Multiconical Intersections and Nondegenerate Ground State in $E \otimes e$ Jahn-Teller Systems

Hiroyasu Koizumi* and Isaac B. Bersuker

Department of Chemistry and Biochemistry, The University of Texas, Austin, Texas 78712

(Received 18 June 1999)

We have investigated the $E \otimes e$ Jahn-Teller problem with large quadratic coupling. Our results reverse the paradigm that, in $E \otimes e$ Jahn-Teller systems, the ground vibronic state should be the same as that of the initial doubly degenerate electronic E term. The E vibronic state is the ground state for small quadratic coupling when the dominant tunneling path between the potential surface minima encircles one central conical intersection, whereas for large quadratic coupling it goes around four conical intersections and the ground state becomes nondegenerate.

PACS numbers: 71.70.Ej, 03.65.Bz, 31.30.Gs, 82.90.+j

There is a widespread belief that the ground state symmetry of any vibronic system is the same as that of the initial degenerate electronic state. The assumed ground state symmetry significantly affects the interpretation of the observed properties of the system. In particular, this assumption lies in the base of the theory of vibronic reduction factors widely used to derive the ground state properties from those of the degenerate electronic state [1,2]. Therefore, the problem of whether the ground state symmetry is that of the initial degenerate electronic state or not is a matter of fundamental importance. The concern about this point has been increased after the finding that for some parameter values the ground vibronic state in the Jahn-Teller $H \otimes h$ problem is nondegenerate [3], which shattered the paradigm that the vibronic ground state should have the same degeneracy and symmetry as the initial degenerate electronic state.

In this Letter, we revisit the $E \otimes e$ Jahn-Teller system with strong vibronic coupling including quadratic and fourth order terms, and examine whether the nondegenerate A symmetry ground state exists or not. Contrary to the experience-based belief, we found that the ground state of this system may be nondegenerate, of A type. It exists in cases where the quadratic vibronic coupling constant is sufficiently large.

In the case of the strong vibronic coupling, the tunneling between the minima of the adiabatic potential of Jahn-Teller systems was first studied by Bersuker [4]. He started from the deep minima of the adiabatic potential of the ground state and diagonalized the full Hamiltonian using the displaced harmonic oscillators as a basis set. The ground state of the system was found in this way to be nondegenerate with the twofold degenerate E tunneling level higher in energy. This result was questioned after the work of O'Brien [5], in which numerical calculations starting from the linear $E \otimes e$ problem and treating quadratic vibronic coupling as a perturbation yield the doubly degenerate E level as the ground term. The subsequent works on the $E \otimes e$ problem followed this scheme and resulted in the E ground state, contributing thus to the formation of the above-mentioned paradigm.

The double degeneracy of the vibronic ground state was first obtained by Longuet-Higgins *et al.* [6]. In the case of strong vibronic coupling with deep potential minima it can be associated with the Berry phase [5,7,8] arising from the conical intersection of the adiabatic potential surface. O'Brien attached a phase factor to the wave function in order to satisfy the sign-change boundary condition [5]. Polinger obtained the E symmetry ground state considering a closed loop around the conical intersection at the center and using the WKB connection formula for the tunneling by imposing an antiperiodic boundary condition [9]. It is also shown by Ham that the sign-change boundary condition required by the Berry phase gives the doubly degenerate ground state [8].

However, in the case of sufficiently strong quadratic coupling, three additional conical intersections on the interminimum barriers come close to the one at the center. Then, two types of important tunneling paths that penetrate the interminimum barrier are possible: one goes through the saddle point between the conical intersections at the center and at the barrier, and the other goes through the saddle point outside of both of them. The dominant tunneling path will be the one that yields the larger tunneling rate between the two. It is plausible that the two types of tunneling paths, mentioned above, form parts of two different stationary semiclassical paths for the path integral representation of the resolvent [10], where one of them encircles the conical intersection at the center only, and the other goes around all four. As shown by Zwanziger and Grant, the electronic wave function does not change sign after the circular transportation along a closed loop that goes outside of all four conical intersections [11]. By employing the same type of argument as that of Polinger [9] for this closed path, it can be easily shown that the ground state of this system is nondegenerate with A symmetry. Then we can assume that the change of the ground state symmetry and degeneracy from A to E is correlated with the change of the dominant tunneling path. We will show below that this is indeed the case and the change of the ground state degeneracy (the A-E level intersection) is directly correlated to the change of the dominant

tunneling path which is estimated by the one-dimensional WKB tunneling rate.

The model Hamiltonian for doubly degenerate electronic states $\{|a\rangle, |b\rangle\}$ of the E representation and doubly degenerate normal vibrational coordinates $Q_1 = \rho\cos\theta, Q_2 = \rho\sin\theta$ of the E representation is given by

$$H = H_0 + H_1 + H_2, \tag{1}$$

where

$$H_0 = \sum_{e=a,b} h_{2\mathrm{DHO}}|e\rangle\langle e|, \tag{2}$$

where $h_{2\mathrm{DHO}}$ the Hamiltonian for the two-dimensional isotropic harmonic oscillator,

$$h_{2\mathrm{DHO}} = -\frac{1}{2}\frac{\partial^2}{\partial\rho^2} - \frac{1}{2\rho}\frac{\partial}{\partial\rho} - \frac{1}{2\rho^2}\frac{\partial^2}{\partial\theta^2} + \frac{1}{2}\rho^2, \tag{3}$$

H_1 is the vibronic interaction Hamiltonian given by

$$H_1 = \left(k\rho e^{-i\theta} + \frac{1}{2}g\rho^2 e^{i2\theta}\right)|a\rangle\langle b| + \mathrm{H.c.}, \tag{4}$$

and H_2 is the fourth order term

$$H_2 = \sum_{e=a,b} f\rho^4|e\rangle\langle e|. \tag{5}$$

This term is included in order to have a bound ground state for a large quadratic coupling constant $g \geq 1$ [12].

The adiabatic potential surfaces are obtained as

$$U_\pm = \frac{1}{2}\rho^2 + f\rho^4 \pm \sqrt{k^2\rho^2 + kg\rho^3\cos 3\theta + \frac{1}{4}g^2\rho^4}, \tag{6}$$

with double-valued adiabatic electronic wave functions $|\varphi_+\rangle = (e^{-i\alpha/2}|a\rangle + e^{i\alpha/2}|b\rangle)/\sqrt{2}$ and $|\varphi_-\rangle = (e^{-i\alpha/2}|a\rangle - e^{i\alpha/2}|b\rangle)/\sqrt{2}$, for U_+ and U_-, respectively, where $\alpha = \tan^{-1}[(k\sin\theta - 0.5g\rho\sin 2\theta)/(k\cos\theta + 0.5g\rho\cos 2\theta)]$.

We diagonalize the Hamiltonian (1) numerically using the basis set $|e\rangle \otimes \langle\rho, \theta|v, m\rangle$, $e = a, b$, $v = 1, 2, \ldots, m = v - 1, v - 3, \ldots, -v + 1$, where

$$\langle\rho, \theta|v, m\rangle = (-1)^n\left(\frac{n!e^{-\rho^2}}{\pi(n + |m|)!}\right)^{1/2}\rho^{|m|}L_n^{|m|}(\rho^2)e^{-im\theta}, \tag{7}$$

with $n = (v - |m| - 1)/2$. The basis functions $\langle\rho, \theta|v, m\rangle$ are eigenfunctions for the two-dimensional harmonic oscillator Hamiltonian $h_{2\mathrm{DHO}}$ with eigenvalues $E_{vm} = v$. Nonzero matrix elements for the linear vibronic coupling term $\rho e^{-i\theta}$ are given by [6,13]

$$\langle v, m|\rho e^{-i\theta}|v + 1, m + 1\rangle = \sqrt{(v + m + 1)/2},$$
$$\langle v, m|\rho e^{-i\theta}|v - 1, m + 1\rangle = \sqrt{(v - m - 1)/2}, \tag{8}$$

and matrix elements for $\rho e^{i\theta}$, $\rho^2 e^{-i2\theta}$, $\rho^2 e^{i2\theta}$, and ρ^4 can be calculated using Eq. (8).

Let us start with the $f = 0$ case. In this case, the quadratic coupling parameter g must be smaller than 1 in order to have the U_- value bounded from below. In Fig. 1(a), vibronic energies for the lowest eight states of the $k = 0$ and the $f = 0$ case are shown [14]. At $g = 0.918$ the crossing of the lowest E and the lowest A energy levels occurs and the nondegenerate A state becomes the lowest for $g > 0.918$. Even when $k \neq 0$ (a small linear coupling term is turned on), the A state becomes the ground state at large g values. With $k = 0.1$, the ground state becomes an A state when g is larger than 0.922 [Fig. (b)]. If the quadratic coupling parameter g is larger than 1, the fourth order terms must be included. In Fig. 1(c), the case $k = 0.5$ and $f = 0.5$ is shown. The crossing of the lowest E and A states occurs at $g = 4.50$.

Now let us consider the situation where the vibronic coupling is very strong, and the ground state nuclear dynamics is considered to be performed on the single potential surface with deep minima. In this case, the energy difference between the lowest A and E states is considered as due to the tunneling splitting [4,9]. The relevant potential energy surface is given by $V = U_- + H_{\mathrm{BH}}$, where H_{BH} is the Born-Huang term [15] (or centrifugal energy [2]) given by

$$H_{\mathrm{BH}} = \frac{1}{2}\sum_{i=1}^{2}\left\langle\frac{\partial\varphi_-}{\partial Q_i}\middle|\frac{\partial\varphi_-}{\partial Q_i}\right\rangle = \frac{1}{8}(\nabla\alpha)^2, \tag{9}$$

where

$$\nabla\alpha = \frac{-kg\sin 3\theta\,\mathbf{e}_\rho + (2k^2\rho^{-1} - k^2\rho - kg\cos 3\theta)\mathbf{e}_\theta}{2k^2 + \frac{1}{2}g^2\rho^2 + 2kg\rho\cos 3\theta}. \tag{10}$$

The potential energy surfaces $U_\pm$ exhibit a conical intersection at the center $\rho = 0$ and three peripheral ones at $(Q_1, Q_2) = \{2kg^{-1}\cos[3^{-1}(2n + 1)\pi], 2kg^{-1}\sin[3^{-1}(2n + 1)\pi]\}, n = 0, 1, 2$ (Fig. 2) [16]. At each conical intersection (Q_{1c}, Q_{2c}), H_{BH} provides a

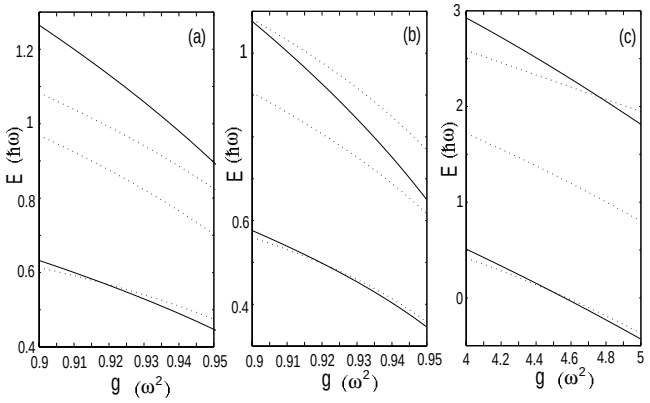

FIG. 1. Energies for the lowest eight vibronic states versus the quadratic coupling constant g. Solid and dotted lines denote nondegenerate and doubly degenerate states, respectively. (a) $k = 0, f = 0$; (b) $k = 0.1, f = 0$; (c) $k = 0.5, f = 0.5$.

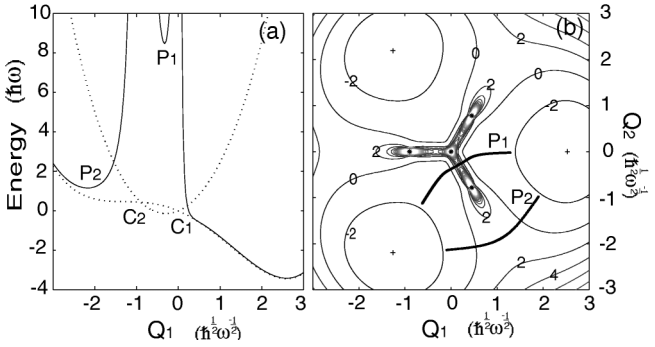

FIG. 2. Potential surface of the $E \otimes e$ system for $k = 0.9$, $g = 2$, and $f = 0.05$. (a) Cross section of the potential surfaces V (solid line) and $U_{\pm}$ (dotted line) at $Q_2 = 0$. C_1 and C_2 indicate conical intersections, while P_1 and P_2 indicate two saddle points on V. (b) Contour plot of the potential surface V. "$*$" and "$+$" indicate a conical intersection and a minimum, respectively. Two steepest decent tunneling paths P_1 and P_2 are shown by thick lines.

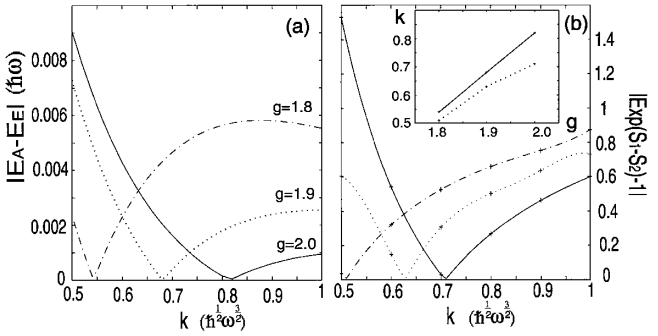

FIG. 3. (a) The absolute values of the energy difference $|E_A - E_E|$ between the lowest A and E levels, and (b) the ratios of the tunneling rates via P_1 and P_2 paths (plotted as $|\exp(S_1 - S_2) - 1|$) as functions of k for $f = 0.05$ and three values of $g = 2.0, 1.9,$ and 1.8. Calculated points are indicated by "$+$" and polynomially interpolated curves for $g = 2.0, 1.9,$ and 1.8 cases are depicted by solid, dotted, and dash-dotted lines, respectively, in (b). Inset: The g versus k values at the crossing points $E_A = E_E$ (solid line) and at $S_1 = S_2$ (dotted line).

diverging term proportional to $[(Q_1 - Q_{1c})^2 + (Q_2 - Q_{2c})^2]^{-1} \equiv \rho_c^{-2}$ because the adiabatic wave function depends on the circular angle around the conical intersection $\theta_c \equiv \tan^{-1}[(Q_2 - Q_{2c})/(Q_1 - Q_{1c})]$, which gives rise to the contribution proportional to $|\rho_c^{-1} \partial |\varphi_-\rangle / \partial \theta_c|^2$. Thus, the access of the nuclear motion to conical intersections is prohibited. A fictitious magnetic field that gives rise to the appearance of the Berry phase and causes the sign change of the wave function exists at each conical intersection.

Two steepest decent paths that connect nearby minima through two different saddle points, one between the conical intersections at the center and at the barrier (P_1) and the other outside both of them (P_2) for the values $k = 0.9$, $g = 2.0$, and $f = 0.05$, are shown in Fig. 2. As is seen from Fig. 2(a), H_{BH} gives a large contribution to energy near the conical intersections and makes the barrier for the path P_1 significantly higher than that for the path P_2. As a result, the barrier for P_1 is high and thin, while that for P_2 is characterized as low and thick.

The absolute values of the energy difference between the lowest A and E states for three values $g = 2.0, 1.9, 1.8$ and $f = 0.05$ by varying k from 0.5 to 1 are shown in Fig. 3(a). The triply degenerate ground state intersection points are obtained at $k = 0.82$, 0.68, and 0.54 for $g = 2.0$, 1.9, and 1.8, respectively. If k is larger than this value, the ground state is E, and if it is smaller the ground state is A symmetry.

We estimate the tunneling rate for P_1 and P_2 using the WKB method given by

$$\exp(-S_i) = \exp\left(-\int_{P_i} \sqrt{2(V - E)}\, dq\right), \qquad i = 1, 2. \tag{11}$$

In Fig. 3(b), $|\exp(S_1 - S_2) - 1|$ and the correlation of the g versus k values at the intersection points $E_A = E_E$ with the corresponding values at $S_1 = S_2$ are shown. A qualitatively good correlation between the crossing points of energy levels $E_A = E_E$ and by equitunneling rate points via the two paths $S_1 = S_2$ is obtained [Fig. 3(b), inset]. Note that the present estimate of the tunneling rate based on the one-dimensional WKB is not very accurate. A more accurate estimate including the multidimensionality of the tunneling [17] may yield a quantitatively better correlation. This strong correlation between the change of the degeneracy of the ground state and the change of the dominant tunneling path suggests that the former is caused by the latter through the change of boundary condition on the wave function, which gives us a clear explanation of the origin of the energy level E-A crossover as due to the presence of two alternative tunneling passes which yield two Berry phases, π and 4π, respectively.

The change of ground state symmetry and degeneracy as a function of intermolecular interactions seems to be of general importance. For instance, it follows from the crystal field theory that the ground state symmetry changes with the strength of the crystal (or ligand) field; the phenomenon is known as spin crossover and it has significant implications in magnetic materials [18]. The energy level crossover discussed above may be regarded as a part of this general understanding.

In summary, we confirmed the existence of the nondegenerate vibronic ground state in the $E \otimes e$ Jahn-Teller systems first suggested in [4]. It exists in cases where the quadratic coupling constant is sufficiently large [19]. We have also elucidated the mechanism of the E-A energy level crossover by demonstrating the correlation between the change of the degeneracy of the tunneling-split ground state and the change of the dominant tunneling path: one goes through the saddle point between the conical

intersections at the center and at the barrier, the other goes through the saddle point outside of both of them.

The authors acknowledge fruitful discussion with Dr. V. Z. Polinger and Dr. H. Köppel. H. K. is supported in part by the travel grant from Hyogo prefectural government in Japan.

*On leave of absence from Faculty of Science, Himeji Institute of Technology, Kamigori, Ako-gun, Hyogo 678-1297, Japan.

[1] R. Englman, *The Jahn-Teller Effect in Molecules and Crystals* (Wiley, New York, 1972).

[2] I. B. Bersuker and V. Z. Polinger, *Vibronic Interactions in Molecules and Crystals* (Springer-Verlag, Berlin, 1989).

[3] M. C. P. Moate, C. M. O'Brien, J. L. Dunn, C. A. Bates, Y. M. Liu, and V. Z. Polinger, Phys. Rev. Lett. **77**, 4362 (1996).

[4] I. B. Bersuker, Opt. Spectrosc. **11**, 319 (1961); Zh. Eksp. Teor. Fiz. **43**, 1315 (1962) [Sov. Phys. JETP **16**, 933 (1963)].

[5] M. C. M. O'Brien, Proc. R. Soc. London A **281**, 323 (1964).

[6] H. C. Longuet-Higgins, U. Öpik, M. H. L. Pryce, and R. A. Sack, Proc. R. Soc. London A **244**, 45 (1958).

[7] M. V. Berry, Proc. R. Soc. London A **392**, 45 (1984).

[8] F. S. Ham, Phys. Rev. Lett. **58**, 725 (1987).

[9] V. Z. Polinger, Sov. Phys. Solid State **16**, 1676 (1975).

[10] See, for example, J. W. Negele and H. Orland, *Quantum Many-Particle Systems* (Perseus Books, Reading, MA, 1988), Sect. 7.4.

[11] J. W. Zwanziger and E. R. Grant, J. Chem. Phys. **87**, 2954 (1987).

[12] The units of energy, time, length, and mass-weighted length (for normal coordinates) in the present Letter are given by $\hbar\omega$, ω^{-1}, $(\hbar/m\omega)^{1/2}$, and $(\hbar/\omega)^{1/2}$, respectively, where $\hbar\omega$ and m are the energy quantum and mass for the two dimensional harmonic oscillator, respectively.

[13] H. Koizumi and S. Sugano, J. Chem. Phys. **101**, 4903 (1994); **103**, 7651(E) (1995).

[14] The lowest A state for the $k = 0$ and $f = 0$ case has the energy $2\sqrt{1 - g}$ with the eigenfunction $\Phi_A = (1/\sqrt{2})(|a\rangle \otimes e^{i\theta} - |b\rangle \otimes e^{-i\theta})\rho\langle\rho, \theta|2, 0\rangle$.

[15] M. Born and K. Huang, *Dynamical Theory of Crystal Lattices* (Oxford University, London, 1954), App. VIII.

[16] For $k \neq 0$ and $g = 0$ values, three peripheral conical intersections are considered to exist at $\lim_{g\to 0} 2kg^{-1} = \infty$, while for the $k = 0$ and $g \neq 0$ all four conical intersections merge into one Renner–Teller-type crossing. This latter situation is actually found at near regular tetrahedral configurations in the H_4 system [H. Koizumi *et al.* (unpublished)].

[17] See, for example, H. Ushiyama and K. Takatsuka, J. Chem. Phys. **106**, 7023 (1997), and references therein.

[18] See, for example, I. B. Bersuker, *Electronic Structure and Properties of Transition Metal Compounds* (Wiley, New York, 1996).

[19] Using a variational method, Bersuker observed the E-A energy level crossing for large quadratic coupling in 1972, but to avoid publication of a possible inaccuracy only the data for smaller quadratic couplings before the crossing, were published [I. B. Bersuker, Cord. Chem. Rev. **14**, 357 (1975), see p. 390].