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Assisted Adiabatic Passage Revisited†

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We report the results of studies of various aspects of the counter diabatic field paradigm, a recipe that generates adiabatic population transfer between levels by assisting a given field so that the total field generates the population transfer that the adiabatic approximation suggests for the given field. The sensitivity of this recipe to the pulse parameters and to Gaussian stochastic phase fluctuations between the fields has been investigated. Ladder-climbing population transfer between the vibrational levels of a nonrotating Morse oscillator is examined, and a numerical demonstration of the efficiency of the scheme is given.

1. Introduction

There is considerable interest in methods that efficiently transfer population between an initial state and a selected target state of a molecule.[1] Two such methods are adiabatic population transfer[2] and optimal-shaped field-induced transfer.[1]

The adiabatic population transfer methods differ from the field optimization methods in their simplicity and their relative stability with respect to changes in the field parameters. Yet the adiabatic transfer methods have the drawback that there is an inverse proportionality between the peak intensity and the duration of a pulse[3] that generates complete population transfer. Indeed, the field strength of a short duration pulse that generates adiabatic population transfer may be so large that it also generates an undesirable competing process such as multiphoton ionization. This is a serious drawback since controlled population transfer competes with many secondary processes that can cause significant degradation of the yield of population in the target state. If the time scales of the secondary processes are shorter than the control field duration , then it is almost certain that the desired population transfer will be inefficient.

In ref 4 Unanyan et. al. and later in ref 5, we have proposed a method, the counter diabatic field paradigm, to assist adiabatic population transfer generated with short pulses that are less intense than the field that generates complete population transfer. The idea is quite simple. Given a field that would generate adiabatic population transfer, if strong enough, but which does not generate complete transfer because of lack of intensity, can one find another field, which is called the counter diabatic field (CDF), such that when it is combined with the first field one can recover adiabaticity? The answer is yes, and a simple derivation of how to find that field is given in the next section.

The previous paragraph implies that adiabatic population transfer can be generated through CDFs even if the first applied field is arbitrarily weak. Although that statement is mathematically accurate, use of the CDF procedure is often not feasible. A detailed analysis reveals that for weak initial fields the CDF must be stronger than the single field required for adiabatic population transfer. However, there is an intensity interval in which both the first field and the CDF can be 1 order of magnitude weaker than that required for adiabatic population transfer with a single field.

There are other questions about the CDF that need to be examined. Is the pulse profile that recovers adiabaticity of population transfer unique for a given parametrization? How sensitive is the population transfer to the inaccuracy in the pulse profile? And most important, to what extent do the phase fluctuations in the applied fields affect the efficiency of population transfer? We have previously applied the CDF scheme to a two-level system driven with a chirped field. It is reasonable to now ask: under what circumstances can the CDF scheme be applied to ladder-climbing[6,7] population transfer?

In what follows in section 2, we derive the CDF formalism and its application to a two-level system driven with a chirped field. Section 3 deals with the sensitivity of population transfer to alterations in the CDF pulse profile. In section 4, the influence of incoherence between the initial field and the CDF is calculated using a simple Gaussian colored noise model. In section 5, we show that under certain circumstances population transfer in a model three-level system can be regarded as sequential applications of CDFs as described in section 2. After comparison of analytical and approximate solutions for the CDF, we extend the methodology to generate population transfer between levels in a Morse oscillator.

2. Formalism

A quantitative account of assisted adiabatic passage is given in this section. We first define a time-dependent unitary transformation $U(t)$ between a static and orthonormal basis set S and a dynamic basis set $\mathscr{D}(t)$ such that

$$\mathscr{D}(t) = U(t)S \tag{1}$$

The unitarity of $U(t)$ and orthonormality of S guarantee the orthonormality of $\mathscr{D}(t)$. Any vector $|\psi(t)\rangle$ expressed in the span of S can be expressed in terms of the vectors in $\mathscr{D}(t)$ using the transformation

$$|\tilde{\psi}(t)\rangle \equiv U(t)|\psi(t)\rangle \tag{2}$$

If $|\psi(t)\rangle$ satisfies the time-dependent Schrödinger equation with Hamiltonian $H(t)$, then the analogous equation of motion for $|\tilde{\psi}(t)\rangle$ is

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

If one requires that the columns of $U^{\dagger}(t)$ be the eigenvectors of $H(t)$, then the first term on the right-hand side of eq 3 is a diagonal matrix. The adiabatic approximation[8] states that if the operator norm of $iU(t)\dot{U}^{\dagger}(t)$ remains small compared to $U(t)H(t)U^{\dagger}(t)$ then the time evolution of an initial superposition of eigenstates of $H(t)$, denoted $\{|\ k\rangle_t\}$, remains unchanged apart from the phases

$$|\tilde{\psi}(t)\rangle = \sum_k c_k(t)|k\rangle_t \quad (4)$$

where

$$c_k(t) \approx c_k(t_{\rm init}) \exp\left[-\frac{i}{\hbar}\int_{t_{\rm init}}^{t} \epsilon_k(s)\,{\rm d}s\right] \quad (5)$$

with the eigenvalues $\{\epsilon_k(t)\}$ of $H(t)$. Although the regime of validity of the adiabatic approximation can be achieved, the strength and the duration of the field must change in an inversely proportional manner in order to maintain adiabatic population transfer. Specifically, if one is interested in adiabatic population transfer with pulses of short duration, then the field strength becomes very large. To achieve adiabatic population transfer with weak and short pulses, we introduce a field (CDF) that operates in the direction opposite to $-iU\dot{U}^{\dagger}$, the generator of nonadiabatic effects, thereby assisting adiabatic population transfer.

The derivation of the CDF starts with a redefinition of the total Hamiltonian without changing the unitary transformation operator $U(t)$

$$H(t) \rightarrow H(t) + H_{\rm CD}(t) \quad (6)$$

Then the effective Hamiltonian for $|\tilde{\psi}(t)\rangle$ is given by

$$H_{\rm eff}(t) \equiv U(t)H(t)U^{\dagger}(t) + U(t)H_{\rm CD}(t)U^{\dagger}(t) - i\hbar U(t)\frac{\partial U^{\dagger}(t)}{\partial t} \quad (7)$$

If we further demand perfect adiabaticity by setting

$$U(t)H_{\rm CD}(t)U^{\dagger}(t) - i\hbar U(t)\frac{\partial U^{\dagger}(t)}{\partial t} = 0 \quad (8)$$

then we can easily deduce that

$$H_{\rm CD}(t) = i\hbar \frac{\partial U^{\dagger}(t)}{\partial t} U(t) \quad (9)$$

Note that the formalism above is exact and, no matter what $H(t)$ is, this equation will always give a CDF that together with the first field recovers perfect adiabatic population transfer.

In our previous work,[5] we implemented this method for a two-level system driven by a chirped field. The question of population transfer with chirped pulses has been adressed, for instance, by Guerin et. al.,[9] who determined the optimized pulse profile that guarantees an efficient population transfer to the target state. In ref 5, we sought and in this paper investigate further a control field that is not mathematically optimal but rather the one that precisely restores adiabaticity. Since in this report we will investigate the flexibility of assisted adiabatic passage with respect to the pulse parameters and phase fluctuations and apply it to adiabatic ladder climbing, we present a review of the findings of ref 5. Let the total Hamiltonian of the two-level system be

$$H(t) = \frac{\omega_{21}}{2}[-|1\rangle\langle 1| + |2\rangle\langle 2|] + V(t)[|1\rangle\langle 2| + |2\rangle\langle 1|] \quad (10)$$

where ω_{21} is the transition frequency and $V(t) = \Omega\cos(\omega t + \alpha t^2)$, with Ω the Rabi frequency, ω the carrier frequency, and α the linear chirp. We set $\hbar = 1$ throughout the analysis. We solve the time-dependent Schrödinger equation

$$i\dot{\mathbf{a}}(t) = H(t)\mathbf{a}(t) \quad (11)$$

We assume our pulse parameters are within the range of validity[10] of the rotating field approximation and define

$$\tilde{a}_1(t) \equiv a_1(t)\exp[-i(\omega t + \alpha t^2)/2] \quad (12)$$

$$\tilde{a}_2(t) \equiv a_2(t)\exp[i(\omega t + \alpha t^2)/2] \quad (13)$$

Within the rotating field approximation, the Schrödinger equation has the effective Hamiltonian

$$H_{\rm RFA}(t) = \frac{1}{2}\begin{bmatrix} \Delta(t) & \Omega \\ \Omega & -\Delta(t) \end{bmatrix} \quad (14)$$

where the time-dependent detuning is defined through $\Delta(t) \equiv \omega - \omega_{21} + 2\alpha t$. The eigenvalues of $H_{\rm RFA}(t)$ are given by

$$\omega_{\pm} = \pm\frac{1}{2}\sqrt{\Delta^2(t) + \Omega^2} \quad (15)$$

with eigenvectors (assuming $\Omega > 0$)

$$|-\rangle = -\sin(\Theta/2)|1\rangle + \cos(\Theta/2)|2\rangle \quad (16)$$

$$|+\rangle = \cos(\Theta/2)|1\rangle + \sin(\Theta/2)|2\rangle \quad (17)$$

where $0 \le \Theta < \pi$ is defined as the root of the nonlinear relation

$$\tan\Theta = \frac{\Omega}{\Delta(t)} \quad (18)$$

If $\Delta(0)$ and α have opposite signs and the rate of chirp is sufficiently small, then the adiabatic approximation is valid, and the dynamics of population transfer from $|-\rangle$ can be followed. If one applies the CDF method to this problem, then $H_{\rm CD}(t)$ in the bare state basis is given by

$$H_{\rm CD}(t) = \frac{i\dot{\Theta}(t)}{2}\begin{bmatrix} 0 & -1 \\ 1 & 0 \end{bmatrix} \quad (19)$$

Inverting the rotating field approximation for the total field that maintains adiabatic population transfer we have

$$V_{\rm tot}(t) = \Omega\cos(\omega t + \alpha t^2) + \dot{\Theta}(t)\sin(\omega t + \alpha t^2) \quad (20)$$

where the Lorentzian profile of the CDF is explicitly given by

$$\dot{\Theta}(t) = -\frac{1}{\tau}\frac{1}{1+(\Delta(t)/\Omega)^2} \quad (21)$$

where $\tau \equiv |\Omega/2\alpha|$. Note that the CDF is a π pulse, i.e.,

$$\int_{-\infty}^{\infty} |\dot{\Theta}(t)|\,{\rm d}t = \pi \quad (22)$$

However, unlike pulses with sinosoidal oscillating parts, being a π pulse is not enough to carry out 100% population transfer for chirped fields. In fact, as reported previously,[5] the CDF alone cannot generate an efficient population transfer. Note also that there is a well-defined phase relation between the first field and the CDF. If this phase relation is not maintained, then the efficiency of population transfer degrades.[5]

3. Pulse Profile

The CDF pulse is a Lorentzian peaked at $t_R = (\omega_{21} - \omega)/2\alpha$. When one can prepare a pulse with exactly that shape, complete population transfer is guaranteed. In this section, we explore the sensitivity of adiabatic population transfer to the CDF pulse parameters. We redefine the total system field interaction as

$$V_{tot}(t) = \Omega \cos(\omega t + \alpha t^2) + L(t) \sin(\omega t + \alpha t^2) \tag{23}$$

Within the rotating field approximation and using the dressed state basis as given in the previous section, the equation of motion has the effective Hamiltonian

$$H_{eff}(t) = \begin{bmatrix} \omega_-(t) & 0 \\ 0 & \omega_+(t) \end{bmatrix} + \frac{1}{2} D(t) \begin{bmatrix} 0 & 1 \\ -1 & 0 \end{bmatrix} \tag{24}$$

where the difference functional is defined by $D(t) \equiv (L(t) - \dot{\Theta}(t))$. Defining the integral

$$I(t) \equiv \int_{t_{init}}^{t} \omega_+(s)\, ds \tag{25}$$

and expressing the wave function in the interaction representation

$$|\psi(t)\rangle = a_-^{int}(t) \exp[iI(t)]|-\rangle + a_+^{int}(t) \exp[-iI(t)]|+\rangle \tag{26}$$

we have the following equation of motion

$$\dot{\mathbf{a}}(t) = \mathbf{W}(t)\mathbf{a}(t) \tag{27}$$

In eq 27

$$\mathbf{W}(t) \equiv \frac{D(t)}{2} \begin{bmatrix} 0 & \exp[-2iI(t)] \\ -\exp[2iI(t)] & 0 \end{bmatrix} \tag{28}$$

and

$$\mathbf{a}^T(t) = [a_-^{int}(t) a_+^{int}(t)]$$

If the field generates perfect adiabatic following, then the dressed state $|+\rangle$ is always empty. Hence the population in $|+\rangle$ as $t \to \infty$ is a good monitor of the efficiency of the adiabatic population transfer. Our experience with the dressed state basis sets and finiteness of $D(t)$ indicates that eq 27 can be solved iteratively. Somewhat slower but numerically exact methods, such as a fourth order Runge Kutta method, can also be used. If one decomposes the vector $\boldsymbol{a}(t)$ as follows

$$\mathbf{a}(t) = \mathbf{a}^{(0)}(t) + \mathbf{a}^{(1)}(t) + \mathbf{a}^{(2)}(t) + \cdots \tag{29}$$

substitutes this expansion into eq 27, and matches the orders of the resulting terms, then one finds the usual perturbation solution (for $n > 0$)

$$\mathbf{a}^{(n)}(t) = \int_{t_{init}}^{t} \mathbf{W}(s)\mathbf{a}^{(n-1)}(s)\, ds \tag{30}$$

The zeroth order term in this development of the solution must be time-independent, and we choose $a_-^{int,(0)} = 1$ and $a_+^{int,(0)} = 0$.

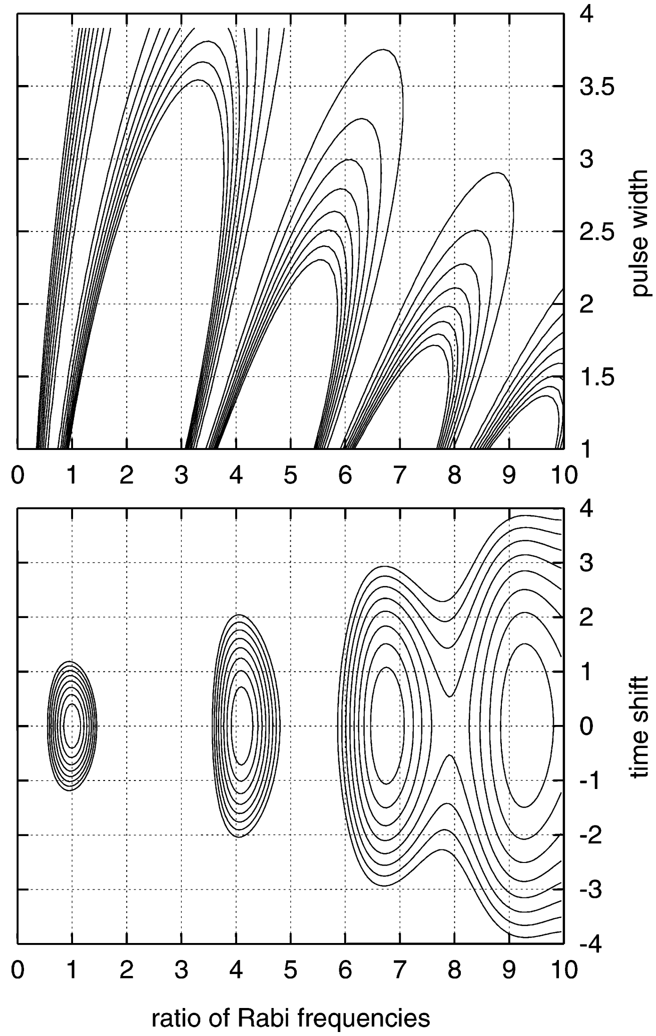

Figure 1. The sensitivity of counter diabatic field paradigm to pulse parameters. Top panel: Contour plot of the yield, the population in the target state. The pulse width is plotted against the ratio of intensities. At every contour, the yield decreases 1%. Note that 100% yield is achieved at (1.0,2.0). Bottom panel: Contour plot of sensitivity of yield with respect to intensity and time shift. The point (1.0,0.0) is where 100% yield is achieved. At every contour, the yield deccreases 1%. The parameters are $\Omega = 0.4$ UT and $\alpha = 0.1$ UT^2. With these parameters, the pulse width of $\dot{\Theta}$ becomes 2 TU.

Note that if $D(t) = 0$, i.e., the case where we achieve perfect adiabatic following, then all of the higher-order terms vanish.

We assume that $L(t)$ has the following form

$$L(t) = I_L \frac{1}{1 + \left(\frac{t - t_0 - t_L}{\tau_L}\right)^2} \tag{31}$$

with I_L the peak Rabi frequency of the test field. We define I_0 to be the peak intensity of the CDF. The ratio I_L/I_0 is the parameter we vary. τ_L is the pulse width of the field, t_0 is the location of the peak of the CDF, and t_L is the temporal deviation from that peak.

Fully converged solutions of eq 27 are displayed in Figure 1. We arranged the parameters such that the width of counter diabatic pulse is 2 time units (TU). This fixes the frequency unit as UT $\equiv$ TU^{-1}. The contour plots of Figure 1 reveal that (1) the counter diabatic field is not unique, i.e., the field we have calculated in section 2 is not the only one that can restore the adiabaticity of population transfer. However, other solutions that restore the adiabaticity of population transfer lie on the more intense or wider side of the parameter space, which makes them unfavorable choices. (2) The success of the CDF will not be significantly affected if one cannot precisely prepare a pulse with specified intensity, width, and peak location.

4. Assisted Adiabatic Passage with Incoherent Laser Sources

The sensitivity of the counter diabatic field paradigm to variation of the fixed relative phase between the two fields was explored in ref 5. In a typical experiment with pulses of short duration, the phases of the fields are likely to fluctuate. Therefore, in this section, we further explore the sensitivity of assisted adiabatic passage to fluctuations in the phases of the fields by assuming a stochastic contribution to the phase. We redefine the total interaction such that

$$V(t) = \Omega \cos(\omega t + \alpha t^2 + \delta(t)) + \dot{\Theta}(t) \sin(\omega t + \alpha t^2 + \delta_{\mathrm{CD}}(t)) \quad (32)$$

where δ and δ_{CD} are defined through

$$\dot{\delta}(t) = \epsilon(t) \quad \dot{\delta}_{\mathrm{CD}}(t) = \epsilon_{\mathrm{CD}}(t) \quad (33)$$

and $\epsilon(t)$ is an exponentially correlated Gaussian process with root-mean-square modulation β and correlation time $\tau = 1/\Gamma$

$$\langle \epsilon(t)\epsilon(t')\rangle = \langle \epsilon_{\mathrm{CD}}(t)\epsilon_{\mathrm{CD}}(t')\rangle = \beta^2 \exp[-|t - t'|/\tau] \quad (34)$$

There are accurate algorithms to generate exponentially correlated Gaussian deviates. As long as one is careful with the time increment in the simulation so that it is smaller than the correlation time of the noise, the algorithm of Fox et. al.[11] is suitable for our purposes.

Within the rotating field approximation, the total Hamiltonian now becomes

$$H_{\mathrm{RFA}}(t) = \frac{1}{2}\begin{bmatrix} \Delta(t) + \epsilon(t) & \Omega \\ \Omega & -\Delta(t) - \epsilon(t) \end{bmatrix} + \frac{\dot{\Theta}(t)}{2i}\begin{bmatrix} 0 & \mathrm{e}^{i(\delta_{\mathrm{CD}}-\delta)} \\ -\mathrm{e}^{-i(\delta_{\mathrm{CD}}-\delta)} & 0 \end{bmatrix} \quad (35)$$

The stochastic Schrödinger equation under H_{RFA} was solved many times with statistically independent $\epsilon(t)$ and $\epsilon_{\mathrm{CD}}(t)$, and the norms $|a_1(t)|^2$ and $|a_2(t)|^2$ were averaged until convergence was achieved. The population transfer yield is assumed to be the value of $|a_2(t{\to}\infty)|^2$. We show in Figure 2 the yield of population transfer with incoherent CDFs. In the absence of any CDF, a population transfer of 70% is achieved for the initial field we have used. Thus, any yield less than 70% represents a serious degradation of the population transfer by the noise. The conclusion one can draw from the calculations is simple. As long as the root-mean-square of the deviates, $\langle \epsilon^2\rangle^{1/2}$, is small with respect to the Rabi frequency, Ω, the degradation of population transfer yield is small. When $\langle \epsilon^2\rangle^{1/2}$ becomes comparable to the Rabi frequency, the degradation is most significant when the correlation time $1/\Gamma$ of the noise is close to the total transfer time. When $\langle \epsilon^2\rangle^{1/2}$ greatly exceeds the Rabi frequency, the cases $\beta = 1.0$ and $\beta = 2.0$ behave qualitatively the same irrespective of modulation frequency Γ.

The results shown in Figure 2, in principle, can be tested for accuracy using a cumulant expansion[12] for $\langle \rho(t)\rangle$, the ensemble average of the density matrix. The cumulant method for a given

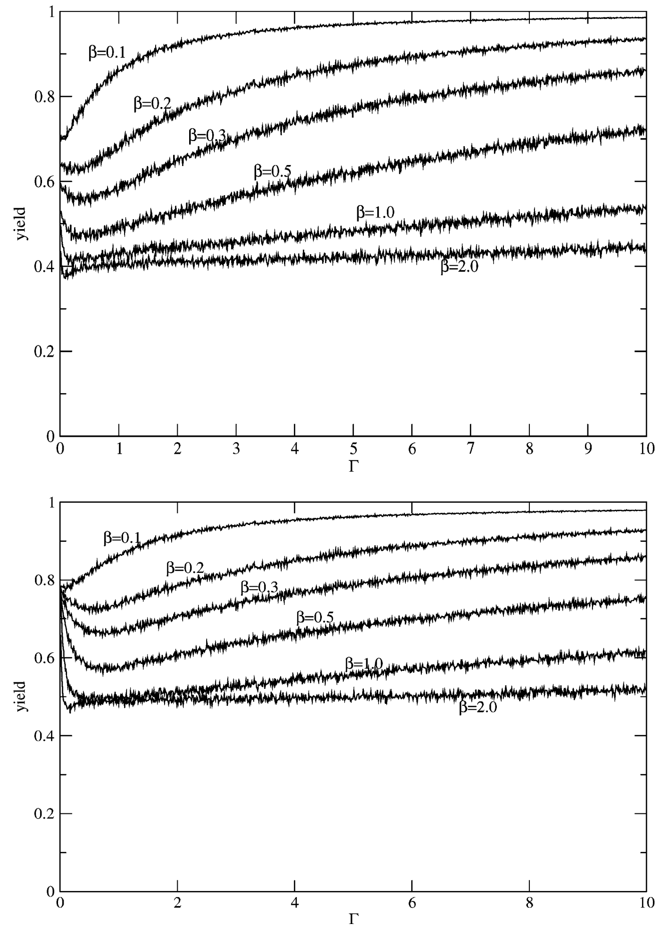

Figure 2. Display of sensitivity of population transfer to phase fluctuations in the laser sources. Yield is plotted against modulation frequency (inverse of correlation time). The Rabi frequencies for the panels are $\Omega = 0.3$ UT (top) and $\Omega = 0.5$ UT (bottom).

nonstochastic Hamiltonian has been tested and compared in performance against perturbation theory by Pechukas and Light.[13] For stochastic Hamiltonians, various cumulant methods have been developed[12] and applied to, for example, modeling the effect of dephasing in magnetic resonance[14] and optical processes.[15] Yatsenko et. al.[16] treated a similar problem of the influence of incoherence on STIRAP and used perturbation theory to provide a comparison for their Monte Carlo calculations. Whether one attempts a perturbation calculation or a cumulant expansion, there is a fundamental difference between the problem we have addressed and straightforward calculations using stochastic dephasing models. In the non-Markovian dephasing calculations, the stochastic variable enters the Hamiltonian as a linear term, whereas in our problem it is strictly nonlinear. This of course has consequences. Despite the nonlinearity, the ensemble averages required can be calculated[17] by exploiting the Gaussian nature of the modulation, but unlike the linear dephasing case the first order cumulant does not vanish. Even then, in our experience, the results of first-order cumulant theory accurately predict the $\Gamma \to 0$ limit while it behaves poorly for other Γ, the latter thereby requiring use of the next order treatment. The computation of averages and the integrals in the second-order cumulant equation are very cumbersome to tackle because 9 operators in the second-order Liouvillian, a total of 82 integrals, and ensemble averages are required with a quadratic scaling of computational complexity. We close this section by noting that a first-order cumulant theory can yield agreement in the static ($\Gamma \to 0$) limit for this strongly nonlinear problem, but the higher-order expansions needed to obtain a better agreement is too tedious to tackle.

5. Sequential Assisted Adiabatic Passage: Extension to Population Transfer by Ladder Climbing

One obvious extension of adiabatic population transfer in a two-level system is Raman chirped adiabatic passage[6] where a nonresonant field that has a time-dependent effective frequency sweeps through the transition frequencies of a nonrotating Morse oscillator and excites it from the ground vibrational state to higher vibrational states. In a Morse oscillator, as one goes to higher excited states the transition frequencies decrease. Thus, if one starts with a field that has a carrier frequency that is larger than the frequency of the first transition ($\omega > \omega_{10}$) and the rate of change of effective frequency is negative ($\alpha < 0$), then one can sequentially excite the oscillator from the ground vibrational state to any desired excited vibrational state.

The chirped nature of the excitation suggests that the nonadiabaticity of the population transfer generated by the field per se can be suppressed via a CDF which is similar to the one explored in the previous sections. Furthermore, as we demonstrate in this section, the CDF can, to a very good approximation, be regarded as the sequential application of the CDF that was described for a two-level system. For the sake of simplicity, we first describe the case for a three-level system and then generalize the results of our findings to the multilevel Morse oscillator.

A three-level system, like the two-level system, is a useful example in the exploration of assisted adiabatic passage since there exist analytical expressions for the eigenvalues and therefore the eigenvectors of a three by three Hamiltonian.[18] The Hamiltonian of this system is given by

$$H(t) = H_0 - \mu E(t) \tag{36}$$

where

$$H_0 = \sum_{k=1}^{3} \omega_k |k\rangle\langle k| \tag{37}$$

with ω_k the eigenenergies. Moreover

$$\mu = -\mu_{12}[|1\rangle\langle 2| + |2\rangle\langle 1|] - \mu_{23}[|2\rangle\langle 3| + |3\rangle\langle 2|] \tag{38}$$

with μ_{12} and μ_{23} the transition dipole moments, and $E(t) = E_0 \cos(\omega t + \alpha t^2)$ is the electric field.

The Hamiltonian within the rotating field approximation is given by

$$H_{\mathrm{RFA}}(t) = \begin{bmatrix} 0 & \Omega_p/2 & 0 \\ \Omega_p/2 & \Delta_2(t) & \Omega_S/2 \\ 0 & \Omega_S/2 & \Delta_2(t) + \Delta_3(t) \end{bmatrix} \tag{39}$$

where

$$\Delta_2(t) = \omega_{21} - \omega - 2\alpha t$$

$$\Delta_3(t) = \omega_{32} - \omega - 2\alpha t$$

$$\Omega_p = \mu_{12} E_0$$

and

$$\Omega_S = \mu_{32} E_0$$

The eigenvalues $\epsilon_i(t)$ of $H_{\mathrm{RFA}}(t)$ are the roots of

$$\epsilon^3 - \epsilon^2(2\Delta_2 + \Delta_3) + \epsilon(\Delta_2(\Delta_2 + \Delta_3) - (\Omega_p^{\ 2} + \Omega_S^{\ 2})/4) + \frac{\Omega_p^{\ 2}}{4}(\Delta_2 + \Delta_3) = 0 \tag{40}$$

and can be calculated analytically via a cosine transformation.[19] Once the eigenvalues are obtained, the normalized eigenvectors are given by

$$|\epsilon_i(t)\rangle = \frac{1}{N(t)} \begin{bmatrix} \Omega_p(\Delta_2 + \Delta_3 - \epsilon_i) \\ 2\epsilon_i(\Delta_2 + \Delta_3 - \epsilon_i) \\ -\Omega_S \epsilon_i \end{bmatrix} \tag{41}$$

where $N(t) = \sqrt{(4\epsilon_i^{\ 2} + \Omega_p^{\ 2})(\Delta_2 + \Delta_3 - \epsilon_i)^2 + \Omega_S^{\ 2}\epsilon_i^{\ 2}}$. After the eigenvectors are calculated, the calculation of the CDF is straightforward using eq 9. Although it is possible to obtain analytic expressions for the matrix elements of the CDF Hamiltonian, little insight is gained from the rather cumbersome expressions.

We now ask if the CDF of a three-level system can be regarded as equivalent to the CDFs that generate two sequential two-level system population transfers. For that purpose, we define the approximate counter diabatic field Hamiltonian matrix elements as

$$L_{p,S}(t) = \frac{\dfrac{\Omega_{p,S}}{2\alpha}}{\left(\dfrac{\Omega_{p,S}}{2\alpha}\right)^2 + \left(t + \dfrac{\omega - \omega_{21,32}}{2\alpha}\right)^2} \tag{42}$$

These functions are to be compared with the exact expressions. We know[5] a priori that the diagonal matrix elements of $H_{\mathrm{CD}}(t)$ are zero. By virtue of Hermiticity, this leaves us with the three off-diagonal elements, namely, $H_{\mathrm{CD},12}$, $H_{\mathrm{CD},13}$, and $H_{\mathrm{CD},23}$. The representation of three-level system ladder climbing as two sequential two-level system population transfers with chirped fields is accurate if (1) $H_{\mathrm{CD},\,12}(t) \approx L_p(t)$, (2) $H_{\mathrm{CD},23}(t) \approx L_S(t)$, and (3) $|H_{\mathrm{CD},13}(t)| \ll |H_{\mathrm{CD},12}(t)|$ and $|H_{\mathrm{CD},13}(t)| \ll |\,H_{\mathrm{CD},\,23}(t)|$

The third condition, which demands either zero or very insignificant coupling between the initial state and the target state, cannot be met in a STIRAP[4,5] type population transfer, and hence a pragmatic application of assisted adiabatic passage is not feasible for STIRAP. As it turns out, the third condition is fulfilled in chirped adiabatic passage.

Figure 3 displays the results of a test calculation of population transfer in a three-level system. The system parameters are set to mimic the ground, first, and second excited vibrational states of the HF molecule. The top two panels of Figure 3 reveal that the approximation $L_{p,S}(t) \approx H_{\mathrm{CD},12/23}(t)$ is very accurate as the two pulse profiles are almost indistinguishable. Moreover, the third condition that $|H_{\mathrm{CD},13}|$ is small with respect to other matrix elements is also satisfied; indeed it turns out to be 1 order of magnitude smaller than the other matrix elements in each case. We infer that the CDF needed for three-level population transfer can be regarded as the CDF needed for two sequential population transfers between two-level systems. The bottom two panels of Figure 3 display the restoration of adiabatic population transfer. On the bottom left, the adiabatic three-level system population dynamics suffers from the lack of intensity as well as the short duration of the excitation. On the bottom right, the nonadiabatic effects are suppressed by the approximate counter diabatic pulses. The neglect of $H_{\mathrm{CD},13}$ in the dynamics manifests

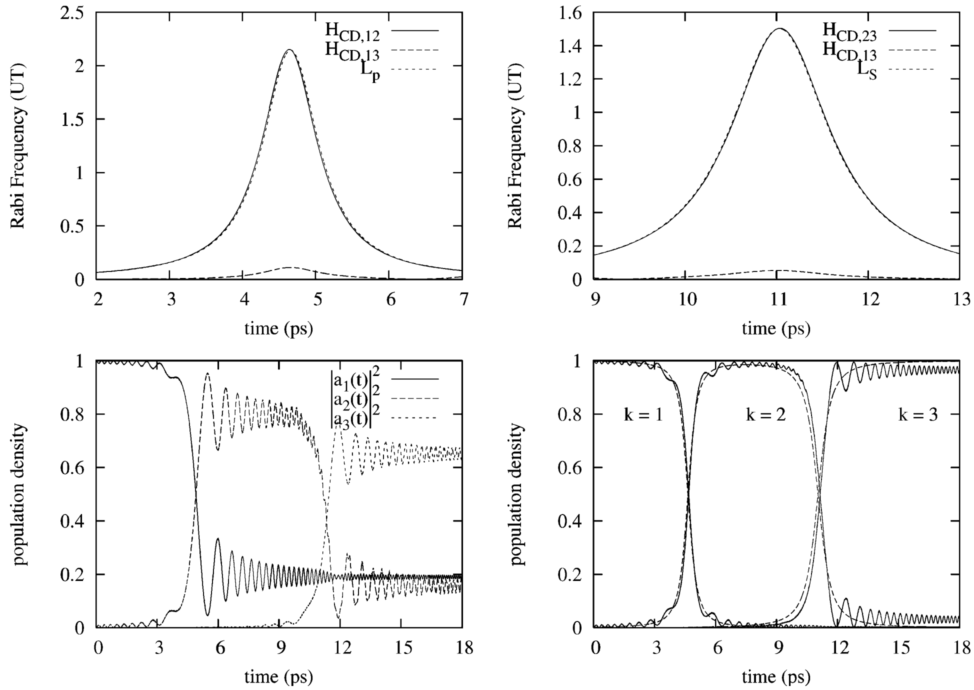

Figure 3. Ladder climbing in a three-level system. Top-left panel: Comparison of the calculated ($H_{CD,12}(t)$) and approximated ($L_p(t)$) counter diabatic fields and coupling ($H_{CD,13}(t)$) between initial and target states. Calculated and approximated CDFs are indistinguishable, and $H_{CD,13}(t)$ appears to be 1 order of magnitude smaller. Top-right panel: A similar calculation for the 2 → 3 transition. Again, $H_{CD,13}(t)$ and $L_S(t)$ are indistinguishable while $H_{CD,13}(t)$ is much smaller. Bottom-left panel: The three-level system population dynamics in the absence of counter diabatic fields $L_{p,S}(t)$. Bottom-right panel: Three-level system population dynamics in the presence of counter diabatic fields. The dashed lines are the results obtained from the adiabatic approximation. The parameters are $\omega_{21} = 0.0181$ au, $\omega_{32} = 0.0173$ au, $\mu_{12} = -0.0385$ au, $\mu_{23} = 0.0551$ au, $E_0 = 0.0015$ au, which corresponds to 0.077 V/Å, $\alpha = -1.5 \times 10^9$ au, and 1 UT $\equiv 10^{12}$ s^{-1}.

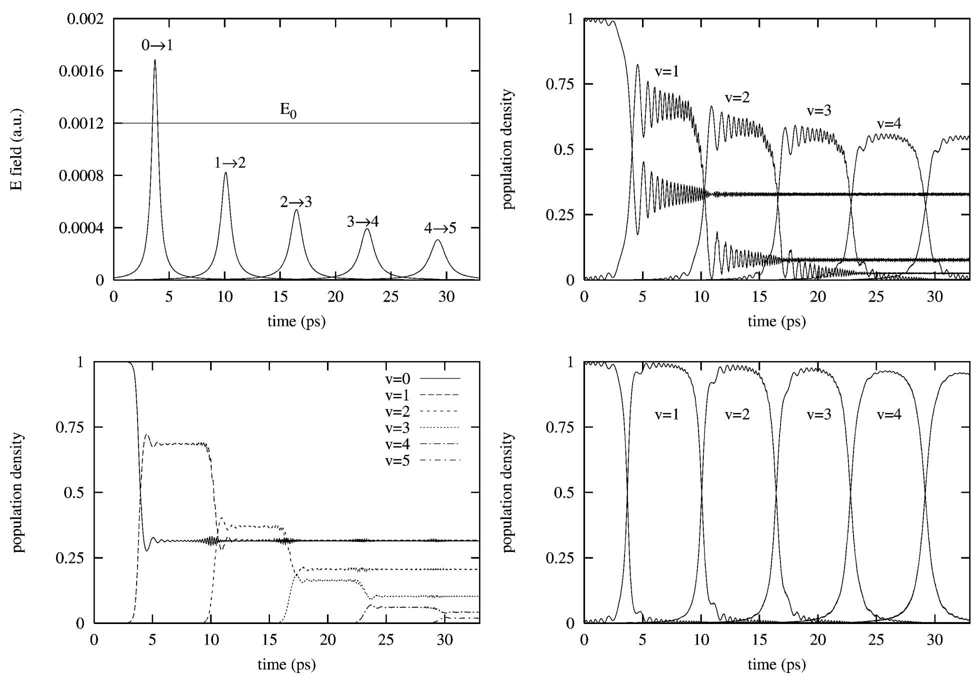

Figure 4. Vibrational ladder climbing via assisted adiabatic passage in ground electronic potential energy surface of HF. Top-left panel: The strength of E_0 and counter diabatic fields. Top-right panel: The vibrational dynamics in the presence of E_0 and absence of Lorentzian (approximated) counter diabatic fields. Bottom-left panel: The vibrational dynamics in the absence of E_0 and presence of Lorentzian pulses. Bottom-right panel: The vibrational dynamics when E_0 and all of the Lorentzian pulses are combined.

itself as ripples in the norms and a slight decrease in the ultimate yield of the population transfer. As for the field strengths, we have chosen the maximum value of the field of the bottom-left panel in Figure 3 to be 0.0015 au (0.077 V/Å). This in turn results in peak values of $L_{p,\max} = 0.0014$ au and $L_{S,\max} = 0.0007$ au.

Figure 4 shows the use of CDFs in vibrational ladder climbing. The system is a nonrotating Morse oscillator[7]

$$V(r) = D(1 - \exp[-a(r - r_0)])^2 \tag{43}$$

whose parameters ($D = 6.125$ eV, $a = 1.1741 a_0^{-1}$, and $r_0 =$

$1.7329a_0$) mimic the ground electronic potential energy surface of the HF molecule. The system field interaction is of the electric dipole type, $H_{\text{int}}(t) = \mu E_0 \cos(\omega t + \alpha t^2)$. The dipole moment operator is assumed to have a linear form, $\mu = d_1 x$ where $d_1 = 0.786$ Db/a_0 and $x = r - r_0$. The time-dependent Schrödinger equation was integrated with the split operator technique.[20] Only the population transfer dynamics of the first six vibrational states are shown. As the top-right and bottom-left panels of Figure 4 clearly show, neither the original system field interaction nor the approximate CDFs alone suffice, in terms of their strength and/or duration, to generate adiabatic population transfer. Only their combination, as shown in the bottom-right panel, generates an efficient adiabatic population transfer. It is worth mentioning that none of the approximate fields are too strong compared to E_0. As a matter of fact, only one (for the $0 \rightarrow 1$ transition) exceeds E_0 in strength, and as one goes to higher transitions the counter diabatic pulses tend to weaken. Although this could be an artifact of the linear dipole moment function, which becomes unrealistic for large r, the dipole moment function is reliable for transitions between the lower states, and in the cases of the $0 \rightarrow 1$ and $1 \rightarrow 2$ transitions we do not observe excessively strong counter diabatic fields.

6. Conclusion

We have explored various aspects and extensions of assisted adiabatic passage, a population transfer method that is designed to generate adiabatic population transfer under unfavorable conditions. Our results can be summarized as follows:

(1) A flexible window of error in the pulse parameters (the pulse width, location of the peak, and intensity) is available within which adiabatic population transfer can be maintained.

(2) The CDF in our formalism is not unique, but among other pulses that are parametrized in the same manner it is the one with the least intensity that restores adiabatic population transfer.

(3) Depending upon how the root-mean square (rms) width and the frequency of modulation compare with the Rabi frequency, the decrease in population transfer efficiency due to incoherence between the initial field and the CDF can be significant. Specifically, if the rms width of the modulation is comparable to or larger than the Rabi frequency, then the CDF method fails. The phase sensitivity of the CDF method is not surprising since the CDF is defined as “a field that clears the diabatic effects as they are generated.”

(4) The chirped CDF developed for the two-level system has been extended to many-level systems through approximating the topology of a many-level system as sequential two-level systems. Specifically, the CDF for adiabatic population transfer in a Morse oscillator by ladder climbing has been calculated.

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(3) There is no simple rule that quantifies the validity of the adiabatic approximation. However, from experimental and numerical experience one infers that if the peak Rabi frequency Ω_{max} and full width at half-maximum τ, a quantity proportional to the duration, of the pulse satisfy $\Omega_{\text{max}}\tau \geq 10$ then the adiabatic approximation is valid. See refs 1 and 2 in the context of optical control and ref 8 for a more general discussion.

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