Exact zero-point energy shift in the $e \otimes (n\ E)$, $t \otimes (n\ H)$ many modes dynamic Jahn-Teller systems at strong coupling

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Abstract

We find the exact semiclassical (strong coupling) zero-point energy shifts applicable to the $e \otimes (n\ E)$ and $t \otimes (n\ H)$ dynamic Jahn-Teller problems, for an arbitrary number $n$ of discrete vibrational modes simultaneously coupled to one single electronic level. We also obtain an analytical formula for the frequency of the resulting normal modes, which has an attractive and apparently general Slater-Koster form. The limits of validity of this approach are assessed by comparison with O’Brien’s previous effective-mode approach, and with accurate numerical diagonalizations. Numerical values obtained for $t \otimes (n\ H)$ with $n = 8$ and coupling constants appropriate to $C_{60}$ are used for this purpose, and are discussed in the context of fullerene.

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I. INTRODUCTION

The dynamical Jahn-Teller (DJT) effect, where one degenerate electronic level is nontrivially coupled to vibrational modes, represents perhaps the simplest type of problem where the Born-Oppenheimer approximation is invalid in principle, and a quantum mechanical treatment of the full electron-ion system is essential. Even for the simplest DJT case, true closed-form solutions have only been obtained for a restricted set of coupling values [1]. In spite of that, the DJT physics of a single vibrational mode coupled to the electronic state is quite well understood [2] for all known symmetries, through analytic expansions valid in the opposite limits of strong and weak coupling, and otherwise through numerical diagonalization for intermediate values of the coupling. In a large number of cases of practical interest there are however many vibrational modes, coupled simultaneously to the same degenerate electronic state. This many-modes case has been extensively studied theoretically [3–5]. In particular, a first group of studies considers in detail the case of an impurity-related localized degenerate level interacting with the continuum of phonons in a crystal [3,5], while a second class of studies concentrates on the case of a finite, discrete set of vibrational modes [4,6,7]. In the present paper we revisit the second type of problem, having in mind in particular the case of an isolated molecule/cluster/ion with a finite (although possibly large) number $n$ of vibrational modes participating.

To begin with, we recall the two special limits in which the many-modes problem is trivially solved [5]. First, the case of all modes having the same symmetry and frequency, is simply reduced, by means of a rotation in the vibrational space, to the equivalent problem of a single mode coupled with the total coupling intensity, plus $n-1$ uncoupled modes. Secondly, in the weak-coupling limit, degenerate perturbation theory applies, and contributions from different modes linearly superpose. Intermode interactions appear only at fourth and higher order in the couplings.

The more realistic case of many modes with the same symmetry and different frequencies and couplings was apparently first addressed systematically by O'Brien [4] in the other customary limit, i.e., the strong-coupling semiclassic expansion. Her approach relies on the concept of replacing the $n$ real modes with a single effective mode, perturbed by weak residual off-diagonal contributions. In this way one obtains an approximation which has been very useful, notably [7] in the calculation of spectral shapes and reduction factors. Nonetheless, as we will show below, there is no well-defined limiting case where that approximation become exact in a controlled manner, except for the equal-frequency case.

In this work we demonstrate an alternative approach, which is exact in the semiclassical (strong e-v coupling) limit, and applicable from strong to intermediate couplings. Rather than working in general, we address directly two specific and physically important cases of many-modes DJT, namely the linear $e \otimes (nE)$ and $t \otimes (n \ H)$. Our method relies on
a detailed analysis of the Born-Oppenheimer (BO) potential surface around its minimum, and of the normal frequencies of the classical small oscillations of the e-v coupled system. These frequencies, in turn, determine residual zero-point quantum correction to the classical motion on the BO surface. Comparison with the effective-mode approach \[4\] reveals that the latter, not taking into account these corrections, contains a systematic deviation in the strong-coupling limit, which we discuss in detail in Sec. II B. Inclusion of these corrections generates the leading term of the exact strong-coupling expansion of the JT energy gain as a function of inverse coupling (Eq. (16)). As a very useful byproduct, we also obtain a detailed description of the low-energy vibronic spectrum, which is again accurate in the strong coupling limit. Finally, in order to provide a numerical application, we deliberately choose in Sec. III a borderline case of intermediate coupling, namely the negative ion of C\(_{60}\). That is a \(t \otimes (n H)\) DJT problem, with \(n = 8\), for which both exact and effective mode alternative calculations are feasible. Due to intermediate coupling, our approximation will not, of course, be particularly accurate. Nonetheless, being able to judge the sign and size of the deviation is especially useful in assessing errors, particularly in a case like this, which stretches a little beyond the reasonable borders of validity.

II. THE \(E \otimes (NE)\) SYSTEM

We consider first the \(e \otimes E\) linear JT Hamiltonian, a basic textbook \[2,5,8\] example of DJT, as well as a relevant model in many molecules and crystals. For convenience, we shall adopt the notations of Ref. \[4\]. The Hamiltonian operator for the \(n\)-modes problem is

\[
H = \frac{1}{2} \sum_i \omega_i (\vec{p}_i^2 + \vec{q}_i^2) + \sum_i \left( c_{x\sigma}^\dagger c_{y\sigma} + c_{y\sigma}^\dagger c_{x\sigma} \right) \sum_k k_i \omega_i \left( \begin{array}{cc} q_{i1} & q_{i2} \\ q_{i2} & -q_{i1} \end{array} \right) \left( \begin{array}{c} c_{x\sigma} \\ c_{y\sigma} \end{array} \right),
\]

(1)

where \(\omega_i\) is the frequency and \(k_i\) is the dimensionless coupling strength of the twofold-degenerate mode \(i\). \(\vec{q}_i\) is a vector notation for the two normal coordinates \(q_{i1}\) and \(q_{i2}\) of mode \(i\), and \(\vec{p}_i\) are the corresponding conjugate momenta. \(x\) and \(y\) label the two degenerate electronic states. The sums should be understood as \(\sum_{i=1}^n\). Note that we use the second-quantized notation for the fermions, and the coordinate description for the vibrational degrees of freedom. We also set \(\hbar = 1\), thus making no distinctions between (angular) frequencies and energies.

As a first step, we treat the \(\vec{q}_i\) as classical coordinates, and study the (lowest) Born-Oppenheimer potential surface:

\[
V (\vec{q}_i) = \frac{1}{2} \sum_i \omega_i (\vec{q}_i)^2 + \min_\psi \langle \psi | \sum_i k_i \omega_i \left( q_{i1}(c_{x\sigma}^\dagger c_x - c_{y\sigma}^\dagger c_y) + q_{i2}(c_{x\sigma}^\dagger c_y + c_{y\sigma}^\dagger c_x) \right) | \psi \rangle
\]

(2)

The minimum over the fermionic degree of freedom \(|\psi\rangle\) is the lowest eigenvalue of the 2\(\times\)2 electronic problem representing one fermion in the degenerate level, which is
\[- \left( \sum_i k_i^2 \omega_i^2 q_i^2 + 2 \sum_{i<j} k_i k_j \omega_i \omega_j \bar{q}_i \cdot \bar{q}_j \right)^{1/2} \]  \]. The lowest BO surface is conveniently rewritten in polar coordinates \( \vec{q}_i = (q_i \cos \theta_i, q_i \sin \theta_i) \) as

\[
V(q_i, \theta_i) = \frac{1}{2} \sum_i \omega_i q_i^2 - \frac{1}{2} \sum_i k_i^2 \omega_i^2 q_i^2 + 2 \sum_{i<j} k_i k_j \omega_i \omega_j q_i q_j \cos(\theta_i - \theta_j) \]  \right\}^{1/2} \quad (3)

In this form, the minima of \( V \), corresponding to the classical stable equilibrium configurations of the system, are straightforwardly discussed. In order to minimize \( V \), the argument of the square root should be maximum, which is obtained when all \( \theta_i - \theta_j \) simultaneously vanish. In this case, for all cosines equal to one, the square root can be explicitly executed, to obtain separate dependences on the different \( q_i \)'s. The minimum of \( V \) is therefore obtained for

\[
q_i^{\min} = k_i \\
\theta_i^{\min} = \theta, \quad (4)
\]

where \( \theta \) is arbitrary. As form (3) explicitly shows, the potential energy is independent of the common rotation angle \( \theta = \sum_i \theta_i/n \). This implies in particular that the configurations of minimum potential energy constitute a continuous manifold, parametrized by \( \theta \), with the topology of a circle, exactly the same as in the one-mode problem. This result was to be expected also on the basis of more abstract considerations \[9\], and we shall return to it below, when analyzing the small oscillations around the minimum.

The value of the potential at the minimum is the classical JT energy gain

\[
E_{\text{class}} = - \frac{1}{2} \sum_i k_i^2 \omega_i = - \frac{1}{2} k_{\text{eff}}^2 \omega_{\text{eff}}, \quad (5)
\]

where we have introduced, following Ref. \[4\], \( k_{\text{eff}} = \sum_i k_i^2 \) and \( \omega_{\text{eff}} = \sum_i k_i^2 \omega_i / k_{\text{eff}}^2 \).

This was just a re-derivation of well-known results. The next step is to compute the quantum corrections to this classical result. The quantum corrections add to \( E_{\text{class}} \) in the form of a strong-coupling expansion in negative powers of \( k_{\text{eff}} \). The leading term, of order zero, is a shift independent of \( k_{\text{eff}} \), due to the change of zero-point energy of the system following the JT coupling.

This is most easily illustrated in the case of just one mode. The ground-state energy of Eq. \( (1) \), \( E(k_1 = 0) \) (no JT coupling), is just the zero-point energy of the (two-fold degenerate) mode, amounting to \( 2 \cdot \frac{1}{2} \omega_1 \). On the other hand, when the coupling is very strong, the dynamics factorizes into a radial harmonic mode plus a free pseudo-rotation. The harmonic zero-point energy is now only \( \frac{1}{2} \omega_1 \). For a single mode, the total JT energy gain is therefore, as is well known,

\[
E_{\text{JT}} - E(k_1 = 0) = E_{\text{class}} - \frac{1}{2} \omega_1 + \frac{1}{2} \omega_1 k_1^{-2} j^2 + O \left( k_1^{-4} \right), \quad (6)
\]
where \( E_{\text{class}} = -\frac{1}{2} k^2 \omega_1 \) term represents the lowering of the BO potential minimum, \(-\frac{1}{2} \omega_1\) representing the zero-point energy gain, and the \( j(= \pm \frac{1}{2} \) for the ground state) term is the residual zero-point energy associated with quantization of the (pseudo-rotational) \( \theta \) motion.

In the rest of this section we wish to generalize the second and third term in Eq. (5) to the many-modes case.

### A. The semiclassical expansion

We now extend this kind of semiclassical expansion to the many-modes case. It is clear that the zero-point energy for zero coupling \( E(k_i = 0) = 2 \times \frac{1}{2} \sum_i \omega_i \). To determine the zero-point energy for the motion around the many-modes potential minimum in the finite coupling case, we expand the BO potential to second order about the minimum in the \( \vec{x} \equiv (q_1, q_2, ..., \theta_1, \theta_2, ...) \) coordinates, and compute the classical normal modes of vibration:

\[
V(\vec{x}) = E_{\text{class}} + \frac{1}{2} \sum_{\mu,\nu}^{2n} (x_\mu - x_\mu^{\text{min}}) \left( \frac{\partial^2 V}{\partial x_\mu \partial x_\nu} \right)_{x_\nu = x_\nu^{\text{min}}} (x_\nu - x_\nu^{\text{min}}) + O \left( (\vec{x} - \vec{x}^{\text{min}})^3 \right)
\]

where the Hessian matrix of the derivatives is

\[
V_{\mu\nu} = \left. \frac{\partial^2 V}{\partial x_\mu \partial x_\nu} \right|_{\vec{x}^{\text{min}}} = \begin{pmatrix}
\omega_1 & \omega_2 & \cdots & 0 \\
0 & k^2_1 \omega_1 (1 - \Xi k^2_1 \omega_1) & -\Xi k^2_1 \omega_1 k^2_2 \omega_2 & \cdots \\
0 & -\Xi k^2_1 \omega_1 k^2_2 \omega_2 & k^2_2 \omega_2 (1 - \Xi k^2_2 \omega_2) & \cdots \\
\cdots & \cdots & \cdots & \cdots
\end{pmatrix},
\]

and \( \Xi = (\sum_i k^2_i \omega_i)^{-1} \).

The kinetic energy for these coordinates is

\[
E_{\text{kin}}(\vec{x}, \dot{\vec{x}}) = \frac{1}{2} \sum_{\mu,\nu}^{2n} \dot{x}_\mu T_{\mu\nu}(\vec{x}) \dot{x}_\nu
\]

where

\[
T(\vec{x})_{\mu\nu} = \begin{pmatrix}
\omega_1^{-1} & \omega_2^{-1} & \cdots & 0 \\
0 & \omega_1^{-1} q_1^2 & \omega_2^{-1} q_2^2 & \cdots
\end{pmatrix},
\]
The normal frequencies $\omega^2$ and vibronic modes are obtained as eigenvalues and eigenvectors of the matrix

$$
T \left( \vec{r}^{\text{min}} \right)^{-1} \cdot V = \begin{pmatrix}
\omega_1^2 & 0 & \cdots & 0 \\
\omega_2^2 & 0 & \cdots & 0 \\
\vdots & \vdots & \ddots & \vdots \\
0 & \omega_1^2 - \Xi k_1^2 \omega_1^3 & \cdots & -\Xi k_2^2 \omega_1 \omega_2^2 \\
0 & -\Xi k_1^2 \omega_1 \omega_2^2 & \omega_2^2 & \Xi k_2^2 \omega_2^3 \\
\vdots & \vdots & \vdots & \ddots \\
0 & \Xi k_1^2 \omega_1 \omega_2^2 & 0 & \omega_2^2 & \cdots \\
\vdots & \vdots & \vdots & \vdots & \ddots
\end{pmatrix}
$$

(11)

This matrix is non Hermitian, but has real eigenvalues. The block-diagonal form shows that the small oscillations of the radial and angular variables are uncoupled. Each radial coordinate $q_i$ corresponds directly to one radial mode of the same frequency $\omega_i$ as the uncoupled modes. On the contrary, the dynamics of the angular variables are intercoupled through the off-diagonal elements in Eq. (11). The secular equation for the angular eigenvector of components $x_i$ and eigenfrequency $\nu^2$ is

$$
\nu^2 x_i = \omega_i^2 x_i - \Xi \omega_i^2 \sum_j k_j^2 \omega_j x_j
$$

(12)

with the solution

$$
x_i = \text{const} \cdot \frac{\omega_i^2}{\omega_i^2 - \nu^2}
$$

(13)

where the corresponding $\nu^2$ is a solution of the equation

$$
\Xi \sum_j \frac{k_j^2 \omega_j^3}{\omega_j^2 - \nu^2} = 1 .
$$

(14)

As a simple graphical analysis suggests, this equation has as many solutions $\nu_j^2$ as original modes. For any frequencies $\omega_j$ and couplings $k_j$, the lowest solution is $\nu_1 = 0$, corresponding to an eigenvector $x_i = (1, 1, 1, ...)$, i.e. to the totally symmetrical coordinate ($\sum \theta_i/n$): it represents the “soft mode” of pseudo-rotation along the circular JT valley. If the other solutions $\nu_j$ are sorted in ascending order of frequency, the inequality $\omega_{j-1} \leq \nu_j \leq \omega_j$ can be seen to hold. In the special case of modes of the same frequency $\omega_{j-1} = \omega_j$, the implied equality $\nu_j = \omega_j$ is also true. Indeed, a set of $d$ modes with equal frequencies can be rewritten as a single coupled mode, plus $d - 1$ uncoupled ones: the unchanged frequencies $\nu_j = \omega_j$ correspond therefore to the angular part of the uncoupled modes. In the simple, but instructive, case of $n = 2$ modes, the (single) nonzero angular frequency is

$$
\nu_2 = \left[ \omega_1 \omega_2 (k_2^2 \omega_1 + k_1^2 \omega_2) / (k_1^2 \omega_1 + k_2^2 \omega_2) \right]^{1/2} .
$$

(15)
This expression for the new angular frequency has the form of a weighted geometrical mean between the unperturbed frequencies, with such weights that $\nu_1$ is attracted towards the frequency of the mode with weaker coupling. This is reasonable because the frequency of any mode whose coupling is exactly zero should of course remain exactly unchanged. The frequencies $\nu_j$ display the same behavior in the general case: the new modes $\nu_j$ are located in the intervals between neighboring frequencies $\omega_{j-1}$, $\omega_j$, attracted towards the mode with weaker coupling strength $k_j$. In the limiting case $k_j = 0$, therefore, $\nu_j$ restores smoothly the twofold-degeneracy of the uncoupled mode $\omega_j$. For a point impurity coupled to the phonon continuum, equations analogous to Eq. (14) were derived earlier [5], but apparently not put to practical use. Here, we will use our eigenvalue equation (14) for the calculation of vibron frequencies, and of the associated zero-point energy.

We underline, incidentally, that this equation has a very familiar form, namely that of a Slater-Koster scattering problem for a separable potential, or of a collective-mode equation [10], or of a BCS gap equation [11]. By coupling to the same electronic state, the different vibrational modes get effectively coupled to each other by a kind of separable “attractive $\delta$-function” potential. The lowest bound state is forced to zero frequency, $\nu_1 = 0$, by what appears to be an exact sum rule, related to the O(2) symmetry of the Hamiltonian (1), corresponding to the independence of the energy of the angle $\theta$. In the BCS case, broken gauge invariance and Goldstone’s theorem give rise to a formally similar sum rule. A universal feature of linear JT systems, the zero mode is also present in the phonon continuum case [5].

In the evaluation of the zero-point energy, the normal angular frequencies appear only as a sum:

$$E_{JT} - E(k_i = 0) = -\frac{1}{2} k_{\text{eff}}^2 \omega_{\text{eff}} + \frac{1}{2} \left( \sum_i \omega_i + \sum_{\text{angular modes } \nu_j} \nu_j \right) - \sum_i \omega_i + O(k_{\text{eff}}^{-2})$$

$$= -\frac{1}{2} k_{\text{eff}}^2 \omega_{\text{eff}} + \frac{1}{2} \sum_j (\nu_j - \omega_j) + O(k_{\text{eff}}^{-2}).$$

(16)

This main result is not in “closed form”, since the $\nu_j$ are defined implicitly as the solutions of Eq. (14). However this is a very marginal shortcoming, involving in each specific case the simple solution of a numerical equation, explicitly given in terms of the parameters $\omega_j$ and $k_j$. We also remark that a rescaling of all the couplings $k_j \rightarrow \alpha k_j$ brings no change to the secular equation (12): the angular frequencies $\nu_j$, therefore, do not depend on $k_{\text{eff}}$, but only on the ratios among the couplings. Thus, in particular, the $\sum \nu_j - \omega_j$ zero-point term is really a term of order zero in $k_{\text{eff}}$, as it should.

This approach provides quite naturally the detailed structure of the spectrum of the excited states in the strong-coupling many-modes case. All the uncoupled frequencies $\omega_i$ persist as radial frequencies in the DJT spectrum, while new harmonic angular modes of interme-
diate frequencies $\nu_j$ (solutions of Eq. (14)) appear in between, as illustrated schematically in Fig. 1.

In addition to these main spectral structure, the zero-frequency mode $\nu_1$ introduces an entire ladder of low-energy excitations, corresponding to the quantization of the pseudo-rotation around the manifold of minimum BO potential. We write these excitations in terms of the “moment of inertia” of the pseudo-rotor associated with the $\sum \theta_i$ coordinate [5]:

$$E^{\text{rot}}(m) = \frac{1}{2 \sum k_i^2 \omega_i^{-1}} \cdot m^2$$  \hspace{1cm} (17)

where the allowed values of $m$ are $m = \pm \frac{1}{2}, \pm \frac{3}{2}, ...$, as required by the Berry-phase prescription. $E^{\text{rot}}(m)$ adds to $E_{JT}$ to give the low-energy states. In particular, the energy of the (twofold degenerate) ground state is given in this scheme by

$$E_{GS} \approx E_{JT} + E^{\text{rot}} \left( \pm \frac{1}{2} \right).$$  \hspace{1cm} (18)

**B. Numerical calculations for $e \otimes (nE)$**

The relative accuracy of the results just derived and of O’Brien’s effective-mode approximation [4]

$$E_{JT,\text{eff}}^{(0)} - E_{JT}(k_i = 0) = -\frac{1}{2} k_{\text{eff}}^2 \omega_{\text{eff}} - \frac{1}{2} \omega_{\text{eff}} - \frac{1}{4} \frac{\overline{\omega}^2 - \omega_{\text{eff}}^2}{\omega_{\text{eff}}} + O(k_{\text{eff}}^{-2})$$

$$= -\frac{1}{2} k_{\text{eff}}^2 \omega_{\text{eff}} - \frac{1}{4} \frac{\overline{\omega}^2 + \omega_{\text{eff}}^2}{\omega_{\text{eff}}} + O(k_{\text{eff}}^{-2})$$  \hspace{1cm} (19)

where $\overline{\omega} = \sum_i k_i^2 \omega_i^2 / k_{\text{eff}}^2$, can be assessed by comparison with the exact numerical diagonalization results of [4] on a truncated oscillator basis. The ground-state energy obtained by numerical diagonalization is a variational estimate of the exact ground-state energy. It converges very rapidly as the number $N$ of included oscillator states exceeds $k_{\text{eff}}^2$. In practice, for $k_{\text{eff}}^2 \approx 100$, inclusion of $N = 100$ quanta in the oscillators ladder yields an accuracy of order $10^{-8} \omega_{\text{eff}}$, largely sufficient for our purposes.

For the case of only two modes, where an explicit form (13) is available for $\nu_2$, the difference between the two is

$$E_{JT,\text{eff}}^{(0)} - E_{JT} = -\frac{1}{4} \frac{\overline{\omega}^2 + \omega_{\text{eff}}^2}{\omega_{\text{eff}}} + \frac{1}{2} (\omega_1 + \omega_2 - \nu_2) + O(k_{\text{eff}}^{-2})$$  \hspace{1cm} (20)

As a first example, we consider the case of two modes with similar frequencies, such that $\omega_2 - \omega_1 = \delta \omega$ is a small parameter. The difference in ground-state energy give by the two approximations is
\[ \frac{E^{(0)}_{JT, \text{eff}} - E_{JT}}{\omega_{\text{eff}}} \approx \left( \frac{k_1 k_2 \delta \omega}{2 \omega_{\text{eff}} k_{\text{eff}}^2} \right)^4 + 2 \left( k_2^2 - k_1^2 \right) \left( k_1 k_2 \right)^4 \left( \frac{\delta \omega}{2 \omega_{\text{eff}} k_{\text{eff}}^2} \right)^5 + \ldots \] (21)

This difference is therefore very small for small \( \delta \omega \): in this limit the two expressions are essentially coincident, and we verified that they both agree with the exact numerical ground-state energy at strong coupling. This is not surprising, since we know that the effective-mode result is exact in the trivial case of equal frequencies \[5\], and it confirms that also our expansion is correct in this limit.

Moving to the more interesting situation of very different frequencies, for example \( \omega_2 = 10 \cdot \omega_1 \), we find that the correction becomes more important (\( \sim 5\% \omega_{\text{eff}} \)). Fig. 2 shows the error of the approximate expressions \( \Delta E = E_{\text{approx}} - E_{\text{exact}}^{\text{ground}} \) for the ground-state energy at different values of the coupling. Our approximate formula (16) converges systematically (from below) to the exact energy modulo corrections \( \sim k_{\text{eff}}^{-2} \). The effective mode expression (19) differs from Eq. (10) for a quantity depending on the individual frequencies and on the ratio between the couplings, but not on the total coupling strength \( k_{\text{eff}}^{-2} \). This difference introduces a systematic shift in the strong-coupling limit of the the expression (19).

In the extreme case of very small frequency ratio \( \omega_1 / \omega_2 (<< \left[ \frac{k_1}{k_2} + \frac{k_2}{k_1} \right]^{-2} ) \), the systematic shift introduced by Eq. (19) becomes as large as

\[ \frac{E^{(0)}_{JT, \text{eff}} - E_{JT}}{\omega_{\text{eff}}} \approx \frac{1}{4} \left( \frac{k_1}{k_2} \right)^2 - \frac{1}{2} \left[ \frac{k_1}{k_2} + \left( \frac{k_1}{k_2} \right)^3 \right] \left( \frac{\omega_1}{\omega_2} \right)^{1/2} + \frac{1}{2} \left[ 1 + \left( \frac{k_1}{k_2} \right)^2 \right] \frac{\omega_1}{\omega_2} + \ldots , \] (22)

which is a relevant fraction of \( \omega_{\text{eff}} \).

A third example (Fig. 3) illustrates the validity of the method for the case of three modes. For a rather large frequency spread \( \omega_2 - \omega_{\text{eff}} \sim 2 \), the approximate formula (16) still converges to the exact energy, but not monotonically in \( k_{\text{eff}} \).

An interesting observation suggested by Figs. 2 and 3 is that, for weak enough coupling—say \( k_{\text{eff}} \lesssim 3 \), the effective-mode theory, owing to the systematic shift discussed above, can yield better agreement with the exact ground-state energy than our method, which is instead superior at strong coupling. Thus the effective-mode method and the present one are to some extent complementary.

Besides the ground state, the Lanczos technique employed for diagonalization easily generates a few low-lying excited states. These accurate excitation energies can be compared with our approximate frequencies \( \nu_i \)’s. In Fig. 4 we report the excitation energy of the low-lying \( m=\pm \frac{1}{2} \) states. These energies show a clear convergence to the fundamentals, overtones and combination states of \( \omega_1 \) and \( \nu_1 \), as expected from the theory. Above each of these origins, higher-\( m \) states form pseudorotational ladders, as determined by \( E^{\text{rot}}(m) \). In Fig. 4 we represent for clarity only the \( m = \pm \frac{3}{2} \) excitation above the ground state, and compare it with the theoretical value given by Eq. (17). Interestingly, a parallel comparison with the effective-mode model shows that, even though the ground-state energy estimates in the two
models differ, the values of the pseudorotational quantum of energy (expressed in completely different forms) are numerically coincident [12].

We stress that our adiabatic potential (2) does not explicitly include centrifugal terms, unlike what is customarily done away from strong coupling. Reference [5], for example, describes a self-consistent prescription for embodying these terms at the outset. For the sake of completeness we include in Fig. 4 the excitation energy to the first \( m = \pm \frac{3}{2} \) pseudorotational state obtained through that method. The self-consistent procedure renormalizes the inertial moment, eliminating the \( k^{-2} \) divergence at weak coupling, but it ends up providing a worse approximation to the exact energy in the region of intermediate to strong coupling. Hence, inclusion of centrifugal terms does not appear to be useful in this regime. Concerning the \( O(k^{-2}) \) terms, we note that, while in Fig. 2 the pseudorotational contribution \( E_{\text{rot}}(\pm \frac{1}{2}) \) shifts the approximate ground-state energy closer to the exact one, in Fig. 3 for \( k_{\text{eff}} \gtrsim 4 \) the error of the approximate expression (14) is positive: thus addition of the pseudorotational contribution moves the approximation further away from the correct value. We conclude that the pseudorotational contribution as given by Eq. (17), contrary to the single-mode case, does not exhaust all the \( O(k^{-2}) \) corrections to the truncated expansion (16). We will not further investigate such terms in the present work.

III. MANY MODES \( T \otimes (N H) \)

After the basic \( e \otimes (nE) \) system, treated in the previous sections, we wish now to consider a second, different case, to illustrate how much of the procedure used can be carried over. The interaction of an orbital triplet (t) with a set of fivefold vibrational modes (\( H \) icosahedral representations) is our next choice. As we shall see, apart from some technical differences, we will be able to follow very closely the approach that proved successful for the \( e \otimes (nE) \) case.

We start with the Hamiltonian operator [13][14]

\[
H = \frac{1}{2} \sum_i \omega_i \left( \vec{p}_i^2 + q_i^2 \right) + \frac{1}{2} \sum_{\sigma} \left( c_{x\sigma}^\dagger \left( q_{i1} - \sqrt{3} q_{i4} \right) - \sqrt{3} q_{i3} - \sqrt{3} q_{i2} \right) \left( \begin{array}{cccc}
 1 & 1 & 1 & 1
\end{array} \right) c_{z\sigma}
\]

where now the three degenerate electronic states are labeled \( x, y, z \), and \( \vec{q}_i \) indicate a five-dimensional vector of components \( (q_{i1},...q_{i5}) \). Reference [14] introduces a polar parametrization of the five-dimensional space of one single mode \( i \) in terms of a radial coordinate \( q_i \), plus four angles \( \alpha_i, \theta_i, \phi_i, \) and \( \gamma_i \). The same work [14] reports for a single mode \( i \), the expression for the lowest electronic eigenvalue of the one-electron matrix in terms of these coordinates:
\(- \cos(\alpha_i) k_i \omega_i q_i \). (24)

The BO potential (obtained adding \(\sum q_i^2 / 2\) to the electronic part) is therefore independent of \(\theta_i, \phi_i,\) and \(\gamma_i,\) but it depends explicitly on the angle \(\alpha_i.\) In particular, it is minimum at \(q_i = k_i, \alpha_i = 0.\) For this special value, the angular parametrization of \(\vec{q}_i\) becomes singular, the coordinate \(\vec{q}_i\) being independent of the angle \(\gamma_i.\) The DJT valley of \(t \otimes (nH)\) is thus, as well known, two-dimensional, parametrized by \(\theta_i, \phi_i.\)

Now, let us move on to \(n > 1\) fivefold modes. Consider the vector \(\sum_i k_i \omega_i \vec{q}_i\) intervening in the JT coupling matrix (23): if we indicate with \(\alpha, \theta, \phi, \) and \(\gamma\) the corresponding set of polar angles, the lowest electronic eigenvalue for the general case writes

\[- \cos(\alpha) \left| \sum_i k_i \omega_i \vec{q}_i \right| = - \cos(\alpha) \left( \sum_i k_i^2 \omega_i^2 q_i^2 + 2 \sum_{i<j} k_i k_j \omega_i \omega_j \vec{q}_i \cdot \vec{q}_j \right)^{1/2}. (25)\]

The minimization of the corresponding the BO potential, function of \(5n\) variables, is therefore very similar to the analogous for Eq. (2): here the electronic term is expressed as the negative of a product, where both terms can be maximized at the same time. As a result, at the BO minimum, \(\alpha = 0,\) and all the \(\vec{q}_i\) should align with one another in a common direction:

\[
\begin{align*}
q_i^\text{min} & = k_i \\
\alpha_i^\text{min} & = \alpha = 0 \\
\theta_i^\text{min} & = \theta \\
\phi_i^\text{min} & = \phi \\
\gamma_i^\text{min} & = \gamma
\end{align*}
\] (26)

Again the trough is two dimensional, parametrized by \(\theta, \phi,\) since \(\gamma\) is singular as discussed in the one mode case above. The expression (5) for the classical JT energy gain holds in the \(t \otimes (nH)\) case.

The next step is to generate the quantum corrections to the classical result. For this purpose we need the harmonic frequencies of oscillation around the minimum (26). Here a completely analytical approach, as in Sec. II, fails, for two reasons. As a first point, the factor \(\cos(\alpha),\) contributing to the Hessian matrix \(\frac{\partial^2 V}{\partial x_{\mu} \partial x_{\nu}},\) is unavailable as an explicit expression in terms of the coordinates \(\vec{x} = (q_1, q_2, ..., \alpha_1, \alpha_2, ..., \theta_1, ...).\) Secondly, the parametrization is singular right at the minimum, thus it cannot generate all the angular modes.

We resort therefore to an alternative, more numerical approach. We express explicitly the lowest electronic eigenvalue in \textit{Cartesian} coordinates \(\vec{x} = (q_{11}, ..., q_{15}, q_{21}, ..., q_{n5})\) compute the \(5n \times 5n\) Hessian matrix (at an arbitrary minimum point in the trough) and the kinetic matrix [see Eq. (7), (9)], and diagonalize the product \(T (x^\text{min})^{-1} \cdot V [\text{see Eq. (14)].}\) For \(n = 2,\) the calculation can be done analytically, choosing some special points in the
minimum manifold \([26]\), such as \(\theta = 0, \phi = \text{anything} \) \([\text{i.e. } \vec{q}_i = (k_i, 0, 0, 0)]\), or \(\theta = \pi/4, \phi = \pi/2 \) \([\text{i.e. } \vec{q}_i = (k_i/4, 0, 0, -k_i\sqrt{3}/4, k_i\sqrt{3}/2)]\). The resulting matrix has two threefold-degenerate eigenvalues of frequency \(\omega_1\) and \(\omega_2\) respectively, a twofold eigenvalue \(\nu_1 = 0\), and a second twofold eigenvalue of frequency \(\nu_2\) given by Eq. (13). The eigenvalues are of course independent of the choice of the minimum point around which the expansion is done. In the general case of larger \(n\), we diagonalized numerically the dynamical matrix, obtaining for any choice of the frequencies and couplings \(n\) threefold-degenerate eigenvalues \(\omega_1, ... , \omega_n\), and \(n\) new twofold-degenerate eigenvalues, which we called \(\nu_i\). Again we have always \(\nu_1 = 0\), and all \(\nu_i\)'s are located between subsequent modes \(\omega_{i-1}\) and \(\omega_i\). Thus, directed by the similarity with the \(e \otimes (n E)\) case, we verified by substitution that the new frequencies \(\nu_i\) are solutions of Eq. (14).

From the above analysis we conclude therefore that (i) in analogy to the \(e \otimes (n E)\) case, each original frequency \(\omega_i\) is still present in the e-v coupled spectrum; (ii) in \(t \otimes (n H)\) each \(\omega_i\) corresponds not just to the radial degrees of freedom, but includes pairs of coupled angular modes as well, for a total degeneracy of three; (iii) new harmonic vibron modes \(\nu_i\) appear at the same frequencies – dictated by the same equation (14) – as in the \(e \otimes (n E)\) case (see Fig. 1); (iv) in the \(t \otimes (n H)\) case, the new modes \(\nu_i\) are all twofold degenerate; (v) in particular, the lowest new frequency \(\nu_1 = 0\) again corresponds to the free pseudorotation around the minimum trough; (vi) finally, the semiclassical DJT energy gain, in analogy to Eq. (16), is for this case:

\[
E_{\text{JT}} - E(k_i = 0) = -\frac{1}{2} k_{\text{eff}}^2 \omega_{\text{eff}} + \frac{1}{2} \left( 3 \sum_i \omega_i + 2 \sum_j \nu_j \right) - \frac{5}{2} \sum_i \omega_i + \mathcal{O}(k_{\text{eff}}^{-2})
\]

\[
= -\frac{1}{2} k_{\text{eff}}^2 \omega_{\text{eff}} + \sum_j (\nu_j - \omega_j) + \mathcal{O}(k_{\text{eff}}^{-2}) \quad . \tag{27}
\]

A. \(C_{60}^-\): a case of intermediate coupling \(t \otimes (n H)\)

As an application, chosen to test the limits of applicability of our approximation, we consider the DJT problem of the fullerene anion \([13,15–17]\), where a single electron in a \(t_{1u}\) electronic state couples to \(n = 8\) \(H_g\) vibrational modes. The frequencies and couplings of the eight modes differ strongly, and none of the couplings is particularly large. The numerical values of the parameters for the \(C_{60}^-\) ion, the same adopted in our previous work \([17]\), are reported in Table I. The table gives also the new vibron frequencies \(\nu_j\) of the the coupled system, calculated within our approximation. Note that mode 6 does not give rise to a new frequency, since its coupling is vanishingly small. On the basis on these numbers, we have computed the ground-state energy gain in the approximation (27), and we report it in
Table II, along with the corresponding values in the effective-mode scheme, as presented in Ref. [14], and with the exact result, obtained by Lanczos diagonalization [17,18].

We note that the two approximations, the effective mode and ours, are essentially equivalent, both of them in error by some 25% relative to the exact result. The approximate energy gains, in particular, correct in excess the initial classical JT gain $|E_{\text{class}}|$ (too small, by about a factor $1/2$) and are now 25% too large. The reason for this is that the vibron zero-point energy, here larger than the classical energy gain itself, overestimates the true quantum correction, indicating important higher-order corrections. This reflects the fact that, in $C_{60}^-$, $k_{\text{eff}}$ is only slightly larger than unity, since the individual couplings are rather weak, so that a semiclassical expansion truncated omitting terms of $O(k_{\text{eff}}^{-2})(\approx 250 \text{cm}^{-1})$ and higher is quite far from convergence. Qualitatively, this regime corresponds to the region $k_{\text{eff}}^2 \approx 2.5$ in Fig. 3.

In the detail, the effective-mode energy is a few wave numbers better than our approximation. The reason for that is the asymptotic shift previously discussed for the $e \otimes (nE)$ case, and illustrated in Figs. 4 and 3, which makes the effective mode competitive when the coupling is weaker.

If in addition we consider the contribution, of order $k_{\text{eff}}^{-2}$, of pseudo-rotations, we can translate Eq. (17) to:

$$E^{\text{rot}}(L) = \frac{1}{6 \sum k_i^2 \omega_i^{-1}} \cdot L \cdot (L + 1).$$  (28)

The inclusion of this contribution ($60.1 \text{cm}^{-1}$) for the $L = 1$ ground state [13] brings the semiclassical estimate of the ground-state energy gain to within 20% of the exact numerical value (Table II). Note however that, according to (28), the first-excited ($L = 3$) pseudorotational state should be found at $\sim 300 \text{cm}^{-1}$ above the ground state, that is slightly above $\omega_1$. This confirms that the fullerene ion is really in an intermediate-coupling situation, rather far from all approximate limiting regimes.

IV. DISCUSSION

O’Brien’s approach – based on an “effective-mode” picture – is available in the literature for the description of the low-energy states of a many-modes JT system. It introduces a fictitious, effective single mode, treating perturbatively the residual corrections. This approach, conceptually attractive as it is (and exact in the limit of equal frequencies $\omega_i = \omega$) [5], is not completely satisfactory, particularly when the spread of the frequencies is sizable, and couplings are large. In that case, the effective-mode expression [13] for the ground-state energy gain has a deviation which may be a large fraction of the effective frequency $\omega_{\text{eff}}$. This shift, for given frequencies and ratios among the couplings, is independent of $k_{\text{eff}}$, therefore
the inclusion of higher power corrections in \( k_{\text{eff}}^{-2} \) to Eq. (19), such as those of Eq. (44) of Ref. [4] cannot correct the asymptotic behavior at large \( k_{\text{eff}} \).

We have introduced a semiclassical treatment of the many-modes problem, which corrects the difficulties of the effective-mode model. We have applied this method to two specific JT cases making it clear that, with straightforward modifications, it can be extended to other DJT systems. The method is based on the approximate calculation of the new vibron normal mode frequencies \( \nu_i \) arising after DJT coupling. Of these modes, \( n - 1 \) fall in the intervals between successive original bare mode frequencies, the remaining one is a zero mode \( \nu_1 = 0 \). The approximate \( \nu_i \)'s are again solutions of a collective-mode–type equation [10], already obtained in an equivalent form in previous studies of the continuum case [4]. Numerical tests confirm this picture, including the recovery of the original, unperturbed frequencies \( \omega_i \)'s in the strong-coupling spectrum.

In particular, we obtain expressions (16,27), in terms of these frequencies, for the ground-state energy which are exact in the strong-coupling limit. At finite coupling, our formulas introduce an error of the order \( k_{\text{eff}}^{-2} \), which is only partly corrected by the term Eqs. (17),(28) of pseudorotation along the BO minimum trough with the associated Berry phase constraints [13]. However, in cases with strong enough coupling for our expansion to hold for the potential, the expressions to order \( O(k_{\text{eff}}^0) \) gives satisfactory results, and will not need further refinement.

We provide ample numerical verification for our expectations in the \( e \otimes (n E) \) case. A detailed numerical test of the result for the case of \( t \otimes (n H) \) would be rather difficult, because of the explosion of the basis set size, which occurs when many vibron states are included, as necessary at strong coupling. The case of \( C_{60} \), not a very strongly-coupled system, therefore amenable to exact diagonalization, shows that our approach provides results for the energy gain which are basically equivalent to those of the effective-mode approximation.

More interesting would be a direct experimental confirmation of the new vibron frequencies which we have found. The ideal test system could be a molecular system where the couplings to a few (2 or 3) modes are known, reasonably strong, controlled, and possibly switchable on and off (for example upon doping): in such a situation, infrared/Raman spectroscopy should easily evidence the birth of new modes. Benzenoid cations might represent a suitable systems for such future investigations.

The present formulation of course neglects a large set of effects potentially capable of modifying the picture to some degree, especially on the low- and high-energy ends of the vibronic spectra. The most obvious limitation regards the assumed harmonicity of the “small oscillations” [3], and the neglect from the beginning of nonlinear terms in (1). In fact, there is no truly flat JT valley in a real system. The effect of valley warping is to localize the pseudorotational motion into a discrete set of minima. The importance of this phenomenon is determined by the relative value of the pseudorotational energy \( E_{\text{rot}} \) and the height of
the barriers between minima. Initially the warping will affect mostly the zero-energy mode, but for very large JT distortions, the whole shape of the BO surface will change. As a consequence, our results apply best to a strong-coupling case where the large value of $k_{\text{eff}}$ is given by the addition of many individually small contributions $k_i$, such that the distortion of each mode’s coordinate remains small, and the effect of higher-order terms is therefore weak.

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TABLES

| i | $\omega_i$(cm$^{-1}$) | $k_i$ | $\frac{1}{2}k_i^2\omega_i$(cm$^{-1}$) | $\nu_i$(cm$^{-1}$) |
|---|---|---|---|---|
| 1 | 270.0 | 0.868 | 101.71 | 0.0 |
| 2 | 430.5 | 0.924 | 183.78 | 329.5 |
| 3 | 708.5 | 0.405 | 58.11 | 633.8 |
| 4 | 772.5 | 0.448 | 77.52 | 742.3 |
| 5 | 1099.0 | 0.325 | 58.04 | 1031.8 |
| 6 | 1248.0 | 0.000 | 0.00 | 1248.0 |
| 7 | 1426.0 | 0.368 | 96.56 | 1302.4 |
| 8 | 1575.0 | 0.368 | 106.65 | 1519.0 |

$\omega_{\text{eff}} = 581.1$, $k_{\text{eff}} = 1.532$, $E_{\text{class}} = \sum \frac{1}{2}k_i^2\omega_i = 682.36$

TABLE I. The frequency/coupling parameters for many-modes DJT of $C_{60}^-$. The last line combines them to give the effective parameters introduced in Ref. [4]. With $k_{\text{eff}}^2 = 2.35$, $C_{60}^-$ is indeed an intermediate-coupling system. The last column reports the new frequencies of the DJT-coupled system.

| DJT energy gain | this work | Ref. [1,14] | exact [17] |
|-----------------|-----------|-------------|-------------|
| order $k_{\text{eff}}^2$ | $-\frac{1}{2}\sum k_i^2\omega_i = -682.4$ | the same | |
| order $k_{\text{eff}}^0$ | $\sum(\nu_j - \omega_j) = -722.8$ | $-\frac{1}{2}\frac{\omega^2 + \omega_{\text{eff}}^2}{\omega_{\text{eff}}} = -713.4$ | |
| pseudorotation $k_{\text{eff}}^{-2}$ term | $\left(3\sum k_i^2\omega_i^{-1}\right)^{-1} = 60.1$ | the same | |
| Total gain (no pseudorotation) | -1405.1 | -1395.8 | |
| Total gain (including pseudorotation) | -1345.0 | -1335.7 | -1125.7 |

TABLE II. The relevant ground-state energetics (in cm$^{-1}$) for the many-modes DJT of $C_{60}^-$, in the present model and as obtained in the cited works by O'Brien. The classical potential-lowering term, the lowest order quantum corrections, and the pseudorotational contribution are listed. Finally, the strong-coupling energy gains (up to order $k_{\text{eff}}^0$, and including the pseudorotational correction) are compared to the result of Lanczos diagonalization.
FIG. 1. A schematic picture of the spectrum of vibronic levels of a coupled many-modes JT system, in the strong-coupling limit. For simplicity, only the harmonic one-phonon (fundamental) states are drawn. The thin lines represent a few low-lying pseudorotational levels. In the $e \otimes (n E)$ case the harmonic vibrations are nondegenerate, but all the states acquire a twofold degeneracy when the pseudorotation is considered. The $\omega_i$ and $\nu_i$ fundamentals in $t \otimes (n H)$ are threefold and twofold degenerate, respectively, and these degeneracies combine further with those of the “soft” states of pseudorotation around the trough.
FIG. 2. The difference between the approximate expressions and the exact ground-state energy, obtained by Lanczos diagonalization including up to $N = 100$ oscillator states, for two modes of frequencies $\omega_2 = 10 \cdot \omega_1$, as a function of the total JT coupling strength $k_{\text{eff}}^2 = 2k_1^2 = 2k_2^2$. The figure shows the semiclassical expression (16), its correction including the pseudo-rotation contribution (18), and the effective-mode formula (19), with also the complete version – Eq. (44) of Ref. [4] – including the $k_{\text{eff}}^{-2}$ correction.
FIG. 3. The difference between the approximate expressions and the exact ground-state energy, obtained by Lanczos diagonalization including up to \( N = 40 \) oscillator states, for \( n = 3 \) modes of frequencies \( \omega_1 = \omega_2/100 = \omega_3/120 \), and couplings \( k_1 = 2k_2 = 2k_3 \), as a function of \( k_{\text{eff}}^2 \). The semiclassical expression (16) and its correction including the pseudo-rotation contribution (18) are indistinguishable on the scale of the figure. The figure shows also \( \Delta E \) for the perturbative formula (19), and for the version including the \( k_{\text{eff}}^{-2} \) correction.
FIG. 4. Excitation energy (solid lines) of selected low-lying excited states for \( n = 2 \) modes of frequencies \( \omega_1 = 1, \omega_2 = 3 \), and coupling ratio \( k_1 = \frac{1}{2} k_2 \) (solid lines). The four lowest \( m = \pm \frac{1}{2} \) states and the lowest \( m = \pm \frac{3}{2} \) state are drawn, and compared with the theoretical previons (dashed lines) and assignments of our model, valid at strong coupling. The dotted line represents the excitation energy of the lowest \( m = \pm \frac{3}{2} \) state including the self-consistent centrifugal correction of Ref. [5].
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