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LETTER TO THE EDITOR

The distorted Jahn–Teller effect

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Abstract. In Jahn–Teller (JT) systems with N equivalent sites on which electrons (holes) may localize, one encounters the interaction of many electronic states through JT vibrations. The total multi-dimensional Hamiltonian is reduced to N equivalent Hamiltonians of low dimension and distorted symmetry. Explicit examples are presented and general implications discussed.

The Jahn–Teller (JT) effect [1] describes the interaction of degenerate electronic states through non-totally symmetric, usually degenerate, nuclear modes. This effect plays a central role in explaining the structure and dynamics of solids and molecules in degenerate electronic states [2, 3]. The well known JT Hamiltonian which linearly couples the two components of an electronic state of, for instance, E symmetry reads [2, 4]

$$H = H_0 \underline{1} + \begin{pmatrix} E_E - \kappa x & \kappa y \\ \kappa y & E_E + \kappa x \end{pmatrix} \tag{1}$$

where x and y denote the two components of the degenerate coupling vibrational coordinate with momenta p_x and p_y and $H_0 = \omega(p_x^2 + p_y^2 + x^2 + y^2)/2$, where ω is the unperturbed vibrational frequency. $\underline{1}$ stands for a unit matrix, κ is the JT coupling constant and E_E is the electronic energy.

Although the Hamiltonian (1) has a simple appearance, it cannot be solved in closed form. In particular, the electronic transformation which brings the matrix (1) into diagonal form explicitly depends on the coordinates x and y. Consequently, the JT effect describes non-adiabatic effects which can have a severe impact on the dynamics of the system as demonstrated in many cases [2–5]. Another consequence of (1) is the appearance of a now very popular geometrical phase factor [6] in the adiabatic electronic states [4, 7, 8]. We should mention that quadratic or higher coupling terms not shown in (1) may also contribute [2, 9]. Within the approximations of (1) there is a constant of the motion (vibronic angular momentum) and, correspondingly, a rotational symmetry of the adiabatic potential energy surfaces.

In the following we wish to point out and to demonstrate that the JT Hamiltonian may take a less symmetric form in composite systems. Here we have in mind systems the wavefunction of which is to a very good approximation a direct product $|L\rangle \otimes |D\rangle$ of a wavefunction $|L\rangle$ describing localized (quasi)particles and $|D\rangle$ describing the remaining ones. Examples are the core electrons which constitute $|L\rangle$ and the valence electrons described by $|D\rangle$, or localized magnetic impurities in a solid (or a cluster) and the delocalized band electrons. A JT effect is supposed to be operative in the

subspace of the wavefunctions $|D\rangle$ while the localization in the subspace $|L\rangle$ can be cast into the language of pseudo-JT theory [10, 5] with a special relation between the coupling constants. Separate transformations on $|L\rangle$ and $|D\rangle$ then help to considerably simplify the problem. We start with the subspace of wavefunctions $|L\rangle$ for which new results will also be derived.

To keep the discussion as transparent as possible we illustrate our general arguments with the aid of a specific point group: D_{3h} with three equivalent centres. An electron (or hole) localized on these centres can be either in a degenerate E or in a totally symmetric A_1 state, and the Hamiltonian (2) applies

$$H = H_0 1 + \begin{bmatrix} E_E - \kappa x & \kappa y & \lambda y \\ \kappa y & E_E + \kappa x & -\lambda x \\ \lambda y & -\lambda x & E_A \end{bmatrix} \tag{2}$$

where λ is the pseudo-JT coupling constant. Because of the localization, the energies E_E and E_{A_1} will be nearly identical. For instance, the core fluorine electrons of BF_3 constitute E and A_1 core orbitals whose orbital energies are separated by less than 0.0007 eV [11] and we may put $E_E = E_{A_1}$ for all practical purposes. In analogy one may derive relations between the JT and pseudo-JT coupling constants. Requiring that the localized electronic states remain decoupled also for finite nuclear displacements, we find $\lambda = \sqrt{2}\kappa$ in our case. Similar relations hold for the quadratic and higher coupling constants not shown in (2).

Inserting $E \equiv E_E = E_{A_1}$ and $\lambda = \sqrt{2}\kappa$ into the matrix Hamiltonian (2) we may now diagonalize this electronic matrix by a transformation which is *independent* of the nuclear coordinates. The transformed Hamiltonian $S_L H S_L^\dagger$ is diagonal with elements H_i, $i = 1, 2, 3$. It is sufficient to know one of these operators, for instance,

$$H_1 = E + H_0 + 2\kappa x + \delta_+(x^2 + y^2) + \delta_-(x^2 - y^2). \tag{3}$$

The other two operators in nuclear space H_2 and H_3 can be obtained from (3) by rotating (x, y) by $2\pi/3$ and $4\pi/3$, respectively. Note that H_0 is invariant under rotations. For completeness, the quadratic JT coupling constants δ_+ and δ_- have been taken into account in the derivation of the H_i although they have not been shown explicitly in (1) and (2). Higher coupling constants can be included analogously.

The three operators H_i are the Hamiltonians for the nuclear motion in the transformed electronic states obtained by application of S_L. Inspection of this transformation (S_L is determined from $\tilde{S}_L$ by normalizing the columns)

$$\tilde{S}_L = \begin{bmatrix} 1 & 1 & 1 \\ -1 & 1 & 1 \\ 0 & -2 & 1 \end{bmatrix} \tag{4}$$

reveals that the original electronic states of E and A_1 symmetry have been transformed to three *symmetry broken* states, where in each of these states the electron (or hole) is localized on a single site. In our case the pseudo-JT Hamiltonian (2) thus describes dynamical on-site localization. The transformation S_L is universal for the D_{3h} point group with three equivalent sites. Similarly simple transformations prevail for other point groups and/or a different number of equivalent sites. The dimension N of the pseudo-JT Hamiltonian will always be the number of the equivalent sites and the on-site localization transformation S_L solves the problem and leads to N one-dimensional

Hamiltonians H_i. For example, $N = 6$ for benzene (C_6H_6) and the pseudo-JT Hamiltonian describes the coupling of six states: two doubly-degenerate E and two non-degenerate A states. All the H_i can be determined from one of them by simple symmetry operations. Related symmetry breaking in connection with on-site localization may also occur in non-JT systems [12, 17].

The on-site pseudo-JT Hamiltonian H_1 in (3) describes two harmonic oscillators. Interestingly, one of them is shifted along one component of the degenerate nuclear mode. The degeneracy of the nuclear JT vibration is lifted and the vibrational frequencies are different along the x and y directions. In particular, because of the electronic symmetry breaking discussed above the adiabatic potential energy surfaces of the H_i are analytic at the origin, in contrast to those of the JT Hamiltonian [2]. A typical contour plot of the potential energy surfaces of our H is shown in figure 1. In spite of the fact that three surfaces intersect (this usually leads to a breakdown of the Born-Oppenheimer approximation), the nuclear motion on them is decoupled as demonstrated above. Every surface corresponds to one of the H_i.
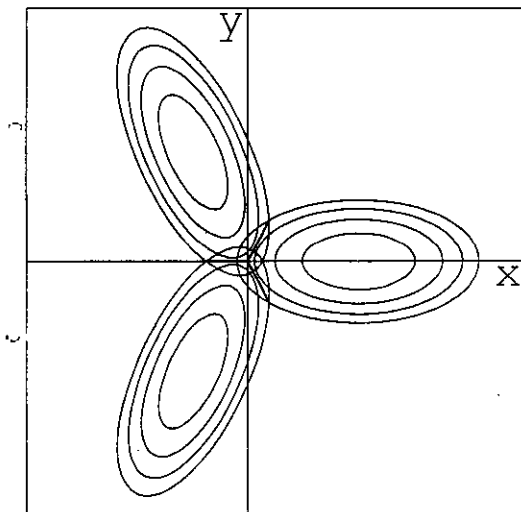

Figure 1. The contour plot of the potential energy surfaces of H in (2) for D_{3h} systems with localized electrons or, equivalently, of the H_i in (3). The solid lines are the lines of intersection.

The spectrum of H in (2) for our systems is simpler than that of the JT spectrum of (1) although the former describes the interaction of three electronic states. Being a shifted oscillator, the Hamiltonian (3) may give rise to strong excitations of quanta of the JT vibration which can lead to a broad spectrum. This may explain the hitherto unexplained observations [13] that the fluorine 1s lines in XPS experiments of BF_3 and CF_4 are much broader than the boron and carbon 1s lines. In the former case the JT vibration is inevitably activated via the above discussed on-site pseudo-JT effect.

Until now we have considered the situation where the JT effect is due to the electrons (holes) in the $|L\rangle$ manifold. The on-site localization principle found for these JT systems prepares the ground for the treatment of the more complex problem of electronic excitations between the $|L\rangle$ and $|D\rangle$ manifolds. Here, we may discern between two types of excitations. If the excited structure in $|D\rangle$ is non-degenerate, the excitation

problem becomes formally identical to the one discussed above and needs no further discussion. If, on the other hand, the excited state in $|D\rangle$ is degenerate as indicated above, the vibronic coupling problem becomes much more complex as more states are involved. Let us return to our D_{3h} example with three equivalent centres. The excitation of the vibronically coupling A_1 and E states of $|L\rangle$ to, for example, an A_1 state of $|D\rangle$ leads again to the same pseudo-JT problem as in (2) because of the symmetry product rules $E \otimes A_1 = E$ and $A_1 \otimes A_1 = A_1$. The specific values of the coupling constants $\lambda = \sqrt{2}\kappa$ and energies $E_E = E_A$, of course, depend on the properties of the A_1 state of the $|D\rangle$ subsystem.

The excitation of the A_1 and E states of $|L\rangle$ to an E state of $|D\rangle$ gives rise to six states which are all vibronically coupled to each other. Using the product rules $E \otimes E = E + A_1 + A_2$ and $A_1 \otimes E = E$, we have readily identified the interacting states. In analogy to (2) we may now construct our pseudo-JT Hamiltonian for these states. Using symmetry arguments [2] we arrive at

$$H = H_0 \underline{1} + \begin{bmatrix} E_E - \kappa_1 x & \kappa_1 y & \lambda_1 y & \chi_1 x & -\kappa_{12}x & \kappa_{12}y \\ & E_E + \kappa_1 x & -\lambda_1 x & \chi_1 y & \kappa_{12}y & \kappa_{12}x \\ & & E_{A_1} & 0 & \lambda_2 y & -\lambda_2 x \\ & \text{hc} & & E_{A_2} & \chi_2 x & \chi_2 y \\ & & & & E_E - \kappa_2 x & \kappa_2 y \\ & & & & & E_E + \kappa_2 x \end{bmatrix} \tag{5}$$

where the subscripts on the coupling constants help to identify the states (the E state arising from $E \otimes E$ has the subscript 1). In analogy to the discussion below equation (2) we can derive relations among the coupling constants and energies. Of course, all energies are equal. The seven coupling constants can be expressed by two only:

$$\kappa_{12} = \lambda_2 = \chi_2 \qquad \kappa_1 = 0, \lambda_1 = \kappa_2 + \kappa_{12} \qquad \chi_1 = \kappa_2 - \kappa_{12}.$$

In spite of the above simplifications the reduction of the six-dimensional Hamiltonian (5) seems complicated. In benzene, for instance, the analogous H will be 12-dimensional and one can easily conceive of even more involved examples. We note, however, that the reduction can be done in two steps. The electronic states which span the Hamiltonian H transform according to the irreducible symmetry representations of the point group and may thus not necessarily have the desired form $|L\rangle \otimes |D\rangle$, but a simple transformation R_{LD} can bring them into this form. More details will be given elsewhere [18]. The final transformation T is determined by applying R_{LD} followed by the on-site localization transformation S_L. The Hamiltonian H is reduced by the transformation $THT^\dagger$ to N Hamiltonians H_i, $i = 1, 2, \ldots, N$, of dimension n, where n is the degree of degeneracy of the excited state in $|D\rangle$. In the case of our explicit D_{3h} example, $N = 3$ and $n = 2$. Again, it is sufficient to know one of the H_i:

$$H_1 = H_0 \underline{1} + \begin{bmatrix} E - (\kappa_2 - 2\kappa_{12})x & \kappa_2 y \\ \kappa_2 y & E + (\kappa_2 + 2\kappa_{12})x \end{bmatrix}. \tag{6}$$

The other two Hamiltonians can be obtained by rotating (x, y) *as well as* the electronic states in (6) by $2\pi/3$ and $4\pi/3$. The result (6) can be understood using our result (3). The Hamiltonian (5) and its reduction shed light on the origin of the underlying vibronic coupling problem and make clear how κ_2 and κ_{12} are to be computed in actual cases.

The reduction of multi-dimensional Hamiltonians to equivalent Hamiltonians of low dimension is the central result of this work. The Hamiltonian (6) describes the complicated vibronic motion in the excited state. The symmetry of (6) is lower than that of the JT problem (1) because of the existence of κ_{12}: putting $\kappa_{12} = 0$ leads to a pure JT effect. The symmetry breaking which originates from the localization of the electrons (holes) in the subsystem $|L\rangle$ is also reflected in the adiabatic potential energy surfaces of (6)

$$V_\pm(x, y) = E + \omega(x^2 + y^2)/2 + 2\kappa_{12}x \pm [(\kappa_2)^2 x^2 + (\kappa_2)^2 y^2]^{1/2} \tag{7}$$

drawn in figure 2. Unlike the surfaces of (1), $V_\pm$ are shifted in the x direction and are not rotationally symmetric in x and y. The spectrum of H_1 is expected to be very different from a JT spectrum and to exhibit richer structures.
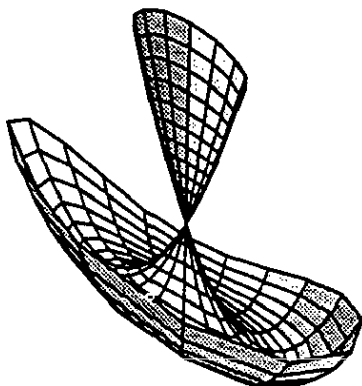

Figure 2. The potential energy surfaces of the distorted JT Hamiltonian (6).

In a JT system with N equivalent sites on which electrons (holes) may localize one encounters the interaction of many electronic states through the JT vibrations. It is demonstrated that the total Hamiltonian can be reduced to N equivalent Hamiltonians of low dimension n, where n is the degree of degeneracy of the state of the non-localized electrons. It is only by this reduction that the complicated multi-state vibronic coupling problem becomes tractable, in particular when several JT vibrations are active.

The resulting N Hamiltonians describe the complex vibronic dynamics of the system and exhibit a lower symmetry than related JT Hamiltonians. Their spectra are less regular than the JT spectra and may exhibit the signature of quantum chaos encountered in other low symmetry vibronic coupling cases [14].

The present theory is applicable also in the case where several JT and totally symmetric vibrations are active. In particular, the latter vibrations decouple [12] and can be considered separately.

One specific application which suggests itself is K-shell excitation spectroscopy where a core electron is excited to a vacant orbital. Recent experiments [15-17] on adsorbed and gas phase molecules have revealed interesting vibronic structures which are difficult to explain without theory [17]. If the molecule is JT active and, in particular, the vacant orbital degenerate, the present theory provides the relevant working equations and makes the computations of the spectra feasible.

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