Adiabatic Population Transfer with Control Fields

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This paper explores the benefit of using time dependent basis sets in the description of adiabatic population transfer between molecular states. Using a time dependent basis set formalism, we develop a counter-diabatic field paradigm that generates adiabatic population transfer for apparently unfavorable conditions. We also describe a time dependent perturbation approach to account for the effect of stochastic dephasing on adiabatic population transfer.

1. Introduction

Optical control of molecular dynamics can be achieved in a variety of ways,[1] some of which[3,8,9] use very strong fields. When a material quantum system such as a molecule interacts with a strong optical field, a description of the molecular dynamics that uses the basis states of the isolated molecule in field-free space requires a direct integration of the time dependent Schrödinger equation. Because the applied field is strong, a perturbation treatment of the dynamics can require inclusion of high-order terms and usually is very slowly convergent. One plausible alternative approach[2] to the description of the dynamical evolution of the molecule in the presence of a strong field is to use, instead of the isolated molecule basis states, time dependent basis states, for example, the adiabatic states of the coupled molecule−field system. We call the Hamiltonian that supports these adiabatic states the transformed Hamiltonian.

When the time evolution of the molecule−field system is very nearly described by the time evolution of one adiabatic state, i.e., one eigenstate of the transformed Hamiltonian, it is reasonable to expect that when there are not too large deviations of the system time evolution from that described by this eigenstate, these can be treated as perturbations. Deviations of the type envisaged can be generated by breakdown of the conditions required for adiabatic following. This approach to the analysis of time dependent problems is not new. However, the point of view we take in this paper is different from that previously taken. Specifically, in this paper we explore the use of a transformation of the representation of the Hamiltonian to a time dependent basis set to design a field that generates adiabatic population transfer from one state of a molecule to another when such population transfer is nonadiabatic in the basis states of the original Hamiltonian.

A transformation of the system Hamiltonian of the type just suggested generates an effective Hamiltonian with operators of two types. The first operator type is associated with the adiabatic following of the field by the molecular motion; it is a diagonal operator. The second operator type describes the deviations of the molecular dynamics from adiabatic following of the field; these are off-diagonal operators. The situation we are interested in is one in which the adiabatic representation is a very good zeroth-order description of the transfer of population between states of a molecule, but there are nonzero off-diagonal terms corresponding, e.g., to dephasing and/or relaxation that generate deviations from adiabatic behavior. The structure of the transformation equations and the effective Hamiltonian suggests the following question. Suppose we are given a field, the zero-order field, that is known to generate adiabatic transfer of population between states of a molecule when the dynamical perturbations are absent. When dynamical perturbations are present, the zero-order field no longer generates perfect adiabatic population transfer. Can we find another field that, when combined with the zero-order field, will restore the adiabatic character of the desired population transfer? In section 3 we answer this question and we give a simple formulation of a counter-diabatic field paradigm that can generate the field which, when combined with the zero-order field, generates perfect adiabatic population transfer. In section 5 we demonstrate how this analysis can be applied to the description of STIRAP generated adiabatic population transfer between states of a molecule when the states of the molecule are subject to stochastic dephasing.

2. Formalism

Let $|\psi(t)\rangle$ be the state vector of a system whose Hamiltonian is $H(t)$, expressed in terms of basis functions of some static basis set $\mathcal{S}$, and let $U(t)$ be a time dependent unitary transformation. The transformed basis set $\mathcal{D}(t) = U(t)\mathcal{S}$ is time dependent, but the unitarity of $U(t)$ guarantees that $\mathcal{D}$ is an orthonormal set provided the set $\mathcal{S}$ is. The transformed state vector is

$$|\tilde{\psi}(t)\rangle = U(t)|\psi(t)\rangle \tag{1}$$

To obtain the equation of motion of $|\tilde{\psi}(t)\rangle$, we begin with the time dependent Schrödinger equation for $|\psi(t)\rangle$ and write $|\psi(t)\rangle = U^{\dagger}(t)|\tilde{\psi}(t)\rangle$:

$$U(t)i\hbar\frac{\partial(U^{\dagger}(t)|\tilde{\psi}(t)\rangle)}{\partial t} = U(t)\,H(t)(U^{\dagger}(t)|\tilde{\psi}(t)\rangle) \tag{2}$$

Using the product rule for derivatives and the unitarity of the transformation, and rearranging the terms so that they mimic the time dependent Schrödinger equation, we arrive at[2]

$$i\hbar\frac{\partial|\tilde{\psi}(t)\rangle}{\partial t} = \left[U(t)\,H(t)\,U^{\dagger}(t) - i\hbar U(t)\frac{\partial U^{\dagger}(t)}{\partial t}\right]|\tilde{\psi}(t)\rangle \tag{3}$$

Equation 3 is the equation of motion for $|\tilde{\psi}(t)\rangle$ that represents the evolution in terms of the dynamic basis $\mathcal{D}$; it is isomorphous with the time dependent Schrödinger equation that represents

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the time evolution in the basis $\mathcal{S}$. Because our primary interest is in adiabatic population transfer, we exploit this formalism for that problem.

To study adiabatic population transfer in the absence of dephasing and/or other stochastic perturbations, the pragmatic choice is that $\mathcal{D}$ and rows of $U(t)$ consist of the eigenvectors of

$$H(t) = H_S + H_{SF}(t) \tag{4}$$

where H_S is the isolated system Hamiltonian and H_{SF} is the system field interaction. The matrix $U(t)\ H(t)\ U^\dagger(t)$ is diagonal. If $U(t)(\partial U^\dagger/\partial t)$ is negligible compared to the differences between the eigenvalues $\epsilon_i(t)$ of $H(t)$, the adiabatic approximation is valid. Put another way, if the molecular state that is prepared has only one nonzero component in one of the adiabatic states of $U(t)\ H(t)\ U^\dagger(t)$, and if the matrix elements satisfy

$$\hbar\left|U(t)\frac{\partial U^\dagger(t)}{\partial t}\right|_{ij} \ll |\epsilon_i(t) - \epsilon_j(t)| \tag{5}$$

then the population transfer is adiabatic. Let the density matrices in the static and dynamic basis sets be, respectively, $\sigma_S(t) \equiv |\psi(t)\rangle\langle\psi(t)|$ and $\sigma_D(t) \equiv |\tilde{\psi}(t)\rangle\langle\tilde{\psi}(t)|$. Then

$$\sigma_S(t) = |\psi(t)\rangle\langle\psi(t)| = U^\dagger(t)|\tilde{\psi}(t)\rangle\langle\tilde{\psi}(t)|U(t) = U^\dagger(t)\ \sigma_D(t)\ U(t) \tag{6}$$

The density matrix in the static basis set representation satisfies the Liouville−von Neumann equation

$$i\hbar\frac{\partial\sigma_S(t)}{\partial t} = [H(t),\sigma_S(t)] \tag{7}$$

Expressing $\sigma_S(t)$ in terms of $\sigma_D(t)$ we find

$$i\hbar\frac{\partial(U^\dagger(t)\ \sigma_S(t)\ U(t))}{\partial t} = [H(t),U^\dagger(t)\ \sigma_D(t)\ U(t)] \tag{8}$$

and carrying out the differentiation we arrive at

$$i\hbar\frac{\partial\sigma_D}{\partial t} = (UHU^\dagger\sigma_D - \sigma_D UHU^\dagger) - i\hbar\left(U\frac{\partial U^\dagger}{\partial t}\sigma_D + \sigma_D\frac{\partial U}{\partial t}U^\dagger\right) \tag{9}$$

If one uses the anti-Hermiticity[4] of $U\dot{U}^\dagger$, eq 9 can be reduced to

$$i\hbar\frac{\partial\sigma_D(t)}{\partial t} = \left[U(t)\ H(t)\ U^\dagger(t) - i\hbar U(t)\frac{\partial U^\dagger(t)}{\partial t}, \sigma_D(t)\right] \tag{10}$$

Note that the Liouville−von Neumann equation derived for $\sigma_D(t)$ is the same as would be obtained by use of the effective Hamiltonian of eq 3 for $|\tilde{\psi}(t)\rangle$.

3. Implementing Adiabatic Transfer of Population under Unfavorable Conditions

In general, adiabatic population transfer between molecular states is possible when changes in the molecule−field interaction are slow relative to $T \approx \hbar/\Delta E$, where ΔE is the energy separation of the relevant levels of the field-free system. If a relaxation process occurs in the molecule on a time scale comparable to T, the field that is applied to generate the population transfer must have duration considerably less than T, with the consequence that to generate complete population transfer, the field intensity must be very large. For example, the widely used STIRAP[3] population transfer method requires, for all practical purposes,

$$\tau\Omega_{max} \geq 10 \tag{11}$$

if the population transfer is to be adiabatic and complete. Here τ is the pulse width and Ω is the Rabi frequency. If τ is made small to avert the intervention of a competing relaxation process, the field intensity needed to drive complete population transfer may excite competing (e.g., multiphoton) processes in the molecule. In the case that the field strength needed to drive adiabatic population transfer also drives unwanted competetive processes, we seek a second field that, when combined with the first field, generates the desired adiabatic population transfer. We call this second field "counter-diabatic", because it works to undo the effects of nonadiabaticity on the population transfer. In other words we seek a second field to maintain perfect adiabaticity[2] of population transfer.

We now illustrate the use of a time dependent basis set to design a field that generates adiabatic population transfer between molecular states under unfavorable conditions by examining a simple two-level system. Two-level systems have been studied theoretically and experimentally by many investigators; see for example ref 7 and the references therein. However, our motivation is to restore the adiabaticity of population transfer with a simple interference scheme, not optimize a set for parameters of the pulse(s) that maximize the transfer efficiency. The formalism set out below is valid for every system in state space representation. The derivation of the Hamiltonian associated with the molecule−counter-diabatic field interaction, $H_{CD}(t)$, is straightforward. In the situation under consideration, adiabatic population transfer cannot be generated by $H_S + H_{SF}(t)$. The application of the counter-diabatic field that restores adiabatic population transfer between the states of H_S changes the total Hamiltonian $H(t)$ to have the form

$$H(t) = H_S + H_{SF}(t) + H_{CD}(t) \tag{12}$$

We retain the definition of $U(t)$ as the unitary operator whose rows consist of the eigenvectors of $H_S + H_{SF}(t)$. Then the operator $[U(t)\ H(t)\ U^\dagger(t) - i\hbar U(t)\ \partial U^\dagger(t)/\partial t]$ takes the form

$$\mathbf{H}(t) = U(t)(H_S + H_{SF}(t))U^\dagger(t) + U(t)\ H_{CD}(t)\ U^\dagger(t) - i\hbar U(t)\frac{\partial U^\dagger(t)}{\partial t} \tag{13}$$

We know a priori that $U(t)(H_S + H_{SF}(t))U^\dagger(t)$ is diagonal. Then, if the remaining part of the operator satisfies

$$U(t)\ H_{CD}(t)\ U^\dagger(t) - i\hbar U(t)\frac{\partial U^\dagger(t)}{\partial t} = 0 \tag{14}$$

at all times, population placed initially in an adiabatic state remains in that particular state. In that case there will be adiabatic transfer of population between the states of H_S. Equation 14 is easily rearranged to read

$$H_{CD}(t) = i\hbar\frac{\partial U^\dagger(t)}{\partial t}U(t) \tag{15}$$

As a simple example, we now apply this counter-diabatic field paradigm to a two-level system driven by a chirped field with uniform profile. The counter-diabatic field for this system,

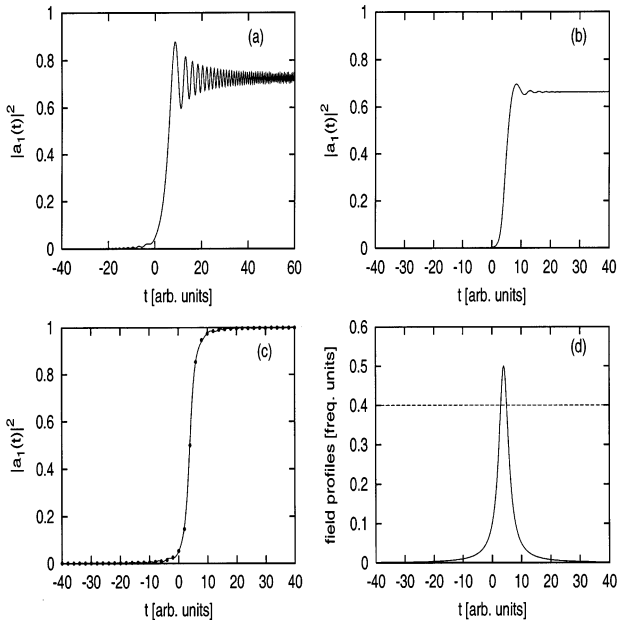

Figure 1. Use of the counter-diabatic field paradigm in a two-level system driven by a chirped field. In (a)−(c) the time dependent Schrödinger equation is integrated without any approximation. (a) shows the probability of observing the system in the excited state under the action of $H_{SF}(t)$, (b) shows the probability of observing the system in the excited state under the action of $H_{CD}(t)$, and (c) shows the excited-state population dynamics of the system under the action of $H_{SF}(t) + H_{CD}(t)$. The solid line is the direct integration, and the points are the adiabatic approximation for $H_{SF}(t)$. The parameters are $\Omega = 0.4$, $\alpha = 0.1$, $\omega = 1300$, $\omega_L = \omega - 2\Omega$. (d) shows the counter-diabatic field profile (solid line) and the profile of H_{SF} (dashed lone).

calculated under the rotating wave approximation (see Appendix A), is given by

$$H_{CD}(t) = i\hbar\frac{\partial U^{\dagger}(t)}{\partial t}U(t) = \hbar\frac{\dot{\Theta}(t)}{2}\begin{bmatrix}0 & -i\\ i & 0\end{bmatrix} \qquad (16)$$

Note that the $H_{CD}(t)$ given above is within the rotating wave approxiamtion, which only gives us the envelope of the counter-diabatic field. One has to invert the rotating wave approximation by using the transformation of Appendix A to obtain the oscillating part so that

$$H_{CD}(t) = +\hbar\dot{\Theta}(t)\sin(\omega_L t + \alpha t^2)[|0\rangle\langle 1| + |1\rangle\langle 0|] \quad (17)$$

Using equation (85) from Appendix A, we find

$$\dot{\Theta}(t) = -\frac{\frac{\Omega}{2\alpha}}{\left(\frac{\Omega}{2\alpha}\right)^2 + \left(t + \frac{\omega_L - \omega}{2\alpha}\right)^2} \qquad (18)$$

Thus, in the case under consideration, the envelope of the counter-diabatic field is a Lorentzian peaked at $t_R = (\omega - \omega_L)/2\alpha$ with a width of $\Omega/2\alpha$ and an absolute maximum of $2\alpha/\Omega$. Notice also that

$$\int_{-\infty}^{\infty}|\dot{\Theta}(t)|\,dt = \pi \qquad (19)$$

i.e., $H_{CD}(t)$ is a π pulse.

We show in panels a−c of Figure 1 the solutions of the time dependent Schrödinger equation in the basis states of H_S for various fields. The solutions displayed were obtained without use of the rotating wave approximation; they are exact. Panels a and b reveal that neither $H_{SF}(t)$ nor $H_{CD}(t)$ can generate adiabatic population transfer in this two-state system transfer. However, their combination

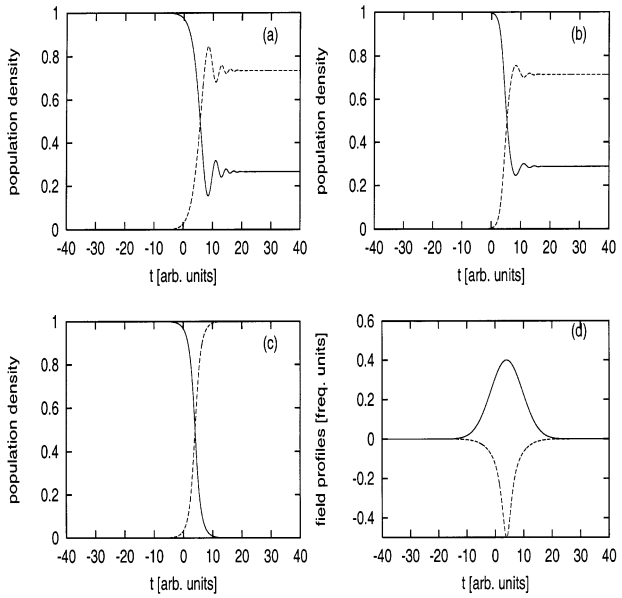

Figure 2. Use of the counter-diabatic field paradigm in a two-level system driven by a chirped field which has a Gaussian profile. In (a)−(c) the time dependent Schrödinger equation is integrated without any approximation. The solid lines are the population in the ground state, and the dashed ones correspond to the population on excited state. (a) shows the two-level system dynamics under the action of $H_{SF}(t)$, (b) shows the two-level system dynamics under the action of $H_{CD}(t)$, and (c) shows the excited-state population dynamics of the system under the action of $H_{SF}(t) + H_{CD}(t)$. (d) shows the counter-diabatic field profile (dashed line) and the profile of H_{SF} (solid line). The parameters are $\Omega_{max} = 0.4$, $\alpha = 0.1$, $\omega = 1300$, $\omega_L = \omega - 2\Omega$, $f = 0.1$.

$$H_{SF}(t) + H_{CD}(t) = \hbar(\Omega\cos(\omega_L t + \alpha t^2) + \dot{\Theta}(t)\sin(w_L t + \alpha t^2))[|0\rangle\langle 1| + |1\rangle\langle 0|] \quad (20)$$

generates complete adiabatic transfer of population between states $|0\rangle$ and $|1\rangle$. Note that the relative phase between $H_{CD}(t)$ and $H_{SF}(t)$ plays an important role in the shaping of the field that generates the adiabatic population transfer. It has been known for some time that, in the limit that $\alpha \ll \Omega^2$, $H_{SF}(t)$ alone can generate adiabatic transfer of population, but at the expense of increased pulse duration (inversely proportional to α). This parameter range is undesirable when there is competition with population transfer due to relaxation processes. In the other limit, $\alpha \gg \Omega^2$, $H_{CD}(t)$ can generate adiabatic population transfer, but at the price of requiring very short pulse duration and very large field amplitude. In the intermediate parameter domain, where $\alpha \approx \Omega^2$, neither $H_{SF}(t)$ nor $H_{CD}(t)$ can generate complete adiabatic population transfer, although $H_{SF}(t) + H_{CD}(t)$ does it perfectly.

Calculations similar to that of Figure 1 are performed for a chirped field with a Gaussian profile and the results are displayed in Figure 2. Specifically, we used the following functional form for the time dependent Rabi frequency

$$\Omega(t) = \Omega_{max}\exp[-f\Omega_{max}{}^2(t - t_R)^2] \qquad (21)$$

where $0 < f < 1$. Note that the counter-diabatic field suggested by this procedure is neither too intense nor too short when compared with the Gaussian pulse. The ideas just described in this section could be extended to the experimenatlly realized[8,9]

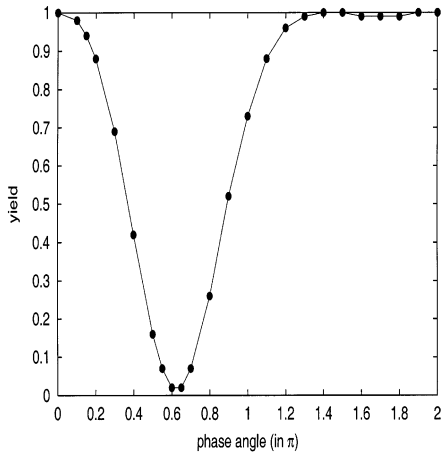

Figure 3. Phase sensitivity of the counter-diabatic field paradigm. The asymptotic yield is plotted against the phase angle, δ, between $H_{SF}(t) = \hbar\Omega \cos(\omega_L t + \alpha t^2)$ and $H_{CD}(t) = \dot{\Theta}(t) \sin(\omega_L t + \alpha t^2 + \delta)$. The parameters given in Figure 1 are used in the calculations.

vibrational ladder climbing scenario[5,6] to restore the adiabaticity of dynamics as well as to reduce the intensity of the pulses.

The simple analysis just described is valid for every α so long as neither the Rabi frequency, Ω, nor the maximum intensity of the counter-diabatic field, $2\alpha/\Omega$, is comparable with the transition frequency. In those cases the rotating wave approximation is no longer valid. This parameter regime is mostly not of concern, because we seldom drive systems with fields that are so intense that the Rabi frequency is comparable with the transition frequency in optical transitions. An analogous treatment of population transfer between two states in a three-state system suggests a generalization of the STIRAP process. Specifically, it is found that the counter-diabatic field must couple the initial state and the target state. When all three states are coupled by radiative transitions, ordinary STIRAP generated population transfer does not occur because the STIRAP process requires that there be no direct coupling between the initial state and the target state.

Another delicate issue that must be addressed is the phase sensitivity of this population transfer scenario. Note that when the oscillating part of $H_{SF}(t)$ is a cosine function, $H_{CD}(t)$ turns out to be a sine; i.e., there has to be a well-defined phase between two fields for the scenario to be valid. Because, by definition, the counter-diabatic field is intended to undo the nonadiabatic effects at every time t, this should not come as a surprise. In Figure 3 we demonstrate the phase sensitivity of the proposed scenario. Depending on the fixed phase between $H_S(t)$ and $H_{CD}(t)$ the yield or the asymptotic value of population in the excited state as $t \rightarrow \infty$ can be varied between 1 and almost zero.

4. Perturbative Treatment of Nonadiabaticity

A second purpose of this article is to use the time dependent basis set formalism to describe the inefficiency of population transfer generated by stochastic dephasing, specifically STIRAP. Before addressing this issue we seek to establish criteria for the accuracy range of the perturbation expansion as a function of pulse parameters. Time dependent perturbation theory,[10] which has been studied extensively, is not needed to evaluate the effect of nonadiabatic coupling on population transfer. However, for the purposes of this paper we must carry out these calculations to establish emprical guidelines pertaining to the accuracy and reliability of a certain order of a perturbation expansion. These guidelines will be followed in the next section when we examine the perturbative treatment of stochastic dephasing in a STIRAP scenario.

We note that $U(t)\ H(t)\ U^\dagger(t)$ is diagonal and $-i\hbar U(t)\ \dot{U}^\dagger(t)$ cannot have diagonal entries[4] for a purely real transformation. Let $\tilde{c}_j(t)$ be an element of the state vector $|\tilde{\psi}(t)\rangle$ defined by

$$\tilde{c}_j(t) \equiv b_j(t) \exp\left[-\frac{i}{\hbar}\int_{t_i}^{t} \epsilon_j(t')\, dt'\right] \tag{22}$$

Then the equation of motion of $b_j(t)$ is

$$i\hbar \dot{b}_j(t) = \sum_k \exp\left[\frac{i}{\hbar}\int_{t_i}^{t} \epsilon_{jk}(t')\, dt'\right](-i\hbar U(t)\ \dot{U}^\dagger(t))_{jk} b_k(t) \tag{23}$$

where $\epsilon_{jk}(t) = \epsilon_j(t) - \epsilon_k(t)$. First we set

$$-i\hbar U(t)\ \dot{U}(t)^\dagger \equiv \lambda W(t) \tag{24}$$

where λ is assumed to be a small parameter, and then expand $b_j(t)$ as follows:

$$b_j(t) = b_j^{(0)}(t) + \lambda b_j^{(1)}(t) + \lambda^2 b_j^{(2)}(t) + \cdots \tag{25}$$

In the zeroth-order approximation, the adiabatic limit, the system remains in state $|i\rangle_t$ of the basis set $\mathscr{D}$. Then for all $t \geq t_i$

$$b_j^{(0)}(t) = \delta_{ij} \tag{26}$$

The first-order term in the perturbation expansion gives

$$b_j^{(1)}(t) = -\int_{t_i}^{t} dt' \exp\left[\frac{i}{\hbar}\int_{t_i}^{t'} \epsilon_{ji}(t_1)\, dt_1\right](U(t')\ \dot{U}^\dagger(t'))_{ji} \tag{27}$$

A higher order expression for $b_j(t)$ can be obtained from the following recursion relation:

$$b_j^{(r)}(t) = -\sum_k \int_{t_i}^{t} dt' \times \exp\left[\frac{i}{\hbar}\int_{t_i}^{t'} \epsilon_{jk}(t_1)\, dt_1\right](U(t')\ \dot{U}^\dagger(t'))_{jk} b_k^{(r-1)}(t') \tag{28}$$

We will assume that the occurrence of nonzero population in states other than the initial state and the target state is a signature of the breakdown in adiabatic population transfer. For the measure of that breakdown we take

$$\not{p}(t) \equiv \sum_{j \neq i} |b_j(t)|^2 \tag{29}$$

As an example, we examine the breakdown of adiabatic population transfer in a STIRAP type pulse arrangement. A brief recap of the three-level STIRAP process is given in Appendix B. For the sake of simplicity we use Rabi frequencies of the form

$$\Omega_{p,S}(t) = A e^{-(t-t_{p,S})^2/\tau^2} \tag{30}$$

with $t_p = 0$ and $t_S = -\tau$. The nonadiabaticity of population transfer associated with the field used is determined by

$$\dot{\Theta}(t) = \frac{\dot{\Omega}_p(t)\ \Omega_S(t) - \Omega_p(t)\ \dot{\Omega}_S(t)}{\Omega_p{}^2(t) + \Omega_S{}^2(t)} = -\frac{2t_S}{\tau^2}\frac{\Omega_p(t)\ \Omega_S(t)}{\Omega_p{}^2(t) + \Omega_S{}^2(t)} \tag{31}$$

The natural choice of time unit is the width of a pulse, so we set 1 TU $= \tau$. The components of the basis vectors of $\mathscr{D}$ are

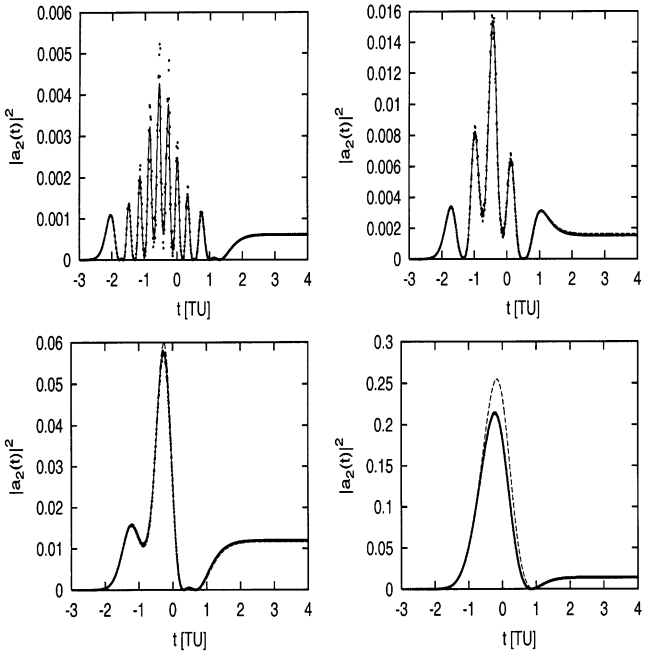

Figure 4. Perturbative treatment of nonadiabaticity in a three-level STIRAP system. The dashed lines are the predictions of first-order perturbation theory for the population of state $|2\rangle$. The bold dots are the direct integration of the time dependent Schrödinger equation in basis $\mathcal{S}$ with no approximation. The solid lines, mostly indistinguishable from the dots, are the result of a third-order calculation. The maximum Rabi frequencies are (top-left) $A = 20$ TU^{-1}, (top-right) $A = 10$ TU^{-1}, (bottom-left) $A = 5$ TU^{-1}, and (bottom-right) $A = 2.5$ TU^{-1}.

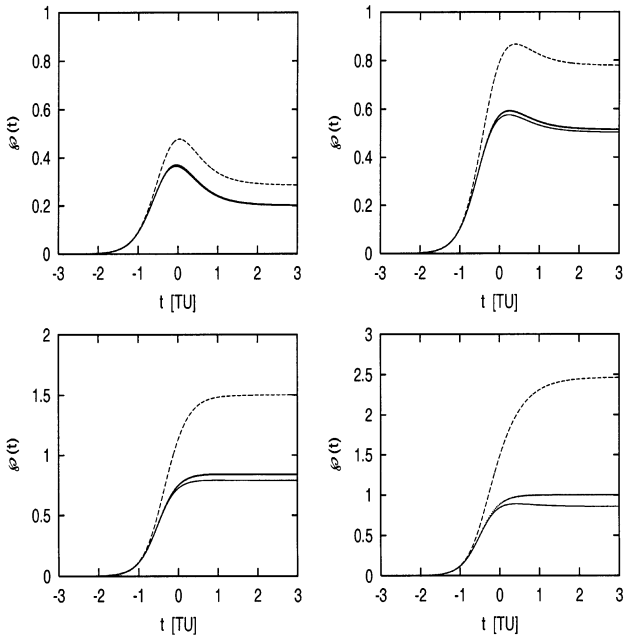

Figure 5. Perturbative treatment of nonadiabatic population transfer in a three-level STIRAP system. The solid lines are the predictions of third-order perturbation theory for $\wp(t)$, and the dashed lines are predicted from a first-order calculation. The bold dots are calculated values of $\wp(t)$ from direct integration of time dependent Schrödinger equation in basis $\mathcal{S}$ with no approximation. The maximum Rabi frequencies are (top-left) $A = 2.0$ TU^{-1}, (top-right) $A = 1.5$ TU^{-1}, (bottom-left) $A = 1.0$ TU^{-1}, and (bottom-right) $A = 0.05$ TU^{-1}.

given by

$$b_+^{(1)}(t) = \frac{1}{\sqrt{2}}\int_{t_i}^{t} dt' \exp[i\int_{t_i}^{t'} dt_1\, \epsilon_+(t_1)]\dot{\Theta}(t') \qquad (32)$$

$$b_-^{(1)}(t) = [b_+^{(1)}(t)]^* \qquad (33)$$

$$b_0^{(1)}(t) = 0 \qquad (34)$$

The signature of nonadiabatic population transfer in a three-state STIRAP population transfer is nonzero population in state $|2\rangle$, because in the limit where there is adiabatic transfer of population from state $|1\rangle$ to state $|3\rangle$, there is never any population in state $|2\rangle$. The correction calculated with first-order perturbation theory yields $b_+^{(1)}(t)$. When this result is transformed to the basis states of H_S, we find

$$a_2(t) = \frac{1}{\sqrt{2}}(\tilde{c}_+(t) - \tilde{c}_-(t)) \qquad (35)$$

Figure 4 displays the results of the perturbation calculations and comparisons with exact numerical calculations of the time dependent population of state $|2\rangle$. The agreement is very good in all cases, and the asymptotic population is very accurately predicted. In this case it can be shown that the second-order terms for $b_\pm^{(2)}(t)$, from eq 28, vanish, so the calculated values of $b_\pm^{(1)}(t)$ are accurate to second order. For near-adiabatic population transfer a perturbation theory treatment using time dependent basis states is more robust than conventional perturbation theory. For instance, the first-order perturbation theory analysis described above accurately predicts the time dependence of the population of state $|2\rangle$, but conventional first-order perturbation theory fails in every respect. According to conventional time dependent perturbation theory

$$a_2^{(1)}(t) = -i\int_{t_i}^{t} dt'\, e^{i\omega_{21}t'}\Omega_p(t') \qquad (36)$$

i.e., the more intense the pump pulse, the more population stays in state $|2\rangle$, which is in contradiction with reality. Moreover, first-order conventional perturbation theory is totally blind to the Stokes field. A third-order perturbation theory calculation of the breakdown in adiabatic population transfer is based on

$$\wp(t) = |\tilde{c}_-(t)|^2 + |\tilde{c}_+(t)|^2 = |b_-(t)|^2 + |b_+(t)|^2 \qquad (37)$$

The numerically exact representation of the time dependent population in the basis states of H_S was transformed via

$$\tilde{c}_\pm(t) = \frac{1}{\sqrt{2}}a_1(t)\sin\Theta \pm \frac{1}{\sqrt{2}}a_2(t) + \frac{1}{\sqrt{2}}a_3(t)\cos\Theta \qquad (38)$$

to provide data for comparison. Figure 5 displays the results of the third-order preturbation calculations for $\wp(t)$. The parameters used in the calculations were chosen so that the population transfer is not adiabatic. The smallest nonadiabatic population transfer, about 20%, is displayed in the top right panel. As the nonadiabatic population transfer increases, the first-order perturbation theory results deviate significantly from the exact values. However, the third-order perturbation theory results do provide accurate predictions.

5. Perturbative Treatment of Stochastic Dephasing

We now consider the influence of stochastic dephasing[12−14] on adiabatic population transfer. To account for decoherence effects, we formulate the theory using a density matrix representation. We treat pure dephasing via introduction of the

phenomenological operator[11]

$$H_D(t) = \hbar(\delta\omega_1(t)|1\rangle\langle 1| + \delta\omega_2(t)|2\rangle\langle 2| + \delta\omega_3(t)|3\rangle\langle 3|) \quad (39)$$

where $\delta\omega_i(t)$ is a stochastic process that is ergodic, stationary, and independent. Then

$$\langle \delta\omega_i(t)\rangle = 0 \quad (40)$$

and

$$\langle \delta\omega_i(t)\, \delta\omega_j(t')\rangle = \delta_{ij}\Delta^2 \exp[-|t - t'|/\tau_c] \quad (41)$$

where Δ is the root-mean-square value of $\delta\omega_i(t)$ and τ_c is the decay time of autocorrelation. The brackets $\langle\cdots\rangle$ define an ensemble average over the stochastic process $\delta\omega_i(t)$. The equation of motion for the density matrix in the $\mathcal{S}$ basis is

$$i\hbar\frac{\partial\rho_S(t)}{\partial t} = [H_S + H_{SF}(t) + H_D(t), \rho_S(t)] \quad (42)$$

where

$$H_S = \sum_{k=1}^{3} E_k|k\rangle\langle k| \quad (43)$$

and

$$H_{SF}(t) = 2\hbar\Omega_p(t)\cos(\omega_p t)[|1\rangle\langle 2| + |2\rangle\langle 1|] + 2\hbar\Omega_S(t)\cos(\omega_S t)[|2\rangle\langle 3| + |3\rangle\langle 2|] \quad (44)$$

Transformation of the matrix elements of ρ_S to the interaction representation yields

$$[\rho_S]_{ij} \rightarrow [\rho_S]_{ij}\exp\left[-i\frac{E_i - E_j}{\hbar}t\right] \quad (45)$$

After introduction of the rotating wave approximation for resonant fields, the equation of motion in the basis states of H_S becomes

$$i\hbar\frac{\partial\rho_S(t)}{\partial t} = [H_{RWA}(t) + H_D(t), \rho_S(t)] \quad (46)$$

where $H_{RWA}(t)$ is given in Appendix B. We use the same transformation as in the previous section. In the time dependent basis-state representation the equation of motion is

$$i\hbar\frac{\partial\rho_D(t)}{\partial t} = \left[U(t)\, H_{RWA}(t)\, U^\dagger(t) + U(t)\, H_D(t)\, U^\dagger(t) - i\hbar U(t)\frac{\partial U^\dagger(t)}{\partial t}, \rho_D(t)\right] \quad (47)$$

We know that $U(t)\, H_{RWA}(t)\, U^\dagger(t)$ has only diagonal entries whose values are the eigenvalues of $H_{RWA}(t)$. The dephasing operator transforms as

$$U(t)\, H_D(t)\, U^\dagger(t) = \begin{bmatrix} \eta(t) & \gamma(t) & \beta(t) \\ \gamma(t) & \alpha(t) & \gamma(t) \\ \beta(t) & \gamma(t) & \eta(t) \end{bmatrix} \quad (48)$$

where the matrix elements are defined through

$$\alpha(t) = \delta\omega_1(t)\cos^2\Theta + \delta\omega_3(t)\sin^2\Theta \quad (49)$$

$$\gamma(t) = \frac{\sin 2\Theta}{2\sqrt{2}}(\delta\omega_1(t) - \delta\omega_3(t)) \quad (50)$$

$$\beta(t) = \frac{1}{2}(\delta\omega_1(t)\sin^2\Theta - \delta\omega_2(t) + \delta\omega_3(t)\cos^2\Theta) \quad (51)$$

$$\eta(t) = \frac{1}{2}(\delta\omega_1(t)\sin^2\Theta + \delta\omega_2(t) + \delta\omega_3(t)\cos^2\Theta) \quad (52)$$

The third term in the commutator, which represents the nonadiabatic population transfer induced by the field, is also given in Appendix B.

Before we start the perturbation analysis we transform to the interaction representation via

$$[\rho_D(t)]_{ij} \rightarrow [\rho_D(t)]_{ij}\exp[-i\int_{t_i}^{t}(\epsilon_i(t_1) - \epsilon_j(t_1))\, dt_1] \quad (53)$$

and for convenience we define

$$I(t_1,t_2) \equiv \exp[-i\int_{t_1}^{t_2}\epsilon_+(t)\, dt] \quad (54)$$

Then the equations of motion for the matrix elements of $\rho_D(t)$ are given by

$$i\dot\rho_{++}(t) = \beta(t)[\rho_{-+}(t)(I^2(t_i,t))^* - \rho_{+-}(t)\, I^2(t_i,t)] + \gamma(t)[\rho_{0+}(t)(I(t_i,t))^* - \rho_{+0}I(t_i,t)] + \frac{i\dot\Theta(t)}{\sqrt{2}}[\rho_{+0}(t)I(t_i,t) + \rho_{0+}(t)(I(t_i,t))^*] \quad (55)$$

$$i\dot\rho_{0\,0}(t) = \gamma(t)[(\rho_{-0}(t) - \rho_{0+}(t))(I(t_i,t))^* + (\rho_{+0}(t) - \rho_{0-}(t))I(t_i,t)] - \frac{i\dot\Theta(t)}{\sqrt{2}}[(\rho_{-0}(t) + \rho_{0+}(t))(I(t_i,t))^* + (\rho_{+0}(t) + \rho_{0-}(t))I(t_i,t)] \quad (56)$$

$$i\dot\rho_{--}(t) = \beta(t)[\rho_{+-}(t)I^2(t_i,t) - \rho_{-+}(t)(I^2(t_i,t))^*] + \gamma(t)[\rho_{0-}(t)I(t_i,t) - \rho_{-0}(t)(I(t_i,t))^*] + \frac{i\dot\Theta(t)}{\sqrt{2}}[\rho_{-0}(t)(I(t_i,t))^* + \rho_{0-}(t)I(t_i,t)] \quad (57)$$

$$i\dot\rho_{+0}(t) = \beta(t)\rho_{-0}(t)(I^2(t_i,t))^* + [\eta(t) - \alpha(t)]\rho_{+0}(t) - \frac{1}{2}[2\gamma(t) + i\sqrt{2}\dot\Theta(t)][\rho_{+-}(t)I(t_i,t) + (\rho_{++}(t) - \rho_{00}(t))(I(t_i,t))^*] \quad (58)$$

$$i\dot\rho_{-0}(t) = \beta(t)\rho_{+0}(t)I^2(t_i,t) + [\eta(t) - \alpha(t)]\rho_{-0}(t) - \frac{1}{2}[2\gamma(t) + i\sqrt{2}\dot\Theta(t)][\rho_{-+}(t)(I(t_i,t))^* + (\rho_{--}(t) - \rho_{00}(t))I(t_i,t)] \quad (59)$$

$$i\dot\rho_{-+}(t) = \beta(t)I^2(t_i,t)[\rho_{++}(t) - \rho_{--}(t)] + \gamma(t)I(t_i,t)[\rho_{0+}(t) - \rho_{-0}(t_i,t)] + \frac{i\dot\Theta(t)I(t_i,t)}{\sqrt{2}}[\rho_{-0}(t) + \rho_{0+}(t)] \quad (60)$$

The equations of motion of $\dot\rho_{0+}$, $\dot\rho_{0-}$, and $\dot\rho_{+-}$ follow from the Hermiticity condition for $\rho_D(t)$. We expand the density matrix to read

$$\rho_{ij}(t) = \rho_{ij}^{(0)}(t) + \rho_{ij}^{(1)}(t) + \rho_{ij}^{(2)}(t) + \cdots \quad (61)$$

and all terms higher than zeroth order are subject to the initial condition

$$\rho_{ij}^{(r)}(t_i) = 0, \qquad r \geq 1 \tag{62}$$

In zeroth order, when stochastic dephasing is absent, the population transfer is adiabatic and

$$\rho_{00}^{(0)}(t) = 1, \qquad \rho_{++}^{(0)}(t) = \rho_{--}^{(0)}(t) = 0 \qquad \text{for} \qquad t \geq t_i \tag{63}$$

$$\rho_{ij}^{(0)}(t) = 0, \qquad \text{for } i \neq j \tag{64}$$

To first order

$$\rho_{++}^{(1)}(t) = \rho_{--}^{(1)}(t) = \rho_{00}^{(1)}(t) = 0 \tag{65}$$

$$\rho_{+0}^{(1)}(t) = [\rho_{0+}^{(1)}(t)]^* = -\frac{\mathrm{i}}{2}\int_{t_i}^{t} \mathrm{d}t'\, (I(t_i,t'))^*[2\gamma(t') + \mathrm{i}\sqrt{2}\dot{\Theta}(t')] \tag{66}$$

$$\rho_{-0}^{(1)}(t) = [\rho_{0-}^{(1)}(t)]^* = -\frac{\mathrm{i}}{2}\int_{t_i}^{t} \mathrm{d}t'\, I(t_i,t')[2\gamma(t') + \mathrm{i}\sqrt{2}\dot{\Theta}(t')] \tag{67}$$

$$\rho_{+-}^{(1)}(t) = \rho_{-+}^{(1)}(t) = 0 \tag{68}$$

Having obtained the first-order approximations for the coherences, we can now calculate the second-order approximation for the norms, $\rho_{++}^{(2)}(t)$ and $\rho_{--}^{(2)}(t)$. The algebraic expressions for these quantities are too lengthy to display here, but their ensemble averages over $\delta\omega_i(t)$, obtained using $\langle\delta\omega_i(t)\rangle = 0$, are

$$\langle\rho_{++}^{(2)}(t)\rangle = \langle\rho_{--}^{(2)}(t)\rangle = 2\mathscr{R}\,[J_a(t) + J_b(t)] \tag{69}$$

where $J_a(t)$ and $J_b(t)$ are given by

$$J_a(t) = \int_{t_i}^{t}\mathrm{d}t'\int_{t_i}^{t'}\mathrm{d}t''\,\langle\gamma(t')\,\gamma(t'')\rangle I(t_i,t')(I(t_i,t''))^* \tag{70}$$

$$J_b(t) = \frac{1}{2}\int_{t_i}^{t}\mathrm{d}t'\int_{t_i}^{t'}\mathrm{d}t''\,\dot{\Theta}(t')\,\dot{\Theta}(t'')\,I(t_i,t')(I(t_i,t''))^* \tag{71}$$

Because $t'' \leq t'$, the correlation function in $J_a(t)$ can be easily shown to be

$$\langle\gamma(t')\,\gamma(t'')\rangle = \frac{1}{8}\sin 2\Theta(t')\sin 2\Theta(t'')(\langle\delta\omega_1(t')\,\delta\omega_1(t'')\rangle + \langle\delta\omega_3(t')\,\delta\omega_3(t'')\rangle) \tag{72}$$

$$= \frac{\Delta^2}{4}\sin 2\Theta(t')\sin 2\Theta(t'')\mathrm{e}^{-(t'-t'')/\tau_c} \tag{73}$$

We are now able to calculate the first nonvanishing contribution to nonadiabatic population transfer:

$$\not{P}(t) = \langle\rho_{++}^{(2)}(t)\rangle + \langle\rho_{--}^{(2)}(t)\rangle = 4\mathscr{R}[J_a(t) + J_b(t)] \tag{74}$$

It is clear that the contribution of $J_b(t)$ to nonadiabatic population transfer is induced by the field, and we have demonstrated that it can be accurately predicted for a STIRAP type pulse arrangement. Moreover, if the population transfer is adiabatic, i.e., the pulse parameters satisfy eq 11, calculation of $J_b(t)$ is not of interest. Accordingly, we concentrate attention on the nonadiabatic population transfer induced by the stochastic dephasing $\not{P}_d(t)$ and define

$$F(t) \equiv \frac{\not{P}_d(t)}{\Delta^2} = \mathscr{R}[\int_{t_i}^{t}\mathrm{d}t'\int_{t_i}^{t'}\mathrm{d}t''\,\mathrm{e}^{-(t'-t'')/\tau_c}I(t_i,t')(I(t_i,t''))^* \times \sin 2\Theta(t')\sin 2\Theta(t'')] \tag{75}$$

Our experience with the model described in the last section suggests that the first nonvanishing order in the perturbation expansion for near-adiabatic or adiabatic population transfer is accurate until the nonadiabaticity reaches 20%. For larger nonadiabatic population transfers calculation of the second nonvanishing order becomes inevitable. Heuristically, we argue that the legitimicy of $F(t)$ as a good guide to nonadiabatic population transfer induced by dephasing becomes questionable for

$$\Delta^2 F(t\rightarrow\infty) \geq 0.2 \tag{76}$$

Once $F(t)$ is calculated, one should restrict the value of Δ, the root-mean-square amplitude of the fluctuations, so as to not violate this condition. For higher values of Δ the next order in the perturbation expansion must be calculated.

Another important parameter of stochastic dephasing is the correlation time τ_c. We have calculated the indirect asymptotic nonadiabatic population transfer induced by stochastic dephasing as a function of $\Gamma \equiv 1/\tau_c$, the average fluctuation frequency. We used the same Rabi frequencies as used in the preceding section. Figure 6 displays the asymptotic nonadiabatic population transfer induced by the field, which we take to be the transfer inefficiency, plotted against fluctuation frequency on both linear and logarithmic scales. It is clear that the transfer inefficiency peaks when the fluctuation frequency is equal to the maximum Rabi frequency. In our previous work[14] we observed and puzzled with the same behavior in a "numerical experiment". Our previous interpretation of this behavior, that a match between the inverse of the pulse width and the fluctuation frequency is relevant to nonadiabatic population transfer, was misleading. Within this formalism it is now clear that a match between the

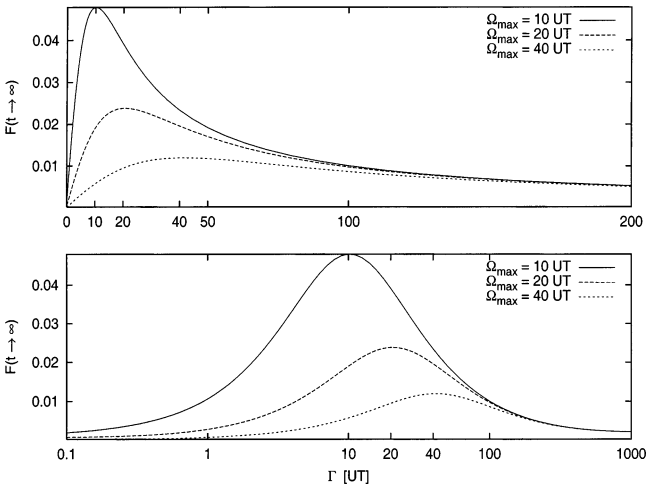

Figure 6. Top panel: transfer inefficiency as a function of modulation frequency ($\Gamma = 1/\tau_c$), on a linear scale. Bottom panel: transfer inefficiency on a logarithmic scale. The transfer inefficiency, which is assumed to be the value of $F(t\rightarrow\infty)$, peaks when the maximum Rabi frequency is equal to the fluctuation frequency. The pulse width is 1 TU, and the time delay between Stokes and pump pulses is -1 TU. Both fields are on resonance with the central transition frequencies.

fluctuation frequency and Rabi frequecy is what really counts for inefficient population transfer to peak.

6. Final Remarks

We have shown that time dependent basis sets can be used to provide a convenient separation of the adiabatic and nonadiabatic evolution of population generated by a particular molecule−field Hamiltonian. This separation helps to describe stochastic dephasing as a perturbation to the adiabatic population transfer scenario. It also provides an insight that permits the design of a field that, in combination with the original field that cannot drive adiabatic population transfer between the molecular states, does generate adiabatic population transfer. This methodology is likely to be useful when it is desirable to generate adiabatic population transfer with very short pulses. A critical feature of the use of the combined initial and counter-diabatic fields is that one must maintain a phase relation between two fields.

Can the counter-diabatic field paradigm we suggest, or a similar methedology, be used to generate selective adiabatic population transfer in a degenerate[15,16] four- or five-level system? The fact that given a population transfer scenario we can always make it perfectly adiabatic under unfavorable conditions increases our optimizm for adiabatic control. However, depending on the topology of problem, the counter-diabatic field might not be a practical one, as turns out to be the case for STIRAP.

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Appendix A: A Two-Level System Driven by a Chirped Field

Consider a two-level system with energy separation $\hbar\omega$ and Hamiltonian

$$H_S = \frac{\hbar\omega}{2}\begin{bmatrix}-1 & 0\\ 0 & 1\end{bmatrix} \tag{77}$$

Furthermore, assume that the electric dipole interaction is given by

$$H_{SF}(t) = \hbar\begin{bmatrix}0 & V(t)\\ V(t) & 0\end{bmatrix} \tag{78}$$

with $V(t) = \Omega(t)\cos(\omega_L t + \alpha t^2)$, ω_L the laser frequency, α the chirp, and $\Omega(t)$ the time independent Rabi frequency. The time dependent Schrödinger equation in the two-level system basis $\mathcal{S} = \{|0\rangle,|1\rangle\}$ is

$$\mathrm{i}|\dot{\psi}(t)\rangle = H(t)|\psi(t)\rangle = [H_S + H_{SF}(t)]|\psi(t)\rangle \tag{79}$$

where $|\psi(t)\rangle = a_0(t)|0\rangle + a_1(t)|1\rangle$ and $|a_i(t)|^2$ is the probability of observing the two-level system in level i. If one defines the following transformation

$$\tilde{a}_0(t) = a_0(t)\mathrm{e}^{-\mathrm{i}(\omega_L t+\alpha t^2)/2}$$

and

$$\tilde{a}_1(t) = a_1(t)\mathrm{e}^{\mathrm{i}(\omega_L t+\alpha t^2)/2} \tag{80}$$

and then uses the rotating wave approximation, the Hamiltomian of the time dependent Schrödinger equation becomes

$$H_{RWA}(t) = \begin{bmatrix}(\omega-\omega_L)/2 + \alpha t & \Omega(t)/2\\ \Omega(t)/2 & -(\omega-\omega_L)/2 - \alpha t\end{bmatrix} \tag{81}$$

The eigenvalues of the above operator are[10]

$$\epsilon_\pm(t) = \pm\frac{1}{2}\sqrt{(\omega-\omega_L-2\alpha t)^2 + \Omega^2} \tag{82}$$

and the corresponding eigenvectors are

$$|+\rangle_t = \cos\frac{\Theta}{2}|0\rangle + \sin\frac{\Theta}{2}|1\rangle \tag{83}$$

$$|-\rangle_t = -\sin\frac{\Theta}{2}|0\rangle + \cos\frac{\Theta}{2}|1\rangle \tag{84}$$

where

$$\tan\Theta = \frac{|\Omega(t)|}{\omega_L + 2\alpha t - \omega} \qquad \text{with} \qquad 0 \le \Theta < \pi \tag{85}$$

If the field starts sufficiently off resonance, i.e., the initial absolute detuning $|\omega_L - \omega|$ is larger than a few times the Rabi frequency, and if $|\alpha|$ is small so that resonance is achieved slowly, the transfer from $|0\rangle$ to $|1\rangle$ is adiabatic. In other words, the entire time dependence of the system can be followed via $|-\rangle_t$. To quantify the description of the rate at which resonance is achieved, and the magnitude of the initial detuning, we define

$$\mathscr{D} = U(t)_{\mathcal{S}} \tag{86}$$

$$\begin{bmatrix}|-\rangle_t\\ |+\rangle_t\end{bmatrix} = \begin{bmatrix}-\sin\frac{\Theta}{2} & \cos\mathrm{q}\frac{\Theta}{2}\\ \cos\frac{\Theta}{2} & \sin\frac{\Theta}{2}\end{bmatrix}\begin{bmatrix}|0\rangle\\ |1\rangle\end{bmatrix} \tag{87}$$

For this particular case $U(t) = U^\dagger(t)$ and

$$U(t)\,H_{RWA}(t)\,U^\dagger(t) = \begin{bmatrix}\epsilon_-(t) & 0\\ 0 & \epsilon_+(t)\end{bmatrix} \tag{88}$$

where the $\epsilon_\pm(t)$ are defined as before. Furthermore the nonadiabaticity

$$-iU(t)\frac{\partial U^\dagger(t)}{\partial t} = \frac{\dot{\Theta}}{2}\begin{bmatrix}0 & -\mathrm{i}\\ -\mathrm{i} & 0\end{bmatrix} \tag{89}$$

Appendix B: Three-Level STIRAP System

For this system ($\hbar = 1$)

$$H_{RWA}(t) = [H_S + H_{SF}(t)]_{RWA} = \hbar\begin{bmatrix}0 & \Omega_p(t) & 0\\ \Omega_p(t) & 0 & \Omega_S(t)\\ 0 & \Omega_S(t) & 0\end{bmatrix} \tag{90}$$

For the sake of simplicity we set the detunings of the pump and Stokes pulses $\Delta_p = \Delta_S = 0$. The eigenvalues and corresponding eigenvectors of $H_{RWA}(t)$ are given by (see the paper by Gaubetz et al. in ref 3)

$$\epsilon_+(t) = \sqrt{[\Omega_p(t)]^2 + [\Omega_S(t)]^2} \qquad \epsilon_0(t) = 0 \qquad \epsilon_-(t) = -\epsilon_+(t) \tag{91}$$

In basis $\mathcal{S} = \{|1\rangle,|2\rangle,|3\rangle\}$

$$\mathcal{D}(t) = U(t)\mathcal{S} \tag{92}$$

$$\begin{bmatrix} |+\rangle_t \\ |0\rangle_t \\ |-\rangle_t \end{bmatrix} = \frac{1}{\sqrt{2}} \begin{bmatrix} \sin\Theta & 1 & \cos\Theta \\ \sqrt{2}\cos\Theta & 0 & -\sqrt{2}\sin\Theta \\ \sin\Theta & -1 & \cos\Theta \end{bmatrix} \begin{bmatrix} |1\rangle \\ |2\rangle \\ |3\rangle \end{bmatrix} \tag{93}$$

where the mixing angle Θ is defined by

$$\tan\Theta = \frac{\Omega_p(t)}{\Omega_S(t)} \tag{94}$$

The nonadiabaticity is then

$$-\mathrm{i}U(t)\,\dot{U}^{\dagger}(t) = \frac{\dot{\Theta}(t)}{\sqrt{2}} \begin{bmatrix} 0 & \mathrm{i} & 0 \\ -\mathrm{i} & 0 & -\mathrm{i} \\ 0 & \mathrm{i} & 0 \end{bmatrix} \tag{95}$$

$|\dot{\Theta}(t)|$ must be much smaller than the energy differences $|\epsilon_-(t) - \epsilon_0(t)|$ and $|\epsilon_+(t) - \epsilon_0(t)|$ for the adiabatic representation to be valid. This is the same condition given by Gaubetz et al.[3]

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(2) Mostafazadeh, A. *Dynamical Invariants, Adiabatic Approximation and the Geometric Phase*; Nova: New York, 2001.

(3) The acronym STIRAP stands for **Sti**mulated **R**aman **A**diabatic **P**assage. The first experimental application of this technique was published in 1990, by U. Gaubetz, P. Rudecki, S. Schiemann, K. Bergmann: *J. Chem. Phys.* **1990**, *92*, 5363−5376. The following reviews and discussions are also useful. Bergmann, K.; Theuer, H.; Shore, B. W. *Rev. Mod. Phys.* **1998**, *70*, 1003−1025. Vitanov, N. V.; Halfmann, T.; Shore, B. W.; Bergmann, K. *Annu. Rev. Phys. Chem.* **2001**, *52*, 763−809. See also chapter 4 of ref 1.

(4) The proof is straightforward. Assume that U is unitary. Then $U\dot{U}^{\dagger} = -\dot{U}U^{\dagger}$. Moreover $(U\dot{U}^{\dagger})^{\dagger} = (\dot{U}^{\dagger})^{\dagger}U^{\dagger} = \dot{U}U^{\dagger} = -(U\dot{U}^{\dagger})$; i.e., $U\dot{U}^{\dagger}$ is anti-Hermitian. An anti-Hermitian operator can only have purely imaginary diagonal elements. Because we defined U to be purely real, we are guaranteed that $U\dot{U}^{\dagger}$ has no nonzero diagonal matrix elements.

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