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Author's Review

The E $\otimes$ ϵ Jahn-Teller Coupling: Models and Manifestations*

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Calculations of the vibronic levels in a Jahn-Teller coupling can be performed using either a crude adiabatic or an adiabatic basis set of electronic states. The experimental manifestations show up in the rotational and vibrational band structures and/or in the molecular shapes, and some examples are given.

INTRODUCTION

A great many papers have in the last years been published which deals with the Jahn-Teller »effect«. Experimentalists have used »effective« Hamiltonians in order to rationalize absorption-and emission-spectra in terms of a number of Jahn-Teller coupling parameters. On the other hand, theoreticians have written down model Hamiltonians and studied the mathematical solutions in great detail. The question is then: how close is the connection between the idealized theoretical solutions and the hard realities of experiments?

The Jahn-Teller theorem asserts that a non-linear molecule cannot be in a stable nuclear conformation, if that conformation will lead to electronic degeneracy. Linear terms in the nuclear displacement coordinates will appear in the expansion of the potential energy, and these can first be eliminated when the degeneracy is lifted.

The theorem tells us that some points in the nuclear configuration space cannot be stable points. Actual molecules or ions which are close to these points are therefore expected to exhibit some singular features. A general mathematical proof of the theorem was given by Ruch and Schönhofer[1] in 1965. Their proof eliminated the need for discussing all actual symmetries as originally done by Jahn and Teller[2]. Other mathematical proofs have been given by Blount[3] and Raghavacharyulu[4]. It transpires that the Jahn-Teller theorem follows logically from the Born-Oppenheimer approximation of the wavefunctions at the molecular equilibrium point in a real molecule. Physically one can understand the theorem by reflecting that in an electronically degenerate state, the electronic charge cloud has different orientations for different components. The linear terms in the nuclear displacement coordinates cannot, therefore, be eliminated for all components[5].

In order to exemplify the quantitative attacks on the problem we shall in this note look at a doubly degenerate E state coupled to a doubly degenerate

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ε vibration. Methods to calculate the vibronic levels in a $E \otimes \varepsilon$ system experiencing a Jahn-Teller coupling were formulated in the late nineteen fifties by Moffitt and Thorson[6] and Longuet-Higgins *et al.*[7]. Their treatments were based on the so-called crude adiabatic approximation to the electronic states. Recently Duch and Segal[8] have, however, used a basis of adiabatic Born-Oppenheimer states in order to calculate the vibronic levels. The differences between these two approximation schemes should become clear in the next section.

THE MODELS

Following Longuet-Higgins[9] we shall write the Hamiltonian for a system as

$$\hat{H} = \hat{T}_N + \hat{H}(r, Q) \tag{1}$$

with $\hat{T}_N$ being the kinetic energy of the nuclei

$$\hat{T}_N = \sum_n \frac{\hat{P}_n^2}{2M_n} \tag{2}$$

and $\hat{H}(r, Q)$ being the »electronic Hamiltonian«

$$\hat{H}(r, Q) = \sum_e \frac{\hat{p}_e^2}{2m} + V(r, Q) \tag{3}$$

$\hat{P}_n$ and $\hat{p}_e$ are the conjugated linear momenta to the nuclear coordinates Q_n and electronic coordinates r, respectively. For the »electronic Hamiltonian« $\hat{H}(r, Q)$ we have the Schrödinger equation

$$\hat{H}(r, Q)\, \psi_i(r, Q) = V_i(Q)\, \psi_i(r, Q) \tag{4}$$

with the solutions $\psi_i(r, Q)$.

Consider now the situation in which the electronic Schrödinger equation, for a certain nuclear configuration Q^0, has a symmetry determined doubly degenerate solution. Using two *adiabatic Born-Oppenheimer wavefunctions* $\psi_1(r, Q)\, \chi_1(Q)$ and $\psi_2(r, Q)\, \chi_2(Q)$ as basis functions, we seek solutions to the wave equation

$$[\hat{T}_N + \hat{H}(r, Q)]\, \Psi = W \Psi \tag{5}$$

where Ψ is taken as

$$\Psi = \psi_1(r, Q)\, \chi_1(Q) + \psi_2(r, Q)\, \chi_2(Q) \tag{6}$$

The »vibrational« functions, $\chi_1(Q)$ and $\chi_2(Q)$, are now to be determined by variation.[9]

Let δ mean a simultaneous, arbitrary, infinitessimal variation of χ_1 and χ_2 and $\langle\ \rangle$ an integration over the electronic coordinates. χ_1 and χ_2 are then determined by

$$\delta \int \langle \psi_1\chi_1 + \psi_2\chi_2 \,|\, \hat{T}_N + \hat{H}(r, Q) - W \,|\, \psi_1\chi_1 + \psi_2\chi_2 \rangle\, dQ = 0 \tag{7}$$

leading to the coupled equations

$$\langle \psi_1 | \hat{T}_N + \hat{H}(r, Q) | \psi_1\chi_1 \rangle + \langle \psi_1 | \hat{T}_N | \psi_2\chi_2 \rangle = W\chi_1 \tag{8}$$

$$\langle \psi_2 | \hat{T}_N + \hat{H}(r, Q) | \psi_2\chi_2 \rangle + \langle \psi_2 | \hat{T}_N | \psi_1\chi_1 \rangle = W\chi_2 \tag{9}$$

We now take Q to denote vibrational symmetry coordinates for a doubly degenerate ε vibration, spanned by Q_a and Q_b. Changing to polar coordinates.

$$Q_a = \varrho \cos\phi \qquad Q_b = \varrho \sin\phi \tag{10}$$

and expanding the matrix-elements in Eqs (8) and (9) we get assuming[9] $\hat{P}_\varrho\psi_1 = \hat{P}_\varrho\psi_2 = 0$ and with M_ε being the effective mass of the doubly degenerate vibration

$$\begin{pmatrix} V_1(\varrho, \phi) + \dfrac{\hbar^2}{8 M_\varepsilon \varrho^2} - \dfrac{\hbar^2}{2 M_\varepsilon} \nabla_\varepsilon^2 & \dfrac{\hbar^2}{2 M_\varepsilon \varrho^2} \dfrac{\partial}{\partial\phi} \\ -\dfrac{\hbar^2}{2 M_\varepsilon \varrho^2} \dfrac{\partial}{\partial\phi} & V_2(\varrho, \phi) + \dfrac{\hbar^2}{8 M_\varepsilon \varrho^2} - \dfrac{\hbar^2}{2 M_\varepsilon} \nabla_\varepsilon^2 \end{pmatrix} \begin{pmatrix} \chi_1 \\ \chi_2 \end{pmatrix} = W \begin{pmatrix} \chi_1 \\ \chi_2 \end{pmatrix} \tag{11}$$

Applying a unitary transformation

$$\hat{U} = \frac{1}{\sqrt{2}} \begin{pmatrix} e^{-\frac{i\phi}{2}} & -ie^{-\frac{i\phi}{2}} \\ e^{\frac{i\phi}{2}} & ie^{\frac{i\phi}{2}} \end{pmatrix} \tag{12}$$

transform the set of coupled equations to

$$\begin{pmatrix} \dfrac{1}{2}(V_1 + V_2) - \dfrac{\hbar^2}{2 M_\varepsilon} \nabla_\varepsilon^2 & e^{-i\phi} \cdot \dfrac{1}{2}(V_1 - V_2) \\ e^{i\phi} \cdot \dfrac{1}{2}(V_1 - V_2) & \dfrac{1}{2}(V_1 + V_2) - \dfrac{\hbar^2}{2 M_\varepsilon} \nabla_\varepsilon^2 \end{pmatrix} \begin{pmatrix} \eta_1 \\ \eta_2 \end{pmatrix} = W \begin{pmatrix} \eta_1 \\ \eta_2 \end{pmatrix} \tag{13}$$

In order to solve the Eqs. (13) η_1 and η_2 are expanded in terms of the solutions to the two dimensional harmonic oscillator. The potentials $\frac{1}{2}(V_1 \pm V_2)$ are calculated by *ab-initio* methods, point by point, and fitted to a power series expansion which incorporates the three-fold modulation of the potential[8]. In the quasiclassical approximation where $\hbar \to 0$, Eq. (13) can be diagonalized, leading to the two potential surfaces $V_1(\rho, \phi)$ and $V_2(\rho, \phi)$.

Returning to the solutions to the Schrödinger equation (5) we now take two *crude adiabatic wavefunctions,* $\psi_1^0(r)$ and $\psi_2^0(r)$, and write for Ψ

$$\Psi = \psi_1^0(r)\,\chi_1(Q) + \psi_2^0(r)\,\chi_2(Q) \tag{14}$$

$\psi_1^0\,(r)$ and $\psi_2^0\,(r)$ are evaluated at a point Q^0. They are assumed to be ortho--normal, but not necessarily degenerate. $\chi_1\,(Q)$ and $\chi_2\,(Q)$ are again to be determined by variation:

$$\delta \int \langle \psi_1^0 \chi_1 + \psi_2^0 \chi_2 \,|\, T_N + \hat{H}\,(r, Q) - W \,|\, \psi_1^0 \chi_1 + \psi_2^0 \chi_2 \rangle \, dQ = 0 \tag{15}$$

The variation leads to the coupled set of equations

$$\begin{pmatrix} T_N + \langle \psi_1^0 \,|\, \hat{H}\,(r, Q) \,|\, \psi_1^0 \rangle & \langle \psi_1^0 \,|\, \hat{H}\,(r, Q) \,|\, \psi_2^0 \rangle \\ \langle \psi_2^0 \,|\, \hat{H}\,(r, Q) \,|\, \psi_1^0 \rangle & T_N + \langle \psi_2^0 \,|\, \hat{H}\,(r, Q) \,|\, \psi_2^0 \rangle \end{pmatrix} \begin{pmatrix} \chi_1 \\ \chi_2 \end{pmatrix} = W \begin{pmatrix} \chi_1 \\ \chi_2 \end{pmatrix} \tag{16}$$

As before Q is taken to denote a doubly degenerate ε vibration, spanned by Q_a and Q_b. Expanding the electronic matrix elements in a Taylor Series in the nuclear coordinates to the second order we get

$$\langle \psi_s^0 \,|\, \hat{H}\,(r, Q) \,|\, \psi_t^0 \rangle = V_{st}^0 \delta_{st} + \langle \psi_s^0 \,|\, \sum_i^{a,b} \left(\frac{\partial \hat{H}}{\partial Q_i}\right)_0 \,|\, \psi_t^0 \rangle\, Q_i + \frac{1}{2} \langle \psi_s^0 \,|\, \sum_{i,j}^{a,b} \left(\frac{\partial^2 \hat{H}}{\partial Q_i \partial Q_j}\right)_0 \,|\, \psi_t^0 \rangle\, Q_i Q_j + \ldots \tag{17}$$

When $V_{11}^0 = V_{22}^0$, ψ_1^0 and ψ_2^0 are degenerate at the point Q^0. This is the situation dealt with by Jahn and Teller. Any actual system will then, according to their theorem, possess a doubly degenerate ε vibration making the linear term in Eq. (17) different from zero.

Let the symmetry determined degeneracy at the point Q^0 be characterized by the presence of a $\hat{C}_2$ and a $\hat{C}_3$ axis. The number of independent electronic matrix elements in the expansion (17) is then three, which we may take as

$$c = - \langle \psi_1^0 \,|\, \left(\frac{\partial \hat{H}}{\partial Q_a}\right)_0 \,|\, \psi_1^0 \rangle \tag{18a}$$

$$\alpha = \langle \psi_1^0 \,|\, \left(\frac{\partial^2 \hat{H}}{\partial Q_a^2}\right)_0 \,|\, \psi_1^0 \rangle \tag{18b}$$

$$\beta = \langle \psi_1^0 \,|\, \left(\frac{\partial^2 \hat{H}}{\partial Q_b^2}\right)_0 \,|\, \psi_1^0 \rangle \tag{18c}$$

Changing to polar coordinates we get that Eq. (16) is transformed into

$$\begin{pmatrix} \hat{T}_N + \frac{1}{2}(\alpha + \beta)\,\varrho^2 & c\varrho e^{-i\phi} - \frac{1}{2}(\alpha - \beta)\,\varrho^2 e^{2i\phi} \\ c\varrho e^{i\phi} - \frac{1}{2}(\alpha - \beta)\,\varrho^2 e^{-2i\phi} & \hat{T}_N + \frac{1}{2}(\alpha + \beta)\,\varrho^2 \end{pmatrix} \begin{pmatrix} \chi_1 \\ \chi_2 \end{pmatrix} = W \begin{pmatrix} \chi_1 \\ \chi_2 \end{pmatrix} \tag{19}$$

The quasiclassical solution, obtained by letting $\hbar \rightarrow 0$ is easily seen to be

$$V = \frac{1}{2} k\varrho^2 \pm \sqrt{c^2\varrho^2 - c\varkappa\varrho^3 \cos 3\phi + \frac{1}{4}\varkappa^2\varrho^4} \tag{20}$$

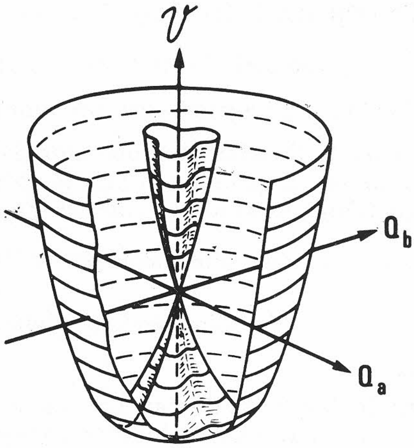

Figure 1. Quasiclassical potential surface for the $E \otimes \epsilon$ system.

with $k = (\alpha + \beta)$ and $\varkappa = (\alpha - \beta)$. The surface is pictured in Figure 1. The two solutions form two sheets of a continous surface which intersect like a double cone at $\varrho = 0$. The three-fold modulation of the potential is a second order effect. The cusp at $\varrho = 0$ is an artifact, introduced by the quasiclassical approximation.

Putting $\varkappa = 0$, the first order Hamiltonian is

$$\hat{H} = \left[- \frac{\hbar^2}{2 M_\varepsilon} \left(\frac{1}{\varrho} \frac{\partial}{\partial \varrho} (\varrho \frac{\partial}{\partial \varrho}) + \frac{1}{\varrho^2} \frac{\partial^2}{\partial \phi^2} + \frac{1}{2} \right) k \varrho^2 \right] \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} + c\varrho \begin{pmatrix} 0 & e^{-i\phi} \\ e^{i\phi} & 0 \end{pmatrix} \qquad (21)$$

This is the model Hamiltonian which has been studied most intensively. It commutes with the operator

$$\hat{j} = \frac{1}{i} \frac{\partial}{\partial \phi} + \frac{1}{2} \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \qquad (22)$$

$\hat{j}$ therefore represents a constant of the motion with half-valued quantum numbers

$$j = \pm \frac{1}{2}, \pm \frac{3}{2}, \pm \frac{5}{2} \dots \qquad (23)$$

and may be looked upon as the total (angular plus electronic) moment.

Actual systems usually have more than one ε vibration. The Jahn-Teller couplings occuring when the same E state is coupled to more than one vibrational motion, cannot be solved independently, because Hamiltonians of the type of Eq. (21) do not commute[10]. The solutions must therefore be obtained by diagonalizing the total Hamiltonian. The total Hamiltonian, commutes of course with the total angular momentum operator:

$$\hat{J} = \sum_u \frac{1}{i} \frac{\partial}{\partial \phi_u} + \frac{1}{2} \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \qquad (24)$$

When the quadratic coupling is included, j ceases to be a good quantum number. The levels $|j| = \frac{2}{3}$ are split to first order, but due to the three-fold symmetry $j' = j$ (modulus 3) is still a good quantum number.

With $c = 0$ the solutions to the Hamilton operator (21) are those of a doubly degenerate harmonic oscillator. Expanding χ_1 and χ_2 on these functions Moffitt and Thorson[6] and Longuet-Higgins *et al.*[7] calculated the energy levels, pictured in Figure 2, as a function of the dimensionless parameter $D = \frac{c^2}{2k\,\hbar\omega} = \frac{\Delta V_{J-T}}{\hbar\omega}$; the Jahn-Teller stabilization energy divided with a quantum of the harmonic vibration.

Analytical solutions to the Hamiltonian (21) have used canonical transformations (Alper and Silbey[11], Wagner[12], Judd and Vogel[13] and Barentzen and Polansky[14]). Variational treatments have been given by Barentzen and Polan-

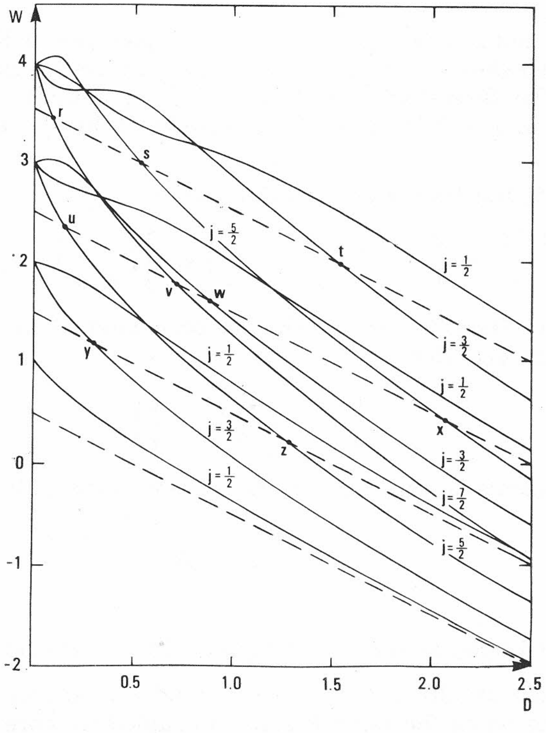

Figure 2. The calculated vibronic eigenvalues to $E \otimes \epsilon$ as a function of D. The points marked with letters, were the curves cross the »base lines« $W = -D + n + \frac{1}{2}$, $n = 0, 1, 2, 3 \ldots$, are the »exact« solutions of Judd[18] and Reik[19]. For instance at the point y, $D = \frac{5}{16}$ with $W = \frac{19}{16}$. The analytical solutions to the vibronic eigenvalue problem was inspired by the precise numerical calculations of Thorson and Moffitt.[32]

sky[15], Ruff and Wagner[16] and Ballhausen[17]. Isolated exact solutions for a number of D values were obtained by Judd[18] and extensions of this work has been performed by Reik and coworkers[19].

THE MANIFESTATIONS

The Jahn-Teller couplings may show up experimentally in

1) The rotational structure of a band.
2) The vibrational structure of a band and
3) The molecular shapes and crystal structures.

As an example of the evidence for rotational Jahn-Teller couplings we shall look at a Rydberg state of H_3. Assuming D_{3h} symmetry, the ground state of H_3 should be ^2E. However, experiments and calculations show H_3 to be unstable, dissociating into $H_2 + H$. Whether the instability can be associated with a Jahn-Teller coupling is a question of metaphysics.

Experiments and calculations have shown that the H_3^+ ions is stable as an equilateral triangle. This indicates that Rydberg states of the H_3 molecule may also be stable. *Ab initio* calculations by King and Morokuma[20] showed that $(2p)$ $^2E'$ was unstable, but that $(3p)$ $^2E'$ was stable in a C_{2v} configuration with $\Delta V_{J-T} = 100$ cm^{-1}. The $\hbar\omega_\varepsilon$ vibration of H_3^+ is 2516 cm^{-1}, leading to a D value of 0.04. The three-fold barrier was estimated to be at most a few wavenumbers.

The extensive analysis of Herzberg and coworkers[21,22] of the electronic emission spectra of H_3 and D_3 succeeded in extracting the rotational data for the $(3p)$ $^2E'$ state. The Jahn-Teller coupling causes a) a first order splitting of the rotational levels (Λ type doubling) b) a shift of other rotational levels (Λ type resonans) and c) a reduction of the Corioli coupling constant. (Child and Longuet-Higgins[23], Child[24], and Child and Strauss[25]). From the observed spectra some ten parameters, more or less influenced by the Jahn-Teller coupling, can be extracted. Neglecting the presence of the three-fold barrier both H_3 and D_3 show a value of $\Delta V_{J-T} = 87$ cm^{-1} for the $(3p)$ $^2E'$ state. Using the *ab-initio* values of $\hbar\omega_\varepsilon$ Herzberg gives $D\,(H_3) = 0.0301$ and $D\,(D_3) = 0.0424$, indicating a weak coupling.

The general interpretation is certainly satisfactory, but one should notice the mixture of high precission experiments with approximate theoretical calculations. The resulting parameter values may not be as precise as the reported number of decimal places indicate.

Using the adiabatic coupling scheme, Eq. (13), Duch and Segal[8], considered the Rydberg transition $^1A_1 \rightarrow {}^1E'$ $(3s)$ in cyclopropane, C_3H_6. Fitting the *ab initio* calculated potential surfaces of the first six excited states to a power series expansion, a complex pattern of sheets with minima and saddle points energies emerges from the calculation. The surfaces of the excited states of cyclopropane are indeed a far cry from the »idealized« picture given by the crude adiabatic expansion. The frequency distribution of the vibronic bands is consequently extremely complex. Their matrix is, however, not correct.[8]

Sears, Miller and Bondybey[26] has studied the fluorescence spectra of 1,3,5-$C_6H_3F_3^+$ and $C_6F_6^+$ in gas phase and in solid Ne matrices. Cooled gas phase laser induced fluorescence spectra of the same ions has been measured by Leach and coworkers[27], with a resolution of 0.1 cm^{-1} between 4500—4700 Å. The relevant data for the Jahn-Teller ground states of ^2E symmetry are therefore very precise. However, they are sparse compared with the number of parameters needed and with the dimensions of the vibronic matrices which must be solved. Some of the hot bands are therefore assigned differently by the two groups.

Theoretically sym. $C_6H_3F_3^+$ have seven, modes of ε symmetry which may show Jahn-Teller activity. If all were included in a linear coupling there would neither be sufficient experimental data to determine the parameters nor would there at present be a computer large enough to diagonalize the relevant matrix. The inclusion of second order terms, where j ceases to be a good quantum number, would not improve the situation.

The quadratic coupling splits the $j = 3/2$ level of a given v state. The american group found that the $v = 1$ in mode 13 in $C_6H_3F_3^+$ shoved a splitting of 12 cm^{-1}. The barrier height is estimated to be 5.3 cm^{-1}. The four mode calculation (Sears *et al.*[26] 1981) using D_i and $\hbar\omega_i$ as parameters, $i = 8, 12, 13, 14$ gave that 3 ε vibrations ($i = 8, 12, 13$) were strongly active, the D values being 0.15, 0.60 and 0.52 respectively. D_{14} was found to be 0.05.

The french group[27] finds that the number of active ε modes are at most five (or seven in the deuterated species). They give $D_{13} = 0.111$.

Configurational instability has played a great role in the structural chemistry associated with Cu^{++} ions. In the system Cu^+ doped into NaF, the Cu^+ lies at the center of an octahedron of F^- ions. Making use of two-photon spectra McClure and coworkers[28] observed the inter-configurational transition $3d^{10} \rightarrow$ $\rightarrow 3d^9 4s$. One of the excited states is of ^1E_g symmetry, and with a Cu^{++} core with a $4s$ electron one would expect it to have a Jahn-Teller coupling similar to that of ^2E_g in Cu^{++}. The strong temperature dependence of the intensity indicate that the transition is vibronic. Cu^+ is therefore located on a center of inversion.

The $^1A_{1g} \rightarrow {}^1E_g$ transition is double humped indicating a $\Delta V_{J-T} = 2250$ cm^{-1}. The average phonon frequency for the ε_g mode in the excited state is $\hbar\omega'_\varepsilon =$ $= 300$ cm^{-1}. D is therefore 7.5, and a strong coupling of the localized movements with the crystal lattice takes place.

For Cu^{++} complexes the elastic properties of the lattice will give rise to an effective interaction between the Cu^{++} ions, leading to co-operative changes in the structure. (Orgel and Dunitz[29], (1957), Gehring and Gehring[30] (1975) and Reinen and Friebel[31] (1979)). The theory of the co-operative interactions is, however, not so well investigated as is the Jahn-Teller couplings of the single species.

CONCLUSIONS

In the treatment of the Jahn-Teller couplings the crude adiabatic approximation has certainly been valuable and has bridged the gap between theory and experiment. However, especially where the density of electronic states is high, cubic, fourth and even six-order terms, can be important when trying to obtain a realistic picture of the potential surfaces. At the risk of losing the transparency of a Taylor Series expansion about the degeneracy point, it must be recommended to calculate the potential, point by point, using an adiabatic basis set. On the other hand, the approximation $\hat{P}_{\varrho} \psi_i = 0$, $i = 1$ and 2, should also be tested before drawing any definite conclusions as to which model gives the best numerical results.

The sophisticated mathematical solutions of the model Jahn-Teller Hamiltonian are certainly impressive. However, they are not really of much help in the interpretation of complex experiments. Even though both theory and experiments dealing with Jahn-Teller couplings have made great strides forward in the last years there is still much which remain to be done, before the models and the manifestations are united.

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SAŽETAK

$E \otimes \epsilon$ Jahn-Tellerovo sprezanje: modeli i manifestacije

Carl J. Ballhausen

Prikazano je stanje umijeća pri rješavanju problema koji nazivamo Jahn-Tellerovim sprezanjem. Konstatirano je da gruba adijabatska aproksimacija predstavlja koristan most između teorije i eksperimenta. No, ako je gustoća elektronskih stanja velika, onda u Taylorovu razvoju treba uzeti u obzir čak članove šestog reda, što je nepraktično. S druge strane, rafinirana matematička rješenja modelnog hamiltonijana nisu korisna u interpretaciji složenih eksperimenata unatoč svojoj impresivnosti. Proizlazi da Jahn-Tellorov problem još uvijek nije riješen na potpuno zadovoljavajući način.