Vibronic energies in C_{60}^{n-} and the Jahn-Teller effect

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(Received 12 September 1995)

When electrons are added to neutral C_{60} they go mainly into a t_{1u} orbital. The energy of such a $(t_{1u})^n$ configuration is affected by a Jahn-Teller interaction with h_g vibrations as well as by the Coulomb interaction that separates the terms. These energies are found for strong, intermediate, and weak coupling; with and without the term splittings. Figures illustrate how the Jahn-Teller interaction inverts the sequence of energy levels. Modifications needed to allow for the configuration interaction with the nearby t_{1g} orbital are indicated. The effect of the existence of eight different h_g modes instead of the one usually included is discussed, and an effective single-mode Hamiltonian is proposed that is shown to give a very good approximation to the energies of low-lying levels. The effect of all this on pairing energies is discussed. A discussion of the effect of warping terms in the Hamiltonian is included.

I. INTRODUCTION

The C_{60} molecule in suitable surroundings can act as a recipient for one or more negative charges. These extra electrons go mainly into a triply degenerate molecular orbital whose symmetry corresponds to the T_{1u} irreducible representation (irrep) of the symmetry group of the molecule, I_h, so that the state with n extra electrons can be described as a $(t_{1u})^n$ configuration outside closed shells. The terms of such a configuration are mostly degenerate in energy, and so their energies can be expected to be further altered by the Jahn-Teller interaction with distortions of the molecular cage. The nature of the distortion and the sizes of the energy shifts will depend on the strength of the Jahn-Teller interaction, the size of the Coulomb interaction producing the term splittings, and the energies of the modes of vibration that are coupled in. It is this collection of problems that are addressed in this paper.

The problem of the effect of Jahn-Teller interactions in states resulting from multiple occupancy of triply degenerate t states has been extensively studied over the last twenty years in connection with the various charge states of the vacancy in silicon (V centers) by Watkins and his collaborators (reviewed by Watkins[1]), and the connection with the similar problem in C_{60}^{n-} was pointed out by Lannoo *et al.*[2] The similarity consists not only in the symmetry type of the electronic orbitals being filled, but also in the symmetry type of the vibrational modes they interact with. The V centers are at sites of cubic symmetry, and the modes of vibration concerned are of two symmetry types ϵ and τ_2, but if the modes are taken to be degenerate in frequency and in interaction strength then the Jahn-Teller Hamiltonian is identical to that for t states with the h_g modes in icosahedral symmetry. In the V centers a considerable amount of experimental evidence has been accumulated, showing that the Jahn-Teller interaction is strong, even strong enough to reverse the expected ordering of the different charge states and to produce (in the terminology of Anderson[3]) ''negative-U'' pairing energies, which are discussed in a review article by Watkins.[4] It has also been shown by Anderson, Ham, and Grossman[5] that the term energies must be taken into account along with the

Jahn-Teller interaction to get a correct fit with experiment.

In C_{60}^{n-}, in contrast with the V centers, we do not have direct measurements of the various energies. It is likely that the Jahn-Teller interaction is not particularly strong relative to the vibrational frequencies, and that the term energies are neither dominant nor negligible. Unlike the V centers, we do not have to consider the different coupling strengths of ϵ and τ_2 vibrations, but because of the higher symmetry the effects of the kinetic energy must be included. Also in C_{60} there are eight h_g modes of very different frequencies, all of which should be included in the Jahn-Teller coupling, and this produces an extra complication.

The problem for C_{60}^{n-} was discussed at length by Auerbach, Manini, and Tosatti,[6] and this study can be regarded as carrying on from there. This paper takes a different line from theirs, in that we work from a basis of the coupled electronic states rather than from a basis of the uncoupled configurations. This makes it easier to consider the effects of the phase of the electronic wave functions, as well as making it simple to include the term energies. Using this basis it is possible to carry a numerical calculation of the energies through all coupling strengths, including the term energies. Where our numerical calculations overlap we agree with Auerbach, Manini, and Tosatti. We differ from them in the details of some small corrections at strong coupling, and in this we are corroborated by the numerical results.

This paper also addresses the question of the eight h_g modes, and shows how an effective single-mode Hamiltonian can be set up that produces a good approximation to the low-lying energies.

Plan of the paper

All the work is built on the by now well-known fact[7] that the Hamiltonian for linear Jahn-Teller coupling of t electronic states to h_g modes is invariant under the operations of the three-dimensional rotation group SO(3), an accidentally higher symmetry than the icosahedral symmetry of the full Hamiltonian. It is also a fact that all angular momentum states up to $L=2$ remain unsplit in the icosahedral group, so if we stick with linear coupling it is possible and convenient
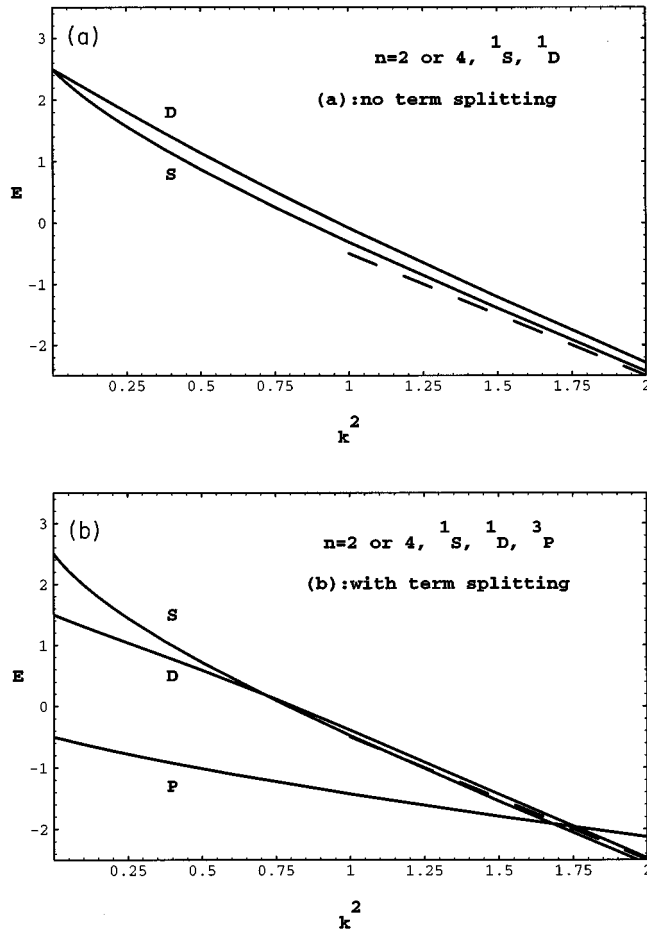
FIG. 1. Calculated energy levels at moderate coupling strength for p^2 and p^4, (a) without and (b) with a term splitting corresponding to $F_2 = \hbar\omega/3$. Energy is in units of $\hbar\omega$. In (b) at $k^2 = 0$ the ^1S electronic state is at $E = 4.5\hbar\omega$, the lowest S state is a one-phonon excitation from ^1D. The dashed line shows the asymptotic energy.

FIG. 2. Calculated energy levels at moderate coupling strength for p^3, (a) without and (b) with a term splitting corresponding to $F_2 = \hbar\omega/3$. Energy is in units of $\hbar\omega$. In (b) at $k^2 = 0$ the ^2P electronic state is at $E = 3.5\hbar\omega$, the lowest P state is a one-phonon excitation from ^2D. The dashed line shows the asymptotic energy.

to use angular momentum labeling throughout, to describe the electronic configurations as p^n and the coupled states as LS coupled terms in the usual spectroscopic notation.

We start in Sec. II with a derivation of the energies in strong coupling. In this section the term energies are assumed to be overridden by the Jahn-Teller interaction, and the vibrational kinetic energy produces a structure of pseudorotations above the potential-energy minimum. C_{60}^{n-} is not expected to be a case of strong coupling, but the results of these calculations are of interest in their own right, and can be tied in with the numerical work, which is valid at all coupling strengths.

In Sec. IV the term splittings are introduced and the numerical work that carries through all coupling strengths is described. The relative energies of all the terms of all the different configurations p^n depend on a single integral of the Coulomb interaction, and the high spin states are always lower than the low spin ones. However, the Jahn-Teller interaction will always reduce the energy of the low spin states more effectively than the high spin states, so the choice of spin of the ground state will be sensitive to the relative strengths of these interactions. Figures 1 and 2 illustrate this effect. This balance has been found to be important in the V
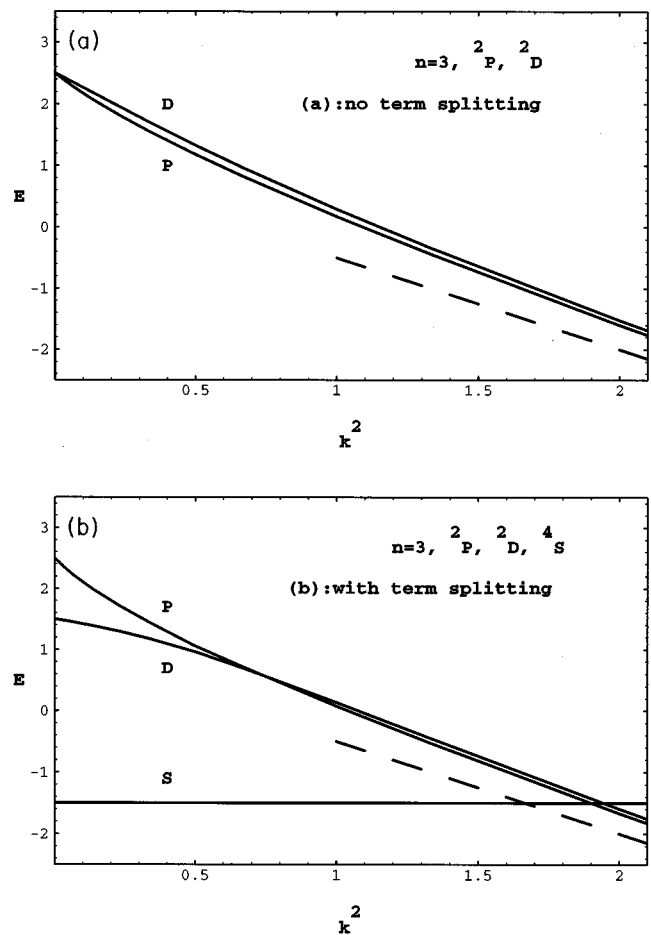
centers in silicon (see the references in the Introduction). The effect of configuration interaction on the energy ordering in C_{60}^{n-} is discussed in Sec. IV B.

In Sec. V the effective Hamiltonian $\mathcal{H}_{\text{eff}}$ is introduced to allow for the coupling to the eight different h_g modes. Some space is devoted to deriving the corrections that are needed to get a good representation of the low-energy levels, and it is shown that these corrections are really quite small, and do not do much to alter the relative energies of the various configurations. We may thus use the single-mode calculations of the earlier sections together with the effective parameters with confidence, though it is important to remember always that this effective Hamiltonian is directed to giving the correct ground state, and is of no use for the spectrum of excited states.

In Sec. VI the effect of a "warping" potential produced by anharmonicities in the vibrational restoring force and higher-order terms in the Jahn-Teller interaction is considered. This term will shift the low-lying energy levels, but it will not split them. In practice, this term is probably not important in C_{60}^{n-} because of the weakness of the Jahn-Teller interaction, but it has been included because the theory is interesting and is new in the context of the multiple electron states.

II. THE LOW-LYING ENERGY LEVELS AT STRONG JAHN-TELLER COUPLING

In this section we start by describing a parametrization of an h_g mode in terms of a set of angles in such a way as to make the best use of the SO(3) invariance (Sec. II A). We then take each configuration of the form p^n in turn and discuss the energy-level structure.

In each case the process starts by setting up the Jahn-Teller interaction as a matrix of the five components of an h_g mode acting from the basis of the electronic states, using the angular parametrization (1), and finding a set of rotations that diagonalize the Jahn-Teller matrix. The choice of the remaining angular parameter that minimizes the lowest root

then puts the system onto a particular SO(3) invariant surface in phase space and forces a form for the kinetic energy. A set of pseudorotational energy levels follows. Finally we bring in the phase changes of the electronic state (the Berry phase) over the surface in phase space, and find a further limitation on the choice of pseudorotational states, leading to a predicted structure of energy levels.

A. The h_g normal modes

The SO(3) invariance of these systems is exploited by making a parametrization of the five components of a set of h_g normal coordinates in the following way:[8]

$$q_1 = q[(\tfrac{3}{2}\cos^2\theta - \tfrac{1}{2})\cos\alpha + (\sqrt{3}/2)\sin^2\theta \ \sin\alpha \ \cos2\gamma],$$

$$q_2 = q[(\sqrt{3}/2)\sin2\theta \ \cos\phi \ \cos\alpha - \tfrac{1}{2}\sin2\theta \ \cos\phi \ \sin\alpha \ \cos2\gamma + \sin\theta \ \sin\phi \ \sin\alpha \ \sin2\gamma],$$

$$q_3 = q[(\sqrt{3}/2)\sin^2\theta \ \sin2\phi \ \cos\alpha + \tfrac{1}{2}(1+\cos^2\theta)\sin2\phi \ \sin\alpha \ \cos2\gamma + \cos\theta \ \cos2\phi \ \sin\alpha \ \sin2\gamma], \quad (1)$$

$$q_4 = q[(\sqrt{3}/2)\sin^2\theta \ \cos2\phi \ \cos\alpha + \tfrac{1}{2}(1+\cos^2\theta)\cos2\phi \ \sin\alpha \ \cos2\gamma - \cos\theta \ \sin2\phi \ \sin\alpha \ \sin2\gamma],$$

$$q_5 = q[(\sqrt{3}/2)\sin2\theta \ \sin\phi \ \cos\alpha - \tfrac{1}{2}\sin2\theta \ \sin\phi \ \sin\alpha \ \cos2\gamma - \sin\theta \ \cos\phi \ \sin\alpha \ \sin2\gamma],$$

where taking $0 \leq q < \infty$, $0 \leq \alpha < \pi/3$, $0 \leq \gamma < \pi$, $0 \leq \theta < \pi/2$, $0 \leq \phi < 2\pi$ ensures that all possible distortions in the five-dimensional phase space are covered without repetition. This parametrization is designed so that $\Sigma q_i^2 = q^2$ and the angles θ, γ, ϕ behave as Euler angles for the rotations.

In terms of these variables the kinetic-energy operator for the normal modes takes the form

$$\mathscr{H}_{KE} = -\frac{1}{2}\left[q^{-4}\frac{\partial}{\partial q}\left(q^4 \frac{\partial}{\partial q}\right) + \frac{1}{q^2\sin3\alpha}\frac{\partial}{\partial\alpha}\left(\sin3\alpha\frac{\partial}{\partial\alpha}\right)\right]$$
$$+ \frac{1}{8q^2}\left[\frac{\lambda_x^2}{\sin^2(\alpha - 2\pi/3)} + \frac{\lambda_y^2}{\sin^2(\alpha + 2\pi/3)} + \frac{\lambda_z^2}{\sin^2\alpha}\right], \quad (2)$$

where $\{\lambda_x, \lambda_y, \lambda_z\}$ are the three components of an angular momentum operator λ within the phonon space. Explicitly,

$$\lambda_x = i \ \cos\gamma\left(\cot\theta\frac{\partial}{\partial\gamma} - \csc\theta\frac{\partial}{\partial\phi}\right) + i \ \sin\gamma\frac{\partial}{\partial\theta},$$

$$\lambda_y = -i \ \sin\gamma\left(\cot\theta\frac{\partial}{\partial\gamma} - \csc\theta\frac{\partial}{\partial\phi}\right) + i \ \cos\gamma\frac{\partial}{\partial\theta}, \quad (3)$$

$$\lambda_z = i \ \frac{\partial}{\partial\gamma}.$$

The potential energy of the uncoupled vibrations is simply $\frac{1}{2}q^2$.

B. The configurations p^1 and p^5

These configurations have already been extensively studied as $T \otimes (\tau_2 \oplus \epsilon)$, p^1 explicitly and p^5 by implication. The Jahn-Teller interaction for p^1 can be written

$$M_T = +\frac{1}{2}k\begin{bmatrix} q_1 - \sqrt{3}q_4 & -\sqrt{3}q_3 & -\sqrt{3}q_2 \\ -\sqrt{3}q_3 & q_1 + \sqrt{3}q_4 & -\sqrt{3}q_5 \\ -\sqrt{3}q_2 & -\sqrt{3}q_5 & -2q_1 \end{bmatrix} \quad (4)$$

and writing this down defines the coupling coefficient k, which reappears throughout this paper. In terms of the variables (1) the linear Jahn-Teller interaction can be written[8]

$$k\mathscr{T}_P^{-1}\begin{bmatrix} \frac{1}{2}q(\cos\alpha - \sqrt{3} \ \sin\alpha) & 0 & 0 \\ 0 & \frac{1}{2}q(\cos\alpha + \sqrt{3} \ \sin\alpha) & 0 \\ 0 & 0 & -q \ \cos\alpha \end{bmatrix}\mathscr{T}_P, \quad (5)$$

where $\mathscr{T}_P$ is an orthogonal matrix given by

$$\mathscr{T}_P = B_P(\gamma) C_P(\theta) D_P(\phi) \qquad (6)$$

and the orthogonal matrices $B_P(\gamma)$, $C_P(\theta)$, and $D_P(\phi)$ are given, together with other rotation matrices, in the Appendix. The matrix $\mathscr{T}_P$ operating on the components of a vector is a general three-dimensional rotation in Euler angle form. From this transformation it is clear that the lowest root of the matrix is $-kq \cos\alpha$, and is constant over all the rotations $\mathscr{T}_P$, and this root is lowest of all when $\alpha = 0$. This transformation also gives eigenvectors for the roots of the matrix, and the eigenvector for this lowest root is

$$|u\rangle = \sin\theta \cos\phi |\xi\rangle + \sin\theta \sin\phi |\eta\rangle + \cos\theta |\zeta\rangle, \qquad (7)$$

where $|\xi\rangle$, $|\eta\rangle$, and $|\zeta\rangle$ are the three components of the electronic p base.

Using the foregoing results we now go ahead and apply the full adiabatic approximation by looking for a solution to the Schrödinger equation in the general form

$$\Psi = \psi(q, \alpha, \gamma, \theta, \phi) u(q, \alpha, \gamma, \theta, \phi, \mathbf{r}), \qquad (8)$$

where u, the electronic wave function, is a vector in the electronic space $\{|\xi\rangle, |\eta\rangle, |\zeta\rangle\}$ and $\mathbf{r}$ represents all the electronic coordinates. Here the vector u is just the eigenvector $|u\rangle$ that has already been calculated (7). When this Ψ is substituted into the Schrödinger equation we get

$$-\tfrac{1}{2}[u\nabla^2\psi + 2\nabla\psi \cdot \nabla u + \psi\nabla^2 u] + (\tfrac{1}{2}q^2 - kq \cos\alpha)\psi u$$
$$= E\psi u, \qquad (9)$$

where $-\tfrac{1}{2}\nabla^2$ is the appropriate vibrational kinetic-energy operator. Applying closure to this equation with u gives

$$-\tfrac{1}{2}\nabla^2\psi - \nabla\psi \cdot \langle u|\nabla u\rangle - \tfrac{1}{2}\psi\langle u|\nabla^2 u\rangle + (\tfrac{1}{2}q^2 - kq \cos\alpha)\psi$$
$$= E\psi. \qquad (10)$$

Because $|u\rangle$ is real, $\langle u|\nabla u\rangle = 0$, but $\langle u|\nabla^2 u\rangle$ must be calculated and included.

First the kinetic-energy operator (2) is adapted to operate in the neighborhood of the minimum surface by taking out a factor $q^{-1}(\sin\alpha/\sin 3\alpha)^{1/2}$, and putting $\alpha = 0$ wherever this does not introduce infinities. The result is

$$\mathscr{H}_{KE} = -\frac{1}{2}\left[\frac{1}{q^2}\frac{\partial}{\partial q}\left(q^2\frac{\partial}{\partial q}\right) + \frac{1}{q^2\sin\alpha}\frac{\partial}{\partial\alpha}\left(\sin\alpha\frac{\partial}{\partial\alpha}\right)\right.$$
$$\left. + \frac{1}{q^2\sin^2\alpha}\frac{\partial^2}{\partial\gamma^2} + \frac{f(\alpha)}{q^2}\right] - \frac{1}{6q^2}\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)\right.$$
$$\left. + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right], \qquad (11)$$

where $f(\alpha) = \tfrac{2}{3}$ at $\alpha = 0$, and this term comes from taking the above factor out of ψ. To get $-\tfrac{1}{2}\langle u|\nabla^2 u\rangle$ only the last line of (11) need be used because $|u\rangle$ depends only on θ and ϕ, and this term is $1/(3q^2)$, which exactly cancels the $f(\alpha)/q^2$ term noted earlier. (This cancellation will not occur in the cases considered later.) The final form of the vibronic Schrödinger equation is thus

$$-\frac{1}{2}\left[\frac{1}{q^2}\frac{\partial}{\partial q}\left(q^2\frac{\partial}{\partial q}\right) + \frac{\partial}{\partial\alpha}\left(\sin\alpha\frac{\partial}{\partial\alpha}\right) + \frac{1}{q^2\sin^2\alpha}\frac{\partial^2}{\partial\gamma^2} - q^2 \right.$$
$$\left. + 2kq\right]\psi - \frac{1}{6q^2}\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right]\psi$$
$$= E\psi. \qquad (12)$$

The first part of (12) is just the Hamiltonian of a three-dimensional harmonic oscillator with a displaced origin, and the energy of its lowest state is $-\tfrac{1}{2}k^2 + \tfrac{3}{2}$. The second part is the Hamiltonian of a rotator, so the formula for the low-lying energies at strong coupling for $n = 1,5$ is

$$E_{1,5} = -\frac{1}{2}k^2 + \frac{3}{2} + \left(\frac{1}{6k^2}\right)L(L+1), \qquad (13)$$

where L is an integer. Finally we must look at the phase changes over the (θ, ϕ) surface. Inspection of the $\{q_i\}$, (1), shows that they are repeated when

$$\gamma \rightarrow \gamma + \pi, \qquad (14)$$

and also under the inversion operation

$$\theta \rightarrow \pi - \theta, \qquad \phi \rightarrow \phi + \pi, \qquad \gamma \rightarrow -\gamma. \qquad (15)$$

The electronic eigenstate (7) is seen to be invariant under (14) and to change sign under (15), and the pseudorotational eigenstates must change sign with the electronic eigenstate to preserve invariance. Thus invariance under these transformations requires L to be odd so that the ground state has $L = 1$.

C. The configurations p^2 and p^4

The terms from these two configurations are ^3P, ^1D, and ^1S.

The high spin state is simple, being yet another P state coupled to the h_g vibrations. The only extra thing we need to know is how the k in this state relates to the single electron k, i.e., we need to work out an extra reduced matrix element. The coupling constant turns out to be $-k$ so that the energies are as given by $E_{1,5}$ above, with a distortion of the opposite sign.

For the low spin states we have a sixfold basis, five D states and one S state. The S state does not have any diagonal Jahn-Teller coupling, but it is coupled to the D states. The Jahn-Teller interaction matrix (partitioned to distinguish the S and D bases) is

$$M_{SD} = -k \begin{bmatrix} 0 & -\sqrt{2}q_1 & -\sqrt{2}q_2 & -\sqrt{2}q_3 & -\sqrt{2}q_4 & -\sqrt{2}q_5 \\ -\sqrt{2}q_1 & q_1 & \frac{1}{2}q_2 & -q_3 & -q_4 & \frac{1}{2}q_5 \\ -\sqrt{2}q_2 & \frac{1}{2}q_2 & \frac{1}{2}q_1 + \frac{\sqrt{3}}{2}q_4 & \frac{\sqrt{3}}{2}q_5 & \frac{\sqrt{3}}{2}q_2 & \frac{\sqrt{3}}{2}q_3 \\ -\sqrt{2}q_3 & -q_3 & \frac{\sqrt{3}}{2}q_5 & -q_1 & 0 & \frac{\sqrt{3}}{2}q_2 \\ -\sqrt{2}q_4 & -q_4 & \frac{\sqrt{3}}{2}q_2 & 0 & -q_1 & -\frac{\sqrt{3}}{2}q_5 \\ \sqrt{2}q_5 & \frac{1}{2}q_5 & \frac{\sqrt{3}}{2}q_3 & \frac{\sqrt{3}}{2}q_2 & -\frac{\sqrt{3}}{2}q_5 & \frac{1}{2}q_1 - \frac{\sqrt{3}}{2}q_4 \end{bmatrix}, \tag{16}$$

where the coupling constants have been calculated as reduced matrix elements in terms of the single-electron coupling constant k. This is put in terms of the parametrization (1) and transformed to a nearly diagonal form by a sequence of orthogonal transformations. This transformation has a block-diagonal form, with a 5×5 block to rotate the D bases, as given in the Appendix, and a 1×1 unit matrix block for the S basis. It is

$$\mathscr{T}_{SD} = A_{SD}(\alpha) B_{SD}(\gamma) C_{SD}(\theta) D_{SD}(\phi), \tag{17}$$

where

$$A_{SD}(\alpha) = \begin{bmatrix} 1 & 0 \\ 0 & A_D(\alpha) \end{bmatrix}, \quad B_{SD}(\gamma) = \begin{bmatrix} 1 & 0 \\ 0 & B_D(\gamma) \end{bmatrix},$$

$$C_{SD}(\theta) = \begin{bmatrix} 1 & 0 \\ 0 & C_D(\theta) \end{bmatrix}, \quad \text{and} \quad D_{SD}(\phi) = \begin{bmatrix} 1 & 0 \\ 0 & D_D(\phi) \end{bmatrix}. \tag{18}$$

Then

$$\mathscr{T}_{SD} [M_{SD}] \mathscr{T}_{SD}^{-1} = [M_{SD}(\alpha)] \tag{19}$$

and the interaction matrix $[M_{SD}(\alpha)]$ takes the form

$$M_{SD}(\alpha) = -kq \begin{bmatrix} 0 & \sqrt{2}\cos\frac{3\alpha}{2} & 0 & 0 & \sqrt{2}\sin\frac{3\alpha}{2} & 0 \\ \sqrt{2}\cos\frac{3\alpha}{2} & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & \cos\left(\alpha - \frac{\pi}{3}\right) & 0 & 0 & 0 \\ 0 & 0 & 0 & -\cos\alpha & 0 & 0 \\ \sqrt{2}\sin\frac{3\alpha}{2} & 0 & 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & 0 & 0 & \cos\left(\alpha + \frac{\pi}{3}\right) \end{bmatrix} \tag{20}$$

This matrix is left incompletely diagonalized to make it obvious where extra terms would have to be put in if the ^1D and ^1S terms were not assumed degenerate in the first place. The lowest value of the lowest eigenvalue of this matrix occurs at $\alpha = 0$, and it is $-2kq$. In this case the eigenvector will be given by a linear combination of the first two columns of the matrix $\mathscr{T}_{SD}^{-1}$ and (still at $\alpha = 0$) this is

$$u = \begin{bmatrix} \frac{1}{\sqrt{3}} \\ \cdots \\ \sqrt{\frac{2}{3}} v_D \end{bmatrix}, \tag{21}$$

where

$$
v_D = \begin{bmatrix} \frac{1}{2}(3\cos^2\theta - 1) \\[12pt] \frac{\sqrt{3}}{2}\sin 2\theta \cos\phi \\[12pt] \sqrt{3}\sin^2\theta \cos\phi \sin\phi \\[12pt] \frac{\sqrt{3}}{2}\sin^2\theta \cos 2\phi \\[12pt] \frac{\sqrt{3}}{2}\sin 2\theta \sin\phi \end{bmatrix}. \tag{22}
$$

Operating on this with (11) gives

$$
-\frac{1}{2}\nabla^2 u = \frac{1}{6q^2}\begin{bmatrix} 0 \\ \cdots \\ 6\sqrt{\frac{3}{3}}v_D \end{bmatrix}, \tag{23}
$$

so $-\frac{1}{2}\langle u|\nabla^2 u\rangle = 2/3q^2$. Finally we get the vibronic Schrödinger equation in this case to be, at $\alpha = 0$,

$$
-\frac{1}{2}\left[\frac{1}{q^2}\frac{\partial}{\partial q}\left(q^2\frac{\partial}{\partial q}\right) + \frac{1}{q^2\sin\alpha}\frac{\partial}{\partial\alpha}\left(\sin\alpha\frac{\partial}{\partial\alpha}\right) + \frac{1}{q^2\sin^2\alpha}\frac{\partial^2}{\partial\gamma^2}\right.
$$
$$
\left. -q^2 + 4kq\right]\psi + \frac{1}{q^2}\left[\frac{2}{3} - \frac{1}{3}\right]\psi - \frac{1}{6q^2}\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)\right.
$$
$$
\left. + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right]\psi = E\psi. \tag{24}
$$

Treating this equation as before gives

$$
E_{2,4} = -2k^2 + \frac{3}{2} + \frac{1}{12k^2} + \left(\frac{1}{24k^2}\right)L(L+1). \tag{25}
$$

This is very similar to the equation for the energy of p^1 (13), but now the electronic eigenstate is invariant under both (14) and (15), and the pseudorotational eigenstates must also be invariant under these transformations, which limits L to be an even integer. Thus the lowest two states are S and D states corresponding to the uncoupled electronic states.[9]

D. The configuration p^3

The terms from this configuration, before coupling, would be ^4S, ^2D, and ^2P. Here the high spin state is trivial, having no Jahn-Teller coupling. For the low spin states we start by finding reduced matrix elements of the Jahn-Teller coupling within and between ^2D and ^2P. The result is that the only nonzero Jahn-Teller coupling is between ^2D and ^2P, the matrix elements coupling P to P or D to D are zero. This absence of diagonal Jahn-Teller terms is noted in the context of cubic symmetry in Ref. 5, and why it happens is discussed in Ref. 10. The interaction matrix in the basis of P and D states is found, using vector coupling coefficients, to be

$$
M_{PD} = \frac{\sqrt{3}}{2}k\begin{bmatrix} 0 & 0 & 0 & \sqrt{3}q_5 & q_3 & -q_2 & q_5 & -q_4-\sqrt{3}q_1 \\ 0 & 0 & 0 & -\sqrt{3}q_2 & -q_4+\sqrt{3}q_1 & q_5 & q_2 & -q_3 \\ 0 & 0 & 0 & 0 & -q_5 & 2q_4 & -2q_3 & q_2 \\ \sqrt{3}q_5 & -\sqrt{3}q_2 & 0 & 0 & 0 & 0 & 0 & 0 \\ q_3 & -q_4+\sqrt{3}q_1 & -q_5 & 0 & 0 & 0 & 0 & 0 \\ -q_2 & q_5 & 2q_4 & 0 & 0 & 0 & 0 & 0 \\ q_5 & q_2 & -2q_3 & 0 & 0 & 0 & 0 & 0 \\ -q_4-\sqrt{3}q_1 & -q_3 & q_2 & 0 & 0 & 0 & 0 & 0 \end{bmatrix}. \tag{26}
$$

This matrix is transformed by a series of rotations in the angles, ϕ, θ, γ, and the 8×8 rotation matrix is made up in block-diagonal form from matrices given in the Appendix as follows:

$$\mathscr{T}_{PD}=\left[\begin{array}{c|c} B_P(\gamma) & 0 \\ \hline 0 & B_D(\gamma) \end{array}\right]\left[\begin{array}{c|c} C_P(\theta) & 0 \\ \hline 0 & C_D(\theta) \end{array}\right]\left[\begin{array}{c|c} D_P(\phi) & 0 \\ \hline 0 & D_D(\phi) \end{array}\right], \tag{27}$$

with the result that

$$M_{PD}(\alpha)=\mathscr{T}_{PD}M_{PD}\mathscr{T}_{PD}^{-1}=\sqrt{3}kq\left[\begin{array}{ccc|ccccc}
0 & 0 & 0 & 0 & 0 & 0 & 0 & -\sin\left(\alpha+\dfrac{\pi}{3}\right) \\
0 & 0 & 0 & 0 & -\sin\left(\alpha-\dfrac{\pi}{3}\right) & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & \sin\alpha & 0 & 0 \\
\hline
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & -\sin\left(\alpha-\dfrac{\pi}{3}\right) & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & \sin\alpha & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
-\sin\left(\alpha+\dfrac{\pi}{3}\right) & 0 & 0 & 0 & 0 & 0 & 0 & 0
\end{array}\right].$$

$$\tag{28}$$

At this stage the matrix is still in block form, so that different energies for the ^2D and ^2P states could be inserted on the diagonal. With these states degenerate the eigenvalues are obviously

$$E=\sqrt{3}kq\{\pm\sin(\alpha+\pi/3),\pm\sin(\alpha-\pi/3),\pm\sin\alpha,0,0\}. \tag{29}$$

All of these roots that are not identically zero have the same minimum energy for some choice of α, and we choose to take $\sin\alpha=1$. The fact that this lies outside the original region $0<\alpha<\pi/3$ does not matter, we are just looking at a different copy of the phase space. With this choice of α the $\{q_i\}$ are given by

$$q_1=q[(\sqrt{3}/2)\sin^2\theta\,\sin2\gamma],$$

$$q_2=q(-\tfrac{1}{2}\sin2\,\cos\phi\,\cos2\gamma+\sin\theta\,\sin\phi\,\sin2\gamma),$$

$$q_3=q[\tfrac{1}{2}(1+\cos^2\theta)\sin2\phi\,\cos2\gamma+\cos\theta\,\cos2\phi\,\sin2\gamma], \tag{30}$$

$$q_4=q[\tfrac{1}{2}(1+\cos^2\theta)\cos2\phi\,\cos2\gamma-\cos\theta\,\sin2\phi\,\sin2\gamma],$$

$$q_5=q(-\tfrac{1}{2}\sin2\theta\,\sin\phi\,\cos2\gamma-\sin\theta\,\cos\phi\,\sin2\gamma),$$

while the eigenstate for the lowest energy comes out as

$$u=\frac{1}{\sqrt{2}}\left[\begin{array}{c}
\sin\theta\,\cos\phi \\
\sin\theta\,\sin\phi \\
\cos\theta \\
\hline
\dfrac{\sqrt{3}}{2}\sin^2\theta\,\sin2\gamma \\
-\cos\theta\,\sin\theta\,\cos\phi\,\sin2\gamma-\sin\theta\,\sin\phi\,\cos2\gamma \\
\tfrac{1}{2}(1+\cos^2\theta)\sin2\phi\,\sin2\gamma-\cos\theta\,\cos2\phi\,\cos2\gamma \\
\tfrac{1}{2}(1+\cos^2\theta)\cos2\phi\,\sin2\gamma+\cos\theta\,\sin2\phi\,\cos2\gamma \\
-\cos\theta\,\sin\theta\,\sin\phi\,\sin2\gamma+\sin\theta\,\cos\phi\,\cos2\gamma
\end{array}\right].$$

$$\tag{31}$$

To find the strong coupling pseudorotational states in this case we must use the appropriate form for the vibrational kinetic energy, which is (2) at $\alpha=\pi/2$. In order to standardize the harmonic oscillator part of the operator this time we take a factor $(q^3\sin3\alpha)^{-1/2}$ out of ψ before setting $\alpha=\pi/2$ and get

$$\mathscr{H}_{\text{KE}}=-\frac{1}{2}\left[\frac{1}{q}\frac{\partial}{\partial q}\left(q\frac{\partial}{\partial q}\right)+\frac{1}{q^2}\frac{\partial^2}{\partial\alpha^2}+\frac{9}{4q^2}\right]$$
$$-\frac{1}{8q^2}[4\lambda_x^2+4\lambda_y^2+\lambda_z^2]. \tag{32}$$

The operator on the second line is a version of the Hamiltonian of the symmetric top. The energies and eigenfunctions of the symmetric top and their relationship to the representations of finite rotations are set out in Chap. 4 of Edmonds.[11] The eigenfunctions are

$$\mathscr{D}_{M,K}^{(L)}(\phi,\theta,\gamma)=e^{i(M\phi+K\gamma)}d_{M,K}^{(L)}(\theta), \tag{33}$$

where L, M, K are integers, $L \geq |M|$, and $L \geq |K|$. With the effective moments of inertia in (32) the kinetic energy eigenvalues are

$$\frac{1}{2q^2}\left[L(L+1) - \frac{3}{4}K^2\right];$$ (34)

to find the $\nabla^2 u$ term we notice that the components of the eigenvector (31) is made up of these symmetric top eigenstates, and if it is written

$$u = \frac{1}{\sqrt{2}}\begin{bmatrix} v_1 \\ \cdots \\ v_2 \end{bmatrix},$$ (35)

then v_1 is composed of states with $L=1$, $K=0$ while v_2 has $L=2$, $K=2$, so

$$-\frac{1}{2}\nabla^2 u = \frac{1}{\sqrt{2}}\frac{1}{2q^2}\begin{bmatrix} 2v_1 \\ \cdots \\ 3v_2 \end{bmatrix},$$ (36)

so that

$$-\langle u|\tfrac{1}{2}\nabla^2 u\rangle = \frac{1}{2q^2}\frac{5}{2}.$$ (37)

The vibronic Schrödinger equation is thus

$$-\frac{1}{2}\left[\frac{1}{q}\frac{\partial}{\partial q}\left(q\frac{\partial}{\partial q}\right) + \frac{1}{q^2}\frac{\partial^2}{\partial \alpha^2} - q^2 + 2\sqrt{3}kq\right]\psi + \frac{1}{q^2}\left[\frac{5}{4} - \frac{9}{8}\right]\psi$$

$$-\frac{1}{8q^2}[4\lambda_x^2 + 4\lambda_y^2 + \lambda_z^2]\psi = E\psi.$$ (38)

The first part of this equation represents a two-dimensional harmonic oscillator with a displaced origin, and the rest the symmetric top, also with the energy origin displaced. Using the value of q at the minimum, $q = \sqrt{3}k$, the energies come out as

$$E_3 = -\frac{3}{2}k^2 + 1 + \frac{1}{24k^2} + \frac{1}{6k^2}[L(L+1) - \tfrac{3}{4}K^2].$$ (39)

The electronic eigenstate (31) is seen to be invariant under (14) and to change sign under (15), and the pseudorotational eigenstates must change sign with the electronic eigenstate to preserve invariance. Thus invariance under (14) requires K to be even, and the sign change under (15) requires the pseudorotational eigenstates to be

$$\Phi_{\text{rot}} = d^{(L)}_{M,K}(\theta)e^{iM\phi}\begin{cases} \cos K\gamma & \text{for } L \text{ odd} \\ \sin K\gamma & \text{for } L \text{ even}. \end{cases}$$ (40)

The lowest state has $L=1$, $K=0$ followed closely in energy by $L=2$, $K=2$; next comes $L=4$, $K=4$ followed by $L=3$, $K=2$. There are no $L=0$ states, and $K=0$ only occurs with odd L.[12]

III. PHYSICAL DISTORTIONS OF THE MOLECULE

Because of the large number of atoms in a C_{60} molecule, a set of h_g normal coordinates can take many forms, but a simple h_g basis approximates to a rotating quadrupole distortion of the sphere. Taking this form we find that the $\alpha = 0$ surface corresponds to an ellipsoidal $(3z^2 - r^2)$ distortion, with the direction of its axis of symmetry given by (θ, ϕ) relative to a fivefold axis. This is the type of pseudorotation to be expected with p^1, p^2, p^4, or p^5. On the other hand, the distortion at $\alpha = \pi/2$, as in p^3, is of $(x^2 - y^2)$ type, which requires the three angles (γ, θ, ϕ) to describe its orientation. This latter is called a bimodal distortion by Auerbach, Manini, and Tosatti.[6]

The sign of k and the type of distortion

For the initial coupling of a single p-type orbital to a single h_g distortion, only the products kq_i enter into the Hamiltonian. We are therefore entitled to take k positive, as we do, allowing the sign to be swallowed up in the definition of the q_i in terms of actual displacements. For instance, the form of (4) shows that there is a minimum at $q_1 = k, q_{i \neq 1} = 0$, and if the shape at the minimum is known, the sign of q_1 follows.

Once k and q_i are fixed in this way the signs are held constant for the rest of the paper. For the configurations p^n the coupling constants are given in terms of the one-electron k, sign and all. The choice of α to give the minimum energy in each case can then be translated into the actual values of the q_i.

IV. INTERMEDIATE COUPLING STRENGTHS, NUMERICAL WORK

The results reported so far have assumed both that the Jahn-Teller interaction is strong compared with the phonon energy ($k \gg 1$) and that the term splitting can be left out. In fact, we can do better than this on both counts.

A. Term energies in p^n

It is possible to express all the term energies for all the terms of p^n, all n, in terms of two parameters which are electrostatic self-energies, just as is done for atomic p^n configurations. In Condon and Shortley[13] these atomic term energies are given as

$p^2 (p^4)$	Energy		p^3	Energy
^1S	$(6)F_0 + 10F_2$		^2P	$3F_0$
^1D	$(6)F_0 + F_2$	and	^2D	$3F_0 - 6F_2$
^3P	$(6)F_0 - 5F_2$		^4S	$3F_0 - 15F_2$

(41)

where F_0 and F_2 are certain integrals of the Coulomb interaction within charge distributions depending on the p wave functions.

Exactly similar expressions can be obtained for molecular orbitals of T_1 symmetry, but the definitions of F_0 and F_2 have to be phrased a little differently. This type of calculation is done for molecular orbitals under cubic symmetry by Sugano, Tanabe, and Kamimura,[14] and their work can be modified to cover the icosahedral orbitals used here. All the integrals required are electrostatic self-energies of charge densities that are products of the T_1 wave functions taken in pairs. As the symmetric product $T_1 \otimes T_1$ contains only

$A \oplus H$, *any product of p or t_1 wave functions can be written as a linear combination of the A and H (S and D) states. The Coulomb energy operator,* $\Sigma_{i>j} e^2/4\pi\epsilon_0 r_{ij}$, *is invariant under space rotations, so only two distinct integrals survive, one for the A product and one for the H product. It turns out that F_0 is three times the self-energy of the A product, while F_2 is 3/2 times the self-energy of the H product. For example, if we represent two components of the T_1 states as ψ_x and ψ_y, then one of the H components of the symmetric product is* $(\psi_x\psi_y + \psi_y\psi_x)/\sqrt{2}$. *The product of the two wave functions produces a charge density* $\rho(\mathbf{r}) = \sqrt{2}\,\psi_x\psi_y$ *and*

$$F_2 = \frac{3}{2}\int\int \rho(\mathbf{r}_1)\frac{e^2}{4\pi\epsilon_0|\mathbf{r}_1 - \mathbf{r}_2|}\rho(\mathbf{r}_2)d\tau_1 d\tau_2. \quad (42)$$

The ψ_i here are to be interpreted as the actual (real) electronic wave functions of the molecular orbitals, a set of atomic p states are a particular example of such orbitals. As self-energies the integrals F_0 and F_2 are intrinsically positive. The fact that the orbitals are spread over the C$_{60}$ sphere will make them rather smaller than similar integrals in atoms.

The effect of including these term splittings at strong Jahn-Teller coupling can be seen by including them in the various interaction matrices. In p^2 and p^4 the Jahn-Teller depression of the ^3P state is 1/4 of that in the combined singlet states, so that at strong Jahn-Teller coupling the ^3P state is above the singlet states, and we have seen that of the singlet states, ^1S is below ^1D. There is thus a complete reversal of the ordering of the states as the Jahn-Teller coupling strength is turned up, as is shown by the calculation illustrated in Fig. 1.

For p^3 there is an uncoupled ^4S state, with no Jahn-Teller interaction. Because of the term splitting between the ^2D and ^2P states themselves, the Jahn-Teller effect will only come in at second order, so if it is weaker than the term splitting it is effectively quenched. A strong Jahn-Teller interaction puts the ^2P state marginally below the ^2D state, and both well below the ^4S, so again the Jahn-Teller interaction reverses the order of the states, as shown in Fig. 2.

B. Term energies in C$_{60}^{n-}$

The p^n model is not really good enough to represent the term splittings in C$_{60}^{n-}$. This is because the next unoccupied orbital above t_{1u}, t_{1g}, is rather close in energy. The result is that configurations other than p^n may be mixed in, and this will alter the simple nature of the configurations assumed here. The effect of this on the term energies has been investigated by Negri, Orlandi, and Zerbetto.[15] These authors have done calculations of the energies of the low excited states of C$_{60}^{n-}$ up to $n=6$ with the inclusion of the t_{1g} states in their base along with the t_{1u} states. They find a different ordering of terms from the Hund's rule ordering of p^n as well as extra terms deriving from other configurations, particularly so when $n>3$ and higher spin states appear. They point out that the energies are all so close that other types of calculation may well give other orderings, but it is worth listing a few of their results to show the sort of thing that happens.

n					
2	^1A_g	^1A_u	$^3T_{1g}$	^1H_g	
	0	0.16	0.19	0.30	
	(^1S)		(^3P)	(^1D)	
3	^4A_u	^4A_g	$^2T_{1u}$	^2H_u	^4H_g
	0	0.10	0.42	0.43	0.45
	(^4S)		(^2P)	(^2D)	
4	^1A_g	$^3T_{1g}$	^1A_u	^1H_g	$^1T_{1u}$
	0	0.01	0.14	0.15	0.16
	(^1S)	(^3P)		(^1D)	
5	^4A_g	$^2T_{1u}$	$^6T_{1u}$	^4A_u	^4T_g ^4H_g
	0	0.01	0.11	0.19	0.21 0.24
		(^2P)			

$$(43)$$

Here the energies are in eV, and the terms that would be expected from p^n are shown in parentheses.

The amount of configuration interaction indicated by the energies in this table will alter the model used in the present calculations in several ways. The accidental SO(3) symmetry will disappear, and with it the simple way all the coupling coefficients depend on one parameter k. Without the symmetry basis the size of the matrices make the type of numerical calculation described in the next section unprofitable, but these calculations do show how interpolation can be used. The Jahn-Teller coupling coefficients within and between terms will additionally depend on the coupling within t_{1g} and there will be pseudo-Jahn-Teller coupling via odd modes of vibration between odd and even terms with the same spin.

It is possible to make some general remarks about the effect of the Jahn-Teller interaction on the terms shown in (43). The magnitude of the Jahn-Teller energy is about 0.1 eV (Ref. 16) as is the average frequency of the h_g modes, so the scale of the term splitting used in Figs. 1(b) and 2(b) is of the correct order for C$_{60}^{n-}$, which should come in in the region of $k^2 = 1$ to 1.5. In $n=2$ and $n=4$ the configuration interaction already makes the $^1A_g(^1S)$ state lowest, and the Jahn-Teller interaction will probably encourage it to remain so. There is experimental evidence that this is so in $n=2$.[17] In $n=4$ the near degeneracy of $^1A_g(^1S)$ and $^3T_{1g}(^3P)$ will allow a linear coupling within the triplet state to make it the ground state if the coupling is really weak, but at the intermediate coupling strength assumed, the coupling in $\{^1A_g(^1S), {}^1H_g(^1D)\}$ can be expected to bring $^1A_g(^1S)$ to the bottom. In $n=3$ the Hund's rule that puts a quartet state lowest is obeyed, and there is the possibility of interaction with the ^4H_g state to push this state down lower than is shown in Fig. 2(b). In $n=5$ the number of nearby quartet states could make the effect of off-diagonal coupling of the ^4A_g state competitive with the effect of linear coupling of $^2T_{1u}(^2P)$.

C. Numerical work

All of the $p^n \otimes h$ systems can be set up as matrices in the uncoupled states for numerical diagonalization, using the SO(5) group for handling the phonon excitations as described in Refs. 8 and 18.

The method involves first taking all the h mode excitations for the n-phonon state, and classifying them according to irreducible representations of SO(5) and SO(3) (angular momentum). This provides a unique labeling system for all the states needed in this study. These states are then coupled to the electronic state or states, and all the coupled states of the required angular momentum are selected out as bases. The Jahn-Teller interaction can then be set out as a matrix within these bases, using angular momentum coupling coefficients together with a limited number of fractional parentage coefficients for SO(5)⊃SO(3), and formulas can be found for a general n. If term energies are to be included they appear on the diagonal of the matrix along with the uncoupled phonon energy. The resulting infinite matrix expands with n, but not as fast as if the symmetry adapted bases had not been used. As what is required here is only the energy of the few lowest states, the application of a Lanczos method to a matrix cutoff at a large value of n is suitable and fast enough for the accuracy of the results to be monitored. To do the extrapolation to find the value of the $1/k^2$ terms in the energies it was found necessary to take a range of coupling strengths to give values of the Jahn-Teller energy of 50 to 100. The cutoff n needed to be somewhat larger than the Jahn-Teller energy.

For p^1 the matrix has already been set up,[8] but now with very much increased computing power at hand, and with the use of the Lanczos method, the calculations can be pushed to a large enough k to verify that, as $1/k^2 \rightarrow 0$, the lowest energy does tend to $E_{1,5}$ [Eq. (13)] with $L=1$.

The matrices for p^3 are simpler and smaller than those for p^2. They are simplified as a result of the lack of Jahn-Teller coupling within ^2P and within ^2D. States with even numbers of phonons associated with ^2P will only couple to states with odd numbers of phonons associated with ^2D, and vice versa. In particular, as no S states can be produced from electronic P states with vibrations of this symmetry, no S states will change energy with Jahn-Teller coupling strength (see Ref. 6, Fig. 6). The matrices that give the lowest P and D states have been set up and run with large enough values of k to verify that the lowest energies are given correctly to order $1/k^2$ by E_3 [Eq. (39)] with $L=1$, $K=0$ and with $L=2$, $K=2$. The term energies have also been included in these matrices, and in Fig. 2 the energies for p^3 are plotted with and without the term splitting. An arbitrary D-P splitting of $2\hbar\omega$ is used, and the diagram shows the reversal of the states as the Jahn-Teller coupling is increased, as described in the previous subsection.

The extra complication in the matrices for p^2 arises from the existence of coupling between S and D, as well as within D. Consequently, there is no segregation of the product states, which makes the matrix for p^2,D significantly larger than the matrix for p^3,D, and two different reduced matrix elements must be introduced to allow for the two types of coupling. These matrices have also been constructed and run at strong coupling, to verify the asymptotic form of the energy, and at weak coupling, with and without term splittings, to provide Fig. 1. Here the choice of parameters is exactly the same as for Fig. 2.

V. MULTIPLE MODES OF VIBRATION, $\mathscr{H}_{\text{eff}}$

At this point we should relax the assumption made so far that there is only one set of h_g modes to be considered. In fact, there are eight h_g vibrational modes in C_{60} spread over a range of frequencies such that the highest frequency is about five times the lowest.[19] The calculated coupling strengths between these modes and the partially occupied t_{1u} orbital vary a good deal between authors, but all the calculations agree that no one mode is much more strongly coupled than all the others. Under these circumstances it makes sense to work in terms of an effective or averaged mode, and it is possible to make a choice that gives the best approximation to the ground-state energy.[20]

The choice goes like this: Assume that there is a set of modes of appropriate symmetry, with the phonon energy of the ith mode $\hbar\omega_i$, and its coupling strength is k_i (this is in the same sort of reduced units that have been used in this paper, so that the Jahn-Teller energy for that particular mode would be proportional to $k_i^2\hbar\omega_i$). Then an orthogonal transformation on the mode coordinates picks out a chosen effective mode whose frequency and coupling strength are defined by

$$\hbar\omega_{\text{eff}}=\hbar\langle\omega\rangle=\frac{\sum_i \hbar\omega_i k_i^2}{\sum_i k_i^2} \quad \text{and} \quad k_{\text{eff}}^2=\sum_i k_i^2. \quad (44)$$

We now find the low-lying energy levels of a Jahn-Teller Hamiltonian of the appropriate form with k_{eff} and ω_{eff} as parameters, called $\mathscr{H}_{\text{eff}}$, and regard all the rest of the original Hamiltonian as a perturbation. The rest of the Hamiltonian consists of a set of normal modes whose frequencies lie between the frequencies of the original modes, and they are coupled to the effective mode by an interaction $\mathscr{H}_I$ that has only off-diagonal matrix elements, and so only introduces a correction by second-order perturbation.

The size of this correction to the eigenstates of $\mathscr{H}_{\text{eff}}$ depends on the mean-square width of the distribution of ω_i's of which $\omega_{\text{eff}}=\langle\omega\rangle$ is a weighted average. The correction is always to lower energy, and it increases with k_{eff} to an upper limit that is some fraction of $\sigma=\hbar(\langle\omega^2\rangle-\langle\omega\rangle^2)/\langle\omega\rangle$ and independant of k_{eff}, reached at about $k_{\text{eff}}=1$. At small k_{eff}, $\mathscr{H}_{\text{eff}}$ is correct up to a correction of order k_{eff}^4. Given some assumption about the distribution of k_i's over the ω_i's it is possible to calculate these corrections at strong and weak coupling as described below for the systems we are concerned with here. Any calculation of the multimode correction at intermediate coupling strengths is prohibitively complicated, but it has been done numerically in a much simpler case,[21] and the correction did vary smoothly between the two regimes in the way described above.

For the sake of having some reasonable corrections to put in the calculations we shall assume here that the eight h_g modes all have the same one-electron Jahn-Teller coupling coefficient k_i, and that their frequencies are uniformly spread between ω and 5ω, with the result that $\omega_{\text{eff}}=\omega/3$, $k_{\text{eff}}^2=8k_i^2$, and $\sigma=4\omega_{\text{eff}}/21$. Each k_i is assumed to be positive, as is k_{eff}, with the signs taken up in the definitions of normal coordinates of each mode, and the distortion associated with ω_{eff} is the sum of distortions proportional to k_i in each mode (see Ref. 20).
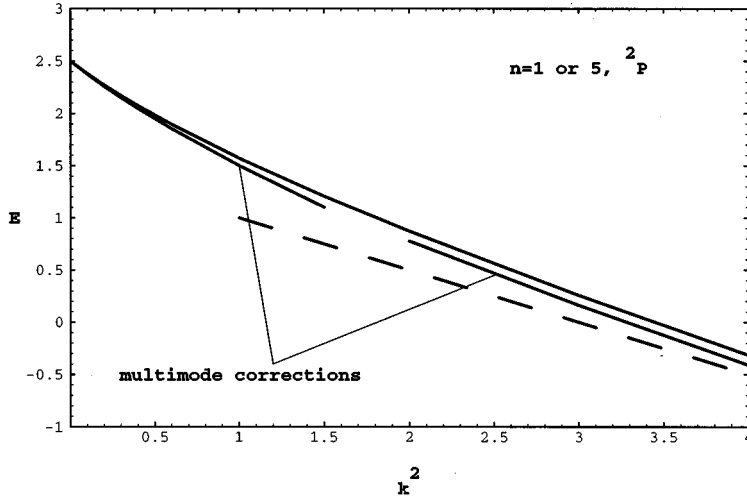
FIG. 3. Calculated lowest energy level for $p \otimes h$. Multimode corrections to $\mathcal{H}_{\text{eff}}$ for the eight h_g modes of C_{60} at weak and strong coupling are shown. The dashed line shows the asymptotic energy.

A. The significance of $\mathcal{H}_{\text{eff}}$

The effective Hamiltonian is chosen in the first place to give the best match to the lowest energy level in the system consistent with the use of a single effective frequency. In particular, it gives correctly the energy of the minimum on the lowest adiabatic potential energy surface (APES), the first term in (13). All the corrections discussed below are concerned with the residual effects of the kinetic-energy terms, though clearly this effective Hamiltonian takes care of many of these too. Hence calculations, such as those by Koga and Morokuma,[16] which work out the Jahn-Teller energy by minimizing the energy under static distortions of the cage, should be interpreted in terms of the effective Hamiltonian. Their Jahn-Teller energy of about 2 kcal/mol in C_{60}^- should be equated with the APES minimum energy of $-\frac{1}{2}k_{\text{eff}}^2 \hbar \omega_{\text{eff}}$. (These authors also calculate the small extra energy produced by a further distortion, the "warping" effect, which is not allowed for here, but see Sec. VI.)

As appears in the following subsections, the corrections that are calculated to the single-mode approximation are really quite small, and do not differ greatly from one configuration to another. They are so similar and unimportant that they have been left out as an unnecessary complication from Figs. 1 and 2; Fig. 3 can serve to show the general effect. This means that the effective Hamiltonian $\mathcal{H}_{\text{eff}}$ works very well on its own for calculations of the low-lying energies, even where, as here, the coupling strength is spread over a rather wide range of frequencies. It was necessary to do the calculations detailed below to justify the use of $\mathcal{H}_{\text{eff}}$, but it is a happy outcome that their results can be neglected.

B. Multimode corrections for p^1, p^5, and p^2, p^4: ^3P

All these P states are relatively simple to work with, and can be treated under one heading. The methods of Ref. 20 for strong coupling can be used straightforwardly. The corrections discussed below are included in the plot of energies in Fig. 3. The corrections at large and small coupling strength are as calculated, and they should presumably be joined by a smooth curve.

1. Strong coupling

At strong coupling the correction to the energy of the lowest APES comes by coupling to the pair of upper surfaces that are at an energy $(3/2)k_{\text{eff}}\hbar\omega_{\text{eff}}q$ above the lowest one, and the minimum occurs at $q = k_{\text{eff}}$, as can be seen from (5). Consequently the energy denominator for this second-order perturbation is $(3/2)k_{\text{eff}}^2\hbar\omega_{\text{eff}}$. The numerator of the second-order perturbation can be found by using the sum rules (25) and (27) of Ref. 20, but as the use of (27) requires some redefinition of the interaction matrices from the usage in this paper we shall work directly from Eqs. (18) and (22) of that paper. Putting these two equations together, and concentrating on the largest terms at strong coupling, we find the required interaction Hamiltonian can be written in the notation of Ref. 20 as

$$\mathcal{H}_I = \sum_{j,i \neq 1} c_i k_{\text{eff}} V^{(j)} \alpha_i^{(j)\dagger}, \tag{45}$$

where $\alpha_i^{(j)\dagger}$ creates one phonon in the background set of normal modes, so this interaction connects the ground state to states with one phonon excited. The matrices $V^{(j)}$ are defined by rewriting (4) in the form

$$M_T = k \sum_j V^{(j)} q_j. \tag{46}$$

The numerator for the second-order perturbation is thus

$$\frac{1}{2}k_{\text{eff}}^2 \sum_i c_i^2 \sum_{j,n} |\langle 0|V^{(j)}|n\rangle|^2, \tag{47}$$

where the sum over n is over the excited APES's and $|0\rangle$ is the vibrational eigenstate on the lowest APES. The extra factor of 1/2 is because Ref. 20, unlike this paper, uses a_i and

$a_i^\dagger$ in the definition of the Jahn-Teller interaction [Eq. (1)]. The sum $\Sigma_{j,n}|\langle 0|V^{(j)}|n\rangle|^2 = \frac{3}{2}$ can be calculated from the eigenvectors that form the matrix in (6), and the sum $\Sigma_i c_i^2$ is $\hbar\omega_{\text{eff}}\sigma$ (σ as defined above). The result of putting all these ingredients into the second-order perturbation produces a correction to the ground-state energy of

$$-\tfrac{1}{2}\sigma, \qquad (48)$$

which is the correction shown in Fig. 3. This calculation is valid for $k_{\text{eff}}^2 \gg 1$, but the numerical work in Ref. 21 suggests that it holds for $k_{\text{eff}}^2 \gtrsim 1$, and that it is also an upper limit on the correction.

2. Weak coupling

At weak coupling, $k_i^2 \ll 1$, the Jahn-Teller interaction first comes in as a second-order perturbation, and the energy to that order is

$$E^{(2)} = -\frac{5}{4}\sum_i k_i^2\omega_i = -\frac{5}{4}k_{\text{eff}}^2\omega_{\text{eff}}. \qquad (49)$$

Consequently the multimode correction to the effective Hamiltonian is a correction to the next order of perturbation, which is fourth order in k_i.

Taking nondegenerate perturbation to fourth order is not usually done explicitly in the textbooks, but the standard methods can be used to give the expression for the correction to the ground state by a perturbation H as

$$E^{(4)} = -\sum_{l,k,n\neq 0}\frac{H_{0l}H_{lk}H_{kn}H_{n0}}{E_l E_k E_n} + \sum_{l,k\neq 0}\frac{H_{0l}H_{l0}H_{0k}H_{k0}}{E_l E_k^2} \qquad (50)$$

as long as $H_{00}=0$ as it is in this case. (Nondegenerate theory can be used because the electronic state belongs to a single irrep of the symmetry group of the Hamiltonian, and so will not be split by perturbation to any order.)

The best way to get the matrix elements to put in here is by using the SO(5)$\supset$SO(3) group chain for the phonon states as is done to prepare the matrices for numerical diagonalization. For a single mode of vibration the ground state is connected to only one singly excited phonon state, with $L=2$, and this in turn is connected to two doubly excited phonon states, with $L=2$ and $L=0$. These matrix elements of the Jahn-Teller interaction are $\sqrt{5/4}k\hbar\omega$, $\sqrt{1/2}k\hbar\omega$, and $\sqrt{7/8}k\hbar\omega$, respectively. It is very easy to substitute these into (50) to give

$$E^{(4)} = -\frac{(\tfrac{5}{4})(\tfrac{1}{2}+\tfrac{7}{8})}{2}k^4\hbar\omega + (\tfrac{5}{4})^2 k^4\hbar\omega \qquad (51)$$

$$= \frac{45}{64}k_{\text{eff}}^4\hbar\omega. \qquad (52)$$

This fourth-order correction is positive, as is usual in dynamic Jahn-Teller systems, corresponding to the fact that the asymptotic value of the energy, $E_{1,5}$ (13), is greater than $E^{(2)}$, which would not be the case with simple linear coupling. Before looking for the multimode correction to $E^{(4)}$, we should also note that the second term in (50) is a product

of two contributions from second-order perturbation, and so is correctly given by $\mathcal{H}_{\text{eff}}$, thus only the first term needs to be reanalyzed.

For the multimode system we need to consider all types of two-phonon states. Those with only one mode excited, at $2\hbar\omega_i$, are as listed above. The states with two different modes excited, at $(\hbar\omega_i + \hbar\omega_j)$, will be made up from products of the two different $L=2$ states, one from one excitation of mode i and one from one excitation of mode j. These products comprise states with $L=2$, $L=1$, and $L=0$, with the important difference that the $L=1$ state is odd under the interchange of i and j, so its matrix elements change sign under this interchange, while the other two states are even. The relative magnitudes of the coupling strengths to these three states can be found using vector coupling coefficients ($6j$ symbols), and the squares are in the ratios 7:9:4. The total coupling strength for these three states is the same as for the excitation of one phonon. Using all this information we start counting diagrams, and after some tedious algebra end up with a multimode correction in fourth order of

$$E_{mm}^{(4)} = -\frac{45}{128}\sum_{i,j}k_i^2 k_j^2\frac{(\omega_i - \omega_j)^2}{\omega_i + \omega_j}. \qquad (53)$$

This is negative definite, as expected, and when calculated with the eight-mode model for C_{60} described above gives a correction

$$E_{mm}^{(4)} = -0.07k_{\text{eff}}^4\hbar\omega_{\text{eff}}, \qquad (54)$$

and this correction is shown in Fig. 3.

C. Multimode corrections in p^2, p^3, and p^4

1. Strong coupling

At strong coupling we assume that the coupling is strong enough to override the term splittings, so that the matrices M_{SD} (16) and M_{PD} (26) can be used exactly as M_T was used in the previous subsection.

For M_{SD} (p^2 and p^4) the lowest root is at $-2kq$, so the minimum is at $q=2k$. The energies of the higher APES's above the lowest one are

$$(\tfrac{3}{2},\tfrac{3}{2},3,3,3)\times 2k^2 \qquad (55)$$

and the quantities $\Sigma_j|\langle 0|V^{(j)}|n\rangle|^2$ are, in the same order,

$$(\tfrac{8}{9},\tfrac{1}{6},\tfrac{8}{3},\tfrac{8}{3},\tfrac{1}{6})\times k^2. \qquad (56)$$

Accordingly, the strong-coupling correction in p^2 and p^4 is

$$-\frac{1}{4}\sigma\left[\frac{8/9}{3/2}+\frac{1/6}{3/2}+2\left(\frac{8/3}{3}\right)+\frac{1/6}{3}\right] = -\frac{137}{216}\sigma. \qquad (57)$$

For M_{PD} (p^3) the lowest root is at $-\sqrt{3}kq$, so the minimum is at $q=\sqrt{3}$. The energies of the higher APES's above the lowest one are

$$(\tfrac{1}{2},\tfrac{1}{2},1,1,\tfrac{3}{2},\tfrac{3}{2},2)\times 3k^2 \qquad (58)$$

and the quantities $\Sigma_j|\langle 0|V^{(j)}|n\rangle|^2$ are, in the same order,

$$(\tfrac{3}{4},\tfrac{3}{4},0,\tfrac{3}{2},0,0,0)\times k^2. \qquad (59)$$

Accordingly, the strong-coupling correction for p^3 is

$$-\frac{1}{6}\sigma\left[2\left(\frac{3/4}{1/2}\right)+\frac{3/2}{1}\right]=-\frac{3}{4}\sigma. \quad (60)$$

Evidently, at strong coupling $\mathscr{H}_{\text{eff}}$ in all these cases remains a very good approximation, only requiring a correction of a similar size to that shown in Fig. 3.

2. Weak coupling

If the term energies are neglected the calculation using $\mathscr{H}_{\text{eff}}$ is still correct to second order, and a fourth-order correction can be calculated by similar methods to those in the previous subsection. However, when term energies are included, the energy denominators in the second-order perturbation are sums of term energies and phonon energies, so simple results such as those in (49) no longer apply. It is therefore more important to have a multimode correction to the second-order energy, and this has to be done explicitly for each particular choice of term energy and distribution of mode coupling.

As an example, we have worked out the second-order perturbation for the ^2D state of p^3, using the same term splitting as in Fig. 2, and the same model of the eight h_g modes as before. The result is a second-order contribution to the energy for this particular case, which comes out in terms of the effective parameters as

$$E_{mm}^{(2)}=-0.544k_{\text{eff}}^2\hbar\omega_{\text{eff}}. \quad (61)$$

This has to be compared with the value in the single-mode approximation

$$E_{\text{eff}}^{(2)}=-0.500k_{\text{eff}}^2\hbar\omega_{\text{eff}}, \quad (62)$$

which gives the initial slope of the ^1D level as plotted in Fig. 2. Clearly, even with this broad spread of vibrational modes coupled, the corrections to the single-mode energies are quite small, but equally clearly the fine details of how the S and D levels are shown changing places are not to be relied on.

The ^3P level shown on Fig. 2 does not have a Jahn-Teller interaction with the singlet states, and the multimode corrections for this level will be the same as are shown in Fig. 3.

VI. "WARPING"

As mentioned in Sec. I, all the calculations reported so far have been made by including a Jahn-Teller interaction that is linear in the phonon coordinates to go with the original harmonic vibrational Hamiltonian. This Hamiltonian is invariant under the rotational operations of the SO(3) group, and it has been by using all the theory that is associated with vibrational symmetry that so much progress has been made. If either the restriction of linear coupling or of harmonic forces is relaxed the symmetry of the Hamiltonian is reduced to icosahedral, and the effect can be adequately represented at strong coupling as if the equipotential $\alpha=$const surface is warped, so that it has energetic hills and holes. Unless the departure from SO(3) symmetry is strong, the warping potential will derive from the lowest-order icosahedral invariant polynomial, which destroys that symmetry. Because the S, P, and D states are not split under icosahedral symmetry

whatever the coupling strength, the warping will have very little qualitative effect. The states will shift a little, but that is all. Nevertheless, it is an interesting theoretical problem. The discussion that follows is all in terms of the strong-coupling theory, but in the absence of any way of calculating the intermediate strength, the best that can be done is to interpolate between strong and weak, and we must remember that these interactions that come in with a higher power of q will be relatively small at weak coupling where the mean value of q is small.

There are two linearly independent third-order polynomials in the $\{q_i\}$ that are invariant under icosahedral symmetry. They can be written

$$I_3^{(1)}=-2q_1^3+q_1(-3q_2^2+6q_3^2+6q_4^2-3q_5^2)-3\sqrt{3}q_2^2q_4$$
$$+3\sqrt{3}q_5^2q_4-6\sqrt{3}q_2q_3q_5 \quad (63)$$

and

$$I_3^{(2)}=-2q_1^3+q_1(-3q_4^2+6q_5^2+6q_2^2-3q_3^2)+3\sqrt{3}q_4^2q_2$$
$$-3\sqrt{3}q_3^2q_2-6\sqrt{3}q_4q_3q_5. \quad (64)$$

The first of these polynomials is also invariant under the SO(3) symmetry, and can be written in terms of the angular parametrization as

$$I_3^{(1)}=-2q^3\cos3\alpha. \quad (65)$$

The second one is in general a much more complicated function of the angular parameters, but on the $\alpha=0$ spherical surface it can be expressed in the form of a sixth-order harmonic function,

$$I_3^{(2)}=V_{\text{icos}}=231z^6-315r^2z^4+105r^4z^2-5r^6$$
$$+42z(x^5-10x^3y^2+5xy^4). \quad (66)$$

This function has extrema that correspond to distortions of the molecular cage of either D_{5d} or D_{3d} symmetry, with either the D_5's at maxima and the D_3's at minima or vice versa. In between are saddle points of D_{2h} symmetry.

A. Warping in p^1 and p^5

This was described in 1989 by Ceulemans and Vanquickenborne,[22] who plotted V_{icos}, the warping potential on the $\alpha=0$ surface. The ground-state symmetries have since been discussed by Wang et al.[23] and by Dunn and Bates.[24] If the warping effect is strong enough to override the kinetic-energy terms introduced in Sec. II, then we must think of the wave function of the lowest vibronic states as being a linear combination of states localized in the minima of the warping potential. Appropriate linear combinations can be constructed by symmetry, and they must be chosen to satisfy the symmetry limitations set out in Sec. II B. There are twelve D_{5d} minima on the sphere, at the vertices of an icosahedron, but as two points on the sphere corresponds to a single point in q space, there are six distinct equilibrium positions. Similarly, if the D_{3d} points, which occur at the twenty vertices of a dodecahedron, are lowest, there are ten different equilibrium positions.

If the six D_{5d} minima are lowest, then with strong warping the states allowed by the symmetry limitations are two triplets, T_{1u} and T_{2u}, with T_{1u} lowest on any reasonable model. This means that introducing a smaller warping potential will split the first excited pseudorotational state, $L=3$, and bring down the T_{2u} component of it towards the ground state. The original T_{1u} or p state may be shifted but it will not be split.

If the ten D_{3d} minima are lowest, then the states allowed with strong warping are T_{1u}, T_{2u}, and G_u. The lowest state is again T_{1u}, while the other two together come from the $L=3$ pseudorotational state. As before the original T_{1u} or p state may be shifted but it will not be split.

B. Warping in p^2 and p^4

Here the phase space to be considered at strong coupling is also $\alpha=0$, as shown in Sec. II C, so the shape of the warping surface is just the same as for p^1 above. The only difference is in the symmetry limitations on the vibronic wave function, which must now be even under inversion on the sphere. The result is that if the six D_{5d} points are minima, then the appropriate linear combinations for the vibronic states are A_g and H_g, or S and D, with the S state lowest, which exactly account for the lowest two pseudorotational states. If the minima are at the ten D_{3d} states, then the linear combinations are of A_g, H_g, and G_g symmetry, which represent the $L=0$, $L=2$, and part of the $L=4$ pseudorotational states. Again the lowest states may be shifted by a moderate amount of warping, but they will not be split, and as their ordering is the same at weak and strong warping we may assume it remains the same throughout.

C. Warping in p^3

This is a different and more complicated problem because the minimum potential occurs at $\alpha=\pi/2$, which also corresponds to $I_3^{(1)}=0$. Equations (30) show that the q's on this surface depend on γ as well as on θ and ϕ, so there is no longer a simple spherical geometry to be exploited. Inspection of (63) and (64) shows that if the condition $I_3^{(1)}=0$ is satisfied for some set of q's it is also satisfied by the same set taken negative. However this inversion operation changes the sign of $I_3^{(2)}$, so the warping energy is symmetrical about zero, and we only need look at one choice of sign for it.

An explicit expression for the warping potential on $\alpha=\pi/2$ can be found in terms of the symmetric top wave functions quoted in Eq. (33), and it is

$$V(\phi,\theta,\gamma)=[\sqrt{11}(\mathscr{D}_{5,6}^{(6)}+\mathscr{D}_{5,-6}^{(6)}-\mathscr{D}_{-5,6}^{(6)}-\mathscr{D}_{-5,-6}^{(6)})$$
$$-\sqrt{7}(\mathscr{D}_{0,6}^{(6)}+\mathscr{D}_{0,-6}^{(6)})]+\sqrt{55}[\sqrt{11}(\mathscr{D}_{5,2}^{(6)}+\mathscr{D}_{5,-2}^{(6)}$$
$$-\mathscr{D}_{-5,2}^{(6)}-\mathscr{D}_{-5,-2}^{(6)})-\sqrt{7}(\mathscr{D}_{0,2}^{(6)}+\mathscr{D}_{0,-2}^{(6)})]. \quad (67)$$

A numerical search shows that the minimum value of $V(\phi,\theta,\gamma)$ is -2, and that it takes that minimum value over a set of six closed loops in $\{\phi,\theta,\gamma\}$ space. The fact that the minimum energy occupies a one-dimensional continuum instead of a set of discrete points as in the cases considered previously means that there will still remain some of the rotational kinetic energy associated with the ground states. It

has not proved possible yet to find an analytical form for the closed loops or to solve the associated Schrödinger equation, but, as in the other cases, warping is not expected to alter the degeneracies of the states, nor shift their energies on anything but a small scale.

VII. ENERGY ORDERING AND "NEGATIVE U"

The big difference between the Jahn-Teller energies in p^1 and p^2 that gives rise to the observed negative U in the V centers in silicon is very obvious from the figures. On the other hand, the advantage of p^2 over p^3 is quite small unless the Jahn-Teller interaction is very strong. (In comparing the figures it should be noted that, while Figs. 1 and 2 are plotted on the same scale, the scale in Fig. 3 is shorter in energy and longer in k^2.) What is not obvious from the figures alone is that their energy origins must be shifted relative to each other because of the repulsion that appears as the integral F_0 in (41), as well as by a multiple of the ionization energy E_p of the t_{1u} molecular orbital. Together these terms add the following energies to the different configurations:

$$\Delta E=-(1,2,3,4,5)E_p+(0,1,3,6,20)F_0, \quad (68)$$

for the configurations (p,p^2,p^3,p^4,p^5), respectively.

The other effect that can be seen from these figures is the effect of the Jahn-Teller interaction in reversing the order of the energy levels within a configuration. It can be seen that, even at these relatively modest term splittings, the coupling strength at which the high spin state is no longer below the low spin states can be well estimated by looking at the asymptotic large-k expressions for the Jahn-Teller energies.

In C_{60}^{n-} with configuration interaction taken into account the discussion in Sec. IV B suggests that the p^n model still gives the correct ground state, except for the case of p^5 where a high spin ground state is likely.

APPENDIX: ROTATION MATRICES

1. Rotation matrices for p states

$$B_P(\gamma)=\begin{bmatrix} \cos\gamma & \sin\gamma & 0 \\ -\sin\gamma & \cos\gamma & 0 \\ 0 & 0 & 1 \end{bmatrix}, \quad (A1)$$

$$C_P(\theta)=\begin{bmatrix} \cos\theta & 0 & -\sin\theta \\ 0 & 1 & 0 \\ \sin\theta & 0 & \cos\theta \end{bmatrix}, \quad (A2)$$

$$D_P(\phi)=\begin{bmatrix} \cos\phi & \sin\phi & 0 \\ -\sin\phi & \cos\phi & 0 \\ 0 & 0 & 1 \end{bmatrix}. \quad (A3)$$

2. Rotation matrices for d states

$$A_D(\alpha) = \begin{bmatrix} \cos\frac{\alpha}{2} & 0 & 0 & \sin\frac{\alpha}{2} & 0 \\ 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 \\ -\sin\frac{\alpha}{2} & 0 & 0 & \cos\frac{\alpha}{2} & 0 \\ 0 & 0 & 0 & 0 & 1 \end{bmatrix}, \quad (A4)$$

$$C_D(\theta) = \begin{bmatrix} (3c^2-1)/2 & -\sqrt{3}sc & 0 & \sqrt{3}s^2/2 & 0 \\ \sqrt{3}sc & (2c^2-1) & 0 & -sc & 0 \\ 0 & 0 & c & 0 & s \\ \sqrt{3}s^2/2 & sc & 0 & (1+c^2)/2 & 0 \\ 0 & 0 & -s & 0 & c \end{bmatrix} \quad (A6)$$

(where $s = \sin\theta$ and $c = \cos\theta$),

$$B_D(\gamma) = \begin{bmatrix} 1 & 0 & 0 & 0 & 0 \\ 0 & \cos\gamma & 0 & 0 & -\sin\gamma \\ 0 & 0 & \cos2\gamma & \sin2\gamma & 0 \\ 0 & 0 & -\sin2\gamma & \cos2\gamma & 0 \\ 0 & \sin\gamma & 0 & 0 & \cos\gamma \end{bmatrix}, \quad (A5)$$

$$D_D(\phi) = \begin{bmatrix} 1 & 0 & 0 & 0 & 0 \\ 0 & \cos\phi & 0 & 0 & -\sin\phi \\ 0 & 0 & \cos2\phi & \sin2\phi & 0 \\ 0 & 0 & -\sin2\phi & \cos2\phi & 0 \\ 0 & \sin\phi & 0 & 0 & \cos\phi \end{bmatrix}. \quad (A7)$$

[1] G.D. Watkins, in *Deep Centers in Semi-conductors*, edited by S.T. Pantelides (Gordon and Breach, New York, 1986), p. 147.

[2] M. Lannoo, G.A. Baraff, M. Schlüter, and D. Tomanek, Phys. Rev. B **44**, 12 106 (1991).

[3] P.W. Anderson, Phys. Rev. Lett. **34**, 953 (1975).

[4] G.D. Watkins, in *Festkörperprobleme XXIV* (Vieweg, Braunschweig, 1984), p. 163.

[5] F.G. Anderson, F.S. Ham, and G. Grossman, Mater. Sci. Forum **83-87**, 475 (1992).

[6] A. Auerbach, N. Manini, and E. Tosatti, Phys. Rev. B **49**, 12 998 (1994).

[7] D.R. Pooler, J. Phys. C **13**, 1197 (1980).

[8] M.C.M. O'Brien, J. Phys. C **4**, 2524 (1971).

[9] This expression for the energy agrees with that of Auerbach, Manini, and Tosatti (Ref. 6) except that they do not have the term in $1/12k^2$. The present result fits the numerical calculations.

[10] A. Ceulemans, *Topics in Current Chemistry* (Springer-Verlag, Berlin, 1994), Vol. 171, p. 27.

[11] A.R. Edmonds, *Angular Momentum in Quantum Mechanics*, 2nd ed. (Princeton University, Princeton, NJ, 1960).

[12] This differs from Auerbach, Manini, and Tosatti (Ref. 6) in the choice of allowed values of L and K, and, in particular, in avoiding the doubling of the degeneracy predicted by those authors. It also differs in including $1/24k^2$. It is in good agreement with the numerical results (Sec. IV) when they are taken to strong coupling.

[13] E.U. Condon and G.H. Shortley, *The Theory of Atomic Spectra* (Cambridge University, Cambridge, England, 1953).

[14] S. Sugano, Y. Tanabe, and H. Kamimura, *Pure and Applied Physics* (Academic Press, New York, 1970), Vol. 33.

[15] F. Negri, G. Orlandi, and F. Zerbetto, J. Am. Chem. Soc. **114**, 2909 (1992).

[16] N. Koga and K. Morokuma, Chem. Phys. Lett. **196**, 191 (1992).

[17] P.C. Trulove, R.T. Carlin, G.R. Eaton, and S.S. Eaton, J. Am. Chem. Soc. **117**, 6265 (1995).

[18] M.C.M. O'Brien, J. Phys. C **9**, 3153 (1976).

[19] See the results from various authors collected in Table II of N. Manini, E. Tosatti, and A. Auerbach, Phys. Rev. B **49**, 13 008 (1994).

[20] M.C.M. O'Brien, J. Phys. C **5**, 2045 (1972).

[21] S.N. Evangelou, M.C.M. O'Brien, and R.S. Perkins, J. Phys. C **13**, 4175 (1980).

[22] A. Ceulemans and L.G. Vanquickenborne, Struct. Bonding **71**, 126 (1989).

[23] C-L. Wang, W-Z. Wang, Y-L. Liu, Z-B. Su, and L. Yu, Phys. Rev. B **50**, 5676 (1994).

[24] J.L. Dunn and C.A. Bates, Phys. Rev. B **52**, 5996 (1995).