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Systematic strong-coupling expansion of the $T \otimes t$ Jahn–Teller system

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Abstract

An analytic approach to the strongly coupled $T \otimes t$ problem is described, which allows a systematic expansion of the Hamiltonian in inverse powers of the coupling parameter K. The approach rests on the construction of a novel vibronic basis causing the Hilbert space to decay into two orthogonal subspaces $\mathcal{L}_1$ and $\mathcal{L}_2$ such that, for strong coupling, the low-lying states in $\mathcal{L}_1$ are separated from all states in $\mathcal{L}_2$ by a large energy gap. This constitutes the basis for the construction of an effective Hamiltonian H_1 defined on $\mathcal{L}_1$ and generated by means of projection operators. The form of H_1 is that of an infinite series in increasing powers of K^{-1}, which is terminated after the terms of $O(K^{-2})$. The eigenvalues of H_1 incorporate those already found by Moffitt and Thorson, including the correct splitting of the t_{2g} vibrations.

1. Introduction

Transition-metal (TM) oxides are notoriously difficult to describe because of a rather close interplay between the spin, orbital, and lattice degrees of freedom (Imada *et al* 1998). This applies, in particular, to the recently investigated titanates $RTiO_3$, where R denotes a rare-earth ion. These compounds possess one t_{2g} electron per site, and their crystal structure is a pseudocubic perovskite with an orthorhombic $GdFeO_3$-type distortion giving rise to a crystal field of nearly trigonal D_{3d} symmetry (Mochizuki and Imada 2003, Cwik *et al* 2003, Pavarini *et al* 2004). The trigonal field, whose strength depends on the degree of distortion, competes with the cubic field (symmetry O_h) resulting from the oxygen ligands surrounding the Ti^{3+} ion, and this competition has been proposed by Mochizuki and Imada (2003, 2004) to be the source of the unusual magnetic and vibronic properties of the titanates. Thus, for example, the strongly distorted $YTiO_3$ shows a ferromagnetic ground state accompanied by a sizeable Jahn–Teller (JT) effect, whereas the less distorted $LaTiO_3$ is antiferromagnetic with no detectable JT coupling. The main effect of the trigonal field is that it causes the TiO_6 octahedra to contract along one of the four threefold axes, which leads to a splitting of the t_{2g} state into a low-lying

a_{1g} and a higher-lying e_g level. Mochizuki and Imada (2004) showed that the occupation of the a_{1g} orbitals well explains the antiferromagnetism in $LaTiO_3$ as well as the isotropic spin-wave spectrum measured by Keimer *et al* (2000). From these results one may conclude that spin–orbit coupling is probably very weak in the whole titanate series; in $YTiO_3$ it is suppressed by the strong JT effect, in $LaTiO_3$ it is also absent because the isotropic spin-wave spectrum indicates that the orbital moment is quenched. At the same time the trigonal field also affects the JT interaction. In the absence of the field the JT coupling would be expected to be of the general type $T \otimes (e + t)$, indicating that the t_{2g} electron couples to both e_g and t_{2g} vibrations. The presence of the field and the concomitant splitting of the t_{2g} level, however, turn the $T \otimes (e + t)$ system into a pseudo-JT effect and eventually render it undetectably small as in $LaTiO_3$. In this paper we concentrate solely on the JT effect in the titanates.

At present, an adequate treatment of the pseudo-JT problem in the titanates is out of reach, and even the pure $T \otimes (e + t)$ system is very difficult. Therefore, as the first step, we further simplify the problem by omitting the coupling to the e_g vibrations leaving the full problem to future study. Thus, the model to be considered here is the $T \otimes t$ JT system describing the vibronic coupling of the electronic t_{2g} triplet to triply degenerate vibrations of the same symmetry. In the basis of the t_{2g} orbitals $\psi_\alpha(\mathbf{r})$ ($\alpha = x, y, z$), the Hamiltonian of the $T \otimes t$ system may be written as (Moffitt and Thorson 1957, Ham 1965, Judd 1974)

$$\mathcal{H} = \tfrac{1}{2}\sum_{l=1}^{3}(P_l^2 + \omega^2 Q_l^2)\tau_0 + K\sum_{l=1}^{3} Q_l\tau_l. \tag{1}$$

Here the first part describes the t_{2g} normal vibrations of frequency ω and the second part represents the *linear* JT coupling, where K denotes the coupling parameter, τ_0 is the 3×3 unit matrix, and

$$\tau_1 = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix}, \qquad \tau_2 = \begin{pmatrix} 0 & 0 & 1 \\ 0 & 0 & 0 \\ 1 & 0 & 0 \end{pmatrix}, \qquad \tau_3 = \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}. \tag{2}$$

The weak-coupling Hamiltonian has been diagonalized by Moffitt and Thorson (1957) by means of a unitary transformation (see also Bersuker and Polinger 1989). The lowest state is found to be a triplet, and this applies to all finite values of K because of the octahedral symmetry of the Hamiltonian. In the limit of infinite coupling, however, the symmetry of the Hamiltonian changes and the ground state is a quartet. This result follows from the topology of the potential-energy surface and has already been obtained by Van Vleck (1939) and Öpik and Pryce (1957). By using classical arguments the latter authors also found that, apart from the lowering of the energy by an amount proportional to K^2, the degenerate t_{2g} vibrations split into a mode of frequency ω and two degenerate modes of frequency $\sqrt{2/3}\omega$. The first steps towards a unified quantum treatment of the mode-splitting problem have been taken by Shultz and Silbey (1976). In a more recent approach, Liu *et al* (1996) tackled the problem by means of a special unitary transformation (scale transformation) and a combination of perturbational and variational techniques.

In this paper we intend to put forward a novel analytic treatment of the $T \otimes t$ problem, which is nonperturbative and leads to a *systematic* expansion in powers of K^{-1} about the strong-coupling limit. Such expansions about the limits of weak and strong coupling might provide an adequate quantitative basis for a proper assessment of the role of the JT effect in the titanates. Our approach rests on a suitably chosen basis of the Hilbert space, i.e., vibronic states constructed with the help of new electronic and vibrational operators. In this basis the Hilbert space decays into two orthogonal subspaces $\mathcal{L}_1$ and $\mathcal{L}_2$ such that, for strong coupling, the low-lying states in $\mathcal{L}_1$ are separated from all states in $\mathcal{L}_2$ by a large energy gap. This constitutes the basis for the construction of an effective Hamiltonian defined on $\mathcal{L}_1$ and generated by means

of projection operators. The eigenvalues of the lowest-order effective Hamiltonian are exactly those given by Moffitt and Thorson (1957), including the correct splitting of the t_{2g} vibrational modes.

In section 2 we prove that the Hamiltonian commutes with a rotation $\mathcal{R}$ of the coordinate system through the angle $\theta = 2\pi/3$ about a threefold axis. The existence of this constant of the motion gives rise to new electronic creation and annihilation operators causing the Hamiltonian to take diagonal form with respect to these operators. The decay of the Hilbert space into the subspaces $\mathcal{L}_1$ and $\mathcal{L}_2$ are the main topic of section 3. To generate the subspaces, we construct projection operators and subsequently use them to decompose the Hamiltonian with respect to $\mathcal{L}_1$ and $\mathcal{L}_2$. The decomposed form of the Hamiltonian constitutes the basis for the strong-coupling expansion in section 4. This is achieved by means of a sequence of unitary transformations, whose effect is to remove those terms from the Hamiltonian giving rise to a coupling of the subspaces. The transformations result in two effective Hamiltonians, H_1 defined on $\mathcal{L}_1$ and H_2 defined on $\mathcal{L}_2$, each having the form of an infinite series in increasing powers of K^{-1}, which we terminate after the terms of $O(K^{-2})$. Subsequently we ignore H_2, since we are only interested in the low-energy part of the spectrum, and solely concentrate on H_1 to obtain its eigenvalues and eigenstates. Finally, our main findings and possible extensions of our treatment are discussed in section 5.

2. The new vibronic basis

Subsequently it proves most convenient to describe the vibrational and orbital degrees of freedom in terms of creation and annihilation operators. The normal vibration l ($l = 1, 2, 3$) is created (annihilated) by the operator $a_l^\dagger$ (a_l), while $c_\alpha^\dagger$ (c_α) creates (annihilates) a spinless electron in the t_{2g} orbital $\psi_\alpha(\mathbf{r})$ ($\alpha = x, y, z$). Hamiltonian (1) may then be written as

$$\hat{H} \equiv \mathcal{H}/(\hbar\omega) = \mathbf{a}^\dagger \cdot \mathbf{a} + 3/2 + k \sum_{l=1}^{3} (a_l^\dagger + a_l)\mathbf{c}^\dagger \cdot \tau_l \cdot \mathbf{c}, \tag{3}$$

where the coupling strength is now expressed by the dimensionless parameter k, while the row vectors $\mathbf{a}^\dagger = (a_1^\dagger a_2^\dagger a_3^\dagger)$ and $\mathbf{c}^\dagger = (c_x^\dagger c_y^\dagger c_z^\dagger)$, as well as their associated column vectors $\mathbf{a}$ and $\mathbf{c}$, have been introduced for convenience.

To simplify the solution of the eigenvalue problem we recall that the invariance of the Hamiltonian with respect to a given group implies that all operations of the group are *conserved quantities*. A set of such quantities, particularly well suited to our purposes, is provided by the threefold rotations $\mathcal{R}_a$ ($a = 1, \ldots, 4$) of O_h describing rotations of the coordinate system through the angle $\theta = 2\pi/3$ about the four threefold axes, whose directions are specified by the nonorthogonal unit vectors (see figure 1)

$$\begin{aligned} \mathbf{e}_1 &= \frac{1}{\sqrt{3}}(111), \qquad & \mathbf{e}_2 &= \frac{1}{\sqrt{3}}(\bar{1}\bar{1}1), \\ \mathbf{e}_3 &= \frac{1}{\sqrt{3}}(\bar{1}1\bar{1}), \qquad & \mathbf{e}_4 &= \frac{1}{\sqrt{3}}(1\bar{1}\bar{1}). \end{aligned} \tag{4}$$

Denoting by $\mathbf{e} = (e_x e_y e_z)$ any of these vectors, we see that the components e_α have the property $|e_\alpha| = 1/\sqrt{3}$ ($\alpha = x, y, z$) and satisfy the relations

$$e_x = \sqrt{3} e_y e_z, \qquad e_y = \sqrt{3} e_x e_z, \qquad e_z = \sqrt{3} e_x e_y. \tag{5}$$

Since all $\mathcal{R}_a$ commute with the Hamiltonian $\hat{H}$, but not among themselves, we select a single rotation $\mathcal{R}$ such that $\hat{H}$ and $\mathcal{R}$ form a *complete set* of commuting operators. Thus, rather than working with the full group O_h, we prefer to select the cyclic (Abelian) subgroup C_3

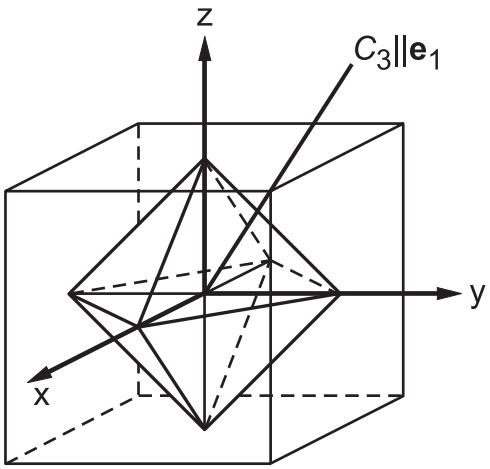

Figure 1. Threefold rotation axis C_3 along the direction $\mathbf{e}_1$.

of threefold rotations generated by $\mathcal{R}$. Below we shall demonstrate that this subgroup alone enables us to achieve a partial diagonalization of the Hamiltonian in the electronic subspace.

First of all, however, we shall prove that $\mathcal{R}$ is indeed a conserved quantity. To this end we recall that in Hilbert space a rotation through $\theta = 2\pi/3$ about an axis along the direction $\mathbf{e}$ is described by the *rotation operator*

$$\mathcal{R} = \exp(\mathrm{i}\theta \mathbf{e} \cdot \mathbf{J}), \tag{6}$$

where $\mathbf{J} = \mathbf{M} + \mathbf{L}$ is the total angular momentum. The *vibrational* and *electronic* angular momenta $\mathbf{M}$ and $\mathbf{L}$, respectively, are defined by the equations (Moffitt and Thorson 1957)

$$\mathbf{M} = \mathbf{a}^\dagger \cdot \boldsymbol{\sigma} \cdot \mathbf{a}, \qquad \mathbf{L} = \mathbf{c}^\dagger \cdot \boldsymbol{\sigma} \cdot \mathbf{c}, \tag{7}$$

where $\boldsymbol{\sigma} = (\sigma_x\, \sigma_y\, \sigma_z)$ denotes a vector, whose components are the matrices

$$\sigma_x = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & -\mathrm{i} \\ 0 & \mathrm{i} & 0 \end{pmatrix}, \qquad \sigma_y = \begin{pmatrix} 0 & 0 & \mathrm{i} \\ 0 & 0 & 0 \\ -\mathrm{i} & 0 & 0 \end{pmatrix}, \qquad \sigma_z = \begin{pmatrix} 0 & -\mathrm{i} & 0 \\ \mathrm{i} & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}. \tag{8}$$

With the help of (7) and (8) the components of $\mathbf{L}$ are readily evaluated and read

$$\begin{aligned} L_x &= \mathbf{c}^\dagger \cdot \sigma_x \cdot \mathbf{c} = -\mathrm{i}(c_y^\dagger c_z - c_z^\dagger c_y), \\ L_y &= \mathbf{c}^\dagger \cdot \sigma_y \cdot \mathbf{c} = -\mathrm{i}(c_z^\dagger c_x - c_x^\dagger c_z), \\ L_z &= \mathbf{c}^\dagger \cdot \sigma_z \cdot \mathbf{c} = -\mathrm{i}(c_x^\dagger c_y - c_y^\dagger c_x), \end{aligned} \tag{9}$$

and quite similar expressions are found for M_x, M_y, M_z. From (9) it follows that $\mathbf{L}^2 = 2$ on the underlying single-electron Hilbert space, implying that $\mathbf{L}$ has the eigenvalue $l = 1$, as is expected for the p-like t_{2g} state. The eigenvalues $m(m+1)$ of $\mathbf{M}^2$ and $j(j+1)$ of $\mathbf{J}^2$ are also known (Moffitt and Thorson 1957, Messiah 1964, Marshalek 1992). Let the eigenvalue $n = n_1 + n_2 + n_3$ of $\mathbf{a}^\dagger \cdot \mathbf{a}$ be given; then m may take the values $n, n-2, \ldots, 0$ or 1, depending on whether n is even or odd, while j follows from the vector model of angular-momentum addition, i.e., $m + l \geqslant j \geqslant |m - l|$. The components (9) satisfy the commutation relations

$$[L_\alpha, c_\beta] = \mathrm{i}\epsilon_{\alpha\beta\gamma} c_\gamma, \tag{10}$$

where $\epsilon_{\alpha\beta\gamma}$ is the Levi-Civita symbol.

As the first step of our proof we need to know how the components of **c** and **a** transform under the action of $\mathcal{R}$. To obtain $\mathcal{R}^\dagger c_x \mathcal{R}$, for example, we employ the commutator expansion

$$e^Z A e^{-Z} = A + [Z, A] + (1/2!)[Z, [Z, A]] + \cdots \tag{11}$$

and make use of (10). A straightforward calculation then yields the expression

$$\mathcal{R}^\dagger c_x \mathcal{R} = (\sqrt{3}/2)[(\sqrt{3}e_x e_y + e_z)c_y + (\sqrt{3}e_x e_z - e_y)c_z],$$

which reduces to $\mathcal{R}^\dagger c_x \mathcal{R} = \sqrt{3}e_z c_y$ by virtue of relations (5). By the same arguments we find that $\mathcal{R}^\dagger c_y \mathcal{R} = \sqrt{3}e_x c_z$ and $\mathcal{R}^\dagger c_z \mathcal{R} = \sqrt{3}e_y c_x$. The transformation behaviour of the boson operators a_l is very similar to that of the fermion operators c_α, both cases differing merely in notation. The results may be written in the compact form

$$\mathcal{R}^\dagger \mathbf{c} \mathcal{R} = \Pi \cdot \mathbf{c}, \tag{12a}$$

$$\mathcal{R}^\dagger \mathbf{a} \mathcal{R} = \Pi \cdot \mathbf{a}, \tag{12b}$$

where the unitary matrix

$$\Pi = \sqrt{3} \begin{pmatrix} 0 & e_z & 0 \\ 0 & 0 & e_x \\ e_y & 0 & 0 \end{pmatrix}. \tag{13}$$

To prove that $\mathcal{R}$ is a conserved quantity, we only show that it leaves the JT coupling

$$H_{\mathrm{JT}} = k(\mathbf{a}^\dagger \cdot \mathbf{t} + \mathbf{t}^\dagger \cdot \mathbf{a})$$

invariant, where we have defined the column vector **t** and the corresponding row vector $\mathbf{t}^\dagger$, whose components are the Hermitian operators $t_l = \mathbf{c}^\dagger \cdot \tau_l \cdot \mathbf{c}$ ($l = 1, 2, 3$). From (12*a*) it then follows that $\mathcal{R}^\dagger t_l \mathcal{R} = \mathbf{c}^\dagger \cdot \Pi^\dagger \tau_l \Pi \cdot \mathbf{c}$, and since the matrices τ_l transform in the same manner as the a_l in (12*b*) (i.e., $\Pi^\dagger \tau_1 \Pi = \sqrt{3}e_z \tau_2$, etc), one readily infers that $\mathcal{R}^\dagger \mathbf{t} \mathcal{R} = \Pi \cdot \mathbf{t}$, $\mathcal{R}^\dagger \mathbf{t}^\dagger \mathcal{R} = \mathbf{t}^\dagger \cdot \Pi^\dagger$. These relations, together with (12*b*) and the unitary property of Π, prove that $\mathcal{R}^\dagger H_{\mathrm{JT}} \mathcal{R} = H_{\mathrm{JT}}$. We thus conclude that $\mathcal{R}^\dagger \hat{H} \mathcal{R} = \hat{H}$, whence it follows that $\mathcal{R}$ is a conserved quantity.

We shall now exploit the Abelian property of the subgroup C_3 to generate new electronic operators such that the Hamiltonian takes diagonal form with respect to these operators. From equations (12) and the relation $\Pi^3 = \tau_0$ it follows that $\mathcal{R}^3 = 1$; hence, $\mathcal{R}$ possesses the three complex eigenvalues

$$r_\kappa = \exp(\mathrm{i}\kappa\theta), \tag{14}$$

where $\kappa = 0, \pm 1$ labels the (one-dimensional) irreducible representations of C_3. Since $\mathcal{R}$ is also unitary, our subgroup consists of the elements $\{\mathcal{R}, \mathcal{R}^2 = \mathcal{R}^{-1} = \mathcal{R}^\dagger, \mathcal{R}^3 = 1\}$, as expected. As the first step we set up the *projection operators* $\mathcal{P}_\kappa$ for selecting the subspace belonging to the eigenvalue (representation) r_κ of $\mathcal{R}$. According to Löwdin (1962),

$$\mathcal{P}_\kappa = \tfrac{1}{3}(1 + r_\kappa^* \mathcal{R} + r_\kappa \mathcal{R}^\dagger), \tag{15a}$$

where r_κ is defined by (14). Apart from being Hermitian, $\mathcal{P}_\kappa$ has the properties

$$\sum_\kappa \mathcal{P}_\kappa = 1, \qquad \mathcal{P}_\kappa P_{\kappa'} = \delta_{\kappa\kappa'} \mathcal{P}_\kappa. \tag{15b}$$

We now use relations (15*b*) and the fact that all parts of (3) commute with $\mathcal{P}_\kappa$ to decompose the Hamiltonian into components acting on the eigenspaces of $\mathcal{R}$ as follows:

$$H = \mathbf{a}^\dagger \cdot \mathbf{a} + 3/2 + \sum_\kappa \mathcal{P}_\kappa H_{\mathrm{JT}} \mathcal{P}_\kappa. \tag{16}$$

This form already demonstrates that the Hamiltonian will take diagonal form with respect to the quantum number κ, and the argument applies equally well to other vibronic operators, provided they commute with $\mathcal{R}$.

To obtain (16) in explicit form, we need to calculate the vectors $\mathbf{c}\mathcal{P}_\kappa$. Using (12*a*) and (15*a*) we find that

$$\begin{aligned}\mathbf{c}\mathcal{P}_\kappa &= \tfrac{1}{3}(\tau_0 + r_\kappa^* \Pi\mathcal{R} + r_\kappa \Pi^\dagger \mathcal{R}^\dagger)\cdot\mathbf{c} \\ &= \frac{1}{\sqrt{3}}\begin{pmatrix} c_x/\sqrt{3} + e_z r_\kappa^* \mathcal{R} c_y + e_y r_\kappa \mathcal{R}^\dagger c_z \\ e_z r_\kappa \mathcal{R}^\dagger c_x + c_y/\sqrt{3} + e_x r_\kappa^* \mathcal{R} c_z \\ e_y r_\kappa^* \mathcal{R} c_x + e_x r_\kappa \mathcal{R}^\dagger c_y + c_z/\sqrt{3}\end{pmatrix}, \end{aligned} \tag{17}$$

and we shall now prove that the operators $\mathcal{R}c_\alpha$ and $\mathcal{R}^\dagger c_\alpha$ on the right-hand side of (17) may be replaced by Rc_α and $R^\dagger c_\alpha$, respectively, where

$$R = \exp(\mathrm{i}\theta \mathbf{e}\cdot\mathbf{M}) \tag{18}$$

acts in the vibrational subspace, since only the vibrational angular momentum $\mathbf{M}$ is involved. To show this, we first observe that the rotation operator (6) factorizes and can be written as $\mathcal{R} = R\tilde{R}$, where R is given by (18) and $\tilde{R} = \exp(\mathrm{i}\theta \mathbf{e}\cdot\mathbf{L})$ is a rotation operator in the electronic subspace. Let $|\Psi\rangle$ be an arbitrary vector of the single-electron Hilbert space,

$$|\Psi\rangle = \sum_\alpha \Psi_\alpha c_\alpha^\dagger |0\rangle,$$

where Ψ_α ($\alpha = x, y, z$) are pure functions of the operators a_l, $a_l^\dagger$ ($l = 1, 2, 3$) and $|0\rangle$ denotes the common vacuum of all particles. If $\mathcal{R}c_\alpha$ is applied to $|\Psi\rangle$ and use is made of the fact that $\tilde{R}$ commutes with Ψ_α, the result is

$$\mathcal{R}c_\alpha|\Psi\rangle = \mathcal{R}\Psi_\alpha|0\rangle = R\Psi_\alpha|0\rangle = Rc_\alpha|\Psi\rangle.$$

Hence, $\mathcal{R}c_\alpha = Rc_\alpha$ on the entire Hilbert space, which proves our claim. The vector (17) may then be written as

$$\mathbf{c}\mathcal{P}_\kappa = \begin{pmatrix} e_x \\ e_y r_\kappa R^\dagger \\ e_z r_\kappa^* R\end{pmatrix} f_\kappa \equiv \mathbf{u}_\kappa f_\kappa, \tag{19}$$

where $\mathbf{u}_\kappa$ is a unit vector ($\mathbf{u}_\kappa^\dagger \cdot \mathbf{u}_\kappa = 1$), while the quantities

$$f_\kappa = e_x c_x + e_y r_\kappa^* R c_y + e_z r_\kappa R^\dagger c_z \tag{20a}$$

behave like ordinary *fermion* operators:

$$\{f_\kappa, f_{\kappa'}^\dagger\} = \delta_{\kappa,\kappa'}, \qquad \{f_\kappa, f_{\kappa'}\} = 0. \tag{20b}$$

However, due to the presence of the operator R in (20*a*), the f_κ, $f_\kappa^\dagger$ *cease to commute* with the vibrational operators a_l, $a_l^\dagger$. This will not entail any problems, provided care is taken of the order of the operators.

To achieve the most convenient form of the Hamiltonian we also introduce, in addition to the new fermion basis, new vibrational modes having the property to bring the rotation operator R to diagonal form. To obtain these, one notices that the exponent in (18) may be written as $\sum_\alpha e_\alpha M_\alpha = \mathbf{a}^\dagger \cdot \mathbf{s} \cdot \mathbf{a}$, where the Hermitian matrix $\mathbf{s} = \sum_\alpha e_\alpha \sigma_\alpha$ has the eigenvalues $0, \pm 1$ and may be brought to diagonal form by means of the unitary matrix

$$\mathbf{T} = \begin{pmatrix} e_x & e_x & e_x \\ e_y \mathrm{e}^{\mathrm{i}\theta} & e_y & e_y \mathrm{e}^{-\mathrm{i}\theta} \\ e_z \mathrm{e}^{-\mathrm{i}\theta} & e_z & e_z \mathrm{e}^{\mathrm{i}\theta}\end{pmatrix}.$$

The eigenvalue equation $\mathbf{T}^\dagger \mathbf{s} \mathbf{T} = \mathbf{\Lambda}$, where $\mathbf{\Lambda}$ denotes the diagonal matrix of the eigenvalues of $\mathbf{s}$, then requires that the new operators b_μ ($\mu = 1, 0, -1$) are related to the a_l ($l = 1, 2, 3$) by means of the equation $\mathbf{a} = \mathbf{T}\cdot\mathbf{b}$, whose explicit form reads

$$\begin{aligned} a_1 &= e_x(b_+ + b_0 + b_-), \\ a_2 &= e_y(\mathrm{e}^{\mathrm{i}\theta} b_+ + b_0 + \mathrm{e}^{-\mathrm{i}\theta} b_-), \\ a_3 &= e_z(\mathrm{e}^{-\mathrm{i}\theta} b_+ + b_0 + \mathrm{e}^{\mathrm{i}\theta} b_-). \end{aligned} \tag{21}$$

Expressed in terms of the b_μ the exponent in (18) becomes $\sum_\alpha e_\alpha M_\alpha = \mathbf{b}^\dagger \cdot \mathbf{\Lambda} \cdot \mathbf{b}$, whereupon the rotation operator R takes the diagonal form

$$R = \exp[\mathrm{i}\theta(N_+ - N_-)], \tag{22}$$

where $N_\mu = b_\mu^\dagger b_\mu$. The new operators satisfy the usual commutation relations for bosons (i.e., $[b_\mu, b_\nu^\dagger] = \delta_{\mu\nu}$ etc) and transform according to the simple formula

$$R^\dagger b_\mu R = \mathrm{e}^{\mathrm{i}\mu\theta} b_\mu, \tag{23}$$

where $\mu = 0, \pm 1$ and $\theta = 2\pi/3$. This relation lends itself to a geometrical interpretation of the new vibrational modes. Since b_0 commutes with R, it must describe a vibration along the direction $\mathbf{e}$ of the threefold rotation axis and will, therefore, be referred to as *longitudinal* mode. The operators b_+ and b_-, on the other hand, describe vibrations orthogonal to $\mathbf{e}$ and will be denoted as *perpendicular* modes.

Finally we show that the Hamiltonian assumes diagonal form with respect to the new fermion basis. This is already implied by the form (16) and explicitly follows after insertion of (19) into (16). The resulting Hamiltonian

$$\begin{aligned} H &= \mathbf{a}^\dagger \cdot \mathbf{a} + 3/2 + k \sum_{l\kappa} f_\kappa^\dagger \mathbf{u}_\kappa^\dagger (a_l^\dagger + a_l) \cdot \tau_l \cdot \mathbf{u}_\kappa f_\kappa \\ &= \mathbf{a}^\dagger \cdot \mathbf{a} + 3/2 + \frac{k}{\sqrt{3}} \sum_\kappa f_\kappa^\dagger [e_x r_\kappa R(a_1^\dagger + a_1) R \\ &\quad + e_y r_\kappa R^\dagger (a_2^\dagger + a_2) + e_z r_\kappa (a_3^\dagger + a_3) R^\dagger + \mathrm{H.c.}] f_\kappa \end{aligned}$$

is manifestly diagonal in the f_κ, $f_\kappa^\dagger$ and reduces to the simpler expression

$$H = \mathbf{a}^\dagger \cdot \mathbf{a} + 3/2 + \sqrt{3} k e_y \sum_\kappa f_\kappa^\dagger [r_\kappa R^\dagger (a_2^\dagger + a_2) + \mathrm{H.c.}] f_\kappa, \tag{24}$$

if use is made of the identities $e_x R(a_1^\dagger + a_1) R = e_y R^\dagger (a_2^\dagger + a_2) = e_z (a_3^\dagger + a_3) R^\dagger$, whose derivation rests on (12*b*) and the relation $R^2 = R^\dagger$. After insertion of (21) into (24) the Hamiltonian loses its explicit dependence on the chosen rotation axis, but still remains implicitly dependent on the direction $\mathbf{e}$ (via the operators f_κ and b_μ):

$$H = \mathbf{b}^\dagger \cdot \mathbf{b} + 3/2 + g \sum_{\kappa\mu} f_\kappa^\dagger (\mathcal{C}_{\kappa+\mu} b_\mu + \mathrm{H.c.}) f_\kappa. \tag{25}$$

Here κ and μ range over the values $0, \pm 1$ and $g \equiv k/\sqrt{3}$, while the operator function $\mathcal{C}_\kappa$ and its counterpart $\mathcal{S}_\kappa$ are defined by the equations

$$\mathcal{C}_\kappa = \mathrm{e}^{\mathrm{i}\kappa\theta} R^\dagger + \mathrm{e}^{-\mathrm{i}\kappa\theta} R = 2\cos[(N_+ - N_- - \kappa)\theta], \tag{26a}$$

$$\mathcal{S}_\kappa = \mathrm{i}(\mathrm{e}^{\mathrm{i}\kappa\theta} R^\dagger - \mathrm{e}^{-\mathrm{i}\kappa\theta} R) = 2\sin[(N_+ - N_- - \kappa)\theta]. \tag{26b}$$

3. Decomposition of the Hamiltonian

The main goal of this section is to demonstrate that the vibronic states, constructed with the help of the new operators f_κ and b_μ obtained above, induce a decay of the entire Hilbert space $\mathcal{L}$ into two orthogonal subspaces $\mathcal{L}_1$ and $\mathcal{L}_2$ such that, for strong coupling, the low-lying states in $\mathcal{L}_1$ are separated from all states in $\mathcal{L}_2$ by a large energy gap.

Insight into the structure of the Hilbert space may be gained from an investigation of the strong-coupling case ($g \gg 1$). To this end we recall the special role played by the longitudinal mode b_0, which commutes with the rotation R and, hence, with $\mathcal{C}_\kappa$. This property may be used

to remove the coupling term $g\sum_\kappa f_\kappa^\dagger(\mathcal{C}_\kappa b_0 + \text{H.c.})f_\kappa$ from Hamiltonian (25) by means of the unitary transformation $W = \sum_\kappa f_\kappa^\dagger W_\kappa f_\kappa$, where

$$W_\kappa = \exp[-g(b_0^\dagger - b_0)\mathcal{C}_\kappa] \tag{27}$$

describes a distortion of the octahedron along the rotation axis **e**. By means of the relations

$$W_\kappa^\dagger \mathbf{b}^\dagger \cdot \mathbf{b} W_\kappa = \mathbf{b}^\dagger \cdot \mathbf{b} - g(b_0^\dagger + b_0)\mathcal{C}_\kappa + g^2\mathcal{C}_\kappa^2, \tag{28a}$$

$$W_\kappa^\dagger (b_0^\dagger + b_0) W_\kappa = b_0^\dagger + b_0 - 2g\mathcal{C}_\kappa, \tag{28b}$$

whose derivation rests on (11), the transformed Hamiltonian is readily obtained as

$$W^\dagger H W = \mathbf{b}^\dagger \cdot \mathbf{b} + 3/2 - g^2 \sum_\kappa f_\kappa^\dagger \mathcal{C}_\kappa^2 f_\kappa + g\sum_\kappa \sum_{\mu=\pm1} f_\kappa^\dagger W_\kappa^\dagger (\mathcal{C}_{\kappa+\mu} b_\mu + \text{H.c.}) W_\kappa f_\kappa. \tag{29}$$

For the subsequent discussion it suffices to consider only the diagonal terms in the first line of (29), whose contribution to the energies is of $O(g^2)$, and to neglect the coupling terms in the second line, which have been shown to provide only small corrections of $O(g^0)$ (Shultz and Silbey 1976). In this approximation the eigenvectors of $W^\dagger H W$ are

$$|\kappa n\rangle \equiv f_\kappa^\dagger \prod_\mu \frac{(b_\mu^\dagger)^{n_\mu}}{\sqrt{n_\mu!}}|0\rangle = f_\kappa^\dagger |n_+ n_0 n_-\rangle, \tag{30}$$

while the corresponding eigenvalues read

$$E_{\kappa n}^{(0)} = n + 3/2 - 4g^2 \cos^2[(n_+ - n_- - \kappa)\theta], \tag{31}$$

where $\kappa = 0, \pm1$ and $n = n_+ + n_0 + n_-$. Since $n_+ - n_- - \kappa$ is an integer and $\theta = 2\pi/3$, the cosine in (31) can only take the values 1 and $-1/2$. This results in two groups of eigenvalues,

$$E_{\kappa n1}^{(0)} = n + 3/2 - 4g^2, \tag{32a}$$

$$E_{\kappa n2}^{(0)} = n + 3/2 - g^2, \tag{32b}$$

being separated from each other by the large energy gap $\Delta = 3g^2$. The *low-energy* form (32*a*) applies if, for given n_+ and n_-, κ is a solution to the equation

$$n_+ - n_- - \kappa = \pm 3m \qquad (m = 0, 1, 2, \ldots), \tag{33}$$

while the *high-energy* form (32*b*) obtains, if κ fails to satisfy criterion (33). It is easy to see that (33) always possesses a *unique* solution κ for any given n_+ and n_-. If $n_+ - n_- = 4$, for example, the only solution to (33) is $\kappa = 1$, while the only solution for $n_+ - n_- = 5$ is $\kappa = -1$. Accordingly, the total Hilbert space $\mathcal{L}$ consists of two orthogonal subspaces $\mathcal{L}_1$ and $\mathcal{L}_2$, where $\mathcal{L}_1$ is spanned by all vectors $|\kappa n\rangle$, equation (30), whose quantum numbers κ, n_+, n_- satisfy criterion (33), whereas $\mathcal{L}_2$ is spanned by all other states so that $\mathcal{L} = \mathcal{L}_1 \oplus \mathcal{L}_2$. Since we are only interested in the low-energy part of the spectrum, the relevant portion of the Hamiltonian is given by its restriction to the subspace $\mathcal{L}_1$.

The most convenient way to generate $\mathcal{L}_1$ and $\mathcal{L}_2$ is by means of projection operators, whose treatment requires some properties of the functions (26). Apart from the cyclic property $\mathcal{C}_{\kappa+3} = \mathcal{C}_\kappa, \mathcal{S}_{\kappa+3} = \mathcal{S}_\kappa$, these operators satisfy numerous identities whose proof follows directly from their definition and the relation $\sum_\kappa e^{i\kappa\theta} = 0$, valid for $\theta = 2\pi/3$. A few identities are listed below, while others will be given when they are needed:

$$\mathcal{C}_\kappa^2 = 2 + \mathcal{C}_\kappa, \tag{34a}$$

$$\sum_\kappa \mathcal{C}_\kappa = \sum_\kappa \mathcal{S}_\kappa = 0. \tag{34b}$$

With the help of $\mathcal{C}_\kappa$ we now define the *projection operators*

$$P_1 = \tfrac{1}{3}\sum_\kappa f_\kappa^\dagger(1+\mathcal{C}_\kappa)f_\kappa, \qquad P_2 = \tfrac{1}{3}\sum_\kappa f_\kappa^\dagger(2-\mathcal{C}_\kappa)f_\kappa, \tag{35}$$

whose basic properties $P_iP_j = \delta_{ij}P_i$, $P_1 + P_2 = 1$, analogous to those in (15*b*), are readily proven with the help of identity (34*a*). These operators generate the subspaces $\mathcal{L}_1$ and $\mathcal{L}_2$ defined above: since $\mathcal{C}_\kappa|\kappa n\rangle = 2|\kappa n\rangle$ if $|\kappa n\rangle \in \mathcal{L}_1$, and $\mathcal{C}_\kappa|\kappa n\rangle = -|\kappa n\rangle$ if $|\kappa n\rangle \in \mathcal{L}_2$, we see that $\mathcal{L}_i$ is an eigenspace of P_i to the eigenvalue 1, while $P_i = 0$ on the complementary subspace. This may be summarized by the symbolic equations $P_i\mathcal{L} = \mathcal{L}_i (i = 1, 2)$.

We now use the projection operators to decompose the Hamiltonian with respect to the subspaces. To this end we recast (25) into the form $H = X_0 + X_1$, where

$$X_0 = \mathbf{b}^\dagger\cdot\mathbf{b} + 3/2 + g\sum_\kappa f_\kappa^\dagger(\mathcal{C}_\kappa b_0 + \text{H.c.})f_\kappa, \tag{36a}$$

$$X_1 = g\sum_\kappa\sum_{\mu=\pm1} f_\kappa^\dagger(\mathcal{C}_{\kappa+\mu}b_\mu + \text{H.c.})f_\kappa. \tag{36b}$$

The decomposition is achieved with the help of the identity $H = (P_1 + P_2)H(P_1 + P_2)$, which requires us to evaluate all products of the form $P_iX_kP_j$, where the $X_k (k = 0, 1)$ are given by equations (36). Starting with X_0, we readily find that

$$P_1X_0P_1 = [\mathbf{b}^\dagger\cdot\mathbf{b} + 3/2 + 2g(b_0^\dagger + b_0)]P_1, \tag{37a}$$

$$P_2X_0P_2 = [\mathbf{b}^\dagger\cdot\mathbf{b} + 3/2 - g(b_0^\dagger + b_0)]P_2, \tag{37b}$$

whereas

$$P_1X_0P_2 = P_2X_0P_1 = 0. \tag{37c}$$

Hence, X_0 is a *pure term* possessing nonzero matrix elements only if the states involved are from the *same* subspace. The derivation of the products $P_iX_1P_j$ rests on the identity $(1 + \mathcal{C}_{\kappa+\mu})(1 + \mathcal{C}_{\kappa-\mu}) = 0$, valid for $\mu = \pm1$. This is obtained from (34*b*) and the relation $\mathcal{C}_{\kappa+\mu}\mathcal{C}_{\kappa-\mu} = \mathcal{C}_\kappa - 1$, which follows directly from definition (26*a*). Using these relations we find that, in contrast to X_0, X_1 mixes states from $\mathcal{L}_1$ and $\mathcal{L}_2$:

$$P_1X_1P_2 = -gP_1Q_+, \qquad P_2X_1P_1 = -gQ_+P_1. \tag{38}$$

Here the operator Q_+ and its companion Q_- are defined as

$$Q_\pm = \pm Q_\pm^\dagger = \sum_\kappa\sum_{\mu=\pm1} f_\kappa^\dagger(b_\mu^\dagger \pm b_\mu)f_\kappa, \tag{39}$$

and their most important properties are

$$P_1Q_\pm = P_1Q_\pm P_2, \qquad P_1Q_\pm P_1 = 0, \tag{40a}$$

$$[\mathbf{b}^\dagger\cdot\mathbf{b}, Q_\pm] = Q_\mp, \qquad [Q_+, Q_-] = 4. \tag{40b}$$

Finally, while X_1 is readily shown to vanish on subspace $\mathcal{L}_1$, i.e., $P_1X_1P_1 = 0$, it does not vanish on $\mathcal{L}_2$, where it takes the form

$$P_2X_1P_2 = (2g/3)\sum_\kappa\sum_{\mu=\pm1} f_\kappa^\dagger[(1+\mathcal{C}_{\kappa+\mu})b_\mu + \text{H.c.}]f_\kappa = (2/3)(gQ_+ + X_1). \tag{41}$$

To achieve a more convenient and transparent expression we multiply (41) on both sides by P_2 again; a straightforward calculation then leads to the simple result

$$P_2X_1P_2 = 2gP_2Q_+P_2. \tag{42}$$

The preceding considerations enable us to write down the Hamiltonian in decomposed form. As we have seen above, this will consist of pure terms as well as *mixing terms*, whose

matrix elements are nonzero only if the states involved are from both $\mathcal{L}_1$ and $\mathcal{L}_2$. Using (37), (38), and (42) the *decomposed Hamiltonian* is obtained as

$$\begin{aligned} H = {} & \mathbf{b}^\dagger \cdot \mathbf{b} + 3/2 + 2gP_2Q_+P_2 \\ & + g(b_0^\dagger + b_0)(2P_1 - P_2) \\ & - g(P_1Q_+ + Q_+P_1). \end{aligned} \tag{43}$$

One recognizes that the operators in the last line are mixing terms, since $P_1Q_+ = P_1Q_+P_2$ by virtue of (40*a*), while all the remaining terms are pure. The next obvious step is to remove the linear coupling term in the second line of (43) by means of the unitary transformation

$$U_0 = \exp[-g(b_0^\dagger - b_0)(2P_1 - P_2)]. \tag{44}$$

The transformed Hamiltonian is readily obtained with the help of (11), and is given by

$$\begin{aligned} U_0^\dagger H U_0 = {} & \mathbf{b}^\dagger \cdot \mathbf{b} + 3/2 - g^2(4P_1 + P_2) \\ & - g(\mathrm{e}^{\Theta}P_1Q_+ + Q_+P_1\mathrm{e}^{-\Theta}) \\ & + 2gP_2Q_+P_2, \end{aligned} \tag{45a}$$

where

$$\Theta = -\Theta^\dagger = 3g(b_0^\dagger - b_0). \tag{45b}$$

4. Systematic strong-coupling expansion

Hamiltonian (45) represents a suitable starting point for a systematic expansion about the strong-coupling limit. The principle of the method is to eliminate the leading mixing terms from the Hamiltonian successively by a sequence of unitary transformations. These are rather easy to handle because of the orthogonality of the projection operators. As the first step, we need to find a transformation which removes the mixing terms in the second line of (45*a*). This will generate an infinite series of pure terms in increasing powers of g^{-1}, and to obtain results beyond those already found by Moffitt and Thorson (1957), we shall terminate the series after the terms of $\mathrm{O}(g^{-2})$. In addition, however, the transformation generates an infinite series of new mixing terms, whose leading members are now of $\mathrm{O}(g^0)$. These are eliminated in the second step by means of another unitary transformation resulting in additional pure terms as well as new mixing terms of lower order. The procedure comes to an end when the new terms generated on $\mathcal{L}_1$ become smaller than $\mathrm{O}(g^{-2})$.

Following these lines we first try to eliminate the mixing terms in the second line of (45*a*) by means of the unitary transformation

$$U_1 = \exp[-(\alpha/g)(\mathrm{e}^{\Theta}P_1Q_+ - Q_+P_1\mathrm{e}^{-\Theta})], \tag{46}$$

where α is fixed by the requirement that the mixing terms should no longer appear in the transformed Hamiltonian. Using (11), (40) and the relation $\mathrm{e}^{\Theta}b_0\mathrm{e}^{-\Theta} = b_0 - 3g$, where Θ is defined by (45*b*), we find that $\alpha = 1/12$. The transformed Hamiltonian assumes the form

$$H^{(1)} \equiv U_1^\dagger U_0^\dagger H U_0 U_1 = H_1^{(1)} + H_2^{(1)} + H_{12}^{(1)}, \tag{47}$$

where

$$\begin{aligned} H_1^{(1)} = {} & (\mathbf{b}^\dagger \cdot \mathbf{b} + 3/2 - 4g^2)P_1 - \tfrac{1}{12}T_+ \\ & + \frac{\alpha}{6g}P_1Q_+^3P_1 - \frac{\alpha}{4g}(b_0^\dagger + b_0)T_+ \\ & + \frac{2\alpha^2}{g^2}P_1 + \frac{\alpha^3}{g^2}T_+^2 + \mathrm{O}(g^{-3}) \end{aligned} \tag{48a}$$

and

$$H_2^{(1)} = (\mathbf{b}^\dagger \cdot \mathbf{b} + 3/2 - g^2) P_2 + 2g P_2 Q_+ P_2 + \tfrac{5}{24} Q_+ P_1 Q_+ - \frac{\alpha^2}{g}(P_2 Q_+^2 P_1 Q_+ + \text{H.c.}) + \frac{3\alpha^2}{g}(b_0^\dagger + b_0) Q_+ P_1 Q_+ + \frac{\alpha^2}{g^2} K - \frac{\alpha^2}{8g^2} Q_+ T_+ Q_+ + \mathrm{O}(g^{-3}) \tag{48b}$$

contain the pure terms, $H_1^{(1)}$ being defined on $\mathcal{L}_1$ and $H_2^{(1)}$ on $\mathcal{L}_2$, while the new mixing terms are all contained in

$$H_{12}^{(1)} = \tfrac{1}{6}(\mathrm{e}^{\Theta} P_1 Q_+^2 P_2 + \text{H.c.}) - \tfrac{1}{4}[(b_0^\dagger + b_0)\mathrm{e}^{\Theta} P_1 Q_+ + \text{H.c.}] - \frac{\alpha}{g}(\mathrm{e}^{\Theta} P_1 Q_- + \text{H.c.}) + \frac{\alpha}{9g}(\mathrm{e}^{\Theta} T_+ Q_+ + \text{H.c.}) - \frac{\alpha^3}{3g^2}(\mathrm{e}^{\Theta} T_+ Q_+^2 P_2 + 3\mathrm{e}^{\Theta} P_1 Q_+^3 P_1 Q_+ + \text{H.c.}) + \frac{2\alpha^3}{g^2}[(b_0^\dagger + b_0)\mathrm{e}^{\Theta} T_+ Q_+ + \text{H.c.}] + \mathrm{O}(g^{-3}). \tag{48c}$$

In these equations we have introduced the Hermitian operators

$$T_+ = P_1 Q_+^2 P_1 \qquad \text{and} \qquad K = \tfrac{1}{2}(Q_+ P_1 Q_- + \text{H.c.}), \tag{49}$$

whose explicit form is readily obtained with the help of (35) and (39). A somewhat lengthy calculation yields the expressions

$$T_+ = 2\mathcal{N} P_1, \tag{50a}$$

$$\mathcal{N} = N_+ + N_- + 1 + b_+^\dagger b_-^\dagger + b_+ b_-, \tag{50b}$$

$$K = P_2 - (N_+ - N_-)\frac{1}{\sqrt{3}} \sum_\kappa f_\kappa^\dagger \mathcal{S}_\kappa f_\kappa, \tag{50c}$$

where $N_\mu = b_\mu^\dagger b_\mu$ ($\mu = \pm$) and $\mathcal{S}_\kappa$ is defined by (26*b*). The operator $\mathcal{N}$ in (50*b*) commutes with the rotation operator (22) and, hence, with both P_1 and P_2.

To gain some insight into the nature of the low-lying eigenvalues of $H^{(1)}$, it is expedient to investigate first a simpler case. This is obtained if all terms smaller than $\mathrm{O}(g^0)$ are omitted in equations (48). Since $H_2^{(1)}$ is irrelevant for the low-lying eigenvalues and the contribution of the mixing terms to $H^{(1)}$ is only of $\mathrm{O}(g^{-2})$, the effective Hamiltonian H_1 on $\mathcal{L}_1$ is simply given by the terms in the first line of (48*a*):

$$H_1 = (\mathbf{b}^\dagger \cdot \mathbf{b} + 3/2 - 4g^2 - \tfrac{1}{6}\mathcal{N}) P_1 + \mathrm{O}(g^{-1}). \tag{51}$$

A glance at (50*b*) reveals that H_1 is a quadratic form in the vibrational operators, which can be straightforwardly diagonalized by means of the *Bogoliubov transformation*

$$V_0 = \exp[\phi(b_+^\dagger b_-^\dagger - b_+ b_-)]. \tag{52}$$

This commutes with both projection operators and is very similar to the *scale transformation* used by Liu *et al* (1996). Applying formula (11) again, we find the new modes

$$V_0^\dagger b_\pm V_0 = b_\pm \cosh\phi + b_\mp^\dagger \sinh\phi, \tag{53}$$

whose substitution into $V_0^\dagger H_1 V_0$ leads to the Hamiltonian

$$V_0^\dagger H_1 V_0 = \big[N_0 + 1/2 - 4g^2 + (1/6)(N_+ + N_- + 1)(5\cosh 2\phi - \sinh 2\phi) + (1/6)(b_+ b_- + \text{H.c.})(5\sinh 2\phi - \cosh 2\phi)\big] P_1 + \mathrm{O}(g^{-1}). \tag{54}$$

This takes diagonal form if ϕ satisfies the condition $5\sinh 2\phi - \cosh 2\phi = 0$ or

$$\tanh 2\phi = 1/5,$$

implying that

$$\sinh 2\phi = \frac{1}{2\sqrt{6}}, \qquad \cosh 2\phi = \frac{5}{2\sqrt{6}}.$$

Then, since $(5\cosh 2\phi - \sinh 2\phi)/6 = \sqrt{2/3}$, Hamiltonian (54) takes the diagonal form

$$V_0^\dagger H_1 V_0 = \left[N_0 + 1/2 + \sqrt{2/3}(N_+ + N_- + 1) - 4g^2\right] P_1 + \mathrm{O}(g^{-1}), \tag{55}$$

whence we see that the eigenvalues of H_1 are the same as those found by Moffitt and Thorson (1957) from their investigation of the static JT problem.

Returning to the general scheme we now seek to remove the mixing terms of $\mathrm{O}(g^0)$ in the first line of (48*c*). This is achieved by means of the transformations

$$U_{21} = \exp[(\alpha_{21}/g^2)(\mathrm{e}^{\Theta} P_1 Q_+^2 P_2 - \mathrm{H.c.})], \tag{56a}$$

$$U_{22} = \exp\{-(\alpha_{22}/g^2)[(b_0^\dagger + b_0)\mathrm{e}^{\Theta} P_1 Q_+ - \mathrm{H.c.}]\}, \tag{56b}$$

where α_{21} and α_{22} are fixed by the condition that the transformed Hamiltonian should no longer contain mixing terms of $\mathrm{O}(g^0)$. The explicit calculation gives $\alpha_{21} = \alpha/6$ and $\alpha_{22} = \alpha/4$, where $\alpha = 1/12$ as in equations (48). With the notation $U_2 = U_{21}U_{22}$ the transformed Hamiltonian may be recast into the form of equation (47) and written as

$$H^{(2)} = U_2^\dagger H^{(1)} U_2 = H_1^{(2)} + H_2^{(2)} + H_{12}^{(2)}. \tag{57}$$

The relevant Hamiltonian on $\mathcal{L}_1$ is now given by the expression

$$H_1^{(2)} = H_1^{(1)} - \frac{\alpha^2}{3g^2} P_1 Q_+^2 P_2 Q_+^2 P_1 - \frac{3\alpha^2}{4g^2}(b_0^\dagger + b_0)^2 T_+ + \frac{\alpha^2}{g^2}(b_0^\dagger + b_0) P_1 Q_+^3 P_1 + \mathrm{O}(g^{-3}), \tag{58}$$

where $H_1^{(1)}$ is defined by (48*a*). The remaining parts of (57) are discussed in appendix A.

The next step of the procedure would be to eliminate the mixing terms of $\mathrm{O}(g^{-1})$, and equation (A.2) shows that there are already five such terms. Fortunately, however, no further transformations are needed, for a lengthy examination shows that all the remaining mixing terms give rise to new terms on $\mathcal{L}_1$, whose leading members are only of $\mathrm{O}(g^{-3})$ and, hence, are beyond the scope of our treatment. In other words, expression (58) already contains *all* terms of $\mathrm{O}(g^{-2})$ and, thus, is the complete effective Hamiltonian H_1 on $\mathcal{L}_1$. Expression (58) may be simplified by means of the identity

$$P_1 Q_+^2 P_2 Q_+^2 P_1 = 2\mathcal{N}^2 P_1 = \tfrac{1}{2} T_+^2, \tag{59}$$

whose derivation rests on (39), (50*a*) and (50*b*). With the help of (48*a*), (58) and (59), the effective Hamiltonian may finally be written as

$$H_1 \equiv H_1^{(2)} = (\mathbf{b}^\dagger \cdot \mathbf{b} + 3/2 - 4g^2) P_1 - \tfrac{1}{12} T_+ + \frac{\alpha}{6g} P_1 Q_+^3 P_1 - \frac{\alpha}{4g}(b_0^\dagger + b_0) T_+ + \frac{2\alpha^2}{g^2} P_1 - \frac{\alpha^3}{g^2} T_+^2 - \frac{3\alpha^2}{4g^2}(b_0^\dagger + b_0)^2 T_+ + \frac{\alpha^2}{g^2}(b_0^\dagger + b_0) P_1 Q_+^3 P_1 + \mathrm{O}(g^{-3}). \tag{60}$$

This expression represents the strong-coupling expansion of Hamiltonian (45) in powers of g^{-1}, truncated after the terms of $O(g^{-2})$. Although the various terms in (60) have no particular physical meaning, they exhibit a clear trend towards increasing anharmonicity, whose origin is best understood in terms of the potential-energy surface. For growing g this surface has been shown by numerous authors (Van Vleck 1939, Öpik and Pryce 1957, Bersuker and Polinger 1974, Bates *et al* 1987) to develop four equivalent wells located on the rotation axes $\mathbf{e}_a$ given by (4). In the strong-coupling regime considered here, the depth of the wells becomes proportional to g^2, causing the complex to vibrate about one distorted configuration, but the wells are neither harmonic nor isotropic. This explains both the growing anharmonicity with increasing powers of g^{-1} and the splitting of the t_{2g} vibrations. Moreover, the presence of the four equivalent wells also explains the fourfold degeneracy of the ground state in the limit $g \to \infty$, as will be discussed in more detail below.

It still remains to bring the effective Hamiltonian (60) to diagonal form, and it turns out that this can be wholly achieved by means of further unitary transformations. On application of the Bogoliubov transformation (52), the Hamiltonian assumes the form

$$\begin{aligned} V_0^\dagger H_1 V_0 = {} & [N_0 + 1/2 + \sqrt{2/3}(N_+ + N_- + 1) - 4g^2]P_1 \\ & + \frac{\alpha}{6g} e^{3\phi} P_1 Q_+^3 P_1 - \frac{\alpha}{2g} e^{2\phi}(b_0^\dagger + b_0)\mathcal{N} P_1 \\ & + \frac{2\alpha^2}{g^2} P_1 - \frac{\alpha^2}{2g^2}\mathcal{N}^2 P_1 - \frac{3\alpha^2}{2g^2} e^{2\phi}(b_0^\dagger + b_0)^2 \mathcal{N} P_1 \\ & + \frac{\alpha^2}{g^2} e^{3\phi}(b_0^\dagger + b_0) P_1 Q_+^3 P_1 + O(g^{-3}), \end{aligned} \tag{61}$$

where (50*a*) has been used and

$$e^{2\phi} = \sinh 2\phi + \cosh 2\phi = \sqrt{3/2}. \tag{62}$$

To complete the diagonalization, we need to remove the two terms in the second line of (61). As a result of the process, whose details are outlined in appendix B, we finally obtain the *diagonalized effective Hamiltonian*

$$\begin{aligned} V^\dagger H_1 V = {} & [N_0 + 1/2 + \sqrt{2/3}(N_+ + N_- + 1) - 4g^2]P_1 \\ & + \frac{3\alpha^2}{5g^2} P_1 - \frac{\alpha^2}{2g^2}[N_+(N_+ + 1) + N_-(N_- + 1)]P_1 \\ & - \frac{17\alpha^2}{5g^2}[N_+(N_- + 1) + N_-(N_+ + 1)]P_1 \\ & - \frac{18\alpha^2}{5g^2} e^{2\phi}(N_0 + 1/2)(N_+ + N_- + 1) P_1 + O(g^{-3}). \end{aligned} \tag{63}$$

One first observes that each eigenvalue of (63) is $4(n_+ + n_- + 1)$-fold degenerate, where the prefactor is a consequence of the four equivalent wells on the potential-energy surface. The same degeneracy has already been found by Englman *et al* (1970), albeit restricted to the levels without the $O(g^{-2})$ corrections. One further observes that these corrections are always negative. This is expected to lead to a small, but observable, effect on the eigenvalues in intermediate coupling, which seems in fact to be present in the majority of levels computed by Caner and Englman (1966). The effect seems to be absent, however, in the singlet states arising from the tunnelling splitting (see below).

The eigenvectors of H_1 are readily seen to have the form $|\Phi_{\kappa n}\rangle = V|\kappa n\rangle$, where $V = V_0 V_1 V_2$ and $|\kappa n\rangle$ is given by (30). To ensure that $|\Phi_{\kappa n}\rangle$ belongs to the relevant subspace $\mathcal{L}_1$, it suffices to require that $|\kappa n\rangle \in \mathcal{L}_1$. Then, since P_1 commutes with all transformations

V_i ($i = 0, 1, 2$), we have the eigenvalue equation $P_1|\Phi_{\kappa n}\rangle = |\Phi_{\kappa n}\rangle$ showing that $|\Phi_{\kappa n}\rangle \in \mathcal{L}_1$. The most important special case is the ground state $|\Phi_{00}\rangle = V f_0^\dagger |000\rangle$, characterized by the quantum numbers $n_0 = n_\pm = \kappa = 0$, and since these satisfy criterion (33), $|\Phi_{00}\rangle$ is clearly an element of $\mathcal{L}_1$. The ground-state energy E_0 follows from (63) and is given by the expression

$$E_0 = -4g^2 + 1/2 + \sqrt{2/3} - \frac{3\alpha^2}{5g^2}(3e^{2\phi} - 1) + O(g^{-3}) \tag{64}$$

showing that the terms of $O(g^{-2})$ are small because of the tiny prefactor ($3\alpha^2/5 = 1/240$). This takes a six times larger value, however, if our g^2 is replaced by $k^2 = 6g^2$, the coupling parameter used by Englman *et al* (1970).

So far our treatment lacks an important ingredient of the strongly coupled $T \otimes t$ system, which is closely related to the presence of the four equivalent wells mentioned above. Since the eigenvalues of (63) do not depend on the chosen rotation axis **e**, the energy levels are the same for all the wells, but eigenvectors belonging to different wells become *orthogonal* in the limit $g \to \infty$. Hence, in this limit, each eigenvalue is at least fourfold degenerate, implying the fourfold degeneracy of the ground state. For all *finite* values of g the ground-state wave functions have a finite overlap, causing the electron to tunnel between the wells. If tunnelling sets in, our treatment in terms of the subgroup C_3 of rotations about a fixed axis is no longer sufficient, and the full group O_h has to be used instead. The fourfold degenerate ground state will then split into a singlet and a triplet, where the latter turns out to have the lower energy. The singlet–triplet splitting has been calculated by Judd (1974), Shultz and Silbey (1976) and, more recently, by Liu *et al* (1996).

The most convenient way to calculate the splitting within our approach may be outlined as follows. First of all, we recall that our basic operators f_κ and b_μ are dependent on the direction **e** of the chosen rotation axis, as follows from (20*a*) and (21). Hence, all the Hamiltonians derived above also depend on **e**, the only exception being Hamiltonian (3), which has the full cubic symmetry. To keep our formalism as far as possible, Hamiltonian (3) will be used in the form $\hat{H} = (1/4)\sum_{a=1}^{4} H^{(a)}$, where $H^{(a)}$ refers to the direction (or well) $\mathbf{e}_a$ and has the form (43). In strong coupling, its ground-state eigenvector is related to $|\Phi_{00}\rangle$ given above and reads $|\Psi_{00}^{(a)}\rangle = U^{(a)} V^{(a)} f_0^{(a)\dagger} |000\rangle$, where $U^{(a)} = U_0^{(a)} U_1^{(a)} U_2^{(a)}$ denotes the product of the transformations (44), (46) and (56), expressed in terms of the $f_\kappa^{(a)}$ and $b_\mu^{(a)}$. To enable tunnelling, linear combinations of the $|\Psi_{00}^{(a)}\rangle$ must be taken transforming according to irreducible representations of O_h. These linear combinations are then used to calculate the singlet and triplet energies and, thus, the singlet–triplet splitting. Since our $|\Psi_{00}^{(a)}\rangle$ are expected to be accurate ground states in the range from intermediate to strong coupling, our result for the singlet–triplet splitting should be rather close to the numerical findings obtained by Caner and Englman (1966). Work along these lines is in progress.

5. Summary and outlook

Over several decades analytic approaches to the $T \otimes t$ JT effect have been facing two major difficulties. One of these arose from the desire to find a unified quantum treatment of the mode-splitting problem, i.e., the splitting of the degenerate t_{2g} vibrational modes in the strong-coupling regime. The more fundamental issue, however, was the lack of any viable systematic method allowing one to extend the calculation of the spectrum and eigenstates into regions away from the limits of weak and strong coupling. Motivated by these problems, we have developed an analytic approach to the strongly coupled $T \otimes t$ system giving rise to a systematic expansion of the Hamiltonian in inverse powers of the coupling parameter. Such expansions

about the limits of weak and strong coupling might also serve as a first step towards a better understanding of the role of the JT effect in the titanates.

The main ingredient of our treatment is a novel vibronic basis causing the Hilbert space to decay into two orthogonal subspaces $\mathcal{L}_1$ and $\mathcal{L}_2$, which reflect the peculiar energy-level structure in strong coupling. In this range only $\mathcal{L}_1$ is relevant, since the states in $\mathcal{L}_2$ are too high in energy. This leads to the construction of an effective Hamiltonian defined on $\mathcal{L}_1$ and generated by means of projection operators. The eigenvalues of the lowest-order effective Hamiltonian include the correct splitting of the t_{2g} vibrational modes and are exactly the same as those found by Moffitt and Thorson (1957) from their classical treatment of the static JT problem.

Although very little is known about the JT effect in the titanates, our strong-coupling scenario might be appropriate for $YTiO_3$, whereas a weak-coupling approach seems to be more realistic for $LaTiO_3$ at the other end of the series. A convenient starting point for a weak-coupling expansion is provided by equation (25), since in this case there is no justification for the introduction of the subspaces $\mathcal{L}_1$ and $\mathcal{L}_2$. Finally, the influence of the ubiquitous trigonal crystal field as well as the role of the e_g modes should also be investigated.

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Appendix A. Explicit form of $H_2^{(2)}$ and $H_{12}^{(2)}$

In our discussion of the transformed Hamiltonian (57) only the relevant part $H_1^{(2)}$ on subspace $\mathcal{L}_1$ has been written down explicitly (see (58)). For the sake of completeness, the remaining parts of (57) will be given in this appendix. We begin with the Hamiltonian $H_2^{(2)}$ on subspace $\mathcal{L}_2$. This is obtained as

$$\begin{aligned} H_2^{(2)} = H_2^{(1)} &+ \tfrac{15}{32} Q_+ P_1 Q_+ \\ &- \frac{13}{16}\frac{\alpha}{g}(P_2 Q_+^2 P_1 Q_+ + \text{H.c.}) + \frac{39}{16}\frac{\alpha}{g}(b_0^\dagger + b_0) Q_+ P_1 Q_+ \\ &+ \frac{21}{4}\frac{\alpha^2}{g^2} K + \frac{5}{6}\frac{\alpha^2}{g^2} P_2 Q_+^2 P_1 Q_+^2 P_2 - \frac{827}{384}\frac{\alpha^2}{g^2} Q_+ T_+ Q_+ \\ &+ \frac{\alpha^2}{2g^2}(P_2 Q_+ P_2 Q_+^2 P_1 Q_+ + \text{H.c.}) + \frac{33}{8}\frac{\alpha^2}{g^2}(b_0^\dagger + b_0)^2 Q_+ P_1 Q_+ \\ &- \frac{11}{4}\frac{\alpha^2}{g^2}(b_0^\dagger + b_0)(P_2 Q_+^2 P_1 Q_+ + \text{H.c.}) + \text{O}(g^{-3}), \end{aligned} \tag{A.1}$$

where $H_2^{(1)}$ is defined by (48*b*). The new mixing terms generated by the transformation U_2 $(=U_{21}U_{22})$ are contained in the operator

$$\begin{aligned} H_{12}^{(2)} = \bar{H}_{12}^{(1)} &- \frac{\alpha}{3g}(\text{e}^{\Theta} P_1 Q_+^2 P_2 Q_+ P_2 + \text{H.c.}) \\ &+ \frac{\alpha}{g}[(b_0^\dagger + b_0)\text{e}^{\Theta} P_1 Q_+^2 P_2 + \text{H.c.}] - \frac{3\alpha}{4g}[(b_0^\dagger + b_0)^2 \text{e}^{\Theta} P_1 Q_+ + \text{H.c.}] \\ &- \frac{3\alpha^2}{g^2}[(b_0^\dagger + b_0)\text{e}^{\Theta} P_1 Q_- + \text{H.c.}] - \frac{3\alpha^2}{g^2}(b_0^\dagger - b_0)(\text{e}^{\Theta} P_1 Q_+ - \text{H.c.}) \end{aligned}$$

$$+\frac{\alpha^2}{2g^2}[(b_0^\dagger+b_0)\mathrm{e}^{\Theta}T_+Q_+ + \mathrm{H.c.}] - \frac{\alpha^2}{6g^2}(\mathrm{e}^{\Theta}T_+Q_+^2P_2 + \mathrm{H.c.})$$
$$+\frac{4\alpha^2}{g^2}(\mathrm{e}^{\Theta}P_1Q_+Q_-P_2 + \mathrm{H.c.}) - \frac{5\alpha^3}{g^2}(\mathrm{e}^{\Theta}P_1Q_+^3P_1Q_+ + \mathrm{H.c.}) + \mathrm{O}(g^{-3}), \quad (A.2)$$

where $\bar{H}_{12}^{(1)}$ is defined by (48*c*), but without the terms of $\mathrm{O}(g^0)$ in the first line. The preceding equation shows that there are now five mixing terms of $\mathrm{O}(g^{-1})$. Their diagonalization leaves the result of (58) unaltered, as was already claimed in the main text, but does contribute additional terms of $\mathrm{O}(g^{-2})$ to $H_2^{(2)}$, equation (A.1).

Appendix B. Diagonal form of the effective Hamiltonian

The bring the effective Hamiltonian to diagonal form, we need to eliminate the two terms in the second line of (61). The first of these terms, where

$$P_1Q_+^3P_1 = (b_+^{\dagger 3} + 3b_+^{\dagger 2}b_- + 3b_+^\dagger b_-^2 + b_-^3 + \mathrm{H.c.})P_1, \quad (B.1)$$

can be removed by means of the unitary operator

$$V_1 = \exp[-\beta_1(\tfrac{1}{3}b_+^{\dagger 3} + 3b_+^{\dagger 2}b_- - 3b_+^\dagger b_-^2 - \tfrac{1}{3}b_-^3 - \mathrm{H.c.})], \quad (B.2)$$

where $\beta_1 = (\alpha/4g)\mathrm{e}^{\phi}$. This transformation leads to the Hamiltonian

$$V_1^\dagger V_0^\dagger H_1 V_0 V_1 = [N_0 + 1/2 + \sqrt{2/3}(N_+ + N_- + 1) - 4g^2]P_1$$
$$-\frac{\alpha}{2g}\mathrm{e}^{2\phi}(b_0^\dagger + b_0)\mathcal{N}P_1$$
$$+\frac{7\alpha^2}{4g^2}P_1 - \frac{\alpha^2}{2g^2}\mathcal{N}^2P_1 - \frac{3\alpha^2}{2g^2}\mathrm{e}^{2\phi}(b_0^\dagger + b_0)^2\mathcal{N}P_1$$
$$+\frac{3\alpha^2}{8g^2}[N_+^2 + N_-^2 - 12N_+N_- - 5(N_+ + N_-)]P_1 + \mathrm{O}(g^{-3}), \quad (B.3)$$

where purely nondiagonal terms of $\mathrm{O}(g^{-2})$ have been omitted, in agreement with a first-order perturbation treatment. The operator in the second line of (B.3) is conveniently eliminated with the help of two successive transformations V_{21} and V_{22}, where

$$V_{21} = \exp[(\alpha/2g)\mathrm{e}^{2\phi}(b_0^\dagger - b_0)\mathcal{N}]. \quad (B.4)$$

The transformed Hamiltonian assumes the form

$$V_{21}^\dagger V_1^\dagger V_0^\dagger H_1 V_0 V_1 V_{21} = [N_0 + 1/2 + \sqrt{2/3}(N_+ + N_- + 1) - 4g^2]P_1$$
$$+\frac{\alpha}{g}(b_0^\dagger - b_0)(b_+^\dagger b_-^\dagger - b_+b_-)P_1$$
$$+\frac{7\alpha^2}{4g^2}P_1 - \frac{\alpha^2}{g^2}\mathrm{e}^{2\phi}(2N_0 + 1)\mathcal{N}P_1 - \frac{7\alpha^2}{8g^2}\mathcal{N}^2P_1$$
$$+\frac{3\alpha^2}{8g^2}[N_+^2 + N_-^2 - 12N_+N_- - 5(N_+ + N_-)]P_1 + \mathrm{O}(g^{-3}), \quad (B.5)$$

where purely nondiagonal terms of $\mathrm{O}(g^{-2})$ have again been omitted.

Finally, the remaining nondiagonal part in the second line of (B.5) can be removed by means of the unitary operator

$$V_{22} = \exp[\beta_{22}(b_0^\dagger + b_0)(b_+^\dagger b_-^\dagger - \mathrm{H.c.}) + \beta'_{22}(b_0^\dagger - b_0)(b_+^\dagger b_-^\dagger + \mathrm{H.c.})], \quad (B.6)$$

where β_{22} and β'_{22} are fixed by the requirement that the transformed Hamiltonian should not contain terms linear in $b_0^\dagger + b_0$ and $b_0^\dagger - b_0$. This leads to the relations

$$\beta_{22} = 3\alpha/5g \qquad \text{and} \qquad \beta'_{22} = -2\beta_{22}\mathrm{e}^{-2\phi}. \tag{B.7}$$

With the notation $V_2 = V_{21}V_{22}$ and $V = V_0V_1V_2$, the transformed Hamiltonian becomes

$$\begin{aligned} V^\dagger H_1 V = {} & [N_0 + 1/2 + \sqrt{2/3}(N_+ + N_- + 1) - 4g^2]P_1 \\ & + \frac{7\alpha^2}{4g^2}P_1 + \frac{3\alpha^2}{5g^2}(2N_+N_- + N_+ + N_- + 1)P_1 \\ & - \frac{7\alpha^2}{8g^2}(N_+ + N_- + 1 + b_+^\dagger b_-^\dagger + b_+b_-)^2 P_1 \\ & + \frac{3\alpha^2}{8g^2}[N_+^2 + N_-^2 - 12N_+N_- - 5(N_+ + N_-)]P_1 \\ & - \frac{9\alpha^2}{5g^2}\mathrm{e}^{2\phi}(2N_0 + 1)(N_+ + N_- + 1)P_1 + \mathrm{O}(g^{-3}), \end{aligned} \tag{B.8}$$

where (50*b*) has been used. This can be written in the more convenient form (63), if all nondiagonal terms of $\mathrm{O}(g^{-2})$ are omitted in the third line of (B.8).

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