Protecting and accelerating adiabatic passage with time-delayed pulse sequences

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Using numerical simulations of two-photon electronic absorption with femtosecond pulses in Na2 we show that: i) it is possible to avoid the characteristic saturation or dumped Rabi oscillations in the yield of absorption by time-delaying the laser pulses; ii) it is possible to accelerate the onset of adiabatic passage by using the vibrational coherence starting in a wave packet; and iii) it is possible to prepare the initial wave packet in order to achieve full state-selective transitions with broadband pulses. The findings can be used, for instance, to achieve ultrafast adiabatic passage by light-induced potentials and understand its intrinsic robustness.

I. INTRODUCTION

Many technological and chemical processes rely on electronic absorption: spectroscopic methods, photophysical events, laser-triggered reactions, to name a few. The design of linear or nonlinear laser processes that increase the yield of electronic absorption or make it more robust against control parameters or experimental uncertainties is a key drive in the field of Quantum Control[1–4]. One particular family of methods that has received considerable attention is adiabatic passage[5–7].

In adiabatic passage, population inversion between two quantum states can be achieved independently of the precise peak amplitude or pulse duration of the field, provided that the pulse area, that is, the accumulated interaction energy (integrated over time) is sufficiently large. Typically, adiabatic passage can be achieved using chirped pulses[8–11], although transformed-limited (i.e. Gaussian) pulses can be used as well in multiphoton processes. This is the case in the well known Stimulated Raman Adiabatic passage or STIRAP scheme[5–7], as well as in the strong-field scheme of Adiabatic Passage by Light-Induced Potentials or APLIP.[12–20].

Both STIRAP and APLIP were proposed (and in the STIRAP case the scheme has been implemented) using relatively long pulses, such that a single vibrational state is clearly resolved and selected during the adiabatic transition. This makes the transition relatively slow and the whole scheme more difficult to implement in the laboratory, as the coherence of the interaction must be preserved and other possible competing processes have to be decoupled. This is particularly important when the pulses are strong, as in APLIP. APLIP is a very interesting and incredibly robust laser scheme which, however, demands the use of very strong pulses, such that other unwanted transitions (e.g. ionization) usually dominate over the selected APLIP process. The realization of ultrafast adiabatic passage using femtosecond pulses would naturally enhance the applicability of the schemes and the likelihood of implementing APLIP in the laboratory.

However, using femtosecond pulses, such that the process occurs during the natural time-scale of the vibrational motion, poses other challenges, that were recently recognized. A typical example is resonant one-photon absorption between electronic states of molecules using femtosecond pulses. If the pulses are not too short that the nuclear positions are fixed, and not too intense that the potentials are completely distorted by the field, the absorption is highly suppressed[21, 22]. This is a generic behavior of systems with a dense structure of couplings (that is, without very restrictive selections rules) excited by fields whose spectral width is larger than the energy spacing of the levels. Then the initial quantum states are relatively protected from resonant transitions from other manifolds. Only very specific states allow population transfer avoiding the decoupling between the manifolds, induced by Autler-Townes splittings between the unpopulated levels[23–25]. Such states allow fast parallel transfer of population between the manifolds[21, 22].

In this work we will analyze what happens for...
non-resonant two-photon transitions using strong fields, where many assumptions used to prove the decoupling of the electronic excitation do not operate. In particular, the potential energy surface of the molecule can be severely deformed in the presence of the fields, generating light-induced potentials. Then, the energy eigenstates of the field-free Hamiltonian are not a very useful basis to follow the dynamics of the system. Hence, we will study the dynamics in the position representation, solving the time-dependent Schrödinger equation (TDSE) numerically on a grid, using the Split-operator method. As a particular example, we will analyze one- and two-photon excitation of the $A$ and $B$ electronic bands in Na$_2$. The recently developed Geometrical Optimization (GeOp) scheme will then be used to optimize the initial state, starting in a wave packet, in order to maximize the yield of absorption at the lowest possible pulse intensities, using the initial vibrational coherence to exploit parallel transfer.

Our goal is to understand the necessary conditions for inversion of the electronic populations (high yields of electronic absorption) and, secondly, for vibrational state-selective transitions, using strong pulses of increasingly shorter duration. In particular we want to understand if the use of time-delayed pulse sequences which are needed in adiabatic passage, poses an additional advantage or disadvantage with respect to the decoupling of electronic absorption. On the other hand, even for pulses with bandwidth smaller than the vibrational energy spacing, the population transfer can occur below the onset of adiabaticity, reducing the yields of (selective or overall) absorption. For such study we will analyze the performance of APLIP with ultrashort pulses, using the GeOp procedure.

The rest of the manuscript is organized as follows: In section 2 we will summarize the GeOp procedure applied to our problem and we will revisit the case of ultrafast electronic absorption in resonant conditions. The non-resonant case is analyzed in section 3, where we focus on the decisive role of the pulse sequence. In section 4 we study vibrational-state selective APLIP with ultrashort laser pulses and section 5 is the conclusions.

II. GEOMETRICAL OPTIMIZATION

As a numerical example, we will study one- and two-photon absorption in Na$_2$, between the $X$, $A$ and $B$ states, shown in Fig.1. Throughout this work we will assume the Condon limit, $\mu_{XA}(r) = \mu_{AB}(r) = 1$. Here we review the application of the GeOp procedure, applied to wave packet calculations. Using the Born-Oppenheimer approximation, we will follow the dynamics of nuclear wave packets $\psi_{X,A,B}$, starting in $\Psi(0) = (\psi_0^{X},0,0)$, the system ground state. We will use the upper case notation ($\Psi$) for the three-component (vector) nuclear wave function. To simplify the notation, whenever there is only one component different from zero (or if we are only interested in a single component) we will use the same subscripts for the full wave functions as for the components, $\Psi_{X}^{0} = (\psi_{X}^{0},0,0)$, if no confusion is possible. Formally, the solution of the TDSE can be written as $\Psi(T) = U(T,0;\mathcal{E}(t))\Psi(0)$, where $U$ is the time evolution operator. In the simplest GeOp procedure, we maximize the yield of the process for a fixed pulse $\mathcal{E}(t)$ optimizing the initial wave function, $\Psi_{opt}(0) = (\psi_{X}^{opt},0,0) = \Psi_{X}^{opt}$ with restrictions. Typically we require it to be a superposition of a small number of vibrational eigenstates of the ground electronic state $\psi_{X}^{0} = \sum_{j}^{N_c} \alpha_j \psi_{j}^{X}$. Maximizing the overall yield of absorption $\chi$ to e.g. the first electronic band $A$, requires finding the highest eigenvalue of the reduced yield operator $F_{X}^{red}$, with matrix elements

$$F_{j,k}^{red} = \langle \Psi_{X}^{k} | U(T,0;\mathcal{E}(t)) | \Psi_{A}^{0} \rangle \langle \Psi_{A}^{0} | U(T,0;\mathcal{E}(t)) | \Psi_{X}^{k} \rangle$$

(1)

Whereas, e.g. selective excitation of $\psi_{B}^{0}$ requires solving the eigenstates of

$$F_{j,k}^{red} = \langle \Psi_{X}^{k} | U(T,0;\mathcal{E}(t)) | \psi_{B}^{0} \rangle \langle \psi_{B}^{0} | U(T,0;\mathcal{E}(t)) | \Psi_{X}^{k} \rangle$$

(2)

Although we are interested in two-photon processes, for consistency, Fig.2 shows the results of the maximum eigenvalue (optimal yield) for the electronic absorption to the $A$ state using a 650 nm 40 fs full-width half-maximum (fwhm) Gaussian pulse as a function of the peak amplitude. The initial state can be a superposition of the first $N_c$ vibrational eigenstates of the ground potential. (With $N_c = 1$ the dynamics is not optimized.) For the chosen frequency the laser is resonant to the $\nu = 7 \rightarrow \nu' = 0$ transition, but $\sim 8$ vibrational levels can participate in the dynamics. These results are similar to those previously obtained but we are now using wave packet calculations and assume the Condon limit. As expected, the available (within the pulse bandwidth) initially unpopulated vibrational states induce the decoupling between the electronic states. The absorption yield however can be ramped up by optimizing the initial state using its vibrational coherences, with
the yield clearly increasing with $N_c$. Another interesting fact is that the optimization supersedes the pulse area theorem\textsuperscript{[7]}, such that the characteristic Rabi oscillations can be dumped. Obviously the solution is not robust in the adiabatic sense. For each pulse intensity a different optimal wave function must be found.

We have shown that for very long pulses the GeOp procedure cannot yield much better results. On the other hand, for very short pulses GeOp is also not needed. If the pulse duration $\tau$ is so short that there is no vibrational motion involved in the transition, then $\psi_A(\tau) \approx \psi_X(0)$. Since the $\psi_X^j(\tau)$ (for different $j$) are orthogonal, the matrix $F^{\text{red}}$ is practically diagonal, that is, the initial state (and in fact, whatever vibrational eigenstate) decouples the Raman transition and hence avoids the Autler-Townes effect on the electronic absorption. This is the regime where we can speak of vertical transitions.

III. NON-RESONANT TWO-PHOTON EXCITATION

We now turn our attention to non-resonant two-photon excitation of the $B$ state. Fig.3 show the results for different pulse sequences using 40 fs fwhm Gaussian pulses. The frequencies of the pulses are chosen such that the first transition is red-detuned with respect to the resonant excitation of the $A$ band, using 868 nm and 710 nm pulses. The dynamics is solved using the rotating wave approximation\textsuperscript{[7]} \textsuperscript{29}, although for large intensities the approximation is not really valid. In addition, the probability of ionization is neglected. Here we are interested in the qualitative aspects of the process.

Consider first two-photon absorption using coincident pulses, shown in Fig.3(a). As in the results for the one-photon resonant transition, the yield of absorption is dumped by Rabi oscillations, and it can again be improved by using the vibrational coherences optimizing the initial state. The main difference with respect to the results shown in Fig.2 is that the Rabi oscillations are faster, since the effective coupling (the Rabi frequency) depends with the square of the field amplitude, that is, with the field intensity. On the other hand the effect of the vibrational coherence is quite noteworthy and optimizing the amplitudes and phases of the first three vibrational components is typically enough to achieve almost full population inversion.

However, the dynamics is completely different when we use time-delayed pulse sequences. For the results in Fig.3(b) and (c) the time-delay is set to 20 fs. In Fig.3(b) the pulse coupling the $X$ and $A$ electronic states, $E_1(t)$, precedes the pulse coupling the $A$ and $B$ states, $E_2(t)$, whereas for the results in Fig.3(c) the opposite order, with $E_2(t)$ preceding $E_1(t)$ is chosen. The first pulse sequences is sometimes called in intuitive order while the second is considered counter-intuitive. Interestingly, the dynamics proceeds now adiabatically and there are no Rabi oscillations (or very attenuated) in both pulse sequences. The time-delayed pulses exert an effect similar to an effective chirp, facilitating the adiabatic passage of the population, regardless of the dynamic decoupling induced by the initially unpopulated levels within the pulse bandwidth. The transition, however, is not state-selective. The initial state can be optimized accelerating the onset of full adiabatic passage, that is, the effective Rabi frequency becomes larger when the appropriate vibrational coherences are used.

Regarding the order of the sequence, the adiabaticity is better preserved using the intuitive sequence. However, this is due to the choice of pulse frequencies. It is well known that adiabatic passage can proceed through a light-induced potential using a counter-intuitive sequence if the frequencies are chosen such that $\omega_1$ is tuned to the blue of the first electronic band. This is the basis of the APLIP process. In Fig.3(c) we show the results for this case (dotted lines), using pulses of 566 and 1259 nm wavelengths (for $\lambda_1$ and $\lambda_2$, respectively).
FIG. 4: Yield of selective excitation of the ground vibrational level of the $B$ state, as a function of the pulse duration (fwhm), using a counterintuitive pulse sequence with peak amplitude of $\mathcal{E}_0 = 0.01$ a.u.

IV. TOWARD ULTRAFAST SELECTIVE APLIP

We have shown that two-photon transitions with time-delayed pulses and in particular APLIP are intrinsically protected against Autler-Townes decoupling. We have optimized the initial state preparing particular superpositions of vibrational levels to accelerate the onset of the adiabatic passage. However, the transition is not state-selective. Can we use the GeOp procedure to achieve ultrafast selective APLIP?

In Fig. 4 we show the yield of selective excitation of the $\Psi_B^0$ state using the GeOp method [Eq.(2)] with pulses of increasing duration using the APLIP pulse sequence with peak field amplitudes $\mathcal{E}_0 = 0.01$ a.u. and the previous wavelengths. The time-delay is set as half the fwhm. Using pulses longer than 1 ps the APLIP scheme is selective. Although for all cases considered here there is electronic population inversion, excited vibrational levels are increasingly populated using shorter pulses. For durations of 100 fs the selective yield is practically zero. However, starting in optimized superpositions states one can recover the full state-selective population transfer. The number of vibrational levels of the $X$ electronic state that must be included in the optimal initial wave function must increase as the pulses become shorter.

In order to understand the optimization mechanism one must consider the source of adiabaticity in the transfer. In APLIP the initial wave function is propagated on a light-induced potential (LIP) that connects the ground state with the second excited electronic state. During the process the wave packet must remain in the bottom of the LIP, that is, it must be the ground vibrational instantaneous eigenstate of the LIP. This requires the process to be quasi-static. Changes in the LIP must be done so slow as to allow the wave function to adapt, in a Born-Oppenheimer way. If the pulses are short, the changes in the LIP impart a momentum on the wave function inducing vibrational excitation. In Fig. 5 we show the evolution of the average momentum of the system wave function $\langle \Psi(t)|p|\Psi(t)\rangle \equiv \langle p(t) \rangle$. The selective transfer can only be regained when the initial wave packet has an initial (opposite) momentum $\langle p(0) \rangle$ that compensates the effect of the field on the wave function.

The time-symmetry that is apparent in Fig. 5 can also be observed in the dynamics in the position representation shown in Fig. 6, where we use 100 fs (fwhm) pulses with $\mathcal{E}_0 = 0.01$ a.u. Allowing for enough vibrational states in the initial optimized wave function, the GeOp procedure essentially provides the same initial solution as that obtained by propagating backwards in time the target wave function, $\Psi_X^{\text{opt}} \approx U(0,T,\mathcal{E}(t))|\Psi_B^0\rangle$.

V. CONCLUSIONS

The vibrational coherence plays an important role in accelerating electronic absorption. Hence, preparing an initial wave packet opens the gate to new schemes of
ultrafast population inversion\cite{32,33}. In this work we use the recently proposed GeOp procedure to obtain the optimal parameters of the initial wave packet. This is essential in resonant one-photon transitions, as the Autler-Townes splittings considerably reduce the yield of absorption. However, by using time-delayed pulse sequences the yield of non-resonant two-photon absorption is already protected from the Autler-Townes splittings. Time-delayed pulse sequences possess an inherent robustness that make two-photon transitions particularly interesting for quantum control of population transfer. However, an initial wave packet can still be used to reduce the onset of adiabatic passage, making population inversion possible with weaker or shorter fields, which pose additional advantages to the experimental implementation of such schemes. This is particularly the case in APLIP. We have shown that one can prepare ultrafast-

APLIP scenarios with ultrashort pulses and moreover, the APLIP process can be state-selective provided that the initial wave packet overlaps a sufficiently large number of vibrational levels.

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