Nonadiabaticity in stimulated Raman adiabatic passage

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This paper begins with the premise that stimulated Raman adiabatic passage (STIRAP) from one state to another by coupling to an intermediate state necessarily requires some population of that intermediate state. The usual view of the process depends on having no population in the intermediate state, but a simple argument from the time-dependent Schrödinger equation shows that such adiabatic transfer cannot occur. From another perspective, removing the time dependence of the Hamiltonian by making the rotating frame transformation cancels the optical frequency oscillations but does not account for the envelopes of the pulses commonly used for STIRAP. By assuming a small but finite intermediate state amplitude ε_1 in the wave function, the propagator for the evolution between initial and final states is derived. Applying the propagator to the initial state produces a single compact formula for the final intermediate-state population that is readily evaluated for an arbitrary choice of laser pulse parameters. Several plots for various experimental conditions show that under the conditions normally used for STIRAP experiments the effects are typically a few percent or less, but in the end this effect puts an ultimate limit on total efficiency.

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I. INTRODUCTION

The process of moving a population of atoms from one quantum state to another can be made very efficient by a number of techniques. If the two states are connected by a single transition, typically electric dipole, then a π pulse [1,2] can be very effective when there are no inhomogeneous compromising effects such as Doppler shifts or interactions with neighboring atoms. The impact of such deleterious effects can be reduced by a variety of methods, for example, adiabatic rapid passage [1,2].

If the transition between the two states is forbidden or weak, a two-step transition via an intermediate state may have a considerably higher efficiency. Although the ideas of three-level coherences originated in the early 1980s [3,4], their rediscovery and application to population transfer emerged some years later [5,6]. The name stimulated Raman adiabatic passage (STIRAP) first appeared in Ref. [7]. This topic has been described in detail by very many authors: Excellent reviews and discussion are in Refs. [8,9]. The underlying idea is to use a pulsed process but to apply the radiation for the second step before that of the first step. There needs to be some overlap between the two pulses, but the order of their peaks must be counterintuitive to that of a sequential two-step process.

The usual description of the STIRAP is in terms of the adiabatic eigenstates of the Hamiltonian and results in the complete absence of population of any intermediate states. There has been some discussion of nonadiabaticity [10,11] in general terms, but their evaluation has not been presented. What is new and important here is the perturbative calculation of the propagator for the initial state that brings it to the final state, given in a form that can be used for arbitrary laser pulse shapes and in terms that can be readily applied to experimental conditions.

The rest of this section provides an introductory description of the STIRAP process and a description of the conditions that maintain the required adiabaticity. Section II describes a method for calculating the nonadiabaticity of real processes in terms of experimental conditions such as pulse shape and timing (most of its mathematical part is in the Appendix). In Sec. III some of the results are plotted for certain experimental choices, and there is some discussion. We believe that this is the first application of such a method to coherent adiabatic processes in atoms but it is widely applicable and in a later paper we will extend it beyond STIRAP. Section IV summarizes the main points and provides conclusions from the plots.

Although spontaneous emission can disrupt the coherence needed for STIRAP, it is not considered here because the choice of parameters usually makes it less important than the inherent adiabaticity presented below. Nevertheless, the approach of Sec. II can also address the effects of spontaneous emission and will also be presented in a later paper.

A. The STIRAP process

Consider the three-state systems called Λ and ladder as shown in Figs. 1(a) and 1(b) respectively. Assume that the atomic population begins in $|1\rangle$ and the objective is to transfer it to $|3\rangle$ with the highest efficiency. This paper addresses some of the nonadiabatic aspects of STIRAP for accomplishing this. It does not consider the effects of spontaneous emission or other processes that can compromise the atomic coherences produced by the light that have been discussed extensively by others [7,12,13]. Since the intermediate state $|2\rangle$ can undergo spontaneous emission that interrupts the coherence of the STIRAP process, the excitation scheme is designed to minimize its population (in the ladder configuration one chooses $|3\rangle$ to be long-lived, e.g., a Rydberg state).

In general, the Hamiltonian for such a three-state system exposed to two radiation fields that connect one of the states to the other two is given by [8]

$$\mathcal{H}(t) = \frac{\hbar}{2}\begin{bmatrix} 0 & \Omega_p(t) & 0 \\ \Omega_p(t) & -2\Delta_p & \Omega_s(t) \\ 0 & \Omega_s(t) & -2(\Delta_p+\Delta_s) \end{bmatrix} \quad (1)$$

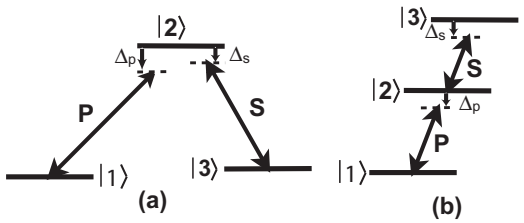

FIG. 1. Two typical three-level systems: the Λ system (a) and the ladder system (b). The labels "p" and "s" derive from the historical usage of Stokes and pump.

in the rotating wave approximation and the rotating frame transformation. Here the time dependence of the Ω's is their pulse envelope shape and spontaneous emission has been left out.

The Ω's connect $|2\rangle$ to both $|1\rangle$ and $|3\rangle$ and are given by $\hbar\Omega_p(t) \equiv |e\vec{\mathcal{E}}_p(t) \cdot \langle 1|\vec{r}\,|2\rangle|$ and similarly for $\Omega_s(t)$. Also, $\vec{\mathcal{E}}(t)$ is the electric field of the light, $\Delta_p \equiv \omega_p - \omega_{21}$ is the detuning of the light at ω_p from exact atomic resonance at ω_{21} (see Fig. 1), and similarly for $\Delta_s \equiv \omega_s - \omega_{23}$.

The resonance condition is $\Delta_p - \Delta_s = 0$ for the Λ configuration and $\Delta_p + \Delta_s = 0$ for the ladder configuration; the remainder of this paper considers only the latter. On resonance one of the eigenvalues of Eq. (1) is clearly 0 for all values of the Ω's, its eigenstate is denoted by $|0(t)\rangle$, and it is given by [8]

$$|0(t)\rangle \equiv \cos\theta(t)\,|1\rangle - \sin\theta(t)\,|3\rangle, \quad \tan\theta(t) \equiv \frac{\Omega_p(t)}{\Omega_s(t)}. \quad (2)$$

Then it is clear that $\mathcal{H}(t)|0(t)\rangle = 0$ at all times. It is convenient to define

$$\Omega' \equiv \sqrt{\Omega_p^2 + \Omega_s^2} = \Omega_p \sin\theta + \Omega_s \cos\theta, \quad (3)$$

where the time dependence has been suppressed.

In the STIRAP process, the initially populated state is $|1\rangle$ and it coincides with $|0(t)\rangle$ for $\theta(t) = 0$. Thus the counterintuitive pulse order provides for the determination of the intial state; the intuitive pulse order would do the reverse. At $t = 0$ a pulse of light tuned near the transition between $|2\rangle$ and $|3\rangle$ with Rabi frequency $\Omega_s(t)$ begins, thereby keeping $\tan\theta(t) = 0$ so that the eigenfunction $|0(t)\rangle$ remains equal to $|1\rangle$. Before this pulse ends a second pulse tuned near the transition between $|2\rangle$ and $|1\rangle$ with Rabi frequency $\Omega_p(t)$ begins, making $\tan\theta(t) \neq 0$ so that $|0(t)\rangle$ becomes the mixture of $|1\rangle$ and $|3\rangle$ given in Eq. (2). The process becomes complete when $\Omega_s(t)$ vanishes before $\Omega_p(t)$ does, making $\tan\theta(t) \to \infty$ and the eigenstate $|0(t)\rangle$ is pure $|3\rangle$. The time dependences of these pulse shapes are chosen so that the actual state vector $\Psi_0(t)$ follows this evolution of the adiabatic eigenstate $|0(t)\rangle$ as closely as possible, thereby transferring the population from $|1\rangle$ to $|3\rangle$ as efficiently as possible. This is the usual description of STIRAP.

B. The conditions for adiabaticity

The usual description of an ideal adiabatic process given above, namely the perfect evolution of $|0\rangle$ from pure $|1\rangle$ to pure $|3\rangle$ and completely independent of $|2\rangle$, is deceptive because $|2\rangle$ plays an important role [14–16]. This is so because perfect adiabaticity is never experimentally possible nor theoretically expected, although some deviations may be compensated [17]. The origin of the role of $|2\rangle$ arises from two sources: (1) Δ_p is not exactly equal to $-\Delta_s$, and (2) the time dependence of the full Hamiltonian has the envelopes of the pulsed light fields in addition their oscillations at the optical frequencies, and this part of the time dependence survives the rotating frame transformation so $\mathcal{H}(t)$ of Eq. (1) still has some time dependence, as indicated.

It is not hard to see how this is necessary because $|0\rangle$ cannot satisfy both sides of the time-dependent Schrödinger equation. Clearly $\mathcal{H}|0\rangle = 0|0\rangle = 0$ for the Hamiltonian of Eq. (1), but $i\hbar\,\partial|0\rangle/\partial t \neq 0$ unless $\theta =$ constant. Since the pulse envelopes Ω_s and Ω_p are time dependent, θ is not constant, but its time dependence escapes the rotating frame transformation. As discussed below, the consequence is that adiabaticity needs to be sacrificed by allowing some small component of $|2\rangle$ in the evolution of $|0\rangle$ under the influence of the light. This is quite evident in several of the published numerical calculations of the STIRAP process, although it may not have been discussed [4,7,14].

Various schemes to minimize the population of $|2\rangle$ have been developed because its undesirable transition back to $|1\rangle$ or other accessible states can compromise the efficiency of the STIRAP process by destroying the phase relation between $|1\rangle$ and $|3\rangle$ [14]. The limits of these STIRAP schemes can be discussed by considering the populations of $|2\rangle$ and $|3\rangle$ in the actual state vector $\Psi_0(t)$ instead of the ideal adiabatic state $|0\rangle$.

For clarity, note that the set of kets $\{|1\rangle,|2\rangle,|3\rangle\}$ are the time-independent bare states of the atom of Fig. 1. The ordered set of kets $\{|+\rangle,|0\rangle,|-\rangle\}$ are the adiabatic eigenstates of $\mathcal{H}(t)$ of Eq. (1), where $|0\rangle$ is the idealized "dark state" of STIRAP, and these are time dependent through $\theta(t)$. Finally, the $\Psi_{\{+,0,-\}}(t)$'s are the set of actual state vectors for the nonideal case. Often the time dependence will not be indicated for clarity. The basis sets $\{|1\rangle,|2\rangle,|3\rangle\}$ and $\{|+\rangle,|0\rangle,|-\rangle\}$ are related by $\{|+\rangle,|0\rangle,|-\rangle\} = \mathcal{U}\{|1\rangle,|2\rangle,|3\rangle\}$ and the unitary transformation $\mathcal{U}$ is given in Eq. (A4).

The populations of $|2\rangle$ and $|3\rangle$ in $\Psi_0(t)$ can be conveniently calculated in any basis: using the eigenfunctions of Eq. (1) is not necessary. Therefore consider a basis set of two other states orthogonal to $|0\rangle$ of Eq. (2) chosen so that they span the Hilbert space. Since these do not need to be eigenfunctions, a good choice is $|2\rangle$ since it is orthogonal to $|0\rangle$ and its population is of special interest here. The third state, $|+\rangle' \equiv \sin\theta(t)\,|1\rangle + \cos\theta(t)\,|3\rangle$, is orthogonal to both $\Psi_0(t)$ and $|2\rangle$. Note that $|+\rangle'$ can be found from $-d|0\rangle/d\theta$ and it represents a $\pi/2$ rotation of $|0\rangle$ in Hilbert space so it is thus orthogonal to $|0\rangle$. Here and onward the time dependence will be omitted.

The focus of STIRAP is the evolution of the state vector $\Psi_0(t)$ under the influence of the changing optical field amplitudes, and using the basis choice above it can be written as

$$\Psi_0(t) = |0\rangle + \varepsilon_1(t)|2\rangle + \varepsilon_2(t)|+\rangle'. \quad (4)$$

Equation (4) uses the ansatz that both $|\varepsilon_1(t)| \ll 1$ and $|\varepsilon_2(t)| \ll 1$ in order to keep the evolution close to the ideal adiabatic case and neglects the correspondingly small normalization correction to $\Psi_0(t)$. Then choosing $\theta' \equiv \theta - \varepsilon_2$ yields the

column vector

$$\Psi_0 \approx [\cos\theta'|1\rangle, \varepsilon_1|2\rangle, \ -\sin\theta'|3\rangle]^T, \tag{5}$$

where the explicit time dependence has been dropped for simplicity.

Insisting that the wave function of Eq. (5) satisfies the time-dependent Schrödinger equation begins by applying the Hamiltonian matrix of Eq. (1) to Ψ_0 to find

$$\mathcal{H}\Psi_0 = \frac{\hbar}{2}[\varepsilon_1\Omega_p|1\rangle, (\varepsilon_2\Omega' - 2\varepsilon_1\Delta_p)|2\rangle, \varepsilon_1\Omega_s|3\rangle]^T, \tag{6}$$

where Eq. (2) has been used twice. If both ε_1 and ε_2, are $\ll 1$, then $\langle\Psi_0|\mathcal{H}|\Psi_0\rangle \ll \hbar\Omega_p$ and $\ll\hbar\Omega_s$ which implies that Ψ_0 is close to the adiabatic eigenstate $|0\rangle$ since $\langle 0|\mathcal{H}|0\rangle = 0$.

The right-hand side of the time-dependent Schrödinger equation, $i\hbar\,\partial/\partial t$, applied to the first and third terms of Eq. (5), can be equated to the corresponding terms of Eq. (6) to give

$$\begin{aligned}\left[-i\hbar\frac{d\theta'}{dt}\sin\theta' = \frac{\hbar}{2}\varepsilon_1\Omega_p\right]|1\rangle;\\ \left[-i\hbar\frac{d\theta'}{dt}\cos\theta' = \frac{\hbar}{2}\varepsilon_1\Omega_s\right]|3\rangle.\end{aligned} \tag{7}$$

The time dependence of θ and θ' is determined by the details of the pulse shape, but if the total pulse overlap time is τ, the average value of $\dot\theta \sim \dot\theta'$ must be $\sim\pi/2\tau$ since θ sweeps smoothly from 0 to $\pi/2$. Now apply $\langle 1|$ to the top line of Eq. (7) to find $-2i\sin\theta'\,\dot\theta' = \varepsilon_1\Omega_p$ and similarly for the second line with $\langle 3|$, square and add the results, and use this average value of $\dot\theta'$ to find $|\varepsilon_1| \approx \pi/(\Omega_0'\tau)$, where Ω_0' is the average value of $\Omega'(t)$ during the pulse overlap time τ. Then the desired condition $|\varepsilon_1| \ll 1$ requires that

$$\Omega_0'\tau \gg \pi. \tag{8}$$

This means that the adiabatic evolution of $\Psi_0(t)$ requires the atom to undergo very many cycles between states $|1\rangle$ and $|3\rangle$ during the pulse overlap time.

In addition to the adiabatic condition above, it is also possible to estimate ε_2. Assume ε_1 varies slowly and smoothly with time during the pulse overlap so that the average value of $\dot\varepsilon_1$ satisfies $\dot\varepsilon_1 \sim \varepsilon_1/\tau$, and use the relation from the time-dependent Schrödinger equation on the middle term of Eq. (5) to find

$$i\hbar\dot\varepsilon_1 = (\hbar/2)(\varepsilon_2\Omega_0' - 2\varepsilon_1\Delta_p) \Rightarrow \varepsilon_2 = 2\varepsilon_1\left(\frac{\Delta_p}{\Omega_0'} + \frac{1}{\Omega_0'\tau}\right). \tag{9}$$

Since $\Omega_0'\tau \gg \pi$, the second term in parentheses above can be neglected relative to Δ_p/Ω_0' unless Δ_p/Ω_0' is very small itself, so $\varepsilon_2 \approx \varepsilon_1(2\Delta_p/\Omega_0')$. As long as Δ_p/Ω_0' is not $\gg 1$, both $\varepsilon_2 \ll 1$ and $\varepsilon_1 \ll 1$, thereby assuring very nearly adiabatic evolution of $\Psi_0(t)$. For $\Delta_p \gg \Omega_0'$, STIRAP fails because it violates the adiabaticity condition and $\Psi_0(t)$ deviates considerably from $|0\rangle$.

II. CALCULATION OF THE NONADIABATICITY

The calculation of the population of the intermediate state $|2\rangle$ contained in $\Psi_0(t)$ as θ sweeps from 0 to $\pi/2$ begins with a closer look at the Schrödinger equation since the evolution of the state vector $\Psi_0(t)$ may not be the same as that of $|0\rangle$. As before, assume that the system starts with $\Psi_0(t) = |1\rangle$ and evolves under the action of the Hamiltonian of Eq. (1). Then calculate how much of $|3\rangle$ is in the final state $\Psi_0(T)$ after Ω' has gone to zero after the interaction time T. This is done by projecting the final state

$$\Psi(T) = \widehat{\mathcal{T}}\{e^{-(i/\hbar)\int_0^T \mathcal{H}(t)dt}\}|1\rangle \tag{10}$$

onto the bare state $\langle 3|$ by calculating $\langle 3|\Psi(T)\rangle$. Here $\widehat{\mathcal{T}}$ indicates time ordering. One way to do this is by calculating the propagator using an approach that is related to path integrals. Begin by defining $t_m \equiv m\Delta t$ and write $\int_0^T$ as a series of integrals over short, equal intervals Δt so it becomes

$$\int_0^T \to \int_{t_{n-1}}^T + \int_{t_{n-2}}^{t_{n-1}} + \int_{t_{n-3}}^{t_{n-2}} + \cdots + \int_0^{t_1}, \tag{11}$$

where $\Delta t \equiv T/n$, and then take $\lim\{n \to \infty\}$.

The next several steps are algebraically complicated so the details of the calculation are relegated to the appendix. In the limit of $n \to \infty$ both Eqs. (11) and (A3) are correct, but the calculation depends on requiring that both $\Delta_p = -\Delta_s \equiv \Delta$ satisfy $\Delta/\Omega_p, \Delta/\Omega_s \leqslant 1/\pi$ so that the perturbation approximation given by the adiabaticity condition of Eq. (9) is satisfied. This also means that during the pulse overlap time, α of Eqs. (A4) and (A5) of the Appendix varies slowly near $\pi/4$ so that neglecting $d\alpha/dt$ in Eq. (A7) there is appropriate. The only time that $d\alpha/dt$ is significant is near the beginning or end of the sequence when only one of the laser frequencies is present and the other is almost off (Gaussian pulses never vanish but other pulse shapes have been studied [14,18]). Then θ is constant near 0 or $\pi/2$ so $\dot\theta$ is negligible here.

The resulting propagator is written as the sum of zeroth-order and first-order terms, and the zeroth-order term $G_{(0)}$ of Eq. (A11) represents the case of perfect adiabaticity. The first-order term $G_{(1)}$ is given by Eq. (A13) and its use requires evaluation using the initial state $|1\rangle$ as shown in Eq. (A2). Of course, $|1\rangle$ is evolved primarily to $|3\rangle$ so the objective of the first-order calculation is to find how much of the final state $\Psi(T)$ is left in $|1\rangle$ after the light pulses end, and also how

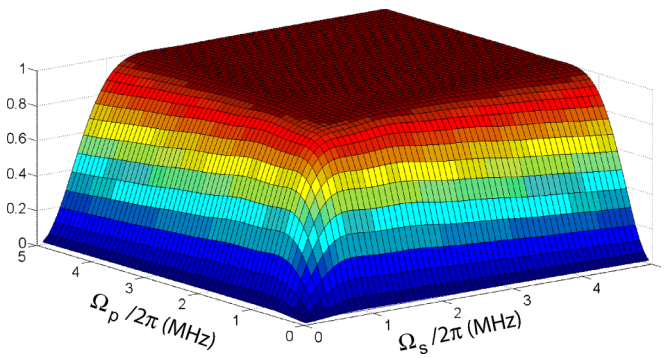

FIG. 2. (Color online) Plot of STIRAP population efficiency found by numerically solving the equation of motion of the density matrix as a function of the two Rabi frequencies Ω_p and Ω_s. The width of each Gaussian pulse was 1 μs, the separation between their peaks was 1.2 μs, and the detuning $\Delta_p = -\Delta_s$ was zero. Clearly the regions of interest are where the Ω's $> 2\pi \times 1.5$ MHz.

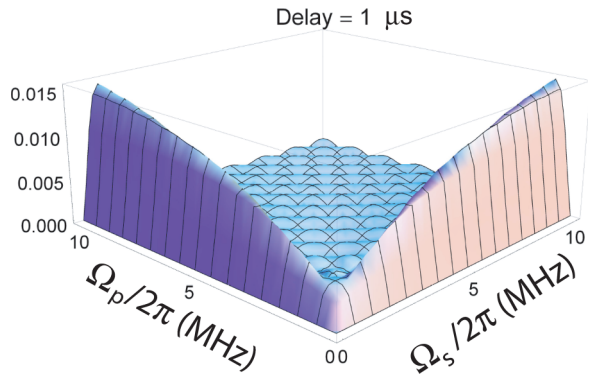

FIG. 3. (Color online) Plot of the amplitude $|\langle 2|\Psi(T)\rangle|$ vs the two Rabi frequencies Ω_s and Ω_p. The width of each Gaussian pulse was 1 μs [for the Rabi frequencies as given in Eq. (12)—the pulse widths are less for the intensities], the detuning $\Delta_p = -\Delta_s$ was $2\pi \times 1$ MHz, and the separation between their peaks was 1 μs. The wave functions are not normalized here so there is an $\sim$1% error in $|\langle 2|\Psi(T)\rangle|$ because of the ε's in Eq. (4). Although Eq. (A15) is not valid for values of either $\Omega < \Delta$, the plot range here goes to zero just to show that the program is well behaved.

much of the final state $\Psi(T)$ is composed of $|2\rangle$ at the end. The ordering of the perturbation method used here is based on powers of $d\theta/dt$, while it is assumed that the effect of $d\alpha/dt$ is much less important. The systematic perturbation method used here is capable of corrections to all orders even though this discussion is restricted to the lowest two for simplicity.

The magnitudes of $\langle 1|\Psi(T)\rangle$ and $\langle 2|\Psi(T)\rangle$ in Eq. (A15) are dictated by the ratio of $\dot{\theta}$ to the eigenvalues $\omega_\pm$ given in Eq. (A6) and is very similar to the result of Ref. [11]. It comes from integrating the exponential of Eq. (A15) and is estimated in Eq. (A16) to be much less than unity for the adiabatic condition of Eq. (8). All the other terms of Eq. (A15) are of order unity.

The essential result, given by Eq. (A15), is just the final-state overlap on the intermediate state, $\langle 2|\Psi(T)\rangle$, in terms of the experimental pulse intensities, shapes, and overlap, as well as the detuning for the resonant case where $\Delta_p + \Delta_s = 0$. A similar calculation would yield $\langle 1|\Psi(T)\rangle$.

III. RESULTS

The results are evaluated in parameter regions where STIRAP is found to be quite efficient. Such regions have been described before in many places [8,9], but we repeated the calculations as shown in Fig. 2. It shows that the efficiency is better than 90% in regions where the Ω's are larger than 2π times a few MHz for the chosen laser timing parameters.

A MATHEMATICA code has been written to evaluate Eq. (A15) as different parameters are varied. In our experiments, the STIRAP laser beams have Gaussian intensity profiles and they cross a beam of metastable 2^3S He atoms perpendicularly [19,20]. Therefore the evaluation of Eq. (A15) begins with Gaussian pulses having time dependence of the form

$$\Omega_k(t) = \Omega_{0,k} e^{-(\frac{t-t_{0,k}}{t_G})^2}, \tag{12}$$

where k stands for s or p, and the pulses can have varying relative delays t_0. In all these calculations both Gaussian pulse widths [t_G of Eq. (12)] were chosen to be 1 μs, and the pump pulse center was at 6 μs while the Stokes pulse was moved earlier by the various specified delays. The total evolution time was 12 μs. In these first cases plotted below, the detunings are chosen so $\Delta_s = -\Delta_p = 2\pi \times 1$ MHz so that they are small compared to the Ω's over a wide range of the plots.

The plot of Fig. 3 shows how the magnitude $|\langle 2|\Psi(T)\rangle|$ depends on the two Rabi frequencies Ω_s and Ω_p. Clearly the nonadiabaticity is relatively large in the regions having Rabi frequencies that are too small to be of interest here. Moreover, the picture is consistent with Fig. 2 that shows a sharp decrease in the STIRAP efficiency in this region. (The efficiency decrease in Fig. 2 is much larger than the peak value of $|\langle 2|\Psi(T)\rangle|$ in Fig. 3 because nonadiabaticity is not the only reason STIRAP is less efficient at low Ω's.)

One prominent feature of Fig. 3 is the oscillatory behavior at larger values of the Ω's, a point that has been made by many other authors [14,15,18]. It derives from the $\cos\alpha(T)$ of Eq. (A15) [see Eq. (A5)]. These ripples run diagonally in the figure because α depends on both Ω_s and Ω_p through Ω'. Also note that $|\langle 2|\Psi(T)\rangle|$ vanishes when either $\Omega = 0$.

The behavior of $|\langle 2|\Psi(T)\rangle|$ is more easily seen in the plots of Fig. 4 that are limited to regions where the Ω's are both larger

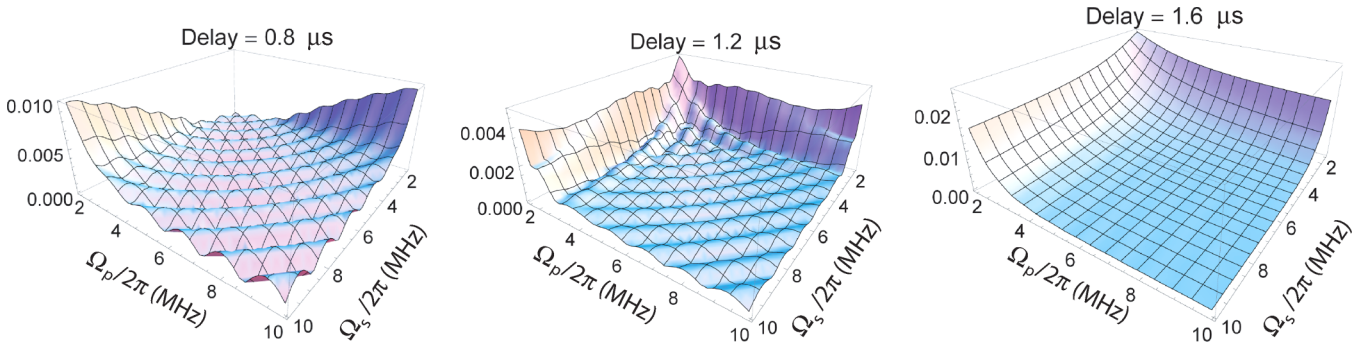

FIG. 4. (Color online) Plot of the amplitude $|\langle 2|\Psi(T)\rangle|$ vs the two Rabi frequencies Ω_s and Ω_p for various delay times between the pulses. As in Fig. 3, the width of each Gaussian pulse was 1 μs, and the detuning $\Delta_p = -\Delta_s$ was $2\pi \times 1$ MHz. The oscillations damp out at large pulse separations because $\alpha(t)$ varies considerably during the gap between them and thus averages over them. Also, neglecting $d\alpha/dt$ is not a good approximation in this region of large delay. The wave functions are not normalized here so there is an $\sim$1% error in $|\langle 2|\Psi(T)\rangle|$ because of the ε's in Eq. (4).

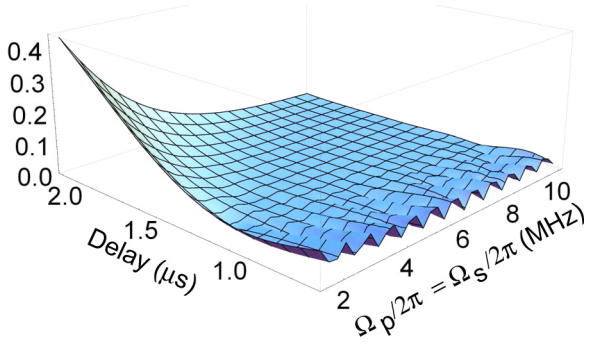

FIG. 5. (Color online) Plot of the amplitude $|\langle 2|\Psi(T)\rangle|$ vs Rabi frequencies and delay is shown. The Rabi frequencies are same for both beams and the detuning is very small: $\Delta_p = -\Delta_s = 2\pi \times 0.25$ MHz. Note that the ripples are quite prominent near short delays but damp out at larger values (see Fig. 4).

than $\sim 2\pi \times 1.5$ MHz, and the plots are turned around with the origin in back to show the behavior at larger values of the Ω's. The three plots are for different values of the delay between the pulse peaks. When the delay is too small the pulses overlap too much and there is significant population excited into $|2\rangle$. When the delay is too large there is not sufficient coherence established between $|1\rangle$ and $|3\rangle$. It was recognized early in the study of STIRAP that the optimal delay is approximately 1.2 times the pulse widths (when they are equal) [7] and this has been corroborated by measurements in neon (see Ref. [8]).

In Figs. 3 and 4 the detuning was fixed at ± 1 MHz for each laser beam so that $\Delta_p + \Delta_s = 0$. Now consider the effects of the detuning, maintaining final-state resonance to satisfy the conditions of Sec. I A. Figure 5 show a plot of the magnitude of $|\langle 2|\Psi(T)\rangle|$ at very small detuning, holding the two Rabi frequencies equal, vs the delay between the pulse peaks. Clearly its magnitude is much larger than those of Figs. 3 and 4, and the reason is that the small detuning allows for significant excitation into $|2\rangle$ at any value of the delay. The oscillatory behavior is quite evident out to moderate values of the delay.

Figure 6 shows the evolution of this behavior for different values of the detuning $\Delta_p = -\Delta_s$. The changes of the vertical axis scale are dramatic: As the detuning changes from 0.5 to 1.5 MHz (top row) the peak nonadiabaticity decreases by a factor of 20, and another factor of 25 going to 2.5 MHz (bottom row). At large detunings [Fig. 6(f)] the nonadiabaticity is minuscule, but it still is optimum at a delay of about 1.2 μs for large Rabi frequencies. This does not mean that STIRAP becomes more efficient, but only that this nonadiabatic part becomes less important. As discussed in Sec. I B, both Δ_p and Δ_s must be much smaller than Ω_s and Ω_p to preserve adiabaticity. In Fig. 6(f), both detunings are $\sim 2\pi \times 3$ MHz while $\Omega' \sim 2\pi \times 14$ MHz at its maximum (furthest corner).

IV. SUMMARY AND CONCLUSIONS

The usual idealized description of STIRAP does not include the time dependence of the shape of the pulse envelopes because the rotating frame transformation eliminates only the time dependence at the optical frequencies (of course, the pulse ordering must be counterintuitive) and therefore does not consider the nonadiabaticity associated with the envelopes' temporal variation. Here it is shown that this traditional description can be slightly modified to accommodate such an effect by allowing a small population in the intermediate state. The consequence precludes the usual analytic solutions of the Schrödinger equation so a perturbative approach is developed (in the Appendix).

It begins by calculating a propagator in infinitesimal time steps and then expanding it in orders of the characteristic time of the pulse envelopes. The result is a single compact formula for the final intermediate-state population that is readily evaluated for an arbitrary choice of laser pulse parameters [Eq. (A15)]. The evaluation is easily changed to find the time dependence of this population.

Plots of a few conditions are chosen to be presented. They are restricted to Gaussian pulses of equal widths with delays in

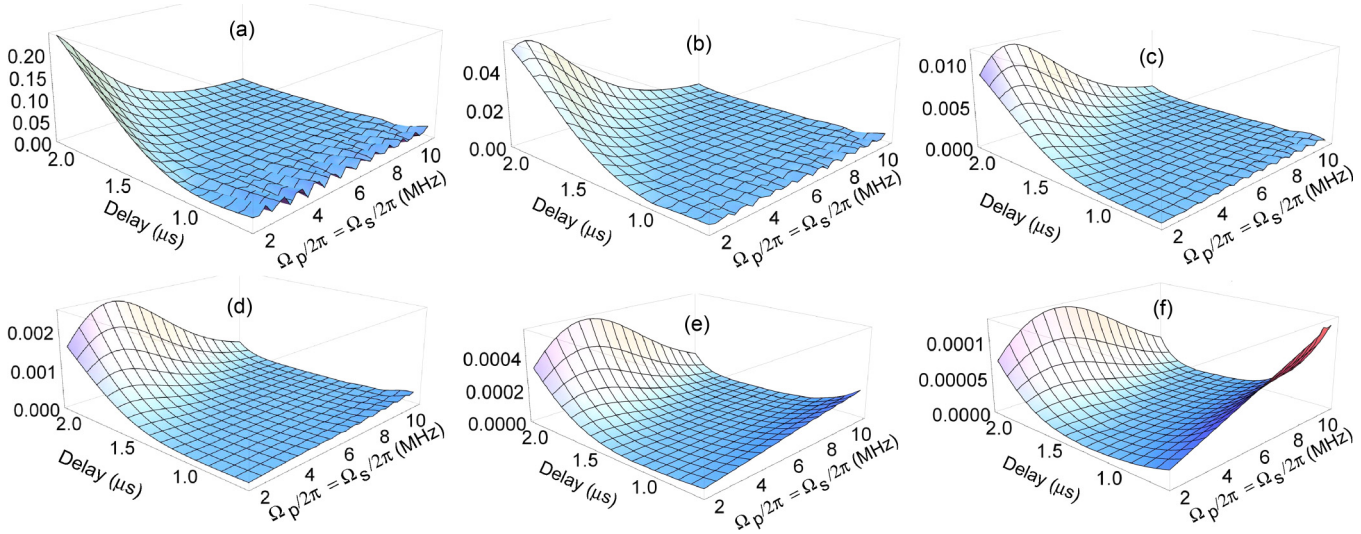

FIG. 6. (Color online) Plots of the amplitude $|\langle 2|\Psi(T)\rangle|$ vs Rabi frequencies and delay. In parts (a) through (f) the values of the detuning $\Delta_p/(2\pi) = -\Delta_s/(2\pi) = \Delta/(2\pi)$ are 0.5, 1.0, 1.5, 2.0, 2.5, and 3.0 MHz respectively.

a range suitable for STIRAP, but they can easily be altered. The peak Rabi frequencies of each pulse are varied over a range consistent with the usual adiabatic conditions of STIRAP, although these can be changed as well. In all calculations, the effect of spontaneous emission from the intermediate is omitted even though it is slightly populated, but this can be included if desired. Since we are modeling an experiment whose intermediate-state lifetime is about 1/10 of the pulse widths and separation, and the intermediate state population is typically below 1%, including it would not change our results here. The effects of the calculated nonadiabaticity are in the few percent range but that this effect could place a limit on the ultimate efficiency of STIRAP. Moreover, this effect could become important for pulse shapes having rapid variations during their overlap time.

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APPENDIX

1. Simplifying the summation

The exponential of the sum obtained by putting Eq. (11) into Eq. (10) is replaced by a product of exponentials as

$$\widehat{\mathcal{T}}\left\{e^{-(i/\hbar)\int_{t_{n-1}}^{T}\mathcal{H}(t_{n-1})dt}e^{-(i/\hbar)\int_{t_{n-2}}^{t_{n-1}}\mathcal{H}(t_{n-2})dt}\cdots e^{-(i/\hbar)\int_{0}^{t_1}\mathcal{H}(0)dt}\right\}. \tag{A1}$$

In the $\lim\{n\to\infty\}$ each integral becomes small enough so that the expansion of each exponential into a series requires retention of only the first two terms. Moreover, for the very short time interval Δt one can replace $\int_{t_m}^{t_{m+1}}\mathcal{H}(t_m)dt$ by $\mathcal{H}(t_m)\Delta t$ so the projection of the final state onto $\langle 3|$ becomes (note the time ordering)

$$\langle 3|\Psi(T)\rangle = \lim_{n\to\infty}\langle 3|\prod_{m=n}^{1}\left[1-\frac{i}{\hbar}\mathcal{H}(t_m)\Delta t\right]|1\rangle. \tag{A2}$$

To evaluate the product of Eq. (A2) in the limit of $n\to\infty$, start by inserting the unit operator in the adiabatic basis set $\sum_{j=1}^{3}|j(t_m)\rangle\langle j(t_m)|$, where $j=\{+,0,-\}$, between each factor of the product using the value of each $j(t_m)$ of the set at the appropriate time t_m. Then each factor in the resulting product of Eq. (A2) can be written as a number having the form

$$g_{kj}^{(m)}(t_m) = \langle k(t_{m+1})|\left[1-\frac{i}{\hbar}\mathcal{H}(t_m)\Delta t\right]|j(t_m)\rangle. \tag{A3}$$

Next, note that the $\lim(n\to\infty)$ allows the expansion $\langle k(t_{m+1})| \approx \langle k(t_m)| + \Delta t d\langle k(t_m)|/dt$ and the complex conjugate of the Schrödinger equation gives $-i\hbar\, d\langle k(t_m)|/dt = E_k(t_m)\langle k(t_m)| \equiv \hbar\omega_k(t_m)\langle k(t_m)|$.

For completeness the full set of eigenfunctions of the $|k(t_m)\rangle$'s can be written as

$$\begin{aligned}
|+\rangle &= \sin\theta\sin\alpha\,|1\rangle + \cos\alpha\,|2\rangle + \cos\theta\sin\alpha\,|3\rangle,\\
|0\rangle &= \cos\theta\,|1\rangle - \sin\theta\,|3\rangle \qquad [\text{as in Eq. (2)}],\\
|-\rangle &= \sin\theta\cos\alpha\,|1\rangle - \sin\alpha\,|2\rangle + \cos\theta\cos\alpha\,|3\rangle,
\end{aligned} \tag{A4}$$

where

$$\tan 2\alpha \equiv \Omega'/\Delta_p\,. \tag{A5}$$

The eigenvalues ω_i are given by

$$\begin{aligned}
E_i &= \hbar\omega_\pm = \frac{\hbar}{2}[\Delta \pm \sqrt{\Omega'^2+\Delta^2}]\\
&\equiv \frac{\hbar}{2}[\Delta\pm\Omega''] \quad \text{and} \quad \omega_0 = 0,
\end{aligned} \tag{A6}$$

and the time derivatives (the $|k\rangle$'s are time-dependent through $\theta(t)$)

$$\begin{aligned}
d|+\rangle/dt &= \dot\theta\,\sin\alpha\,[\cos\theta\,|1\rangle - \sin\theta\,|3\rangle] = \dot\theta\,\sin\alpha\,|0\rangle,\\
d|0\rangle/dt &= -\dot\theta\,[\sin\theta\,|1\rangle + \cos\theta\,|3\rangle]\\
&= -\dot\theta\,[\sin\alpha\,|+\rangle + \cos\alpha\,|-\rangle],\\
d|-\rangle/dt &= \dot\theta\,\cos\alpha\,[\cos\theta\,|1\rangle - \sin\theta\,|3\rangle] = \dot\theta\,\cos\alpha\,|0\rangle.
\end{aligned} \tag{A7}$$

Here the time dependence is also suppressed for clarity. The adiabaticity condition of Eq. (8) leads to $\tan 2\alpha \gg 1$. Thus Eq. (A5) means that $\alpha \approx \pi/4$ during the pulse overlap time and so $d\alpha/dt$ is neglected in Eqs. (A7).

2. Evaluating each term

Now consider the nine terms $g_{kj}^{(m)}(t_m)$ of Eq. (A3) (both k and j have values $\{+,0,-\}$). Their numerical values can be written in a 3×3 array as

$$g^{(m)}(t_m) = \begin{bmatrix} 1-i\omega_+(t_m)\Delta t & \dot\theta\Delta t\sin\alpha & 0\\ -\dot\theta\Delta t\sin\alpha & 1 & -\dot\theta\Delta t\cos\alpha\\ 0 & \dot\theta\Delta t\cos\alpha & 1-i\omega_-(t_m)\Delta t\end{bmatrix} \tag{A8}$$

after considerable careful algebra [15]. Using the definition given in Eq. (A3), Eq. (A9) shows how to evaluate these terms in the first row:

$$\begin{aligned}
g_{++}^{(m)}(t_m) &= \{\dot\theta\Delta t\,\sin\alpha\,\langle 0| + \langle +|\}\left[1-\frac{i}{\hbar}\mathcal{H}(t_m)\Delta t\right]|+\rangle\\
&= 1-i\omega_+(t_m)\Delta t,\\
g_{+0}^{(m)}(t_m) &= \{\dot\theta\Delta t\,\sin\alpha\,\langle 0| + \langle +|\}\left[1-\frac{i}{\hbar}\mathcal{H}(t_m)\Delta t\right]|0\rangle\\
&= \dot\theta\Delta t\sin\alpha,\\
g_{+-}^{(m)}(t_m) &= \{\dot\theta\Delta t\,\sin\alpha\,\langle 0| + \langle +|\}\left[1-\frac{i}{\hbar}\mathcal{H}(t_m)\Delta t\right]|-\rangle\\
&= 0.
\end{aligned} \tag{A9}$$

The utility of writing the $g^{(m)}(t_m)$'s as an array [see Eq. (A8)] emerges by considering the summations inserted as unit operators in Eq. (A2). Each of the summations over the $|j(t_m)\rangle$'s is evaluated at a different time t_m so that the terms involving the Hamiltonian $\mathcal{H}(t_m)$ do not necessarily commute. Even so, it is possible to move the summation signs to the left in the expression because the $|j(t_m)\rangle$'s are distinguishable. With that in mind, examination of the summations shows that

treating the arrays of $g^{(m)}(t_m)$'s as matrices, and performing matrix multiplication of them, produces the desired result.

3. Perturbative approach to lowest orders

Although matrix multiplication of the $g^{(m)}(t_m)$'s is straightforward, the limit $n \to \infty$ makes the multiplication a daunting process. Nevertheless, the adiabaticity criterion $\dot{\theta} \ll \Omega_0'/2$ near the end of Sec. I B above, and the eigenvalues of Eq. (A6) having Ω_0' and ω_j of the same order, suggest that the ω_j's $\gg \dot{\theta}$ so a perturbative approach to Eq. (A8) is in order. Its first step for evaluating the $g^{(m)}(t_m)$'s is to separate each of them into the two terms $g_{(0)}^{(m)}(t_m)$ and $g_{(1)}^{(m)}(t_m)$ as

$$g^{(m)}(t_m) \equiv g_{(0)}^{(m)}(t_m) + g_{(1)}^{(m)}(t_m) = \begin{bmatrix} (1 - i\omega_+(t_m)\Delta t) & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & (1 - i\omega_-(t_m)\Delta t) \end{bmatrix}$$
$$+ \dot{\theta}(t_m)\Delta t \begin{bmatrix} 0 & \sin\alpha(t_m) & 0 \\ -\sin\alpha(t_m) & 0 & -\cos\alpha(t_m) \\ 0 & \cos\alpha(t_m) & 0 \end{bmatrix}. \tag{A10}$$

Then the lowest order term in the product of all these $g^{(m)}$'s in Eq. (A10) is given by

$$G_{(0)} = \lim_{n\to\infty} \prod_{m=n}^{1} g_{(0)}^{(m)}(t_m). \tag{A11}$$

Since each $g_{(0)}^{(m)}(t_m)$ is diagonal, $G_{(0)}$ is a diagonal matrix having corner elements equal to the product of their binomial elements as given in Eq. (A10). Moreover, each of these has the form $1 - i\eta$ where $\eta \ll 1$ so they can be replaced by $e^{-i\eta}$. In the product of these resulting exponentials the sum of the exponents can be replaced by the integral $-i\int_0^T \omega_\pm(t)dt$ so that $G_{(0)}$ has a simple form.

The next order term in the product of the $g^{(m)}(t_m)$'s is first order in $\dot{\theta}$ and has a sum of n terms, each of which has products of $n-1$ factors of the form $e^{-i\eta}$ and one having the form $\dot{\theta}\Delta t \sin\alpha$ (or $\cos\alpha$) from $g_{(1)}^{(m)}$. However, the matrices $g_{(0)}^{(m)}$ and $g_{(1)}^{(m)}$ do not commute so some care is needed. The mth term of the sum is given by

$$G_{(1)}^{(m)} = \dot{\theta}(t_m)\Delta t \begin{bmatrix} e^{-i\int_{t_m}^T \omega_+(t)dt} & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & e^{-i\int_{t_m}^T \omega_-(t)dt} \end{bmatrix}$$
$$\times \begin{bmatrix} 0 & \sin\alpha(t_m) & 0 \\ -\sin\alpha(t_m) & 0 & -\cos\alpha(t_m) \\ 0 & \cos\alpha(t_m) & 0 \end{bmatrix} \begin{bmatrix} e^{-i\int_0^{t_m} \omega_+(t)dt} & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & e^{-i\int_0^{t_m} \omega_-(t)dt} \end{bmatrix}. \tag{A12}$$

Summing these over all m can also be replaced by an integral. Begin by multiplying out the three matrices of Eq. (A12) and then integrate the product to get the final result for the first-order term in the product of all the $g^{(m)}$'s as

$$G_{(1)} = \int_0^T dt_\mu\, \dot{\theta}(t_\mu) \begin{bmatrix} 0 & \sin\alpha(t_\mu)e^{-i\int_{t_\mu}^T \omega_+(t)dt} & 0 \\ -\sin\alpha(t_\mu)e^{-i\int_0^{t_\mu} \omega_+(t)dt} & 0 & -\cos\alpha(t_\mu)e^{-i\int_0^{t_\mu} \omega_-(t)dt} \\ 0 & \cos\alpha(t_\mu)e^{-i\int_{t_\mu}^T \omega_-(t)dt} & 0 \end{bmatrix}. \tag{A13}$$

4. Evaluating the propagator

What remains to be done to calculate the nonadiabaticity of the process is evaluation of the end terms of Eq. (A2) after the insertion of the identity operators. Substituting the results above into $\langle 3|\Psi(T)\rangle$ gives

$$\langle 3|\Psi(T)\rangle = \sum_{j=1}^{3}\sum_{j'=1}^{3} \langle 3|j(T)\rangle (G_{(\mathrm{tot})}) \langle j'(0)|1\rangle, \tag{A14}$$

where the explicit time dependence of the $|j\rangle$'s has been restored and the 3×3 array $G_{(\mathrm{tot})} \equiv G_{(0)} + G_{(1)}$ depends on both j and j'. Thus there are nine terms in Eq. (A14), for example, the term for $j, j' = +, 0$ is $\langle 3|+(T)\rangle G_{+0} \langle 0(0)|1\rangle$. The evaluation is simplified by noting that, at $t = 0$, the wave function is pure $\langle 0(0)| = \langle 1|$ because neither $\langle +(0)|$ nor $\langle -(0)|$ have any component of $\langle 1|$ when $\theta = 0$ [see Eq. (A4)]. Thus six of the nine terms vanish because of the factor $\langle j'(0)|1\rangle$ of Eq. (A14). For the three remaining terms, $j' = 0(0)$ and $\langle 0(0)|1\rangle =$ unity.

Moreover, $\langle 3|j(T)\rangle$ vanishes for two of the surviving terms having $j = +$ or $-$ because $\theta = \pi/2$ at the time T, leaving only $\langle 3|0(T)\rangle (G_{00}) \langle 0(0)|1\rangle = 1$ as the surviving term. Here G_{00} is the center element of the matrix $G_{(\mathrm{tot})}$ (it is 1 from $G_{(0)}$ and 0 from $G_{(1)}$). The lowest order term in the perturbative

expansion uses only $G_{(0)}$, which is diagonal, so a similar calculation shows that both $\langle 1|\Psi(T)\rangle$ and $\langle 2|\Psi(T)\rangle$ vanish in lowest order. Thus the projection of the final state on $\langle 3|$, namely $\langle 3|\Psi(T)\rangle$, is exactly unity corresponding to perfect adiabaticity in this lowest order approximation.

By contrast, in the next order, $G_{(1)}$ has only off-diagonal elements so the two terms with $\langle 1|\Psi(T)\rangle$ and $\langle 2|\Psi(T)\rangle$ that vanished in zeroth order because $G_{(0)}$ is diagonal need to be re-examined. The factor $\langle j'(0)|1\rangle$ still vanishes for the same six terms as before in Eq. (A14) at $t = 0$, and also $\langle 2|0\rangle$ vanishes for all times. As an example of this next step, one surviving term is $\langle 2|+(T)\rangle(\,G_{+0}\,)\langle 0(0)|1\rangle$ and another would have $\langle 2|-(T)\rangle$ in place of the first factor. Since $\langle 2|+(T)\rangle$ is just $\cos\alpha(T)$, the G_{+0} term is given by

$$\langle 2|\Psi(T)\rangle = \cos\alpha(T)\int_0^T dt_\mu\,\dot\theta_\mu\,\sin\alpha(t_\mu)\,e^{-i\int_{t_\mu}^T\omega_+(t)dt}. \tag{A15}$$

A rough estimate of this quantity can be had by choosing the Ω'' of Eq. (A6) to be constant during the interaction time. Thus ω_+ is constant and the integral $\int_0^{t_\mu}\omega_+(t)dt$ is simply $\omega_+ t_\mu$. Then, continuing with the approximation that $\cos\alpha(t_\mu)$ can be replaced by $\cos\alpha(T)$ and $\dot\theta = \pi/2\tau = $ const. as well, yields

$$\begin{aligned}\langle 2|\Psi(T)\rangle &= \frac{\pi}{4}\frac{\sin 2\alpha}{\tau}\int_0^T e^{-i\omega_+ t_\mu}dt_\mu \\ &\approx \frac{\pi}{4\omega_+ T}\frac{\sin 2\alpha}{}\,[\sin\omega_+ T - i(1+\cos\omega_+ T)]\end{aligned} \tag{A16}$$

for $\tau = T$. The imaginary part of this first-order estimate represents nothing more than a phase shift.

It is important here that $\langle 3|\Psi(T)\rangle = 1$ and $\langle 2|\Psi(T)\rangle$ and similarly $\langle 1|\Psi(T)\rangle$ are not zero, so the total needs to be normalized. Since ω_+ is of the same order as Ω', the adiabaticity constraint of Eq. (8) requires that these $\langle 2|\Psi(T)\rangle$ and $\langle 1|\Psi(T)\rangle \ll 1$ so that normalization will make only a small correction to the magnitudes of the results.

5. Higher order perturbation calculation

Equation (A10) contains only the two lowest orders of a series expansion that can be generalized. We use $\dot\theta$ as the expansion parameter because it is always small compared with the ω's of Eq. (A6) and write $G_{(0)}$ as in Eq. (A11). Then the mth terms of the higher orders are

$$G_{(1)}^{(m)} = \lim_{n\to\infty}\left\{\prod_{\mu=m}^{n} g_{(0)}^{(\mu)}(t_\mu)\right\}\left\{g_{(1)}^{(m)}(t_m)\right\}\left\{\prod_{\mu=m}^{1} g_{(0)}^{(\mu)}(t_\mu)\right\}$$

as in Eq. (A12) and

$$\begin{aligned}G_{(2)}^{(m,m')} = \lim_{n\to\infty}&\left\{\prod_{\mu=n}^{m} g_{(0)}^{(\mu)}(t_\mu)\right\}\left\{g_{(1)}^{(m)}(t_m)\right\}\left\{\prod_{\mu=m}^{m'} g_{(0)}^{(\mu)}(t_\mu)\right\} \\ &\times\left\{g_{(1)}^{(m')}(t_{m'})\right\}\left\{\prod_{\mu=m'}^{0} g_{(0)}^{(\mu)}(t_\mu)\right\},\end{aligned} \tag{A17}$$

and similarly for $G_{(3)}^{(m,m',m'')}$ and higher. Each succeeding term has one higher power of $\dot\theta$. Of course, evaluation of $G_{(2)}$ requires sums over both m and m', $m > m'$ that are eventually to be converted into integrals as above.

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