

Chaos-induced breaking of the Franck-Condon approximation

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We investigate the vibrational structure of electronic spectra for the transition from the non-degenerate A state to E states in $E_g \otimes e_g$ Jahn-Teller systems with the trigonal field included. In connection with the underlying chaotic behavior for vibronic energy levels in this model reported by the present authors in Phys.Rev.**E68**(2003)046201, we extend the analysis by Longuet-Higgins et al. to the classically chaotic system. In particular, the triple-humped structure is manifest with increasing the anharmonicity. Such structure is completely inconsistent with the shape obtained from Franck-Condon(FC) approximation, and is caused by the chaos-induced beaking of the FC principle.

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We investigate the vibronic problem in degenerate E_g orbitals of d -levels in transition metal ions coupled with 2-d vibrational modes e_g expressed by coordinates $Q_1(=Q_{e_g u})$ and $Q_2(=Q_{e_g v})$ by taking into account the trigonal distortion. This $E_g \otimes e_g$ model is the typical system[1] showing dynamic Jahn-Teller effects(DJTE), which has been discussed in the field of magnetism for transition-metal ions. In fact, the numerical work was launched [2, 3] by Longuet-Higgins et al[LH] in 1958. Since then, the double-humped vibrational structure of electronically allowed transitions from the electronically non-degenerate ground state A to a Jahn-Teller degenerate state $E_g \otimes e_g$ has been the fundamental subject in optical properties of transition-metal ionic compounds. There the ground state is taken as the level of zero-phonon in A state at zero temperature.

Recently, the present authors[4] found the relationship between the chaotic behavior of this system and the magnetic g -factors of electronic orbital angular momentum as well as features of level statistics for vibronic states. The statistical properties of those levels and the energy dependence of g -factor shed light on the quantum signature of “Chaos” in this Jahn-Teller system.

In the present paper, we first report the novel vibrational structure in the spectra of the transition from the non-degenerate A state to the excited states in the $E_g \otimes e_g$ model. Secondly, the comparative study between vibrational structure in quantum mechanical treatment and the semiclassical one in Condon approximation for the adiabatic potential is made in order to see the role of “Quantum Chaos” [5, 6].

The Hamiltonian matrix \mathcal{H} is expressed as

$$\mathcal{H} = -\frac{\hbar^2}{2} \left(\frac{\partial^2}{\partial Q_1^2} + \frac{\partial^2}{\partial Q_2^2} \right) \mathbf{I} + \frac{1}{2} \omega^2 (Q_1^2 + Q_2^2) \mathbf{I} + k[-Q_1 \sigma_3 + Q_2 \sigma_1] + b Q_1 (Q_1^2 - 3Q_2^2) \mathbf{I}, \quad (1)$$

where \mathbf{I} is the unit matrix and σ_i with $i = 1, 2, 3$ are Pauli matrices. This Hamiltonian operates on φ_u and φ_v bases in E_g state, which are expressed as $|3z^2 - r^2\rangle$ and $|x^2 - y^2\rangle$, respectively. In the third term called “linear Jahn-Teller matrix”, k is the coupling between electronic and vibrational states. The strength of the anharmonic trigonal field is expressed by b of the fourth term.

Without the trigonal field, the second and the linear Jahn-Teller matrix give the adiabatic potential energy surfaces(APES) for axial symmetry: APES is expressed as $(1/2)\omega^2 \rho^2 \pm k\rho$, where $\rho = \sqrt{Q_1^2 + Q_2^2}$. It should be noted that APES is independent on azimuthal angle $\theta = \tan^{-1}(Q_2/Q_1)$. Therefore, APES for the lower branch has the continuous minima whose value is k^2/ω^2 . Such minima draw the circle located at the bottom of the so-called “Mexican Hat” potential. In the vibronic problem, we take into account the first term of (1) in addition to the other static terms. Namely, we treat the vibrational modes e_g as the 2-dimensional harmonic oscillator for quantum mechanics in order to investigate the dynamical effects: Wavefunctions are described as $\phi_{nm} = F_{n|m}(\rho)e^{im\theta}$, where $n = 1, 2, \dots$ and $m = n - 1, n - 3, \dots, n + 1$. Here, $F_{n|m}(\rho)$ is the confluent hypergeometric function[7, 8]. According to the conventional procedure for the degenerate electronic state E_g , we employ the expressions φ_{\pm} of eigenfunctions for 2-dimensional angular momentum, which are transformed from φ_u and φ_v : The transformation is $\varphi_{\pm} = (1/\sqrt{2})(\varphi_u \pm i\varphi_v)$. Thus, the linear Jahn-Teller matrix in (1) is transformed to $\sqrt{2}k\rho e^{i\theta} i\sigma_2$. Using $\phi_{nm}(\rho, \theta)$ and φ_{\pm} , we can express bases of present vibronic wave-

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functions as

$$\Phi_{nm}^{\pm} = \varphi_{\pm} \cdot \phi_{nm}(\rho, \theta). \quad (2)$$

The quantum mechanical expression of the present $E_g \otimes e_g$ model is obtained from the following nonvanishing elements:

$$\begin{aligned} & \langle \phi_{n,m} | \rho e^{i\theta} | \phi_{n',m'} \rangle \\ &= \left\{ \frac{\hbar}{2\omega} [n \pm (m-1)] \right\}^{1/2} \delta_{n',n \mp 1} \delta_{m',m-1} \\ & \langle \phi_{n,m} | \rho e^{-i\theta} | \phi_{n',m'} \rangle \\ &= \left\{ \frac{\hbar}{2\omega} [n \pm (m+1)] \right\}^{1/2} \delta_{n',n \pm 1} \delta_{m',m+1}. \end{aligned} \quad (3)$$

If we assign the quantum numbers $j = \pm 1$ to $\Phi_{n,m}^{\pm}$, the Jahn-Teller interaction without the anharmonic term connects the states with the same quantum number, $\ell = m - (1/2)j$ ($j = \pm 1$). The present matrix decomposes into matrices labeled by quantum number ℓ . For any given value of ℓ , m can take two values, $m = \ell - 1/2$ and $\ell + 1/2$ corresponding to $j = -1$ and $+1$, respectively. Thus, the p -th eigenfunction for a given ℓ is expressed as $\Psi_{p,\ell}$. As a result, the total angular momentum ℓ whose values are $\pm 1/2, \pm 3/2, \pm 5/2, \dots$ becomes the good quantum-number in the case of $b = 0$.

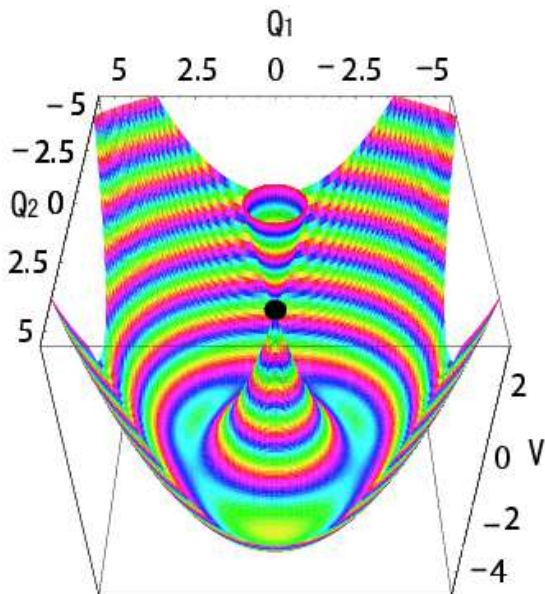


FIG. 1: APES with the trigonal distortion expressed as $bQ_1(Q_1^2 - 3Q_2^2)$. Three minima are induced. The full point means the conical intersection.

In the absence of the trigonal field in (1), LH obtained the vibrational structure appearing in allowed electronic spectra from the non-degenerate electronic state A to $E_g \otimes e_g$ system for various values of k , finding the structure with two intensity maxima in the energy region of $-10\hbar\omega \leq \varepsilon \leq 15\hbar\omega$. This double-humped structure can be explained by the transitions to a pair of branches of APES in the $E_g \otimes e_g$ system.

In this paper, we consider the third term ($b \neq 0$) in (1), which expresses the anharmonicity keeping invariant to any operation in the cubic group. In fact, it gives the trigonal ligand field $\rho^3 \cos 3\theta = Q_1(Q_1^2 - 3Q_2^2)$ to the adiabatic potential as shown in Fig.1: The continuous circular symmetry is destroyed and three minima appear in the lower branch. We shall calculate vibrational structures in the spectra in this case. O'Brien investigated[9] the system (1) with the trigonal field in the low-energy approximation that ρ is fixed to be ρ_0 at the bottom of the Mexican-hat, but gave no discussion on the spectra[9]. Here we numerically calculate eigenvalues and eigenvectors without having recourse to such an approximation in order to obtain the spectra exactly. In this case, the angular momentum ℓ is not a good quantum number: By the trigonal field, the levels for $\ell = 1/2 \pm 3\nu$ (where $\nu = 1, 2, 3, \dots$) are mixed into the levels of $\ell = 1/2$. We get in this way a set of vibronic doublets arising from combinations with $\ell = \pm 1/2, \mp 5/2, \pm 7/2, \mp 11/2, \pm 13/2, \dots$ (where either the upper or lower sign is to be taken throughout). Namely, we treat the doubly degenerate E representations of the symmetry group C_{3v} . On the other hand, solutions with $\ell = \pm 3/2, \pm 9/2, \pm 15/2, \dots$ correspond to identical representation A and B of group C_{3v} : A is the mode with the symmetric composition for $\ell > 0$ and $\ell < 0$, while B with anti-symmetric one.

One of the observable phenomena where the trigonal field plays a notable role is the spectral line shape of a parity-allowed transition in which the final state is $E_g \otimes e_g$ while the initial state is an orbital singlet A . The quantum mechanical calculation of the spectral line-shape is possible if the eigenvectors of the matrix with elements (3) are known. In short, the spectra are made of the probability density to find the first basis $\Phi^- \equiv u_-(\mathbf{r})\phi_{1,0}(\rho, \theta)$ in the final state of the transition.

The calculated vibrational structure in the transition spectra from A to the excited levels are shown in Fig.2(a),(b),(c) and (d), where the strength of the trigonal field b is 0,1.41,2.5 and 5, respectively. Here, the coupling parameter k in (1) is fixed to be 4.47 (i.e., $k^2 = 20$). It is certain that the double-humped structure for $b = 0$ (see Fig.2(a)), composed of transitions only to levels in $\ell = 1/2$, agrees with that in LH[2]. As b increases, however, the double-humped structure changes into the triple-humped one, because of the mixing of levels for $\ell = \mp 5/2, \pm 7/2, \mp 11/2, \dots$ into the excited E state. In other words, an extra new hump appears at the conical interaction, i.e., around the dip of double-humped structures. The central branch in the spectrum is the common result proper to the system with the trigonal field, as shown in Fig.2(b),(c) and (d). This new hump can also be interpreted as ‘‘Quantum Chaos’’ emanating in the region $b \lesssim k$ [4], as explained below.

In order to discuss this triple-humped structure in detail, we calculate semiclassical spectra in Franck-Condon(FC) approximation, which is schematically shown in Fig.3. The physical implication for this approximation is intuitively clear: It shows that the electronic

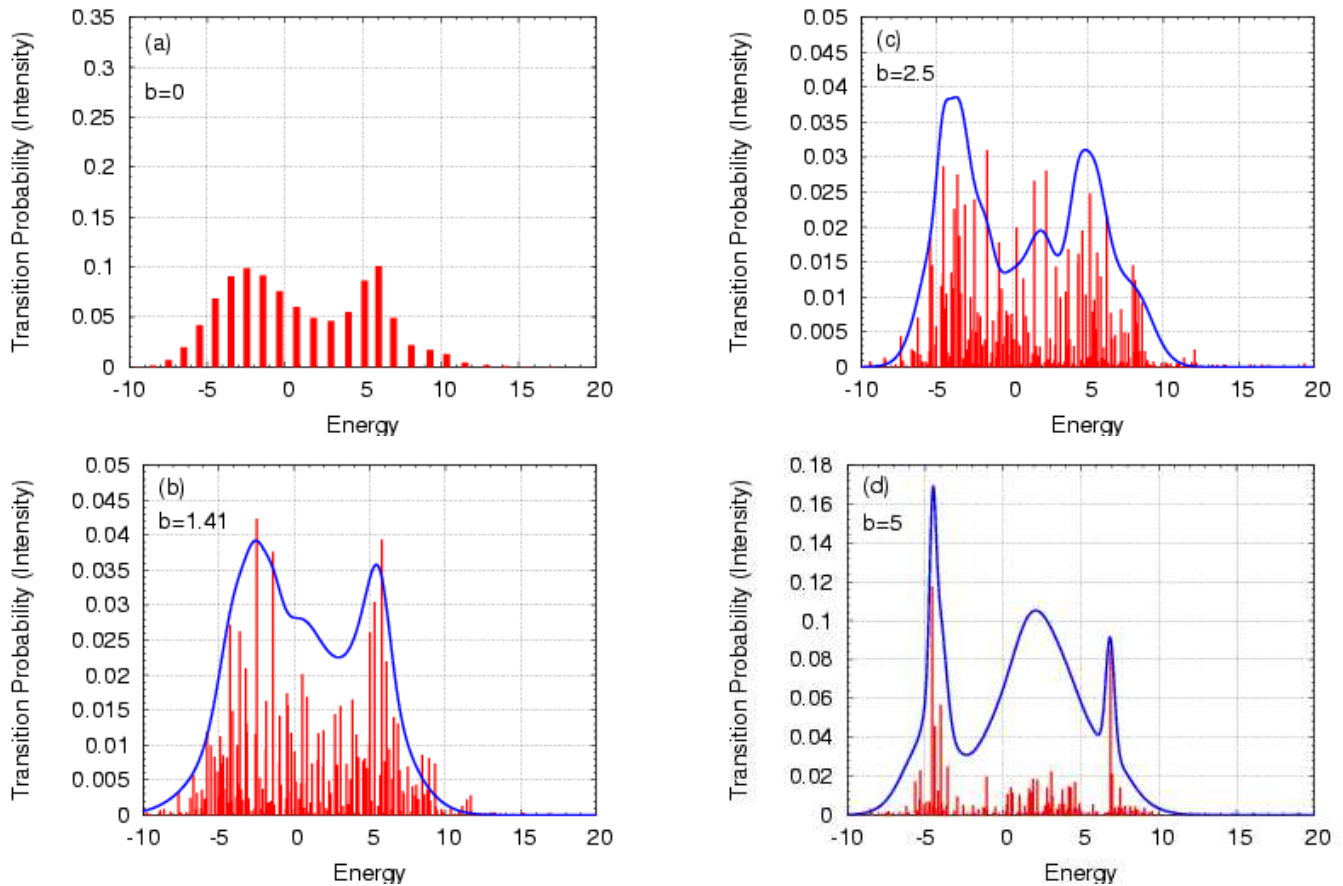


FIG. 2: The calculated vibrational structure in transition spectra from A to $E_g \otimes e_g$ system with the trigonal field are shown in (a)(b)(c)(d), where the strength of the field b is 0,1.41,2.5 and 5, respectively. The coupling k between electronic and vibrational states is fixed to be 4.47. The envelop functions for line-spectra are drawn by solid lines.

transition takes place so rapidly that the nuclear positions do not change during the transition. In fact, the two intensity maxima of the transition spectra without anharmonicity were revealed by Y.Toyozaawa and M.Inoue[10]. They showed the absorption line-shape function for the transition spectrum by using the semiclassical FC approximation. Here, we shall show the consequence of the FC approximation applied explicitly to the system with cases of $b \neq 0$. Namely, APES consists of two branch surfaces as shown in Fig.1, corresponding to

$$\varepsilon_{\pm}(\rho, \theta) = \varepsilon_0 \mp k\rho + b\rho^3 \cos 3\theta \quad (4)$$

where ε_0 is the excitation energy from the ground state A to the excited one E at $\rho = 0$. Within the semiclassical FC approximation, the normalized line-shape function of the optical absorption is given by

$$F(\hbar\omega) = \frac{1}{2} \sum_{\pm} \int \int d\theta \sin\theta d\rho \rho \left(\frac{1}{\pi\kappa T} \right) \times \exp\left(-\frac{\rho^2}{\kappa T}\right) \delta\{\hbar\omega - \varepsilon_{\pm}(\rho, \theta)\}, \quad (5)$$

where κ , T and $\hbar\omega$ are the Boltzmann constant, the absolute temperature and the photon energy, respectively.

Namely κT give the width to line spectra. In the present calculation, we use $\kappa T = 0.72\hbar\omega$. Without anharmonicity the absorption shape function is integrable[10]. ($b = 0$): This gives a line-shape which is completely split into upper and lower parts, as shown in Fig.3. In Fig.4, we show the line shape in FC approximation for $b = 2.5$, which is completely inconsistent with the triple-humped feature in Fig.2(c).

In the presence of the trigonal(anharmonic) potential, the nonadiabatic motion of electron wave packet can show chaotic features with the outstanding occupation probability at the conical intersection due to its subtle distortions. This means the increase of density of state at the energy where the conical intersection locates. Therefore, the transition from A state has extra final states at the level of the conical intersection, i.e., triple-humped structure as a whole. Here a simple application of the FC principle is not justified(see the pertinacious double-humped structure in Fig.4).

As a result of comparative discussion between vibrational structure and the semiclassical spectra in FC approximation, we would like to point out the following fact: The new peak comes from the non-adiabatic dy-

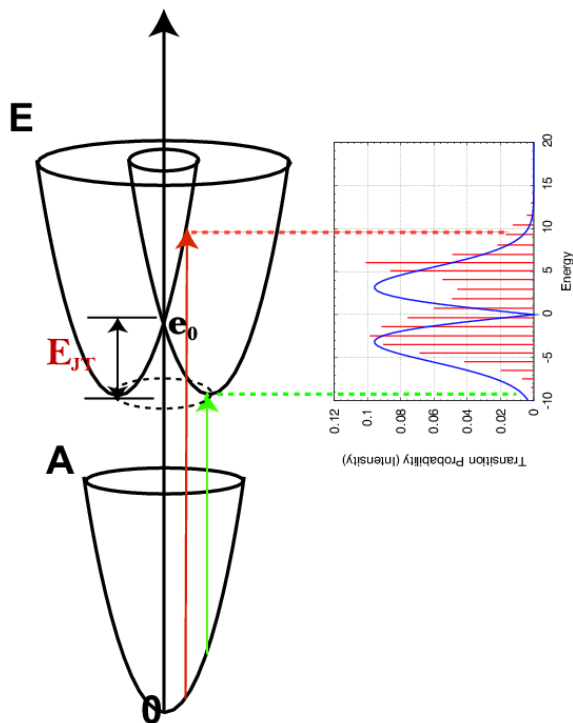


FIG. 3: APES of the electronic states A and E . The spectral line-shape function for the transition from A to E states obtained by the semiclassical Franck-Condon approximation is shown by the solid curve for the typical case of $b = 0$, which has been reported in [10]. This function becomes zero at $\varepsilon = 0$ from mathematical nature of APES at $\rho = 0$. The corresponding vibronic structures are also drawn by dotted lines.

namic mixing to the pair of lower and upper APES for electronic E_g state, which is a typical quantum manifestation of the underlying chaos.

In conclusion, we find a new hump induced by the trigonal field in the transition spectrum, which is manifesting of quantum chaos in vibrations coupled with electronic states in the case of $b = 0$. In the strong coupling limit ($k \gg 1$), the void between a pair of APES is obvious. This fact led to the double-humped structure of LH[2]

in the nonadiabatic spectra of the transition from A to degenerate $E_g \otimes e_g$ states. This spectra can be nicely reproduced by application of the FC principle. However, the anharmonic trigonal term, which yields the new density of states near the energy of the conical intersection, breaks the FC principle.

In the case of the oscillation of magnetic g -factor[4] we assumed the small k value. The quenching of the regular oscillation was also caused by the underlying classical chaos due to anharmonic term. On the contrary, in the present work, we require the k value to be sufficiently large to ensure the double-humped transition spectra due to the obvious splitting of two APES, and chaos in the nonadiabatic electron wave packet plays an essential role.

The relationship between vibrational structures of spectra and chaotic behavior in the present quantum sys-

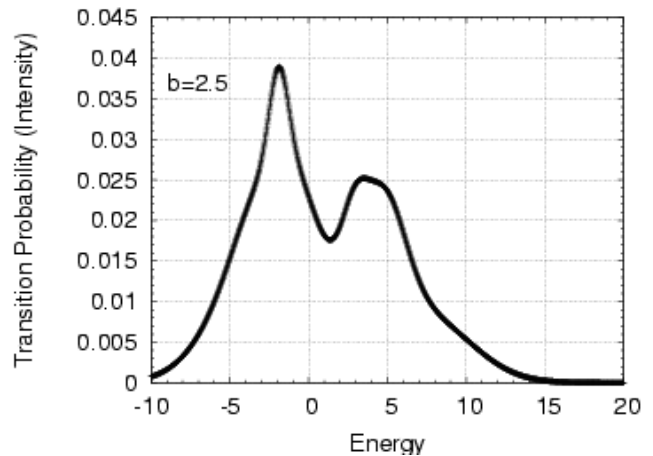


FIG. 4: The shape of spectra for $k = 4.47$ and $b = 2.5$ obtained by Franck-Condon approximation discussed in the text. Temperature is determined to be $0.72\hbar\omega/\kappa$. The shape is completely inconsistent with feature in Fig.2(c).

tem is quite attractive, though there is very much left to study of analyzing this characteristic structure in connection with experimental work for transition-metal ions in compounds.

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