PHYSICAL REVIEW A VOLUME 45, NUMBER 7 1 APRIL 1992

Population transfer with delayed pulses in four-state systems

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(Received 11 September 1991; revised manuscript received 19 November 1991)

We present explicit analytic expressions for adiabatic dressed states which, in suitable limits, produce complete population transfer between initial and final states of a four-state excitation chain without ever placing appreciable population into intermediate states. The population-transfer scheme is a generalization of the three-state stimulated Raman adiabatic passage that makes use of counterintuitive pulse sequences. We demonstrate analytically and numerically that the four-state system differs in a very significant qualitative way from previously studied N-state systems with odd N. In particular, we find that the presence of modest detuning from single-photon resonance is critical to the success of population transfer.

PACS number(s): 42.50.Hz, 33.80.Be, 42.65.Dr

I. INTRODUCTION

For many purposes, in particular collision dynamics and spectroscopy, it is desirable to prepare samples of molecules in which population resides almost entirely in some specified excited state. Such complete population transfer requires coherent excitation by laser radiation [1].

The simplest examples of complete population transfer are to be found in two-state systems [2]. A resonantly tuned pulse will produce complete inversion during the course of Rabi oscillations, whenever the temporal pulse area produces an odd integral number of Rabi cycles (a π pulse is the simplest example) [3–5]. Alternatively, one may sweep the pulse frequency slowly through resonance and thereby achieve complete inversion (adiabatic passage by pulse chirping). The advantages and disadvantages of these alternative schemes are well known [6].

Population transfer in multistate systems can be accomplished by suitable generalization of the π pulse or the chirped adiabatic passage. However, new and more satisfactory schemes become possible when one considers more than two states. With three-state systems a novel technique, stimulated Raman adiabatic passage (STIRAP), makes use of counterintuitive temporal ordering of pulses to produce complete population transfer without placing population into the intermediate state [7,8]. The scheme is particularly attractive since the laser frequency remains constant while the overlap in time of the laser pulses can be conveniently controlled experimentally. It is based upon adiabatically following an instantaneous dressed state that passes continuously from complete identification with the initial molecular state to identification with the final molecular state.

The experimentally demonstrated success of STIRAP in three-state systems [9–11] quite naturally leads one to question whether such a scheme of adiabatic population transfer is possible in more complex multistate systems. We have previously found very simple analytic expressions for the desired approximate adiabatic states for N-state systems with $N>3$ [12]. Those particular solutions are valid for an odd-integer number N of states and also require careful timing of the interaction sequence by a suitable time delay of the laser pulses.

We here display an analytic expression that generalizes the STIRAP process (counter-intuitive pulse ordering, complete population transfer, very small or even negligible population in intermediate states) for a four-state system. From this expression one can readily see the importance of moderate single-photon detuning. We show that, despite the additional complexity of a quartic equation for dressed eigenvalues, it is possible to obtain physical insight comparable to that available for the simpler three-state system.

The four-state version of STIRAP is of interest, e.g., for efficient population transfer to high-angular-momentum states of atoms or for the population of high vibrational levels in electronically excited molecules which, because of small Franck-Condon factors, cannot be reached directly from the vibrational ground state in a one-step process. The transfer process can be accomplished with two or three pulses. Experimental implementation is straightforward, as in the case of three-state STIRAP [9–11]. When particles in a molecular

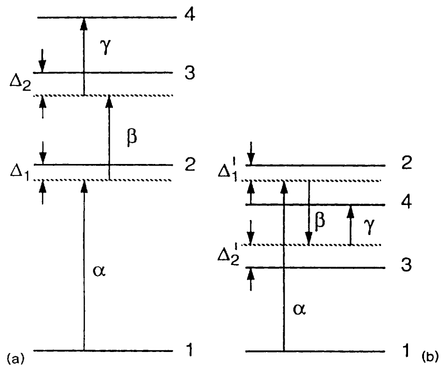

FIG. 1. (a) The "ladder" and (b) the N-type configurations of a chainwise-connected four-level system. The Rabi frequencies of the 1-2, 2-3, and 3-4 transitions are denoted by α, β, and γ, respectively, and Δ_i are the accumulated detunings from state i.

beam cross continuous laser beams at right angle, the correct timing of the interaction sequence is imposed by suitable spatial displacement of the laser beam axes. If the process is induced with pulsed laser in particle beams or in the bulk the interaction sequence can be controlled by suitable time delay of the pulses.

We present analysis of the more general three-pulse case. The two-pulse case is obtained when two out of three pulses are identical. The four-state excitation chain from a low-lying state has various possible configurations (see Fig. 1). Each of these chains is described by a tridiagonal 4×4 Hamiltonian matrix; they differ only in the expressions for diagonal elements. We assume throughout our discussion that the population initially resides entirely at one end of the chain, in state 1. Our objective is to place population into state 4.

In atomic excitation the successive states typically have well-defined parity. Unlike the three-state system, where the final state of the chain has the same parity as the initial state (and hence may be relatively stable to radiative decay), the final state of a four-state chain has opposite parity from the initial state. It may therefore be also linked by a single-photon transition to the initial state, if other selection rules permit. The ladder configuration is particularly important because it corresponds to the well studied frequency-tripling process, in which three low-energy photons are converted into one high-energy photon.

II. BACKGROUND AND NOTATION

From previous work [5,10,13] it is known that important insight into the flow of population in a multistate system can be gained from analytical solutions of the Schrödinger equation. The more complicated density matrix equation is required only if quantitative results including radiative or collisional decay channels are important. The description of coherent excitation makes use of a vector $\mathbf{C}(t)$ whose components, the complex-valued probability amplitudes $C_k(t)$, yield state populations $P_k(t)$ as absolute squares, $P_k(t)=|C_k(t)|^2$.

The probability amplitudes are, for any multistate system, solutions of the time-dependent Schrödinger matrix equation

$$i\hbar\frac{d}{dt}\mathbf{C}(t)=H(t)\mathbf{C}(t)\ . \tag{1}$$

The solution $\mathbf{C}(t)$ of Eq. (1) can always be represented in a basis of adiabatic dressed states, defined as eigenvectors of the instantaneous Hamiltonian

$$H(t)\mathbf{V}^{(k)}(t)=\hbar\omega_k(t)\mathbf{V}^{(k)}(t)\ . \tag{2}$$

The construction reads

$$\mathbf{C}(t)=\sum_k \eta_k(t)\mathbf{V}^{(k)}(t)\exp\left[-i\int_0^t\omega_k(t')dt'\right] \tag{3}$$

with the initial condition

$$\mathbf{C}(0)=\sum_k \eta_k(0)\mathbf{V}^{(k)}(0)\ . \tag{4}$$

The adiabatic theorem [14] states that if the Hamiltonian varies sufficiently slowly, as expressed by the inequality

$$R_{km}\equiv\left|\mathbf{V}^{(k)}\cdot\frac{d}{dt}\mathbf{V}^{(m)}\right|\ll|\omega_k-\omega_m| \tag{5}$$

then the coefficients $\eta(t)$ can be taken as constant (the adiabatic approximation) and the solution can be written for all time as

$$\mathbf{C}(t)=\sum_k \eta_k(0)\mathbf{V}^{(k)}(t)\exp\left[-i\int_0^t\omega_k(t')dt'\right]\ . \tag{6}$$

This analytic relation is the key step of methods that rely on adiabatic behavior. It places all time dependence into basis dressed states and phases. The result is applicable, in principle, to any nondegenerate multistate system (not just to an excitation chain of levels).

III. THE FOUR-LEVEL HAMILTONIAN

The Hamiltonian for a system of four states connected in a chain is a tridiagonal matrix. We shall assume in all that follows that the various frequencies (Bohr and laser) are such that a three-photon resonance condition always applies. Under this condition the general form for the rotating-wave-approximation Hamiltonian may be taken to be

$$H(t)=\hbar\begin{bmatrix}0 & \alpha(t) & 0 & 0\\ \alpha(t) & \Delta_1 & \beta(t) & 0\\ 0 & \beta(t) & \Delta_2 & \gamma(t)\\ 0 & 0 & \gamma(t) & 0\end{bmatrix} \tag{7}$$

where 2α, 2β, and 2γ are the (time-varying) Rabi frequencies of the first, second, and third transitions, respectively, as shown in Fig. 1 for "ladder" and N-type configurations. The diagonal elements Δ_1 and Δ_2 are the 1-2 and 1-3 detunings; they may be time dependent but in our present analysis are constants.

IV. LARGE DETUNING

If the detuning Δ_k are large compared to the Rabi frequencies α, β, and γ, then we can use adiabatic elimination to reduce the four coupled equations to two equations for an effective two-state system (states 1,4). The effective Rabi frequency and effective detunings are easily obtained (by setting to zero the time derivatives of intermediate-state amplitudes):

$$\Omega_{\text{eff}}=\alpha\beta\gamma/(\Delta_1\Delta_2-\beta^2)\ ,$$
$$\Delta_{\text{eff}}=(\Delta_1\gamma^2-\Delta_2\alpha^2)/(\Delta_1\Delta_2-\beta^2)\ . \quad (8)$$

This result resembles the well-known two-photon resonance in a three-state system with large intermediate detunings [10]. The two-state system has the following properties.

(1) The effective interaction between states 1 and 4 is nonzero only if *all* the individual Rabi frequencies are simultaneously present.

(2) If the pulsed fields of α and γ form a delayed pattern, then the effective detuning will sweep through the effective two-state resonance ($\Delta_{\text{eff}}=0$). This is demonstrated in Fig. 2 where Δ_{eff} and Ω_{eff} which result from the delayed pattern of the Rabi frequencies α and γ are displayed. If the sweeping of Δ_{eff} is carried out adiabatically, then the populations of state 1 and state 4 will be inverted.

(3) The adiabatic condition requires pulses which are long compared to the inverse of the Rabi frequencies.

(4) The lifetimes of the intermediate levels do not affect the population transfer between levels 1 and 4 because they are not populated at any time.

It was shown [8,10] that in the three-state case, the delayed-pulse inversion is successful also when the intermediate detuning vanishes. It is only necessary that the second-transition laser appears first in time. In this case the probability amplitude vector $\mathbf{C}(t)$ "follows" the dressed state that has null eigenvalue, $\omega(t)=0$. It turns out that in this resonant case the adiabatic condition becomes much less restrictive and large Rabi frequencies compensate for short pulses. The peculiar sequence of laser appearance is termed as the "counterintuitive" scheme or stimulated Raman adiabatic passage [10].

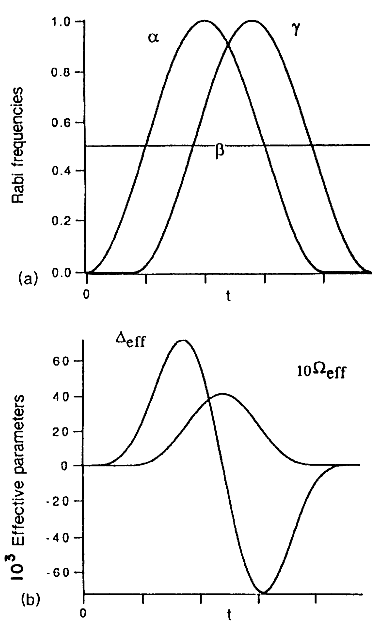

FIG. 2. (a) The temporal variation of the Rabi frequencies in the four-state delayed-pulse scheme. The pulses α and γ must partially overlap while β needs only to be present during the overlap time. Normalized time and frequencies are used ($t'=\alpha_0 t$ and $\alpha'=\alpha/\alpha_0$, $\beta'=\beta/\alpha_0$, $\gamma'=\gamma/\alpha_0$ where α_0 is the peak Rabi frequency of laser 1), but for simplicity of notation primes are omitted. (b) The equivalent effective two-state system (for large intermediate detunings; $\Delta_1=\Delta_2=10$) is characterized by a chirp of $\Delta_{\text{eff}}(t)$ and a pulse-shaped $\Omega_{\text{eff}}(t)$.

V. THE GENERAL CASE

In order to see what happens for "small" detunings in the four-state case we investigate the dressed states of the Hamiltonian. The four-state eigenvalue equation is

$$\omega^4+b_3\omega^3+b_2\omega^2+b_1\omega^1+b_0=0\ ,$$
$$b_3=-(\Delta_1+\Delta_2)\ ,$$
$$b_2=\Delta_1\Delta_2-(\alpha^2+\beta^2+\gamma^2)\ , \quad (9)$$
$$b_1=\alpha^2\Delta_2+\gamma^2\Delta_1\ ,$$
$$b_0=\alpha^2\gamma^2\ .$$

The four eigenvalues of Eq. (9) are [15]

$$\omega_k=[-B_k+(-1)^k(B_k^2-4C_k)^{1/2}]/2,\quad k=1,2,3,4 \quad (10)$$

where

$$B_k=\left[\frac{b_3}{2}+(-1)^{t_k}\left[\frac{b_3^2}{4}+z-b_2\right]^{1/2}\right]\ ,$$
$$C_k\left[\frac{z}{2}+(-1)^{t_k}\left[\frac{z^2}{4}-b_0\right]^{1/2}\right]\ , \quad (11)$$
$$t_k=\begin{cases}0, & k=1,2\\ 1, & k=3,4\end{cases}$$

and z is the real root of the following cubic equation:

$$\zeta^3+a_2\zeta^2+a_1\zeta^1+a_0=0\ ,$$
$$a_2=-b_2\ , \quad (12)$$
$$a_1=b_1b_3-4b_0\ ,$$
$$a_0=-(b_1^2+b_0b_3^2-4b_0b_2)\ .$$

If all the cubic roots are real, z is the one which leads to real coefficients B_k and C_k of Eq. (11). This root, z, will be specified later for our particular cases of interest.

The corresponding eigenvectors are

$$\mathbf{V}^{(k)}=\frac{1}{N_k}\begin{bmatrix}\alpha\beta\omega_k\\ \beta\omega_k^2\\ -\omega_k[\alpha^2+\omega_k(\Delta_1-\omega_k)]\\ -\gamma[\alpha^2+\omega_k(\Delta_1-\omega_k)]\end{bmatrix} \tag{13}$$

where N_k is a normalization factor. The arbitrary phases that must be specified to complete the definitions of eigenvectors are here taken to make all components real numbers. The time dependence of these vectors comes from that of the pulses $\alpha(t)$, $\beta(t)$, and $\gamma(t)$ as well as of the eigenvalues $\omega(t)$.

Analytical substitution of ω_k of Eqs. (10)–(12) into the formula for $\mathbf{V}^{(k)}$ yields very complicated expressions. However, our interest is in some simple specific limits which, as we shall see, lead to complete population transfer, by adiabatic passage, as produced by delayed pulses.

We wish to obtain the eigenvector that initially has only a single component (that of state 1). We will show that with the present choices for the diagonal elements of the Hamiltonian (as fixed by our choice of phases) this desired eigenvector is characterized by having a null eigenvalue initially.

It is easily seen from Eqs (10), (12), and (11) that if either α or γ vanishes, then $b_0=0$, and the Hamiltonian has a null eigenvalue, $\omega_1=0$. This has important consequences as noted below. If $\alpha=\gamma=0$, then independent of β the Hamiltonian has two null eigenvalues, $\omega_1=0$ and $\omega_3=0$.

If either α or γ is nonzero and β is also nonzero, then b_1, b_2, and b_3 are nonzero. In this case all a_i (including a_0) and the roots z_i of Eq. (12) are nonzero as well.

Unlike the case when the number of states N is an odd integer [12], the N-state Hamiltonian for even N lacks the symmetry which allows $\omega(t)=0$ for all t. Nevertheless, we will see that the adiabatic condition can still be fulfilled easily: the system follows the initially populated eigenvector and the pulses produce complete population transfer with only small transient populations in the intermediate levels.

For our analysis we will need only the following limits obtained from Eqs. (10)–(13); when $\alpha\to 0$ and $\gamma\neq 0$ then $\omega_1 \Longrightarrow 0$ and $N_1 \Longrightarrow 0$ yielding

$$V_1^{(k)}=\frac{\alpha\beta\omega_k}{N_k}\to\delta_{k,1} \ . \tag{14a}$$

If now $\gamma\to 0$ we have also $\omega_3, N_3\to 0$ and

$$V_4^{(k)}=\frac{-\omega_k[\alpha^2+\omega_k(\Delta_1-\omega_k)]}{N_k}\to-\delta_{k,3} \ , \tag{14b}$$

whereas when $\gamma\to 0$ and $\alpha\neq 0$ then $\omega_1, N_1\to 0$ yields

$$V_4^{(k)}=\frac{-\omega_k[\alpha^2+\omega_k(\Delta_1-\omega_k)]}{N_k}\to\delta_{k,1} \ . \tag{15a}$$

If now $\alpha\to 0$ we have also $\omega_3, N_3\to 0$ and

$$V_1^{(k)}-\frac{\alpha\beta\omega_k}{N_k}\to\delta_{k,3} \ . \tag{15b}$$

These limits can also be seen in Fig. 3 where we display the eigenvectors $\mathbf{V}^{(1)}$ and $\mathbf{V}^{(3)}$ versus time, which correspond to the delay pattern of Fig. 4(a).

As we shall see, for delayed-pulse schemes, four distinct times are of particular importance: (1) $t=0$—the leading pulse appears; (2) $t=t_1$—the delayed pulse appears; (3) $t=T$—the leading pulse disappears; and (4) $t=T+t_2$—the delayed pulse disappears (we take $t_1=t_2$). The three fields of Fig. 4(a) start from zero at $t=0$ when the leading laser has just been turned on. At this point the Hamiltonian matrix, Eq. (7), is diagonal,

$$H(0)=\begin{bmatrix}0 & & & \\ & \Delta_1 & & \\ & & \Delta_2 & \\ & & & 0\end{bmatrix} , \tag{16}$$

and the eigenvalue $\omega=0$ is double degenerate:

$$\begin{aligned}&\omega_1(0)=\omega_3(0)=0 \ ,\\ &\omega_2(0)=\Delta_2,\quad \omega_4(0)=\Delta_1 \quad \text{for } \Delta_2\leq\Delta_1 \ ,\\ &\omega_2(0)=\Delta_1,\quad \omega_4(0)=\Delta_2 \quad \text{for } \Delta_1\leq\Delta_2 \ .\end{aligned} \tag{17}$$

At this time both $\mathbf{V}^{(1)}(0)$ and $\mathbf{V}^{(3)}(0)$ have null eigenvalues, $\omega=0$. As the leading pulse is increasing the degeneracy is removed [see Fig. 4(b)]: the eigenvalue ω_3 is changing *but* ω_1 (associated with $b_0=\alpha^2\gamma^2=0$) *remains zero until the delayed laser is turned on at* $t=t_1$. Later, at $t=T$, the first pulse disappears. From this time on we have again $\omega_1=0$. The vector space of null eigenvalues becomes degenerate again only at the end of the process

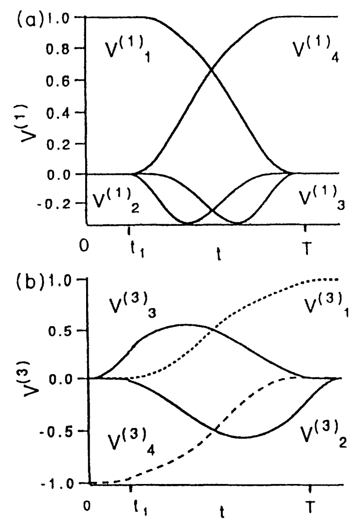

FIG. 3. The time evolution of the eigenvectors $\mathbf{V}^{(1)}$ and $\mathbf{V}^{(3)}$. The driving fields are displayed in Fig. 4 together with the corresponding eigenvalues, where the leading pulse starts and ends at $t=0$ and $t=T$, respectively, and the delayed pulse is shifted by t_1. In the respective limits of Eqs. (14) $|\mathbf{V}_1^{(1)}|=|\mathbf{V}_4^{(3)}|=1$, while for the limits (15) $|\mathbf{V}_4^{(1)}|=|\mathbf{V}_1^{(3)}|=1$. These limits dictate the adiabatic inversion schemes in the counterintuitive and intuitive sequences. Normalized time and frequencies as in Fig. 2 are used.

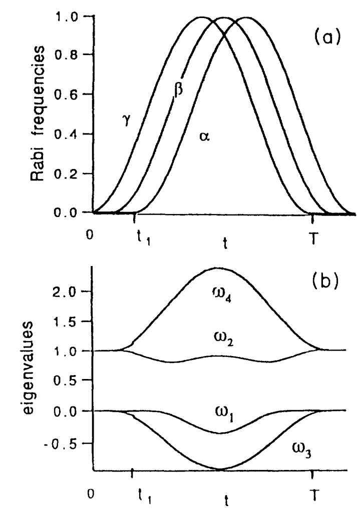

FIG. 4. The delayed-pulse scheme for a counterintuitive sequence where the laser γ of the third transition appears first. ω_k are the Hamiltonian's eigenvalues [see Eq. (7)]. The eigenvalues ω_1 and ω_3 are initially degenerate but the degeneracy is removed completely at t_1 where the delayed α pulse appears. The evolution of the corresponding eigenvectors is displayed in Fig. 3. Normalized time and frequencies as in Fig. 2 (with $\omega_k \Longrightarrow \omega_k/\alpha_0$) are used.

$(t=T+t_1)$ when the delayed pulse vanishes as well. The intermediate laser β only has to be present during the overlap time $(t_1<t<T)$ of α and γ. It may have any shape that changes adiabatically. In particular when applied to a two-laser scheme, the field part of the Rabi frequency β may be identical to one of the laser fields of α or γ (see Sec. IX).

We consider now the two choices for pulse sequences: (a) The "counterintuitive" scheme (γ precedes α)

$$\alpha(t_1)=0,\quad \gamma(t_1)\neq 0,\quad \alpha(T)\neq 0,\quad \gamma(T)=0\ . \tag{18}$$

(b) The "intuitive" scheme (α precedes γ)

$$\gamma(t_1)=0,\quad \alpha(t_1)\neq 0,\quad \gamma(T)\neq 0,\quad \alpha(T)=0\ . \tag{19}$$

Each of these schemes will be discussed separately.

VI. THE "COUNTERINTUITIVE" SCHEME

Let us first consider case (a) in which pulse γ, connecting states 3 and 4 (see Fig. 1), appears first while the pulse α, connecting states 1 and 2, is delayed as shown in Fig. 4(a). In this case it is the $k=1$ dressed state $\mathbf{V}^{(1)}(t)$ which leads to complete population transfer. To see this we need only to look at the initial and final conditions. It is immediately seen from Eqs. (18), (14a), and (15a) and from Fig. 3 that this eigenvector has the following initial and final components:

$$\mathbf{V}^{(1)}(0)=\begin{bmatrix}1\\0\\0\\0\end{bmatrix},\quad \mathbf{V}^{(1)}(T)=\begin{bmatrix}0\\0\\0\\0\\1\end{bmatrix}\ . \tag{20}$$

If initially all the population is in state 1, the initial condition obeys the relation

$$\mathbf{C}(t\le t_1)=\mathbf{V}^{(1)}(t\le t_1)=\mathbf{V}^{(1)}(0) \tag{21}$$

and under the adiabatic conditions the solution (6) for all t is

$$\mathbf{C}(t)=\mathbf{V}^{(1)}(t)\exp\left[-i\int_0^t \omega_1 dt\right]\ . \tag{22}$$

Thus the population is not affected at all until the delayed pulse α is turned on at t_1. Thereafter the population develops to complete inversion at $t=T$.

The fulfillment of the adiabatic evolution is demonstrated in Figs. 5(a)–5(d). These figures present the convergence of the numerical solution of Eq. (1) to the analytic formula for the components of the dressed state $\mathbf{V}^{(1)}(t)$ [Eq. (13)].

The pulse shapes used for this example have the form

$$\begin{aligned}
\alpha(t)&=\alpha_0\sin^2\left[\frac{\pi(t-D_1)}{T}\right],\quad D_1\le t\le T+D_1\\
\beta(t)&=\beta_0\sin^2\left[\frac{\pi(t-D_2)}{T}\right],\quad D_2\le t\le T+D_2\\
\gamma(t)&=\gamma_0\sin^2\left[\frac{\pi(t-D_3)}{T}\right],\quad D_3\le t\le T+D_3
\end{aligned} \tag{23}$$

with the delays $D_3=0$, $D_2=0.1T$, $D_1=0.2T$, the amplitudes of the Rabi frequencies $\alpha_0=\beta_0=\gamma_0=1$, and the detunings $\Delta_1=\Delta_2=1$. Note that the exact pulse shapes are irrelevant as long as the adiabatic condition of Eq. (5) is fulfilled.

Since the results are invariant to the scaling $t'=\Omega_0 t$, and $\alpha'=\alpha/\Omega_0$, $\beta'=\beta/\Omega_0$, $\gamma'=\gamma/\Omega_0$, where Ω_0 is any chosen frequency, we have used these dimensionless quantities in the figures but have omitted the primes for simplicity of notation. Our choice of $\alpha_0=1$ amounts to choosing $\Omega_0=\alpha_0$ (the peak Rabi frequency of laser 1).

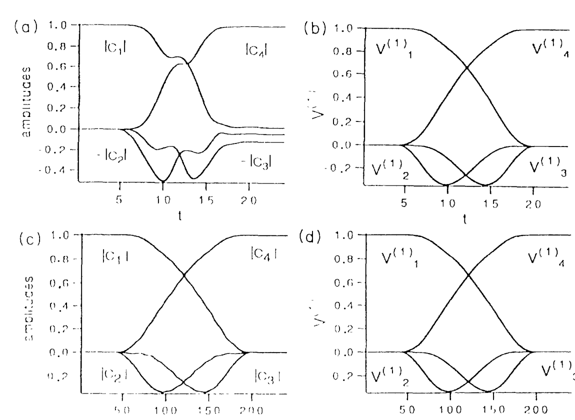

FIG. 5. The convergence of the vector of probability amplitudes $\mathbf{C}(t)$ into the dressed state $\mathbf{V}^{(1)}(t)$ as the duration time of the driving pulses is increased from $T=20$ (top) to 200 (bottom). The pulses' shapes are as in Fig. 4(a). Normalized time and frequencies as in Fig. 2 are used.

From Fig. 5 we see that as the pulse duration time T is increased from $T=20$ to 200 the adiabatic condition becomes better satisfied and the numerical solutions become almost indistinguishable from those derived from the analytic expression for $\mathbf{V}^{(1)}$.

We also notice from Figs. 4 and 5 that the dressed state $\mathbf{V}^{(1)}(t)$ remains unchanged until the third pulse appears at $t_1=0.2T$. At this time the eigenvalue ω_1 is far enough from ω_3 so the adiabatic conditions (5) are obeyed. The solution follows the dressed state $\mathbf{V}^{(1)}(t)$.

It is interesting to note that although *the populations of the intermediate states* are nonzero during the process, they *are small* for these realistic conditions. Thus decays from these states should not affect significantly the evolution of the system. This can be further improved by optimizing the parameters such as pulse shapes, proper delays, and laser intensities and detunings.

A crucial observation that we have made is that, unlike the three-state delayed-pulse scheme which preferred single-photon resonance in the counterintuitive scheme, we must avoid here exact single-photon resonance with any of the intermediate states. *Some small detuning with these states must be present.* More precisely for the counterintuitive scheme where γ appears first we need $\Delta_1\neq 0$ at $t=t_1$ and $\Delta_2\neq 0$ at $t=T$ (If it is α which leads, then the opposite $\Delta_2\neq 0$ at $t=t_1$ and $\Delta_1\neq 0$ at $t=T$ is required.) The effect of $\Delta_i=0$ becomes obvious, again, from the eigenvalue Eqs. (10) and (13). We first see [in Eq. (17)] that the vector space of null eigenvalues is initially triply degenerate, with $\omega_2=\omega_1=\omega_3=0$. However *this degeneracy is not removed until the delayed pulse appears at* $t=t_1$. In this case we have $b_1=\alpha^2\Delta_2+\gamma^2\Delta_1=0$ and the cubic equation (8) reduces to $\zeta^3-b_2\zeta^2=0$ leading to either $z=0$ or b_2 for all $t<t_1$. Thus ω_2 (as well as ω_1) remains zero for all $t<t_1$ and both $\mathbf{V}^{(1)}$ and $\mathbf{V}^{(2)}$ remain unchanged and degenerate during that time. As the delayed pulse appears, the components of these dressed states start oscillating. This is illustrated in Fig. 6 which displays the evolution of the system under the pulses of Fig. 4(a) for the case where $\Delta_1=0$ at all times, in particular at $t=t_1=40$. The vector $\mathbf{C}(t)$ cannot follow these oscillations adiabatically and starts oscillating between these two eigenvectors. Then the amount of population transfer deepens critically on experimental parameters such as Rabi frequencies, pulse widths, and pulse delays. The phases

$$\exp\left(-i\int_0^t \omega_k dt\right)$$

in Eq. (6) (which have no effect when a single eigenvector is populated) add here to the oscillatory behavior and inversion fails. The condition $\Delta_2\neq 0$ at $t=T$ is required to avoid such mixing at the end of the process.

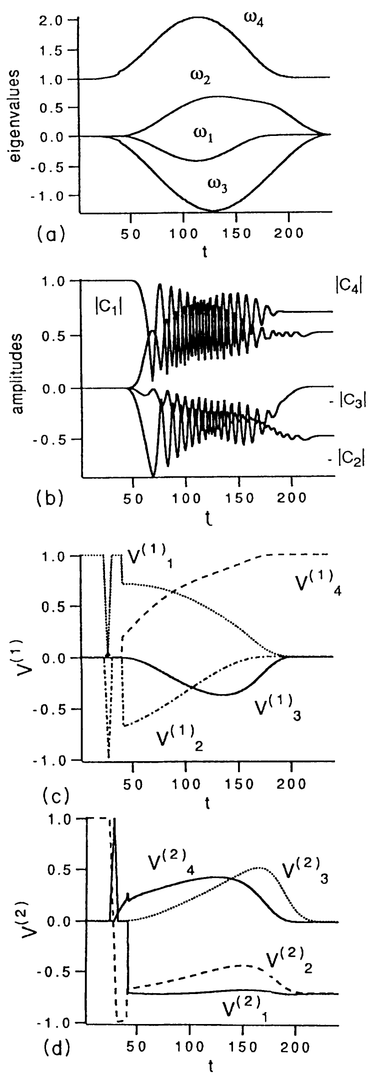

FIG. 6. The breakdown of the adiabatic evolution due to the one-photon resonance $\Delta_1=0$, under the counterintuitive pulse sequence of Fig. 4(a). The eigenvalues of $\mathbf{V}^{(1)}$, $\mathbf{V}^{(3)}$, and $\mathbf{V}^{(2)}$ are degenerate initially with $\omega_1(0)=\omega_3(0)=\omega_2(0)=0$. Whereas the degeneracy with ω_3 is immediately removed, the remaining double degeneracy stays until the delayed pulse appears, yielding oscillations between the degenerate dressed states $\mathbf{V}^{(1)}$ and $\mathbf{V}^{(2)}$. Normalized time and frequencies as in Fig. 2 are used.

VII. THE "INTUITIVE" SCHEME

As we have already seen from Eq. (8), for very large intermediate-state detunings Δ_1 and Δ_2 complete population transfer can be produced for either ordering of the sequencing of the pulses α and γ. However, to produce adiabatic following when the detunings are large (compared with the peak Rabi frequency) the pulse areas must also be relatively large. In the preceding section we have seen that with small detunings the counterintuitive scheme allows adiabatic passage. In this section we investigate the "intuitive" scheme (where α appears first) with small detunings.

The coefficients b_i of Eq. (9) (and therefore also the eigenvalues ω_k) are invariant under the exchange of pairs $\Delta_2,\alpha \Longleftrightarrow \Delta_1,\gamma$. They are thus not affected if we reverse the order of the pulses (with the concomitant exchange $\Delta_2\Longleftrightarrow\Delta_1$). The components of the dressed states $\mathbf{V}^{(k)}$ provided by Eq. (13) are obviously not invariant under this exchange. For the intuitive scheme we see from the limits of Eqs. (14b) and (15b) that the initial probability vector $\mathbf{C}(0)$ follows eigenvector $\mathbf{V}^{(3)}$ of the initially degenerate null eigenvalues. However, as we have already remarked, although the eigenvalue $\omega_1(t)$ remains zero, the eigenvalue $\omega_3(t)$ departs from zero when the leading pulse arrives. Therefore the vector $\mathbf{C}(t)$ follows $\mathbf{V}^{(3)}$ with no interruption. From Eqs. (14b) and (15b) we see also that $\mathbf{V}^{(3)}$ inverts the populations at $t=T$. All this is illustrated in Fig. 7, which displays the evolution of the intuitive scheme. We notice that at this adiabatic rate ($T=20$) the evolution of the populations is not smooth and that the intermediate components are appreciably large. From comparison between Figs. 4, 5, and 7 we see that, similar to the three-state case, the superiority of the counterintuitive scheme has two aspects: (1) The adiabatic condition requires smaller pulse areas, and (2) the population of the intermediate states is much smaller during the process, thereby avoiding decays from these states.

As with counterintuitive pulse sequences, the intuitive sequence requires some initial and final detunings for smooth adiabatic following. Clearly, if $\Delta_1=0$ the first transition is on resonance and 1-2 Rabi oscillations occur. The initial vector $\mathbf{C}(0)$ is a combination of $\mathbf{V}^{(2)}(0)$ and $\mathbf{V}^{(3)}(0)$, so that from the very beginning the phases dictate oscillatory behavior. The interesting new observation here is that according to Eqs. (10), (13), and (17) we require $\Delta_2\neq 0$ at $t=t_1$ and $\Delta_1\neq 0$ at $t=T$. This is because $\Delta_2=0$ at $t=0$ leads to $\omega_2(0)=\omega_1(0)=\omega_3(0)=0$. Whereas ω_3 subsequently departs from zero, the other eigenvalues ω_1 and ω_2 remain degenerate for all $t<t_1$. Consequently population oscillations begin when the delayed pulse α appears.

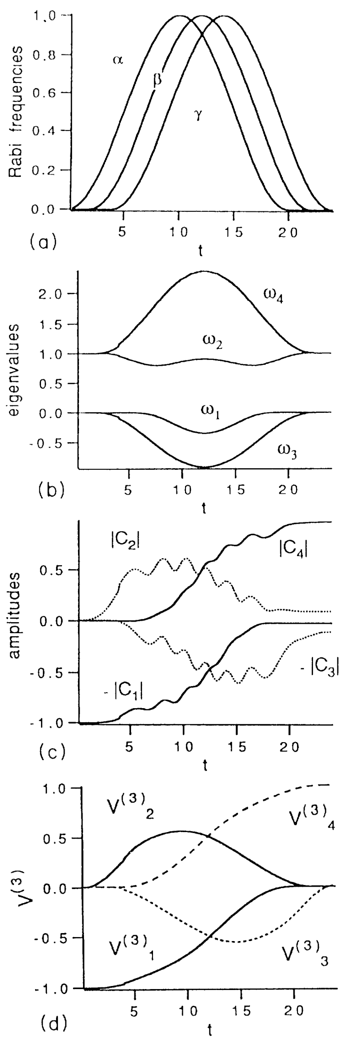

FIG. 7. The evolution under the intuitive sequence of pulses. The dressed state which meets the initial condition is $\mathbf{V}^{(3)}$. Under the adiabatic conditions it leads to complete inversion. However, the evolution is not smooth and the intermediate components are appreciably populated. Comparison with Fig. 5 indicates that the counterintuitive scheme is preferable. Normalized time and frequencies as in Fig. 2 are used.

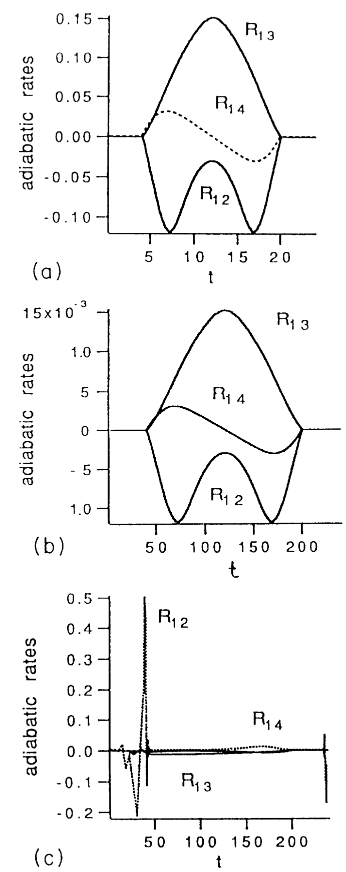

FIG. 8. The adiabatic condition of Eq. (5). Here (a) and (b) display the adiabatic rates $R_{1m}\equiv\mathbf{V}^{(1)+}\cdot(d/dt)\mathbf{V}^{(m)}$ of Fig. 5, for the "short," $T=20$, and "long," $T=200$, pulses (upper panels). The shapes are identical but for longer pulse areas the magnitude of the nonadiabatic coupling elements decreases. The lowest panel, (c), displays the adiabatic condition for the single-photon resonance case of Fig. 6. The point of the breakdown of the adiabatic evolution is clear from the large derivatives of the corresponding dressed states. Normalized time and frequencies as in Fig. 2 are used.

VIII. FURTHER DETAILS ON ADIABATIC EVOLUTION

The adiabatic criterion [Eq. (5)] is a sufficient condition. With the proper initial condition it ensures adiabatic evolution of the atomic or molecular system. It is not a necessary condition. A good example is shown in Fig. 4 where the initial dressed states $\mathbf{V}^{(1)}(0)$ and $\mathbf{V}^{(3)}(0)$ are degenerate but depart from one another without any effect on the dressed states or population. In general when the duration of the pulses is scaled up, the eigenvalues follow the same instantaneous values but at different times (see Fig. 5), whereas the derivatives of the dressed states become smaller by the scaling factor. The adiabatic condition [Eq. (5)] is then better fulfilled. This fact is demonstrated in Figs. 8(a) and 8(b), which present the adiabatic rates R_{km} of Eq. (5) for the evolution of the system of Fig. 4. It is seen that as the criterion is improved the probability amplitude vector converges to the dressed state which matched the initial conditions. In contrast Fig. 8(c) demonstrates the failure of the adiabatic evolution due to the occurrence of the degeneracy of $\mathbf{V}^{(1)}$ and $\mathbf{V}^{(2)}$ resulting from single-photon resonance as demonstrated in Fig. 6. It is seen that at the time $t_1=40$, where the delayed pulse appears, the derivatives of the relevant dressed state become very high, and the failure of the adiabatic condition leads in this case to the collapse of the adiabatic evolution.

IX. COUNTERINTUITIVE SCHEME INVOLVING ONLY TWO LASERS

With regard to experimental implementation of complete population transfer in a four-level system, it is important to realize that the process can be induced with two lasers only. In fact, since it is the only purpose of the pulse β (see Fig. 1) to provide a link between the first and third steps of the radiative coupling, β may coincide with either α or γ. Furthermore, since the frequency of the laser, associated with the pulse β, should not be in exact resonance with the corresponding transition, pulse α or γ can also provide the intermediate coupling step even if the levels 1–4 are not equally spaced. This scheme is in particular promising for excitation of molecular vibra-

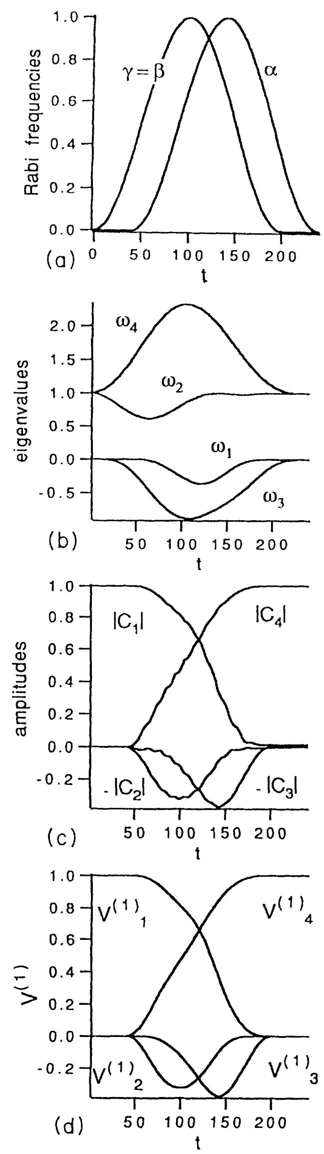

FIG. 9. The four-level STIRAP process with only two driving fields with $\beta=\gamma$. The evolution of the system is only little affected by changes in β as seen by comparison with Fig. 5. Normalized times and frequencies as in Fig. 2 are used.

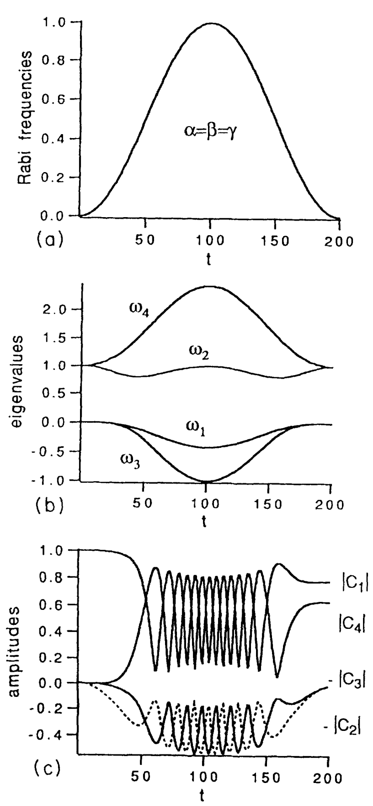

FIG. 10. Evolution of the eigenvalues and amplitudes for fully overlapping pulses. Here, a pronounced Rabi oscillation occurs. Normalized time and frequencies as in Fig. 2 are used.

tional levels using infrared photons [11]. Figure 9 shows an example of the time evolution of the system for the case where γ and β are produced by the same laser. Clearly, there are minor quantitative differences when compared to the case when β does not coincide with α or γ (see Fig. 5), but the success of the population-transfer process is nevertheless obvious.

X. OVERLAPPING PULSES

For completeness, we also show in Fig. 10 results for complete overlapping of the pulses. As seen from Eq. (8), for large detunings, such overlap leads to near-resonance effective two-level Rabi oscillations between levels 1 and 4. In Fig. 10 the pulses overlap while the detuning is relatively small. The result is Rabi oscillations which involve the intermediate levels as well.

XI. CONCLUSIONS

From the analysis of the analytical results of a four-level system (see Fig. 1) coupled by two or three laser fields we draw the following conclusions. As in the experimentally demonstrated three-level case, efficient and selective population transfer from the initial to the final level can be achieved by suitable timing of the interaction. For efficient population transfer, the interaction with the laser connecting levels 3 and 4 has to come first, while interaction with laser connecting levels 1 and 2 should be last (see Fig. 4).

Essential features of the population-transfer process from level 1 to level 4 can be derived from analytical solutions for pulsed excitation of a four-state system. Although the general expressions are complicated, the essential properties can be recognized by examining limiting cases only.

Unlike the analytic solutions for N-state systems with odd-integer N, the STIRAP-type solutions for a four-state system require moderate constant detunings of intermediate steps. The detunings are not large—they are comparable to the peak of the Rabi frequency.

Both the intuitive and the counterintuitive pulse sequences will permit complete population transfer. The difference between the two is that the counterintuitive sequence will essentially place no population into the intermediate states, and may use smaller pulse areas.

It is also possible to achieve successful population transfer using two distinct pulse shapes, when the field of β coincides with the field of either α or γ. This configuration corresponds, for instance, to a $(2+1)$ or $(1+2)$ excitation scheme, respectively, and is of interest in particular for vibrational excitation of molecules by ir radiation [11].

ACKNOWLEDGMENTS

This work was completed at the occasion of a visit of J.O. and B.W.S. to Kaiserslautern, supported through the visiting scientists program of the Sonderforschungsbereich SFB 91 "Energy transfer in Atomic and Molecular Collisions" of the Deutsche Forschungsgemeinschaft. The work of J. Oreg and S. Rosenwaks is supported by the Israel Council for Higher Education. The work of B. W. Shore is supported by the U.S. Department of Energy at Lawrence Livermore National Laboratory under Contract No. W-7405-Eng-48.

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