Adiabatically reduced coupled equations for intramolecular dynamics calculations

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(Received 20 September 1985; accepted 14 November 1985)

"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

[a] Contribution No. 7291.

 0021-9606/86/042254-08$02.10

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 $\{|\varphi_j\rangle\}$ $(j=1,...,n)$ of states nearly resonant (and/or strongly interacting), a linear combination of which constitutes the initial state, and into a set $\{|\varphi_k\rangle\}$ $(k=n+1,...,n+m)$ 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

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

and

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

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, $\langle H\rangle\mathbf{I}^R$ $(\langle H\rangle\mathbf{I}^0)$ is an $n\times n$ $(m\times m)$ diagonal matrix with the elements $\langle H\rangle\delta_{ii'}$, $\mathbf{H}^R$ $(\mathbf{H}^0)$ 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 $\{|\varphi_k\rangle\}$ $(j=1,...,n;\ k=n+1,...,n+m)$. 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

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

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 $(\langle H\rangle\mathbf{I}^0 - \mathbf{H}^0)$ is nonsingular. One thereby obtains

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

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

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

Equation (2.9) is expected to provide an accurate approximation to the true dynamics of the manifold of states $\{|\varphi_j\rangle\}$ $(j=1,...,n)$ 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 $(\langle H\rangle\mathbf{I}^0 - \mathbf{H}^0)^{-1}$ 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 $\{|\varphi_k\rangle\}$ $(k=n+1,...,N)$ had been prediagonalized. In that case, the matrix elements $[(\langle H\rangle\mathbf{I}^0 - \mathbf{H}^0)^{-1}]_{kk'}$ equal $(\langle H\rangle - H_{kk})^{-1}\delta_{kk'}$, and the reduced coupled equations for the $\{|\varphi_j\rangle\}$ states are given by

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

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:

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

where

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

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-reso-

nant 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

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

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

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

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

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]

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

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

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

is then solved for the eigenvalues $\boldsymbol{\lambda}^R_{\rm exact}$. Since the expression for $\mathbf{H}^R_{\rm exact}$ [Eq. (3.4)] involves the matrix $E\mathbf{I}^0$, 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 $\mathbf{H}^R_{\rm exact}$ 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 $E\mathbf{I}^0$ in Eq. (3.4) by the constant matrix $\langle H\rangle\mathbf{I}^0$. 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]

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

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 de-

fined as the level shift operator,[31,33] given by

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

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

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

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

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

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-

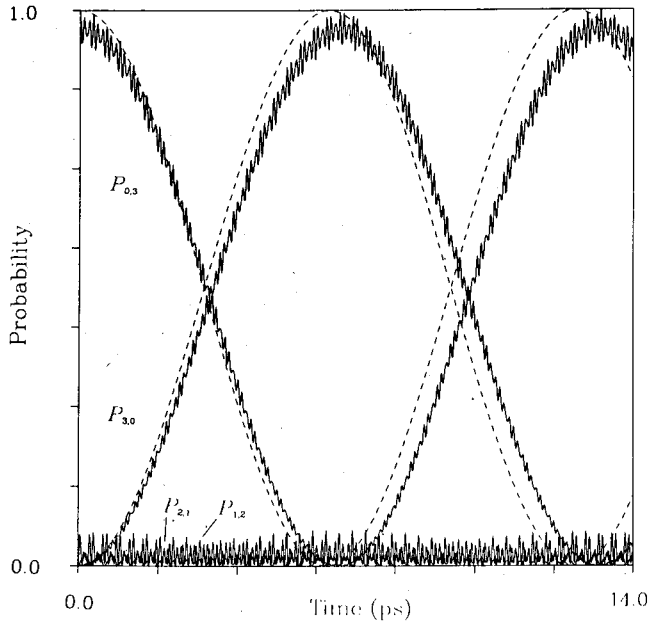

FIG. 1. Local mode probabilities $P_{0,3}$ and $P_{3,0}$ as a function of time for the $|0,3\rangle$ and $|3,0\rangle$ zeroth-order coupled Morse oscillator states, respectively, of Ref. 15. The exact results are given by the solid lines and the approximate results based on Eqs. (4.1) and (4.2) are given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

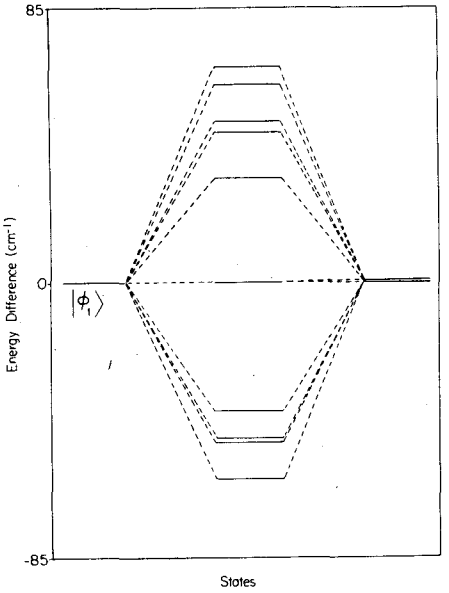

FIG. 2. A schematic of the model system used in Sec. IV B. Dotted lines represent the couplings between the zeroth-order states and $|\varphi_1\rangle$ is the initial state.

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

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

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

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

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]

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

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 **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 **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						
8								24					
9									99				
10										111			
11											114		
12												126	
13													131

[a] **H** is a symmetric matrix.

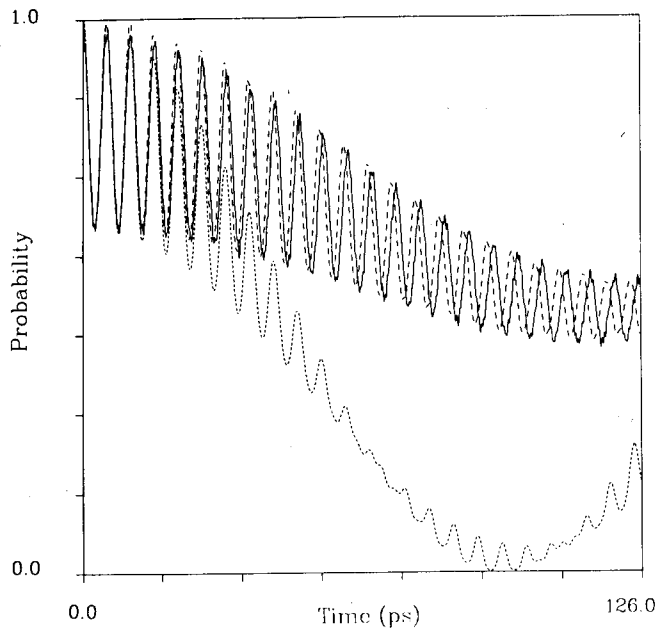

FIG. 3. The $|\varphi_1\rangle$ zeroth-order state probability as a function of time for the model system shown in Fig. 2 and given in Table I. The exact results are given by the solid line, the results obtained using Eq. (2.9) by the dashed line, and the results obtained by integrating the coupled equations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

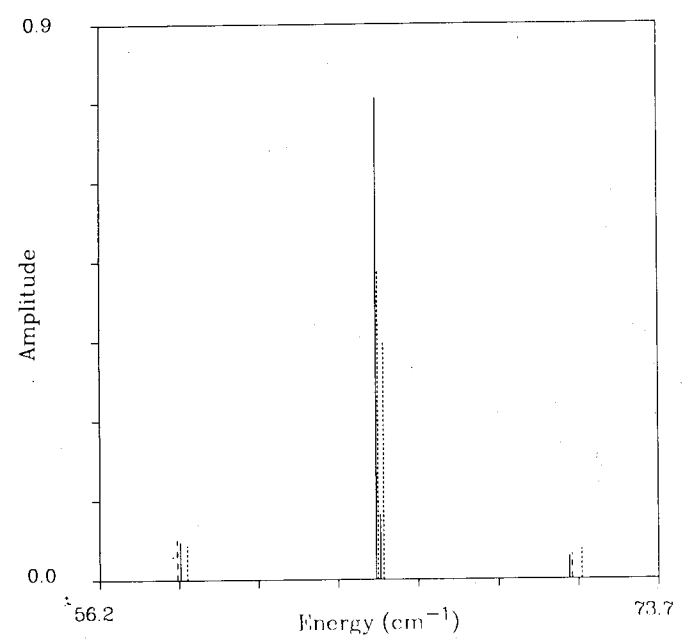

FIG. 4. The Fourier transform spectrum of $b_1(t)$ for the model system of Figs. 2 and 3 and Table I. The labeling of the lines is the same as in Fig. 3. For the two central peaks, the approximate results based on Eq. (2.9) (dashed lines) essentially coincide with the exact results (solid lines) and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

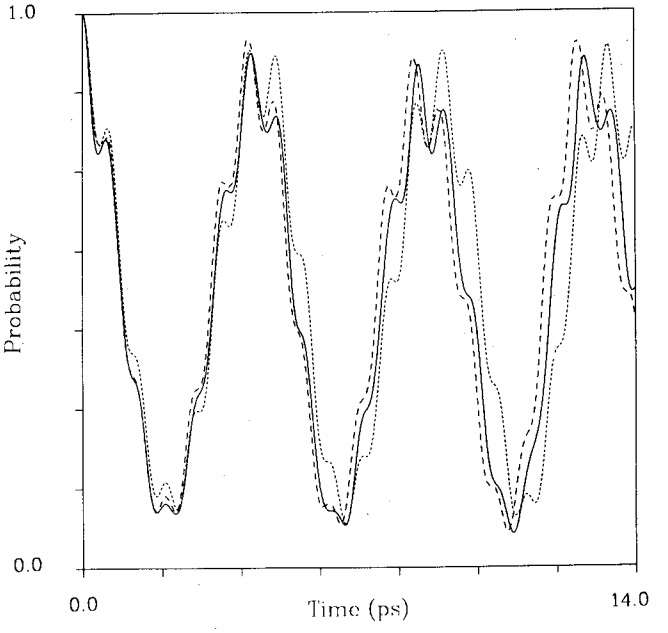

FIG. 5. The $|\varphi_1\rangle$ zeroth-order state probability as a function of time for the model system in Table II. The labeling of the lines is the same as in Fig. 3.

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].

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 \ 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.

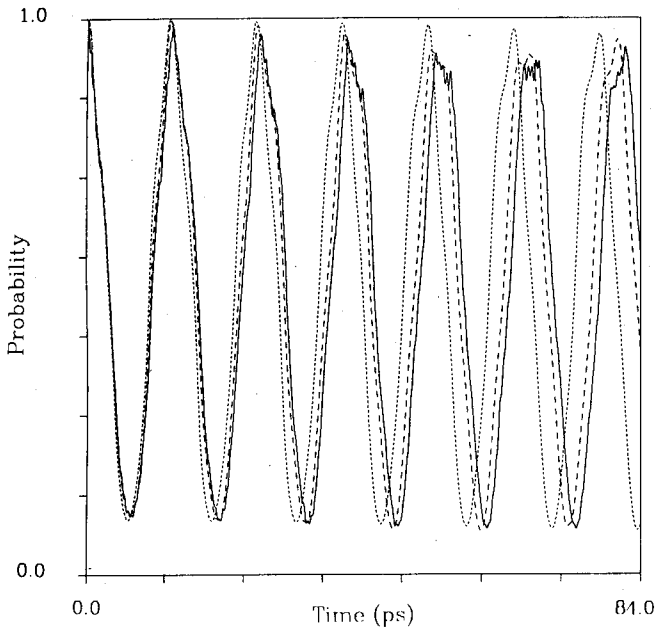

FIG. 6. The $|\varphi_1\rangle$ zeroth-order probability as a function of time for the model system shown in Fig. 2 and given in Table I, except that a diagonal perturbation $V_{11} = 5.0\ \mathrm{cm}^{-1}$ is now added to the Hamiltonian. The exact results are given by the solid line, the results obtained 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]

ACKNOWLEDGMENTS

It is a pleasure to acknowledge the support of this research by the National Science Foundation. GAV would like to thank Dr. S. N. Dixit for several helpful discussions.

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[23]The matrix $\mathbf{H}^0$ is the matrix representation of the total Hamiltonian operator H in the off-resonant manifold $\{|\varphi_k\rangle\}$ of the basis states and is not to be confused with the zeroth-order Hamiltonian matrix $\mathbf{H}_0$.
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[39]The authors of Refs. 15 and 16 assume an approximate time-dependent solution for the local mode probability of the form (in their notation) $\cos^2(\Delta t/2\hbar)$, where Δ is the splitting between the symmetric and asymmetric local mode *eigenstates*. Their exact and approximate values for Δ (our Ω) are given in the text.
[40]S. M. Lederman, G. A. Voth, V. Lopez, and R. A. Marcus (to be submitted).