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Analysis of the $T_{1u}\otimes h_g$ Jahn-Teller system as a model for C_{60} molecules

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The $T_{1u}\otimes h_g$ Jahn-Teller system is studied analytically on an icosahedral cluster model. This system is a model for the effects of vibronic coupling in the C_{60} molecule. Vibronic coupling is very important in this system because both the electronic and vibrational states are of high symmetry. The method employed is to apply a unitary transformation to the Hamiltonian for the system in order to obtain expressions for the states associated with minima in the potential-energy surface. Quadratic coupling terms are included in the Hamiltonian in order to obtain distinct minima located at either pentagonal (D_{5h}) or trigonal (D_{3h}) positions in Q space. These states are good eigenstates of the system as a whole in very strong coupling. For finite couplings, projection operator techniques are then used to obtain explicit expressions for the vibronic ground and inversion states from these basis states for both the pentagonal and trigonal cases. Expressions for the corresponding energies are then derived as a function of the coupling constants. These results are necessary in order to be able to calculate further properties of the system, such as Jahn-Teller reduction factors, which are in turn necessary to explain experimental data on these systems.

I. INTRODUCTION

The discovery of the isolated C_{60} molecule[1] and subsequently the solid form[2] of C_{60} followed by the realization of its superconducting properties[3] led to an explosion of work by experimental and theoretical physicists and chemists in this area. A recent description of the most significant work on these fullerenes can be found in the comprehensive review by Gelfand[4] and in the more general article by Ramirez,[5] for example. In order to understand the superconducting properties of the solid material, much work has appeared about the significance of the electron-phonon interaction (vibronic coupling) within C_{60}.[6–11] Within the last year, interest in the role of the electron-phonon coupling and the resultant Jahn-Teller (JT) effect it induces in C_{60} molecules has continued. Much of this stems from the original work of Ceulemans[12] and subsequent publications.[13–15] The JT problem has also been studied in further detail but from different points of view by a number of other authors.[16–22] However, despite all this work, no papers have been published which give explicit expressions for the vibronic states of such systems and their resultant energies.

Prior to the discovery of C_{60}, virtually all JT work had been undertaken in either octahedral or tetrahedral symmetry, with the exception of Khoplin, Polinger, and Bersuker,[23] who investigated JT effects in icosahedral symmetry. Following the work of Chancey[24] and Cullerne and O'Brien,[25] it became clear that a range of JT problems which had not been considered previously is present in such system because of the existence of four- and five-dimensional representations for both the orbital and phonon states. In this paper, we will investigate the particular case of the $T_{1u}\otimes h_g$ JT problem. This is of considerable interest because when an additional electron is added to the C_{60} molecule, it occupies an excited T_{1u} orbital state.[4]

Understanding the molecular structure of the fullerenes, including within it the vibronic coupling, has other important applications, particularly in relation to the formation of solid C_{60} and hence of superconductivity. Here we mention the very recent work of You, Xie, and Tang[18] on the Raman fine structure involving the intramolecular vibrational modes,[26] the optical absorption,[27,28] vibrational infrared spectra,[29] giant vibrational resonances in A_6C_{60} compounds,[30] and charged phonon absorption.[31] There is also considerable interest in the way C_{60} molecules attach themselves to surfaces. The application of the scanning tunneling microscopy (STM) technique to control the movement of such molecules across silicon surfaces has obvious device applications.[32] Interactions with Ag and In surfaces[33] and with Au surfaces[34] have also been reported.

The C_{60} molecule has a truncated icosahedral structure of I_h symmetry. Many calculations of the undoped molecule have been undertaken to determine the molecular energy spectrum.[4,5] These calculations clearly show that all molecular levels up to and including the molecular orbital of h_u symmetry are filled, and that the unfilled orbital of lowest energy is of t_{1u} symmetry. On doping the molecule with an impurity such as potassium, the additional electron occupies the t_{1u} orbital. In a similar way, when the fullerene solid is formed or when one molecule interacts with another solid surface, for example, the t_{1u} orbital is usually directly involved and is partially or totally filled with the extra electrons. In such cases, it is necessary to take into account the coupling between the electron or electrons in the t_{1u} orbit, which is spread over the entire surface of the molecule, and the vibrations of the molecular cage itself. From group theory, coupling to two A_g and eight H_g modes is expected.

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The above is obviously a very complex problem even allowing for the redundancy of the two A_g modes. However, a model in which a single T_{1u} orbit interacts with a single h_g mode of vibration of a simple icosahedron will be a good starting point for modeling such systems, and can adequately account for virtually all the relevant vibronic properties of the real C_{60} molecule. The vibronic coupling is described therefore as a $T_{1u}\otimes h_g$ JT problem. (For a general review of vibronic interactions, see the book by Bersuker and Polinger.[35])

For many years, the authors have been involved in modeling dynamic JT effects in strongly coupled systems of tetrahedral symmetry (for application to magnetic-ion impurities in III-V semiconductors). They developed an analytical method for solving such problems based on an initial unitary transformation followed by an energy minimization procedure. They then obtained symmetry-adapted vibronic states for the system, and their corresponding energies, using projection operator techniques.[36–40] The work of Cullerne and O'Brien[25] indicated that this transformation method had attractive features which could be applied to the C_{60} molecule. Also, the theoretical method described by Wang and coworkers[20,21] for the $C_{60}{}^{-}$ molecule had some features in common with our transformation method, particularly as it highlights the dynamic properties of the resultant states. However, the latter calculations were restricted to the involvement of minima in Q space of D_{5d} symmetry only (as are most other discussions), and some of the important details, such as the positions of the minima in Q space, were not given. The primary object of this paper is to apply our transformation method to the $T_{1u}\otimes h_g$ JT problem and obtain explicit expressions for the states. Minima of both D_{3d} and D_{5d} symmetries will be considered.

The ultimate aim of this work is to set up a model from which fundamental explanations of some of the experimental data obtained by others and summarized above can be explained. In particular, we mention the calculation of the electron-phonon coupling constants[22] from an analysis of photoemission spectra of $C_{60}{}^{-}$ and the lowering of the total energy for $C_{60}{}^{n-}$ due to electron-phonon coupling.[41]

II. THE HAMILTONIAN AND TRANSFORMATION METHOD

A. Definitions

In principle, the formulation of the $T\otimes h$ JT problem is well known to be the same as that for the cubic $T\otimes(e+t_2)$ JT problem in the special case when the couplings to the e and t_2 modes are the same. However, following the work of Fowler and Ceulemans,[42] it is more appropriate for I_h symmetry to define the equivalent of the cubic e modes $\theta_z=\theta$ and $\epsilon_z=\epsilon$ in a different manner to that for the cubic systems, such that they are the linear combinations

$$\begin{aligned}\epsilon&=\sqrt{\tfrac{3}{8}}d_{x^2-y^2}-\sqrt{\tfrac{5}{8}}d_{3z^2-r^2}\,,\\ \theta&=\sqrt{\tfrac{3}{8}}d_{3z^2-r^2}+\sqrt{\tfrac{5}{8}}d_{x^2-y^2}\end{aligned}\tag{2.1}$$

of the hydrogenlike $d_{(3z^2-r^2)}$ and $d_{(x^2-y^2)}$ functions. It will also be useful to work with combinations of them corresponding to functions associated with the x and y axes:

$$\begin{aligned}\theta_x&=-\tfrac{1}{2}\theta+\frac{\sqrt{3}}{2}\epsilon\,,\quad \theta_y=-\tfrac{1}{2}\theta-\frac{\sqrt{3}}{2}\epsilon\,,\\ \epsilon_x&=-\frac{\sqrt{3}}{2}\theta-\tfrac{1}{2}\epsilon\,,\quad \epsilon_y=\frac{\sqrt{3}}{2}\theta-\tfrac{1}{2}\epsilon\,.\end{aligned}\tag{2.2}$$

In the following, these labels, together with 4, 5, and 6, which denote the equivalent of the t_2-type modes of cubic symmetry transforming like yz, zx, and xy, respectively, will be used to denote the five components transforming like H. In particular, they will be attached to the displacements Q and their conjugate momenta P.

Using the tables in Ref. 42, it can be seen that the linear interaction Hamiltonian for the $T\otimes h$ system can be written as a matrix acting on the set of electronic basis states (x,y,z) in the form

$$\mathcal{H}_1=V_1\begin{bmatrix}\frac{1}{2\sqrt{5}}[\sqrt{3}\phi^{-1}Q_\theta+\phi^2Q_\epsilon] & \sqrt{\tfrac{3}{10}}Q_6 & \sqrt{\tfrac{3}{10}}Q_5\\ \sqrt{\tfrac{3}{10}}Q_6 & -\frac{1}{2\sqrt{5}}[\sqrt{3}\phi Q_\theta+\phi^{-2}Q_\epsilon] & \sqrt{\tfrac{3}{10}}Q_4\\ \sqrt{\tfrac{3}{10}}Q_5 & \sqrt{\tfrac{3}{10}}Q_4 & \tfrac{1}{2}[\sqrt{\tfrac{3}{5}}Q_\theta-Q_\epsilon]\end{bmatrix},\tag{2.3}$$

where $\phi=\frac{1}{2}(1+\sqrt{5})$ is the golden mean, and V_1 is the linear vibronic coupling constant.

Analysis of the potential-energy surface using numerical means[13,25] shows that when only linear coupling and harmonic terms are included, there is a continuous spherical equal-energy surface. (This statement is also true if more than one h mode is included in the analysis.) However, when small anharmonic and quadratic coupling terms are added,[13] the minimum-energy surface is warped to give local minima.

In this paper, we will consider the effects of the two types of quadratic couplings which are possible in these systems. Again, using the tables in Ref. 42, the Hamiltonians for the two forms of quadratic coupling with coupling constants V_2 and V_3 are written as

$$\mathcal{H}_2=V_2\begin{bmatrix} \tfrac{1}{2}\phi^{-1}\sqrt{\tfrac{3}{5}}A_1+\dfrac{\phi^2}{2\sqrt{5}}A_2 & -\sqrt{\tfrac{3}{5}}Q_\epsilon Q_6 & \tfrac{1}{2}\sqrt{\tfrac{3}{5}}(-\sqrt{3}Q_\theta+Q_\epsilon)Q_5 \\ -\sqrt{\tfrac{3}{5}}Q_\epsilon Q_6 & -\tfrac{1}{2}\phi\sqrt{\tfrac{3}{5}}A_1-\dfrac{1}{2}\dfrac{\phi^{-2}}{\sqrt{5}}A_2 & \tfrac{1}{2}\sqrt{\tfrac{3}{5}}(\sqrt{3}Q_\theta+Q_\epsilon)Q_4 \\ \tfrac{1}{2}\sqrt{\tfrac{3}{5}}(-\sqrt{3}Q_\theta+Q_\epsilon)Q_5 & \tfrac{1}{2}\sqrt{\tfrac{3}{5}}(\sqrt{3}Q_\theta+Q_\epsilon)Q_4 & \tfrac{1}{2}\sqrt{\tfrac{3}{5}}A_1-\tfrac{1}{2}A_2 \end{bmatrix} \tag{2.4}$$

and

$$\mathcal{H}_3=V_3\begin{bmatrix} \tfrac{1}{2}\phi^{-1}\sqrt{\tfrac{3}{5}}B_1+\dfrac{\phi^2}{2\sqrt{5}}B_2 & \sqrt{\tfrac{1}{5}}(Q_\theta Q_6-\sqrt{2}Q_4Q_5) & C_1 \\ \sqrt{\tfrac{1}{5}}(Q_\theta Q_6-\sqrt{2}Q_4Q_5) & -\tfrac{1}{2}\phi\sqrt{\tfrac{3}{5}}B_1-\dfrac{1}{2}\dfrac{\phi^{-2}}{\sqrt{5}}B_2 & D_1 \\ C_1 & D_1 & \tfrac{1}{2}\sqrt{\tfrac{3}{5}}B_1-\tfrac{1}{2}B_2 \end{bmatrix}, \tag{2.5}$$

where

$$\begin{aligned} A_1&=\sqrt{\tfrac{1}{2}}Q_\theta Q_\epsilon+\sqrt{\tfrac{3}{8}}(Q_4^2-Q_5^2)\ ,\\ A_2&=\sqrt{\tfrac{1}{8}}(Q_\theta^2-Q_\epsilon^2+Q_4^2+Q_5^2-2Q_6^2)\ ,\\ B_1&=\sqrt{\tfrac{3}{8}}(Q_\theta^2-Q_\epsilon^2)-\sqrt{\tfrac{1}{24}}(Q_4^2+Q_5^2-2Q_6^2)\ ,\\ B_2&=-\sqrt{\tfrac{3}{2}}Q_\theta Q_\epsilon+\sqrt{\tfrac{1}{8}}(Q_4^2-Q_5^2)\ ,\\ C_1&=-\tfrac{1}{2}\sqrt{\tfrac{1}{5}}[(Q_\theta+\sqrt{3}Q_\epsilon)Q_5+2\sqrt{2}Q_4Q_6]\ ,\\ D_1&=-\tfrac{1}{2}\sqrt{\tfrac{1}{5}}[(Q_\theta-\sqrt{3}Q_\epsilon)Q_4+2\sqrt{2}Q_5Q_6]\ . \end{aligned} \tag{2.6}$$

As usual, the Hamiltonian describing the vibrations is

$$\mathcal{H}_{\text{vib}}=\tfrac{1}{2}\sum_i\left[\frac{P_i^2}{\mu}+\mu\omega^2Q_i^2\right], \tag{2.7}$$

where μ is the mass of each of the nuclei at the corners of the icosahedron with the sum taken over all modes (θ, ϵ, 4, 5, and 6). The total Hamiltonian for the system is thus

$$\mathcal{H}=\mathcal{H}_1+\mathcal{H}_2+\mathcal{H}_3+\mathcal{H}_{\text{vib}}\ .$$

B. The transformation and energy minimization

According to the transformation method,[36] a unitary transformation of the form

$$U=\exp\left[i\sum_j\alpha_jP_j\right] \tag{2.8}$$

can be applied to $\mathcal{H}$. This transformation has the effect of displacing each of the coordinates Q_j to the points (Q_j-$\alpha_j\hbar$). This in turn leads to a transformed Hamiltonian $\tilde{\mathcal{H}}=U^{-1}\mathcal{H}U$ which can be split into a contribution $\tilde{\mathcal{H}}_1$ which does not contain any P_j's or Q_j's, and hence does not contain any phonon operators, and a second part $\tilde{\mathcal{H}}_2$ which contains all remaining terms. It follows that $\tilde{\mathcal{H}}_1$ is a good Hamiltonian for determining the ground states of the system. Further work[38] shows that the Hamiltonian is also a good basis for determining excited states.

It is convenient to eliminate some of the constants in $\mathcal{H}$ by defining

$$\begin{aligned} a_i&=\frac{\mu\hbar\omega^2}{V_1}\alpha_i\ ,\quad E'=\frac{\mu\omega^2}{V_1^2}E\ ,\\ V_2'&=\frac{V_2}{\mu\omega^2}\ ,\quad V_3'=\frac{V_3}{\mu\omega^2}\ . \end{aligned} \tag{2.9}$$

$\tilde{\mathcal{H}}_1$ can then be obtained from $\mathcal{H}$ by replacing the Q_j by $-a_j$, V_2 by V_2', and V_3 by V_3', omitting V_1 from $\mathcal{H}_1$ and writing $\mathcal{H}_{\text{vib}}$ as $\frac{1}{2}\sum a_i^2$. The resulting Hamiltonian $\tilde{\mathcal{H}}_1$ will be written as a 3×3 matrix with elements a_{ij}. Subsequent results will be expressed in terms of the parameters

$$K_1=-\frac{\sqrt{\hbar}V_1}{\sqrt{2\mu\omega}}\ ,\quad K_i=\frac{V_i\hbar}{2\mu\omega}\quad(i=2,3)\ . \tag{2.10}$$

By diagonalizing $\tilde{\mathcal{H}}_1$, an expression for E' as a function of a_i can thus be found in the form

$$E'=\frac{I}{3}+\lambda\ , \tag{2.11}$$

where λ are the roots of the cubic equation:

$$\lambda^3+3p\lambda+2q=0\ , \tag{2.12}$$

with

$$3p=J-\frac{I^2}{3}\ ,\quad 2q=\frac{2I^3}{27}-\frac{IJ}{3}+K\ , \tag{2.13}$$

where

$$\begin{aligned} I&=-(a_{11}+a_{22}+a_{33})\ ,\\ J&=(a_{11}a_{22}+a_{11}a_{33}+a_{22}a_{33})-(a_{12}^2+a_{13}^2+a_{23}^2),\\ K&=-a_{11}a_{22}a_{33}-2a_{12}a_{13}a_{23}+a_{11}a_{23}^2\\ &\quad+a_{22}a_{13}^2+a_{33}a_{12}^2\ . \end{aligned} \tag{2.14}$$

The solutions are $\lambda=u+v$, where

$$\begin{aligned} u^3&=-q+\sqrt{q^2+p^3}\ ,\\ v^3&=-q-\sqrt{q^2+p^3}\ . \end{aligned} \tag{2.15}$$

The five equations which define the minima in E' can then be written down by differentiating this expression with respect to a_i. After much algebra, we find that these equations can be written in the form

$$\begin{aligned}
&-12\sqrt{10}a_\theta-\sqrt{6}y+V_2'[\sqrt{3}ya_\epsilon-za_\theta+3\sqrt{2}(\mu_3a_4-\mu_2a_5)]+V_3'[3ya_\theta+\sqrt{3}za_\epsilon+\sqrt{2}(2\mu_1a_6-\mu_2a_5-\mu_3a_4)]=0\ ,\\
&-12\sqrt{10}a_\epsilon+\sqrt{2}z+V_2'[\sqrt{3}ya_\theta+za_\epsilon+\sqrt{6}(\mu_3a_4+\mu_2a_5-2\mu_1a_6)]+V_3'[-3ya_\epsilon+\sqrt{3}za_\theta+\sqrt{6}(\mu_3a_4-\mu_2a_5)]=0\ ,\\
&-12\sqrt{10}a_4-2\sqrt{3}\mu_3+V_2'[a_4(3y-z)-2\sqrt{6}\mu_3a_{\epsilon x}]+V_3'[-a_4(y+z)+2\sqrt{2}\mu_3a_{\theta x}-4(\mu_1a_5+\mu_2a_6)]=0\ ,\\
&-12\sqrt{10}a_5-2\sqrt{3}\mu_2-V_2'[a_5(3y+z)+2\sqrt{6}\mu_2a_{\epsilon y}]+V_3'[a_5(z-y)+2\sqrt{2}\mu_3a_{\theta y}-4(\mu_1a_4+\mu_3a_6)]=0\ ,\\
&-12\sqrt{10}a_6-2\sqrt{3}\mu_1+V_2'[2a_6z-2\sqrt{6}\mu_1a_\epsilon]+V_3[2a_6y+2\sqrt{2}\mu_1a_\theta-4(\mu_2a_4+\mu_3a_5)]=0\ ,
\end{aligned}\tag{2.16}$$

where the combinations $a_{\theta x}$, etc. are as given in (2.2) and

$$\begin{aligned}
y&=[-\phi^{-1}a_{11}+\phi a_{22}-a_{33}]\delta\\
&\quad+[\phi^{-1}(a_{23}^2-a_{22}a_{33})-\phi(a_{13}^2-a_{11}a_{33})\\
&\qquad+(a_{12}^2-a_{11}a_{22})]\alpha\ ,\\
z&=[\phi^2a_{11}-\phi^{-2}a_{22}-\sqrt{5}a_{33}]\delta\\
&\quad+[-\phi^2(a_{23}^2-a_{22}a_{33})+\phi^{-2}(a_{13}^2-a_{11}a_{33})\\
&\qquad+\sqrt{5}(a_{12}^2-a_{11}a_{22})]\alpha\ ,\\
\mu_1&=-2a_{12}\delta+2(a_{12}a_{33}-a_{13}a_{23})\alpha\ ,\\
\mu_2&=-2a_{13}\delta+2(a_{13}a_{22}-a_{12}a_{23})\alpha\ ,\\
\mu_3&=-2a_{23}\delta+2(a_{23}a_{11}-a_{12}a_{13})\alpha\ ,
\end{aligned}\tag{2.17}$$

with

$$\begin{aligned}
\delta&=\beta-\frac{I\alpha}{3}\ ,\\
\alpha&=\left[\frac{1}{u^2}+\frac{1}{v^2}\right]-\frac{q}{\sqrt{q^2+p^3}}\left[\frac{1}{u^2}-\frac{1}{v^2}\right]\ ,\\
\beta&=-\frac{p^2}{\sqrt{q^2+p^3}}\left[\frac{1}{u^2}-\frac{1}{v^2}\right]\ .
\end{aligned}\tag{2.18}$$

Unfortunately, these equations are highly nonlinear and cannot be solved for the general case using analytical means.

The potential-energy surface is known to contain either minima of D_{5d} symmetry and maxima of D_{3d} symmetry or *vice versa*[13,43] (and referred to as pentagonal and trigonal epikernels, respectively, in Ref. 13), depending on the parameters in the nonlinear perturbations. Cullerne and O'Brien[43] showed that these minima or maxima correspond to the corners of an icosahedron or dodecahedron, respectively, when mapped onto the original spherical potential-energy surface. The only other points which could possibly be minima are the so-called dihedral points of D_{2h} symmetry. Thus we can restrict our attempt at solving Eqs. (2.16) by searching specifically for solutions which will give eigenstates corresponding to the trigonal, pentagonal, or dihedral points in the potential-energy surface. In all of these cases, the equations can be easily solved.

III. TRANSFORMATION PROPERTIES OF ICOSADHEDRA AND DODECAHEDRA

In order to obtain the states associated with each of the minima, it is first necessary to write down the coordinates of the corners of the icosahedron and dodecahedron which both belong to the I_h group. We choose the same coordinate system for both in which Oz is a twofold axis such that each edge of the icosahedron has a length of two units. As in Refs. 36 and 37, it is possible to write down the form of both the electronic orbital states and phonon states associated with each corner of the icosahedron and dodecahedron from these coordinates based exclusively on the transformation properties of the corners.

A. The icosahedron

The coordinates of the 12 corners of the icosahedron using the above coordinate system are shown in Fig. 1. Six of these coordinates are given explicitly in Table I; the remaining six coordinates are obtained by inversion through the center of the icosahedron such that the corner labeled A, at the point $(0,\phi,1)$ for example, becomes $\bar{A}$ at the point $(0,-\phi,-1)$. (We note that the coordinates given in Table I are very similar to those given in Boyle and Parker[44] and Mermin[45] but with small changes introduced in order to systematize our subsequent calculations.) There will be a minimum in energy

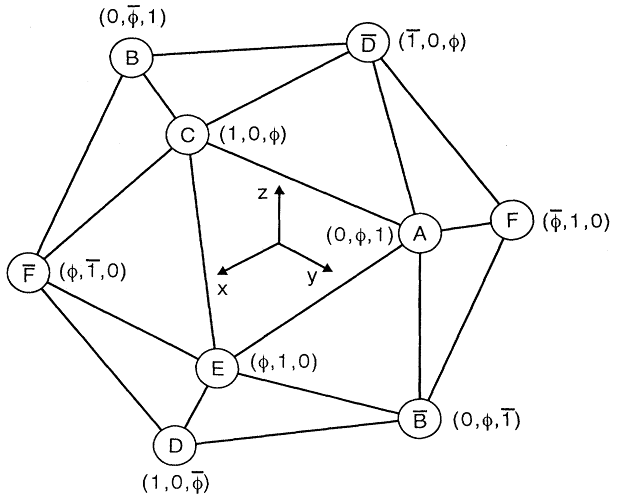

FIG. 1. The icosahedron showing the coordinates of the corners.

TABLE I. States for pentagonal minima.

Label	Coordinate	Electronic state	Phonon state	a_θ	a_ϵ	a_4	a_5	a_6
A	$(0,\phi,1)$	$z+\phi y$	$yz+\sqrt{\frac{2}{3}}\epsilon_x$	$-\beta/\sqrt{2}$	$-\beta/\sqrt{6}$	β	0	0
B	$(0,-\phi,1)$	$z-\phi y$	$-yz+\sqrt{\frac{2}{3}}\epsilon_x$	$-\beta/\sqrt{2}$	$-\beta/\sqrt{6}$	$-\beta$	0	0
C	$(1,0,\phi)$	$x+\phi z$	$zx+\sqrt{\frac{2}{3}}\epsilon_y$	$\beta/\sqrt{2}$	$-\beta/\sqrt{6}$	0	β	0
D	$(1,0,-\phi)$	$x-\phi z$	$-zx+\sqrt{\frac{2}{3}}\epsilon_y$	$\beta/\sqrt{2}$	$-\beta/\sqrt{6}$	0	$-\beta$	0
E	$(\phi,1,0)$	$y+\phi x$	$xy+\sqrt{\frac{2}{3}}\epsilon_z$	0	$\beta\sqrt{\frac{2}{3}}$	0	0	β
F	$(-\phi,1,0)$	$y-\phi x$	$-xy+\sqrt{\frac{2}{3}}\epsilon_z$	0	$\beta\sqrt{\frac{2}{3}}$	0	0	$-\beta$

corresponding to each of these six coordinates. The minima have D_{5d} symmetry, so will be called pentagonal wells. The resultant states are given in columns 3 and 4 of Table I. (Throughout, we ignore all normalizing factors in electronic and phonon states, as they complicate the expressions and will automatically drop out of the energy results.)

B. The dodecahedron

As the corners of the dodecahedron lie at the center of each equilateral triangle forming the icosahedron, their coordinates are easily obtained. Table II gives the coordinates of ten of the 20 corners of the dodecahedron. Again, the associated electronic and phonon states associated with wells at trigonal points in Q space of D_{3d} symmetry follow automatically, and are given in Table II. (A factor of ϕ^2 has been removed from each electronic state compared to the coordinates for simplicity.)

C. Analytical form for the vibronic states

The method described above yields electronic and phonon states having correct transformation properties associated with particular wells in Q space. However, it does not give the absolute positions of these wells but this information is sufficient to allow Eqs. (2.16) to be solved. This allows the values of a_j (which give the well positions) to be found, as indicated below. We consider wells associated with the pentagonal and trigonal wells in turn.

1. Pentagonal minima

Consider the (un-normalized) pentagonal electronic states $|y\pm\phi x\rangle$. The condition that these are eigenstates results in the additional identity

$$a_{11}-a_{22}=\pm a_{12}\ . \tag{3.1}$$

The phonon part of the state contains ϵ- and 6-type excitations only. This implies that only a_ϵ and a_6 are nonzero. It is then a simple matter to show that $a_\epsilon=\pm\sqrt{\frac{2}{3}}a_6$, as would be expected independently from the form of the phonon state shown in Table I. Equations (2.16) are then readily solved with the result $a_\epsilon=\sqrt{\frac{2}{3}}\beta$ and $a_6=\pm\beta$, where

$$\beta=\frac{\sqrt{6}}{(5-4\sqrt{2}V_2')}\ . \tag{3.2}$$

Hence these states are found to have energy

$$E_I'=-\frac{1}{(5-4\sqrt{2}V_2')}\ . \tag{3.3}$$

Thus if V_2' is positive, the states are lower in energy than the linear-coupling value of $E'=-\frac{1}{5}$. All of the states contained in Table I have this same energy. It should be noted also that the energy and eigenstates are independent of the second form of quadratic coupling V_3'.

Table I shows the values of a_i which specify the positions of each well. The full states appropriate in the transformed picture may be written in the form $|A;0\rangle$, for example, where A is the (un-normalized) orbital state and 0 denotes that all the h oscillators are in their ground

TABLE II. States for trigonal minima.

Group	Number	Coordinate	Electronic state	Phonon state	a_θ	a_ϵ	a_4	a_5	a_6
I	a	$(0,\phi,\phi^3)$	$\phi^{-1}y+\phi z$	$yz-\sqrt{2}\theta_x$	$\gamma/\sqrt{2}$	$-\gamma\sqrt{\frac{3}{2}}$	γ	0	0
	b	$(0,-\phi,\phi^3)$	$-\phi^{-1}y+\phi z$	$-yz-\sqrt{2}\theta_x$	$\gamma/\sqrt{2}$	$-\gamma\sqrt{\frac{3}{2}}$	$-\gamma$	0	0
	c	$(\phi^3,0,\phi)$	$\phi^{-1}z+\phi x$	$zx-\sqrt{2}\theta_y$	$\gamma/\sqrt{2}$	$\gamma\sqrt{\frac{3}{2}}$	0	γ	0
	d	$(\phi^3,0,-\phi)$	$-\phi^{-1}z+\phi x$	$-zx-\sqrt{2}\theta_y$	$\gamma/\sqrt{2}$	$\gamma\sqrt{\frac{3}{2}}$	0	$-\gamma$	0
	e	$(\phi,\phi^3,0)$	$\phi^{-1}x+\phi y$	$xy-\sqrt{2}\theta_z$	$-\gamma\sqrt{2}$	0	0	0	γ
	f	$(-\phi,\phi^3,0)$	$-\phi^{-1}x+\phi y$	$-xy-\sqrt{2}\theta_z$	$-\gamma\sqrt{2}$	0	0	0	$-\gamma$
II	g	(ϕ^2,ϕ^2,ϕ^2)	$(x+y+z)$	$yz+zx+xy$	0	0	γ	γ	γ
	h	$(-\phi^2,\phi^2,\phi^2)$	$(-x+y+z)$	$yz-zx-xy$	0	0	γ	$-\gamma$	$-\gamma$
	i	$(\phi^2,-\phi^2,\phi^2)$	$(x-y+z)$	$-yz+zx-xy$	0	0	$-\gamma$	γ	$-\gamma$
	j	$(\phi^2,\phi^2,-\phi^2)$	$(x+y-z)$	$-yz-zx+xy$	0	0	$-\gamma$	$-\gamma$	γ

state. States $|A';0\rangle$ appropriate to the untransformed picture can be obtained by multiplying the transformed states by the value U_A of U appropriate to that well by substituting with the particular values of a_j. Thus

$$|A';0\rangle = U_A |A;0\rangle \ , \tag{3.4}$$

for example. As U_A contains phonon excitations, this results in states which are automatically vibronic.

2. *Trigonal minima*

The group-I un-normalized states e and f ($|\pm\phi^{-1}x+\phi y\rangle$) must satisfy the condition

$$\sqrt{5}a_{12} = \mp(a_{11}-a_{22}) \tag{3.5}$$

in order to be eigenstates. Together with the fact that, from group-theoretical arguments, they are expected to involve θ- and 6-type excitations only, it can be established that $a_6 = \mp a_\theta/\sqrt{2}$ and hence, by substituting into (2.16), that $a_\theta = -\sqrt{2}\gamma$ and $a_6 = \pm\gamma$, where

$$\gamma = \frac{\sqrt{2}}{(\sqrt{15}-4\sqrt{\tfrac{2}{3}}V'_3)} \ . \tag{3.6}$$

The group-II state g is only an eigenstate if $(a_{11}+a_{13}) = (a_{22}+a_{23})$ and also if $(a_{12}+a_{22}) = (a_{13}+a_{33})$. This leads to the result $a_4 = a_5 = a_6 = \gamma$.

The positions of the wells for all of the states in groups I and II are given in Table II. Each state is found to have the energy

$$E'_D = -\frac{1}{(5-4\sqrt{10}V'_3/3)} \ , \tag{3.7}$$

which is lower than the linear-coupling value of $-\frac{1}{5}$ when V'_3 is positive. The energy and eigenstates are independent of the first form of quadratic coupling V_2. As in the case of the pentagonal states given in (3.4), states appropriate to the untransformed picture such as $|a';0\rangle$ are obtained by multiplying normalized transformed states $|a;0\rangle$ by U_a such that $|a';0\rangle = U_a|a;0\rangle$. Again, this state is automatically vibronic in character.

D. Dihedral points

As mentioned above, the only positions which can possibly become minima other than the tetragonal and pentagonal points are the dihedral points of D_{2h} symmetry. One such point would have the orbital state $|z\rangle$. For this to be a turning point, it is necessary to set $a_4 = a_5 = a_6 = 0$, and thus

$$a_\theta = \tfrac{1}{2}\sqrt{\tfrac{3}{5}}\,\frac{1+V'_2/\sqrt{2}+V'_3/\sqrt{10}}{1-V'^2_2/5-3V'^2_3/5}$$

and (3.8)

$$a_\epsilon = -\frac{1}{2}\,\frac{1-V'_2/5\sqrt{2}+3V'_3/\sqrt{10}}{1-V'^2_2/5-3V'^2_3/5} \ .$$

This results in an energy for these states of

$$E' = -\frac{1}{5}\,\frac{1+V'_2/4\sqrt{2}+9V'_3/4\sqrt{10}}{1-V'^2_2/5-3V'^2_3/5} \ . \tag{3.9}$$

However, for this point to be an absolute minimum, the value for E' given in (3.9) must be less than both E'_I in (3.3) and E'_D in (3.7). This implies that

$$3V'_2 < \sqrt{5}V'_3 \quad \text{and} \quad \sqrt{5}V'_3 < 3V'_2 \ , \tag{3.10}$$

which is obviously contradictory. Hence it can be concluded that these points can never become absolute minima, and can thus be discounted. It has been verified that the same conclusion also holds when anharmonic terms are included to first order.

IV. PROJECTION OPERATORS AND SYMMETRY-ADAPTED STATES

The results obtained above give vibronic states associated with the minima. These are good eigenstates of the system as a whole in infinite coupling. However, in finite coupling, it is necessary to take combinations of these vibronic states which transform among themselves with the required symmetry. Such states can be constructed using projection operators as described in Hallam, Bates, and Dunn,[46] for example. The principle used is that the projection operator method generates a set of symmetry-adapted states from a set of nonsymmetrized states Ψ by operating on Ψ with the projection operator $\rho^{(i)}_{ts}$ given by

$$\rho^{(i)}_{ts} = \frac{d_i}{g}\sum_R D^i(R)^*_{ts}R \ , \tag{4.1}$$

where g is the order of the group, d_i is the dimension of the representation of symmetry Γ_i, R is an element of the icosahedral group I_h, and $D^i(R)_{ts}$ is the tsth element of the matrix representation of R.

Our interest is centered on the T_{1u} electronic state of the C_{60} molecule. One of the ground states localized in one of the wells (such as $|A';0\rangle$) is taken as the state Ψ, and (4.1) is used to determine the required vibronic states of symmetry T_{1u} containing a component localized in that well. This procedure to obtain vibronic states has been carried out for both the pentagonal and trigonal sets of wells. All 60 matrices of the I_h group belonging to the T_{1u} representation are needed. While some of the required matrices are given in McLellan,[47] insufficient detail is presented from which all the others may be derived. Consequently the full set has been obtained by determining the way in which each corner of the icosahedron shown in Fig. 1 is translated into another corner or remains unchanged as a result of the 60 allowed symmetry operations of the I_h group.

A. Vibronic states belonging to the pentagonal wells

Consider first the wells which correspond to the corners of the icosahedron when mapped onto the original spherical potential-energy surface. Following the procedure outlined above, the T_{1u} symmetry-adapted ground vibronic states obtained from the pentagonal minima are found to be

$$
\begin{aligned}
|T^I_{1ux}\rangle &= N^I_{T1u}[\phi^{-1}(|C';0\rangle+|D';0\rangle) \\
&\quad +(|E';0\rangle-|F';0\rangle)]\,, \\
|T^I_{1uy}\rangle &= N^I_{T1u}[\phi^{-1}(|E';0\rangle+|F';0\rangle) \\
&\quad +(|A';0\rangle-|B';0\rangle)]\,, \\
|T^I_{1uz}\rangle &= N^I_{T1u}[\phi^{-1}(|A';0\rangle+|B';0\rangle) \\
&\quad +(|C';0\rangle-|D';0\rangle)]\,,
\end{aligned}
\tag{4.2}
$$

where N^I_{T1u} is the normalization constant. N^I_{T1u} can be determined after using the identity

$$\exp[k(b_i^+-b_i)]=\exp(kb_i^+)\exp(-kb_i)\exp(-k^2/2) \tag{4.3}$$

and expanding the exponentials $\exp(kb_i^+)$ and $\exp(-kb_i)$ as power series,[36,37] with the result

$$N^I_{T1u}=[10(1+S_I)]^{-1/2}\,, \tag{4.4}$$

where

$$S_I=\exp\left[-2\left[\beta\frac{K_1}{\hbar\omega}\right]^2\right] \tag{4.5}$$

is the phonon overlap between any two states.

The first excited vibronic state for finite coupling has the same energy as the T_{1u} vibronic ground state in the infinite coupling limit as all of the oscillators are in their ground states. Such a state is often referred to as the inversion state and has T_{2u} symmetry. A similar method to that for the T_{1u} states can formally be used to derive these states, but that requires knowledge of the 60 matrices for the T_{2u} irreducible representation. However, an alternative simpler procedure is to use the orthogonality property of the T_{1u} and T_{2u} states. The three components of the T_{2u} vibronic states are thus found to be

$$
\begin{aligned}
|T^I_{2ux}\rangle &= N^I_{T2u}[(|C';0\rangle+|D';0\rangle) \\
&\quad -\phi^{-1}(|E';0\rangle-|F';0\rangle)]\,, \\
|T^I_{2uy}\rangle &= N^I_{T2u}[(|E';0\rangle+|F';0\rangle) \\
&\quad -\phi^{-1}(|A':0\rangle-|B';0\rangle)]\,, \\
|T^I_{2uz}\rangle &= N^I_{T2u}[(|A';0\rangle+|B';0\rangle) \\
&\quad -\phi^{-1}(|C';0\rangle-|D';0\rangle)]\,,
\end{aligned}
\tag{4.6}
$$

where

$$N^I_{T2u}=[10(1-S_I)]^{-1/2} \tag{4.7}$$

is the normalizing factor (evaluated in the same manner as above).

B. Vibronic states belonging to the trigonal wells

For the trigonal wells, the symmetry-adapted T_{1u} vibronic ground states are

$$
\begin{aligned}
|T^D_{1ux}\rangle &= N^D_{T1u}[-\phi^2(|c';0\rangle+|d';0\rangle)+(|f'0\rangle-|e';0\rangle)+\phi(-|g';0\rangle+|h';0\rangle-|i';0\rangle-|j';0\rangle)]\,, \\
|T^D_{1uy}\rangle &= N^D_{T1u}[-\phi^2(|e';0\rangle+|f';0\rangle)+(|b';0\rangle-|a';0\rangle)+\phi(-|g';0\rangle-|h';0\rangle+|i';0\rangle-|j';0\rangle)]\,, \\
|T^D_{1uz}\rangle &= N^D_{T1u}[-\phi^2(|a';0\rangle+|b';0\rangle)+(|d';0\rangle-|c';0\rangle)+\phi(-|g';0\rangle-|h';0\rangle-|i';0\rangle+|j';0\rangle)]\,,
\end{aligned}
\tag{4.8}
$$

where

$$N^D_{T1u}=[10\phi^2(3+5S_D+2S_D^2)]^{-1/2}\,, \tag{4.9}$$

and where

$$S_D=\exp\left[-2\left[\gamma\frac{K_1}{\hbar\omega}\right]^2\right]\,. \tag{4.10}$$

The phonon overlaps between any two wells are either S_D or S_D^2.

In this case, there are two inversion levels, one of symmetry T_{2u} and one of symmetry G_u. As there are two inversion levels, orthogonality alone cannot be used to determine the appropriate combinations of states. The states can be derived systematically using the 60 matrices for T_{2u} and the 60 matrices for G_u. However, a much simpler method has been used by noting that it seems likely that the T_{2u} states are composed of the same basis states, and in a similar combination, as the corresponding T_{1u} states. This suggests that, in order to be orthogonal to the T_{1u} states, the symmetry-adapted combinations must be

$$
\begin{aligned}
|T^D_{2ux}\rangle &= N^D_{T2u}[\phi^{-2}(|c';0\rangle+|d';0\rangle)-(|f';0\rangle-|e';0\rangle)+\phi^{-1}(-|g';0\rangle+|h';0\rangle-|i';0\rangle-|j';0\rangle)]\,, \\
|T^D_{2uy}\rangle &= N^D_{T2u}[\phi^{-2}(|e';0\rangle+|f';0\rangle)-(|b';0\rangle-|a';0\rangle)+\phi^{-1}(-|g';0\rangle-|h';0\rangle+|i';0\rangle-|j';0\rangle)]\,, \\
|T^D_{2uz}\rangle &= N^D_{T2u}[\phi^{-2}(|a';0\rangle+|b';0\rangle)-(|d';0\rangle-|c';0\rangle)+\phi^{-1}(-|g';0\rangle-|h';0\rangle-|i';0\rangle+|j';0\rangle)]\,,
\end{aligned}
\tag{4.11}
$$

where

$$N^D_{T2u}=[10\phi^{-2}(3-5S_D+2S_D^2)]^{-1/2}\,. \tag{4.12}$$

In order to be orthogonal to both T_{1u} and T_{2u}, the G_u vibronic states must then be

$$\begin{aligned}
|G^D_{ua}\rangle &= \sqrt{5}N^D_{Gu}[\,|g';0\rangle - |h';0\rangle - |i';0\rangle - |j';0\rangle\,]\ ,\\
|G^D_{ux}\rangle &= N^D_{Gu}[2(|a';0\rangle + |b';0\rangle - |c';0\rangle + |d';0\rangle) + (-|g';0\rangle - |h';0\rangle - |i';0\rangle + |j';0\rangle)]\ ,\\
|G^D_{uy}\rangle &= N^D_{Gu}[2(|e';0\rangle + |f';0\rangle + |b';0\rangle - |a';0\rangle) + (-|g';0\rangle - |h';0\rangle + |i';0\rangle - |j';0\rangle)]\ ,\\
|G^D_{uz}\rangle &= N^D_{Gu}[2(|c';0\rangle + |d';0\rangle + |f';0\rangle - |e';0\rangle) + (-|g';0\rangle + |h';0\rangle - |i';0\rangle - |j';0\rangle)]\ ,
\end{aligned} \tag{4.13}$$

where

$$N^D_{Gu} = [60(1-S_D^2)]^{-1/2}\ . \tag{4.14}$$

The calculations of energies below will show that all of the proposed T_{2u} states have the same energy as each other, and that the G_u states also have the same energy as each other but a different energy from the T_{2u} states. This confirms that the correct combinations have indeed been identified.

V. ENERGIES OF THE SYMMETRY-ADAPTED STATES

The energies of all of the above states can be found after evaluating the matrix elements of the full Hamiltonian $\mathcal{H}$ between all relevant pairs of untransformed vibronic states $|X';0\rangle$. This can be done[37] by writing the operators in second-quantized form, using the commutation relation

$$(b_i + b_i^+)^n \exp[k(b_i - b_i^+)] = \exp[k(b_i - b_i^+)][(b_i + b_i^+) - 2k]^n \tag{5.1}$$

and its complex conjugate, applying the identity (4.3) and then expanding the exponentials in U_i's, as was done for the evaluation of the oscillator overlaps.

A. Energies of the pentagonal vibronic states

It is found that the matrix elements of $\mathcal{H}$ between the state associated with any one of the pentagonal wells and itself can be expressed in the form $\sqrt{5}\phi H^I_{11}$, where

$$H^I_{11} = \tfrac{5}{2}\hbar\omega + \frac{K_1^2}{\hbar\omega}\beta\left(-2\sqrt{\tfrac{2}{3}} + \tfrac{5}{3}\beta\right) - \frac{8\sqrt{2}}{3}K_2\beta^2\ . \tag{5.2}$$

The matrix element between any two different wells is found to be $\pm\phi H^I_{12}$, where

$$H^I_{12} = S_I\left[\frac{5}{2}\hbar\omega - \frac{K_1^2}{\hbar\omega}\beta\left[2\sqrt{\tfrac{2}{3}} + \frac{\beta}{3}\right] - \frac{2\sqrt{2}}{3}K_2\beta^2 - 2\sqrt{\tfrac{2}{5}}K_3\beta^2\right]\ . \tag{5.3}$$

The energies of the T^I_{1u} states are thus found to be

$$E^I_{T1u} = 10N^{I2}_{T1u}(H^I_{11} + H^I_{12}) = \frac{(H^I_{11} + H^I_{12})}{(1+S_I)}\ . \tag{5.4}$$

Similarly, the energies of the T^I_{2u} states are found to be

$$E^I_{T2u} + 10N^{I2}_{T2u}(H^I_{11} - H^I_{12}) = \frac{(H^I_{11} - H^I_{12})}{(1-S_I)}\ . \tag{5.5}$$

Figure 2 shows a plot of the energy of the T^I_{2u} state relative to the T^I_{1u} state for the case of zero quadratic coupling (i.e., $V_2' = V_3' = 0$). The T^I_{2u} inversion level can be seen to be $\hbar\omega$ above the ground state in the weak-coupling limit, and degenerate with the ground state in the strong-coupling limit, as would be expected.

B. Energies of the trigonal states

The matrix elements of $\mathcal{H}$ between the state associated with any one of the trigonal wells and itself can be expressed in the form $3H^D_{11}$, where

$$H^D_{11} = \tfrac{5}{2}\hbar\omega + \frac{K_1^2}{\hbar\omega}\gamma\left(-2\sqrt{\tfrac{6}{5}} + 3\gamma\right) - 8\sqrt{\tfrac{2}{5}}K_3\gamma^2\ . \tag{5.6}$$

Similarly, the matrix elements between any two different states is either $\pm\sqrt{5}H^D_{12}$, where

$$H^D_{12} = S_D\left\{\tfrac{5}{2}\hbar\omega + \frac{K_1^2}{\hbar\omega}\gamma\left(-2\sqrt{\tfrac{6}{5}} + \gamma\right) - \frac{2\sqrt{2}}{5}K_2\gamma^2 - 6\sqrt{\tfrac{2}{5}}K_3\gamma^2\right] \tag{5.7}$$

or $\pm H^D_{13}$, where

$$H^D_{13} = S_D^2\left\{\tfrac{5}{2}\hbar\omega - \frac{K_1^2}{\hbar\omega}\gamma\left(2\sqrt{\tfrac{6}{5}} + \gamma\right) - 2\sqrt{2}K_2\gamma^2 - 2\sqrt{\tfrac{2}{5}}K_3\gamma^2\right]\ . \tag{5.8}$$

The energies of the T^D_{1u} states are thus found to be

$$\begin{aligned}
E^D_{T1u} &= 10\phi^2(N^D_{T1u})^2(3H^D_{11} + 5H^D_{12} + H^D_{13})\\
&= \frac{(3H^D_{11} + H^D_{12} + 2H^D_{13})}{(3+5S_D+2S_D^2}\ .
\end{aligned} \tag{5.9}$$

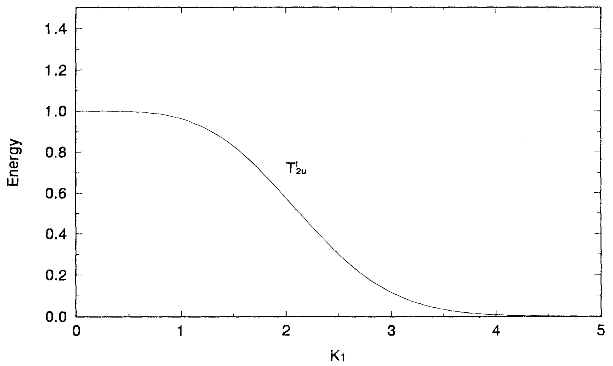

FIG. 2. The energy of the T^I_{2u} inversion level relative to the T^I_{1u} ground state for the states based on the pentagonal minima. (Both axes are given in units of $\hbar\omega$.)

Similarly, the energies of the T_{2u}^{D} states are found to be

$$\begin{aligned} E_{T2u}^{D} &= 10\phi^{-2}(N_{T2u}^{D})^{2}(3H_{11}^{D}-5H_{12}^{D}+2H_{13}^{D}) \\ &= \frac{(3H_{11}^{D}-5H_{12}^{D}+2H_{13}^{D})}{(3-5S_{D}+2S_{D}^{2})} \end{aligned} \tag{5.10}$$

and those of the G_{u}^{D} states to be

$$E_{Gu}^{D}=60N_{Gu}^{D2}(H_{11}^{D}-H_{13}^{D})=\frac{(H_{11}^{D}-H_{13}^{D})}{(1-S_{D}^{2})} . \tag{5.11}$$

Figure 3 shows a plot of the energies of the T_{2u}^{D} and G_{u}^{D} inversion levels relative to that of the T_{1u} state for zero quadratic coupling. Again, the expected results that the inversion levels are $\hbar\omega$ above the ground state in the weak-coupling limit, and also degenerate with the ground state in the strong-coupling limit, are seen to be satisfied.

Figure 3 also shows the energies of the T_{1u}^{I} and T_{2u}^{I} states (again when $V_2'=V_3'=0$) relative to the energy of the T_{1u}^{D} state. It can be seen that the T_{1u} ground states for both the pentagonal and trigonal minima have the same energy in very weak and very strong coupling, but that the T_{1u} state for the trigonal minima is lowest in energy for intermediate coupling strengths. However, in order to know which state is lowest in a real C_{60} molecule, it would be necessary to know the relative strengths of the V_2 and V_3 quadratic coupling constants, and also to evaluate the effect of other perturbations such as anharmonicity which have not been considered in this paper.

VI. DISCUSSION

In this paper, minima in the potential-energy surface for the $T_{1u}\otimes h_g$ Jahn-Teller system have been found of both D_{5d} (pentagonal) and D_{3d} (trigonal) symmetries using analytical means. States associated with each of the wells have been deduced, and are appropriate eigenstates of the system in the strong-coupling limit. Symmetry-adapted states for the ground and inversion level(s) appropriate for finite couplings have then been constructed using projection operator techniques, and their energies evaluated. The method adopted is very similar to that used earlier by the authors in their studies of tetrahedral centers, particularly for the cases of $E\otimes e$ (Refs. 40 and 48) and for $T\otimes(e+t_2)$ for both the orthorhombic case[46] and when the trigonal and tetragonal wells coexist.[49] As in the $T\otimes h$ case, the wells were generated by the second-order vibronic couplings which warped an otherwise continuous equal-energy surface. The importance of such second-order terms was pointed out by Bersuker and Polinger,[35] and it is also clearly demonstrated here. The simplification of using a $T_{1u}\otimes h_{1g}$ model as a good approximation for what should be a $T_{1u}\otimes 8h_g$ model for C_{60} is justified partially by previous work[50] on the multimode JT effect, but further investigations are needed to verify this.

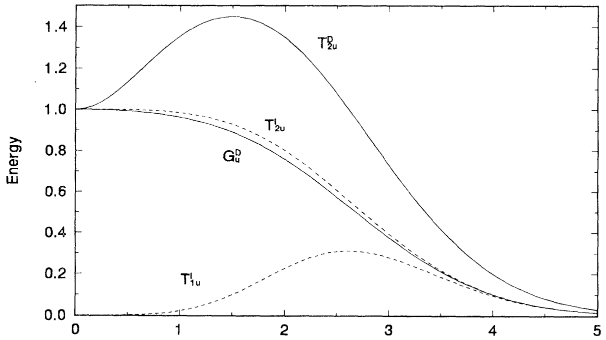

FIG. 3. The energy of the T_{2u}^{D} and G_{u}^{D} inversion levels relative to the T_{1u}^{D} ground state for the states based on the trigonal minima (solid lines). The energies of the T_{1u}^{I} and T_{2u}^{I} states are also plotted relative to the T_{1u}^{D} state (dashed lines). (Both axes are given in units of $\hbar\omega$.)

Although our calculations above begin by calculating the positions of the wells, which is in effect a static JT model, the introduction of tunneling automatically converts the problem to that of a dynamic JT model. The physical reason for the tunneling is that other perturbations are present, such as spin-orbit coupling, which generate the finite overlaps between states localized in the wells. In many of the experiments cited in Sec. I, it was concluded that the JT effect was dynamic.

To our knowledge, this is the first time that vibronic states and their energies have been written down in an explicit algebraic form for systems of icosahedral symmetry. Wang *et al.*[20] give expressions which are equivalent to those given here in Eqs. (5.4) and (5.5) for the energies of the T_{1u} and T_{2u} vibronic states associated with the pentagonal minima, but they do not give explicit expressions for the states themselves or for the matrix elements H_{ij} in terms of the fundamental constants. These authors obtain expressions for their vibronic states using degenerate perturbation theory and symmetry arguments in comparison to our method of using projection operators. It is therefore not possible to compare the results directly. Also, we note that they used the fivefold axis of the icosahedron as O_z, which meant that the form of their states is different from our own. However, the procedures adopted by Wang and co-workers[20,21] appear to resemble closely that given here, in that their origin-shifting unitary operator U^{β} for their well β is very similar in both appearance and effect to our unitary operator U given in (2.8). The major difference appears to be that the positions of the wells given here are defined explicitly through the parameters α_j, whereas those of Wang *et al.* are given through the c numbers via the gap equation. As explicit expressions for these quantities are not given, again no direct comparison between the results obtained can be made. However, there is one significant difference between the two approaches in that Wang *et al.* assume that the wells are of pentagonal symmetry only, and they do not consider the possibility of trigonal wells.

We found previously that, for magnetic impurity ions in semiconducting hosts, the procedure of solving the JT problem by a unitary transformation followed by an energy minimization and the construction of symmetry-adapted states from appropriate projection operators was very successful. The same conclusions apply in the case of the $T_{1u}\otimes h_g$ JT problem considered here. The states automatically have the correct symmetry properties, and are automatically vibronic in character on account of operators such as U_A acting on the state $|A;0\rangle$ according to Eq. (3.4). The other advantage of the method is that expressions for the energies of the vibronic states can be determined entirely by analytical methods, and graphs such as those in Figs. 2 and 3 are very easily obtained. However, many more calculations are needed before direct comparison between our first results and experiment can be undertaken.

An additional problem for the future is to evaluate the first-order JT reduction factors for the $T_{1u}\otimes h_g$ system. These in turn can be used in effective Hamiltonians to help interpret the results of experiments such as EPR and the measured phonon spectrum on real examples of these JT systems, such as the C_{60} molecule. In addition, the methods developed in this paper can be used (after much algebraic manipulation) to obtain expressions for the excited states of these systems, and subsequently to determine second-order JT reduction factors.

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