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SOME REMARKS ON PSEUDO-JAHN–TELLER COUPLINGS AND MOLECULAR STRUCTURES

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CONTENTS

A. SYNOPSIS

The basic theory of pseudo-Jahn–Teller couplings is reviewed, and an instructive model system is treated in some detail. It transpires that whereas one should be very cautious of using these couplings to explain molecular topological features, they offer a convenient framework for a discussion of the electronic structures of complex dimers. To account for the strength of the first-order pseudo-Jahn–Teller couplings, a dimensionless parameter Φ is introduced, and an inequality is found which determines whether or not a system possesses a potential curve exhibiting a double minimum. The magnitude of Φ also determines the shape of the charge transfer band in mixed-valence complexes.

B. PREAMBLE

As a science, chemistry is infinitely complicated. Broad generalizations are therefore only of limited value. The more we want to understand molecular behaviour in detail the more sophisticated we need to be. The dynamics of a few simple systems can be calculated with great accuracy.

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Those systems are in turn expanded into parameterized models of chemical behaviour: a limited number of parameters are used to account for a manifold of manifestations. In principle we all know, quoting Dirac, that all of chemistry is calculable. As active chemists we know also that this is a statement which needs to be taken with more than a grain of salt!

In a molecule the masses of the nuclei are very much larger than the masses of the electrons whilst the coulombic forces between all the particles are comparable. It follows that the motions of the electrons are much faster than the motions of the nuclei and this fact is the basis for the calculation of molecular structures in the Born–Oppenheimer approximation. When calculating the electronic structures the motions of the nuclei are neglected: the nuclear coordinates are treated as parameters. A potential surface for the motion of the nuclei is thereby obtained, and re-introducing the kinetic energy of the nuclei, the vibrational Schrödinger equation can be solved. In this way the nuclear and electronic motions are separated and a variational molecular wavefunction can be written as a single product

$$\Psi_{i,v} = \psi_i(q,Q)\chi_v(Q) \tag{1}$$

where q and Q are the electronic and the nuclear coordinates, respectively. Such a form of the wavefunction is often referred to as a Born–Oppenheimer state function.

For a non-degenerate electronic state at the molecular equilibrium point Q^0, a single product function of the type in eqn. (1) is empirically a good approximation to the true wavefunction. However, in the cases where we have symmetry-determined electronic degeneracy, that is, where for a certain nuclear conformation, Q^0, the states $\psi_1(q, Q^0)$, $\psi_2(q, Q^0)\ldots$ have the same electronic energy W^0, the Born–Oppenheimer approximation breaks down completely. A strong coupling of the electronic and vibrational motions will then take place between the members of the Born–Oppenheimer states spanning the degenerate state. This situation is dealt with under the heading of Jahn–Teller couplings with which we shall not be concerned here [1].

Degeneracies or no degeneracies, vibrational–electronic couplings will on the other hand always occur between the various Born–Oppenheimer states. Depending upon the strength of the couplings, these will manifest themselves in various ways. However, it is important to realize that the "existence" of vibrational–electronic couplings is a consequence of the use of the Born–Oppenheimer approximation.

A vibronic coupling model for dimers goes back to the work of Moffitt and Witkowski [2] in 1960 and to Fulton and Gouterman [3] in 1961. It was used by Piepho, Krausz and Schatz [4] in 1978 to account for the absorption band profiles of mixed-valence complexes. Their model has since been

developed and extended by the work of, for instance, Wong, Schatz and Piepho [5,6] and Prassides, Schatz, Wong and Day [7], to name but a few. All these authors took as their starting point an electronic–vibrational coupling between the two localized metal centres in the complex. However, I shall advocate here that a clearer understanding of the nature of the coupling can be reached by considering the electronic structures in the system as the outcome of a coupling between two non-degenerate molecular electronic states of the entire entity. Such a point of view focuses the attention upon the so-called pseudo-Jahn–Teller couplings.

One of the advantages is that such a treatment clearly delineates which vibrations are active in the couplings and to what order. This treatment shows which vibrations act as "reaction coordinates" during an electron transfer from one centre to the other. Certain molecular topological proposals which have been put forward using pseudo-Jahn–Teller couplings are also clarified [8,9].

C. THE FORMALISM

The molecular Schrödinger equation is

$$\mathscr{H}\Psi(q, Q) = W\Psi(q, Q) \tag{2}$$

with

$$\mathscr{H} = \hat{T}_N + \hat{T}_e + V(q, Q) \tag{3}$$

Here $\hat{T}_N$ is the kinetic energy of the N nuclei, $\hat{T}_e$ the kinetic energy of n electrons and $V(q, Q)$ is the total potential energy in the electronic and nuclear coordinates (q, Q), respectively. The momenta and masses of the nuclei and electrons are designated by upper and lower cases:

$$\hat{T}_N = \sum_N \frac{\hat{P}_N^2}{2M_N} \tag{4}$$

$$\hat{T}_e = \sum_n \frac{\hat{p}_n^2}{2m_e} \tag{5}$$

Suppose now that all the nuclear masses are infinitely heavy. Clearly this means that $\hat{T}_N = 0$, and we can solve for the electronic Schrödinger equation:

$$\mathscr{H}(Q)\Psi_i(q, Q) = W_i(Q)\psi_i(q, Q) \tag{6}$$

where

$$\mathscr{H}(Q) = \hat{T}_e + V(q, Q) \tag{7}$$

The electronic energies $W_i(Q)$ and the electronic wavefunctions $\psi_i(q, Q)$ contain the nuclear positions Q as parameters: they are indeed continuous functions of the $3N$ nuclear coordinates. The wavefunctions $\psi_i(q, Q)$ are further normalized to unity in the electronic space

$$\int |\psi_i(q, Q)|^2 \, dq = 1 \tag{8}$$

When a single Born–Oppenheimer state $\Psi_{1v} = \psi_1(q, Q)\chi_v(Q)$ suffices for the description of the ground state, the stable configuration point $\tilde{Q}^0$ is determined by $[\partial W_1/\partial Q]_{Q=\tilde{Q}^0} = 0$.

In what follows we want to draw on the theory of symmetry. We therefore solve eqn. (6) for a certain fixed nuclear conformation Q^0, which need not be the molecular equilibrium point

$$\left[\hat{T}_e + V(q, Q^0)\right]\psi_i^0(q) = W_i^0\psi_i^0(q) \tag{9}$$

and obtain an orthonormal set of so-called crude adiabatic solutions $\psi_i^0(q)$, $i = 1, 2 \cdots$ with energies $W_1^0 < W_2^0 < \cdots$. We shall here suppose (being only interested in the pseudo-Jahn–Teller couplings) that the wavefunctions $\psi_i^0(q)$ are electronically non-degenerate and real. These wavefunctions, as well as the vibrational symmetry coordinates, can therefore be characterized in the point group peculiar to the Q^0 nuclear conformation.

The pseudo-Jahn–Teller coupling between two non-degenerate crude Born–Oppenheimer states is now handled using a variational wavefunction made up of a linear combination of the two states in question:

$$\Psi(q, Q) = \psi_1^0(q)\chi_1(Q) + \psi_2^0(q)\chi_2(Q) \tag{10}$$

where $\chi_1(Q)$ and $\chi_2(Q)$ can be looked upon as variational functions to be determined by substituting eqn. (10) into eqn. (2). Multiplying from the left with ψ_1^0 and ψ_2^0 and integrating over the electronic space we obtain the set of coupled equations:

$$\begin{bmatrix} \hat{T}_N + \langle\psi_1^0|\mathscr{H}(Q)|\psi_1^0\rangle & \langle\psi_1^0|\mathscr{H}(Q)|\psi_2^0\rangle \\ \langle\psi_2^0|\mathscr{H}(Q)|\psi_1^0\rangle & \hat{T}_N + \langle\psi_2^0|\mathscr{H}(Q)|\psi_2^0\rangle \end{bmatrix}\begin{bmatrix}\chi_1(Q)\\ \chi_2(Q)\end{bmatrix} = W\begin{bmatrix}\chi_1(Q)\\ \chi_2(Q)\end{bmatrix} \tag{11}$$

In order to calculate the electronic matrix elements in eqn. (11) we expand the electronic Hamiltonian $\mathscr{H}(Q)$ in the $3N - 6$ vibrational symmetry coordinates peculiar to the Q^0 nuclear conformation. To second order we have

$$\mathscr{H}(Q) = \hat{T}_e + V(q, Q^0) + \sum_t^{3N-6} Q_t\left[\frac{\partial V}{\partial Q_t}\right]_0 + \tfrac{1}{2}\sum_{s,t}^{3N-6} Q_sQ_t\left[\frac{\partial^2 V}{\partial Q_s\partial Q_t}\right] + \cdots \tag{12}$$

To simplify matters and in order to bring out the principal features of the coupling, we now assume that only two vibrations are "active" in the system: Q_1, being totally symmetric and Q_2, being non-degenerate, non-totally symmetric. $V(q, Q)$, as a part of the Hamiltonian, must transform like a totally symmetric representation. Therefore $[\partial V/\partial Q_t]_0$ must transform like Q_t and $[\partial^2 V/\partial Q_s \partial Q_t]_0$ like $Q_s Q_t$. The products $|\psi_1^0(q)|^2$ and $|\psi_2^0(q)|^2$ transform like a totally symmetric function. For the diagonal matrix elements in eqn. (11) we have therefore in general to the second order

$$\langle \psi_1^0 | \mathscr{H}(Q) | \psi_1^0 \rangle = W_1^0 + c_{111} Q_1 + \tfrac{1}{2} k_{111} Q_1^2 + \tfrac{1}{2} k_{112} Q_2^2 \tag{13}$$

$$\langle \psi_2^0 | \mathscr{H}(Q) | \psi_2^0 \rangle = W_2^0 + c_{221} Q_1 + \tfrac{1}{2} k_{221} Q_1^2 + \tfrac{1}{2} k_{222} Q_2^2 \tag{14}$$

where

$$\begin{aligned} c_{111} &= \langle \psi_1^0 | \left[\frac{\partial V}{\partial Q_1}\right]_0 | \psi_1^0 \rangle \qquad c_{221} = \langle \psi_2^0 | \left[\frac{\partial V}{\partial Q_1}\right]_0 | \psi_2^0 \rangle \\ k_{111} &= \langle \psi_1^0 | \left[\frac{\partial^2 V}{\partial Q_1^2}\right]_0 | \psi_1^0 \rangle \qquad k_{221} = \langle \psi_2^0 | \left[\frac{\partial^2 V}{\partial Q_1^2}\right]_0 | \psi_2^0 \rangle \\ k_{112} &= \langle \psi_1^0 | \left[\frac{\partial^2 V}{\partial Q_2^2}\right]_0 | \psi_1^0 \rangle \qquad k_{222} = \langle \psi_2^0 | \left[\frac{\partial^2 V}{\partial Q_2^2}\right] | \psi_2^0 \rangle \end{aligned} \tag{15a–15f}$$

The off-diagonal matrix element $\langle \psi_1^0 | \mathscr{H}(Q) | \psi_2^0 \rangle$ is, however, dependent upon whether ψ_1^0 and ψ_2^0 transform alike, in which case the product function $\psi_1^0 \psi_2^0$ transforms like Q_1 or whether they transform differently, in which case we take their product to transform like Q_2. In the first case

$$\langle \psi_1^0 | \mathscr{H}(Q) | \psi_2^0 \rangle = c_{121} Q_1 + \tfrac{1}{2} k_{121} Q_1^2 + \tfrac{1}{2} k_{122} Q_2^2 \tag{16}$$

and in the second case

$$\langle \psi_1^0 | \mathscr{H}(Q) | \psi_2^0 \rangle = c_{122} Q_2 + \tfrac{1}{2} \gamma Q_1 Q_2 \tag{17}$$

where

$$\begin{aligned} c_{121} &= \langle \psi_1^0 | \left[\frac{\partial V}{\partial Q_1}\right]_0 | \psi_2^0 \rangle \qquad c_{122} = \langle \psi_1^0 | \left[\frac{\partial V}{\partial Q_2}\right]_0 | \psi_2^0 \rangle \\ k_{121} &= \langle \psi_1^0 | \left[\frac{\partial^2 V}{\partial Q_1^2}\right]_0 | \psi_2^0 \rangle \qquad k_{122} = \langle \psi_1^0 | \left[\frac{\partial^2 V}{\partial Q_2^2}\right]_0 | \psi_2^0 \rangle \\ \gamma &= \langle \psi_1^0 | \left[\frac{\partial^2 V}{\partial Q_1 \partial Q_2}\right]_0 | \psi_2^0 \rangle \end{aligned} \tag{18a–18e}$$

It should be noticed that the only cross-term in the two vibrations occurs in the γ term in the off-diagonal matrix element.

Without loss of generality we can put $W_1^0 = 0$ and $c_{111} = 0$. This just corresponds to choosing Q^0 such that the $\psi_1^0(Q)$ state is stable with regard to the breathing motion. In the first case, the potential function is therefore given by

$$V_1 = \begin{bmatrix} \frac{1}{2}k_{111}Q_1^2 + \frac{1}{2}k_{112}Q_2^2 & c_{121}Q_1 + \frac{1}{2}k_{121}Q_1^2 + \frac{1}{2}k_{122}Q_2^2 \\ c_{121}Q_1 + \frac{1}{2}k_{121}Q_1^2 + \frac{1}{2}k_{122}Q_2^2 & W_2^0 + c_{221}Q_1 + \frac{1}{2}k_{221}Q_1^2 + \frac{1}{2}k_{222}Q_2^2 \end{bmatrix} \tag{19}$$

and in the second

$$V_2 = \begin{bmatrix} \frac{1}{2}k_{111}Q_1^2 + \frac{1}{2}k_{112}Q_2^2 & c_{122}Q_2 + \frac{1}{2}\gamma Q_1 Q_2 \\ c_{122}Q_2 + \frac{1}{2}\gamma Q_1 Q_2 & W_2^0 + c_{221}Q_1 + \frac{1}{2}k_{221}Q_1^2 + \frac{1}{2}k_{222}Q_2^2 \end{bmatrix} \tag{20}$$

D. THE POTENTIAL SURFACES. FIRST CASE

Cutting V_1 with a plane $Q_1 = C$

$$V_1 = \begin{bmatrix} \frac{1}{2}k_{111}C^2 + \frac{1}{2}k_{112}Q_2^2 & c_{121}C + \frac{1}{2}k_{121}C^2 + \frac{1}{2}k_{122}Q_2^2 \\ c_{121}C + \frac{1}{2}k_{121}C^2 + \frac{1}{2}k_{122}Q_2^2 & W_2^0 + c_{221}C + \frac{1}{2}k_{221}C^2 + \frac{1}{2}k_{222}Q_2^2 \end{bmatrix} \tag{21}$$

It should be noted that the potential is symmetrical around $Q_2 = 0$. Diagonalizing V_1 and for simplicity putting $C = 0$ and $k_{112} = k_{222} = k_2$, we obtain

$$V_1 = \tfrac{1}{2}W_2^0 + \tfrac{1}{2}k_2Q_2^2 \pm \tfrac{1}{2}\left[\left(W_2^0\right)^2 + k_{122}^2Q_2^4\right]^{1/2} \tag{22}$$

To find the extremum points we differentiate and put the result equal to zero:

$$Q_2\left\{k_2 \pm \frac{k_{122}^2Q_2^2}{\left[\left(W_2^0\right)^2 + k_{122}^2Q_2^4\right]^{1/2}}\right\} = 0 \tag{23}$$

Both the upper and lower potential sheets have minima at $Q_2 = 0$, and the lower surface has two maxima at

$$Q_2^2 = \frac{k_2W_2^0}{k_{122}}\left(k_{122}^2 - k_2^2\right)^{-1/2} \tag{24}$$

provided $k_{122} > k_2$. The potential sheets in Q_2 therefore have the appearance shown in Fig. 1a or 1b. The height of the barrier is

$$\Delta V_1 = \tfrac{1}{2}W_2^0\left\{1 - \left[1 - \left(\frac{k_2}{k_{122}}\right)^2\right]^{1/2}\right\} \tag{25}$$

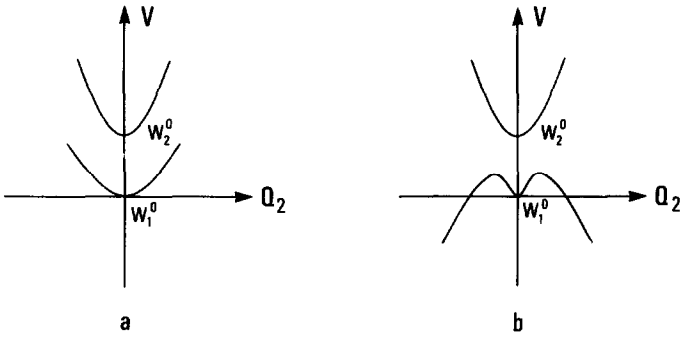

Fig. 1. Potential sheets in the first case for (a) $k_{122} < k_2$ and (b) $k_{122} > k_2$. $Q_1 = 0$

With $k_{122} > k_2$ the system is therefore unstable towards vibrations in Q_2 space. The conclusions are therefore that either the system is unstable with respect to motions in Q_2 space, or that the second-order coupling term $\frac{1}{2}k_{122}Q_2^2$ only gives rise to anharmonicity in the Q_2 potential.

The same situation prevails for the motions in Q_1. With $k_{121} > k_{111} \approx k_{221}$, instability occurs, as is readily seen. With $k_{121} < k_{111} \approx k_{221}$ we may therefore concentrate upon the first-order term in the coupling and put $k_{121} = k_{122} = 0$ in order to extract the principal features. In the first case, with the second-order coupling terms being zero and $k_{112} = k_{222} = k_2$, we have

$$V_1 = \begin{bmatrix} \frac{1}{2}k_{111}Q_1^2 & c_{121}Q_1 \\ c_{121}Q_1 & W_2^0 + c_{221}Q_1 + \frac{1}{2}k_{221}Q_1^2 \end{bmatrix} + \frac{1}{2}k_2Q_2^2\begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix} \tag{26}$$

The V_1 potential is then harmonic in the Q_2 coordinate and the vibrational energy in the two coordinates can be separated.

We first look at the case where $k_{111} = k_{222} = k_1$. Diagonalizing

$$V_1 = \frac{1}{2}k_1Q_1^2 + \frac{c_{221}}{2}Q_1 + \frac{W_2^0}{2} \pm \frac{1}{2}\left[\left(W_2^0 + c_{221}Q_1\right)^2 + 4c_{121}^2Q_1^2\right]^{1/2} + \frac{1}{2}k_2Q_2^2 \tag{27}$$

This potential has the appearance shown in Fig. 2. Clearly it is the c_{221} term which introduces the asymmetry in the potential. Eliminating the asymmetry in Q_1 by putting $c_{221} = 0$

$$V_1 = \begin{bmatrix} \frac{1}{2}k_{111}Q_1^2 & c_{121}Q_1 \\ c_{121}Q_1 & W_2^0 + \frac{1}{2}k_{221}Q_1^2 \end{bmatrix} + \frac{1}{2}k_2Q_2^2\begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix} \tag{28}$$

Applying the unitary transformation

$$U = \frac{1}{\sqrt{2}}\begin{bmatrix} 1 & -1 \\ -1 & -1 \end{bmatrix} \tag{29}$$

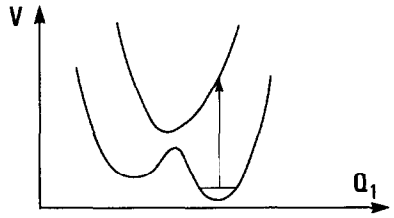

Fig. 2. The potential sheets in the first case with $Q_2 = 0$.

to the potential V_1 of eqn. (28) we obtain

$$V_1 = \begin{bmatrix} \frac{1}{4}(k_{111}+k_{221})Q_1^2 + \frac{W_2^0}{2} - \frac{c_{121}}{2}Q_1 & \frac{W_2^0}{2} + \frac{1}{4}(k_{221}-k_{111})Q_1^2 \\ \frac{W_2^0}{2} + \frac{1}{4}(k_{221}-k_{111})Q_1^2 & \frac{1}{4}(k_{111}+k_{221})Q_1^2 + \frac{W_2^0}{2} + \frac{c_{121}}{2}Q_1 \end{bmatrix} + \frac{1}{2}k_2 Q_2^2 \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix} \tag{30}$$

Putting $\frac{1}{2}(k_{111}+k_{221}) = k_1$ and $\frac{1}{2}(k_{221}-k_{111}) = \mathscr{K}$ and subtracting $\frac{1}{2}W_2^0 - c_{122}^2/2k_1$ from the diagonal we obtain

$$V_1 = \begin{bmatrix} \frac{1}{2}k_1\left(Q_1 - \frac{c_{121}}{k_1}\right)^2 & \frac{W_2^0}{2} + \frac{1}{2}\mathscr{K}Q_1^2 \\ \frac{W_2^0}{2} + \frac{1}{2}\mathscr{K}Q_1^2 & \frac{1}{2}k_1\left(Q_1 + \frac{c_{121}}{k_1}\right)^2 \end{bmatrix} + \frac{1}{2}k_2 Q_1^2 \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix} \tag{31}$$

We observe that the V_1 potential of eqn. (31) is equivalent to two identical but displaced harmonic oscillators interacting through the term $\frac{1}{2}(W_2^0 + \mathscr{K}Q_1^2)$.

Calling $c_{121} = c_1$, the diagonal form of the potential V_1 in eqn. (31) is

$$V_1 = \frac{1}{2}k_1 Q_1^2 + \frac{1}{2}\frac{c_1^2}{k_1} \pm \frac{1}{2}\left(4c_1^2 Q_1^2 + \left(W_2^0 + \mathscr{K}Q_1^2\right)^2\right)^{1/2} \tag{32}$$

This potential has been pictured in Fig. 3 for various values of the parameters.

We now define the dimensionless parameters D and Φ as

$$D = \frac{c_1^2}{2k_1\hbar\omega} \tag{33}$$

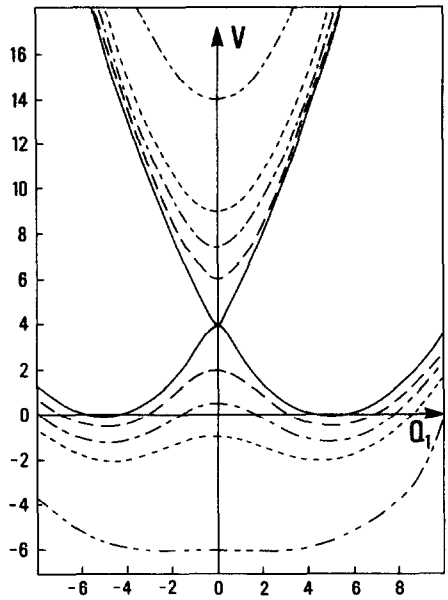

Fig. 3. The potential of eqn. (32) pictured for $\mathscr{K}/k = \frac{1}{4}$, $D = 4$ and $\Phi = 0$, $\frac{1}{4}$, $\frac{7}{16}$, $\frac{5}{8}$ and $\frac{5}{4}$ as counted from the inflection point.

and

$$\Phi = \frac{W_2^0}{4D\hbar\omega} \tag{34}$$

D is equivalent to the Huang–Rhys factor [11] which governs the bandwidth, and Φ turns out to be the parameter which is a measure of the first-order pseudo-Jahn–Teller couplings.

Differentiating the potential of eqn. (32) twice we find

$$\left[\frac{d^2V}{dQ_1^2}\right]_{Q_1=0} = k_1\left[1 \pm \left(\Phi^{-1} + \frac{\mathscr{K}}{k_1}\right)\right] \tag{35}$$

Evidently the force constant for the upper potential is always positive. For the lower potential

$$k = k_1\left[1 - \left(\frac{1}{\Phi} + \frac{\mathscr{K}}{k_1}\right)\right] \tag{36}$$

k is negative, corresponding to the occurrence of a double minimum on the potential curve, provided

$$\Phi\left(1 - \frac{\mathscr{K}}{k_1}\right) < 1 \tag{37}$$

which is therefore the condition for the presence of a double minimum on the lower potential. By differentiating the lower potential we find

$$Q_{\min}^2 = \frac{c_1^2}{k_1^2}\left\{\frac{1}{1-\mathscr{K}^2/k_1^2} - \left[\left(1+\frac{\mathscr{K}}{k_1}2\Phi\right)^{1/2} - \left(\frac{1}{1-\mathscr{K}^2/k_1^2}\right)^{1/2}\right]^2\right\} \tag{38}$$

For $\mathscr{K}/k_1$ small, $Q_{\min} \approx \pm c_1/k_1$. With

$$\mathscr{K} = (1-\Phi^{-1})k_1 \tag{39}$$

we find, however, that $Q_{\min} = 0$. The inclusion of the second-order coupling term therefore "shrinks" the distance between the double minima.

The vertical transition from the lower to the upper potential surface occurs at

$$\Delta W = 4D\hbar\omega\left(\frac{k_1^2 - 2\mathscr{K}k_1\Phi}{k^2-\mathscr{K}^2}\right)^{1/2} \tag{40}$$

which, for $\mathscr{K}$ small, equals $4D\hbar\omega[1+(\mathscr{K}/k_1)W_2^0]$. For $\mathscr{K} \geqslant (1-\Phi^{-1})k_1$ the energy separation is W_2^0. The barrier height ΔV is given by

$$\Delta V = D\hbar\omega\left\{1-2\Phi+\mathscr{K}^2\left[\left(k_1^2+2\mathscr{K}k_1\Phi\right)^{1/2} - \left(k_1^2-\mathscr{K}^2\right)^{1/2}\right]^2\right\} \tag{41}$$

which for $\mathscr{K}$ small becomes

$$\Delta V \approx D\hbar\omega\left[(1-\Phi)^2 + \frac{\mathscr{K}}{k_1}\Phi\right] \tag{42}$$

and, for $\mathscr{K} = (1-\Phi^{-1})k_1$, equals zero. Clearly a small value of $\mathscr{K}$ raises the potential barrier, whereas a large value lowers it.

E. THE POTENTIAL SURFACES. SECOND CASE

In order to bring out the principal features in this case, we take V_2 of eqn. (20):

$$V_2 = \begin{bmatrix} \frac{1}{2}k_1Q_1^2 + \frac{1}{2}k_2Q_2^2 & c_{122}Q_2 + \frac{1}{2}\gamma Q_1Q_2 \\ c_{122}Q_2 + \frac{1}{2}\gamma Q_1Q_2 & W_2^0 + c_{221}Q_1 + \frac{1}{2}k_1Q_1^2 + \frac{1}{2}k_2Q_2^2 \end{bmatrix} \tag{43}$$

where we have put $k_{112} = k_{222} = k_2$ and $k_{111} = k_{221} = k_1$. Diagonalizing

$$V_2 = \tfrac{1}{2}k_1Q_1^2 + \frac{c_{221}}{2} + \tfrac{1}{2}k_2Q_2^2 + \frac{W_2^2}{2}$$
$$\pm\tfrac{1}{2}\left[\left(W_2^0 + c_{221}Q_1\right)^2 + 4Q_2^2\left(c_{122}+\tfrac{1}{2}\gamma Q_1\right)^2\right]^{1/2} \tag{44}$$

We observe that the V_2 potential is symmetrical in the plane $Q_2 = 0$ with

$V_2^{\text{lower}} = \frac{1}{2}k_1Q_1^2$. It should also be noted that at the plane $Q_1 = -2c_{122}/\gamma$ we have

$$V_2^{\text{lower}} = \tfrac{1}{2}k_2Q_2^2 + \frac{2k_1c_{122}^2}{\gamma^2} \tag{45}$$

Cutting V_2 with a plane $Q_1 = \Omega$ equal to a constant, we have for the lower surface

$$V_2 = \tfrac{1}{2}k_1\Omega^2 + \frac{c_{221}}{2}\Omega + \tfrac{1}{2}k_2Q_2^2 + \frac{W_2^0}{2}$$
$$-\tfrac{1}{2}\left[\left(W_2^0 + c_{221}\Omega\right)^2 + 4Q_2^2\left(c_{122} + \tfrac{1}{2}\gamma\Omega\right)^2\right]^{1/2} \tag{46}$$

Assuming $(c_{122} + \frac{1}{2}\gamma\Omega) \neq 0$, two minima are found at

$$Q_2^{\min} = \pm\left[\frac{\left(c_{122} + \frac{1}{2}\gamma\Omega\right)^2}{k_2^2} - \frac{\left(W_2^0 + c_{221}\Omega\right)^2}{4\left(c_{122} + \frac{1}{2}\gamma\Omega\right)^2}\right]^{1/2} \tag{47}$$

provided

$$W_2^0 + c_{122}\Omega < \frac{2\left(c_{122} + \frac{1}{2}\gamma\Omega\right)^2}{k_2} \tag{48}$$

A closer analysis then shows that with

$$k_2c_{221}^2 + 2\gamma^2W_2^0 > 4\gamma c_{221}c_{122} \tag{49}$$

there are two relative minima for all values of Ω except $\Omega = -2c_{122}/\gamma$ where there is only one minimum. The lower potential is pictured in Fig. 4.

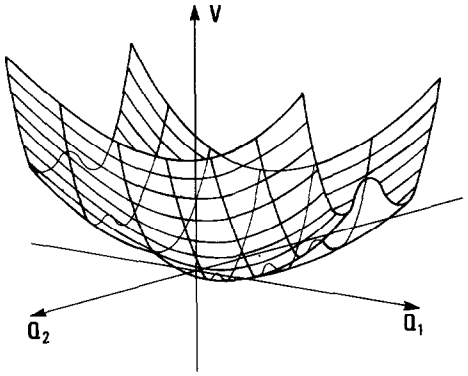

Fig. 4. The V_2 potential with $k_2c_{221}^2 + 2\gamma^2W_2^2 > 4\gamma c_{221}c_{122}$.

With the second-order coupling term $\gamma = 0$, the diagonalized V_2 potential is

$$V_2 = \tfrac{1}{2}k_1Q_1^2 + \tfrac{1}{2}c_{221}Q_1 + \tfrac{1}{2}k_2Q_2^2 + \tfrac{1}{2}W_2^0 \pm \tfrac{1}{2}\left[\left(W_2^0 + c_{221}Q_1\right)^2 + 4c_{122}^2Q_2^2\right]^{1/2} \tag{50}$$

Only with $c_{221} = 0$ is it possible to decouple the potential into a sum of two potentials in Q_1 and Q_2, respectively, to obtain the potential

$$V_2 = \tfrac{1}{2}k_1Q_1^2 + \tfrac{1}{2}k_2Q_2^2 + \tfrac{1}{2}W_2^0 \pm \tfrac{1}{2}\left[\left(W_2^0\right)^2 + 4c_{122}^2Q_2^2\right]^{1/2} \tag{51}$$

This is similar to that of V_1 in eqn. (32) with $\mathscr{K} = 0$, but with Q_1 and Q_2 reversed.

F. STRUCTURAL CONCLUSIONS

The outcome of this investigation into the workings of pseudo-Jahn–Teller couplings is therefore that the potential curves for a stable molecule may or may not possess a double minimum. From symmetry considerations alone, nothing can be predicted: only a priori calculations of Φ, k, γ and $\mathscr{K}$, evaluating the potential surfaces of an imaginary conformation of the atoms in the molecule, can settle the question. Furthermore, for minima widely separated on the potential curve, a perturbation procedure becomes nonsensical.

In the theory of stereochemistry the temptation is to start with the known structure and argue backwards [8,9]. If pseudo-Jahn–Teller couplings are to be invoked as being of stereochemical importance the proof that this is so is an experimental observation of a double minimum in the potential curve. A structural interchange is then possible through a kinetic transition state. In the two limits where the barrier is either very low or very high compared with a vibrational quantum, it serves, however, no purpose to use a topological description based on a pseudo-Jahn–Teller coupling, and such arguments border on the metaphysical. A single Born–Oppenheimer state, tied to the known molecular structure, will suffice. However, a detectable double minimum is a signal that the wavefunction is built up from at least two Born–Oppenheimer states.

G. THE VIBRATIONAL LEVELS

With V_1 being given in eqn. (31) and putting $c_{121} = c_1$, the Hamiltonian is

$$\mathscr{H} = \begin{bmatrix} \hat{T}_1 + \tfrac{1}{2}k_1\left(Q_1 - \dfrac{c_1}{k_1}\right)^2 & \tfrac{1}{2}\left(W_2^0 + \mathscr{K}Q_1^2\right) \\ \tfrac{1}{2}\left(W_2^0 + \mathscr{K}Q_1^2\right) & \hat{T}_1 + \tfrac{1}{2}k_1\left(Q_1 + \dfrac{c_1}{k_1}\right)^2 \end{bmatrix} + \left(\hat{T}_2 + \tfrac{1}{2}k_2Q_2^2\right)\begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix} \tag{52}$$

with

$$\hat{T}_1 = -\frac{\hbar^2}{2\mu_1}\frac{\partial^2}{\partial Q_1^2} \qquad \text{and} \qquad \hat{T}_2 = -\frac{\hbar^2}{2\mu_2}\frac{\partial^2}{\partial Q_2^2} \tag{53}$$

The total vibrational energy is therefore given as a sum of the energy in the harmonic Q_2 term and the energy W obtained by solving the coupled equations of eqn. (54) in Q_1:

$$\begin{bmatrix} \hat{T}_1 + \frac{1}{2}k_1\left(Q_1 - \frac{c_1}{k_1}\right)^2 & \frac{1}{2}\left(W_2^0 + \mathscr{K}Q_1^2\right) \\ \frac{1}{2}\left(W_2^0 + \mathscr{K}Q_1^2\right) & \hat{T}_1 + \frac{1}{2}k_1\left(Q_1 + \frac{c_1}{k_1}\right)^2 \end{bmatrix} \begin{bmatrix} \chi_1 \\ \chi_2 \end{bmatrix} = W \begin{bmatrix} \chi_1 \\ \chi_2 \end{bmatrix} \tag{54}$$

Because $\hat{T}_1$ does not commute with V_1, the Schrödinger equation (eqn. (54)) cannot be diagonalized as can V_1 in the semiclassical approximation. Strictly speaking, there is therefore no "upper" and "lower" potential function associated with eqn. (54). Nevertheless, adopting the Franck–Condon approximation, the most likely internal transition is that from the lowest vibrational level ($T = 0$) up to the place where the vertical transition "hits" the semiclassical upper potential surface. This is indeed the transition (see Figs. 2 and 5) which is associated with an intervalence transition [10].

With $\mathscr{K} = 0$, the Q_1 potential of eqn. (31) is equivalent to the Piepho, Krausz and Schatz potential [4]. We observe, as did Piepho et al., that the coupling of two Born–Oppenheimer states with different force constants still leads to a symmetrical lower potential curve, at the same time introducing a second-order coupling equal to $\mathscr{K}Q_1^2$. The value of $\mathscr{K}$ is here considered to be an independent parameter. The most important point of difference in our treatments is that they employ what Piepho et al. call a set of "dimer normal coordinates". These are not too well defined and should be contrasted with our use of the conventional normal vibrational modes associated with the entire ion.

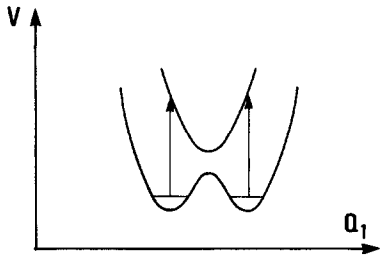

Fig. 5. The vertical transition for the V_1 potential of eqn. (54).

To obtain the solutions to eqn. (54) we observe that with no off-diagonal coupling term present, χ_1 and χ_2 would be harmonic oscillator functions displaced by respectively c_1/k_1 and $-c_1/k_1$. The energy for the degenerate oscillators is

$$W = \hbar\omega\left(v + \tfrac{1}{2}\right) \qquad v = 0, 1, 2, \ldots \qquad \omega = \left(\frac{k_1}{\mu_1}\right)^{1/2} \tag{55}$$

It is therefore natural to expand χ_1 and χ_2 in terms of the complete sets of harmonic oscillator functions centered at $(Q_1 - c_1/k_1)$, centre a, and $(Q_1 + c_1/k_1)$, centre b, respectively:

$$\chi_1 = \sum_{i=0}^{\infty} a_i \chi_i^a\left(Q_1 - \frac{c_1}{k_1}\right) \qquad \text{and} \qquad \chi_2 = \sum_{j=0}^{\infty} b_j \chi_j^b\left(Q_1 + \frac{c_1}{k_1}\right) \tag{56}$$

Then substituting eqn. (56) into eqn. (54) with

$$V^{(1)} = \tfrac{1}{2}\left(W_2^0 + \mathscr{K} Q_1^2\right) \tag{57}$$

$$(\mathscr{H}_a - W)\sum_{i=0}^{\infty} a_i \chi_i^a + V^{(1)} \sum_{j=0}^{\infty} b_j \chi_j^b = 0 \tag{58a}$$

$$V^{(1)} \sum_{i=0}^{\infty} a_i \chi_i^a + (\mathscr{H}_b - W)\sum_{j=0}^{\infty} b_j \chi_j^b = 0 \tag{58b}$$

Multiplying eqn. (58a) from the left with χ_i^a and eqn. (58b) with χ_j^b and integrating

$$(W_i - W)a_i + \sum_{j=0}^{\infty} \langle \chi_i^a | V^{(1)} | \chi_j^b \rangle b_j = 0 \tag{59a}$$

$$\sum_{i=0}^{\infty} \langle \chi_j^b | V^{(1)} | \chi_i^a \rangle a_i + (W_j - W) b_j = 0 \tag{59b}$$

we obtain an infinite homogeneous set of linear equations in a_i and b_j, $i = 0, 1, 2$, and $j = 0, 1, 2, \cdots$. With

$$V_{ij} = \langle \chi_i^a | V^{(1)} | \chi_j^b \rangle = (-1)^{i+j} \langle \chi_j^a | V^{(1)} | \chi_i^b \rangle \tag{60}$$

we obtain the secular equation

$$\begin{vmatrix}
\frac{1}{2}\hbar\omega_1 - W & V_{00} & 0 & V_{01} & 0 & V_{02} & \cdots \\
V_{00} & \frac{1}{2}\hbar\omega_1 - W & -V_{01} & 0 & V_{02} & 0 & \cdots \\
0 & -V_{01} & 3/2\hbar\omega_1 - W & V_{11} & 0 & V_{12} & \cdots \\
V_{01} & 0 & V_{11} & 3/2\hbar\omega_1 - W & -V_{12} & 0 & \cdots \\
0 & V_{02} & 0 & -V_{12} & 5/2\hbar\omega_1 - W & V_{22} & \cdots \\
V_{02} & 0 & V_{12} & 0 & V_{22} & 5/2\hbar\omega_1 - W & \cdots \\
\cdots & \cdots & \cdots & \cdots & \cdots & \cdots & \cdots
\end{vmatrix} = 0 \tag{61}$$

To first order, the energies of the zeroth-order degenerate levels, $(v_1 + \frac{1}{2})\hbar\omega_1$, are therefore given by

$$W_v = \left(v_1 + \tfrac{1}{2}\right)\hbar\omega_1 \mp V_{vv} \tag{62}$$

which is good so long as W_v is much less than the height of the potential barrier and $V_{vv} < \hbar\omega$. To second order the two lowest levels are given by

$$W_0^{\mp} = \tfrac{1}{2}\hbar\omega_1 \mp V_{00} - \sum_{j=1}^{\infty} \frac{V_{0j}^2}{j\hbar\omega_1} \tag{63}$$

Introducing harmonic oscillator functions and the $V^{(1)}$ potential of eqn. (57), we calculate

$$V_{0j} = \sqrt{\frac{1}{j!}}\ \mathrm{e}^{-2D}(4D)^{j/2}\left\{\tfrac{1}{2}W_2^0 + \tfrac{1}{4}\frac{\mathscr{K}}{k_1}\hbar\omega_1\left[1 + \frac{j(j-1)}{4D}\right]\right\} \tag{64}$$

and

$$W_0^{\mp} = \tfrac{1}{2}\hbar\omega_1 \mp \mathrm{e}^{-2D}\left(\tfrac{1}{2}W_2^0 + \tfrac{1}{4}\frac{\mathscr{K}}{k}\hbar\omega_1\right) - \frac{\left(W_2^0\right)^2 \mathrm{e}^{-4D}}{4\hbar\omega_1} \sum_{j=1}^{\infty} \frac{(4D)^j\left[1 + \tfrac{1}{2}\dfrac{\mathscr{K}\hbar\omega_1}{kW_2^0}\left[1 + \dfrac{j(j-1)}{4D}\right]\right]^2}{j(j!)} \tag{65}$$

which for the Huang–Rhys factor $D \to 0$ gives

$$W_0^{\mp} = \tfrac{1}{2}\hbar\omega_1 \mp \tfrac{1}{2}\left(W_2^0 + \tfrac{1}{2}\frac{\mathscr{K}}{k}\hbar\omega_1\right) - \tfrac{1}{16}\hbar\omega_1\frac{\mathscr{K}^2}{k^2} \tag{66}$$

The splitting, equal to W_2^0, of the two lowest vibrational levels found in the uncoupled Born–Oppenheimer states is seen to be quenched by the action of a pseudo-Jahn–Teller coupling. Furthermore, with D large, the splitting is very small.

The complete set of vibrational levels is obtained by solving eqn. (61) numerically. The wavefunctions are also obtained by this procedure, and in order to estimate the intensities of the intramolecular transitions the necessary Franck–Condon factors are evaluated. Even though the secular equation (eqn. (60)) looks different from that of Piepho et al. [4] we obtain, of course, (with $\mathscr{K} = 0$) the same results as they did, since our two Hamiltonians are related to each other by means of a unitary transformation.

The charge transfer band in a binuclear complex will have its maximum at the frequency of the corresponding vertical transition (Figs. 2 and 5). When Φ and $\mathscr{K}$ are small one expects to observe the charge transfer band with a width proportional to the Huang–Rhys factor of D [11]. With

increasing Φ the vibrational density of the $v = 0$ level on the lower potential surface will move towards $Q_1 = 0$. In the limit when $\Phi(1 - \mathscr{K}/k_1) > 1$, both the upper and the lower potential have their minima at $Q_1 = 0$, but with different force constants. In that case, most of the intensity will be concentrated in the 0–0 line. We may therefore expect that the charge transfer band in a pseudo-Jahn–Teller coupled system will be quite narrow and more unsymmetrical than the other type of charge transfer band found for instance in ferrocene or permanganate, where D is large. This expectation is borne out by experiments [12] and by numerical calculations [4].

H. CONCLUSIONS

Unfortunately, the parameters which govern the pseudo-Jahn–Teller couplings between two Born–Oppenheimer states are elusive quantities and are difficult to estimate a priori. However, we have seen that the occurrence of a double minimum in a potential curve can be associated with the workings of a pseudo-Jahn–Teller coupling between two Born–Oppenheimer states. Provided such minima are observed experimentally, the topological shape of the molecule or ion can probably be inferred as a manifestation of such couplings.

A parameterized description of the electronic structures of binuclear complexes, using the framework of pseudo-Jahn–Teller couplings, has the merit that it joins the discussion directly to the standard Born–Oppenheimer approximation. In particular, it treats the molecule or ion as one entity, thereby playing down the somewhat artificial distinction of a double minimum in the potential function. Indeed, for Φ large, two coupled states will tend to align on top of each other, only displaced in electronic energy, and in this process the double minimum is wholly or in part eliminated. An extensive review of multimode molecular dynamics has been given by Köppel et al. [13] of which our discussion here is but a small part.

Using a semiclassical approach we have arrived at the same conclusions as to the appearance of the charge transfer band in binuclear complexes as did Piepho et al. [4]. Whether their intuitive introduction of the inherent couplings is more appealing than our more formal treatment is finally a question of taste. In her recent fine paper, to which the referee turned my attention, Piepho [14] has indeed re-formulated their original approach so that the similarities with our treatment here are striking. Thus, Edgar's words in King Lear, "Ripeness is all", are worth remembering.

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