

# 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,<sup>a)</sup> Pasadena, California 91125

(Received 20 June 1986; accepted 22 July 1986)

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,<sup>1</sup> vibrational,<sup>2</sup> and rovibrational<sup>3</sup> 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,<sup>4</sup> 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<sup>5</sup> 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,<sup>6</sup> as well as Chang and Wyatt,<sup>7</sup> 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<sup>8</sup> have developed an approximate dynamical approach which is based on a partitioning<sup>8,9</sup> 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.<sup>8</sup> 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.<sup>8</sup> 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.<sup>10</sup> The relationship of the present effective Hamiltonian to that given by Lee and Suzuki<sup>11</sup> and to the partitioning formalism of Löwdin<sup>12</sup> 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<sup>8,13</sup>

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

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  $\{|\varphi_i\rangle\}$

<sup>a)</sup> Contribution No. 7434.

basis, the following coupled first-order differential equations for the amplitudes  $b_i(t)$  are obtained:

$$\frac{db_j(t)}{dt} = i\langle H \rangle b_j(t) - i \sum_{i=1}^N H_{ji} b_i(t), \quad (2)$$

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<sup>8</sup>

$$\frac{d}{dt} \mathbf{b}^R(t) = i(\langle H \rangle \mathbf{1}^R - \mathbf{H}^R) \mathbf{b}^R(t) - i \mathbf{V}^{RO} \mathbf{b}^O(t), \quad (3)$$

$$\frac{d}{dt} \mathbf{b}^O(t) = i(\langle H \rangle \mathbf{1}^O - \mathbf{H}^O) \mathbf{b}^O(t) - i \mathbf{V}^{OR} \mathbf{b}^R(t). \quad (4)$$

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.<sup>8</sup> 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

$$\mathbf{V}^{RO} \mathbf{b}^O(t) = i \frac{d}{dt} \mathbf{b}^R(t) + (\langle H \rangle \mathbf{1}^R - \mathbf{H}^R) \mathbf{b}^R(t) \quad (5)$$

and Eq. (4) can also be rearranged to give

$$\mathbf{b}^O(t) = -i(\langle H \rangle \mathbf{1}^O - \mathbf{H}^O)^{-1} \frac{d}{dt} \mathbf{b}^O(t) + (\langle H \rangle \mathbf{1}^O - \mathbf{H}^O)^{-1} \mathbf{V}^{OR} \mathbf{b}^R(t). \quad (6)$$

As a mentioned before, the zeroth-order adiabatic approximation used in Ref. 8 was

$$\frac{d}{dt} \mathbf{b}^O(t) \simeq 0, \quad (7)$$

which, when substituted into Eq. (6), yields

$$\mathbf{b}^O(t) \simeq (\langle H \rangle \mathbf{1}^O - \mathbf{H}^O)^{-1} \mathbf{V}^{OR} \mathbf{b}^R(t). \quad (8)$$

Substitution of this expression for  $\mathbf{b}^O(t)$  into Eq. (3) gives

$$\frac{d}{dt} \mathbf{b}^R(t) \simeq -i \mathbf{H}_{\text{eff},0}^R \mathbf{b}^R(t), \quad (9)$$

where the zeroth-order effective Hamiltonian is given by

$$\mathbf{H}_{\text{eff},0}^R = \mathbf{H}^R - \langle H \rangle \mathbf{1}^R + \mathbf{V}^{RO} (\langle H \rangle \mathbf{1}^O - \mathbf{H}^O)^{-1} \mathbf{V}^{OR}. \quad (10)$$

An iterative formula for the general  $n$ th-order effective Hamiltonian,  $\mathbf{H}_{\text{eff},n}^R$ , may be derived as shown below, for which the corresponding coupled equations are given by

$$\frac{d}{dt} \mathbf{b}^R(t) \simeq -i \mathbf{H}_{\text{eff},n}^R \mathbf{b}^R(t), \quad (11)$$

where

$$\mathbf{H}_{\text{eff},n}^R = [\mathbf{1}^R + \mathbf{F}^{-1} (\mathbf{H}_{\text{eff},n-1}^R + \langle H \rangle \mathbf{1}^R - \mathbf{H}^R)]^{-1} \mathbf{H}_{\text{eff},0}^R \quad (12)$$

and

$$\mathbf{F}^{-1} = \mathbf{V}^{RO} (\langle H \rangle \mathbf{1}^O - \mathbf{H}^O)^{-1} (\mathbf{V}^{RO})^{-1}. \quad (13)$$

Equations (11)–(13) constitute the central result of the present paper.

To derive Eqs. (11)–(13), Eq. (5) is first rewritten as

$$\mathbf{b}^O(t) \simeq (\mathbf{V}^{RO})^{-1} (\mathbf{H}_{\text{eff},n-1}^R + \langle H \rangle \mathbf{1}^R - \mathbf{H}^R) \mathbf{b}^R(t), \quad (14)$$

where  $(\mathbf{V}^{RO})^{-1}$  is a “left” inverse, and  $i d\mathbf{b}^R(t)/dt$  in Eq. (5) has been taken to be equal to  $\mathbf{H}_{\text{eff},n-1}^R \mathbf{b}^R(t)$  (i.e., it is taken from the previous iteration). For example, the first-order approximation to  $\mathbf{b}^O(t)$  is obtained by replacing  $i d\mathbf{b}^R(t)/dt$  in Eq. (5) by  $\mathbf{H}_{\text{eff},0}^R \mathbf{b}^R(t)$ . 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

$$\begin{aligned} \mathbf{b}^O(t) \simeq & -i(\langle H \rangle \mathbf{1}^O - \mathbf{H}^O)^{-1} (\mathbf{V}^{RO})^{-1} (\mathbf{H}_{\text{eff},n-1}^R \\ & + \langle H \rangle \mathbf{1}^R - \mathbf{H}^R) \frac{d}{dt} \mathbf{b}^R(t) \\ & + (\langle H \rangle \mathbf{1}^O - \mathbf{H}^O)^{-1} \mathbf{V}^{OR} \mathbf{b}^R(t). \end{aligned} \quad (15)$$

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  $n$ th-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.<sup>8</sup>) 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  $(\langle H \rangle \mathbf{1}^O - \mathbf{H}^O)$ .<sup>8</sup>

The following notation is introduced here to simplify the expressions for the effective Hamiltonians:

$$\mathbf{V}_0 = \mathbf{H}_{\text{eff},0}^R,$$

$$\mathbf{V}_i = \mathbf{V}^{RO}(\langle H \rangle \mathbf{1}^O - \mathbf{H}^O)^{-(i+1)} \mathbf{V}^{OR}, \quad i \geq 1. \quad (16)$$

For example, the first-order effective Hamiltonian is now given by

$$\begin{aligned} \mathbf{H}_{\text{eff},1}^R &= [\mathbf{1}^R + \mathbf{V}^{RO}(\langle H \rangle \mathbf{1}^O - \mathbf{H}^O)^{-2} \mathbf{V}^{OR}]^{-1} \mathbf{H}_{\text{eff},0}^R \\ &= (\mathbf{1}^R + \mathbf{V}_1)^{-1} \mathbf{V}_0, \end{aligned} \quad (17)$$

and the second-order effective Hamiltonian by

$$\mathbf{H}_{\text{eff},2}^R = [\mathbf{1}^R + \mathbf{V}_1 - \mathbf{V}_2 (\mathbf{1}^R + \mathbf{V}_1)^{-1} \mathbf{V}_0]^{-1} \mathbf{V}_0. \quad (18)$$

### 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  $E$ ):

$$\begin{aligned} (\langle H \rangle \mathbf{1}^O - \mathbf{H}^O)^{-1} &= (\langle H \rangle \mathbf{1}^O - E^O)^{-1} \\ &\times \sum_{n=0}^{\infty} [\mathbf{V}^O(\langle H \rangle \mathbf{1}^O - E^O)^{-1}]^n, \end{aligned} \quad (19)$$

where the matrix  $\mathbf{H}^O$  has been separated into  $E^O + \mathbf{V}^O$ , with  $E^O$  containing the diagonal elements of  $\mathbf{H}^O$  and  $\mathbf{V}^O$  containing the off-diagonal elements of  $\mathbf{H}^O$ . Since the matrix  $(\langle H \rangle \mathbf{1}^O - E^O)$  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  $\mathbf{H}_{\text{eff},2}^R$  in powers of  $\mathbf{V}_i$  is given by

$$\mathbf{H}_{\text{eff},2}^R = \sum_{m=0}^{\infty} \left[ \mathbf{V}_2 \sum_{n=0}^{\infty} (-\mathbf{V}_1)^n \mathbf{V}_0 - \mathbf{V}_1 \right]^m \mathbf{V}_0. \quad (20)$$

With the further definition of

$$\mathbf{V}'_i = [\mathbf{1}^R + \mathbf{V}_1]^{-1} \mathbf{V}_i, \quad i \geq 0, \quad (21)$$

the second-order effective Hamiltonian may be rewritten as

$$\mathbf{H}_{\text{eff},2}^R = (\mathbf{1}^R - \mathbf{V}'_2 \mathbf{V}'_0)^{-1} \mathbf{V}'_0. \quad (22)$$

A final series expansion which may prove useful is one in powers of  $\mathbf{V}'_i$  (see, e.g., Ref. 10), which for  $\mathbf{H}_{\text{eff},2}^R$  is given by

$$\mathbf{H}_{\text{eff},2}^R = \sum_{n=0}^{\infty} (\mathbf{V}'_2 \mathbf{V}'_0)^n \mathbf{V}'_0. \quad (23)$$

### 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<sup>10-12,14-16</sup> for determining eigenvalues using effective Hamiltonians is discussed next. For the purpose of comparison, the preceding dynamical analysis of Sec. II B may be viewed as a complementary way of determining an effective Hamiltonian, although the focus of the present pa-

per 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,<sup>14,15</sup> given in the present notation<sup>17</sup> by

$$\begin{aligned} \mathbf{H}_{\text{eff}}^R &= \mathbf{H}^R - \lambda \mathbf{1}^R + \sum_{n=0}^{\infty} \frac{d^n}{(dE)^n} \mathbf{V}^{RO} (E \mathbf{1}^O - \mathbf{H}^O)^{-1} \\ &\times \mathbf{V}^{OR} \Big|_{E=\lambda} \frac{1}{n!} (\mathbf{H}_{\text{eff}}^R)^n. \end{aligned} \quad (24)$$

In this equation, the quantity  $\lambda$  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  $\lambda$  is nontrivial.<sup>17</sup> 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<sup>10-12,14-16</sup> can also be shown, noting that we have replaced their  $\lambda$  by our  $\langle H \rangle$ .

Schucan and Weidenmüller<sup>10</sup> (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<sup>17</sup>:

$$\mathbf{H}_{\text{eff}}^R = [\mathbf{1}^R + \mathbf{F}^{-1}(\mathbf{H}_{\text{eff}}^R + \lambda \mathbf{1}^R - \mathbf{H}^R)]^{-1} \mathbf{V}_0, \quad (25)$$

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  $\lambda$  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<sup>10</sup> to the implicit equation for  $\mathbf{H}_{\text{eff}}^R$  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  $n$ th-order effective Hamiltonian shows that  $\mathbf{H}_{\text{eff},n}^R$  is just the  $n$ th 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  $n$ th order forms of Eqs. (20) and (23) by making the choice  $\lambda = \langle H \rangle$ . Discussions of the convergence 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<sup>11</sup> 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,<sup>16,17</sup> is given in the present notation [Eq. (16)] by

$$\begin{aligned} \mathbf{H}_0 &= \mathbf{V}_0, \\ \mathbf{H}_n &= \left[ \mathbf{1}^R + \mathbf{V}_1 - \sum_{m=2}^n (-)^m \mathbf{V}_m \prod_{k=n-m+2}^n \mathbf{H}_{k-1} \right]^{-1} \mathbf{V}_0, \\ n &\geq 1, \end{aligned} \quad (26)$$

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  $\lambda$ . In Appendix A, it is shown that the present  $\mathbf{H}_{\text{eff},n}^R$  is equivalent to the  $n$ th-order effective Hamiltonian  $\mathbf{H}_n$  of Lee and Suzuki,<sup>11</sup> 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.<sup>12</sup> The exact partitioned Hamiltonian is given in the present notation by<sup>8</sup>

$$\mathbf{H}_{\text{exact}}^R = \mathbf{H}^R + \mathbf{V}^{RO}(E\mathbf{1}^O - \mathbf{H}^O)^{-1}\mathbf{V}^{OR}, \quad (27)$$

where the constant factor  $-\langle H \rangle \mathbf{1}^R$  has been omitted. The eigenvalues are then determined by solving the secular equation

$$\det |\mathbf{H}_{\text{exact}}^R - E\mathbf{1}^R| = 0, \quad (28)$$

which, due to the dependence of  $\mathbf{H}_{\text{exact}}^R$  on  $E$ , may require the use of a root search technique such as the Newton–Raphson method.<sup>12</sup>

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 equa-

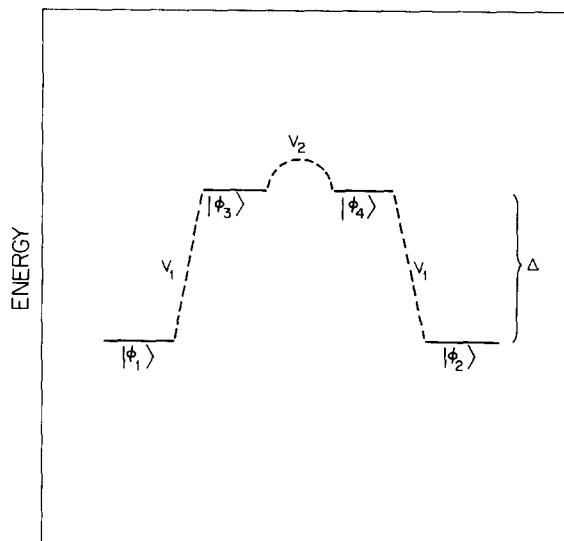


FIG. 1. A schematic diagram of the four-state model system used in Sec. IV. Dotted lines denote the couplings between the zeroth-order states, and  $|\varphi_1\rangle$  is the initial state.

tions, 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  $\text{H}_2\text{O}$ .<sup>8,20</sup> In the present model, the relevant matrix elements are given by  $\mathbf{H}^R = E_1\mathbf{1}^R$ ,  $H_{ii}^O = E_i + \Delta$ ,  $H_{12}^O = H_{21}^O = V_2$ , and  $V_{ij}^{RO} = V_{ij}^{OR} = V_1\delta_{ij}$ .

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:

$$P_1(t) = |b_1^R(t)|^2 = \cos^2(\Omega_1 t/2), \quad (i=0,1), \quad (29)$$

where the zeroth- and first-order effective frequencies  $\Omega_0$  and  $\Omega_1$  are given, respectively, by

$$\Omega_0 = \left| \frac{2V_1^2 V_2}{\Delta^2 - V_2^2} \right|, \quad (30)$$

$$\Omega_1 = \left| \frac{2(\Delta^2 - V_2^2)\{[(\Delta^2 - V_2^2)^2 + V_1^2(\Delta^2 + V_2^2)]V_1^2 V_2 - 2\Delta^2 V_1^4 V_2\}}{[(\Delta^2 - V_2^2)^2 + V_1^2(\Delta^2 + V_2^2)]^2 - 4\Delta^2 V_1^4 V_2^2} \right|. \quad (31)$$

An analogous analytical formula for the second-order effective frequency  $\Omega_2$  can be obtained from Eq. (18), although it is omitted here for brevity. The “exact” frequency<sup>21</sup> which would appear instead of  $\Omega_i$  in Eq. (29) is denoted below by  $\Omega$ .

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  $V_1 = -43.9$ ,  $V_2 = -50.6$ ,  $\Delta = 337.7 \text{ cm}^{-1}$ . For these parameters, the

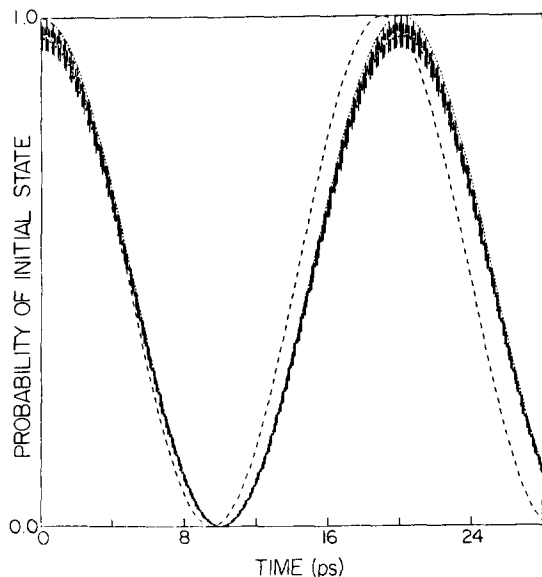


FIG. 2. Initial state probability  $P_1(t)$  for the model system shown in Fig. 1, with  $\Delta = 337.7$ ,  $V_1 = -43.9$ , and  $V_2 = -50.6$   $\text{cm}^{-1}$ . The exact results are given by the solid line, the zeroth-order results by the long dashed line, and the first-order results by the short dashed line.

values of  $\Omega_0$ ,  $\Delta_1$ , and  $\Omega_2$  were calculated to be 1.7495, 1.6588, and 1.6614  $\text{cm}^{-1}$ , respectively, while the result for  $\Omega$  is 1.6613  $\text{cm}^{-1}$ . 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  $\Delta$  decreased to 150  $\text{cm}^{-1}$ . In this case, the values of  $\Omega_0$ ,  $\Omega_1$ , and  $\Omega_2$  were calculated to be 9.781, 7.056, and 7.481  $\text{cm}^{-1}$ , respectively, while the result for  $\Omega$  is 7.426  $\text{cm}^{-1}$ . 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

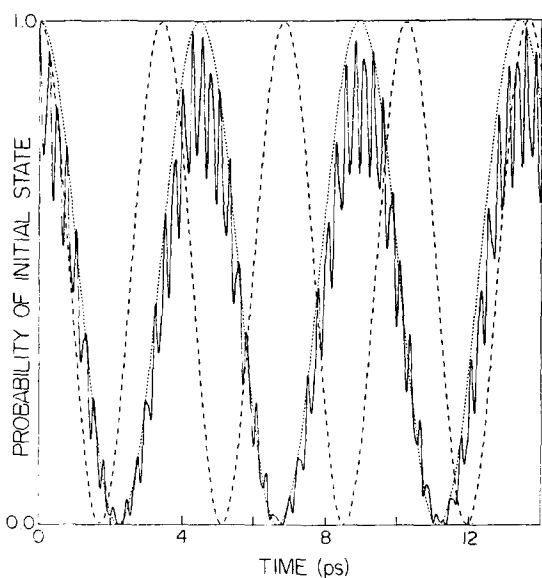


FIG. 3. Initial state probability  $P_1(t)$  for the model system shown in Fig. 1, with  $\Delta = 150.0$ ,  $V_1 = -43.9$ , and  $V_2 = 50.6$   $\text{cm}^{-1}$ . The exact results are given by the solid line, the zeroth-order results by the long dashed line, and the second-order results by the short dashed line.

TABLE I. Eigenvalues for the resonant subspace in the four-state model system.

$\Delta^a$	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

<sup>a</sup>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  $\text{cm}^{-1}$ .

off-resonant subspace having 45 states. The initial state energy  $H_{11}^R$  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  $-55 < H_{ii}^O < -10$   $\text{cm}^{-1}$  and  $10 < H_{ii}^O < 55$   $\text{cm}^{-1}$ . 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

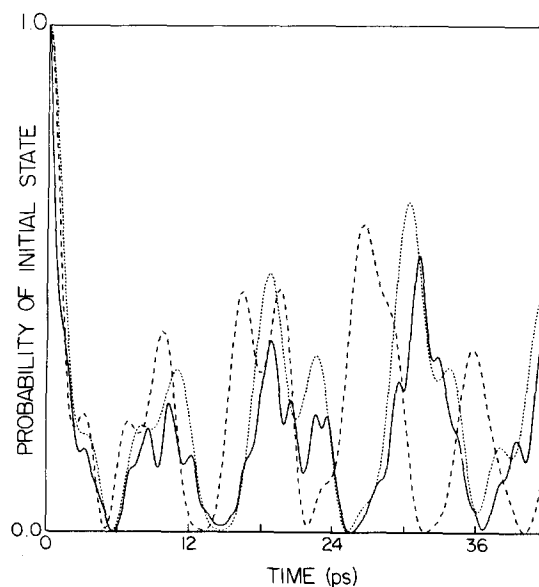


FIG. 4. Initial state probability  $P_1(t)$  for the second model system discussed in Sec. IV of the text. The exact results are given by the solid line, the zeroth-order results by the long dashed line, and the first-order results by the short dashed line.

TABLE II. Eigenvalues for the resonant subspace in the 55-state model system.<sup>a</sup>

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

<sup>a</sup>All units are  $\text{cm}^{-1}$ .

$$f_R = 1 - \frac{1}{N_R} \sum_{i=1}^{N_R} M_{ii}, \quad (32)$$

where the matrix  $\mathbf{M}$  is

$$\mathbf{M} = \mathbf{V}^{RO} (\langle H \rangle \mathbf{1}^O - \mathbf{H}^O)^{-2} \mathbf{V}^{OR}. \quad (33)$$

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  $f_R$ .

## 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

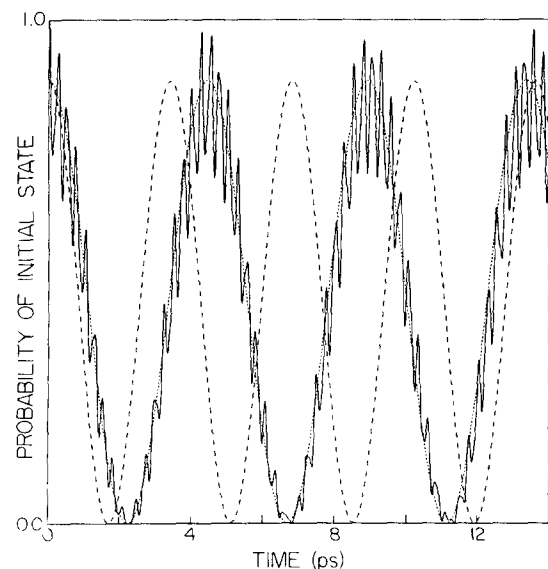


FIG. 5. "Corrected" initial state probability  $P_1(t) \times f_R$  for the model system shown in Fig. 1, with  $\Delta = 150.0$ ,  $V_1 = -43.9$ , and  $V_2 = -50.6 \text{ cm}^{-1}$ . The exact results (with no correction factor) are given by the solid line, the zeroth-order results by the long dashed line, and the second-order results by the short dashed line.

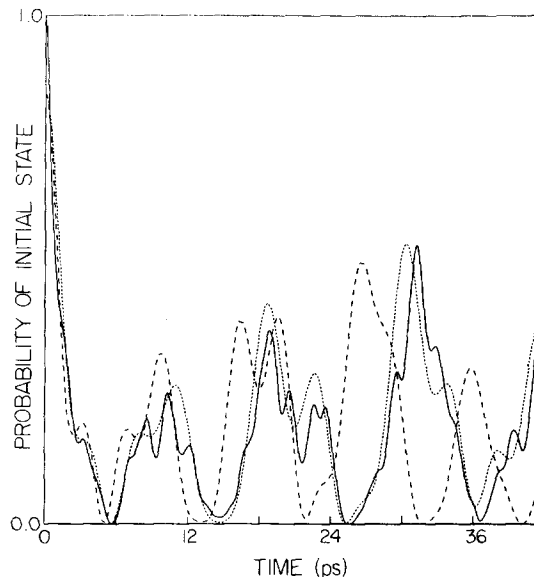


FIG. 6. Corrected initial state probability  $P_1(t) \times f_R$  for the second model system discussed in Sec. IV of the text. The exact results (with no correction factor) are given by the solid line, the zeroth-order results by the long dashed line, and the first-order results by the short dashed line.

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.

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  $\langle H \rangle$  ( $= H_{11}^R = 0$ ) 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  $n$ th-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  $(\mathbf{H}_{\text{eff},n}^R + \mathbf{H}_{\text{eff},n}^{R\dagger})/2$ . This simple symmetrization of the effective Hamiltonian has been used in nuclear physics applications,<sup>19</sup> 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.<sup>14,15,19</sup>

## 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<sup>8</sup> and is related to several effective Hamiltonian techniques<sup>10-12,14-16,18,19</sup> 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,<sup>8</sup> (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.

## ACKNOWLEDGMENTS

It is a pleasure to acknowledge support of this research by the National Science Foundation. SJK gratefully acknowledges the support of a Natural Sciences and Engineering Research Council of Canada Postgraduate Scholarship, 1984-1986.

## APPENDIX A: EQUIVALENCE OF EQ. (12) TO EQ. (26)

It is given that  $\mathbf{H}_0 = \mathbf{H}_{\text{eff},0}^R$ , and so using the method of induction, the equality of the two effective Hamiltonians  $\mathbf{H}_{\text{eff},n}^R$  and  $\mathbf{H}_n$  [Eqs. (12) and (26), respectively] may be established by assuming that  $\mathbf{H}_{\text{eff},n}^R = \mathbf{H}_n$  and then showing that  $\mathbf{H}_{\text{eff},n+1}^R = \mathbf{H}_{n+1}$ .

Equation (12), with  $n$  replaced by  $n+1$  and setting  $\mathbf{H}_{\text{eff},n}^R = \mathbf{H}_n$ , yields

$$\mathbf{H}_{\text{eff},n+1}^R = [\mathbf{1}^R + \mathbf{F}^{-1}(\mathbf{H}_n + \langle H \rangle \mathbf{1}^R - \mathbf{H}^R)]^{-1} \mathbf{F}^{-1} \mathbf{F} \mathbf{V}_0 \\ = [\mathbf{F} + \mathbf{H}_n + \langle H \rangle \mathbf{1}^R - \mathbf{H}^R]^{-1} \mathbf{F} \mathbf{V}_0, \quad (\text{A1})$$

recalling Eq. (16) for  $\mathbf{V}_0$ . There is also the identity,

$$\mathbf{H}_n = \mathbf{V}_0 - (\mathbf{V}_0 \mathbf{H}_n^{-1} - \mathbf{1}^R) \mathbf{H}_n \\ = \mathbf{V}_0 - [(\mathbf{H}_n \mathbf{V}_0^{-1})^{-1} - \mathbf{1}^R] \mathbf{H}_n. \quad (\text{A2})$$

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

$$\mathbf{H}_n = \mathbf{V}_0 - \left[ \mathbf{V}_1 - \sum_{m=2}^n (-)^m \mathbf{V}_m \prod_{k=n-m+2}^n \mathbf{H}_{k-1} \right] \mathbf{H}_n \\ = \mathbf{V}_0 - \sum_{m=2}^{n+1} (-)^m \mathbf{V}_{m-1} \prod_{k=n-m+3}^{n+1} \mathbf{H}_{k-1}, \quad (\text{A3})$$

upon using Eq. (16). Substituting this expression for  $\mathbf{H}_n$  into Eq. (A1) yields

$$\mathbf{H}_{\text{eff},n+1}^R \\ = [\mathbf{F} + \mathbf{V}_0 + \langle H \rangle \mathbf{1}^R - \mathbf{H}^R \\ - \sum_{m=2}^{n+1} (-)^m \mathbf{V}_{m-1} \prod_{k=n-m+3}^{n+1} \mathbf{H}_{k-1}]^{-1} \mathbf{F} \mathbf{V}_0. \quad (\text{A4})$$

Observing that

$$\mathbf{F} \mathbf{V}_1 = \mathbf{V}_0 + \langle H \rangle \mathbf{1}^R - \mathbf{H}^R \quad (\text{A5})$$

and

$$\mathbf{F} \mathbf{V}_m = \mathbf{V}_{m-1}, \quad (m \geq 2), \quad (\text{A6})$$

one sees that Eq. (A4) may be rewritten as

$$\mathbf{H}_{\text{eff},n+1}^R = \left\{ \mathbf{F} \left[ \mathbf{1}^R + \mathbf{V}_1 - \sum_{m=2}^{n+1} (-)^m \mathbf{V}_m \right. \right. \\ \left. \left. \times \prod_{k=n-m+3}^{n+1} \mathbf{H}_{k-1} \right] \right\}^{-1} \mathbf{F} \mathbf{V}_0 \\ = \mathbf{H}_{n+1} \mathbf{V}_0^{-1} \mathbf{F}^{-1} \mathbf{F} \mathbf{V}_0 \\ = \mathbf{H}_{n+1}, \quad (\text{A7})$$

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

$$P_R(t) + P_O(t) = 1, \quad (\text{B1})$$

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

$$P_R(t) = \mathbf{b}^R \dagger(t) \mathbf{b}^R(t) \quad \text{and} \quad P_O(t) = \mathbf{b}^O \dagger(t) \mathbf{b}^O(t), \quad (\text{B2})$$

respectively. If the probabilities are now long-time-averaged, the average resonant state probability  $\bar{P}_R$  is given from Eq. (B1) as

$$\bar{P}_R = 1 - \bar{P}_O, \quad (\text{B3})$$

where  $\bar{P}_R$  and  $\bar{P}_O$  are given by

$$\bar{P}_i = \lim_{\tau \rightarrow \infty} \frac{1}{\tau} \int_0^\tau P_i(t) dt, \quad (i = R, O). \quad (\text{B4})$$

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

$$\bar{P}_O \simeq \lim_{\tau \rightarrow \infty} \left[ \frac{1}{\tau} \sum_{i=1}^{N_R} M_{ii} \int_0^\tau |b_i^R(t)|^2 dt \right. \\ \left. + \frac{1}{\tau} \sum_{i=1}^{N_R} \sum_{j \neq i}^{N_R} M_{ij} \int_0^\tau b_i^{R*}(t) b_j^R(t) dt \right], \quad (\text{B5})$$

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

$$|\varphi_i^R\rangle \simeq \sum_{n=1}^{N_R} C_{in} |\psi_n^R\rangle. \quad (\text{B6})$$

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

$$\lim_{\tau \rightarrow \infty} \frac{1}{\tau} \sum_{i=1}^{N_R} M_{ii} \int_0^\tau |b_i^R(t)|^2 dt \simeq \frac{1}{N_R} \sum_{i=1}^{N_R} M_{ii}. \quad (\text{B7})$$

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:

$$\bar{P}_O \simeq \frac{1}{N_R} \sum_{i=1}^{N_R} M_{ii}. \quad (\text{B8})$$

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

$$f_R \equiv 1 - \bar{P}_O, \quad (\text{B9})$$

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.<sup>8</sup>

<sup>1</sup>For reviews, see K. F. Freed, *Top. Appl. Phys.* **15**, 23 (1976); P. Avouris, W. M. Gelbart, and M. A. El-Sayed, *Chem. Rev.* **77**, 793 (1977); S. Mukamel and J. Jortner, in *Excited States*, edited by E. C. Lim (Academic, New York, 1977), Vol. 3, p. 57; W. Rhodes, *J. Phys. Chem.* **87**, 30 (1983), and references cited therein.

<sup>2</sup>For reviews, see V. E. Bondybey, *Annu. Rev. Phys. Chem.* **35**, 591 (1984); F. F. Crim, *ibid.* **35**, 657 (1984); E. B. Stechel and E. J. Heller, *ibid.* **35**, 563 (1984); R. E. Smalley, *J. Phys. Chem.* **86**, 3504 (1982); M. L. Sage and J. Jortner, *Adv. Chem. Phys.* **47**, 293 (1981); S. A. Rice, *ibid.* **47**, 117 (1981).

<sup>3</sup>See, for example, K. T. Chen, B. E. Forch, and E. C. Lim, *Chem. Phys. Lett.* **99**, 98 (1983); N. L. Garland and E. K. C. Lee, *Faraday Discuss. Chem. Soc.* **75**, 377 (1983); A. Lorincz, D. D. Smith, F. Novak, R. Kosloff, D. J. Tannor, and S. A. Rice, *J. Chem. Phys.* **82**, 1067 (1985); P. M. Felker and A. H. Zewail, *ibid.* **82**, 2994 (1985).

<sup>4</sup>We are concerned here with quantum mechanical approaches and hence will not consider the many useful semiclassical and classical approaches.

<sup>5</sup>A. Nauts and R. E. Wyatt, *Phys. Rev. Lett.* **51**, 2238 (1983); *Phys. Rev. A* **30**, 872 (1984); I. Schek and R. E. Wyatt, *J. Chem. Phys.* **83**, 3028, 4650 (1985); **84**, 4497 (1986); K. F. Milfeld, J. Castillo, and R. E. Wyatt, *ibid.* **83**, 1617 (1985).

<sup>6</sup>J. V. Tietz and S. -I. Chu, *Chem. Phys. Lett.* **101**, 446 (1983).

<sup>7</sup>J. Chang and R. E. Wyatt, *Chem. Phys. Lett.* **121**, 307 (1985).

<sup>8</sup>G. A. Voth and R. A. Marcus, *J. Chem. Phys.* **84**, 2254 (1986).

<sup>9</sup>For a related, but somewhat different, partitioning approach to that given in Ref. 8, see R. A. White, A. Altenberger-Siczek, and J. C. Light, *J. Chem. Phys.* **59**, 200 (1973).

<sup>10</sup>(a) T. H. Schucan and H. A. Weidenmüller, *Ann. Phys.* **73**, 108 (1972); (b) **76**, 483 (1973).

<sup>11</sup>(a) S. Y. Lee and K. Suzuki, *Phys. Lett. B* **91**, 173 (1980); (b) K. Suzuki and S. Y. Lee, *Prog. Theor. Phys.* **64**, 2091 (1980). These authors use the notation  $\mathbf{R}_n$  in place of  $\mathbf{H}_n$ .

<sup>12</sup>P. O. Löwdin, in *Perturbation Theory and Its Applications in Quantum Mechanics*, edited by C. H. Wilcox (Wiley, New York, 1966), p. 255 and references cited therein.

<sup>13</sup>The expansion of the wave function  $|\Psi(t)\rangle$  in Eq. (1) is assumed to be composed of a finite number ( $= N$ ) of basis states. In theory, an infinite number of basis states are required to completely represent most Hamiltonians, but, in practice, the basis set is usually truncated.

<sup>14</sup>J. Des Cloiseaux, *Nucl. Phys.* **20**, 321 (1960).

<sup>15</sup>B. H. Brandow, *Rev. Mod. Phys.* **39**, 771 (1967); in *Lectures in Theoretical Physics*, edited by K. T. Mahanthappa (Gordon and Breach, New York, 1969), Vol. 11; *Ann. Phys.* **57**, 214 (1970).

<sup>16</sup>T. T. S. Kuo, in *Lecture Notes in Physics*, edited by T. T. S. Kuo (Springer, Berlin, 1981), Vol. 144, p. 248.

<sup>17</sup>Note that in this article the resonant subspace is not necessarily degenerate and for this reason the Des Cloiseaux expansion is slightly modified here as discussed in Ref. 10(a). For the case of a degenerate subspace of energy  $E_0$ , the choice  $\lambda = E_0$  is used. Similar remarks apply to most of the expansions of Schucan and Weidenmüller and Lee and Suzuki, as given here. We have adopted the notation and partitioning scheme from Ref. 8.

<sup>18</sup>D. J. Klein, *J. Chem. Phys.* **61**, 786 (1974).

<sup>19</sup>B. H. Brandow, *Int. J. Quantum Chem.* **15**, 207 (1979).

<sup>20</sup>J. S. Hutchinson, E. L. Sibert III, and J. T. Hynes, *J. Chem. Phys.* **81**, 1314 (1984).

<sup>21</sup>The “exact” frequency was determined from the splittings of the resonant state eigenstates (cf. Table I).