Adiabatic approximation for the density matrix

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An adiabatic approximation for the Liouville density-matrix equation which includes decay terms is developed. The adiabatic approximation employs the eigenvectors of the non-normal Liouville operator. The approximation is valid when there exists a complete set of eigenvectors of the non-normal Liouville operator (i.e., the eigenvectors span the density-matrix space), the time rate of change of the Liouville operator is small, and an auxiliary matrix is nonsingular. Numerical examples are presented involving efficient population transfer in a molecule by stimulated Raman scattering, with the intermediate level of the molecule decaying on a time scale that is fast compared with the pulse durations of the pump and Stokes fields. The adiabatic density-matrix approximation can be simply used to determine the density matrix for atomic or molecular systems interacting with cw electromagnetic fields when spontaneous emission or other decay mechanisms prevail.

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I. INTRODUCTION

The object of this paper is to develop an adiabatic density-matrix approximation (ADMA) for systems in which the effects of decay are explicitly incorporated by inclusion of a decay term into the Liouville equation (sometimes called the Bloch equation), which describes the dynamics of the system. The present approximation differs from the well-known adiabatic following approximation for density matrices [1], which treats the case when a time-varying field (or fields) is tuned far from resonance. Here, the treatment is in terms of the slow variation of the eigenvectors of the Liouville operator, and is similar to the treatment for slow variation of the eigenvectors of the Hamiltonian in the adiabatic Hamiltonian approximation (AHA) [2].

After developing the ADMA we apply it to describe the dynamics of population transfer in molecular systems by stimulated Raman scattering with time-varying pump and Stokes fields. We consider the case when the temporal duration of the fields is long compared with the decay time of the intermediate level of the Raman transition. One might expect that efficient population transfer would not be possible, since decay out of the manifold of levels can significantly reduce the population. Yet, efficient population transfer to the terminal level of the Raman transition would be possible if the intermediate level were not populated during the course of the dynamics. Recent interest in adiabatic approximations has been rekindled in part by the experiments of Bergmann and co-workers, which demonstrate that nearly complete population transfer in atoms or molecules can be achieved using Raman scattering with the fundamental laser beam temporally delayed relative to the Stokes-shifted laser beam, but partially overlapping it [3,4]. The rationale for these experimental findings is given in terms of the adiabatic approximation, wherein an electric-field-dressed eigenstate evolves from the ground molecular state to the terminal molecular state as a time-dependent linear combination of the ground and terminal states with zero amplitude of the intermediate excited state [5–9]. However, the adiabatic approximation that has been used to explain these phenomena treats the system within the context of an adiabatic *Hamiltonian* approximation [2] without the explicit inclusion of decay of the intermediate excited state due to spontaneous emission (or other nonradiative processes). One wonders whether an ADMA yields results similar to the AHA. Here, we shall use the ADMA that explicitly contains the effects of decay to describe the observed phenomena. We demonstrate that, without decay of the terminal state (or the initial state), the results of the AHA are basically identical to the ADMA results for the three-level problem discussed in the numerical example. However, the ADMA is capable of describing a broader range of phenomena than the AHA. For example, we use the ADMA to treat a case with decay of the terminal state of the Raman transition. Then, the electric-field-dressed eigenstate of the Liouville operator (i.e., the adiabatic density-matrix component) that evolves from the ground state develops a decaying component. The AHA is not capable of treating this case. Another more trivial example is the case of problems with atomic or molecular systems interacting with cw electromagnetic fields when spontaneous emission or other decay mechanisms are included in the description. In this case, the eigenstate of the Liouville operator with zero eigenvalue is the desired cw density matrix, so often used in describing optical resonance and nonlinear optics [10]. Thus the regime of validity of the ADMA is wider than the AHA because it can incorporate decay.

A density-matrix description of the dynamics is necessary when incomplete information regarding a subsystem results due to averaging over degrees of freedom associat-

ed with the remainder of the system (i.e., the bath). The averaging can result in a mixed state of the subsystem, which cannot be described in terms of a wave function. The quantum-mechanical description of such mixed states is in terms of a density matrix [11]. The equation of motion for the density matrix is called the Liouville–von Neumann equation, or the Bloch density-matrix equation. Reduction schemes for eliminating the degrees of freedom of the bath have been studied by many authors [12–15]. In the context of the interaction of light with matter, optical Bloch equations have become a standard method to determine the dynamics of a system described by a finite number of states that undergo interactions with degrees of freedom, such as the modes of the radiation field participating in spontaneous emission that have been reduced out of the problem [16]. The elimination of the bath degrees of freedom leads to expressions for the lifetime of the excited states and the line shape of the transitions between the states of the subsystem [17].

The Liouville (Bloch) equation with decay incorporated is given by

$$\frac{d}{dt}\rho=-\frac{i}{\hbar}[H(t),\rho]-\Gamma(t)\rho \ . \tag{1}$$

Written explicitly in terms of components, this equation takes the form

$$\frac{d}{dt}\rho_{ij}=-\frac{i}{\hbar}[H(t)_{ik}\rho_{kj}-\rho_{ik}H(t)_{kj}]-\Gamma_{ijkl}(t)\rho_{kl} \ , \tag{2}$$

where the summation convention is assumed, and $i,j,k,l=1,2,\ldots,N$. We develop an adiabatic approximation of this system of equations. The Liouville density-matrix equation can be viewed as a matrix differential equation, with ρ_{ij} considered a vector and the $N^2\times N^2$ linear operator $Z_{ij,kl}(t)$,

$$Z_{ij,kl}(t)=-\frac{i}{\hbar}[H(t)_{ik}\delta_{lj}-\delta_{ik}H(t)_{lj}]-\Gamma_{ijkl}(t) \ , \tag{3}$$

appearing on the right-hand side of the equation is a matrix operating on the vector ρ_{kl}. Hence Eq. (2) takes the form

$$\frac{d}{dt}\rho_{ij}=Z_{ij,kl}(t)\rho_{kl} \ . \tag{4}$$

The operator Z is often written as $Z=-iL$, and L is called the generalized Liouville operator, which is the generator of the solution of Eq. (1).

II. ADIABATIC APPROXIMATION

Let us express $\rho_{ij}(t)$ as a sum over "adiabatic" matrices $\rho_{ij}^{\alpha}(t)$. We shall use matrices $\rho_{ij}^{\alpha}(t)$ that are eigenvectors of the linear operator $Z_{ij,kl}(t)$. Here ij is taken as the first index of the matrix $Z(t)$, kl is taken as the second index, $\rho_{ij}^{\alpha}(t)$ is an eigenvector of the matrix $Z(t)$,

$$Z_{ij,kl}(t)\rho_{kl}^{\alpha}(t)=\rho_{ij}^{\alpha}(t)z^{\alpha}(t) \ , \tag{5}$$

and $z^{\alpha}(t)$ is an eigenvalue of $Z(t)$. We choose to expand the density matrix $\rho_{ij}(t)$ in terms of $\rho_{ij}^{\alpha}(t)$ in the form

$$\rho_{ij}(t)=\sum_{\alpha}[a(t)]_{\alpha}\rho_{ij}^{\alpha}(t)\exp\left[\int_{z}^{t}z^{\alpha}(t')dt'\right] \ . \tag{6}$$

When this expansion is substituted into Eq. (2), we obtain

$$\sum_{\alpha}\left[\frac{d[a(t)]_{\alpha}}{dt}\rho_{ij}^{\alpha}(t)+a(t)_{\alpha}\frac{d}{dt}\rho_{ij}^{\alpha}(t)\right]\times\exp\left[\int^{t}z^{\alpha}(t')dt'\right]=0 \ . \tag{7}$$

If the operator Z is normal, i.e., $Z(t)[Z(t)]^{\dagger}=[Z(t)]^{\dagger}Z(t)$, where the dagger represents Hermitian conjugation, there exists a unitary eigenvector matrix, and the eigenvectors can be orthogonalized [18],

$$\langle\rho^{\beta}(t)|\rho^{\alpha}(t)\rangle=\delta_{\beta\alpha} \ . \tag{8}$$

Hence, upon taking the inner product of Eq. (7) with $\rho^{\beta}(t)$, we obtain

$$\frac{d[a(t)]_{\beta}}{dt}=-\sum_{\alpha}\left[\left\langle\rho^{\beta}(t)\left|\frac{d}{dt}\rho^{\alpha}(t)\right.\right\rangle\times\exp\left[\int^{t}[z^{\alpha}(t')-z^{\beta}(t')]dt'\right]\times[a(t)]_{\alpha}\right] \ . \tag{9}$$

Moreover, $\langle\rho^{\beta}(t)|(d/dt)\rho^{\alpha}(t)\rangle$ can be expressed in terms of matrix elements of $dZ(t)/dt$, provided the eigenvalues z^{α} are distinct [2]. Equation (9) then takes the form

$$\frac{d[a(t)]_{\beta}}{dt}=\sum_{\alpha}\left[\frac{\left\langle\rho^{\beta}(t)\left|\frac{dZ(t)}{dt}\right|\rho^{\alpha}(t)\right\rangle}{z^{\beta}(t)-z^{\alpha}(t)}\times\exp\left[\int^{t}[z^{\alpha}(t')-z^{\beta}(t')]dt'\right]\times[a(t)]_{\alpha}\right] \ . \tag{10}$$

Without decay, i.e., when $\Gamma_{klnm}(t)=0$, the Z operator is normal. This is demonstrated in Appendix A. However, for the case without decay, there is no reason to adopt a density-matrix treatment since it is equivalent to the much simpler wave-function treatment.

With decay included, our operator $Z(t)$ is non-normal. Specifically, we consider a decay matrix Γ with the following properties. Let γ_{in} be the decay rate of state n into state i. For the decay terms appearing in the equations for the population density-matrix elements $\rho_{ii}(t)$,

$$\Gamma_{iinm}=\begin{cases}-\gamma_{in}\delta_{nm} & \text{for } i<n\\ \left[\sum_{n<i}\gamma_{ni}\right]\delta_{nm} & \text{for } i=n\\ 0 & \text{for } i>n \ .\end{cases} \tag{11}$$

For the decay terms appearing in the off-diagonal density-matrix elements $\rho_{ij}(t)$ with $i\neq j$,

$$\Gamma_{ijnm}=\left[\left[\sum_{n<i}\gamma_{ni}+\sum_{n<j}\gamma_{nj}\right]\Big/2\right]\delta_{in}\delta_{jm} \ . \tag{12}$$

With this type of decay matrix (which is often employed in atomic and molecular applications involving spontaneous emission of excited-state levels), the $Z(t)$ operator is non-normal (see Appendix A). Moreover, generalizations of the decay matrix, e.g., by inclusion of decay to states outside the N levels under consideration [9], or inclusion of proper dephasing terms [15] into the polarization decay Γ_{ijnm}, also produce a $Z(t)$ operator that is non-normal.

Now, the eigenvectors of a non-normal operator cannot be orthogonalized, but they *may* or *may not* form a complete basis of states that span the density-matrix space [17]. No general theorem regarding the linear dependence or independence of the eigenvectors of non-normal matrices exists. Hence a numerical check to confirm whether the eigenvectors of $Z(t)$ are linearly independent must be performed by evaluating the determinant of the eigenvector matrix during the temporal evolution (the determinant of the eigenvector matrix in general varies throughout the course of the evolution). *If there exists a complete basis consisting of eigenvectors of Z,* we obtain the following equation instead of Eq. (9):

$$\frac{d[a(t)]_\gamma}{dt}=-\sum_\alpha\sum_\beta\left[\langle\rho^\beta(t)|\rho^\gamma(t)\rangle^{-1}\left\langle\rho^\beta(t)\left|\frac{d}{dt}\rho^\alpha(t)\right\rangle\exp\left[\int^t[z^\alpha(t')-z^\gamma(t')]dt'\right][a(t)]_\alpha\right]. \tag{13}$$

(Note that the matrix $\langle\rho^\beta(t)|\rho^\gamma(t)\rangle$ is nonsingular if the eigenvectors are linearly independent.) Moreover, the term $\langle\rho^\beta(t)|(d/dt)\rho^\alpha(t)\rangle$ is proportional to terms of the form $\langle\rho^\gamma(t)|d\mathbf{Z}(t)/dt|\rho^\alpha(t)\rangle$ and $\langle\rho^\gamma(t)|\rho^\alpha(t)\rangle dz^\alpha(t)/dt$ (see Appendix B). Hence, $\langle\rho^\beta(t)|(d/dt)\rho^\alpha(t)\rangle$ is vanishingly small if the matrix $Z(t)$ varies sufficiently slowly, provided the **D** matrix defined in Appendix B does not become singular. Therefore, $da_\gamma/dt=0$ and

$$[a(t)]_\gamma=[a(0)]_\gamma\ . \tag{14}$$

Thus, if the system starts at $t=0$ in the state

$$\rho_{ij}(0)=\sum_\alpha[a(0)]_\alpha\rho_{ij}^\alpha(0)\ , \tag{15}$$

within the ADMA it evolves into

$$\rho_{ij}(t)=\sum_\alpha[a(0)]_\alpha\rho_{ij}^\alpha(t)\exp\left[\int^t z^\alpha(t')dt'\right]. \tag{16}$$

This generalizes the Hamiltonian adiabatic theorem to the adiabatic density-matrix theorem for systems with decay incorporated via inclusion of a phenomenological decay matrix $\Gamma(t)$ into the Liouville equation, provided (a) the eigenvectors $\rho_{ij}^\alpha(t)$ of the Z operator are linearly independent, and (b) the **D** matrix defined in Appendix B does not become singular. The latter condition replaces the condition that was necessary for the adiabatic Hamiltonian approximation, that eigenvalues are distinct. Here **D** is a complex matrix; hence the condition should be easier to meet since the real and imaginary parts of the determinant of **D** must both vanish for **D** to be singular.

An alternative to Eq. (13) can be obtained if, instead of taking the inner product of Eq. (7) with $\rho^\beta(t)$, we take the inner product with the eigenvectors of $Z^\dagger$ [which is similar to taking the inner product with the left eigenvectors of the operator Z (see Appendix B)].

III. NUMERICAL EXAMPLES

We consider a three-level (Λ configuration) system, g, a, and b, interacting with a pump and a Stokes laser field. The ground- and excited-state levels g and a are optically coupled by a time-dependent pump field that is in resonance with the transition, or nearly in resonance, and the excited and terminal levels a and b are optically coupled by a time-dependent Stokes radiation field in resonance with this transition, or nearly in resonance [3,9]. The Liouville equation for the density matrix of the three-level system interacting with the two optical time-dependent pulses is given by Eq. (1) where $H=H_0-E(t)\mu$, $E(t)=A(t)\exp[i(k_1x-\omega_1t)]+B(t)\exp[i(k_2x-\omega_2t)]+\text{c.c.}$, and μ is the transition dipole moment matrix for the system. The Rabi frequencies for the two transitions are given in terms of the transition dipole moments and field strengths by $\Omega_p(t)=A(t)\mu_{ag}/\hbar$ and $\Omega_s(t)=B(t)\mu_{ab}/\hbar$. The decay matrix is taken to have only the following nonvanishing elements, $\Gamma_{gg,aa}$ $(=\gamma_{ga})$, $\Gamma_{bb,aa}$ $(=\gamma_{ba})$, $\Gamma_{ag,ag}$, $\Gamma_{ba,ba}$, and the decay of state a to states not included in the three-level system with decay rate $\gamma_{\text{out},a}$. Thus, the full decay rate of state a is $(\gamma_{ga}+\gamma_{ba}+\gamma_{\text{out},a})$ $(\approx 8.0\times10^7\ \text{s}^{-1})$, and the decay rates of the polarizations are $\Gamma_{ag,ag}=\Gamma_{ba,ba}=(\gamma_{ga}+\gamma_{ba}+\gamma_{\text{out},a})/2$. Upon expanding the elements of the density matrix ρ_{ij} in slowly varying envelopes that oscillate at Fourier frequencies $l\omega_1+m\omega_2$ and $\rho_{ij}^{(l,m)}$ and making the rotating-wave approximation, we obtain the following set of equations governing the dynamics of the system [19,9]:

$$i\partial_t\rho_{ag}^{(1,0)}=(\omega_{ag}-\omega_1-i\Gamma_{ag})\rho_{ag}^{(1,0)}-\Omega_s\rho_{bg}^{(1,-1)}-\Omega_p(\rho_{gg}^{(0,0)}-\rho_{aa}^{(0,0)})\ , \tag{17}$$

$$i\partial_t\rho_{ba}^{(0,-1)}=(\omega_2-\omega_{ab}-i\Gamma_{ab})\rho_{ba}^{(0,-1)}+\Omega_p^*\rho_{bg}^{(1,-1)}-\Omega_s^*(\rho_{aa}^{(0,0)}-\rho_{bb}^{(0,0)})\ , \tag{18}$$

$$i\partial_t\rho_{bg}^{(1,-1)}=(\omega_{bg}+\omega_2-\omega_1-i\Gamma_{bg})\rho_{bg}^{(1,-1)}-\Omega_s^*\rho_{ag}^{(1,0)}+\Omega_p\rho_{ba}^{(0,-1)}\ , \tag{19}$$

$$i\partial_t\rho_{gg}^{(0,0)}=-[\Omega_p^*\mu_{ag}(\rho_{ag}^{(1,0)})-\text{c.c.}]+i\gamma_{gb}\rho_{bb}^{(0,0)}+i\gamma\rho_{aa}^{(0,0)}\ , \tag{20}$$

$$i\partial_t \rho_{bb}^{(0,0)} = [\Omega_s(\rho_{ba}^{(0,-1)}) - \text{c.c.}] - i\gamma_{gb}\rho_{bb}^{(0,0)} + i\gamma_{ba}\rho_{aa}^{(0,0)} , \quad (21)$$

$$i\partial_t \rho_{aa}^{(0,0)} = -i\partial_t \rho_{gg}^{(0,0)} - i\partial_t \rho_{bb}^{(0,0)} - i\gamma_{\text{out},a}\rho_{aa}^{(0,0)} . \quad (22)$$

Here, the Rabi frequencies are functions of time and are taken to vary slowly in time with a Gaussian functional form

$$\Omega_p(t) = A(t)\mu_{ag}/\hbar = \Omega_{p,0}\exp\left[\frac{-(t-t_p)^2}{2\sigma^2}\right] , \quad (23)$$

$$\Omega_s(t) = B(t)\mu_{ab}/\hbar = \Omega_{s,0}\exp\left[\frac{-[t-(t_p+\Delta t)]^2}{2\sigma}\right] . \quad (24)$$

Equations (17)–(22) are of the form given in Eq. (2). They can be solved using the adiabatic approximation given in Eq. (6), in terms of the eigenvectors to the matrix equation obtained by setting the derivatives with respect to time in Eqs. (17)–(22) equal to zero. We shall carry out the adiabatic density approximation and compare it with the numerical solution of the full Liouville equation and with the adiabatic Hamiltonian approximation for a number of different sets of parameters. The numerical values for the decay rates, the transition dipole moments, and the other parameters employed in the calculations are presented in Ref. [9], with the exception of the Rabi frequencies $\Omega_{p,0}$ and $\Omega_{s,0}$, which are increased by a factor of 100 and are taken here to be 12.9×10^9 and 8.7×10^9 s^{-1}, respectively. The increased Rabi frequencies make the criteria for validity of the adiabatic approximation more easily achievable, as discussed below.

The adiabatic *Hamiltonian* approximation is given in terms of the dressed-state basis $|g,N_p(t),N_s(t)\rangle$, $|a,N_p(t)-1,N_s(t)\rangle$, and $|b,N_p(t)-1,N_s(t)+1\rangle$, where N_i refers to the number of photons in field E_i. The dressed-state Hamiltonian in this basis is given by

$$[H(t)]_{\text{dress}} = \begin{bmatrix} 0 & \Omega_p(t) & 0 \\ \Omega_p(t) & \Delta_p & \Omega_s(t) \\ 0 & \Omega_s(t) & \Delta_s \end{bmatrix} , \quad (25)$$

where the constant diagonal matrix corresponding to the energy of the state $|g,N_p(t),N_s(t)\rangle, E_g + N_p(t)\hbar\omega_p + N_s(t)\hbar\omega_s$ has been removed. This Hamiltonian can be diagonalized to obtain the eigenvectors and eigenvalues of the Hamiltonian as a function of time.

We first consider the on-resonance case $\Delta_p = \Delta_s = 0$, when $\Delta t = -2.5\sigma$ (i.e., the Stokes field precedes the pump field by 2.5 pulse durations). Figure 1 shows the Rabi frequencies $\Omega_p(t)$ and $\Omega_s(t)$ and the calculated eigenfunctions of the Hamiltonian. There are three eigenvalues, two of which are symmetrically displaced about zero, and one that is equal to zero for all time. According to the Hamiltonian adiabatic theorem, a state of the system that begins in an eigenvector will remain in this eigenvector as long as the criteria for validity of the Hamiltonian adiabatic theorem remains valid [2]. The eigenvector corresponding to the zero eigenvalue begins at early times with all the population in state g [actually,

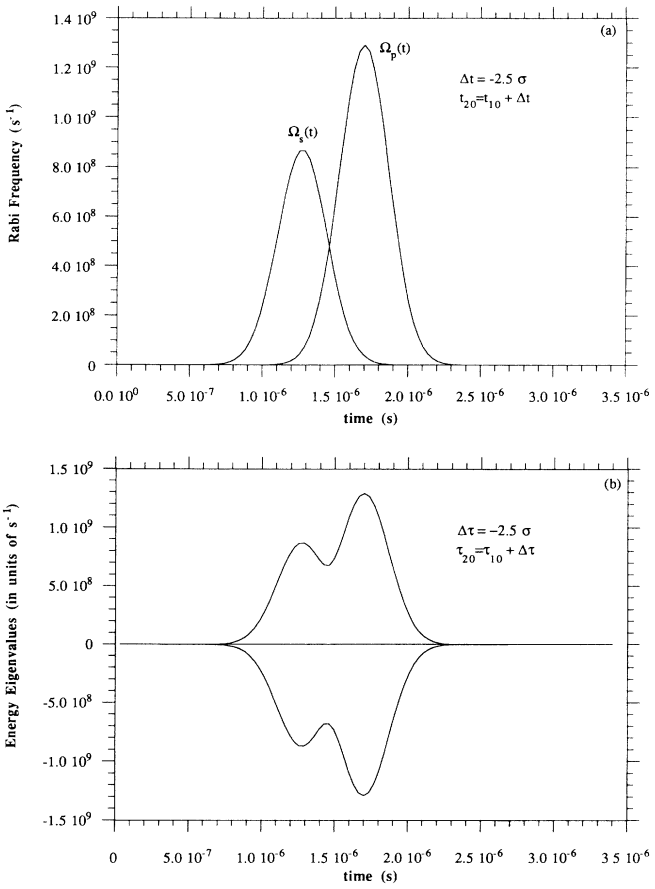

FIG. 1. (a) Rabi frequencies $\Omega_p(t)$ and $\Omega_s(t)$ vs time when $\Delta t = -2.5\sigma$; (b) eigenvalues of the on-resonance Hamiltonian, Eq. (25), when $\Delta t = -2.5\sigma$.

to be more precise we should say in state $|g,N_p(t),N_s(t)\rangle$], and ends with all the population in state b [$|b,N_p(t)-1,N_s(t)+1\rangle$] with no population in state a [$|a,N_p(t)-1,N_s(t)\rangle$] throughout the course of the evolution. The population of levels g, b, and a as a function of time, as obtained from the adiabatic Hamiltonian approximation, is virtually identical to those shown in

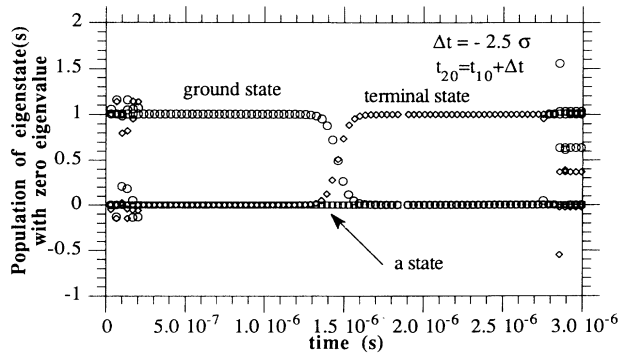

FIG. 2. Populations (diagonal elements) of the "adiabatic" matrices, $\rho_{ij}^{\alpha}(t)$ with eigenvalue $z^{\alpha}(t)=0$ vs time for the off-resonance case $\Delta_p = \Delta_s = 0$, when $\Delta t = -2.5\sigma$.

Fig. 2 (actually, this figure was calculated using the ADMA as discussed below, but the populations obtained with the adiabatic Hamiltonian approximation are indistinguishable from those in Fig. 2 on the scale of the figure).

We now proceed to the ADMA for the on-resonance case and for $\Delta t = -2.5\sigma$. At early times, but times at which the Rabi frequencies $\Omega_p(t)$ and $\Omega_s(t)$ are not vanishingly small (i.e., not too early), the adiabatic matrix $\rho_{ij}^{\alpha}(t)$ with eigenvalue $z^{\alpha}(t)=0$ has all of the population in the ground state. At the end of the dynamical process, this matrix has all of the population in the terminal state. Figure 2 shows the diagonal elements of the "adiabatic" matrices $\rho_{ij}^{\alpha}(t)$ with eigenvalue $z^{\alpha}(t)=0$ as a function of time. For times t, $4.0\times10^{-7}\ \text{s} < t < 2.5\times10^{-6}$ s, only one such eigenvector $\rho_{ij}^{\alpha}(t)$ exists. However, at the very beginning and at the very end of the process, more than one eigenvector has zero eigenvalue, as shown in the figure. When the laser intensities vanish, the Z operator is not only non-normal but the eigenvectors of the $Z(t)$ operator do not span the space, and a spectral decomposition of the operator is no longer possible. Fortunately, the eigenvectors of $Z(t)$ in this case are linearly independent once the Rabi frequencies become finite.

We also numerically calculated the density-matrix equations (17)–(22) to obtain the populations. The population of levels g, b, and a as a function of time is virtually identical to those shown in Fig. 2 (i.e., the smooth curves in the temporal region $4.0\times10^{-7}\ \text{s} < t < 2.5\times10^{-6}$ s, see Ref. [9]), so we shall not reproduce the results here. Note that the excited-state population remains zero throughout the dynamics and therefore complete population transfer without loss occurs.

Calculations for off-resonance fields $\Delta_p=\Delta_s=400$ MHz (the overall transition $g\rightarrow a$ is still on resonance, but the $g\rightarrow b$ and the $b\rightarrow a$ transitions are both off-resonance by 400 MHz) and for $\Delta t=-2.5\sigma$ yield results virtually identical to the on-resonant results. This is because these detunings are small compared with the Rabi frequencies. However, the structure of the "spurious eigenvectors" at early and late times is considerably different, as shown in Fig. 3. These eigenvectors are not truly eigenvectors and therefore we have called them spurious.

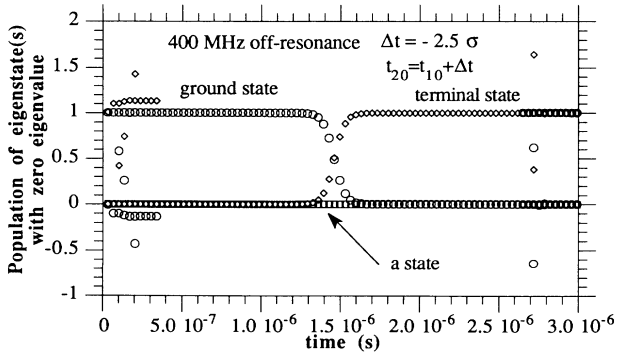

FIG. 3. Populations (diagonal elements) of the "adiabatic" matrices, $\rho_{ij}^{\alpha}(t)$ with eigenvalue $z^{\alpha}(t)=0$ vs time for the on-resonance case $\Delta_p=\Delta_s=400$ MHz, when $\Delta t=-2.5\sigma$.

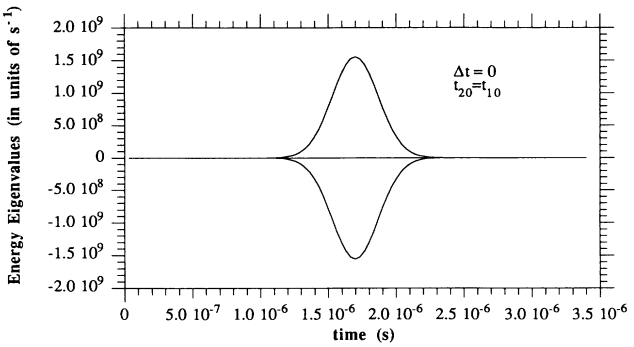

FIG. 4. Eigenvalues of the on-resonance Hamiltonian Eq. (25), when $\Delta t=0$.

When the temporal shift of the Stokes field and the pump field is varied but kept negative, $\Delta t<0$, similarly high transfer efficiencies result provided the Stokes field and the pump field overlap somewhat. As long as $\Delta t<0$, the eigenvector corresponding to the zero eigenvalue begins with all the population in state g and evolves so that all the population is in the terminal state at the completion of the dynamics.

We now consider the on-resonance case $\Delta_p=\Delta_s=0$, when $\Delta t=0$ (the Stokes and the pump pulses are coincident). Note that for this case, the Hamiltonian can be written as a constant matrix time, with a time-dependent scale factor multiplying it (but this is not true of the Z operator, which also contains the decay contribution). Figure 4 shows the calculated eigenfunctions of the Hamiltonian. Again, two eigenvalues are symmetrically displaced about zero, and one is equal to zero for all time. In this case, the eigenfunctions of the Hamiltonian do not vary in time. For the eigenvector with zero eigenvalue, the terminal-state population equals 0.687, the ground-state population is 0.313, and the excited-state population equals 0. It is possible to take a linear combination of eigenvectors of the Hamiltonian that starts in the ground state, but this linear combination will stay in the ground state within the context of the Hamiltonian adiabatic approximation, since the eigenvectors do not change with time for this case. Figure 5 shows the diagonal elements of the adiabatic matrices $\rho_{ij}^{\alpha}(t)$ with eigenvector $z^{\alpha}(t)=0$.

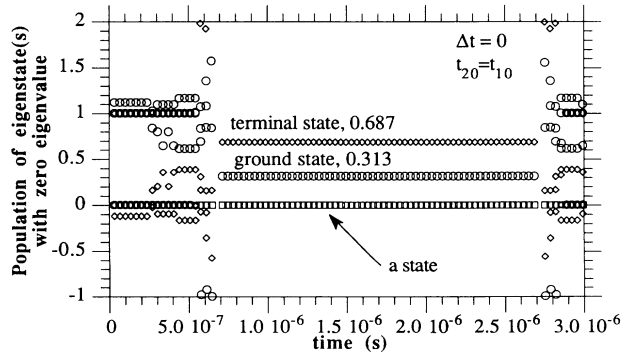

FIG. 5. Populations (diagonal elements) of the "adiabatic" matrices, $\rho_{ij}^{\alpha}(t)$ with eigenvalue $z^{\alpha}(t)=0$ vs time for the on-resonance case $\Delta_p=\Delta_s=0$, when $\Delta t=0$.

Once again, for times t, 4.0×10^{-7} s$<t<2.5\times10^{-6}$ s, only one such eigenvector $\rho_{ij}^{\alpha}(t)$ exists, and the numerical value of the populations in this eigenvalue is equal to the populations obtained from the adiabatic Hamiltonian approximation. Figure 5 shows that at the beginning of time and at the end of the evolution, more than one eigenvector has zero eigenvalue. These eigenvectors are spurious. In these temporal regions, an expansion of the Z operator in the adiabatic eigenvectors $\rho_{ij}^{\alpha}(t)$ is not complete. Figure 6 shows the numerical solution of Eqs. (17)–(22) for this case. Here neither the Hamiltonian nor the Liouville adiabatic approximations is adequate to describe the dynamics. The asymptotic populations of the levels is given by $\rho_{gg}(t$ large$)=0.114$, $\rho_{aa}(t$ large$)=0.252$, $\rho_{bb}(t$ large$)=0$. The system behaves very nonadiabatically. For finite detuning $\Delta_p=\Delta_s=400$ MHz and $\Delta t=0$, the adiabatic Hamiltonian and adiabatic Liouville solutions are very similar to that shown in Fig. 5 for the on-resonance case (the detuning is very small compared to the Rabi frequencies), but the full numerical solution of Eqs. (17)–(22) is quite different from that of the full numerical solution in the on-resonance case, as shown in Fig. 7. The time dependence of the process is sensitive to small changes in the diagonal elements of the Hamiltonian. The asymptotic populations of the levels is given by $\rho_{gg}(t$ large$)=0.140$, $\rho_{aa}(t$ large$)=0.230$, and $\rho_{bb}(t$ large$)=0$.

For $\Delta t>0$, the eigenvector (of the Hamiltonian or of the Z operator) with zero eigenvalue starts off with all the population in the terminal level and evolves to large times with all the population in the ground state. To begin at an early time with all the population in the ground state, a linear combination of eigenvectors with nonzero eigenvalues is necessary. Such an eigenvector of the Z operator decays, i.e., the eigenvalue is complex and the real part of the eigenvalue indicates the decay rate. Hence, for pulse durations large compared with the decay rate, the loss due to decay precludes efficient population transfer to the terminal level. We shall not undertake the analysis of these cases here.

It is of interest to consider the case when the Rabi frequencies are decreased to the point that they become comparable to or smaller than the decay rates γ. Intriguingly, the nature of the eigenvector with zero eigenvalue

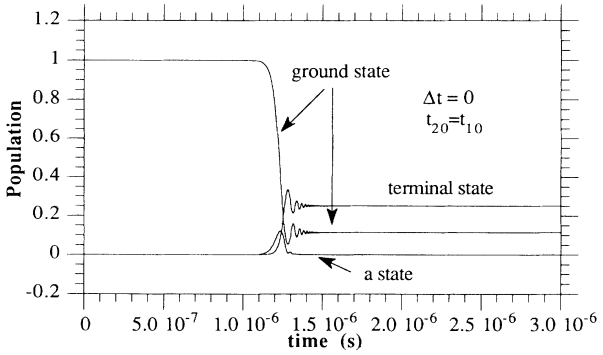

FIG. 6. Numerical solution of the Liouville equations (17)–(22) for $\Delta_p=\Delta_s=0$, when $\Delta t=0$.

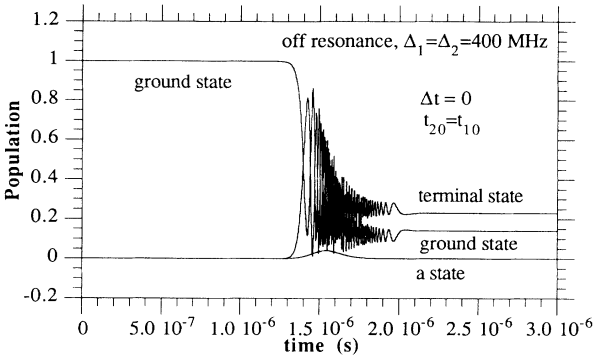

FIG. 7. Numerical solution of the Liouville equations (17)–(22) for $\Delta_p=\Delta_s=400$ MHz, when $\Delta t=0$.

hardly changes if both Rabi frequencies $\Omega_p(t)$ and $\Omega_s(t)$ are simultaneously multiplied by the small factor. For example, reducing the Rabi frequencies $\Omega_p(t)$ and $\Omega_s(t)$ by a factor of 10^4 ($\Omega_{p,0}=12.9\times10^5$ and $\Omega_{s,0}=8.7\times10^5$ s^{-1}) and recalculating the probabilities for on-resonance and off-resonance $\Delta t<0$ cases shown in Figs. 2 and 3 yields results that are almost identical to those in the figures. Now, however, the criteria for validity of the adiabatic approximation are not met, and the numerical calculation looks nothing like the ADMA results.

We now introduce decay of state b, the terminal state of the Raman transition, and redo the off-resonance $\Delta t=-2.5\sigma$ case shown in Fig. 3. We let level b decay out of the three-level manifold with decay rate $\gamma_{\text{out},b}=1.0\times10^6$ s^{-1}. The ADMA results now decay in time. The eigenvalue $z^1(t)$ of the eigenstate of the Liouville operator that evolves from the ground state $\rho_{ij}^1(t)$ develops a decaying component; the real part of the eigenvalue becomes negative as the admixture of state b in the eigenstate becomes significant, as shown in Fig. 8, but the imaginary part remains zero. The diagonal elements of the adiabatic matrix $\rho_{ii}^1(t)$ is shown in Fig. 9. The full adiabatic density matrix is given by

$$\rho_{ij}(t)=\rho_{ij}^1(t)\exp\left[\int^t z^1(t')dt'\right], \tag{26}$$

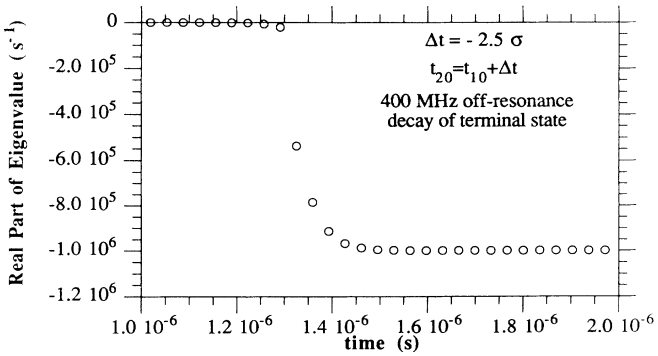

FIG. 8. Real part of the eigenvalue $z^1(t)$ of the eigenstate of the Liouville operator that evolves from the ground state vs time for $\Delta_p=\Delta_s=400$ MHz, when $\Delta t=-2.5\sigma$ and state b decays outs of the three-level manifold.

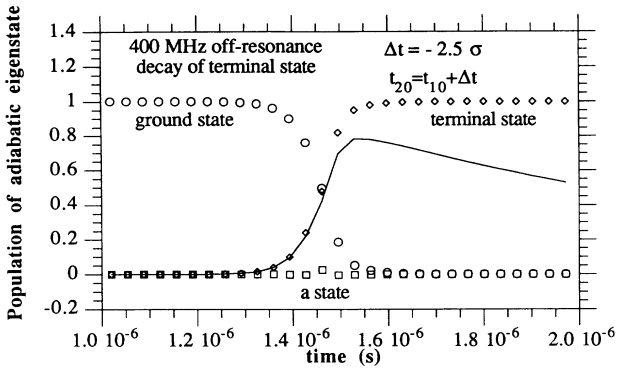

FIG. 9. Populations (diagonal elements) of the adiabatic density matrix evolving from the ground state for $\Delta_p=\Delta_s=400$ MHz, when $\Delta t=-2.5\sigma$ and state b decays out of the three-level manifold. The circles, squares, and diamonds indicate the populations $\rho_{ii}^{1}(t)$, and the solid curve indicates the full adiabatic population $\rho_{bb}(t)$.

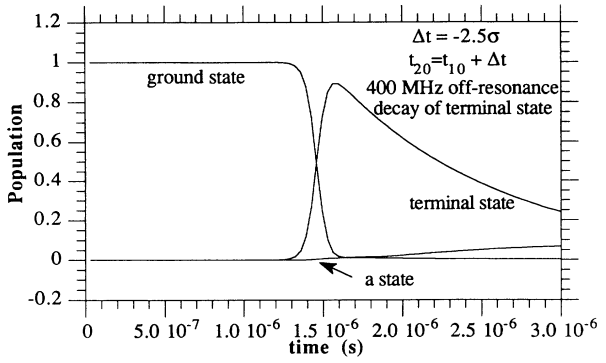

FIG. 10. Numerical solution of the Liouville equations (17)–(22) for $\Delta_p=\Delta_s=400$ MHz, when $\Delta t=-2.5\sigma$ and state b decays out of the three-level manifold.

and the population of state b decays in time due to the exponential factor, as shown by the solid curve in Fig. 9, i.e., the reduction of $\rho_{aa}^{1}(t)$ in obtaining $\rho_{aa}(t)$ is due to the exponential factor in Eq. (26). Figure 10 shows the populations versus time obtained from the full numerical solution of the density-matrix equations (17)–(22). Clearly, the comparison of the ADMA and the numerical results is very good (note the different time scales of Figs. 9 and 10). The numerical results do have a feature that is not present in the ADMA for times larger than 2×10^{-6} s. The ground state is somewhat repopulated for times 2×10^{-6} s $<t<3\times10^{-6}$ s by the optical coupling of the a state and the g state, and the repopulation terminates for times larger than 3×10^{-6} s because the optical fields are too small beyond this time. This repopulation does not occur in the ADMA results; it constitutes a nonadiabatic process. Nevertheless, the ADMA accounts for most of the dynamics in this case.

We should mention that the ADMA can be used to obtain the density matrix for problems involving cw electromagnetic fields coupled with atomic and molecular states when spontaneous emission or other decay mechanisms are included in the description. In this case, the eigenstate of the Liouville operator with zero eigenvalue is the desired cw density matrix. An algorithm to obtain only this eigenstate of the Liouville operator is easily implemented, and this is a simple method for numerically obtaining the cw density matrix.

IV. SUMMARY AND CONCLUSION

The Liouville operator with decay is non-normal. Hence, there is no general theorem that ensures that the eigenvalues of the Liouville operator will be linearly independent and span the space of the density matrix. If the eigenvectors of the Liouville operator are linearly independent, the time rate of change of the Liouville operator is small, and the **D** matrix of Appendix B is nonsingular, the ADMA [Eq. (16)] can be used to calculate the rate of change of the coefficients of the adiabatic matrices appearing in the expansion of the density matrix. The linear independence (or dependence) of the eigenvectors of the Liouville operator may vary during the temporal evolution of the problem. Hence, no guarantee of meeting the conditions for validity of the ADMA exists, just as no guarantee of meeting the conditions for validity of the adiabatic Hamiltonian approximation exists. In the examples presented, the eigenvectors of the Liouville operator are linearly independent once the Rabi frequencies become nonvanishing. Asymptotically, when the Rabi frequencies vanish, the eigenvectors are no longer linearly independent. Nevertheless, the ADMA was successfully used to determine the dynamics for the case in which the Stokes pulse preceded the pump pulse. The results for the case of simultaneous Stokes and pump pulses $\Delta t=0$ indicate that caution should be used in attempting to apply the ADMA. For this case, the adiabatic Hamiltonian approximation and the ADMA both fail to describe the dynamics. Hence, even when the eigenvectors of the Liouville operator are linearly independent, the ADMA may fail to describe the dynamics correctly.

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APPENDIX A

We show that the $Z(t)$ matrix is normal when the decay matrix vanishes, and is non-normal when a decay matrix with the conditions specified in Eqs. (13) and (14) is included. We consider a real Hamiltonian matrix. Hence, the Hermitian condition $H=H^{\dagger}$ yields $H_{ij}=H_{ji}$. We form $ZZ^{\dagger}$:

$$Z_{ij,kl}Z^{\dagger}_{kl,nm}=\left[-\frac{i}{\hbar}\{[H(t)]_{ik}\delta_{lj}-\delta_{ij}[H(t)]_{lj}\}-\Gamma_{ijkl}\right]\left[\frac{i}{\hbar}\{[H(t)]_{nk}\delta_{lm}-\delta_{nk}[H(t)]_{lm}\}-\Gamma_{nmkl}\right],$$

$$=\left[\frac{1}{\hbar^2}\{[H(t)]_{nk}[H(t)]_{ik}\delta_{jm}-[H(t)]_{in}[H(t)]_{jm}\}-\frac{1}{\hbar^2}\{[H(t)]_{m}[H(t)]_{ni}-\delta_{ni}[H(t)]_{lj}[H(t)]_{lm}\}\right.$$

$$\left.-\frac{i}{\hbar}\{\Gamma_{ijkm}[H(t)]_{nk}-\Gamma_{ijnl}[H(t)]_{lm}\}+\frac{i}{\hbar}\{[H(t)]_{ik}\Gamma_{nmkj}-[H(t)]_{lj}\Gamma_{nmil}\}+\Gamma_{ijkl}\Gamma_{nmkl}\right], \tag{A1}$$

$$Z^{\dagger}_{lj,kl}Z_{kl,nm}=\left[\frac{i}{\hbar}\{[H(t)]_{ki}\delta_{jl}-\delta_{ki}[H(t)]_{il}\}-\Gamma_{klij}\right]\left[-\frac{i}{\hbar}\{[H(t)]_{kn}\delta_{ml}-\delta_{kn}[H(t)]_{ml}\}-\Gamma_{klnm}\right],$$

$$=\left[\frac{1}{\hbar^2}\{[H(t)]_{ki}[H(t)]_{kn}\delta_{mj}-[H(t)_{ni}[H(t)]_{mj}\}-\frac{1}{\hbar^2}\{[H(t)]_{jm}[H(t)]_{in}-\delta_{ni}[H(t)]_{jl}[H(t)]_{ml}\}\right.$$

$$\left.+\frac{i}{\hbar}\{\Gamma_{kmij}[H(t)]_{kn}-\Gamma_{nlij}[H(t)]_{ml}\}-\frac{i}{\hbar}\{[H(t)]_{ki}\Gamma_{kjnm}-[H(t)]_{jl}\Gamma_{ilnm}\}+\Gamma_{klij}\Gamma_{klnm}\right]. \tag{A2}$$

Using the Hermitivity of the Hamiltonian, Eq. (A2) yields

$$Z^{\dagger}_{ij,kl}Z_{kl,nm}=\left[\frac{1}{\hbar^2}\{[H(t)]_{nk}[H(t)]_{ik}\delta_{jm}-[H(t)]_{in}[H(t)]_{jm}\}-\frac{1}{\hbar^2}\{[H(t)]_{mj}[H(t)]_{ni}-\delta_{ni}[H(t)]_{ij}[H(t)]_{lm}\}\right.$$

$$\left.+\frac{i}{\hbar}\{\Gamma_{kmij}[H(t)]_{nk}-\Gamma_{nlij}[H(t)]_{lm}\}-\frac{i}{\hbar}\{[H(t)]_{ik}\Gamma_{kjnm}-[H(t)]_{jl}\Gamma_{ilnm}\}+\Gamma_{klij}\Gamma_{klnm}\right]. \tag{A3}$$

If the Γ matrix vanishes, it is clear that $ZZ^{\dagger}=Z^{\dagger}Z$, as is readily seen by comparing (A1) with (A3). Otherwise, using the relationships (11) and (12) and performing the necessary algebra, it is easily demonstrated that the Z matrix is non-normal.

APPENDIX B

We calculate the quantity $\langle\rho^{\gamma}(t)|(d/dt)\rho^{\alpha}(t)\rangle$ in terms of $\langle\rho^{\beta}(t)|d\mathbf{Z}(t)/dt|\rho^{\alpha}(t)\rangle$ and dz^{α}/dt. To do so we take the time derivative of Eq. (5) to obtain

$$\frac{dZ_{ijkl}(t)}{dt}\rho^{\alpha}_{kl}(t)+Z_{ijkl}(t)\frac{d}{dt}\rho^{\alpha}_{kl}(t)=\frac{dz^{\alpha}(t)}{dt}\rho^{\alpha}_{ij}(t)+z^{\alpha}(t)\frac{d}{dt}\rho^{\alpha}_{ij}(t)\ , \tag{B1}$$

or, upon rearranging,

$$[Z_{ijkl}(t)-\delta_{kl}\delta_{lj}z^{\alpha}(t)]\frac{d}{dt}\rho^{\alpha}_{kl}(t)=\frac{dz^{\alpha}(t)}{dt}\rho^{\alpha}_{ij}(t)-\frac{dZ_{ijkl}(t)}{dt}\rho^{\alpha}_{kl}(t)\ . \tag{B2}$$

Taking the inner product of this equation with $\rho^{\beta}(t)$ we obtain

$$\left\langle\rho^{\beta}(t)\left|[\mathbf{Z}(t)-\mathbf{1}z^{\alpha}(t)]\right|\frac{d}{dt}\rho^{\alpha}(t)\right\rangle=\langle\rho^{\beta}(t)|\rho^{\alpha}(t)\rangle\frac{dz^{\alpha}(t)}{dt}-\left\langle\rho^{\beta}(t)\left|\frac{d\mathbf{Z}(t)}{dt}\right|\rho^{\alpha}(t)\right\rangle\ . \tag{B3}$$

Upon using the definition of Hermitian transpose and rearranging, we find

$$\left\langle[\mathbf{Z}(t)]^{\dagger}\rho^{\beta}(t)\left|\frac{d}{dt}\rho^{\alpha}(t)\right\rangle-z^{\alpha}(t)\left\langle\rho^{\beta}(t)\left|\frac{d}{dt}\rho^{\alpha}(t)\right\rangle\right.\right.=\langle\rho^{\beta}(t)|\rho^{\alpha}(t)\rangle\frac{dz^{\alpha}(t)}{dt}-\left\langle\rho^{\beta}(t)\left|\frac{d\mathbf{Z}(t)}{dt}\right|\rho^{\alpha}(t)\right\rangle\ . \tag{B4}$$

Now, $[\mathbf{Z}(t)]^{\dagger}\rho^{\beta}(t)$ can be written in terms of the eigenvectors of the Z operator, provided the eigenvectors are linearly independent, and therefore

$$[\mathbf{Z}(t)]^{\dagger}\rho^{\beta}(t)=C_{\beta\gamma}(t)\rho^{\gamma}(t)\ . \tag{B5}$$

Upon substituting this into Eq. (B4) we obtain

$$\{[C_{\beta\gamma}(t)]^{*}-z^{\alpha}(t)\delta_{\beta\gamma}\}\left\langle\rho^{\gamma}(t)\left|\frac{d}{dt}\rho^{\alpha}(t)\right\rangle\right.=\langle\rho^{\beta}(t)|\rho^{\alpha}(t)\rangle\frac{dz^{\alpha}(t)}{dt}-\left\langle\rho^{\beta}(t)\left|\frac{d\mathbf{Z}(t)}{dt}\right|\rho^{\alpha}(t)\right\rangle\ . \tag{B6}$$

Defining the $\mathbf{D}$ matrix,

$$D_{\beta\gamma}(\alpha;t)=\{[C_{\beta\gamma}(t)]^{*}-z^{\alpha}(t)\delta_{\beta\gamma}\}\ , \tag{B7}$$

we find that

$$\left\langle \rho^{\gamma}(t) \left| \frac{d}{dt}\rho^{\alpha}(t) \right\rangle = [D_{\gamma\beta}(\alpha;t)]^{-1} \times \left[\langle \rho^{\beta}(t)|\rho^{\alpha}(t)\rangle \frac{dz^{\alpha}(t)}{dt} - \left\langle \rho^{\beta}(t) \left| \frac{d\mathbf{Z}(t)}{dt} \right| \rho^{\alpha}(t) \right\rangle \right] , \quad \text{(B8)}$$

provided that the inverse of the **D** matrix exists. This proviso is similar to the proviso mentioned after Eq. (9) in connection with the adiabatic Hamiltonian approximation, that the eigenvalues are distinct.

As mentioned in the text, an alternative to Eq. (13) can be obtained if instead of taking the inner product of Eq. (7) with $\rho^{\beta}(t)$, we take the inner product with the eigenvectors of $Z^{\dagger}$ to obtain

$$\frac{d[a(t)]_{\gamma}}{dt} = -\sum_{\alpha}\sum_{\beta} \left[\langle \eta^{\beta}(t)|\rho^{\gamma}(t)\rangle^{-1} \left\langle \eta^{\beta}(t) \left| \frac{d}{dt}\rho^{\alpha}(t) \right\rangle \exp\left[\int^{t} [z^{\alpha}(t')-z^{\gamma}(t')]dt' \right] [a(t)]_{\alpha} \right] , \quad \text{(B9)}$$

where $\eta^{\beta}(t)$ is an eigenvector of $Z^{\dagger}$,

$$[\mathbf{Z}(t)]^{\dagger}\eta^{\beta}(t) = \zeta^{\alpha}(t)\eta^{\beta}(t) . \quad \text{(B10)}$$

To calculate the quantity $\langle \eta^{\beta}(t)|(d/dt)\rho^{\alpha}(t)\rangle$, we take the inner product of Eq. (B2) with $\eta^{\beta}(t)$ to obtain

$$\{[\zeta^{\beta}(t)]^{*} - z^{\alpha}(t)\} \left\langle \eta^{\beta}(t) \left| \frac{d}{dt}\rho^{\alpha}(t) \right\rangle = \langle \eta^{\beta}(t)|\rho^{\alpha}(t)\rangle \frac{dz^{\alpha}(t)}{dt} - \left\langle \eta^{\beta}(t) \left| \frac{d\mathbf{Z}(t)}{dt} \right| \rho^{\alpha}(t) \right\rangle ,$$

and hence,

$$\left\langle \eta^{\gamma}(t) \left| \frac{d}{dt}\rho^{\alpha}(t) \right\rangle = [D_{\gamma\beta}(\alpha;t)]^{-1} \times \left[\langle \eta^{\beta}(t)|\rho^{\alpha}(t)\rangle \frac{dz^{\alpha}(t)}{dt} - \left\langle \eta^{\beta}(t) \left| \frac{d\mathbf{Z}(t)}{dt} \right| \rho^{\alpha}(t) \right\rangle \right] ,$$

where $D_{\gamma\beta}(\alpha;t) = \{[\zeta^{\beta}(t)]^{*} - z^{\alpha}(t)\}\delta_{\gamma\beta}$. The proviso is now much more similar in form to that of the adiabatic Hamiltonian approximation. Of course, one must now calculate the eigenvectors of Z and $Z^{\dagger}$ to test the validity of the approximation.

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