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ADIABATIC EXCITATION OF MULTILEVEL SYSTEMS

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Adiabatic excitation of multilevel systems

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We derive and discuss the behavior of several multilevel models relevant to the problem of molecular multiphoton excitation under the action of a quasimonochromatic laser field, the amplitude of which rises slowly and falls rapidly on a certain internal time scale. Our method is suitable for the numerical solution of problems involving the adiabatic excitation of large multilevel systems. We find adiabatic inversion to be a general characteristic of the models considered. The fact that adiabatic inversion is accompanied by marked qualitative and quantitative changes in the expectation value of the dipole operator makes our results useful for understanding the propagation of laser pulses. An explicit expression that is especially convenient for numerical evaluation is presented for determining the limiting internal time scale, which is determined by the energy levels and transition moments of the system and the laser frequency. We illustrate the criterion for adiabatic inversion by applying it to a particular multilevel model. From a density-matrix treatment we conclude that collisional damping destroys the coherence required for adiabatic inversion. On the basis of our results we believe that the adiabatic approximation may be appropriate for some experiments of current interest.

I. INTRODUCTION

Methods for achieving selective excitation of atoms and molecules have received much attention during the past decade, chiefly because of the potential applications of these methods in spectroscopy, laser chemistry, and laser isotope separation.[1] In this paper we discuss the physical principles of a method of adiabatic excitation in which the laser electric field amplitude is varied slowly in comparison with an internal response time of a multilevel atom or molecule. The systems considered here consist of a single ground state with bands of closely spaced levels lying above it (Fig. 1). Such a system is a schematic representation of the energy levels of many systems of physical or chemical interest, such as an atom (in which the splitting of the sublevels within each band results from the fine or hyperfine interaction) or a molecule (in which the splittings result from vibration-rotation and anharmonic interactions). We find that adiabatic inversion, in which population is transferred from the ground state to higher energy levels with nearly 100% efficiency, is a universal characteristic of these systems. Furthermore, the degree of excitation is sharply frequency dependent, making adiabatic excitation a possible candidate for use in laser chemistry or isotope separation as well as in the selective preparation of states for spectroscopy. We find also that adiabatic inversion is accompanied by substantial changes in the index of refraction of a gas containing the active atoms or molecules. In addition to affecting the propagation of a laser beam through optically thick samples, these changes may afford a means for detecting adiabatic inversion.

Adiabatic excitation is accomplished through irradiating an atom or a molecule with one or more time-varying fields whose frequencies and field strengths vary sufficiently slowly for the system to adjust continuously and reversibly to the new conditions, but sufficiently rapidly to avoid disruption of the necessary atomic or molecular coherence by collisions. Because of the reversibility of adiabatic excitation, a nonadiabatic change of conditions is required to preserve an adiabatically achieved excitation after the cutoff of the pulse causing the excitation. Such a nonadiabatic change can be accomplished by a sudden cutoff of the laser pulse, as well as by other means.

Adiabatic excitation through slow changes in the laser pulse amplitude as considered here occurs or can be induced in many systems of current interest. Experiments in which the atoms or molecules of an atomic beam ex

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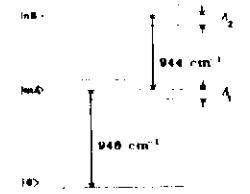

FIG. 1. Schematic energy-level diagram of the multilevel systems considered in this paper. $\delta_1 = 0.1$ cm^{-1} and $\delta_2 = 0.08$ cm^{-1}.

perience a gradually rising (and then falling) laser field amplitude may satisfy the conditions for adiabatic excitation in some cases. As we show below, experiments on multiphoton excitation of low-lying vibrational states of polyatomic molecules may be better described in the adiabatic approximation than in the opposite (sudden) approximation, in which the laser electric field amplitude is assumed to change instantaneously from zero to a finite value. Finally, deliberately induced state-selective adiabatic inversion in molecular or atomic systems may find applications in laser chemistry and isotope separation or in atomic and molecular spectroscopy.

Adiabatic excitation is well known in the field of nuclear magnetic resonance, where adiabatic inversion (fast passage) takes place when a dc field producing an energy-level splitting is slowly varied in such a way as to move the resonance of the system through the frequency of the applied radiofrequency field.[2] The adiabatic approximation was applied to a two-level atom by Treacy,[3] who found that adiabatic inversion could be induced by a laser pulse whose frequency varied slowly from below resonance to above it (or vice versa). Treacy and Demaria[4] later confirmed this result experimentally in NH_3 and SF_6. Grischkowsky and Loy later predicted adiabatic inversion on a two-photon transition using variations in field strength alone.[5] One- and two-photon adiabatic inversion was demonstrated experimentally by Loy using a dc Stark field to shift the energy levels during the pulse.[6,7] More recently, Hulet and Kleppner demonstrated adiabatic inversion using the Rydberg states of lithium.[8] Using a dc Stark field to shift the energy levels and a microwave field to induce transitions, they were able to populate the $n = |m| = 19$ states with nearly 100% efficiency. Courtens and Szöke made use of the adiabatic approximation in their analysis of resonance scattering and resonance fluorescence.[9] The theoretical work of Kuz'min and Sazonov is of particular importance.[10–12] They applied the adiabatic approximation to a number of multilevel systems using variations of field strength alone, and found adiabatic inversion to be a common phenomenon. They also noted its sharp frequency dependence as a possible basis for laser isotope separation. A somewhat different approach was taken by Hioe, who considered adiabatic excitation using the density matrix, and conservation laws on the trace of powers of the density matrix.[13] He found adiabatic inversion could be induced in ladder systems using simultaneous variations in field strength and frequency of incident laser pulses.

In this paper we derive and discuss the behavior of several multilevel models relevant to the problem of molecular multiphoton excitation under the action of a single slowly varying laser field. In Sec. II, which lays the foundation for describing the dynamics of multilevel systems under the adiabatic approximation, the equations of motion are derived and the adiabatic approximation is introduced and explained. We develop a general formalism suitable for the numerical solution of problems involving adiabatic excitation of large multilevel systems. Thus we are not limited to two- or three-level systems or simple ladders, nor to limiting cases of small or large field strengths. We also present expressions for physical observables, such as the expectation value of the dipole operator. In Sec. III these results will be applied to some model systems. In our previous work[14] and in this paper we consider appreciably more complicated systems than previous authors, and show that adiabatic inversion is not limited to a few very simple systems. We also evaluate the polarization as a function of laser field strength and frequency, an observable not considered by previous authors except for two-level systems. We find that marked qualitative changes occur in the polarization as the field strength is raised to values at which adiabatic inversion takes place. Section IV addresses the question of how slowly a perturbing field must be varied to be within the adiabatic approximation. An explicit expression especially convenient for numerical evaluation is developed for determining this important restriction. The expression is not tied to a particular number of bands or levels, and while we limit ourselves to variations in a single laser field strength, the criterion is easily generalized to include variations in laser frequency or an externally applied dc field. We apply the expression to one of the examples of Sec. III and compare it with a time-dependent numerical solution of the Schrödinger equation in order to verify its validity, and give some insight into the consequences of violating it. Based on the results of this example we believe the adiabatic approximation must be taken seriously when evaluating the behavior of multilevel systems for many laser pulses currently in use. Finally, in Sec. V we clarify the effects of collisional damping on the adiabatic approximation by presenting a density-matrix formulation of the adiabatic equations of motion. We find that the presence of damping destroys the adiabatic character of the interaction as the density matrix approaches its steady-state value with multiple time scales. We illustrate this property by presenting a time-dependent solution of the density-matrix equations of motion which explicitly shows the decay of the adiabatic character of a particular multilevel system as the effects of damping set in.

II. THE ADIABATIC APPROXIMATION AND ITS APPLICATION TO MULTILEVEL SYSTEMS

The multilevel systems under consideration in this paper are all of the form portrayed by Fig. 1 and consist of a single ground state and bands of discrete, nearly degenerate levels spaced at almost equal intervals. Such a system is a schematic representation of many systems of chemical or physical interest, such as the levels of a spherical-top molecule (SF_6 or UF_6) that are radiatively connected under the approximate selection rule $\Delta R = 0$. The eigenstates may be denoted by $|mA\rangle$, where m labels the bands and A labels the levels within a band. A general state of the system may be expressed in the Schrödinger picture as a superposition of these eigenstates,

$$\psi(t) = \sum_{m,A} c_{mA}(t)\,|mA\rangle\ . \tag{1}$$

The total Hamiltonian is of the form

$$H = H_0 - \mu E_0(t)\cos(\omega t)\ , \tag{2}$$

where H_0 is the unperturbed Hamiltonian, μ is the component of the dipole operator parallel to the electric field, and $E_0(t)\cos(\omega t)$ is the incident laser field, composed of a rapidly varying carrier of frequency ω modulated by a slowly varying envelope $E_0(t)$. Taking matrix elements of both sides of (1), making the transformation

$$c_{mA} = \tilde{c}_{mA}e^{-im\omega t}\ , \tag{3}$$

and neglecting rapidly varying terms [the rotating-wave approximation (RWA)] gives an equation of the $\tilde{c}$'s of the form

$$\frac{d\tilde{\xi}}{dt} = iH^{\text{eff}}\tilde{\xi}\ , \tag{4}$$

where $\tilde{\xi}$ is a column vector formed from the coefficients $\tilde{c}_{mA}$, and the effective RWA Hamiltonian H^{eff} is given by

$$H^{\text{eff}} = \Delta + \Omega\ . \tag{5}$$

Δ is a diagonal matrix of detunings, $\Delta_{mA,mA} = m\omega - E_{mA}/\hbar$; Ω is an off-diagonal matrix of radiative couplings, $\Omega_{mA,m'A'} = \mu_{mA,m'A'}E_0(t)/2\hbar$; and $\mu_{mA,m'A'}$ is an element of the matrix μ of dipole transition moments. Only matrix elements between adjacent bands of levels will be taken as nonzero:

$$\mu_{mA,m'A'} = \mu_{mA,m'A}\delta_{m,m'\pm1}\ . \tag{6}$$

Two limiting cases may be distinguished in the multilevel dynamical problem posed in Eq. (4). In the sudden approximation the field is assumed to be turned on or off rapidly in comparison with the response time of the system, so that immediately afterwards the system is still in the same state as it was just before the field was switched on or off. For a two-level system the case of rapid switching on gives rise to phenomena such as Rabi oscillations between the upper and lower levels. The sudden approximation, which has been employed extensively in studies of multiphoton excitation, is discussed briefly in Appendix B, where we also show that an inversion of excitation produced adiabatically can be preserved by switching the field off rapidly. In the opposite limit, the adiabatic approximation, the field is varied slowly on an internal time scale established by the dynamics of the system. This allows the system to adjust continuously and reversibly to variations in external parameters such as the field strength or the frequency of a laser pulse. The calculation of the internal time scale on which the external field's amplitude and phase must vary slowly in order for the adiabatic approximation to be valid, which is one of the main goals of this paper, is described in Sec. IV.

Central to the adiabatic approximation are the so-called dressed states, which are the eigenvectors of H^{eff} for a given field strength and frequency, with eigenvalues λ:

$$H^{\text{eff}}\,|a(\lambda)\rangle = \lambda\,|a(\lambda)\rangle\ . \tag{7}$$

The column vectors $\tilde{\xi}$ representing such states take the form

$$\tilde{\xi}(t) = g(\lambda)e^{i\lambda t} \quad \text{or} \quad \tilde{c}_{mA}(t) = a_{mA}(\lambda)e^{i\lambda t}\ , \tag{8}$$

where the column vector $g(\lambda)$ is independent of time but depends parametrically upon the field strength E_0 and the frequency ω. Since the elements of H^{eff} are real and all of the λ's are real, the vectors $g(\lambda)$ can be chosen to have real components. As the field strength goes to zero, H^{eff} becomes diagonal and the dressed states reduce to the unperturbed eigenstates apart from a time-dependent phase factor. The excited unperturbed eigenstates have eigenvalues Δ_{mA} while the ground eigenstate has eigenvalue zero. If the system is initially in one of the unperturbed eigenstates with $E_0 = 0$, then the adiabatic theorem of quantum mechanics[15] guarantees that as E_0 is increased from zero the system will remain in the dressed state derived from the initial state by continuity, provided the field strength and frequency are varied sufficiently slowly. We shall speak of this particular dressed state as being "correlated" with the initial state. For example, the dressed state $|a(\lambda_0)\rangle$ correlated with the ground state has an eigenvalue λ_0 that approaches zero as E_0 approaches zero. In practice, if one assumes that the eigenvalues of H^{eff} do not cross one another as functions of E_0 and ω, an assumption which holds for the systems considered here, matching a given dressed state with the unperturbed eigenstate whence it was derived is a matter of ordering the eigenvalues from lowest to highest and recognizing that the position of a given dressed state's eigenvalue will remain the same as when the field strength was zero.

The extensive use of the sudden approximation in calculations of multiphoton excitation has created a climate in which certain natural properties of adiabatically evolving states may seem surprising at first. For example, as the field increases adiabatically from zero, the system remaining in a single dressed state, the populations in the unperturbed eigenstates are given by $|a_{mA}(\lambda_0)|^2$ and are therefore independent of time aside from their parametric dependence on E_0 and ω. Thus no Rabi oscillations occur in the adiabatic approximation. Adiabatic excitation is also a reversible process: if the field is adiabatically decreased to zero after reaching some maximum field strength, population excited into other levels will move smoothly back into the initial state, thus leaving the system in its original condition. Thus, if any excitation is to persist after the passage of a laser pulse of a given frequency, one must violate the adiabatic condition somewhere within the pulse. For example, a sharp cutoff of $E_0(t)$ after a slow rise can trap population in excited levels. We give examples of the trapping of population in Sec. IV and in a forthcoming paper on the applications of adiabatic excitation to laser isotope separation and laser chemistry.

Previous discussion of adiabatic excitation have generally concentrated on the populations $|\tilde{c}_{mA}(t)|^2 = |c_{mA}(t)|^2$ of the original (unperturbed) states. However, there is another physically important quantity that can be calculated straightforwardly under the adiabatic approximation: the dipole moment induced in the system by the laser field, or, equivalently, the induced macroscopic polarization (dipole moment per unit volume). For laser pulses with a sufficiently slowly varying amplitude $E_0(t)$, the polarization induced in the medium during the passage of the pulse can be approximated by the polarization calculated under the adiabatic approximation. The polarization, in turn, gives rise to a contribution to the index of

refraction. The source term in the wave equation describing the spatial propagation of a laser pulse amplitude $E_0(z,t)$ (in the approximation of slowly varying amplitude and phase) is proportional to the complex polarization

$$\mathcal{P} = S + iC , \tag{9a}$$

where C and S are the slowly varying in-phase and quadrature components of the real polarization

$$P(t) = C(t)\cos(\omega t) + S(t)\sin(\omega t) . \tag{9b}$$

In Appendix A we show that the complex polarization for a multilevel system is given by

$$\mathcal{P} = 2iN_0 \sum_{m,A,B} \tilde{c}^*_{m,A}\tilde{c}_{m-1,B}\mu_{m,A;m-1,B} \tag{10}$$

where N_0 is the density of atoms or molecules. In published numerical calculations of pulse propagation, the polarization has usually been calculated by direct solution of the Schrödinger equation and subsequent evaluation of the expectation value of the dipole moment. Since calculating the refractive index requires much less computational effort than solving the Schrödinger equation, the adiabatic approximation is attractive as an ingredient of a propagation calculation for slowly varying pulses. One of the motivations of this work was to prepare the way for extending earlier work on pulse propagation under the adiabatic-following approximation from two-level to multilevel systems. Because all components of a given dressed-state eigenvector contain a time dependence of the form $e^{i\lambda t}$, the complex polarization for a system in a unique dressed state can be shown from Eqs. (8) and (10) to be pure imaginary and to be given by

$$\mathcal{P} = 2iN_0 \sum_{m,A,A'} a_{m,A}(\lambda_0)a_{m-1,A'}(\lambda_0)\mu_{m,A;m-1,A'} \tag{11a}$$

implying that the real polarization is in phase with the field. Thus the susceptibility

$$\chi = P(t)/E(t) \tag{11b}$$

is real, and there is a real refractive index $n = (1+4\pi\chi)^{1/2} \approx 1 + 2\pi\chi$ for $\chi \ll 1$ (cgs units). In the adiabatic approximation, then, the system is purely dispersive.

Accounting for the effects of collisions and other damping processes is beyond the scope of Eq. (4). We show in Sec. V that the adiabatic processes that are the primary concern of this paper occur only on time scales that are short compared to the decay times established by the damping processes; in the language of nuclear magnetic resonance, we are discussing the "adiabatic rapid passage" of multilevel systems.

In summary, we have outlined a procedure for solving problems under the adiabatic approximation which is suitable for numerical evaluation and sufficiently general to include multilevel systems of realistic complexity. Briefly, this procedure consists of calculating the eigenvectors and eigenvalues of H^{dr}, ordering the eigenvalues to match dressed states with initial states, and calculating physical properties from the dressed states as functions of field strength and frequency. The given expressions for the populations and polarization yield as immediate consequences of adiabatic excitation that there are no Rabi oscillations in the populations, and the polarization is in phase with the applied field. We now consider some examples of multilevel systems in order to demonstrate several other general properties of adiabatic excitation which are not readily apparent from the form of the basic expressions for the observables.

III. EXAMPLES OF MULTILEVEL SYSTEMS UNDER THE ADIABATIC APPROXIMATION

The simple multilevel system composed of a single ground state with a single band of N levels above it, which will henceforth be referred to as a $(1,N)$ system, exhibits many of the features present in more complex systems while remaining fairly tractable by analytic methods. The $(1,N)$ system has been the prototype of studies of intramolecular relaxation for many years.[16] In this section we derive analytically and calculate numerically the behavior of the populations and the dipole expectation value (polarization) of $(1,N)$ and $(1,M,N)$ systems subject to an adiabatically varying quasimonochromatic laser field. In particular, we show that adiabatic inversion occurs in a $(1,N)$ system whenever the laser frequency ω is tuned so that $\hbar\omega$ falls within the upper band of levels, and that under these circumstances a strong population inversion is accompanied by a nearly vanishing polarization. More complex behavior occurs in $(1,M,N)$ systems, where the ground state can be adiabatically depleted but where different excited states can be populated, depending on the laser field amplitude. In order to provide a basis for judging whether adiabatic excitation may be important in experiments on infrared multiphoton excitation, we have chosen energy-level spacings and dipole transition moments that are approximately those of the well-studied molecule SF_6.[17]

The eigenvector-eigenvalue equations for the $(1,N)$ system are of the form

$$\sum_{i=1}^{N} \Omega_i a_i(\lambda) = \lambda a_0(\lambda) , \tag{12a}$$

$$\Omega_i a_0(\lambda) + \Delta_i a_i(\lambda) = \lambda a_i(\lambda) . \tag{12b}$$

In these equations $\Omega_{0,i}, \Delta_{i}, a_i$ have been written as Ω_i, Δ_i, a_i, since all indices but the last are identical for the nonzero matrix elements. These equations may be rearranged to give

$$a_i(\lambda) = \frac{\Omega_i}{\lambda - \Delta_i} a_0(\lambda) , \tag{13a}$$

$$\lambda = \sum_{i=1}^{N} \frac{\Omega_i^2}{\lambda - \Delta_i} . \tag{13b}$$

Equation (13b) is a well-known implicit equation for the eigenvalues.[18] Placing these eigenvalues into (13a) then yields the eigenvectors, which are the dressed states of the $(1,N)$ system.

Equation (13b) may be solved graphically for the eigenvalues by plotting the right-hand side, henceforth referred to as $F(\lambda)$ versus λ. Superimposing on this graph of $F(\lambda)$ versus λ the diagonal line $\lambda = \lambda$ gives the eigenvalues as the intersection points. An example of such a graph is given in Fig. 2 for a (1,5) system. Numerical details of this system are given later; detailed markings of the axes have been deliberately suppressed to bring out qualitative features of the graph. The dashed vertical lines on the graph are the asymptotes of $F(\lambda)$ occurring at the detunings Δ_i.

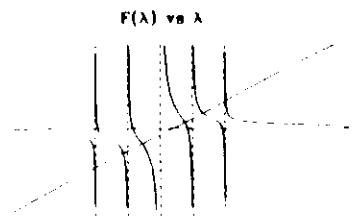

FIG. 2. Graphical solution of the eigenvector-eigenvalue equation for a $(1,N)$ system. The eigenvalues are given by the intersection points of the straight line $\lambda = \lambda$ with $F(\lambda)$.

Understanding the behavior of this plot as the frequency and field strength are changed is of great importance in understanding the behavior of a $(1,N)$ system. The observation that $F(\lambda)$ depends on the field strength only through the factor $(E_0)^2$ in the numerator makes clear the behavior of the eigenvalues for large and small E_0. For small E_0 the curves of $F(\lambda)$ become compressed towards the x axis, the intersection points being nearly equal to the detunings Δ_i for all except one eigenvalue, that correlated with the ground state, which approaches zero. For large E_0 the curves become stretched out and the intersection points for curves between two asymptotes approach the values at which the curves of $F(\lambda)$ cross the x axis, which are independent of E_0. Thus the interior eigenvalues λ approach fixed finite values for large E_0. The intersection points for curves on the far left and right, however, do not approach fixed values but rather grow increasingly large as E_0 becomes larger. The behavior of these two eigenvalues at large field strengths may be found from the eigenvalue equation. If λ is large compared to all Δ_i then one may neglect these Δ_i in the denominator of Eq. (13b) to obtain the expression

$$\lambda = \sum_{i=1}^{N} \frac{\Omega_i^2}{\lambda} \tag{14}$$

or

$$\lambda^2 = \sum_{i=1}^{N} \Omega_i^2 = \frac{1}{4\hbar^2} M^2 E_0^2, \quad M^2 = \sum_{i=1}^{N} \mu_i^2 . \tag{15}$$

Thus the far left (smallest) and right (largest) eigenvalues of Fig. 2 are proportional to the field strength for large E_0.

The frequency dependence of the curves is contained entirely in the Δ_i, so the only effect of increasing or decreasing the frequency is to move the curves and asymptotes for $F(\lambda)$ left or right with respect to the y axis and the diagonal line $\lambda = \lambda$.

The dressed states may be obtained for small and large E_0 using the known behavior of the eigenvalues in these limits. Assuming the system is initially in its ground state, we seek the particular dressed state whose eigenvalue goes to zero as E_0 approaches zero. The eigenvalue of interest, λ_0, is easily identified on the graph of $F(\lambda)$ versus λ. While the relative position of this eigenvalue with respect to all other eigenvalues does depend upon frequency, it does not depend upon the field strength, and thus having identified its position with respect to the other eigenvalues for low fields one also knows it for high fields.

First let E_0 be small enough so that $\lambda_0 \ll \Delta_i$ for all i, and let the frequency of the field be close to the energy of one of the upper levels, i.e., $\Delta_j \ll \Delta_{i\neq j}$. The jth term in Eq. (13b) will then dominate all the other terms because of its small denominator. The eigenvalue equation may then be written

$$\lambda_0^2 - \lambda_0\Delta_j = \Omega_j^2 . \tag{16}$$

This is precisely the eigenvalue equation for a two-level system, and inspection of the eigenvector Eq. (13a) shows that $a_j \gg a_{i\neq j}$. Thus for E_0 small and $\hbar\omega$ sufficiently close to E_j the $(1,N)$ system behaves like a two-level system, with the field connecting only one state at a time with the ground state.

If E_0 is large, the $(1,N)$ system displays radically different behavior. There are two subcases; $\hbar\omega$ above or below the band, and $\hbar\omega$ within the band. Suppose $\hbar\omega$ is below the band ($\hbar\omega < E_i$ for all i). In this case all asymptotes of $F(\lambda)$ versus λ will be to the left of the y axis, so the ground-state-correlated eigenvalue is given by the intersection at the far right. Letting $\lambda \gg \Delta_i$ and using Eq. (15) one finds

$$\lambda_0 = \frac{1}{2\hbar} M E_0 . \tag{17}$$

Substitute this into the eigenvector equation and neglect Δ_i compared with λ to arrive at an expression for the amplitude of the ith state:

$$a_i(\lambda_0) \propto \frac{\mu_i}{M} a_0 . \tag{18}$$

Normalizing the sum of the squares of the a_i to 1 gives $a_0^2(\lambda_0) = \frac{1}{2}$, so that

$$a_i^2(\lambda_0) = \tfrac{1}{2}\mu_i^2/M^2 . \tag{19}$$

Thus the populations in each state attain a limiting saturation value for large E_0. A similar effect holds for the polarization:

$$P_0 = 2N_0 a_0(\lambda_0)\sum_i a_i(\lambda_0)\mu_i = 2N_0 a_0^2 M = N_0 M . \tag{20}$$

Since this value is independent of E_0, the polarization will saturate at a finite value if E_0 is large and $\hbar\omega$ is outside the band.

Now take E_0 large and $\hbar\omega$ inside the band. In this case the ground-state-correlated eigenvalue is determined by an intersection with a curve trapped between two asymptotes. As E_0 gets large the curves of $F(\lambda)$ become nearly vertical lines, so that the eigenvalue approaches a finite value,

equal to the value of λ at which $F(\lambda)$ crosses zero.

The behavior of the probability amplitudes and populations may be seen easily from Eq. (13a). As Ω_j gets large, $|a_j|$ must remain bounded by 1. If λ_0 is near its finite limiting value then the only way of keeping $|a_j|$ bounded in Eq. (12a) is to have $a_0 \to 0$. Thus the population in this limit will move from the ground state to the upper states, producing a population inversion.

To find the polarization, rewrite the eigenvalue Eq. (13b) in the form

$$\lambda = \tfrac{1}{2} E_0 \left| \sum_{i=1}^{N} \frac{\frac{1}{2}\mu_i^2 E_0/\hbar}{\lambda - \Delta_i} \right| . \tag{21}$$

As E_0 approaches infinity, λ remains finite so that the term in parentheses must approach zero. Next construct an expression for the polarization in terms of a_0 from the eigenvector Eq. (13a):

$$P_0 = 2N_0 a_0 \sum_{i=1}^{N} \frac{\frac{1}{2}\mu_i E_0/\hbar}{\lambda - \Delta_i} a_0 \mu_i$$

$$= 2N_0 a_0^2 \left| \sum_{i=1}^{N} \frac{\frac{1}{2}\mu_i^2 E_0/\hbar}{\lambda - \Delta_i} \right| . \tag{22}$$

The quantity in parentheses is identical to the quantity in parentheses of Eq. (21). Since the latter quantity goes to zero for large E_0 and when $\lambda = \lambda_0$, and since a_0^2 is bounded by unity, the polarization must also go to zero at this frequency for large E_0. A special case of our general results for the high-field-strength $(1,N)$ systems has been derived by Kuz'min and Sazonov[12] for a (1,2) system.

The results of a numerical solution of the eigenvector-eigenvalue equations are given in Figs. 3–7 for a (1,5) system. The levels in the band are spaced 0.1 cm^{-1} apart, and the spacing between the ground state and the center of the band is 948 cm^{-1}. The square of the matrix element of the dipole operator between the ground state and an excited state is largest between the center level and the ground state, and falls off toward the edge of the band as a Lorentzian with a half-width at half maximum

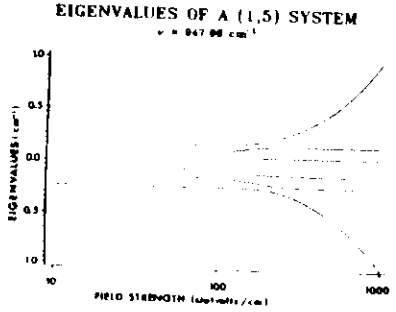

FIG. 3. Eigenvalues of a (1,5) system vs field strength at $\nu = 947.96$ cm^{-1}. Note the two outside values diverge while the interior values approach a finite limit

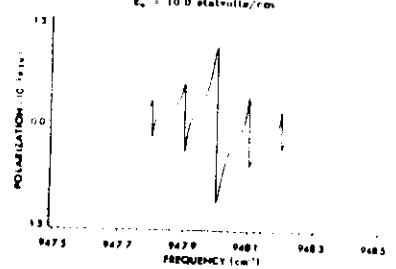

FIG. 4. Polarization of a (1,5) system vs frequency at a field strength of 10 statvolts/cm (0.012 MW/cm^2). At this relatively low field strength the system behaves much like a series of two-level systems.

(HWHM) of 0.05 cm^{-1}. The matrix elements satisfy

$$\sum_i \mu_i^2 = (0.4 \text{ debye})^2 .$$

Figure 3 displays the eigenvalues of H^{eff} as functions of field strength at a frequency of 947.96 cm^{-1}, which is well inside the band. Note that the eigenvalue curves do not cross one another, and that as E_0 gets large the highest and lowest eigenvalues diverge while all others approach limiting values. Figure 4 shows the behavior of the polarization [Eq. (11a)] for an assumed density $N_0 = 3.54 \times 10^{15}$ cm^{-3} at a relatively low field strength (10 statvolts/cm corresponding to a power of 0.012 MW/cm^2); the graph is reminiscent of the behavior of a series of two-level systems. The discontinuities in the curve at the exactly resonant frequencies arise from the assumed adiabatic character of the field and the absence of damping. Figure 5 shows the polarization at a relatively high value of the field (300 statvolts/cm corresponding to 11 MW/cm^2). Here the finite value of the polarization outside the band and its nearly zero value inside the band

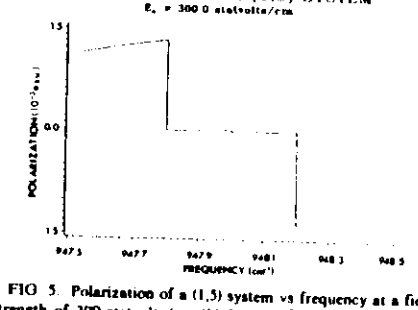

FIG. 5. Polarization of a (1,5) system vs frequency at a field strength of 300 statvolts/cm (11 MW/cm^2). At this relatively high field strength the polarization within the band uniformly approaches zero while the polarization outside the band saturates at a finite value

are clearly shown by the steplike behavior of the polarization. The washing out of the structure in the center of the band will also be found in a more complex system to be considered below.

Figures 6 and 7 show the populations of the levels as functions of field strength. With a laser frequency outside the band, $\bar{\nu} = 947.67$ cm^{-1}, the populations clearly display the saturation behavior predicted analytically. Inside the band, $\bar{\nu} = 947.96$ cm^{-1}, the phenomenon of adiabatic inversion is clearly displayed. At a field strength around 100 statvolts/cm (1.2 MW/cm^2) the population makes a clear shift from the ground state to the upper band.

The existence of adiabatic inversion and the interesting behavior of the polarization in the $(1,N)$ system lead naturally to the question of whether these effects will make their appearance in more complicated systems. A simple extension of the $(1,N)$ system is obtained by adding another band to form a $(1,M,N)$ system. While numerical calculations for the $(1,M,N)$ system are essentially no more difficult to perform than calculations for the simple $(1,N)$ system, analytic calculations rapidly become intractable. Thus only some general observations about this system will be made before moving to a presentation of numerical solutions.

The eigenvector-eigenvalue equations for the $(1,M,N)$ system take the following form:

$$\sum_{i=1}^{N} \Omega_{0,1i} a_{1i} = \lambda a_0 , \tag{23a}$$

$$\sum_{j=1}^{N} \Omega_{1m,2j} a_{2j} + \Omega_{1m,0} a_0 + \Delta_{1m} a_{1m} = \lambda a_{1m} , \tag{23b}$$

$$\sum_{k=1}^{N} \Omega_{2n,1k} a_{1k} + \Delta_{2n} a_{2n} = \lambda a_{2n} , \quad 1 \le m \le M , \; 1 \le n \le N . \tag{23c}$$

Equation (23b) would be the same as Eq. (12b) if not for the term involving the amplitudes a_{2j}. Thus one expects this system to behave like a $(1,N)$ system if one may neglect this term. Dropping this term and substituting the resulting expression for a_{1m} into Eq. (23c) yields an equation for a_{2n}:

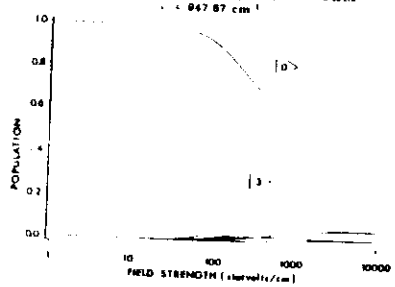

FIG. 6. Population of the states of a (1,5) system vs field strength at $\nu = 947.67$ cm^{-1}. The laser frequency is tuned below the band of levels and thus no adiabatic inversion occurs.

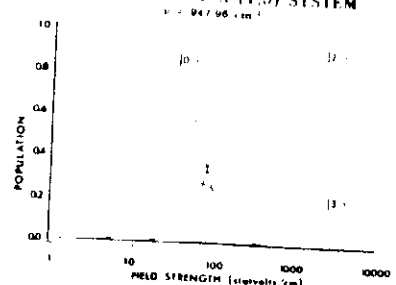

FIG. 7. Population of the states of a (1,5) systems vs field strength at $\nu = 947.96$ cm^{-1}. The laser frequency is tuned within the band and adiabatic inversion occurs around 100 statvolts/cm (1.2 MW/cm^2).

$$a_{2n} \cong \frac{\sum_{k=1}^{M} \Omega_{2n,1k} a_{1k}}{\lambda - \Delta_{2n}}$$

$$\cong \sum_{k=1}^{M} \frac{\Omega_{2n,1k}\Omega_{1k,0} a_0}{(\lambda - \Delta_{1k})(\lambda - \Delta_{2n})} . \tag{24}$$

Crudely speaking, amplitudes of states in the second band are seen to depend on the square of the field strengths, while amplitudes in the first band depend on the first power. Thus one expects the system to behave as a $(1,N)$ system for low enough field strengths, provided the denominator in Eq. (24) is not near zero.

If λ in Eq. (24) is sufficiently close to Δ_{2n} for some frequency and field strength, the amplitude a_{2n} will be large, representing adiabatic inversion into the upper band. This possibility is clearly seen in the numerical solutions, which we now discuss.

Figures 8–11 show graphs of polarization versus laser frequency calculated numerically for a (1,5,5) system. The levels in the central band are 0.1 cm^{-1} apart while

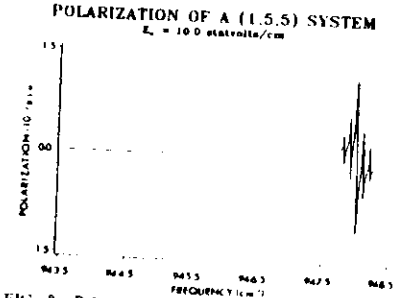

FIG. 8. Polarization of a (1,5,5) system vs frequency at $E_0 = 10$ statvolts/cm (0.012 MW/cm^2). Only the interaction with the lower band of states is apparent

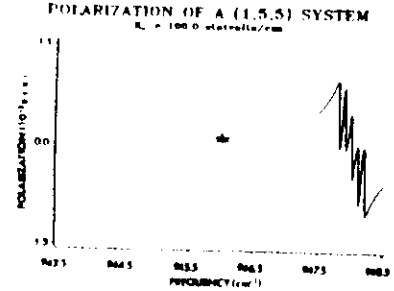

FIG. 9. Polarization of a (1,5,5) system vs frequency at $E_0 = 100$ statvolts/cm (1.2 MW/cm^2). The interaction with the upper band is apparent around 946 cm^{-1}.

for the upper band they are 0.08 cm^{-1} apart. The dipole matrix elements satisfy

$$\sum_{A,A'} (\mu_{m,A,m+1,A'})^2 = (0.4 \text{ debye})^2$$

for both $m = 0$ and $m = 1$. The difference in energy between the ground state and the center of the central band is 948 cm^{-1} while that between the central band and the upper band is 944 cm^{-1}. Figure 8 with $E_0 = 10.0$ statvolts/cm (0.012 MW/cm^2) has $\Omega \sim 10^{-2}$ cm^{-1}, which is an order of magnitude less than the detunings. Thus one expects the ground state and central band to dominate the behavior of the polarization; a comparison of this graph with Fig. 4 for a (1,5) system shows that the two systems have a similar appearance at this field strength. Figure 9 with $E_0 = 100.0$ statvolts/cm (1.2 MW/cm^2) has $\Omega \sim \Delta$; the effects of the two-photon resonance at $\nu = 946$ cm^{-1} are clearly evident, while the behavior at 948 cm^{-1} still has the same character as that of a (1,5) system. Figure 10 with $E_0 = 320$ statvolts/cm (12 MW/cm^2) clearly displays the polarization going to zero when the frequency is inside the lower band. Figure 11 with $E_0 = 2000$ statvolts/cm (480 MW/cm^2) and $\Omega \gg \Delta$ shows the effect

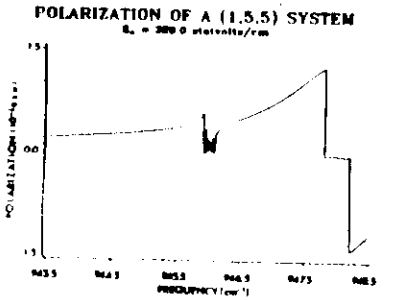

FIG. 10. Polarization of a (1,5,5) system vs frequency at $E_0 = 320$ statvolts/cm (12 MW/cm^2). The interaction with the upper band is very pronounced, while the lower band is showing signs of adiabatic inversion.

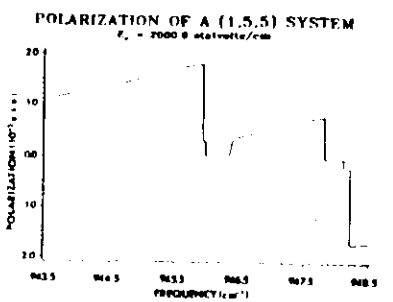

FIG. 11. Polarization of a (1,5,5) system vs frequency at $E_0 = 2000$ statvolts/cm (480 MW/cm^2). The upper band is showing signs of adiabatic inversion just as the lower band is.

on the polarization of a population inversion for $946.13 \lesssim \nu \lesssim 946.4$; the polarization approaches zero in this region.

Figures 12 and 13 demonstrate adiabatic population inversion of this system for two different frequencies. At $\nu = 946.4$ cm^{-1} the population moves to the highest state of the upper band when E_0 rises above 1500 statvolts/cm (270 MW/cm^2), while at $\nu = 947.96$ cm^{-1} the population is seen to move to the second and third states of the central band at a much lower field strength, $E_0 = 100$ statvolts/cm (1.2 MW/cm^2). As the field strength is raised above 2000 statvolts/cm (480 MW/cm^2), however, the population moves into other states of the system.

The results presented in Figs. 3–7 illustrate the fact that under conditions of adiabatic excitation the ground-state population and dipole expectation value (polarization) of a $(1,N)$ system show the same behavior as for a two-level system when the laser frequency is tuned outside the band, but show a completely different behavior (population inversion accompanied by a vanishing polarization) when the laser frequency is such that $\hbar\omega$ lies within the band. For a $(1,M,N)$ system, the ground-state population can be depleted through adiabatic excitation when the

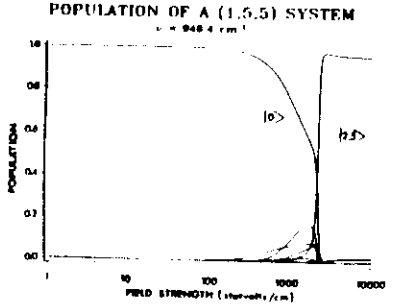

FIG. 12. Population of the states of a (1,5,5) system vs field strength at $\nu = 946.4$ cm^{-1}. A sharp adiabatic inversion occurs near a field strength of 2000 statvolts/cm (480 MW/cm^2).

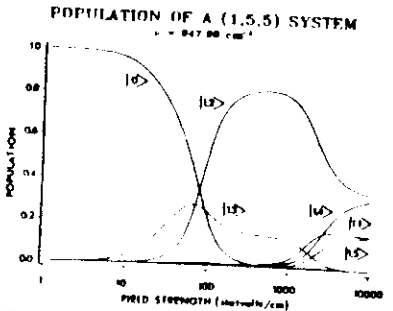

FIG. 13. Population of the states of a (1,5,5) system at $\nu = 947.96$ cm^{-1}. Adiabatic inversion into the lower band takes place near 100 statvolts/cm (1.2 MW/cm^2). At field strengths higher than 1000 statvolts/cm (120 MW/cm^2) the population makes further transitions within the lower band.

laser frequency lies in a certain interval (determined by the field strength) between the one-photon and two-photon resonances. In the latter case the state that receives the population is determined by both the laser frequency and the field strength. High state-selectivity is therefore possible, as will be discussed in greater detail in a forthcoming paper.

For both $(1,N)$ and $(1,M,N)$ systems, there are values of laser frequency and field strength for which the polarization nearly vanishes. In these regions a propagating laser field will therefore experience little phase change as a result of its interaction with the atomic or molecular systems. In particular, self-focusing and self-defocusing should be minimal under these conditions.

IV. CONDITIONS FOR VALIDITY OF THE ADIABATIC APPROXIMATION

The results presented have assumed the validity of the adiabatic approximation, in which a multilevel system is assumed to remain in a dressed state for sufficiently slow variations in the effective Hamiltonian. To use the adiabatic approximation effectively, one needs a criterion for evaluating how slow is slow enough. In this section a general criterion for the validity of the adiabatic approximation[15] will be applied to the multilevel systems discussed in this paper. Special cases of this criterion have been discussed previously in the context of two-level systems.[9]

Messiah's adiabatic condition[15] explicitly shows the probability of finding a multilevel system in a dressed state other than that in which it originally started. If the system is assumed to be in its ground state at zero field, then the probability P_{0i} of finding it in a dressed state $|\lambda_i\rangle$ different from the ground-state-correlated state $|\lambda_0\rangle$ at nonzero field is bounded by

$$P_{0i} \leq \left| \frac{\langle \lambda_0 | dH^{\text{eff}}/dt | \lambda_i \rangle}{(\lambda_0 - \lambda_i)^2} \right|^2 . \tag{25}$$

If the adiabatic approximation is to be valid one requires that $P_{0i} \ll 1$ for all $|\lambda_i\rangle \neq |\lambda_0\rangle$. This may be expressed in the form

$$\sum_{i(\neq 0)} \left| \frac{\langle \lambda_0 | dH^{\text{eff}}/dt | \lambda_i \rangle}{(\lambda_0 - \lambda_i)^2} \right|^2 \ll 1 \tag{26}$$

A convenient form of this condition may be obtained when the frequency of the field is held fixed so that the entire time dependence of H^{eff} is carried by the field strength. Express H^{eff} and dH^{eff}/dt as

$$H^{\text{eff}} = \Delta + \frac{\mu}{2\hbar} E_0 , \tag{27a}$$

$$\dot{H}^{\text{eff}} = \frac{\mu}{2\hbar} \dot{E}_0 . \tag{27b}$$

These two equations imply that

$$(H^{\text{eff}} - \Delta) \frac{\dot{E}_0}{E_0} = \frac{\mu}{2\hbar} \dot{E}_0 = \dot{H}^{\text{eff}} . \tag{28}$$

H^{eff} is diagonal in the dressed-state basis but Δ is not, so that one obtains

$$\left| \frac{E_0}{\dot{E}_0} \right|^2 \gg \sum_{i(\neq 0)} \left| \frac{\langle \lambda_0 | \Delta | \lambda_i \rangle}{(\lambda_0 - \lambda_i)^2} \right|^2 . \tag{29}$$

Define a quantity T with units of time as $T = (\dot{E}_0/E_0)^{-1}$ to obtain

$$T \gg \tau \equiv \left[\sum_{i(\neq 0)} \left| \frac{\langle \lambda_0 | \Delta | \lambda_i \rangle}{(\lambda_0 - \lambda_i)^2} \right|^2 \right]^{1/2} . \tag{30}$$

Crudely speaking, T is a measure of the minimum rise time permitted an applied laser pulse for the production of adiabatic excitation. Pulses that obey Eq. (30) produce adiabatic excitation, while pulses that strongly violate Eq. (30) (i.e., for which $T \ll \tau$) can be treated in the sudden approximation. A similar equation may be obtained for variations in laser frequency.

In general, an analytic evaluation of Messiah's adiabatic condition is difficult for all but rather elementary systems, some of which appear in Ref. 14. However, the form of Messiah's condition is particularly well suited to numerical evaluation. It is also completely general in the sense that it is not tied to any particular number of bands, levels within the band, or any particular field strength, frequency, or distribution of dipole strengths.

A numerical evaluation of Messiah's condition on variations in field strength for a (1,3) system is displayed in Fig. 14, where the quantity τ (in nanoseconds) is plotted as a function of the laser frequency in cm^{-1} and of the common logarithm of the field strength in statvolts/cm. It is clear that τ is a function of field strength and frequency, so that the maximum permissible rate of variation of E_0 is larger for some frequency–field-strength combinations than for others. The larger values of τ occur at frequencies near resonance and at frequencies and field strengths for which adiabatic inversion occurs, as would be expected from Eq. (30). Note that pulse rise times of the order of 1–10 ns should be well within the adiabatic approximation over the regions in which adiabatic inversion occurs for this system. At other frequency–field-

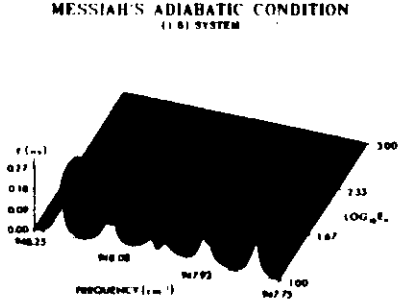

FIG. 14. A plot of Messiah's adiabatic condition τ (ns) as a function of field strength (statvolts/cm) and frequency (cm^{-1}). One requires the rate of change of the field strength (E_0/E_0) to be slow compared to the reciprocal of τ. The peaks in τ usually label the positions of adiabatic inversion.

strength combinations variations of the field may take place on times scales much shorter than 1 ns and still be within the adiabatic approximation.

To test Messiah's condition, we performed numerical solutions of the time-dependent Schrödinger equation under the rotating-wave approximation [Eq. (4)] for a (1,3) system. The field strength was given the form of a Fermi pulse,

$$E_0(t)=\frac{E_0}{1+\exp(-t/\tau_p)} \tag{31}$$

with $-70\le t\le 70$ ns, and the system was initially placed in its ground state. A summary of the results of these calculations for ν equal to 947.82 cm^{-1} is given in Fig. 15 for several values of τ_p. In this figure the net population in the upper band is plotted as a function of time. On the basis of the adiabatic approximation one expects adiabatic inversion to occur at 947.82 cm^{-1} when $E_0\simeq 150$ statvolts/cm (2.7 MW/cm^2) and $\tau_p\ge 1$ ns, as may be verified by inspection of Fig. 14. Figure 15 clearly shows adiabatic behavior for $\tau_p=10$ ns. At $\tau_p=1$ ns the adiabatic

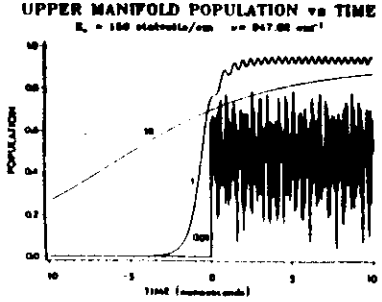

FIG. 15. Total population in the upper band vs time for three Fermi pulses with time constants $\tau_p=10$, 1, and 0.01 ns.

approximation is still quite good apart from a slight ripple arising from the onset of Rabi oscillations associated with small deviations of the system from a dressed state. At $\tau_p=0.01$ ns the Rabi oscillations are very pronounced as the adiabatic approximation breaks down.

The ability to trap population in excited states using pulse envelopes with slow rise times and rapid fall times may be demonstrated with a pulse shape of the form

$$E_0(t)=\frac{2A}{\exp(t/\tau_p)+\exp(-t/\tau_p)}, \tag{32}$$

which approaches zero as $t\to\pm\infty$. The parameter τ_p provides a measure of the rise time and fall time of the pulse. A time-dependent solution of the Schrödinger equation for two sets of parameters is summarized in Fig. 16. In this figure the total population in the upper manifold of a (1,5) system is plotted as a function of time. The solid curve represents a rise time and fall time of 10 ns, with $A=300$ statvolts/cm giving a maximum field strength of 300 statvolts/cm (11 MW/cm^2). Such a pulse is adiabatic for all time and as a consequence the population is seen to adiabatically invert into the upper manifold as the pulse approaches its maximum value, and then revert back to the ground state as the field adiabatically falls to zero. In contrast the dashed curve represents a rise time of 10 ns followed by rapid cutoff of 0.01 ns ($\tau_p=10$ ns for $t<0$ and $\tau_p=0.01$ ns for $t>0$). As before, the population adiabatically inverts into the upper manifold, but as the field strength falls rapidly to zero in the tail of the pulse, the adiabatic condition is violated and the system is trapped in an inverted state.

In view of the rapid variation in field strength permitted by the adiabatic criterion [Eqs. (29)–(30)] for energy-level spacings, transition moments, and laser frequencies that are close to those of interest for real systems such as SF_6, it appears that the adiabatic approximation must be taken seriously in interpreting the behavior of multilevel systems subjected to laboratory laser fields. We note that the self-mode-locked CO_2 laser pulses frequently

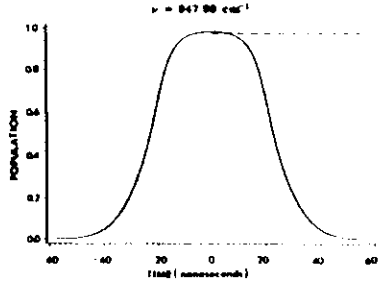

FIG. 16. Total population in the upper band vs time for two different laser pulses at $\nu=947.96$ cm^{-1}. The solid curve results from a pulse with a slow rise and fall time. The dashed curve results from a pulse with a slow rise time and rapid fall time. Note that almost all of the population is trapped in upper levels when the pulse is cutoff sharply

employed in experiments on multiphoton excitation have a temporal fine structure with a subpulse width of roughly 1 ns, while "clean" pulses obtained by the use of an intracavity gain cell[19] have a rise time $T\sim 25-50$ ns. Our calculations show that the clean pulses will produce adiabatic excitation (and deexcitation) of the first few vibrational levels, while the self-mode-locked pulses may violate the adiabaticity criterion; these considerations may help to explain the differences observed in SF_6 (Ref. 20) for excitation with clean pulses versus self-mode-locked pulses.

The calculations of this section demonstrate that it is reasonable to attempt inversion of population from the molecular ground state to a low-lying vibrational state (or from the atomic ground state to an excited state) by adiabatically varying the amplitude of an incident laser field the frequency of which is close (but not exactly equal) to a multiphoton resonance frequency. In order to produce a physically useful inversion, the laser pulse employed must violate the adiabaticity criterion [Eq. (30)] after the laser field amplitude has exceeded the minimum required for an inversion: that is, the laser pulse must rise adiabatically [$T>>\tau$, Eq. (30)] and fall suddenly (in a time short compared to τ). Numerical calculations to be reported in another paper demonstrate that substantial inversions may be produced by this technique.

V. THE DENSITY-MATRIX FORMULATION OF THE ADIABATIC APPROXIMATION

The assumed absence of collisional damping on time scales of interest in adiabatic excitation has made possible an analysis in terms of state vectors rather than the density matrix. However, previous applications of the adiabatic approximation to two-level systems have been performed with the density matrix,[21] chiefly because of the pictorial representation of the density matrix afforded by the model of Feynman, Vernon, and Hellwarth.[22] In the presence of collisional damping, solutions of the density-matrix equation of motion such that $d\rho/dt=0$ are sometimes termed adiabatic, although such solutions are quite distinct from the adiabatic solutions considered here. For the sake of clarity we shall refer to solutions of $d\rho/dt=0$ as steady-state density matrices. In the steady state the system is in a dynamic equilibrium between the collisional decay and the radiative pumping due to the incident field.

In this section, we show (i) that the density matrix of a multilevel system approaches the steady-state density matrix on multiple time scales determined by solving a certain eigenvalue problem; (ii) that in the limit of zero damping, the steady-state density matrix approaches a density matrix describing a system under the adiabatic approximation as described in the preceding sections; and (iii) that adiabatic excitation can be achieved only on time scales that are short compared to any of the characteristic times for the approach of the system to the steady state.

There is a close relationship between the steady-state density matrix and the dressed states. The steady-state approximation (which is sometimes called the adiabatic elimination of atomic variables) consists of replacing the exact solution to the density-matrix equation of motion with the steady-state solution $\bar{\rho}^{ss}$. This approximation is valid as long as the pulse duration (or, for a pulse with a nonsmooth envelope, the time in which the pulse envelope changes significantly) is long compared with both the characteristic response and relaxation times of the system. The limit $\bar{\sigma}^{ss}$ of the steady-state density matrix as the relaxation times approach infinity is diagonal in the dressed-state basis, with populations that are determined only by the initial conditions. If the system is to be described (in the limit of no relaxation) by a wave function rather than by a density matrix, then only one of the diagonal entries in $\bar{\sigma}^{ss}$ can be nonzero. In the latter case the system remains in the dressed state that is correlated with the initial state prior to turning on the laser pulse. In this sense the multilevel adiabatic-following approximation for the wave function is a limiting case of the adiabatic approximation for the density matrix. These points are discussed in detail below. We assume that the density matrix obeys an equation of motion of the standard form

$$\frac{\partial\rho_{uA,vB}}{\partial t}=\left[-\frac{i}{\hbar}(E_{uA}-E_{vB})-\gamma_{uA,vB}(1-\delta_{uv}\delta_{AB})\right]\rho_{uA,vB}+\frac{i}{\hbar}E(t)\sum_{w,C}(\mu_{uA,wC}\rho_{wC,vB}-\rho_{uA,wC}\mu_{wC,vB})+\delta_{uv}\delta_{AB}\sum_{w,C}(\rho_{wC,wC}W_{wC,uA}-\rho_{uA,uA}W_{uA,wC}), \tag{33}$$

where

$$\gamma_{uA,vB}=\gamma_{vB,uA} \tag{34}$$

is the dephasing rate of an off-diagonal density-matrix element and $W_{uA,vB}$ is the rate of population transfer per molecule from u,A to v,B. For a two-level system, we have

$$(T_1)^{-1}=\tfrac{1}{2}(W_{12}+W_{21}), \tag{35}$$

$$(T_2)^{-1}=\gamma_{12}=\gamma_{21}, \tag{36}$$

which are the familiar relaxation constants. We regard the physical origin of the γ's and W's as collisions. The equation of motion (33) is sufficiently general to encompass many systems of interest in multiphoton excitation.

In Appendix C we define a transformed density matrix $\tilde{\rho}$; show that the density-matrix equation of motion [Eq. (33)] can be written as $d\tilde{\rho}/dt=\Delta\tilde{\rho}$ for a certain matrix Δ [Eq. (C5)]; and show that for a constant-amplitude laser field the density matrix can be partitioned into a constant part (equal to the steady-state density matrix) and a decaying part:

$$\tilde{\rho}_{uA,vB}(t)=\tilde{\rho}^{ss}_{uA,vB}+\sum_{\lambda\,(\neq 0)}\sum_{\beta,\gamma}\sum_{C,D}e^{-\lambda(t-t_0)}C_{\beta A,\gamma B}(\lambda)\times D_{\beta C,\gamma D}(\lambda)\tilde{\rho}_{\beta C,\gamma D}(t_0), \tag{37}$$

where the eigenvalues λ are determined by solving the secular Eq. (C15), and should not be confused with the eigen-

values of the dressed states. Thus the density matrix approaches the steady-state density matrix $\tilde{\rho}^{\infty}$ with time constants given by $\mathrm{Re}\lambda$ as λ runs over the set of eigenvalues.

The steady-state density matrix $\tilde{\rho}^{\infty}$ must be determined analytically or numerically from the equations

$$\sum_{\beta,\gamma,D} A_{\alpha A,\beta B,\gamma C,\varphi D}\tilde{\rho}^{\infty}_{\gamma C,\varphi D}=0 \tag{38}$$

together with the trace condition, Eq. (C21). That Eqs. (C21) and (38) determine $\tilde{\rho}^{\infty}$ uniquely follows from the fact that there are $M(M-1)/2$ independent off-diagonal (generally complex) elements of $\tilde{\rho}^{\infty}$ and Eqs. (38) (as may be seen from the explicit form of Δ [Eq. (C5)]) while there are $M-1$ independent diagonal elements of $\tilde{\rho}^{\infty}$ and Eqs. (38) (since the trace condition [Eq. (C21)] implies that one of the diagonal Eqs. (38) can be derived from the others).

As the damping coefficients [γ and W in Eq. (33)] approach zero, A [Eq. (C5)] approaches the matrix

$$A^{(0)}_{\alpha A,\beta C,\varphi D}=i(H^{\mathrm{eff}}_{\alpha A,\beta C}\delta_{\varphi\beta}\delta_{BD}-H^{\mathrm{eff}}_{\varphi B,\varphi D}\delta_{\varphi\beta}\delta_{AC}) . \tag{39}$$

The requirement that the limiting steady-state density matrix

$$\tilde{\rho}^{\infty}=\lim_{\gamma\to 0}\lim_{W\to 0}\tilde{\rho}^{\infty} \tag{40}$$

satisfy $d\tilde{\rho}^{\infty}/dt=\Delta^{(0)}\tilde{\rho}^{\infty}=0$ implies, according to Eqs. (C4) and (39), that $[H^{\mathrm{eff}},\tilde{\sigma}^{\infty}]=0$. A simple calculation then implies that $\tilde{\rho}^{\infty}$ must be diagonal in a basis of eigenvectors $|\lambda\rangle$ of H^{eff}, i.e., that

$$\tilde{\sigma}^{\infty}=\sum_{\lambda}\tilde{\sigma}_{\lambda\lambda}|\lambda\rangle\langle\lambda| . \tag{41}$$

Indeed any set of $\tilde{\sigma}_{\lambda\lambda}$ will give a $\tilde{\sigma}^{\infty}$ that commutes with H^{eff}. Thus the limit expressed in Eq. (40) is nonunique. As expected, the steady-state solution of the density matrix depends on the form of the damping, and not on the initial conditions, however small such damping may be.

The adiabatic approximation of quantum mechanics implies that if the Hamiltonian H^{eff} is changed sufficiently slowly in time (as a result of changes in the amplitude of the incident field, for example), then each dressed state $|\lambda(t)\rangle$ evolves into a unique state $|\lambda(t')\rangle$, which is the dressed state that is correlated with $|\lambda(t)\rangle$:

$$|\lambda(t')\rangle=\Phi(t',t)|\lambda(t)\rangle . \tag{42}$$

Since $\Phi(t',t)$ is the adiabatic evolution operator in the interaction picture given by Eq. (3) or Eq. (C1), the density matrix evolves according to the equation

$$\tilde{\sigma}^{\mathrm{ad}}(t)=\Phi(t,t_0)\tilde{\sigma}^{\mathrm{ad}}[\Phi(t,t_0)]^{\dagger} \tag{43}$$

$$=\sum_{\lambda}\tilde{\sigma}_{\lambda\lambda}|\lambda(t)\rangle\langle\lambda(t)| , \tag{44}$$

where the dressed-state populations $\tilde{\sigma}_{\lambda\lambda}$, in contrast to the steady-state case, are determined by the initial conditions. Evidently Eq. (44) is simply the density-matrix generalization of the adiabatic approximation. When $\tilde{\sigma}_{\lambda\lambda}$ is nonzero only for one λ, we recover the wave-function version of the adiabatic approximation.

In order to demonstrate the results of this section we performed a numerical solution of the density matrix equations of motion under the rotating-wave approximation [Eq. (C2)] for the (1,5) system considered earlier. The soft collision damping rates were taken to be $\gamma_{mA,nB}=\gamma=0.01\ \mathrm{ns}^{-1}$. Hard collisions transferred population from excited states back into the ground state so that $W_{1m,0}=W=0.001\ \mathrm{ns}^{-1}$, while no population transfer was assumed to occur from the ground state to the excited states, $W_{0,1m}=0$. The system was subjected to a laser pulse of the form given by Eq. (31), with $\tau_p=20$ ns and $E_0=300$ statvolts/cm (1 MW/cm^2). The results of this calculation are summarized in Fig. 17. The solid curves give the populations of the individual excited states, while the dashed curve represents the sum of the populations in these states. The solid horizontal line at 0.79 represents the total excited population obtained in a steady state. At first the system is seen to behave adiabatically, with adiabatic inversion occurring at $t=0$ ns. However, the damping soon destroys the coherence of the adiabatic state and the population is seen to approach the steady-state value asymptotically. Furthermore, the presence of damping destroys the rather selective nature of the adiabatic excitation, scattering the population in a more uniform fashion throughout the excited levels.

VI. CONCLUSION

Adiabatic excitation of multilevel systems displays a number of interesting properties, and must be taken seriously in understanding the behavior of atoms and molecules under the actions of laser fields. We have developed a procedure for solving adiabatic problems, based on the dressed states of the rotating-wave Hamiltonian, which is well suited for numerical evaluation. Application of this procedure to two classes of multilevel models has shown adiabatic inversion to be a rather general property of multilevel systems. The inversion is seen to be sharply frequency dependent, and accompanied by substantial qualitative changes in the polarization. An application of Messiah's adiabatic condition provides an explicit criterion for determining the limits of the adiabatic approximation. It is a general criterion for all multilevel systems of the form presented, and is straightforward to evaluate numerically. Application of Messiah's condition to a particular (1,3) system has shown that pulse rise times of the order of 1 ns may be sufficiently slow to lie within the adiabatic approximation. The presence of collisional damping has been found to destroy the adiabatic behavior of a multilevel system. Consequently adiabatic excitation must take place on a time scale short compared to the mean collision time.

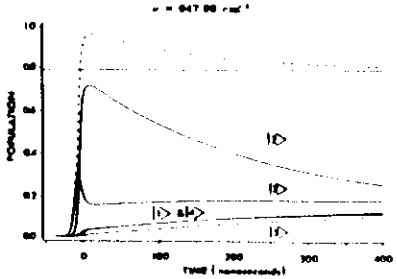

FIG. 17. Population in the upper band vs time in the presence of damping at $\nu=947.96\ \mathrm{cm}^{-1}$. The soft collision rate is $\gamma=10^{-2}\ \mathrm{ns}^{-1}$. The hard collision rate is $W=10^{-3}\ \mathrm{ns}^{-1}$. The dashed curve represents the sum of the populations in the upper band.

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APPENDIX A: POLARIZATION

The polarization density (dipole moment per unit volume) in a dilute medium is given by

$$P(t)=N_0\langle\psi(t)|\mu|\psi(t)\rangle , \tag{A1}$$

where N_0 is the molecular or atomic number density. In terms of the matrix elements of the dipole operator μ, we have

$$P(t)=N_0\sum_{m,n}\sum_{A,B}\exp[i(n-m)\omega t]\tilde{c}_{mA}\tilde{c}^{*}_{nB}\mu_{nB,mA} . \tag{A2}$$

By Eq. (6) this becomes

$$P=N_0\sum_{m,A,B}[\exp(+i\omega t)\tilde{c}_{mA}\tilde{c}^{*}_{m+1,B}\mu_{m+1,B;mA}+\exp(-i\omega t)\tilde{c}_{mA}\tilde{c}^{*}_{m-1,B}\mu_{m-1,B;mA}] . \tag{A3}$$

In order to calculate the complex slowly varying polarization amplitude $\mathscr{P}$ [Eq. (9a)] we must identify the in-phase and quadrature amplitudes C and S (respectively) of Eq. (9b), thus generalizing the result of Icsevgi and Lamb, and Hopf and Scully[7] for a two-level system to the multilevel system considered here.

In the first sum, let $m\to m-1$, interchange A and B and use the fact that the dipole operator is Hermitian to reduce Eq. (A3) to

$$P(t)=C(t)\cos(\omega t)+S(t)\sin(\omega t) , \tag{A4}$$

where

$$C(t)=D+D^{*} ,$$

$$S(t)=i(D-D^{*}) , \tag{A5}$$

and

$$D\equiv N_0\sum_{m,A,B}\tilde{c}^{*}_{mA}\tilde{c}_{m-1,B}\mu_{mA;m-1,B} . \tag{A6}$$

From Eqs. (9), (A5), and (A6), we find that

$$\mathscr{P}(t)=2iD\equiv 2iN_0\sum_{m,A,B}\tilde{c}^{*}_{mA}\tilde{c}_{m-1,B}\mu_{mA,m-1,B} . \tag{A7}$$

APPENDIX B: THE SUDDEN APPROXIMATION

The limiting case of a rapidly-switched-on pulse is one in which the laser field is switched instantaneously from zero to a finite value. In this limit, the state vector at the instant before the pulse is switched on is equal to the state vector at the instant after switching on:

$$|\psi(0)\rangle=\sum_{m,A}\tilde{c}_{mA}(0)|mA\rangle$$

$$=\sum_{m,A,\lambda}\tilde{c}_{mA}(0)a_{mA}(\lambda)|\lambda\rangle \tag{B1}$$

Then the probability amplitudes are subsequently

$$\tilde{c}_{mA}(t)=\sum_{\lambda,m,C}\exp(i\lambda t)a_{mA}(\lambda)a^{*}_{mC}(\lambda)\tilde{c}_{mC}(0)$$

$$=\exp(im\omega t)\langle mA|\psi(t)\rangle . \tag{B2}$$

The populations in the original basis states $|mA\rangle$ are

$$|\tilde{c}_{mA}(t)|^2=\sum_{\lambda,\lambda'}\sum_{m,C}\sum_{m',C'}\exp[i(\lambda-\lambda')t]\times a_{mA}(\lambda)a^{*}_{mC}(\lambda)a^{*}_{m'A}(\lambda')a_{m'C'}(\lambda')\times\tilde{c}_{mC}(0)\tilde{c}^{*}_{m'C'}(0) . \tag{B3}$$

Evidently Rabi oscillations occur at every frequency $\lambda-\lambda'$ for which the corresponding product of amplitudes differs significantly from zero.

If we use the amplitudes of Eq. (B2) in Eq. (10), we obtain for the complex polarization in the sudden approximation

$$\mathscr{P}(t)=i\sum_{\lambda,\lambda'}\mathscr{P}_{\lambda\lambda'}\exp[-i(\lambda-\lambda')t] , \tag{B4}$$

where

$$\mathscr{P}_{\lambda\lambda'}=2iN_0\sum_{m,m'}\sum_{A,B,C,C'}a^{*}_{mA}(\lambda)a_{mC}(\lambda)a^{*}_{m'C'}(\lambda')\times a_{m-1,B}(\lambda')\tilde{c}^{*}_{mC}(0)\tilde{c}_{m'C'}(0)\times\mu_{mA;m-1,B} . \tag{B5}$$

Once again, oscillations occur in $\mathscr{P}$ at every Rabi frequency $\lambda-\lambda'$. Since the response of the medium to the laser field (as summarized in $\mathscr{P}$) contains these additional frequencies, the polarization $\mathscr{P}$ cannot simply be written as $\chi(E_0)E_0$ as in the adiabatic approximation. Thus in the sudden approximation it is not possible to define a susceptibility $\chi(E_0)$ that depends on time only through the variation of E_0 (if any).

If the laser pulse is switched on adiabatically and is then switched off instantaneously at time $t=t_0$, then the state immediately after t_0 is

$$\psi(t_0)=e^{-iH(t_0)}|\lambda_0\rangle$$

$$=\sum_{m,A}d_{mA}|mA\rangle . \tag{B6}$$

The phase $\phi(t)$ is

$$\phi(t) = \int_{-\infty}^{t} \lambda_0(t')dt' , \tag{B7}$$

where the dressed state eigenvalue $\lambda_0(t) = \lambda_0(E_0(t))$ depends on time through the laser field amplitude E_0. We also have

$$d_{mA} = e^{i\phi(t_0)}\langle mA \mid \lambda_0(t_0)\rangle \tag{B8}$$

Since the subsequent evolution of the state vector is given by

$$\psi(t) = \sum_{m,A} d_{mA} e^{-iE_{mA}t/\hbar} \mid mA\rangle \quad (t > t_0) , \tag{B9}$$

the populations in the original basis states $\mid mA\rangle$ for times after the switching-off time t_0 are given by

$$\mid d_{mA} \mid^2 = \mid \langle mA \mid \lambda_0(t_0)\rangle \mid^2 . \tag{B10}$$

thus showing that an adiabatically excited population can be "trapped" in the excited state by rapidly switching off the laser pulse.

APPENDIX C: PROPERTIES OF THE DENSITY MATRIX OF A MULTILEVEL SYSTEM

In order to remove rapidly varying terms in Eq. (33), we make the transformation

$$\rho_{uA,vB} = \exp[-i(u-v)\omega t]\tilde{\rho}_{uA,vB} , \tag{C1}$$

use the rotating-wave approximation, and find that Eq. (33) reduces to

$$\begin{aligned}\frac{\partial\tilde{\rho}_{uA,vB}}{\partial t} = {} & [i(\Delta_{uv} - \Delta_{vB}) - \gamma_{uA,vB}(1 - \delta_{uv}\delta_{AB})]\tilde{\rho}_{uA,vB} \\ & + i\sum_{C}(\Omega_{uA,u+1,C}\tilde{\rho}_{u+1,C,vB} + \Omega_{uA,u-1,C}\tilde{\rho}_{u-1,C,vB} - \tilde{\rho}_{uA,v+1,C}\Omega_{v+1,C,vB} - \rho_{uA,v-1,C}\Omega_{v-1,C,vB}) \\ & + \delta_{uv}\delta_{AB}\sum_{w(\neq u)}\sum_{C}(\tilde{\rho}_{wC,uA}W_{wC,uA} - \tilde{\rho}_{uA,wA}W_{wA,wC}) .\end{aligned} \tag{C2}$$

We note that the causal terms involving the optical field Ω are obtained directly from the effective Hamiltonian and from the basic equation of motion $i\hbar\partial\tilde{\rho}/\partial t = [H^{\text{eff}},\tilde{\rho}]$.

The density matrix Eq. (C2) may be written formally as

$$\frac{\partial\tilde{\rho}_{uA,vB}}{\partial t} = \sum_{p,q}\sum_{C,D} A_{uA,vB;pC,qD}\tilde{\rho}_{pC,qD} , \tag{C3}$$

where the elements of A are sufficiently slowly varying to be considered constant. Equation (C3) may be formally written as a finite-dimensional matrix equation of the form

$$\frac{\partial\tilde{\underline{\rho}}}{\partial t} = \underline{A}\,\tilde{\underline{\rho}} . \tag{C4}$$

where we assume that the basis $\{\mid uA\rangle\}$ has been truncated to M vectors. We then regard $\tilde{\underline{\rho}}$ as an $M^2\times 1$ column vector and $\underline{A}$ as an $M^2\times M^2$ matrix the components of which are

$$\begin{aligned}A_{uA,vB;pC,qD} = {} & +\delta_{up}\delta_{uq}\delta_{AC}\delta_{BD}[i(\Delta_{uA} - \Delta_{vB}) - \gamma_{uA,vB}(1-\delta_{uv}\delta_{AB})] + i\delta_{uq}\delta_{BD}(\delta_{p,u+1}\Omega_{uA,u+1,C} + \delta_{p,u-1}\Omega_{uA,u-1,C}) \\ & - i\delta_{up}\delta_{AC}(\delta_{v,u+1}\Omega_{u+1,D,vB} + \delta_{v,u-1}\Omega_{u-1,D,vB}) \\ & + \delta_{uv}\delta_{pq}\delta_{AB}\delta_{CD}\left[W_{pC,uA}(1-\delta_{pu}\delta_{AC}) + \delta_{pu}\delta_{AC}\sum_{r(\neq u)}\sum_{E}W_{uA,rE}\right] .\end{aligned} \tag{C5}$$

Since Eq. (C4) is linear in $\tilde{\rho}$ and of first order in t, it possesses a solution of the form

$$\tilde{\rho}(t) = U(t,t_0)\tilde{\rho}(t_0) , \tag{C6}$$

where U satisfies the initial condition

$$U(t_0,t_0) = 1 \tag{C7}$$

If we put Eq. (C6) into Eq. (C4) and note that $\tilde{\rho}(t_0)$ is completely arbitrary, we obtain

$$\frac{\partial U}{\partial t} = \underline{A}\,\underline{U} \tag{C8}$$

(Note that $\underline{A}$ is complex.)

In the same spirit as the eigenfunction expansion of ρ used by Goodman and Thiele,[24] we expand U as

$$U_{uA,vB;pC,qD}(t,t_0) = \sum_{\lambda} e^{\lambda(t-t_0)}D_{pC,qD}(\lambda)C_{uA,vB}(\lambda) \tag{C9}$$

The complex numbers λ are determined from an eigenvalue equation derived below.

By Eq. (C7) it follows that

$$\sum_{\lambda} D_{pC,qD}(\lambda)C_{uA,vB}(\lambda) = \delta_{pu}\delta_{qv}\delta_{CA}\delta_{DB} \tag{C10}$$

Thus, the matrix $D_{pC,qD}(\lambda)$ [with columns ordered by λ and rows by (pC,qD)] is a left inverse of the matrix $C_{uA,vB}(\lambda)$ [with rows ordered by λ and columns by (uA,vB)]. Since a left-inverse matrix is also a right inverse, it follows that C and D also obey an orthogonality condition with respect to the index λ of the dressed-state energies:

$$\sum_{u,v}\sum_{A,B} C_{uA,vB}(\lambda)D_{uA,vB}(\lambda') = \delta_{\lambda\lambda'} . \tag{C11}$$

We next show the significance of the matrix C. If we put Eq. (C9) into Eq. (C8), we obtain

$$\begin{aligned}\sum_{\lambda} e^{\lambda(t-t_0)}\lambda D_{rE,sF}(\lambda)C_{uA,vB}(\lambda) = {} & \sum_{\lambda}\sum_{p,q}\sum_{C,D} e^{\lambda(t-t_0)}A_{uA,vB;pC,qD}C_{pC,qD}(\lambda)D_{rE,sF}(\lambda) .\end{aligned} \tag{C12}$$

The above must be true for each distinct eigenvalue λ. Thus

$$\lambda D_{rE,sF}C_{uA,vB} = \sum_{p,q}\sum_{C,D} A_{uA,vB;pC,qD}C_{pC,qD}D_{rE,sF} . \tag{C13}$$

Since the matrix elements of D are the same on both sides, we obtain the eigenvector equation

$$\sum_{p,q}\sum_{C,D}(A_{uA,vB;pC,qD} + \lambda\delta_{up}\delta_{uq}\delta_{AC}\delta_{BD})C_{pC,qD}(\lambda) = 0 , \tag{C14}$$

where the eigenvalues λ are found from the secular equation

$$\det(\underline{A} + \lambda\underline{1}) = 0 , \tag{C15}$$

and the C's are the eigenvectors. The eigenvalues may be either real or complex. We thus see that the solution of the density-matrix equation of motion is

$$\begin{aligned}\rho_{uA,vB}(t) = {} & \sum_{\lambda}\sum_{p,q}\sum_{C,D} e^{-\lambda(t-t_0)}C_{uA,vB}(\lambda) \\ & \times D_{pC,qD}(\lambda)\tilde{\rho}_{pC,qD}(t_0) .\end{aligned} \tag{C16}$$

If we note that $\mathrm{tr}(\tilde{\rho})$ must be constant, i.e.,

$$\sum_{u,A}\frac{\partial\tilde{\rho}_{uA,uA}}{\partial t} = 0 , \tag{C17}$$

it follows that

$$\sum_{u,A}\frac{\partial}{\partial t}U_{uA,uA;pC,qD}(t,t_0) = 0 . \tag{C18}$$

substituting the expression for U given by Eq. (C9) then gives

$$-\lambda\sum_{u,A} e^{-\lambda(t-t_0)}C_{uA,uA}(\lambda) = 0 . \tag{C19}$$

For $\lambda\neq 0$ it follows that

$$\sum_{u,A} C_{uA,uA}(\lambda) = 0 , \tag{C20}$$

while for $\lambda = 0$ we are free to choose

$$\sum_{u,A} C_{uA,uA}(0) = 1 . \tag{C21}$$

Considered as an $M\times M$ matrix, $C(\lambda)$ has unit trace if $\lambda = 0$ and zero trace otherwise. If we set $u = v$ and $A = B$ in Eq. (C10) and sum on u, A, we find that the elements of $D(\lambda)$ can be evaluated for $\lambda = 0$:

$$D_{pC,qD}(0) = \delta_{pq}\delta_{CD} . \tag{C22}$$

The eigenvalue $\lambda = 0$ corresponds to the steady-state solution of Eq. (C2), i.e., the solution $\tilde{\rho}^{ss}$ in which pumping by the field is exactly balanced by collisional relaxation, so that

$$\frac{\partial\tilde{\rho}^{ss}}{\partial t} = 0 . \tag{C23}$$

If $\tilde{\rho}(t_0) = \tilde{\rho}^{ss}$, then $\tilde{\rho}(t) = \tilde{\rho}^{ss}$ for $t > t_0$ by definition of the steady state. Inspection of Eq. (C16) shows that this is possible only if

$$\sum_{p,q}\sum_{C,D} D_{pC,qD}(\lambda)\tilde{\rho}^{ss}_{pC,qD} = \delta_{\lambda,0} \tag{C24}$$

which by Eq. (C11) implies that the $M\times M$ matrix $C(0)$ is the steady-state density matrix:

$$\tilde{\rho}^{ss}_{pC,qD} = C_{pC,qD}(0) . \tag{C25}$$

With this physically important result, the density matrix of Eq. (C16) can be partitioned into a steady-state part and a transient part:

$$\begin{aligned}\tilde{\rho}_{uA,vB}(t) = {} & \tilde{\rho}^{ss}_{uA,vB} + \sum_{\lambda(\neq 0)}\sum_{p,q}\sum_{C,D} e^{-\lambda(t-t_0)}C_{uA,vB}(\lambda) \\ & \times D_{pC,qD}(\lambda)\tilde{\rho}_{pC,qD}(t_0) .\end{aligned} \tag{C26}$$

The transient part (with $\lambda\neq 0$) approaches zero as $(t - t_0)$ becomes large compared to the inverse of the minimum $\mathrm{Re}\lambda$. The approximation of replacing the general $\tilde{\rho}(t)$ by the steady-state $\tilde{\rho}^{ss}$ for all t generalizes the adiabatic elimination of off-diagonal density-matrix components commonly employed for two-level systems.

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