac{1}{4}(g + c + h). \quad (\text{A4})$$

For the PJTE case (C2):

$$Q'_\theta = \frac{1}{2}g(jf - 2)/(f - g'') \quad (\text{A5})$$

$$S' = -\frac{1}{2}h(jf - 2)/(f - g'') \quad (\text{A6})$$

$$Q'_{xy} = -\frac{1}{2}c(jf - 2)/(f - g'') \quad (\text{A7})$$

$$P'^2 = f^2(jf + 2 - 2jg'')(jf - 2)/(f - g'')^2 \quad (\text{A8})$$

$$E_3 = \frac{1}{2}(jf + 2 - 2jg'')(jf - 2)/(f - g'') - j(jf + 1) \quad (\text{A9})$$

$$E_3 = E_2 - \frac{1}{2}(jf + 2 - 2jg'')^2/(f - g'') \quad (\text{A10})$$

$$E_3 = E_1 - \frac{1}{2}(jf - 2)^2/(f - g''). \quad (\text{A11})$$

Comparing  $g''$  with  $g'$  and  $c'$ , when  $g' > c'$  then  $g'' < g'$  and when  $c' > g'$  then  $g'' < c'$ . Comparing (A11) with (30) and (40) respectively, it follows that the 'intermediate' PJTE solution is less stable than either the tetragonal or the trigonal solutions, unless  $g' = c'$  (see section 4). The same applies for the 'intermediate' solution for the JTE (equation (A4)), in agreement with Öpik and Pryce (1957).

For other settings (A9)–(A11) apply as well, so that the previous conclusions remain valid. Of course other components of the normal coordinates may not be equal to zero.

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