

EFFECTIVE POTENTIAL CURVES FOR DEGENERATE VIBRATIONS IN THE JAHN-TELLER EFFECT

BY M. Z. ZGIERSKI

Department of Theoretical Chemistry, Jagellonian University, Cracow*

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The decoupling conditions for the vibronic equation, describing the Jahn-Teller effect in a three atomic molecule, are analysed. It is shown that for vibronic states with sufficiently large projection of the total angular momentum the decoupling procedure is quite accurate and leads to the separate effective potentials for nuclear movements.

It is well known that for degenerate electronic states in molecules the Born-Oppenheimer approximation is invalid. In such cases mixing between electronic and nuclear motions occurs. This situation appears in nonlinear polyatomic molecules which possess at least a C_3 axis of symmetry and the interaction between degenerate electronic motions and degenerate, not totally symmetric vibrations, leads to the Jahn-Teller effect [1]. Because of the failure of the adiabatic approximation, a single-valued potential energy for vibrations coupled with electronic motion does not exist. The situation is similar in the Renner effect [2] and in the vibronic coupling in dimers [3]. We have shown [4, 5] that in limiting cases the two-dimensional vibronic Hamiltonians, describing the vibronic coupling in dimers and the Renner effect, can be reduced to some one-dimensional Hamiltonians with an effective potential energy for vibrations. In dimers this can be done for sufficiently strong interaction between monomers, and for the Renner effect for a sufficiently large projection of the total angular momentum of electrons and nuclei on the long axis of a linear molecule and not too small Renner parameter. Numerical calculations have been performed for dimers [6] and confirm the decoupling procedure used in reference [4].

In this note we shall investigate a similar problem for the Jahn-Teller effect. We consider a three atomic molecule belonging to the C_{3v} symmetry group and suppose that all electronic states are well separated from the two given states under consideration.

The vibronic function for this case is [7]:

$$\Psi(q, Q_+, Q_-, Q_-) = \alpha(Q_+)[\Psi_+(q)\eta_+(Q_+, Q_-) + \Psi_-(q)\eta_-(Q_+, Q_-)], \quad (1)$$

* Address: Zespoły Chemii Teoretycznej, Instytut Chemii UJ, Kraków, Krupnicza 41, Polska.

where Q_+ , Q_- are the normal coordinates of degenerate vibrations which couple with electronic motion, Q_1 is the normal coordinate of the totally symmetric vibration which satisfies the Born-Oppenheimer approximation, and $\Psi_{\pm}(q)$ are the degenerate electronic wave functions.

The equation for functions η_+ , η_- can be obtained from the variational principle, and reads [7]

$$\begin{pmatrix} \frac{1}{2} \lambda Q^2 + \frac{1}{2M Q^2} [(Q P_e)^2 + P_e^2], & k_e e^{-i\Phi} \\ K Q e^{i\Phi}, & \frac{1}{2} \lambda Q^2 + \frac{1}{2M Q^2} [(Q P_e)^2 + P_e^2] \end{pmatrix} \begin{pmatrix} \eta_+ \\ \eta_- \end{pmatrix} = E \begin{pmatrix} \eta_+ \\ \eta_- \end{pmatrix} \quad (2)$$

where

$$W(Q_1) + \frac{1}{2} \lambda Q^2 = \int \Psi_{\pm}^*(q) \mathbf{H}(Q) \Psi_{\pm}(q) dq, \quad (3a)$$

$$k_e e^{-i\Phi} = \int \Psi_+^*(q) \mathbf{H}(Q) \Psi_-(q) dq, \quad (3b)$$

$$Q = (Q_+^2 + Q_-^2)^{1/2}, \quad \Phi = \arctg \frac{Q_+}{Q_-} \quad (3c)$$

$\mathbf{H}(Q)$ is the electronic Hamiltonian which depends parametrically on vibrational coordinates, $W(Q_1)$ is the potential energy curve for the totally symmetric vibration, and k is the Jahn-Teller parameter of distortion. In Eq. (2) we have retained the linear coupling term only, *i.e.*, we have ignored the pseudo-Jahn-Teller effect.

Inserting

$$\begin{aligned} \eta_+ &= e^{i(j - \frac{1}{2})\Phi} \frac{1}{\sqrt{2}} (R_1 - R_2), \\ \eta_- &= e^{i(j + \frac{1}{2})\Phi} \frac{1}{\sqrt{2}} (R_1 + R_2), \end{aligned} \quad (4)$$

$$\chi = \begin{pmatrix} R_1 \\ R_2 \end{pmatrix},$$

into Eq. (2) we obtain

$$\mathbf{H}\chi = E\chi \quad (5)$$

where

$$\mathbf{H} = \left[\frac{1}{2} \lambda Q^2 + \frac{\hbar^2}{2M Q^2} \left(j^2 + \frac{1}{4} \right) + \frac{P_e^2}{2M} - \frac{i\hbar}{2M Q} P_e \right] \mathbf{1} + k Q \sigma_3 - \frac{\hbar^2 j}{2M Q^2} \sigma_1 \quad (6)$$

and $j = \pm 1/2, \pm 3/2, \pm 5/2 \dots = l = 1/2 + A$, where l is the quantum number of the vibrational angular momentum and A is the quantum number of the electronic angular momentum in a given degenerate state. j is the good quantum number in a linear Jahn-Teller effect and the optical transitions between vibronic states which differ in j by ± 1 are allowed.

Introducing the dimensionless quantities

$$q = \varrho \left(\frac{M\omega}{\hbar} \right)^{1/2}, \quad p_e = p(\hbar M\omega)^{-1/2},$$

$$\kappa = \frac{k}{\hbar\omega} \left(\frac{\hbar}{M\omega} \right)^{1/2}, \quad \omega^2 = \frac{\lambda}{M} \quad (7)$$

we obtain

$$\frac{\mathbf{H}}{\hbar\omega} = \left[\frac{1}{2} (p^2 + q^2) - \frac{i}{2q} p + \frac{j^2 + \frac{1}{4}}{2q^2} \right] \mathbf{1} + \kappa \varrho \boldsymbol{\sigma}_3 - \frac{j}{2q^2} \boldsymbol{\sigma}_1 \quad (8)$$

in order to include most of the energy in the diagonal terms of Hamiltonian (8) we transform it by the unitary transformation

$$\mathbf{U} = \cos \varphi \boldsymbol{\sigma}_3 + \sin \varphi \boldsymbol{\sigma}_1$$

$$\text{ctg } 2\varphi = -\frac{2\kappa}{j} q^3 \quad (9)$$

and obtain

$$\mathbf{H}' = \frac{1}{\hbar\omega} \mathbf{U}^+ \mathbf{H} \mathbf{U}, \quad (10)$$

$$\mathbf{H}' = \left[\frac{1}{2} (p^2 + q^2) + \frac{1}{2q^2} \left(j^2 + \frac{1}{4} \right) - \frac{i}{2q} p + \frac{1}{2} \left(\frac{d\varphi}{dq} \right)^2 \right] \mathbf{1} +$$

$$+ \frac{1}{2q^2} (4\kappa^2 \varrho^6 + j^2)^{1/2} \boldsymbol{\sigma}_3 + \frac{d\varphi}{dq} \boldsymbol{\sigma}_2 p - \frac{i}{2} \frac{d^2\varphi}{dq^2} \boldsymbol{\sigma}_2 - \frac{i}{2q} \frac{d\varphi}{dq} \boldsymbol{\sigma}_2. \quad (11)$$

Now, we see that the terms proportional to the $\boldsymbol{\sigma}_2$ matrix, which couple the functions R_1 and R_2 , have upper limits, namely:

$$\frac{d\varphi}{dq} \leq A^{1/2},$$

$$\frac{d^2\varphi}{dq^2} \leq 2.4 A^{1/2}, \quad \frac{1}{q} \frac{d\varphi}{dq} \leq 1.5 A^{1/2} \quad (12)$$

where $A = \kappa/j$. The term proportional to $\boldsymbol{\sigma}_3$ matrix possesses a minimum:

$$\frac{1}{2q^2} \sqrt{4\kappa^2 q^6 + j^2} \geq |j| A^{1/2}. \quad (13)$$

Assuming that the derivatives of R_1 and R_2 are not excessively high, we may neglect the coupling terms, if only in the whole region of the q -space the diagonal term (13) is larger than the nondiagonal ones. This condition is satisfied for

$$\kappa j^2 > 1 \quad \text{and} \quad |j| \geq \frac{3}{2}. \quad (14)$$

Also for vibronic states with the projection of the total angular momentum $|j| \geq \max(\kappa^{-1/2}, 3/2)$ we may seek the functions R_1, R_2 from a one-dimensional effective Schrödinger equation of the form:

$$\left[\frac{1}{2} p^2 + V_{\pm, j}^{\text{eff}}(q) \right] \tilde{R}_{\pm}^j = E_{\pm, j} \tilde{R}_{\pm}^j, \quad (15)$$

where

$$\begin{pmatrix} \tilde{R}_+^j \\ \tilde{R}_-^j \end{pmatrix} = q^{-\frac{1}{2}} (\cos \varphi \sigma_3 + \sin \varphi \sigma_1) \begin{pmatrix} R_1 \\ R_2 \end{pmatrix}, \quad (16)$$

and

$$V_{\pm, j}^{\text{eff}}(q) = \frac{1}{2} q^2 + \frac{j^2}{2q^2} \pm \frac{1}{2q^2} (4\kappa^2 q^6 + j^2)^{1/2}. \quad (17)$$

If we formally put $j = 0$ into Eq. (17) we obtain curves discussed by Longuet-Higgins [7]; of course such vibronic states do not exist. For vibronic states with $|j| = 1/2$ we can never speak, even approximately, about the motion of nuclei on a given potential curve, and only for higher quantum numbers j , and not too small distortion parameter k are the potential curves well separated.

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