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Vibronic coupling by two active modes: A simple, exactly solvable model for the Duschinsky effect*

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The properties of a simple model for the Duschinsky effect are investigated. The model consists of two electronic states coupled by two harmonic oscillators. Weak and strong adiabatic and nonadiabatic coupling limits are defined. If an alternative phase convention is adopted, the two ways of approaching the strong nonadiabatic coupling limit lead paradoxically, in the one-oscillator case, to adiabatic Born–Oppenheimer wavefunctions that are exact eigenstates of the system. Expansion of the adiabatic coupling matrix element as a power series in the normal coordinates in the weak nonadiabatic coupling regime is not possible in the two-oscillator case unless a constraint is placed on the Duschinsky parameter.

I. INTRODUCTION

The realization that conventional theories are inadequate for understanding radiative and nonradiative processes in molecules on a quantitative basis has been responsible for a remarkable resurgence of interest in the theory of vibronic coupling.

One way to gain insight into the range of validity of conventional procedures is to formulate models for vibronic coupling which can be solved exactly and to compare the approximate predictions with the exact ones. Recent work^{1–4} that has been directed along these lines employs a model in which just two electronic states are vibronically coupled. Despite this limitation, which has the important advantage that it guarantees exact solvability, the model possesses a great deal of flexibility. However, consideration so far has only been given to vibronic coupling through a single active vibrational mode. Although one such mode often dominates the vibronic coupling, many physical systems of experimental interest show nonnegligible coupling through a second vibrational mode. Previous work^{5,6} on the Jahn–Teller effect has established that the activity of a second mode can markedly distort the spectral pattern predicted by the first alone.

The effect of including a second but inactive mode in the model has been considered,³ but the more complicated situation where both modes are vibronically active remains to be treated. The latter situation is more complicated because, if a second mode with the same symmetry species is allowed, the normal coordinates for the two electronic states will not generally be the same, but will be rotated with respect to one another. This effect, which is known as the Duschinsky effect,⁷ has been shown^{8,9} to be a necessary consequence of vibronic coupling through two or more active modes.

II. GENERAL CONSIDERATIONS

In this paper we first summarize the basic formalism^{4a} of the model and then specialize it to the case where two modes are vibronically active.

The model is formulated mathematically in terms of both the adiabatic Born–Oppenheimer (ABO)¹⁰ and crude BO (CBO)¹¹ representations. The molecular Hamiltonian is written

$$H_M = T_N + T_e + U, \quad (1)$$

where T_N and T_e are the nuclear and electronic kinetic energy operators, respectively, and U is the potential energy operator. We define the ABO electronic states, to be denoted by $\Phi_m(q; Q)$ and $\Phi_n(q; Q)$, and the ABO vibrational states, to be denoted by $\Lambda_v^{(m)}(Q)$ and $\Lambda_w^{(n)}(Q)$, respectively, by the equations

$$\begin{aligned} \Psi_{mv}(q; Q) &= \Phi_m(q; Q) \Lambda_v^{(m)}(Q), \\ (T_e + U)\Phi_m &= E_m(Q)\Phi_m, \\ (T_N + E_m)\Lambda_v^{(m)} &= \epsilon_{mv} \Lambda_v^{(m)}. \end{aligned} \quad (2)$$

Here q and Q denote the electronic and nuclear coordinates, respectively. We shall use $\langle \rangle$ and $()$ to represent integration over q and Q , respectively, mass-weighted nuclear coordinates, and units such that $\hbar = 1$. The eigenvalues $E_m(Q) \equiv \langle \Phi_m | T_e + U | \Phi_m \rangle$ and $E_n(Q) \equiv \langle \Phi_n | T_e + U | \Phi_n \rangle$ are the potential energy operators for vibrational motion in the states Φ_m and Φ_n , respectively. The ABO states are coupled *nonadiabatically* by T_N and consequently the exact vibronic wavefunctions take the form

$$\Psi_i(q; Q) = \Phi_m(q; Q)\xi_i(Q) + \Phi_n(q; Q)\eta_i(Q), \quad (3)$$

where ξ_i and η_i are solutions to the following coupled differential equations:

$$\begin{pmatrix} T_{mm} + E_m - \epsilon_i & T_{mn} \\ T_{nm} & T_{nn} + E_n - \epsilon_i \end{pmatrix} \begin{pmatrix} \xi_i \\ \eta_i \end{pmatrix} = 0, \quad (4)$$

$$T_{mn} \equiv \langle m | T_N | n \rangle, \text{ etc.}$$

In (4) it is to be understood that T_N operates on all functions to the right.

The electronic CBO states are independent of Q and are assumed to be solutions of the electronic Schrödinger equation at a convenient nuclear configuration, $Q = Q_0$, with appropriate symmetry. We set $Q_0 \equiv 0$ and denote the two electronic CBO states by $\Phi_m^0 \equiv \Phi_m(q; 0)$ and $\Phi_n^0 \equiv \Phi_n(q; 0)$. In contrast to the ABO states, the CBO states are coupled *adiabatically* by the potential energy operator $\Delta U \equiv U(q; Q) - U(q; 0)$ and so in this representation it follows that the exact eigenstates take the form

$$\Psi_i(q; Q) = \Phi_m^0 \xi_i^0 + \Phi_n^0 \eta_i^0, \quad (5)$$

where ξ_i^0 and η_i^0 are the solutions to the following coupled differential equations:

$$\begin{pmatrix} T_N + E_m(0) + U_{mm}(Q) - \epsilon_i & U_{mn}(Q) \\ U_{nm}(Q) & T_N + E_n(0) + U_{nn}(Q) - \epsilon_i \end{pmatrix} \begin{pmatrix} \xi_i^0 \\ \eta_i^0 \end{pmatrix} = 0$$

$$U_{mn} \equiv \langle m^0 | \Delta U | n^0 \rangle, \text{ etc.} \quad (6)$$

The quantities $E_m(0) + U_{mm}(Q)$ and $E_n(0) + U_{nn}(Q)$ are the potential energy operators for vibrational motion in the states Φ_m^0 and Φ_n^0 , respectively.

Writing

$$\begin{pmatrix} \Phi_m \\ \Phi_n \end{pmatrix} = \mathfrak{u} \begin{pmatrix} \Phi_m^0 \\ \Phi_n^0 \end{pmatrix}, \quad (7)$$

where

$$\mathfrak{u} = \begin{pmatrix} \cos\phi & \sin\phi \\ -\sin\phi & \cos\phi \end{pmatrix}, \quad (8)$$

we deduce from the electronic Schrödinger equation that

$$\begin{pmatrix} E_m(0) + U_{mm} & U_{mn} \\ U_{nm} & E_n(0) + U_{nn} \end{pmatrix} \tilde{\mathfrak{u}} = \tilde{\mathfrak{u}} \begin{pmatrix} E_m & 0 \\ 0 & E_n \end{pmatrix}, \quad (9)$$

where $\tilde{\mathfrak{u}}$ is the transpose of \mathfrak{u} . Thus, for example, we have

$$(E_m(0) + U_{mm}) \cos\phi + U_{mn} \sin\phi = E_m \cos\phi, \quad (10)$$

which yields

$$\sin\phi = -\frac{\Delta E_m}{U_{mn}} \cos\phi,$$

$$\Delta E_m \equiv E_m(0) + U_{mm} - E_m. \quad (11)$$

We deduce immediately from Feenberg perturbation theory¹² that the exact expression for E_m is

$$E_m = E_m(0) + U_{mm} + |U_{mn}|^2 / \Delta E_m,$$

$$\Delta E_m \equiv E_m - E_n(0) - U_{nm}. \quad (12)$$

We may write

$$\Delta E_m = E_m - E_n + E_n - E_n(0) - U_{nm} = E_m - E_n - \Delta E_n.$$

However, due to the assumption of only two electronic states, $\Delta E_n = -\Delta E_m$,

$$\Delta E_m = -(E_m - \Delta E_m),$$

$$E_m \equiv E_n - E_m. \quad (13)$$

Since we are free to take U_{mn} to be real, it follows from (12) and (13) that

$$U_{mn}^2 = -\Delta E_m \Delta E_n = (E_m - \Delta E_m) \Delta E_m. \quad (14)$$

Choosing $\Delta E_m \geq 0$, we see that the restriction that U_{mn} be real imposes the condition

$$\Delta E_m \leq 0 \text{ or } E_m \geq \Delta E_m (\geq 0), \quad (\Rightarrow E_n \geq E_m). \quad (15)$$

Only three out of the four vibrational potentials (two adiabatic and two crude adiabatic) can be chosen independently and the choice we make for these three potentials determines the adiabatic coupling through Eq. (14). Hence, if the model is to be internally consistent, we cannot choose the potentials and the coupling

independently of one another.

Since $\cos^2\phi + \sin^2\phi = 1$, it follows from (11) and (14) that

$$\cos^2\phi = -\frac{\Delta E_m}{E_{nm}} = \frac{E_m - \Delta E_m}{E_{nm}}, \quad (16)$$

$$\sin^2\phi = \frac{\Delta E_m}{E_{nm}}. \quad (17)$$

The signs of U_{mn} , $\sin\phi$ and $\cos\phi$ are not independent: the signs chosen for U_{mn} and $\cos\phi$ determine the sign of $\sin\phi$ through Eq. (11). If $U_{mn} > 0$, then either (a) $\cos\phi > 0$ and $\sin\phi < 0$ and therefore $3\pi/2 \leq \phi \leq 2\pi$ or (b) $\cos\phi < 0$ and $\sin\phi > 0$ and therefore $\pi/2 \leq \phi \leq \pi$. In both cases $\tan\phi < 0$. If $U_{mn} < 0$, then either (a) $\cos\phi > 0$ and $\sin\phi > 0$ and therefore $0 \leq \phi \leq \pi/2$, or (b) $\cos\phi < 0$ and $\sin\phi < 0$ and therefore $\pi \leq \phi \leq 3\pi/2$. In both cases $\tan\phi > 0$.

Finally, by substituting (7) into (3) and comparing the result with (5), we deduce that

$$\xi_i^0 = \xi_i \cos\phi - \eta_i \sin\phi,$$

$$\eta_i^0 = \eta_i \cos\phi + \xi_i \sin\phi. \quad (18)$$

III. SPECIFIC MODEL: TWO ACTIVE NORMAL MODES

This completes our summary of the basic formalism of the model. We now turn our attention to the specific problem of interest. We assume that m and n are coupled to one another, but not to the ground state g , by two nondegenerate undisplaced normal modes a and b . Following Sharf and Honig,⁸ we assume that the normal coordinates for the CBO vibrational potentials of states m and n are the same as those (Q_a , Q_b) for the ground state potential. This is equivalent to assuming that the Duschinsky effect arises solely from adiabatic vibronic coupling and that the normal coordinates are not mixed as a result of excitation from the ground state $\Phi_g(q; 0)$ to the excited states $\Phi_m^0(q; 0)$ and $\Phi_n^0(q; 0)$. We write the diagonal matrix elements in the CBO basis as

$$E_i(0) + U_{ii}(Q) = E_i(0) + \frac{1}{2} \Omega_{ia}^2 Q_a^2 + \frac{1}{2} \Omega_{ib}^2 Q_b^2, \quad i = m, n, \quad (19)$$

and the ABO electronic eigenvalue for state m as

$$E_m = E_m(0) + \frac{1}{2} f_{maa}^2 Q_a^2 + f_{mab} Q_a Q_b + \frac{1}{2} f_{mnb}^2 Q_b^2, \quad (20)$$

where the Ω 's are CBO vibrational frequencies and the f 's are constants that characterize the ABO potential for state m in the coordinate system (Q_a , Q_b). Since $-\Delta E_n = \Delta E_m$, it follows that

$$E_n = E_n(0) + U_{nn} + E_m(0) + U_{mm} - E_m$$

$$= E_n(0) + \frac{1}{2} (\Omega_{na}^2 + \Omega_{nb}^2 - f_{maa}^2) Q_a^2$$

$$- f_{mab} Q_a Q_b + \frac{1}{2} (\Omega_{nb}^2 + \Omega_{mb}^2 - f_{mnb}^2) Q_b^2$$

$$\equiv E_n(0) + \frac{1}{2} f_{naa}^2 Q_a^2 + f_{nab} Q_a Q_b + \frac{1}{2} f_{nbb}^2 Q_b^2, \quad (21)$$

$$f_{nii}^2 \equiv \Omega_{ni}^2 + \Omega_{mi}^2 - f_{mii}^2, \quad i = a, b,$$

$$f_{nab} \equiv -f_{mab}.$$

Denoting the normal coordinates in states Φ_m and Φ_n by (Q_{ma} , Q_{mb}) and (Q_{na} , Q_{nb}), respectively, it follows that their vibrational potentials can also be written

$$E_i = E_i(0) + \frac{1}{2} \omega_{ia}^2 Q_{ia}^2 + \frac{1}{2} \omega_{ib}^2 Q_{ib}^2, \quad i = m, n, \quad (22)$$

where the ω 's are ABO vibrational frequencies.

Continuing to work in ground state normal coordinates, we find that

$$\begin{aligned} \Delta E_m &= \frac{1}{2} (\Omega_{ma}^2 - f_{maa}^2) Q_a^2 - f_{mab} Q_a Q_b + \frac{1}{2} (\Omega_{mb}^2 - f_{mbb}^2) Q_b^2, \\ E_{nm} &= E_0 + \frac{1}{2} (f_{naa}^2 - f_{maa}^2) Q_a^2 - 2f_{mab} Q_a Q_b + \frac{1}{2} (f_{nbb}^2 - f_{mbb}^2) Q_b^2, \\ E_0 &\equiv E_n(0) - E_m(0). \end{aligned} \quad (23)$$

It is convenient to introduce the parameters

$$\begin{aligned} A_i &\equiv \frac{1}{2} (\Omega_{mi}^2 - f_{mii}^2), \quad i = a, b, \\ C_i &\equiv \frac{1}{2} (f_{nii}^2 - f_{mii}^2) = 2A_i + \frac{1}{2} (\Omega_{ni}^2 - \Omega_{mi}^2), \quad i = a, b, \\ D &\equiv -f_{mab}. \end{aligned} \quad (24)$$

We then have

$$\begin{aligned} \Delta E_m &= A_a Q_a^2 + D Q_a Q_b + A_b Q_b^2, \\ E_{nm} &= E_0 + C_a Q_a^2 + 2D Q_a Q_b + C_b Q_b^2, \\ -\Delta E_{mn} &= E_{nm} - \Delta E_m = E_0 + (C_a - A_a) Q_a^2 + D Q_a Q_b \\ &\quad + (C_b - A_b) Q_b^2. \end{aligned} \quad (25)$$

Our assumptions and condition (15) require the expressions for ΔE_m and $-\Delta E_{mn}$ to be positive definite. This follows if

$$\begin{aligned} C_a &\geq A_a, \quad 4(C_a - A_a)(C_b - A_b) \geq D^2 \quad (\Rightarrow C_b \geq A_b), \\ A_a &\geq 0, \quad 4A_a A_b \geq D^2 \quad (\Rightarrow A_b \geq 0). \end{aligned} \quad (26)$$

Hence

$$D^2 \leq \min[4A_a A_b, 4(C_a - A_a)(C_b - A_b)]. \quad (27)$$

Substituting (25) into (14), (16), and (17), we get

$$\begin{aligned} U_{mn}^2 &= [E_0 + (C_a - A_a) Q_a^2 + D Q_a Q_b + (C_b - A_b) Q_b^2] (A_a Q_a^2 \\ &\quad + D Q_a Q_b + A_b Q_b^2), \\ \cos^2 \phi &= \frac{E_0 + (C_a - A_a) Q_a^2 + D Q_a Q_b + (C_b - A_b) Q_b^2}{E_0 + C_a Q_a^2 + 2D Q_a Q_b + C_b Q_b^2}, \\ \sin^2 \phi &= \frac{A_a Q_a^2 + D Q_a Q_b + A_b Q_b^2}{E_0 + C_a Q_a^2 + 2D Q_a Q_b + C_b Q_b^2}. \end{aligned} \quad (28)$$

To proceed further, we must define U_{mn} , $\cos \phi$, and $\sin \phi$. The simplest procedure is to write (Definition 1)

$$\begin{aligned} U_{mn} &= \{ [E_0 + (C_a - A_a) Q_a^2 + D Q_a Q_b + (C_b - A_b) Q_b^2] \\ &\quad \times [A_a Q_a^2 + D Q_a Q_b + A_b Q_b^2] \}^{1/2}, \\ \cos \phi &= \left[\frac{E_0 + (C_a - A_a) Q_a^2 + D Q_a Q_b + (C_b - A_b) Q_b^2}{E_0 + C_a Q_a^2 + 2D Q_a Q_b + C_b Q_b^2} \right]^{1/2}, \\ \sin \phi &= - \left(\frac{A_a Q_a^2 + D Q_a Q_b + A_b Q_b^2}{E_0 + C_a Q_a^2 + 2D Q_a Q_b + C_b Q_b^2} \right)^{1/2}, \\ &\quad -\pi/2 \leq \phi \leq 0. \end{aligned} \quad (29)$$

However, noting that

$$\Delta E_m = (A_a^{1/2} Q_a \pm A_b^{1/2} Q_b)^2 + [D \mp 2(A_a A_b)^{1/2}] Q_a Q_b, \quad (30)$$

we see that, if we replace the convention $\sqrt{x^2} = |x|$ with $\sqrt{x^2} = x$, we may also define U_{mn} and $\sin \phi$ as follows (Definition 2):

$$\begin{aligned} U_{mn} &= (A_a^{1/2} Q_a \pm A_b^{1/2} Q_b) \{ [E_0 + (C_a - A_a) Q_a^2 + D Q_a Q_b \\ &\quad + (C_b - A_b) Q_b^2] \{ 1 + [D \mp 2(A_a A_b)^{1/2}] Q_a Q_b / (A_a^{1/2} Q_a \\ &\quad \pm A_b^{1/2} Q_b)^2 \} \}^{1/2}, \end{aligned}$$

$$\begin{aligned} \sin \phi &= - (A_a^{1/2} Q_a \pm A_b^{1/2} Q_b) \\ &\quad \times \left\{ \frac{1 + [D \mp 2(A_a A_b)^{1/2}] Q_a Q_b / (A_a^{1/2} Q_a \pm A_b^{1/2} Q_b)^2}{E_0 + C_a Q_a^2 + 2D Q_a Q_b + C_b Q_b^2} \right\}^{1/2}, \\ &\quad -\pi/2 \leq \phi \leq \pi/2; \end{aligned} \quad (31)$$

$\cos \phi$ is defined as before.

The two definitions correspond to different, but overlapping phase conventions. Except for certain limits, they lead to different vibronic problems with different solutions. In the second case, U_{mn} has the same symmetry as Q_a and Q_b and therefore satisfies the symmetry requirement of Fulton and Gouterman,¹³ irrespective of the symmetry of the modes. This definition corresponds to the one adopted in earlier work.¹⁻⁴

IV. LIMITING BEHAVIOR OF THE MODEL

We will now examine the behavior of the exact wavefunctions in various limiting cases. In what follows, the weak adiabatic coupling limit is defined by $A_a = 0$ and $A_b = 0$, the strong adiabatic coupling limit by $A_a = C_a$ and $A_b = C_b$, the weak nonadiabatic coupling limit by $E_0 \rightarrow \infty$, and the strong nonadiabatic coupling limit by $E_0 = 0$.

In the general limit of weak adiabatic coupling ($A_a \rightarrow 0$ and $A_b \rightarrow 0$), $U_{mn} = 0$ and it follows from Eq. (6) that the exact eigenstates are the functions $\Phi_m^0 |v_m^0\rangle$ and $\Phi_n^0 |w_n^0\rangle$, which we shall call the CBO functions in line with current convention. In the general limit of weak nonadiabatic coupling ($E_0 \rightarrow \infty$), $\cos \phi = 1$, $\sin \phi = 0$, and the ABO functions, $\Phi_m |v_m\rangle$ and $\Phi_n |w_n\rangle$ reduce to the functions $\Phi_m^0 |v_m^0\rangle$ and $\Phi_n^0 |w_n^0\rangle$, respectively. For historical reasons we shall call the latter functions the Herzberg-Teller (HT) functions (rather than the CBO functions^{4a}). The HT functions are very good zeroth-order approximations to the exact eigenstates; the corresponding zeroth-order eigenvalues are

$$\begin{aligned} \epsilon_{mv} &= (v_a + \frac{1}{2}) \omega_{ma} + (v_b + \frac{1}{2}) \omega_{mb}, \\ \epsilon_{nw} &= (w_a + \frac{1}{2}) \omega_{na} + (w_b + \frac{1}{2}) \omega_{nb} + E_0, \end{aligned} \quad (32)$$

respectively. In the weak adiabatic coupling limit the HT functions reduce to the CBO functions. In the strong adiabatic coupling limit ($A_a = C_a$ and $A_b = C_b$), $\omega_{mi} = \Omega_{ni}$, $\omega_{ni} = \Omega_{mi}$, $i = a, b$ and the HT functions reduce to the functions $\Phi_m^0 |v_n^0\rangle$ and $\Phi_n^0 |w_m^0\rangle$. (Note that in these functions $|v_n^0\rangle$ and $|w_m^0\rangle$ have reversed the roles that they take in the CBO functions.)

These conclusions are independent of which definition we choose for U_{mn} and $\sin \phi$. However, Eqs. (29) and (31) do not exhibit the same limiting behavior in the strong nonadiabatic coupling limit ($E_0 \rightarrow 0$). As this limit is approached, U_{mn} , $\cos \phi$ and $\sin \phi$ all become rapidly varying functions of Q_a and Q_b and the ABO approximation breaks down. Both $\cos \phi$ and $\sin \phi$ are defined unambiguously in the limit $E_0 = 0$ so long as neither Q_a nor Q_b is zero. Consider Definition 1 and the case $Q_i = 0$, $i = a$ or b . Equations (29) reduce to

$$U_{mn} = \{A_j Q_j^2 [E_0 + (C_j - A_j) Q_j^2]\}^{1/2},$$

$$\cos \phi = \left[\frac{E_0 + (C_j - A_j) Q_j^2}{E_0 + C_j Q_j^2} \right]^{1/2}, \quad (33)$$

$$\sin \phi = - \left[\frac{A_j Q_j^2}{E_0 + C_j Q_j^2} \right]^{1/2},$$

$$Q_i = 0, \quad j \neq i.$$

At first sight, the values that $\cos \phi$ and $\sin \phi$ take in the limit $E_0 = Q_j = 0$ appear to depend on which limit, $E_0 = 0$ or $Q_j = 0$, is taken first. In the first case we obtain

$$U_{mn} = [A_j(C_j - A_j)]^{1/2} Q_j^2,$$

$$\cos \phi = (1 - A_j/C_j)^{1/2}, \quad (34)$$

$$\sin \phi = -(A_j/C_j)^{1/2},$$

$$E_0 = Q_i = 0, \quad j \neq i,$$

for all Q_j . Both $\cos \phi$ and $\sin \phi$ are thus independent of Q_j in the plane $Q_i = 0$, but are double valued at the point $E_0 = Q_a = Q_b = 0$ unless $A_a/C_a = A_b/C_b$. However, if there were just one oscillator, the ABO electronic wavefunctions would then be independent of the nuclear coordinate, there would be no nonadiabatic coupling, and the ABO vibronic functions would be exact eigenstates of the system. This conclusion is readily confirmed in the CBO approach using Eqs. (3), (6), (18), (19), and (34). A similar situation holds in the two-oscillator case when we take the limit $E_0 = 0$ of Eq. (29) before either of the limits $Q_a = 0$ and $Q_b = 0$ in the following circumstances (in which $A_a/C_a = A_b/C_b$):

(i) The weak adiabatic coupling limit ($A_a = A_b = 0$). As for $E_0 \neq 0$, $U_{mn} = 0$, $\cos \phi = 1$, $\sin \phi = 0$, and the ABO vibronic functions reduce to the CBO functions, the exact eigenstates of the system.

(ii) The special case where $\Omega_{na} = \Omega_{ma}$ and $\Omega_{nb} = \Omega_{mb}$, i. e., the CBO potentials are superposed on one another. Here $C_i = 2A_i$, $i = a, b$, $U_{mn} = A_a Q_a^2 + D Q_a Q_b + A_b Q_b^2$, $\cos \phi = 1/\sqrt{2}$, $\sin \phi = -1/\sqrt{2}$, and the ABO functions, $(\Phi_m^0 - \Phi_n^0 | v_m) / \sqrt{2}$ and $(\Phi_m^0 + \Phi_n^0 | w_n) / \sqrt{2}$, are exact eigenstates of the system.

(iii) The Renner-Teller case^{14,15} defined by $E_0 = 0$, $\Omega_{ma} = \Omega_{mb}$, $\Omega_{na} = \Omega_{nb}$, $\omega_{ma} = \omega_{mb}$, and $\omega_{na} = \omega_{nb}$. Here it follows that

$$A_a = A_b \equiv A, \quad C_a = C_b \equiv C, \quad D = 0,$$

$$U_{mn} = [A(C - A)]^{1/2} (Q_a^2 + Q_b^2), \quad \cos \phi = (1 - A/C)^{1/2},$$

$$\sin \phi = -(A/C)^{1/2},$$

and that the ABO functions

$$[(1 - A/C)^{1/2} \Phi_m^0 - (A/C)^{1/2} \Phi_n^0] | v_m)$$

and

$$[(A/C)^{1/2} \Phi_m^0 + (1 - A/C)^{1/2} \Phi_n^0] | w_n)$$

are exact eigenstates of the system. These functions are also exact eigenstates for the one-oscillator problem.

(iv) The strong adiabatic coupling limit ($A_a = C_a$ and $A_b = C_b$). Here $\omega_{mi} = \Omega_{ni}$, $\omega_{ni} = \Omega_{mi}$, $i = a, b$; $U_{mn} = 0$;

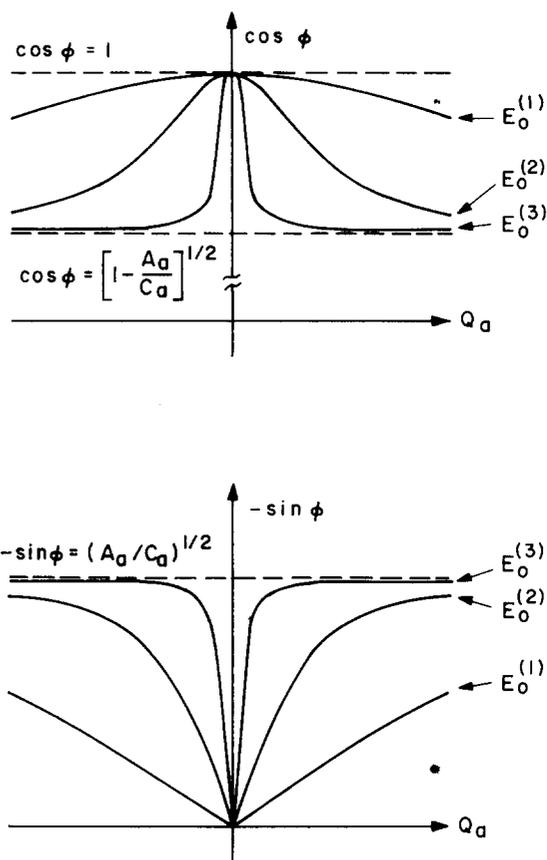


FIG. 1. Sketch of $-\sin \phi$ and $\cos \phi$ as a function of Q_a for $Q_b = 0$. $E_0^{(1)} > E_0^{(2)} > E_0^{(3)} \sim 0$.

$\cos \phi = 0$, $\sin \phi = -1$, and the ABO vibronic functions once again reduce to the CBO functions. These functions are exact eigenstates of the system. Note that these states are quite different from the exact eigenstates deduced above for the system in the strong adiabatic, weak nonadiabatic coupling limit.

As for the one-oscillator problem, our conclusions concerning the nature of the exact eigenstates for these special cases can all be readily verified using the CBO approach.

Now let us examine the situation had we taken the limit $Q_j = 0$ before the limit $E_0 = 0$. We would then have obtained

$$\cos \phi = \begin{cases} (1 - A_j/C_j)^{1/2} & E_0 = 0, \quad Q_j \neq 0, \\ 1 & \forall E_0; \quad Q_j = 0, \end{cases} \quad (35)$$

$$\sin \phi = \begin{cases} -(A_j/C_j)^{1/2} & E_0 = 0, \quad Q_j \neq 0, \\ 0 & \forall E_0; \quad Q_j = 0, \end{cases}$$

$$Q_i = 0, \quad j \neq i.$$

In this case $\cos \phi$ and $\sin \phi$ are not double valued at the point $E_0 = Q_a = Q_b = 0$, but have singularities there unless $A_a = A_b = 0$. The $\cos \phi$ and $-\sin \phi$ [Eqs. (33)] have been sketched as functions of Q_j for $Q_i = 0$ and various finite values of E_0 in Fig. 1. We thus see that if we were to require continuity as $E_0 \rightarrow 0$, we would take the limit $Q_j = 0$ before the limit $E_0 = 0$. However, at the point $E_0 = Q_a = Q_b = 0$, the states Φ_m^0 and Φ_n^0 are degenerate and

not coupled adiabatically. Hence any linear combination of them is an eigenfunction of the electronic Hamiltonian. This implies that any choice of ϕ is allowable. We can therefore remove the singularities in $\cos\phi$ and $\sin\phi$ at this point for one of the oscillators, a say, by writing

$$\begin{aligned} \cos\phi &= \begin{cases} (1 - A_a/C_a)^{1/2} & \forall Q_a; Q_b = 0, \\ (1 - A_b/C_b)^{1/2} & Q_a = 0; Q_b \neq 0, \end{cases} \\ \sin\phi &= \begin{cases} -(A_a/C_a)^{1/2} & \forall Q_a; Q_b = 0, \\ -(A_b/C_b)^{1/2} & Q_a = 0; Q_b \neq 0, \end{cases} \\ E_0 &= 0. \end{aligned} \quad (36)$$

Hence, if a were the only oscillator, the ABO vibronic functions would be exact eigenstates of the system as before when we took the limit $E_0 = 0$ before the limit $Q_j = 0$. Equations (34) and (36) become fully equivalent in the two-oscillator case when we remove the double valuedness from Eqs. (34) in the same way.

Now consider definition 2. As before, $\sin\phi$ is defined unambiguously in the limit $E_0 = 0$ provided neither Q_a nor Q_b is zero. In the case $Q_i = 0$, $i = a, b$, Eqs. (31) (upper sign) reduce to

$$\begin{aligned} U_{mn} &= A_j^{1/2} Q_j [E_0 + (C_j - A_j) Q_j^2]^{1/2}, \\ \sin\phi &= -A_j^{1/2} Q_j (E_0 + C_j Q_j^2)^{-1/2}, \\ Q_i &= 0, \quad j \neq i. \end{aligned} \quad (37)$$

This time, however, the value that $\sin\phi$ takes in the limit $E_0 = Q_j = 0$ depends on which limit, $E_0 = 0$ or $Q_j = 0$, is taken first. In the first case we recover Eqs. (34), provided that we continue to write $\sqrt{x^2} = x$. In the second case we obtain

$$\begin{aligned} U_{mn} &= [A_j(C_j - A_j)]^{1/2} Q_j |Q_j|, \\ \sin\phi &= \begin{cases} -\left(\frac{A_j}{C_j}\right)^{1/2} \frac{Q_j}{|Q_j|} & E_0 = 0, \quad Q_j \neq 0, \\ 0 & \forall E_0, \quad Q_j = 0, \end{cases} \\ Q_i &= 0, \quad j \neq i, \end{aligned} \quad (38)$$

as suggested by sketching U_{mn} and $\sin\phi$ for finite values of E_0 and looking to the requirements for continuity as $E_0 \rightarrow 0$. The $\sin\phi$ thus reduces to a step function rather than to a spike in the planes $Q_a = 0$ and $Q_b = 0$. As a result we cannot take advantage of the properties of Φ_m^0 and Φ_n^0 at the point $E_0 = Q_a = Q_b = 0$ to remove the singularities in both $\cos\phi$ and $\sin\phi$ at this point for one of the oscillators. In this case there is no longer a simple solution to the one-oscillator problem.⁴

V. COMPARISON WITH THE HT EXPANSION METHOD

Extension¹⁶⁻¹⁸ of the HT theory of vibronic coupling^{15,19} to the present problem where two modes are active implicitly assumes that the adiabatic coupling matrix element U_{mn} can be expanded as a power series in (Q_a, Q_b) . This, however, is not generally possible in the model treated here, even in the weak nonadiabatic coupling regime where E_0 is very large and HT theory is usually considered to be valid. In this regime we can take $[(C_a - A_a)Q_a^2 + DQ_aQ_b + (C_b - A_b)Q_b^2]/E_0$ as an expansion parameter and use the binomial expansion to ex-

pand the second factor in Eq. (31) (Definition 2) for U_{mn} as a power series in (Q_a, Q_b) . The third factor cannot be so expanded, but does reduce to unity when $D = \pm 2(A_a A_b)^{1/2}$. It is only in these special cases (and for Definition 2) that we can expand U_{mn} as a power series in (Q_a, Q_b) :

$$\begin{aligned} U_{mn} &= (A_a^{1/2} Q_a + A_b^{1/2} Q_b) E_0^{1/2} \{1 + [(C_a - A_a)Q_a^2 + 2(A_a A_b)^{1/2} Q_a Q_b \\ &\quad + (C_b - A_b)Q_b^2]/E_0\}^{1/2} \\ &= (A_a E_0)^{1/2} Q_a + (A_b E_0)^{1/2} Q_b + \frac{1}{2} E_0^{-1/2} [A_a^{1/2} (C_a - A_a) Q_a^3 \\ &\quad + A_b^{1/2} (C_b + A_b) Q_b^3 + A_a^{1/2} (C_b + A_b) Q_a Q_b^2 \\ &\quad + A_b^{1/2} (C_b - A_b) Q_b^3] + \dots, \\ D &= 2(A_a A_b)^{1/2}. \end{aligned} \quad (39)$$

This conclusion also follows from the fact that Definition 2 for U_{mn} is not analytic at the origin ($Q_a = Q_b = 0$) for nonzero E_0 except when $D = \pm 2(A_a A_b)^{1/2}$.

VI. SIMPLIFICATION TO ONE ACTIVE NORMAL MODE

It is instructive to examine the behavior of Eqs. (31) when the second mode is not vibronically active, i. e., when $A_b = D = 0$. Equations (31) reduce to

$$\begin{aligned} U_{mn} &= A_a^{1/2} Q_a [E_0 + (C_a - A_a) Q_a^2 + C_b Q_b^2]^{1/2}, \\ \cos\phi &= \{[E_0 + (C_a - A_a) Q_a^2 + C_b Q_b^2]/(E_0 + C_a Q_a^2 \\ &\quad + C_b Q_b^2)\}^{1/2}, \\ \sin\phi &= -A_a^{1/2} Q_a / (E_0 + C_a Q_a^2 + C_b Q_b^2)^{1/2}. \end{aligned} \quad (40)$$

These equations should be compared to the corresponding equations [Ref. 4(a), Eqs. (32)] for the model where all modes except a single, active, undisplaced normal mode are neglected. Equations (40) show that if a molecule possesses other undisplaced normal modes which are not vibronically active, these modes nevertheless contribute to the vibronic coupling to the extent that their frequencies are different in the two states. We also see that when Definition 2 is adopted and only one mode is active, U_{mn} is generally analytic at the origin and it is generally possible to expand U_{mn} as a power series in the normal coordinates in the weak nonadiabatic coupling regime.

VII. CONCLUDING REMARKS

The model determines not the adiabatic coupling matrix element U_{mn} but only its square unambiguously. Two different definitions of U_{mn} are possible. They correspond to different phase conventions and generally yield different vibronic problems with different solutions. If the active modes are nontotally symmetric, only one definition satisfies a symmetry requirement.¹³ Only this definition can be linked to the conventional HT treatment of the weak nonadiabatic coupling regime. However, when two modes are active, both definitions of U_{mn} generally have a singularity at the origin. For this reason, it has been argued that in this case neither definition is physically acceptable, but that this difficulty can be surmounted by making U_{mn} complex. We do not see a way to justify the complexity of U_{mn} from some more basic principle since the molecular

Hamiltonian is real and therefore the electronic wavefunctions as well as the normal coordinates can always be chosen to be real. We prefer to conclude that in the model treated here analyticity generally rules out one definition of U_{mn} and places a constraint on the Duschinsky parameter D in the other.

Note added in proof: The assumption that the Duschinsky effect arises solely from adiabatic vibronic coupling is unnecessarily restrictive in the two-state model treated here. For example, this assumption and the constraint imposed by analyticity on the Duschinsky parameter rule out the strong adiabatic coupling limit as a possible limit. This limit becomes accessible when the assumption is removed, and, as we shall show in a future publication, the analysis proceeds in a similar and straightforward manner.

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