# Product Jahn-Teller systems: The $\{T_1 \otimes T_2\} \otimes (e+t_2)$ case

A. Ceulemans and Q. C. Qiu
*Department of Chemistry, Catholic University of Leuven, Celestijnenlaan 200F, B-3001 Leuven, Belgium*
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The product Jahn-Teller (JT) effect is defined as the combined vibronic instability of two open shells which both transform according to degenerate irreducible representations. Such effects are of potential relevance for the study of the excited states in fullerenes and fullerides. We describe here as a prototype the $\{T_1 \otimes T_2\} \otimes (e+t_2)$ product system in cubic symmetry. Stationary points on the potential energy surface are searched under guidance of the epikernel principle. It is shown that the combined activity of the two shells can lead to minima with low ranking subgroup symmetries. If the distorting forces in the two shells have opposite signs a remarkable conflict arises between the epikernel principle and the JT theorem itself, which drives the system in the direction of further symmetry lowering. The icosahedral limit, where coupling to $e$ and $t_2$ modes becomes degenerate, is also studied using the method of the isostationary function. In this limit the product system has rotational symmetry of $SO(3)$ or $SO(3) \otimes SO(2)$ type, depending on the relative signs of the force elements in the two shells.

## I. INTRODUCTION

The Jahn-Teller (JT) effect refers to the vibronic instability of an electronic level which transforms according to a degenerate irreducible representation of a symmetry group.[1] Whenever several electronic levels are energetically close, it may be required to extend the JT treatment to the manifold of all levels involved. Such a case is usually referred to as the pseudo-JT effect, although it might equally well be called a sum-JT problem, since the active manifold now transforms as the *direct sum* of irreducible representations.[2,3] A further possibility arises if the electronic space covers the *direct product* of two degenerate irreducible representations. We propose to call such cases product-JT systems. They are truly second-generation JT problems, since they combine the JT activities of two open shells. Vibronic interactions between shells in a product JT problem take place via coupling to a common phonon system. This coupling has an effective two-particle character, as opposed to sum-JT problems where direct one-particle vibronic interaction elements between shells are allowed. The prime example of a product-JT system is the excited manifold that results from a HOMO $\rightarrow$ LUMO transition, where both the highest occupied molecular orbitals (HOMO) and lowest unoccupied molecular orbitals (LUMO) are degenerate. Let $\Gamma_a$ and $\Gamma_b$ be the symmetry representations of these levels, and $\gamma_i$ be the symmetry of a normal mode. The product problem is then denoted as $\{\Gamma_a \otimes \Gamma_b\} \otimes \{\Sigma \gamma_i\}$, with

$$\gamma_i \in ([\Gamma_a \otimes \Gamma_a] \cup [\Gamma_b \otimes \Gamma_b]). \tag{1.1}$$

Square brackets in this equation denote the symmetrized squares of the $\Gamma$ representations. In principle one might anticipate that transition-metal chemistry would abound with product-JT problems, in view of the ubiquitous $t_{2g} \rightarrow e_g$ transition between the cubic crystal field components of the $d$ shell. However, in these systems interelectronic repulsion between $d$ electrons is usually of the same order of magnitude—if not larger—than the JT stabilization energy. As a result the excited state JT problem often reduces to an isolated subspace of the product space, which can then be treated as a separate JT problem.

This need not be the case in icosahedral fullerenes where repelling electrons are smeared out over a spherical surface. As an example for the excited state of neutral $C_{60}$, with HOMO and LUMO transforming, respectively, as $H_u$ and $T_{1u}$, several terms of the $H_u \otimes T_{1u}$ singlet manifold are being claimed to participate in the JT distorted emitting state.[4] This suggests that the $H_u \otimes T_{1u}$ product problem would be a useful starting point to describe the JT activity in this case.

In the present paper we lay the foundations for the analysis of this complex product problem by studying the product of two $T$-type shells. This logically precedes the more complicated case of the coupling of a five-component $H$-tensor with a three-component $T$ vector. As a prototype we have chosen the $T_1 \otimes T_2$ product problem in cubic symmetry. The results also apply to such icosahedral problems as $T_{1u} \otimes T_{1g}$, which would correspond to the product problem for the excited states of $C_{60}^{6-}$.

## II. THE HAMILTONIAN

### A. The linear Hamiltonian of the $T_1 \otimes (e+t_2)$ and $T_2 \otimes (e+t_2)$ JT systems

The threefold degenerate $T$ representation of the cubic groups couples to doubly degenerate $e$-type and threefold degenerate $t_2$-type vibrations. The bases of the $T_1$ and $T_2$ levels are chosen generally as $(x,y,z)$ and $(\xi,\eta,\zeta)$, respectively, and the linear JT Hamiltonians of the two separate systems can be obtained using the appropriate Clebsch-Gordan coefficients,[5]

$$\mathcal{H}_{linear}^{T_1 \otimes e} = F_{T1e}(Q_\theta \hat{L}_\theta^T + Q_\epsilon \hat{L}_\epsilon^T),$$

$$\mathcal{H}_{linear}^{T_2 \otimes e} = F_{T2e}(Q_\theta \hat{L}_\theta^T + Q_\epsilon \hat{L}_\epsilon^T),$$

$$\mathcal{H}_{linear}^{T_1 \otimes t_2} = F_{T1t}(Q_\xi \hat{L}_\xi^T + Q_\eta \hat{L}_\eta^T + Q_\zeta \hat{L}_\zeta^T),$$

 

$$\mathcal{H}^{T_2\otimes t_2}_{linear}=F_{T2t}(Q_\xi\hat{L}^T_\xi+Q_\eta\hat{L}^T_\eta+Q_\zeta\hat{L}^T_\zeta), \qquad (2.1)$$

where

$$\hat{L}^T_\theta=\frac{1}{2}\begin{pmatrix}-1 & 0 & 0\\ 0 & -1 & 0\\ 0 & 0 & 2\end{pmatrix}, \quad \hat{L}^T_\epsilon=\frac{\sqrt{3}}{2}\begin{pmatrix}1 & 0 & 0\\ 0 & -1 & 0\\ 0 & 0 & 0\end{pmatrix},$$

$$\hat{L}^T_\xi=\frac{1}{\sqrt{2}}\begin{pmatrix}0 & 0 & 0\\ 0 & 0 & -1\\ 0 & -1 & 0\end{pmatrix}, \quad \hat{L}^T_\eta=\frac{1}{\sqrt{2}}\begin{pmatrix}0 & 0 & -1\\ 0 & 0 & 0\\ -1 & 0 & 0\end{pmatrix},$$

$$\hat{L}^T_\zeta=\frac{1}{\sqrt{2}}\begin{pmatrix}0 & -1 & 0\\ -1 & 0 & 0\\ 0 & 0 & 0\end{pmatrix}.$$

These $\hat{L}$ quantities are electronic operators in matrix form. $F_{T1e}, F_{T2e}, F_{T1t}$, and $F_{T2t}$ are called the force elements or vibronic constants for the $T_1\otimes e, T_2\otimes e, T_1\otimes t_2$, and $T_2\otimes t_2$ JT systems, respectively. $Q_\theta$ and $Q_\epsilon$ are the two components of the $e$-type vibrational mode and $Q_\xi, Q_\eta$, and $Q_\zeta$ the three components of the $t_2$-type mode. Note that only one active mode of each symmetry type is considered. The two shells are thus coupled to the same phonon part. As the electronic operators for $T_1$ and $T_2$ symmetries have exactly the same form, we have taken $\hat{L}^{T_1}_p=\hat{L}^{T_2}_p=\hat{L}^T_p$ ($p=\theta,\epsilon,\xi,\eta,\zeta$) for simplicity. Actually, they have been distinguished in the calculations. $\hat{L}^{T_1}_\theta$, for example, operates on the basis of $T_1$ and takes the basis of $T_2$ as constant parameters.

### B. The linear Hamiltonian of the $\{T_1\otimes T_2\}\otimes(e+t_2)$ product system

We now consider the formation of product states, e.g., as a result of a transition from an occupied $T_1$ into an empty $T_2$ shell. In this scheme, the $T_1$ and $T_2$ parts can be identified, respectively, as hole and electron states. The coupling of these states gives rise to a product space with nine orbital components, which will be expressed as $\{x\xi, x\eta, x\zeta, y\xi, y\eta, y\zeta, z\xi, z\eta, z\zeta\}$. The JT activity in this space is readily obtained following the rules for the matrix elements of one-particle operators in a product space. The matrix form of the Hamiltonian $\mathcal{H}^{\{T_1\otimes T_2\}\otimes e}_{linear}$ for the $\{T_1\otimes T_2\}\otimes e$ JT system is a nine-dimensional square matrix with the nonzero matrix elements on the diagonal only:

$$(\mathcal{H}^{\{T_1\otimes T_2\}\otimes e}_{linear})_{11}=\frac{1}{2}(-Q_\theta+\sqrt{3}Q_\epsilon)(F_{T1e}+F_{T2e}),$$

$$(\mathcal{H}^{\{T_1\otimes T_2\}\otimes e}_{linear})_{22}=\frac{1}{2}(-Q_\theta+\sqrt{3}Q_\epsilon)F_{T1e}-\frac{1}{2}(Q_\theta+\sqrt{3}Q_\epsilon)F_{T2e},$$

$$(\mathcal{H}^{\{T_1\otimes T_2\}\otimes e}_{linear})_{33}=\frac{1}{2}(-Q_\theta+\sqrt{3}Q_\epsilon)F_{T1e}+Q_\theta F_{T2e},$$

$$(\mathcal{H}^{\{T_1\otimes T_2\}\otimes e}_{linear})_{44}=-\frac{1}{2}(Q_\theta+\sqrt{3}Q_\epsilon)F_{T1e}+\frac{1}{2}(-Q_\theta+\sqrt{3}Q_\epsilon)F_{T2e},$$

$$(\mathcal{H}^{\{T_1\otimes T_2\}\otimes e}_{linear})_{55}=-\frac{1}{2}(Q_\theta+\sqrt{3}Q_\epsilon)(F_{T1e}+F_{T2e}),$$

$$(\mathcal{H}^{\{T_1\otimes T_2\}\otimes e}_{linear})_{66}=-\frac{1}{2}(Q_\theta+\sqrt{3}Q_\epsilon)F_{T1e}+Q_\theta F_{T2e},$$

$$(\mathcal{H}^{\{T_1\otimes T_2\}\otimes e}_{linear})_{77}=Q_\theta F_{T1e}+\frac{1}{2}(-Q_\theta+\sqrt{3}Q_\epsilon)F_{T2e},$$

$$(\mathcal{H}^{\{T_1\otimes T_2\}\otimes e}_{linear})_{88}=Q_\theta F_{T1e}-\frac{1}{2}(Q_\theta+\sqrt{3}Q_\epsilon)F_{T2e},$$

$$(\mathcal{H}^{\{T_1\otimes T_2\}\otimes e}_{linear})_{99}=Q_\theta(F_{T1e}+F_{T2e}). \qquad (2.2)$$

The matrix form of the linear Hamiltonian for the $\{T_1\otimes T_2\}\otimes t_2$ JT system is given by

$$\mathcal{H}^{\{T_1\otimes T_2\}\otimes t_2}_{linear}=\begin{pmatrix}
0 & Q^{2t}_\zeta & Q^{2t}_\eta & Q^{1t}_\zeta & 0 & 0 & Q^{1t}_\eta & 0 & 0\\
Q^{2t}_\zeta & 0 & Q^{2t}_\xi & 0 & Q^{1t}_\zeta & 0 & 0 & Q^{1t}_\eta & 0\\
Q^{2t}_\eta & Q^{2t}_\xi & 0 & 0 & 0 & Q^{1t}_\zeta & 0 & 0 & Q^{1t}_\eta\\
Q^{1t}_\zeta & 0 & 0 & 0 & Q^{2t}_\zeta & Q^{2t}_\eta & Q^{1t}_\xi & 0 & 0\\
0 & Q^{1t}_\zeta & 0 & Q^{2t}_\zeta & 0 & Q^{2t}_\xi & 0 & Q^{1t}_\xi & 0\\
0 & 0 & Q^{1t}_\zeta & Q^{2t}_\eta & Q^{2t}_\xi & 0 & 0 & 0 & Q^{1t}_\xi\\
Q^{1t}_\eta & 0 & 0 & Q^{1t}_\xi & 0 & 0 & 0 & Q^{2t}_\zeta & Q^{2t}_\eta\\
0 & Q^{1t}_\eta & 0 & 0 & Q^{1t}_\xi & 0 & Q^{2t}_\zeta & 0 & Q^{2t}_\xi\\
0 & 0 & Q^{1t}_\eta & 0 & 0 & Q^{1t}_\xi & Q^{2t}_\eta & Q^{2t}_\xi & 0
\end{pmatrix}, \qquad (2.3)$$

with $Q_\lambda^{it} = -(1/\sqrt{2})F_{Tit}Q_\lambda$ and $i$ is taken as 1 and 2.

### C. The total Hamiltonian of the $\{T_1 \otimes T_2\} \otimes (e+t_2)$ JT system

The total Hamiltonian contains the linear JT terms and the totally symmetric elasticity terms contributed by the vibrational modes. The latter part is expressed as

$$\mathcal{H}_{vib}^{e+t_2} = \mathcal{H}_{vib}^{e} + \mathcal{H}_{vib}^{t_2}, \tag{2.4}$$

with

$$\mathcal{H}_{vib}^{e} = \frac{1}{2}K_E(Q_\theta^2 + Q_\epsilon^2), \quad \mathcal{H}_{vib}^{t_2} = \frac{1}{2}K_T(Q_\xi^2 + Q_\eta^2 + Q_\zeta^2). \tag{2.5}$$

$K_E$ and $K_T$ are the harmonic force constants of the $e$ and $t_2$ type vibrational modes, respectively. The total Hamiltonian of the $\{T_1 \otimes T_2\} \otimes (e+t_2)$ JT system can then be simply written as

$$\mathcal{H} = \mathcal{H}_{vib}^{e+t_2} + \mathcal{H}_{linear}^{\{T_1 \otimes T_2\} \otimes e} + \mathcal{H}_{linear}^{\{T_1 \otimes T_2\} \otimes t_2}. \tag{2.6}$$

## III. EXTREMA ON THE JT SURFACE

Extrema on the JT surface of the separate $T \otimes (e+t_2)$ problem can easily be found by the Öpik and Pryce method,[6] or by the unitary transformation and energy minimization procedure.[7] The same methods can also be applied to the product problem. Generally, the eigenvalue of the Hamiltonian for the system is a function of the vibrational modes, which can be written as

$$\langle E \rangle = \frac{1}{2} \sum_{\Lambda\lambda} K_\Lambda Q_{\Lambda\lambda}^2 + \langle \chi | \mathcal{H}_{linear} | \chi \rangle, \tag{3.1}$$

where $|\chi\rangle$ is the pure electronic state and $\mathcal{H}_{linear}$ is the linear JT Hamiltonian. In principle $\chi$ is a nine-dimensional vector in the $T_1 \otimes T_2$ product space, requiring nine eigenvector coefficients subject to a normalization condition. However, since the present Hamiltonian reduces to a sum of one-particle operators, we can do with a fewer number of coefficients. Indeed, any eigenvector of this Hamiltonian can strictly be written as a simple product of a $T_1$ and a $T_2$ component, i.e.,

$$|\chi\rangle = (x|T_{1x}\rangle + y|T_{1y}\rangle + z|T_{1z}\rangle)(\xi|T_{2\xi}\rangle + \eta|T_{2\eta}\rangle + \zeta|T_{2\zeta}\rangle), \tag{3.2}$$

where only six coefficients are needed, subject to separate particle and hole normalization conditions,

$$x^2 + y^2 + z^2 = 1, \quad \xi^2 + \eta^2 + \zeta^2 = 1. \tag{3.3}$$

$|\chi\rangle$ should further be multiplied by symmetric or antisymmetric spin functions to realize triplet or singlet spin states. These spin parts will not affect the JT treatment. In contrast, if the electron-hole attraction operator is added to the Hamiltonian, the single product nature of $|\chi\rangle$ is lost, and rotations in the full nine-dimensional product space become possible. As we have explained in the Introduction we will not explore such possibility in the present paper.

Minimizing the energy in $Q$ space, positions of the extremal points can be found by the formula

$$||Q_{\Lambda\lambda}|| = -\frac{1}{K_\Lambda} \left\langle \chi \left| \frac{\partial \mathcal{H}_{linear}}{\partial Q_{\Lambda\lambda}} \right| \chi \right\rangle. \tag{3.4}$$

For the $T_1 \otimes T_2$ system, we have

$$\begin{aligned}
||Q_\theta|| &= \frac{1}{2K_E}\{(x^2+y^2-2z^2)F_{T1e} + (\xi^2+\eta^2-2\zeta^2)F_{T2e}\},\\
||Q_\epsilon|| &= -\frac{\sqrt{3}}{2K_E}\{(x^2-y^2)F_{T1e} + (\xi^2-\eta^2)F_{T2e}\},\\
||Q_\xi|| &= \frac{\sqrt{2}}{K_T}(yzF_{T1t} + \eta\zeta F_{T2t}),\\
||Q_\eta|| &= \frac{\sqrt{2}}{K_T}(zxF_{T1t} + \zeta\xi F_{T2t}),\\
||Q_\zeta|| &= \frac{\sqrt{2}}{K_T}(xyF_{T1t} + \xi\eta F_{T2t}).
\end{aligned} \tag{3.5}$$

Substituting $||Q_{\Lambda\lambda}||$ back into $\langle E \rangle$ yields the extrema of the JT surface provided the corresponding eigenvector coefficients are known. The usual recipe to solve this problem is to assume that the JT effect acts in an economic way, removing only those symmetry elements that are directly responsible for the degeneracy. The tendency of the JT forces to conserve as many symmetry elements as possible is known as the *epikernel principle*.[8] Epikernels are intermediate subgroups in the decomposition scheme of the original point group. In line with this principle the extrema of the linear $T \otimes (e+t_2)$ problem are found along tetragonal ($D_{4h}$), trigonal ($D_{3d}$), or orthorhombic ($D_{2h}$) distortions, which are indeed the principal epikernels of the distortion space.[9] In addition the $(e+t_2)$ space also contains lower ranking $C_{2h}$ epikernels, which only become extremal if higher-order coupling terms are included in the Hamiltonian. Two different $C_{2h}$ subgroups have to be considered, corresponding to the two classes of twofold symmetry axes in the cubic group: if the twofold axis is along a tetragonal symmetry axis we will denote the subgroup as $C_{2h}(C_4^2)$, if it is in between these directions we will denote the subgroup as $C_{2h}(C_2)$.

Subsequently, we will apply the same recipe to the product problem and use epikernel symmetries to project extremal eigenvectors. Later on we will introduce the method of the isostationary function to gain a deeper understanding of the structure of the JT surface.

### A. The $\{T_1 \otimes T_2\} \otimes e$ JT system

The structure of the JT surface in the $e$ plane is easily resolved since the corresponding JT Hamiltonian is already in diagonal form [cf. Eq. (2.2)]. Two types of minima may be found, depending on the relative sign of the $F_{T1e}$ and $F_{T2e}$ coupling constants. If $F_{T1e}$ and $F_{T2e}$ have the same sign the lower part of the surface consists of three potential wells with absolute minima along the tetragonal directions. The well positions are given in Table I in terms of the parameters

TABLE I. $\{T_1\otimes T_2\}\otimes e$: $F_{T1e}F_{T2e}>0$, tetragonal minima.

| Label | $(x,y,z)\otimes(\xi,\eta,\zeta)$ | $\lVert Q_\theta \rVert$ | $\lVert Q_\epsilon \rVert$ | Energy |
|---|---|---|---|---|
| $x\xi$ | $(1,0,0)\otimes(1,0,0)$ | $\alpha$ | $-\sqrt{3}\alpha$ | $E_{D_{4h}}$ |
| $y\eta$ | $(0,1,0)\otimes(0,1,0)$ | $\alpha$ | $\sqrt{3}\alpha$ | $E_{D_{4h}}$ |
| $z\zeta$ | $(0,0,1)\otimes(0,0,1)$ | $-2\alpha$ | | $E_{D_{4h}}$ |

$$\alpha=\frac{1}{2K_E}(F_{T1e}+F_{T2e}),$$

$$E_{D_{4h}}=-\frac{1}{2K_E}(F_{T1e}+F_{T2e})^2. \tag{3.6}$$

The electronic states are denoted as $(x,y,z)\otimes(\xi,\eta,\zeta)$ forms. Note that both particle and hole components are only determined up to an arbitrary phase. For $F_{T1e}F_{T2e}<0$, six minima are found in between the tetragonal turning points. These minima have only orthorhombic symmetry. The three $C_2$ axes of this $D_{2h}$ subgroup correspond to the $C_4^2$ elements of the cubic group. We will therefore also denote it as $D_{2h}(3C_4^2)$. This $D_{2h}$ subgroup is the lowest symmetry group that can be attained by an *e*-type distortion. It is also referred to as the *kernel* of the *e* space. The results are given in Table II and involve two further parameters,

$$\beta=\frac{\sqrt{3}}{2K_E}(F_{T1e}-F_{T2e}),$$

$$E_{D_{2h}}=-\frac{1}{2K_E}(F_{T1e}^2-F_{T1e}F_{T2e}+F_{T2e}^2). \tag{3.7}$$

A new feature of the product-JT system which already shows up in this $\{T_1\otimes T_2\}\otimes e$ problem is the appearance of low symmetry absolute minima whenever the JT force elements of the component systems have different signs. This result arises from a conflict between the epikernel principle and the JT theorem itself and will be discussed thoroughly in Sec. V.

### B. The $\{T_1\otimes T_2\}\otimes t_2$ JT system

As for the previous case the crucial feature of the system in $t_2$ space should depend on the relative sign of the hole and particle force elements. If $F_{T1t}$ and $F_{T2t}$ have the same sign, $F_{T1t}F_{T2t}>0$, the trigonal and orthorhombic extrema of the separate $T\otimes t_2$ system are easily retrieved in the product problem as well. Using the parameters

$$\gamma=\frac{\sqrt{2}}{3K_T}(F_{T1t}+F_{T2t}),$$

$$E_{D_{3d}}=-\frac{1}{3K_T}(F_{T1t}+F_{T2t})^2, \tag{3.8}$$

$$E_{D'_{2h}}=-\frac{1}{4K_T}(F_{T1t}+F_{T2t})^2,$$

one obtains the results in Tables III and IV. The trigonal points in the table are absolute minima for equal signs of $F_{T1t}$ and $F_{T2t}$. Under a $D_{3d}$ distortion the nine components of a $T_1\otimes T_2$ product space span $A_1\oplus 2A_2\oplus 3E$ representations. The ground state has $A_2$ symmetry, as it is formed by

TABLE II. $\{T_1\otimes T_2\}\otimes e$: $F_{T1e}F_{T2e}<0$, orthorhombic minima.

| Label | $(x,y,z)\otimes(\xi,\eta,\zeta)$ | $\lVert Q_\theta \rVert$ | $\lVert Q_\epsilon \rVert$ | Energy |
|---|---|---|---|---|
| $x\eta$ | $(1,0,0)\otimes(0,1,0)$ | $\alpha$ | $-\beta$ | $E_{D_{2h}}$ |
| $y\xi$ | $(0,1,0)\otimes(1,0,0)$ | $\alpha$ | $\beta$ | $E_{D_{2h}}$ |
| $x\zeta$ | $(1,0,0)\otimes(0,0,1)$ | $-\frac{1}{2}\alpha+\frac{\sqrt{3}}{2}\beta$ | $-\frac{\sqrt{3}}{2}\alpha-\frac{1}{2}\beta$ | $E_{D_{2h}}$ |
| $y\zeta$ | $(0,1,0)\otimes(0,0,1)$ | $-\frac{1}{2}\alpha+\frac{\sqrt{3}}{2}\beta$ | $\frac{\sqrt{3}}{2}\alpha+\frac{1}{2}\beta$ | $E_{D_{2h}}$ |
| $z\xi$ | $(0,0,1)\otimes(1,0,0)$ | $-\frac{1}{2}\alpha-\frac{\sqrt{3}}{2}\beta$ | $-\frac{\sqrt{3}}{2}\alpha+\frac{1}{2}\beta$ | $E_{D_{2h}}$ |
| $z\eta$ | $(0,0,1)\otimes(0,1,0)$ | $-\frac{1}{2}\alpha-\frac{\sqrt{3}}{2}\beta$ | $\frac{\sqrt{3}}{2}\alpha-\frac{1}{2}\beta$ | $E_{D_{2h}}$ |

TABLE III. $\{T_1\otimes T_2\}\otimes t_2$: $F_{T1t}F_{T2t}>0$, trigonal minima.

| Label | $(x,y,z)\otimes(\xi,\eta,\zeta)$ | $\lVert Q_\xi \rVert$ | $\lVert Q_\eta \rVert$ | $\lVert Q_\zeta \rVert$ | Energy |
|---|---|---|---|---|---|
| xyz | $\frac{1}{\sqrt{3}}(+,+,+)\otimes\frac{1}{\sqrt{3}}(+,+,+)$ [a] | $\gamma$ | $\gamma$ | $\gamma$ | $E_{D_{3d}}$ |
| $\bar{x}yz$ | $\frac{1}{\sqrt{3}}(-,+,+)\otimes\frac{1}{\sqrt{3}}(-,+,+)$ | $\gamma$ | $-\gamma$ | $-\gamma$ | $E_{D_{3d}}$ |
| $x\bar{y}z$ | $\frac{1}{\sqrt{3}}(+,-,+)\otimes\frac{1}{\sqrt{3}}(+,-,+)$ | $-\gamma$ | $\gamma$ | $-\gamma$ | $E_{D_{3d}}$ |
| $xy\bar{z}$ | $\frac{1}{\sqrt{3}}(+,+,-)\otimes\frac{1}{\sqrt{3}}(+,+,-)$ | $-\gamma$ | $-\gamma$ | $\gamma$ | $E_{D_{3d}}$ |

[a]In this and subsequent tables, the "+" and "−" signs will be used in the electronic states to denote "+1" and "−1," respectively.

TABLE IV. $\{T_1\otimes T_2\}\otimes t_2$: $F_{T1t}F_{T2t}>0$, orthorhombic saddle points.

| Label | $(x,y,z)\otimes(\xi,\eta,\zeta)$ | $\lVert Q_\xi \rVert$ | $\lVert Q_\eta \rVert$ | $\lVert Q_\zeta \rVert$ | Energy |
|---|---|---|---|---|---|
| xy | $\frac{1}{\sqrt{2}}(+,+,0)\otimes\frac{1}{\sqrt{2}}(+,+,0)$ | | | $\frac{3}{2}\gamma$ | $E_{D'_{2h}}$ |
| $x\bar{y}$ | $\frac{1}{\sqrt{2}}(+,-,0)\otimes\frac{1}{\sqrt{2}}(+,-,0)$ | | | $-\frac{3}{2}\gamma$ | $E_{D'_{2h}}$ |
| xz | $\frac{1}{\sqrt{2}}(+,0,+)\otimes\frac{1}{\sqrt{2}}(+,0,+)$ | | $\frac{3}{2}\gamma$ | | $E_{D'_{2h}}$ |
| $x\bar{z}$ | $\frac{1}{\sqrt{2}}(+,0,-)\otimes\frac{1}{\sqrt{2}}(+,0,-)$ | | $-\frac{3}{2}\gamma$ | | $E_{D'_{2h}}$ |
| yz | $\frac{1}{\sqrt{2}}(0,+,+)\otimes\frac{1}{\sqrt{2}}(0,+,+)$ | $\frac{3}{2}\gamma$ | | | $E_{D'_{2h}}$ |
| $y\bar{z}$ | $\frac{1}{\sqrt{2}}(0,+,-)\otimes\frac{1}{\sqrt{2}}(0,+,-)$ | $-\frac{3}{2}\gamma$ | | | $E_{D'_{2h}}$ |

TABLE V. $\{T_1 \otimes T_2\} \otimes t_2$: $F_{T1t}F_{T2t} < 0$, orthorhombic extrema.

| Label | $(x,y,z) \otimes (\xi,\eta,\zeta)$ | $\lVert Q_\xi \rVert$ | $\lVert Q_\eta \rVert$ | $\lVert Q_\zeta \rVert$ | Energy |
|---|---|---|---|---|---|
| $\overline{xy}\xi\eta$ | $\frac{1}{\sqrt{2}}(-,+,0) \otimes \frac{1}{\sqrt{2}}(+,+,0)$ | | | $\frac{3}{2}\delta$ | $E_{D''_{2h}}$ |
| $xy\overline{\xi}\eta$ | $\frac{1}{\sqrt{2}}(+,+,0) \otimes \frac{1}{\sqrt{2}}(-,+,0)$ | | | $-\frac{3}{2}\delta$ | $E_{D''_{2h}}$ |
| $\overline{xz}\xi\zeta$ | $\frac{1}{\sqrt{2}}(-,0,+) \otimes \frac{1}{\sqrt{2}}(+,0,+)$ | | $\frac{3}{2}\delta$ | | $E_{D''_{2h}}$ |
| $xz\overline{\xi}\zeta$ | $\frac{1}{\sqrt{2}}(+,0,+) \otimes \frac{1}{\sqrt{2}}(-,0,+)$ | | $-\frac{3}{2}\delta$ | | $E_{D''_{2h}}$ |
| $\overline{yz}\eta\zeta$ | $\frac{1}{\sqrt{2}}(0,-,+) \otimes \frac{1}{\sqrt{2}}(0,+,+)$ | $\frac{3}{2}\delta$ | | | $E_{D''_{2h}}$ |
| $yz\overline{\eta}\zeta$ | $\frac{1}{\sqrt{2}}(0,+,+) \otimes \frac{1}{\sqrt{2}}(0,-,+)$ | $-\frac{3}{2}\delta$ | | | $E_{D''_{2h}}$ |

occupying the orbital singlets of the trigonally splitted $T_1$ and $T_2$ manifolds. The complete set of trigonal energy expressions reads

$$E_0(A_2) = -\frac{1}{3K_T}(F_{T1t}+F_{T2t})^2 = E_{D_{3d}},$$

$$E_1(E) = \frac{1}{3K_T}(2F_{T1t}^2 + F_{T1t}F_{T2t} - F_{T2t}^2),$$

$$E_2(E) = \frac{1}{3K_T}(-F_{T1t}^2 + F_{T1t}F_{T2t} + 2F_{T2t}^2),$$

$$E_3(A_1,A_2,E) = \frac{2}{3K_T}(F_{T1t}+F_{T2t})^2 = -2E_{D_{3d}}. \quad (3.9)$$

Note that the third excited state, $E_3$, is fourfold degenerate. It corresponds to the occupation of the orbital doublets of the trigonally splitted $T_1$ and $T_2$ manifolds.

The orthorhombic extrema obey a $D_{2h}$ symmetry group based on one $C_4^2$ axis and two perpendicular $C_2$ elements. Subsequently, we will use the notation $D_{2h}(C_4^2, 2C_2)$. These extrema turn out to be saddle points. The Hessian matrix for the *xy* isomer in the $t_2$ space is given by

$$\left\{\frac{\partial^2 \mathcal{H}}{\partial Q_i \partial Q_j}\right\}_{i,j=\xi,\eta,\zeta} = \begin{pmatrix} 0 & -K_T & 0 \\ -K_T & 0 & 0 \\ 0 & 0 & K_T \end{pmatrix}.$$

The corresponding eigenvalues are $-7K_T, K_T, K_T$, indicating that there is indeed one direction of negative curvature.

If $F_{T1t}$ and $F_{T2t}$ have different signs the energies of trigonal and orthorhombic points raise and the structure of the surface is completely altered. The lower part of the surface is now dominated by extrema of $D_{2h}(C_4^2, 2C_2)$ and $C_{2h}(C_2)$ symmetry. Details of the electronic vectors, well positions, and energies of these critical points are given in Tables V and VI in terms of the parameters

$$\delta = \frac{\sqrt{2}}{3K_T}(-F_{T1t}+F_{T2t}),$$

TABLE VI. $\{T_1 \otimes T_2\} \otimes t_2$: $F_{T1t}F_{T2t} < 0$, $C_{2h}(C_2)$ extrema.

| Label | $(x,y,z) \otimes (\xi,\eta,\zeta)$ | $\lVert Q_\xi \rVert$ | $\lVert Q_\eta \rVert$ | $\lVert Q_\zeta \rVert$ | Energy |
|---|---|---|---|---|---|
| *a* | $\frac{1}{\sqrt{3}}(-,+,+) \otimes \frac{1}{\sqrt{3}}(+,+,+)$ | $\gamma$ | $\delta$ | $\delta$ | $E_{C_{2h}}$ |
| *b* | $\frac{1}{\sqrt{3}}(+,-,+) \otimes \frac{1}{\sqrt{3}}(+,+,+)$ | $\delta$ | $\gamma$ | $\delta$ | $E_{C_{2h}}$ |
| *c* | $\frac{1}{\sqrt{3}}(+,+,-) \otimes \frac{1}{\sqrt{3}}(+,+,+)$ | $\delta$ | $\delta$ | $\gamma$ | $E_{C_{2h}}$ |
| *d* | $\frac{1}{\sqrt{3}}(+,+,+) \otimes \frac{1}{\sqrt{3}}(+,-,-)$ | $\gamma$ | $-\delta$ | $-\delta$ | $E_{C_{2h}}$ |
| *e* | $\frac{1}{\sqrt{3}}(+,+,+) \otimes \frac{1}{\sqrt{3}}(-,+,-)$ | $-\delta$ | $\gamma$ | $-\delta$ | $E_{C_{2h}}$ |
| *f* | $\frac{1}{\sqrt{3}}(+,+,+) \otimes \frac{1}{\sqrt{3}}(-,-,+)$ | $-\delta$ | $-\delta$ | $\gamma$ | $E_{C_{2h}}$ |
| *g* | $\frac{1}{\sqrt{3}}(-,-,+) \otimes \frac{1}{\sqrt{3}}(-,+,-)$ | $-\gamma$ | $\delta$ | $-\delta$ | $E_{C_{2h}}$ |
| *h* | $\frac{1}{\sqrt{3}}(-,-,+) \otimes \frac{1}{\sqrt{3}}(-,+,+)$ | $\delta$ | $-\gamma$ | $-\delta$ | $E_{C_{2h}}$ |
| *i* | $\frac{1}{\sqrt{3}}(-,+,-) \otimes \frac{1}{\sqrt{3}}(-,+,+)$ | $\delta$ | $-\delta$ | $-\gamma$ | $E_{C_{2h}}$ |
| *j* | $\frac{1}{\sqrt{3}}(-,+,-) \otimes \frac{1}{\sqrt{3}}(+,+,-)$ | $-\gamma$ | $-\delta$ | $-\delta$ | $E_{C_{2h}}$ |
| *k* | $\frac{1}{\sqrt{3}}(+,-,-) \otimes \frac{1}{\sqrt{3}}(+,+,-)$ | $-\delta$ | $-\gamma$ | $\delta$ | $E_{C_{2h}}$ |
| *l* | $\frac{1}{\sqrt{3}}(+,-,-) \otimes \frac{1}{\sqrt{3}}(-,+,-)$ | $-\delta$ | $\delta$ | $-\gamma$ | $E_{C_{2h}}$ |

$$E_{D''_{2h}} = -\frac{1}{4K_T}(F_{T1t}-F_{T2t})^2, \quad (3.10)$$

$$E_{C_{2h}} = -\frac{1}{3K_T}\left(F_{T1t}^2 - \frac{2}{3}F_{T1t}F_{T2t} + F_{T2t}^2\right).$$

Note that different orthorhombic eigenstates are used in Tables IV and V. In $D_{2h}(C_4^2, 2C_2)$, $T_1$ subduces $B_1 \oplus B_2 \oplus B_3$ representations versus $A \oplus B_2 \oplus B_3$ for $T_2$, yielding a direct product of type $2A \oplus 3B_1 \oplus 2B_2 \oplus 2B_3$. In Table IV, the orthorhombic ground states, with energy $E_{D'_{2h}}$, are of *B* symmetry, while the eigenvectors in Table V with energy $E_{D''_{2h}}$, are of *A*-type symmetry.

To identify the symmetry of the 12 points in Table VI we consider as an example the point labeled *f*. To reach this point the distortion first acts along the $Q_\zeta$ direction, which reduces the symmetry already to a $D_{2h}$ subgroup based on the axes $(C_4^z)^2, C_2^{xy}, C_2^{x\bar{y}}$. The distortion then continues along the $Q_\xi + Q_\eta$ direction, thus further destroying the $(C_4^z)^2$ and $C_2^{x\bar{y}}$ elements. The point *f* is thus characterized by a $C_{2h}$ subgroup, based on the $C_2^{xy}$ symmetry element. Note that the corresponding eigenvector is antisymmetric under this twofold rotation axis. For $F_{T1t}F_{T2t} < 0$, both the $D''_{2h}$ and $C_{2h}$ points can be absolute minima depending on the relevant vibronic coupling constants. The possible minima of the $\{T_2 \otimes T_2\} \otimes t_2$ problem as a function of the two force elements are displayed in Fig. 1. The boundaries of the $D_{2h}$ and $C_{2h}$ phases correspond to the straight lines

$$F_{T1t} = -3F_{T2t}, \quad F_{T1t} = -\frac{1}{3}F_{T2t}. \tag{3.11}$$

### C. The $\{T_1 \otimes T_2\} \otimes (e+t_2)$ JT system

We now proceed to the extremal analysis of the combined $(e+t_2)$ space, using the epikernel principle as a guideline.

#### 1. $D_{3d}, D_{4h}, D_{2h}(3C_4^2)$ points

The trigonal, tetragonal, and $D_{2h}(3C_4^2)$ points belong entirely to the $e$ or $t_2$ subspaces which implies that the previous solutions remain unaltered when the $\{T_1 \otimes T_2\}$ problem is considered in its full generality.

#### 2. $D_{2h}(C_4^2, 2C_2)$

In this orthorhombic subgroup the $T_1$ and $T_2$ states subduce $B_1 \oplus B_2 \oplus B_3$ and $A \oplus B_2 \oplus B_3$ components respectively. For $D_{2h}(C_2^z, C_2^{xy}, C_2^{\bar{x}y})$ one has

$$T_1 : B_1 : |T_{1z}\rangle,$$

$$B_2 : \frac{1}{\sqrt{2}}\{|T_{1x}\rangle + |T_{1y}\rangle\}, \tag{3.12}$$

$$B_3 : \frac{1}{\sqrt{2}}\{|T_{1x}\rangle - |T_{1y}\rangle\};$$

$$T_2 : A : |T_{2\zeta}\rangle,$$

$$B_2 : \frac{1}{\sqrt{2}}\{|T_{2\xi}\rangle - |T_{2\eta}\rangle\}, \tag{3.13}$$

$$B_3 : \frac{1}{\sqrt{2}}\{|T_{2\xi}\rangle + |T_{2\eta}\rangle\}.$$

Out of these we can form nine product states. The $B_1 \otimes A$ combination $(0,0,1) \otimes (0,0,1)$ is in fact a tetragonal eigenvector, which was already considered in Table I. Of the remaining products the interchange of $B_2$ and $B_3$ labels is an equivalence operation. Indeed for each orthorhombic distortion with a given $C_4^2$ principal axis there exists an equivalent distortion where the two remaining $C_2$ axes, which discriminate $B_2$ and $B_3$, are swapped. This leaves four nontrivial orthorhombic $\{T_1 \otimes T_2\}$ product states: $B_1 \otimes B_2, B_2 \otimes A, B_2 \otimes B_2, B_2 \otimes B_3$. Each of these gives rise to a set of six equivalent extremal points, with the following respective energies:

$$E_{D_{2h}}^{B_1B_2} = -\frac{1}{2K_E}\left(F_{T1e}^2 - F_{T1e}F_{T2e} + \tfrac{1}{4}F_{T2e}^2\right) - \frac{F_{T2t}^2}{4K_T},$$

$$E_{D_{2h}}^{B_2A} = -\frac{1}{2K_E}\left(\tfrac{1}{4}F_{T1e}^2 - F_{T1e}F_{T2e} + F_{T2e}^2\right) - \frac{F_{T1t}^2}{4K_T},$$

$$E_{D_{2h}}^{B_2B_2} = -\frac{1}{8K_E}(F_{T1e} + F_{T2e})^2 - \frac{1}{4K_T}(F_{T1t} - F_{T2t})^2,$$

$$E_{D_{2h}}^{B_2B_3} = -\frac{1}{8K_E}(F_{T1e} + F_{T2e})^2 - \frac{1}{4K_T}(F_{T1t} + F_{T2t})^2. \tag{3.14}$$

The corresponding eigenvectors and distortions in terms of the previously defined parameters $\alpha, \beta, \gamma$, and $\delta$ are given in Table VII. If both $F_{T1e}F_{T2e} > 0$ and $F_{T1t}F_{T2t} > 0$ the $B_2 \otimes B_3$ combination definitely is favored. As in the case of the separate $T \otimes (e+t_2)$ problem, parameter values for which the trigonal and tetragonal wells have the same depth automatically imply a coexistence of these minima with $B_2 \otimes B_3$ type orthorhombic points.

For $F_{T1e}F_{T2e} > 0$ and $F_{T1t}F_{T2t} < 0$ there is a change of the orthorhombic ground state from $B_2 \otimes B_3$ to $B_2 \otimes B_2$. Finally the other combinations $B_1 \otimes B_2$ and $B_2 \otimes A$ only will become ground states in cases with dominant coupling to tetragonal modes with $F_{T1e}F_{T2e} < 0$ and the proper values of $F_{T2t}$ or $F_{T1t}$. This coupling regime is close to the $D_{2h}(3C_4^2)$ solution; the energetic distance between the two is given by

$$E_{D_{2h}}^{B_1B_2} - E_{D_{2h}} = \frac{3}{4}\left(\frac{F_{T2e}^2}{2K_E} - \frac{F_{T2t}^2}{3K_T}\right), \tag{3.15}$$

$$E_{D_{2h}}^{B_2A} - E_{D_{2h}} = \frac{3}{4}\left(\frac{F_{T1e}^2}{2K_E} - \frac{F_{T1t}^2}{3K_T}\right). \tag{3.16}$$

#### 3. $C_{2h}(C_2)$

Consider a $C_{2h}$ subgroup based on the twofold rotation axis $C_2^{xy}$, situated in the $xy$ plane between $x$ and $y$ directions. Possible nontrivial eigenvectors of this symmetry operation are

$$A \otimes A : \left(\frac{1}{\sqrt{2}}, \frac{1}{\sqrt{2}}, 0\right) \otimes \left(\frac{\cos\varphi}{\sqrt{2}}, -\frac{\cos\varphi}{\sqrt{2}}, \sin\varphi\right),$$

$$B \otimes B : \left(\frac{\cos\varphi}{\sqrt{2}}, -\frac{\cos\varphi}{\sqrt{2}}, \sin\varphi\right) \otimes \left(\frac{1}{\sqrt{2}}, \frac{1}{\sqrt{2}}, 0\right), \tag{3.17}$$

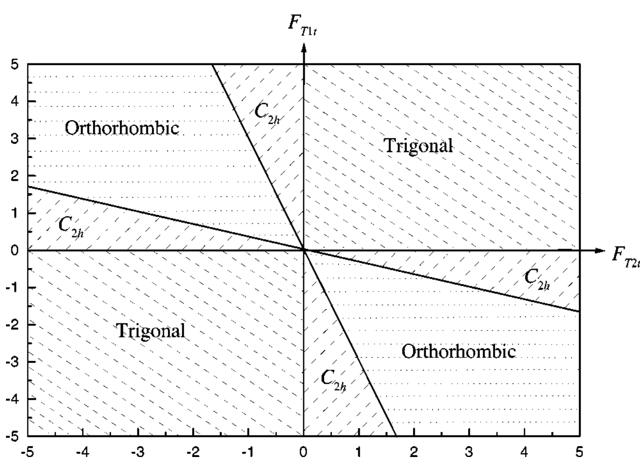


FIG. 1. Regions of existence of absolute minima of different symmetries for the $\{T_1 \otimes T_2\} \otimes t_2$ JT system.

TABLE VII. Orthorhombic extrema of the $\{T_1\otimes T_2\}\otimes(e+t_2)$ problem.

| Label | $(x,y,z)\otimes(\xi,\eta,\zeta)$ | $\lvert\lvert Q_\theta\rvert\rvert$ | $\lvert\lvert Q_\epsilon\rvert\rvert$ | $\lvert\lvert Q_\xi\rvert\rvert$ | $\lvert\lvert Q_\eta\rvert\rvert$ | $\lvert\lvert Q_\zeta\rvert\rvert$ | Conditions | Energy |
|---|---|---|---|---|---|---|---|---|
| 1 | $(1,0,0)\otimes\frac{1}{\sqrt{2}}(0,+,+)$ | $\frac{1}{4}\alpha+\frac{\sqrt{3}}{4}\beta$ | $-\frac{\sqrt{3}}{4}\alpha-\frac{3}{4}\beta$ | $\frac{3}{4}(\gamma+\delta)$ | | | $F_{T1e}F_{T2e}<0$ | $E_{D_{2h}}^{B_1B_2}$ |
| 2 | $(1,0,0)\otimes\frac{1}{\sqrt{2}}(0,-,+)$ | $\frac{1}{4}\alpha+\frac{\sqrt{3}}{4}\beta$ | $-\frac{\sqrt{3}}{4}\alpha-\frac{3}{4}\beta$ | $-\frac{3}{4}(\gamma+\delta)$ | | | $F_{T1e}F_{T2e}<0$ | $E_{D_{2h}}^{B_1B_2}$ |
| 3 | $(0,1,0)\otimes\frac{1}{\sqrt{2}}(+,0,+)$ | $\frac{1}{4}\alpha+\frac{\sqrt{3}}{4}\beta$ | $\frac{\sqrt{3}}{4}\alpha+\frac{3}{4}\beta$ | | $\frac{3}{4}(\gamma+\delta)$ | | $F_{T1e}F_{T2e}<0$ | $E_{D_{2h}}^{B_1B_2}$ |
| 4 | $(0,1,0)\otimes\frac{1}{\sqrt{2}}(-,0,+)$ | $\frac{1}{4}\alpha+\frac{\sqrt{3}}{4}\beta$ | $\frac{\sqrt{3}}{4}\alpha+\frac{3}{4}\beta$ | | $-\frac{3}{4}(\gamma+\delta)$ | | $F_{T1e}F_{T2e}<0$ | $E_{D_{2h}}^{B_1B_2}$ |
| 5 | $(0,0,1)\otimes\frac{1}{\sqrt{2}}(+,+,0)$ | $-\frac{1}{2}\alpha-\frac{\sqrt{3}}{2}\beta$ | | | | $\frac{3}{4}(\gamma+\delta)$ | $F_{T1e}F_{T2e}<0$ | $E_{D_{2h}}^{B_1B_2}$ |
| 6 | $(0,0,1)\otimes\frac{1}{\sqrt{2}}(-,+,0)$ | $-\frac{1}{2}\alpha-\frac{\sqrt{3}}{2}\beta$ | | | | $-\frac{3}{4}(\gamma+\delta)$ | $F_{T1e}F_{T2e}<0$ | $E_{D_{2h}}^{B_1B_2}$ |
| 1 | $\frac{1}{\sqrt{2}}(0,-,+)\otimes(1,0,0)$ | $\frac{1}{4}\alpha-\frac{\sqrt{3}}{4}\beta$ | $-\frac{\sqrt{3}}{4}\alpha+\frac{3}{4}\beta$ | $-\frac{3}{4}(\gamma-\delta)$ | | | $F_{T1e}F_{T2e}<0$ | $E_{D_{2h}}^{B_2A}$ |
| 2 | $\frac{1}{\sqrt{2}}(0,+,+)\otimes(1,0,0)$ | $\frac{1}{4}\alpha-\frac{\sqrt{3}}{4}\beta$ | $-\frac{\sqrt{3}}{4}\alpha+\frac{3}{4}\beta$ | $\frac{3}{4}(\gamma-\delta)$ | | | $F_{T1e}F_{T2e}<0$ | $E_{D_{2h}}^{B_2A}$ |
| 3 | $\frac{1}{\sqrt{2}}(+,0,+)\otimes(0,1,0)$ | $\frac{1}{4}\alpha-\frac{\sqrt{3}}{4}\beta$ | $\frac{\sqrt{3}}{4}\alpha-\frac{3}{4}\beta$ | | $\frac{3}{4}(\gamma-\delta)$ | | $F_{T1e}F_{T2e}<0$ | $E_{D_{2h}}^{B_2A}$ |
| 4 | $\frac{1}{\sqrt{2}}(-,0,+)\otimes(0,1,0)$ | $\frac{1}{4}\alpha-\frac{\sqrt{3}}{4}\beta$ | $\frac{\sqrt{3}}{4}\alpha-\frac{3}{4}\beta$ | | $-\frac{3}{4}(\gamma-\delta)$ | | $F_{T1e}F_{T2e}<0$ | $E_{D_{2h}}^{B_2A}$ |
| 5 | $\frac{1}{\sqrt{2}}(+,+,0)\otimes(0,0,1)$ | $-\frac{1}{2}\alpha+\frac{\sqrt{3}}{2}\beta$ | | | | $\frac{3}{4}(\gamma-\delta)$ | $F_{T1e}F_{T2e}<0$ | $E_{D_{2h}}^{B_2A}$ |
| 6 | $\frac{1}{\sqrt{2}}(-,+,0)\otimes(0,0,1)$ | $-\frac{1}{2}\alpha+\frac{\sqrt{3}}{2}\beta$ | | | | $-\frac{3}{4}(\gamma-\delta)$ | $F_{T1e}F_{T2e}<0$ | $E_{D_{2h}}^{B_2A}$ |
| 1 | $\frac{1}{\sqrt{2}}(-,+,0)\otimes\frac{1}{\sqrt{2}}(+,+,0)$ | $\alpha$ | | | | $\frac{3}{2}\delta$ | $F_{T1t}F_{T2t}<0$ | $E_{D_{2h}}^{B_2B_2}$ |
| 2 | $\frac{1}{\sqrt{2}}(+,+,0)\otimes\frac{1}{\sqrt{2}}(-,+,0)$ | $\alpha$ | | | | $-\frac{3}{2}\delta$ | $F_{T1t}F_{T2t}<0$ | $E_{D_{2h}}^{B_2B_2}$ |
| 3 | $\frac{1}{\sqrt{2}}(-,0,+)\otimes\frac{1}{\sqrt{2}}(+,0,+)$ | $-\frac{1}{2}\alpha$ | $-\frac{\sqrt{3}}{2}\alpha$ | | $\frac{3}{2}\delta$ | | $F_{T1t}F_{T2t}<0$ | $E_{D_{2h}}^{B_2B_2}$ |
| 4 | $\frac{1}{\sqrt{2}}(+,0,+)\otimes\frac{1}{\sqrt{2}}(-,0,+)$ | $-\frac{1}{2}\alpha$ | $-\frac{\sqrt{3}}{2}\alpha$ | | $-\frac{3}{2}\delta$ | | $F_{T1t}F_{T2t}<0$ | $E_{D_{2h}}^{B_2B_2}$ |
| 5 | $\frac{1}{\sqrt{2}}(0,-,+)\otimes\frac{1}{\sqrt{2}}(0,+,+)$ | $-\frac{1}{2}\alpha$ | $\frac{\sqrt{3}}{2}\alpha$ | $\frac{3}{2}\delta$ | | | $F_{T1t}F_{T2t}<0$ | $E_{D_{2h}}^{B_2B_2}$ |
| 6 | $\frac{1}{\sqrt{2}}(0,+,+)\otimes\frac{1}{\sqrt{2}}(0,+,-)$ | $-\frac{1}{2}\alpha$ | $\frac{\sqrt{3}}{2}\alpha$ | $-\frac{3}{2}\delta$ | | | $F_{T1t}F_{T2t}<0$ | $E_{D_{2h}}^{B_2B_2}$ |
| 1 | $\frac{1}{\sqrt{2}}(+,+,0)\otimes\frac{1}{\sqrt{2}}(+,+,0)$ | $\alpha$ | | | | $\frac{3}{2}\gamma$ | $F_{T1t}F_{T2t}>0$ | $E_{D_{2h}}^{B_2B_3}$ |
| 2 | $\frac{1}{\sqrt{2}}(+,-,0)\otimes\frac{1}{\sqrt{2}}(+,-,0)$ | $\alpha$ | | | | $-\frac{3}{2}\gamma$ | $F_{T1t}F_{T2t}>0$ | $E_{D_{2h}}^{B_2B_3}$ |
| 3 | $\frac{1}{\sqrt{2}}(+,0,+)\otimes\frac{1}{\sqrt{2}}(+,0,+)$ | $-\frac{1}{2}\alpha$ | $-\frac{\sqrt{3}}{2}\alpha$ | | $\frac{3}{2}\gamma$ | | $F_{T1t}F_{T2t}>0$ | $E_{D_{2h}}^{B_2B_3}$ |
| 4 | $\frac{1}{\sqrt{2}}(+,0,-)\otimes\frac{1}{\sqrt{2}}(+,0,-)$ | $-\frac{1}{2}\alpha$ | $-\frac{\sqrt{3}}{2}\alpha$ | | $-\frac{3}{2}\gamma$ | | $F_{T1t}F_{T2t}>0$ | $E_{D_{2h}}^{B_2B_3}$ |
| 5 | $\frac{1}{\sqrt{2}}(0,+,+)\otimes\frac{1}{\sqrt{2}}(0,+,+)$ | $-\frac{1}{2}\alpha$ | $\frac{\sqrt{3}}{2}\alpha$ | $\frac{3}{2}\gamma$ | | | $F_{T1t}F_{T2t}>0$ | $E_{D_{2h}}^{B_2B_3}$ |
| 6 | $\frac{1}{\sqrt{2}}(0,+,-)\otimes\frac{1}{\sqrt{2}}(0,+,-)$ | $-\frac{1}{2}\alpha$ | $\frac{\sqrt{3}}{2}\alpha$ | $-\frac{3}{2}\gamma$ | | | $F_{T1t}F_{T2t}>0$ | $E_{D_{2h}}^{B_2B_3}$ |

TABLE VIII. Numerical results for $B\otimes A$ minima of $C_{2h}(C_2)$ symmetry.

| Label | 1 | 2 | 3 | 4 | 5 | 6 |
|---|---|---|---|---|---|---|
| $F_{T1e}$ [a] | 2.4 | 2.4 | 0.1 | 0.1 | −3.1 | 1.0 |
| $F_{T2e}$ [a] | 0.1 | 0.6 | 3.1 | 3.1 | 0.1 | −2.0 |
| $F_{T1t}$ [a] | 0.1 | −4.5 | 2.5 | −2.5 | 2.5 | −2.0 |
| $F_{T2t}$ [a] | 5.2 | 0.2 | 2.2 | 2.2 | −2.2 | 2.0 |
| $\varphi$ | 88.33° | 41.62° | 39.77° | 41.13° | 105.51° | 151.12° |
| $\chi$ | 35.82° | 110.80° | 69.57° | 103.85° | 38.70° | 68.28° |
| $\|\|Q_\theta\|\|$ | −2.398 | −0.875 | −2.545 | −2.848 | 2.759 | 1.739 |
| $\|\|Q_\epsilon\|\|$ | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| $\|\|Q_\xi\|\|$ | −2.470 | 2.301 | −1.949 | 1.750 | 1.718 | −1.533 |
| $\|\|Q_\eta\|\|$ | 2.470 | −2.301 | 1.949 | −1.750 | −1.718 | 1.533 |
| $\|\|Q_\zeta\|\|$ | −2.418 | 1.760 | −1.234 | 0.914 | 0.821 | 0.891 |
| HEV(1) | 1.0 | 1.0 | 1.0 | 1.0 | 1.0 | 1.0 |
| HEV(2) | 0.999 | 0.998 | 0.956 | 0.976 | 0.955 | 0.988 |
| HEV(3) | 0.996 | 0.905 | 0.828 | 0.849 | 0.896 | 0.582 |
| HEV(4) | 0.675 | 0.388 | 0.394 | 0.577 | 0.452 | 0.118 |
| HEV(5) | 0.656 | 0.193 | 0.348 | 0.217 | 0.161 | 0.099 |
| Energy | −11.902 | −7.226 | −7.797 | −7.537 | −7.093 | −4.260 |

[a] $K_E$ and $K_T$ are set equal to 1.

$$B\otimes A:\left(\frac{\cos\varphi}{\sqrt{2}},-\frac{\cos\varphi}{\sqrt{2}},\sin\varphi\right)\otimes\left(\frac{\cos\chi}{\sqrt{2}},-\frac{\cos\chi}{\sqrt{2}},\sin\chi\right).$$

Although the $A\otimes A$ and $B\otimes B$ products are both totally symmetric, they cannot form a linear combination since it takes a two-particle operator to connect these states. For the $A\otimes A$ and $B\otimes B$ cases one finds the trivial solutions with $\varphi=0$ and $\pi/2$ that correspond to the orthorhombic points already considered (see Table VII). In addition they yield a genuine $C_{2h}(C_2)$ point as well. For $A\otimes A$ it appears for

$$\cos^2\varphi=\frac{2}{3}\left(1-\frac{3F_{T1e}F_{T2e}K_T-2F_{T1t}F_{T2t}K_E}{2(3F_{T2e}^2K_T-2F_{T2t}^2K_E)}\right), \tag{3.18}$$

and similarly for $B\otimes B$ with the appropriate substitution $F_{T2e}/F_{T1e}$ and $F_{T2t}/F_{T1t}$. These points of course only exists if the expression in the right-hand side of the equation has a value in the [0,1] interval.

The most interesting extrema are found on the $B\otimes A$ sheet. If we factor out solutions with higher epikernel symmetries, the extremal conditions on the $\varphi$ and $\chi$ angles can be converted into a single quintic equation in $\cos 2\varphi$. This equation cannot be solved in general but numerical tests clearly show that one can easily find parameter values for which these $C_{2h}(C_2)$ points become absolute minima. In Table VIII we list several examples, which were solved by a standard numerical minimization procedure on the hypersurface. In each of these cases the $C_{2h}(C_2)$ point corresponds to the absolute minimum, all Hessian eigenvalues (HEV) being positive. Quite remarkably sign differences between the vibronic parameters are no condition sine qua non for the existence of a solution with such low epikernel symmetry. A case in point is the third example: both $F_{T1t}$ and $F_{T2t}$ have pronounced positive values, which is in favor of a trigonal minimum. Note that the $T_1$ vector is indeed very close to a trigonal eigenvector ($\varphi=39.77°$ as compared to 35.26° for an ideal trigonal eigenvector). On the other hand, the $T_2$ state is subject to a strong tetragonal distortion due to larger values of $F_{T2e}$. These two opposing trends are seen to yield a $C_{2h}$ optimum, which is the largest common subgroup of tetragonal and trigonal distortions. Once again this example shows that the preference for minima with high epikernel symmetries is not a characteristic of product-JT systems. We will come back to this point in Sec. V.

#### 4. $C_{2h}(C_4^2)$

Finally we investigate the alternative $C_{2h}$ epikernel, based on a fourfold symmetry direction. For the $z$ direction, three possible eigenvectors have to be examined,

$$\begin{aligned}&B\otimes A:(\cos\varphi,\sin\varphi,0)\otimes(0,0,1),\\&A\otimes B:(0,0,1)\otimes(\cos\varphi,\sin\varphi,0),\\&B\otimes B:(\cos\varphi,\sin\varphi,0)\otimes(\cos\chi,\sin\chi,0),\end{aligned} \tag{3.19}$$

where $\varphi$ and $\chi$ are to be determined from extremal conditions. For the $B\otimes A$ and $A\otimes B$ cases only trivial solutions are found with $\varphi=n\pi/4$ $(n=0,1,2,3)$. These solutions have, in fact, orthorhombic symmetry and were already described in the foregoing sections. For the third case further trivial solutions are also retrieved with $\varphi=\chi=n\pi/4$ and $\varphi=\chi+\pi/2=n\pi/4$ $(n=0,1,2,3)$. However, in this case a genuine $C_{2h}$ solution is also found. The extremal conditions that determine this solution can be reduced to

$$\cos 2\varphi(2F_{T1t}'^2-3F_{T1e}'^2)-3\cos 2\chi F_{T1e}'F_{T2e}'+2\cot 2\varphi\sin 2\chi F_{T1t}'F_{T2t}'=0,$$

$$\cos 2\chi(2F_{T2t}'^2-3F_{T2e}'^2)-3\cos 2\varphi F_{T1e}'F_{T2e}'+2\cot 2\chi\sin 2\varphi F_{T1t}'F_{T2t}'=0,$$

where

TABLE IX. Analytical results for $B\otimes B$ extrema of $C_{2h}(C_4^2)$ symmetry.

| Label | 1 | 2 | 3 | 4 | 5 | 6 |
|---|---|---|---|---|---|---|
| $F_{T1e}$ [a] | 1.6 | 1.6 | 1.0 | 1.0 | 0.4 | 0.1 |
| $F_{T2e}$ [a] | 0.2 | 0.6 | 2.0 | 2.0 | 3.2 | 1.2 |
| $F_{T1t}$ [a] | −1.7 | −0.5 | 3.0 | 0.5 | 4.0 | 2.1 |
| $F_{T2t}$ [a] | 0.5 | 1.5 | 0.5 | 3.0 | −0.5 | 0.1 |
| $\varphi$ | −72.05° | −87.17° | 33.97° | 83.21° | −48.41° | 43.84° |
| $\chi$ | 60.21° | 77.79° | 5.81° | 72.04° | 86.28° | 2.79° |
| $\|\|Q_\theta\|\|$ | 0.900 | 1.100 | 1.500 | 1.500 | 1.800 | 0.650 |
| $\|\|Q_\epsilon\|\|$ | 1.210 | 1.786 | −2.022 | 2.245 | 2.790 | −1.038 |
| $\|\|Q_\xi\|\|$ | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| $\|\|Q_\eta\|\|$ | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| $\|\|Q_\zeta\|\|$ | 1.010 | 0.694 | 2.037 | 1.327 | −2.854 | 1.491 |
| HEV(1) | 1.0 | 1.0 | 1.0 | 1.0 | 1.0 | 1.0 |
| HEV(2) | 1.0 | 1.0 | 1.0 | 1.0 | 1.0 | 1.0 |
| HEV(3) | 0.847 | 0.993 | 0.993 | 0.998 | 0.992 | 0.998 |
| HEV(4) | 0.104 | 0.272 | 0.658 | 0.090 | 0.939 | 0.981 |
| HEV(5) | 0.092 | −0.077 | −0.326 | −0.024 | −0.745 | −0.909 |
| $E_{C_{2h}(C_4^2)}$ | −1.647 | −2.441 | −5.244 | −4.525 | −9.583 | −1.861 |
| $E_{C_{2h}(C_2)}$ [b] | * | *−2.447* | *−5.482* | *−4.532* | *−10.592* | *−2.197* |

[a] $K_E=K_T=1$.

[b] Energies given in this row were obtained by numerical minimization of the total Hamiltonian, using a wide range of starting coordinates. The asterisk denotes that no minimum energy with $C_{2h}(C_2)$ symmetry is found.

$$F'_{Tis}=F_{Tis}/\sqrt{K_S} \quad (i=1,2;s=e,t). \tag{3.20}$$

This remarkable system of equations can be solved analytically. The results can be written in terms of the parameters

$$\sigma_0=F'^2_{T1t}F'^2_{T2e}-F'^2_{T1e}F'^2_{T2t},$$

$$\sigma_i=3F'^2_{Tie}-2F'^2_{Tit} \quad (i=1,2), \tag{3.21}$$

$$\rho_s=\frac{F'^2_{T1s}\sigma_2^2-F'^2_{T2s}\sigma_1^2}{\sigma_0} \quad (s=e,t).$$

After much algebra, the meaningful sets of solutions are found to be

$$(\cos 2\varphi,\cos 2\chi)=\left(-\frac{F'_{T1e}}{\sigma_1},+\frac{F'_{T2e}}{\sigma_2}\right)\sqrt{\rho_t},$$

$$(\cos 2\varphi,\cos 2\chi)=\left(+\frac{F'_{T1e}}{\sigma_1},-\frac{F'_{T2e}}{\sigma_2}\right)\sqrt{\rho_t}. \tag{3.22}$$

It is found that these two sets of values of $\varphi$ and $\chi$ give the same energy. Substituting the solutions back into Eqs. (3.5) and (3.1), the energy expression for the $B\otimes B$ symmetry is obtained

$$E_{C_{2h}(C_4^2)}=-\frac{1}{4}\Bigg\{F'^2_{T1t}\left(2F'^2_{T2t}\left|\frac{\rho_e}{\sigma_1\sigma_2}\right|-\frac{F'^2_{T1t}}{\sigma_1^2}\rho_e\right)+\rho_t\left[\frac{3F'^2_{T1e}}{2\sigma_1}\left(\frac{F'^2_{T1e}}{\sigma_1}-\frac{2F'^2_{T2e}}{\sigma_2}\right)+\frac{F'^2_{T2e}}{2\sigma_2}\right]+F'^2_{T2t}-E_{D_{4h}}\Bigg\}. \tag{3.23}$$

Physical solutions exist only on the condition that $\rho_t>0$. In order to illustrate the details of these extrema, a sample is listed in Table IX. Parameters $\varphi$ and $\chi$ are restricted between $-\pi/2$ and $\pi/2$ and match numerical tests properly. It is found that usually these extrema are coexistent with $C_{2h}(C_2)$ minima on the potential energy surface. In all such examples the minima of the latter type were found to be a little bit lower. In contrast the first set of parameters in Table IX refers to a case where the $C_{2h}(C_4^2)$ minimum is the absolute minimum and where no coexistent $C_{2h}(C_2)$ minimum was found. It should be noted that each of the $C_{2h}(C_4^2)$ points in Table IX has 12 copies in the space of the distortion parameters.

## IV. THE ISOSTATIONARY FUNCTION AND THE EQUAL COUPLING CASE

Substituting the stationary coordinates $||Q_{\Lambda\lambda}||$ back into the energy expression $\langle E\rangle$ yields a function $\langle ||E||\rangle$ which was shown to have the same extremal points as the actual JT surface and was therefore called the isostationary function.[10] The proof of isostationary properties was later extended to bilinear terms and multimode effects.[11] The isostationary function not only provides the theoretical foundation for the Öpik and Pryce procedure but it also offers a compact view of the structure of the hypersurface. For the $T_1\otimes T_2$ system it consists of separate $e$ and $t_2$ parts and is given by

$$\begin{aligned}\langle\|E\|\rangle = &-\frac{1}{2K_E}\{[1-3(y^2z^2+z^2x^2+x^2y^2)]F_{T1e}^2\\ &+[-1+3(z^2\zeta^2+y^2\eta^2+x^2\xi^2)]F_{T1e}F_{T2e}\\ &+[1-3(\eta^2\zeta^2+\zeta^2\xi^2+\xi^2\eta^2)]F_{T2e}^2\}\\ &-\frac{1}{3K_T}\{3(y^2z^2+z^2x^2+x^2y^2)F_{T1t}^2\\ &+6(yz\eta\zeta+xz\xi\zeta+xy\xi\eta)F_{T1t}F_{T2t}\\ &+3(\eta^2\zeta^2+\zeta^2\xi^2+\xi^2\eta^2)F_{T2t}^2\}.\end{aligned} \tag{4.1}$$

This expression is a fourth rank tensor of the eigenvector coefficients. For the parent $T\otimes(e+t_2)$ system it is well known that the tensorial part in the isostationary function vanishes when the tetragonal and trigonal minima have the same depth. In this equal coupling case, the JT surface exhibit a minimal energy trough which allows for free rotation of the distortion mode around the high symmetry point.[12] This is the standard behavior of an orbital triplet in icosahedral symmetry where the $e$ and $t_2$ modes are degenerate. If we transpose the equal coupling conditions to our product system, we must require

$$\frac{F_{T1t}^2}{3K_T}=\frac{F_{T1e}^2}{2K_E},\quad \frac{F_{T2t}^2}{3K_T}=\frac{F_{T2e}^2}{2K_E}. \tag{4.2}$$

This implies that the cross terms will be equal in absolute value

$$\frac{F_{T1t}F_{T2t}}{3K_T}=\pm\frac{F_{T1e}F_{T2e}}{2K_E}. \tag{4.3}$$

We will further assume that in this equation the plus sign applies. This corresponds to the assumption of icosahedral symmetry. The isostationary function then becomes

$$\begin{aligned}\langle\|E\|\rangle = &-\frac{1}{2K_E}\{F_{T1e}^2+F_{T2e}^2\\ &+[-1+3(z\zeta+y\eta+x\xi)^2]F_{T1e}F_{T2e}\}.\end{aligned} \tag{4.4}$$

Consider the hole and particle functions to be vectors in a common three-dimensional space. Since both are normalized one has

$$z\zeta+y\eta+x\xi=\cos\omega, \tag{4.5}$$

where $\omega$ is the angle between them. The function then reduces to

$$\langle\|E\|\rangle=-\frac{1}{2K_E}\{F_{T1e}^2+F_{T2e}^2+(-1+3\cos^2\omega)F_{T1e}F_{T2e}\}. \tag{4.6}$$

Two extrema are possible, depending on the sign of the cross term. If $F_{T1e}$ and $F_{T2e}$ have the same sign—i.e., if the JT forces of the hole and particle act in the same sense—the isostationary function becomes minimal for $\omega=0$

$$\langle\|E\|\rangle|_{\omega=0}=-\frac{1}{2K_E}(F_{T1e}+F_{T2e})^2. \tag{4.7}$$

The two vectors are then aligned and this pair can freely rotate. This corresponds to the motion of the JT system in a two-dimensional trough. This trough contains the tetragonal and trigonal points described, respectively, in Tables I and III, as well as the orthorhombic points of type $B_2\otimes B_3$ listed in Table VII. Note that under equal coupling conditions the corresponding energies $E_{D_{4h}}$,$E_{D_{3d}}$, and $E_{D_{2h}}^{B_2B_3}$ [Eqs. (3.6), (3.8), and (3.14)] are indeed degenerate.

On the other hand, if $F_{T1e}$ and $F_{T2e}$ have opposite signs the JT energy becomes minimal for $\omega=\pi/2$

$$\langle\|E\|\rangle|_{\omega=\pi/2}=-\frac{1}{2K_E}(F_{T1e}^2-F_{T1e}F_{T2e}+F_{T2e}^2). \tag{4.8}$$

Now the hole and particle vectors are at right angles of each other. The free rotation of the pair has $SO(3)\otimes SO(2)$ symmetry, which yields a three-dimensional trough. Hence when the JT forces of the hole and particle components act in opposite senses the corresponding wave vectors cannot rotate in phase but are kept perpendicular to each other. Special points on this trough correspond to the lower ranking epikernels $D_{2h}$ and $C_{2h}$. We have encountered them in the previous section in Tables II and VII. Note that the corresponding energies $E_{D_{2h}}$,$E_{D_{2h}}^{B_1B_2}$,$E_{D_{2h}}^{B_2A}$, and $E_{D_{2h}}^{B_2B_2}$ [Eqs. (3.7) and (3.14)] all reduce to the same form under equal coupling conditions.

## V. DISCUSSION

As the present survey of a model product system shows, the physics of the coupled system is quite varied. If the two shells have similar sets of coupling parameters the classical high symmetry solutions of the separate open shells are easily retrieved. However, if the two shells develop pronounced distortions towards different epikernels, lower symmetry solutions may be found that correspond to the intersection of the epikernels involved. Such a case is exemplified in example 1 of Table VIII: the trigonal force element $F_{T2t}$ pulls this system into $D_{3d}$ symmetry, but the strong tetragonal force element $F_{T1e}$ simultaneously exerts a strong force towards $D_{4h}$. As a result neither $D_{4h}$ nor $D_{3d}$ symmetry is a solution and not even the $D_{2h}$ epikernel which is at the borderline of trigonal and tetragonal phases for the separate shells. Instead it is found that the absolute minimum has only $C_{2h}(C_2)$ symmetry, which is the intersection of $D_{4h}$ and $D_{3d}$ subgroups.

Pronounced symmetry lowering will also result if the two shells tend to distort the system along the same epikernel but in opposite directions. This occurs if the signs of the force elements are different. The equal coupling limit, presented in the previous section, presents a clear example of the importance of this sign difference. The appearance of low symmetry minima when adding equisymmetric forces is quite disturbing because it violates the epikernel principle. We will

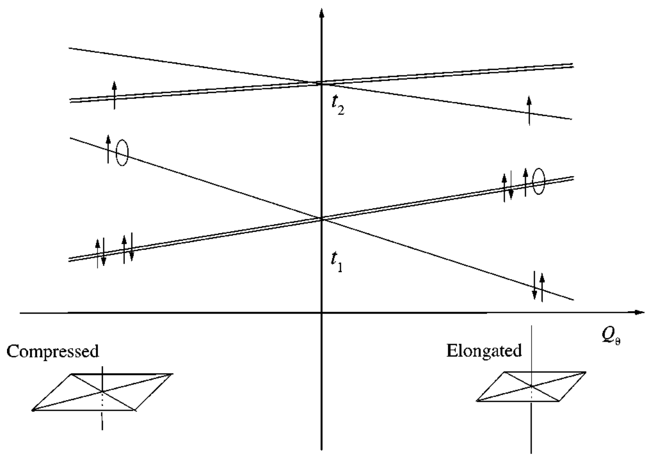


FIG. 2. Two-shell system of type $t_1^5 t_2^1$. The $t_1$ shell induces a tetragonal compression while the $t_2$ shell favors the tetragonal elongation.

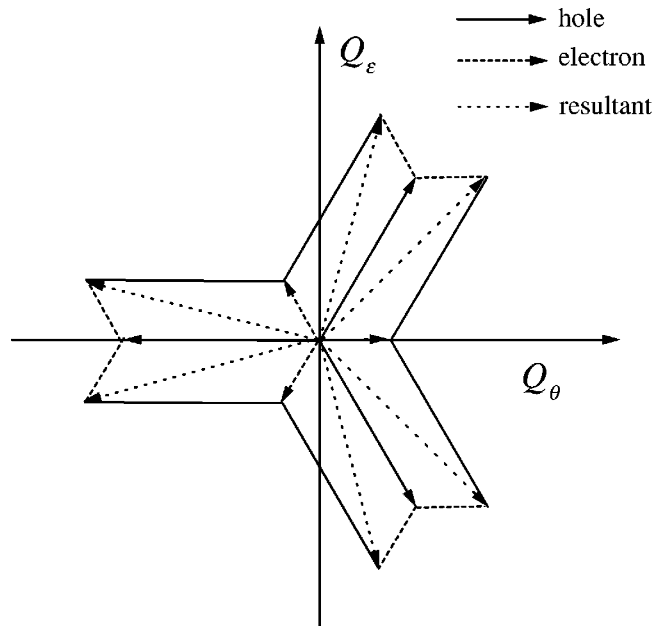


FIG. 3. The orthorhombic distortions in the $Q_\theta$ and $Q_\epsilon$ plane caused by the dominant JT forces of the hole and particle. The resultant vectors are the sums of the hole and particle vectors with the choice of the smallest angle between them.

now analyze more closely how a breaking of symmetry may arise from a sign change. Consider the simple case of the $\{T_1 \otimes T_2\} \otimes e$ problem with $F_{T1e} F_{T2e} < 0$. Both separate shells will have a preference for a $D_{4h}$ epikernel, but—because of the sign difference—along opposite directions. In Fig. 2 we depict as an example an excited $t_1^5 t_2$ configuration in which the hole component has a strong tendency to distort the system in the negative $Q_\theta$ direction (tetragonal compression) versus a weak tendency towards a positive $Q_\theta$ distortion (tetragonal elongation) for the particle component.

The force elements $F_{T1e}$ and $F_{T2e}$ thus have opposite signs. The remarkable consequence of this difference is that no matter in which $Q_\theta$ direction the system will distort the ground state will remain degenerate; if the system is tetragonally compressed, the degeneracy is due to the $t_2$ electron; if it is tetragonally elongated the degeneracy stems from the $t_1$ hole. The relative coupling strength does not influence this outcome, only the signs are important. In view of the JT theorem itself the system thus must further distort to a lower symmetry in which this degeneracy is lifted. This is indeed what happens, the compromise being a superposition of a tetragonal compression induced by the hole along one $C_4$ direction and a small tetragonal elongation, due to the electron, along a different $C_4$ direction.

The resultant symmetry group is only $D_{2h}(3C_4^2)$, which is the highest common subgroup of two $D_{4h}$ groups with different principal axes. The stationary coordinates for this case are found in Table II. They indeed correspond to sums of tetragonal distortion vectors pointing along different tetragonal directions. In Fig. 3 we illustrate this result in a schematic way. The figure represents the distortion vector in the $(Q_\theta, Q_\epsilon)$ plane for the dominant JT forces of the hole and the particle. Because of the sign differences these vectors are antiparallel. The dotted vectors denote the resultant orthorhombic distortions which give rise to six equivalent minima. By combining distortions along different tetragonal directions the system benefits from stabilization of both its hole and particle component, which is worth the sacrifice of a few symmetry elements.

## VI. CONCLUSION

The paper presents an analysis of a product-JT system composed of two triply degenerate shells. It is designed for cubic systems but can also be applied to icosahedral ones by imposing equal coupling conditions. The most interesting result is that opposite signs for the JT force elements in the separate shells lead to resultant distortions in the direction of lower ranking epikernels.

It is the purpose of this paper to extend the analysis to the icosahedral $T \otimes H$ product problem which occurs in the excited manifold of $C_{60}$. Interestingly, existing model calculations for the excited state of $C_{60}$ point to relaxation along low ranking epikernel coordinates.[13] Whether or not this can be explained by a product-JT effect will be the subject of further investigation.

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