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Reduction of the effective manifold of states in models of multiphoton laser-induced dissociation and chemistry

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In the N-level atom (or molecule) model, a set of conditions are developed whereby (i) a band of reaction channels can be approximated by a single reaction channel, and (ii) this single reaction channel can be approximated by a population-loss term. The reactions are restricted to those which remove the system from the laser-excited ladder.

I. INTRODUCTION

There is an increasingly extensive literature[1] on experiments in laser-induced chemistry and dissociation, and several methods[1,2] have been developed for predicting the results of these experiments. One method, commonly referred to as the N-level atom (or molecule) model, considers the energy levels of the molecular system (reactants and products) to be known, and couples these levels by one or more of the following: (i) light tuned to the neighborhood of the resonance frequencies, (ii) intramolecular energy transfer processes connecting levels near resonance, (iii) intermolecular energy transfer processes and/or chemical reactions levels near resonance. Population loss and dephasing terms are added phenomologically.

The usefulness of this model is attested to by the growing list of general formalisms[3] with respect to it, and to its use in both analytical and computational solutions,[4] in the literature. One of the major difficulties in using this model is the large number of levels that are generally involved in real molecular systems. As the number of levels involved is large, one requires exceedingly large core computers (and computer budgets) for the computations. This problem has led us to consider conditions whereby (i) a band of reaction channels can be approximated by a single reaction channel, and (ii) when this resultant channel can be approximated by a population-loss term.

In a previous paper[4(a)] we considered the well-studied[5] two-level model coupled to a dense manifold of states as a simplified model of laser-induced chemistry and dissociation, and developed criteria for the reduction of the effective number of levels in this system. In particular, a laser-driven molecular species A, represented as a two-level system, was taken to react forming finite-level molecular species B. Criteria were developed that, when satisfied, enabled this model to be approximated by a two-level molecular A system reacting to form a single-level molecular species B. Further criteria were then developed which, when satisfied, enabled this model to be approximated by a two-level molecular species A with irreversible population loss.

In this paper we extend this concept to a laser driven N-level molecular species A (reactant), in which each of the levels k can react, producing a finite level B_k (product) molecular species. Both the A and B molecules are also able to be connected to reservoir degrees of freedom. We shall develop criteria whereby the finite-level B_k species can be approximated by a single-level B_k species. Further criteria will be developed whereby these single-level B_k species can be approximated by irreversible population loss out of level k of the A system.

We shall confine ourselves to systems where the reaction eliminates the system from the excitation ladder. Examples of systems satisfying this criteria are those (i) involving radiationless transitions, to an excited electronic state, such as singlet to triplet (as frequently occur in polyatomic molecules, for example, in the aromatic hydrocarbons); (ii) involving collisional dissociation processes; (iii) involving chemical reactions wherein the final molecular species is (are) not the same as the original molecular species; (iv) and those wherein one laser excites a specific vibrational manifold of the system, while a second laser excites a vibrationally excited level to an electronically excited level of the system. Energy transfer mechanisms not satisfying this criteria are those involving nonlaser induced excitations or deexcitations taking place within the laser excited ladder. Examples are energy transfer mechanisms involving intramolecular or intermolecular V-V or V-R processes.

In Sec. II we will derive the conditions for the approximation of a reaction band by a single reaction level. In Sec. III we will derive the conditions for the approximation of this single reaction level by a simple population-loss term. Section IV will be our conclusions.

II. REDUCTION OF A BAND OF LEVELS TO A SINGLE LEVEL

In this section we shall derive the conditions whereby a system with several multilevel reaction (and/or excitation) channels can be approximated by one in which these multilevel channels can be replaced by single-level channels. We start by examining the equations for the total multilevel system. We will then consider the equations for an identical system except that one level in the laser-excited system is coupled only to a single reaction (and/or excitation) level of the product system. By comparing the resultant solutions of both systems we will derive the conditions whereby the first system can be approximated by the latter one. By successive use of this method, many of the multilevel channels may be able to be approximated by single-level channels.

Consider a collection of laser-pumped molecules of type A with a finite number N of accessible, "undressed" modal levels k having energy ϵ_k, reacting to form molecules of type B_k having a finite number M_k of accessible, undressed modal levels j, having energy η_{kj}. This system is shown in Fig. 1(a). The classically treated laser field of carrier frequency ω_0 and amplitude E pumps the molecules of type A into their accessible levels with a coupling strength $\omega_{k',k}$, equal to one-half the Rabi frequency for the transition $k \leftrightarrow k'$,

$$\omega_{k',k}=\frac{1}{2}\mu_{k'k}E \;, \tag{1}$$

where $\mu_{k'k}$ is the matrix element of the transition dipole moment of A between levels k and k'. The reaction rate of an A molecule in level k with energy ϵ_k reacting to produce a B_k molecule in level j, B_{kj} with energy η_{kj} is specified by the parameter g_{kj}. Population loss of level k of the A molecules via interaction with reservoir degrees of freedom is represented by a decay rate γ_k^A; population loss of level j of the B_k molecules B_{kj} via interaction with reservoir degrees of freedom is specified by a decay rate γ_{kj}. Using the operator format developed by Bowden *et al.*,[6] of a method employed by Silverman and Pipkin,[7] the Hamiltonian of this sytem is given by

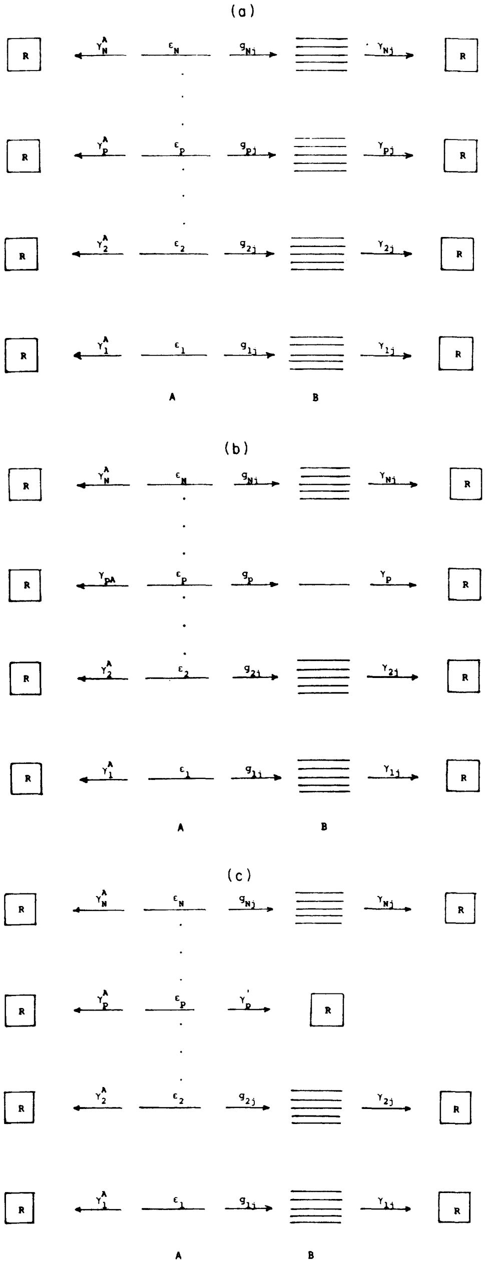

FIG. 1. Schematic diagram of a laser-pumped N-level A molecule reacting to form B molecules. Both the A and B molecular levels are coupled to reservoirs. (a) Original system, (b) the B_p levels are approximated by a single level, (c) the B_p level is approximated by a coupling to a reservoir.

$$H=\sum_{k=1}^{N}\epsilon_k a_k^\dagger a_k+\sum_{k=1}^{N}\sum_{j=1}^{M_k}\eta_{kj}b_j^\dagger b_j+\sum_{k=1}^{N}\sum_{k'=k+1}^{N}\omega_{k',k}(e^{-i\omega_0 t}a_{k'}^\dagger a_k+e^{i\omega_0 t}a_k^\dagger a_{k'})$$
$$+\sum_{k=1}^{N}\sum_{j=1}^{M_k}(g_{kj}a_k b_{kj}^\dagger+g_{kj}^* a_k^\dagger b_{kj})+R\equiv H+R \;, \tag{2}$$

where R is the coupling of the A and B molecules to reservoir degrees of freedom, and the rotating-wave approximation has been assumed. Notationally, $a_k^\dagger$ and a_k are, respectively, the (Bose) creation and annihilation operators[3(a),3(d),3(e)] for the kth level of the A molecules, and similarly the $b_j^\dagger$ and b_j are, respectively, the (Bose) creation and annihilation operators for the jth level of the B molecules. Transforming to the interaction picture and neglecting the rapidly oscillating components, we obtain the following hierarchy of $N+\sum_{k=1}^{N} M_k$ (complex) coupled linear first-order differential equations for the equation of motion for the amplitudes $a_k(t)$, and $b_{kj}(t)$ of the various states of the A and B manifolds, respectively:

$$\dot{a}_1=-i\omega_{1,2}a_2\exp(-i\Omega_{1,2}t)-i\sum_{j=1}^{N_1} g_{1j}^{*}b_{1j}\exp(-i\sigma_{1j}t)-\gamma_1^A a_1 \;, \tag{3a}$$

$$\vdots$$

$$\begin{aligned}\dot{a}_k=&-i\omega_{k-1,k}a_{k-1}\exp(i\Omega_{k-1,k}t)-i\omega_{k,k+1}a_{k+1}\exp(-i\Omega_{k,k+1}t)\\ &-i\sum_{j=1}^{M_k} g_{kj}^{*}b_{kj}\exp(-i\sigma_{kj}t)-\gamma_k^A a_k,\quad k=2,\ldots,N-1\end{aligned} \tag{3b}$$

$$\vdots$$

$$\dot{a}_N=-i\omega_{N-1,N}a_{N-1}\exp(i\Omega_{N-1,N}t)-i\sum_{j=1}^{M_N} g_{Nj}^{*}b_{Nj}\exp(-i\sigma_{Nj}t)-\gamma_N^A a_N \;, \tag{3c}$$

$$\dot{b}_{kj}=-ig_{kj}a_k\exp(i\sigma_{kj}t)-\gamma_{kj}b_{kj},\quad j=1,\ldots,M_k;\quad k=1,\ldots,N \tag{3d}$$

where the dot denotes the derivative with respect to the time $\Omega_{i,n}$ is the laser detuning between the ith and nth level, given by

$$\Omega_{i,n}=\epsilon_n-\epsilon_i-(n-i)\omega_0 \;,$$

and $\sigma_{k,k+1}$ is the reaction energy deficit given by $\sigma_{kj}=\eta_{kj}-\epsilon_k$. We shall assume that initially all the A molecules are in the ground state $[a_1(0)=1,\ a_i(0)=0,\ i=2,\ldots,N]$, that no B molecules are present $[b_{kj}(0)=0,\ j=1,\ldots,M_k]$, and we shall arbitrarily set all the phase angles equal to zero at $t=0$. Taking the Laplace transform we can solve (see Appendix A) for $a_k(s)$, the Laplace transform of $a_k(t)$, obtaining

$$a_k(s+i\Omega_{1k})=\frac{\prod_{l=1}^{k-1}(-i\omega_{l,l+1})}{C_kD_k+\omega_{k-1,k}^2D_{k-1}},\quad k=1,\ldots,N \tag{4a}$$

$$b_{kj}(s+i\Omega_{1k}+i\sigma_{kj})=\frac{(-ig_{kj})\prod_{l=1}^{k-1}(-i\omega_{l,l+1})}{(s+i\Omega_{1k}+i\sigma_{kj}+\gamma_{kj})\left[D_{k+1}+\dfrac{\omega_{k,k+1}^2}{C_{k+1}}D_k\right]} \;, \tag{4b}$$

where

$$C_k=s+i\Omega_{1k}+\frac{\omega_{k,k+1}^2}{C_{k+1}}+\gamma_k^A+G_k \;, \tag{5a}$$

$$\begin{aligned}D_k=&\,(s+i\Omega_{1(k-1)}+G_{k-1}+\gamma_{k-1}^A)D_{k-1}\\ &+\omega_{k-2,k-1}^2D_{k-2} \;,\end{aligned} \tag{5b}$$

in which

$$G_k=\sum_{j=1}^{M_k}\frac{|g_{kj}|^2}{[(s+\gamma_{kj})+i(\Omega_{1k}+\sigma_{kj})]} \;, \tag{6a}$$

$$\prod_{l=1}^{0}(-i\omega_{l,l+1})\equiv 1 \;, \tag{6b}$$

and

$$(\omega_{N,N+1}^2/C_{N+1})\equiv 0,\quad \omega_{0,1}^2D_0\equiv 0,\quad D_1=1 \;. \tag{6c}$$

We now compare the above system with a system of laser-pumped N-level A molecules [Fig. 1(b)], in which every level $k\neq p$ is the same as the above system, but level p, which can be connected to A reservoir degrees of freedom so as to undergo population loss at a decay rate γ_p^A, can also react to produce only a single-level B_p (product) molecule, which is, in turn, coupled to reservoir degrees of freedom so as to undergo a population loss at a decay rate γ_p. Namely, every level $k \neq p$ is the same for both systems, and we are attempting to replace the band of levels B_{pj} in the first system, by a single level B_p in the second system.

The equations of motion for the operator amplitudes for the second system are identical to those of the first system, Eqs. (3) for $k \neq p$, with the equation for the pth level being

$$\begin{aligned}\dot{a}_p = & -i\omega_{p-1,p}a_{p-1}\exp(i\Omega_{p-1,p}t) \\ & -i\omega_{p,p+1}a_{p+1}\exp(-i\Omega_{p,p+1}t) \\ & -ig_p^* b_p \exp(-i\sigma_p t) - \gamma_p^A a_p \end{aligned} \tag{3b$'$}$$

and

$$\dot{b}_p = -ig_p a_p \exp(i\sigma_p t) - \gamma_p b_p \ , \tag{3d$'$}$$

where σ_p, the reaction energy deficit, is given by $\sigma_p = \eta_p - \epsilon_p$. Assume the same initial conditions as the previous case. Taking the Laplace transform, we obtain Eqs. (4) for all levels $k \neq p$, and for level p

$$a_p(s+i\Omega_{1p}) = \frac{\prod_{l=1}^{p-1}(-i\omega_{l,l+1})}{C_pD_p + \omega_{p-1,p}D_{p-1}} \ , \tag{4a$'$}$$

$$b_p(s+i\Omega_{1p}+i\sigma_p) = \frac{(-ig_p)\prod_{l=1}^{p-1}(-i\omega_{l,l+1})}{(s+i\Omega_{1p}+i\sigma_p+\gamma_p)\left[D_{p+1} + \dfrac{\omega_{p,p+1}^2}{C_{p+1}}D_p\right]} \ , \tag{4b$'$}$$

where Eqs. (5a) and (5b) and (6a)–(6c) hold for $k \neq p$ and G_p is given by

$$G_p = \frac{|g_p|^2}{s+i\Omega_{1p}+i\sigma_p+\gamma_p} \ , \tag{6a$'$}$$

where γ_p is the population-loss term of level B_p and represents the coupling of B_p to its reservoir.

Let us now compare the solutions for both systems. The A system interacts with b_p only through a_p. Therefore, as can be seen from Eqs. (3) [or, alternatively, Eqs. (A1)], if the solutions of a_p given by Eqs. (4a) and (4a′) are equivalent, then the total solutions for both systems will be equivalent. Now the only difference between the solution of Eq. (4a) with $k=p$, and that of Eq. (4a′) is the G_p term given for the two systems by Eqs. (6a) and (6a′), respectively. This difference will show up in the solutions for the respective roots of Eq. (4a) with $k=p$, and Eq. (4a′). Now the G_p terms will only be important when the denominator of either Eq. (4a) with $k=p$, or Eq. (4a′) with G_p set equal to zero, is less than, or of the same order as G_p; namely, relatively small. Therefore, let the roots of Eq. (4a) with $k=p$ and Eq. (4a′), where $G_p=0$, be specified by $s=R_l+iI_l$, where R_l and I_l are real numbers. Substituting these roots into Eqs. (6a) and (6a′) and rationalizing the results, one obtains from Eq. (6a) for $k=p$

$$G_p = \sum_{j=1}^{M_p} \frac{|g_{pj}|^2[(R_l+\gamma_{pj}) - i(I_l+\Omega_{1p}+\sigma_{pj})]}{[(R_l+\gamma_{pj})^2+(I_l+\Omega_{1p}+\sigma_{pj})^2]} \tag{7a}$$

and from Eq. (6a′),

$$G_p = \frac{|g_p|^2[(R_l+\gamma_p) - i(I_l+\Omega_{1p}+\sigma_p)]}{[(R_l+\gamma_p)^2+(I_l+\Omega_{1p}+\sigma_p)^2]} \ . \tag{7a$'$}$$

These two equations will obviously be equivalent if

$$\begin{aligned} &\sigma_{pj} \simeq \sigma_{pk}, \quad j,k=1,\ldots,M_p \\ &\gamma_{pj} = \gamma_{pk}, \quad j,k=1,\ldots,M_p \end{aligned} \tag{8a}$$

and we set

$$\begin{aligned} &\sigma_p = \sigma_{pj} \ , \\ &\gamma_p = \gamma_{pj} \ , \\ &|g_p|^2 = \sum_{j=1}^{M_p} |g_{pj}|^2 \ . \end{aligned} \tag{8b}$$

More generally, these two equations will be equivalent if

$$\begin{aligned} &(R_l+\gamma_{pj})^2+(I_l+\Omega_{1p}+\sigma_{pj})^2 \\ &\quad \simeq (R_l+\gamma_p)^2+(I_l+\Omega_{1p}+\sigma_p)^2 \ , \quad \text{for all } l \end{aligned} \tag{9a}$$

and we set

$$
\begin{aligned}
|g_p|^2 &= \sum_{j=1}^{M_p} |g_{pj}|^2 \,, \\
\gamma_p &= \sum_{j=1}^{M_p} \frac{|g_{pj}|^2 \gamma_{pj}}{|g_p|^2} \,,
\end{aligned}
\tag{9b}
$$

and

$$\sigma_p = \sum_{j=1}^{M_p} \frac{|g_{pj}|^2 \sigma_{pj}}{|g_p|^2} \,.$$

By equating the numerators we are fitting the amplitudes of the various terms in the solutions. As the denominators, by Eq. (9a), are required to be approximately the same, the approximations of Eqs. (9b) should be slightly better than those of Eqs. (8b). We note that owing to the similarity between the parameters g_n and $\omega_{k'n}$ in Eq. (2), similar types of approximations, Eqs. (8) and (9), are applicable to laser pumping, i.e., we may be able to approximate a band of laser-pumped levels by a single laser-pumped level.

What errors might we expect from these approximations? A formal solution of Eq. (3d) [or Eq. (3d′)] is

$$b_{pj}(t') = b_{pj}(0)\exp(-\gamma_{pj}t') + \int_0^{t'} -ig_{pj}a_p(t'')\exp(i\sigma_{pj}t'')\exp[-\gamma_{pj}(t'-t'')]dt'' \,. \tag{10}$$

Substituting this expression into a formal solution for Eq. (3b) with $k=p$ [or Eq. (3b′)] we obtain

$$
\begin{aligned}
a_p(t) = {} & a_p(0)\exp(-\gamma_p^A t) \\
& + \int_0^t \Bigg[-i\omega_{p-1,p}a_{p-1}(t')\exp(i\Omega_{p-1,p}t') - i\omega_{p,p+1}a_{p+1}(t')\exp(-i\Omega_{p,p+1}t') - ig_p^* b_p(0)\exp(-\gamma_p t') \\
& \qquad - \int_0^{t'} \sum_{j=1}^{M_p} |g_{pj}|^2 a_p(t'')\exp[i\sigma_{pj}(t''-t')]\exp[-\gamma_{pj}(t'-t'')]dt'' \Bigg] \exp[-\gamma_p^A(t-t')]dt' \,.
\end{aligned}
\tag{11}
$$

The difference between the formal solutions of Eq. (3b) with $k=p$, and of Eq. (3b′), is

$$
\begin{aligned}
& \int_0^{t'} \sum_{j=1}^{M_p} |g_{pj}|^2 a_p(t'')\exp[i\sigma_{pj}(t''-t')]\exp[-\gamma_{pj}(t'-t'')]dt'' \\
& \qquad \text{vs} \int_0^{t'} |g_p|^2 a_p(t'')\exp[i\sigma_p(t''-t')]\exp[-\gamma_p(t'-t'')]dt'' \,.
\end{aligned}
\tag{12}
$$

Let us consider when these solutions differ. Firstly, until $a_p(t'')$ reaches some significant value, both solutions will make no contribution. Set

$$\Delta t = t'-t'', \quad \Delta\sigma_{pj} = \sigma_{pj} - \sigma_p \,. \tag{13}$$

If the γ's are negligible, the solutions will be approximately the same for time intervals Δt, where

$$\Delta\sigma_{pj}\Delta t \le \text{some fraction of } \pi \,, \quad \text{say } \pi/10, \text{ for any } j \,. \tag{14}$$

Let us now consider the effect of the γ's. Assume all the γ_{pj}'s are approximately equal to γ_p. The γ's are damping coefficients, with damping times of the order, $\Delta t \simeq 1/\gamma_p$. Thus, from Eq. (14) the solutions will be approximately the same if

$$\gamma_p \ge 10\frac{\Delta\sigma_{pj}}{\pi} \,, \quad \text{for all } j \,. \tag{15}$$

Therefore, for negligible decay rates out of the B_p system, the approximation should be good until a time of the order of $\pi/(10\Delta\sigma)$ past the time the level was significantly populated. If the decay rates out of the B_p system satisfy Eq. (15), then the approximation should be reasonable, in general. Since Eq. (14) generally gives rather short times, its use is somewhat limited. The condition Eq. (15) assures that the population decays before the frequency differences, $\Delta\sigma_{pj}$, cause significant differences in the time dependences of the population amplitudes, wherein whose equations the σ_{pj}'s appear in the form $\sin\sigma_{pj}t$ and $\cos\sigma_{pj}t$. In particular, we note that the approximation of a large or infinite number of level *B* system with no (or negligible) decay terms present, by a smaller number of level *B* system, must be used with care. An example would be the approximation of the continuum in models of laser-induced dissociation (using this method with $g_{nj} \rightarrow \omega_{p,v}$ where v is the continuum level) by a finite number of levels with no decay terms present.

In conclusion, we have shown that if the original system has a band of levels B_{pj} for which the reaction energy deficits σ_{pj} are approximately equal, or if $(\sigma_p - \sigma_{pj})$ is negligible compared to other rate parameters, and if the decay rates γ_{pj} from these levels are approximately equal, then the $N+\sum_k M_k$ level system can be approximated by an appropriate $N+1+\sum_{k \neq p} M_k$ level system. These assumptions frequently hold for reactive processes. One technique useful in determining the applicability of Eqs. (9) is given in Appendix B. As noted previously, in addition to reaction this method can also be applied when a second laser causes the transition between the laser-pumped A system, and the B system.

Once the $N+\sum_k M_k$ level system has been reduced to an $N+1+\sum_{k \neq p} M_k$ level system, there may exist conditions such that the $N+1+\sum_{k \neq p} M_k$ level system may be reduced to an $N+2+\sum_{k \neq p_1,p_2} M_k$ level system, etc. By repeating this approximation method successively for all p levels desired, the original A system with several levels coupled to multilevel reaction (or laser-pumped) channels may be able to be approximated by one wherein several of these levels are only coupled to single reaction (or laser-pumped) channels.

Let us now consider the application of this method to a hypothetical system, the parameters of which are given in Table I. The total population of the A system is given in Fig. 2(a); the population of the A system's first, fifth, and seventh levels are given in Figs. 2(b)—2(d), respectively. Starting with the 20-total-level system the restriction, Eq. (15), is satisfied for the A system level 5. We can thus apply the approximation Eq. (9b) and thereby obtain the 16-level system. The differences between the graphs of the 20- and the 16-total-level systems, in the scale of Fig. 2, are too small to be seen. (In Fig. 2 we only plotted the graphs of the 20-total-level system.) The level populations of the A system in the 20-total-level system are thus well approximated by those of the 16-total-level system. The restriction of Eq. (15) is not satisfied for the A system level 7. Figures 2 show the result of using the approximation (9b) anyway, thereby reducing the 16-total-level system to a 12-total-level system. As can be seen, the results are not as good as those of the previous reduction, where the restriction was satisfied.

III. REDUCTION OF A SINGLE LEVEL TO A POPULATION-LOSS TERM

Having reduced the band of levels to a single level, let us now find when this single level can be approximated by a population-loss term. Thus, consider an $N+1+\sum_{k \neq p} M_k$ level system in which the

TABLE I. Parameters for the hypothetical level systems. All parameters not explicitly given are taken to be equal to zero. $\epsilon_i=1000(i-1)$; $i=1,10$. $\omega_{i,i+1}=1.0$; $i=1,9$. $\gamma_{10}^A=0.1$.

Levels 20	16	12	11	10
$\eta_{51}=3998$	$\eta_{51}=3998$			
$\eta_{52}=3999$	$\eta_{52}=3999$			
$\eta_{53}=4000$	$\eta_{53}=4000$	$\eta_5=4000$	$\eta_5=4000$	
$\eta_{54}=4001$	$\eta_{54}=4001$	$\gamma_5=0.5$	$\gamma_5=0.5$	$\gamma_5^A=2.0$
$\eta_{55}=4002$	$\eta_{55}=4002$			
$g_{5i}=1/\sqrt{5}$; $i=1,5$	$g_{5i}=1/\sqrt{5}$; $i=1,5$			
$\gamma_i=0.5$; $i=1,5$	$\gamma_i=0.5$; $i=1,5$			
$\eta_{71}=6001.6$				
$\eta_{72}=6001.7$				
$\eta_{73}=6001.8$				
$\eta_{74}=6001.9$	$\eta_7=6001.90909$	$\eta_7=6001.90909$	$\gamma_7^A=\frac{1}{3}$	$\gamma_7^A=\frac{1}{3}$
$\eta_{75}=6002.0$	$\gamma_7=6$	$\gamma_7=6$		
$g_{7i}=(\frac{2}{55})^{1/2}i$; $i=1,5$				
$g_{7i}=6$; $i=1,5$				

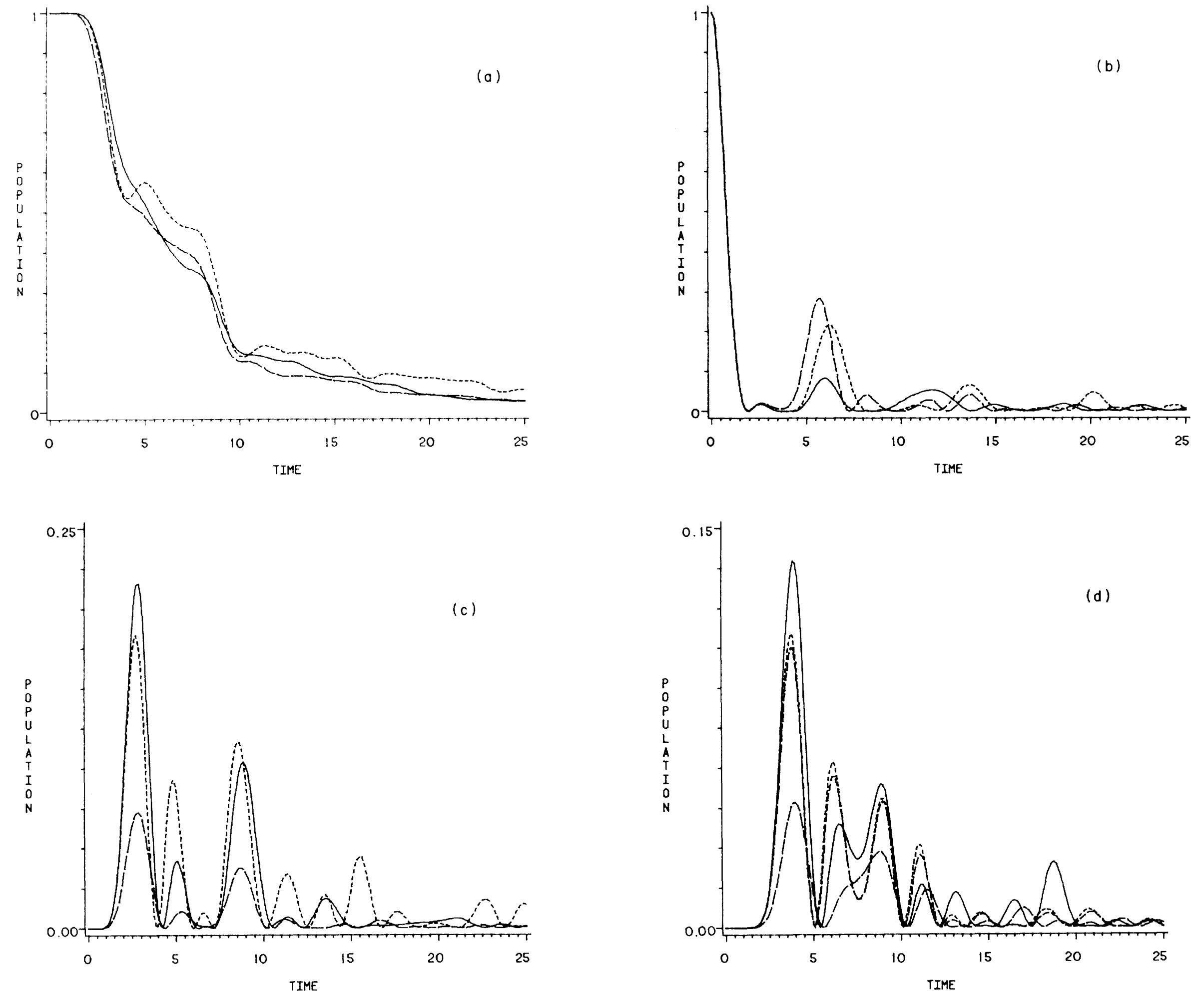

FIG. 2. Plot of population vs time for the systems consisting of 20 and 16 (——), (a)–(d) 12 (- - -) and (a)–(c) 11 (- - -), (d) 11 (— — —), and 10 (———) total levels. (a) Total population, (b) 1st level, (c) 5th level, (d) 7th level, of the A system.

A molecule's pth level is only coupled to reservoir degrees of freedom so as to undergo loss of population at the rate $\gamma_p^A+\gamma_p'$; namely, the previous loss rate γ_p^A plus an additional loss rate γ_p' which will be used to approximate the B_p level. The equations of motion for the amplitudes of the operators of this system are given by Eqs. (3) for $k\neq p$, with the equation for the pth level being

$$\dot{a}_p=-\omega_{p-1,p}a_{p-1}\exp(i\Omega_{p-1,p}t)-i\omega_{p,p+1}a_{p+1}\exp(-i\Omega_{p,p+1}t)-(\gamma_p^A+\gamma_p')a_p\ . \tag{3b''}$$

Assume the same initial conditions as in the previous systems. Taking the Laplace transform, we obtain Eqs. (4) for all levels $k\neq p$, and for level p

$$a_p(s+i\Omega_{1p})=\frac{\prod_{l=1}^{p-1}(-i\omega_{l,l+1})}{\left[s+i\Omega_{1p}+\frac{\omega_{p,p+1}^2}{C_{p+1}}+\gamma_p^A+\gamma_p'\right]D_p+\omega_{p-1,p}^2D_{p-1}}\ . \tag{4a''}$$

We want to compare the solutions for this system with the solutions for the one-level p reaction channel system. The levels for $p \neq k$ interact with the pth level through a_p. Therefore, as can be seen from Eqs. (3) [or, alternatively, Eqs. (A1)], if the solutions of a_p given by Eqs. (4a') and (4a'') are equivalent, then the total solutions for both systems will be equivalent. The only difference between these two solutions is the G_p term in Eq. (4a') versus the γ'_p term in Eq. (4a''). As in the previous case, these terms will be important in their respective equations only when the denominators of these equations with $G_p = 0$ and $\gamma'_p = 0$, respectively, are of the same order or less than G_p and γ'_p, respectively; namely, relatively small. Therefore, let the roots of Eq. (4a') with $G_p = 0$, and Eq. (4a'') with $\gamma'_p = 0$ be specified by $s = R_l + iI_l$, where R_l and I_l are real numbers. Substituting these roots into Eq. (7a') and setting it equal to γ'_p we obtain the requirement

$$G_p = \frac{|g_p|^2[(R_l+\gamma_p) - i(I_l + \Omega_{1p} + \sigma_p)]}{(R_l+\gamma_p)^2 + (I_l + \Omega_{1p} + \sigma_p)^2} = \gamma'_p \ . \tag{16}$$

Now consider the case when

$$\gamma_p \gg \text{ other rate constants} \tag{17}$$

and thus

$$\gamma_p \gg R_l, \ I_l, \ |g_p|^2, \ \sigma_p, \ \Omega_{1p} \ , \quad \text{for all } l \ . \tag{18}$$

Then the imaginary component is relatively small as it is proportional to $|g_p|^2/(\gamma_p)^2$, and thus can be neglected. Therefore, if we set

$$\gamma'_p = \mathrm{Re}\gamma'_p = \frac{|g_p|^2}{\gamma_p} \tag{19}$$

Eq. (16) will approximately be satisfied.

What errors might we expect from this approximation? A formal solution of Eq. (3b') is given by Eq. (11) with $M_p = 1$. Assuming γ_p is sufficiently large, such that, as in Eq. (15),

$$\gamma_p \geq \frac{10}{\pi}\sigma_p \ , \tag{20}$$

and assuming

$$a_p(t'') \simeq a_p(t') \ \text{ for all } \ t' - t'' \leq \frac{1}{\gamma_p} \tag{21}$$

then neglecting $\exp[-\gamma_p(t'-t'')]$ for intervals $t'-t'' > 1/\gamma_p$ and using Eq. (19),

$$\int_0^{t'} |g_p|^2 a_p(t'')\exp[i\sigma_p(t''-t')]\exp[-\gamma_p(t'-t'')]dt'' \simeq \gamma'_p a_p(t')[1-\exp(-\gamma_p t')] \ . \tag{22}$$

Substituting this expression into Eq. (11) (with $M_p = 1$), and differentiating the resulting equation with respect to t, we obtain

$$\begin{aligned} \dot{a}_p(t) = {} & -i\omega_{p-1,p}a_{p-1}(t)\exp(i\Omega_{p-1,p}t) - i\omega_{p,p+1}a_{p+1}(t)\exp(-i\Omega_{p,p+1}t) - ig_p^* b_p(0)\exp(-\gamma_p t) \\ & - \gamma'_p a_p(t)[1-\exp(-\gamma_p t)] - \gamma_p^A a_p(t) \ . \end{aligned} \tag{23}$$

Since terms proportional to $\exp(-\gamma_p t)$ can be neglected for $t \gg 1/\gamma_p$, and since we assumed $a_p(t)$ does not vary significantly over the time interval $t \leq 1/\gamma_p$, the terms proportional to $\exp(-\gamma_p t)$ can be ignored, and Eq. (23), which was obtained from Eq. (3b'), becomes Eq. (3b''). Thus, we see what errors are introduced by our assumptions. The requirement that $a_p(t)$ be approximately constant over the time interval $1/\gamma_p$ implies that γ_p be greater than all other rate parameters affecting $a_p(t)$, and is therefore satisfied by Eq. (18). For a specific system, one can see if the approximation of Eq. (19) will work, either by (i) solving for the roots $s = R_l + iI_l$ (with $G_{\mathrm{p}i} = 0$, $i = 1, \ldots, M_i$) and checking if Eq. (18) is satisfied, or (ii) knowing that γ_p satisfies Eq. (20), and γ'_p is relatively small for the system under consideration, use the approximation, Eq. (19) and check to see that $a_p(t)$ is approximately constant over any time interval $1/\gamma_p$. Thus, we can only approximate a single-level reaction channel by a decay term if the decay out of the reaction product is relatively very fast. Physically, this requirement simply states that the population loss of the product must be sufficiently fast that we can ignore any reaction from the product B back into system A. The condition Eq. (17) is much more restrictive than the approximation of many reaction channels by a single channel, Eq. (15). In particular, Eq. (15) only requires γ_p to be significantly greater than the spread in the reaction deficits, $\Delta\sigma_{pj}$. On the other hand, Eq. (17) requires γ_p to be greater than $|g_p|^2$, Ω_p, and σ_p itself, as well as the R_l and I_l, for all l.

Some systems may have two or more levels in which the decay rates γ_k^B are relatively large for several levels k, compared to the other rate parameters of the system. Consider the case when two levels p and q have relatively large decay rates γ_p^B and γ_q^B, respectively. From Eq. (4a′) one can readily see that a_p will only be affected by γ_q^B through the C's and the D's. From Eq. (5a) C_p will be influenced by G_p only when G_p is relatively large, which from Eq. (6a′) will only occur when the real part of $s \simeq -\gamma_p^B$. From Eq. (5a), when $s = -\gamma_p^B$, C_p will be relatively large due to the $s = -\gamma_p^B$ term itself. Owing to the recursion relation, Eq. (5a) other C's can only be affected by ω^2/C. Thus (since the ω's $\ll \gamma_p^B, \gamma_q^B$), other C's will not be substantially affected by the G_p term in C_p. From Eq. (5b) one can see that a similar situation exists for the D terms. Thus, G_p will only significantly affect the a_p term, and G_q will only significantly affect the a_q term. Therefore, the requirements derived in Eqs. (16)–(19) will hold for each level p and q. One can also see this generalization from Eq. (23). This process can be extended to any arbitrary number of levels. Thus, the single reaction levels in systems which have relatively large decay rates γ_k^B for several levels k can be approximated by decay terms provided the parameters of each of the levels approximated satisfies Eq. (17) (where the large γ^B's are excluded from the "other rate constants").

Let us now consider the application of these approximations to the hypothetical 12-level system, the parameters of which are given in Table I. In the first reduction, the approximation of the coupling of the 7th A level to a B system, by a population-loss term, γ_7 is sufficiently large such that the approximation, Eq. (19), can be used. The results are shown in Fig. 2. The differences between the graphs of the 12- and 11-total-level systems, in the scale of Figs. 2(a)–2(c), are too small to be seen. [In those figures we only plotted the graphs of the 12-total-level system. In Fig. 2(d) the discrepancies are greater, and both graphs are plotted.] The level populations of the A system in the 12-total-level systems are thus well approximated by those of the 11-total-level system. In the second reduction, the approximation of the coupling of the 5th A level to a B system, by a population-loss term, γ_5 is not sufficiently large to enable the approximation, Eq. (19), to be used. Figures 2 show the result of using the approximation of Eq. (19) anyway, thereby reducing the 11-total-level system to a 10-total-level system. As can be seen, the results are not as good as those of the previous reduction, where the restriction was satisfied.

IV. CONCLUSION

We have thus derived conditions as to when a system of reaction channels can be approximated by a single level, and when that single level can be approximated by a population-loss (decay) term. While we did it for a single level p, the method can be used sequentially to eliminate as many bands of levels as is feasible. We would also like to note that this method is not limited to reaction channels only. As can be seen from the structure of the equations of motion Eqs. (3), it can also be used to eliminate levels coupled by the laser, i.e., $g_{Nj} \rightarrow \omega_{Nj}; \sigma_{Nj} \rightarrow \Omega_{Nj}$.

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APPENDIX A

Taking the Laplace transform of Eqs. (3) and changing $a_k(s)$ to $a_k(s+i\Omega_{1k})$ we obtain the set of equations

$$(s+\gamma_1^A)a_1(s) = 1 - i\omega_{1,2}a_2(s+i\Omega_{12}) - i\sum_{j=1}^{M_1} g_{1j}b_{1j}(s+i\sigma_{1j}) \,, \tag{A1a}$$

$$\vdots$$

$$\begin{aligned}(s+i\Omega_{1k}^A+\gamma_k)a_k(s+i\Omega_{1k}) = {} & -i\omega_{k-1,k}a_{k-1}(s+i\Omega_{1(k-1)}) - i\omega_{k,k+1}a_{k+1}(s+i\Omega_{1(k+1)}) \\ & -i\sum_{j=1}^{M_k} g_{kj}^* b_{kj}(s+i\sigma_{kj}+i\Omega_{1k}), \quad k=2,\ldots,N-1\end{aligned} \tag{A1b}$$

$$\vdots$$

$$(s+i\Omega_{1N}+\gamma_N^A)a_N(s+i\Omega_{1N}) = -i\omega_{N-1}a_{N-1}(s+i\Omega_{1(N-1)}) - i\sum_{j=1}^{M_N} g_{Nj}^* b_{Nj}(s+i\sigma_{Nj}+i\Omega_{1N}) \,, \tag{A1c}$$

$$(s+i\Omega_{1k}+i\sigma_{kj}+\gamma_j^A)b_{kj}(s+i\Omega_{1k}+i\sigma_{kj}) = -ig_{kj}^* a_k(s+i\Omega_{1k}) \,. \tag{A1d}$$

Assume a solution of the form

$$a_k(s+i\Omega_{1k})=\frac{\prod_{l=1}^{k-1}(-i\omega_{l,l+1})}{C_kD_k+\omega_{k-1,k}^2D_{k-1}}\ , \tag{A2a}$$

$$b_{kj}(s+i\Omega_{1k}+i\sigma_{kj})=\frac{(-ig_{kj})\prod_{l=1}^{k-1}(-i\omega_{l,l+1})}{(s+i\Omega_{1k}+i\sigma_{kj}+\gamma_{kj})\left[D_{k+1}+\dfrac{\omega_{k,k+1}^2}{C_{k+1}}D_k\right]}\ , \tag{A2b}$$

where

$$C_k=s+i\Omega_{1k}+\frac{\omega_{k,k+1}^2}{C_{k+1}}+G_k+\gamma_k^A \tag{A3}$$

in which

$$G_k=\frac{\sum_{j=1}^{M_j}|g_{kj}|^2}{(s+i\Omega_{1k}+i\sigma_{kj}+\gamma_{kj})}\ , \tag{A4}$$

$$\prod_{l=1}^{0}(-i\omega_{l,l+1})=1\ , \tag{A5}$$

and D_k will be defined shortly. Substituting Eqs. (A2) into Eq. (A1b) we can obtain

$$\frac{(s+i\Omega_{1k}+\gamma_k^A)}{(C_kD_k+\omega_{k-1,k}^2D_{k-1})}=\frac{1}{(C_{k-1}D_{k-1}+\omega_{k-2,k-1}^2D_{k-2})}-\frac{\omega_{k,k+1}^2}{(C_{k+1}D_{k+1}+\omega_{k,k+1}^2D_k)}$$
$$-\frac{G_k}{\left[D_{k+1}+\dfrac{\omega_{k,k+1}^2}{C_{k+1}}D_k\right]}\ . \tag{A6}$$

Define D_k such that

$$C_kD_k+\omega_{k-1,k}^2D_{k-1}=D_{k+1}+\frac{\omega_{k,k+1}^2D_k}{C_{k+1}} \tag{A7}$$

or by substituting Eq. (A3) for the C_k's, and letting $k\to k-1$,

$$D_k=(s+i\Omega_{1(k-1)}+G_{k-1}+\gamma_{k-1}^A)D_{k-1}$$
$$+\omega_{k-2,k-1}^2D_{k-2}\ . \tag{A8}$$

Substituting Eq. (A7) into Eq. (A6) gives us Eq. (A3). Thus we have consistency and the a_k's and b_k's given by Eq. (A2) are the solutions of the set of Eqs. (A1).

As Eqs. (A3) and (A7) define the C_k's and D_k's as recursion relations, we must give some initial values. Since $\omega_{N,N+1}^2=0$, the series for C_k, Eq. (A3) is cut off at C_N by setting $(\omega_{N,N+1}^2/C_{N+1})=0$. Then C_N is given by Eq. (A3), and all other C_k's starting with C_{N-1} and proceeding to C_1 can also be obtained from Eq. (A3).

Now lets consider the recursion relation for the D_k's Eq. (A8). Start with D_1. Substituting Eq. (A2) into Eq. (A1a), setting $\omega_{0,1}=0$, and thus $\omega_{0,1}D_0=0$, we obtain

$$\frac{s+\gamma_1^A}{C_1D_1}=1-\frac{\omega_{1,2}^2}{C_2D_2+\omega_{1,2}^2D_1}-\frac{G_1}{D_2+\dfrac{\omega_{1,2}^2}{C_2}D_1}\ . \tag{A9}$$

Substituting Eq. (A7) into Eq. (A9), using Eq. (A3) and then Eq. (A7), all with $k=1$, we obtain

$$s+\gamma_1^A+G_1+\frac{\omega_{1,2}^2}{C_2}=D_2+\frac{\omega_{1,2}^2D_1}{C_2}$$

or from Eqs. (A3) and (A7)

$$C_1=D_2+\frac{\omega_{1,2}^2D_1}{C_2}=C_1D_1\ . \tag{A10}$$

Thus,

$$D_1 = 1\ . \tag{A11}$$

Using Eq. (A8) we can then obtain the D_k's for $k=2$ to $k=N$.

APPENDIX B

From the theory of the solution of a system of linearly coupled equations, one knows that the roots of Eq. (9a) are the same as those obtained by requiring the determinant of the matrix (R) formed by the coefficients of the Laplace transforms of the equation of motion as given in Eq. (A1) to be zero.

Let (S) be a matrix where $S^{ii}=s$ and all other elements $S^{ij}=0$, $i\neq j$. Set

$$(A)=(R)-(S)\ . \tag{B1}$$

In estimating the quantities to be used in Eq. (9a) it is convenient to make use of a theorem by Gersgorin[8,9] and one by Bendixson-Kirsch.[10] The Gersgorin theorem states that the characteristic roots of a real matrix B must lie inside the circles of center b^{ii} and radius $\sum_{j\neq i} |b^{ij}|$ for $i=1,2,\ldots,N$.

The matrix (A), given by Eq. (A1), can be written in the form $B+iC$, where B and C are Hermitian. Let the characteristic roots of B be contained between b_1 and b_2 and those of C be between c_1 and c_2. Then all the characteristic roots of A will be contained within the rectangle in the complex plane bound by b_1+ic_1, b_1+ic_2, b_2+ic_1, b_2+ic_2 (Bendixson-Hirsch). By using this technique one can readily determine when the conditions, Eq. (9a), are satisfied.

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