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LETTER TO THE EDITOR

A scale transformation in $T \otimes t_2$ Jahn–Teller systems

Y M Liu†, C A Bates†, J L Dunn† and V Z Polinger†‡

† Physics Department, University of Nottingham, Nottingham NG7 2RD, UK
‡ MSC Division, BYU-Hawaii Campus, Laie, Hawaii 96762–1294, USA

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Abstract. The $T \otimes t$ Jahn–Teller (JT) system has been studied previously by many authors. It is well known that the potential energy surface for this system contains four equivalent wells in strong coupling. The wells are not isotropic. In the strong coupling limit, the vibrational t-mode splits into an a_1-mode of frequency ω_T and an e-mode of frequency $\sqrt{(2/3)}\omega_T$. However, it is difficult to incorporate this anisotropic effect into analytical models. Previously, the current authors have used a unitary shift transformation and energy minimization procedure to model many moderately to strongly coupled JT systems. However, the part of the Hamiltonian which produces the anisotropy was not treated fully. We now present a modification of this procedure for the $T \otimes t$ system in which a scale transformation is applied in addition to the shift transformation. This is shown to introduce anisotropy automatically into the problem. We show that the correct frequencies are obtained in the infinite coupling limit. Symmetry-adapted combinations of the states associated with the wells are taken to obtain expressions for the T_1 ground state and A_2 inversion level. The inversion splitting between them is compared with existing results. We then discuss how the scale transformation method can be applied to other JT systems (for which the limiting frequencies are unknown), such as those in the I_h symmetry which applies to the C_{60} molecule.

The current authors [1, 2, 3, 4] previously developed a method for studying strongly coupled Jahn–Teller (JT) systems in which a unitary shift transformation U (here called U_d) is applied to the Hamiltonian which has the effect of displacing the origin of the phonon coordinates. The transformation contains parameters α_j, which can be fixed by minimizing the total energy of the system. This determines the positions of wells in the potential energy surface. The states localized in the wells can then be written in the original untransformed basis by multiplying them by the value of U_d appropriate to that well. However, this method does not take into account the shape of the potential energy surface around the minima. If the full Hamiltonian is included, the degeneracy of the vibrational frequency of the phonon modes will (in general) be lifted and so anisotropy introduced into the system. The anisotropy is important as JT systems must be described by vibronic states containing both electronic and vibrational coordinates. The changes in frequency of the local modes will alter the vibrational contributions to the vibronic states, which in turn will affect other important properties of the system, such as reduction factors.

The frequencies of the local modes in the strong coupling limit can be determined using the method of Öpik and Pryce [5]. States can then be written down to incorporate the effects of anisotropy by multiplying the states at the minima by harmonic oscillator functions reflecting the strong-coupling frequencies. However, the results are only valid at strong coupling, and the advantages of the transformation approach are lost. The aim of this letter is to show how the unitary transformation method can be modified to include anisotropy for all moderate to strong JT couplings by the addition of a new scale transformation. Results will be given for the cubic $T_1 \otimes t_2$ JT system. It will be shown that the frequencies of the

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local modes reduce to those predicted using the Öpik and Pryce method [5] in the strong coupling limit.

As in the original transformation method, the states localized in the wells are good eigenstates of the system as a whole in strong coupling. In finite coupling, the system will tunnel between states of equivalent energy, so linear combinations of the states in the wells must be taken. This can be achieved using projection operators. Results will be given for the T_1 ground states and the associated A_2 inversion level. The tunnelling splitting between these states will be calculated and compared to existing results (both with and without anisotropy).

The linear vibronic Hamiltonian for the $T_1 \otimes t_2$ JT system may be written as [1]

$$\mathcal{H} = \frac{1}{2}\sum_j \left[\frac{P_j^2}{\mu} + \mu\omega_T^2 Q_j^2\right] I - \sqrt{\frac{3}{2}}\sum_j V_T Q_j \tau_j \tag{1}$$

where V_T is the linear coupling constant, μ is the mass and ω_T the frequency of the t_2 mode. P_j and Q_j are the momenta and coordinates, respectively, of each of the components j of the t_2 mode, which will be labelled 4, 5 and 6. I and τ_j are matrices defined in terms of a basis (x, y, z) as

$$\begin{aligned} I &= \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \quad \tau_4 = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix} \\ \tau_5 &= \begin{pmatrix} 0 & 0 & 1 \\ 0 & 0 & 0 \\ 1 & 0 & 0 \end{pmatrix} \quad \tau_6 = \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} \end{aligned} \tag{2}$$

and Q_j and P_j can be written in the second quantized form

$$Q_j = -\sqrt{\frac{\hbar}{2\mu\omega_T}}(b_j^\dagger + b_j) \qquad P_j = -\mathrm{i}\sqrt{\frac{\hbar\mu\omega_T}{2}}(b_j^\dagger - b_j) \tag{3}$$

where $b_j^\dagger$ and b_j create and destroy, respectively, phonons of symmetry j. The vibronic Hamiltonian (1) can thus be converted into the second quantized form

$$\mathcal{H} = \sum_j \hbar\omega_T \left(b_j^\dagger b_j + \frac{1}{2}\right) I + \sum_j K_T (b_j^\dagger + b_j)\tau_j \tag{4}$$

where

$$K_T = \sqrt{\frac{3\hbar}{8\mu\omega_T}} V_T. \tag{5}$$

We now introduce a shift transformation

$$U_d = \exp\left(\sum_j \alpha_j (b_j - b_j^\dagger)\right) \tag{6}$$

to displace the origin of phonon coordinates, and a scale transformation

$$U_s = \exp\left(\sum_{ij} \Lambda_{ij} (b_i b_j - b_i^\dagger b_j^\dagger)\right) \tag{7}$$

to take account of the anisotropy of the local vibrational modes. The α_j and Λ_{ij} are parameters whose values are to be determined.

Using the formula

$$e^{-S}Ae^{S} = A + \frac{1}{1!}[A, S] + \frac{1}{2!}[[A, S], S] + \dots \tag{8}$$

we can deduce that

$$U_d^{\dagger} b_j U_d = b_j - \alpha_j \quad \text{and} \quad U_s^{\dagger} b_j U_s = \sum_i \left(b_i (\cosh 2\Lambda)_{ij} - b_i^{\dagger} (\sinh 2\Lambda)_{ij} \right). \tag{9}$$

The transformations of $b_j^{\dagger}$ can be obtained by simply taking the Hermitian conjugate of equation (9). We thus find that the vibronic Hamiltonian can be written in the form

$$\tilde{\mathcal{H}} = U_s^{\dagger} U_d^{\dagger} \mathcal{H} U_d U_s = \tilde{\mathcal{H}}_1 + \tilde{\mathcal{H}}_2 + \tilde{\mathcal{H}}_3 \tag{10}$$

where

$$\begin{aligned} \tilde{\mathcal{H}}_1 &= \tfrac{3}{2}\hbar\omega_T I + \textstyle\sum_j \left(\hbar\omega_T [\alpha_j^2 + (\sinh 2\Lambda)_{jj}^2] I - 2K_T \alpha_j \tau_j \right) \\ &\quad + \textstyle\sum_{ij} \hbar\omega_T b_i^{\dagger} b_j (\cosh 4\Lambda)_{ij} I \\ \tilde{\mathcal{H}}_2 &= \textstyle\sum_{ij} (-\hbar\omega_T \alpha_j I + K_T \tau_j)(b_i^{\dagger} + b_i)(\mathrm{e}^{-2\Lambda})_{ij} \\ \tilde{\mathcal{H}}_3 &= -\tfrac{1}{2} \textstyle\sum_{ij} \hbar\omega_T (b_i^{\dagger} b_j^{\dagger} + b_i b_j)(\sinh 4\Lambda)_{ij} I. \end{aligned} \tag{11}$$

$\tilde{\mathcal{H}}_1$ describes couplings within the ground states (with no phonons) so is a good Hamiltonian for determining the ground states of the system. $\tilde{\mathcal{H}}_2$ contains couplings to excited states with one phonon, so can be later treated as a perturbation. $\tilde{\mathcal{H}}_3$ contains higher-order couplings, so can be neglected to second order in perturbation theory. When all the elements Λ_{ij} are zero, this result reduces to that given in Bates *et al* [1] for application of the unitary transformation alone.

We may fix the α_j by solving $\varphi^{\dagger}(\partial\tilde{\mathcal{H}}_1/\partial\alpha_j)\varphi = 0$ [5]. As no terms contain both α_j and Λ_{ij}, this gives the same result for the positions of the wells as in the case without the scale transformation [1]. There are thus four possible solutions. The wells are labelled $k = a, b, c$ and d and have associated electronic states φ_k given by $(1/\sqrt{3})(x, y, -z)$, $(1/\sqrt{3})(x, -y, z)$, $(1/\sqrt{3})(-x, y, z)$ and $(1/\sqrt{3})(-x, -y, -z)$. The shift parameters are $(\alpha_4, \alpha_5, \alpha_6) = \beta\boldsymbol{v}$, where $\boldsymbol{v} = (1, 1, -1)$, $(1, -1, 1)$, $(-1, 1, 1)$ and $(-1, -1, -1)$ respectively.

The wells on the lowest potential energy sheet in Q-space have C_{3v} symmetry. At these minima, the vibrational modes of t_2 symmetry will be reduced to $a_1 \oplus e$. Therefore, a judicious choice of Λ is

$$\Lambda = \frac{1}{4} S_k^{\dagger} \begin{pmatrix} \ln\lambda_a & 0 & 0 \\ 0 & \ln\lambda_e & 0 \\ 0 & 0 & \ln\lambda_e \end{pmatrix} S_k \tag{12}$$

where the S_k are unitary matrices which reduce the t_2 modes of the T_d group into the local

modes of a_1 and e symmetries for a well k. They are found to be

$$\begin{aligned} S_a &= \frac{1}{\sqrt{6}}\begin{pmatrix} \sqrt{2} & \sqrt{2} & -\sqrt{2} \\ -\sqrt{3} & \sqrt{3} & 0 \\ 1 & 1 & 2 \end{pmatrix} \\ S_b &= \frac{1}{\sqrt{6}}\begin{pmatrix} \sqrt{2} & -\sqrt{2} & \sqrt{2} \\ -\sqrt{3} & -\sqrt{3} & 0 \\ 1 & -1 & -2 \end{pmatrix} \\ S_c &= \frac{1}{\sqrt{6}}\begin{pmatrix} -\sqrt{2} & \sqrt{2} & \sqrt{2} \\ \sqrt{3} & \sqrt{3} & 0 \\ -1 & 1 & -2 \end{pmatrix} \\ S_d &= \frac{1}{\sqrt{6}}\begin{pmatrix} -\sqrt{2} & -\sqrt{2} & -\sqrt{2} \\ \sqrt{3} & -\sqrt{3} & 0 \\ -1 & -1 & 2 \end{pmatrix}. \end{aligned} \tag{13}$$

The scale transformation parameters λ_a and λ_e in the matrix Λ can be fixed by taking into account $\tilde{\mathcal{H}}_2$ via second-order perturbation theory. This can be performed in any one of the four equivalent wells. We will illustrate the results for the well a. In this well, the ground vibronic state is $|\varphi_a; 000\rangle$ and its energy is

$$E_0 = -E_{JT} + \frac{1}{4}\hbar\omega_T\left[\lambda_a + \lambda_a^{-1} + 2(\lambda_e + \lambda_e^{-1})\right] \tag{14}$$

where $E_{JT} = 4K_T^2/3\hbar\omega_T$ is the Jahn–Teller energy. This vibronic state is coupled in second-order perturbation theory to the excited states $|\varphi_i; n_4, n_5, n_6\rangle$ $(i = 1, 2)$, where $\varphi_1 = (1/\sqrt{2})(-x, y, 0)$ and $\varphi_2 = (1/\sqrt{6})(x, y, 2z)$. Thus the ground state energy, correct to second order, is $E = E_0 + \Delta$, where

$$\Delta = \sum_{i,n_4,n_5,n_6} \frac{|\langle\varphi_i; n_4 n_5 n_6|\tilde{\mathcal{H}}_2|\varphi_a; 000\rangle|^2}{E_0 - E_i} = -\frac{E_{JT}}{2\lambda_e\,(1 + 3E_{JT}/\hbar\omega_T)}. \tag{15}$$

The scale transformation parameters are determined by setting $\partial E/\partial\lambda_a = 0$ and $\partial E/\partial\lambda_e = 0$ and using the matrix elements of the symmetric matrices $\mathrm{e}^{\pm 2\Lambda}$ in well a:

$$\begin{aligned} (\mathrm{e}^{\pm 2\Lambda})_{ii} &= \frac{1}{3}(\lambda_a^{\pm 1/2} + 2\lambda_e^{\pm 1/2}) \qquad (i = 4, 5, 6) \\ (\mathrm{e}^{\pm 2\Lambda})_{45} &= -(\mathrm{e}^{\pm 2\Lambda})_{56} = -(\mathrm{e}^{\pm 2\Lambda})_{64} = \frac{1}{3}(\lambda_a^{\pm 1/2} - \lambda_e^{\pm 1/2}). \end{aligned} \tag{16}$$

We thus find that

$$\lambda_a = 1 \qquad \lambda_e = \sqrt{\frac{1 + 2E_{JT}/\hbar\omega_T}{1 + 3E_{JT}/\hbar\omega_T}}. \tag{17}$$

It can be seen that the vibrational frequency of the e modes lies between ω_T (in weak coupling) and $\sqrt{(2/3)}\omega_T$ (in strong coupling). One main advantage of the scale transformation method is that other methods [3, 6] have to do, in principle, an infinite order perturbation calculation to obtain this result.

The ground state energy can be seen to take the limits

$$E|_{K_T\to 0} = \frac{3}{2}\hbar\omega_T \qquad E|_{K_T\to\infty} = -E_{JT} + \frac{1}{2}\hbar\omega_T\left(1 + 2\sqrt{\frac{2}{3}}\right). \tag{18}$$

The weak coupling result is the same as would be predicted in the absence of anisotropy. The strong coupling result is the same as would be expected for one mode of frequency ω_T and two modes of frequency $\sqrt{(2/3)}\omega_T$.

The vibronic states associated with the wells can be written in the untransformed picture in the form

$$|\Psi_k\rangle = U_d^{(k)} U_s^{(k)} |\varphi_k; 000\rangle \qquad (k = a, b, c, d). \tag{19}$$

Linear combinations of these states must be taken to allow for tunnelling between the wells in finite coupling. These can be obtained using projection operator techniques, and are the same as those obtained in our previous work [1, 2]. We thus find a T_1 triplet ground state and an A_2 singlet inversion (or tunnelling) level, given by

$$\begin{aligned} |T_{1x}\rangle &= N_t[-|\Psi_a\rangle - |\Psi_b\rangle + |\Psi_c\rangle + |\Psi_d\rangle] \\ |T_{1y}\rangle &= N_t[-|\Psi_a\rangle + |\Psi_b\rangle - |\Psi_c\rangle + |\Psi_d\rangle] \\ |T_{1z}\rangle &= N_t[|\Psi_a\rangle - |\Psi_b\rangle - |\Psi_c\rangle + |\Psi_d\rangle] \\ |A_2\rangle &= N_a[|\Psi_a\rangle + |\Psi_b\rangle + |\Psi_c\rangle + |\Psi_d\rangle] \end{aligned} \tag{20}$$

where N_t and N_a are normalization constants. Both the normalization constants and the energies of the states can be evaluated after standard commutation relationships have been taken into account. We find that the energies of the states are given by

$$\begin{aligned} E_{T_1} &= \langle T_{1z}|\mathcal{H}|T_{1z}\rangle = \frac{H_{11} - H_{12}}{1 + S_t/3} \\ E_{A_2} &= \langle A_2|\mathcal{H}|A_2\rangle = \frac{H_{11} + 3H_{12}}{1 - S_t} \end{aligned} \tag{21}$$

where $H_{11} = E_0$ and

$$H_{12} = \frac{1}{3} S_t \left[\frac{3(1 + 2\lambda_e^2 + 4\lambda_e)}{(1 + 2\lambda_e)^2} E_{JT} - \frac{\hbar\omega_T}{2} \left(1 + 2\lambda_e + \frac{1 - \lambda_e^2}{1 + 2\lambda_e} - \frac{(\lambda_e^3 + \lambda_e^2 - \lambda_e - 1)}{\lambda_e(2 + \lambda_e)} \right) \right]. \tag{22}$$

S_t is the phonon overlap between the vibrational states associated with any two different wells i and j, and is given by

$$S_t = \langle 000|U_s^{(i)\dagger} U_d^{(i)\dagger} U_d^{(j)} U_s^{(j)}|000\rangle = 3c(\lambda_e) \exp\left(-b(\lambda_e) \frac{E_{JT}}{\hbar\omega_T} \right) \tag{23}$$

where

$$c(\lambda_e) = \sqrt{\frac{\lambda_e}{(1 + 2\lambda_e)(2 + \lambda_e)}} \quad \text{and} \quad b(\lambda_e) = \frac{4\lambda_e}{1 + 2\lambda_e}. \tag{24}$$

We thus find that the inversion splitting $\delta (= E_{A_2} - E_{T_1})$ is given by

$$\delta = \frac{2S_t}{(1 + 2\lambda_e)(3 + S_t)(1 - S_t)} \left[\frac{(1 - \lambda_e^2)^2}{\lambda_e(2 + \lambda_e)} \hbar\omega_T + 4 \frac{(1 + 4\lambda_e + \lambda_e^2)}{(1 + 2\lambda_e)} E_{JT} \right]. \tag{25}$$

In the strong coupling limit, δ can be written in the simpler form

$$\delta = a(\lambda_e) E_{JT} \exp\left(-b(\lambda_e) \frac{E_{JT}}{\hbar\omega_T} \right) \tag{26}$$

where

$$a(\lambda_e) = 8 \left(1 - \frac{3\lambda_e^2}{(1 + 2\lambda_e)^2} \right) c(\lambda_e). \tag{27}$$

When the strong-coupling value of $\lambda_e = \sqrt{(2/3)}$ is substituted into this expression, a and b are then constants and the form of the expression is the same as that obtained by other authors. More specifically, we obtain the values $a = 1.8887$ and $b = 1.2404$. These are very close to the results of the analytical perturbation calculations of Schulz and Silbey [6], who obtained the results $a = 1.89$ and $b = 1.2405$ when anisotropic frequencies of ω_T and $\sqrt{(2/3)}\omega_T$ were used. Our value of b is identical to that obtained by Bersuker and Polinger [9] and references therein for the 'harmonic approximation' (although the former approximate the numerical value of b to 1.24). The value of b is also in close agreement with the numerical results of Caner and Englman [7]] (who obtain 1.2405 for $E_{JT}/\hbar\omega_T < 4$ and 1.2 for $E_{JT}/\hbar\omega_T > 4$), although they obtain values of 1.32 and 1.2 respectively for a.

The results do differ from those of more recent accurate calculations for finite coupling. Polinger *et al* [10] obtain results both by numerical integration and an analytical WKB method to try to determine the contributions to the inversion splitting from tunnelling and 'hopping'. Numerical calculations of O'Brien [11] showed that in the region near $E_{JT}/\hbar\omega_T = 6$, $a \approx 0.7$ and $b \approx 1.1$. However, she suggests that the factor in front of the exponential should not be proportional to $E_{JT} = 2k_\tau^2/3\hbar\omega_T$, but some factor raised to a lower power of E_{JT} at stronger coupling. However, she concluded that more accurate calculations are needed to get a true asymptotic form. O'Brien [8] and Polinger [12] suggested that the prefactor should depend on powers of k_τ and $k_\tau^{1.07}$ respectively, rather than on E_{JT}, for k_τ between 2 and 8. From our results, it is clear that the prefactor contains terms depending in a non-trivial manner on both E_{JT} and $\hbar\omega_T$, and that no simple asymptotic form exists.

Polinger [12], using numerical integration of the WKB theory, suggested that $b = 1.098$, in agreement with O'Brien [11]. Our value of b lies between the limits of 1.2404 in strong coupling and 1.33 in weak coupling, and so can never approach the values near 1 suggested by these authors. This must be attributed to the fact that our method is strictly only valid in very strong coupling; higher-order corrections from the neglect of $\tilde{\mathcal{H}}_2$ in the transformed Hamiltonian would need to be included to obtain results to a higher degree of accuracy. We may conclude that, for a relatively simple analytical calculation, the results are very reasonable. Although more sophisticated methods may produce more accurate results for the inversion splitting, the difficulty in obtaining a full set of excited states mean that they cannot be used for the calculation of second-order reduction factors, for example.

The main aim of this letter was to illustrate how a new scale transformation method can be applied in addition to the shift transformation used in previous work [1, 2, 3, 4] in order to incorporate the effects of anisotropy into models of strongly coupled JT systems. It has been applied to the well known case of the cubic $T \otimes t$ JT system to illustrate that the method is valid. Work has just been prepared in which the method is applied to the states associated with the pentagonal (D_{5d}) wells which can arise in the $T \otimes h$ system in icosahedral symmetry (I_h). The effects of anisotropy in this system are as yet unknown. We hope also to be able to extend the method to the trigonal (D_{3d}) wells of this system in the near future. The above method requires some modification in this case, as the reduction of the h_g mode contains a repeated irreducible representation. The results of both cases should help in the understanding of the fullerene C_{60} and related compounds, where it is known that such a JT effect can be exhibited.

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