Front. Phys. China (2007) 1: 51—54
DOI 10.1007/s11467-007-0019-2

RESEARCH ARTICLE

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Studies of the doubly degenerate product Jahn-Teller system

Abstract The static product Jahn-Teller (JT) system with two doubly-degenerate electronic open shells coupling to a single *e*-mode is further studied in the electronic space using the isostationary function method and the energy minimization procedure. These effects are vividly described by the coupling of two electronic vectors that belong to two different *E*-spaces. The energy levels in the trough positions are also investigated and it is found that the two doubly degenerate electronic levels are generally lifted by the product JT coupling.

Keywords product Jahn-Teller effect, vibronic coupling, electron and phonon interactions

PACS numbers 70.70.Ej, 63.20.Kr, 71.38.-k

1 Introduction

It is well known that the interactions between a degenerate electronic level and the vibrational modes of atoms can lower the symmetry of the Jahn-Teller (JT) system [1] and the degeneracy of the electronic level will be lifted. For the two electronic doubly-degenerate coupling system, it has been initially studied using the operatorization and unitary transformation approaches [2], but the potential surface of the system still needs further study.

The doubly degenerate product JT system considered in this paper contains two *E* electronic open shells and one *e*-type vibrational mode. These two electronic doubly-degenerate shells are coupled to the single *e*-mode, forming one-center product JT system, denoted as $\{E\otimes E\}\otimes e$. The structures on the lowest potential energy surface of the product JT system should be related to the properties of the separate $E\otimes e$ JT systems, but some parameters have to be obtained to reflect the interactions between the two electronic shells. It is known that such phenomena can be easily seen in cubic symmetry but probably exist as well in fullerene-related families as the separate $E\otimes e$ JT system was also formed in C_{70}^{3-} molecules [3]. The JT problem with two open electronic shells was described as cooperative JT phenomena [4] and explored as the vibronic intercenter interaction on a trigonal two-center system [5]. The similarities and differences between the one and two-center treatments were studied in Ref. [6]. In the present paper, we investigate the structures on the lowest JT surface, the excited levels and their symmetry properties in the product JT system.

2 The Hamiltonian

The effective vibronic Hamiltonian of a JT system is usually written as the coupling of the electronic operators and their corresponding vibrational modes [7]. The two components of the electronic bases of the doubly degenerate JT system are transformed as $(3z^2-r^2)$ and (x^2-y^2), which are labeled as θ and ε respectively. For several doublet electronic states coupling to one vibrational e mode, the linear vibronic Hamiltonian of a particular electronic doublet (*i*th for example) coupling to the e mode, denoted as $E_i\otimes e$, can be written as

$$\mathcal{H}_{\mathrm{lin}}^{E^{(i)}}=F_{ie}(Q_\theta\hat{L}_\theta^{(i)}+Q_\varepsilon\hat{L}_\varepsilon^{(i)}),\quad i=1,2,\cdots \tag{1}$$

where F_{ie} is the *i*th vibronic coupling constant; Q_θ and Q_ε are the two components of the vibrational *e*-mode; $\hat{L}_\theta^{(i)}$ and $\hat{L}_\varepsilon^{(i)}$ (i = 1, 2, $\cdots$) are the electronic operators, which have the same form of the irreducible representation matrix for different i, expressed as

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Received December 3, 2006

$$\hat{L}_{\theta}^{(i)}=\begin{pmatrix}1 & 0\\ 0 & -1\end{pmatrix},\quad \hat{L}_{\theta}^{(i)}=\begin{pmatrix}0 & 1\\ 1 & 0\end{pmatrix} \tag{2}$$

Here we consider $i = 2$, the electronic states in each E-space, denoted by $|\psi_E\rangle$, can be written as

$$|\psi_{E_i}\rangle=\theta_i\,|E_{\theta_i}\rangle+\varepsilon_i\,|E_{\varepsilon i}\rangle,\quad i=1,2 \tag{3}$$

These states are orthonormal and they could form a four dimensional space by coupling. The linear vibronic Hamiltonian for the $\{E\otimes E\}\otimes e$ product JT system can be constructed according to the coupling basis, given as

$$\mathcal{H}_{\text{lin}}=\begin{pmatrix}Q_\theta(F_{1e}+F_{2e}) & Q_\varepsilon F_{2e} & Q_\varepsilon F_{1e} & 0\\ Q_\varepsilon F_{2e} & Q_\theta(F_{1e}-F_{2e}) & 0 & Q_\varepsilon F_{1e}\\ Q_\varepsilon F_{1e} & 0 & -Q_\theta(F_{1e}-F_{2e}) & Q_\varepsilon F_{2e}\\ 0 & Q_\varepsilon F_{1e} & Q_\varepsilon F_{2e} & -Q_\theta(F_{1e}+F_{2e})\end{pmatrix} \tag{4}$$

The total Hamiltonian for the product JT system should also include the vibrational potential energy related to the e mode and it is given by

$$\mathcal{H}=\mathcal{H}_{\text{vib}}+\mathcal{H}_{\text{lin}} \tag{5}$$

where $\mathcal{H}_{\text{vib}}=\frac{1}{2}K_E(Q_\theta^2+Q_\varepsilon^2)\hat{I}$ is the vibrational potential energy of the system. $\hat{I}$ is 4×4 unit matrix and K_E is the harmonic force constant of the e-type vibrational mode.

3 Structures of potential JT surface

Extrema on the JT surface of separate problem can be found by the Öpik and Pryce method [8] in the vibronic space. The energy of the system can be obtained by evaluating the expectation value of the total Hamiltonain for the system

$$\langle E\rangle=\frac{1}{2}K_E(Q_\theta^2+Q_\varepsilon^2)+\langle\psi\,|\mathcal{H}_{\text{lin}}|\,\psi\rangle \tag{6}$$

where $|\psi\rangle=|\psi_{E_1}\rangle\,|\psi_{E_2}\rangle$. The positions of the extremal points, usually referred to as stationary coordinates, can be obtained by minimizing the energy in Q-space:

$$\left\|Q_\gamma\right\|=-\frac{1}{K_E}\langle\psi\,|\frac{\partial\mathcal{H}_{\text{lin}}}{\partial Q_\gamma}|\,\psi\rangle \tag{7}$$

Expressing $|\psi\rangle$ in matrix form and working out the above simultaneous equations, the stationary coordinates can be obtained in the form:

$$\begin{aligned}\left\|Q_\theta\right\|&=\frac{1}{K_E}\left[(\varepsilon_1^2-\theta_1^2)F_{1e}+(\varepsilon_2^2-\theta_2^2)F_{2e}\right]\\ \left\|Q_\varepsilon\right\|&=-\frac{2}{K_E}(\varepsilon_1\theta_1F_{1e}+\varepsilon_2\theta_2F_{2e})\end{aligned} \tag{8}$$

where the normalization conditions of the electronic parameters have been used. Substituting Eq. (8) back into the Eq. (6), the energy of the system becomes a function of the electronic parameters, the vibronic coupling and the harmonic force constants. Such an energy expression is called isostationary function which was proved to contain all information of the potential energy surface of the JT system [9].

Based on the illustration in Fig. 1, the electronic parameters can be expressed as the two rotational angles, denoted by α and β respectively, in the separate electronic spaces, given by

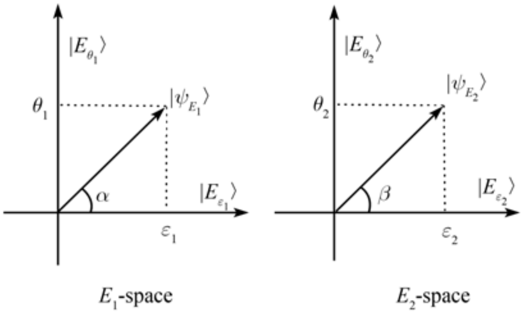

Fig. 1 The schematic discription of the electronic vectors and parameters in separate electronic spaces. The variation of α and β represents the rotations of $|\psi_{E_1}\rangle$ and $|\psi_{E_2}\rangle$ in the electronic space.

$$\theta_1=\sin\alpha,\quad \varepsilon_1=\cos\alpha,\quad \theta_2=\sin\beta,\quad \varepsilon_2=\cos\beta \tag{9}$$

With the above expressions of the electronic parameters, the isostationary function for the product JT system can be worked out as

$$\langle\|E\|\rangle=-\frac{1}{2K_E}\left(F_{1e}^2+2\cos[2(\alpha-\beta)]F_{1e}F_{2e}+F_{2e}^2\right) \tag{10}$$

Two extremal energies can be easily obtained from the isostationary function by minimization procedure:

$$\begin{aligned}\langle\|E\|\rangle_{\alpha-\beta=0}&=-\frac{1}{2K_E}(F_{1e}+F_{2e})^2\\ \langle\|E\|\rangle_{\alpha-\beta=\frac{\pi}{2}}&=-\frac{1}{2K_E}(F_{1e}-F_{2e})^2\end{aligned} \tag{11}$$

These energies are obviously trough energies in the electronic space as the results are just related to the angle between the two electronic vectors. In the electronic space, when the two electronic vectors rotate in-phase, the isostationary function will show the lowest energy of the JT system if $F_{1e}F_{2e}>0$. On the other hand, if the two force constants have different signs, the lowest energy will occur only on the condition that the two electronic vectors keep perpendicular. Obviously the interaction between the two electronic levels is through the term of $F_{1e}F_{2e}$. This physical picture explains that as long as the two electronic doublets couple to the same e mode no matter in coherent or independent way, they will affect each other. Consequently, we conclude that the two electronic doublets interact in nature as long as the common e mode exists.

4 The energy levels in troughs

It is known that without considering the vibronic coupling effects, there exist two doubly degenerate electronic levels in the product JT system. Substituting Eq. (9) into the stationary coordinates (8) and then into the total Hamiltonian Eq. (5), the eigenvalues of the total Hamiltonian in the extremal position can be obtained as

$$E_{a\pm} = \frac{1}{2K_E}\left[f(\alpha,\beta) \pm 2\sqrt{(F_{1e}+F_{2e})^2 f(\alpha,\beta)} \right] \tag{12}$$

$$E_{b\pm} = \frac{1}{2K_E}\left[f(\alpha,\beta) \pm 2\sqrt{(F_{1e}-F_{2e})^2 f(\alpha,\beta)} \right] \tag{13}$$

where

$$f(\alpha,\beta) = F_{1e}^2 + 2\cos[2(\alpha-\beta)]F_{1e}F_{2e} + F_{2e}^2 \tag{14}$$

Each of the above eigenvalues represents a potential energy sheet. As these energy sheets correspond to the same stationary coordinates, energy sheet in higher position can be recognized as the excited state in such a position. Making use of the method of Lagrange multipliers, extremum energies can be calculated. Note that many extremum values can be obtained from different potential sheets and the lowest ones interest us only. It is found that there are two lowest energies which are corresponding to $\alpha - \beta = \pm 2n\pi$ (n = 0, 1, 2, ⋯) and $\alpha-\beta = \pm\frac{(2n+1)\pi}{2}\,(n=0,1,2,\cdots)$ respectively. It is instructive to give the corresponding excited states for each of the trough energies. For $\alpha-\beta = 2n\pi\,(n=0,1,2,\cdots)$, the lowest energy should be in Eq. (12) we have

$$\begin{aligned} E_{a1} &= -\frac{1}{2K_E}(F_{1e}+F_{2e})^2 \\ E_{a2} &= \frac{1}{2K_E}(3F_{1e}^2 + 2F_{1e}F_{2e} - F_{2e}^2) \\ E_{a3} &= \frac{1}{2K_E}(-F_{1e}^2 + 2F_{1e}F_{2e} + 3F_{2e}^2) \\ E_{a4} &= \frac{3}{2K_E}(F_{1e}+F_{2e})^2 \end{aligned} \tag{15}$$

There are four energy levels in the trough and the lowest one is obviously corresponding to the $F_{1e}F_{2e} > 0$. For $\alpha-\beta = \pm\frac{(2n+1)\pi}{2}\,(n=0,1,2,\cdots)$, we obtain

$$\begin{aligned} E_{b1} &= -\frac{1}{2K_E}(F_{1e}-F_{2e})^2 \\ E_{b2} &= \frac{1}{2K_E}(-3F_{1e}^2 + 2F_{1e}F_{2e} - F_{2e}^2) \\ E_{b3} &= \frac{1}{2K_E}(F_{1e}^2 + 2F_{1e}F_{2e} - 3F_{2e}^2) \\ E_{b4} &= \frac{3}{2K_E}(F_{1e}-F_{2e})^2 \end{aligned} \tag{16}$$

It is easy to work out that when the two vibronic coupling constants F_{1e} and F_{2e} have different signs, E_{b1} is the lowest energy in the trough and in this case, the two electronic vectors are coupled in the way of mutual orthogonality. On the other hand, if the two coupling constants have the same sign, E_{a1} is the lowest energy in the product JT system and the two electronic vectors are coupled in in-phase. Taking the $F_{1e}F_{2e} > 0$ trough as an example, the four potential energy surfaces join together at the origin point of F_{1e} and F_{2e} plane. Both cases of $F_{1e} = 0$ and $F_{2e} = 0$ are not interesting to us as we want both of them to be non-zero. In such a case, the degeneracy of the energies in the trough happens for $E_{a2} = E_{a3}$ only. such a degeneracy occurs at $F_{1e} = F_{2e}$ and is referred to as crossover degeneracy. Detailed illustrations are given in Fig. 2.

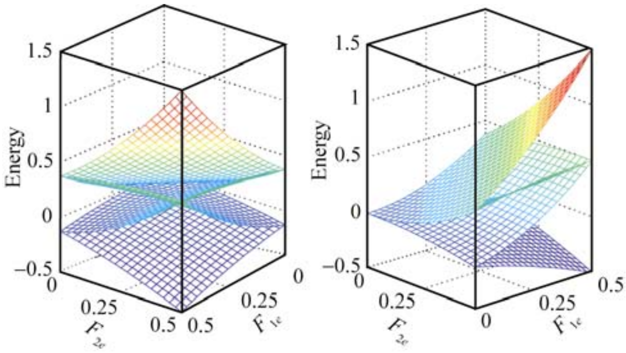

Fig. 2 Plot of adiabatic potential surfaces in the in-phase trough. The two plots show the same set of potential energy sheets but viewed from different angle.

At last, we focus our discussion on the lowest potential energy sheets for both cases. On the F_{1e} and F_{2e} plane, the two ground energies are located in different regions. The result is shown in Fig. 3. If the two coupling constants drop on lines which belong to a same square in Fig. 3, the product JT system has the same energy. Therefore, the squares in Fig.3 can be recognized as energy contour lines.

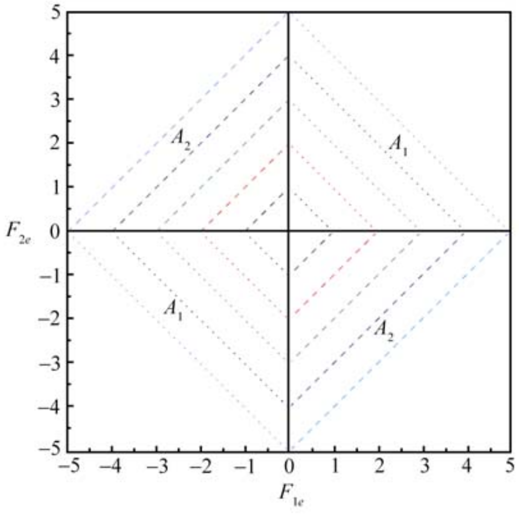

Fig. 3 Plot of equi-energy lines in the coupling constant space. Symmetry is also shown in different regions. Lines constructing a same square give the same energy for the product JT system.

5 Discussions

It can be seen from the last section that the energy gap between the highest excited and ground levels in the two troughs are always the four times in value of the ground energy. The four levels in the two troughs are generally split except for the so-called “crossover” degeneracy when E_2 is equal to E_3. On the other hand, though the two troughs are formed from the same product JT system, their ground potential energy sheets should not have the same symmetry as they are constructed from the different coupling of the two electronic bases. Details of this part could be searched from the isostationary function. It is found that the ground state in the in-phase trough has A_1 symmetry and that in the other trough has A_2 symmetry as it is subjected to a sign change under inversion operation. It should be pointed out that these two troughs cannot be formed simultaneously and the tunnelling splitting effect between the two troughs should not exist in such a product JT system. However, like the separate $E \otimes e$ JT problem, the trough will probably be warped into wells while the second-order perturbations are introduced into the JT system. When the linear vibronic coupling is very strong, i.e., the magnitudes of F_{1e} and F_{2e} are very large, the quadratic coupling effects may not be simply ignored. As mentioned above, the system will probably have minima and then the ground energy expressions calculated in this paper are not valid any more. Therefore, new calculations with quadratic coupling effect should be carried out. This quadratic vibronic coupling problem, as a prototype of the product JT systems, including their reduction factors, excited states, the anisotropic effects and their frequency splitting in wells, will form a basis of future investigations.

Acknowledgements The author would like to thank Professor A. Ceulemans and Dr. L. F. Chibotaru for many helpful discussions. This research was supported by the Natural Science Foundation of Guangdong Province of China (Grant No. 34613).

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