A generalized approach to the control of the evolution of a molecular system

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The theory of active control of molecular motion by use of shaped laser pulses is developed emphasizing the role of interference and using thermodynamic analogies. Attention is focused on the control of the dynamics in a system with n states coupled by radiation, and the phase relations which generate particular control schemes are derived. Among the new results reported is an optimal control scheme which constrains the value of the phase. The n-state model can be considered to represent a molecule with n electronic potential energy surfaces and an arbitrary number of degrees of freedom or as the skeleton spectrum of system where each level in the spectrum can be associated with a specific set of quantum numbers for all of the degrees of freedom. We show how the control of the dynamics of an n-state molecule can be represented in terms of the control of the dynamics of a precisely defined surrogate fewer state system. This reduction is illustrated by use of a surrogate two state system to describe the dynamics of population transfer in a three state system. © *1996 American Institute of Physics.* [S0021-9606(96)02314-0]

I. INTRODUCTION

Finding ways to control the selection of products of a chemical reaction is, arguably, the essence of chemistry. The intensive studies of synthetic methodology carried out over the past two centuries have led to the development of numerous methods for generating desired chemical species. Most of these methods rely on amplifying the yield of the desired product by adjusting the equilibrium between reactants that do and do not form the desired species so as to favor the former, or by adjusting the rates of competing reactions which form different species from the same reactant so as to enhance the formation of the desired species, or by combinations of these methods. All of these methods are fundamentally macroscopic in the sense that they depend on the statistical, incoherent, properties of a many molecule system, e.g., collisions between reactant molecules and between reactant and solvent molecules. In contrast, this paper discusses the influence on product selectivity generated by active control of the molecular dynamics and, more generally, the active control of the temporal evolution of complex molecular systems.

Much of the study of active control of quantum molecular dynamics has been stimulated by advances in laser technology, in molecular spectroscopy, and in our understanding of molecular dynamics. The developments in laser technology we refer to include methods for the generation of very short pulses, of shaped pulses, of pulses with a well-defined phase relationship, of very pure monochromatic light fields, and of very high intensity light fields. The application of these and other laser technologies to molecular spectroscopy has yielded both a wealth of information concerning molecular potential energy surfaces and an increased awareness that interference effects can be used to guide system evolution. Simply put, it is now recognized that the dynamics of a strongly coupled light–matter system can be influenced by alteration of the temporal and spectral distributions of the radiation coupled to the system. The underlying principle of the new approach to controlling product selectivity in a reaction is different from that used in earlier attempts to achieve ‘‘bond selective chemistry.’’ The new approach is based on exploitation of quantum interference effects whereas the old approaches are, typically, based on trying to create a situation in which the rate of bond breakage will greatly exceed the rate of transfer of energy from the excited bond to the rest of the molecule.

Two different ways of using quantum mechanical interference to control product selectivity in a chemical reaction have been proposed.[1–8]

Suppose there are two independent excitation pathways between a specified initial state of a molecule and a specified final state of the products; these might be transitions involving absorption of one and three photons, respectively.[2,3] Quantum theory requires that the probability of forming the specified product is proportional to the square of the sum of the transition amplitudes for the two pathways; because the amplitudes can have different signs, the magnitude of that probability is determined by the extent of their interference. For example, when one- and three-photon transitions generate the independent pathways between the initial and final states, the extent of interference can be controlled by altering the relative phase of the two excitation sources. The situation is analogous to the formation of a diffraction pattern in a two-slit experiment in that the excited state amplitude in each molecule is the sum of the excitation amplitudes generated by two routes which are not distinguished from each other by measurement. Using this method, Gordon and coworkers have reported an example of control of the population of a level in HCl, and also of the ratio of concentrations of the products in the branching photodissociation of HI to form HI^+ and I^+.[4,5] These results provide experimental confirmation of the Brumer–Shapiro control scheme.[2,3]

The selectivity of product formation in a chemical reaction can also be influenced via interference in the time domain.[6] In the simplest case, when only two electronic potential energy surfaces are involved, an incident (first) pulse of light transfers probability amplitude from the electronic ground state to the excited state, creating a coherent wave packet on the excited state potential energy surface. That wave packet then evolves on the excited state potential energy surface. A second pulse of light, incident after an interval t, will, depending on the position and momentum of the wave packet, select a particular reaction channel. This control scheme has been demonstrated[7] with respect to the competition between ionization and dissociative ionization of Na_2, namely, $Na_2 \rightarrow Na_2^+ + e$ vs $Na_2 \rightarrow Na^+ + Na$, by varying the time delay between the first and second pulses. The result obtained is an experimental confirmation of the Tannor–Rice control scheme.[6]

It is also possible to modulate the product yield via interference between two impulsive excitation pulses with a variable time delay between them.[8] In this case the second pulse of the sequence, whose phase is locked to that of the first one, also creates amplitude in the excited electronic state, which is in superposition with the initial, propagated, amplitude. This intramolecular superposition of amplitudes is subject to interference; whether the interference is constructive or destructive, giving rise to larger or smaller excited state population for a given interpulse delay, depends on the optical phase difference between the two pulses and on the detailed nature of the evolution of the initial amplitude. This situation is also analogous to a two-slit experiment. The method described, which is a variant of the Tannor–Rice scheme, has been used to control the population of a level of I_2.[8] The success of this experiment confirms that it is possible to control population flow with interference that is local in time.

In principle, the methods available for guiding the evolution of a quantum system by coupling it to an external field are not restricted to the use of a time-independent field or a simple pulse sequence. If the goal to be achieved is, say, maximization of the amount of a product in a reaction, the design of the external field which accomplishes the goal is an inverse problem: Given the target product and the quantum mechanical equations of motion, calculate the guiding field which is required. The solution to this inverse problem is very likely not unique, which for the case under consideration is a strength since it is then plausible that one of the possible guide fields is more easily generated than others.

The methodology used in calculations of the field required to maximize a particular product yield is optimal control theory.[9–11] It is usually found that the optimal guiding field has a complicated spectral and temporal structure whose efficiency is determined by the extent of interference between the amplitudes associated with its different spectral and temporal components. In the model problems studied to date it is predicted that the use of an optimal guide field can increase the desired product yield by many orders of magnitude relative to the yield from a two-pulse control field.[12]

To facilitate understanding of possible strategies for directing molecular evolution, it is important to study the generic aspects of control of both population and energy transfer between potential energy surfaces. For example, if one wishes to increase the yield of a chemical species, one has to understand how to control population transfer on one electronic potential energy surface and population transfer from one surface to another surface. If, on the other hand, one wishes to coherently excite or to de-excite the motion of the molecule on the ground electronic state potential energy surface, it is necessary to control the energy flow within the molecule. It is worth noting that it is possible to combine the control processes for several elementary processes to achieve quite elaborate control schemes, including constraints on the dynamics, e.g., control of radiation damage.[13,14]

In principle, the general formalism for designing fields that optimally control particular aspects of the molecular dynamics is applicable to systems with an arbitrary number of degrees of freedom. However, in practice, the utility and accuracy of the application of the formalism to an n-degree of freedom system is limited by lack of knowledge of the system Hamiltonian (e.g., the complete Born–Oppenheimer potential energy surfaces and the regions where the Born–Oppenheimer approximation is inapplicable), by the complexity of the system spectrum when n is large, and by the difficulty of finding a global minimum in n degrees of freedom. Accordingly, it is of considerable interest to develop a reduced description of the dynamics, which focuses attention on a subset of the most important degrees of freedom and treats the other degrees of freedom as a background to which the subset is coupled. This reduction is useful only if it suggests accurate approximations which permit analysis of the dynamics of the subsystem with weak perturbations from the background. Note that the preceding argument has been phrased in terms of the dynamics of a complicated molecule with n degrees of freedom, but it also applies to a molecule embedded in a solvent.

In this paper we present an overview of a formalism for active control of molecular dynamics that differs from previous formulations in its emphasis on the relationship between the role of interferences and the quasithermodynamic character of the control process. We also present a reduced space formalism for the design of control fields and a simple test of that formalism.

II. BACKGROUND INFORMATION: THE TWO STATE SYSTEM

To provide background for our analysis of the n-state system, in this section we sketch the formalism for active control of a molecule coupled to the radiation field when only two electronic states of the molecule play roles in the reaction dynamics, e.g., the ground electronic state and the first excited electronic state. Details of the analysis can be found elsewhere.[15]

The density operator describing the state of the system can be represented as[16]

$$\rho=\rho_{\mathbf{g}}\otimes\mathbf{P_g}+\rho_{\mathbf{e}}\otimes\mathbf{P_e}+\rho_{\mathbf{i}}\otimes\mathbf{S}_{+}+\rho_{\mathbf{i}}^{+}\otimes\mathbf{S}_{-}, \tag{2.1}$$

where $\rho_{\mathbf{j}}$ is the density operator for state $\mathbf{j}\in\mathbf{g}$, $\mathbf{e}$ ($\mathbf{g}$ refers to the ground state and $\mathbf{e}$ to the excited state), the symbol $\otimes$ denotes the tensor product, $\mathbf{P_j}$ is a projection operator on surface $\mathbf{j}\in\mathbf{g}$, $\mathbf{e}$, and the $\mathbf{S}_{\pm}$ are raising and lowering operators that transfer amplitude from one surface to another. The first two terms in Eq. (2.1) represent the state of the molecules with population on the ground and excited surfaces, while the last two terms represent the electronic coherence induced by the radiation field. It is convenient to represent the Hamiltonian of the system as the sum of internal Hamiltonians, $\mathbf{H_0}=\mathbf{H_g}\otimes\mathbf{P_g}+\mathbf{H_e}\otimes\mathbf{P_e}$, and a radiative coupling interaction term which control the transfer of amplitude between the two electronic manifolds,

$$\mathbf{V_t}=-\mu\otimes\{\mathbf{S}_{+}\epsilon(t)+\mathbf{S}_{-}\epsilon^{*}(t)\}, \tag{2.2}$$

where μ is the transition dipole moment operator and $\epsilon(t)$ represents a semiclassical time dependent radiation field. It is via control of the spectral composition, the time profile of the field amplitude and the phase of the field that we can control the evolution of the molecule. When intramolecular coupling of electronic manifolds is included in the Hamiltonian, radiationless transitions within the molecule can be included in the group of dynamical processes to be controlled.

The evolution of the molecule is described by the generalized Liouville–von Neumann equation[16]

$$\frac{\partial\rho}{\partial t}=-\frac{i}{\hbar}[\mathbf{H},\rho]+\mathbf{L}_D\rho, \tag{2.3}$$

where $\mathbf{L}_D$ is an operator representing the dissipative coupling of the system to background states. Equation (2.3) describes the dynamics of an open quantum mechanical system under the assumption that the evolution operator defines a dynamical semigroup.[17–20] The source of the dissipative term $\mathbf{L}_D\rho$ is the reduction of the combined system and bath dynamics to the dynamics of the system only. The semigroup formalism provides an explicit form for the dissipative operator $\mathbf{L}_D$, but we shall not need that detailed form for most of our considerations. Note that the first term in Eq. (2.3) describes the unitary dynamics supported by the Hamiltonian.

The mechanism by which control of the dynamical evolution of our model molecule is achieved is the alteration, by variation of the external field, of population, and energy transfers between its two electronic states. This mechanism is, in a sense, analogous to the control of transformation of the equilibrium states of a macroscopic system by altering population and energy transfers between macroscopic states via variation of external parameters. Accordingly, it is interesting to examine the exchange of energy between the molecule and the external field, and to relate that energy exchange to alteration in the populations of the molecular states. The rate of change of energy is

$$\frac{d\langle E\rangle}{dt}=\left\langle\frac{\partial\mathbf{H}}{\partial t}\right\rangle+\langle\mathbf{L}_D^{*}\mathbf{H}\rangle, \tag{2.4}$$

since $[\mathbf{H},\,\mathbf{H}]=0$. Eq. (2.4) is a version of the first law of thermodynamics,[15,21–23] written in terms of the time rate of change of the energy and the power

$$P=\left\langle\frac{\partial\mathbf{H}}{\partial t}\right\rangle, \tag{2.5}$$

which is the time derivative of the work, and the heat flow

$$\mathbf{J}=\frac{dQ}{dt}=\langle\mathbf{L}_D^{*}\mathbf{H}\rangle. \tag{2.6}$$

With these definitions, the power absorbed from the field into the system becomes

$$\begin{aligned}P&=-\left\langle\mu\otimes\left\{\mathbf{S}_{+}\frac{\partial\epsilon}{\partial t}+\mathbf{S}_{-}\frac{\partial\epsilon^{*}}{\partial t}\right\}\right\rangle\\&=-2\,\mathrm{Re}\left\{\langle\mu\otimes\mathbf{S}_{+}\rangle\frac{\partial\epsilon}{\partial t}\right\}.\end{aligned} \tag{2.7}$$

In Eq. (2.7), $\langle\mu\otimes\mathbf{S}_{+}\rangle$ is the expectation value of the instantaneous transition dipole moment; variation of its value provides the means for controlling the molecular evolution.

For the two state system under consideration it can be shown that the flow of population from the ground state satisfies

$$\frac{dN_g}{dt}=-\frac{i}{\hbar}\langle\mu\otimes\{\mathbf{S}_{+}\epsilon-\mathbf{S}_{-}\epsilon^{*}\}\rangle=\frac{2}{\hbar}\,\mathrm{Im}\{\langle\mu\otimes\mathbf{S}_{+}\rangle\epsilon\} \tag{2.8}$$

when nonradiative couplings between the ground and excited state surfaces are ignored, i.e., $\mathbf{L}_D^{*}\mathbf{P}_g=0$. The flow of energy from the ground state can also be calculated when it is assumed that the rate of electronic dephasing is small, i.e., $\mathbf{L}_D^{*}\mathbf{P}_g\approx 0$ and/or the rate of pure vibrational dephasing is small, i.e., $\mathbf{L}_D^{*}\mathbf{H}_g\approx 0$. These conditions apply when the rate of relaxation to equilibrium is small relative to the rate of loss of phase coherence. Under these conditions

$$\frac{dE_g}{dt}=\frac{2}{\hbar}\,\mathrm{Im}(\langle\mu\mathbf{H_g}\otimes\mathbf{S}_{+}\rangle\varepsilon) \tag{2.9}$$

and

$$\mathbf{F}=2\,\mathrm{Re}\left(\left\langle\frac{\partial\mu}{\partial\mathbf{x}}\otimes\mathbf{S}_{+}\right\rangle\varepsilon\right), \tag{2.10}$$

where $\mathbf{x}$ represents the internal coordinates of the molecule, is the internal force which the electromagnetic field exerts on the molecule.

Molecular transfer processes can be promoted either by controlling the field $\varepsilon(t)$ or its time derivative. We note that the transfer equations (2.8) and (2.9) have similar structure, namely, each contains the imaginary part of a product of a molecular expectation value $\langle \mathbf{X} \rangle$ and the field ε. Equation (2.7) has an analagous structure; transfer is controlled by the real part of the product of a molecular expectation value and the time derivative of the field. For convenience we rewrite Eq. (2.8) in the form

$$\frac{dN_g}{dt} = \frac{2}{\hbar} |\langle \mu \otimes \mathbf{S}_+ \rangle||\varepsilon| \sin(\phi_\mu + \phi_\varepsilon), \tag{2.11}$$

where ϕ_μ is the phase angle of the instantaneous dipole moment and ϕ_ε is the phase angle of the radiation field. The overall phase angle in Eq. (2.11) is the sum of the phase angle of the induced polarization of the molecule and the phase angle of the polarization of the light. In a similar way

$$P = -2|\langle \mu \otimes \mathbf{S}_+ \rangle| \left| \frac{\partial \varepsilon}{\partial t} \right| \cos(\phi_\mu + \phi_{\dot{\varepsilon}}) \tag{2.12}$$

and

$$\frac{dE_g}{dt} = \frac{2}{\hbar} |\langle \mu \mathbf{H_g} \otimes \mathbf{S}_+ \rangle||\varepsilon| \sin(\phi_{\mu \mathbf{H}} + \phi_\varepsilon), \tag{2.13}$$

where $\phi_{\mu \mathbf{H}}$ is the phase angle of $\langle \mu \mathbf{H_g} \otimes \mathbf{S}_+ \rangle$. We also have

$$\mathbf{F} = 2 \left| \left\langle \frac{\partial \mu}{\partial \mathbf{x}} \otimes \mathbf{S}_+ \right\rangle \right| |\varepsilon| \cos(\phi_{\mu'} + \phi_\varepsilon), \tag{2.14}$$

where $\phi_{\mu'}$ is the phase angle of $\langle \partial\mu/\partial\mathbf{x} \otimes \mathbf{S}_+ \rangle$. Equations (2.11)–(2.14) clearly show that the sum of the phase angles generates the following possibilities for control of the dynamics:

$$\begin{aligned} \phi_\mu + \phi_{\dot{\varepsilon}} &= 0 \quad \text{for maximum energy transfer} \\ &= \pi \quad \text{for maximum energy emission,} \end{aligned} \tag{2.15}$$

$$\begin{aligned} \phi_\mu + \phi_\varepsilon &= \pi/2 \quad \text{for maximum positive population transfer} \\ &= -\pi/2 \quad \text{for maximum negative population transfer,} \end{aligned} \tag{2.16}$$

$$\begin{aligned} \phi_{\mu \mathbf{H}} + \phi_\varepsilon &= \pi/2 \quad \text{for maximum energy transfer to the ground state surface} \\ &= -\pi/2 \quad \text{for maximum energy removal from the ground state surface,} \end{aligned} \tag{2.17}$$

$$\begin{aligned} \phi_{\mu'} + \phi_\varepsilon &= 0 \quad \text{for maximum positive force} \\ &= \pi \quad \text{for maximum negative force.} \end{aligned} \tag{2.18}$$

Control of population transfer using the relation displayed in Eq. (2.16) has been demonstrated experimentally by Sherer *et al.*[8] In this experiment gaseous I_2 was irradiated with two short (femtosecond) laser pulses; the first pulse transfers population from the ground state potential energy surface to the excited state potential energy surface, thereby creating an instantaneous transition dipole moment. The instantaneous transition dipole moment is modulated by the molecular vibration on the excited state surface. At the proper instant, when the instantaneous transition dipole moment expectation value is maximized, a second pulse is applied. The direction of population transfer is then controlled by changing the phase of the second pulse relative to that of the first pulse.

In contrast with the conditions (2.15)–(2.18), when we wish to prevent transfer of population or energy the phase angle relations are:

$$\phi_\mu + \phi_{\dot{\varepsilon}} = \pm \pi/2 \quad \text{for zero total energy transfer,} \tag{2.19}$$

$$\phi_\mu + \phi_\varepsilon = 0, \pi \quad \text{for zero population transfer,} \tag{2.20}$$

$$\phi_{\mu \mathbf{H}} + \phi_\varepsilon = 0, \pi \quad \text{for zero change in the ground state energy,} \tag{2.21}$$

$$\phi_{\mu'} + \phi_\varepsilon = \pm \pi/2 \quad \text{for zero force.} \tag{2.22}$$

Examination of the control conditions (2.19)–(2.22) shows that there are two values of the sum of phase angles for which zero transfer occurs. In principle, then, one can simultaneously block the transfer of, say, the energy, and select the direction of the transfer of the population. One particularly interesting case is the definition of the phase angles for zero total power absorption. Since no energy is absorbed or emitted from the field these conditions define laser catalysis.[24]

A note of caution must be inserted at this point. It appears, at first sight, that there is a meaning which can be attached to the absolute phase of the field and to the phases of the molecular expectation values. However, it must be remembered that the phase of the molecular quantity is induced by the radiation field prior to the present time. Therefore, all phases must be related to the phase of a previous pulse which synchronizes the molecular clock with the field clock. With this synchronization it is possible to understand how quantum mechanical interference between events which are induced in the past propagates and can be used to control energy and/or population transfer at a later time. From the experimental perspective, both the amplitude and the phase of the light must be controlled.

III. GLOBAL CONTROL OF DYNAMICS

We now seek the optimal strategy for transfer of an observable with minimum power consumption under the restriction of zero population transfer. Consider the following functional for a ground state quantity $\langle \mathbf{A_g} \rangle$:

$$\Theta = \frac{d\langle \mathbf{A_g} \otimes \mathbf{P}_g \rangle}{dt} + W|\varepsilon|^2, \tag{3.1}$$

where W is a penalty function imposed by the power consumption. The globally optimal solution can be obtained by varying the ground state quantity $\Theta = \langle \mathbf{A_g} \rangle$ at a specific final time t_f with the following constraints:

(a) The evolution of the system is governed by the Liouville–von Neumann equation (2.3).

(b) There is zero population transfer so $\delta N_g = 0$.

(c) The power consumption is bounded by $E = \int_0^{t_f} |\varepsilon|^2\, dt$.

Taking account of the constraints by the method of Lagrange multipliers, the functional to be minimized takes the form

$$\Theta^* = \mathrm{Tr}\{\mathbf{A_g} \otimes \mathbf{P_g} \rho(t_f)\} + \int_0^{t_f} \mathrm{Tr}\left\{ \left(\frac{\partial \rho}{\partial t} - \mathbf{L}\rho \right) \mathbf{B} + \lambda |\varepsilon|^2 \right\} dt, \tag{3.2}$$

where $\mathbf{B}$ is an operator Lagrange multiplier and λ is a scalar Lagrange multiplier. The variation of Θ^* is with respect to ρ and $|\varepsilon|$. The condition $dN_g/dt = 0$ determines the phase of ε through Eq. (2.20). It therefore is omitted from the variation. Taking the variation of Eq. (3.2) and integrating by parts leads to the following equations:

(a) A forward equation for the density operator,

$$\frac{\partial \rho}{\partial t} = \mathbf{L}\rho, \tag{3.3}$$

subject to the initial condition $\rho = \rho(0)$.

(b) A backward equation for the Lagrange operator $\mathbf{B}$,

$$-\frac{\partial \mathbf{B}}{\partial t} = \mathbf{L}^* \mathbf{B}, \tag{3.4}$$

subject to the final condition $\mathbf{B}(t_f) = \mathbf{A_g} \otimes \mathbf{P_g}$. The dissipative part of Eq. (3.4) is symmetric in time, meaning that dissipation takes place in the forward as well as in the backward evolution.

(c) A condition on the field

$$|\varepsilon(t)| = \frac{1}{2\lambda} \mathrm{Tr}\left\{ \frac{\partial \mathbf{L}\rho(t)}{\partial |\varepsilon|} \mathbf{B}(t) \right\} = -\frac{1}{2\lambda} \left\langle \frac{\partial \mathbf{L}^* \mathbf{B}(t)}{\partial |\varepsilon|} \right\rangle. \tag{3.5}$$

Equation (3.5) can be interpreted as the scalar product of a forward moving density and a backward moving time-dependent operator. The optimal field at time t is determined by a time-dependent objective function propagated from the target time t_f backwards to time t. A first order perturbation approach to obtain a similar equation for optimal control in Liouville space has been derived in a different method by Yan *et al.*[25]

In dissipative dynamics, the backwards propagating target operator decays into a stationary operator and, therefore, $\mathbf{L}^* \mathbf{B}(-\infty) = 0$. This leads to loss of control, as can be seen from Eq. (3.5).

Thus far we have not made explicit use of the phase constraint which defines the control of a particular dynamical process, e.g., relationships (2.19)–(2.22). Although we have used a constraint on the energy while minimizing, via the variational calculus, $\langle \mathbf{A_g} \otimes \mathbf{P_g} \rangle$ on the ground surface, this procedure yields only the variational solution for the amplitude of electric field; the variational solution for the field phase is lost. However, the phase of the field is constrained by the condition on dN_g/dt, through Eq. (2.20). In general, if the goal is to minimize some dynamical function without consideration of the changes of any other observables, then we do not need to explicitly specify any of the phase relationships exhibited by the field.

We now examine the formalism needed to explicitly include a constraint on the phase of the field in the optimization procedure.

Consider the case where we try to minimize the ground surface energy under the condition of zero population transfer, for which we have the phase relation

$$\phi_\varepsilon + \phi_\mu = 0. \tag{3.6}$$

To incorporate Eq. (3.6) as a constraint in the variational calculation of the optimal field, we represent the electric field as $\varepsilon(t) = A_\varepsilon(t) e^{i\phi_\varepsilon(t)}$, and the objective functional as

$$\Theta^* = \mathrm{Tr}\{\mathbf{H}_g \otimes \mathbf{P}_g \rho(t_f)\} + \int_0^{t_f} \mathrm{Tr}\left\{ \left(\frac{\partial \rho}{\partial t} - \mathbf{L}\rho \right) \mathbf{B} \right\} dt + \lambda_1 \int_0^{t_f} A_\varepsilon^2\, dt + \lambda_2 \int_0^{t_f} (\phi_\varepsilon + \phi_\mu)^2\, dt, \tag{3.7}$$

where $\mathbf{B}$ is the operator Lagrange multiplier introduced earlier and λ_1, λ_2 are two scalar Langrange multipliers. We note that the time average of $\phi_\varepsilon + \phi_\mu$ vanishes but the time average of $(\phi_\varepsilon + \phi_\mu)^2$ is positive definite, hence the form that appears in Eq. (3.7).

Taking the variation of Θ^* with respect to ρ, A_ε, and ϕ_ε leads to the following equation for the phase, in addition to the Eqs. (3.3)–(3.5) for $\rho(t)$, $\mathbf{B}(t)$ and $A_\varepsilon(t)$:

$$\phi_\varepsilon + \phi_\mu = \frac{1}{2\lambda_2} \mathrm{Tr}\left\{ \frac{\partial \mathbf{L}\rho}{\partial \phi_\varepsilon} \mathbf{B}(t) \right\}. \tag{3.8}$$

Equation (3.8) explicitly describes how the time evolution of the phase angles must vary so as to minimize the value of $(\phi_\varepsilon + \phi_\mu)^2$ to satisfy the constraint of zero population transfer between potential energy surfaces. Note that control of the field phase is critically influenced by the backward propagation of the target function $\mathbf{B}(t)$.

IV. THE TRANSFER EQUATIONS FOR A SYSTEM WITH MORE THAN TWO ELECTRONIC SURFACES

There are several different ways one can view the dynamics in a system with n states. For example, the n states could represent the n electronic potential energy surfaces in a molecule with an arbitrary number of degrees of freedom. Alternatively, the n states could be a skeleton spectrum representation in which each level corresponds to a particular set of quantum numbers of a many degree of freedom system. We shall use, for the most part, the n-state molecule view, but the reader should keep in mind the other view.

Consider, then, a molecule with n electronic states. For the purpose of deducing the control conditions we will examine the extreme (and unlikely) case in which every possible pair of these electronic states is connected via the radiation field and a nonzero transition dipole moment. If the molecule is coupled to a radiation field which is a superposition of individual fields, each of which is resonant with a dipole allowed transition between two surfaces, the density operator of the system can be represented in the form

$$\begin{aligned}\rho &= \sum_{i=1}^{n} \rho_{ii} \otimes \mathbf{P}_{ii} + \sum_{1 \leqslant i,j \leqslant n} \rho_{ij} \otimes \mathbf{S}_{ij} \\ &= \sum_{i=1}^{n} \rho_{ii} \otimes \mathbf{P}_{ii} + \sum_{1 \leqslant i<j \leqslant n} (\rho_{ij} \otimes \mathbf{S}_{ij} + \rho_{ij}^{*} \otimes \mathbf{S}_{ij}^{+}), \qquad (4.1)\end{aligned}$$

where ρ_{ii} is the projection operator onto surface i, $i \in (1,\ldots,n)$ and the $\mathbf{S}_{ij}$ and $\mathbf{S}_{ij}^{+}$ are lowering and raising operators in the basis of the connected states i and j.

The Hamiltonian of the n-state system is

$$\begin{aligned}\mathbf{H} = \mathbf{H}_o + \mathbf{V}_t = \sum_{i=1}^{n} \mathbf{H}_{ii} \otimes \mathbf{P}_{\mathbf{ii}} \\ - \sum_{1 \leqslant i<j \leqslant n} \mu_{ij} \otimes [\mathbf{S}_{ij} \varepsilon(t) + \mathbf{S}_{ij}^{+} \varepsilon^{*}(t)],\end{aligned} \qquad (4.2)$$

where μ_{ij} is the transition dipole moment between states i and j and $\epsilon(t)$ is the semiclassical representation of the radiation field.

We find that the power absorbed from the field by the system is

$$\begin{aligned}P &= -\sum_{1 \leqslant i<j \leqslant n} \left\langle \mu_{ij} \otimes \left(\mathbf{S}_{ij} \frac{\partial \varepsilon}{\partial t} + \mathbf{S}_{ij}^{+} \frac{\partial \varepsilon^{*}}{\partial t} \right) \right\rangle \\ &= -2\,\mathrm{Re}\left(\sum_{1 \leqslant i<j \leqslant n} \langle \mu_{ij} \otimes \mathbf{S}_{ij} \rangle \frac{\partial \varepsilon}{\partial t} \right) \\ &= -2 \sum_{1 \leqslant i<j \leqslant n} |\langle \mu_{ij} \otimes \mathbf{S}_{ij} \rangle| |\dot{\varepsilon}| \cos(\phi_{\mu_{ij}} + \phi_{\dot{\varepsilon}}), \qquad (4.3)\end{aligned}$$

and that the flow of population from the ground state $(i=1)$ to the rest of the electronic states $(i>1)$ is, with neglect of the dissipative coupling of the n-state system to the bath states,

$$\begin{aligned}\frac{dN_g}{dt} &= \frac{i}{\hbar} \langle [\mathbf{H}, \mathbf{P}_{11}] \rangle \\ &= -\frac{i}{\hbar} \sum_{1<i \leqslant n} (\langle \mu_{i1} \otimes \mathbf{S}_{i1} \rangle \varepsilon - \langle \mu_{1i} \otimes \mathbf{S}_{1i} \rangle \varepsilon^{*}) \\ &= \frac{2}{\hbar} \sum_{1<i \leqslant n} \mathrm{Im}(\langle \mu_{1i} \otimes \mathbf{S}_{1i} \rangle \varepsilon) \\ &= \frac{2}{\hbar} \sum_{1<i \leqslant n} |\langle \mu_{1i} \otimes \mathbf{S}_{i1} \rangle| |\varepsilon| \sin(\phi_{\mu_{1i}} + \phi_{\varepsilon}). \qquad (4.4)\end{aligned}$$

Finally, the flow of energy from the ground state is

$$\begin{aligned}\frac{dE_g}{dt} &= \frac{2}{\hbar} \sum_{1<i \leqslant n} \mathrm{Im}(\langle \mu_{1i} \mathbf{H}_{11} \otimes \mathbf{S}_{i1} \rangle \varepsilon) \\ &= \frac{2}{\hbar} \sum_{1<i \leqslant n} |\langle \mu_{1i} \mathbf{H}_{11} \otimes \mathbf{S}_{i1} \rangle| |\varepsilon| \sin(\phi_{\mu_{1i}\mathbf{H}_{11}} + \phi_{\varepsilon}),\end{aligned} \qquad (4.5)$$

and the internal force which the radiation field exerts on the molecule takes the form

$$\begin{aligned}\mathbf{F} &= 2\,\mathrm{Re}\left(\sum_{1 \leqslant i<j \leqslant n} \left\langle \frac{\partial \mu_{ij}}{\partial \mathbf{x}} \otimes \mathbf{S}_{ij} \right\rangle \epsilon \right) \\ &= 2 \sum_{1 \leqslant i<j \leqslant n} \left| \frac{\partial \mu_{ij}}{\partial \mathbf{x}} \otimes \mathbf{S}_{ij} \right| |\epsilon| \cos(\phi'_{\mu_{ij}} + \phi_{\epsilon}). \qquad (4.6)\end{aligned}$$

The phase angle conditions for control of the system dynamics follow directly from the above. For example, the analogues of Eqs. (2.15)–(2.18) are

$$\begin{aligned}&\phi_{\mu_{ij}} + \phi_{\dot{\epsilon}_{ij}} = 0 \quad \text{for maximum energy absorption} \\ &\phi_{\mu_{ij}} + \phi_{\dot{\epsilon}_{ij}} = \pi \quad \text{for maximum energy emission}\end{aligned} \qquad (4.7)$$

for $1 \leqslant i<j \leqslant n$, where ϵ_{ij} is the resonant electric field component between states i and j;

$$\begin{aligned}&\phi_{\mu_{1i}} + \phi_{\epsilon_{1i}} = \pi/2 \quad \text{for maximum positive population transfer} \\ &\phi_{\mu_{1i}} + \phi_{\epsilon_{1i}} = -\pi/2 \quad \text{for maximum negative population transfer}\end{aligned} \qquad (4.8)$$

for $1<i \leqslant n$, where ϵ_{1i} is the resonant field component between the ground state and excited state i;

$$\begin{aligned}&\phi_{\mu_{1i}\mathbf{H}_{11}} + \phi_{\epsilon_{1i}} = \pi/2 \quad \text{for maximum energy transfer to ground state surface} \\ &\phi_{\mu_{1i}\mathbf{H}_{11}} + \phi_{\epsilon_{1i}} = -\pi/2 \quad \text{for maximum energy removal from ground state surface}\end{aligned} \qquad (4.9)$$

for $1<i\leqslant n$;

$$\begin{aligned}\phi'_{\mu_{ij}}+\phi_{\epsilon_{ij}}&=0 \quad \text{for maximum positive force}\\ \phi'_{\mu_{ij}}+\phi_{\epsilon_{ij}}&=\pi \quad \text{for maximum negative force}\end{aligned} \tag{4.10}$$

for $1\leqslant i<j\leqslant n$.

The above relations define the conditions for concurrent control of population and energy transfers between all of the states of the system which are connected by dipole allowed transitions. It is unlikely that a situation that complicated will ever be encountered. In the n-state molecule view, which has been emphasized above, typically, not all pairs of states are connected with nonzero transition dipole moments. In the skeleton spectrum view, there is usually a small subset of states (doorway states) connected by transition dipole moments to the ground state, and a dense background of states that either have zero transition dipole moments or very small transition dipole moments with ground state, with the doorway states and the background states only weakly coupled. In both cases, when only some pairs of states are coupled with nonzero transition dipole moments the appropriate control conditions are simplified.

V. REDUCTION OF THE DYNAMICS OF AN *n*-STATE SYSTEM TO THE DYNAMICS OF AN EQUIVALENT SMALLER SYSTEM

There is an interesting analogy between the analysis presented in this section and the optics of thin films. In thin film optics, Herpin's theorem[26] states that a symmetrical multilayer stack is equivalent to a single layer with an effective refractive index (called the Herpin index) and an effective phase thickness. We shall develop a representation of the population dynamics of an n-state system in terms of the properties of a surrogate system with fewer states. The states of the surrogate system must, of course, be defined in terms of the n states of the full system, so we are really developing an alternative representation of the n state system. However, we expect the formal relations which define the reduction of n to, say, m states to be of value in guiding the generation of accurate approximations to the dynamics of the full n state system.

The reduction procedure can be defined using the Schrodinger representation of the dynamics of the n-state system. The molecular wave function of the n-state system can be written as a superposition of the electronic eigenfunctions $\{u_n(\mathbf{r})\}$, which yields

$$\psi(\mathbf{r},t)=\sum_n C_n(t)u_n(\mathbf{r})e^{-i\omega_n t}. \tag{5.1}$$

Insertion of Eq. (5.1) into the Schrodinger equation yields the following equations of motion for the coefficients C_n:[27]

$$\dot{C}_n(t)=-\frac{i}{\hbar}\sum_k C_k(t)V_{nk}e^{-i\omega_{kn}t}, \tag{5.2}$$

where $V_{nk}=\langle u_n|V|u_k\rangle$ and $\omega_{kn}=\omega_k-\omega_n$.

We assume that the molecule-field coupling is dominated by the dipole transition interaction $V_{nk}=-\mu_{nk}E$, where μ_{nk} is the transition dipole matrix element. Of course, $\mu_{nk}=\mu_{el}f_{nk}$, where $f_{nk}=\int d\mathbf{r}u_n^*(\mathbf{r})u_k(\mathbf{r})$ is the Franck–Condon factor between electronic surfaces n and k.[28] The resonant continuous electric field $E(t)$ can be written in the form

$$E(t)=\frac{E_0}{2}\sum_{1\leqslant j<i\leqslant n}(e^{i\gamma_{ij}t}+e^{-i\gamma_{ij}t}). \tag{5.3}$$

Adopting the rotating wave approximation (RWA) and introducing the detuning frequency $\Delta\omega_{nk}=\omega_{nk}-\gamma_{nk}$ and the Rabi frequency $M_{nk}=-(\mu_{nk}E_0)/(\hbar)$, we find the following equations of motion:

$$\dot{C}_n(t)+i\sum_{k\in(1,\ldots,n)}^{k\neq n}M_{nk}(t)C_k(t)=0, \tag{5.4}$$

where the $M_{nk}(t)$ are the elements of the $n\times n$ time-dependent matrix

$$\mathbf{M}(t)=\frac{1}{2}\begin{pmatrix}0 & M_{12}e^{-i\Delta\omega_{21}t} & \cdots M_{1n}e^{-i\Delta\omega_{n1}t}\\ M_{21}e^{i\Delta\omega_{21}t} & 0 & \cdots M_{2n}e^{-i\Delta\omega_{n2}t}\\ \vdots & \vdots & \vdots\\ M_{n1}e^{i\Delta\omega_{n1}t} & M_{n2}e^{i\Delta\omega_{n2}t} & \cdots 0\end{pmatrix}. \tag{5.5}$$

For the case of zero detuning of the radiation field, $\mathbf{M}(t)$ becomes time-independent

$$M=\frac{1}{2}\begin{pmatrix}0 & M_{12} & \cdots M_{1n}\\ M_{21} & 0 & \cdots M_{2n}\\ \vdots & \vdots & \vdots\\ M_{n1} & M_{n2} & \cdots 0\end{pmatrix} \tag{5.6}$$

and the equation of motion for the population coefficient of the nth electronic state is given by

$$\dot{C}_n(t)+i\sum_{k\in(1,\ldots,n)}^{k\neq n}M_{nk}C_k(t)=0. \tag{5.7}$$

If all of the states of the system are equally strongly coupled to each other, the system dynamics can only be described by completely-solving the above equations. However, it is common (especially in an n-state system) that some pairs of states are strongly coupled and other pairs of states are weakly coupled. Then we expect that the population transfers among strongly coupled states dominate the system dynamics, and that it should be possible to study the n-state system dynamics in the subspace of strongly coupled states with a correction from the influence of the weakly coupled states.

The reduction scheme we use to define the surrogate fewer state system follows the method proposed by Shore.[29] The scheme has a compact form when we introduce two orthogonal projection operators, P and Q, and work in the frequency domain instead of the time domain. The time evolution matrix for the n-state system dynamics, $U(t)$, and its Fourier transform, $G(\omega)$, satisfy the following equations:

$$\left(\frac{d}{dt}+i\mathbf{M}\right)U(t)=0$$
$$(\omega\mathbf{I}-\mathbf{M})G(\omega)=1, \tag{5.8}$$

where ω is the frequency domain variable and $\mathbf{I}$ is the $n\times n$ unit matrix.

Let P be the projection operator onto the subspace composed of the states having stronger couplings within which we try to approximate the system dynamics, and let Q be the projection operator onto the remaining states. Then

$$P+Q=1,\ P^2=P,\ Q^2=Q,\quad \text{and } PQ=QP=0. \tag{5.9}$$

We are interested in evaluating the matrix elements of $G(\omega)$ within the subspace of P states in the frequency domain. Multiplying both sides of the equation for $G(\omega)$ in Eq. (5.8) by $P+Q=1$ we find

$$(\omega\mathbf{I}-\mathbf{M})PG(\omega)+(\omega\mathbf{I}-\mathbf{M})QG(\omega)=P+Q. \tag{5.10}$$

Further multiplying by P from the right and Q from the left yields

$$Q(\omega\mathbf{I}-\mathbf{M})PG(\omega)P+Q(\omega\mathbf{I}-\mathbf{M})QG(\omega)P=0, \tag{5.11}$$

from which we obtain

$$QG(\omega)P=Q[Q(\omega\mathbf{I}-\mathbf{M})Q]^{-1}Q\mathbf{M}PG(\omega)P. \tag{5.12}$$

Note that we require the inverse of the matrix $\omega\mathbf{I}-\mathbf{M}$ within the Q subspace. Now multiplying both sides of Eq. (5.10) by P, we find

$$P(\omega\mathbf{I}-\mathbf{M})PG(\omega)P+P(\omega\mathbf{I}-\mathbf{M})QG(\omega)P=P. \tag{5.13}$$

Substituting $QG(\omega)P$ from Eq. (5.12) into Eq. (5.13) yields

$$P(\omega\mathbf{I}-\mathbf{M})PG(\omega)P-P\mathbf{M}Q[Q(\omega\mathbf{I}-\mathbf{M})Q]^{-1}$$
$$\times Q\mathbf{M}PG(\omega)P=P, \tag{5.14}$$

and multiplying Eq. (5.14) by P on both sides yields

$$P\{\omega\mathbf{I}-P\mathbf{M}P-P\mathbf{M}Q[Q(\omega\mathbf{I}-\mathbf{M})Q]^{-1}Q\mathbf{M}P\}$$
$$\times PG(\omega)P=P. \tag{5.15}$$

We now write

$$\tilde{\mathbf{M}}(\omega)=P\mathbf{M}P+P\mathbf{M}Q[Q(\omega\mathbf{I}-\mathbf{M})Q]^{-1}Q\mathbf{M}P, \tag{5.16}$$

which generates a representation of the frequency domain time evolution operator within P space

$$PG(\omega)P=P[\omega\mathbf{I}-\tilde{\mathbf{M}}(\omega)]^{-1}P. \tag{5.17}$$

From $PG(\omega)P$ we can get the time evolution operator $PU(t)P$ by use of a Fourier transform. These localized operators permit the construction of those portions of the time evolved state vectors that lie within the subspace of P states. The influence of the remaining states (Q states) occurs through the action of the operator $\tilde{\mathbf{M}}(\omega)$.

The preceding analysis is just a transformation of one representation of the n-state problem to another representation. To be useful, the new representation must admit the use of simplifying approximations not suggested by the original representation. One such approximation is to replace the frequency variable ω in $\tilde{\mathbf{M}}(\omega)$ in Eq. (5.16) by a typical P-space eigenfrequency, say ω_1^0. We thereby obtain the frequency-independent effective operator

$$\tilde{\mathbf{M}}=P\mathbf{M}P+P\mathbf{M}Q[Q(\omega_1^0I-\mathbf{M})Q]^{-1}Q\mathbf{M}P. \tag{5.18}$$

Note that the original matrix elements $P\mathbf{M}P$ associated with the P-space state population dynamics have to be modified to include the influence of Q-space states. Viewed in the time domain, the replacement of $\tilde{\mathbf{M}}(\omega)$ by $\tilde{\mathbf{M}}$ washes out the details of the time variation within Q space. For this approximation to be useful all strongly coupled states should be included in the P space and the Q space should not include any states that couple strongly to the P space. We now find that the population dynamics of the m levels within the P subspace is governed by the equations of motion

$$\dot{C}_m(t)+i\sum_{k\in(1,\ldots,m)}^{k\neq m}\tilde{M}_{mk}C_k(t)=0. \tag{5.19}$$

Although we have phrased the preceding argument in terms of the dynamics of a complicated molecule with n degrees of freedom, it also applies to a molecule embedded in a solvent.

We now connect the analysis given above with the equation of motion displayed in Eq. (2.3). That equation of motion follows from subdivision of a system into an open subsystem S, with Hamiltonian $\mathbf{H}_S$, and a complementary reservoir R with Hamiltonian $\mathbf{H}_R$, such that the complete system Hamiltonian $\mathbf{H}$ is given by

$$\mathbf{H}=\mathbf{H}_S\otimes\mathbf{I}_R+\mathbf{I}_S\otimes\mathbf{H}_R+\mathbf{H}_{SR}. \tag{5.20}$$

When the coupling between S and R is weak the evolution of the open system S, due to the internal dynamics of S and the interaction with the reservoir R, can be described in density matrix form by

$$\frac{\partial\rho_S(t)}{\partial t}=\mathbf{L}\rho_S(t)=-\frac{i}{\hbar}[\mathbf{H}_S,\rho_S]+\mathbf{L}_D(\rho_S) \tag{5.21}$$

as stated in Sec. II. Now writing

$$\rho_S(t)=\Lambda_t\rho_S(0) \tag{5.22}$$

we find

$$\Lambda_t=e^{\mathbf{L}t},\quad t\geqslant 0 \tag{5.23}$$

which we require to satisfy the semigroup condition[19,30]

$$\Lambda_t\Lambda_\tau=\Lambda_{t+\tau}. \tag{5.24}$$

Hence $\mathbf{L}$ is a semigroup generator.

Returning to the formal reduction procedure described at the beginning of this section, we note again that the operator $\tilde{\mathbf{M}}(\omega)$, which is a function of the frequency variable ω, incorporates all of the dynamics associated with evolution of the n-state system, and the formalism merely reorganizes the exact representation of the n-state population transfer dynamics. The formalism, as such, does not demand that the m states in the P subspace are strongly coupled to each other and that the $(n-m)$ states in the Q subspace are weakly coupled to those in the P subspace. The use of a typical unperturbed eigenfrequency of the P subspace, ω_1^0, to replace the variable frequency ω in $\tilde{\mathbf{M}}(\omega)$, by virtue of washing out the details of the time variation within the Q subspace, generates the separation of the total system into a strongly coupled subsystem which is weakly coupled to a reservoir. In general, we expect this approximation will lead to a loss of time reversibility, hence can be used to explore an explicit form for the operator $\mathbf{L}_D$.

Given Eq. (5.19), it is straightforward to obtain the corresponding density matrix form of the equation of motion. The density matrix element for the mth state population in the P subspace, ρ_{mm}, is defined by $\rho_{mm}=C_m C_m^*$, from which we find the time variation

$$\begin{aligned}\frac{\partial\rho_{mm}}{\partial t}&=\dot{C}_m C_m^*+C_m\dot{C}_m^*\\&=-i\sum_k \tilde{M}_{mk}(\rho_{km}-\rho_{mk})\\&=-i\sum_k (P\mathbf{M}P)_{mk}(\rho_{km}-\rho_{mk})\\&\quad+i\sum_{k,} (P\mathbf{M}Q)_{mn}[Q(\omega_1^0-\mathbf{M})Q]_{n1}^{-1}\\&\quad\times(Q\mathbf{M}P)_{1k}(\rho_{mk}-\rho_{km}).\end{aligned}\tag{5.25}$$

A comparison of Eqs. (5.25) and (5.21) yields

$$\frac{\partial\rho_{mm}}{\partial t}=-\frac{i}{\hbar}\sum_k [(\mathbf{H}_S)_{mk}\rho_{km}-\rho_{mk}(\mathbf{H}_S)_{km}]+\mathbf{L}_D(\rho)_{mm},\tag{5.26}$$

where, in the rotating wave approximation, $\mathbf{L}_D$ has the representation

$$\begin{aligned}\mathbf{L}_D(\rho)_{mm}=i\sum_{k,n,1} (P\mathbf{M}Q)_{mn}[Q(\omega_1^0-\mathbf{M})Q]_{n1}^{-1}\\\times(Q\mathbf{M}P)_{1k}(\rho_{mk}-\rho_{km}).\end{aligned}\tag{5.27}$$

VI. THE TRANSFER EQUATIONS FOR A SYSTEM WITH THREE ELECTRONIC STATES

As an example of the formalism outlined in Sec. IV, in this section we examine the excitation dynamics of a molecule with three electronic states coupled to a radiation field.[29,31,32] The results obtained from this analysis will be used as the benchmark for a test of the reduced dynamics formalism described in Sec. V. We note that the three level system is of interest in its own right, e.g., to analyze the two-step excitation of a molecule through an intermediate electronic state.

Using the Heisenberg representation it is straightforward to extend the formalism set out in Sec. II to a molecule with three electronic states. The result of the analysis is a set of multiple phase relationships, each involving the phase angle of the individual transition dipole moment and the phase angle of the coupled radiation field.

For example, if we assume electric dipole transitions are allowed between the ground state surface, denoted 1, and the first excited state surface, denoted 2, and between the ground state surface and the second excited state surface, denoted 3, the condition for maximum positive population transfers from the ground state surface is

$$\begin{aligned}\phi_{\mu_{12}}+\phi_{\epsilon_1}&=\pi/2,\\\phi_{\mu_{13}}+\phi_{\epsilon_2}&=\pi/2,\end{aligned}\tag{6.1}$$

and the condition for maximum negative population transfers is

$$\begin{aligned}\phi_{\mu_{12}}+\phi_{\epsilon_1}&=-\pi/2,\\\phi_{\mu_{13}}+\phi_{\epsilon_2}&=-\pi/2,\end{aligned}\tag{6.2}$$

where ϵ_1 and ϵ_2 are the fields generating the 1→2 and 2→3 transitions, respectively.

The conditions stated in Eqs. (6.1) and (6.2) induce population transfers into (out of) the ground state surface that have the same direction. We can also generate two-way population transfers, e.g., a maximum positive population transfer between state 1 and state 2, and a maximum negative population transfer between state 1 and state 3 (or vice versa). The necessary conditions are

$$\begin{aligned}\phi_{\mu_{12}}+\phi_{\epsilon_1}&=\pi/2,\\\phi_{\mu_{13}}+\phi_{\epsilon_2}&=-\pi/2.\end{aligned}\tag{6.3}$$

Clearly, there are interesting opportunities for the control of the population transfer dynamics in a three state system.

We now examine the Schrodinger representation of the dynamics of a three state system. The equations of motion for the population coefficients are, according to Eq. (5.7),

$$\begin{aligned}i\dot{C}_1(t)&=\tfrac{1}{2}[M_{12}C_2(t)e^{-i\Delta\omega_{21}t}+M_{13}C_3(t)e^{-i\Delta\omega_{31}t}],\\i\dot{C}_2(t)&=\tfrac{1}{2}[M_{12}C_1(t)e^{i\Delta\omega_{21}t}+M_{23}C_3(t)e^{-i\Delta\omega_{32}t}],\\i\dot{C}_3(t)&=\tfrac{1}{2}[M_{13}C_1(t)e^{i\Delta\omega_{31}t}+M_{23}C_2(t)e^{i\Delta\omega_{32}t}].\end{aligned}\tag{6.4}$$

A. Analytical solution for a partially decoupled three state system

It is difficult to obtain a general analytic solution to the set of equations (6.4). However, when one transition dipole moment is zero an analytic solution can be found. Let $M_{23}=0$. Then

$$\begin{aligned}i\dot{C}_1(t)&=\tfrac{1}{2}[M_{12}C_2(t)e^{-i\Delta\omega_{21}t}+M_{13}C_3(t)e^{-i\Delta\omega_{31}t}],\\i\dot{C}_2(t)&=\tfrac{1}{2}M_{12}e^{i\Delta\omega_{21}t}C_1(t)\\i\dot{C}_3(t)&=\tfrac{1}{2}M_{13}e^{i\Delta\omega_{31}t}C_1(t).\end{aligned}\tag{6.5}$$

If we substitute the trial solutions

$$C_1(t)=C_1^0 e^{-i(\lambda+\Delta\omega_{21}+\Delta\omega_{31})t/2},$$
$$C_2(t)=C_2^0 e^{-i(\lambda+\Delta\omega_{21}+\Delta\omega_{31})t/2}, \tag{6.6}$$
$$C_3(t)=C_3^0 e^{-i(\lambda+\Delta\omega_{21}-\Delta\omega_{31})t/2}$$

into Eq. (6.5), we obtain the following algebraic equations:

$$(\lambda+\Delta\omega_{21}+\Delta\omega_{31})C_1^0+M_{12}C_2^0+M_{13}C_3^0=0,$$
$$M_{12}C_1^0+(\lambda-\Delta\omega_{21}+\Delta\omega_{31})C_2^0=0, \tag{6.7}$$
$$M_{13}C_1^0+(\lambda+\Delta\omega_{21}-\Delta\omega_{31})C_3^0=0.$$

The set of equations (6.7) define an eigenvalue problem. In the special case when $\Delta\omega_{21}=\Delta\omega_{31}=\Delta\omega$ the eigenvalues are found to be

$$\lambda_1=0;$$
$$\lambda_{2,3}=-\Delta\omega\pm R, \tag{6.8}$$

where $R=\sqrt{\Delta\omega^2+M_{12}^2+M_{13}^2}$. After normalization, which imposes the condition $|C_1^0|^2+|C_2^0|^2+|C_3^0|^2=1$, the null eigenvector is found to be

$$(C_1^0,C_2^0,C_3^0)=\frac{1}{\sqrt{M_{12}^2+M_{13}^2}}\,(0,-M_{13},M_{12}), \tag{6.9}$$

while the other two eigenvectors are found to be

$$\left(\mp\sqrt{\frac{R\pm\Delta\omega}{2R}},\ \frac{M_{12}}{\sqrt{2R(R\pm\Delta\omega)}},\ \frac{M_{13}}{\sqrt{2R(R\pm\Delta\omega)}}\right). \tag{6.10}$$

The physical interpretations of the situations these eigenmodes describe are very interesting. The first eigenmode corresponds to transfer of all of the ground state amplitude to the other two excited states, and the distribution of amplitude between the two excited states is unusual in that the stronger the dipole coupling of an excited state with the ground state the less populated it is. To interpret the situations described by the other two eigenmodes we note that when the detuning frequency $\Delta\omega$ approaches zero, the probabilities

$$(|C_1^0|^2,|C_1^0|^2,|C_2^0|^2)$$
$$=\left(\frac{R\pm\Delta\omega}{2R},\frac{M_{12}^2}{2R(R\pm\Delta\omega)},\frac{M_{13}^2}{2R(R\pm\Delta\omega)}\right) \tag{6.11}$$

converge to

$$\left(\frac{1}{2},\frac{1}{2}\frac{M_{12}^2}{M_{12}^2+M_{13}^2},\frac{1}{2}\frac{M_{13}^2}{M_{12}^2+M_{13}^2}\right), \tag{6.12}$$

which implies that half of the probability amplitude is trapped in the ground state while the other half is shared between the two excited states according to the magnitudes of their coupling with ground state surface. For nonzero detuning, one eigenmode describes the situation with more than half of the probability amplitude in the ground state while the other eigenmode describes the opposite effect.

B. Solution for the fully coupled three state system

An analytic solution for the dynamics of a fully coupled three state system can only be obtained when all of the detunings are zero, in which case the equations of motion become ordinary differential equations. When the detunings are nonzero the dynamics can be studied using perturbation theory.

Suppose that the initial conditions are $C_1(0)=1$ and $C_2(0)=C_3(0)=0$, i.e., the system is in the ground state at time $t=0$. Then the equations of motion (6.4) become

$$i\dot{C}_1(t)=0,$$
$$i\dot{C}_2(t)=\tfrac{1}{2}\,M_{12}e^{i\Delta\omega_{21}t}, \tag{6.13}$$
$$i\dot{C}_3(t)=\tfrac{1}{2}\,M_{13}e^{i\Delta\omega_{31}t},$$

which can be solved by iteration. To second order we find

$$C_1(t)\approx C_1^{(0)}(t)+C_1^{(1)}(t)+C_1^{(2)}(t)$$
$$=1+\frac{M_{12}^2+M_{13}^2}{4\Delta\omega^2}\,(e^{-i\Delta\omega t}+i\Delta\omega t-1),$$

$$C_2(t)\approx-\frac{M_{12}}{2\Delta\omega}\,(e^{i\Delta\omega t}-1)+\frac{M_{23}M_{13}}{4\Delta\omega^2}\,(e^{-i\Delta\omega t}+i\Delta\omega t-1) \tag{6.14}$$

$$C_3(t)\approx-\frac{M_{13}}{2\Delta\omega}\,(e^{i\Delta\omega t}-1)+\frac{M_{12}M_{23}}{8\Delta\omega^2}\,(e^{i\Delta\omega t}-1)^2.$$

Note that the perturbation parameter is the ratio of the Rabi frequency M_{nk} to the detuning frequency $\Delta\omega$.

The temporal evolution of the populations of the three states of the system are displayed in Fig. 1(a). We note that the induced resonant transitions oscillate with approximately the detuning frequency $\Delta\omega$ and that the first excited state is populated more than is the second excited state. In Fig. 1(b) we show the change of population of the first excited state as the detuning frequency is raised. It can be seen that the population decreases rapidly as the detuning increases, which justifies the use of the rotating wave approximation.

VII. MOLECULE–LASER PULSE INTERACTION

In this section we report a numerical study of the population transfer dynamics induced by the interaction of a three state molecule with a short pulse of radiation.

A. Single pulse dynamics

The equations of motion for the probability amplitudes are obtained as before, with the interaction term now of the form

$$V_{nk}=-\mu_{nk}E(t)=-\tfrac{1}{2}\mu_{nk}S_1(t)E_1(e^{i\gamma_{nk}t}+e^{-i\gamma_{nk}t}), \tag{7.1}$$

where $S_1(t)$ is the shape function of pulse 1, E_1 its amplitude and γ_{nk} is the carrier frequency. We choose for the shape function $S_1(t)=\exp(-(t-\tau_1)^2/\sigma_1^2)$, where σ_1 is the width of the pulse. As before, we choose the initial conditions $C_1(0)=1$ and $C_2(0)=C_3(0)=0$. A direct application of first order perturbation theory yields

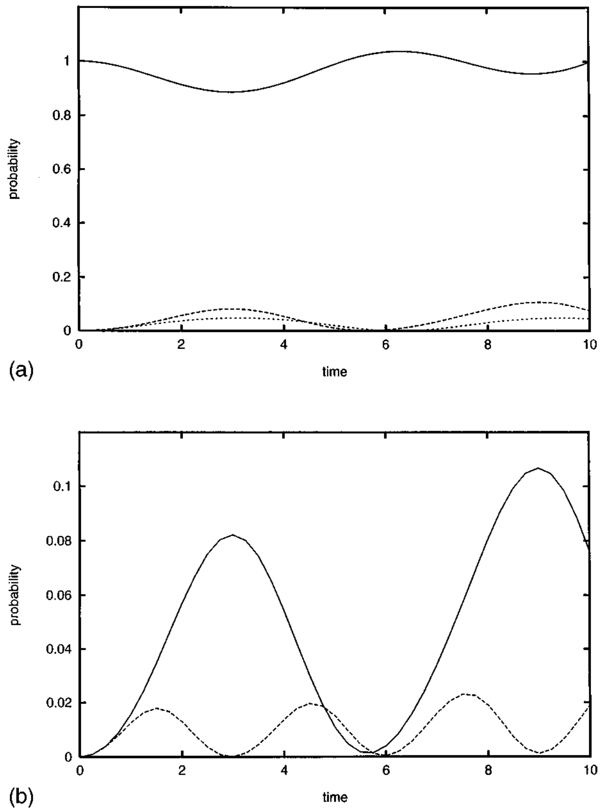

FIG. 1. The probability profiles for three state system coupled with monochromatic fields, on ground state surface (—), first excited state surface (---) and second excited state surface (---). All M_{nk} are made equal to a constant M and $M/\Delta\omega=1/4$. (b) The probability profile on the first excited state surface as detuning frequency increases from $\Delta\omega_{21}=1$ (—) to $\Delta\omega_{21}=2$ (---).

$$\begin{aligned}C_2^{(1)}(t)&=\frac{i\mu_{21}E_1}{2\hbar}\int_0^t \exp\left(-\frac{(\tau-\tau_1)^2}{\sigma_1^2}+i\Delta\omega_{21}\tau\right)d\tau\\&=-\frac{\mu_{21}E_1}{2\hbar}\frac{\sqrt{\pi}}{2}\sigma_1\exp\left(-\frac{\sigma_1^2\Delta\omega_{21}^2}{4}+i\Delta\omega_{21}\tau_1\right)\\&\quad\times\left[\operatorname{erfi}\left(\frac{\sigma_1^2\Delta\omega_{21}-2i\tau_1}{2\sigma_1}\right)\right.\\&\quad\left.-\operatorname{erfi}\left(\frac{\sigma_1^2\Delta\omega_{21}-2i(t-\tau_1)}{2\sigma_1}\right)\right],\end{aligned}\tag{7.2}$$

where $\operatorname{erfi}(z)$, the complex error integral, is defined as

$$\operatorname{erfi}(z)=-\frac{2i}{\sqrt{\pi}}\int_0^{iz}e^{-x^2}\,dx.\tag{7.3}$$

We note that $\operatorname{erfi}(z)=-i\operatorname{erf}(iz)$ with $\operatorname{erf}(z)=2/\sqrt{\pi}\int_0^z e^{-x^2}\,dx$, the standard error integral. Variants of (7.2) have been published by several investigators.[28,33]

A typical temporal evolution of the population of the first excited state is displayed in Fig. 2(a), where the central peak time, the width of the pulse and the detuning frequency are all set to be 1. Note that the population of the excited state saturates in about two time units, i.e., in a time which is about twice the pulse width.

To study the influence of detuning of the radiation field on the temporal evolution of the excited state population, we apply a pulse with $\sigma_1=1$ and $\tau_1=1$ and three different detuning frequencies, $\Delta\omega_{21}=1$, 2, and 3. The time evolution of the excited state population is displayed in Fig. 2(b). As expected, the population decreases rapidly as the detuning increases and its asymptotic value drops to near zero for large detuning. Furthermore, the course of the time evolution of the excited state population is different for different detunings. When $\Delta\omega$ is small the excited state population rises smoothly to its asymptotic value. However, when $\Delta\omega$ is large the excited state population does not rise monotonically. For small t the population growth follows the radiation field in almost the same manner as when $\Delta\omega$ is small but at later time the system starts to diminish the overshooting portion of population. In the extreme case when $\Delta\omega$ is very large the population of the excited state after interaction of the system with the radiation pulse is essentially zero, but it is not zero during the interaction with the pulse. In this case the excited state plays the role of a virtual state.

The influence of pulse width on the excited state population can be studied by applying to the three state system radiation pulses which have same amplitude but different widths. The temporal evolutions of the state populations are displayed in Fig. 2(c). Clearly, our narrowest pulse generates an increase in the excited state population to its asymptotic value without overshoot, but the wider pulses generate, at some intermediate time, an overshoot in the excited state population as a function of time. This result arises as follows. Let $t\rightarrow\infty$ and suppose the pulse is not present prior to $t=0$. Under these conditions $C_2^{(1)}(t)$ becomes

$$C_2^{(1)}(t)=\frac{i\mu_{21}E_1}{2\hbar}\int_{-\infty}^{\infty}\exp\left(-\frac{(\tau-\tau_1)^2}{\sigma_1^2}\right)e^{i\Delta\omega_{21}\tau}\,d\tau.\tag{7.4}$$

This integral is, apart from the factor $(i\mu_{21}E_1)/(2\hbar)$, the Fourier transform of the pulse shape function

$$\exp\left(-\frac{(\tau-\tau_1)^2}{\sigma_1^2}\right),$$

which illustrates that what matters in producing lasting excitation is the magnitude of the Fourier component of the pulse shape function at the detuning frequency $\Delta\omega_{21}$. Because the spectral content of a pulse is inversely proportional to its temporal width, short duration pulses generate greater asymptotic excitation than do long pulses.

B. Double pulse dynamics

Tannor and Rice[6] proposed the use of two pulses, with a variable separation, to enhance the formation of a selected product in a branching chemical reaction. Scherer *et al.*[8] have developed "wave packet interferometry" to control, in addition to the time delay, the relative phase shift between a pair of femtosecond pulses, thereby fully exploiting the coherence properties of laser light. In this subsection we will study two examples of the response of a molecule to two radiation pulses.

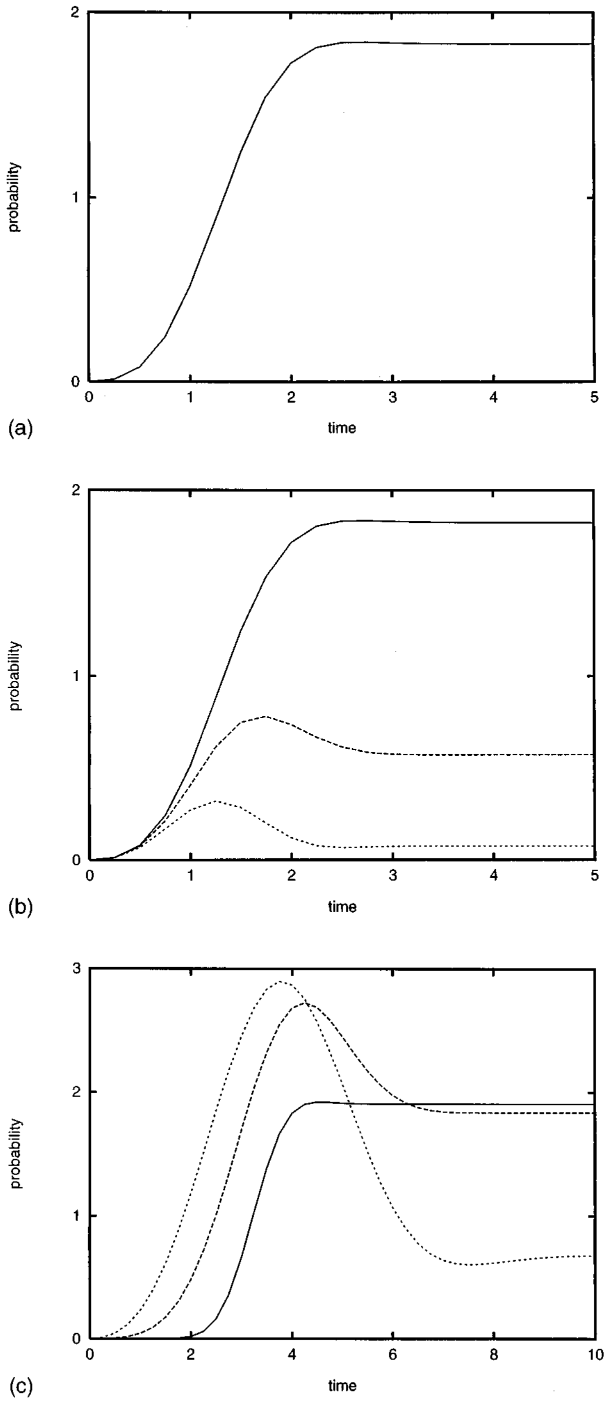

FIG. 2. (a) The population profile on the first excited state surface induced by a single Gaussian pulse with $\sigma_1=1$, $\tau_1=1$ and $\Delta\omega_{21}=1$. The actual drawing is $|C_2^{(1)}(t)|^2$ divided by a constant factor $|\mu_{21}E_1/2\hbar|^2$, which is similarly applied in all the following graphs. (b) The excited population profiles by a single pulse with various detuning frequencies $\Delta\omega_{21}=1$ (—), $\Delta\omega_{21}=2$ (---) and $\Delta\omega_{21}=3$ (---). (c) The excited population profiles by a single pulse ($\tau_1=3$ and $\Delta\omega_{21}=1$) with different widths $\sigma_1=1$ (—), $\sigma_1=2$ (---) and $\sigma_1=3$ (---).

1. Zero relative phase shift between two pulses

If the two pulses that interact with the molecule have no relative phase shift, the probability amplitude on the first excited state surface is

$$C_2^{(1)}(t)=\frac{i\mu_{21}E_1}{2\hbar}\int_0^t\left[\exp\left(-\frac{(\tau-\tau_1)^2}{\sigma_1^2}\right)+\exp\left(-\frac{(\tau-\tau_2)^2}{\sigma_2^2}\right)\right]e^{i\Delta\omega_{21}\tau}\,d\tau. \tag{7.5}$$

Consider two pulses, one centered at $\tau_1=1$ and the other at $\tau_2=2$ or $\tau_2=3$. The excited state population for this case is displayed in Fig. 3(a), which shows that the population transfer is larger for $\Delta\tau=1$ than for $\Delta\tau=2$. In fact, the asymptotic population of the excited state is a periodic function of the delay between the pulses, as shown in Fig. 3(b). For the parameters we have used, the excited state population has maxima at $\Delta\tau=0.25$ and 6.5 and a minimum at $\Delta\tau=3.25$. Figure 3(b) also can be interpreted as an interference pattern with variable pumping and dumping as the delay time between the pulses is changed.

2. Nonzero relative phase shift between two pulses

Suppose there is a relative phase shift ϕ between two Gaussian pulses that interact with a molecule. Then

$$C_2^{(1)}(t)=\frac{i\mu_{21}E_1}{2\hbar}\int_0^t\left[\exp\left(-\frac{(\tau-\tau_1)^2}{\sigma_1^2}\right)+\exp\left(-\frac{(\tau-\tau_2)^2}{\sigma_2^2}-i\phi\right)\right]e^{i\Delta\omega_{21}\tau}\,d\tau. \tag{7.6}$$

For simplicity, we assume that $\sigma_1=\sigma_2=1$. First consider the situation when $\Delta\omega_{21}=0$. In this case it can be shown that the excited state population is proportional to cos ϕ, i.e., that there is constructive interference at $\phi=2n\pi$ and destructive interference at $\phi=(2n+1)\pi$. The excited state population is displayed in Fig. 3(c) for various ϕ. Note that when $\phi=\pi$ the excited state acts like a virtual state.

When the detuning frequency is not zero the interference condition becomes more complicated, and the population maxima and minima no longer occur at exactly $\phi=2n\pi$ and $\phi=(2n+1)\pi$, respectively. The excited state population when $\Delta\omega_{21}=1$ is shown in Fig. 3(d). For this particular detuning the excited state population can be shown to be proportional to $\cos^2(1-\phi)/(2)$, hence has a maximum at $\phi=1$, accidentally equal to $\Delta\omega$ at this detuning frequency. We note that when $\phi=\pi$ the population increases following the onset of each of the pulses.

In general, when the detunings are nonzero in magnitude, no simple relationships between $\Delta\omega$ and ϕ are found.

VIII. REDUCTION OF A THREE STATE SYSTEM TO AN EFFECTIVE TWO STATE SYSTEM

In this section we use the reduction of a three state system to a surrogate two state system as an example to illustrate the formalism outlined in Sec V.

The equations of motion for the proability amplitudes in a three state system for the case of zero detuning are

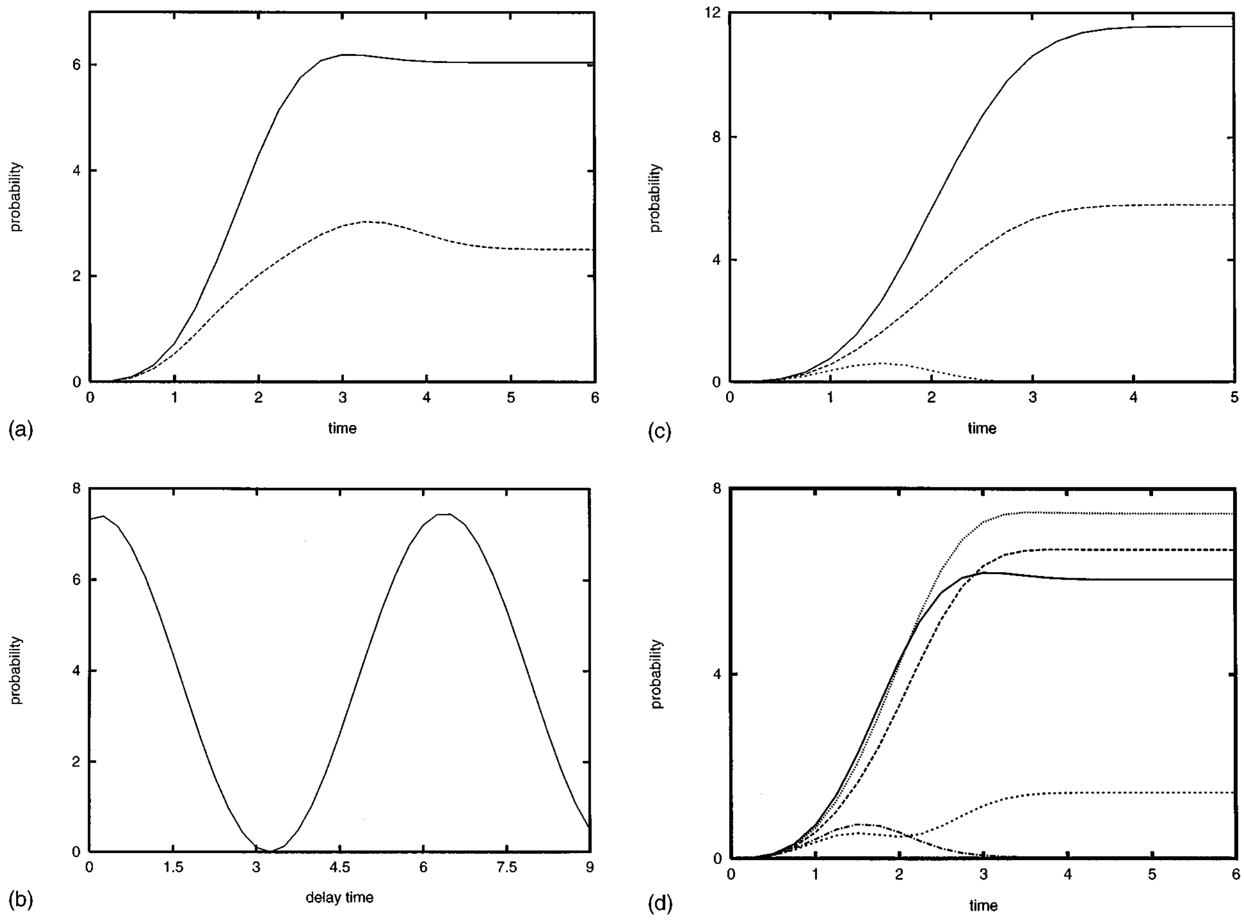

FIG. 3. (a) The population profiles on first excited state surface by double Gaussian pulses with delay time $\Delta\tau=1$ (—) and $\Delta\tau=2$ (---) between them. Two pulses have same width at $\sigma=1$ and detuning frequency is at $\Delta\omega_{21}=1$. (b) The population interference pattern when varying delay time between double pulses. The parameters for the pulses are the same as in (a). (c) The excited population profiles by double pulses at zero detuning with relative phase shift $\phi=0$ (—), $\phi=\pi/2$ (---) and $\phi=\pi$ (---). (d) The excited population profiles by double pulses at nonzero detuning $\Delta\omega_{21}=1$ with relative phase shift $\phi=0$ (—), $\phi=\pi/2$ (---), $\phi=\pi$ (---), $\phi=1$ (···), and $\phi=\pi+1$ (-·-·).

$$
\begin{aligned}
i\dot{C}_1(t)&=\tfrac{1}{2}[M_{12}C_2(t)+M_{13}C_3(t)],\\
i\dot{C}_2(t)&=\tfrac{1}{2}[M_{12}C_1(t)+M_{23}C_3(t)],\\
i\dot{C}_3(t)&=\tfrac{1}{2}[M_{13}C_1(t)+M_{23}C_2(t)],
\end{aligned}
\tag{8.1}
$$

which we cast into matrix form

$$\dot{C}_n(t)+i\sum_{k=1,2,3}^{k\neq n} M_{nk}C_k(t)=0 \tag{8.2}$$

with

$$\mathbf{M}=\frac{1}{2}\begin{pmatrix} 0 & M_{12} & M_{13}\\ M_{12} & 0 & M_{23}\\ M_{13} & M_{23} & 0\end{pmatrix}.$$

Suppose, for the model system under consideration, that state 3 is weakly coupled with states 1 and 2. Then we expect that population transfer between state 1 and state 2 will dominate the dynamics, with only a small contribution from population transfer to and from state 3. Under such circumstances, the three state system can be reduced to a two state system with a correction to the dynamics from the influence of the third state.

Following the formalism outlined in Sec. V, P is chosen to be the projection operator onto the subspace composed of state 1 and state 2, and Q the projection operator onto state 3. The first term in $\tilde{\mathbf{M}}$ [see Eq.(5.18)] is

$$P\mathbf{M}P=\frac{1}{2}\begin{pmatrix} 0 & M_{12}\\ M_{12} & 0\end{pmatrix},$$

which is a submatrix describing the system dynamics in the absence of state 3. The second term is $P\mathbf{M}Q^{-1}[Q(\omega_1^0\mathbf{I}-\mathbf{M})Q]^{-1}Q\mathbf{M}P$, which describes the correction to the subsystem dynamics arising from the coupling to state 3. We note that in this case $P\mathbf{M}Q=\frac{1}{2}\binom{M_{13}}{M_{23}}$, $Q\mathbf{M}P=\frac{1}{2}(M_{13}M_{23})$, and $[Q(\omega\mathbf{I}-\mathbf{M})Q]^{-1}=1/\omega$. The frequency domain variable ω can be replaced by a typical eigenfrequency of the P subspace, which is $\frac{1}{2}M_{12}$ here. Therefore, for surrogate two state system we have

$$\tilde{\mathbf{M}}=\frac{1}{2}\begin{pmatrix} \dfrac{M_{13}^2}{M_{12}} & M_{12}+\dfrac{M_{13}M_{23}}{M_{12}}\\ M_{12}+\dfrac{M_{13}M_{23}}{M_{12}} & \dfrac{M_{23}^2}{M_{12}}\end{pmatrix}.$$

To see how good this approximation is, we supply a simple numerical demonstration. Suppose the coupling of state 3 with states 1 and 2 is one-tenth of the coupling between state 1 and state 2, i.e., $M_{13}=M_{23}=(M_{12}/10)=-(1/10)$. Then the exact system dynamics is governed by the coupled equations of motion for the three states, i.e.,

$$\begin{aligned}\dot{C}_1(t)&=0.5i[C_2(t)+0.1C_3(t)],\\ \dot{C}_2(t)&=0.5i[C_1(t)+0.1C_3(t)],\\ \dot{C}_3(t)&=0.5i[0.1C_1(t)+0.1C_2(t)],\end{aligned} \tag{8.3}$$

and the approximate system dynamics is governed by the two coupled equations of motion for the two surrogate states, i.e.,

$$\begin{aligned}\dot{C}_1(t)&=i[0.005C_1(t)+0.505C_2(t)]\\ \dot{C}_2(t)&=i[0.505C_1(t)+0.005C_2(t)].\end{aligned} \tag{8.4}$$

The values of $|C_1(t)|^2$ and $|C_2(t)|^2$ obtained from Eqs. (8.3) and (8.4) are compared in Figs. 4(a) and 4(b). The amplitudes and periods of the temporal evolution predicted by the two approaches to the system dynamics are seen to agree quite well. The differences seen in the amplitudes are a consequence of the replacement of the exact eigenfrequencies of the Rabi frequency matrix with a typical eigenfrequency from the P subspace.

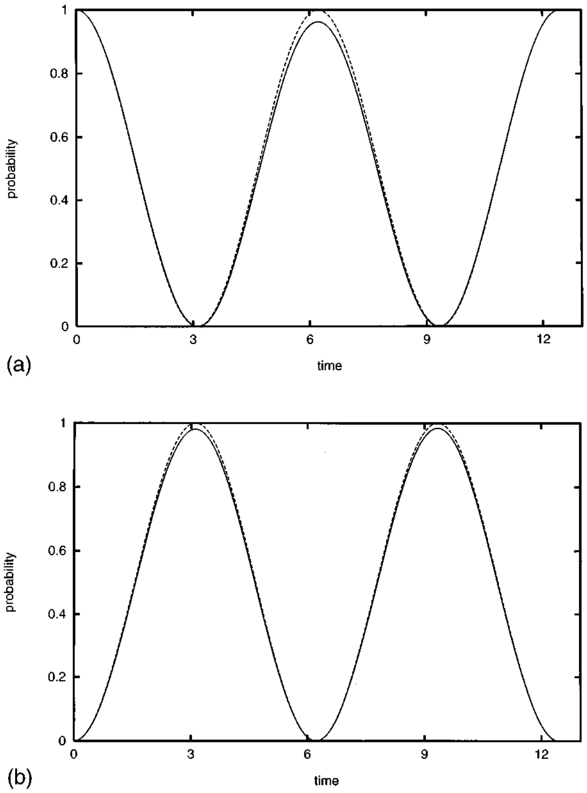

FIG. 4. (a) The probability $|C_1(t)|^2$ on ground state surface from solving exact three state dynamics (—) and effective two state dynamics (---). The initial condition is $C_1(0)=1$ and $C_2(0)=C_3(0)=0$. (b) The probability $|C_2(t)|^2$ on first excited state surface with the same notations as in (a).

IX. DISCUSSION

We have dispersed our comments about the formal analysis throughout the text so there remain only a few remarks to be added. It is important to re-emphasize that all of the control processes we have studied are based on quantum mechanical interference phenomena. Interference is a global phenomenon which, in the context of a time dependent description, implies that events in the past interfere with events in the present. However, it is easier to understand the character of a control mechanism using a local time description, since one can then optimize the transfer of the desired quantity. The links between the local and global pictures are the phases of the molecular expectation values, the most important of which is the nonvanishing instantaneous transition dipole moment $\langle\mu\otimes\mathbf{S}_+\rangle$, which itself shows that a crutial condition for control is the maintenance of well defined phase relation between amplitude on the ground and excited state potential energy surfaces. Any degradation of that phase coherence reduces the efficiency of the control procedure. The most important dephasing mechanism will be determined by the backward propagation of the target function $\mathbf{B}(t)$ [Eqs. (3.7)–(3.8)]. We note that, in general, achievement of control requires the use of two components of the dipole operator.

The description of the interaction of light with a system with two electronic surfaces which we have developed is in many senses analogous to the thermodynamic description of two systems which can transfer mass and energy via external work. Indeed, it is possible to develop versions of the first, second, and third law of thermodynamics for this case.[15] The thermodynamic analysis leads to the identification of processes which transfer energy without transfer of mass and vice versa. An interesting consequence of the analysis is the prediction that it should be possible to build a pulsed laser with an active medium which does not require population inversion. The next step in the development of this analysis is the formulation of a quantum theory of the control of the dynamics of an arbitrary system which includes a consistent thermodynamic description of the system; this formalism could provide a thermodynamic guide to the control of molecular dynamics.

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