Theoretical Studies of Intramolecular Dynamics and Energy Redistribution

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Gregory Alan Voth

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Abstract

By virtue of various theoretical techniques, the fundamental mechanisms responsible for intramolecular vibrational energy redistribution (IVR) in isolated molecules are studied in this thesis. One such mechanism, the nonlinear resonance, is examined in some detail for several systems. In particular, nonlinear stretch–bend resonances in a series of isotopically substituted methanes are predicted to have a large effect on the spectral properties of those molecules. By using a semiclassical analysis, the general properties of stretch–bend interactions are further examined, and the quantum mechanical manifestations of classical resonances are characterized in detail. A related problem, the role of classical resonances in the multiphoton absorption process by an anharmonic oscillator, is also analyzed.

In addition, it is demonstrated that the quantum mechanical coupled equations which describe the fundamental IVR process may be simplified. This simplification is achieved by virtue of an "adiabatic" approximation for those state amplitudes which are sufficiently off-resonant with (i.e., different in energy from) the experimentally prepared quantum state. The approximate coupled equations are based on an effective Hamiltonian which contains renormalized self–energies and interactions between the zeroth–order quantum states. This formalism may be applied to describe the quasidissipative flow of probability out of an initially prepared vibrational state in a large molecule, and it may also be adapted to treat multiphoton absorption processes in polyatomic molecules when one or more lasers are present.

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Introduction

The research presented in this dissertation is centered around providing a theoretical description of the nonlinear interactions and energy exchange mechanisms between vibrational modes in polyatomic molecules. Understanding and characterizing these mechanisms is of particular importance to the so-called "laser selective" chemistry.[1] That is, if the selective laser excitation and localization of energy in specific vibrational degrees of freedom of a molecule is to be achieved, it is critical that the mechanisms of intramolecular vibrational energy redistribution (IVR) be explored and understood. At the fundamental level, highly excited and nonlinearly coupled oscillators exhibit extremely rich quantum and classical mechanics and thereby pose many interesting questions to the theoretician.

In the past ten years or so, it has become increasingly clear that vibrational resonances in both classical[2] and quantum[3] mechanics are of paramount importance to the IVR phenomenon.[3–8] A substantial portion of this dissertation is therefore devoted to characterizing the effect of resonances on the vibrational dynamics of molecules: Classical, semiclassical, and quantum mechanical techniques are utilized to treat this problem. At the quantum mechanical level in particular, the effects of resonant versus off-resonant interactions are strikingly different, and this situation allows for a simplification of the intramolecular dynamics problem. In addition, a molecular system interacting with a radiation field may be treated in a similar way since the total Hamiltonian in this case is isomorphic with Hamiltonians which give rise to IVR in isolated molecules (i.e., the field simply contributes additional coupled degrees of freedom).

In Chapter 1, a theoretical analysis of the vibrational states of the isotopically substituted methanes CHD_3, CHT_3, and CH_3D is presented.[4] This work was motivated by the high C-H overtone spectrum of CHD_3 obtained experimentally by Perry *et al.*[5] The C-H overtone spectrum consists of simple two-level Fermi resonances which show very selective and strong zeroth-order state mixing between the "pure" overtone state $|v, 0, 0, ..., 0\rangle$ ($v = 5, 6$) and a single 1:2 resonant combination state $|v-1, 2, 0, ..., 0\rangle$, having two quanta in a bending mode. This severely restricted state mixing is quite interesting since the density of zeroth-order vibrational states with the appropriate symmetry to interact with the pure C-H overtone state is approximately 35 states per cm^{-1}. The observed state mixing behavior thereby appears to be quite "non-statistical" and hence due to a specific and selective resonant coupling mechanism.

A theoretical explanation for the selective coupling behavior observed in CHD_3 is proposed in Chapter 1 which is based on a curvilinear coordinate treatment of the quantum mechanical vibrational state problem.[4,6,7] The analysis in that chapter uncovers selective and strong dynamical coupling between the C-H stretch and a particular normal mode involving H-C-D bending motions. The experimental results on CHD_3 are fit quite well by the theoretical model, and similar behavior is predicted for the C-H stretching states of CHT_3. In addition, the possible origins of the more extensive state mixing observed[5] in CH_3D are discussed. As a whole, the work in Chapter 1 serves to further advance the understanding of stretch-bend interactions and the breakdown of localized excitations in molecules.[3–8] In general, it is found that a specific and identifiable dynamical coupling mechanism is much more important for determining the state mixing in CHD_3 than is the total density of vibrational states.

The quantum mechanical study in Chapter 1 of the resonant stretch-bend interactions in CHD_3, as well as the multitude of similar resonances observed experimentally in other molecules (see, e.g., references cited in Ref. 8), provides motivation for the development of a semiclassical theory of the 1:2 stretch-bend Fermi resonance.[8] In Chapter 2, three semiclassical treatments are used to characterize a model having a Morse oscillator stretching mode coupled nonlinearly to a harmonic bending mode. These three treatments include a diagonalization of a semiclassical Hamiltonian matrix, a two-state solution of an approximate Schrödinger equation obtained from a classically averaged Hamiltonian in action-angle variables, and a uniform semiclassical solution.[9] The results of the semiclassical calculations give good agreement with the quantum results and are, in general, considerably easier to obtain. By virtue of the uniform semiclassical analysis, analytic formulas are also derived for the eigenvalue splittings and the overlaps of the wavefunctions with the zeroth-order basis functions. The eigenvalue splittings are measured experimentally in a Fermi resonance doublet, while the overlaps are important, for instance, in determining the relative intensities of the spectral peaks within a doublet (see, e.g., Refs. 4 and 5). These analytic formulas, in conjunction with the corresponding classical resonance analysis,[2,3,8,9] are found to be valuable in relating molecular parameters, such as the perturbation strength and the stretching mode anharmonicity, to the observed quantum behavior.

In Chapter 3, an examination of the effect of small classical resonances on the quantum mechanics of nonlinearly coupled oscillator systems is presented.[10] It is well known that there are many classical resonances in such systems, but most resonances occupy only a small volume in the energetically allowed phase space (see, e.g., Ref. 2). It is therefore examined how the quantum mechanics of the coupled oscillator system is affected as the width of a classical resonance is increased in classical phase space (specifically, in action-angle space). In particular, in Chapter 3 an analysis of the eigenvalue spectrum and basis function mixing of a resonant oscillator system is performed. By using a suitably modified uniform semiclassical treatment for an $n : m$ resonance,[8–10] it can be demonstrated analytically that the quantum mechanics not only "smooths over" small resonances with widths less than $n\hbar$, but also that there is a rather abrupt change as the resonance width increases past $n\hbar$.[10] This result represents an explicit confirmation of some ideas proposed by other authors.[3,9,11]

Another interesting and related physical problem is the vibrational excitation of an anharmonic oscillator by radiation.[12] In Chapter 4, it is demonstrated that a uniform semiclassical analysis can be performed using a "dressed state" picture.[12,13] Consequently, some interesting and useful results regarding the interrelationship of the classical and quantum mechanics of the oscillator-field system are obtained. In particular, the uniform semiclassical analysis yields resonance frequencies (i.e., field frequencies where the maximum absorption occurs) which are essentially exact. Moreover, the quantum one– and two–photon Rabi frequencies are related via the semiclassical analysis to the Fourier components of the dipole moment function evaluated in a special way.[12] By using analytic means, or by computing classical trajectories with the appropriate initial conditions (as determined by the semiclassical theory), these Fourier components are usually much easier to obtain than the corresponding quantum matrix elements.[12,14] The semiclassically calculated Rabi frequencies (and hence absorption intensities) are also found to be in excellent agreement with the exact quantum results. The uniform semiclassical analysis provides a justification of sorts for the use of Fourier components of the dipole moment in the calculation of one-photon absorption intensities.[14] Perhaps most significantly, the appropriate Fourier components needed to calculate two-photon absorption intensities semiclassically are derived for the first time.

A complete quantum mechanical description of IVR processes in polyatomic molecules is quite complicated and requires considerable theoretical effort. In Chapter 5, an approximate method is developed for calculating the quantum dynamics of initially prepared nonstationary states in polyatomic molecules.[15] This method is based on the integration of a set of "adiabatically reduced" coupled equations for the time-dependent amplitudes of a set of zeroth-order basis functions. The derivation of these approximate coupled equations relies on a partitioning of the basis states into two subsets: One subset consists of those zeroth-order states that are resonant with and/or strongly coupled to the initial state, while the other subset is taken as being those states that are off-resonant with and weakly coupled to the initial state. In the proper "rotating frame" representation,[15] the probability of the evolving nonstationary state is found to not contain any appreciable amplitude from the off-resonant, weakly coupled subset of basis states (on the relevant time scale of interest[15]). This interesting property of resonant versus off-resonant zeroth-order state amplitudes allows one to accurately calculate the dynamics using an effective Hamiltonian matrix. Since this effective Hamiltonian has the same dimension as the resonant and/or strongly coupled subspace, the method of Chapter 5 may reduce considerably the number of coupled equations that must be integrated.[15] It is also found that the off-resonant, weakly coupled states can have a suprisingly important influence on the dynamics of the initial state.[15,16] The method of Chapter 5 is extended to treat non-orthogonal basis sets in Appendix I, and an iterative method for determining more accurate effective Hamiltonians[17] is discussed in Appendix II.

Based on the theory of Chapter 5, approximate coupled equations are derived in Chapter 6 which describe the interaction of a molecular system with one or more continuous wave lasers.[18] This problem is of particular interest because there are numerous multilaser, "pump–probe" experiments which are capable of probing various aspects of molecular excitation and energy redistribution processes (see, e.g., references cited in Ref. 18). The formulation of the approximate coupled equations is based on a time-independent dressed state Hamiltonian[13] which includes the radiation field as a set of harmonic oscillators coupled to the molecule. By virtue of the adiabatic approximation implemented in Chapter 5, an effective dressed state Hamiltonian may be formulated for a set of resonant, or near resonant, dressed molecular states. This effective Hamiltonian contains the generalized Rabi frequencies and AC Stark shifts[13] to all orders in the perturbation strength. It is also demonstrated in Chapter 6 that an expansion of the effective Hamiltonian in terms of the perturbation strength allows for simplified calculations of the relevant effective dressed state matrix elements.

In the final Chapter of this thesis, an approximate theory is developed which describes the exponential decay of an experimentally prepared state in a large polyatomic molecule undergoing IVR. This behavior, which thus far has been observed in a majority of experimental studies on IVR,[19] is also predicted by the well known radiationless transitions theory.[20] The derivation of exponential decay behavior in isolated molecules given in Chapter 7 does not rely on a resolvent operator approach (as does the usual theory[20]). Instead, it relies on the adiabatic approximation[15,21] given in Chapter 5 and is based on somewhat different physical intuition than that employed in previous IVR theories.[20] The present theory also gives an expression for the exponential decay rate which differs from the usual Golden Rule rate expression.[20,22] In fact, the theory allows for bottlenecks in the intramolecular decay rate which are not directly predicted by the usual Golden Rule–type theories. Furthermore, the decay rate derived in Chapter 7 is written in terms of an "intramolecular width" parameter which is related to the number of intramolecular "bath" states participating in the IVR. The possible experimental determination of this parameter is discussed in Chapter 7. The theory presented in Chapter 7 offers an alternative approach to IVR problems in large molecules, and it yields results that differ somewhat from previous theories.[20]

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Chapter 1: The Highly Excited C–H Stretching States of CHD_3, CHT_3, and CH_3D

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The highly excited C–H stretching states of CHD_3, CHT_3, and CH_3D

Gregory A. Voth, R. A. Marcus, and A. H. Zewail[a]
Arthur Amos Noyes Laboratory of Chemical Physics,[b] *California Institute of Technology, Pasadena, California 91125*

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Unlike many other molecules having local modes, the highly excited C–H stretching states of CHD_3 show well resolved experimental spectra and simple Fermi resonance behavior. In this paper the local mode features in this prototype molecule are examined using a curvilinear coordinate approach. Theory and experiment are used to identify the vibrational state coupling. Both kinetic and potential terms are employed in order to characterize the coupling of the C–H stretch to various other vibrational modes, notably those including D–C–H bending. Predictions are also made for CHT_3 and the role of dynamical coupling on the vibrational states of CH_3D explored. Implications of these findings for mode-specific and other couplings are discussed.

I. INTRODUCTION

The highly excited vibrational states of C–H stretching modes in many molecules have been the subject of considerable interest in recent years.[1] The local mode description[1] has been used to treat these C–H oscillator systems and has had considerable success in doing so. Of particular relevance to the present paper are the experimental results of Perry *et al.*[2] which, for CHD_3, indicate the specific coupling of the C–H stretch to a bending normal mode. For other molecules, this type of coupling has been discussed previously by several authors.[3] The local mode description has recently been extended to handle such couplings,[4] using curvilinear coordinate systems.[5–7] These coordinate systems present a natural way of treating molecular vibrations and provide physical insight into the coupling mechanisms between vibrational states. To such vibrational couplings have been attributed the calculated breakdown of localized C–H stretching vibrations,[1–4,8,9] the observed linewidths of aromatic (~ 100–$200\ cm^{-1}$) and aliphatic ($\sim 20\ cm^{-1}$) local mode transitions,[4,9–11] and the postulated onset of extensive intramolecular relaxation.[4,9,12,13]

With these aspects in mind, the highly excited C–H stretching vibrations in CHD_3, CHT_3, and CH_3D are studied in the present paper. Recent experimental evidence[2] has suggested that in CHD_3 there are extremely narrow linewidths ($< 1\ cm^{-1}$) and very limited state mixing at a high level of C–H vibrational excitation. An analysis of this spectral data was performed in terms of a simple Fermi resonance between the C–H stretch and a bending normal mode.[2] In the present paper, using a curvilinear coordinate treatment, a theoretical analysis is presented for the vibrational eigenstate problem which includes kinetic and potential energy coupling terms. An explanation for the observed spectrum of CHD_3 is proposed and, in turn, predictions are made for the high overtone C–H stretching spectrum of CHT_3. In addition, the difference between the relatively simple CHD_3 spectrum and the highly congested spectrum[2] for CH_3D is discussed in terms of the different dynamical vibrational mode couplings in these two molecular species.

An outline of the present paper is as follows: A brief review of the relevant experimental data[2] is given in Sec. II. In Sec. III, the curvilinear coordinate formalism is applied to CHD_3 and CHT_3, and couplings between the C–H stretching vibration and other normal modes of these molecules are described. In Sec. IV, the dynamical coupling of the C–H stretching states to bending normal modes in CH_3D is examined. Concluding remarks appear in Sec. V.

II. CHD_3 AND CH_3D: SUMMARY OF THE EXPERIMENTAL RESULTS

Recently, using photoacoustic spectroscopy, the high C–H overtones of methane and of its isotopic derivatives CH_3D, CH_2D_2, and CHD_3 have been studied by Perry *et al.*[2] Some results obtained for CHD_3 and CH_3D, both of which have very different spectra, can be summarized as follows:

The CHD_3 overtones corresponding in zeroth order to five, six, and seven quanta in the C–H stretch have remarkable simplicity.[2] For $v = 5$ and $v = 6$, the spectra have a simple two level Fermi resonance structure (e.g., Fig. 1 for $v = 6$). For $v = 7$, the spectrum is more congested, but it appears to be essentially a three level Fermi resonance.[2] When the quantity $\Delta E_{ov}/v$ is plotted vs v, ΔE_{ov} being the excitation of the C–H overtone in excess of the zero-point

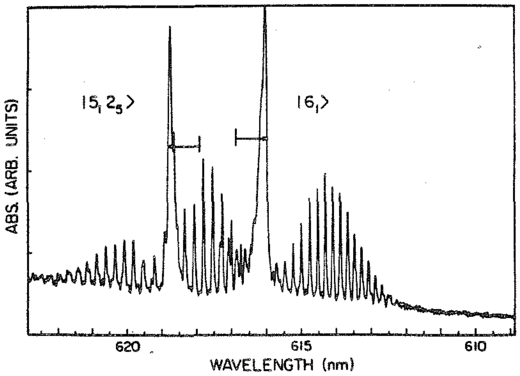

FIG. 1. Experimental $v = 6$ C–H overtone spectrum for CHD_3 (taken from Ref. 2).

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[a] Camille and Henry Dreyfus Teacher–Scholar.

[b] Contribution no. 7057.

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energy, one obtains[2] an excellent Birge–Sponer line,[1] but with deviations in the $v = 5$, 6, and 7 regions where these Fermi resonances become important. Also, the CHD_3 spectra clearly show the P-, Q-, and R-like branches expected for a symmetric top molecule with parallel type vibrational/rotational transitions.[14] Considering the size of the molecule involved and the density of vibrational states, the simplicity of these spectra is quite interesting.

The spectrum at $v = 6$ for CH_3D (Fig. 2), on the other hand, is strikingly different from that for CHD_3 at the same level of excitation. This transition has a spectral envelope with a width at half-maximum of approximately 150 cm^{-1}. The excitation of the C–H stretching states in this molecule corresponds to both parallel and perpendicular type vibrational/rotational transitions[14] and therefore has more complicated selection rules than that for CHD_3. The level structure underneath the spectral envelope at $v = 6$ is expected to be quite complicated for this and other reasons.

Several compelling questions arise from the experimental data on these two molecules. For instance, why do the $v = 5$ and $v = 6$ transitions in CHD_3 have such a remarkably simple level structure? A harmonic state count[15] yields a density of A_1 symmetry vibrational states of about 35 states/cm^{-1} at the energy of the $v = 6$ transition. There are, thereby, many vibrational states with the proper symmetry to couple with the C–H stretch (which has A_1 symmetry) via Fermi resonance interactions. The behavior actually observed is highly nonstatistical, however, since very few states are significantly coupled. In addition, the observed CHD_3 spectrum at $v = 6$ is very different from the corresponding CH_3D spectrum, and a knowledge of the mechanism that causes the high degree of congestion in the latter is of particular interest.

III. THEORY FOR CHD_3, CHT_3

A. Curvilinear formalism: qualitative analysis for CHD_3

The general expression for the classical vibrational Hamiltonian in curvilinear interval valence displacement coordinates[5,7] is

$$H(\mathbf{x},\mathbf{p}) = \frac{1}{2}\sum_{ij}^{N} G_{ij}(\mathbf{x}) p_i\, p_j + V(\mathbf{x}), \tag{3.1}$$

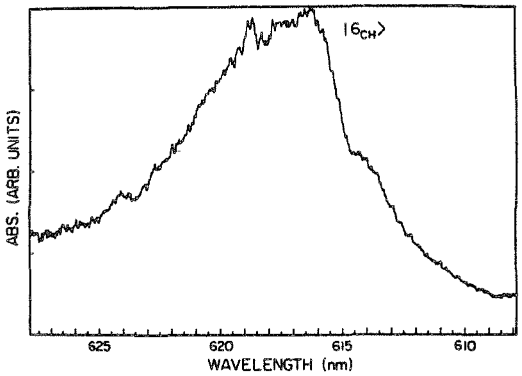

FIG. 2. Experimental $v = 6$ C–H overtone spectrum for CH_3D (taken from Ref. 2).

where the $G_{ij}(\mathbf{x})$ are the Wilson G-matrix elements[16] which, in the curvilinear coordinate approach, are dynamical functions of the curvilinear displacement coordinates $\mathbf{x}$, and $V(\mathbf{x})$ is some Born–Oppenheimer potential energy surface for the molecular vibrations. In the rectilinear coordinate approach,[6,7,16] the G-matrix elements are treated as constants and the potential $V(\mathbf{x})$ contains extra contributions to compensate for this restriction.

For any particular molecular vibrational problem, one must usually make some approximation for the potential energy function $V(\mathbf{x})$, since this quantity is rarely known accurately. For the analysis of the vibrations in CHD_3, it will first be assumed that the single C–H stretching mode may be described by a Morse oscillator potential energy function[17] and that the remaining vibrations are adequately described by harmonic (quadratic) potentials. The coupling between modes is then qualitatively described by the dynamical dependence of the G-matrix terms in Eq. (3.1). It will be shown later in this paper that, in addition to these G-matrix couplings, higher order (i.e., higher than quadratic) curvilinear potential energy terms are needed in order to explain more quantitatively the observed spectra of CHD_3.

The corresponding quantum mechanical Hamiltonian to Eq. (3.1) may be defined in effect by substituting the momentum operator $\hat{p}_i = (\hbar/i)\partial/\partial x_i$ for p_i in Eq. (3.1). This step is not rigorously exact, but it is an excellent approximation for the limit of relatively small amplitude molecular vibrations. A discussion of this appears in Ref. 7.

The Hamiltonian [Eq. (3.1)] for CHD_3 may be straightforwardly transformed into

$$H = H_0 + V', \tag{3.2}$$

where

$$H_0 = H_m(r,p) + \frac{1}{2}\sum_{i=2}^{9} (P_i^2 + \omega_i^2 Q_i^2) \tag{3.3a}$$

and the perturbation V' is given by

$$V' = \frac{1}{2}\sum_{i=2}^{9} [\widetilde{G}_{ii}(\mathbf{x}) - 1] P_i^2 + \frac{1}{2}\sum_{i=2}^{9}\sum_{j=2}^{9} \widetilde{G}_{ij}(\mathbf{x}) P_i P_j. \tag{3.3b}$$

In these equations, $H_m(r,p)$ is the Morse oscillator Hamiltonian[17,18] for the C–H stretch with displacement coordinate r and conjugate momentum p; the $\frac{1}{2}(P_i^2 + \omega_i^2 Q_i^2)$ are the harmonic oscillator Hamiltonians for the eight curvilinear normal mode vibrations in CHD_3. Also, the $\widetilde{G}_{ij}$'s are the G-matrix terms transformed via a normal mode transformation[16]

$$\widetilde{G}_{ij}(\mathbf{x}) = \sum_{l=1}^{9}\sum_{m=1}^{9} L_{il}^{-1} \overline{G}_{lm}(\mathbf{x}) L_{jm}^{-1}, \tag{3.4}$$

where the $\overline{G}_{lm}$'s are the G-matrix terms transformed via a symmetry coordinate transformation[16]

$$\overline{G}_{lm}(\mathbf{x}) = \sum_{i=1}^{9}\sum_{j=1}^{9} U_{li} G_{ij}(\mathbf{x}) U_{mj}. \tag{3.5}$$

The coefficients U_{li} and L_{il}^{-1}, etc. in these equations are the elements of the matrices $\mathbf{U}$ and $\mathbf{L}^{-1}$ that define the transformations

$$\mathbf{q} = \mathbf{U}\mathbf{x}, \quad \mathbf{Q} = \mathbf{L}^{-1}\mathbf{q} \tag{3.6}$$

TABLE I. Internal symmetry coordinates for $CHD_3(CHT_3)$.[a]

$$q_1^{A_1} = r$$
$$q_2^{A_1} = \frac{1}{\sqrt{3}}(r_1 + r_2 + r_3)$$
$$q_3^{A_1} = \frac{1}{\sqrt{6}}(\alpha_1 + \alpha_2 + \alpha_3 - \beta_1 - \beta_2 - \beta_3)$$
$$q_4^{E_a} = \frac{1}{\sqrt{6}}(2r_1 - r_2 - r_3)$$
$$q_5^{E_a} = \frac{1}{\sqrt{6}}(2\alpha_1 - \alpha_2 - \alpha_3)$$
$$q_6^{E_a} = \frac{1}{\sqrt{6}}(2\beta_1 - \beta_2 - \beta_3)$$
$$q_7^{E_b} = \frac{1}{\sqrt{2}}(r_2 - r_3)$$
$$q_8^{E_b} = \frac{1}{\sqrt{2}}(\alpha_2 - \alpha_3)$$
$$q_9^{E_b} = \frac{1}{\sqrt{2}}(\beta_2 - \beta_3)$$

[a] r is defined here to be the C–H bond displacement coordinate, r_i the C–D(T) bond displacement coordinates, α_i the D–C–D(T–C–T) angles opposite r_i, and β_i the H–C–D(T) angles that include the r_i bond.

to curvilinear symmetry coordinates **q** and normal coordinates **Q**, respectively. The symmetry coordinates for CHD_3 are given in Table I while the $\mathbf{L}^{-1}$ matrix is the standard normal mode matrix calculated by the methods of Ref. 16 with all internal coordinates in the G-matrix terms evaluated at their equilibrium value. In order that the C–H coordinate r be treated as a local mode coordinate, the transformation coefficient L_{11}^{-1}, where coordinate 1 is defined as r, is set equal to unity and the coefficients L_{1i}^{-1}, L_{i1}^{-1} are set equal to zero for $i \neq 1$. This approximation does not diagonalize all the off-diagonal quadratic perturbation terms, leaving terms proportional to rQ_i and pP_i. However, the present calculations show these to be very small and they may be safely neglected. This approximation has been known since the early days of normal mode theory[8] and is a good one due to the high frequency of the C–H stretching vibrations; they are essentially adiabatic from the rest of the normal modes of a molecule when coupling terms of quadratic order only are treated. Thus, to quadratic order, the C–H stretching vibrations may be treated separately rather than included in the zeroth order normal mode analysis.

A principal approximation of this paper is to treat the dynamical G-matrix elements in Eqs. (3.1) and (3.3b) as functions of the C–H displacement coordinate r only. This approximation is assumed to be valid because, for the states of experimental interest in CHD_3,[2] the C–H stretching local mode is the only vibrational mode with appreciable amplitude. The other internal coordinates of the molecule are taken to be at their equilibrium values when evaluating these G-matrix elements. Such an approximation simplifies the treatment of the vibrations in CHD_3 and allows for a straightforward physical interpretation of the coupling of the C–H stretch to various normal modes.

The normal modes with possible coupling to the C–H stretching local mode in CHD_3 consist of two nondegenerate A_1 symmetry modes with harmonic frequencies $\omega_2 = 2185$ cm^{-1} and $\omega_3 = 1042$ cm^{-1} and three doubly degenerate E symmetry modes with frequencies $\omega_4 = 2337$ cm^{-1}, $\omega_5 = 1335$ cm^{-1}, and $\omega_6 = 1070$ cm^{-1}. These modes couple with varying degrees to the C–H stretching local mode as a result of the G-matrix terms in Eq. (3.3b).

Since a full matrix diagonalization of the Hamiltonian [Eq. (3.2)] in a suitable basis is impractical due to the large number of vibrational degrees of freedom in this molecule, a simpler, more transparent approach was taken to determine which modes couple strongly to the C–H stretch. This approach was to determine the strength of the coupling of the "pure" C–H stretching states $|v,0,...,0\rangle$ to resonant "doorway states"[4,9] such as $|v-1,v_2,v_3,...,v_9\rangle$. The degree to which two such zeroth order states mix was determined by simple diagonalizations of 2×2 matrices of the Hamiltonian [Eq. (3.2)] represented in this basis. For the nondegenerate A_1 symmetry normal mode states, a nondegenerate harmonic oscillator basis[19] was used, while, for the doubly degenerate E symmetry normal mode states, a doubly degenerate harmonic oscillator basis[19] was employed. The C–H stretching local mode basis states were taken to be Morse oscillator eigenfunctions.[17,18] The Morse oscillator matrix elements of the G-matrix coupling terms [Eq. (3.3b)] were calculated by numerical quadrature, rather than using the expansion employed in Refs. 4(a) and 7 of these terms in a Taylor series. It was found that this numerical integration avoided problems due to the slow convergence of the series expansion terms. Details of this integration procedure are described in Appendix A.

B. Vibrational analysis for CHD_3 and CHT_3

Two key features of the vibrational state mixing as described by pure G-matrix coupling are first summarized. They were investigated and found to simplify the analysis considerably:

(1) The two A_1 symmetry normal modes are rigorously decoupled from the C–H stretch because the G-matrix terms in Eq. (3.4) for these modes are independent of the C–H displacement coordinate r. While this behavior is not necessarily evident from Eq. (3.4), it may be shown by demonstrating the independence of the A_1 symmetry normal mode frequencies from the C–H bond length using standard normal mode techniques.[16]

(2) It is found in the calculations that the doubly degenerate E symmetry modes with harmonic frequencies $\omega_4 = 2337$ cm^{-1} and $\omega_6 = 1070$ cm^{-1} have extremely weak coupling to the C–H stretch via G-matrix terms. They also have no low order resonance condition with this mode for $v = 1$–6. Accordingly, coupling to these modes corresponds to effects of second order. For example, the states $|6\rangle|0,0\rangle_i$ and $|5\rangle|2,0\rangle_i$ (both of A_1 symmetry), where a doubly degenerate harmonic oscillator basis $|n,l\rangle_i$ is used for the particular E symmetry normal mode i, are coupled. However, the ratio of the matrix element that couples these two states (with $\hbar = 1$)

$$V_{12} = \omega_i \langle v-1|\tilde{G}_{i,i}(r)|v\rangle/2 \qquad (3.7)$$

to the energy difference between them is straightforwardly calculated for $v = 6$ to be 0.002 for coupling to E mode 4 and 0.019 for coupling to E mode 6. Thus, these vibrational modes only weakly couple by G-matrix terms to the pure C–

H stretch and may be ignored in the present analysis.

The remaining doubly degenerate E symmetry normal mode is found in the calculations to be strongly coupled to the C–H stretch, with an average off-diagonal matrix element of the $\widetilde{G}_{i,i}$ coupling term of $\sim 100\ \text{cm}^{-1}$ in the range $v = 3$–6. Moreover, the harmonic frequency ω_5 of this normal mode satisfies a 1:2 nonlinear resonance condition with the C–H vibrational frequency at the $v = 5$ and 6 level of excitation. As a result, the states $|v\rangle|0,0\rangle$ and $|v-1\rangle|2,0\rangle$ in this energy regime are approximately degenerate in zeroth order. This bending mode involves the E symmetry deformation of the H–C–D angles and it thus interacts strongly with the C–H stretch via the curvilinear G-matrix coupling effect. The physical origin for this effect is due to the effective mass for the H–C–D bend, as described by the inverse of the G-matrix term, being increased when the local mode is excited and the C–H bond is lengthened. No other normal modes of the molecule satisfy both a low order resonance condition and the condition that the H–C–D bend be included in their motion.

One further possibility to be considered is the coupling of the pure C–H stretching state to A_1 symmetry combination states by terms like $\widetilde{G}_{ij}(r)P_iP_j$ in Eq. (3.3b). These combination states have the form $|v-1,\ldots,v_i,v_j,\ldots\rangle$, where the normal mode quantum numbers other than v_i and v_j are zero. The combination state having $v_5 = 1$, $v_6 = 1$ is the only state found to have both an approximate zeroth order degeneracy and a nonnegligible interaction with the pure state $|v,0,0,\ldots\rangle$. In the calculations, it becomes important only for a level of excitation in the C–H oscillator corresponding to at least seven quanta in zeroth order. For six quanta in the C–H stretch, this combination state is sufficiently detuned from the C–H stretching state energy so as to have only a small second order effect on the splitting ($< 5\ \text{cm}^{-1}$) and the relative intensity ($< 3\%$) of the Fermi resonance found in this spectral region.

The results of the above analysis indicate that the C–H stretch selectively interacts with the doubly degenerate bending normal mode with harmonic frequency $\omega_5 = 1335\ \text{cm}^{-1}$, thereby simplifying the quantitative treatment of the C–H stretching states (i.e., only three degrees of freedom need be considered). However, since the magnitude of the pure curvilinear G-matrix interaction ($\sim 100\ \text{cm}^{-1}$) is larger than what is observed experimentally ($\sim 35\ \text{cm}^{-1}$), the potential energy is postulated to have an important cancellation effect within these matrix elements. Because the available high order force constants[20(a)] relevant to the Fermi resonances at $v = 5$ and 6 were found to be inadequate, only first order effects (in terms of degenerate perturbation theory) were treated. As will be shown later for CHD$_3$, this first order treatment is useful in determining both the energies and the relative intensities of the pure C–H stretching mode states and of combination levels involving the C–H stretch and the H–C–D bending mode.

The Hamiltonian for the coupled C–H stretch and doubly degenerate bending mode is

$$H = H_0 + V' \tag{3.8}$$

with

$$H_0 = H_m(r,p) + \tfrac{1}{2}[(P_1^2 + P_2^2) + \omega_5^2(Q_1^2 + Q_2^2)] \tag{3.9}$$

and

$$V' = \tfrac{1}{2}[\widetilde{G}_{5,5}(r) - 1](P_1^2 + P_2^2) + \frac{F_3}{2} r(Q_1^2 + Q_2^2) + \frac{F_4}{4} r^2(Q_1^2 + Q_2^2), \tag{3.10}$$

where Q_1 and Q_2 are the degenerate pair of normal mode coordinates for the bending mode with conjugate momenta P_1 and P_2, $H_m(r,p)$ is the C–H stretch Morse oscillator Hamiltonian, and F_3 and F_4 are the cubic and quartic force constants, respectively, for the interaction of the C–H stretch with the bend.

The basis states of the zeroth order Hamiltonian [Eq. (3.9)] are the states $|v\rangle|n,l\rangle_5$, where $|v\rangle$ are the Morse oscillator eigenfunctions[18] for the C–H stretch and $|n,l\rangle_5$ is the doubly degenerate harmonic oscillator basis[19] for the ν_5 bending mode. The Fermi resonances in CHD$_3$ are presumed to involve the pure C–H stretching state $|v\rangle|0,0\rangle_5$ of A_1 symmetry interacting with the A_1 combination state $|v-1\rangle|2,0\rangle_5$. The relevant matrix elements for the bending normal mode are (in units of $\hbar = 1$)[19]:

$$\langle n,0|P_1^2 + P_2^2|n+2,0\rangle = (n+2)\omega_5/2, \tag{3.11a}$$

$$\langle n,0|Q_1^2 + Q_2^2|n+2,0\rangle = -(n+2)/(2\omega_5), \tag{3.11b}$$

$$\langle n,0|P_1^2 + P_2^2|n,0\rangle = (n+1)\omega_5, \tag{3.11c}$$

and

$$\langle n,0|Q_1^2 + Q_2^2|n,0\rangle = (n+1)/\omega_5. \tag{3.11d}$$

The 2×2 Fermi resonance matrix for this treatment is

$$\begin{pmatrix} H_{11} & H_{12} \\ H_{21} & H_{22} \end{pmatrix} = \begin{pmatrix} H_1 + V_{11} & V_{12} \\ V_{12}^* & H_2 + V_{22} \end{pmatrix}, \tag{3.12}$$

where (with $\hbar = 1$)

$$H_1 = (v - \tfrac{1}{2})\omega_1 - (v - \tfrac{1}{2})^2\omega_1\chi + 3\omega_5, \tag{3.13a}$$

$$H_2 = (v + \tfrac{1}{2})\omega_1 - (v + \tfrac{1}{2})^2\omega_1\chi + \omega_5, \tag{3.13b}$$

$$V_{11} = \frac{3\omega_5}{2}\langle v-1|[\widetilde{G}_{5,5}(r) - 1]|v-1\rangle + \frac{3}{\omega_5}\left(\frac{F_3}{2}\langle v-1|r|v-1\rangle + \frac{F_4}{4}\langle v-1|r^2|v-1\rangle\right), \tag{3.13c}$$

$$V_{22} = \frac{\omega_5}{2}\langle v|[\widetilde{G}_{5,5}(r) - 1]|v\rangle + \frac{1}{\omega_5}\left(\frac{F_3}{2}\langle v|r|v\rangle + \frac{F_4}{4}\langle v|r^2|v\rangle\right), \tag{3.13d}$$

and

$$V_{12} = \frac{\omega_5}{2}\langle v-1|\widetilde{G}_{5,5}(r)|v\rangle - \frac{1}{\omega_5}\left(\frac{F_3}{2}\langle v-1|r|v\rangle + \frac{F_4}{4}\langle v-1|r^2|v\rangle\right). \tag{3.13e}$$

The Morse matrix elements of the normal mode-transformed G-matrix element $\widetilde{G}_{5,5}(r)$ [Eq. (3.4)] were calculated by numerical quadrature, as in Appendix A. The matrix elements of r and r^2, known analytically,[18,21] are discussed in Appendix B. Both the cubic and quartic terms, involving the Morse matrix elements $\langle v|r|v-1\rangle$ and $\langle v|r^2|v-1\rangle$, respectively, were found to be nonnegligible for $v = 5$ or 6. The force constants in these terms were determined by a nonlinear least squares parameter fit[22] of the calculated values to the experimental data for $v = 1$ through $v = 6$. This fit was performed using a 2×2 matrix, as in Eq. (3.12), to calculate the energies of the C–H overtones and combinations at each energy level through $v = 6$. Using a grid of values for F_3 and F_4, the minimum of the least squares function was found. Since only first order effects were considered in this treatment, the cubic and quartic force constants obtained in such an least squares analysis represent a first order estimate.

The kinetic and potential perturbation contributions to the diagonal elements in Eq. (3.12) also contributed in this calculation. The contribution from the G-matrix terms to the matrix elements V_{ii} represents, in effect, a modification of the bending mode's harmonic frequency ω_5,[23,24] namely,

$$H_{ii} = E_v^m + (n+1)\omega_5' + \langle v|V_{\text{pot}}'|v\rangle, \tag{3.14a}$$

where

$$\omega_5' = \omega_5\left\{1 + \frac{1}{2}\left[\langle v|\widetilde{G}_{5,5}(r)|v\rangle - 1\right]\right\} \tag{3.14b}$$

and E_v^m is the energy of the Morse oscillator with v quanta. Since the diagonal element $\langle v|\widetilde{G}_{5,5}(r)|v\rangle$ is always less than unity (i.e., the effective mass of the bend increases with increasing v), the effective harmonic frequency ω_5' of the bending mode decreases with increasing v. For the CHD_3 molecule, the potential energy term has a similar effect except that it is somewhat more complicated in form. Both contributions give rise, as a result, to an effective anharmonicity for the C–H overtones.[23,24] For the point of view of that interpretation, the values of ω_1 and $\omega_1\chi$ taken from experimentally measured Birge–Sponer lines may deviate somewhat from the "true" Morse parameters for the C–H mode, as is shown later for CHD_3.

The effect of the coupling of the above $|v-1\rangle|2,0\rangle_5$ states to A_1 symmetry states like $|v-2\rangle|4,0\rangle_5$, with four quanta in the bending mode, was also examined. These couplings can, in principle, have a large effect, as was suggested recently for benzene.[4] In the case of CHD_3, however, these states are strongly detuned from the principal Fermi resonance due, in part, to the diagonal first order energy corrections just mentioned [Eqs. (3.14a) and (3.14b)]. Moreover, these states seem to be particularly sensitive to second order corrections from off-resonant states such as $|v-1\rangle|4,0\rangle_5$ or $|v-3\rangle|4,0\rangle_5$. These corrections tend to lower the energy of these states even more so that they are further detuned from the principal Fermi resonance.

To explore such effects, diagonalizations of 27×27 secular determinants for the Hamiltonian [Eq. (3.8)], including states with four quanta in the bending mode and as many as nine C–H stretching quanta, were performed. Since it is computationally expensive to use a 27×27 matrix diagonalization in the determination of the force constants F_3 and F_4 by the nonlinear least squares fitting procedure described previously, two separate approaches to this problem were taken. The first approach was to determine the values of F_3 and F_4 using a 2×2 matrix such as Eq. (3.12) at each level of C–H excitation ($v = 1$–6) in conjunction with the force constant fitting procedure discussed previously. A 27×27 matrix was subsequently diagonalized utilizing the force constants thus obtained. The second approach was to extend the nonlinear least squares fitting procedure to include the diagonalization of a 3×3 matrix (including the states with four bending quanta) at each level of C–H excitation. The force constants obtained in this fit were then used in a diagonalization of a 27×27 secular determinant.

The results of all four calculations are shown in Table II together with the experimental values. It is evident that the results for the simple 2×2 treatment and the subsequent 27×27 diagonalization are consistent with the experimental values and with each other (i.e., the results do not differ significantly between the 2×2 and the 27×27 treatment). Interestingly enough, as one can see from Table II, the 3×3 treatment does not fit the experimental data as well nor are the 3×3 results consistent with the subsequent 27×27 matrix diagonalization using those parameters. These results indicate that the simple 2×2 procedure is the best way to fit the experimental data.

Both 27×27 matrix diagonalizations exhibit the strong second order detuning effect of the $|v-2\rangle|4,0\rangle_5$ states mentioned previously. For the diagonalization utilizing the parameters obtained from the 2×2 fitting procedure, this energy shift for the $v = 6$ region was estimated from second order nondegenerate perturbation theory to be

$$\Delta^{(2)} = \frac{|V_{12}|^2}{E_1^{(0)} - E_2^{(0)}} + \frac{|V_{13}|^2}{E_1^{(0)} - E_3^{(0)}} \simeq -80\ \text{cm}^{-1},$$

TABLE II. Comparison of theoretical results.

	$v = 5$ splitting[c] (cm^{-1})	$v = 6$ splitting[c] (cm^{-1})	$v = 5$ rel. intensity	$v = 6$ rel. intensity
Expt.	133	74	18 ± 8%	55 ± 10%
2×2	117	79	9%	43%
27×27[a]	131	78	7%	40%
3×3	99	59	13%	97%
27×27[b]	138	84	7%	25%

[a] Calculated using parameters from 2×2 fit.

[b] Calculated using parameters from 3×3 fit.

[c] Fermi resonance splittings between eigenstates of $|v\rangle|0,0\rangle$ and $|v-1\rangle|2,0\rangle$ parentage.

TABLE III. Molecular parameters for $CHD_3(CHT_3)$.

	Morse harmonic freq. ω_1(cm^{-1})[a]	Morse anharmonicity $\omega_1\chi$ (cm^{-1})[b]	ν_5 mode harmonic freq. (cm^{-1})[c]	Cubic force constant F_3 (a.u.)[d]	Quartic force constant F_4 (a.u.)[d]
CHD_3	3133	58.08	1335	-2.03×10^{-5}	1.83×10^{-5}
CHT_3	3133	58.08	1273	-1.82×10^{-5}	1.64×10^{-5}

[a] From Ref. 20(a).
[b] From Ref. 25.
[c] Calculated from the quadratic force constants given in Ref. 20(a).
[d] As determined from least squares parameter fit.

where 1 denotes the state $|4\rangle|4,0\rangle_5$, 2 denotes the state $|5\rangle|4,0\rangle_5$, and 3 denotes the state $|3\rangle|4,0\rangle_5$. The exact 27×27 treatment, in this case, has a shift for this state of $\simeq -120\ \mathrm{cm}^{-1}$ instead of $-80\ \mathrm{cm}^{-1}$. Due to this detuning effect, we conclude that the states with four quanta in the bend are not important to the observed Fermi resonances.

C. Results for CHD_3

The energies of the C–H stretch overtones for CHD_3, as calculated from the 2×2 fitting procedure given in Sec. III B and utilizing the molecular parameters from Table III, are compared with the experimental results in Table IV. The results are in good agreement with experiment for both the pure C–H stretching states and the combination levels. The corresponding theoretical least squares Birge–Sponer line (in cm^{-1}) through the $v = 6$ overtone is given by $\Delta E_{0v}/v = 3047 - 57.56v$. This line was determined by using a linear least squares fit to the calculated points for $v = 1$ through 4 and fits the theoretical data very well except at $v = 5$ and 6, where a deviation is expected due to the onset of the Fermi resonances. As compared with Ref. 25, where a fit was obtained for the $v = 1$–4 C–H overtones, there is, from a phenomenological point of view, two new pieces of experimental data, namely the splittings at $v = 5$ and 6, and two new parameters introduced into the fit. Of course, this does not require that the model will automatically fit the data, but it does nevertheless. The main virtue, we believe, of the present analysis is that it describes the physics of the problem. In particular, it is found that the treatment of the dynamical (i.e., G-matrix) coupling does not quantitatively explain the Fermi resonances, i.e., the force constants F_3 and F_4 should be included. Such force constants are ultimately to be compared with *ab initio* calculations. Other treatments which either do not employ curvilinear coordinates and/or potential energy contributions of cubic order or higher can be considered to be more phenomenological.

In Table V, the relative intensities for the two Fermi resonances at $v = 5$ and $v = 6$ are listed along with the off-diagonal matrix elements and the detunings of the diagonal matrix elements. In calculating these relative intensities, the dipole moment for the C–H stretching transitions was assumed to be a function of only the C–H oscillator coordinate r.[1(c)] As a result, the relative intensity of the two states involved in the Fermi resonance is determined by the overlap of the zeroth order pure C–H stretching state with the actual eigenstates. The relative intensity is thus defined as

$$I_r = (b/a)^2\times 100\%, \tag{3.15}$$

where

$$a = |\langle v,0|\psi_0\rangle|, \quad b = |\langle v,0|\psi_2\rangle|. \tag{3.16}$$

Here, $|v,0\rangle$ denotes the zeroth order pure C–H stretching state $|v\rangle|0,0\rangle_5$, ψ_0 is the eigenstate of $|v\rangle|0,0\rangle_5$ parentage, and ψ_2 is the eigenstate of $|v-1\rangle|2,0\rangle_5$ combination state parentage. These relative intensities in Table V are in reasonable agreement with the experimental results, but the discrepancy is larger than that for the splittings. This discrepancy may reflect slight inaccuracies in the zeroth order detunings and/or off-diagonal electrical anharmonicity terms contained in the actual dipole moment function. A theoretical spectrum (at $v = 6$) employing the above results

TABLE IV. Energies of C–H overtones and combinations for $CHD_3(CHT_3)$.

State[a]	CHD_3 expt.[b] (cm^{-1})	CHD_3 calc. (cm^{-1})	CHT_3 calc. (cm^{-1})
$|1,0\rangle$	2 992	2 990	2 990
$|2,0\rangle$	5 865	5 864	5 865
$|3,0\rangle$	8 623	8 624	8 624
$|4,0\rangle$	11 267	11 269	11 269
$|4,2\rangle$	13 668	13 684	13 558
$|5,0\rangle$	13 801	13 801	13 800
$|5,2\rangle$	16 156	16 149	16 029
$|6,0\rangle$	16 230	16 228	16 218

[a] Refers to the zero-order parentage of the state. This notation denotes the states $|v\rangle|n,0\rangle$ (with $l = 0$ in all cases).
[b] Taken from Ref. 2.

TABLE V. Relative intensities, off-diagonal matrix elements, and diagonal detunings[a] for CHD_3 and CHT_3.

Molecule and energy level	Expt. relative intensity[b]	Calc. relative intensity	Off diagonal matrix element V_{12} (cm^{-1})	Diagonal detuning δ (cm^{-1})
CHD_3 $v=5$	18 ± 8%	9%	− 32	98
CHT_3 $v=5$	···	4%	− 47	223
CHD_3 $v=6$	55 ± 10%	43%	− 36	31
CHT_3 $v=6$	···	9%	− 52	159

[a] The diagonal detuning is defined from Eq. (3.12) as $\delta = (H_2 + V_{22}) - (H_1 + V_{11})$.
[b] Taken from Ref. 2.

and the measured excited state rotational constants from Ref. 2 is shown in Fig. 3. The main discrepancy with the experimental spectrum (shown in Fig. 1) is due to the differences in the relative intensities.

The diagonal first order perturbation contributions [Eq. (3.13d)] to the pure C–H stretching energies are given in Table VI. One sees that, according to the results, these terms contribute even for the fundamental transition. Furthermore, the G matrix and the potential energy contributions are of comparable magnitude for all excitations. Indeed, the effective Morse parameters $\omega_1 = 3105$ cm^{-1} and $\omega_1 \chi = 57.56$ cm^{-1} calculated from the theoretical Birge–Sponer line for CHD_3 are quite different from the actual values given for the Morse oscillator in Table III. This difference reflects the diagonal first order perturbation effect. Thus, as noted before, parameters for the C–H bond Morse oscillator potential functions obtained from experimental Birge–Sponer plots should be used with this in mind: they are effective parameters.

The procedure used for calculating the C–H overtones and Fermi resonance combinations was extended to the $v = 7$ region where now both the ν_5 and ν_6 modes couple to the C–H stretch. A 3×3 matrix was used with the zeroth order A_1 symmetry basis states (with energies $E_{c^0} < E_{b^0} < E_{a^0}$)

$$|a^0\rangle = |6\rangle |2,0\rangle_5 |0,0\rangle_6, \tag{3.17a}$$

$$|b^0\rangle = |7\rangle |0,0\rangle_5 |0,0\rangle_6, \tag{3.17b}$$

$$|c^0\rangle = |6\rangle \left[\frac{1}{\sqrt{2}} (|1,-1\rangle_5, |1,1\rangle_6 + |1,1\rangle_5 |1,-1\rangle_6) \right], \tag{3.17c}$$

where the notation $|v\rangle |n,l\rangle_5 |n',l'\rangle_6$ represents the Morse oscillator eigenket for the C–H mode, the $|n,l\rangle$ eigenket for the fifth normal mode ($\omega_5 = 1335$ cm^{-1}), and the $|n,l\rangle$ eigenket for the sixth normal mode ($\omega_6 = 1070$ cm^{-1}), respectively. The term

$$V_{56} = \tilde{G}_{56}(r)(P_{5,1} P_{6,1} + P_{5,2} P_{6,2}) + F_{56} r (Q_{5,1} Q_{6,1} + Q_{5,2} Q_{6,2}) \tag{3.18}$$

was added to the perturbation given in Eq. (3.10).[20(b)] This perturbation term is responsible for the coupling of the $|c^0\rangle$ state to the $|a^0\rangle$ and $|b^0\rangle$ states. The subscripts 5 and 6 have been added here to distinguish between the two normal modes while, as before, the subscripts 1 and 2 in Eq. (3.18) refer to the degenerate pairs of coordinates and momenta for these vibrations. Diagonalization of the 3×3 matrix gave perturbed states $|a\rangle$, $|b\rangle$, and $|c\rangle$ with splittings $\Delta_{bc} \sim 110$ cm^{-1} and $\Delta_{ab} \sim 55$ cm^{-1}. The experimental results from Ref. 2 give splittings of ~120 and ~60 cm^{-1}, respectively. No quantitative comparison of the relative intensities could be made since they were not obtained experimentally for this level. Nevertheless, the theoretical results suggest that the intensity may be distributed approximately uniformly over the three levels in qualitative agreement with what may be seen from visual inspection of the spectrum at $v = 7$.[2]

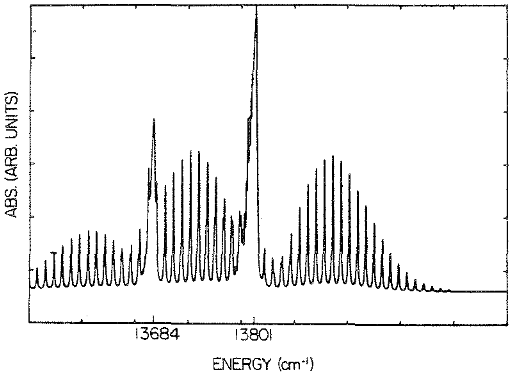

FIG. 3. Theoretical $v = 6$ C–H overtone spectrum for CHD_3.

D. Results for CHT_3

The theoretical treatment of Sec. III A for the $v = 1$–6 transitions in CHD_3 was applied to CHT_3 to investigate the effect of the isotopic substitution D to T. It was again concluded that the fifth normal mode is the only vibration interacting strongly with the C–H stretch by G-matrix coupling and that the simplified treatment of Sec. III B may be applied to CHT_3. The cubic and quartic force constants found

TABLE VI. Calculated first order diagonal corrections to the local mode states in CHD_3.

Zero-order local mode state v	$\tilde{G}$-matrix contribution (cm^{-1})	Potential energy contribution (cm^{-1})	Total correction (cm^{-1})
1	-20	-21	-41
2	-34	-35	-69
3	-48	-47	-95
4	-62	-59	-121
5	-76	-69	-145
6	-90	-78	-168

for CHD_3 were transformed to the CHT_3 normal mode coordinate system with the aid of the transformation in Appendix C. The results for the energies are given in Table IV. The relative intensities of the Fermi resonances, the off-diagonal matrix elements, and the detunings of the diagonal matrix elements are given in Table V. This model predicts significantly less intensity sharing by the combination states in the $v = 5$ and 6 regions than in CHD_3 due to a detuning of the Fermi resonance: the fifth normal mode for CHT_3 has a harmonic frequency of only $\omega_5 = 1273$ cm^{-1} as opposed to 1335 cm^{-1} for CHD_3. This effect far outweighs the contribution due to the increased magnitude of the off-diagonal matrix element (as seen in Table V) and results in a much "purer" C–H stretching state at $v = 5$ and 6.

This analysis of CHT_3 raises two interesting questions. First, the density of vibrational states would obviously be higher for CHT_3 than for CHD_3. Thus, CHT_3 presents a case in which the experimental verification of the results predicted by this model would indicate that the density of states need not predominate in determining the degree of state mixing in structually similar molecules. Rather, the degree of mixing of states may be determined primarily by a specific physical mechanism, as in the case of CHD_3. Second, CHT_3 has the possibility of having 1:3 nonlinear resonance conditions between the C–H stretch, an A_1 mode ($\omega_3 = 905$ cm^{-1}), or a doubly degenerate E mode ($\omega_6 = 900$ cm^{-1}). This resonance condition is possible around the $v = 3$ or 4 level of excitation in the C–H mode. However, the sixth mode involves almost entirely T–C–T bending and C–T stretching motions and so is not expected to be physically coupled to the C–H stretch. The third mode, on the other hand, involves both the H–C–T and the T–C–T bending, but, as was found for the A_1 symmetry modes in CHD_3, it has no G-matrix element providing coupling to the C–H stretch. In addition, the resonant $|v-1,3\rangle_i$ states of either mode cannot couple directly to the pure C–H stretching states via the perturbation terms like those given in Eq. (3.10) as long as the harmonic oscillator basis is a good one for those normal modes. Experimental observation of significant 1:3 Fermi resonances in this molecule would indicate that the simple theoretical/physical picture presented in Eqs. (3.8)–(3.13e) needs extension. Possible extensions include a dynamical dependence of the G-matrix term in Eq. (3.10) on the normal mode Q_6 or the presence of significant fourth order force constants proportional to rQ_3^3 or rQ_6^3 in the potential energy function.

A curvilinear coordinate treatment is next used to estimate the vibrational state mixing in CH_3D.

IV. THEORY FOR CH_3D

A. Vibrational analysis

The CH_3D molecule has three equivalent C–H oscillators, so it is useful to prediagonalize the CH_3 local mode problem[1] before treating the interactions of these modes with the bending normal modes. The properly symmetrized zeroth order local mode basis states for C_{3v} symmetry were found using the method of Halonen and Child.[21,25] For the sake of brevity, these basis states are not presented here, but they consist in general of the A_1, A_2, E_a, and E_b linear combinations of different permutations of the unsymmetrized local mode state

$$|v_1,v_2,v_3\rangle, \tag{4.1}$$

where the subscripts 1, 2, and 3 refer to the Morse oscillator basis states for the three C–H bonds. The corresponding C–H local mode Hamiltonian is

$$H_m = H_m^0 + V'_m, \tag{4.2}$$

where

$$H_m^0 = \sum_i^3 H_i(p_i,r_i) \tag{4.3}$$

and

$$V'_m = \sum_{i>j}^3 G_{ij}\, p_i\, p_j + \sum_{i>j}^3 F_{ij} r_i\, r_j, \tag{4.4}$$

and may be diagonalized in the symmetrized local mode basis. In these equations, $H_i(p_i,r_i)$ is a Morse oscillator Hamiltonian with curvilinear bond displacement coordinate r_i and conjugate momentum p_i; G_{ij} and F_{ij} are the off-diagonal G-matrix element and the off-diagonal quadratic force constant, respectively, for two C–H stretching local modes i and j. The G-matrix element used in this calculation may be found analytically,[16] the quadratic stretch–stretch interaction force constant was obtained from the Gray and Robiette potential energy surface,[20(c)] and the Morse parameters are the same as those used for CHD_3 (Table III). The eigenvalues and eigenfunctions of this Hamiltonian were calculated for manifolds with $v = 4$, 5, and 6 total quanta in the C–H stretches.[21,25] Couplings by the perturbation term (4.4) between manifolds of states with different total v were neglected since they are far off resonance. Each manifold of states has four independent blocks of A_1, A_2, E_a, and E_b symmetry, and the properly symmetrized "pure" local mode states (i.e., symmetrized linear combinations of $|v,0,0\rangle$) are nearly degenerate for all blocks that included such states (there is one pure state each in the A_1, E_a, and E_b blocks).

The interaction of the prediagonalized local mode states with the bending degrees of freedom was next calculated. This step is usually omitted in the customary local mode treatment[1,21,25] but, as was learned in the CHD_3 analysis, is useful in understanding the breakdown of localized C–H stretching vibrations. As a first step, the interaction of the CH_3 local modes with the bending vibrations was calculated using only the G-matrix coupling technique presented in Sec. III A. Due to the limited experimental resolution of individual vibrational lines at $v = 6$ in this molecule, a treatment of the potential energy contributions to the state coupling was not attempted.

The description of the normal modes was made by performing a standard normal mode analysis[16] on the quadratic Hamiltonian

$$H_N = \frac{1}{2}\sum_{i,j}{}' G_{ij}(\mathbf{x}_0)p_i\, p_j + \frac{1}{2}\sum_{i,j}{}' F_{ij}q_iq_j, \tag{4.5}$$

where the primes on the summations indicate a summation over all internal symmetry coordinates q_i (see Table VII) other than the three C–H stretching coordinates. This treatment defines three normal modes with harmonic frequencies $\omega_3 = 1366\ \mathrm{cm}^{-1}$, $\omega_5 = 1524\ \mathrm{cm}^{-1}$, and $\omega_6 = 1222\ \mathrm{cm}^{-1}$ that are in approximate 1:2 nonlinear resonance with the C–H stretches. The fifth and sixth vibrations are both doubly degenerate modes of E symmetry while the third vibration is the A_1 symmetry umbrella mode.[20(a)] As for CHD_3, the C–H stretching coordinates are treated separately when defining the zeroth order oscillator basis.

The curvilinear Hamiltonian used for this problem, containing the third, fifth, and sixth normal modes and the C–H local modes, is

$$H = H_0 + V' + V_d, \tag{4.6a}$$

where

$$\begin{aligned} H_0 = H_m &+ \frac{1}{2}(P_3^2 + \omega_3^2 Q_3^2) \\ &+ \frac{1}{2}[(P_{5,1}^2 + P_{5,2}^2) + \omega_5^2(Q_{5,1}^2 + Q_{5,2}^2)] \qquad (4.6\mathrm{b}) \\ &+ \frac{1}{2}[(P_{6,1}^2 + P_{6,2}^2) + \omega_6^2(Q_{6,1}^2 + Q_{6,2}^2)], \end{aligned}$$

$$\begin{aligned} V' = \frac{1}{2}&[\widetilde{G}_{3,3}(r_1,r_2,r_3) - 1] \\ &+ \frac{1}{2}\sum_{n=1}^{2}[\widetilde{G}_{5,5;n}(r_1,r_2,r_3) - 1]P_{5,n}^2 \\ &+ \frac{1}{2}\sum_{n=1}^{2}[\widetilde{G}_{6,6;n}(r_1,r_2,r_3) - 1]P_{6,n}^2 \qquad (4.6\mathrm{c}) \\ &+ \sum_{n=1}^{2}\widetilde{G}_{5,6;n}(r_1,r_2,r_3)P_{5,n}\, P_{6,n}, \end{aligned}$$

and the diagonal matrix element of the V_d potential energy term is written as

$$\langle v_3|V_d|v_3\rangle = -(v_3 + \tfrac{1}{2})^2\omega_3\chi_3. \tag{4.6d}$$

Here, H_m is the C–H local mode Hamiltonian from Eq. (4.2), $\widetilde{G}_{3,3}(r_1,r_2,r_3)$ is the normal mode transformed G-matrix element [Eq. (3.4)] for the nondegenerate A_1 mode, $\widetilde{G}_{i,i;n}(r_1,r_2,r_3)$ is the normal mode transformed G-matrix element for doubly degenerate normal mode i with degenerate partner n, and $\widetilde{G}_{5,6;n}(r_1,r_2,r_3)$ is the G-matrix cross term for the degenerate normal modes 5 and 6 and degenerate partner n. All of these G-matrix elements are assumed to depend only on the three C–H bond lengths r_1, r_2, and r_3. This approximation is analogous to the one made for CHD_3, where the C–H mode was taken to be the only vibration with appreciable amplitude. The $|v_3\rangle$ ket denotes a vibrational state of the A_1 mode such that $\langle v_3|V_d|v_3\rangle$ has the effect of a diagonal anharmonicity with the adjustable anharmonicity parameter $\omega_3\chi_3$. The work of Gray and Robiette[20(a)] suggests that this anharmonicity is significant and should not be neglected; an approximate value of 20 cm^{-1} was chosen for this parameter. The other matrix elements of this vibrational mode are still treated in the harmonic limit, however, because this anharmonicity is not large enough to cause significant deviations from harmonic oscillator values.

TABLE VII. Internal symmetry coordinates for CH_3D.[a]

$q_1 = r$

$q_2 = r_1$

$q_3 = r_2$

$q_4 = r_3$

$q_5 = \frac{1}{\sqrt{6}}(\alpha_1 + \alpha_2 + \alpha_3 - \beta_1 - \beta_2 - \beta_3)$

$q_6 = \frac{1}{\sqrt{6}}(2\alpha_1 - \alpha_2 - \alpha_3)$

$q_7 = \frac{1}{\sqrt{6}}(2\beta_1 - \beta_2 - \beta_3)$

$q_8 = \frac{1}{\sqrt{2}}(\alpha_2 - \alpha_3)$

$q_9 = \frac{1}{\sqrt{2}}(\beta_2 - \beta_3)$

[a] The coordinates are defined the same way as in Table I except that r is now the C–D displacement coordinate and r_i is a C–H displacement coordinate.

The basis states defined by the zeroth order Hamiltonian [Eq. (4.6b)] are

$$|\psi\rangle = |v,j,\Gamma\rangle|v_3\rangle|n_5,l_5\rangle|n_6,l_6\rangle, \tag{4.7}$$

where $|v,j,\Gamma\rangle$ represents the jth eigenket (ordered by increasing energy) of the prediagonalized CH_3 local mode Hamiltonian H_m [Eq. (4.2)] from the manifold with v total C–H stretching quanta and symmetry Γ. Also, $|v_3\rangle$ is the nondegenerate harmonic oscillator basis for the third mode and $|n_i,l_i\rangle$ is the doubly degenerate harmonic oscillator basis for the fifth and sixth modes.

The matrix elements for the doubly degenerate bending modes were calculated in the same way as those for CHD_3/CHT_3 [Eqs. (3.10a)–(3.10c)] while the nondegenerate matrix elements were calculated from standard harmonic oscillator formulas.[19] The matrix elements

$$\langle v',j',\Gamma|\widetilde{G}_{i,i;n}(r_1,r_2,r_3)|v,j,\Gamma\rangle, \tag{4.8}$$

in the prediagonalized local mode basis set $|v,j,\Gamma\rangle$, were nontrivial and could have required copious quantities of computer time. Several simplifications which made the evaluation of Eq. (4.8) tractable are given in Appendix D.

B. Results for CH_3D

In the notation of Eq. (4.7), the pure local mode state for $v = 6$ is

$$|\psi_1\rangle = |6,1,\Gamma\rangle|0\rangle|0,0\rangle|0,0\rangle, \tag{4.9}$$

where $|v,1,\Gamma\rangle$ is defined as the symmetrized state of pure local mode parentage and of Γ symmetry. These pure states are always lowest in energy within a manifold with v total quanta [i.e., in the notation of Eq. (4.7), they are denoted by $j = 1$]. The only zeroth order states with less than or equal to four quanta in the bending modes found in the calculations to strongly interact by G-matrix coupling with this state are

$$|\psi_2\rangle = |5,1,\Gamma\rangle|2\rangle|0,0\rangle|0,0\rangle, \tag{4.10a}$$

$$|\psi_3\rangle = |5,1,\Gamma\rangle|0\rangle|0,0\rangle|2,0\rangle, \tag{4.10b}$$

and

$$|\psi_4\rangle = |4,1,\Gamma\rangle|4\rangle|0,0\rangle|0,0\rangle, \tag{4.10c}$$

where Γ denotes states of A_1, E_a, or E_b symmetry. In the calculations, it was also found that no states from Eq. (4.7) containing local mode combination states[1] are found to mix to any appreciable extent with the states (4.9) and (4.10a)–(4.10c) when the full matrix diagonalization (including the bending degrees of freedom) is performed.

An approximate theoretical spectral envelope was calculated for the $v = 6$ overtone of CH_3D at 300 K (see Fig. 4). Standard selection rules for parallel and perpendicular type vibrational/rotational transitions in symmetric top molecules were used.[14] Moreover, as in the case of CHD_3, the body fixed C–H stretching dipole moment operator was assumed to have the form[1,21]

$$\mu(\mathbf{r}) = \sum_{i=1}^{3} \mu(r_i)\mathbf{e}_{r_i}, \tag{4.11}$$

where $\mathbf{e}_{r_i}$ is a unit vector directed along the ith C–H bond. The overlaps of the molecular eigenstates with the zeroth order pure C–H stretching state thus determine the relative intensities of the vibrational transitions. For Fig. 4, the individual vibrational/rotational lines were given a Lorentzian shape with a width at half-maximum of 1 cm^{-1}, as was determined experimentally.[2] A value of -0.2 cm^{-1} was assumed for the ground to excited state rotational constant difference $\Delta B = (B_v - B_0)$, representing a crude estimate of the change in the rotational constant in going to the excited state. The overall spectral envelope is not particularly sensitive to changes in the value of this parameter.

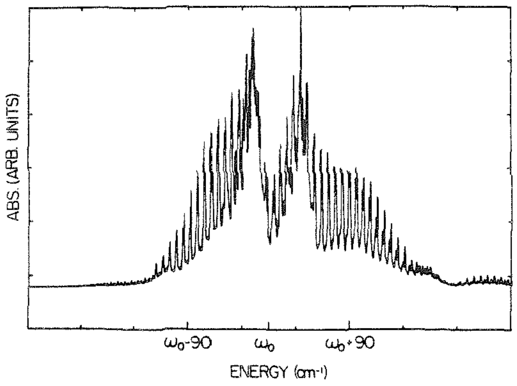

FIG. 4. Theoretical C–H overtone spectrum for CH_3D. The rotational contours were calculated using the rotational constants $B \simeq 3.88$ cm^{-1} and $A \simeq 5.25$ cm^{-1} [Ref. 20(a)] and the excited state rotational constant difference $\Delta B \simeq -0.2$ cm^{-1}. The individual vibrational/rotational transitions were given a Lorentzian line shape with a width at half-maximum of 1 cm^{-1}.

When compared with the experimental spectrum in Fig. 2, two features of the theoretical spectral envelope in Fig. 4 are immediately apparent. First, the two main peaks of the experimental envelope presumably correspond to states of zeroth order parentage $|6,1,\Gamma\rangle|0\rangle|0,0\rangle|0,0\rangle$ for the eigenstate to higher energy and $|5,1,\Gamma\rangle|0\rangle|0,0\rangle|2,0\rangle$ for the eigenstate to lower energy, with an experimental splitting of ~ 60 cm^{-1}. The theoretical spectrum has these same states present with a splitting of ~ 50 cm^{-1}. Moreover, the relative heights of the two peaks seem to be in qualitative agreement for the two spectra. A second feature is that the theoretical spectrum is noticeably less congested than the experimental one. We have considered the Coriolis interactions among only the pure local mode states and found them to be very ineffective in contributing to the observed spectral congestion (Appendix E).

For the theoretical spectrum at $v = 6$ shown in Fig. 5, a Lorentzian line shape for each vibrational/rotational transition with a width of 30 cm^{-1} was assumed and is much closer in appearance to the experimental one. If one assumes a high degree of level mixing of the ro-vibrational states at $v = 6$, then the "Golden Rule" formula $(2\pi/\hbar)\langle V\rangle^2\rho_{rv}$ may be used for the rate constant k for decay of the excitation. The homogeneous linewidth $\Delta\bar{\nu}$ is then given by $k/2\pi c$,[26] where c is the speed of light. Using the expression $(2J+1)\rho_v(\Gamma)$ for the average density of ro-vibrational states ρ_{rv} with symmetry Γ and rotational quantum number J,[27] typical values of the effective coupling element $\langle V\rangle$ needed to give linewidths of 30 cm^{-1} are found to be on the order of 0.1–1.0 cm^{-1}, depending on the value of J and the symmetry Γ. (Note the difference in magnitude of these matrix elements coupling to individual bath states as compared to those coupling the stretch to the bend in CHD_3). In these calculations, values of 1.85, 1.85, and 7.40 states/cm^{-1} were used for the density $\rho_v(\Gamma)$ of A_1, A_2, and E symmetry vibrational states, respectively, at the energy of the $v = 6$ transition.[15] Whether the physical origin of the extra broadening in Fig. 5 is due to higher order potential energy and/or Coriolis interactions is at present not known. It should, however,

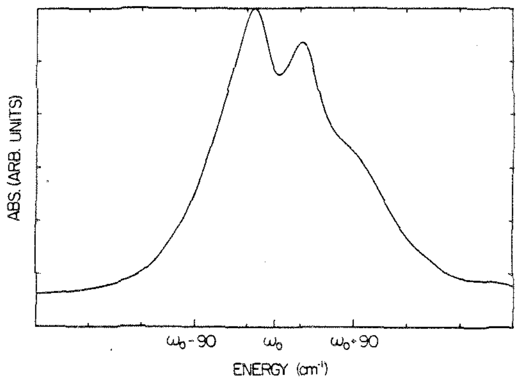

FIG. 5. Theoretical C–H overtone spectrum for CH_3D including a broadening of 30 cm^{-1} for each vibrational/rotational transition.

be mentioned that thermal congestion may be the source of the observed broadening in this molecule provided there are small but not negligible Coriolis interactions.

V. CONCLUDING REMARKS

In this paper, a theoretical analysis of the C–H stretching vibrations in CHD_3, CHT_3, and CH_3D was performed. The various coupling mechanisms in these molecules resulting from dynamical and, in the case of CHD_3 and CHT_3, potential energy interactions were considered. For CHD_3, the simplicity of the observed C–H overtone spectrum was qualitatively explained by treating the curvilinear G-matrix coupling[4] of the C–H stretch with the other vibrational normal modes, but this coupling is seen to be too large to quantitatively explain the Fermi resonances with the ν_5 mode. Potential energy contributions are therefore assumed to contribute a cancellation effect within the interaction matrix elements between zeroth order states. It was further concluded that the existence of a low order resonance condition between the C–H stretch and the other vibrations was crucial in determining the degree of vibrational mode coupling in these molecules. In CHD_3, it was deduced from the calculations that the C–H stretching local mode selectively interacts by these mechanisms with only one doubly degenerate normal mode involving D–C–H bending. Another approach to the present problem is the rectilinear coordinate method used by Quack *et al.*[28,29] for the C–H stretching states in the CHX_3 species (where X = D, F, etc.).

Predictions for CHT_3 are also presented, using the same model as for CHD_3, the only difference being in the normal mode frequencies due to the isotopic substitution D to T. The predictions of this model indicate the existence of a purer C–H stretching mode than was found for CHD_3 because the 1:2 resonance condition between the C–H stretch and the bend is detuned upon isotopic substitution. It is suggested that more subtle vibrational state mixing effects such as higher order resonances with other normal modes, weak potential energy couplings, and a higher density of states may be present in this molecule, although our model indicates that these are not important. The results presented in this paper for CHD_3 and CHT_3, together with the work of Sibert *et al.*[4] on the benzene local modes suggests it is possible that many intermediate and large size molecules may exhibit interesting behavior that only the detailed examination of the vibrational state coupling can reveal. One possibility is that certain molecular systems may be thought of as decoupled or very weakly coupled subsets of strongly interacting vibrational modes. There are implications of this picture for vibrational energy redistribution[12] and laser selective chemistry.[13] In fact, the results presented here are consistent with the recent observation in anthracene[30] of simple quantum beats, indicating that only a few (~ 3) levels are involved in the coupling even though the total density of states is quite high.

For CH_3D, it is found that the pure C–H stretching local modes do, in fact, mix to a greater degree by G-matrix coupling with bending normal modes than was found in CHD_3. It was also shown that local mode combination states[1] were not significantly coupled to these pure local modes. Thus, the present model suggests that the energy flow from an initially excited zeroth order nonstationary state like Eq. (4.9) would go almost exclusively into the bending degrees of freedom coupled to the C–H stretches and not into local mode combination states. This picture is similar to that presented by several authors[4,9] for C_6H_6.

While the calculated spectral envelope (Fig. 4) for CH_3D is congested due to vibrational/rotational transitions, we were unable to explain the observed high degree of spectral congestion (see Fig. 2) using pure G-matrix coupling effects. Potential energy or Coriolis couplings between the rovibrational states may be responsible for the added degree of congestion observed experimentally in this molecule.

ACKNOWLEDGMENTS

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APPENDIX A: INTEGRATION OF THE $\tilde{G}$ MATRIX ELEMENTS FOR CHD_3, CHT_3

The matrix elements $\langle v|\tilde{G}_{5,5}(r)|v'\rangle$ appearing in Eqs. (3.7) and (3.13c)–(3.13e) were calculated as follows: Computer subroutines were written (1) to calculate the G matrix[16] for a general tetrahedral molecule, the input parameters being the atomic masses and the bond lengths; (2) to calculate the normal mode matrix $\mathbf{L}^{-1}$ for all the displacement coordinates at their equilibrium value; (3) to perform the symmetry coordinate transformation [Eq. (3.5)] and the normal mode transformation [Eq. (3.4)]; (4) to calculate the value of the integrand $\psi_v^*(r)\tilde{G}_{5,5}(r)\psi_{v'}(r)$ from the matrix element $\langle v|\tilde{G}_{5,5}(r)|v'\rangle$ for an arbitrary value of the C–H bond displacement coordinate r, ψ_v and $\psi_{v'}$ being the Morse oscillator eigenfunctions[17,18]; and (5) to numerically integrate the integral $\langle v|\tilde{G}_{5,5}(r)|v'\rangle$ using Gaussian quadrature[31] for the classically allowed region and Laguerre quadrature[31] for the classically unallowed region. These subroutines were linked into a main computer code such that a value of $\tilde{G}_{5,5}(r)$ could be calculated at each r and the numerical integration in (5) performed. It was found that 64-point Gaussian quadrature and 30-point Laguerre quadrature gave values for the integrals converged to at least six decimal places.

APPENDIX B: MORSE MATRIX ELEMENTS FOR r AND r^2

The Morse matrix elements in Ref. 21 for $r \equiv (R - R_0)$ were simplified to give

$$\langle v+j|r|v\rangle = \frac{(-1)^{j+1}}{a} \frac{[(k-2v-1)(k-2v-2j-1)]^{1/2}}{j(k-2v-j-1)} \times \left[\frac{(v+j)(v+j-1)\ldots(v+1)}{(k-v-1)(k-v-2)\ldots(k-v-j)}\right]^{1/2} \tag{B1}$$

and

$$\langle v|r|v\rangle = \frac{1}{a}\left[\ln k - \left(\sum_{m=1}^{p-1} \frac{1}{(p-m)+z} + \Phi(1+z)\right)\right.$$

$$+\sum_{j=1}^{v}\frac{1}{(k-v-j)}(1-\delta_{v0})\Bigg], \tag{B2}$$

where $\Phi(x)$ is the digamma function,[32] k denotes $\omega/\omega\chi$, and a denotes $(2\mu\omega\chi)^{1/2}/\hbar$. Also, μ is the reduced mass of the two particles having an internuclear separation R and

$$z=k-\mathrm{Int}(k), \quad p=\mathrm{Int}(k)-1-2v, \tag{B3}$$

where Int(k) is the integer nearest to k from below.

The off-diagonal Morse matrix elements of r^2 are given by Gallas in Ref. 18(a). However, the diagonal matrix elements of r^2, when calculated from the formula given by Gallas,[18(a)] can in general pose serious numerical difficulties [see Ref. 18(b)]. They were instead calculated from the formula

$$\langle v|r^2|v\rangle \simeq \sum_{j\{\mathrm{bound}\}}\langle v|r|j\rangle\langle j|r|v\rangle, \tag{B4}$$

which assumes an approximate completeness relation

$$\sum_{j\{\mathrm{bound}\}}|j\rangle\langle j|\simeq 1 \tag{B5}$$

for the Morse oscillator bound states. For relatively low values of v, it is not expected that the contribution in Eq. (B4) from the continuum wave functions is significant.

APPENDIX C: TRANSFORMATION OF FORCE CONSTANTS FOR CHD_3 TO CHT_3

The transformation of the cubic and quartic force constants from CHD_3 normal mode coordinates to CHT_3 normal mode coordinates was performed in a straightforward way using the equations

$$\mathbf{q}=\mathbf{L}\mathbf{Q}, \quad \mathbf{q}=\mathbf{L}'\mathbf{Q}', \tag{C1}$$

where the primed quantities refer to CHT_3, the unprimed quantities refer to CHD_3, the **Q**'s are the normal modes, and the **q**'s are the internal symmetry coordinates (Table I). Equating the two expressions in Eq. (C1), one obtains

$$\mathbf{Q}=\mathbf{L}^{-1}\mathbf{L}'\mathbf{Q}', \tag{C2}$$

i.e.,

$$\mathbf{Q}=\mathbf{A}\mathbf{Q}', \tag{C3}$$

where

$$\mathbf{A}=\mathbf{L}^{-1}\mathbf{L}'. \tag{C4}$$

The cubic and quartic force constants for CHT_3 are then easily found to be

$$F'_{nlm}=\sum_{ijk}F_{ijk}A_{in}A_{jl}A_{km} \tag{C5}$$

and

$$F'_{nlmp}=\sum_{hijk}F_{hijk}A_{hn}A_{il}A_{jm}A_{kp}. \tag{C6}$$

In this case, A_{11} is defined to be equal to unity and the other A_{1i} and A_{i1} are set equal to zero. This was done because coordinate 1 is taken to be the local mode C–H stretching coordinate, and the normal mode transformation is performed independently of this coordinate.

APPENDIX D: MATRIX ELEMENTS OF $\widetilde{G}$ FOR CH_3D

Let $\widetilde{G}_{ij}(r_1,r_2,r_3)$ be any general normal mode transformed G-matrix element from Eq. (4.6c). The matrix elements [Eq. (4.8)] between CH_3 local mode states j and j' from manifolds with total C–H stretching quanta v and v' [the Γ indices from Eq. (4.8) have been suppressed] are

$$\langle v'j'|\widetilde{G}_{ij}|v,j\rangle=\sum_{i'=0}^{N'_0}\sum_{i=1}^{N_0}C^{j',v'*}_{i',v'}\mathbf{G}_{i',i}C^{j;v}_{i;v}, \tag{D1}$$

where N_0 is the number of symmetrized zeroth order wave functions for the manifold with v C–H stretching quanta and

$$C^{j;v}_{i;v}=\langle v,i_0|v,j\rangle, \tag{D2}$$

with $|v,i_0\rangle$ being the symmetrized zeroth order wave function:

$$|v,i_0\rangle=\sum_{p}^{N_p}C^{i;v}_{p;v}|p;v\rangle. \tag{D3}$$

In Eq. (D3),

$$C^{i;v}_{p;v}=\langle p;v|v,i_0\rangle\equiv\text{the symmetrization coefficients,}^{25} \tag{D4}$$

and N_p is the number of different permutations p of the unsymmetrized local mode state $|p;v\rangle$ with v total C–H quanta [in an abbreviated notation for Eq. (4.1)]. Furthermore,

$$\mathbf{G}_{i',i}=\sum_{p=1}^{N_p}\sum_{p'=1}^{N'_p}C^{i';v'*}_{p';v'}\langle p';v'|\widetilde{G}_{ij}|p;v\rangle C^{i;v}_{p;v}. \tag{D5}$$

The matrix elements $\langle p';v'|\widetilde{G}_{ij}|p;v\rangle$ were computed numerically by the following procedure: (1) the standard G matrix in internal valence coordinates is calculated in terms of the atomic masses and the quantities $\langle v_i|r_i^{-1}|v'_i\rangle\delta_{v_jv'_j}\delta_{v_kv'_k}$, $\langle v_i|r_i^{-2}|v'_i\rangle\delta_{v_jv'_j}\delta_{v_kv'_k}$, and $\langle v_iv_j|(r_i\,r_j)^{-1}|v'_iv'_j\rangle\delta_{v_kv'_k}$, where $|v_i\rangle$, $|v'_i\rangle$, etc. are Morse oscillator eigenfunctions[17,18] appropriate to the states $|p;v\rangle$ and $|p';v'\rangle$; (2) the symmetry coordinate transformation [Eq. (3.5)] is performed with the symmetry coordinates from Table VII; (3) the normal mode transformation [Eq. (3.4)] is performed with the $\mathbf{L}^{-1}$ matrix calculated from the normal mode analysis of Eq. (4.5). As before, the three C–H coordinates were excluded from this transformation. The ijth term of this matrix of values corresponds to the matrix element $\langle p';v'|\widetilde{G}_{ij}|p;v\rangle$. This procedure yields values for the matrix elements in Eq. (D1) efficiently and economically. A direct multidimensional numerical integration in terms of the three C–H coordinates was anticipated to be too expensive and, because of the dependence on several coordinates, probably inaccurate.

APPENDIX E: CORIOLIS INTERACTION AND LOCAL MODE DEGENERACY

In order to determine whether Coriolis interactions can strongly effect the threefold near degeneracy of the zeroth order states in Eqs. (4.9)–(4.10c) for the present model of CH_3D, a simple calculation was performed to estimate these effects for the pure A_1, E_a, and E_b symmetrized zeroth order CH_3 local mode states[25]

$$|\psi_1;A_1\rangle = \frac{1}{\sqrt{3}}(|v,0,0\rangle + |0,v,0\rangle + |0,0,v\rangle), \tag{E1}$$

$$|\psi_2;E_a\rangle = \frac{1}{\sqrt{6}}(2|v,0,0\rangle - |0,v,0\rangle - |0,0,v\rangle), \tag{E2}$$

and

$$|\psi_3;E_b\rangle = \frac{1}{\sqrt{2}}(|0,v,0\rangle - |0,0,v\rangle). \tag{E3}$$

In this calculation, a rectilinear coordinate treatment was used due to the relative simplicity of the equations in this approach.[33] In addition, it is well known that the description of molecular vibrations in the curvilinear coordinate approach differs most strongly from the rectilinear treatment only for the bending modes.[5,6] For these reasons and because we only desire to estimate these rotational effects, the rectilinear coordinate approach is well suited to our purpose.

The first order Coriolis effect is described in the small amplitude limit by the vibration/rotation coupling term[33]

$$V_{vr} = -\frac{\hat{P}_z \hat{p}_z}{I_z}, \tag{E4}$$

where $\hat{P}_z$ is the z projection of the rotational angular momentum, $\hat{p}_z$ is the z projection of the vibrational angular momentum, and I_z is the z component of the inertia tensor (taken as a constant). The orientation of the molecule is such that the z axis in the body fixed coordinate system is along the symmetry axis of the molecule. The contribution to this term from the CH_3 local mode coordinates r_1, r_2, and r_3 is

$$V'_{vr} = -\frac{\hat{P}_z}{I_z}\sum_{i<j}^{3}\zeta^z_{ij}(\hat{r}_i\hat{p}_j - \hat{r}_j\hat{p}_i), \tag{E5}$$

where the ζ^z_{ij} are the Coriolis zeta constants,[33,34] and $\hat{p}_i$ is the momentum operator conjugate to $\hat{r}_i$. The first order matrix elements are then (with $\hbar = 1$)

$$E^{(1)} = -\frac{K}{I_z}\langle\psi_i;\Gamma|C(\hat{\mathbf{r}},\hat{\mathbf{p}})|\psi_{i'};\Gamma'\rangle, \tag{E6}$$

where $C(\hat{\mathbf{r}},\hat{\mathbf{p}})$ is the summation term in Eq. (E5) and the states $|\psi_i;\Gamma\rangle$ are states from Eqs. (E1)–(E3). The zeta constants for the coordinate system defined by the normal mode transformation of Eq. (4.5) (excluding the C–H coordinates) and the three C–H stretching coordinates were calculated using standard techniques.[34] The values for these constants were found to be $\zeta^z_{12} = -\zeta^z_{13} = \zeta^z_{23} = 0.06$. The values of the x and y zeta constants ζ^x_{ij} and ζ^y_{ij} were also calculated and found to be even smaller. As a check of the present method, a complete normal mode calculation was performed (including the C–H coordinates), and we reproduced exactly all of the relevant normal mode zeta constants for CH_3D (see Table VI of Ref. 20).

In standard normal mode theory,[33] the matrix element [Eq. (E6)] between doubly degenerate normal modes of E symmetry yields the value $-(K/I_z)(\pm l_i)\delta_{ii'}\delta_{\Gamma\Gamma'}$, where l_i is the magnitude of the vibrational angular momentum of degenerate state i, and hence splits the degeneracy of this mode due to the difference in the values of the diagonal elements. For the local mode states [Eqs. (E1)–(E3)], the matrix element in Eq. (E6) was evaluated numerically. It was found that the only nonzero first order matrix element is between the E_a state [Eq. (E2)] and the E_b state [Eq. (E3)] and, for $v = 6$, that it is extremely small ($\sim 4\times10^{-7}$ cm^{-1}).

The second order Coriolis interactions of the states in Eqs. (E1)–(E3) with the symmetrized zeroth order local mode combination states of $|5,1,0\rangle$ parentage were next calculated. To do this, a Van Vleck transformation[35] through second order was employed in order to treat the problem by a simple 2×2 matrix for the states (E2) and (E3) with $v = 6$. The only nonzero perturbations were the first order corrections just described and diagonal second order corrections arising from the coupling to the E symmetry combination states of $|5,1,0\rangle$ parentage. These interactions were again found to be very small ($\sim 10^{-2}$ cm^{-1}). It is clear that, while the degeneracy of the local mode states (E1)–(E3) is lifted by the Coriolis interactions, this effect is expected to be entirely negligible on the scale of Fig. 4 and thus contributes little to the observed spectral congestion. The weakness of these interactions is primarily due to the smallness of the zeta constants ζ^z_{ij} for the local mode coordinates appearing in Eq. (E5) and because the local mode states presumably have very little vibrational angular momentum. Whether Coriolis effects are important for the pure local mode states in other molecules with different symmetries remains an open question.[36] It is also again emphasized that the above calculations assume the local axial symmetry of the CH_3 group in the CH_3D molecule.

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Chapter 2: Semiclassical Theory of Fermi Resonance Between Stretching and Bending Modes in Polyatomic Molecules

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Semiclassical theory of Fermi resonance between stretching and bending modes in polyatomic molecules

Gregory A. Voth and R. A. Marcus
A. A. Noyes Laboratory of Chemical Physics, California Institute of Technology,[a] *Pasadena, California 91125*

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Approximate semiclassical solutions are developed for a system of a Morse oscillator coupled to a harmonic oscillator via a nonlinear perturbation. This system serves as a model for the interaction of an excited stretching mode with a bending mode in a polyatomic molecule. Three semiclassical methods are used to treat this model. In particular, a matrix diagonalization, a two-state model, and a uniform semiclassical approximation (USC) based on Mathieu functions are each used to determine the splittings and state mixing involved in these stretch–bend Fermi resonances. For small perturbations, approximate analytic semiclassical expressions are obtained for the system treated. These analytic expressions are given for the splittings using a two-state or USC method and for the overlaps of the zeroth order states with the eigenstates of the molecule using a USC method.

I. INTRODUCTION

The present paper treats the 1:2 resonant interaction of a stretching mode with a bending mode in a polyatomic molecule. This system is modeled classically using a resonance Hamiltonian[1–6] to describe the nonlinear interaction of a Morse oscillator stretching vibration with a harmonic bending vibration. Several semiclassical methods are used to obtain information about the quantum Fermi resonance resulting from this nonlinear interaction. The results of these methods are compared with each other, with those obtained from a recent uniform semiclassical treatment,[7] and with the exact quantum results.

The experimental incidence of 1:2 stretch–bend Fermi resonance is widespread, the best known being that in CO_2.[8] Previous discussions of these resonances are many, e.g., Ref. 9, and they have appeared more recently in the local mode literature.[10] The model of a local mode C–H stretch interacting resonantly with bending normal modes has also been proposed as a theoretical explanation for the observed Fermi resonances in CHD_3[11,12] and for the C–H overtone linewidths in benzene.[13] These Fermi resonances are related to the existence of one (or more) *classical* resonance conditions.[1–6] The quantum mechanical implications of an *isolated* classical resonance have been discussed by a number of authors,[3,7,14–27] including their relation to avoided crossings[14,24,25] and to Fermi resonances.[3,7,14,22]

A straightforward semiclassical matrix technique is presented in Sec. II to treat Fermi resonant systems. Two other semiclassical methods, namely, a semiclassical two-state solution and a uniform semiclassical approximation (USC), are also formulated later in Sec. IV that are based on an effective classical resonance Hamiltonian for the nonlinear interaction of a Morse with a harmonic oscillator (Sec. III). These latter two methods may be used to calculate analytically the splittings between the eigenstates of the system and the overlaps of the zeroth order wave functions with the actual eigenfunctions. The three semiclassical methods are applied in Sec. V to a model of a C–H stretching local mode interacting resonantly with a bending mode in a dihalomethane molecule. The results of these calculations, and those obtained using the method of Ref. 7, are discussed in Sec. VI, and concluding remarks are given in Sec. VII.

II. SEMICLASSICAL MATRIX DIAGONALIZATION

The classical Hamiltonian for a coupled Morse and harmonic oscillator may be written in action-angle variables as[7]

$$H(I_1, I_2, \theta_1, \theta_2) = I_1\omega_1^0 - I_1^2\omega_1^0\chi + I_2\omega_2^0 + V(I_1, I_2, \theta_1, \theta_2), \tag{2.1}$$

where I_1 and I_2 are the action variables[28] for the Morse and harmonic oscillators, respectively. θ_1 and θ_2 are the angles conjugate to I_1 and I_2, ω_1^0 and ω_2^0 are the zeroth order harmonic angular frequencies of the Morse and harmonic oscillators, respectively, $\omega_1^0\chi$ is the anharmonicity of the Morse oscillator, and $V(I_1, I_2, \theta_1, \theta_2)$ is the perturbation.[29] ($\hbar$ is set equal to 1 throughout the present paper.)

One can use a semiclassical matrix treatment[30] of the Fermi resonance problem for the Hamiltonian (2.1) in action-angle variables using, as a basis, the semiclassical wave functions[25,31]

$$\Psi^{(0)}_{n_1, n_2} = \frac{1}{2\pi}\exp[i(n_1\theta_1 + n_2\theta_2)] \tag{2.2}$$

for the angle representation of the zeroth order states $|n_1, n_2\rangle$, where $|n_1\rangle$ and $|n_2\rangle$ are the zeroth order eigenfunctions for the Morse and harmonic oscillators, respectively. The semiclassical action and angle operators[25,31] $\hat{I}_k$ and $\hat{\theta}_k$ in the angle representation acting on these wave functions yield

$$\hat{I}_k\,\Psi^{(0)}_{n_1, n_2} = I_k\Psi^{(0)}_{n_1, n_2} \text{ and } \hat{\theta}_k\Psi^{(0)}_{n_1, n_2} = \theta_k\Psi^{(0)}_{n_1, n_2}, \tag{2.3}$$

where I_k and θ_k are the classical variables. The I_k are related to the quantum numbers n_k by $I_k = n_k + \frac{1}{2}$ in the case of an oscillator, be it Morse or harmonic.

The semiclassical wave functions are useful because the matrix elements of the perturbation have the form of Fourier components

$$V_{lm}(\mathbf{I}) = \frac{1}{(2\pi)^2}\int_0^{2\pi}\int_0^{2\pi} V(\mathbf{I}, \boldsymbol{\theta})e^{-i(l\theta_1 + m\theta_2)}\,d\theta_1\,d\theta_2. \tag{2.4}$$

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If, e.g., the resonant interaction of the three states $|n, 0\rangle$, $|n-1,2\rangle$, and $|n-2, 4\rangle$ is considered, the Hamiltonian represented in this restricted basis has the following diagonal element H_{ii} for the zeroth order state i:

$$H_{ii} = (n_1^i + \tfrac{1}{2})\omega_1^0 - (n_1^i + \tfrac{1}{2})^2\omega_1^0\chi + (n_2^i + \tfrac{1}{2})\omega_2^0 + V_{00}(I_1^i, I_2^i), \tag{2.5}$$

where $(n_1^i, n_2^i) = (n, 0)$, $(n-1, 2)$, or $(n-2, 4)$. The diagonal perturbation term V_{00} is the $(l = 0, m = 0)$ Fourier component [Eq. (2.4)] evaluated at the actions $I_1^i = (n_1^i + \frac{1}{2})$, $I_2^i = (n_2^i + \frac{1}{2})$. The off-diagonal perturbation terms H_{ij} between the states i and j have the form

$$H_{ij} = \frac{1}{(2\pi)^2}\int_0^{2\pi}\int_0^{2\pi} e^{-i(n_1^i\theta_1 + n_2^i\theta_2)} \times V(\hat{\mathbf{I}}, \hat{\theta})e^{i(n_1^j\theta_1 + n_2^j\theta_2)}\, d\theta_1\, d\theta_2, \tag{2.6}$$

which is the Fourier component $V_{lm}(I_1^j, I_2^j)$ of the perturbation with $l = n_1^i - n_1^j$ and $m = n_2^i - n_2^j$. These semiclassical matrix elements are approximate and usually not exactly Hermitian since $H_{ij} = V_{lm}(I_1^j, I_2^j) \neq V_{lm}(I_1^i, I_2^i) = H_{ji}^*$. These matrix elements may be made Hermitian in an *ad hoc* way by evaluating them at any fixed value of the actions [e.g., at the resonance center (I_1^r, I_2^r)] or at an intermediate value of the actions between any pair of states i and j, using, for instance, the arithmetic mean $(I_k^i + I_k^j)/2$, where $(k = 1, 2)$.[32] The latter approximation has been used successfully in the calculation of transition dipole matrix elements for Morse[33] and other[34] oscillators and has been employed in a description of isolated avoided crossings.[24] Semiclassical expressions for the matrix elements are frequently simpler to compute than the corresponding quantum mechanical ones. The resulting semiclassical matrix may then be diagonalized numerically to find the eigenvalues and eigenvectors as is done for standard quantum mechanical matrices.

Comparison of the method presented in this section with exact quantum results are given later in Sec. V. In Sec. IV, we formulate a different semiclassical method based on a classical analysis and an effective Hamiltonian given in the next section.

III. THEORY: CLASSICAL RESONANCE TREATMENT

A. Treatment of the perturbation

The perturbation of these coupled oscillator systems is, as usual,[1–6] expanded in a complex-valued Fourier series

$$V(I_1, I_2, \theta_1, \theta_2) = \sum_{l=-\infty}^{\infty}\sum_{m=-\infty}^{\infty} V_{lm}(I_1, I_2)e^{i(l\theta_1 + m\theta_2)}, \tag{3.1}$$

where $V_{lm}(I_1, I_2)$ is given by Eq. (2.4). The $V_{00}(I_1, I_2)$ Fourier component is the analog of a quantum mechanical "diagonal" first order perturbation correction. These corrections have been discussed previously[11,13,35,36] within the context of stretch–bend interactions in molecules and are found to modify the zeroth order oscillator frequencies, sometimes appreciably. To include the effect of this perturbation, a new zeroth order Hamiltonian may be defined as

$$H^{(0)}(I_1, I_2) = I_1\omega_1^0 - I_1^2\omega_1^0\chi + I_2\omega_2^0 + V_{00}(I_1, I_2). \tag{3.2}$$

(This Hamiltonian is the same as that in Ref. 7, except that the V_{00} term is taken as a constant there, namely, its value at certain zeroth order "resonant actions" described later in the Results section.)

Hamilton's equations for the angle variables, based on $H^{(0)}$, yield

$$\dot{\theta}_1 = \omega_1(I_1, I_2) = \omega_1^0 - 2I_1\omega_1^0\chi + \partial V_{00}(I_1, I_2)/\partial I_1, \tag{3.3}$$

$$\dot{\theta}_2 = \omega_2(I_1, I_2) = \omega_2^0 + \partial V_{00}(I_1, I_2)/\partial I_2, \tag{3.4}$$

and that I_1 and I_2 are constants of the motion for $H^{(0)}$ since this zeroth order Hamiltonian contains no angle variables. Since I_1 and I_2 are functions of E_1^0 and E_2^0 (the zeroth order energies of the Morse and harmonic oscillators, respectively), Eqs. (3.3) and (3.4) may be rewritten as

$$\omega_1(I_1, I_2) = (\omega_1^0 - 2I_1\omega_1^0\chi)f, \tag{3.5}$$

$$\omega_2(I_1, I_2) = \omega_2^0\, g, \tag{3.6}$$

where

$$f = [1 + \partial V_{00}(E_1^0, E_2^0)/\partial E_1^0],$$
$$g = [1 + \partial V_{00}(E_1^0, E_2^0)/\partial E_2^0]. \tag{3.7}$$

When the angle-dependent perturbation terms from Eq. (3.1) are included in the equations of motion, the actions I_1 and I_2 are no longer constants of the motion. In the presence of a nonlinear resonance, these actions slowly oscillate near or about their value at the resonance center[1–6] (I_1^r, I_2^r). If the factors f and g in Eqs. (3.5) and (3.6) are approximated as the "average" constants f^r and g^r [given by Eq. (3.7) evaluated at the resonance center], one obtains an *effective* zeroth order Hamiltonian

$$H_0(I_1, I_2) = I_1\omega_1 - I_1^2\omega_1\chi + I_2\omega_2, \tag{3.8}$$

where ω_1, $\omega_1\chi$, and ω_2 denote $\omega_1^0 f^r$, $\omega_1^0\chi f^r$, and $\omega_2^0 g^r$, respectively. These effective oscillator parameters are the classical analog to those obtained empirically from the analysis of experimental absorption spectra (cf. discussion in Refs. 11, 13, 35, and 36).

The particular classical resonance to be examined here is the 1:2 resonance defined by the condition

$$\omega_1(I_1^r) \simeq 2\omega_2, \tag{3.9}$$

where

$$\omega_1(I_1^r) = (\partial H_0/\partial I_1)_{I_1 = I_1^r} = \omega_1 - 2I_1^r\,\omega_1\chi \tag{3.10}$$

is the (modified) nonlinear angular frequency of the Morse oscillator at the center of the resonance. The use of these modified oscillator frequencies yields values for the resonant actions different from those predicted by the zeroth order Hamiltonian alone [Eq. (2.1) with $V = 0$]. An accurate approximate method for finding the values of the resonant actions I_1^r and I_2^r, a nonlinear problem, is given in Appendix A.

The resonance condition (3.9) prompts a canonical transformation of the zeroth order action-angle variables in which there is now a "slow" variable α (low frequency coordinate)[1–7]:

$$2\alpha = \theta_1 - 2\theta_2 + \delta, \quad \beta = \theta_2, \tag{3.11}$$

$$I_\alpha = 2I_1, \quad I_\beta = 2I_1 + I_2. \tag{3.12}$$

The δ in Eq. (3.11) is chosen to simplify later the final expression (3.16) and to make the canonical transformation used in

Ref. 7 suitable for any general perturbation.[29]

The transformation (3.12) applied to Eq. (3.8) yields the effective zeroth order Hamiltonian in the new action variables I_α and I_β as

$$H_0(I_\alpha, I_\beta) = I_\alpha \Omega - \omega_1 \chi' I_\alpha^2 + I_\beta \omega_2, \qquad (3.13)$$

where

$$\Omega = (\omega_1 - 2\omega_2)/2, \; \chi' = \chi/4. \qquad (3.14)$$

As is standard in the theory of classical resonances,[1–6] all highly oscillating terms in the Fourier expansion (3.1) are omitted, leaving the terms appropriate to the 1:2 resonance of the form $\exp[\pm ik(\theta_1 - 2\theta_2)]$, where k equals (1, 2, ...), in addition to the V_{00} term discussed earlier. As usual,[1–6] only the lowest nonzero k term is then retained, allowing Eq. (3.1) to be written approximately as

$$V(I_1, I_2, \theta_1, \theta_2) \simeq 2\mathrm{Re}\{ V_{1-2}(I_1, I_2) e^{i(\theta_1 - 2\theta_2)} \} \qquad (3.15)$$

when the lowest term is $k = 1$. (In other cases, the $k = 1$ term may be zero and a term for $k > 1$ is required.) Since the perturbation in Eq. (2.1) is real, the relation $V_{lm}^* = V_{-l-m}$ was used in obtaining Eq. (3.15). If $2V_{1-2}$ is written as $V_0 e^{i\gamma}$, with $V_0 \equiv 2|V_{1-2}|$, then Eq. (3.15) may be written as

$$V \simeq - V_0 \cos 2\alpha \qquad (3.16)$$

when one chooses δ in Eq. (3.11) to equal $\gamma + \pi$ to obtain the negative sign in Eq. (3.16).

B. Classical resonance Hamiltonian

Equations (3.13) and (3.16), evaluated at the resonant actions (I_1^r, I_2^r), yield a resonance Hamiltonian[1–6] for the 1:2 resonance[37]

$$H_R = \omega_1 \chi' I_\alpha^2 - I_\alpha \Omega + V_0 \cos 2\alpha = E_R. \qquad (3.17)$$

The total Hamiltonian H in Eq. (2.1) is then approximately given by

$$H_{\text{eff}} = I_\beta \omega_2 - H_R, \qquad (3.18)$$

which will henceforth be termed the "effective" Hamiltonian. Since I_β is a constant of the motion in this approximation, $I_\beta \omega_2$ is a constant. The phase plane behavior of Eq. (3.17) is discussed in Appendix B.

From Eqs. (3.9), (3.10), and (3.14), the resonant action I_1^r is given by $\Omega / \omega_1 \chi$. Since, semiclassically, I_1 equals $(n_1 + \frac{1}{2})$, a resonant Morse "quantum number" n_1^r may be defined by

$$n_1^r = (\Omega / \omega_1 \chi) - \tfrac{1}{2}. \qquad (3.19)$$

In general, n_1^r is not an integer.

The two-state and uniform approximation solutions introduced in the next section are based on the effective Hamiltonian (3.18).

IV. THEORY: SEMICLASSICAL METHODS BASED ON H_{eff}

A. Two-state solution

Introduction of the action operator[25,31] $\hat{I}_\alpha = (1/i) d/d\alpha + 1$ into the classical resonance Hamiltonian [Eq. (3.17)] yields the semiclassical Schrödinger equation[7]

$$\frac{d^2\psi}{d\alpha^2} - 2i(\xi - 1) \frac{d\psi}{d\alpha} + [A - 2q \cos 2\alpha] \psi = 0, \qquad (4.1)$$

with α being in the interval $(0, \pi)$ and

$$\xi = 2\Omega / \omega_1 \chi = 2n_1^r + 1,$$

$$A = [4(\Omega + E_R)/\omega_1 \chi] - 1,$$

$$q = 2V_0/\omega_1 \chi. \qquad (4.2)$$

For the model oscillator system considered in the present paper, the near 1:2 resonance condition can lead to a near degeneracy between the zeroth order states $|n, 0\rangle$ and $|n - 1,2\rangle$ for some value of n. In many cases of experimental interest, these two states may be the most important states involved in a Fermi resonance. For this reason, and because it is desirable to obtain a simple analytic solution, a two-state solution for Eq. (4.1) of the form

$$\psi \simeq a\psi_n^{(0)} + b\psi_{n-1}^{(0)} \qquad (4.3)$$

is considered first, where a and b are constants to be determined and where $\psi_n^{(0)}$ equals $\pi^{-1/2} \exp[2in\alpha]$ and $\psi_{n-1}^{(0)}$ equals $\pi^{-1/2} \exp[2i(n - 1)\alpha]$ (e.g., Refs. 25 and 31). When Eq. (4.1) is diagonalized in this basis, the eigenvalues are given by

$$A^{\pm} = A_0 \pm \tfrac{1}{2}(4q^2 + d^2)^{1/2}, \qquad (4.4)$$

where

$$A_0 = - [4(n_1^r)^2 - \nu^2(n) + 2\nu(n) - 2], \qquad (4.5)$$

$$d = 4[1 - \nu(n)], \; \nu(n) = 2(n - n_1^r), \qquad (4.6)$$

and q is given in Eq. (4.2). In terms of Eq. (3.19), this $\nu(n)$ is twice the "distance" of the eigenstate with quantum number $n_1 = n$ from the center of the resonance n_1^r.

The approximate splitting ΔE of these two eigenstates by the Fermi resonance is therby found from Eqs. (4.2) and (4.4)–(4.6) to be

$$\Delta E = \omega_1 \chi' (4q^2 + d^2)^{1/2}, \qquad (4.7)$$

and the two approximate eigenfunctions are[38]

$$\psi^+ = a\psi_n^{(0)} + b\psi_{n-1}^{(0)}, \qquad (4.8)$$

$$\psi^- = - b\psi_n^{(0)} + a\psi_{n-1}^{(0)}, \qquad (4.9)$$

where

$$a = [(\Gamma + d)/2\Gamma]^{1/2},$$

$$b = [(\Gamma - d)/2\Gamma]^{1/2},$$

$$\Gamma = (4q^2 + d^2)^{1/2}. \qquad (4.10)$$

Calculations employing Eqs. (4.7)–(4.10) involve determining n_1^r from Eq. (3.19) and q from Eq. (4.2), both of which are readily obtained.

The two-state solution presented in this section is not, in general, the same as a semiclassical 2 × 2 matrix diagonalization using the method of Sec. II. The difference between these two methods results from the use in the present section of a resonance Hamiltonian (3.17) based on the effective Hamiltonian (3.18), while the method of Sec. II is based directly on the original Hamiltonian (2.1).

B. Uniform semiclassical approximation (USC)

A uniform approximation for the present coupled oscillator system is obtained by converting Eq. (4.1) to the standard Mathieu equation.[7,25] A function $F(\alpha)$, defined by[25]

$$F(\alpha) = \exp[i(1-\xi)\alpha]\psi(\alpha), \tag{4.11}$$

is used for this purpose: It satisfies Mathieu's equation[39(a)]

$$\frac{d^2F(\alpha)}{d\alpha^2} + [a_\nu - 2q\cos 2\alpha]F(\alpha) = 0, \tag{4.12}$$

where

$$a_\nu = (\xi-1)^2 + A = 4[(\Omega/\omega_1\chi)^2 + E_R/\omega_1\chi], \tag{4.13}$$

and ν is the order of the Mathieu equation.[39(a),40] Equation (4.13) is rearranged to give the energy of the rotor Hamiltonian H_R as

$$E_R = a_\nu\omega_1\chi' - (n_1^r + \tfrac{1}{2})\Omega. \tag{4.14}$$

Semiclassical expressions for the Fermi resonance splittings between the eigenstates of the Hamiltonian may be obtained from Eq. (4.14). In general, one is concerned with a resonant progression of nearly degenerate zeroth order states $|n_1,n_2\rangle$ for the zeroth order Hamiltonian (2.1): $|n,0\rangle$, $|n-1,2\rangle$, $|n-2,4\rangle$, etc. The action I_β from Eq. (3.12) semiclassically equals $2n_1 + n_2 + 3/2$ and remains constant along this progression. For any two states of orders ν_1 and ν_2 involved in this resonant progression, the splittings are given from Eq. (4.14) as

$$|\Delta E_{1-2}| = |a_{\nu_1} - a_{\nu_2}|\omega_1\chi', \tag{4.15}$$

where[40]

$$\nu_i \equiv \nu(n_1^{(i)}) = 2(n_1^{(i)} - n_1^r) \quad (i = 1, 2). \tag{4.16}$$

For example, one uses $n_1^{(1)} = n$ and $n_1^{(2)} = n-1$ in calculating the splitting between the nearly degenerate states $|n,0\rangle$ and $|n-1,2\rangle$. The characteristic values a_ν of the Mathieu equation may be obtained from expansions[39(b)] (if q is small), from tables,[41,42] or from semiclassical phase integral arguments.[43]

When the relevant dipole moment operator is assumed to be a function of the C–H stretching coordinate only, the overlap (squared) of the zeroth order pure local mode state $|n,0\rangle$ with the actual eigenstates describes the Fermi resonance intensity sharing,[11,13,35,44] and so is of interest. When q is small enough, an expansion[39(c),42] for the solution $F(\alpha)$ of the Mathieu equation (4.12) may be used. From the definition of the wave function $\psi(\alpha)$ in Eq. (4.11), and using Eq. (4.2) for ξ and the expression for ν in Ref. 40, the unnormalized wave function may be written as

$$\psi_{n_1}(\alpha) \sim e^{2in_1\alpha} - \frac{q}{4}\left[\frac{e^{2i(n_1+1)\alpha}}{[\nu(n_1)+1]} - \frac{e^{2i(n_1-1)\alpha}}{[\nu(n_1)-1]}\right] + \frac{q^2}{32}\left[\frac{e^{2i(n_1+2)\alpha}}{[\nu(n_1)+1][\nu(n_1)+2]} + \frac{e^{2i(n_1-2)\alpha}}{[\nu(n_1)-1][\nu(n_1)-2]}\right] + \cdots. \tag{4.17}$$

Equation (4.17) properly normalized (cf. Appendix C) yields the following formulas for the overlaps of the zeroth order $|n,0\rangle$ local mode state with the eigenstates of $|n,0\rangle$, $|n-1,2\rangle$, and $|n-2,4\rangle$ parentage:

$$\int_0^\pi \psi_n^{(0)*}(\alpha)\psi_n(\alpha)d\alpha = \sqrt{\pi}N_n, \tag{4.18}$$

$$\int_0^\pi \psi_n^{(0)*}(\alpha)\psi_{n-1}(\alpha)d\alpha = -\sqrt{\pi}N_{n-1}\left[\frac{q}{4[\nu(n-1)+1]}\right], \tag{4.19}$$

and

$$\int_0^\pi \psi_n^{(0)*}(\alpha)\psi_{n-2}(\alpha)d\alpha = \sqrt{\pi}N_{n-2}\left[\frac{q^2}{32[\nu(n-2)+1][\nu(n-2)+2]}\right]. \tag{4.20}$$

Here, $\psi_n^{(0)}(\alpha)$ denotes $\pi^{-1/2}\exp[2in\alpha]$ and is the properly normalized zeroth order local mode state $|n,0\rangle$, and ψ_m $(m = n, n-1, n-2)$ is the approximate normalized eigenstate based on Eq. (4.17). It is also of interest to determine the overlap of the zeroth order state $|n-2,4\rangle$ with the eigenstate $\psi_{n-1}(\alpha)$. This overlap is given by

$$\int_0^\pi \psi_{n-2}^{(0)*}(\alpha)\psi_{n-1}(\alpha)d\alpha = \sqrt{\pi}N_{n-1}\left[\frac{q}{4[\nu(n-1)-1]}\right], \tag{4.21}$$

where $\psi_{n-2}^{(0)}$ denotes $\pi^{-1/2}\exp[2i(n-2)\alpha]$. At or very close to the actual avoided crossing point between two states, some of overlaps in Eqs. (4.18)–(4.21) are not suitable for computation and a different expression is used.[45]

V. APPLICATION

A. The model Hamiltonian

As an application, we consider a model Hamiltonian for a single C–H stretch interacting with a bending mode involving the C–H bond in a dihalomethane molecule. In curvilinear coordinates,[46] such a Hamiltonian may be phenomenologically written as[46(a)]

$$H = \frac{1}{2\mu}P_R^2 + D[1-\exp(-aR)]^2 + \frac{1}{2}(P^2 + \omega_2^{02}Q^2) - \frac{\lambda}{2}RP^2, \tag{5.1}$$

where R and Q are, respectively, the curvilinear displacement coordinates for the C–H stretch and for the bend, P_R and P are their conjugate momenta, μ is the reduced mass of the C–H bond, D and a are the C–H Morse parameters, λ is a coupling constant, and ω_2^0 is the zeroth order angular frequency of the bending mode. The constant λ generally has a complicated dependence[13,46(a)] on the atomic masses, equilibrium bond angles and lengths, and the bending normal coordinate[47] coefficients L_{ij}^{-1}. This coupling constant will be treated as a variable parameter in the present paper.

For energies in the vicinity of the $|3,0\rangle$ state, it is assumed in this model that only one of the C–H local mode vibrations need be considered.[35] For these energies, the quantum mechanical eigenvalues for the symmetric and asymmetric combinations[35] of local modes in the dihalomethanes become virtually degenerate, and hence the two CH's in the molecule have negligible direct coupling to each other.

The Fourier expansion for the displacement coordinate R of a Morse oscillator is given in Ref. 48. Since the bending mode is a harmonic oscillator [cf. Eq. (5.1)], a suitable transformation to action-angle variables is to set Q and P equal to $(2I_2/\omega_2^0)^{1/2}\sin\theta_2$ and $(2I_2\omega_2^0)^{1/2}\cos\theta_2$, respectively. This transformation yields the (1, -2) and (0,0) Fourier components

$$V_{1-2}(I_1,I_2) = \frac{I_2\omega_2^0\lambda}{4a}\left(\frac{1-(1-y)^{1/2}}{y^{1/2}}\right) \tag{5.2}$$

and

$$V_{00}(I_1,I_2) = -\frac{I_2\omega_2^0\lambda}{2a}\ln\left(\frac{1+(1-y)^{1/2}}{2(1-y)}\right). \tag{5.3}$$

where $y = E_1^0/D$, and E_1^0 and D are the energy and dissociation energy of the zeroth order Morse oscillator, respectively. These expressions may be used in Eqs. (2.5), (2.6), (3.7), and (3.16).

B. Calculations

Calculations were performed for the resonant interaction of the $|3,0\rangle$, $|2,2\rangle$, and $|1,4\rangle$ states for the model Hamiltonian (5.1). The values used in Eqs. (5.1)–(5.3) for ω_1^0, $\omega_1^0\chi$, D and a, obtained from the data of of Ref. 35, were 3143, 63.2, 39 076 cm^{-1}, and 0.988 a.u., respectively. The zeroth order bend frequency ω_2^0 was not determined there, but is estimated to be ~ 1400 cm^{-1}. The coupling parameter λ was allowed to vary in the present calculations to yield quantum off-diagonal matrix elements between the zeroth order states $|3,0\rangle$ and $|2,2\rangle$ in the range of 5–30 cm^{-1}. The resonant actions I_1^r and I_2^r used in evaluating the USC and two-state solutions were determined by the method described in Appendix A.

The Fermi resonant splittings and overlaps were calculated as a function of λ using the three semiclassical methods presented in the previous sections. For the two-state and 3×3 semiclassical matrix treatment, calculations were performed using both the resonant and mean actions (cf. Sec. II) to evaluate the 3×3 semiclassical off-diagonal matrix elements and to obtain q for the two-state calculation (Sec. IV A). In all cases, diagonalizations of quantum mechanical 2×2, 3×3, and 78×78 matrices were performed for comparison.

C. Results

The calculated splittings between the eigenstates of $|3,0\rangle$ and $|2,2\rangle$ parentage and between the eigenstates of $|3,0\rangle$ and $|1,4\rangle$ parentage are shown in Tables I and II, respectively. In Table III, the exact and the present uniform semiclassical (USC) results are compared with those obtained by the method of Ref. 7 (USC^0). As in Ref. 7, the resonant actions for the USC^0 calculation were found using the zeroth order frequencies, i.e., using Eq. (A1) instead of Eq. (3.9). The "diagonal" perturbation term V_{00} was then taken, in the USC^0 method, as a constant value evaluated at these zeroth order resonant actions. Also shown in Table III, for comparison with and for analyzing the method of Ref. 7, are results from a quantum mechanical 3×3 matrix diagonalization method ($3\times 3^{Q^0}$) having the diagonal first order perturbation corrections taken as a constant (e.g., zero). In addition, the relative overlaps of the zeroth order states $\psi_i^{(0)}$ with the actual eigenstates ψ_j, defined as $|\langle\psi_i^{(0)}|\psi_j\rangle|/|\langle\psi_i^{(0)}|\psi_i\rangle|$, are given in Table IV for two values of λ. For the various two-state calculations, the calculated splittings between the eigenstates of $|3,0\rangle$ and $|2,2\rangle$ parentage are given in Table V as a function of λ.

TABLE I. Splittings (in cm^{-1}) between states of $|3,0\rangle$ and $|2,2\rangle$ parentage.

λ (a.u.)	78×78^Q	3×3^Q	$3\times 3^{sc^a}$	$3\times 3^{sc^b}$	USC^c
0.037	31.0	31.1	31.3	31.8	33.4
0.077	30.8	31.1	31.9	33.5	35.5
0.121	35.4	35.8	37.4	40.1	41.5
0.170	43.1	43.8	46.1	49.2	49.7
0.227	53.0	54.4	57.4	59.8	59.1

[a] Calculated with Fourier components [Eq. (2.6)] evaluated at mean actions for each pair of states.

[b] Calculated with Fourier components [Eq. (2.6)] evaluated at the resonant actions.

[c] Uniform semiclassical calculation (cf. Sec. IV B) based on $H_{\rm eff}$ [Eq. (3.18)].

TABLE II. Splittings (in cm^{-1}) between states of $|3,0\rangle$ and $|1,4\rangle$ parentage.

λ (a.u.)	78×78^Q	3×3^Q	$3\times 3^{sc^a}$	$3\times 3^{sc^b}$	USC^c
0.037	61.9	62.3	62.2	61.2	64.1
0.077	69.8	71.5	71.2	66.9	73.3
0.121	78.0	82.2	81.7	71.9	82.3
0.170	87.8	95.7	95.1	77.4	92.2
0.227	100.4	113.8	113.2	84.1	103.1

[a] Calculated with Fourier components [Eq. (2.6)] evaluated at mean actions for each pair of states.

[b] Calculated with Fourier components [Eq. (2.6)] evaluated at the resonant actions.

[c] See footnote c of Table I.

VI. DISCUSSION

The quantum 3×3 and converged (78×78) results are seen from Tables I, II, and IV to be in good agreement (except at high λ where the discrepancy in Table II is ~ 10 cm^{-1}). Thus, the present Fermi resonance is well characterized by considering only the interaction of the three zeroth order states $|3,0\rangle$, $|2,2\rangle$, and $|1,4\rangle$. For the splittings, the 3×3 and USC semiclassical methods in Tables I and II yield results comparable to each other and in reasonable agree-

TABLE III. Calculated splittings (in cm^{-1}) of $|3,0\rangle$ and $|2,2\rangle$ states by exact quantum, zero order uniform semiclassical (USC^0),[a] zero order $3\times 3^{Q^0}$ quantum,[b] and effective uniform semiclassical (USC)[c] methods.

λ (a.u.)	78×78^Q	$3\times 3^{Q^0}$	USC^0 [Ref. 7]	USC (Present)
0.037	31.0	38.3	38.7	33.4
0.077	30.8	44.4	45.7	35.5
0.121	35.4	53.7	55.9	41.5
0.170	43.1	65.7	68.1	49.7
0.227	53.0	80.6	> 80[d]	59.1

[a] Using zeroth order frequencies [cf. Eq. (2.1)] to calculate I_1^r, I_2^r, ν, and q.

[b] Calculated by setting all diagonal perturbations equal to zero in the 3×3 quantum matrix.

[c] See footnote c of Table I.

[d] This value is estimated from the tables given in Ref. 41. The values of q there go to 2.5 whereas q equals 2.54 for the present USC^0 method (with $\lambda = 0.227$).

TABLE IV. Relative overlaps.[a]

λ (a.u.)	Rel. overlap[a]	78×78^Q	3×3^Q	$3\times3^{SC^b}$	USC[c]
0.037					
	2:3	0.154	0.154	0.163	0.205
	1:3	0.008	0.008	0.008	0.007
	2:1	0.100	0.099	0.100	0.065
0.077					
	2:3	0.347	0.344	0.359	0.507
	1:3	0.029	0.028	0.030	0.023
	2:1	0.189	0.186	0.186	0.111

[a] Relative overlap $j{:}i$ is defined as $|\langle\psi_i^{(0)}|\psi_j\rangle|/|\langle\psi_i^{(0)}|\psi_i\rangle|$, where $|\psi_{i(j)}\rangle$ is the eigenstate of zeroth order $|\psi_{i(j)}^{(0)}\rangle$ parentage. States 3, 2, and 1 are defined as $|3, 0\rangle$, $|2, 2\rangle$, and $|1, 4\rangle$, respectively.

[b] Calculated with Fourier components [Eq. (2.6)] evaluated using mean actions for each pair of states.

[c] Present USC method (see footnote c of Table I).

ment with the quantum mechanical values. The results shown in Tables I–V indicate that, of the semiclassical two-state, 3×3, and USC methods, the 3×3 one using mean actions in the evaluation of the Fourier components appears to be the most accurate for calculating *both* the splittings and the relative intensities. In addition, the results in Table III for the USC^0 method of Ref. 7 show that the nonconstancy of the diagonal perturbation term V_{00} has an appreciable effect for the system studied.

Of the two-state calculations, the quantum 2×2 values [based on the original Hamiltonian (5.1)] and the semiclassical two-state ones based on $H_{\rm eff}$ [Eq. (3.18)] and employing mean actions in the calculation of the Fourier components are in better agreement than those based on $H_{\rm eff}$ and resonant actions. Diagonalizations of semiclassical 2×2 matrices were also performed using the method of Sec. II. These results were essentially the same as those in Table V based on $H_{\rm eff}$ and mean actions. Thus, for the present model Hamiltonian (5.1), the two-state (Sec. IV A) and 2×2 (Sec. II) methods are essentially equivalent, although this is not necessarily the case in general.

The 3×3 (and 78×78) basis set calculations show that the $|1, 4\rangle$ state mixes significantly with the other zeroth order states. Thus, the two-state treatments are incorrect for determining the eigenfunctions, and hence the overlaps (relative intensities), although they yield reasonable values for the eigenvalues (splittings) in Table V.

The semiclassical matrix calculations in Tables I–V indicate the principal weakness of the uniform approximation.

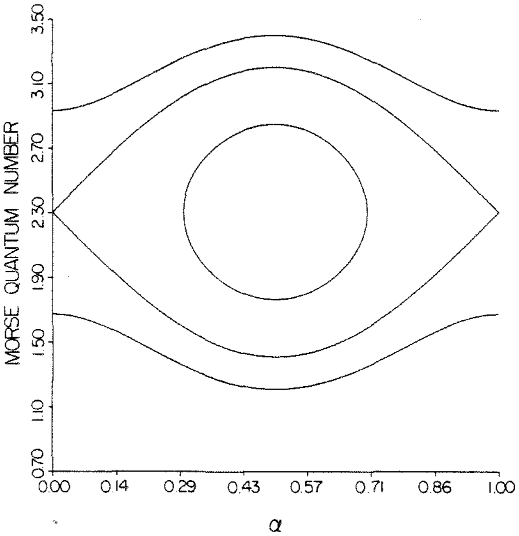

FIG. 1. An (n_1, α) phase plane portrait of the rotor Hamiltonian (B2) for the model Hamiltonian (5.1). The angle variable α is given in fractions of π.

In the derivation of the Mathieu equation and its corresponding solutions, q, and hence the $1, -2$ Fourier component, was approximated as a constant, i.e., it was evaluated at the resonance center. This approximation assumes, in effect, that all the matrix elements such as $\langle n, 0|V|n-1, 2\rangle$ and $\langle n-1, 2|V|n-2, 4\rangle$ have the same average value. The semiclassical matrix technique employing mean actions for the evaluation of individual matrix elements H_{ij} avoids this restriction of constant Fourier components and thus obtains better agreement with the purely quantum treatments in the general case. Nevertheless, the USC is useful because, when q is small and expansions[39(b)–39(c)] may be used for a_v and $F(\alpha)$ of the Mathieu equation, it yields approximate analytic solutions. These solutions may also provide some additional physical insight when coupled with the classical analysis presented in Sec. III and Appendix B.

As an example of this latter point, one may consider the dependence of the Fermi resonances on the classical resonance width [Eq. (B3)]. Examination of the classical (n_α, α) surfaces of section in Figs. 1 and 2 for the Hamiltonian (5.1) with $q = 0.8$ shows that the states $|3, 0\rangle$ and $|2, 2\rangle$, with $n_1 = 3$ and $n_1 = 2$, are within the width of the resonance.

TABLE V. Splittings (in cm^{-1}) between states of $|3, 0\rangle$ and $|2, 2\rangle$ parentage using two-state solutions.

λ (a.u.)	78×78^Q	2×2^Q	Two-state$^{SC^a}$	Two-state$^{SC^b}$
0.037	31.0	30.2	33.2	32.3
0.077	30.8	28.4	35.4	32.3
0.121	35.4	32.8	42.0	37.3
0.170	43.1	43.1	51.5	47.0
0.227	53.0	58.6	62.7	61.3

[a] Calculated using the method of Sec. IV A based on the effective Hamiltonian $H_{\rm eff}$ [Eq. (3.18)] and using resonant actions in the evaluation of q [Eq. (4.2)].

[b] Calculated using the method of Sec. IV A based on the effective Hamiltonian $H_{\rm eff}$ [Eq. (3.18)] and using the mean actions between the states $|3, 0\rangle$ and $|2, 2\rangle$ in evaluating q [Eq. (4.2)].

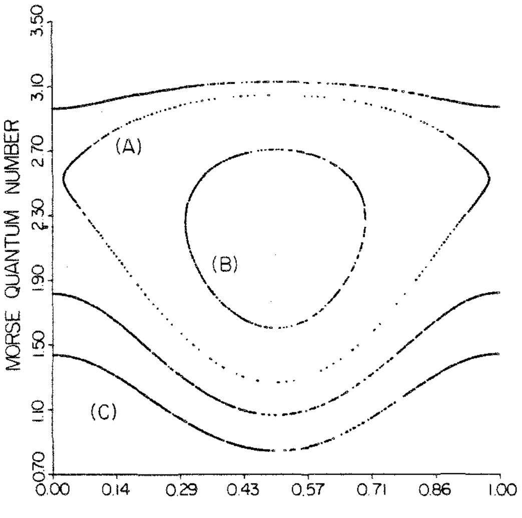

FIG. 2. An (n_1, α) surface of section for the Hamiltonian (5.1) taken for $P = 0$, $Q > 0$, and $\lambda = 0.077$ a.u. $(q = 0.8)$. Trajectories labeled (A), (B), and (C) are for initial condition corresponding to $n_1 = 3$, $n_1 = 2$, and $n_1 = 1$, respectively. All trajectories have $I_\beta = 2n_1 + n_2 + 3/2 = 7.5$. The angle variable α is given in fractions of π.

Hence, one would expect significant mixing for these states, and this is indeed found to be the case (cf. Table IV for $\lambda = 0.077$). On the other hand, the state $|1, 4\rangle$, with $n_1 = 1$, is well outside the classical resonance zone and does not mix strongly with the $|3, 0\rangle$ or $|2, 2\rangle$ states. One obtains similar conclusions about the degree of state mixing from purely quantum mechanical arguments by comparing the coupling elements H_{ij} to the diagonal energy differences $E_i - E_j$. However, when many states are involved, the semiclassical phase plane picture allows one to estimate the degree of coupling by a single quantity, the width of the resonance [Eq. (B3)].

VII. CONCLUDING REMARKS

The semiclassical methods presented in this paper all involve the use of the Fourier components of the perturbation, some of which exist in analytic form[33,34,48] or are straightforward to evaluate in the typical case by numerical quadrature. For the calculation described in Sec. V, the semiclassical matrix elements (i.e., Fourier components) were analytic and could be evaluated by the use of a hand calculator. The quantum mechanical Morse matrix elements of, for instance r or r^2, while analytic,[49] are more complicated to compute. The semiclassical techniques can therefore be particularly useful when one wishes to use relatively simple methods for comparison with experimental absorption spectra: In actual experiments, the rovibrational structure may only be partially resolved (e.g., Ref. 35), and so a quick and approximate estimation of the Fermi resonance splittings and relative intensities can be helpful in fitting the data to various models.

ACKNOWLEDGMENT

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APPENDIX A: APPROXIMATE EVALUATION OF THE RESONANT ACTIONS

The solution of Eqs. (3.9) and (3.12) to calculate the resonant actions I_1^r and I_2^r involves the determination of the angle-independent effective oscillator frequencies from Eqs. (3.5)–(3.7). One recalls that these frequencies are nonlinearly dependent on the resonant actions I_1^r and I_2^r, so the following approximate root finding procedure was used to determine them: (1) A value for the zeroth order resonant action $I_1^{r^0}$ was determined from the zeroth order resonance condition

$$\omega_1^0 - 2I_1^{r^0}\omega_1^0\chi = 2\omega_2^0, \tag{A1}$$

and $I_2^{r^0}$ was found from Eq. (3.12) (one recalls that I_β is taken as a constant of the motion). (2) The zeroth order values of $I_1^{r^0}$ and $I_2^{r^0}$ were used to calculate the constants g^{r^0} and f^{r^0} from Eq. (3.7). (3) Approximate values for I_1^r and I_2^r were calculated from Eqs. (3.9) and (3.12) using g^{r^0} and f^{r^0} in determining the frequencies [Eqs. (3.5) and (3.6)] for the effective zeroth order Hamiltonian [Eq. (3.8)]. If desired, this procedure may then be iterated. However, for the model Hamiltonian given by Eq. (5.1), one iteration was sufficient to determine I_1^r and I_2^r to within 5% of the exact numerically calculated values and was the procedure used in the present paper.

APPENDIX B: PHASE PLANE BEHAVIOR OF THE RESONANCE HAMILTONIAN

The analysis of the (I_α, α) phase plane behavior for the resonance Hamiltonian [Eq. (3.17)] is standard. For a given energy E_R of the α motion in Eq. (3.17), I_α is given by

$$I_\alpha = I_\alpha^r \pm 2[\Omega^2 + \omega_1\chi(E_R - V_0 \cos 2\alpha)]^{1/2}/\omega_1\chi, \tag{B1}$$

where, from Eqs. (3.9), (3.10), (3.12), and (3.14), I_α^r denotes $2\Omega/\omega_1\chi$. Since $I_\alpha = 2I_1$ and, semiclassically, $I_1 = (n_1 + \frac{1}{2})$, a phase plane portrait for the Morse "quantum number" n_1 may be generated from Eq. (B1) as a function of α:

$$n_1 = n_1^r \pm [\Omega^2 + \omega_1\chi(E_R - V_0 \cos 2\alpha)]^{1/2}/\omega_1\chi, \tag{B2}$$

where n_1^r is given by Eq. (3.19).

Figure 1 shows an (n_1, α) phase plane plot on the interval $(0, \pi)$ for the three different types of motion of Eq. (B2). This idealized behavior for the full Hamiltonian (2.1) is identical to that for a pendulum or "rotor" Hamiltonian.[1–6] The curves that pass through a single point at $\alpha = 0$ and π correspond to the separatrix trajectory. The phase plane curves in Fig. 1 above and below the separatrix correspond to "rotations" in the (n_1, α) space. These are motions in which the action $I_1 = I_\alpha/2$ (or the quantum number $n_1 = I_1 - \frac{1}{2}$) varies only slightly over a cycle of motion. Thereby, there is relatively little classical energy transfer between the Morse and harmonic oscillators. The phase plane curves inside the separatrix represent motions in which n_1 varies greatly over a cycle of motion and thus reflects a large transfer of energy. Such a large variation in n_1 is expected for any initial n_1 within the resonance width

$$\Delta n_1 = \Delta I_1 = 2(2V_0/\omega_1\chi)^{1/2} = 2\sqrt{q}, \tag{B3}$$

defined by the separatrix trajectory.[1–6] The width of the resonance increases with increasing coupling element V_0 and with decreasing effective anharmonicity $\omega_1\chi$ of the Morse oscillator. The less the anharmonicity, the less the states in the progression $|n, 0\rangle$, $|n-1,2\rangle$, etc. pass out of resonance.

In Fig. 2, an (n_1, α) surface of section (e.g., Ref. 17) of the Hamiltonian (5.1) is shown for actual classical trajectories having initial conditions corresponding to $I_B = 7.5$ and $n_1 = 1$ to 3.6. For this model Hamiltonian, this plot shows the "rotor" or "pendulum" behavior, although it is somewhat distorted from Fig. 1. For larger perturbations, the surface of section becomes increasingly distorted from the idealized behavior shown in Fig. 1 (cf. discussion in Ref. 25).

A few remarks on the rate of classical and quantum energy exchange among the oscillators are perhaps in order. For a classical resonance Hamiltonian [e.g., Eq. (3.17)], there is extensive classical energy exchange when the system is within the cosine well. (I_α changes considerably during the latter motion.) The frequency of the oscillatory energy exchange is then obtained by expanding the cos 2α term about its minimum and is found to be porportional to the square root of the coefficient of the cosine term in Eq. (3.17) [i.e., it is proportional to the square root of the $(1, -2)$ Fourier component of the perturbation]. Quantum mechanically, this *type* of energy exchange is expected to be approached when the initial wave packet consists of many eigenstates. When there are only two or three states, as in the present analysis, the frequency of energy exchange between zeroth order states is, in the case of an exact zeroth order degeneracy, proportional to the coupling matrix elements between the states. In the semiclassical limit, these matrix elements correspond to the Fourier components of the cosine perturbation term in Eq. (3.17). As a result, the quantum energy exchange frequency may be thought of, in the case of an exact resonance, as being proportional to the coefficient rather than, as in the purely classical case, the square root of the coefficient of the cosine function. Thus, it is expected that, in any wave packet analysis, one must distinguish between the classical (i.e., many quantum states) and highly quantum (i.e., few quantum states) cases.

APPENDIX C: NORMALIZATION OF THE WAVE FUNCTION (4.17)

A normalized wave function $N_{n_1}\psi_{n_1}(\alpha)$ satisfies

$$N_{n_1}^2 \int_0^\pi \psi_{n_1}^*(\alpha)\psi_{n_1}(\alpha)d\alpha = 1. \tag{C1}$$

By truncating the expansion (4.17) at terms of order q^2 and using Eq. (C1), $N_{n_1}^2$ is found to be given from

$$\frac{1}{N_{n_1}^2\pi} \simeq 1 + \frac{q^2}{16}\left[\frac{1}{[\nu(n_1)+1]^2} + \frac{1}{[\nu(n_1)-1]^2}\right] + \frac{q^4}{1024}\left[\frac{1}{[\nu(n_1)+1]^2[\nu(n_1)+2]^2} + \frac{1}{[\nu(n_1)-1]^2[\nu(n_1)-2]^2}\right]. \tag{C2}$$

The normalization series in Eq. (C2) may be "slow" to converge for one of the semiclassical eigenstates $\psi_j(\alpha)$ involved in the resonance, an example being when $\nu(n_1) \pm m$ is small relative to q^{2m} for that state ($m = 1, 2$). In that case, one can determine the other overlaps $\langle \psi_{n_1}^{(0)} | \psi_j \rangle$ of nonnegligible magnitude and then use the normalization condition for the Fermi resonance

$$\sum_j |\langle \psi_{n_1}^{(0)} | \psi_j \rangle|^2 = 1 \tag{C3}$$

to determine the absolute value of the unknown overlap. This approximation was tested in quantum mechanical calculations discussed in Sec. V and found to agree with the exact results in the system chosen to within 2%. The semiclassical wave functions are not suitable for determining the overlaps with the zeroth order states when the normalization series (C2) does not converge for several of the semiclassical eigenstates.

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Chapter 3: On the Relationship of Classical Resonances to the Quantum Mechanics of Coupled Oscillator Systems

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I. Introduction

The quantum mechanical implications of isolated classical resonances[1-5] in coupled oscillator systems have been discussed by a number of authors.[6-26] For example, classical resonances have been related by a variety of techniques to avoided crossings[9-12] and Fermi resonances.[13-18] It is found in general that a large classical resonance zone has a pronounced effect on the eigenvalues and eigenfunctions of a coupled oscillator system.[4,6-25] As a result, the character of the quantum mechanical solution for such a system can be quite different from that described by the "zeroth-order" Hamiltonian H_0.[27] Of course, it is always possible that quantum effects such as tunnelling can significantly modify the eigenvalues and eigenfunctions of an oscillator system even when no classical resonances are present.

In the usual *classical* treatment of resonances in two dimensions (e.g., ref 3), one chooses a zeroth-order Hamiltonian $H_0(I_1,I_2)$ for which a set $(I_1,I_2,\theta_1,\theta_2)$ of action-angle variables exists and then examines the effect of the resonant perturbation on the dynamics of the total Hamiltonian $H(I_1,I_2,\theta_1,\theta_2)$. In order to do this, the perturbation is usually expanded in a double Fourier series in the zeroth-order angle variables (θ_1,θ_2).[28] The Hamiltonian thereby contains terms having, in principle, all combinations of these angles, including a term containing solely the "slow" or "resonant" angle variable θ_r. This angle is given by[1-4]

$$\theta_r = n\theta_1 - m\theta_2 \quad . \tag{1}$$

The slow angle reflects the resonance condition (i.e., frequency commensurability) for the full dynamics of H such that

$$\frac{d}{dt}(n\theta_1 - m\theta_2) \simeq n\omega_1^0(I_1^r,I_2^r) - m\omega_2^0(I_1^r,I_2^r) = 0 \quad , \tag{2}$$

where $\omega_i^0(I_1^r,I_2^r)$ is a zeroth-order frequency $\partial H_0/\partial I_i$, and (I_1^r,I_2^r) are the resonant zeroth-order action variables that give rise to the resonance condition (eq 2). All other combination terms of the angles θ_1 and θ_2 in the Fourier expansion of the perturbation are rapidly oscillating "fast" terms,[1,3,4] and hence averaging over θ_1 (or θ_2) effectively removes their contribution to the dynamics of H. By virtue of a suitable canonical transformation and, if necessary, a Taylor series expansion of the angle-averaged Hamiltonian $\bar{H}(I_1,I_2,\theta_r)$ about the resonant action variables (I_1^r,I_2^r), the standard Chirikov analysis[1] reduces $\bar{H}(I_1,I_2,\theta_r)$ to a constant term[29] plus an effective "hindered rotor" Hamiltonian. This rotor Hamiltonian contains the slow angle θ_r and its canonically conjugate action.

As a result of the Chirikov analysis, the zeroth-order actions (I_1,I_2) for resonant classical trajectories are predicted to oscillate periodically about their resonant values (I_1^r,I_2^r). The range of initial values of (I_1,I_2) giving this oscillatory behavior define resonance "widths" ΔI_i centered about I_i^r $(i = 1,2)$. These widths are found to be proportional to the square root of the $V_{n,-m}(I_1,I_2)$ Fourier component of the perturbation evaluated at $(I_1,I_2) = (I_1^r,I_2^r)$.[1,3,8-10,12,17,18,21] Any classical trajectory having actions within the range $I_i^r \pm \frac{1}{2}\Delta I_i$ $(i=1,2)$ is thereby found to be strongly affected by the resonance. A typical nonlinearly coupled oscillator system has many classical resonances, but most of these are of negligible width (see, e.g., refs 3, 7, and 8).

Quantum mechanically, the existence of a classical $n:m$ resonance condition at approximately the energy of the zeroth-order state $|\psi^{(0)}_{n_1,n_2}> = |\psi^{(0)}_{j,k}>$ implies the existence of near degeneracies in the manifold of states $|\psi^{(0)}_{j,k}>$, $|\psi^{(0)}_{j\pm n,k\mp m}>$, $|\psi^{(0)}_{j\pm 2n,k\mp 2m}>$, etc., where $mn_1 + nn_2$ equals a positive constant.[29] It has been proposed[4,7-10] that these zeroth-order states will not strongly mix or "feel" the classical resonance if the widths ΔI_1 and ΔI_2, in units of $\hbar = 1$, are less than n and m, respectively.[30] That this is intuitively reasonable is seen by considering the semiclassical quantization condition for the zeroth-order oscillator actions:

$$I_i = n_i + 1/2 \quad , \qquad (i = 1, 2) \quad , \tag{3}$$

where n_i is a positive integer (or zero), and I_i is the usual action variable J_i[31] divided by 2π. Thus, if a classical resonance for the I_i action variables is weak, the widths ΔI_i are less than n and m, respectively, and it is not possible for at least two quantum states from the nearly degenerate manifold to be contained in the width of the resonance. As a result, one expects little mixing of the zeroth-order eigenfunctions and relatively small changes in the eigenvalue spectrum. This proposed behavior is expected to be a direct manifestation of an action-angle-like uncertainty principle (which has not as yet been rigorously formulated) and suggests that quantum mechanical wavefunctions will "smooth over" structures in classical phase space that have negligible measure (e.g., weak resonances).[7–10]

In the present paper, the effect of small classical resonance zones on the quantum eigenvalues and eigenfunctions of a general class of two-dimensional coupled oscillator systems is explicitly examined. In section II, a classical resonance Hamiltonian will first be formulated for these systems using standard techniques.[1,3] In section III, a uniform semiclassical approximation that has been found useful for a semiclassical description of coupled local modes in H_2O,[21] avoided crossings,[12] and Fermi resonances[17,18,24] will be used to quantize the resonance Hamiltonian. The analysis of sections II and III is based on techniques which have been developed by a number of authors, and it is included here for the purpose of continuity and completeness. New results are presented in section IV which demonstrate analytically the dependence of the quantum eigenvalues and eigenfunctions on the classical resonance width. These results indicate directly how the quantum mechanics is affected by the existence of small classical resonances. Concluding remarks are given in section V.

II. Classical Resonance Theory

In the present paper, a particular class of two-dimensional coupled oscillator Hamiltonians will be treated. In action-angle variables, these Hamiltonians are of the form

$$H = I_1\omega_1 - I_1^2\omega_1\chi_1 + I_2\omega_2 - I_2^2\omega_2\chi_2 + \lambda I_1 I_2 + V(I_1,I_2,\theta_1,\theta_2) \quad , \tag{4}$$

where ω_1, $\omega_1\chi_1$, ω_2, $\omega_2\chi_2$, and λ are constants,[32] (I_i,θ_i) are the zeroth-order action-angle variables for H_0 (i.e., for $V = 0$), and $V(I_1,I_2,\theta_1,\theta_2)$ is the perturbation. Examples of Hamiltonians of this kind include those for two coupled Morse oscillators,[21,23,26] for a Morse coupled to a harmonic oscillator,[15-18] and for a nonlinear oscillator system treated to low order by classical perturbation theory (e.g., refs 12 and 24). The validity of using low order classical perturbation expansions to semiclassically treat resonant systems has been discussed recently within the context of a uniform semiclassical analysis.[25]

If an $n:m$ resonance condition exists (cf. eq 2), the perturbation may, as stated before, be averaged over the fast angles, leaving the approximate term

$$V(I_1,I_2,\theta_1,\theta_2) \simeq 2\,\mathrm{Re}\{V_{n,-m}(I_1,I_2)\exp[i(n\theta_1 - m\theta_2)]\} \quad . \tag{5}$$

This expression may be made into an action-independent one by evaluating (I_1,I_2) at the resonance center (I_1^r,I_2^r).[1,3] This approximation is usually a good one (e.g., ref 18), although it was recently found to give qualitatively incorrect results in a classical model of formaldehyde.[33] Since the treatment in the present paper is concerned with weak perturbations, it will be assumed that the averaging of the perturbation over the fast angles and the subsequent evaluation of $V_{n,-m}(I_1,I_2)$ at the resonance center provides an accurate approximation to $V(I_1,I_2,\theta_1,\theta_2)$.

The resonance condition (eq 2) suggests a canonical transformation to a set of new action-angle variables $(I_\alpha, I_\beta, \alpha, \beta)$ given by

$$I_\alpha = 2I_1/n \quad , \quad 2\alpha = n\theta_1 - m\theta_2 + \delta \quad , \tag{6}$$

$$I_\beta = mI_1 + nI_2 \quad , \quad \beta = \theta_2/n \quad , \tag{7}$$

where δ is a constant chosen to give the perturbation a negative sign in the following analysis. The angle 2α is seen by comparison of eqs 1 and 6 to be the "slow" or resonant angle θ_r, and the approximate expression in eq 5 for the perturbation can hence be written as[18]

$$V \simeq -V_0 \cos 2\alpha \quad , \tag{8}$$

where $V_0 \equiv 2|V_{n,-m}(I_1^r, I_2^r)|$, and δ is chosen as in ref 18. The fast-angle-averaged Hamiltonian $\bar{H}$ in the new action-angle variables is thereby given from eqs 4 - 8 as

$$\bar{H}(I_\alpha, I_\beta, \alpha) = I_\alpha\Omega - I_\alpha^2\omega_\alpha\chi_\alpha + I_\beta\omega_\beta - I_\beta^2\omega_\beta\chi_\beta - V_0 \cos 2\alpha \quad , \tag{9}$$

where

$$\begin{aligned} \Omega &= \frac{n\omega_1 - m\omega_2}{2} + \left[\frac{m\omega_2\chi_2}{n} + \frac{\lambda}{2}\right] I_\beta \quad , \\ \omega_\alpha\chi_\alpha &= (n^2\omega_1\chi_1 + m^2\omega_2\chi_2 + nm\lambda)/4 \quad , \\ \omega_\beta &= \omega_2/n \quad , \quad \omega_\beta\chi_\beta = \omega_2\chi_2/n^2 \quad . \end{aligned} \tag{10}$$

The action variable I_β is inferred to be an approximate constant of the motion for the resonant dynamics of the full Hamiltonian since its conjugate angle β does not appear in the fast angle-averaged Hamiltonian $\bar{H}$ (eq 9).

A resonance Hamiltonian[1-4] H_R may be defined from eq 9 as

$$H_R = I_\alpha^2\omega_\alpha\chi_\alpha - I_\alpha\Omega + V_0 \cos 2\alpha = E_R \tag{11}$$

such that

$$\bar{H} = I_\beta \omega_\beta - I_\beta^2 \omega_\beta \chi_\beta - H_R \tag{12}$$

The analysis of the "hindered rotor" Hamiltonian in eq 11 is standard (see, e.g., refs 3,8-10,18,21). For a given conserved action I_β and rotor energy E_R, the (I_α,α) phase-plane curves for eq 11 are given by

$$I_\alpha = I_\alpha^r \pm [(I_\alpha^r)^2 + (E_R - V_0 \cos 2\alpha)/(\omega_\alpha \chi_\alpha)]^{1/2} \quad , \tag{13}$$

where the resonant value I_α^r is given by

$$I_\alpha^r = \Omega/(2\omega_\alpha \chi_\alpha) \quad , \tag{14}$$

and the angle α is taken on the interval $(0,\pi)$. The action I_α given by eq 13 can either have oscillatory or "rotational" behavior.[1,3,12,18,21] The oscillatory behavior gives closed curves centered about $(I_\alpha^r,\pi/2)$ in the (I_α,α) phase plane (see, e.g., ref 18) and indicates that the two oscillators are in classical resonance (i.e., the action I_α oscillates periodically about I_α^r). The "rotational" behavior gives curves of approximately constant I_α vs. α and occurs when the two oscillators are out of resonance. The (I_α,α) curve that separates the oscillatory and rotational types of motion is the separatrix trajectory[1,3,12,18,21] which has a rotor energy E_R^S given by

$$E_R^S = V_0 - \Omega^2/(4\omega_\alpha \chi_\alpha) \quad . \tag{15}$$

The two possible values of I_α on the separatrix curve, evaluated at $\alpha = \pi/2$, define the width of the resonance ΔI_α,[1,3] given in this instance by

$$\Delta I_\alpha = 4\sqrt{q} \quad , \tag{16}$$

where

$$q \equiv V_0/(2\omega_\alpha \chi_\alpha) \quad . \tag{17}$$

Any trajectory having an action I_α within the range $I_\alpha^r \pm \frac{1}{2}\Delta I_\alpha$ will be strongly in the resonance, and I_α will hence exhibit oscillatory behavior.[1-4,8-12,17,18,21]

Using the canonical transformation given in eqs 6 and 7, the resonant action and resonance width may be found for the action I_1. These quantities are given by

$$I_1^r = n\Omega/(4\omega_\alpha\chi_\alpha) \quad , \tag{18}$$

and

$$\Delta I_1 = 2n\sqrt{q} \quad . \tag{19}$$

In the present analysis, the action variable conjugate to the slow angle 2α was chosen to be directly proportional to I_1 (cf. eq 6), although one could just as easily choose I_2 for this purpose. For the above treatment, the resonant value I_2^r of I_2 may be found using eq 18 and the (constant) value for I_β (cf. eq 7). A width ΔI_2 for the action I_2 may also be found from an analogous resonance analysis to that given above. In addition, using eqs 3 and 18, it will be found useful later to define resonant "quantum numbers" given by

$$n_1^r = I_1^r - \frac{1}{2} \ ; \quad n_2^r = I_2^r - \frac{1}{2} \quad . \tag{20}$$

These numbers are not in general integers.

As mentioned in the Introduction, the resonance condition in eq 2 implies that, for a given I_1^r and I_2^r, there exists a near degeneracy between the zeroth-order quantum basis states of H_0 in the manifold with $mn_1 + nn_2$ equal to a constant.[29] The correspondence of the quantum near-degeneracy of these states with the existence of the classical resonance condition (eq 2) results from the fact that

$$n\omega_1^0(I_1^r+\delta_1 I_1, I_2^r+\delta_2 I_2) - m\omega_2^0(I_1^r+\delta_1 I_1, I_2^r+\delta_2 I_2) \simeq \Delta E^{(0)} \quad . \tag{21}$$

Here, $\Delta E^{(0)}$ is a (small) zeroth-order Bohr frequency between two adjacent basis states in the nearly degenerate manifold (e.g., $|\psi_{j,k}^{(0)}>$ and $|\psi_{j-n,k+m}^{(0)}>$), $\omega_i^0(I_1^r+\delta_1 I_1, I_2^r+\delta_2 I_2)$ is a zeroth-order classical frequency $\partial H_0/\partial I_i$, and $(I_1^r+\delta_1 I_1, I_2^r+\delta_2 I_2)$ are values of the action variables very near (I_1^r, I_2^r). For a specific system, a similar result is discussed in Appendix B of ref 12.

In the following section, a uniform semiclassical analysis, developed by several authors[12,17,18,21,24] to quantize specific hindered rotor-like resonance Hamiltonians, will be used to quantize the general n:m resonance Hamiltonian (eq 11).

III. Uniform Semiclassical Treatment

The approximate classical Hamiltonian (eq 9) may be quantized by converting it into a wave equation[12,17,18,21,24] using semiclassical action operators.[34] The approximate operators $\hat{I}_\alpha$ and $\hat{I}_\beta$ corresponding to the classical variables I_α and I_β may be chosen in the angle representation to be

$$\hat{I}_\alpha \equiv \frac{1}{i}\frac{d}{d\alpha} + \frac{1}{n} \, , \quad \hat{I}_\beta \equiv \frac{1}{i}\frac{d}{d\beta} + \frac{m+n}{2} \quad , \tag{22}$$

where $\hbar$ equals unity. The wave function $|\Psi>$ which satisfies the Schrödinger equation obtained via substitution of the above operators in the angle-averaged Hamiltonian (eq 9) is separable and written in the angle representation as

$$<\alpha,\beta|\Psi> = \Psi(\alpha,\beta) = \psi(\alpha)\varphi(\beta) \quad . \tag{23}$$

Here, $\varphi(\beta)$ equals $\exp[i\int_0^\beta (I_\beta - \frac{n+m}{2})\, d\beta]$ (aside from a normalization factor) and is a function of the conserved action I_β, while $\psi(\alpha)$ satisfies the differential equation

$$\frac{d^2\psi(\alpha)}{d\alpha^2} - 2i(2n_1^\tau/n)\frac{d\psi(\alpha)}{d\alpha} + (A - 2q\cos 2\alpha)\psi(\alpha) = 0 \quad . \tag{24}$$

In eq 24, n_1^τ is the resonant "quantum number" defined in eq 20, q is defined in eq 17, and A is given by

$$A = (\Omega/n + E_R)/(\omega_\alpha \chi_\alpha) - 1/n^2 \quad . \tag{25}$$

Using a function $F(\alpha)$, defined as

$$F(\alpha) = \exp(-2in_1^\tau \alpha/n)\psi(\alpha) \quad , \tag{26}$$

equation 25 may be transformed into a Mathieu equation of order ν for $F(\alpha)$:[12,17,18,24,35]

$$\frac{d^2F(\alpha)}{d\alpha^2} + (a_\nu - 2q\cos 2\alpha)F(\alpha) = 0 \quad , \tag{27}$$

where the characteristic eigenvalue[35] a_ν is

$$a_\nu = (2n_1^\tau/n)^2 + A \quad . \tag{28}$$

The order ν of the Mathieu equation[35] is found, for instance, by the method of ref 18 to be

$$\nu = \nu(n_1) = 2(n_1 - n_1^\tau)/n \quad . \tag{29}$$

The order $\nu(n_1)$ is a function of the zeroth-order quantum number n_1 because the solution of the zeroth-order Mathieu equation (i.e., with $q = 0$), along with eq 26, must give the WKB wavefunction $\psi_{n_1}^{(0)}(\alpha) = (n\pi)^{-1/2}\exp(2in_1\alpha/n)$.[18] In general, $\nu(n_1)$ is not an integer.

The energy E_R of the quantized resonance Hamiltonian is given from eqs 25 and 28 by

$$E_R = a_\nu \omega_\alpha \chi_\alpha - (n_1^\tau + 1/2)\Omega/n \quad . \tag{30}$$

When q is small and $\nu(n_1)$ is not an integer, an expansion for a_ν may be used,[35] which yields

$$E_R \simeq \left[\nu(n_1)^2 + \frac{q^2}{2[\nu(n_1)^2 - 1]}\right]\omega_a\chi_a - (n_1^r + ½)\Omega/n \quad , \tag{31}$$

where the expansion has been truncated to second order in q.

Under the same conditions, the unnormalized uniform semiclassical wave function $\psi_{n_1}^{un}(\alpha)$ for the α-motion may be obtained using an expansion[35] for $F(\alpha)$ in terms of q along with eq 26. The wave function is given to second order in q by

$$\psi_{n_1}^{un}(\alpha) \simeq e^{2in_1\alpha/n} - \frac{q}{4}\left[\frac{e^{2i(n_1+n)\alpha/n}}{[\nu(n_1)+1]} - \frac{e^{2i(n_1-n)\alpha/n}}{[\nu(n_1)-1]}\right]$$

$$+ \frac{q^2}{32}\left[\frac{e^{2i(n_1+2n)\alpha/n}}{[\nu(n_1)+1][\nu(n_1)+2]} - \frac{e^{2i(n_1-2n)\alpha/n}}{[\nu(n_1)-1][\nu(n_1)-2]}\right] . \tag{32}$$

The normalized wave functions $\psi_{n_1}(\alpha) = N_{n_1}\psi_{n_1}^{un}(\alpha)$ are found by normalizing eq 32. The normalization factor N_{n_1} is given to second order in q by

$$N_{n_1} = [(n\pi)(1 + q^2B_{n_1}/16)]^{-½} \quad , \tag{33}$$

where

$$B_{n_1} \equiv \left[\frac{1}{[\nu(n_1)+1]^2} + \frac{1}{[\nu(n_1)-1]^2}\right] \tag{34}$$

The uniform semiclassical wave functions $\psi_{n_1}(\alpha)$ for the α-motion henceforth have an n_1 subscript since they are related via the Mathieu equation analysis to the zeroth-order states $\psi_{n_1}^{(0)}(\alpha)$.

IV. The Effect of Small Resonance Zones on the Eigenvalues and Eigenfunctions

The width ΔI_1 of the $n:m$ classical resonance zone is given in eq 19 in terms of the parameter q. In the following analysis, the effect of small resonance zones, and hence small q, on the uniform semiclassical eigenvalues and eigenfunctions will be examined. By treating ΔI_1 as a variable parameter, one may examine such properties as the splitting of the eigenstates or the mixing of the zeroth-order wave functions as the resonance width increases. In this way, information is obtained on how weak classical resonances influence the quantum properties of a nonlinear oscillator system.

Nonlinear resonances can have a pronounced effect on the eigenvalue spectrum of coupled oscillator systems.[6-26] (Consider, for example, the simple Fermi resonance.[13-18]) The splittings ΔE between the adjacent semiclassical eigenstates $|\psi_{j,k}>$ and $|\psi_{j\pm n,k\mp m}>$ of zeroth-order parentage $|\psi^{(0)}_{j,k}>$ and $|\psi^{(0)}_{j\pm n,k\mp m}>$, respectively, are, for fixed I_β, given from eqs 12 and 30 by

$$\Delta E = E_{j,k} - E_{j\pm n,k\mp m} = -[a_{\nu(j)} - a_{\nu(j\pm n)}]\omega_\alpha\chi_\alpha \quad . \qquad (35)$$

Using the expansion (eq 31) to second order in q for a_ν,[36] the splitting may be written approximately as

$$\Delta E \simeq [\nu(j\pm n)^2 - \nu(j)^2]\omega_\alpha\chi_\alpha + q^2 C_j\omega_\alpha\chi_\alpha/2 \quad , \qquad (36)$$

where

$$C_j \equiv \left[\frac{1}{[\nu(j\pm n)^2-1]} - \frac{1}{[\nu(j)^2-1]}\right] \quad . \qquad (37)$$

In eqs 35 - 37, the orders $\nu(j)$ and $\nu(j\pm n)$ correspond to the solutions of the Mathieu equation (eq 27) having zeroth-order state parentage $|\psi_{j,k}^{(0)}>$ and $|\psi_{j\pm n,k\mp m}^{(0)}>$, respectively. In addition, as the reader may easily verify, the term $[\nu(j\pm n)^2 - \nu(j)^2]\omega_\alpha \chi_\alpha$ in eq 36 is just the (exact) zeroth-order energy difference $\Delta E^{(0)}$ between these two states. Using the definition given in eq 19 for the resonance width ΔI_1 in terms of q, the splitting of the two states due to the perturbation may be written as[36]

$$\Delta E - \Delta E^{(0)} = \frac{(\Delta I_1/n)^4 C_j \omega_\alpha \chi_\alpha}{32} \quad . \tag{38}$$

Also of interest are the squared overlaps of the zeroth-order basis functions with the actual eigenfunctions. These squared overlaps are of importance in determining, for instance, the effect of resonances on the probability amplitude distributions and the nodal patterns of the wavefunctions.[6,9-11,22] Also, for dipole moment functions aligned along a particular vibrational coordinate, they are crucial in understanding the relative intensities of absorption lines in the vicinity of an overtone transition.[15,16,18]

Due to the separability of the total semiclassical wave function $\Psi(\alpha,\beta)$ (eq 23), the following analysis needs only involve the wave function for the α−motion (i.e., the wave function for the β−motion is the same for all nearly degenerate states having the same I_β). Hence, the overlap squared of, for instance, the basis function $|\psi_{j,k}^{(0)}>$ with the eigenfunction $|\psi_{j,k}>$ (i.e., that of predominantly $|\psi_{j,k}^{(0)}>$ parentage) is determined from the semiclassical analysis to be

$$|<\psi_{j,k}^{(0)}|\psi_{j,k}>|^2 = \left| \int_0^{n\pi} \psi_j^{(0)*}(\alpha)\psi_j(\alpha)\, d\alpha \right|^2 = n\pi N_j^2 \quad . \tag{39}$$

Here, the zeroth-order semiclassical wave function $\psi_j^{(0)}(\alpha)$ in the angle representation equals $(n\pi)^{-1/2}\exp(2ji\alpha/n)$, $\psi_j(\alpha)$ is the normalized uniform semiclassical wave function given in eqs 32 and 34, and the normalization factor N_j is given by eq 33. Similarly, the overlap squared of the zeroth-order state $|\psi_{j,k}^{(0)}>$ with the eigenfunction of $|\psi_{j\pm n,k\mp m}^{(0)}>$ parentage is given semiclassically by

$$|<\psi_{j,k}^{(0)}|\psi_{j\pm n,k\mp m}>|^2 = \left|\int_0^{n\pi} \psi_j^{(0)*}(\alpha)\psi_{j\pm n}(\alpha)\, d\alpha\right|^2$$

$$= n\pi N_{j\pm n}^2\left[\frac{q^2}{16[\nu(j\pm n)\mp 1]^2}\right] , \tag{40}$$

For small enough q, the normalization factors in eqs 39 and 40 may be expanded about $q = 0$, and the definition of ΔI_1 given in eq 19 used to yield

$$|<\psi_{j,k}^{(0)}|\psi_{j,k}>|^2 \simeq 1 - \frac{(\Delta I_1/n)^4 B_j}{256} \tag{41}$$

and

$$|<\psi_{j,k}^{(0)}|\psi_{j\pm n,k\mp m}>|^2 \simeq \frac{(\Delta I_1/n)^4}{256}\left[B_j - \frac{1}{[\nu(j)\mp 1]^2}\right] \tag{42}$$

In eqs 41 and 42, B_j is the value of eq 34 for the specific quantum number j, and the fact that $\nu(j\pm n)$ equals $\nu(j) \pm 2$ has been used. An alternate derivation of eqs 41 and 42, along with a discussion of the limits of their validity, is given in the Appendix. Also, by an analysis similar to that given in this section, one can derive formulas analogous to eqs 38, 41, and 42 in terms of $(\Delta I_2/m)^4$, provided one initially chooses I_α equal to $2I_2/m$ and β equal to θ_1/m in eqs 6 and 7.

V. Concluding Remarks

The formulas given in eqs 38 and 41 - 42 for, respectively, the eigenvalue splittings and the mixing of the basis functions are particularly revealing. One sees by examination of these expressions that their dependence on the ratio $\Delta I_1/n$ is to the *fourth* power. Hence, the argument[4,7-10] that the quantum states should not "feel" the effect of small classical resonances with $\Delta I_1 \ll n$ (or equivalently $\Delta I_2 \ll m$) is explicitly confirmed by eqs 38, 41, and 42. More specifically, for any classical resonance with a width in I_1-space significantly less than n, the corrections to the zeroth-order eigenvalues and eigenfunctions are negligibly small. (The exception to this statement is when the two states are identically at the avoided crossing point.[37]) As the width ΔI_1 increases to be on the order of n, a rather abrupt change in the eigenvalues and eigenfunctions will occur due to their dependence on $\Delta I_1/n$ to the fourth power. This is a manifestation of the fact that the $n:m$ resonance can begin to contain two quantum states as the width ΔI_1 increases past n.[7-10] In addition, the overall effect of the classical resonance on the quantum properties given in eqs 38, 41, and 42 is modulated by the constants C_j (eq 38) or B_j (eqs 41 and 42). These constants reflect the energy detuning of the zeroth-order states and hence decrease in value with increasing "distance" from the avoided crossing point. Figure 1 shows the behavior of the squared overlaps, given by eqs 41 and 42, as a function of increasing resonance width for two states near the center of a 1:2 Fermi resonance.

The analysis of the present paper indicates that the quantum mechanics of a nonlinear oscillator system is not sensitive to any weak, isolated classical resonances that will distort small regions of classical phase space. In fact, one might also speculate from the present results that the quantum mechanics may "smooth over" the small regions of classically irregular or chaotic behavior that occur when two or more small classical resonance zones overlap.[1-10,38] However, a quantitative relationship between overlapping classical resonances, classical chaos, and quantum chaos (if it exists) is at present not known. (Some qualitative relationships between these phenomena have certainly been proposed.[5-10]) For realistic molecular oscillator systems, it is also not clear to what degree classical resonances are responsible for significant basis function mixing and eigenvalue changes, or, rather, if these effects can for the most part be attributed to purely quantum mechanical mechanisms. Further studies in this regard may prove quite informative.

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Appendix: An Alternate Derivation of the Overlap Formulas

Under the appropriate circumstances to be specified below, the normalized wave functions $|\psi_{j,k}>$, $|\psi_{j-n,k+m}>$, and $|\psi_{j+n,k-m}>$ of the full Hamiltonian (eq 4) may be written approximately using first-order perturbation theory as

$$|\psi_{j,k}> \simeq N'_{j,k}\left[|\psi_{j,k}^{(0)}> + \frac{<\psi_{j-n,k+m}^{(0)}|V|\psi_{j,k}^{(0)}>}{E_{j,k}^{(0)} - E_{j-n,k+m}^{(0)}}|\psi_{j-n,k+m}^{(0)}> \right.$$

$$\left. + \frac{<\psi_{j+n,k-m}^{(0)}|V|\psi_{j,k}^{(0)}>}{E_{j,k}^{(0)} - E_{j+n,k-m}^{(0)}}|\psi_{j+n,k-m}^{(0)}>\right] \qquad (A1)$$

and

$$|\psi_{j\pm n,k\mp m}> \simeq N'_{j\pm n,k\mp m}\left[|\psi_{j\pm n,k\mp m}^{(0)}> + \frac{<\psi_{j,k}^{(0)}|V|\psi_{j\pm n,k\mp m}^{(0)}>}{E_{j\pm n,k\mp m}^{(0)} - E_{j,k}^{(0)}}|\psi_{j,k}^{(0)}>\right] \qquad (A2)$$

where N'_{n_1,n_2} is a normalization factor (which differs by a factor of $(n\pi)^{-1/2}$ from eq 33), and the zeroth-order wave functions $|\psi_{n_1,n_2}^{(0)}>$ are taken to be WKB wave functions in action-angle variables.[12,18,21,34] These wave functions are defined, in the angle representation, as

$$<\theta_1,\theta_2|\psi_{j,k}^{(0)}> = (2\pi)^{-1}\exp[i(j\,\theta_1 + k\,\theta_2)] \qquad (A3)$$

and

$$<\theta_1,\theta_2|\psi_{j\pm n,k\mp m}^{(0)}> = (2\pi)^{-1}\exp[i(j\pm n)\theta_1 + i(k\mp m)\theta_2] \quad . \qquad (A4)$$

In eqs A1 - A4, we consider only the zeroth-order wave functions $|\psi_{j,k}^{(0)}>$ and $|\psi_{j\pm n,k\mp m}^{(0)}>$ with quantum numbers (n_1,n_2) equal to (j,k) and $(j\pm n,k\mp m)$, respectively. These wave functions are assumed to be from a nearly resonant manifold of states having a constant value of I_β[29] but also having weak couplings (i.e., a weak resonance). These states are moreover assumed to have the strongest mixing due to "direct", or classical-like, first order couplings between the basis states with zeroth-order quantum numbers n_1 and n_2 differing by n and m, respectively (cf. discussion in the Introduction and ref 30). For a given conserved action I_β,[29] the center of the classical resonance is also assumed to be given by resonant "quantum numbers" (eq 20) close to the zeroth-order quantum numbers of the $|\psi_{j,k}^{(0)}>$ state.

For WKB basis functions, the matrix elements of the perturbation appearing in eqs A1 and A2 have the form of Fourier components,[18] e.g.,

$$<\psi_{j+n,k-m}^{(0)}|V|\psi_{j,k}^{(0)}> = \frac{1}{(2\pi)^2}\int_0^{2\pi}\int_0^{2\pi} d\theta_1 d\theta_2 V(I^{int},\theta)e^{-i(n\theta_1 - m\theta_2)}$$

$$= V_{n,-m}(I^{int}) \quad , \tag{A5}$$

where $I^{int} \equiv (I_1^{int}, I_2^{int})$ are some intermediate values of the actions chosen, as in ref 18, to give good agreement between the Fourier component and the quantum matrix element (and also to make the former Hermitian [18]). If the zeroth-order states described by the wavefunctions in eqs A3 and A4 are near the center of the classical resonance, and if the width of the resonance contains only two or three quantum states, the choice $(I_1^{int}, I_2^{int}) = (I_1^r, I_2^r)$ (i.e., the resonant actions) gives good agreement between the WKB and exact matrix elements.[18] The relationship of the Fourier components evaluated in this way to the width of the classical resonance is given in eqs 8 and 16 - 19. Using that relationship, and the (exact) expression given in eq 36 for the zeroth-order energy differences that appear in the denominators of the perturbation expansion terms, the approximate wave functions may be rewritten as

$$|\psi_{j,k}> = N'_{j,k}\left[|\psi^{(0)}_{j,k}> - \frac{qe^{i\gamma}}{4[\nu(j)-1]}\,|\psi^{(0)}_{j-n,k+m}> + \frac{qe^{-i\gamma}}{4[\nu(j)+1]}\,|\psi^{(0)}_{j+n,k-m}> \right] \tag{A6}$$

and

$$|\psi_{j\pm n,k\mp m}> = N'_{j\pm n,k\mp m}\left[|\psi^{(0)}_{j\pm n,k\mp m}> \mp \frac{qe^{\mp i\gamma}}{4[\nu(j)\pm 1]}|\psi^{(0)}_{j,k}> \right] . \tag{A7}$$

The phase $e^{\pm i\gamma}$ in eqs A6 and A7 is defined as in ref 18, and the number $\nu(j)$ is the order of the Mathieu equation (eq 29) for $n_1 = j$ (cf. discussion following eq 37).

The squared overlaps of interest in the present paper are hence given by

$$|<\psi^{(0)}_{j,k}|\psi_{j,k}>|^2 = |N'_{j,k}|^2 \tag{A8}$$

and

$$|<\psi^{(0)}_{j,k}|\psi_{j\pm n,k\mp m}>|^2 = \left| N'_{j\pm n,k\mp m}\frac{qe^{\mp i\gamma}}{4[\nu(j)\pm 1]}\right|^2 , \tag{A9}$$

which, upon expansion to second order about $q = 0$, yield the same expressions as are given in the text (eqs 41 and 42). These overlap formulas are valid as long as the two zeroth-order states $|\psi^{(0)}_{j,k}>$ and $|\psi^{(0)}_{j\pm n,k\mp m}>$ are, for a given I_β, near the center of the classical resonance and not directly at their avoided crossing point.[36] It was also assumed in the derivation given in this Appendix that the width ΔI_1 of the resonance was small ($< n$) and therefore that q was small.

A final point with regard to the limits of validity of eqs 41 and 42 of the text concerns the contribution to these formulas from unphysical "states" in the uniform semiclassical wavefunction (eq 32). These unphysical states correspond to zeroth-order WKB wave functions (cf. eqs A3 and A4) with negative quantum numbers.[39] For example, it is known for the n:m resonance that the constant action I_β equals $mn_1 + nn_2 + (n+m)/2$ for states in the nearly degenerate resonant manifold.[29] Therefore, a resonance having resonant "quantum numbers" $(n_1^r, n_2^r) \simeq (j - n\varepsilon, 0 + m\varepsilon)$, where ε is a small parameter, would give $I_\beta \simeq mj + (n+m)/2$. As a result, an α–motion state $\psi_{n_1}(\alpha)$ with $n_1 = j + n$ would, for constant I_β, require n_2 to equal $-m$ and would thereby be unphysical. In this special case, the uniform semiclassical wave function would indeed have a contribution $\sim \exp[2i(j + n)\alpha/n]$ as can be seen by inspection of eq 32. A similar statement may also be made for the case in which $(n_1^r, n_2^r) \simeq (0, k)$, and, in that instance, an unphysical state with a negative n_1 would contribute to the uniform semiclassical wave function.

In both of the cases mentioned above, the unphysical states have a small contribution to the normalization factor N_{n_1} (eqs 33 and 34) and would therefore lead to slight errors in the overlap formulas (eqs 41 and 42). Suppose, however, that one is considering the interaction of the two physical zeroth-order states that are nearest the center of the classical resonance, e.g., $|\psi_{j,0}^{(0)}>$ and $|\psi_{j-n,m}^{(0)}>$. This situation supposes that the resonant quantum numbers (n_1^r, n_2^r) are some values intermediate between $(j, 0)$ and $(j - n, m)$, but not those giving an avoided crossing.[36,37] The contribution from these physical states to the normalization factor N_{n_1} (eqs 33 and 35) will then be much larger than that from any unphysical state(s). (The unphysical zeroth-order state in the present example would be $|\psi_{j+n,-m}^{(0)}>$.) More specifically, the factor $[\nu(j) - 1]^{-2}$ in eqs 33 and 34 corresponding to the contribution from the physical zeroth-order state $\psi_{j-n}^{(0)}(\alpha)$ to the normalization factor for the eigenstate $\psi_j(\alpha)$ will be much larger than that for any unphysical states. (The two interacting physical states are near, but not at, their avoided crossing point.[12,36,37] Hence, the term $\sim [\nu(j) - 1]^{-2}$ in N_j corresponding to the contribution from the physical zeroth-order state $|\psi^{(0)}_{j-n,m}>$ to the normalization of $|\psi_{j,0}>$ is large since $[\nu(j) - 1] < 1$ in that case. The term $\sim [\nu(j) + 1]^{-2}$ corresponding to the contribution from the unphysical zeroth-order state $|\psi^{(0)}_{j+n,-m}>$ to the normalization of the $|\psi_{j,0}>$ eigenstate will be much smaller.)

In the alternative derivation of the overlap formulas given in this Appendix, any unphysical zeroth-order states with negative quantum numbers for n_1 or n_2 are omitted by *fiat*.[39]

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(28) An alternative route to the resonance Hamiltonian might involve use of Birkhoff-Gustavson classical perturbation theory (see, e.g., Appendix A in ref 12 and ref 24).

(29) This term arises from the approximate constant of the motion $I_\beta = mI_1 + nI_2$ for the full Hamiltonian H. The action I_β is rigorously a positive constant in the angle-averaged Hamiltonian $\bar{H}$ since its canonically conjugate angle variable does not appear there. For the case of the 1:2 Fermi resonance, I_β equals $2I_1 + I_2$ (see, e.g., refs 17 and 18). Semiclassically, since $I_i = (n_i + 1/2)$, where $(i = 1, 2)$, we have the "constant of the motion" $mn_1 + nn_2$ for the resonant zeroth-order quantum states.

(30) It is possible, however, that the classical resonance widths ΔI_i may be zero because the $V_{n,-m}$ Fourier component is zero. The zeroth-order quantum states with $mn_1 + nn_2 = \text{const.}$ are still nearly degenerate because of eq 2 and can mix due to purely quantum effects. In particular, if $V_{n,-m}$ is zero, then there is expected to be no "direct" or first order quantum coupling elements between the states in that nearly degenerate manifold. The state mixing may therefore be due to higher order coupling effects (i.e., coupling through off-resonant intermediate or "virtual" states). A non-zero $V_{n,-m}$ Fourier component can be directly related via WKB wave functions to the existence of first order coupling matrix elements between the quantum states $|\psi^{(0)}_{j,k}>$, $|\psi^{(0)}_{j\pm n,k\mp m}>$, etc. (see, e.g., ref 18 for the 1:2 Fermi resonance or ref 21b for a 1:1 resonance).

(31) See, e.g., Goldstein, H. "Classical Mechanics"; Addison-Wesley: Reading, Mass., 1980, p. 457.

(32) These constants are general in the present context and are not necessarily related to Morse oscillator constants (e.g., ref 18). This notation was chosen to follow that used in a previous semiclassical treatment of the Fermi resonance (ref 18).

(33) Gray, S. K.; Child, M. S. *Mol. Phys.* **1984** , 53 , 961.

(34) Marcus, R. A. *Chem. Phys. Lett.* **1970** , 7, 525; Berry, M. V. *Philos. Trans. R. Soc. London, Ser. B* **1977** , 287, 237.

(35) McLachlan, N. W. "Theory and Applications of Mathieu Functions", Dover Publications: New York, 1964, pp. 19-20. See also, refs 12, 18,

and 24.

(36) In the derivation given in Sections III and IV, the orders $\nu(j)$ and $\nu(j \pm n)$ of the Mathieu equation (eq 27) are assumed to be fractional. When the two orders are integers such that $\nu(j)$ equals $-\nu(j \pm n)$, the zeroth-order splitting $\Delta E^{(0)}$ equals zero and the two levels are at the avoided crossing point (cf. ref 12). In that case, none of the formulas given in eqs 31 - 33, 36, and 38 are applicable. To treat such a system, Mathieu functions of integral order (cf. ref 35, Chap. 2) must be used. Since the avoided crossing point is a special case, it is not treated in the present paper.

(37) Directly at the avoided crossing point between two quantum levels, the basis functions will mix in nearly equal proportion because of the exact zeroth-order degeneracy. However, for avoided crossings due to a classical resonance (cf. ref 12), the level repulsion will be very small for small $\Delta I_1 / n$. (This result was also predicted, in terms of the parameter q, in ref 12.)

(38) For apparent examples of quantum "smoothing" over reasonably small regions of classical chaos, see, e.g., Shirts, R. B.; Reinhardt, W. P. *J. Chem. Phys.* **1982** , 77, 5204; Skodje, R. T.; Borondo, F.; Reinhardt, W. P. *J. Chem. Phys.* **1985** , 82, 4611, and references cited therein.

(39) See, e.g., Augustin, S. D.; Rabitz, H. *J. Chem. Phys.* **1979** , 71, 4956; Gray, S. K. *Chem. Phys.* **1984** , 83, 125, and references cited therein.

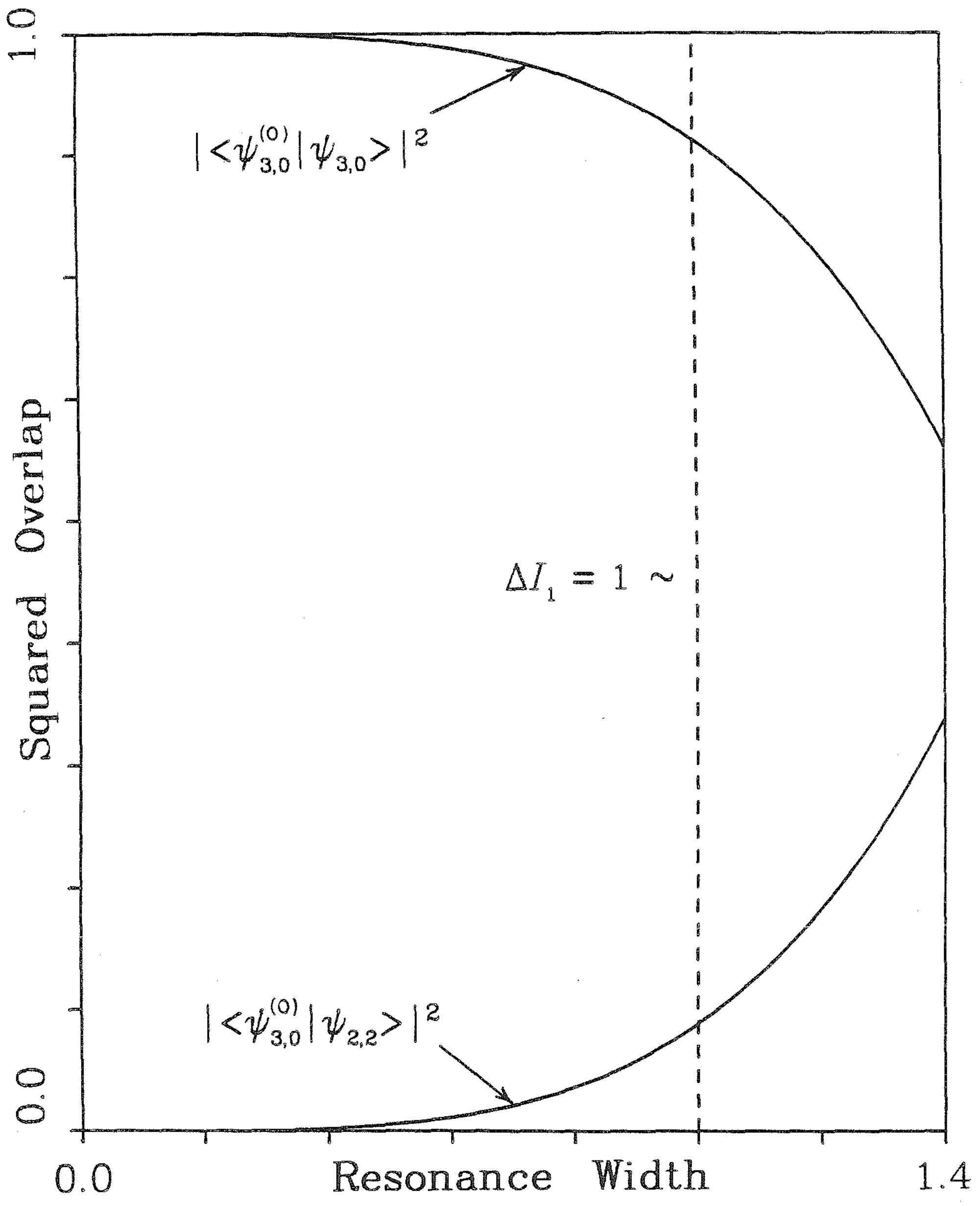

Figure 1. The squared overlaps $|\langle\psi^{(0)}_{3,0}|\psi_{3,0}\rangle|^2$ and $|\langle\psi^{(0)}_{3,0}|\psi_{2,2}\rangle|^2$ as a function of ΔI_1 for a 1:2 Fermi resonance with $n_1^r = 2.4$. The value of $\Delta I_1 = 1$ is marked by the vertical dashed line.

Chapter 4: Semiclassical Dressed State Theory for the Vibrational Excitation of a Morse Oscillator by Radiation

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Introduction

In the present paper, uniform semiclassical expressions are obtained for the resonant and Rabi frequencies for one- and two-photon absorption by a Morse oscillator. The correspondence of the results for these frequencies with quantum mechanical dressed state theory[1] is described. This semiclassical treatment is derived for a diatomic molecule and is then adapted to the excitation of an isolated vibrational state in a polyatomic molecule. Experimental or theoretical studies of CH_3F,[2] O_3,[3] BCl_3,[4] and SO_2[5] and of certain local mode molecules such as HDO[6a] and CHD_3[6b] suggest that such state-to-state behavior can be observed at low energies in some polyatomic molecules.

Many studies in the past few years[7,8] have been devoted to the development of exact and approximate quantum mechanical treatments for the vibrational excitation of a single anharmonic oscillator by an electromagnetic radiation field.[9] In addition, there have been several classical and quantum resonance studies of related driven oscillator systems,[8,10-17] including the early work by Chirikov[15] Shuryak,[16] and Zaslavsky.[17] Recently, Gray[18] discussed the semiclassical aspects of a Morse oscillator driven by a classical radiation field by formulating the matrix representation of an appropriate classical resonance Hamiltonian[14-21] using WKB wavefunctions[22] for the basis states. A uniform semiclassical "dressed state" approach is developed in the present paper that circumvents the use of a multilevel matrix treatment (e.g., ref 18) to describe the absorption of two (or more) photons. An alternative semiclassical approach for an explicitly time-dependent Hamiltonian is presented in the Appendix.

Classical Resonance Hamiltonian

The energy-conserving Hamiltonian for the dipole interaction of a Morse oscillator with a classical radiation field is[13,23]

$$H = H_m(r,p) + \frac{1}{2}(P^2+\omega^2 Q^2) - (4\pi\omega^2/V_c)^{1/2}\mu(r)Q \quad , \tag{1}$$

where P and Q are the abstract momentum and coordinate of the field, respectively, ω is the angular frequency of the field, V_c is the volume of the radiation cavity, $\mu(r)$ is the dipole moment, and H_m is the zeroth order Hamiltonian for a Morse oscillator[24] with displacement coordinate r and conjugate momentum p.

If a canonical transformation is made to Morse oscillator action-angle variables (I_m,θ_m)[25] and to harmonic oscillator action-angle variables (I_f,θ_f) for the field, given in the latter case by $Q = (2I_f/\omega)^{1/2}\cos\theta_f$ and $P = -(2I_f\omega)^{1/2}\sin\theta_f$, eq 1 is transformed to

$$H = I_m\omega_m^0 - I_m^2\omega_m^0\chi + I_f\omega - E_o\mu(I_m,\theta_m)\cos\theta_f \quad , \tag{2}$$

where ω_m^0 and $\omega_m^0\chi$ are the harmonic angular frequency and anharmonicity, respectively, of the Morse oscillator and $E_o = (8\pi I_f\omega/V_c)^{1/2}$ is defined as the field strength.[11,12] The actions I_i in eq 2 are defined as the usual action variables[26] divided by 2π and $\hbar = 1$ throughout the present paper.

A 1:1 resonance condition[15-17,19] exists when, for the value I_m^r of the action I_m, the frequency of the Morse oscillator $\omega_m = (\partial H_m/\partial I_m)_{I_m=I_m^r}$ satisfies

$$\omega_m(I_m^r) = \omega_m^0 - 2I_m^r\omega_m^0\chi \simeq \omega \quad . \tag{3}$$

When nonlinear coupling between oscillator modes is present and there is a near 1:1 resonance, the variable $\theta_m - \theta_f$ is a "slow" angle.[15-17,19] By virtue of eq 3, this angle satisfies

$$\frac{d}{dt}(\theta_m - \theta_f) \simeq 0 \quad . \tag{4}$$

This condition suggests a canonical transformation[15-17,19] such as

$$I_\alpha = 2I_m \;, \quad I_\beta = I_m + I_f \quad , \tag{5}$$

$$2\alpha = \theta_m - \theta_f + \delta \;, \quad \beta = \theta_f \quad , \tag{6}$$

where δ is a constant chosen as in ref 27 to ensure a real, negative contibution for the last term in eq 8 below (e.g., for the linear dipole approximation used later, δ equals π). The zeroth order Hamiltonian in the new action-angle variables becomes

$$H_0(I_\alpha, I_\beta) = I_\alpha\Omega - \omega_m^0\chi' I_\alpha^2 + I_\beta\omega \quad , \tag{7}$$

where $\Omega = (\omega_m^0 - \omega)/2$ and $\chi' = \chi/4$. The perturbation term in eq 2 $-E_o\mu(I_m,\theta_m)\cos\theta_f$ is then expanded in a complex-valued double Fourier series in θ_m and θ_f, expressed in terms of the new angle variables α and β, and averaged over the "fast" variable β. Only the terms having the "slow angle" variable 2α will remain after this averaging,[15-17,19] so the Hamiltonian for this 1:1 resonance system becomes

$$H = I_\alpha\Omega - \omega_m^0\chi' I_\alpha^2 + I_\beta\omega - V_o\cos 2\alpha \quad , \tag{8}$$

where V_o denotes $|2V_{1-1}(I_m^r, I_f)|$: V_{1-1} is the (1,-1) Fourier component, $-(2\pi)^{-2}\int_0^{2\pi}\int_0^{2\pi} E_o\mu(I_m^r,\theta_m)\cos\theta_f\, e^{-i(\theta_m-\theta_f)}\,d\theta_m\, d\theta_f$, evaluated at the resonance center[15-17,19] $I_m = I_m^r$ and at any I_f.

Because the angle β conjugate to the total action of the system I_β does not appear in eq 8, I_β is a constant of the motion in this approximation. The Hamiltonian (8) may then be written as

$$H = I_\beta\omega - H_R = E \quad , \tag{9}$$

where E is the total energy and H_R is a "resonance" Hamiltonian:[15-17,19]

$$H_R = E_R = \omega_m^0\chi' I_\alpha^2 - I_\alpha\Omega + V_o\cos 2\alpha \quad . \tag{10}$$

The quantity V_o in eq 10, given earlier, may be rewritten as

$$V_o = \left|\frac{E_o}{2\pi}\int_0^{2\pi}\mu(I_m^r,\theta_m)e^{-i\theta_m}\,d\theta_m\right| = E_o\tilde{\mu} \quad , \tag{11}$$

which is simply the field strength E_o times the fundamental Fourier component $\tilde{\mu}$ of the dipole moment function evaluated at the center of the resonance.

Uniform Semiclassical Approximation

The oscillator-field system may be quantized by converting eq 9 into a Schrödinger equation. To do this, the I_i's are replaced by semiclassical action operators,[21,22] given by $(1/i)\,d/d\alpha + 1$ for the α motion and by $(1/i)\,d/d\beta + 1$ for the β motion. For a separable semiclassical basis $\psi(\alpha)\varphi(\beta)$, this procedure yields the semiclassical Schrödinger equations for $\psi(\alpha)$ and $\varphi(\beta)$:

$$\frac{d\varphi}{d\beta} - i[E_\beta/\omega - 1]\,\varphi = 0 \quad , \tag{12}$$

where $E_\beta = I_\beta\omega$, and

$$\frac{d^2\psi}{d\alpha^2} - 2i(\xi-1)\frac{d\psi}{d\alpha} + [A - 2q\cos 2\alpha]\,\psi = 0 \quad , \tag{13}$$

where

$$\xi = 2\Omega/\omega_m^0\chi = 2I_m^r , \quad A = [4(\Omega+E_\beta-E)/\omega_m^0\chi] - 1 , \quad q = 2V_o/\omega_m^0\chi \, . \tag{14}$$

Solution of eq 12 yields an equation for the (normalized) primitive semiclassical wavefunction[22] $(2\pi)^{-1/2}\exp[i(I_\beta-1)\beta]$. Equation 13 may be solved by defining an auxilary function $F(\alpha)$, given by[21]

$$F(\alpha) = \exp[i(1-\xi)\alpha]\psi(\alpha) \quad , \tag{15}$$

and introducing it into eq 13. One thus obtains Mathieu's equation[28,29] for $F(\alpha)$:

$$\frac{d^2F(\alpha)}{d\alpha^2} + [a_\nu - 2q\cos 2\alpha]F(\alpha) = 0 \quad , \tag{16}$$

where

$$a_\nu = (\xi-1)^2 + A \quad . \tag{17}$$

The order ν of the Mathieu equation[28,29] is given by[30]

$$\nu = 2I_m - \xi = 2(I_m - I_m^T) \quad , \tag{18}$$

which is, in general, not an integer. The solutions of eq 16 together with eqs 12, 14, and 17 give the uniform semiclassical eigenvalues for the Hamiltonian (1) as

$$E = E_\beta + I_m^T\,\Omega - a_\nu\omega_m^0\chi' \quad . \tag{19}$$

Semiclassical Dressed State Description

When the semiclassical eigenvalues of the Hamiltonian (1) as given by eq 19 are plotted as a function of the field frequency ω and at constant E_0, they exhibit avoided crossings, as in Figure 1. The frequencies ω at which these avoided crossings occur may be obtained from the semiclassical uniform approximation formula (eq 16); namely they occur when the orders of the Mathieu equation correspond to integers[21,28] such that

$$\nu = -\nu' \quad . \tag{20}$$

Here, ν and ν' correspond to the two different states involved in the avoided crossing. Typically, the characteristic values a_ν and b_ν of the Mathieu equation (eq 16) are associated with these states.[21,28,29]

The interpretation of the states involved in an avoided crossing may be clarified by considering the quantum numbers associated with the zeroth order actions:

$$\begin{aligned} I_m &= (n_m + \tfrac{1}{2}) \quad , \quad I_f = N + n \quad , \\ I'_m &= (n'_m + \tfrac{1}{2}) \quad , \quad I'_f = N \quad , \end{aligned} \tag{21}$$

where N is a very large number of "background" photons for the typical laser cavity,[31] n is the number of photons to be absorbed ($n \ll N$), and n_m (n'_m) is the quantum number of the Morse oscillator. These quantum numbers in eq 21 are associated with the zeroth order semiclassical eigenstates,[22] denoted in this section by $|n_m, N+n>$ and $|n'_m, N>$. A further simplification may be made since N is normally so large that it may be taken as a constant and hence the field strength $E_0 \equiv (8\pi N\omega/V_c)^{1/2}$ is constant.[11,12,32]

For a two-level model,[33] an isolated avoided crossing[21] of the eigenvalues indicates a zeroth order degeneracy between the basis states (e.g., $|n_m, N+n>$ and $|n'_m, N>$ in the present instance) at the avoided crossing. Therefore, for non-zero coupling between the field and the oscillator, the avoided crossing condition identifies the resonant excitation frequency where the Morse state $|n_m>$ absorbs n photons and is excited to the state $|n'_m>$.

The avoided crossing condition is given by eq 20 and is satisfied whenever ξ equals $n_m + n'_m + 1$[21] or, from eq 14,

$$I_m^r = (n_m + n_m' + 1)/2 \quad . \tag{22}$$

This I_m^r is seen to be the mean action $\bar{I}_m$ between the two levels undergoing the avoided crossing. Hence, eq 22 together with eq 3 indicates that, at a field frequency

$$\omega = \omega_m^0 - 2\bar{I}_m \, \omega_m^0 \chi \quad , \tag{23}$$

a field induced resonance between states with Morse quantum numbers n_m and n_m' occurs. It has been noted (e.g., ref 34) that n times the classical frequency in eq 23 corresponds exactly to the quantum mechanical resonant excitation (or Bohr) frequency, $\omega_{n_m' n_m} \equiv E_{n_m'} - E_{n_m}$, between the two Morse oscillator levels with energies $E_{n_m'}$ and E_{n_m}.

The splittings between states at isolated avoided crossings are,[21,28] for small enough q (the typical case in the present problem[35]),

$$(n_m \to n_m+1) \quad \Delta E_1 = \frac{(a_1 - b_1)\omega_m^0 \chi}{4} = V_o + O(q^3) \quad , \tag{24a}$$

$$(n_m \to n_m+2) \quad \Delta E_2 = \frac{(a_2 - b_2)\omega_m^0 \chi}{4} = \frac{V_o^2}{2\omega_m^0 \chi} + O(q^4) \quad , \tag{24b}$$

and so on for higher order transitions. One recalls from eqs 11 and 22 that the V_o's in eqs 24a and 24b are functions of n_m and n_m'. When the system is initially in one of the zeroth order states involved in the avoided crossing, the splittings ΔE_n of the eigenvalues give the characteristic Rabi frequency ω_R for oscillation between these zeroth order states.[33] One may demonstrate this as follows:

Suppose at $t = 0$ the system is in an initial state $|\psi(0)>$ that may be expressed as a linear combination of only two "exact" semiclassical wavefunctions $|a>$ and $|b>$. Due to the coupling between the field and the oscillator, this state evolves in time as

$$|\psi(t)\rangle = e^{-iH_{sc}t}|\psi(0)\rangle = C_a|a\rangle e^{-iE_a t} + C_b|b\rangle e^{-iE_b t} \ , \tag{25}$$

where C_a equals $\langle a|\psi(0)\rangle$, C_b equals $\langle b|\psi(0)\rangle$, and H_{sc} is the semiclassical Hamiltonian (9) (expressed, as in the previous section, in terms of semiclassical action-angle operators). The probability amplitude $|\langle\psi(0)|\psi(t)\rangle|^2$ for the state $|\psi(0)\rangle$ oscillates in time as $\cos^2([E_a - E_b]t/2)$, where $E_a > E_b$. If the field frequency ω is such that the exact states $|a\rangle$ and $|b\rangle$ are at an avoided crossing, then their splitting $\Delta E_n \equiv E_a - E_b$ is defined as the Rabi frequency ω_R.[33]

When $|\psi(0)\rangle$ is taken to be the "unexcited" dressed state $|n_m, N+n\rangle$, the probability for being in the excited dressed state $|n_m', N\rangle$ is given by[33]

$$P_{n_m' n_m}(t) = |\langle n_m', N|e^{-iH_{sc}t}|n_m, N+n\rangle|^2 \ , \tag{26}$$

while the probability for being in the state $|n_m, N+n\rangle$ is given by

$$P_{n_m n_m}(t) = |\langle n_m, N+n|e^{-iH_{sc}t}|n_m, N+n\rangle|^2 \ . \tag{27}$$

For the present two-level model, the energy absorption[8] $\langle E(t)\rangle - \langle E(0)\rangle$ of the Morse oscillator starting in the state $|n_m\rangle$ is given by

$$\begin{aligned}\langle\psi(t)|H_m|\psi(t)\rangle - E_{n_m} &\simeq E_{n_m'} P_{n_m' n_m}(t) + E_{n_m}[P_{n_m n_m}(t) - 1] \\ &= \omega_{n_m' n_m} P_{n_m' n_m}(t) \ .\end{aligned} \tag{28}$$

This field-induced oscillation between zeroth order states describes the time-varying absorption process of n photons by the Morse oscillator. It has recently been demonstrated numerically that a two-level Rabi model is a good approximation at (or close to) resonance even for large laser intensities (e.g., 44 TW/cm^2).[8]

Relationship to Quantum Dressed State Theory

In the quantum dressed state picture,[1] the classical Hamiltonian in eq (1) is quantized by first replacing the classical variables (p, r, P, Q) with the quantum mechanical operators ($\hat{p}$, $\hat{r}$, $\hat{P}$, $\hat{Q}$) and then solving the matrix representation of the quantum counterpart of eq (1) for the eigenvalues and eigenvectors. When plotted vs. ω, an avoided crossing of two eigenvalues of this matrix (the dressed state matrix[1,36]) identifies, as already noted for the semiclassical case, a resonant excitation frequency, and the splitting between the states at the avoided crossing is the Rabi frequency of the transition.[1] For a given field frequency ω, the correspondence of the quantum Rabi and resonant excitation frequencies with those obtained by the semiclassical treatment in the previous section may be demonstrated as follows:

To describe an isolated quantum mechanical avoided crossing corresponding to an n-photon transition, it is convenient to transform the full dressed state matrix H via a Van Vleck transformation[37] $\mathrm{T}^{-1}\mathrm{H}\,\mathrm{T}$ of order k (where $k \geq n$). This transformation serves to diagonalize H to order k except for any zeroth order states that are degenerate or nearly degenerate. This procedure is ideal for the present purpose of treating an isolated avoided crossing, since here one is dealing with a case where only two zeroth order states are degenerate or nearly degenerate. Specifically, if an isolated avoided crossing between two levels, as in Figure 1, occurs in a small frequency interval $\Delta\omega$, there are only two states in that interval which are nearly degenerate amid the vast number of states in H. The Van Vleck transformation then yields a matrix G that is diagonal to k^{th} order except for a 2 × 2 submatrix

$$\begin{bmatrix} G_{n_m' n_m'} & G_{n_m' n_m} \\ G_{n_m n_m'} & G_{n_m n_m} \end{bmatrix} = \begin{bmatrix} E_{n_m'} + N\omega & V^{(k)} \\ V^{(k)*} & E_{n_m} + (N+n)\omega \end{bmatrix} \tag{29}$$

that includes the two degenerate or nearly degenerate quantum states $|n_m', N>$ and $|n_m, N+n>$. In eq 29, E_{n_m} ($E_{n_m'}$) is the energy of a quantum mechanical Morse oscillator eigenstate $|n_m>$ ($|n_m'>$), $V^{(k)}$ is the perturbation coupling of order k between states, and N, n, and ω are as defined previously. There are, in general, some diagonal perturbation corrections, but, for realistic laser intensities (< 1 TW/cm^2), they are estimated to have a negligible effect on the resonant excitation frequencies.[37] The contribution from the off-resonant components of the matrix H is shifted via the Van Vleck transformation to the coupling term $V^{(k)}$. Expressions for the coupling elements $V^{(k)}$ through third order ($k = 3$) may be found in ref 37. In general, a coupling element of at least order n is necessary to induce an n-photon transition (i.e., $V^{(k)}$, where $k < n$, would be equal to zero for the n-photon transition). Higher order terms ($k > n$) usually have a negligible contribution for such transitions, so only terms $V^{(n)}$ of n^{th} order will be considered.[38]

The two diagonal elements of the matrix (29) become degenerate and hence undergo an avoided crossing when $n\omega$ equals $\omega_{n_m' n_m}$. As in the semiclassical case, there is a field induced resonant transition between Morse oscillator states $|n_m>$ and $|n_m'>$ at this frequency. In the previous section, n times the semiclassically calculated resonance frequency (eq 23) was stated to correspond exactly with the quantum value for $\omega_{n_m' n_m}$. This may be demonstrated by considering the quantum expression for $\omega_{n_m' n_m}$:

$$\omega_{n_m' n_m} = (n_m' - n_m)\omega_m^0 - (n_m' - n_m)(n_m' + n_m + 1)\omega_m^0 \chi \quad . \qquad (30)$$

For the 1:1 resonance, this is simply $n\omega$, where ω is the classical frequency in eq 23 and n equals $n_m' - n_m$.

At the resonant field frequency, the matrix (29) yields the time-dependent Rabi flopping formula[33] $\sim \sin^2(\omega_R t/2)$ for the probability of being in the dressed Morse oscillator state $|n_m', N>$ after starting in dressed state $|n_m, N+n>$, where the quantum Rabi frequency ω_R for n photon absorption equals $2|V^{(n)}|$.[33] It is seen from eqs 24a, 24b, and 29 that, at resonance, the semiclassically calculated Rabi frequency ΔE_n is to be compared, in this approximation, to the quantum Rabi frequency $2|V^{(n)}|$. These quantities are now considered for two specific cases:

a) One-photon absorption

The semiclassical one-photon Rabi frequency is given by eq 24a as $E_o\tilde{\mu}$, whereas the quantum one-photon Rabi frequency is given by[39] $E_o<n_m'|\hat{\mu}|n_m>$ with n_m' equal to $n_m + 1$. In this case, the Morse oscillator matrix element $<n_m'|\hat{\mu}|n_m>$ appearing in the quantum mechanical quantity $V^{(1)}$ is to be compared with the fundamental Fourier component $\tilde{\mu}$ (cf. eq 11) evaluated at the mean action $\bar{I}_m = n_m + 1$ for the one-photon transition. The same semiclassical Rabi frequency for one-photon absorption in terms of a Fourier component has been obtained by a somewhat different argument.[18] These Fourier components have recently been shown to give excellent agreement with the quantum matrix elements for Morse[34,40] and other[40,41] oscillators. Using HF Morse parameters[7a] and a linear dipole approximation, values of $<n_m+1|r|n_1>$ and $\tilde{r}(\bar{I}_m)$ are compared in Table I.

b) Two-photon absorption

The semiclassical two-photon Rabi frequency is given by eq 24b as $(E_o\tilde{\mu})^2/2\omega_m^0\chi$. For this case, $\tilde{\mu}$ is the fundamental Fourier component of the dipole moment function evaluated at the mean action $\bar{I}_m = (2n_m + 3)/2$ for the two-photon transition between the Morse states $|n_m>$ and $|n_m+2>$. It is clear that the semiclassical two-photon Rabi frequency has the proper dependence on the field strength[42] unlike a previous semiclassical study.[18] Moreover, this quantity is inversely dependent on $\omega_m^0\chi$, reflecting the detuning of the two-photon resonance by the Morse anharmonicity.

To demonstrate the correspondence of the semiclassical Rabi frequency with the quantum result, the quantum two-photon coupling element $V^{(2)}$ is examined. This coupling term for the resonant field frequency $2\omega = \omega_{n_m^{'}n_m}$, where $n_m^{'} = n_m + 2$, and for large N is given by[43]

$$V^{(2)} = \frac{E_o^2}{4}\sum_p\left[\frac{<n_m+2|\hat{\mu}|p><p\,|\hat{\mu}|n_m>}{\omega - \omega_{pn_m}}\right] \quad , \qquad (31)$$

with E_o being a constant. Using the resonance condition (eq 23) and noting that the term with $<n_m+2|\hat{\mu}|n_m+1><n_m+1|\hat{\mu}|n_m>$ is the dominant contribution to the sum over Morse states $|p>$,[44] the quantum two-photon Rabi frequency is given approximately by

$$2|V^{(2)}| \simeq \frac{E_o^2}{2\omega_m^0\chi}<n_m+2|\hat{\mu}|n_m+1><n_m+1|\hat{\mu}|n_m> \quad . \qquad (32)$$

From eqs 24b and 32, the agreement between the semiclassical and quantum Rabi frequencies is expected to be good if

$$[\tilde{\mu}\,(\bar{I}_m)]^2 \simeq <n_m+2|\hat{\mu}|n_m+1><n_m+1|\hat{\mu}|n_m> \quad . \qquad (33)$$

A comparison of these two quantities for HF and a linear dipole approximation is given in Table II.

Adaptation to a Polyatomic Molecule

For a non-rotating polyatomic molecule in a radiation field, it is assumed that the Hamiltonian may be written as

$$H = H_o(\boldsymbol{I}) + I_f\,\omega - \boldsymbol{E}_o\cdot\boldsymbol{\mu}(\boldsymbol{I},\boldsymbol{\theta})\cos\theta_f \quad . \tag{34}$$

Here, I_f and θ_f refer to the radiation field as before, and the $(\boldsymbol{I},\boldsymbol{\theta})$ form a set of "good" action-angle variables describing perhaps Morse-like vibrational modes with no internal resonances.[15,19] These variables may be obtained, for instance, by perturbative or other approximate methods. If there is a resonance between the field and some vibrational frequency $\omega_m = \partial H_o/\partial I_m$ of the molecule, I_m being the m^{th} action with conjugate angle θ_m, then the angle variable $\theta_m - \theta_f$ becomes a "slow" angle. If the Hamiltonian H in eq 34 is averaged over all molecular angle variables θ_i except θ_m and *if* H_o can be expanded in a Taylor series in I_m about $I_m = 0$, one obtains

$$H = H_m(I_m,\boldsymbol{I}') + I_f\,\omega - \boldsymbol{E}_o\cdot\bar{\boldsymbol{\mu}}(\boldsymbol{I},\theta_m)\cos\theta_f + H_o'(\boldsymbol{I}') \quad , \tag{35}$$

where $H_o'(\boldsymbol{I}')$ is a constant term for the set of actions $\boldsymbol{I}'$ excluding I_m. If H_m is truncated at a quadratic function of I_m (which may depend on $\boldsymbol{I}'$), the Hamiltonian in eq 35 has the form of eq 2, but ω_m^0 now denotes $(\partial H_o/\partial I_m)_{I_m=0}$ and $\omega_m^0\chi$ denotes $\frac{1}{2}(\partial^2 H_o/\partial I_m^2)_{I_m=0}$.

Discussion

A semiclassical treatment of one- and two-photon absorption by a

Morse oscillator has been presented in this paper that has a direct correspondence with the quantum mechanical dressed state approach. The use of the Mathieu function uniform approximation allows one to calculate the Rabi and resonant excitation frequencies directly from eqs 23 - 24b without the use of a multistate matrix treatment. For this reason, the present uniform semiclassical method is useful for characterizing multiphoton absorption processes in a simple way. In addition, it has been noted[18] that, for realistic laser intensities (< 1 TW/cm^2), two-photon absorption may correspond to a non-classical path. (More specifically, classical calculations[8] have shown no two-photon absorption). This fact indicates the usefulness of an appropriate uniformization procedure to treat such a process purely semiclassically, for such a uniform approximation permits quantum mechanical tunneling.

It has been noted[18] that the solutions of the Mathieu equation (eq 16) contain contributions from unphysical "states" corresponding to negative quantum numbers. This problem arises whenever primitive semiclassical wavefunctions in an (approximate) action-angle representation[22] are used. In the case of an oscillator, one usually omits, by fiat, states with negative principal quantum numbers. In the present case, however, these "states" are distant in energy and found not to have a significant contribution. A similar situation would occur in other uses of Mathieu functions, e.g., in a description of molecular Fermi resonances.[27]

The uniform semiclassical technique presented in this paper is not applicable in the regime of overlapping classical resonances[15-17,19,20] and/or overlapping avoided crossings (e.g., ref 20). When there are overlapping classical resonances, the dynamics are thought to be chaotic classically,[15-17,19,20] and, when there are overlapping avoided crossings, the system may in some sense be regarded as quantum mechanically chaotic (e.g., ref 20). One could use, however, a multilevel semiclassical matrix treatment[18] when a simple two-level treatment is not applicable.

The uniform semiclassical method allows one to calculate the absorption probabilities using the Fourier components of the dipole moment function, some of which exist in analytic form.[40,45] In some cases, this may be preferable to calculating the more complicated quantum dipole matrix elements for the Morse oscillator.[46] When not determined analytically, the Fourier components for any general dipole moment function may be found numerically by integrating a classical trajectory with the appropriate mean action as an initial condition and then calculating the power spectrum of $\mu(t)$.[34,41,47]

Acknowledgement

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Appendix: An Alternative Semiclassical Approach

It has been noted[11-13] that the time-independent[23] and time-dependent, classical radiation field[9] formulations of the molecule-field Hamiltonian are equivalent when the number of photons N is large. For completeness, we derive here the semiclassical Schrödinger equation (eq 13) starting from the time-dependent, classical radiation field point of view.

The time-dependent Hamiltonian for the interaction of a Morse oscillator with a classical radiation field is given by[9]

$$H(r,p,t) = H_m(r,p) - E_o\mu(r)\cos \omega t \quad , \tag{A1}$$

where $H_m(r,p)$ is the Morse oscillator Hamiltonian in terms of the displacement coordinate r and its conjugate momentum p. Written in Morse oscillator action-angle variables (I_m,θ_m),[25] eq A1 becomes

$$H(I_m,\theta_m,t) = I_m\omega_m^0 - I_m^2\omega_m^0\chi - E_o\mu(I_m,\theta_m)\cos \omega t \quad . \tag{A2}$$

The formulation of the resonance Hamiltonian for the 1:1 resonance is performed in two steps. First, the $V = -E_o\mu(I_m,\theta_m)\cos \omega t$ perturbation term is expanded in a Fourier series in θ_m; the result is expressed in terms of the "slow" angle variable $\theta_m - \omega t$ and averaged over all remaining functions of θ_m. Second, the time-dependent canonical transformation

$$I_\alpha = 2I_m \; , \quad 2\alpha = \theta_m - \omega t + \delta \tag{A3}$$

is introduced to yield a new set of action-angle variables (I_α,α) appropriate for the 1:1 resonance. This transformation is generated by the F_2-type generating function (e.g., ref 18 and ref 26, p.383)

$$F_2 = I_\alpha(\theta_m - \omega t + \delta)/2 \tag{A4}$$

and thus gives the new Hamiltonian K from the expression

$$K = H(I_\alpha, \alpha, t) + \partial F_2 / \partial t \quad . \tag{A5}$$

The new Hamiltonian K now given by

$$K = I_\alpha(\omega_m^0 - \omega)/2 - I_\alpha^2 \omega_m^0 \chi / 4 - V_o \cos 2\alpha \quad , \tag{A6}$$

where V_o is the same as in eq 11 of the text. Using the definitions of Ω and χ' given previously, the resonance Hamiltonian is written as

$$H_R = -K = \omega_m^0 \chi' I_\alpha^2 - I_\alpha \Omega + V_o \cos 2\alpha \quad , \tag{A7}$$

which is identical to eq 9 of the text minus the constant $I_\beta \omega$ term. Gray[18] has obtained a very similar, but not identical (because of the use of a slightly different canonical transformation), resonance Hamiltonian.

As in the text, introduction of the semiclassical action operator $(1/i)d/d\alpha + 1$ into eq A7 yields eq 13. As a result, both the time-dependent, classical radiation field and time-independent formulations yield the same uniform semiclassical Mathieu equation and hence the same semiclassical resonant and Rabi frequencies.

The direct correspondence of the time-independent semiclassical formulation with the quantum dressed state theory is presented in the text. The time-dependent, classical radiation field Hamiltonian (A1) may be converted to a time-independent Floquet matrix[49] that is formally equivalent[49,50] to the quantum dressed state matrix when N is large. The language of avoided crossings may then be used in relation to the so-called quasi-energies[50] of this Floquet matrix.

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(31) The zero point energy of the field mode is not written explicitly here since $N \gg \frac{1}{2}$. For a photon energy of ~ 1000 cm^{-1}, the photon densi-

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(35) For HF Morse parameters[7a] and a laser intensity of 1 TW/cm^2,[18] the expansions for a_ν and b_ν in ref 28, p. 16, are found to be rapidly convergent.

(36) This matrix is defined as the matrix representation of the Hamiltonian (1) using the quantum "dressed state" basis[1] $|p,j>$, where $|p>$ and $|j>$ denote a Morse oscillator eigenstate with quantum number p and a harmonic oscillator photon state with occupation number j, respectively.

(37) The Van Vleck transformation is given, for example, in J.E. Wollrab, "Rotational Spectra and Molecular Structure", Academic Press, New York, 1967, Appendix 7. In the matrix (29), the diagonal self energy corrections for the typical Morse oscillator had a negligible effect on the resonant excitation frequencies for the system treated and have been neglected (e.g., for a laser intensity of 1 TW/cm^2, the one- and two-photon peaks for HF show virtually no shifts from the expected zero-order Morse oscillator resonant excitation frequencies[8]).

(38) For the perturbation $V = -(4\pi\omega^2/V_c)^{1/2}\mu(r)Q$ in eq 1, the quantum one- and two-photon matrix elements are given at resonance by $V^{(1)} = \langle n_m^{'},N\,|\,V\,|\,n_m,N+1\rangle$ and

$$V^{(2)} = \sum_j{}' \sum_p{}' \frac{\langle n_m^{'},N\,|\,V\,|\,p,j\rangle\langle p,j\,|\,V\,|\,n_m,N+2\rangle}{(N+2-j)\omega \; - \; \omega_{pn_m}} \;,$$

respectively. The summations in the latter case are over the photon states $|j\rangle$ and Morse oscillator states $|p\rangle$, excluding those appearing in the diagonal elements of eq 29. The equality at resonance $2\omega = \omega_{n_m^{'}n_m}$ has been used here to simplify the expression for $V^{(2)}$ in ref 37. For the general case of the field tuned slightly off-resonance from the two-photon transition frequency $\omega_{n_m^{'}n_m}$, $V^{(2)}$ is given by the above expression with an added multiplicative factor $(d_{pj}+\Delta/2)/(d_{pj}+\Delta)$, where d_{pj} is the denominator term from above, and Δ is identified as $\omega_{n_m^{\prime}n_m} - 2\omega$.

(39) From footnote 38, $V^{(1)}$ is given by $-(4\pi\omega^2/V_c)^{1/2}\langle n_m^{'}\,|\,\mu\,|\,n_m\rangle\langle N\,|\,Q\,|\,N+1\rangle$. Using harmonic oscillator selection rules for the field mode, this expression reduces to $-(8\pi(N+1)\omega/V_c)^{1/2}\langle n_m^{'}\,|\,\mu\,|\,n_m\rangle/2$. Since $N \gg 1$ and N equals I_f, $V^{(1)}$ may be written as $-E_o\langle n_m^{'}\,|\,\mu\,|\,n_m\rangle/2$, where $E_o = (8\pi I_f\,\omega/V_c)^{1/2}$ as in the text.

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(44) Including only the nearly resonant term for the dressed state $|n_m+1,N+1>$ (cf. footnote 36) is similar to making the rotating wave approximation (RWA). For a discussion of the usual RWA, see ref 48 below. A discussion of the RWA in relation to dressed state theory is given in ref 1, p. 18. **Using the parameters for HF given in ref 7a and a laser intensity of 1 TW/cm^2, the neglected terms in the summation (eq 31) were found to contribute less than 5% to the Rabi frequency.**

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TABLE I: Quantum $\langle n_m + 1|r|n_m\rangle$ vs. Semiclassical $\tilde{r}(\bar{I}_m)$

n_m	Q (a. u.)	SC (a. u.)
0	0.1246	0.1246
1	0.1781	0.1781
2	0.2205	0.2205
3	0.2575	0.2576
4	0.2912	0.2913
5	0.3228	0.3229

TABLE II: Quantum $\langle n_m + 2|r|n_m + 1\rangle\langle n_m + 1|r|n_m\rangle$ vs. Semiclassical $[\tilde{r}(I_m)]^2$

n_m	Q (a. u.)	SC (a. u.)
0	0. 0222	0. 0235
1	0. 0393	0. 0401
2	0. 0568	0. 0574
3	0. 0750	0. 0755
4	0. 0940	0. 0945
5	0. 1139	0. 1143

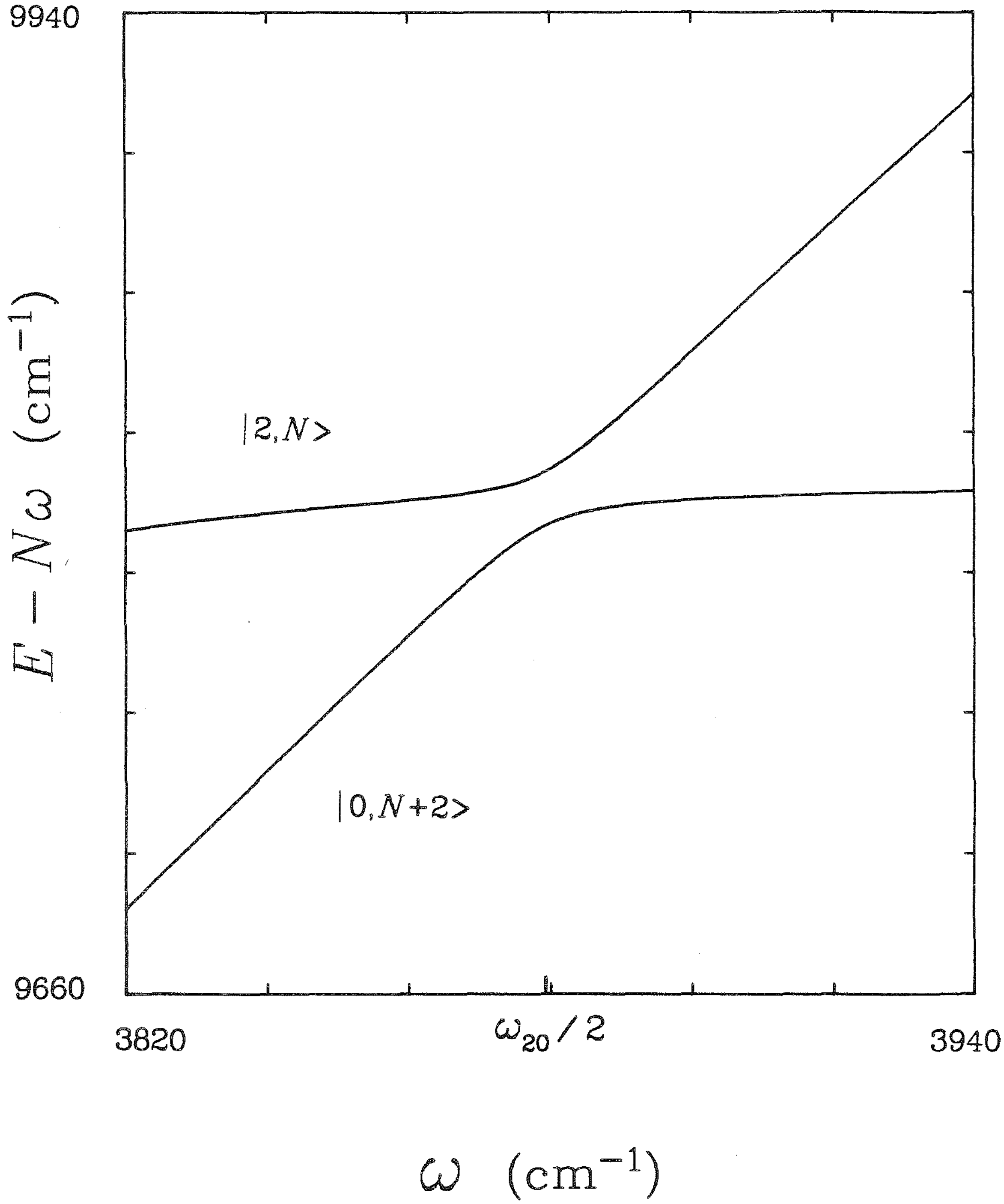

Figure 1. A semiclassical two-photon avoided crossing of the dressed states $|0,N+2>$ and $|2,N>$. The resonant excitation frequency $\omega_{20}/2 = 3879$ cm^{-1} is indicated by the location of the avoided crossing.

Chapter 5: Adiabatically Reduced Coupled Equations for Intramolecular Dynamics Calculations

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Adiabatically reduced coupled equations for intramolecular dynamics calculations

Gregory A. Voth and R. A. Marcus
Arthur Amos Noyes Laboratory of Chemical Physics, California Institute of Technology,[a] *Pasadena, California 91125*

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"Adiabatically reduced" coupled equations are derived to obtain an approximate quantum mechanical solution for the dynamics of nonstationary states in isolated polyatomic molecules. Under suitable conditions, the number of such equations is considerably less than the number of coupled equations needed in practice for the exact calculation. The relationship of the present technique to several other methods, including the partitioning method, is discussed, and specific applications of the present treatment are given.

I. INTRODUCTION

In recent years, there has been much experimental and theoretical interest in the quantum dynamics of initially prepared nonstationary vibronic,[1,2] rovibronic,[3] rovibrational,[4] and vibrational[5–16] states in isolated polyatomic molecules. The richness of the underlying dynamics is evident, e.g., in recent experimental results on the evolution of initially prepared vibronic states in anthracene.[7,8] In these experiments, periodic few-state quantum evolution or "beating" was observed at low excess energies, and dissipative[17] intramolecular vibrational energy redistribution (IVR) was detected at higher energies.

Theoretically, the exact treatment of the dynamical evolution of initially prepared zeroth-order states is, in principle, straightforward (e.g., Refs. 1–16). In practice, it is usually quite difficult or not computationally feasible due to the large number of states in a typical molecule.[18] For this reason, a variety of approximate or phenomenological methods have been devised to treat these problems, ranging from few-level treatments for sparse level densities (e.g., Ref. 7) to Bixon–Jortner-like models[19] for large level densities. In general, it is often assumed that any zeroth-order states coupled weakly to and/or reasonably off-resonant from the initially prepared state do not significantly affect the subsequent evolution of that initial state (e.g., Refs. 12 and 14). An important exception to this situation is when the weakly coupled states provide the *only* coupling pathway of the initial state to other resonant states.[15,20] This latter effect, which has been discussed only recently within the context of IVR,[15,20] has also been suggested as being particularly important in the direct multiphoton excitation of few-level quantum systems (e.g., Ref. 21). Model calculations, given below, also show that weakly coupled/off-resonant states[22(a)] can have an important effect on the dynamical evolution of initially prepared states even when there is *direct* coupling to resonant or nearly resonant states.

With the advent of increasingly high resolution spectroscopy and real-time experiments such as those in Refs. 7 and 8, the usefulness of detailed and accurate dynamical calculations is apparent. In Sec. II, reduced coupled equations are derived that allow one to solve for the dynamics of a strongly coupled and/or resonant subset of states that includes the initial state. In suitable circumstances, this treatment considerably reduces the number of coupled equations needed in a typical calculation by using an effective Hamiltonian. The relationship of this effective Hamiltonian to those obtained by several existing techniques is discussed in Sec. III, and the theory is applied in Sec. IV to some model systems. A discussion of the results is given in Sec. V, along with concluding remarks in Sec. VI.

II. THEORY: ADIABATICALLY REDUCED COUPLED EQUATIONS

The general solution $|\Psi(t)\rangle$ of the time-dependent Schrödinger equation may be written in terms of a time-dependent phase factor and a new function $|\psi(t)\rangle$ (with $\hbar = 1$):

$$|\Psi(t)\rangle = |\psi(t)\rangle \exp(-i\langle H\rangle t), \tag{2.1}$$

where $\langle H\rangle$ is the time-independent mean energy of the nonstationary state given by

$$\langle H\rangle = \langle\Psi(t)|H|\Psi(t)\rangle. \tag{2.2}$$

This separation of the phase factor $\exp(-i\langle H\rangle t)$ from the time-dependent wave function represents a type of interaction representation for a nonstationary state in which the phase due to the mean energy of the initial state is removed from $|\Psi(t)\rangle$. If the second time-dependent factor $|\psi(t)\rangle$ is then expanded in terms of some orthonormal zeroth-order basis as

$$|\psi(t)\rangle = \sum_{i=1}^{N} b_i(t)|\varphi_i\rangle, \tag{2.3}$$

the following coupled equations are obtained:

$$\frac{db_j(t)}{dt} = i\langle H\rangle b_j(t) - i\sum_{i=1}^{N} b_i(t)H_{ji}. \tag{2.4}$$

In Eq. (2.4), the coefficients $b_j(t)$ are the time-dependent amplitudes of the zeroth-order states $|\varphi_j\rangle$, H_{ji} equals the matrix element $\langle\varphi_j|H|\varphi_i\rangle$ of the total Hamiltonian $H = H_0 + V$, and $|\varphi_i\rangle$ is an eigenstate of H_0. The usefulness of a coupled equations approach for determining the dynamics of nonstationary states has been discussed recently.[12,14] In particular, it allows the inclusion of more basis states in the

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[a] Contribution No. 7291.

calculations because an internal computer storage of large matrices is not required. In addition, the dynamics of the zeroth-order states are obtained directly from the amplitudes $b_j(t)$ rather than from an expansion in terms of the eigenstates and eigenvectors of the total Hamiltonian, the latter usually being obtained by a previous matrix diagonalization.[18]

It is now assumed that the complete set of zeroth-order states may usefully be partitioned into a set $\{|\varphi_j\rangle\}$ $(j=1,\ldots,n)$ of states nearly resonant (and/or strongly interacting), a linear combination of which constitutes the initial state, and into a set $\{|\varphi_k\rangle\}$ $(k=n+1,\ldots,n+m)$ of states off-resonant and/or weakly coupled[22(a)] to the manifold $\{|\varphi_j\rangle\}$. (In the simplest case, the initial state is one of the $|\varphi_j\rangle$'s.) The coupled equations for the two sets of states may be written in vector-matrix notation as

$$\frac{d}{dt}\mathbf{b}^R(t)=i(\langle H\rangle\mathbf{1}^R-\mathbf{H}^R)\mathbf{b}^R(t)-i\mathbf{V}^{R0}\mathbf{b}^0(t) \qquad (2.5)$$

and

$$\frac{d}{dt}\mathbf{b}^0(t)=i(\langle H\rangle\mathbf{1}^0-\mathbf{H}^0)\mathbf{b}^0(t)-i\mathbf{V}^{0R}\mathbf{b}^R(t), \qquad (2.6)$$

where $\mathbf{b}^R(t)$ $[\mathbf{b}^0(t)]$ is an n (m)-dimensional column vector containing the amplitudes for the resonant (off-resonant) states, $\langle H\rangle\mathbf{1}^R$ $(\langle H\rangle\mathbf{1}^0)$ is an $n\times n$ $(m\times m)$ diagonal matrix with the elements $\langle H\rangle\delta_{ir}$, $\mathbf{H}^R$ $(\mathbf{H}^0)$ is the $n\times n$ $(m\times m)$ Hamiltonian matrix for the resonant (off-resonant) states,[23] and $\mathbf{V}^{R0}$ $(\mathbf{V}^{0R})$ is an $n\times m$ $(m\times n)$ matrix composed of the coupling matrix elements $\langle\varphi_j|V|\varphi_k\rangle$ $(\langle\varphi_k|V|\varphi_j\rangle)$ between the two manifolds $\{|\varphi_j\rangle\}$ and $\{|\varphi_k\rangle\}$ $(j=1,\ldots,n;\ k=n+1,\ldots,n+m)$. The summation limit N in Eq. (2.4) equals $n+m$.

If the off-resonant/weakly coupled amplitudes $\mathbf{b}^0(t)$ remain negligible in magnitude throughout the course of the dynamics, then the derivative in Eq. (2.6) satisfies

$$\frac{d}{dt}\mathbf{b}^0(t)\simeq 0. \qquad (2.7)$$

Specifically, it is intended that Eq. (2.7) be valid over any relevant time scale of interest [e.g., for some fraction of time needed for an appreciable change in the resonant amplitudes $\mathbf{b}^R(t)$ to occur]. That is, $d\mathbf{b}^0(t)/dt$ is, on the average, zero on this time scale.[22(b)] This approximation is similar in spirit to those sometimes used in this study of the dynamics of direct multiphoton absorption by multilevel quantum mechanical systems.[24] It is also similar to the steady-state approximation used in solving reaction rate equations in chemical kinetics.

By virtue of Eqs. (2.6) and (2.7), the amplitudes $\mathbf{b}^0(t)$ may be solved for in terms of the amplitudes $\mathbf{b}^R(t)$ provided the matrix $(\langle H\rangle\mathbf{1}^0-\mathbf{H}^0)$ is nonsingular. One thereby obtains

$$\mathbf{b}^0(t)=(\langle H\rangle\mathbf{1}^0-\mathbf{H}^0)^{-1}\mathbf{V}^{0R}\mathbf{b}^R(t). \qquad (2.8)$$

From Eqs. (2.5) and (2.8), the reduced coupled equations for the desired amplitudes $\mathbf{b}^R(t)$ are thus given by

$$\frac{d}{dt}\mathbf{b}^R(t) =i[\langle H\rangle\mathbf{1}^R-\mathbf{H}^R-\mathbf{V}^{R0}(\langle H\rangle\mathbf{1}^0-\mathbf{H}^0)^{-1}\mathbf{V}^{0R}]\mathbf{b}^R(t). \qquad (2.9)$$

Equation (2.9) is expected to provide an accurate approximation to the true dynamics of the manifold of states $\{|\varphi_j\rangle\}$ $(j=1,\ldots,n)$ provided the amplitudes $\mathbf{b}^0(t)$, as determined by the exact dynamics, remain small. When the approximate dynamics are obtained by integrating the reduced coupled equations in Eq. (2.9), an *a posteriori* error estimate may be obtained by calculating $\mathbf{b}^0(t)$ via Eq. (2.8) [i.e., the elements of $\mathbf{b}^0(t)$ obtained in this way should remain small]. The amplitudes $\mathbf{b}^0(t)$ are clearly small, for instance, if all of the elements of the matrix $(\langle H\rangle\mathbf{1}^0-\mathbf{H}^0)^{-1}$ are small. In some cases, such a condition may be too restrictive because sign variations in these elements, as well as in $\mathbf{V}^{0R}$ and $\mathbf{b}^R(t)$, may lead to some cancellation.

The *reduced coupled equations* [Eq. (2.9)] have a particularly simple form when there is no coupling among the states in the off-resonant manifold $\{|\varphi_k\rangle\}$. This would be the case, for instance, if the manifold $\{|\varphi_k\rangle\}$ $(k=n+1,\ldots,N)$ had been prediagonalized. In that case, the matrix elements $[(\langle H\rangle\mathbf{1}^0-\mathbf{H}^0)^{-1}]_{kk'}$ equal $(\langle H\rangle-H_{kk})^{-1}\delta_{kk'}$, and the reduced coupled equations for the $\{|\varphi_j\rangle\}$ states are given by

$$\frac{db_j(t)}{dt}=i\langle H\rangle b_j(t) -i\sum_{i=1}^{n}\left(H_{ji}+\sum_{k=n+1}^{N}\frac{V_{jk}\,V_{ki}}{\langle H\rangle-H_{kk}}\right)b_i(t). \qquad (2.10)$$

If the strongly coupled manifold of states $\{|\varphi_j\rangle\}$ is weakly and smoothly coupled to a quasicontinuous background of states in the $\{|\varphi_k\rangle\}$ manifold, the summation over the $|\varphi_k\rangle$ states in Eq. (2.10) may be approximated by an integral:

$$\sum_{k=n+1}^{N}\frac{V_{jk}\,V_{ki}}{\langle H\rangle-H_{kk}}\simeq\int_{\Delta_{\min}}^{\Delta_{\max}}\rho(\Delta)f(\Delta)d\Delta, \qquad (2.11)$$

where

$$f(\Delta)\equiv V_{jk}(\Delta)V_{ki}(\Delta)/\Delta, \qquad (2.12)$$

and the integration limits $\Delta_{\min}$ to $\Delta_{\max}$ span the range of energy differences $\Delta\equiv\langle H\rangle-H_{kk}$. Equations (2.11) and (2.12) lead to a dependence of the coupled equations for the $\{|\varphi_j\rangle\}$ *manifold on the density* $\rho(\Delta)$ *of* $|\varphi_k\rangle$ *states*. Thus, in addition to the possible "dissipative" effect of a background quasicontinuum states,[17] the $\{|\varphi_j\rangle\}$ states can also experience this added dynamical effect. In the quantum beats found experimentally in anthracene,[7,8] the simple dynamics observed between the two or three vibronic levels may be due either to a very weak, nondissipative interaction with the background quasicontinuum of states, or to a direct coupling of those few "relevant" levels to each other, or to both.

In related treatments,[24] a reduction of the original coupled equations [e.g., Eq. (2.4)] to new equations in some subspace has sometimes been called "adiabatic elimination" or "adiabatic following." The adiabatic connotation in the present context is that the perturbation due to the off-resonant states has distorted the subspace of interest, but its dimension (characterized by a set of quantum numbers) remains intact. When the interaction representation given by Eq. (2.1) is used, the dynamics describing the coupling of the "resonant" subspace, which includes the initial state, to the off-resonant states involves large energy differences and hence large frequencies relative those characterizing that resonant subspace. In this general way, the separation and reduction of the coupled equations can be termed an adiabatic reduction.

In the next section the relationship of the present method to several existing quantum mechanical methods is discussed. For brevity, we have not included a discussion of the many useful semiclassical techniques that are present in the literature.

III. RELATIONSHIP TO OTHER QUANTUM TECHNIQUES

A. Partitioning methods

In order to relate the formalism of Sec. II to Hamiltonian matrix partitioning methods, the solution of the coupled differential equations in Eq. (2.9) is written as

$$\mathbf{b}^R(t) = \mathbf{U}\exp(-i\boldsymbol{\lambda}^R t)\mathbf{U}^\dagger\mathbf{b}^R(0), \tag{3.1}$$

where

$$\exp(-i\boldsymbol{\lambda}^R t) = \mathbf{U}^\dagger\exp(-i\mathbf{H}^R_{\text{eff}}\, t)\mathbf{U}. \tag{3.2}$$

In Eq. (3.2), $\mathbf{H}^R_{\text{eff}}$ is the effective Hamiltonian matrix for the (resonant) $\{|\varphi_j\rangle\}$ manifold given from Eq. (2.9) by

$$\mathbf{H}^R_{\text{eff}} = \mathbf{H}^R + \mathbf{V}^{R0}(\langle H\rangle\mathbf{1}^0 - \mathbf{H}^0)^{-1}\mathbf{V}^{0R} - \langle H\rangle\mathbf{1}^R, \tag{3.3}$$

and $\mathbf{U}$ and $\boldsymbol{\lambda}^R$ are, respectively, the unitary matrix of eigenvectors and the diagonal matrix of eigenvalues of $\mathbf{H}^R_{\text{eff}}$.

Several partitioning methods have been used to solve the matrix-eigenvalue problem for the time-independent Schrödinger equation (e.g., Refs. 25–27). It was shown[25] how a finite-dimensional Hamiltonian matrix can be formally partitioned into a new Hamiltonian for a particular subspace of interest (here, the resonant manifold $\{|\varphi_j\rangle\}$). For the problem discussed in Sec. II, the exact partitioned Hamiltonian would be[28]

$$\mathbf{H}^R_{\text{exact}} = \mathbf{H}^R + \mathbf{V}^{R0}(E\mathbf{1}^0 - \mathbf{H}^0)^{-1}\mathbf{V}^{0R}. \tag{3.4}$$

In an exact treatment of the eigenvalue problem, the secular equation

$$\det|\mathbf{H}^R_{\text{exact}} - E\mathbf{1}^R| = 0 \tag{3.5}$$

is then solved for the eigenvalues $\boldsymbol{\lambda}^R_{\text{exact}}$. Since the expression for $\mathbf{H}^R_{\text{exact}}$ [Eq. (3.4)] involves the matrix $E\mathbf{1}^0$, the solution for the roots λ_i of Eq. (3.5) is still a complicated problem, although the reduced dimension of the secular determinant may be helpful. As a result, a number of related iterative and perturbative schemes have been devised[25,27,29,30] to simplify the solution of Eq. (3.5). For a nondegenerate energy level, the matrix $\mathbf{H}^R_{\text{exact}}$ has one element and these methods are potentially quite powerful, while for degenerate or nearly degenerate levels, approximate approaches based on Eqs. (3.4) and (3.5) are more difficult and have met with varying degrees of success (cf. discussion in Refs. 27 and 30).

The method developed in the present paper amounts to defining an effective Hamiltonian by replacing the matrix $E\mathbf{1}^0$ in Eq. (3.4) by the constant matrix $\langle H\rangle\mathbf{1}^0$. This method yields eigenvalues for the $\{|\varphi_j\rangle\}$ manifold which depend on $\langle H\rangle$ and hence the initial nonstationary state. The correct eigenvalues are, of course, independent of the initial conditions. The present choice of $\langle H\rangle$ in Eq. (3.3) arose from a dynamical, rather than a static, analysis and provides an approximate or "average" representation of the exact eigensolutions of Eq. (3.5). The dynamics of the initial state are thus obtained using an effective Hamiltonian [Eq. (3.3)] rather than by performing an accurate determination of the roots of Eq. (3.5). The effective Hamiltonian given by Eq. (3.3) may not, therefore, be the method of choice when the primary purpose is to obtain highly accurate eigenvalues of the exact Hamiltonian [Eq. (3.5)]. However, it is useful in obtaining approximate, and simplified, solutions for the dynamics.

The above partitioning formalism [Eqs. (3.3)–(3.5)] is also closely related to a resolvent plus projection operator treatment of the dynamics.[31] For this purpose, it is useful to introduce here the projection operators for the $\{|\varphi_j\rangle\}$ and $\{|\varphi_k\rangle\}$ manifolds:

$$P = \sum_{j=1}^{n}|\varphi_j\rangle\langle\varphi_j|, \quad Q = \sum_{k=n+1}^{N}|\varphi_k\rangle\langle\varphi_k|. \tag{3.6}$$

These projection operators have the usual properties that $P^2(Q^2)$ equals $P(Q)$ and that $PQ(QP)$ equals zero. Using $N\times N$ matrix representations $\mathbf{P}$ and $\mathbf{Q}$ of these operators in the zeroth-order basis, where the elements of $\mathbf{P}$ for $j>n$ and of $\mathbf{Q}$ for $k<n+1$ are all zeros, the coupled equations in Eq. (2.9) for the states spanned by the operator $\mathbf{P}$ may be written as

$$\frac{d}{dt}\mathbf{Pb}(t) = i\langle H\rangle\mathbf{Pb}(t) - i\,\mathbf{P}[\mathbf{H} + \mathbf{VQ}(\langle H\rangle\mathbf{1} - \mathbf{QHQ})^{-1}\mathbf{QV}]\mathbf{Pb}(t), \tag{3.7}$$

where $\mathbf{V}$ is the coupling matrix, and all matrices are N-dimensional. By inspection of Eq. (3.7), it is seen that the dynamics of the amplitudes $\mathbf{Pb}(t)$ are determined by the effective Hamiltonian[32]

$$\mathbf{H}_{\text{eff}} = \mathbf{P}[\mathbf{H} + \mathbf{VQ}(\langle H\rangle\mathbf{1} - \mathbf{QHQ})^{-1}\mathbf{QV} - \langle H\rangle]\mathbf{P}. \tag{3.8}$$

We next compare this result with that based on the resolvent operator. Using an earlier partitioning formalism,[26,33] the amplitudes $\mathbf{Pb}(t)$ for the exact problem have been expressed[31] in terms of a projection of the resolvent operator. These exact amplitudes $b_j(t)$ are given in terms of the resolvent operator $G(E)$ by[31]

$$b_j(t) = \frac{1}{2\pi i}\int_C dE\, e^{-iEt}\langle\varphi_j|PG(E)P|\varphi_i\rangle, \tag{3.9}$$

where the integration contour C runs from $+\infty$ to $-\infty$ and is infinitesimally above the real energy axis where the singularities in $G(E)$ occur; $|\varphi_i\rangle$ is taken here as the initial state. The partitioned resolvent operator $PG(E)P$ for the amplitudes of the $\{|\varphi_j\rangle\}$ states may be written as[31]

$$PG(E)P = [E - PH_0P - PR(E)P]^{-1}P, \tag{3.10}$$

where H_0 is the zeroth-order Hamiltonian, and $R(E)$ is defined as the level shift operator,[31,33] given by

$$R(E) \equiv V + VQ(E - QHQ)^{-1}QV. \qquad (3.11)$$

Equations (3.9)–(3.11) provide an exact expression for the amplitudes of the states spanned by the projector P. In this formalism, the operator $R(E)$ in Eqs. (3.10) and (3.11) is responsible for the shifts and couplings of the energy levels in the $\{|\varphi_j\rangle\}$ manifold, including the contributions from the off-resonant $\{|\varphi_k\rangle\}$ states. A number of authors [e.g., Refs. 1(a) and 1(c), and references therein] have used this formalism to describe formally the competing radiationless and radiative decay dynamics of initially prepared vibronic states in polyatomic molecules.[34] Several authors[1(a),31,33] have also discussed the smooth energy dependence of $R(E)$ when the projection operator P spans one[1(a),33] or two[31] states. In addition, when P spans a number of states, it has been suggested [Ref. 1(a), p. 86] that an effective resolvent operator in Eq. (3.9) could be defined by treating $R(E)$ as an energy-independent operator evaluated at the average zeroth-order energy of those states in P. The perturbation theory based on the projection operator approach (e.g., Ref. 33 and references cited therein) has also been further developed[35] using an iterative scheme and continued fractions.

The present approximation, given by Eq. (3.7), may be written in terms of a resolvent operator formalism for the effective Hamiltonian in Eq. (3.8). The approximate amplitudes $b_j(t)$ for the resonant states are thereby given by

$$b_j(t) = \frac{1}{2\pi i}\int_C dE\, e^{-i(E - \langle H\rangle)t}\langle\varphi_j|PG_{\text{eff}}(E)P|\varphi_i\rangle, \qquad (3.12)$$

where $PG_{\text{eff}}(E)P$ is the effective resolvent operator for the P space:

$$PG_{\text{eff}}(E)P = [E - PH_0P - PR(\langle H\rangle)P]^{-1}P, \qquad (3.13)$$

and the $\langle H\rangle$ in the exponential term of Eq. (3.12) simply describes a constant shift of the energy levels. The relation of the approximation developed in Sec. II to this formalism is clear: It simplifies the evaluation of the poles of the resolvent operator in Eq. (3.9) by evaluating the level shift operator $R(E)$ at the mean energy of the nonstationary state $E = \langle H\rangle$ and hence making it energy independent.

The present approximation is also complimentary to a recent method developed by Schultheis *et al.*[36] These authors derive an approximate solution of the time-dependent Schrödinger equation based on a partitioning of the Hamiltonian and a conversion of the exact Schrödinger equations for the P and Q spaces into second order differential equations. Their method is accurate for short time solutions, including those for problems in which the Q space dissipates some probability from the P space (i.e., from the subspace of interest). The method of the present paper, however, relies on the fact that the Q space cannot dissipate the P space probability because these two spaces are defined as being detuned in energy from each other.[22] The method of Schultheis *et al.*[36] has been found useful in treating systems where the perturbation acts for a small time duration and where it may be desirable to have states in the P space which are nearly degenerate with some states in the Q space. Such a system was found, e.g., in heavy ion collisions.[36]

B. Van Vleck-like approaches

As discussed by Killingbeck,[27] the Van Vleck approach to degenerate or nearly degenerate perturbation theory (e.g., Ref. 37) is based on transformation theory rather than partitioning techniques. The usual procedure is to find a unitary transformation of order n that block diagonalizes the Hamiltonian to order n and hence leaves an effective Hamiltonian for the degenerate or nearly degenerate submatrix of interest. To the extent that such a method is accurate, the effective Hamiltonian matrix for the resonant $\{|\varphi_j\rangle\}$ states could be used in Eqs. (3.1) and (3.2) to determine the dynamics of that subsystem of interest. However, as noted elsewhere,[25] this approach relies on expansions in orders of a perturbation parameter, whereas a partitioning approach based on Eqs. (3.3) or (3.4) does not. In particular examples having strong couplings in the off-resonant manifold of states $\{|\varphi_k\rangle\}$, we have found that the Van Vleck treatment of the dynamics gave qualitatively incorrect results for the initial state probabilities in several model systems, whereas the approach developed in Sec. II and based on Eq. (2.9) continued to give accurate results.[38]

IV. APPLICATIONS

A. Coupled Morse oscillator systems: Local mode evolution

Recently, Hutchinson *et al.*[15] have discussed the dynamics of two-degrees-of-freedom coupled Morse oscillator systems. Of particular relevance to the present work is their dynamical study of the quantum local mode states in these systems in which they gave an approximate numerical solu-

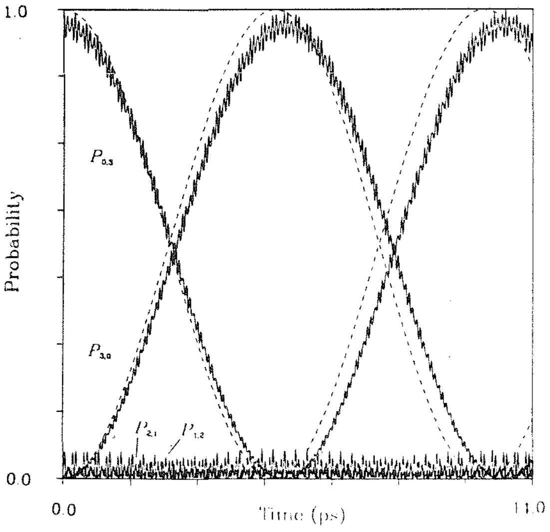

FIG. 1. Local mode probabilities $P_{0,3}$ and $P_{3,0}$ as a function of time for the $|0,3\rangle$ and $|3,0\rangle$ zeroth-order coupled Morse oscillator states, respectively, of Ref. 15. The exact results are given by the solid lines and the approximate results based on Eqs. (4.1) and (4.2) are given by the dashed lines. The exact probabilities $P_{1,2}$ and $P_{2,1}$ of the $|2,1\rangle$ and $|1,2\rangle$ zeroth-order states, respectively, are shown for comparison with the local mode probabilities.

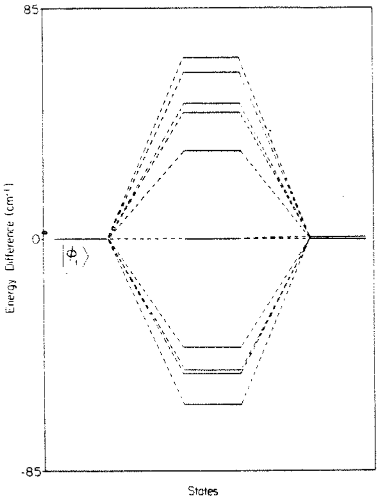

FIG. 2. A schematic of the model system used in Sec. IV B. Dotted lines represent the couplings between the zeroth-order states and $|\varphi_1\rangle$ is the initial state.

tion based on time-independent perturbation theory and a truncated basis set. Equation (2.9) may be used to solve the equations for the dynamics of the zeroth-order Morse oscillator local mode states $|0,n\rangle$ ($|n,0\rangle$), with n quanta initially in one bond. For example, in the case of the $|0,3\rangle$ state, the time-dependent probabilities of these states are given analytically from Eq. (2.9) by

$$P_{0,3}(t) = \cos^2(\Omega t/2); \quad P_{3,0}(t) = \sin^2(\Omega t/2), \tag{4.1}$$

where $P_{0,3}$ ($P_{3,0}$) is the probability $|b_j(t)|^2$ of being in the $|0,3\rangle$ ($|3,0\rangle$) state, and the oscillation frequency Ω is given by

$$\Omega = 2[V_4 + (2V_1 V_3\Delta + V_3^2 V_2 + V_1^2 V_2)/(\Delta^2 - V_2^2)]. \tag{4.2}$$

In Eq. (4.2), V_1, V_2, V_3, and V_4 equal $\langle 1,2|V|0,3\rangle$, $\langle 1,2|V|2,1\rangle$, $\langle 2,1|V|0,3\rangle$, and $\langle 3,0|V|0,3\rangle$, respectively, and Δ is the zeroth-order detuning between the states $|0,3\rangle$ ($|3,0\rangle$) and $|1,2\rangle$ ($|2,1\rangle$). The restricted number of basis states used here are the same as those employed in the analysis of Ref. 15, and the states $|1,2\rangle$ and $|2,1\rangle$ are treated in the formalism of Sec. II as the "off-resonant" $\{|\varphi_k\rangle\}$ manifold. For the values of the above matrix elements and Δ given in Ref. 15, Ω is calculated to be 2.66 cm^{-1}, whereas the exact result[15,16,39] was reported to be 2.7 cm^{-1}. A result for Ω based on time-independent perturbation theory is given analytically by[15,39]

$$\Omega = 2[V_4 + (2V_1 V_3\Delta + V_1^2 V_2)/\Delta^2] \tag{4.3}$$

and equals 2.6 cm^{-1}. In Fig. 1, the time dependence of the exact (solid lines) and adiabatically reduced coupled equations (dashed lines) probabilities is shown. The probabilities of the off-resonant $|2,1\rangle$ and $|1,2\rangle$ states are also shown for comparison with the local mode $|3,0\rangle$ and $|0,3\rangle$ probabilities. As is also discussed in Sec. II, it is seen from the $P_{2,1}(t)$ [$P_{1,2}(t)$] plot in Fig. 1 that $dP_{2,1}(t)/dt$, and hence $d\mathbf{b}^0(t)/dt$ [Eq. (2.6)], can oscillate quite rapidly in time but, on the average, is equal to zero for the time scale of interest. As a result, $P_{2,1}(t)$, and hence the magnitude of $\mathbf{b}^0(t)$, remains small throughout the course of the relevant dynamics.

B. Model calculations

Time-dependent calculations were performed for the model 13-level system depicted schematically in Fig. 2. This model is chosen to represent a physically reasonable few-level quantum dynamical system in a polyatomic molecule. Three levels were taken to be nearly degenerate and significantly coupled to each other as well as to the initial state (shown as $|\varphi_1\rangle$ in Fig. 2). Nine other levels were placed randomly in a region 30–70 cm^{-1} above and below the four-level subsystem. The elements of the Hamiltonian matrix $\mathbf{H}$ used in the exact coupled equations [Eqs. (2.4)] for this system are given in Table I. Shown in Fig. 3 is the evolution of the initial state probability $|b_1(t)|^2$ for the exact dynamics (solid line), the adiabatically reduced coupled equations dynamics (dashed line), and the isolated (i.e., neglecting the nine off-resonant states) four-state dynamics (dotted line). In Fig. 4, the Fourier transform spectrum of the initial state amplitude $b_1(t)$ is given. In addition, the evolution of the $|\varphi_1\rangle$ state probability is shown in Fig. 5 for a somewhat different model system (cf. Table II). This model was chosen

TABLE I. The Hamiltonian matrix $\mathbf{H}$ (in cm^{-1}) for the model system in Figs. 2 and 3.[a]

i \ j	1	2	3	4	5	6	7	8	9	10	11	12	13
1	65	2	0	0	1	2	2	1	2	1	1	3	3
2		65	3	5	0	0	0	0	0	0	0	0	0
3			64.9	0	1	2	2	1	2	1	2	3	1
4				65.5	1	1	1	2	1	3	3	2	1
5					2								
6						13							
7							15				0		
8								24					
9									99				
10										111			
11											114		
12												126	
13													131

[a] $\mathbf{H}$ is a symmetric matrix.

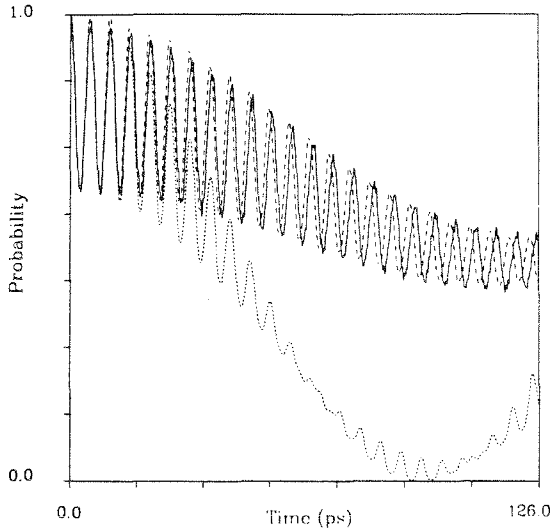

FIG. 3. The $|\varphi_1\rangle$ zeroth-order state probability as a function of time for the model system shown in Fig. 2 and given in Table I. The exact results are given by the solid line, the results obtained using Eq. (2.9) by the dashed line, and the results obtained by integrating the coupled equations [Eq. (2.4)] for the four resonant states while neglecting the nine off-resonant states are given by the dotted line.

so that the four states of interest are no longer nearly degenerate. In Fig. 6, the $|\varphi_1\rangle$ probability is shown for a model system having the same couplings and zeroth-order energies as in Table I but with an added diagonal perturbation term $V_{11} = 5.0\ \text{cm}^{-1}$. Here, the solid line is the exact result, the dashed line is the result calculated by integrating Eq. (2.9), and the dotted line is now the result calculated by equations similar to Eq. (2.9) except using the energy E_1^0 of the zeroth-order state $|\varphi_1\rangle$ instead of $\langle H \rangle$ in Eq. (2.9) [i.e., using a phase factor $\exp(-iE_1^0 t)$ instead of $\exp(-i\langle H \rangle t)$ in Eq. (2.1) and then solving for the reduced equations as in Sec. II based on this choice of phase].

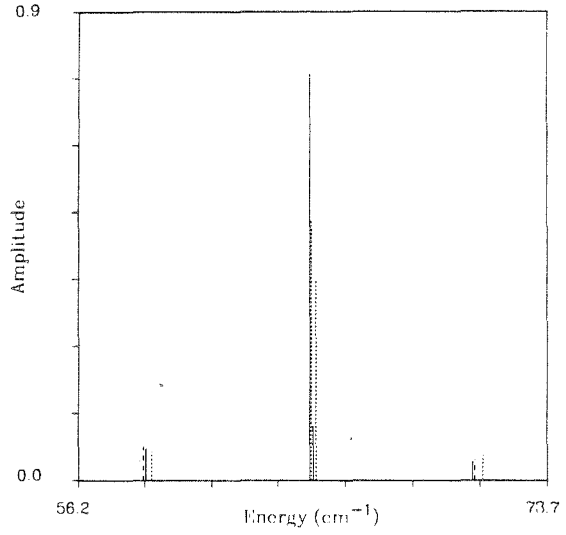

FIG. 4. The Fourier transform spectrum of $b_1(t)$ for the model system of Figs. 2 and 3 and Table I. The labeling of the lines is the same as in Fig. 3. For the two central peaks, the approximate results based on Eq. (2.9) (dashed lines) essentially coincide with the exact results (solid lines) and are hidden by the latter.

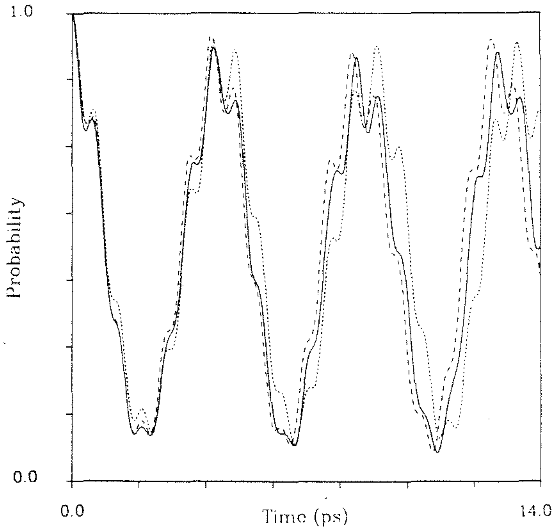

FIG. 5. The $|\varphi_1\rangle$ zeroth-order state probability as a function of time for the model system in Table II. The labeling of the lines is the same as in Fig. 3.

V. DISCUSSION

It is clear from the results shown in Fig. 3 that the off-resonant states can qualitatively effect the dynamics of the initial state and that the approximate coupled equations in Eq. (2.9) give accurate results for this system. The influence of the off-resonant states in the frequency domain is seen in the Fourier transform spectrum of $b_1(t)$ shown in Fig. 4. In particular, the relative Fourier amplitude of the two central peaks is significantly changed by the presence of the off-resonant states and hence the time-dependent probability amplitude in Fig. 3 is also changed. It is also interesting that the frequency components of $b_1(t)$ are not as sensitive to the off-resonant states as are the Fourier amplitudes. This fact is probably due to the zeroth-order near degeneracy of the four

TABLE II. Hamiltonian submatrix (in cm^{-1}) for the model system in Fig. 5.[a]

$i \setminus j$	1	2	3	4
1	65	10	0	0
2		100	11	9
3			70	0
4				75

[a] The submatrix is for the four strongly interacting states (cf. discussion in Sec. IV B) and is a symmetric matrix. The remainder of the Hamiltonian is the same as in Table I.

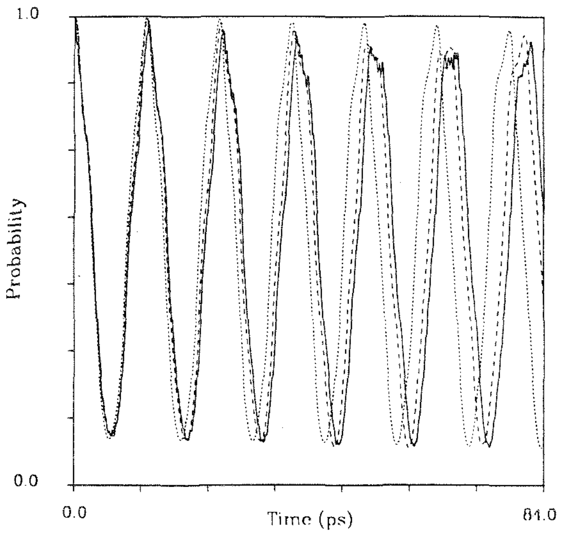

FIG. 6. The $|\varphi_1\rangle$ zeroth-order probability as a function of time for the model system shown in Fig. 2 and given in Table I, except that a diagonal perturbation $V_{11} = 5.0\ \mathrm{cm}^{-1}$ is now added to the Hamiltonian. The exact results are given by the solid line, the results obtained using Eq. (2.9) by the dashed line, and the results obtained by using Eqs. (2.1) through (2.9) with a phase $\exp(-iE_1^0\, t)$ (cf. discussion in Secs. IV B and V) are given by the dotted line.

resonant states shown in Fig. 2; i.e., the wave functions and hence the Fourier amplitudes are quite sensitive to small detunings in the energy. The dynamics of the initial state for the nondegenerate system (cf. Table II) shown in Fig. 5 is less susceptible to the presence of the off-resonant states, but those states nevertheless have an important effect. For this system, the reduced coupled equations also prove to be accurate.

In Fig. 6, a comparison of the initial state dynamics for two possible choices of the reference or interaction phase in Eq. (2.1) is shown. In that system, a diagonal perturbation V_{11} of 5 cm^{-1} was added to distinguish between the choices of $E_1^0\, t$ and $\langle H \rangle t$ for the phase. From Fig. 6, one sees that the latter choice (dashed line rather than dotted line) is a better one for that system, and thus far we have found this choice of phase to give the best results in other model calculations. Other choices for the phase in Eq. (2.1) such as the average zeroth-order energy $(E_j^0)_{\mathrm{av}}\, t$ or the average expectation value $(\langle H \rangle_j)_{\mathrm{av}}\, t$, where av denotes an arithmetic average over the $|\varphi_j\rangle$'s, were also tested. In general, they did not give as accurate results as did the choice of $\langle H \rangle t$. However, as is evident in Fig. 6, the approximate dynamics based on Eq. (2.9) were not strongly sensitive to the choice of the reference phase in Eq. (2.1) (i.e., the results did not differ strongly for these different phases). This behavior is a manifestation of the smooth energy dependence mentioned previously by several authors[1(a),31,33,35] in regard to the level shift operator $R(E)$ discussed in Sec. III A.

For the model systems in the present paper, the approximate approach based on Eq. (2.9) used approximately eight times less computer time than was required for the exact calculations in Figs. 3 and 5. In general, when there are many off-resonant/weakly coupled states, one can expect a considerable savings in computer time by using the reduced coupled equations in Eq. (2.9), although the inversion of the matrix $(\langle H \rangle \mathbf{I}^0 - \mathbf{H}^0)$ may require some CPU time. In some cases, an approximate approach based on those equations may allow a practical treatment of problems that cannot as yet be treated by an exact calculation.

VI. CONCLUDING REMARKS

Adiabatically reduced coupled equations have been derived for the propagation of nonstationary states in polyatomic molecules. In appropriate cases, the present method allows one to significantly reduce the number of coupled equations included in a time-dependent calculation. It was found that the adiabatically reduced coupled equations gave an accurate approximation to the dynamics for coupled Morse oscillator local mode states and for the model systems presented in Sec. IV B. Moreover, strong dynamical effects due to the presence of off-resonant states were found for these model systems. Other model calculations performed by us have, in general, exhibited significant dynamical contributions from the off-resonant states, and similar results have been discussed by Hutchinson *et al.*[15,20] from a time-independent point of view. An application of the methods presented in this paper to the problem of energy transfer between ligands of a heavy atom will be given elsewhere.[40]

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Chapter 6: Approximate Coupled Equations for Multiphoton Processes Induced by One or More Lasers

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1. Introduction

With the advent of powerful lasers, experimental techniques based on nonlinear optical processes have rapidly developed. In particular, the experimentalist now has at his or her disposal many experimental probes of molecular systems based on multiphoton processes stimulated by one or more lasers [1-4]. These experimental probes typically involve the multiphoton excitation, ionization, and/or dissociation of molecules [1]. There are also numerous experiments based on, for example, optical double resonance [2], double frequency pulsed NMR [3], or stimulated emission pumping [4] techniques.

The basic theory of resonant multiphoton processes between two molecular levels has also been developed [5,6]. However, in the case of one or more intense laser fields interacting with a multi-level quantum system, the accurate description of multiphoton processes can be a difficult problem and must usually be treated by a many-state numerical calculation.* Promising numerical approaches capable of treating in an efficient way the general intense field multiphoton problem include the many-mode Floquet theory [7] and the RRGM method [8]. In view of the numerous experimental techniques based on multiphoton processes, theories which simplify the detailed calculation of state-to-state multiphoton processes are potentially quite useful.

Central to the usual non-perturbative, though approximate, theory of resonant multiphoton processes is the procedure of adiabatic elimination, in one form or another [9,10], of the off-resonant intermediate states from the quantum mechanical equations of motion. This approximate treatment is primarily based on the physical property that the off-resonant intermediate states cannot build up significant amplitude for any length of time [9]. Within the context of multiphoton processes, adiabatic elimination has generally been applied to the density matrix equations based on time-dependent "semiclassical" Hamiltonians, i.e., those Hamiltonians in

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* There have been numerous calculations of state-to-state multiphoton processes. It is beyond the scope of the present letter to reference all of those studies here.

which the molecular system is treated quantum mechanically and the radiation field is treated classically. For some relatively simple cases (i.e., simple field-molecule resonance conditions), the adiabatic elimination procedure yields approximate, yet accurate, analytic results for the state probabilities and/or other physical properties of the system [5,6,9,10].

Recently, an adiabatic approximation for time-independent Hamiltonians has been shown to be useful for intramolecular dynamics calculations [11]. The salient features of the latter theory are (1) the number of coupled equations that must be integrated to obtain a reasonable description of the dynamics is reduced, perhaps considerably, and (2) the adiabatic approximation in the intramolecular context can be related in a specific way to several well known time-independent partitioning and projection operator techniques [11].

In the present letter, an approximate set of coupled equations based on the theory of ref. [11] will be developed to treat the several laser (i.e., many-mode), multiphoton dynamics of a general laser-molecule system in a time-independent Hamiltonian framework. Dressed state theory [12] will be used to formulate the appropriate fully quantum mechanical time-independent Hamiltonian. The dressed state approach has recently been found to be particularly useful for treating intense field multiphoton effects in NO [13] and for calculating dynamic polarizabilities [14]. The adiabatic elimination procedure used in ref. [11] will then be performed based on a partitioning of the Hamiltonian into resonant and off-resonant subspaces, and the approximate coupled equations will be derived. The central result of the present paper is given in eqs. (7) and (8) below.

The usefulness of the present formalism is that many-mode multiphoton processes may be treated to arbitrary orders of the perturbation, albeit approximately, without resorting to the usual rotating wave-like approximations (RWA) commonly used in semiclassical multiphoton theories [6]. The so-called generalized rotating wave approximation (GRWA) appropriate for multiphoton processes in one or more classical laser fields is not unique when there is no unique field-molecule resonance condition and can thereby be difficult to formulate [6]. (See, however, ref. [15] for a somewhat different approach). In particular, more subtle non-RWA effects such as dynamical Stark shifts, appropriately generalized to the multiple laser case, can be treated in a systematic fashion using the time-independent Hamiltonian. (For the more standard approach based on semiclassical Hamiltonians, see Appendix A of ref. [9].) The relationship to other quantum techniques is also readily established [11,16]: The present approach is complementary to approximate multiphoton formulations [17] based on the pole approximation for the resolvent operator [11,18].

2. Theory

The quantum mechanical Hamiltonian for a molecule interacting with M radiation field modes may be written as [19]

$$\hat{H} = \hat{H}_m + \sum_{k=1}^{M} \hbar\omega_k \hat{a}_k^\dagger \hat{a}_k + \hat{V} \quad , \tag{1}$$

where $\hat{H}_m$ is the molecular Hamiltonian operator, and each $\hbar\omega_k \hat{a}_k^\dagger \hat{a}_k$ term is a radiation field mode Hamiltonian of frequency ω_k, written here in terms of the harmonic oscillator creation and annihilation operators $\hat{a}_k^\dagger$ and $\hat{a}_k$, respectively. The field-molecule coupling operator $\hat{V}$ is given in the dipole approximation by [19]

$$\hat{V} = i \sum_{k=1}^{M} (2\pi\hbar\omega_k/V_c)^{1/2} \hat{\mu} \cdot \hat{e}_k (\hat{a}_k^\dagger - \hat{a}_k) \quad , \tag{2}$$

where $\hat{\mu} \cdot \hat{e}_k$ is the scalar product of the molecular dipole moment (vector) operator $\hat{\mu}$ times the polarization vector $\hat{e}_k$ of field mode k, and V_c is the volume of the radiation cavity.

The dressed state basis [12] for the field-molecule Hamiltonian in the absence of the interaction $\hat{V}$ is written as $|\varphi_i\rangle = |\{n_m\}, N_1, \ldots, N_M\rangle$, where $\{n_m\}$ denote the quantum numbers for the molecular levels, and N_k, $(k = 1, \ldots, M)$, are the photon occupation numbers for the field modes. In the present picture, the system is assumed at time $t = 0$ to be in the initial dressed state $|\{n_m\}, N_1, \ldots, N_M\rangle$ at which time the interaction $\hat{V}$ is turned on instantaneously. The resulting dynamics induced by the field-molecule interaction thereby involves transitions to the other dressed states $|\{n'_m\}, N'_1, \ldots, N'_M\rangle$ [12]. This non-stationary dynamical process describes the absorption and stimulated emission of radiation by the molecule. An exact calculation of the state amplitudes during the multiphoton dynamics involves either the diagonalization of the dressed state Hamiltonian matrix to obtain the representation of the propagator in terms of the eigenvalues and eigenvectors (see, e.g., ref. [14]), or the numerical solution of a set of coupled first-order ordinary differential equations. An approximate approach based on the latter method is developed in what follows.

In the presence of the interaction $\hat{V}$, the general time-dependent wavefunction may be expanded [11] in terms of N_c dressed state basis functions as**

$$|\Psi(t)\rangle \;=\; exp(-\frac{i}{\hbar}\langle H\rangle\, t) \sum_{i=1}^{N_c} b_i(t)\, |\varphi_i\rangle \quad , \tag{3}$$

where the expectation value of $\hat{H}$ for the dressed state initial condition $|\Psi(0)\rangle = |\varphi_1\rangle = |\{n_m\}, N_1, \ldots, N_M\rangle$ is given by

$$\langle H\rangle \;=\; \epsilon_{\{n_m\}} + \sum_{k=1}^{M} N_k \hbar\omega_k \quad . \tag{4}$$

In eq. (4), $\epsilon_{\{n_m\}}$ is the energy of the initial molecular level having the quantum numbers $\{n_m\}$. Substitution of eq. (3) for $|\Psi(t)\rangle$ into the time-dependent Schrödinger

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** In practice, one selects for the full dressed state basis those states which are coupled to the initial dressed state by reasonably low-order resonant and off-resonant multiphoton processes, depending of course on the strength of the interaction. Such a selection procedure is physically motivated and hence limits the dimension of the total dressed state Hamiltonian matrix.

equation and using the orthonormal properties of the dressed state basis yields the coupled first-order differential equations for the amplitudes $b_j(t)$:

$$i\hbar\frac{db_j(t)}{dt} = \sum_{i=1}^{N_c}(H_{ji} - \langle H\rangle\,\delta_{ij})b_i(t) \quad . \tag{5}$$

The matrix elements H_{ji} are simply the matrix elements of the total Hamiltonian [eq. (1)] represented in the dressed state basis.

Following the treatment of ref. [11], the basis states are now partitioned into two subsets. One subset includes those dressed states that are resonant with and/or strongly coupled to the initial state, while the other subset contains all other states (i.e., those states sufficiently off-resonant with the initial state [11]). For example, one might use a simple criterion for including states in the resonant manifold such as including all dressed states of zeroth-order energy E_i^0 that satisfy the condition

$$\left|\epsilon_{\{n_m\}} + \sum_{k=1}^{M} N_k\hbar\omega_k - E_i^0\right| \leq \eta \quad , \tag{6}$$

where η is a generalized detuning parameter which may be adjusted depending on the strength of the field-molecule interaction. A more detailed partitioning scheme could, for instance, be based on artificial intelligence algorithms [20]. In matrix notation, the Hamiltonian sub-matrix containing the initial state and those states satisfying eq. (6) is denoted by $\mathbf{H}^{\mathrm{R}}$, the sub-matrix with the off-resonant states by $\mathbf{H}^{\mathrm{O}}$, and the coupling matrices between the two subspaces by $\mathbf{V}^{\mathrm{RO}}$ and $\mathbf{V}^{\mathrm{OR}}$. The latter two matrices are simply Hermitian conjugates of each other. Once the appropriate partitioning is determined, the adiabatically reduced coupled equations for the resonant ("R") dressed state amplitudes $\mathbf{b}^{\mathrm{R}}(t)$ may be derived using the adiabatic approximation of ref. [11]. The resulting coupled equations for the resonant subspace are given by

$$i\hbar\frac{d\mathbf{b}^{\mathrm{R}}(t)}{dt} = (\mathbf{H}^{\mathrm{R}}_{\mathrm{eff}} - \langle H\rangle\,\mathbf{1}^{\mathrm{R}})\mathbf{b}^{\mathrm{R}}(t) \quad , \tag{7}$$

where the effective dressed state Hamiltonian $\mathbf{H}^{\mathrm{R}}_{\mathrm{eff}}$ is given by

$$\mathbf{H}^{\mathrm{R}}_{\mathrm{eff}} = \mathbf{H}^{\mathrm{R}} + \mathbf{V}^{\mathrm{RO}}(\langle H\rangle\,\mathbf{1}^{\mathrm{O}} - \mathbf{H}^{\mathrm{O}})^{-1}\mathbf{V}^{\mathrm{OR}} \quad , \tag{8}$$

and $\mathbf{b}^{\mathrm{R}}(t)$ is the column vector containing the amplitudes for the resonant dressed states. The matrices $\mathbf{1}^{\mathrm{R}}$ and $\mathbf{1}^{\mathrm{O}}$ are identity matrices having the dimensions of the resonant and off-resonant subspaces, respectively. The conditions for validity of eq. (7) are discussed in ref. [11].

The effective coupled equations in eq. (7) are initial condition dependent because the number $\langle H\rangle$ [eq. (4)] depends on the initial dressed state of the field-molecule system. However, the number of coupled equations that must be integrated is given by the dimension of $\mathbf{H}^{\mathrm{R}}$ *only*. This approach is expected to be most useful when there are a few distinct dressed states that satisfy the resonance criterion [cf. eq. (6)] and for moderate laser intensities ($\sim 10^6 - 10^{10}$ W/cm^2), depending on the magnitude of the dipole matrix element. Of course, for processes involving high laser intensities and/or numerous resonance conditions, one has the flexibility of including more and more states in the resonant Hamiltonian $\mathbf{H}^{\mathrm{R}}$ (vs. $\mathbf{H}^{\mathrm{O}}$) in order to obtain increasingly accurate results.

The effective Hamiltonian in eq. (8) describes the interactions between the dressed states in the resonant manifold to all orders and is therefore particularly useful for an approximate and simplified numerical solution of the many-mode, many-state problem. However, a useful expansion [21] of the second term of the right hand side of eq. (8) may be employed to further simplify the results and to avoid the inversion of the matrix $(\langle H\rangle\,\mathbf{1}^{\mathrm{O}} - \mathbf{H}^{\mathrm{O}})$. Writing the off-resonant Hamiltonian matrix $\mathbf{H}^{\mathrm{O}}$ as $\mathbf{E}^{\mathrm{O}} + \mathbf{V}^{\mathrm{O}}$, the inverse of the matrix $(\langle H\rangle\,\mathbf{1}^{\mathrm{O}} - \mathbf{H}^{\mathrm{O}})$ may be represented by a power series as

$$(\langle H\rangle\,\mathbf{1}^{\mathrm{O}} - \mathbf{H}^{\mathrm{O}})^{-1} = \Delta\mathbf{E}^{-1}\left[\sum_{m=0}^{\infty}(\mathbf{V}^{\mathrm{O}}\Delta\mathbf{E}^{-1})^{m}\right] \quad , \tag{9}$$

where $\Delta\mathbf{E}$ is defined as the diagonal matrix $(\langle H\rangle\,\mathbf{1}^{\mathrm{O}} - \mathbf{E}^{\mathrm{O}})$, which is trivial to invert, and $\mathbf{V}^{\mathrm{O}}$ is the matrix of couplings among the off-resonant dressed states.

Using this expansion in eq. (8), one obtains the expanded effective dressed state Hamiltonian

$$\mathrm{H}^{\mathrm{R}}_{\mathrm{eff}} = \mathrm{H}^{\mathrm{R}} + \sum_{m=0}^{\infty} \mathrm{V}^{\mathrm{RO}} \Delta \mathrm{E}^{-1} \left(\mathrm{V}^{\mathrm{O}} \Delta \mathrm{E}^{-1} \right)^{m} \mathrm{V}^{\mathrm{OR}} \quad . \tag{10}$$

This expansion brings in, term by term, increasingly higher order couplings between the states in the resonant dressed state manifold. Thereby, each higher order term in the summation involves increasingly complicated "virtual state" configurations [12]. The off-diagonal matrix elements of $\mathrm{H}^{\mathrm{R}}_{\mathrm{eff}}$ provide the generalized Rabi frequencies for the multiphoton transitions [5,6,9], while the diagonal elements contain the radiative shift terms corresponding to the generalized dynamical Stark shifts. If rapidly convergent [21], eq. (10) is expected to be particularly useful for calculations performed on high speed vector supercomputers because it involves repeated matrix multiplications.

The form of the coupling matrix elements in the dressed state picture may also be simplified for laser fields of normal or higher intensity (see, e.g., refs. [12] and [22]). The matrix elements $V_{i'i}$ of the perturbation $\hat{V}$ [eq. (2)] between the dressed states $|\{n'_m\}, N'_1, \ldots, N'_M\rangle$ and $|\{n_m\}, N_1, \ldots, N_M\rangle$ are given by

$$\begin{aligned} V_{i'i} &= i \sum_{k=1}^{M} \left(2\pi \hbar \omega_k / V_c \right)^{1/2} \langle \{n'_m\} | \, \hat{\mu} \cdot \hat{e}_k \, | \{n_m\} \rangle \\ &\qquad \times \left(\delta_{N'_k, N_k+1} \sqrt{N_k + 1} - \delta_{N'_k, N_k-1} \sqrt{N_k} \right) \quad . \end{aligned} \tag{11}$$

However, since the classical radiation field strength $E_{\mathrm{o}k}$ for mode k is given by [12,22]

$$E_{\mathrm{o}k} = \left(8\pi N_k \hbar \omega_k / V_c \right)^{1/2} \quad , \tag{12}$$

and since $\sqrt{(N_k + m)} \simeq \sqrt{N_k}$ for $N_k \gg m$, the matrix elements $V_{i'i}$ can be written to a very good approximation (see, e.g., ref. [22]) as

$$V_{i'i} \simeq \frac{i}{2} \sum_{k=1}^{M} E_{\mathrm{o}k} \langle \{n'_m\} | \, \hat{\mu} \cdot \hat{e}_k \, | \{n_m\} \rangle \left(\delta_{N'_k, N_k+1} - \delta_{N'_k, N_k-1} \right) \quad . \tag{13}$$

This form of $V_{i'i}$ simplifies the calculation of the summation terms in eq. (10). Moreover, when the field-molecule coupling is written in this way, the relationship of dressed state theory to time-independent Floquet theory has been noted by several authors (see, e.g., ref. [23]). Equation (12) also determines the relationship between the laboratory quantity E_{ok} and the initial state photon occupation numbers N_k ($k = 1, \ldots, M$) used in the dressed state calculations [e.g., eqs. (6)-(10)].

3. Summary

Approximate coupled equations have been presented which can simplify the calculation of state-to-state multiphoton processes in molecular systems. These coupled equations are based on a partitioning of the time-independent dressed state Hamiltonian matrix into resonant and off-resonant sub-blocks, and on a subsequent adiabatic elimination of the off-resonant state amplitudes [11] from the coupled equations arising from that Hamiltonian. The partitioning scheme offers one the flexibility to obtain increasingly accurate results by numerically integrating any number of dressed state amplitudes exactly, while treating the remaining amplitudes in an effective way. Artificial intelligence algorithms [20] could prove to be particularly useful in that regard.

An expansion of the effective Hamiltonian in terms of the perturbation strength may also be performed which brings in, order by order, the generalized Rabi frequencies and dynamical Stark shifts for multiphoton transitions between states in the resonant subspace of interest. This latter expansion approach is similar in spirit to the Generalized Van Vleck (GVV) perturbation theory treatment of dressed state [22] and semiclassical Floquet [7,24] matrix treatments, although the GVV method is based on perturbative unitary transformation theory rather than the partitioning approach (cf. discussion in ref. [11] and references cited therein). The present approach is also complementary (see, e.g., refs [11] and [18]) to resolvent operator approaches for the multiphoton problem based on the pole approximation [17].

In view of the recent experimental results on the multiphoton dynamical Stark effect in molecules [13], and the success of dressed state theory in treating this effect in NO [13], the present theory may prove to be quite useful in the interpretation of future experimental results along these lines. In particular, one should be able to reduce the full dressed state matrix to a smaller matrix containing only the resonant states, examine the generalized Rabi frequencies and Stark shifts for these states order by order, and then integrate the coupled equations to obtain the detailed dynamical results for the state-to-state transition amplitudes. If necessary, suitable time-averaging and/or coarse graining of the results could then be performed. Further work to extend the present approximate treatment to include dressed state theories which incorporate resonance fluorescence [25] may also prove useful.

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Chapter 7: Quasidissipative Behavior in Isolated Molecular Systems

I. INTRODUCTION

The flow of probability from a metastable quantum state into a dense set of "receptor" states has been discussed by many authors. In fact, the basic theory of metastable state decay may be found in most textbooks on Quantum Mechanics (see, e.g., Refs. 1–3) and dates back to the seminal work of Wigner and Weisskopf.[4] The standard treatments of a decaying metastable state are based on certain physically motivated pole approximations which simplify the energy dependence of the resolvent operator (see, e.g., Ref. 5). The time-dependent behavior of the decaying state is then obtained via inverse Laplace transformation of the simplified integral equation. In this way, the approximate time-dependent probability of the initial state is found to obey the exponential decay law $P(t) \sim exp(-\Gamma t)$, having a decay rate Γ which is given by the "Golden Rule" expression[1,2]

$$\Gamma \;=\; 2\pi \left\langle |V|^2 \right\rangle \rho(E_i) \quad . \tag{1.1}$$

Here, $\left\langle |V|^2 \right\rangle$ is the average of the absolute square of the matrix elements coupling the initial state to the receptor states,[6] $\rho(E_i)$ is the density of receptor states at the energy E_i of the initially prepared state, and $\hbar$ equals unity. For short times, this result agrees, of course, with that obtained from time-dependent perturbation theory (see, e.g., Refs. 1–3).

In the field of intramolecular dynamics, the decay of probability of initally prepared quantum states in "large" molecules is a subject of great interest. For example, there is an extensive literature on the dynamics of electronic radiationless transitions[7] in molecular systems (i.e., redistribution of electronic energy). The theoretical approach to these problems is also based largely on approximate resolvent operator approaches (see, e.g., Ref. 7), and results similar to those mentioned above have been derived. More specifically, Golden Rule exponential decay rates are predicted for initially prepared states in large molecules which undergo electronic radiationless transitions and have large densities of states.[7,8] The theory of electronic radiationless transitions has been rather successful in explaining experimental trends and results (see, e.g., Ref. 7).

The phenomenon of intramolecular *vibrational* energy redistribution (IVR) is perhaps more subtle than that for electronic energy redistribution because, in the former case, the coupling mechanisms are more diverse and not as well characterized as in the latter case. Nevertheless, "real time" experiments which probe the process of IVR in large molecules have suggested that exponential decay of initially prepared states is the norm at moderate to high energies (see, e.g., Refs. 9 and 10). Theoretical studies,[11–14] many of which are based on the same formalism developed to treat electronic radiationless transitions,[11,12] also predict that exponential decay of the initial state is the most probable behavior in large molecules. It is perhaps useful then to ask the following question: Given that the probability of an initially prepared state in a large molecule is expected to decay exponentially, can a quantum dynamical theory be formulated which not only predicts this behavior, but also allows one to calculate the IVR decay rate more accurately than is given by the Golden Rule? It is the purpose of this chapter to demonstrate that, upon consideration of the basic phenomenology of IVR processes, it is indeed possible to derive a somewhat more flexible and general formula for the decay rate.

The theoretical approach used in this chapter represents an extension of the theory developed in Chapter 5 and is intended to be complementary to those approaches based on resolvent operator equations.[1–5,7,12] The present approach is based on the adiabatic approximation, which has been related by previous authors to certain pole approximations for the resolvent (see, e.g., Refs. 15 and 16). This chapter is organized as follows: In Sec. II, the basic phenomenology of IVR in large molecules is discussed and the present theory is derived. In Sec. III, the relationship between average coupling matrix elements for different basis sets is examined, and the relevance of those results to the theory of Sec. II is indicated. A discussion of the results is given in Sec. IV, and concluding remarks appear in Sec. V.

II. THEORY

It is first assumed that there exists a zeroth-order orthonormal basis set which captures the essential features of the molecular (i.e., nuclear) motions of a large molecule in a given Born–Oppenheimer electronic state. An example of such a basis set would be the harmonic normal modes of the molecule, and the present approach does not preclude a treatment of molecular rotations. As usual, the zeroth-order basis $\{|\varphi_i\rangle\}$ satisfies the time-independent Schrödinger equation for the zeroth-order Hamiltonian H_0:

$$H_0\,|\varphi_i\rangle \;=\; E_i\,|\varphi_i\rangle \quad , \tag{2.1}$$

where E_i is the zeroth-order energy of the state $|\varphi_i\rangle$. The coupling term V in the total Hamiltonian H $(= H_0 + V)$ introduces couplings between the zeroth-order states.

It is also assumed that one of the zeroth-order states carries all of the oscillator strength for a radiative transition from the ground state. Therefore, this is the state that is prepared by an appropriate pulsed laser excitation and is the state that subsequently undergoes IVR (cf. discussion in Ref. 9 by Bloembergen and Zewail). The coupling between the zeroth-order states is responsible for the flow of probability from the initially prepared state. By virtue of that coupling, the initial state interacts with a set of other states, which interact with even more states, and so on. This "tier" structure of the basis states is suggested to give rise to the basic phenomenology of intramolecular vibrational (and rotational) energy flow.[17] A tier structure has been invoked, for example, in the numerical analyses of IVR in benzene[13] and hydrocarbon chains,[14] and is not inconsistent with experimental results on anthracene and t–stilbene at higher energies,[9] p–difluorobenzene,[10,11] and tetramethyldioxetane.[18] Most of the earlier approximate resolvent operator treatments[12] of IVR are also based on various simple tier models.[19]

In order to exploit the basic phenomenology of IVR, the basis set is partitioned into three unique sets: The inital state (denoted by "P"), those states which are coupled to the initial state (denoted by "Q"), and the remaining states (denoted by "Q' "). It is assumed that the Q'−space contains many states since the present analysis is concerned with the large molecule limit. If the general time-dependent wavefunction $|\Psi(t)\rangle$ is expanded as[15]

$$|\Psi(t)\rangle \;=\; exp(-i\,\langle H\rangle\,t)\sum_{i=1}^{N} b_i(t)\,|\varphi_i\rangle \quad , \tag{2.2}$$

where $\langle H\rangle$ equals the expectation value of the energy for the initial state, then the coupled differential equations for the amplitiudes $b_i(t)$ are given by

$$i\,\frac{d}{dt}\mathbf{b}^P(t) \;=\; \mathbf{V}^{PQ}\mathbf{b}^Q(t) \quad , \tag{2.3}$$

$$i\,\frac{d}{dt}\mathbf{b}^Q(t) \;=\; \mathbf{V}^{QP}\mathbf{b}^P(t) \;+\; (\mathbf{H}^Q - \langle H\rangle\,\mathbf{1}^Q)\mathbf{b}^Q(t) \;+\; \mathbf{V}^{QQ'}\mathbf{b}^{Q'}(t) \quad , \tag{2.4}$$

$$i\,\frac{d}{dt}\mathbf{b}^{Q'}(t) \;=\; \mathbf{V}^{Q'Q}\mathbf{b}^Q(t) \;+\; (\mathbf{H}^{Q'} - \langle H\rangle\,\mathbf{1}^{Q'})\mathbf{b}^{Q'}(t) \quad . \tag{2.5}$$

In these equations, the previously mentioned partitioning scheme has been implemented, and vector-matrix notation has been used. (The superscripts identify the different subspaces.) The **1**'s are identity matrices, the **b**'s contain the state amplitudes, the **H**'s contain the different Hamiltonian matrix sub-blocks, and the **V**'s contain the coupling matrices between the different subspaces. The dimensions of the P, Q, and Q' subspaces are given by the numbers N_P, N_Q, and $N_{Q'}$, respectively. For simplicity, N_P equals unity in the present analysis, but this is not a crucial restriction.

It is now assumed that there are so many states in the Q'−manifold that the derivatives $d\mathbf{b}^{Q'}/dt$ satisfy the approximate relation

$$\frac{d}{dt}\mathbf{b}^{Q'}(t) \;\simeq\; \mathbf{0} \quad . \tag{2.6}$$

This approximation is based on the assumption that the probability will flow slowly and uniformly into the Q' states, and hence the individual Q' state probabilities will have magnitudes of the order $1/N_{Q'}$. Similar approximations have been used to eliminate the continuum state's contribution to the density matrix equations describing the multiphoton ionization of atoms (see, e.g., Ref. 20). It is also noted here that the physical basis for this approximation differs somewhat from that used in Chapter 5 and Ref. 15.

By virtue of the approximation given in Eq. (2.6), the Q' amplitudes are found from Eq. (2.5) to be

$$\mathbf{b}^{Q'}(t) \simeq (\langle H \rangle \mathbf{1}^{Q'} - \mathbf{H}^{Q'})^{-1}\mathbf{V}^{Q'Q}\mathbf{b}^{Q}(t) \quad . \tag{2.7}$$

If the states in the Q' subspace are thought of as being "prediagonalized" (i.e., the matrix $\mathbf{H}^{Q'}$ is prediagonalized), then Eq. (2.7) simplifies to

$$\mathbf{b}^{Q'}(t) \simeq (\langle H \rangle \mathbf{1}^{Q'} - \mathbf{E}^{Q'})^{-1}\mathbf{V}^{Q'Q}\mathbf{b}^{Q}(t) \quad , \tag{2.8}$$

where $\mathbf{E}^{Q'}$ is a diagonal matrix containing the prediagonalized Q'–space state energies $E_k^{Q'}$. The approximate expression for $\mathbf{b}^{Q'}(t)$ given in Eq (2.8) is then inserted into Eq. (2.4) for $d\mathbf{b}^{Q}/dt$, yielding

$$\begin{aligned} i\,\frac{d}{dt}\mathbf{b}^{Q}(t) \simeq\ & \mathbf{V}^{QP}\mathbf{b}^{P}(t) + (\mathbf{H}^{Q} - \langle H \rangle \mathbf{1}^{Q})\mathbf{b}^{Q}(t) \\ & + \mathbf{V}^{QQ'}(\langle H \rangle \mathbf{1}^{Q'} - \mathbf{E}^{Q'})^{-1}\mathbf{V}^{Q'Q}\mathbf{b}^{Q}(t) \quad , \end{aligned} \tag{2.9}$$

where now the amplitudes $\mathbf{b}^{Q'}(t)$ do not appear explicitly in this equation.

The elements of the matrix $\mathbf{V}^{QQ'}(\langle H \rangle \mathbf{1}^{Q'} - \mathbf{E}^{Q'})^{-1}\mathbf{V}^{Q'Q}$ in Eq. (2.9) are particularly simple because $\mathbf{E}^{Q'}$ is a diagonal (i.e., prediagonalized) matrix. They are given by

$$\left[\mathbf{V}^{QQ'}(\langle H \rangle \mathbf{1}^{Q'} - \mathbf{E}^{Q'})^{-1}\mathbf{V}^{Q'Q}\right]_{ij} = \sum_{k=1}^{N_{Q'}} \frac{V_{ik}^{QQ'}V_{kj}^{Q'Q}}{\langle H \rangle - E_k^{Q'}} \quad . \tag{2.10}$$

The matrix elements $V_{ik}^{QQ'}$ (and $V_{kj}^{Q'Q}$) give the couplings between the Q–space states and the prediagonalized Q'–space states. In principle, obtaining these $Q - Q'$ matrix elements would require the actual diagonalization of the very large Q' sub-block of the Hamiltonian matrix $\mathbf{H}^{Q'}$. (An extremely difficult task!) However, it will be shown in the next section that this is not required in the present theory.

Since the density of Q' states is assumed to be large, the Q'–space energy spectrum may be treated as continuous and the *diagonal* terms in Eq. (2.10) written as a contour integrals,[3,20] i.e., as

$$\sum_{k=1}^{N_{Q'}} \frac{V_{ik}^{QQ'} V_{ki}^{Q'Q}}{\langle H \rangle - E_k^{Q'}} \simeq \lim_{\varepsilon \to 0^+} \int_{-\infty}^{\infty} \frac{\langle |V_i^{QQ'}(E^{Q'})|^2 \rangle}{\langle H \rangle - E^{Q'} + i\varepsilon} \rho_{Q'}(E^{Q'}) dE^{Q'} \quad , \tag{2.11}$$

where $\rho_{Q'}(E^{Q'})$ is the density of Q' states, and $\langle |V_i^{QQ'}(E^{Q'})|^2 \rangle$ is the average of the absolute squared matrix element which couples the Q–space state $|\varphi_i^Q\rangle$ to the Q'–space states at the energy $E^{Q'}$. The condition that the Q'–space states are prediagonalized *is crucial* to making the above approximation. [That is, the prediagonalization condition allows the sum to be converted to the simple intergral in Eq. (2.11).] In Sec. III, it will be shown that the prediagonalization of the Q'–space is not necessary in order to apply an approximate form of the present theory [Eqs. (2.22) and (2.27)].

In Eq. (2.11), the function $\langle |V_i^{QQ'}(E^{Q'})|^2 \rangle \rho_{Q'}(E^{Q'})$ is assumed to be a well behaved function in the neighborhood of $E^{Q'} = \langle H \rangle$ and sufficiently decaying for large values of $|E^{Q'} - \langle H \rangle|$. By using the property (e.g., Ref. 2, p. 1470)

$$\lim_{\varepsilon \to 0^+} \int_{-\infty}^{\infty} \frac{f(x)}{x \pm i\varepsilon} dx = P.P. \int_{-\infty}^{\infty} \frac{f(x)}{x} dx \mp i\pi \int_{-\infty}^{\infty} f(x) \delta(x) dx \quad , \tag{2.12}$$

where $\delta(x)$ is the Dirac delta–function and "*P.P.*" denotes the Cauchy principal part, the integral in Eq. (2.11) may be performed, yielding

$$\sum_{k=1}^{N_{Q'}} \frac{V_{ik}^{QQ'} V_{ki}^{Q'Q}}{\langle H \rangle - E_k^{Q'}} \simeq \Delta_i^Q - \frac{i}{2} \Gamma_i^Q \quad . \tag{2.13}$$

In Eq. (2.13), Δ_i^Q represents a shift in the energy of the Q–space state $|\varphi_i^Q\rangle$ which equals

$$\Delta_i^Q = P.P. \int_{-\infty}^{\infty} \frac{\langle |V_i^{QQ'}(E^{Q'})|^2 \rangle}{\langle H \rangle - E^{Q'}} \rho_{Q'}(E^{Q'}) dE^{Q'} \quad , \tag{2.14}$$

and Γ_i^Q is that state's decay "width"

$$\Gamma_i^Q \; = \; 2\pi \big\langle \big| V_i^{QQ'}(\langle H \rangle) \big|^2 \big\rangle \rho_{Q'}(\langle H \rangle) \; . \tag{2.15}$$

In the present treatment, the energy shifts Δ_i^Q are assumed to be small due to the postulated "smooth" coupling to the quasicontinuous Q'–space, and hence they are neglected. (Alternatively, the zeroth-order energies E_i^Q of the Q–space states might be "renormalized" so as to contain the shifts Δ_i^Q).

The off-diagonal elements in Eq. (2.10) require a somewhat different approach: In general, the terms $V_{ik}^{QQ'} V_{kj}^{Q'Q}$ are expected to have essentially random signs for realistic molecular systems. Thus, when summing over the Q'–state index k, the simplest approximation is to assume that the sign variations are random enough so as to cause a cancellation of terms. Thus, the off-diagonal terms in eq. (2.10) may be taken to be quite small and are thereby neglected. It is unlikely that a more detailed analysis of these off-diagonal elements would yield significant *low-order* corrections to the end result, although this aspect of the theory may warrant further study.

If the function $\big\langle \big| V_i^{QQ'}(\langle H \rangle) \big|^2 \big\rangle \rho_{Q'}(\langle H \rangle)$ in Eq. (2.15) could be determined accurately, the decay widths Γ_i^Q could, in principle, reflect rather subtle properties of the couplings between the $Q-$ and $Q'-$manifolds. However, the calculation of these quantities is not much easier than solving the entire problem numerically, i.e., it is only slightly easier than a diagonalization of the entire Hamiltonian matrix. Therefore, an approximation is introduced into Eq. (2.15) by substituting $\langle |V_i^{QQ'}|^2 \rangle$ for $\big\langle \big| V_i^{QQ'}(\langle H \rangle) \big|^2 \big\rangle$, where $\langle |V_i^{QQ'}|^2 \rangle$ is the *average* of the squared coupling elements between the state $|\varphi_i^Q\rangle$ in the Q–manifold and *all of the states in the Q'–manifold.* The decay widths Γ_i^Q are then given by the functions $2\pi \langle |V_i^{QQ'}|^2 \rangle \rho_{Q'}(\langle H \rangle)$. If the $Q - Q'$ subspace couplings are fairly random, some justification for this approximation is suggested from random coupling models.[12] In addition, in Sec. III this approximation will be shown to be crucial to the simplification of the present theory.

By virtue of the above approximation, the coupled equations for the Q–space amplitudes are given by

$$i\frac{d}{dt}\mathbf{b}^Q(t) \;\simeq\; (\mathbf{H}^Q - \langle H\rangle\,\mathbf{1}^Q - i\mathbf{\Gamma}^Q/2)\mathbf{b}^Q(t) \;+\; \mathbf{V}^{QP}\mathbf{b}^P(t) \quad , \tag{2.16}$$

where $\mathbf{\Gamma}^Q$ is a diagonal matrix containing the Q–space widths Γ_i^Q. If the widths Γ_i^Q are equal to or larger than the Q–space energy level spacings, then one may treat the derivatives in Eq. (2.16) in a manner analogous to that given in Eq. (2.6). That is, if

$$\Gamma_i^Q \;\geq\; 1/\rho_Q(E_i^Q) \quad , \tag{2.17}$$

where $\rho_Q(E_i^Q)$ is the density of Q–space states at the energy E_i^Q, then it is expected that $d\mathbf{b}^Q/dt \simeq \mathbf{0}$ is a good approximation for the Q–space amplitude derivatives.[21] By applying this approximation to Eq. (2.16), one obtains

$$\mathbf{b}^Q(t) \;\simeq\; (\langle H\rangle\,\mathbf{1}^Q - \mathbf{H}^Q + i\mathbf{\Gamma}^Q/2)^{-1}\mathbf{V}^{QP}\mathbf{b}^P(t) \quad . \tag{2.18}$$

Upon insertion of this approximate expression for $\mathbf{b}^Q(t)$ into Eq. (2.3), an approximate differential equation for the amplitude $\mathbf{b}^P(t)$ is obtained:

$$i\frac{d}{dt}\mathbf{b}^P(t) \;\simeq\; \mathbf{V}^{PQ}(\langle H\rangle\,\mathbf{1}^Q - \mathbf{H}^Q + i\mathbf{\Gamma}^Q/2)^{-1}\mathbf{V}^{QP}\mathbf{b}^P(t) \quad . \tag{2.19}$$

Provided the off-diagonal elements of the matrix $\mathbf{H}^Q$ are smaller than the magnitude of the diagonal elements of the $(\langle H\rangle\,\mathbf{1}^Q - \mathbf{H}^Q + i\mathbf{\Gamma}^Q/2)$ matrix, the inverse in Eq. (2.19) may be expanded in a series as

$$(\langle H\rangle\,\mathbf{1}^Q - \mathbf{H}^Q + i\mathbf{\Gamma}^Q/2)^{-1} \;=\; (\Delta\mathbf{E} + i\mathbf{\Gamma}^Q/2)^{-1}\sum_{m=0}^{\infty}\left[\mathbf{V}^Q(\Delta\mathbf{E} + i\mathbf{\Gamma}^Q/2)^{-1}\right]^m , \tag{2.20}$$

where $\Delta\mathbf{E}$ is defined as the diagonal matrix $(\langle H\rangle\,\mathbf{1}^Q - \mathbf{E}^Q)$, $\mathbf{E}^Q$ is the matrix consisting of the diagonal elements of $\mathbf{H}^Q$, and $\mathbf{V}^Q$ is the matrix containing the off-diagonal elements of $\mathbf{H}^Q$. For a description of the decay dynamics of an initially prepared state in the large molecule limit, it is not expected that the couplings between the Q–space states are of particular importance.

A particularly simple expression for the $\mathbf{b}^P(t)$ differential equation [Eq. (2.19)] is obtained if only the $m = 0$ term in Eq. (2.20) is retained:

$$i\,\frac{db_j^P(t)}{dt} \;\simeq\; \left[\sum_{i=1}^{N_Q} \frac{V_{ji}^{PQ}V_{ij}^{QP}}{\Delta E_i + i\Gamma_i^Q/2}\right] b_j^P(t) \;, \tag{2.21}$$

where ΔE_i is a diagonal element of the $(\langle H\rangle\,\mathbf{1}^Q - \mathbf{E}^Q)$ matrix, and

$$\Gamma_i^Q \;\simeq\; 2\pi\big\langle|V_i^{QQ'}|^2\big\rangle\rho_{Q'}(\langle H\rangle) \;. \tag{2.22}$$

In Eq. (2.22), $\big\langle|V_i^{QQ'}|^2\big\rangle$ is the average of the squared matrix elements between the $Q-$space state $|\varphi_i^Q\rangle$ and all of the prediagonalized $Q'-$space states. It is again noted here that in the present analysis the $P-$space has only one state $|\varphi_j^P\rangle$ (i.e., the initial state).

Equation (2.21) may be further simplified by separating the real and imaginary parts of the right-hand-side. Thus,

$$i\,\frac{db_j^P(t)}{dt} \;\simeq\; (\Delta_j^P \;-\; i\Gamma_j^P/2)\; b_j^P(t) \;, \tag{2.23}$$

where

$$\Delta_j^P \;=\; \sum_{i=1}^{N_Q} \Delta E_i\, \frac{V_{ji}^{PQ}V_{ij}^{QP}}{\Delta E_i^2 + (\Gamma_i^Q/2)^2} \;, \tag{2.24}$$

and

$$\Gamma_j^P \;=\; \sum_{i=1}^{N_Q} \Gamma_i^Q\, \frac{V_{ji}^{PQ}V_{ij}^{QP}}{\Delta E_i^2 + (\Gamma_i^Q/2)^2} \;. \tag{2.25}$$

The factor Δ_j^P in Eq. (2.23) contributes an overall phase to the time-dependent amplitude, while the width Γ_j^P gives the decay rate. Hence, the time-dependent probability $P_j(t)$ of the initial state is given by

$$P_j(t) \;\simeq\; exp(-\Gamma_j^P t) \;, \tag{2.26}$$

where Γ_j^P is given in Eq. (2.25), and $\hbar$ equals unity. This expression is the central result of the present chapter. Provided that the "P" state carries all of the oscillator strength for a radiative transition from the ground state, the Fourier transform of $b_j^P(t)$ is proportional to the spectral lineshape of that state.[22] In this case, the Fourier transform will give a Lorentzian lineshape with a fwhm of $\Gamma_j^P/2$.

A useful approximate expression for the rate Γ_j^P may be derived from Eq. (2.25) and is given by an average of the squared coupling elements over a unit normalized Lorentzian distribution function $L(\Delta E_i\,;\langle\Gamma^Q\rangle)$. That is,

$$\Gamma_j^P \simeq 2\pi \sum_{i=1}^{N_Q} |V_{ij}^{QP}|^2 L(\Delta E_i\,;\langle\Gamma^Q\rangle) \quad , \tag{2.27}$$

where

$$L(\Delta E_i\,;\langle\Gamma^Q\rangle) = \frac{1}{2\pi}\,\frac{\langle\Gamma^Q\rangle}{\Delta E_i^2 + \left(\langle\Gamma^Q\rangle/2\right)^2} \quad . \tag{2.28}$$

The Q−state widths Γ_i^Q in Eqs. (2.22) and (2.25) have been replaced in Eqs. (2.27) and (2.28) by the average Q−state width

$$\langle\Gamma^Q\rangle = 2\pi\langle\langle|V^{QQ'}|^2\rangle\rangle\rho_{Q'}(\langle H\rangle) \quad , \tag{2.29}$$

where the quantity $\langle\langle|V^{QQ'}|^2\rangle\rangle$ is explicitly written as

$$\langle\langle|V^{QQ'}|^2\rangle\rangle = \frac{1}{N_Q N_{Q'}} \sum_{i=1}^{N_Q}\sum_{k=1}^{N_{Q'}} |V_{ik}^{QQ'}|^2 \quad . \tag{2.30}$$

This "double" average is simply the average of all of the squared coupling elements in the $\mathbf{V}^{QQ'}$ Hamiltonian matrix sub-block. Equations (2.27)–(2.30) are expected to give a good approximation to Eq. (2.25) when there are many non-zero matrix elements between the Q− and Q'−spaces.

For a dense set of Q states and very weak coupling between the Q and Q' subspaces, the usual Golden Rule decay rate may be obtained by first converting Eq. (2.27) into an integral:

$$\Gamma_j^P \simeq 2\pi \int \langle|V_j^{QP}(E^Q)|^2\rangle L(\Delta E;\langle\Gamma^Q\rangle)\rho_Q(E^Q)dE^Q \quad . \tag{2.31}$$

If the E^Q–dependent term $\langle |V_j^{QP}(E^Q)|^2 \rangle$ is replaced by its average $\langle |V_j^{QP}|^2 \rangle$ over all couplings between the P– and Q–space states, one obtains

$$\Gamma_j^P \simeq 2\pi \langle |V_j^{QP}|^2 \rangle \int L(\Delta E; \langle \Gamma^Q \rangle) \rho_Q(E^Q) dE^Q \quad . \tag{2.32}$$

For weak $Q - Q'$ couplings, the width $\langle \Gamma^Q \rangle$ of the Lorentzian function [Eq. (2.28)] is sharply peaked about $\Delta E = 0$ (i.e., $E^Q = \langle H \rangle$). Therefore, the usual Golden Rule expression is obtained as the approximate result:

$$\Gamma_j^P \simeq 2\pi \langle |V_j^{QP}|^2 \rangle \rho_Q(\langle H \rangle) \quad . \tag{2.33}$$

It is expected, however, that in a realistic system the Q–space will not be particularly dense and will also have significant couplings to the Q'–space.

It is also possible to generalize the present results to include more than one state in the P–manifold. This case is important when there are a few basis states, including the initial state, that are strongly coupled together, or when the initial excitation forms a linear combination of basis states. The suitably generalized forms of Eqs. (2.23)–(2.25) are given by

$$i \frac{db_j^P(t)}{dt} \simeq \sum_{j'=1}^{N_P} \left(H_{jj'}^P - \langle H \rangle \delta_{jj'} + \Delta_{jj'}^P - i\Gamma_{jj'}^P/2 \right) b_{j'}^P(t) \quad , \tag{2.34}$$

where $H_{jj'}^P$ are Hamiltonian matrix elements for the P–space, and the generalized shifts and widths are given respectively by

$$\Delta_{jj'}^P = \sum_{i=1}^{N_Q} \Delta E_i \frac{V_{ji}^{PQ} V_{ij'}^{QP}}{\Delta E_i^2 + (\Gamma_i^Q/2)^2} \quad , \tag{2.35}$$

and

$$\Gamma_{jj'}^P = \sum_{i=1}^{N_Q} \Gamma_i^Q \frac{V_{ji}^{PQ} V_{ij'}^{QP}}{\Delta E_i^2 + (\Gamma_i^Q/2)^2} \quad . \tag{2.36}$$

Coupled differential equations of this form can give rise to such interesting behavior as biexponential decay of the initial state probability.

In the next section, a rigorous result which simplifies the numerical evaluation of Eqs. (2.25), (2.27), (2.35), and (2.36) will be derived.

III. AVERAGE MATRIX ELEMENTS

A calculation of the two approximate results for the decay rate of the initially prepared "P" state [Eqs. (2.25) and (2.27)] is a relatively straightforward matter except for the evaluation of the quantities Γ_i^Q and $\langle\Gamma^Q\rangle$, respectively. More specifically, in a typical calculation one can probably determine the "P" initial state, the "Q" states that are coupled to the initial state, and the value of the coupling elements between the P and Q states. However, depending on which approximate result one uses, the widths Γ_i^Q or $\langle\Gamma^Q\rangle$ of the $Q-$space states $|\varphi_i^Q\rangle$ must also be explicitly calculated. These quantities involve a calculation of, in the former case, the average [cf. Eq. (2.22)]

$$\langle|V_i^{QQ'}|^2\rangle = \frac{1}{N_{Q'}}\sum_{k=1}^{N_{Q'}}|V_{ik}^{QQ'}|^2 , \tag{3.1}$$

and, in the latter case, the further average [cf. Eqs. (2.29)–(2.30)]

$$\langle\langle|V^{QQ'}|^2\rangle\rangle = \frac{1}{N_Q}\sum_{i=1}^{N_Q}\langle|V_i^{QQ'}|^2\rangle . \tag{3.2}$$

The coupling elements in Eqs. (3.1) and (3.2) describe the couplings between the zeroth-order $Q-$space states $|\varphi_i^Q\rangle$ and the *many* prediagonalized $Q'-$space states. As mentioned before, in order to calculate each of the $Q-Q'$ matrix elements individually requires that one actually *prediagonalize* the entire $Q'-$space Hamiltonian to find the $Q'-$space eigenvectors. This is clearly a difficult, if not impossible, task for any large molecule. It is therefore important to consider in more detail the explicit expression for the averages in Eqs. (3.1) and (3.2).

The explicit form of the prediagonalized Q'−space wavefunction $|\psi_k^{Q'}\rangle$ is given by

$$|\psi_k^{Q'}\rangle = \sum_{n=1}^{N_{Q'}} U_{nk}|\varphi_n^{Q'}\rangle \quad , \tag{3.3}$$

where $\{|\varphi_n^{Q'}\rangle\}$ is the Q'−space zeroth-order basis, and the coefficients U_{nk} contain the overlaps $\langle\varphi_n^{Q'}|\psi_k^{Q'}\rangle$. The matrix $\mathbf{U}$ contains a column of coefficients U_{nk} for each state $|\psi_k^{Q'}\rangle$ and diagonalizes the Q'−space Hamiltonian sub-block $\mathbf{H}^{Q'}$:

$$\mathbf{U}^\dagger\mathbf{H}^{Q'}\mathbf{U} = \mathbf{E}^{Q'} \quad . \tag{3.4}$$

In this equation, the diagonal matrix $\mathbf{E}^{Q'}$ contains the prediagonalized Q'−space energies $E_k^{Q'}$.

By virtue of Eq. (3.3), the expression for the matrix element which couples the Q−space state $|\varphi_i^Q\rangle$ to the prediagonalized Q'−space state $|\psi_k^{Q'}\rangle$ is found in terms of the zeroth-order basis to be

$$V_{ik}^{QQ'} = \sum_{n=1}^{N_{Q'}} U_{nk}v_{in}^{QQ'} \quad , \tag{3.5}$$

where $v_{in}^{QQ'}$ is the matrix element $\langle\varphi_i^Q|V|\varphi_n^{Q'}\rangle$ between *zeroth-order* states. The absolute value squared of this matrix element may be written as

$$|V_{ik}^{QQ'}|^2 = \sum_{n=1}^{N_{Q'}} \left|U_{nk}\right|^2|v_{in}^{QQ'}|^2 + \sum_{n=1}^{N_{Q'}}\sum_{m\neq n}^{N_{Q'}} U_{nk}U_{km}^\dagger v_{im}^{QQ'*}v_{in}^{QQ'} \quad . \tag{3.6}$$

In order to calculate the approximate Q−space widths in Eq. (2.22), one evaluates Eq. (3.1). However, by using Eq. (3.6), this equation can be written more explicitly as

$$\langle|V_i^{QQ'}|^2\rangle = \frac{1}{N_{Q'}} \sum_{k=1}^{N_{Q'}} \left[\sum_{n=1}^{N_{Q'}} \left|U_{nk}\right|^2|v_{in}^{QQ'}|^2 + \sum_{n=1}^{N_{Q'}}\sum_{m\neq n}^{N_{Q'}} U_{nk}U_{km}^\dagger v_{im}^{QQ'*}v_{in}^{QQ'} \right] \quad . \tag{3.7}$$

Equation (3.7) may be easily rewritten as

$$\langle |V_i^{QQ'}|^2 \rangle = \frac{1}{N_{Q'}} \sum_{n=1}^{N_{Q'}} A_{nn} |v_{in}^{QQ'}|^2 + \frac{1}{N_{Q'}} \sum_{n=1}^{N_{Q'}} \sum_{m \neq n}^{N_{Q'}} A_{nm} v_{in}^{QQ'} v_{im}^{QQ'*} \quad , \tag{3.8}$$

where

$$A_{nm} = \sum_{k=1}^{N_{Q'}} U_{nk} U_{km}^{\dagger} \quad . \tag{3.9}$$

Since **U** is the unitary transformation matrix that diagonalizes $\mathbf{H}^{Q'}$ [cf. Eq. (3.4)], it is easy to show that A_{nm} equals the Kronecker delta δ_{nm}. Hence,

$$\langle |V_i^{QQ'}|^2 \rangle = \frac{1}{N_{Q'}} \sum_{n=1}^{N_{Q'}} |v_{in}^{QQ'}|^2 = \langle |v_i^{QQ'}|^2 \rangle \quad , \tag{3.10}$$

where $\langle |v_i^{QQ'}|^2 \rangle$ is the average coupling element between the zeroth-order Q−space state $|\varphi_i^Q\rangle$ and the zeroth-order Q'−space states $\{|\varphi_n^{Q'}\rangle\}$. This result significantly simplifies the evaluation of Eqs. (3.1) and (3.2) and hence the application of the present theory because *no diagonalizations are now required* in order to calculate the relevant quantities in Eqs. (2.23)–(2.36).

IV. DISCUSSION

The present theory is most useful when detailed theoretical information is available regarding the initial state, those "first tier" states that are coupled directly to the initial state, and the magnitudes of the couplings between them. Given that knowledge, the approximate result in Eq. (2.27) for the IVR decay rate is particularly useful for a comparison with experiment. That is, the experimental decay rate could be fit to a function of the form given in Eq. (2.27), provided one could calculate theoretically the $Q-P$ couplings V_{ij}^{QP}. The "intramolecular width" parameter $\langle \Gamma^Q \rangle$ could then be determined from the combined experimental and theoretical results. Alternatively, one could evaluate $\langle\Gamma^Q\rangle$ [Eqs. (2.29) and (2.30)] directly from the zeroth-order matrix elements and an estimate[23] of $\rho_{Q'}(\langle H\rangle)$, calculate the decay rate [Eq. (2.27)] using the theoretical value for $\langle\Gamma^Q\rangle$, and then compare the result with the experimental value.

By virtue of its form, the parameter $\langle\Gamma^Q\rangle$ [Eq. (2.29)] provides valuable information regarding the degree of coupling (or mixing) among the intramolecular "bath" states. It is also interesting to note that the additional parameter $\langle\Gamma^Q\rangle\rho_{Q'}^{av}$, where $\rho_{Q'}^{av}$ is the average density of Q'−space states over the width $\langle\Gamma^Q\rangle$, gives an estimate of the total number of Q'−space bath states that participate in the IVR.[24] A comparison of the value of $\langle\Gamma^Q\rangle\rho_{Q'}^{av}$ with the total density of states at the mean energy $\langle H\rangle$ of the initial state $\left[\rho(\langle H\rangle)\right]$ provides information regarding the degree to which interactions with off-resonant states (i.e., with energies $E_i \neq \langle H\rangle$) are important (see, e.g., Ref. 11). It should be mentioned that $\langle\Gamma^Q\rangle$ *is not* the homogeneous spectral linewidth[12,13] of the initial state. Rather, $\langle\Gamma^Q\rangle$ reflects properties of the intramolecular bath states.

The approximate formulas for the decay rate [Eqs. (2.25) or (2.27)] also suggest the possibility of bottlenecks in the flow of probability out of the initial state. In particular, if the energies E_i^Q of the Q−space states are outside of the intramolecular width $\langle\Gamma^Q\rangle$ of the initial state, then the exponential decay rate is diminished. This effect is shown more clearly by considering the relative contributions $\delta\Gamma_j^P$ to the rate in Eq. (2.27) from a state $|\varphi_0^Q\rangle$ which is degenerate with the initial state, and from a state $|\varphi_i^Q\rangle$ which is outside of the intramolecular width (i.e., $|E_i - \langle H\rangle\,| = |\Delta E_i| \gg \langle\Gamma^Q\rangle/2$). It may be shown that the ratio of these state's contributions to the decay rate is given by

$$\frac{\delta\Gamma_i^P}{\delta\Gamma_0^P} \simeq \frac{|V_{ji}^{PQ}|^2}{|V_{j0}^{PQ}|^2}\left(\frac{\langle\Gamma^Q\rangle}{2\Delta E_i}\right)^2 . \tag{4.1}$$

Thus, the contribution to the decay rate for first tier (Q−space) states outside of the width $\langle\Gamma^Q\rangle$ diminishes rapidly with increasing energy difference ΔE_i.

On the other hand, Q–space states $\left|\varphi_i^Q\right\rangle$ that are within the intramolecular width $\left\langle\Gamma^Q\right\rangle$ can contribute considerably to the initial state's decay rate. In that case (i.e., $\Delta E_i \ll \left\langle\Gamma^Q\right\rangle/2$), it can also be shown that those state's contributions to the decay rate are insensitive functions of their zeroth-order energies. The relative contributions $\delta\Gamma_i^P$ and $\delta\Gamma_0^P$ to the initial state's decay rate are found to be given in this case by

$$\frac{\delta\Gamma_i^P}{\delta\Gamma_0^P} \simeq \frac{\left|V_{ji}^{PQ}\right|^2}{\left|V_{j0}^{PQ}\right|^2}\left[1 - \left(\frac{2\Delta E_i}{\left\langle\Gamma^Q\right\rangle}\right)^2\right] , \tag{4.2}$$

where all quantities are as defined in the previous paragraph. For states with $\Delta E_i \ll \left\langle\Gamma^Q\right\rangle/2$, it is clear from Eq. (4.2) that those state's contribution to the rate is only weakly dependent on their energy. For a typical large molecule,[13] $\left\langle\Gamma^Q\right\rangle$ may be on the order of 10–100 cm^{-1}, so Eq. (4.2) raises some interesting questions concerning the relevance of different energy level distributions[25] to IVR rates.

The present theory may also be applied to calculate the decay rates of the C-H overtone states in benzene.[13] By using the theoretical values for the energy differences ΔE_i and coupling elements V_{ij}^{QP} given by Sibert *et al.*,[13] the decay lifetimes ($\equiv \hbar/\Gamma_j^P$) of the $v_{CH} = 5$, 6, and 9 overtones were calculated from Eq. (2.27) to be 0.065, 0.052, and 0.154 ps, respectively. The values calculated numerically by Sibert *et al.* were 0.062, 0.067, and 0.160 ps, respectively. In the present calculations, a value for $\left\langle\Gamma^Q\right\rangle$ of 100 cm^{-1} was used for calculating the $v = 5$ and 6 overtone lifetimes, while a value of 150 cm^{-1} was used for the $v = 9$ overtone. These widths were taken to be the same as the phenomenological decay widths used in the detailed time-dependent calculations of Sibert *et. al.* The agreement between the two sets of results is quite encouraging. By using a value of 150 cm^{-1} instead of 100 cm^{-1} for $\left\langle\Gamma^Q\right\rangle$ in Eq. (2.27), the $v = 5$ and 6 overtone lifetimes were calculated to be 0.064 and 0.063 ps, respectively. (The widths used by Sibert *et al.* should not necessarily be the same as $\left\langle\Gamma^Q\right\rangle$, but it is expected that these two numbers should be reasonably close in value.)

V. CONCLUDING REMARKS

In Eqs. (2.25) and (2.27), approximate results have been given for the exponential IVR decay rate of an initially prepared zeroth-order state in a large polyatomic molecule. In addition, the appropriate generalized coupled equations for several strongly coupled states are given in Eqs. (2.34)–(2.36). The derivation of these approximate results was based on a partitioning of the zeroth-order Hilbert space into three subsets which are, respectively, the initial state ("P"), those states which are directly coupled to the initial state ("Q"), and all remaining states ("Q' "). The procedure of adiabatic elimination[15,16] was then used on the Q'–space amplitudes to simplify the coupled differential equations for those states. By treating the Q'–space states as being prediagonalized, the appropriate sum over Q'–space states in Eq. (2.10) was treated as a contour integral [cf. Eq. (2.11)], and the decay width Γ_i^Q due to the "background" Q'–space states [Eq. (2.22)] was obtained. By virtue of an expansion [Eq. (2.20)] and the subsequent adiabatic elimination of the Q-space states from the coupled equations, the approximate decay rate Γ_j^P for the intial P–space state was derived [Eq. (2.25)]. [An approximation given in Eqs. (2.27)–(2.29) further simplified the result for Γ_j^P.] In Sec. III, it was also demonstrated that no prediagonalization of the Q'–space states is necessary in order to determine the relevant decay widths in the present theory.

The approximate results for the IVR decay rate Γ_j^P [Eqs. (2.25) or (2.27)] are more detailed in form than the usual Golden Rule expression [Eq. (1.1)]. This fact is because the matrix elements for the first tier Q–space states that are directly coupled to the initial state are treated explicitly. Nevertleless, no diagonalizations of matrices or integrations of coupled equations are required in the present theory [unless desired: cf. Eqs. (2.34)–(2.36)]. In addition, the value of the intramolecular width $\langle \Gamma^Q \rangle$ in Eq. (2.29) is a potentially useful parameter which may be calculated by averaging matrix elements [cf. Eq. (2.30)] or, more importantly, by comparison with experimental results.

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(19) Rovibrational states from other electronic manifolds may also contribute to the various tiers of states in the intramolecular coupling scheme. In that case, the IVR process stimulates electronic energy redistribution. Experimental results indicating this interesting effect have been obtained for several large molecules [see, e.g., U. Schubert, E. Riedle, H. J. Neusser, and E. W. Schlag, J. Chem. Phys. **84**, 6182 (1986); A. Amirav, J. Jortner, S. Okajima, and E. C. Lim, Chem. Phys. Lett. **126**, 487 (1986), and references cited therein.]

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(21) This condition has been suggested as the criterion for having an effective quasicontinuum of states in electronic radiationless transitions theory (see, e.g., Ref. 7). In that case, the widths Γ_i^Q arise from the phenomenological radiative lifetimes of the molecular vibronic states.

(22) By using a complementary resolvent operator approach, Heller and Mukamel (Ref. 12) have derived a similar lineshape expression for the specific case of bond mode overtone excitation in molecules with several such modes (e.g., benzene).

(23) For example, by using the Whitten-Rabinovitch formula [see, e.g., P. J. Robinson and K. A. Holbrook, *Unimolecular Reactions* (Wiley, New York, 1972), p. 131].

(24) The parameter $\langle \Gamma^Q \rangle \rho_{Q'}^{av}$ is somewhat different from, but related to, the parameter N employed by Dolson, *et al.* (Ref. 11). The latter parameter, defined as $2\pi \langle V_{sl}^2 \rangle \rho^2$, is based on a model having an initial state $|\varphi_s\rangle$ coupled to a single tier of $|\varphi_l\rangle$ states with an average density ρ. The parameter N provides a measure of the number of $|\varphi_l\rangle$ states that participate in the IVR of the $|\varphi_s\rangle$ state. To the extent that we view the $|\varphi_l\rangle$ states as being the prediagonalized bath states (i.e., $Q + Q'$ states), these two parameters should have similar interpretations.

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Appendix I: Adiabatically Reduced Coupled Equations for Non-orthogonal Basis Sets

For certain applications, it may be desirable to use a non-orthogonal basis set expansion of the time-dependent wave function,* i.e.,

$$|\Psi(t)\rangle \;=\; exp(-i\,\langle H\rangle\,t)\sum_{i=1}^{N} b_i(t)\,|\varphi_i\rangle \quad , \tag{I.1}$$

where $\hbar$ equals unity, and $\langle H\rangle$ is the expectation value of the energy for the initial state. This expansion is similar to that given in Eqs. (2.1) and (2.3) of Chapter 5, except that now the overlaps $\langle\varphi_i|\varphi_j\rangle$ equal a value S_{ij} rather than the Kronecker delta δ_{ij}.

By substituting Eq. (I.1) into the time-dependent Schrödinger equation and multiplying from the left by $exp(i\,\langle H\rangle\,t)\,\langle\varphi_j|$, the following coupled equations for the amplitudes $b_i(t)$ are obtained:

$$i\mathbf{S}\frac{d}{dt}\,\mathbf{b}(t) \;=\; (\mathbf{H} \;-\; \langle H\rangle\,\mathbf{S})\mathbf{b}(t) \quad , \tag{I.2}$$

where $\mathbf{H}$ is the Hamiltonian matrix represented in the non-orthogonal basis $\{|\varphi_i\rangle\}$, $\mathbf{b}(t)$ is a vector containing the amplitudes $b_i(t)$, and $\mathbf{S}$ is the overlap matrix composed of the elements S_{ij}. The initial conditions for Eq. (I.2) are given by the vector $\mathbf{b}(0) = \mathbf{S}^{-1}\mathbf{a}(0)$, where the vector $\mathbf{a}(0)$ has the elements $a_i(0) = \langle\varphi_i|\psi(0)\rangle$.

Equation (I.2) may be rewritten as

$$i\frac{d}{dt}\,\mathbf{b}(t) \;=\; (\mathbf{A} \;-\; \langle H\rangle\,\mathbf{1})\mathbf{b}(t) \quad , \tag{I.3}$$

where the matrix $\mathbf{A}$ is defined as $\mathbf{S}^{-1}\mathbf{H}$. The matrix $\mathbf{A}$ determines the time evolution of the non-orthogonal basis state amplitudes $\mathbf{b}(t)$ in the same way that $\mathbf{H}$, when represented in an orthogonal basis, determines the state amplitudes in the

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* See, for example, T. J. Park and J. C. Light, J. Chem. Phys. **85**, 5870 (1986).

theory of Chapter 5. In the present instance, therefore, a partitioning of the state amplitudes into resonant/strongly coupled and off-resonant/weakly coupled subspaces may be performed based on an examination of the elements of the matrix **A** relative to the value of the initial state energy $\langle H \rangle$ (cf. Chap. 5). The adiabatic treatment of Chapter 5 may then be utilized by taking care to use the partitioned matrix **A** rather than present $\mathbb{H}$ (which is represented in a non-orthogonal basis). It is hence a relatively straightforward matter to adapt the theory of Chapter 5 to treat non-orthogonal basis sets.

Appendix II: Iteratively Determined Effective Hamiltonians for the Adiabatically Reduced Coupled Equations Approach to Intramolecular Dynamics Calculations

[The text of this Appendix appeared in: S. J. Klippenstein, G. A. Voth, and R. A. Marcus, J. Chem. Phys. **85**, 5019 (1986).]

Iteratively determined effective Hamiltonians for the adiabatically reduced coupled equations approach to intramolecular dynamics calculations

Stephen J. Klippenstein, Gregory A. Voth, and R. A. Marcus
Arthur Amos Noyes Laboratory of Chemical Physics, California Institute of Technology,[a] *Pasadena, California 91125*

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An iterative procedure is proposed for determining increasingly accurate effective Hamiltonians for use in the adiabatically reduced coupled equations approach to intramolecular dynamics calculations [J. Chem. Phys. **84**, 2254 (1986)]. The relationships between this iterative determination of the effective Hamiltonian, which is based on an adiabatic approximation, and some other partitioning methods for determining an effective Hamiltonian are discussed. The present iterative procedure provides accurate agreement with the exact dynamics for the two specific model systems studied.

I. INTRODUCTION

In recent years, there has been considerable theoretical and experimental interest in the quantum dynamics of initially prepared nonstationary states in isolated polyatomic molecules. More specifically, the time-evolution of initially prepared states resulting from vibronic,[1] vibrational,[2] and rovibrational[3] coupling mechanisms is of particular interest. The "exact" treatment of the dynamics of these states requires, in typical situations, the numerical diagonalization of a Hamiltonian matrix having a very large number of basis states. Since there are, at present, computational limitations on the size of matrices which can be diagonalized, methods which reduce the size of the Hamiltonian matrix to be diagonalized, or, alternatively, new methods for determining the quantum dynamics,[4] must be developed.

By virtue of clever numerical methods, several authors have been able to increase the number of basis states which may be included in a typical calculation. For example, Nauts and Wyatt[5] have developed the recursive residue generation method (RRGM) to determine the relevant time-dependent transition amplitudes directly without requiring the diagonalization of the Hamiltonian matrix. Moreover, Tietz and Chu,[6] as well as Chang and Wyatt,[7] have implemented artificial intelligence algorithms in their studies of multiphoton excitation of molecules which allowed them to consider a large number of basis states and then to include in their dynamical calculations only those states which had the largest effect on the dynamics. These methods represent potentially quite powerful numerical approaches for obtaining the dynamics of nonstationary states.

Recently, Voth and Marcus[8] have developed an approximate dynamical approach which is based on a partitioning[8,9] of the basis set into a subset of states which are resonant and/or strongly interacting with the initial state, and a subset of states containing the remaining off-resonant/weakly coupled states.[8] Their approach then treats the off-resonant/weakly coupled states in an effective manner by virtue of an adiabatic approximation. This latter method also allows one to determine the dynamics directly by integrating the effective coupled equations and hence does not rely on a calculation (and computer storage) of the eigenvalues and eigenvectors of the system.

In this article, an iterative scheme is applied to the adiabatically reduced coupled equations approach of Voth and Marcus.[8] With each iterative step, new effective coupled equations for the resonant/strongly coupled subspace are obtained, and hence a new effective Hamiltonian is derived. If the initial adiabatic approximation is a good one (cf. Discussion in Ref. 8), the resulting dynamics calculated from the effective coupled equations exhibit accurate agreement with the exact dynamics.

The derivation of the reduced coupled equations is reviewed in Sec. II and the iterative scheme is presented there. In Sec. III the present time-dependent method for determining the effective coupled equations is shown to be related to the iterative solution of an equation for the effective interaction in nuclei derived from a time-independent viewpoint by Schucan and Weidenmüller.[10] The relationship of the present effective Hamiltonian to that given by Lee and Suzuki[11] and to the partitioning formalism of Löwdin[12] is also discussed in Sec. III. An application of the effective coupled equations to two model problems is given in Sec. IV, and the results are discussed in Sec. V. Concluding remarks appear in Sec. VI.

II. THEORY

A. Coupled equations

The time-dependent wave function (in atomic units) is expanded as[8,13]

$$|\Psi(t)\rangle = \exp(-i\langle H\rangle t)\sum_{i=1}^{N} b_i(t)|\varphi_i\rangle , \qquad (1)$$

where the basis states $|\varphi_i\rangle$ are eigenfunctions of a suitably chosen zeroth-order Hamiltonian H_0, and $\langle H\rangle$ is the expectation value of the total Hamiltonian $H(=H_0+V)$, defined as $\langle H\rangle = \langle\Psi(t)|H|\Psi(t)\rangle$. By substituting this expansion for $|\Psi(t)\rangle$ into the time-dependent Schrödinger equation and using the orthonormal properties of the $\{|\varphi_i\rangle\}$

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[a] Contribution No. 7434.

basis, the following coupled first-order differential equations for the amplitudes $b_i(t)$ are obtained:

$$\frac{db_j(t)}{dt} = i\langle H\rangle b_j(t) - i\sum_{i=1}^{N} H_{ji} b_i(t)\,, \tag{2}$$

where $H_{ji} = \langle \varphi_j | H | \varphi_i \rangle$.

The zeroth-order basis is now partitioned into a subset of states which are nearly resonant with and/or strongly coupled to the initial state and another subset containing all remaining off-resonant/weakly coupled states. The coupled equations may then be written in vector-matrix notation as[8]

$$\frac{d}{dt}\mathbf{b}^R(t) = i(\langle H\rangle \mathbf{1}^{\mathrm{R}} - \mathbf{H}^R)\mathbf{b}^R(t) - i\mathbf{V}^{RO}\mathbf{b}^O(t)\,, \tag{3}$$

$$\frac{d}{dt}\mathbf{b}^O(t) = i(\langle H\rangle \mathbf{1}^O - \mathbf{H}^O)\mathbf{b}^O(t) - i\mathbf{V}^{OR} b^R(t)\,. \tag{4}$$

By denoting the dimension of the resonant/strongly coupled subspace by N_R and the off-resonant/weakly coupled subspace by N_O, the quantities in Eqs. (3) and (4) are defined as follows: $\mathbf{b}^R(t)\,[\mathbf{b}^O(t)]$ is an $N_R\,(N_O)$-dimensional column vector containing the amplitudes for the resonant (off-resonant) states, $\mathbf{1}^R(\mathbf{1}^O)$ is the $N_R \times N_R\,(N_O \times N_O)$ identity matrix, $\mathbf{H}^R(\mathbf{H}^O)$ is the $N_R \times N_R\,(N_O \times N_O)$ Hamiltonian submatrix for the resonant (off-resonant) states, and $\mathbf{V}^{RO}(\mathbf{V}^{OR})$ is the $N_R \times N_O\,(N_O \times N_R)$ coupling matrix between the two subspaces.

B. Iterative scheme for the effective coupled equations

The adiabatic approximation given in Ref. 8 was based on the physical property that the off-resonant amplitudes $\mathbf{b}^O(t)$ will remain negligibly small during the time evolution and hence the derivatives $d\mathbf{b}^O(t)/dt$ in Eq. (4) are effectively equal to zero. The validity of this approximation depends on the partitioning scheme, and the reader is referred to Ref. 8 for further details in that regard. With the approximation of $d\mathbf{b}^O(t)/dt \simeq 0$, which hereafter will be termed the "zeroth-order" approximation, effective coupled equations for calculating the dynamics of the resonant amplitudes may be derived.[8] It will be shown here how increasingly accurate higher-order effective coupled equations can be derived iteratively by obtaining improved approximations for the off-resonant derivatives in Eq. (4).

Equation (3) can be rewritten in the form

$$\mathbf{V}^{RO}\mathbf{b}^O(t) = i\frac{d}{dt}\mathbf{b}^R(t) + (\langle H\rangle \mathbf{1}^R - \mathbf{H}^R)\mathbf{b}^R(t) \tag{5}$$

and Eq. (4) can also be rearranged to give

$$\mathbf{b}^O(t) = -i(\langle H\rangle \mathbf{1}^O - \mathbf{H}^O)^{-1}\frac{d}{dt}\mathbf{b}^O(t) + (\langle H\rangle \mathbf{1}^O - \mathbf{H}^O)^{-1}\mathbf{V}^{OR}\mathbf{b}^R(t)\,. \tag{6}$$

As a metioned before, the zeroth-order adiabatic approximation used in Ref. 8 was

$$\frac{d}{dt}\mathbf{b}^O(t) \simeq 0, \tag{7}$$

which, when substituted into Eq. (6), yields

$$\mathbf{b}^O(t) \simeq (\langle H\rangle \mathbf{1}^O - \mathbf{H}^O)^{-1}\mathbf{V}^{OR}\mathbf{b}^R(t)\,. \tag{8}$$

Substitution of this expression for $\mathbf{b}^O(t)$ into Eq. (3) gives

$$\frac{d}{dt}\mathbf{b}^R(t) \simeq -i\mathbf{H}^R_{\mathrm{eff},0}\,\mathbf{b}^R(t)\,, \tag{9}$$

where the zeroth-order effective Hamiltonian is given by

$$\mathbf{H}^R_{\mathrm{eff},0} = \mathbf{H}^R - \langle H\rangle \mathbf{1}^R + \mathbf{V}^{RO}(\langle H\rangle \mathbf{1}^O - \mathbf{H}^O)^{-1}\mathbf{V}^{OR}\,. \tag{10}$$

An iterative formula for the general nth-order effective Hamiltonian, $\mathbf{H}^R_{\mathrm{eff},n}$, may be derived as shown below, for which the corresponding coupled equations are given by

$$\frac{d}{dt}\mathbf{b}^R(t) \simeq -i\mathbf{H}^R_{\mathrm{eff},n}\,\mathbf{b}^R(t)\,, \tag{11}$$

where

$$\mathbf{H}^R_{\mathrm{eff},n} = [\mathbf{1}^R + \mathbf{F}^{-1}(\mathbf{H}^R_{\mathrm{eff},n-1} + \langle H\rangle \mathbf{1}^R - \mathbf{H}^R)]^{-1}\mathbf{H}^R_{\mathrm{eff},0} \tag{12}$$

and

$$\mathbf{F}^{-1} = \mathbf{V}^{RO}(\langle H\rangle \mathbf{1}^O - \mathbf{H}^O)^{-1}(\mathbf{V}^{RO})^{-1}. \tag{13}$$

Equations (11)–(13) constitute the central result of the present paper.

To derive Eqs. (11)–(13), Eq. (5) is first rewritten as

$$\mathbf{b}^O(t) \simeq (\mathbf{V}^{RO})^{-1}(\mathbf{H}^R_{\mathrm{eff},n-1} + \langle H\rangle \mathbf{1}^R - \mathbf{H}^R)\mathbf{b}^R(t)\,, \tag{14}$$

where $(\mathbf{V}^{RO})^{-1}$ is a "left" inverse, and $id\mathbf{b}^R(t)/dt$ in Eq. (5) has been taken to be equal to $\mathbf{H}^R_{\mathrm{eff},n-1}\mathbf{b}^R(t)$ (i.e., it is taken from the previous iteration). For example, the first-order approximation to $\mathbf{b}^O(t)$ is obtained by replacing $id\mathbf{b}^R(t)/dt$ in Eq. (5) by $\mathbf{H}^R_{\mathrm{eff},0}\mathbf{b}^R(t)$. By taking the derivative of Eq. (14) and then substituting the resulting expression for $d\mathbf{b}^O(t)/dt$ into Eq. (6), an approximation for $\mathbf{b}^O(t)$ is obtained, namely

$$\begin{aligned}\mathbf{b}^O(t) \simeq{}& -i(\langle H\rangle \mathbf{1}^O - \mathbf{H}^O)^{-1}(\mathbf{V}^{RO})^{-1}(\mathbf{H}^R_{\mathrm{eff},n-1} \\ &+ \langle H\rangle \mathbf{1}^R - \mathbf{H}^R)\frac{d}{dt}\mathbf{b}^R(t) \\ &+ (\langle H\rangle \mathbf{1}^O - \mathbf{H}^O)^{-1}\mathbf{V}^{OR}\mathbf{b}^R(t)\,.\end{aligned} \tag{15}$$

Substitution of Eq. (15) for the off-resonant amplitudes into Eq. (3) and collecting the terms for $d\mathbf{b}^R(t)/dt$ yields the nth-order effective coupled equations given by Eqs. (11)–(13).

The present iterative procedure can be repeated *ad infinitum* to give, in principle, better and better approximations to the off-resonant amplitudes and hence to give more and more accurate effective coupled equations. However, the accuracy of the coupled equations determined from this procedure depends crucially on how good the initial choice for the time derivatives of the off-resonant states is. (This choice was zero in the present case.[8]) When the initial approximation for those derivatives is not a sufficiently accurate one, the iterative procedure may give qualitatively incorrect results for the dynamics. From the nature of the iterative formula, it is clear that the convergence properties depend very much on the "magnitude" of $\mathbf{V}^{RO}$ (or $\mathbf{V}^{OR}$) relative to the magnitude of $(\langle H\rangle \mathbf{1}^O - \mathbf{H}^O)$.[8]

The following notation is introduced here to simplify the expressions for the effective Hamiltonians:

$$\mathbf{V}_0 = \mathbf{H}^R_{\mathrm{eff},0}\,,$$

$$\mathbf{V}_i = \mathbf{V}^{RO}(\langle H\rangle \mathbf{1}^O - \mathbf{H}^O)^{-(i+1)}\mathbf{V}^{OR}, \quad i \geqslant 1. \tag{16}$$

For example, the first-order effective Hamiltonian is now given by

$$\begin{aligned}\mathbf{H}^R_{\text{eff},1} &= [\mathbf{1}^R + \mathbf{V}^{RO}(\langle H\rangle \mathbf{1}^O - \mathbf{H}^O)^{-2}\mathbf{V}^{OR}]^{-1}\mathbf{H}^R_{\text{eff},0}\\ &= (\mathbf{1}^R + \mathbf{V}_1)^{-1}\mathbf{V}_0\,,\end{aligned} \tag{17}$$

and the second-order effective Hamiltonian by

$$\mathbf{H}^R_{\text{eff},2} = [\mathbf{1}^R + \mathbf{V}_1 - \mathbf{V}_2(\mathbf{1}^R + \mathbf{V}_1)^{-1}\mathbf{V}_0]^{-1}\mathbf{V}_0\,. \tag{18}$$

C. Expansions of the effective Hamiltonian

The effective Hamiltonian determined from the present iterative procedure may be expanded in various ways. For example, due to computational limitations, it may not always be desirable to invert the matrix $(\langle H\rangle \mathbf{1}^O - \mathbf{H}^O)$ present in $\mathbf{V}_i$ [Eq. (16)]. In that case, the following expansion could prove useful (e.g., Ref. 12, with $\langle H\rangle$ replaced by an energy eigenvalue E):

$$(\langle H\rangle \mathbf{1}^O - \mathbf{H}^O)^{-1} = (\langle H\rangle \mathbf{1}^O - \mathbf{E}^O)^{-1} \times \sum_{n=0}^{\infty} [\mathbf{V}^O(\langle H\rangle \mathbf{1}^O - \mathbf{E}^O)^{-1}]^n, \tag{19}$$

where the matrix $\mathbf{H}^O$ has been separated into $\mathbf{E}^O + \mathbf{V}^O$, with $\mathbf{E}^O$ containing the diagonal elements of $\mathbf{H}^O$ and $\mathbf{V}^O$ containing the off-diagonal elements of $\mathbf{H}^O$. Since the matrix $(\langle H\rangle \mathbf{1}^O - \mathbf{E}^O)$ is a diagonal matrix and thereby trivial to invert, each of the terms in the expansion may be straightforwardly evaluated.

Another expansion which may prove useful is a series expansion in powers of $\mathbf{V}_i$ [cf. Eq. (16), and see, e.g., Ref. 10]. For example, the series expansion of $\mathbf{H}^R_{\text{eff},2}$ in powers of $\mathbf{V}_i$ is given by

$$\mathbf{H}^R_{\text{eff},2} = \sum_{m=0}^{\infty}\left[\mathbf{V}_2 \sum_{n=0}^{\infty}(-\mathbf{V}_1)^n\mathbf{V}_0 - \mathbf{V}_1\right]^m \mathbf{V}_0\,. \tag{20}$$

With the further definition of

$$\mathbf{V}'_i = [\mathbf{1}^R + \mathbf{V}_1]^{-1}\mathbf{V}_i, \quad i \geqslant 0, \tag{21}$$

the second-order effective Hamiltonian may be rewritten as

$$\mathbf{H}^R_{\text{eff},2} = (\mathbf{1}^R - \mathbf{V}'_2\mathbf{V}'_0)^{-1}\mathbf{V}'_0\,. \tag{22}$$

A final series expansion which may prove useful is one in powers of $\mathbf{V}'_i$ (see, e.g., Ref. 10), which for $\mathbf{H}^R_{\text{eff},2}$ is given by

$$\mathbf{H}^R_{\text{eff},2} = \sum_{n=0}^{\infty}(\mathbf{V}'_2\mathbf{V}'_0)^n\mathbf{V}'_0\,. \tag{23}$$

III. RELATIONSHIP TO OTHER PARTITIONING TECHNIQUES

The relationship between the present time-dependent method for determining the effective coupled equations, and hence the effective Hamiltonian, and some time-independent methods[10–12,14–16] for determining eigenvalues using effective Hamiltonians is discussed next. For the purpose of comparison, the preceeding dynamical analysis of Sec. II B may be viewed as a complementary way of determining an effective Hamiltonian, although the focus of the present paper is towards a determination of the dynamics rather than the eigenvalues.

Several authors (e.g., Refs. 10, 11, 14–16) have used partitioning techniques to construct an effective interaction Hamiltonian for the determination of a subset of energy levels in nuclei. A summary of the work in this field is given in Ref. 16. One frequently used formula for determining the effective interactions is the Des Cloiseaux and Brandow expansion,[14,15] given in the present notation[17] by

$$\mathbf{H}^R_{\text{eff}} = \mathbf{H}^R - \lambda\,\mathbf{1}^R + \sum_{n=0}^{\infty}\frac{d^n}{(dE)^n}\mathbf{V}^{RO}(E\,\mathbf{1}^O - \mathbf{H}^O)^{-1} \times \mathbf{V}^{OR}\bigg|_{E=\lambda}\frac{1}{n!}(\mathbf{H}^R_{\text{eff}})^n\,. \tag{24}$$

In this equation, the quantity λ is taken to be a general parameter which should, in principle, be chosen to give the best agreement between the eigenvalues of the effective Hamiltonian and the corresponding eigenvalues of the exact Hamiltonian. For a nondegenerate resonant subspace, deciding upon the appropriate choice of λ is nontrivial.[17] Following our analysis in Ref. 8, we make the choice $\lambda = \langle H\rangle$, since it gave the most accurate effective coupled equations for calculating the resonant state *dynamics*. The relationship of the effective Hamiltonians determined by the present iterative scheme to those determined by previous authors[10–12,14–16] can also be shown, noting that we have replaced their λ by our $\langle H\rangle$.

Schucan and Weidenmüller[10] (SW) have considered the application of partitioning techniques to the determination of energy levels in nuclei. SW derived the following equation for the effective interaction[17]:

$$\mathbf{H}^R_{\text{eff}} = [\mathbf{1}^R + \mathbf{F}^{-1}(\mathbf{H}^R_{\text{eff}} + \lambda\,\mathbf{1}^R - \mathbf{H}^R)]^{-1}\mathbf{V}_0\,, \tag{25}$$

where this $\mathbf{F}^{-1}$ denotes $\mathbf{V}^{RO}(\lambda\,\mathbf{1}^O - \mathbf{H}^O)^{-1}(\mathbf{V}^{RO})^{-1}$, and $\mathbf{V}_0$ is given in terms of λ by $\mathbf{H}^R - \lambda\,\mathbf{1}^R + \mathbf{V}^{RO}(\lambda\,\mathbf{1}^O - \mathbf{H}^O)^{-1}\mathbf{V}^{OR}$. This equation is equivalent[10] to the implicit equation for $\mathbf{H}^R_{\text{eff}}$ given by the Des Cloiseaux and Brandow expansion [Eq. (24)]. Comparison of Eq. (25) above for the SW effective interaction with Eq. (12) for the present nth-order effective Hamiltonian shows that $\mathbf{H}^R_{\text{eff},n}$ is just the nth iterative solution to Eq. (25), with the *specific* choice of $\lambda = \langle H\rangle$. SW discuss solving Eq. (25) iteratively, and, by making expansions in powers of $\mathbf{V}_i$'s or $\mathbf{V}'_i$'s, they derive series expansions for the effective Hamiltonian which are similarly related to nth order forms of Eqs. (20) and (23) by making the choice $\lambda = \langle H\rangle$. Discussions of the covergence properties of the eigenvalues of the unexpanded and various expanded forms of the effective Hamiltonians are given in Refs. 10, 11, and 14–16, for example.

Recently, Lee and Suzuki[11] have derived an iterative formula for an effective Hamiltonian $\mathbf{H}_n$ for use in obtaining the eigenvalues in the case of a degenerate subspace. This formula, generalized to the case of a nondegenerate subspace,[16,17] is given in the present notation [Eq. (16)] by

$$\begin{aligned}\mathbf{H}_0 &= \mathbf{V}_0,\\ \mathbf{H}_n &= \left[\mathbf{1}^R + \mathbf{V}_1 - \sum_{m=2}^{n}(-)^m\mathbf{V}_m \prod_{k=n-m+2}^{n}\mathbf{H}_{k-1}\right]^{-1}\mathbf{V}_0,\\ &\quad n \geqslant 1,\end{aligned} \tag{26}$$

with V_0 given as in the expression following Eq. (25) and with the V_i's for $i > 0$ given by Eq. (16) and having the $\langle H \rangle$ replaced by λ. In Appendix A, it is shown that the present $\mathrm{H}^R_{\mathrm{eff},n}$ is equivalent to the nth-order effective Hamiltonian H_n of Lee and Suzuki,[11] given by Eq. (26), once the specific choice of $\lambda = \langle H \rangle$ is made.

The eigenvalues obtained from the present iterative scheme for the effective Hamiltonian are also related to the Newton–Raphson technique for determining the eigenvalues for the exact partitioned Hamiltonian of Löwdin.[12] The exact partitioned Hamiltonian is given in the present notation by[8]

$$\mathrm{H}^R_{\mathrm{exact}} = \mathrm{H}^R + \mathrm{V}^{RO}(E\mathbf{1}^O - \mathrm{H}^O)^{-1}\mathrm{V}^{OR}, \tag{27}$$

where the constant factor $-\langle H \rangle \mathbf{1}^R$ has been omitted. The eigenvalues are then determined by solving the secular equation

$$\det |\mathrm{H}^R_{\mathrm{exact}} - E\mathbf{1}^R| = 0, \tag{28}$$

which, due to the dependence of $\mathrm{H}^R_{\mathrm{exact}}$ on E, may require the use of a root search technique such as the Newton–Raphson method.[12]

The relationship between the Newton–Raphson solution to the above secular equation and the present effective Hamiltonian method may be established in the case of a one-dimensional resonant subspace. In this situation, the expression for the eigenvalue derived from the first-order effective Hamiltonian is identical with the expression derived from the first iteration of the Newton–Raphson method with the initial guess for E of $\langle H \rangle$. However, the relationship between the higher-order effective Hamiltonians and further iterations of the Newton–Raphson method (as well as for resonant subspaces of dimension greater than one) requires further investigation.

The effective Hamiltonian method for determining eigenvalues is also related to various other formulations of degenerate or nearly degenerate perturbation theory. These relationships are not as relevant to the dynamical analysis of the present paper and will not be discussed here. Further discussions in that regard are given in Refs. 18 and 19.

IV. APPLICATIONS

In order to illustrate the possible applications of this technique and the accuracy of the effective coupled equations, two model systems are considered here. The zeroth-order energy levels and couplings for the first system studied are depicted schematically in Fig. 1. The four basis states for this system are separated into two resonant states $|\varphi_1\rangle$ and $|\varphi_2\rangle$ and two off-resonant states $|\varphi_3\rangle$ and $|\varphi_4\rangle$. The state $|\varphi_1\rangle$ is taken to be the initially prepared state. This effective two-level model has features in common with the energy transfer dynamics of the local mode states in a model of H_2O.[8,20] In the present model, the relevant matrix elements are given by $\mathrm{H}^R = E_1\mathbf{1}^R, H^O_{ii} = E_1 + \Delta, H^O_{12} = H^O_{21} = V_2$, and $V^{RO}_{ij} = V^{OR}_{ij} = V_1\delta_{ij}$.

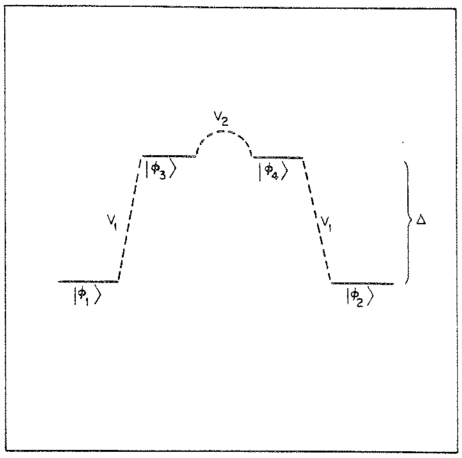

FIG. 1. A schematic diagram of the four-state model system used in Sec. IV. Dotted lines denote the couplings between the zeroth-order states, and $|\varphi_1\rangle$ is the initial state.

By using the formulas for the zeroth- and first-order effective Hamiltonians given in Eqs. (10) and (17), the following analytic result for the time-dependent probability $P_1(t)$ of the initial zeroth-order state is obtained:

$$P_1(t) = |b^R_1(t)|^2 = \cos^2(\Omega_i t/2), \quad (i=0,1), \tag{29}$$

where the zeroth- and first-order effective frequencies Ω_0 and Ω_1 are given, respectively, by

$$\Omega_0 = \left| \frac{2V_1^2 V_2}{\Delta^2 - V_2^2} \right|, \tag{30}$$

$$\Omega_1 = \left| \frac{2(\Delta^2 - V_2^2)\{[(\Delta^2 - V_2^2)^2 + V_1^2(\Delta^2 + V_2^2)]V_1^2 V_2 - 2\Delta^2 V_1^4 V_2\}}{[(\Delta^2 - V_2^2)^2 + V_1^2(\Delta^2 + V_2^2)]^2 - 4\Delta^2 V_1^4 V_2^2} \right|. \tag{31}$$

An analogous analytical formula for the second-order effective frequency Ω_2 can be obtained from Eq. (18), although it is omitted here for brevity. The "exact" frequency[21] which would appear instead of Ω_i in Eq. (29) is denoted below by Ω.

The time evolution of $P_1(t)$ is plotted in Fig. 2 for the exact, zeroth-, and first-order coupled equations. The parameters used in making this plot were $V_1 = -43.9$, $V_2 = -50.6$, $\Delta = 337.7\ \mathrm{cm}^{-1}$. For these parameters, the

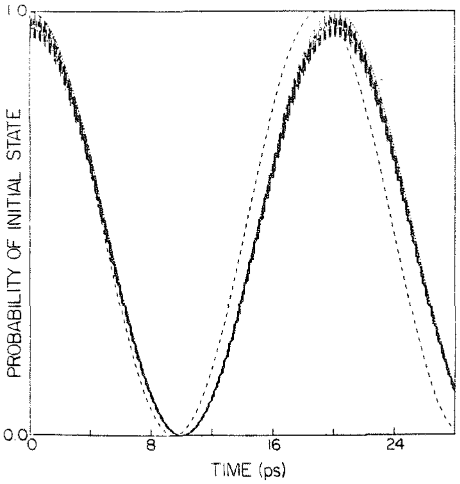

FIG. 2. Initial state probability $P_1(t)$ for the model system shown in Fig. 1, with $\Delta = 337.7$, $V_1 = -43.9$, and $V_2 = -50.6\ \text{cm}^{-1}$. The exact results are given by the solid line, the zeroth-order results by the long dashed line, and the first-order results by the short dashed line.

TABLE I. Eigenvalues for the resonant subspace in the four-state model system.

Δ^a	Exact	Second	First	Zeroth
337.7	− 6.562 66	− 6.562 74	− 6.559 32	− 6.712 68
	− 4.901 33	− 4.901 34	− 4.900 56	− 4.963 20
150.0	− 16.612 14	− 16.667 92	− 16.223 89	− 19.388 43
	− 9.186 53	− 9.187 33	− 9.168 14	− 9.607 23

[a] The other parameters in the four-state model were $V_1 = -43.9$ and $V_2 = -50.6\ \text{cm}^{-1}$. All units are in cm^{-1}.

values of Ω_0, Δ_1, and Ω_2 were calculated to be 1.7495, 1.6588, and 1.6614 cm^{-1}, respectively, while the result for Ω is 1.6613 cm^{-1}. In Fig. 3, the initial state probability $P_1(t)$ is plotted once again, but now for the exact, zeroth-, and second-order coupled equations, and with the zeroth-order detuning Δ decreased to 150 cm^{-1}. In this case, the values of Ω_0, Ω_1, and Ω_2 were calculated to be 9.781, 7.056, and 7.481 cm^{-1}, respectively, while the result for Ω is 7.426 cm^{-1}. In Table I, the resonant subspace eigenvalues for the above two sets of parameters, as calculated from the exact, zeroth-, first-, and second-order effective Hamiltonians, are given.

The second model system considered consists of 55 basis states, with the resonant subspace having 10 states and the off-resonant subspace having 45 states. The initial state energy H^R_{11} was arbitrarily set equal to zero and all the other diagonal elements of $\mathbf{H}^R$ were chosen to have random values between $\pm 10\ \text{cm}^{-1}$. The diagonal elements of $\mathbf{H}^O$ were chosen randomly within the limits $-55 < \mathbf{H}^O_{ii} \leqslant -10\ \text{cm}^{-1}$ and $10 \leqslant \mathbf{H}^O_{ii} < 55\ \text{cm}^{-1}$. The off-diagonal elements of $\mathbf{H}^R$, $\mathbf{H}^O$, and all the elements of $\mathbf{V}^{RO}$ and $\mathbf{V}^{OR}$ were chosen randomly to be between $\pm 2\ \text{cm}^{-1}$. These matrices were made to be Hermitian. The initial state probability $P_1(t)$ as calculated by the exact, zeroth-, and first-order coupled equations is plotted in Fig. 4 for this system. In Table II, the eigenvalues for the resonant subspace, as calculated from the exact Hamiltonian, and the zeroth- and first-order effective Hamiltonians, are given.

The probabilities in Figs. 2–4 obtained by integration of the effective coupled equations are seen to remain somewhat above the peaks and valleys of the exact probability curves. It is perhaps desirable to have the effective probability curves follow the "average" of the exact curves. For this purpose, a correction factor f_R, derived in Appendix B, may be used. This factor takes into account the small fraction of probability remaining, on the average, in the off-resonant states (cf. Appendix B) and is given by

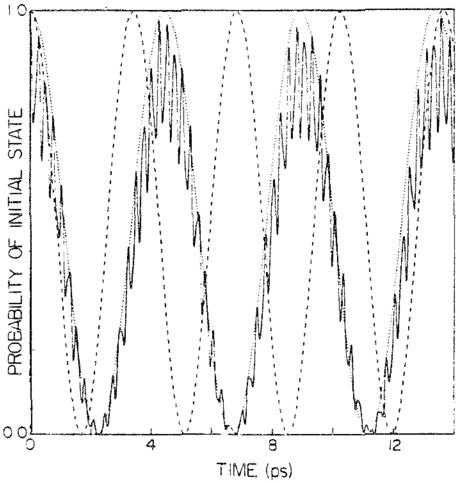

FIG. 3. Initial state probability $P_1(t)$ for the model system shown in Fig. 1, with $\Delta = 150.0$, $V_1 = -43.9$, and $V_2 = 50.6\ \text{cm}^{-1}$. The exact results are given by the solid line, the zeroth-order results by the long dashed line, and the second-order results by the short dashed line.

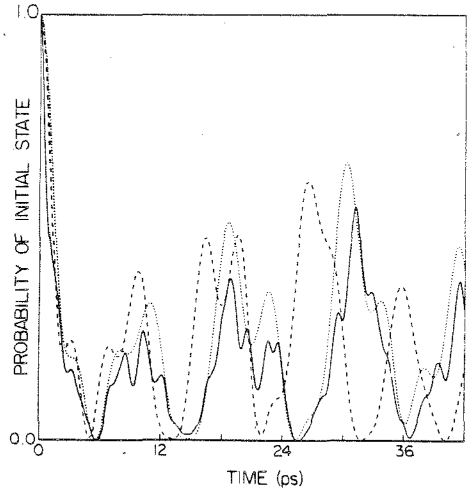

FIG. 4. Initial state probability $P_1(t)$ for the second model system discussed in Sec. IV of the text. The exact results are given by the solid line, the zeroth-order results by the long dashed line, and the first-order results by the short dashed line.

TABLE II. Eigenvalues for the resonant subspace in the 55-state model system.[a]

Exact	First	Zeroth
− 7.8342	− 8.1506	− 9.1006
− 3.4768	− 3.5308	− 4.1809
− 2.6149	− 2.6338	− 2.9832
− 1.3356	− 1.3344	− 1.5533
0.6269	0.6268	0.7097
1.1780	1.1811	1.3642
4.5006	4.3520	5.3627
5.9862	6.1315	6.8652
6.1681	6.2137	7.3159
7.6073	7.7074	8.5667

[a] All units are cm^{-1}.

$$f_R = 1 - \frac{1}{N_R} \sum_{i=1}^{N_R} M_{ii}\,, \tag{32}$$

where the matrix $\mathbf{M}$ is

$$\mathbf{M} = \mathbf{V}^{RO}(\langle H \rangle \mathbf{1}^{O} - \mathbf{H}^{O})^{-2}\mathbf{V}^{OR}\,. \tag{33}$$

In Figs. 5 and 6, all the initial state probabilities from Figs. 3 and 4 are plotted, but the approximate ones are now multiplied by the overall correction factor f_R.

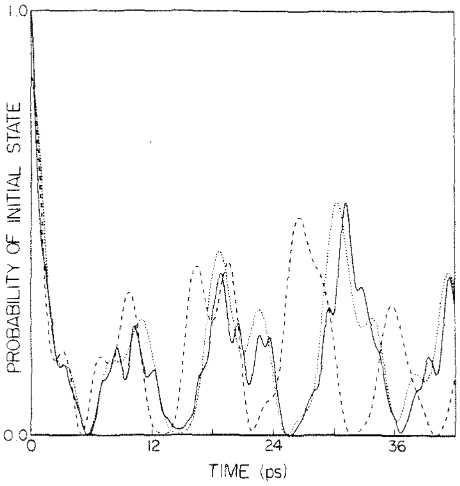

FIG. 6. Corrected initial state probability $P_1(t) \times f_R$ for the second model system discussed in Sec. IV of the text. The exact results (with no correction factor) are given by the solid line, the zeroth-order results by the long dashed line, and the first-order results by the short dashed line.

V. DISCUSSION

From the results shown in Figs. 2–6, it is clear that by using such higher-order effective Hamiltonians one can obtain more accurate approximations to the dynamics than by just using the zeroth-order one. In addition, the results shown in Fig. 3 indicate that, even in the case of an interaction with the off-resonant states which is fairly large relative to the splitting between the resonant and off-resonant subspaces, the approximate resonant state dynamics obtained from a higher-order effective Hamiltonian may still be able to reproduce the most important trends in the dynamics. However, in each case it is also apparent that the zeroth-order approximation gives a reasonably good description of the correct average behavior, apart from a shift in the oscillation frequency. As mentioned before, this situation is necessary for the higher-order effective coupled equations to be accurate. In addition, Figs. 5 and 6 indicate that the correction factor f_R [Eq. (32)] is indeed useful for obtaining better average dynamics.

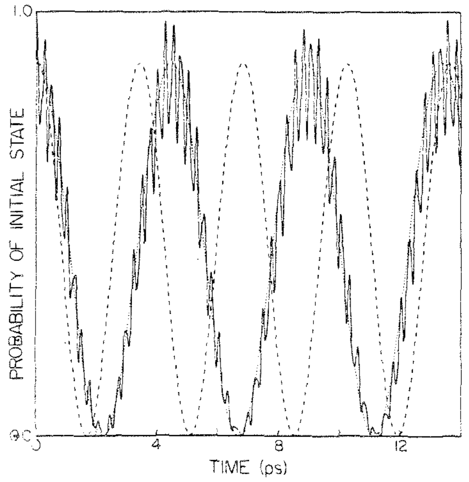

FIG. 5. "Corrected" initial state probability $P_1(t) \times f_R$ for the model system shown in Fig. 1, with $\Delta = 150.0$, $V_1 = -43.9$, and $V_2 = -50.6\ \text{cm}^{-1}$. The exact results (with no correction factor) are given by the solid line, the zeroth-order results by the long dashed line, and the second-order results by the short dashed line.

An inspection of the results given in Table I shows that the eigenvalues in the effective two-level model become more accurate with successive steps in the iteration procedure. From the results given in Table II for the second model system, one can again see that the eigenvalues which are obtained from the first-order effective Hamiltonian are more accurate than those obtained from the zeroth-order effective Hamiltonian, with the ones closest to the initial state energy $\langle H \rangle$ $(= H^{R}_{11} = 0)$ being the most accurately determined. In addition, calculations for this and other model systems have shown that more accurate dynamics and eigenvalues may also be obtained by increasing the dimension of the resonant subspace relative to the dimension of the off-resonant subspace. This result illustrates the potential power of a combined partitioning and iterative formalism.

It is also noted here that although the zeroth-order effective Hamiltonian is Hermitian, since $\mathbf{H}$ is Hermitian, the nth-order effective Hamiltonian is not in general Hermitian. If desirable, this situation can be remedied in various ways. For example, a Hermitian effective Hamiltonian may be obtained by defining it to be $(\mathbf{H}^{R}_{\text{eff},n} + \mathbf{H}^{R\dagger}_{\text{eff},n})/2$. This simple symmetrization of the effective Hamiltonian has been used in nuclear physics applications,[19] but was found in those applications and in the present dynamical calculations to have a negligible effect. Other alternatives in this regard include transformations which make the initial non-Hermitian effective Hamiltonian Hermitian.[14,15,19]

VI. CONCLUDING REMARKS

An iterative procedure for obtaining increasingly accurate effective coupled equations has been presented in the present paper. This procedure extends the adiabatic approximation developed by Voth and Marcus[8] and is related to several effective Hamiltonian techniques[10–12,14–16,18,19] used predominantly in the nuclear physics literature. A general prescription for obtaining the effective coupled equations, and hence an effective Hamiltonian, has been formulated. This prescription may be used to calculate the dynamics of a subset of resonant/strongly coupled states (relative to the initially prepared state). The model calculations performed to test the accuracy of the iterative procedure indeed yielded very encouraging results.

The results presented in this paper suggest the following possibilities for use of the higher-order effective coupled equations in intramolecular dynamics calculations: (1) as a test for the usefulness/accuracy of the zeroth-order adiabatically reduced coupled equations approach,[8] (2) as a means for obtaining more accurate dynamics in any given application of the zeroth-order coupled equations, and (3) as a means to obtain the approximate intramolecular dynamics in a situation where, due to computational limitations, one cannot obtain convergence of the zeroth-order dynamics by simply increasing the dimension of the resonant subspace. It is planned to give specific applications of the present theory in later publications.

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APPENDIX A: EQUIVALENCE OF EQ. (12) TO EQ. (26)

It is given that $\mathbf{H}_0 = \mathbf{H}^R_{\text{eff},0}$, and so using the method of induction, the equality of the two effective Hamiltonians $\mathbf{H}^R_{\text{eff},n}$ and $\mathbf{H}_n$ [Eqs. (12) and (26), respectively] may be established by assuming that $\mathbf{H}^R_{\text{eff},n} = \mathbf{H}_n$ and then showing that $\mathbf{H}^R_{\text{eff},n+1} = \mathbf{H}_{n+1}$.

Equation (12), with n replaced by $n+1$ and setting $\mathbf{H}^R_{\text{eff},n} = \mathbf{H}_n$, yields

$$\begin{aligned}\mathbf{H}^R_{\text{eff},n+1} &= [\mathbf{1}^R + \mathbf{F}^{-1}(\mathbf{H}_n + \langle H\rangle\mathbf{1}^R - \mathbf{H}^R)]^{-1}\mathbf{F}^{-1}\mathbf{F}\mathbf{V}_0\\ &= [\mathbf{F} + \mathbf{H}_n + \langle H\rangle\mathbf{1}^R - \mathbf{H}^R]^{-1}\mathbf{F}\mathbf{V}_0, \qquad (\text{A1})\end{aligned}$$

recalling Eq. (16) for $\mathbf{V}_0$. There is also the identity,

$$\begin{aligned}\mathbf{H}_n &= \mathbf{V}_0 - (\mathbf{V}_0\mathbf{H}_n^{-1} - \mathbf{1}^R)\mathbf{H}_n\\ &= \mathbf{V}_0 - [(\mathbf{H}_n\mathbf{V}_0^{-1})^{-1} - \mathbf{1}^R]\mathbf{H}_n. \qquad (\text{A2})\end{aligned}$$

Introducing the expression for $\mathbf{H}_n$, given by Eq. (26), into the first $\mathbf{H}_n$ term on the right-hand side of Eq. (A2) yields

$$\begin{aligned}\mathbf{H}_n &= \mathbf{V}_0 - \left[\mathbf{V}_1 - \sum_{m=2}^{n}(-)^m\mathbf{V}_m \prod_{k=n-m+2}^{n}\mathbf{H}_{k-1}\right]\mathbf{H}_n\\ &= \mathbf{V}_0 - \sum_{m=2}^{n+1}(-)^m\mathbf{V}_{m-1}\prod_{k=n-m+3}^{n+1}\mathbf{H}_{k-1}, \qquad (\text{A3})\end{aligned}$$

upon using Eq. (16). Substituting this expression for $\mathbf{H}_n$ into Eq. (A1) yields

$$\begin{aligned}\mathbf{H}^R_{\text{eff},n+1} &= \Big[\mathbf{F} + \mathbf{V}_0 + \langle H\rangle\mathbf{1}^R - \mathbf{H}^R\\ &\quad - \sum_{m=2}^{n+1}(-)^m\mathbf{V}_{m-1}\prod_{k=n-m+3}^{n+1}\mathbf{H}_{k-1}\Big]^{-1}\mathbf{F}\mathbf{V}_0. \qquad (\text{A4})\end{aligned}$$

Observing that

$$\mathbf{F}\mathbf{V}_1 = \mathbf{V}_0 + \langle H\rangle\mathbf{1}^R - \mathbf{H}^R \qquad (\text{A5})$$

and

$$\mathbf{F}\mathbf{V}_m = \mathbf{V}_{m-1}, \quad (m\geqslant 2), \qquad (\text{A6})$$

one sees that Eq. (A4) may be rewritten as

$$\begin{aligned}\mathbf{H}^R_{\text{eff},n+1} &= \left\{\mathbf{F}\left[\mathbf{1}^R + \mathbf{V}_1 - \sum_{m=2}^{n+1}(-)^m\mathbf{V}_m \times \prod_{k=n-m+3}^{n+1}\mathbf{H}_{k-1}\right]\right\}^{-1}\mathbf{F}\mathbf{V}_0\\ &= \mathbf{H}_{n+1}\mathbf{V}_0^{-1}\mathbf{F}^{-1}\mathbf{F}\mathbf{V}_0\\ &= \mathbf{H}_{n+1}, \qquad (\text{A7})\end{aligned}$$

upon using a result for the produce of inverses, and introducing Eq. (26) (for $n+1$ instead of n).

APPENDIX B: DERIVATION OF THE CORRECTION FACTOR f_R

The total probability $\langle\Psi(t)|\Psi(t)\rangle$ of the quantum dynamical system satisfies the condition

$$P_R(t) + P_O(t) = 1, \qquad (\text{B1})$$

where $P_R(t)$ and $P_O(t)$ are the resonant and off-resonant basis state probabilities, respectively (cf. Sec. II A). The latter two quantities may be written in terms of the vectors containing the resonant and off-resonant state amplitudes as

$$P_R(t) = \mathbf{b}^{R\dagger}(t)\mathbf{b}^R(t) \quad \text{and} \quad P_O(t) = \mathbf{b}^{O\dagger}(t)\mathbf{b}^O(t), \qquad (\text{B2})$$

respectively. If the probabilities are now long-time-averaged, the average resonant state probability $\overline{P}_R$ is given from Eq. (B1) as

$$\overline{P}_R = 1 - \overline{P}_O, \qquad (\text{B3})$$

where $\overline{P}_R$ and $\overline{P}_O$ are given by

$$\overline{P}_i = \lim_{\tau\to\infty}\frac{1}{\tau}\int_0^\tau P_i(t)dt, \quad (i = R,O). \qquad (\text{B4})$$

By virtue of Eq. (B2) and the "zeroth-order" adiabatic approximation for the amplitudes $\mathbf{b}^O(t)$ [Eq. (8)], the long-time-averaged off-resonant state probability may be approximated as

$$\begin{aligned}\overline{P}_O \simeq \lim_{\tau\to\infty}\Bigg[&\frac{1}{\tau}\sum_{i=1}^{N_R}M_{ii}\int_0^\tau |b_i^R(t)|^2dt\\ &+ \frac{1}{\tau}\sum_{i=1}^{N_R}\sum_{j\neq i}^{N_R}M_{ij}\int_0^\tau b_i^{R*}(t)b_j^R(t)dt\Bigg], \qquad (\text{B5})\end{aligned}$$

where the matrix $\mathbf{M}$ is given by Eq. (33) of the text, and N_R is the dimension of the resonant subspace (cf. Sec. II A).

This expression could, in principle, be evaluated from an actual dynamical calculation of the vector $\mathbf{b}^R(t)$ using the effective coupled equations [Eqs. (11)–(13)].

It is desirable, however, to obtain simple approximations for the long-time averages of $|b_i^R(t)|^2$ and $b_i^{R*}(t)b_j^R(t)$ and to thereby simplify Eq. (B5). To achieve this goal, the resonant state basis functions $|\varphi_i^R\rangle$ are assumed to be adequately described as a linear combination of the resonant state eigenfunctions $|\psi_n^R\rangle$, i.e., as

$$|\varphi_i^R\rangle \simeq \sum_{n=1}^{N_R} C_{in}|\psi_n^R\rangle. \tag{B6}$$

It is assumed here that the contributions from the off-resonant basis functions $|\varphi_i^O\rangle$ to the resonant eigenfunctions $|\psi_n^R\rangle$ are small. With the further assumption of strong mixing among the resonant basis functions due to the perturbation and their near degeneracy, the magnitude of the expansion coefficients $|C_{in}|$ may be approximated by $1/\sqrt{N_R}$. By virtue of these latter two approximations and the fact that $b_i^R(t) = \langle\varphi_i^R|\Psi(t)\rangle$, the first term in Eq. (B5) becomes

$$\lim_{\tau\to\infty}\frac{1}{\tau}\sum_{i=1}^{N_R} M_{ii}\int_0^\tau |b_i^R(t)|^2 dt \simeq \frac{1}{N_R}\sum_{i=1}^{N_R} M_{ii}. \tag{B7}$$

The second term in Eq. (B5) is assumed to be approximately equal to zero since each $b_i^{R*}(t)b_j^R(t)$ term, with $i\neq j$, is highly oscillatory. With the above approximations for the long-time averages in Eq. (B5), the simple approximate formula for $\bar{P}_O$ is obtained:

$$\bar{P}_O \simeq \frac{1}{N_R}\sum_{i=1}^{N_R} M_{ii}. \tag{B8}$$

If dynamics calculations are performed using the effective coupled equations [Eqs. (11)–(13)] and an initial state probability normalized to unity, the results of Eq. (B3) and (B8) suggest that the calculated resonant state probabilities should be multiplied by the correction factor

$$f_R \equiv 1 - \bar{P}_O, \tag{B9}$$

where $\bar{P}_O$ is given by Eq. (B8). The factor f_R corrects phenomenologically for the small fraction of probability which is present, on the average, in the off-resonant "virtual" states.[8]

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