Exact diagonalization for the vibronic levels of dynamic Yahn-Teller systems –E_g orbitals with e_g modes in trigonal fields–

Hisatsugu Yamasaki [a], Yuhei Natsume [a,1],

[a] *Graduate School of Science and Technology, Chiba-University, Inage-ku, Chiba, 263-8522 Japan*

Abstract

The electronic states of degenerate E_g orbitals of d-levels in transition-metal ions coupled with vibrational modes of e_g are discussed on the basis of numerical calculation. This is the typical system of dynamic Jahn-Teller effects(DYTE): As the coupling of these electronic states E_g with e_g vibrational modes expressed as Q_1 and Q_2 is essentially non-adiabatic, we obtain structures of vibronic levels by the method of exact diagonalization. In addition, we investigate vibronic levels for systems in low-symmetric potentials, where the trigonal fields expressed as $b \cdot (Q_1^3 - 3Q_1Q_2^2)$ are taken into account. Using these results, we discuss features in level-structures for systems of DYTE.

Key words: dynamic Jahn-Teller effects; vibronic states; trigonal fields

---

1. Introduction

We investigate the electronic states of degenerate E_g orbitals of d-levels in transition-metal ions coupled with vibrational modes of e_g expressed as Q_1 and Q_2. This is the typical system of dynamic Jahn-Teller effects (DYTE), which has been traditionally discussed in the field of magnetism in transition-metal compounds. [1]. The Hamiltonian Matrix H for bases of E_g orbitals is expressed as

$$H = -\frac{\hbar^2}{2}(\frac{\partial^2}{\partial Q_1^2} + \frac{\partial^2}{\partial Q_2^2})\mathbf{I} + k \begin{bmatrix} Q_1 & Q_2 \\ Q_2 & -Q_1 \end{bmatrix} + \frac{1}{2}\omega^2(Q_1^2 + Q_2^2)\mathbf{I}, \qquad (1)$$

where $\mathbf{I}$ is the unit matrix. Bases of electronic orbitals E_g are determined to be $u = |3z^2 - r^2>$ and $v = |x^2 - y^2>$. Here, k is the coupling parameter between electronic states and vibrational modes. As well confirmed, the corresponding adiabatic potential of (1) has the Mexican-hut shape as shown in Fig.1, where $Q_1 = \rho\cos\theta$ and $Q_2 = \rho\sin\theta$. The minimum occurs at $\rho = \rho_0 = k/\omega^2$ with an arbitrary value of θ. The energy of the minimum is $k^2/2\omega^2$. Namely no static point is given on this potential. In fact, vibronic levels for quantum Hamiltonian has been discussed [2] as the problem of DYTE on the basis of numerical calculation in rather small dimensional Hamiltonian matrices. Recently, this model has been investigated from the viewpoint of the geometric phase.[3] Further, the effect of the trigonal fields expressed as the anharmonic term $-(b/3)(Q_1^3 - 3Q_1Q_2^2)$ has been also analysed as to some low-lying levels [4]. In short, she has adopted the low-energy approximation in which electronic states are confined at ρ_0.

2. Present calculation

In this work, we perform the exact diagonalization of the vibronic Hamiltonian without the approximation used in previous papers [2,4]. As results, we can make

---

[1] Corresponding author. E-mail:natsume@science.s.chiba-u.ac.jp

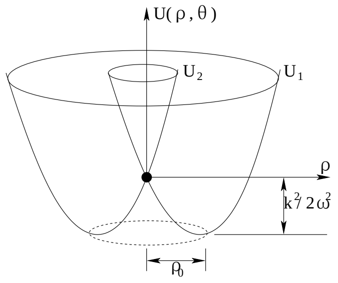

Fig. 1. The adiabatic potential of Mexican-hut shape. Here, ρ is $\sqrt{Q_1^2+Q_2^2}$. The potential has the minimum at ρ at $\rho_0 = k/\omega^2$.

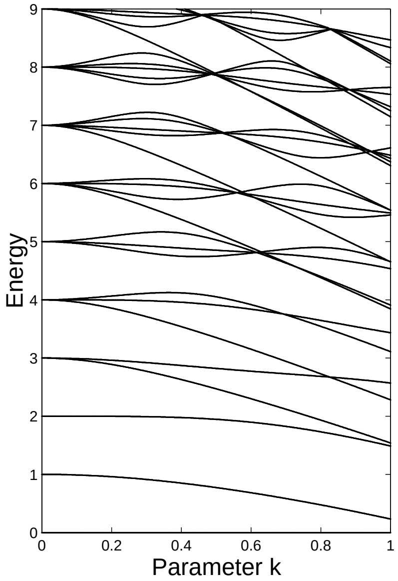

Fig. 2. The dependence of vibronic levels on the coupling parameter k between electronic states and vibrational modes. Here, the trigonal field is not considered.

quantitative discussion of DYTE in comparison with observations in magnetic compounds.[5]

3. Results and discussion

In Fig.2, we show the dependence of vibronic levels on the coupling parameter k between electronic states and vibrational modes. Here, the trigonal field is not considered. In this case, the energy matrix decomposes into the matrices labeled by quantum number of the total angular momentum ℓ which is half-integers of $m+\frac{1}{2}$ and $m-\frac{1}{2}$. Here, m denotes two-dimensional angular momentum in the space of (Q_1, Q_2). The fractional angular momentums is caused by the degenerate electronic states E_g, The doubly degenerate electronic states treated here are non-Kramers doublets having non-vanishing orbital angular momentum, though significant repellings appear with increasing k. Because of properties by the non-adiabatic coupling between electric states and vibrational modes (Q_1, Q_2), the characteristic re-appearances of the degeneracy are clearly found with increasing k. The fact that ℓ with these values of half-integers is conserved originates from the the axial symmetry of the adiabatic potential in Fig.1.

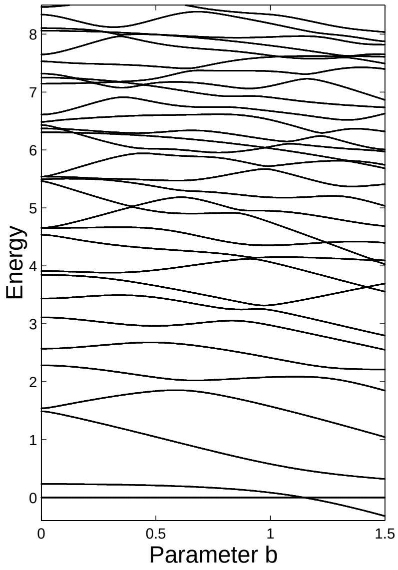

Fig. 3. Level structures for the case with the trigonal field. The value of k is fixed to be 1. The dependence on the strength of trigonal field b is shown. Here, the braking of the axial symmetry induces the additional splittings.

Further, level structures for the case with the trigonal field are illustrated in Fig.3, where the dependence on the strength of trigonal field b is shown. The value of k is fixed to be 1. Here, the braking of above axial symmetry induces the additional splittings: Each level can be assigned as A,B or E representation of C_{3v} symmetry. We can find more vigorously repelling of vibronic levels than that shown in Fig.2. Orbital angular momenta are almost quenched as b increases. In particular, vigorously repellings near at $b = 1$ should be noted.

References

[1] S. Sugano, Y. Tanabe and H. Kamimura, *Multiplets of Transition-Metal Ions in Crystals.* Academic Press, (1970) Chapter 9.

[2] H.C.Longuet-Higgins, U. Öpik, M.H.L. Pryce and R.A. Sack, Proc.Roy.Soc. **A244** (1958) 1.

[3] C.Alen.Mead, Rev.Mod.Phys. **64**(1992) 51.

[4] M.C.M.O'Breien, Proc.Roy.Soc. **A281** (1964) 323.

[5] S.Washimiya, Phys.Rev.Lett. **28**(1972) 556.