Further studies of anisotropy in the $T_{1u}\otimes h_g$ Jahn-Teller system

Q. C. Qiu, J. L. Dunn, C. A. Bates, and Y. M. Liu
Physics Department, University of Nottingham, University Park, Nottingham NG7 2RD, United Kingdom
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In the linear $T_{1u}\otimes h_g$ Jahn-Teller system, the adiabatic potential energy surface (APES) is a trough. However, in real systems, quadratic coupling will be present, which warps the APES to give wells of either D_{3d} or D_{5d} symmetry. The degeneracy of the vibrations within the wells is also lifted. This anisotropy has recently been investigated in the $T_{1u}\otimes h_g$ system, and expressions for the frequencies in both types of wells obtained in the strong coupling limit using the method of Öpik and Pryce. A scale transformation procedure was then used to incorporate these results into expressions for the states in the wells and their associated energies. However, this calculation did not allow for second-order perturbation effects and is only valid in the strong coupling limit. In this paper, a revised scale transformation procedure is developed for the D_{5d} wells, which allows expressions for the anisotropic frequencies to be obtained without employing the Öpik and Pryce procedure. An expression is obtained for the phonon overlap that is correct to second-order and is not restricted to the strong coupling limit. Results are then obtained for the ground-state energies and inversion splitting. For D_{3d} wells, the previous results are improved by application of a modified scale transformation procedure and overlaps correct to second order obtained. The results obtained in this paper are of interest in studies of the C_{60}^- anion state of the C_{60} molecule, which is known to occupy a T_{1u} orbital ground state.
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I. INTRODUCTION

The discovery of the C_{60} molecule,[1] and later other fullerenes[1–3] such as C_{180} and C_{240}, opened up a whole new area of study of physical effects in icosahedral (I_h) symmetry. Only a few examples of this very high symmetry were previously known in nature and hence very few studies had been undertaken concerning it. One area of current interest is that of Jahn-Teller (JT) effects, in which highly degenerate orbital states are coupled to highly degenerate vibrational modes. Fourfold and fivefold degeneracies are possible in I_h symmetry; these are not found in other symmetries. $T_{1u}\otimes h_g$ JT systems are of particular interest because molecular orbital calculations indicate that the lowest-energy unfilled orbital in a C_{60} molecule is of T_{1u} symmetry. Hence this system could be a model for C_{60}^-.

In linear coupling, the adiabatic potential energy surface (APES) for the $T_{1u}\otimes h_g$ JT system consists of a trough of SO(3) symmetry. This has been studied by several authors.[4,5] However, quadratic coupling must also be present in all real systems to at least some degree. This will warp the trough to produce wells of either D_{3d} or D_{5d} symmetry, depending upon the strengths of the two possible forms of quadratic coupling.[5–10] It also lifts the degeneracy of the local phonon modes in the wells. This in turn changes the vibronic states of the system as a whole, which then affects further properties of JT systems such as tunneling splittings and reduction factors.

Anisotropic effects such as those induced by quadratic coupling are known to be important in cubic systems (Ref. 11 and references therein). If the quadratic coupling is small, its effect can be treated as a perturbation on the linear coupling states. However, if this is not the case it must be included in the analysis from the beginning. The effects of anisotropy in the $T_{1u}\otimes h_g$ system, as induced by quadratic coupling, have recently been considered in this manner for the first time, firstly for the D_{5d} wells[12] and secondly for the D_{3d} wells.[13] Expressions for the reduced local vibrational frequencies were obtained using the method of Öpik and Pryce,[14] following procedures that are well known for cubic systems. Expressions for the states associated with the wells neglecting the anisotropic effect had already been obtained,[12,13] following the unitary shift transformation approach of Bates, Dunn, and Sigmund.[15] Anisotropy was then included in these states by applying an additional scale transformation incorporating the new local vibrational frequencies. However, due to the nature of the Öpik and Pryce procedure, the results obtained in Refs. 12 and 13 are strictly valid only in the infinite coupling limit.

In the current paper, a modified version of the scale transformation method will be developed and applied to the states associated with both the D_{5d} and D_{3d} wells. The method to be used for the D_{5d} wells follows that developed originally for the $T\otimes t_2$ system in cubic symmetry.[16] Values for the local vibrational frequencies are obtained without using the Öpik and Pryce method, and hence the results are not restricted to the strong coupling limit. In Ref. 12, the results obtained were taken to zeroth order in perturbation theory only. However, it will be shown here that significant correction terms arise when the calculation is repeated to second order in perturbation theory. This calculation is nontrivial because the ground states used now involve contributions from excited phonon states. This vastly complicates the evaluation of the necessary overlap factors and matrix elements, which now depend upon both of the second-order coupling coefficients rather than just one as in the simple case. In this paper, the magnitudes of the corrections to the isotropic result from these second-order effects and from including the correct local frequencies will be calculated and compared.

Equivalent results for the D_{3d} wells cannot be obtained using the scale transformation directly due to a repeated irreducible representation in the reduction in symmetry of the h_g mode. However, an alternative procedure will be developed that also allows results to be obtained that are not restricted to infinite coupling. Firstly, the reduced infinite coupling frequencies as obtained using the Öpik and Pryce method will be used to generate the diagonalizing matrices (called *S* matrices) that arise as part of the scale transformation method. With these known, new expressions for the frequencies not restricted to infinite coupling will be obtained by solving the original problem using the scale transformation. Results will be obtained that are correct to second order in perturbation theory.

This paper begins by setting up the vibronic Hamiltonian for the $T_{1u}\otimes h_g$ JT system[6] including the two quadratic coupling terms. A brief discussion of the application of the unitary shift and scale transformation procedures to this system is then given. The local frequency problem is then solved for the D_{5d} wells and then the D_{3d} wells using the methods described above. In both cases, phonon overlap integrals will be calculated to second order. Finally, expressions for the tunneling splittings are obtained, and the results both including and neglecting the revised frequencies compared to the isotropic case.

II. BACKGROUND THEORY

The components j of the h vibrational mode will be labeled θ, ε, 4, 5, and 6. In order to get the simplest matrices of H symmetry,[17] the components θ and ε will be chosen to be linear combinations of the standard components used in cubic symmetry, namely,

$$d_{z^2}=\tfrac{1}{2}\sqrt{\tfrac{3}{2}}H_\theta-\tfrac{1}{2}\sqrt{\tfrac{5}{2}}H_\varepsilon,$$
$$d_{x^2-y^2}=\tfrac{1}{2}\sqrt{\tfrac{5}{2}}H_\theta+\tfrac{1}{2}\sqrt{\tfrac{3}{2}}H_\varepsilon. \tag{2.1}$$

The orbital triplet T_{1u} is modeled using an isomorphic $l=1$ operator, and its three components will be labeled *x*, *y*, and *z*.

A. The Hamiltonian

The total vibronic Hamiltonian of the system including two quadratic terms can be written down in terms of collective displacements Q_i and corresponding conjugate momenta P_i. As the calculations to be described here involve the evaluation of rather complicated phonon overlaps, we find it convenient to write the Hamiltonian in second quantized operator form. Following Ref. 6, we express it in the form

$$\mathcal{H}=\mathcal{H}_{\rm vib}+\mathcal{H}_1+\mathcal{H}_2+\mathcal{H}_3, \tag{2.2}$$

where $\mathcal{H}_{\rm vib}$ is the vibrational Hamiltonian, $\mathcal{H}_1$ the linear interaction Hamiltonian and $\mathcal{H}_2$ and $\mathcal{H}_3$ the two quadratic coupling Hamiltonians. Thus in second quantized form,

$$\mathcal{H}_{\rm vib}=\sum_j \hbar\omega\left(b_j^\dagger b_j+\frac{1}{2}\right)\hat{L}_{A_1} \quad (j=\theta,\varepsilon,4,5,6), \tag{2.3}$$

where ω is the frequency of vibration, $b_j^\dagger$ and b_j are phonon creation and annihilation operators, respectively. The linear term of the Hamiltonian is

$$\mathcal{H}_1=K_1\sum_j (b_j^\dagger+b_j)\hat{L}_{Hj} \tag{2.4}$$

and the two quadratic terms are

$$\mathcal{H}_2=K_2\sum_j A_j'\hat{L}_{Hj} \quad \text{and} \quad \mathcal{H}_3=K_3\sum_j B_j'\hat{L}_{Hj}, \tag{2.5}$$

respectively. The coefficients K_i are defined by the relations

$$K_1=-\sqrt{\hbar/2\mu\omega}V_1 \quad \text{and} \quad K_i=\frac{V_i\hbar}{2\mu\omega}=\frac{1}{2}\hbar\omega V_i' \quad (i=2,3), \tag{2.6}$$

where $V_i'=V_i/\mu\omega^2$, V_1 is the linear coupling constant and V_2 and V_3 are the quadratic coupling coefficients. $\hat{L}_{A_1}$ is the unit operator and

$$\hat{L}_{H\theta}=\tfrac{1}{2}\sqrt{\tfrac{3}{5}}(\phi^{-1}c_1^\dagger c_1-\phi c_2^\dagger c_2+c_3^\dagger c_3),$$
$$\hat{L}_{H\varepsilon}=\tfrac{1}{2}\sqrt{\tfrac{1}{5}}(\phi^2 c_1^\dagger c_1-\phi^{-2}c_2^\dagger c_2-\sqrt{5}c_3^\dagger c_3),$$
$$\hat{L}_{H4}=\sqrt{\tfrac{3}{10}}(c_2^\dagger c_3+c_3^\dagger c_2),$$
$$\hat{L}_{H5}=\sqrt{\tfrac{3}{10}}(c_3^\dagger c_1+c_1^\dagger c_3), \tag{2.7}$$
$$\hat{L}_{H6}=\sqrt{\tfrac{3}{10}}(c_1^\dagger c_2+c_2^\dagger c_1),$$
$$A_j'=\sum_{mp} a_{mp}^j(b_m^\dagger+b_m)(b_p^\dagger+b_p),$$
$$B_j'=\sum_{mp} b_{mp}^j(b_m^\dagger+b_m)(b_p^\dagger+b_p),$$

where $\phi=\frac{1}{2}(1+\sqrt{5})$ is the golden mean, $c_1^\dagger$, $c_2^\dagger$, and $c_3^\dagger$ are orbital creation operators acting on the pure electronic basis states $|x\rangle$, $|y\rangle$, and $|z\rangle$, of T_{1u} symmetry to create *x*, *y*, and *z*, respectively, and a_{mp}^j and b_{mp}^j $(j,m,p=\theta,\varepsilon,4,5,6)$ are coefficients whose nonzero terms are

$$a_{\theta\varepsilon}^\theta=\sqrt{\tfrac{1}{2}}, \quad a_{44}^\theta=-a_{55}^\theta=\sqrt{\tfrac{3}{8}},$$
$$a_{\theta\theta}^\varepsilon=-a_{\varepsilon\varepsilon}^\varepsilon=a_{44}^\varepsilon=a_{55}^\varepsilon=-\tfrac{1}{2}\ a_{66}^\varepsilon=\sqrt{\tfrac{1}{8}},$$
$$a_{\theta4}^4=-a_{\theta5}^5=\sqrt{\tfrac{3}{2}}, \quad a_{\varepsilon4}^4=a_{\varepsilon5}^5=\sqrt{\tfrac{1}{2}}, \quad a_{\varepsilon6}^6=-\sqrt{2},$$
$$b_{\theta\theta}^\theta=-b_{\varepsilon\varepsilon}^\theta=\sqrt{\tfrac{3}{8}},\ b_{44}^\theta=b_{55}^\theta=-\tfrac{1}{2}\ b_{66}^\theta=-\sqrt{\tfrac{1}{24}}, \tag{2.8}$$
$$b_{\theta\varepsilon}^\varepsilon=-\sqrt{\tfrac{3}{2}}, \quad b_{44}^\varepsilon=-b_{55}^\varepsilon=\sqrt{\tfrac{1}{8}},$$
$$b_{\theta4}^4=b_{\theta5}^5=-\sqrt{\tfrac{1}{6}}, \quad b_{\theta6}^6=\sqrt{\tfrac{2}{3}}, \quad b_{\varepsilon4}^4=-b_{\varepsilon5}^5=\sqrt{\tfrac{1}{2}},$$
$$b_{56}^4=b_{46}^5=-2\sqrt{\tfrac{1}{3}}, \quad b_{45}^6=-2\sqrt{\tfrac{1}{3}}.$$

B. Unitary shift and scale transformations

In very strong coupling, the system becomes frozen into one of the minima in the APES at low temperatures.[15] At

finite coupling, it is possible to employ the crude adiabatic approximation and construct states for the whole system from a linear combination of the strong coupling states. Hence it is important to be able to obtain accurate expressions for the infinite coupling states.

Previously,[6] the positions of the minima in the APES have been determined by applying a unitary shift transformation U_d to the original Hamiltonian. For well k, this has the form

$$U_d^{(k)}=\exp\left\{ i\sum_j \alpha_j^{(k)}P_j\right\}\equiv\exp\left\{\sum_j C_j^{(k)}(b_j-b_j^\dagger)\right\}, \tag{2.9}$$

where $C_j^{(k)}=-\sqrt{\mu\hbar\omega/2}\alpha_j^{(k)}=(K_1/\hbar\omega)\ a_j^{(k)}$. The resultant transformed Hamiltonian can be split into two parts. The first part contains the α_j as free parameters but no phonon operators, and so it can be used to determine the energy of the ground state of the system. Values for the α_j (or equivalently the a_j) are then chosen to minimize the energy of the system. This has the effect of fixing the system into one of the potential energy minima, because the transformation displaces the origin of the nuclear coordinates to $\tilde{Q}_j=U_d^\dagger Q_j U_d=Q_j-\alpha_j\hbar$. Infinite-coupling states can then be written down by multiplying the original basis states by $U_d^{(k)}$. These zeroth-order states are good as a first approximation, and have been used successfully to describe many properties of a range of different JT systems. However, they do not incorporate corrections due to anisotropy in the wells.

In strong coupling, the fivefold degeneracy of the vibrational h_g mode is lifted as the symmetry is reduced from I_h to D_{5d} or D_{3d}. It has been difficult previously to incorporate the anisotropic effects induced by the lifting of this degeneracy into analytical models. Recently,[16] an extension of the shift transformation method has been developed to automatically introduce anisotropy into the $T\otimes t_2$ JT problem in cubic symmetry. This involved applying an additional scale transformation, which for well k has the form

$$\begin{aligned}U_s^{(k)}&=\exp\left\{\frac{i}{\hbar}\sum_{ij}A_{ij}^{(k)}(Q_iP_j+P_jQ_i)\right\}\\&=\exp\left\{\sum_{ij}\Lambda_{ij}^{(k)}(b_ib_j-b_i^\dagger b_j^\dagger)\right\},\end{aligned} \tag{2.10}$$

where $\Lambda_{ij}^{(k)}=A_{ij}^{(k)}\sqrt{\omega_j/\omega_i}$ are transformation parameters whose values must be determined. It can be proved that the eigenvalues of the matrix Λ are identical to those of A, so it is possible to work with either in subsequent calculations. No terms in the new transformed Hamiltonian contain both α_j and Λ_{ij}, so the α_j can be fixed to take the same values as with the shift transformation alone.

In the case of the $T\otimes t_2$ JT system, values for the Λ_{ij} were fixed by minimization of the total energy taking into account the previously neglected part of the transformed Hamiltonian to second order in perturbation theory. However, difficulties arise in applying this method directly to the $T_{1u}\otimes h_g$ JT system due to the higher fivefold degeneracy and the necessity to include quadratic couplings in the problem in order to generate wells rather than a trough. Only a simplified version of this procedure has been developed so far,[2,13] using the result that in infinite coupling it is possible to determine values for the local frequencies using the Öpik and Pryce method. These were used to bypass the need to fix values for the parameters Λ_{ij} in the scale transformation. We will now develop the scale transformation theory for both sets of wells.

Using the formula

$$e^{-B}Ae^B=A+\frac{1}{1!}[A,B]+\frac{1}{2!}[[A,B],B]+\cdots, \tag{2.11}$$

it is easy to show that

$$U_s^\dagger b_j U_s=\sum_i\ [b_i(\cosh 2\Lambda)_{ij}-b_i^\dagger(\sinh 2\Lambda)_{ij}], \tag{2.12}$$

where $(\cosh 2\Lambda)_{ij}$ means the (i,j)th element of the matrix $\cosh 2\Lambda$ (and similarly for $\sinh 2\Lambda$). The matrices $f(\Gamma)$ where $f=\cosh$, sinh, or exp can be defined[18] in terms of power series expansions, or via a matrix $\mathbf{P}$ which brings $f(\Gamma)$ to a diagonal form Γ' by the relationship

$$f(\Gamma)=\mathbf{P}f(\Gamma')\mathbf{P}^{-1}. \tag{2.13}$$

The corresponding transformation for $b_j^\dagger$ can be obtained by taking the Hermitian conjugate of the equation above. Consequently,

$$U_s^\dagger(b_j^\dagger+b_j)U_s=\sum_i\ (b_i^\dagger+b_i)(e^{-2\Lambda})_{ij}. \tag{2.14}$$

The full transformed Hamiltonian is therefore $\tilde{\mathcal{H}}=U_s^\dagger U_d^\dagger\mathcal{H}U_dU_s=\tilde{\mathcal{H}}_1+\tilde{\mathcal{H}}_2+\tilde{\mathcal{H}}_3$, where in this case

$$\begin{aligned}\tilde{\mathcal{H}}_1=\sum_j\ \Bigg[&\hbar\omega\left(C_jC_j+\tfrac{1}{2}\right)\hat{L}_{A_1}-2K_1C_j\hat{L}_{Hj}\\&+\sum_{mp}\ 4(K_2a_{mp}^j+K_3b_{mp}^j)C_mC_p\hat{L}_{Hj}\Bigg],\end{aligned} \tag{2.15}$$

$$\begin{aligned}\tilde{\mathcal{H}}_2=\sum_j\ \Bigg[&\hbar\omega(\sinh 2\Lambda)_{jj}^2\hat{L}_{A_1}\\&+\sum_{mp}\ (K_2a_{mp}^j+K_3b_{mp}^j)(e^{-4\Lambda})_{mp}\hat{L}_{Hj}\Bigg]\\&+\sum_{ij}\ (b_j^\dagger+b_j)\Bigg[(-\hbar\omega C_j\hat{L}_{A_1}+K_1\hat{L}_{Hj})(e^{-2\Lambda})_{ij}\\&-2\sum_{mp}\ (K_2a_{mp}^j+K_3b_{mp}^j)[C_p(e^{-2\Lambda})_{im}\\&+C_m(e^{-2\Lambda})_{ip}]\hat{L}_{Hj}\Bigg],\end{aligned}$$

$$\tilde{\mathcal{H}}_3=\sum_{ij}\ [b_i^\dagger b_j(\cosh 4\Lambda)_{ij}-\tfrac{1}{2}(b_i^\dagger b_j^\dagger+b_i b_j)$$
$$\times(\sinh 4\Lambda)_{ij}]\hat{L}_{A_1}+\sum_j\ \sum_{mp}\ (K_2 a^j_{mp}+K_3 b^j_{mp})$$
$$\times\sum_{ks}\ (b_k^\dagger b_s^\dagger+b_k b_s+b_k^\dagger b_s+b_s^\dagger b_k)$$
$$\times(e^{-2\Lambda})_{km}(e^{-2\Lambda})_{sp}\hat{L}_{Hj}\,.$$

As $\tilde{\mathcal{H}}_1$ contains no phonon creation and annihilation operators, it can be used to describe the vibronic ground states of the system. $\tilde{\mathcal{H}}_2$ contains two contributions: one of them, like $\tilde{\mathcal{H}}_1$, also contains no phonon operators. This describes anisotropic corrections to the ground-state energy produced by the scale transformation. The other term contains one-phonon creation and annihilation operators, and so describes couplings to excited states with one phonon excitation (as with the shift transformation alone). $\tilde{\mathcal{H}}_2$ may be treated as a first-order perturbation correction to the ground states. $\tilde{\mathcal{H}}_3$ describes the higher-order vibronic coupling and it is only necessary to calculate its effects in higher-order perturbations. We note that the results are consistent with those neglecting anisotropy because when all the elements Λ_{ij} above are set to zero, the results become identical to those of the shift transformation alone.

In order to evaluate the overlaps between different vibronic states, it will be necessary to know the effect of U_s on the collective displacements Q_i. It can be proved that

$$U_s Q_m=\exp\left\{\sum_i\ A_{ii}\right\}\sum_i\ \exp\{2A\}_{im}Q_i\,,$$
$$U_s\sum_m\ Q_m^2=\exp\left\{\sum_i\ A_{ii}\right\}\sum_{im}\ \exp\{4A\}_{im}Q_iQ_m\,. \tag{2.16}$$

Therefore, for any differentiable function $f(Q_i)$ of Q_i,

$$U_s f(Q_m)=\exp\left\{\sum_i\ A_{ii}\right\}f\left(\sum_i\ \exp\{2\Lambda\}_{im}Q_i\right),$$
$$U_s f\left(\sum_m\ Q_m^2\right)=\exp\left\{\sum_i\ A_{ii}\right\}f\left(\sum_{i,m}\ \exp\{4A\}_{im}Q_iQ_m\right). \tag{2.17}$$

Before the calculations can be performed, it is necessary to know how to write down vibronic states associated with the wells with respect to the transformed Hamiltonian. In the transformed space, the zeroth-order ground electronic state in well k is denoted by $|X_0^{(k)};0\rangle$ where the ''0'' represents no phonon excitations and $X_0^{(k)}$ represents the electronic state. Equivalent states including phonon excitations are written in the form $|X_0^{(k)};X_p\rangle$. In Ref. 6, explicit expressions for the electronic states $X_0^{(k)}$ were obtained. In this reference, the electronic states for the ten D_{3d} wells were labeled a to j and the states for the six D_{5d} wells labeled A to F. The states are of A_{2u} symmetry in both cases. Here, the effect of $\tilde{\mathcal{H}}_2$ on the ground state of the system will be calculated using perturbation theory. This involves correcting the zeroth-order states by coupling to first-order excited states in the wells containing at most one-phonon excitation.[16] We will therefore add subscripts A_0, etc. to the state labels to indicate that the states are zeroth-order ground states. We will illustrate the method of calculation by reference to the well A for D_{5d} minima. The corrected energy in this well is

$$E=E_0+\langle A_0;0|\tilde{\mathcal{H}}_2|A_0;0\rangle+\sum_i\ \frac{|\langle A_i|\tilde{\mathcal{H}}_2|A_0;0\rangle|^2}{E_0-E_i}, \tag{2.18}$$

where $|A_i\rangle$ represent all components of the relevant first-order excited states in the wells, with corresponding energies E_i, and E_0 is the ground-state energy in well A (calculated from $E_0=\langle A_0;0|\tilde{\mathcal{H}}_1|A_0;0\rangle$). Explicit expressions for the excited electronic states, which are of E_{1u} symmetry for the D_{5d} wells and E_u symmetry for the D_{3d} wells, are given in Table I.

TABLE I. Excited electronic states in (a) D_{5d} wells (b) D_{3d} wells.

D_{5d} well	Electronic excited states X_i
A	$(1,0,0),(0,1,-\phi)$
B	$(1,0,0),(0,1,\phi)$
C	$(0,1,0),(-\phi,0,1)$
D	$(0,1,0),(\phi,0,1)$
E	$(0,0,1),(1,-\phi,0)$
F	$(0,0,1),(1,\phi,0)$
D_{3d} well	Electronic excited states X_i
a	$(1,0,0),(0,-\phi,\phi^{-1})$
b	$(1,0,0),(0,\phi,\phi^{-1})$
c	$(0,1,0),(-\phi^{-1},0,\phi)$
d	$(0,1,0),(\phi^{-1},0,\phi)$
e	$(0,0,1),(-\phi,\phi^{-1},0)$
f	$(0,0,1),(\phi,\phi^{-1},0)$
g	$(1,0,-1),(1,-2,1)$
h	$(0,1,-1),(2,1,1)$
i	$(-1,0,1),(1,2,1)$
j	$(1,0,1),(-1,2,1)$

It is also necessary to write down states in the original untransformed space. This can be achieved by applying the transformation operators to the transformed vibronic states. The zeroth-order untransformed states associated with each well will be written as

$$|X_0^{(k)\prime};X_p\rangle=U_s^{(k)}U_d^{(k)}|X_0^{(k)};X_p\rangle. \tag{2.19}$$

As in previous work, we note that because the U's contain phonon operators, the untransformed ground states are vibronic in nature even when there are no phonon excitations present in the transformed picture.

III. CALCULATION OF LOCAL FREQUENCIES

A. The local frequency problem for D_{5d} minima

In principle, the scale transformation parameters Λ_{ij} can be determined by minimizing E with respect to Λ_{ij}. The matrix Λ can be treated with the aid of group theory. It is known that the irreducible representations of the I_h group

will be reduced under D_{5d} symmetry to the sum $a_1 \oplus e_1 \oplus e_2$. The frequency ω of the mode in each well is therefore reduced to three values, ω_a, ω_{e_1}, and ω_{e_2}. These will be written in terms of scaled frequencies $\lambda_i = \omega_i/\omega$. As the splittings are the same in each well, the frequencies will also be the same in each well. The matrices Λ will be different. However, they are connected by a unitary transformation.

In order to illustrate the effect of the scale transformation, we first investigate its effect on the zeroth-order wave functions of a simple harmonic operator (SHO). In the coordinate representation, these wave functions can be written in the form

$$\psi(Q_i) = N_0 \exp\left\{ -\frac{\mu\omega}{\hbar} Q_i^2 \right\}, \tag{3.1}$$

where N_0 is a normalization factor. The scale transformation operator U_s in Eq. (2.10) is a product of operators U_{ij} due to each element A_{ij} of the matrix A. It can be shown that for the diagonal elements,

$$\begin{aligned} U_{ii}\psi(Q_i) &= \lambda_i^{1/4} N_0 \exp\left\{ -\frac{\mu\omega}{\hbar} \lambda_i Q_i^2 \right\} \\ &\equiv \lambda_i^{1/4} N_0 \exp\left\{ -\frac{\mu\omega_i}{\hbar} Q_i^2 \right\}, \end{aligned} \tag{3.2}$$

where λ_i are new parameters defined by the relationship

$$\Lambda_{ii} = \tfrac{1}{4} \ln \lambda_i. \tag{3.3}$$

λ_i is thus the ratio of the anisotropic local frequency ω_i of the i mode to the original isotropic frequency ω. Comparing with Eq. (3.1), it can be seen that the effect of the scale transformation has been to change the original isotropic frequency ω to the local value ω_i.

The above analysis for the part of U_s due to Λ_{ii} acting on a SHO wave function in the coordinate representation suggests that it is reasonable to choose $\frac{1}{4} \ln \lambda_i$ as the eigenvalues of the matrix $\Lambda^{(k)}$ in the general case. Thus we have

$$\Lambda^{(k)} = \tfrac{1}{4} S_k^{\dagger} [\ln \lambda_i] S_k, \tag{3.4}$$

where $[\ln \lambda_i]$ represents the diagonal matrix with $i = a_1$, e_1, and e_2 and S_k is a unitary matrix that has two functions. Firstly, it can block diagonalize ten representation matrices of H symmetry of the I_h group. The ten matrices form a subgroup D_{5d} of the I_h group. Secondly, it can reduce the h_g modes of I_h symmetry into local modes a_{1g}, e_{1g}, and e_{2g}.

It is necessary now to determine an expression for the energy E of the system as a function of λ_a, λ_{e_1}, and λ_{e_2}. In calculating the second-order correction to E, we must consider the excited states with energies $E_0 + \hbar\omega$ (degeneracy 5), $E_{E_{1u}}$ (degeneracy 2), and $E_{E_{1u}} + \hbar\omega$ (degeneracy 10), where $E_{E_{1u}}$ is the energy of the excited electronic E_{1u} state with no phonon excitations. However, it is found that the states defining the first two of these sets of energy levels make no overall contribution to the total energy E. To illustrate the calculation involving the third set, we will use well A. We must determine E using the transformed Hamiltonian in Eq. (2.15), which in turn involves handling the matrices $\exp(2\Lambda)$, etc. according to Eq. (2.13) (as described in Joshi[18]). In particular,

$$\exp\{\pm n\Lambda\} = S_A^{\dagger} [\lambda_i^{\pm n/4}] S_A, \tag{3.5}$$

where $[\lambda_i]$ represents the diagonal matrix with $i = a_1$, e_1, and e_2 and S_A is the unitary matrix found previously by Liu *et al.*[12] (using group theory) to be

$$S_A = \frac{1}{\sqrt{10}} \begin{pmatrix} -\sqrt{3} & -1 & \sqrt{6} & 0 & 0 \\ \phi^2 & -\sqrt{3}\phi^{-1} & \sqrt{2} & 0 & 0 \\ 0 & 0 & 0 & \sqrt{10/(\phi+2)} & \phi\sqrt{10/(\phi+2)} \\ \phi^{-2} & \sqrt{3}\phi & \sqrt{2} & 0 & 0 \\ 0 & 0 & 0 & -\phi\sqrt{10/(\phi+2)} & \sqrt{10/(\phi+2)} \end{pmatrix}. \tag{3.6}$$

The sinh and cosh functions can be expressed in terms of exponentials. Thus we obtain the result

$$\begin{aligned} E_{D_{5d}} = E_0 &+ \frac{1}{2}\hbar\omega \left(\frac{\lambda_a}{2} + \frac{1}{2\lambda_a} + \lambda_{e_1} + \frac{1}{\lambda_{e_1}} + \lambda_{e_2} + \frac{1}{\lambda_{e_2}} - 5 \right) \\ &+ \frac{\sqrt{2}}{10} \left[V_2' \left(\frac{1}{\lambda_{e_1}} + \frac{1}{\lambda_{e_2}} - \frac{2}{\lambda_a} \right) - \sqrt{5} V_3' \left(\frac{1}{\lambda_{e_1}} - \frac{1}{\lambda_{e_2}} \right) \right] \\ &- \frac{1}{5} \frac{1}{\lambda_{e_1}} \frac{K_1^2}{\hbar\omega} \frac{[\sqrt{3} + \beta(V_2' + \sqrt{5}V_3')]^2}{\Delta_{5d}}, \end{aligned} \tag{3.7}$$

where

$$\Delta_{5d} = 1 + \sqrt{2} \left(\frac{K_1}{\hbar\omega} \right)^2 \beta(\sqrt{3} + 2\beta V_2'). \tag{3.8}$$

The correct set of ratios of frequencies should be chosen to ensure that the energy is a minimum. Therefore, values for the parameters λ_a, λ_{e_1}, and λ_{e2} are fixed by solving the three equations $\partial E/\partial \lambda_i = 0$. From perturbation theory, the

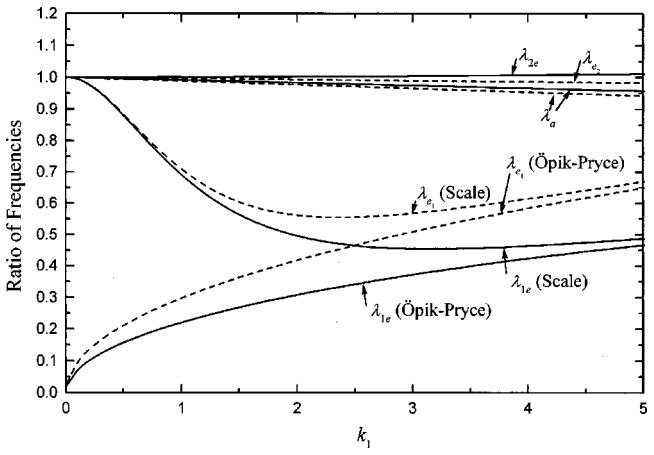

FIG. 1. A comparison of the scaled frequencies λ_i obtained after the Öpik-Pryce method and after the scale transformation. The dashed lines are the results for the D_{5d} wells with $K_2=-K_3=0.01K_1$ and the solid lines are for the D_{3d} wells with $K_2=-K_3=-0.01K_1$.

first-order term gives the correction to the zeroth-order and the second-order terms give the corrections to first order. We finally obtain the results

$$\lambda_a^2=1-\tfrac{4}{5}\sqrt{2}V_2',$$

$$\lambda_{e_2}^2=1+\tfrac{1}{5}\sqrt{2}V_2'+\frac{2}{5}\sqrt{10}V_3', \tag{3.9}$$

$$\lambda_{e_1}^2=1+\frac{1}{5}\sqrt{2}V_2'\frac{1+\sqrt{2}(K_1/\hbar\omega)^2\beta(3\sqrt{3}+\beta V_2')}{\Delta_{5d}}-\frac{1}{5}\sqrt{10}V_3'\frac{1+\sqrt{2}(K_1/\hbar\omega)^2\beta(3\sqrt{3}+\sqrt{5}\beta V_2')}{\Delta_{5d}}-\frac{6}{5}\frac{(K_1/\hbar\omega)^2}{\Delta_{5d}},$$

where

$$\beta=\frac{\sqrt{6}}{5-4\sqrt{2}V_2'}. \tag{3.10}$$

The formulas obtained for λ_a and λ_{e_2} are identical to the results using the Öpik-Pryce method. Figure 1 shows a plot of these results as a function of the linear coupling strength $k_1=K_1/\hbar\omega$ for the quadratic coupling constants in the ratios $K_2=-K_3=0.01K_1$ (dashed lines). The figure also shows the results obtained for λ_{e_1} using both the scale transformation and Öpik-Pryce methods. This shows that the primary difference between the two approaches is that the result obtained using the scale transformation correctly tends to 1 in weak coupling, whilst the Öpik-Pryce result tends to zero. This is because the latter is a strong coupling procedure.

For very weak coupling (i.e., $K_1\rightarrow 0$), the second-order contributions can be neglected and the results obtained are identical to the first-order results. In the infinite coupling limit (i.e., $K_1\rightarrow\infty$), and if we take $V_2'=V_3'=0$, we have $\lambda_a=\lambda_{e_2}=1$ and $\lambda_{e_1}=0$. This correctly describes the appearance of the trough in five-dimensional phonon space when quadratic coupling is neglected. The two vibrational modes with E_1 symmetry have been completely quenched by the strong linear vibronic coupling. However, even if the two quadratic coupling terms in the total Hamiltonian of the $T_{1u}\otimes h_g$ JT system are ignored, the perfect trough appears at infinite coupling only. Away from the limit $K_1\rightarrow\infty$, ω_{e_1} does not take its ideal values of 0 but varies according to the relationship

$$\lambda_{e_1}^2=\frac{1}{1+6(K_1/\hbar\omega)^{2/5}}. \tag{3.11}$$

The above results are consistent with the view that in the absence of vibronic coupling, the vibrational space is isotropic and the frequencies in all directions are exactly the same. When linear vibronic coupling is added, the isotropic vibrational space will be broken gradually according to the strength of the coupling. When the strength increases, the two-dimensional trough becomes deeper.

B. The local frequency problem for D_{3d} minima

For D_{3d} minima, the h_g vibrational modes with I_h symmetry can be reduced into $a_g\oplus 2e_g$. Solving the local frequency problem involves constructing S matrices for the D_{3d} minima. However, as the D_{3d} subgroup contains a repeated representation, proper S matrices cannot be found using group theory alone. Group theory cannot distinguish between the two e_g modes and so the resulting S matrix can only block diagonalize Λ. This suggests that suitable S matrices to make Λ diagonal must be found using the Öpik and Pryce method. These matrices can then be applied using the scale transformation procedure, thus allowing revised expressions for the frequencies to be obtained that are not restricted to the strong coupling limit.

1. The Öpik-Pryce method

The values of the frequencies in infinite coupling can be derived using the method of Öpik and Pryce,[14] as described in detail for D_{5d} wells in Ref. 12. Brief preliminary details were also given for D_{3d} wells in Ref. 13. The potential energy U that generates the APES is expanded as a power series in $q_{\Gamma\gamma}=Q_{\Gamma\gamma}-Q_{\Gamma\gamma}^{(k)}$ about the minimum at the well position $Q^{(k)}$ up to second order. The first- and second-order contributions are treated as perturbations, and a corrected energy up to second order obtained. This is written in a matrix form:

$$E=E_0(Q^{(k)})+\frac{1}{2}(q_{\Gamma_1\gamma_1}q_{\Gamma_1\gamma_2}\cdots)M\begin{pmatrix}q_{\Gamma_1\gamma_1}\\ q_{\Gamma_1\gamma_2}\\ \vdots\end{pmatrix}, \tag{3.12}$$

where the matrix M is given explicitly in Ref. 12. As the matrix elements have the same dimension as $\mu\omega^2$, they are therefore written as $\mu\omega_{\Gamma_1}^2,\mu\omega_{\Gamma_2}^2,\ldots$. In general, the matrix M can be diagonalized using a proper unitary transformation

(quantum mechanically, this operation changes M from one representation to another.). The diagonalized matrix can be expressed as

$$\tilde{M} = SMS^{-1} = \mu\omega^2 \begin{pmatrix} \lambda_{\Gamma_1}^2 & & & \\ & \ddots & & \\ & & \lambda_{\Gamma_2}^2 & \\ & & & \ddots \end{pmatrix}, \tag{3.13}$$

where $\lambda_\Gamma = \omega_\Gamma/\omega$. In the case of the D_{5d} wells, the resulting eigenvalues were then found. Normalizing each eigenstate and substituting the corresponding electronic states and the positions of the wells allowed the S matrices to be determined.

For the D_{3d} minima, it would appear first that the procedure should follow that above for D_{5d} wells. The required S matrices can be determined following the procedure described in the appendix of Ref. 12. The electronic states, energies, and the positions of the D_{3d} wells are known so can be used to obtain the corresponding M matrices. However, unlike in the D_{5d} case, these M matrices cannot be diagonalized directly. However, the S matrices can block diagonalize the M matrices as the M matrices have I_h symmetry and the S matrices block diagonalize the h_g representative matrices that form a D_{3d} subgroup of I_h. We will illustrate the procedure using well a as an example. As a first step, we use the matrix S_{a_1} given by

$$S_{a_1} = \frac{1}{\sqrt{6}} \begin{pmatrix} 1 & -\sqrt{3} & \sqrt{2} & 0 & 0 \\ 2 & 0 & -\sqrt{2} & 0 & 0 \\ 0 & 0 & 0 & \sqrt{6} & 0 \\ 1 & \sqrt{3} & \sqrt{2} & 0 & 0 \\ 0 & 0 & 0 & 0 & -\sqrt{6} \end{pmatrix} \tag{3.14}$$

to operate on M. The block-diagonal matrix $\tilde{M}'$,

$$\tilde{M}' = S_{a_1} M S_{a_1}^{\dagger}, \tag{3.15}$$

is obtained. The second step is to determine the eigenvalues and eigenvectors of $\tilde{M}'$ and to find the final form of $\tilde{M}$. On normalizing and simplifying the eigenvectors, a proper unitary matrix S_{a_2} that diagonalizes $\tilde{M}'$ is obtained. This has the form

$$S_{a_2} = \begin{pmatrix} 1 & 0 & 0 & 0 & 0 \\ 0 & xy & 0 & y & 0 \\ 0 & 0 & xy & 0 & y \\ 0 & 0 & -y & 0 & xy \\ 0 & -y & 0 & xy & 0 \end{pmatrix}, \tag{3.16}$$

where

$$x = \frac{1}{2}\frac{Q_1 Q_2 Q_3 Q_4}{Q_5}, \quad y = \frac{1}{\sqrt{1+x^2}}$$

and where

$$\begin{aligned} Q_1 &= 45\sqrt{5} + 108\sqrt{10}V_2' - 150\sqrt{2}V_3' + 18\sqrt{5}V_2'^2 \\ &\quad + 42\sqrt{5}V_3'^2 - 204V_2'V_3' + W_2, \\ Q_2 &= -45 + 6\sqrt{10}V_3' + 18V_2'^2 + 26V_3'^2 + 12\sqrt{5}V_2'V_3', \\ Q_3 &= -45 + 6\sqrt{10}V_3' + 18V_2'^2 + 26V_3'^2 - 12\sqrt{5}V_2'V_3', \\ Q_4 &= -45 - 6\sqrt{10}V_3' + 18V_2'^2 + 26V_3'^2 + 12\sqrt{5}V_2'V_3', \\ Q_5 &= 45^4 - 6561000V_2'^2 + 3936600V_2'^4 - 1049760V_2'^6 \\ &\quad + 104976V_2'^8 - 10935000V_3'^2 + 9622800V_2'^2V_3'^2 \\ &\quad - 2449440V_3'^2V_2'^4 + 139968V_2'^6V_3'^2 + 10027800V_3'^4 \\ &\quad - 4393440V_3'^4V_2'^2 + 484704V_2'^4V_3'^4 - 3650400V_3'^6 \\ &\quad + 292032V_3'^6V_2'^2 + 456976V_3'^8 \end{aligned} \tag{3.17}$$

with

$$\begin{aligned} W_2 = (&18225 + 48600\sqrt{2}V_2' - 11340\sqrt{10}V_3' + 118260V_2'^2 \\ &+ 55980V_3'^2 - 78840\sqrt{5}V_2'V_3' + 19440\sqrt{2}V_2'^3 \\ &- 13848\sqrt{10}V_3'^3 + 109440\sqrt{2}V_2'V_3'^2 - 50328\sqrt{10}V_3'V_2'^2 \\ &+ 2916V_2'^4 + 11524V_3'^4 - 19632\sqrt{5}V_2'V_3'^3 \\ &- 9072\sqrt{5}V_3'V_2'^3 + 55800V_2'^2V_3'^2)^{1/2}. \end{aligned}$$

Hence, the matrix M has been diagonalized using S_{a_1} (to make M block diagonal) and then, using S_{a_2}, the block-diagonalized form of M is fully diagonalized. Thus the unitary matrix S_a that diagonalizes the M matrix for the D_{3d} well a is given by

$$\begin{aligned} S_a &= S_{a_2} S_{a_1} \\ &= \begin{pmatrix} \frac{1}{\sqrt{6}} & -\frac{1}{\sqrt{2}} & \frac{1}{\sqrt{3}} & 0 & 0 \\ \frac{2(x+1)y}{\sqrt{6}} & \frac{y}{\sqrt{2}} & -\frac{(x-1)y}{\sqrt{3}} & 0 & 0 \\ 0 & 0 & 0 & xy & -y \\ 0 & 0 & 0 & -y & -xy \\ \frac{(-2+x)y}{\sqrt{6}} & \frac{xy}{\sqrt{2}} & \frac{(1+x)y}{\sqrt{3}} & 0 & 0 \end{pmatrix}. \end{aligned} \tag{3.18}$$

This S_a matrix reduces the h_g modes into a_g, $1e_g$ and $2e_g$ modes as it diagonalizes M. It will therefore also diagonalize the matrix Λ of well a as they have the same properties. For the D_{5d} case at infinite coupling, the eigenvalues of Λ and M differed only by a factor of $\mu\omega^2$. Also, we know that if S_a cannot diagonalize Λ, the results obtained in the infinite coupling limit will be inconsistent with those derived using the Öpik and Pryce method. Conversely, if it can diagonalize Λ,

the results should agree. Therefore, for the D_{3d} case, we have sufficient reason to use S_a instead of S_{a_1} in our scale transformation method.

2. Evaluation of local frequencies for D_{3d} wells

Using S_a instead of S_{a_1}, and on substituting the electronic states, their corresponding energies and the position of well a into Eq. (2.16), we obtain the result

$$\begin{aligned}E_{D_{3d}}=E_0+\frac{1}{2}\hbar\omega\left(\frac{\lambda_a}{2}+\frac{1}{2\lambda_a}+\lambda_{1e}+\frac{1}{\lambda_{1e}}+\lambda_{2e}+\frac{1}{\lambda_{2e}}-5\right)\\+\frac{1}{\sqrt{10}}\frac{1-x^2}{1+x^2}V_2'\left(\frac{1}{\lambda_{1e}}-\frac{1}{\lambda_{2e}}\right)+\frac{1}{3\sqrt{10}}\\\times V_3'\left(\frac{1}{\lambda_{1e}}+\frac{1}{\lambda_{2e}}-\frac{2}{\lambda_a}\right)+\frac{2}{5}\sqrt{10}\frac{x}{1+x^2}\\\times V_3'\left(\frac{1}{\lambda_{1e}}-\frac{1}{\lambda_{2e}}\right)-\frac{1}{3\Delta_{3d}}\frac{K_1^2}{\hbar\omega}\\\times\left\{\frac{\phi^2}{\lambda_{1e}}[a_1+\gamma(a_2V_2'+a_3V_3')]^2\right.\\\left.+\frac{\phi^{-2}}{\lambda_{2e}}[a_1'+\gamma(a_2'V_2'+a_3'V_3')]^2\right\},\end{aligned}\tag{3.19}$$

where

$$\gamma=\frac{\sqrt{2}}{\sqrt{15}-4\sqrt{\frac{2}{3}}V_3'},$$

$$\Delta_{3d}=(1+x^2)\left[5+3\sqrt{10}\left(\frac{K_1}{\hbar\omega}\right)^2\gamma(\sqrt{3}+2\gamma V_3')\right],\tag{3.20}$$

$$a_1=-\sqrt{3}(x-\phi^{-2}),\quad a_2=-3(x+\phi^{-2}),\quad a_3=x\phi^{-3}+\phi,$$

$$a_1'=\sqrt{3}(x+\phi^2),\quad a_2'=-3(x-\phi^2),\quad a_3'=x\phi^3-\phi^{-1}.$$

The final expressions for the local frequencies are thus

$$\lambda_a^2=1-\tfrac{4}{15}\sqrt{10}V_3',$$

$$\begin{aligned}\lambda_{ie}^2=1\pm\frac{1}{5}\sqrt{10}V_2'\left\{\frac{1-x^2}{1+x^2}+\frac{2\sqrt{10}}{\Delta_{3d}}\gamma\left(\frac{K_1}{\hbar\omega}\right)^2(1\pm x\phi^{\pm2})f_i\right\}\\+\frac{1}{15}\sqrt{10}V_3'\left\{1\pm\frac{4x}{1+x^2}\mp\frac{2\sqrt{10}}{\Delta_{3d}}\gamma\left(\frac{K_1}{\hbar\omega}\right)^2\right.\\\left.\times(\phi^{\pm3}\pm x\phi^{\mp1})f_i\right\}-\frac{2}{\Delta_{3d}}\phi^{\pm2}\left(\frac{K_1}{\hbar\omega}\right)^2(x\mp\phi^{\mp2})^2,\end{aligned}\tag{3.21}$$

where the upper sign corresponds to $i=1$ and the lower sign to $i=2$, and

$$f_i=\begin{cases}\frac{1}{2}\gamma(a_2V_2'+a_3V_3')+a_1 & \text{for } i=1\\ \frac{1}{2}\gamma(a_2'V_2'+a_3'V_3')+a_1' & \text{for } i=2.\end{cases}\tag{3.22}$$

A plot of the above frequencies for $K_2=-K_3=-0.01K_1$ is shown in Fig. 1 (solid lines). The formula for λ_a is identical to that obtained using the Öpik-Pryce method. The result for λ_{2e} is not identical, but the difference in the magnitude is very small and cannot be observed for this range of couplings. The Öpik-Pryce result for λ_{1e} is also shown in Fig. 1. It can be seen that, as for the D_{5d} results, the primary difference is in correctly predicting that λ_{1e} tends to 1 in weak coupling, while the Öpik-Pryce results tends to 0.

It is easy to see that when $K_1=V_2'=V_3'=0$, the frequencies coincide with the isotropic results (i.e., $\lambda_a=\lambda_{1e}=\lambda_{2e}=1$). When K_1 approaches infinity and $V_2'=V_3'=0$, we get $\lambda_a=\lambda_{2e}=1$ and $\lambda_{1e}=0$. Under this condition, wells do not exist but a two-dimensional trough is formed in the five-dimensional phonon space. This is known to be the correct result for linear coupling. Furthermore, when $V_2'=V_3'=0$ and K_1 is finite, the results are identical to those obtained for the D_{5d} wells in the absence of quadratic coupling. It can also be shown that when V_2' and V_3' are nonzero but finite, the results obtained converge with those obtained using the Öpik-Pryce method as K_1 tends to infinity. The results for λ_a and λ_{2e} converge very quickly, while the convergence of λ_{1e} is much slower; the difference is around 0.01 at $K_1/\hbar\omega=10$. The consistency of the two methods under the condition $K_1\to\infty$ helps to verify that the results obtained using the S matrices as described above are indeed valid.

IV. PHONON OVERLAPS

A. Results for D_{5d} wells

The results obtained so far give the local reduced frequencies of the h_g mode in the wells. It is interesting to investigate how the inclusion of anisotropy alters the overlaps between the well states. In the last section, perturbation theory was applied, keeping terms up to second order in the expression for the energy. Accordingly, the zeroth-order approximate states are not appropriate for these further calculations but revised states taken to second order must be used. For example, the appropriate states for the D_{5d} wells labeled A and B are

$$\begin{aligned}|A\rangle=|A_0;0\rangle+{\sum_{i\alpha}}'a_{i\alpha}^{(1)}|A_i;1_\alpha\rangle-a_0^{(2)}|A_0;0\rangle\\+{\sum_{m\gamma}}'a_{m\gamma}^{(2)}|A_m;1_\gamma\rangle,\\|B\rangle=|B_0;0\rangle+{\sum_{i\alpha}}'b_{i\alpha}^{(1)}|B_i;1_\alpha\rangle-b_0^{(2)}|B_0;0\rangle\\+{\sum_{m\gamma}}'b_{m\gamma}^{(2)}|B_m;1_\gamma\rangle,\end{aligned}\tag{4.1}$$

where

$$a_{i\alpha}^{(1)}=\frac{\langle A_0;0|\tilde{\mathcal{H}}_2|A_i;1_\alpha\rangle}{E_0-E_{i\alpha}},$$

$$a_0^{(2)}=\frac{1}{2}\sum_{i\alpha}{}'(a_{i\alpha}^{(1)})^2, \tag{4.2}$$

$$a_{m\gamma}^{(2)}=\sum_{i\gamma'}{}'\frac{\langle A_m;1_\gamma|\tilde{\mathcal{H}}_2|A_i;1_{\gamma'}\rangle\langle A_i;1_{\gamma'}|\tilde{\mathcal{H}}_2|A_0;0\rangle}{(E_0-E_{m\gamma})(E_0-E_{i\gamma'})}-\frac{\langle A_m;1_\gamma|\tilde{\mathcal{H}}_2|A_0;0\langle A_0;0|\tilde{\mathcal{H}}_2|A_0;0\rangle}{(E_0-E_{m\gamma})^2}.$$

and where the prime on the summation indicates that the electronic ground state is excluded. 1_α, 1_γ, and $1_{\gamma'}$, indicate single phonon excitations of any symmetry. The coefficients $b_{1\alpha}^{(1)}$, $b_0^{(2)}$, and $b_{m\gamma}^{(2)}$ are obtained from Eq. (4.2) by simply replacing A by B.

The phonon overlap between any two different wells of D_{5d} symmetry up to second order is

$$\begin{aligned}S_{AB}&=\frac{\langle A|U_s^{(A)^+}U_d^{(A)^+}U_d^{(B)}U_s^{(B)}|B\rangle}{\langle A_0|B_0\rangle}\\&=S_{00}^{AB}+\frac{1}{\langle A_0|B_0\rangle}\Bigg\{\sum_{i\alpha}{}'\langle A_i|B_0\rangle a_{i\alpha}^{(1)}S_{\alpha 0}^{AB}\\&\quad+\sum_{i\gamma}{}'\langle A_0|B_i\rangle b_{i\gamma}^{(1)}S_{0\gamma}^{AB}-\langle A_0|B_0\rangle(a_0^{(2)}+b_0^{(2)})S_{00}^{AB}\\&\quad+\sum_{ij\alpha\gamma}{}'\langle A_i|B_j\rangle a_{i\alpha}^{(1)}b_{j\gamma}^{(1)}S_{\alpha\gamma}^{AB}+\sum_{m\alpha}{}'\langle A_m|B_0\rangle a_{m\alpha}^{(2)}S_{\alpha 0}^{AB}\\&\quad+\sum_{m\gamma}{}'\langle A_0|B_m\rangle b_{m\gamma}^{(2)}S_{0\gamma}^{AB}\Bigg\},\end{aligned} \tag{4.3}$$

where S_{ij}^{AB} is defined as $\langle 1_i|U_s^{(A)^+}U_d^{(A)^+}U_d^{(B)}U_s^{(B)}|1_j\rangle$. These can be evaluated as

$$S_{00}^{AB}=N_a^2\left(\frac{\pi^n}{\det(W)}\right)^{1/2}\times\exp\left\{-\rho W^{AB}+\frac{1}{4}\sum B_i^{AB}(W^{-1})_{ij}B_j^{AB}\right\},$$

$$S_{\alpha 0}^{AB}=-\left(\frac{2\mu\omega}{\hbar}\right)^{1/2}S_{00}^{AB}[(e^{2\Lambda})^A(\tfrac{1}{2}W^{-1}B^{AB}-Q^A)]_\alpha,$$

$$S_{0\gamma}^{AB}=-\left(\frac{2\mu\omega}{\hbar}\right)^{1/2}S_{00}^{AB}[(e^{2\Lambda})^B(\tfrac{1}{2}W^{-1}B^{AB}-Q^B)]_\gamma,$$

$$\begin{aligned}S_{\alpha\gamma}^{AB}=\frac{2\mu\omega}{\hbar}S_{00}^{AB}\{&[\tfrac{1}{2}(e^{2\Lambda})^AW^{-1}(e^{2\Lambda})^B]_{\alpha\gamma}\\&+\tfrac{1}{4}[(e^{2\Lambda})^AW^{-1}B^{AB}]_\alpha[(e^{2\Lambda})^BW^{-1}B^{AB}]_\gamma\\&-\tfrac{1}{2}[(e^{2\Lambda})^AQ^A]_\alpha[(e^{2\Lambda})^BW^{-1}B^{AB}]_\gamma\\&-\tfrac{1}{2}[(e^{2\Lambda})^AW^{-1}B^{AB}]_\alpha[(e^{2\Lambda})^BQ^B]_\gamma\\&+[(e^{2\Lambda})^AQ^A]_\alpha[(e^{2\Lambda})^BQ^B]_\gamma\},\end{aligned} \tag{4.4}$$

where

$$N_a=\frac{(\mu\omega/\pi\hbar)^{n/4}}{\sqrt{\det(e^{-2\Lambda})}},\quad W^{AB}=(Q^A)^+W^AQ^A+(Q^B)^+W^BQ^B,$$

$$W^A=S_A^\dagger e^{4\Lambda}S_A,\quad W^B=S_B^\dagger e^{4\Lambda}S_B,$$

$$(Q^{A,B})^\dagger=\frac{V_1}{\mu\omega^2}[a_\theta^{(A,B)},a_\varepsilon^{(A,B)},a_4^{(A,B)},a_5^{(A,B)},a_6^{(A,B)}], \tag{4.5}$$

$$B^{AB}=2\rho(W^AQ^A+W^BQ^B),\quad W=\rho(W^A+W^B),$$

$$(e^{m\Lambda})^\Gamma=S_\Gamma^+[\lambda_i^{m/4}]S_\Gamma,\quad \rho=\frac{\mu\omega}{2\hbar},$$

with Γ labeling the wells, m are natural numbers, and n denotes the number of phonon modes ($n=5$ for the h_g modes). Thus

$$S_{00}^{AB}=\frac{5\sqrt{5}\sqrt{\nu_1\lambda_{e1}\lambda_{e2}}\,\exp\{-10(K_1\beta/\hbar\omega)^2\nu_1\}}{\sqrt{(3\lambda_a+\lambda_{e1}+\lambda_{e2})(\lambda_{e1}+\phi^2\lambda_{e2})(\lambda_{e1}+\phi^{-2}\lambda_{e2})}}, \tag{4.6}$$

where

$$\nu_1=\frac{\lambda_a\lambda_{e1}\lambda_{e2}}{3\lambda_{e1}\lambda_{e2}+\lambda_a\lambda_{e1}+\lambda_a\lambda_{e2}}. \tag{4.7}$$

A calculation of the last two terms in Eq. (4.3) shows that the two contributions cancel each other out. The full analytical expression for the overlap S_{AB} is very complicated so it will not be given here. However, all contributions will be included in the subsequent calculations. The result for the overlap neglecting the second-order contributions is simpler to write down and can be expressed in the form

$$S_{AB}=S_{00}^{AB}\left[1-\frac{2}{5}\frac{f_{AB}}{\lambda_{e1}}\left(\frac{K_1}{\hbar\omega}\right)^2(20\beta\nu_1+f_{AB})\right], \tag{4.8}$$

where

$$f_{AB}=-\frac{\sqrt{3}-\beta(V_2'-\sqrt{5}V_3')}{\sqrt{2}\Delta_{5d}}. \tag{4.9}$$

It is interesting to compare the magnitude of the overlap calculated here with the zeroth-order overlap obtained using the original shift transformation only. It is also interesting to calculate the overlap that is obtained using the shift transformation alone but including perturbation corrections. This enables us to estimate the relative corrections from the scale transformation and due to performing the calculations to higher order. Figure 2 shows a plot of the overlap as a function of the linear coupling constant for $K_2=-K_3=0.01K_1$. These values for the quadratic coupling constants ensure that the D_{5d} wells remain minima. It can be seen that both effects are of similar orders of magnitude. The scale transformation is particularly important at strong couplings; this is to be expected as it is in this region that the shape of the well and hence the anisotropic effects are the largest. Conversely, the perturbation effects are largest at weak couplings. This is again to be expected as the states used were derived using a

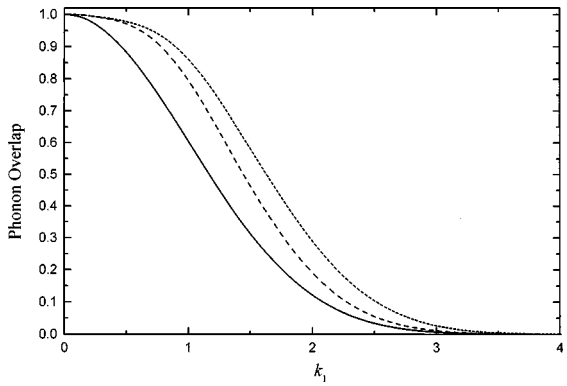

FIG. 2. A plot of the overlap S_{AB} for D_{5d} wells obtained including the shift transformation only (solid line), the shift transformation and perturbation corrections (long-dashed line), and the shift and scale transformations plus perturbation corrections (short-dashed line). The results are plotted for $K_2=-K_3=0.01K_1$.

strong-coupling model. It is only because the combined states reproduce the correct weak coupling limit that the results in this region are valid at all. It is not surprising that perturbation effects are relatively large here.

B. Results for D_{3d} wells

For D_{3d} wells, the calculation can be performed in a similar way using the proper S matrices found using group theory in conjunction with the Öpik and Pryce method. As in the equivalent zeroth-order calculation,[6] there are found to be two different overlaps between wells for this system. Although the calculations have been performed to second order, the results are again very complex so the analytical forms are only given here to first order. Thus,

$$S_{ab}=f_0(x,\lambda)[1-f_1(x,\lambda)-f_2(x,\lambda)]\exp\left\{-6\gamma^2\nu_2^2\left(\frac{K_1}{\hbar\omega}\right)^2\right\}, \tag{4.10}$$

$$S_{ac}=f_0'(x,\lambda)[1-f_1'(x,\lambda)-f_2(x,\lambda)]\times\exp\left\{-24\gamma^2\nu_2'^2\left(\frac{K_1}{\hbar\omega}\right)^2\right\},$$

where

$$\nu_2=\left[\frac{(x^2+1)\lambda_a\lambda_{1e}\lambda_{2e}}{\lambda_{1e}\lambda_{2e}(x^2+1)+\lambda_{2e}\lambda_a(x-1)^2+\lambda_a\lambda_{1e}(x+1)^2}\right]^{1/2},$$

$$\nu_2'=\left[\frac{(x^2+1)\lambda_a\lambda_{1e}\lambda_{2e}}{\lambda_a\lambda_{2e}(x^2+x+1)+\lambda_{1e}\lambda_a(x^2-x+1)+4\lambda_{1e}\lambda_{2e}(x^2+1)}\right]^{1/2},$$

$$f_0(x,\lambda)=\frac{3(x^2+1)\nu_2\nu_3}{\sqrt{(\lambda_{2e}+\lambda_{1e}x^2)(\lambda_{1e}+\lambda_{2e}x^2)}}, \tag{4.11}$$

$$f_0'(x,\lambda)=\frac{12(x^2+1)\nu_2'\nu_3'}{\sqrt{[\lambda_{2e}(x^2+x+1)+\lambda_{1e}(x^2-x+1)][\lambda_{1e}(x^2+x+1)+\lambda_{2e}(x^2-x+1)]}},$$

$$f_1(x,\lambda)=\frac{4\sqrt{2}\nu_2^2\gamma}{\lambda_{1e}\lambda_{2e}\Delta_{3d}}\left(\frac{K_1}{\hbar\omega}\right)^2\{(x-1)\lambda_{2e}\phi[a_1+\gamma(a_2V_2'+a_3V_3')]-(x+1)\lambda_{1e}\phi^{-1}[a_1'+\gamma(a_2'V_2'+a_3'V_3')]\},$$

$$f_1'(x,\lambda)=\frac{\sqrt{10}\nu_2'^2\gamma}{\lambda_{1e}\lambda_{2e}\Delta_{3d}}\left(\frac{K_1}{\hbar\omega}\right)^2\{(x\phi^4+2\sqrt{5}+1)\lambda_{2e}[a_1+\gamma(a_2V_2'+a_3V_3')]-(x\phi^{-4}+2\sqrt{5}-1)\lambda_{1e}[a_1'+\gamma(a_2'V_2'+a_3'V_3')]\},$$

$$f_2(x,\lambda)=\frac{5}{3}\frac{1+x^2}{\lambda_{1e}\lambda_{2e}\Delta_{3d}^2}\left(\frac{K_1}{\hbar\omega}\right)^2\{\lambda_{2e}\phi^2[a_1+\gamma(a_2V_2'+a_3V_3')]^2-\lambda_{1e}\phi^{-2}[a_1'+\gamma(a_2'V_2'+a_3'V_3')]^2\},$$

and where

$$\nu_3=\left[\frac{(x^2+1)\lambda_{1e}\lambda_{2e}}{\lambda_a(x^2+1)+\lambda_{1e}(x-1)^2+\lambda_{2e}(x+1)^2}\right]^{1/2}, \tag{4.12}$$

$$\nu_3'=\left[\frac{(x^2+1)\lambda_{1e}\lambda_{2e}}{4\lambda_a(x^2+1)+\lambda_{1e}(x^2+x+1)+\lambda_{2e}(x^2-x+1)}\right]^{1/2}$$

Figure 3 shows a plot of the overlaps S_{ab} and S_{ac} as a function of the linear coupling strength using the full results correct to second order. Quadratic coupling parameters have been chosen to ensure the D_{3d} wells are minima. As for the D_{5d} wells (Fig. 2), it can be seen that the additional corrections due to taking the calculations to second-order and to including the scale transformation are of similar orders of magnitude.

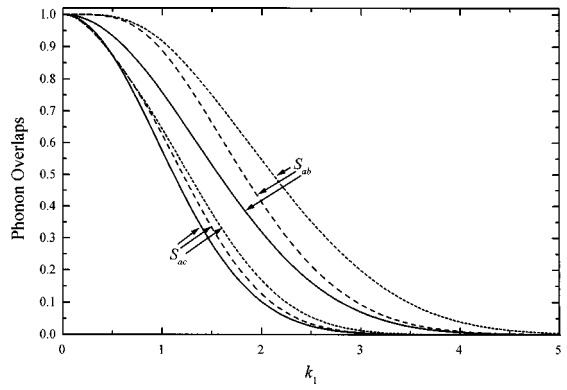

FIG. 3. A plot of the overlaps for D_{3d} wells obtained including the shift transformation only (solid lines), the shift transformation and perturbation corrections (long-dashed lines), and the shift and scale transformations plus perturbation corrections (short-dashed lines). The results are plotted for $K_2=-K_3=-0.01K_1$. The upper curves are for S_{ab} and the lower curves for S_{ac}.

V. TUNNELING SPLITTINGS

The states associated with the wells are only good eigenstates of the system as a whole in infinite coupling. For finite couplings, the system will tunnel between equivalent wells. It is therefore necessary to construct symmetry-adapted combinations of the well states. This has been performed using projection operators[19] for the zeroth-order states. The forms of the symmetry-adapted states, their energies, and the tunnelling splittings between them will all be affected by inclusion of the scale transformation operator.

For both types of wells, the ground state is a triplet of T_{1u} symmetry, derived from an original orbital state of T_{1u} symmetry. For D_{5d} wells, there is a tunneling state of T_{2u} symmetry, and for the D_{3d} wells, there are tunneling states of T_{2u} and G_u symmetries. Explicit expressions for these states in terms of the zeroth-order states associated with the wells were given in Ref. 6. (We note that in this reference, the labels $|G^D_{ux}\rangle$ and $|G^D_{uz}\rangle$ were inadvertently inverted. Also, the sign of $|G^D_{ua}\rangle$ should be changed in order to make the phase factor of the components of the G state consistent.)

Figure 4 shows a plot of the zeroth-order tunneling splitting between the T_{1u} ground state and the T_{2u} excited state as a function of the linear coupling strength for the D_{5d} wells. The graph gives the results of (i) Ref. 6 using the shift transformation only, (ii) Ref. 12, in which a simplified scale transformation procedure was used to incorporate the Öpik-Pryce frequencies into the problem, and (iii) the current calculation, in which the scale transformation is included properly. Figure 5 shows a similar plot for the T_{2u} and G_u tunneling states for D_{3d} wells. It can be seen that methods (ii) and (iii) coincide in strong coupling, which is to be expected as the current results coincide with the Öpik-Pryce results in this regime. However, methods (i) and (iii) coincide in the weak coupling limit. This is because both the current method and the original method of a shift transformation alone predict the correct frequencies in this limit, whereas the Öpik-Pryce method does not. Hence we can see that the current method has incorporated the most important features of both strong and weak coupling. In particular, it removes the problem of the result including the scale transformation to zeroth order[12] tending to infinity in weak coupling, which is obviously physically incorrect.

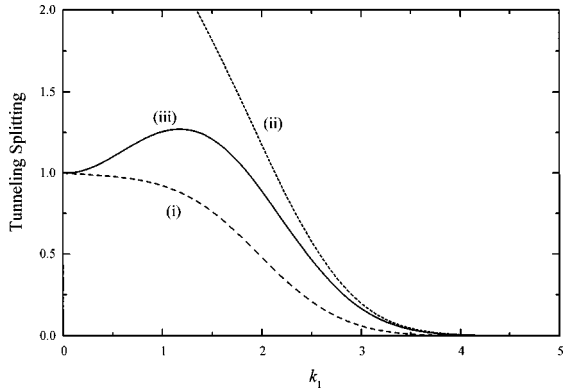

FIG. 4. A plot of the zeroth-order tunneling splitting for D_{5d} wells for $K_2=-K_3=0.01K_1$ obtained using (i) the shift transformation only (long-dashed line), (ii) the simplified scale transformation to incorporate the Öpik-Pryce frequencies (short-dashed line), and (iii) the full scale transformation procedure (solid line).

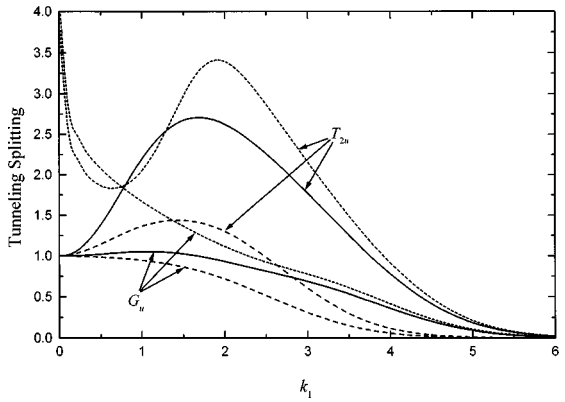

FIG. 5. A plot of the zeroth-order tunneling splittings for D_{3d} wells for $K_2=-K_3=-0.01K_1$ obtained using (i) the shift transformation only (long-dashed line), (ii) the simplified scale transformation to incorporate the Öpik-Pryce frequencies (short-dashed line), and (iii) the full scale transformation procedure (solid line). Results are shown for both the T_{2u} and G_u tunneling levels.

As expressions for the phonon overlap have been obtained correct to second order, it would obviously be desirable to obtain an expression for the inversion splitting correct to second order also. However, the first- and second-order corrections to the well states include one-phonon excitations. If these revised states are substituted into the expressions for the symmetry-adapted states obtained previously, it is found that the correct symmetries are broken. A full calculation of new symmetry-adapted states and their energies would therefore be required, which becomes prohibitively complicated. They would be particularly involved for this system as it is necessary to include two quadratic couplings in order to ensure the existence of wells. However, as an approximation, it is possible to calculate revised energies neglecting the symmetry-breaking first-order contributions to the otherwise symmetrized states, both with and without the scale transformation. It is found that the second-order results converge with the corresponding zeroth-order results in strong coupling, with the former being lower than the latter for all

coupling strengths. However, in weak coupling, the second-order results both tend to a limit considerably less than the expected $\hbar\omega$. The limits with the scale transformation are all correct in zeroth order, and the limits attained in second order are the same both with and without the scale transformation. We can therefore conclude that the effect arises due to the perturbation corrections rather than the scale transformation itself.

VI. CONCLUSION

The main aim of this paper has been to incorporate the effects of anisotropy into an analytical model for the quadratic $T_{1u}\otimes h_g$ JT system in a manner that is not restricted to the strong coupling limit. Although anisotropy must always be present in real systems, this has not been attempted previously. Expressions for the overlaps between different wells have been obtained for both the D_{5d} and D_{3d} cases. These results differ from results obtained previously in two respects. Firstly, a scale transformation method has been developed that incorporates anisotropic effects into the problem without restricting the calculations to the strong coupling limit. Secondly, the calculations have been carried out to second order in perturbation theory. Plots of the overlaps show that both factors result in corrections to the simple isotropic result of similar orders of magnitude. In weak coupling, the scale transformation corrections are smallest, because the anisotropic variations in the frequencies are smallest in this regime. Conversely, in strong coupling the changes introduced by the scale transformation dominate. Therefore, it is indeed necessary to incorporate both additional features in our model.

The energies of the ground and first excited states for the $T_{1u}\otimes h_g$ JT system have previously been calculated for both D_{3d} and D_{5d} wells to zeroth order by incorporating frequencies obtained using the Öpik-Pryce method for strong coupling. However, these results predict tunnelling splittings that tend to infinity in weak coupling, which is obviously physically incorrect. Our results obtained using the scale transformation procedure have been shown to exhibit the same behavior in strong coupling as obtained using the Öpik-Pryce method. However, they also exhibit the correct limiting behavior in weak coupling.

Unfortunately, calculations of the energies correct to second order are prohibitively complicated because the correct well states to this order in perturbation theory include one-phonon excitations, which means that new symmetry-adapted states must be derived. The construction of symmetry-adapted states and subsequent calculations using them are much more complicated for icosahedral systems than for cubic systems. In cubic symmetry, a set of well states can be written down such that when one state is acted upon by any of the group operations, it is transformed into one of the other states in the set (or into itself). In icosahedral symmetry, this is not possible because the transformation of a set of phonon states from one well to another always creates a new set of phonon states that is a linear combination of the original phonon states. This means that the results are inevitably immensely complicated. Currently, work is under way in which different combinations of θ, ε, 4, 5, and 6 are used to define the excited states in each well. However, this is a far from trivial task and cannot be attempted in this paper. Also, until energy expressions correct to second-order have been obtained, the calculation of further properties such as first-order reduction factors can only be undertaken in a simplified manner.

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