Coherent Control of Multiphoton Transitions with Femtosecond pulse shaping

S. Abbas Hosseini and Debabrata Goswami

Tata Institute of Fundamental Research, Homi Bhabha Road, Mumbai 400 005, India.

(June 1, 2003)

Abstract

We explore the effects of ultrafast shaped pulses for two-level systems that do not have a single photon resonance by developing a multiphoton density-matrix approach. We take advantage of the fact that the dynamics of the intermediate virtual states are absent within our laser pulse timescales. Under these conditions, the multiphoton results are similar to the single photon and that it is possible to extend the single photon coherent control ideas to develop multiphoton coherent control.
I. INTRODUCTION

Use of optimally shaped pulses to guide the time evolution of a system and thereby control its future is an active field of research in recent years [1]- [16]. Such developments have been spurred by technological breakthroughs permitting arbitrarily amplitude modulated laser pulses with 20-30 fs resolution and pulse energies ranging to almost hundred microjoules—either in the time domain or in the frequency domain. In most practical cases, computer optimizations are used to generate the useful shapes [1]- [7], since even approximate analytical solutions exist only for very specialized cases [7]- [12]. Such computer simulations have resulted in generating quite complicated theoretical waveforms that can break strong bonds [1]- [4], localize excitation [13]. Most of these interesting calculations involve intense pulses, which do not operate in the linear response regime. Actual photo-chemical processes with such intense pulses that operate beyond the linear response region often involve multiphoton effects. Unfortunately, multiphoton interactions typically induce additional complications and have not yet been explored much theoretically for coherent control purposes. In fact, most models for coherent control deal with light-matter interaction at the single-photon level. However, some recent experiments show that they can even simplify quantum interference effects; e.g., how Cs atoms can be made to absorb or not absorb light with non-resonant two-photon excitation with shaped optical pulses [14,15]. The experimental results have been treated with a perturbation model that works under the resonant condition. However, a more complete theoretical treatment of multiphoton interactions for developing multiphoton coherent control is quite complex and is far from complete. In fact, the lack of such a theoretical basis is also evident from the fact that in the classic demonstration of control of multiphoton ionization process, an experimentally optimized feedback pulse shaping was found to provide the best-desired yield [16]. In the present work, we develop a density matrix approach to multiphoton processes that do not have any lower-order process and demonstrate that can also explain the off-resonance behavior.

We present results, which show that this would be a promising approach. We first apply
the approach to the two-photon scenario in a simple two-level system (e.g., any narrow, single-photon transition line that is only multiphoton allowed). We then generalize the results to the case where only one N-photon \((N \geq 2\), which is multiphoton\) transition is possible and none of the \((N-1)\) photon transition can exist. Under these conditions, we show that most of the waveforms produce the same results as the single photon case [18]. With care, therefore, we predict that it will be possible to extend some of the single photon coherent control ideas to develop multiphoton coherent control. We explore the various frequency-swept pulses into the multiphoton domain, which have been previously shown to be successful in inducing robust inversions under single-photon adiabatic conditions. We also investigate the case of phase modulated overlapped Gaussian pulses for two-photon transition (in the spirit of a “dark” pulse of Meshulach and Silberberg, which they defined as “a single burst of optical field” that does not produce any net population transfer [15]). We show that the two-photon dark pulses, which are a result of smoothly varying phase modulation, can be explained by invoking the well-established concept of single photon adiabatic rapid passage (ARP) [17,18] to the multiphoton framework. In fact, the ARP explanation allows us to generalize the results to the N-photon case and show that such dark pulses are a result of the Stark shifting of the resonant \(N^{th}\) photon transition. The extension of the concept of ARP into the multiphoton domain has very important consequences in generating inherent robust processes.

II. FORMALISM

The simplest model describing a molecular system is an isolated two-level system or ensemble without relaxation or inhomogeneities. This simple model often turns out to be a very practical model for most systems interacting with the femtosecond laser pulses as the magnitude of the relaxation processes are immensely large as compared to the femtosecond interaction time. Let us consider a linearly polarized pulse is being applied to the \(|1>\to|2>\) transition, where \(|1>\) and \(|2>\) represent the ground and excited eigenlevels, respectively,
of the field-free Hamiltonian. In case of single photon interactions (Fig. 1a), the total laboratory-frame Hamiltonian for such two-level system under the effect of an applied laser field, \( E(t) = \varepsilon(t) e^{i[\omega(t) t + \phi(t)]} \) can be written as [10,17]:

\[
H = \begin{pmatrix}
E_1 & V_{12} \\
V_{21} & E_2
\end{pmatrix} = \begin{pmatrix}
\hbar \omega_1 & \mu E \\
\mu E^* & \hbar \omega_2
\end{pmatrix} = \hbar \begin{pmatrix}
-\frac{\omega_R}{2} & \frac{\mu \varepsilon}{\hbar} e^{i(\omega t + \phi)} \\
\frac{\mu \varepsilon^*}{\hbar} e^{-i(\omega t + \phi)} & \omega_R/2
\end{pmatrix}
\]

(1)

where \( \omega_R = \omega_2 - \omega_1 \) is resonance frequency, \( V_{12} \) and \( V_{21} \) are the negative interaction potentials and \( \hbar \omega_1, \hbar \omega_2 \) are the energies of ground \( (E_1) \) and excited state \( (E_2) \) respectively, and \( \mu \) is the transition dipole moment of the \( |1> \rightarrow |2> \) transition. In analogy to this single photon interaction as given in Eqn. (1), the interaction potential under the effect of an applied laser field, in two-photon absorption case (Fig. 1b) can be written as:

\[
V(t) = \mu_{1m} \varepsilon(t) e^{i(\omega t + \phi(t))} |1> \langle m| \mu_{m2} \varepsilon(t) e^{i(\omega t + \phi(t))} |m> \langle 2| + c.c.
\]

(2)

where \( m \) is the virtual state. Let us, for simplicity, take the transition dipole moment between the ground state to the virtual state to be equal to the transition dipole moment between the virtual state and excited state \( (\mu_{1m} = \mu_{m2} = \mu) \). In fact, we have verified in our simulations that the trend of the results is preserved even when we relax this simplification. In any event, for developing the initial model, the above said simplification allows us to take \( \mu \) as a common factor and we can rewrite Eqn. (2) as:

\[
V(t) = (\mu \varepsilon(t))^2 e^{2i(\omega t + \phi(t))} |1> \langle 2| + c.c.
\]

(3)

since for normalized states, \( <m|m> = 1 \). Using similar arguments for the \( N \)-photon case (Fig. 1c), the interaction potential can be written as:

\[
V(t) = (\mu \varepsilon(t))^N e^{iN(\omega t + \phi(t))} |1> \langle 2| + c.c.
\]

(4)

Thus, the total laboratory-frame \( N \)-photon Hamiltonian will be:

\[
H = \begin{pmatrix}
\hbar \omega_1 & (\mu E)^N \\
(\mu E^*)^N & \hbar \omega_2
\end{pmatrix} = \hbar \begin{pmatrix}
-\frac{\omega_R}{2} & \frac{(\mu \varepsilon)^N}{\hbar} e^{iN(\omega t + \phi)} \\
\frac{(\mu \varepsilon^*)^N}{\hbar} e^{-iN(\omega t + \phi)} & \omega_R/2
\end{pmatrix}
\]

(5)
The virtual levels for the two-photon (or N-photon) case can exist anywhere within the bandwidth $\Delta \omega$ of the applied laser pulse (Fig. 1) and the individual virtual state dynamics is of no consequence.

In analogy to the single photon case [11,12], there are two different ways to transform the elements of the above laboratory frame N-photon Hamiltonian (Eqn. (5)) into a rotating frame of reference. Any time-dependent transformation function $T$ can be applied on both sides of the Schrödinger equation as follows:

$$T \left( i \hbar \frac{\partial}{\partial t} \Psi = H \Psi \right)$$

$$i \hbar \frac{\partial}{\partial t} (T \Psi) - i \hbar \frac{\partial T}{\partial t} (T^{-1} T) \Psi = TH (T^{-1} T) \Psi$$

$$i \hbar \frac{\partial}{\partial t} (T \Psi) = \left[ THT^{-1} + i \hbar \frac{\partial T}{\partial t} T^{-1} \right] (T \Psi)$$

which results the following transformation equation:

$$H^{\text{Transformed}} = THT^{-1} + i \hbar T^{-1} \frac{\partial T}{\partial t}$$

The usual frame of reference would be to rotate at $N\omega$. This is the phase-modulated (PM) frame of reference, which can be derived from the Hamiltonian $H$ of Eqn. (5) by the transformation:

$$T^{PM} = \begin{pmatrix} e^{-iN\frac{\phi}{2}} & 0 \\ 0 & e^{iN\frac{\phi}{2}} \end{pmatrix}$$

Using of Eqn. (7), the transformed Hamiltonian in the PM frame is:

$$H^{PM} = \hbar \begin{pmatrix} \Delta & \frac{\mu(\varepsilon(t))^N}{\hbar} e^{iN\phi} \\ \frac{\mu(\varepsilon^*(t))^N}{\hbar} e^{-iN\phi} & 0 \end{pmatrix}$$

under the assumption that the transient dipole moment of the individual intermediate virtual states in the multiphon ladder all add up constructively to the final state transition dipole moment and can be approximated to a constant ($\mu$) over the N-photon electric field interaction. This approximation is particularly valid for the case of multiphoton interaction with femtosecond pulses where no intermediate virtual level dynamics can be observed. Thus, we define multiphoton Rabi Frequency, as the complex conjugate pairs: $\Omega(t) = \mu(\varepsilon(t))^N / \hbar$
and $\Omega^*(t) = \mu_\ast(t)$, and the time-independent multiphoton detuning as: $\Delta = \omega_R - N\omega$ (Fig. 1c). However, in order to investigate the off-resonance behavior of continuously modulated pulses, in the single photon case, it is useful to perform an alternate rotating-frame transformation to a frequency modulated (FM) frame with the transformation function:

$$T^{FM} = \begin{pmatrix} e^{-iN\omega t/2} & 0 \\ 0 & e^{iN\omega t/2} \end{pmatrix}$$

(10)

to transform the N-photon laboratory Hamiltonian in Eqn. (5) to the FM frame as:

$$H^{FM} = \hbar \begin{pmatrix} \Delta + N\dot{\phi}(t) & \frac{\mu_\ast(t)}{\hbar} \frac{\mu(t)\ast(t)}{\hbar} \\ \frac{\mu(t)\ast(t)}{\hbar} & 0 \end{pmatrix} = \hbar \begin{pmatrix} \Delta + N\dot{\phi}(t) & \Omega \\ \Omega^* & 0 \end{pmatrix}$$

(11)

The time derivative of the phase function $\dot{\phi}(t)$, i.e., frequency modulation, appears as an additional resonance offset over and above the time-independent detuning $\Delta$, while the direction of the field in the orthogonal plane remains fixed. The time evolution of the unrelaxed two-level system can then be evaluated by integrating the Liouville equation [10,17]:

$$\frac{d\rho(t)}{dt} = \frac{i}{\hbar} [\rho(t), H^{FM}(t)]$$

(12)

where $\rho(t)$ is a $2\times2$ density matrix whose diagonal elements represent populations in the ground and excited states and off-diagonal elements represent coherent superposition of states. This approach has been very successful in solving many single-photon inversion processes for arbitrarily shaped amplitude and frequency modulated pulses [12], [13]. We have just extended the same arguments to the multiphoton case.

The simulations are performed with a laser pulse that either has (a) a Gaussian intensity profile or (b) a hyperbolic secant intensity profile which have the following respective forms:

(a) $$I(t) = I_0 \exp \left[ -8 \ln 2 \left( t/\tau \right)^2 \right]$$

implies $$\varepsilon(t) = \varepsilon_0 \exp \left[ -4 \ln 2 \left( t/\tau \right)^2 \right]$$

(b) $$I(t) = I_0 \text{sech}^2 \left[ \left\{ 2 \ln \left( 2 + \sqrt{3} \right) \right\} (t/\tau) \right]$$

implies $$\varepsilon(t) = \varepsilon_0 \text{sech} \left[ \left\{ 2 \ln \left( 2 + \sqrt{3} \right) \right\} (t/\tau) \right]$$

(13)
where $\tau$ is the full width at half maximum, and $I(t)$ is the pulse intensity. This is because most of the commercially available pulsed laser sources have these intrinsic laser parameters. We choose a range of frequency sweeps, such as (c) the linear frequency sweep for the Gaussian amplitude, (d) the hyperbolic tangent sweep for the hyperbolic secant amplitude, and they have the following respective forms:

\[
(c) \quad \dot{\phi}(t) = bt \\
(d) \quad \dot{\phi}(t) = b \left\{ 2 \ln \left( 2 + \sqrt{3} \right) \right\} \tanh \left[ \left\{ 2 \ln \left( 2 + \sqrt{3} \right) \right\} (t/\tau) \right]
\]

where $b$ is a constant. Such pulses have been shown to invert population through ARP in single photon case and so we choose to use these particular shapes for the multiphoton case.

We also use the shaped overlapping Gaussian pulses for a two-photon transition similar to the ones used by Meshulach and Silberberg. In their case the frequency sweep is given by:

\[
\dot{\phi}(t) = \begin{cases} 
  b & t \geq t_0 \\
  -b & t < t_0 
\end{cases}
\]

where $t_0$ is the midpoint of the pulse. This pulse does not satisfy the ARP condition and is quite susceptible to the changes in the pulse amplitude profile and our results show this in the next section. However, if we instead use smoothly varying linear frequency sweeps, either changing monotonically as in Eqn. (14c), or linearly approaching and going away from resonance as given by:

\[
\dot{\phi}(t) = bt, \text{ where } b \text{ changes sign at } t_0
\]

These pulses satisfy the ARP conditions as explained in the next section. Dark pulses given by Eqn (16) are thus quite insensitive to the changes in the pulse amplitude profile. We also extend our calculations to the N-photon case in a simple two-level type of system that supports only an $N^{th}$ photon transition and show how the phase switches effect the population cycling. These generalizations would become evident when we examine the results based on the ARP extended to multiphoton case.
III. RESULTS & DISCUSSION

The population evaluation in a simple two level system without relaxation for one photon absorption (N=1) is shown in Fig. 2 for the pulse shapes given by Eqns. (13) and (14). Excitation exactly on resonance creates a complete population inversion when the pulse area (the time integral of the Rabi frequency) equals $\pi$. However, the population oscillates between the ground and excited state as sine function with respect to the Rabi frequency. These oscillations are not desirable in most cases involving real atoms or molecules. They are washed out by inhomogeneous broadening, the transverse Gaussian profile of the laser, and (in the molecular case) different values of $\mu \varepsilon$. For a single-photon case, as discussed in Ref. [18], frequency modulated pulses can instead produce adiabatic inversion, which avoids these complications. A linearly frequency swept (chirped) laser pulse can be generated by sweeping from far above resonance to far below resonance (blue to red sweeps), or alternatively from far below resonance to far above resonance (red to blue sweeps). When the frequency sweep is sufficiently slow such that the irradiated system can evolve with the applied sweep, the transitions are “adiabatic”. If this adiabatic process is faster than the characteristic relaxation time of the system, a smooth population inversion occurs with the evolution of the pulse, which is the well-known ARP.

Let us now extend the effect of such laser pulses (given by Eqns. (13) and (14)) to a two-photon (N=2) case as derived in our Hamiltonian of Eqn. (11). Fig. 3 shows the plots of the upper state population ($\rho_{22}$) as a function of applied Rabi frequency and detuning for two photon absorption case in the absence of one photon absorption. We find that the results are qualitatively the same as the one-photon absorption. In fact, our simulations show that for such a simple case of a two-level system, where only an $N^{th}$ photon transition is possible, we can extend our single-photon results to the N-photon case. The difference lies in the Rabi frequency scaling. Thus, for this simple case as defined here, we are able to invoke the concept of ARP for multiphoton interaction.

We next use the overlapping Gaussian pulses (when the overlap is complete it collapses
into a single Gaussian) with different phase relationships. Our simulation shows that for shaped overlapping Gaussian pulses the excited state population depends on the form of the frequency sweep. In figure 4a, for the shaped pulse without sweep the population of excited state oscillates symmetrically. For a simple monotonically increasing or decreasing sweep around resonance, it behaves like a Gaussian pulse with linear sweep (Fig. 4b). These results essentially confirm another important implication of the adiabatic principle: that the exact amplitude of the pulse is not very important under the adiabatic limit. Again, for this simple case, we are able to invoke the concept of ARP for multiphoton interaction to explain the inversion.

The phase modulated overlapped Gaussian pulses are of interest since Meshulach and Silberberg had experimentally switched the phase of the second pulse with respect to the first pulse and demonstrated two-photon excited state population modulation. However, the phase switch in their pulse shapes was abrupt as given by Eqn. (15), and thus did not satisfy the ARP condition. As a result the population transfer with such pulses are very heavily dependent on the actual shape of the pulse. Figs. 5 shows that the upper state population for two photon absorption in the absence of one photon absorption is heavily dependent on the nature of the phase step, the intensity and the extent of overlap of the pulses. At some particular phase switch, there is no excited-state population, and they called it the dark pulse. We show that it is indeed true for a specific overlapped amplitude profile and intensity for a given phase switching position. These dark pulses, however, are sensitive to the exact nature of the amplitude profile and intensity.

If instead we choose a smoothly varying linear frequency sweeping to the two-photon resonance and then away from resonance, as given by Eqn. (16), the results are quite robust to the exact nature of the amplitude profile and intensity (Fig. 6). At detuning zero and for small values of Rabi frequency, we have some population in excited state. However, when the intensity of applied pulse increases, the excited state population returns to zero. In other words, we are sending shaped pulse into the two-level system but finally there is no excited-state population. Curiously enough, for such pulses, the population is asymmetric
about detuning from resonance. In fact, Fig. 6 clearly shows that the population transfer occurs at some non-zero detuning values at higher Rabi frequencies when it does not have any excitation at resonance and behaves as a dark pulse. This result can be understood by examining the evolution of the dressed states [17]-[19] with time (Fig. 7). When the effect of the pulse cannot be felt by the system at very early or and at very late times with respect to the presence of the pulse, each dressed state essentially corresponds to the single bare state ($|\alpha\rangle \rightarrow |1\rangle$ and $|\beta\rangle \rightarrow |2\rangle$). It is only during the pulse that the dressed states change in composition and evolve as a linear combination of the two bare states. The proximity of these dressed states during the pulse essentially determines the population exchange. The higher Rabi frequencies cause a stark shift in the dressed states so that at resonance there is no population exchange. Under such stark shifted condition, resonance occurs at some specific non-zero detuning value where Rabi oscillations are seen in Fig. 6. These results are completely general for a simple case of a two-level system, where only an N$^{th}$ photon transition is possible. The phase change of the overlapping Gaussian pulses essentially provide an additional parameter to control the population evolution of a simple two-level type of system that supports only an N$^{th}$ photon transition.

IV. CONCLUSIONS

In this paper, we have explored the effects of ultrafast shaped pulses for two-level systems that do not have a single photon resonance by developing a multiphoton density-matrix approach. We took advantage of the fact that dynamics of the intermediate virtual states are absent in the femtosecond timescales, and demonstrated that many multiphoton results can be surprising similar to the well-known single photon results. When we extend the ARP to the multiphoton condition, robust population inversion and dark pulses become possible that are insensitive to the exact profile of the applied electric field. We have shown, therefore, that it is possible to extend the single photon coherent control ideas to develop femtosecond multiphoton coherent control.
REFERENCES


FIGURES

FIG. 1. Schematic of (a) single, (b) two and (c) multiphoton processes, respectively. Symbols and notations are defined in text.

FIG. 2. Comparison of the excited state population for a single photon excitation as a function of Rabi frequency, for (a) a Gaussian pulse (solid curve: without any frequency sweep; dashed curve: with linear frequency sweep), and (b) a hyperbolic secant pulse (solid curve: without any frequency sweep; dashed curve: with hyperbolic tangent frequency sweep).

FIG. 3. Excited state population for 2-photon excitation as a function of Rabi frequency and detuning for: (a) transform-limited Gaussian pulse; (b) bandwidth equivalent linearly frequency-swept Gaussian pulse; (c) transform-limited hyperbolic secant pulse; and (d) hyperbolic secant pulse with hyperbolic tangent frequency sweep.

FIG. 4. (a) Excited state population for 2-photon excitation as a function of Rabi frequency and detuning for Shaped overlapped Gaussian pulse without sweep. (b) Excited state population for 2-photon excitation as a function of Rabi frequency and detuning for shaped overlapped Gaussian pulse with a monotonically increasing linear sweep.

FIG. 5. Excited state population for 2-photon excitation as a function of phase step position (i.e., detuning) normalized to the pulse FWHM, $\tau$, for two different Rabi frequencies in the case of pulses with phase steps as given by Eqn. 15. The results are heavily subjective to the choice of parameters (as we show for the two Rabi frequencies used in this Fig. that differ by less than 5%), and are thus non-adiabatic, as discussed in the text.

FIG. 6. Excited state population for 2-photon excitation as a function of Rabi frequency and detuning for shaped overlapped Gaussian pulse with a sweep linearly approaching and going away from resonance as given by Eqn. 16. A contour plot (b) is shown for the 3-D surface plot (a) to better represent that the population exchange occurs at some detuned position for high Rabi frequencies.

FIG. 7. Energies of the two dressed states evolving with time for the shaped Gaussian pulse whose population evolution is shown in Fig. 6 at a high Rabi frequency for (a) no net population transfer at resonance, (b) the Stark-shifted frequency (detuned from resonance on one direction) where the Rabi oscillations occur, (c) the Stark-shifted frequency equally detuned from resonance to the other side where no Rabi oscillations occur.