Dark pulses for resonant two-photon transitions

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We investigate the excitation of an atom or molecule via two-photon absorption induced by an ultrashort laser pulse in the perturbative intensity regime. We show that the probability for a resonant transition, i.e., with an intermediate state within the spectral width of the pulse, can be reduced to zero by pulses having a θ-phase step at a certain detuning $\delta\omega$ from the central frequency. Our theoretical predictions are confirmed by numerical calculations for the $4s \rightarrow 4d$ transition in the potassium atom.

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I. INTRODUCTION

Ultrashort laser pulses are nowadays used as an effective tool to steer quantum processes in atoms and molecules [1]. The central idea of quantum control is to provide schemes to either maximize or minimize the probability of a transition; a variety of such control schemes have been proposed and demonstrated [2,3]. For example, the pathway to a desired final state can be controlled by the time delay between two pulses [4,5]. Other prominent control schemes are based on the interference between two different pathways (e.g., one-photon vs three-photon interference) to a final channel [6] or on the coherent population transfer among quantum states using the technique of stimulated Raman adiabatic passage [7].

The ability to generate ultrashort laser pulses with almost arbitrary temporal shape through the manipulation of the spectral phases and amplitudes of the different frequency components of the pulse [8] has further expanded the range of quantum control [9,10]. In the nonperturbative high intensity regime it is difficult to theoretically assess the field parameters relevant for the control of a multiphoton transition and/or the possible degree of control. Significant progress has been, however, achieved in the case of perturbative two-photon transitions [11–14]. It has been shown that in a two-level system the two-photon absorption can be annihilated by tailoring the spectral phase function of the laser pulse [11,12]. Since no net transition is induced, such pulses are also called dark pulses. For transitions involving an intermediate resonance, with shaped laser pulses the two-photon absorption probability could be significantly enhanced beyond the level achieved with transform-limited pulses [13].

In this work we revisit the problem of resonant two-photon transitions and show that even in this case it is possible to form a dark pulse. The paper is organized as follows: In the next section we outline the theoretical formulation for the resonant and nonresonant two-photon transitions in the perturbative intensity regime. We then discuss the possibility to induce a net-zero transition probability in the general case and identify the so-called θ-phase step pulses as a simple pulse form to annihilate the resonant two-photon absorption. Finally, we confirm our theoretical predictions by numerical results for the $4s \rightarrow 4d$ transition in the potassium atom.

II. DARK PULSES AND θ-PHASE STEP MODULATION

We consider a laser induced transition between two bound states of an atom or a molecule, e.g., between the ground state $|g\rangle$ and an excited state $|f\rangle$. The laser pulse is assumed to be linearly polarized, given by its electric field $\boldsymbol{E}(t) = E(t)\hat{z}$, with a central frequency ω_L which equals half the transition frequency $\omega_f - \omega_g$. At sufficiently low field intensities the transition probability is given by the second-order term of the perturbation series (for a general derivation see the Appendix, Hartree atomic units are used: $e=m=\hbar=1$):

$$P_{f,g} = |A_{f,g}|^2 = \left| -i \sum_m \langle f|\hat{z}|m\rangle\langle m|\hat{z}|g\rangle \times \int \frac{\tilde{E}(\omega_L+\omega')\tilde{E}(\omega_L-\omega')}{\omega_g+\omega_L+\omega'-\omega_m+i0} d\omega' \right|^2, \quad (1)$$

where $\tilde{E}(\omega)$ is the Fourier transform of the pulse and the summation or integration is over a complete set of eigenstates $\{|m\rangle\}$ with frequencies ω_m.

If all intermediate states are off-resonant, i.e., $\omega_g+\omega_L-\omega_m$ for each m is much larger than the spectral width of the pulse $\Delta\omega$, in the denominator of Eq. (1) ω' can be approximated by 0 and the delta term in the expansion of the singularity can be neglected. Thus $P_{f,g}$ can be approximated by [12]

$$P_{f,g}^{(nonres)} \approx \left| -i \sum_m \frac{\langle f|\hat{z}|m\rangle\langle m|\hat{z}|g\rangle}{\omega_g+\omega_L-\omega_m} \times \int \tilde{E}(\omega_L+\omega')\tilde{E}(\omega_L-\omega')d\omega' \right|^2. \quad (2)$$

As is evident from Eq. (2) and has been shown by Meshulach and Silberberg [11,12] the probability for a nonresonant two-photon transition is maximized for any antisymmetric spectral phase distribution around the central laser frequency ω_L including the transform limited pulse as a special case. On the other hand, the power spectrum of the pulse can be tailored such that the pulse induces a zero net probability to find the system in the excited state. Pulses with a π-phase step at a certain detuning, defined by

$$\tilde{E}(\omega) = \begin{cases} \tilde{E}_{\mathrm{TL}}(\omega) & \text{for} \quad |\omega| > \omega_L + \delta\omega \\ e^{i\pi}\tilde{E}_{\mathrm{TL}}(\omega) & \text{for} \quad |\omega| < \omega_L + \delta\omega \end{cases}, \tag{3}$$

where $\delta\omega$ is the detuning parameter controlling the position of the step and $\tilde{E}_{\mathrm{TL}}(\omega)$ is the transform limited Gaussian pulse, are particular simple examples of such so-called dark pulses [11,12,14].

In the (general) case of a resonant transition Eq. (1) can be written as a sum of two terms [13]:

$$P_{f,g}^{(res)} = \left| -\frac{i}{2}\sum_m \langle f|\hat{z}|m\rangle\langle m|\hat{z}|g\rangle \times \left\{ \pi\tilde{E}(\omega_f - \omega_m)\tilde{E}(\omega_m - \omega_g) + i\mathcal{P}\int \frac{\tilde{E}(\omega_f - \omega')\tilde{E}(\omega' - \omega_g)}{\omega' - \omega_m} d\omega' \right\} \right|^2, \tag{4}$$

where $\mathcal{P}$ is Cauchy's principal value. The first term depends on the spectral components of the pulse at the resonant frequencies and determines the real part of the amplitude, while the second term contains an integration over all the other frequencies and sets the imaginary part. It is the second term which enables an enhancement of the transition probability beyond the level achieved by the transform limited pulse as shown by Dudovich *et al.* [13].

We now turn to our objective to finding a dark pulse for a resonant two-photon transition. As can be seen from Eq. (4) the amplitude of such a transition is, in general, complex. In order to control (annihilate) both values, namely the real and the imaginary part of the amplitude, two control parameters are needed. As we will show below, this can be achieved in a simple way by pulses with a θ-phase step at a certain detuning $\delta\omega$, defined as

$$\tilde{E}(\omega) = \begin{cases} \tilde{E}_{\mathrm{TL}}(\omega) & \text{for } |\omega| > \omega_L + \delta\omega \\ e^{\pm i\theta}\tilde{E}_{\mathrm{TL}}(\omega) & \text{for } |\omega| < \omega_L + \delta\omega \end{cases}, \tag{5}$$

where the positive (negative) sign applies for the positive (negative) part of the Fourier frequency spectrum. This reflects that the two parts of the spectrum are complex conjugate to each other, since the electric field is a real valued quantity. Thus in the experiment both parts are addressed simultaneously by the same parameter θ.

Please note that the set of pulses, defined by Eq. (5), includes the transform limited pulse (for $\theta=0$) and pulses with a π-phase step (for $\theta=\pi$) as special cases. All pulses of this set have the same energy, since they differ in their phases, but not in their amplitudes. From Eq. (1) it is easy to see that

$$A_{f,g}(\delta\omega, \theta) = \exp(2i\theta)A_{f,g}(-\delta\omega, -\theta), \tag{6}$$

where $A_{f,g}(\delta\omega, \theta)$ is the transition amplitude obtained using a pulse with a θ-phase step at $\delta\omega$. Therefore we may restrict our analysis to phase steps at negative values of $\delta\omega$, having in mind that Eq. (6) determines a second (set of) solution(s) at positive detunings.

In order to simplify the further discussion, we now restrict our analysis to two-photon transitions with *one* intermediate resonant state. For this case the effect of the θ-phase step modulation is illustrated in Fig. 1(a), where the real and the imaginary parts of the transition amplitude induced by certain modulated pulses are exemplified. Any θ-phase step at an arbitrary detuning $\delta\omega$ influences the real and/or the imaginary part of the complex transition amplitude.

Let us discuss a few special cases: First, it easily seen from Eq. (4) that for a θ-phase step at the central frequency ω_L ($\delta\omega=0$) the absolute square of the amplitude is independent of the value of θ [see circle with zero as center in Fig. 1(a)]. Thus all pulses of this subgroup will induce the same transition probability as the transform limited (Gaussian) pulse independent of the phase step [cf. Fig. 1(c)]. We may note parenthetically that the same applies for the unimportant cases of an application of the phase step at a detuning outside the pulse spectrum ($|\delta\omega| \gg \Delta\omega$).

Next, application of a π-phase step as a function of the step position $\delta\omega$ does continously change the imaginary part of the amplitude. On the other hand the real part switches between two values for $|\delta\omega| < |\omega_L - \omega_m|$ and $|\delta\omega| > |\omega_L - \omega_m|$, respectively. This is illustrated by the vertical lines in Fig. 1. Note that the original transform limited (Gaussian) pulse corresponds to a pulse with a π-phase step below the pulse spectrum ($\delta\omega \ll -\Delta\omega$). The imaginary part of the amplitude and the corresponding transition probability [cf. Fig. 1(b)] tends to infinity as $|\delta\omega|$ approaches the resonance $|\omega_L - \omega_m|$. The probability of a resonant transition cannot be vanished using pulses having a π-phase step.

Finally, a variation of θ between 0 and 2π at any detuning $\delta\omega$ will result in a loop in the complex amplitude plane. The result for the transform limited pulse ($\theta=0$) is on each of these loops. The smaller the parameter $\delta\omega$, the smaller is the radius of the loop, since the variations from the amplitude obtained with the transform limited pulse are smaller [see also the numerical results in Fig. 4(a)].

From the analysis above it is clear that at negative detunings there exists a pair of parameters $(\theta_{dark}, \delta\omega_{dark})$ for which the amplitude of the resonant two-photon transition is zero. Due to the relation in Eq. (6) a second pair is given by $(-\theta_{dark}, -\delta\omega_{dark})$. Thus there are two dark pulses in the set of pulses defined by Eq. (5). The corresponding parameters can be determined by variation in an experiment or by numerical simulations, as shown in the next section.

III. NUMERICAL RESULTS FOR THE $4s \rightarrow 4d$ TRANSITION IN POTASSIUM ATOM

In this section we will verify our theoretical conclusions by results of numerical calculations. We have chosen the potassium atom for our numerical studies, since it has one valence electron and can be treated as single-active-electron atom (similar to the hydrogen atom). The relevant energy levels in the potassium atom are shown in Fig. 2. A two-photon transition in the K atom between the ground state $[4S_{1/2}(4s)]$ and the $4D_{5/2,3/2}(4d)$ state can be induced by a laser pulse with a central wavelength of 730 nm. The energy differences to the intermediate $4P_{3/2}(4p)$ state correspond to 770 nm ($4S$ state) and 694 nm ($4D$ state). This transition is well suited for our considerations, since the intermediate state is resonant for short pulses with a large bandwidth but

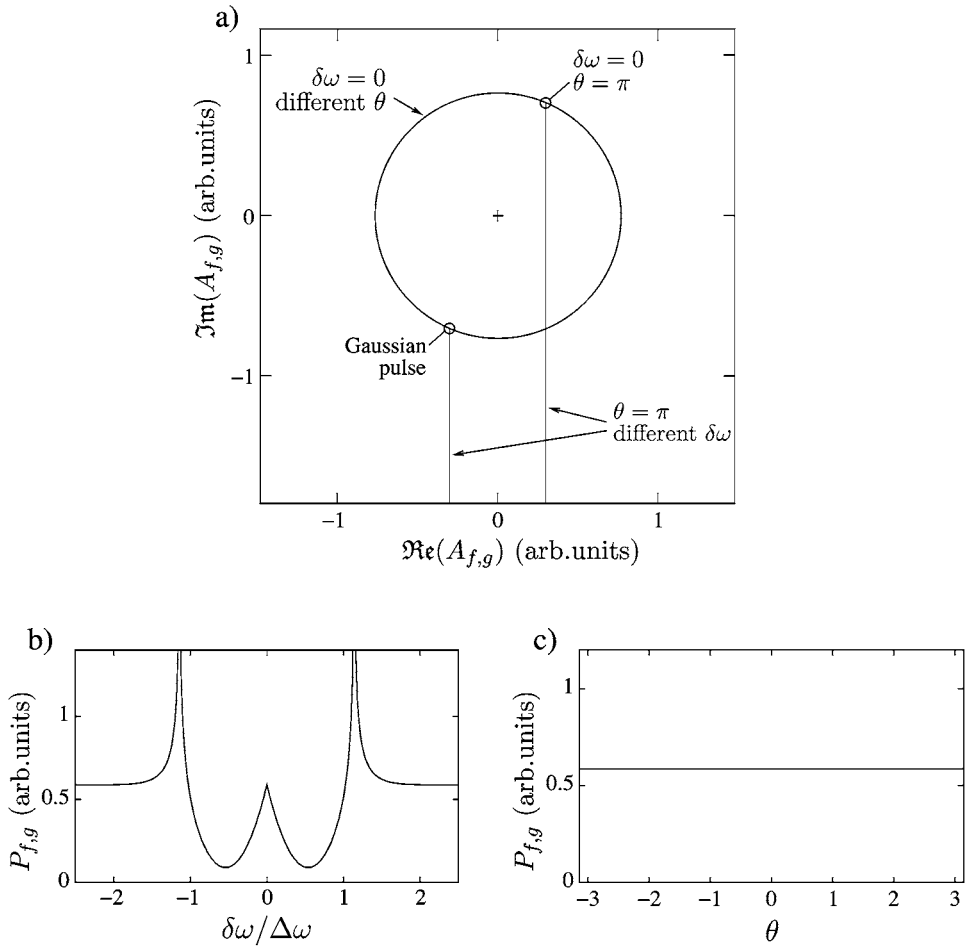

FIG. 1. (a) Imaginary vs real part of resonant two-photon transition amplitudes $A_{f,g}$. Shown are examples for the transform limited (Gaussian) pulse, pulses with θ-phase steps at the central frequency ω_L (circle), and pulses with a π-phase step at different detunings $\delta\omega/\Delta\omega$ from the central frequency (lines). Transition probabilities (b) as a function of the detuning for pulses with a π-phase step and (c) as a function of θ for pulses with a θ-phase step at the central frequency.

almost nonresonant for long pulses having a small bandwidth. For the actual calculations we have considered pulses with transform-limited durations (FWHM) of 35 optical cycles (or bandwidth of 6.5 nm) and 7 optical cycles (or bandwidth of 31 nm), respectively.

A. Theoretical description

To obtain the time-dependent amplitudes of the different states, $a_n(t)$, we first expand the wave function in a basis of atomic eigenstates $\{|n\rangle\}$:

$$|\psi(t)\rangle = \sum_n a_n(t)|n\rangle. \tag{7}$$

The basis set used in the actual simulations covers a large number of bound states of the potassium atom, namely $4s$-$46s$, $4p$-$21p$, $3d$-$46d$, $4f$-$14f$, $5g$. The neglect of higher Rydberg states and the continuum does not influence the conclusions concerning dark pulses with θ-phase steps.

Using the expansion in Eq. (7) in the time-dependent Schrödinger equation of the one-electron atom interacting with an external field one obtains a set of coupled ordinary

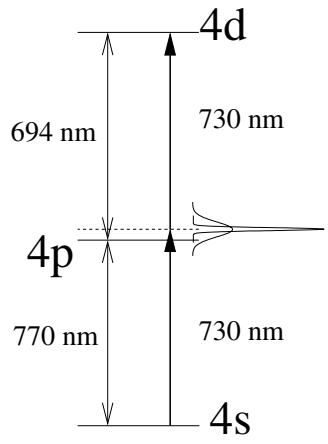

FIG. 2. Energy-level diagram of two-photon transitions in a potassium atom. Note that the $4p$ level lies well within the spectrum of the shorter pulse [7 optical cycles; bandwidth: 31 nm full width at half maximum (FWHM)], but outside the bandwidth of the longer pulse (35 optical cycles; bandwidth: 6.5 nm FWHM).

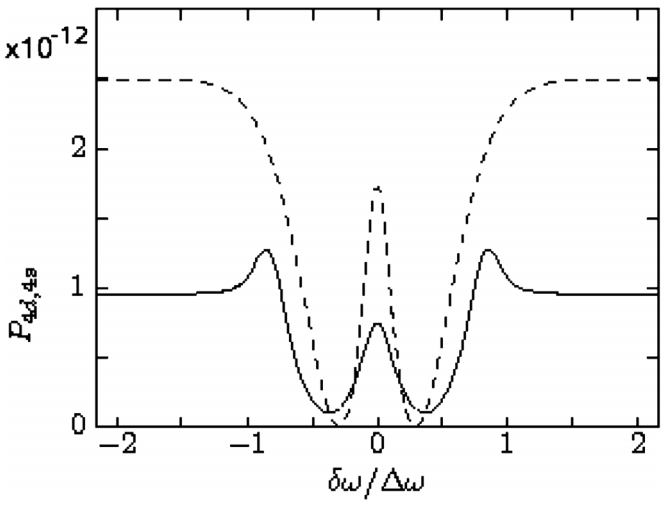

FIG. 3. The population in the excited $4d$ state for long and short π-phase step pulses at different step position $\delta\omega$ (scaled in units of $\Delta\omega$). The solid curve corresponds to the transition induced by the short resonant laser pulse, while the dashed line represents the results obtained for the long nonresonant pulse.

differential equations for the time-dependent coefficients $a_n(t)$, which can be solved using standard techniques. The numerical results presented below are obtained using the velocity gauge, which in general have been found [15] to provide more accurate results than the length gauge. For a one-electron atom, the transition amplitude between two states $|n,l\rangle$ and $|n',l'\rangle$ in the velocity gauge is related to those in the length gauge by [16]

$$\langle n',l'|\hat{p}_z|n,l\rangle \approx i(E_{n'}-E_n)\langle n',l'|\hat{z}|n,l\rangle. \tag{8}$$

The latter are obtained from the averaged oscillator strengths $S^{(NIST)}_{n'l',nl}$ given in the *NIST Atomic Spectra Database*, via [16]

$$\langle n',l'|\hat{z}|n,l\rangle = \pm\sqrt{S^{(NIST)}_{n'l',nl}}\frac{l_{\max}}{\sqrt{2l_{\max}(4l^2_{\max}-1)}}, \tag{9}$$

where $l_{\max}=\max(l,l')$. The negative sign applies for $n=n'$ and the positive otherwise.

B. Amplitudes for θ-phase step pulses

In Figs. 3 and 4 we present the results for the excitation to the $4d$ state of the K atom for pulses with different phase steps. Before we turn to the general case, let us discuss the results for the conventional π-phase step pulses, shown in Fig. 3. Plotted are the transition probabilities as a function of the step function $\delta\omega$ induced by the long nonresonant (FWHM of 35 optical cycles, dashed line) and the short resonant (FWHM of 7 optical cycles, solid line) pulses. The peak intensities were chosen to be 3×10^6 W/cm^2 (short pulse) and 1.34×10^6 W/cm^2 (long pulse), such that both pulses have the same energy.

As can be seen from Fig. 3, the transition probability has two zeros for the long pulse (dashed line), which confirms the results of earlier studies [11,12,14] that a nonresonant two-photon absorption can be annihilated using π pulses. In

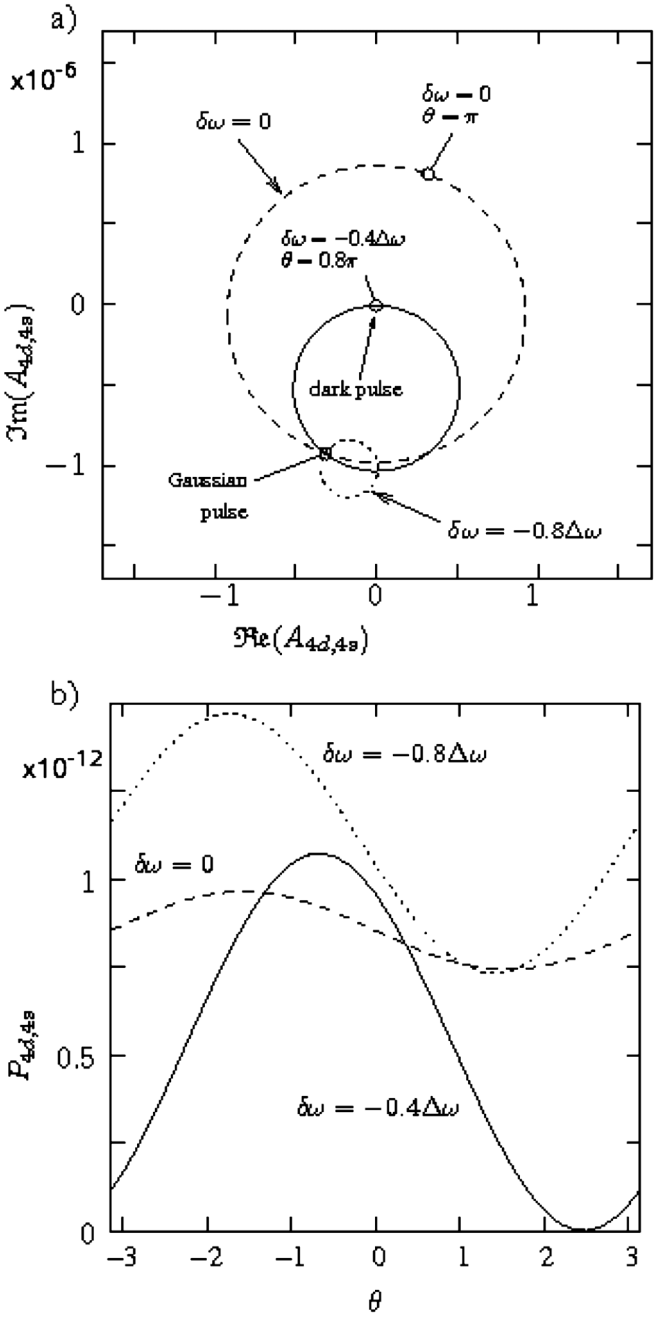

FIG. 4. (a) The imaginary (vertical axis) vs the real (horizontal axis) part of the final amplitude of the $4d$ state and (b) the transition probabilities as a function of θ for application of the θ-phase step function at different detunings $\delta\omega$ used for the short resonant laser pulse.

contrast, in the case of the resonant two-photon transition induced by the short pulse (solid line) the final state population does not vanish independent of the π-phase step position. Thus for a resonant two-photon transition there does not exist a dark π pulse. Note that in the latter case the numerical results do not reproduce the "infinite" enhancement of the imaginary part, as predicted by Eq. (1) for a π-phase step at the resonance. This is due to the fact that in the actual calculations we have smoothed the phase step over a small frequency window.

The probability for the resonant transition can, however, be annihilated as soon as phase steps with values different from $\theta=\pi$ are used. This is demonstrated through the numerical results in Fig. 4. Shown are the transition amplitude [panel (a)] and the final-state populations [panel (b)] for changes of θ between 0 and 2π at certain step positions $\delta\omega$. The numerical results are found to fully confirm our theoretical conclusions, discussed in Sec. II. Changes of θ result in a loop for the amplitude in the complex plane. Any θ-phase step at the central frequency ($\delta\omega=0$, dashed lines) results in almost the same transition probability, the small variation from this trend in the numerical results is again due to the smoothening of the phase step over a small frequency window. The smaller the parameter $\delta\omega$, the smaller is the radius of the loop in the amplitude representation. And, finally, the goal to form a dark pulse for the $4s \rightarrow 4d$ transition in the K atom via the intermediate resonant $4p$ state is indeed achieved for $\theta_{dark}=0.8\pi$ and $\delta\omega_{dark}=-0.4\Delta\omega$ (solid line). Our numerical calculations (results not shown) confirm that a second dark pulse is given by $\theta_{dark}=-0.8\pi$ and $\delta\omega_{dark}=0.4\Delta\omega$, as expected from Eq. (6).

C. Summary

To summarize, we have studied the general case of a two-photon transition including an intermediate state within the spectral width of the pulse. We have shown that the transition probability can be annihilated by tailoring the spectral phase of the pulse. Pulses with a θ-phase step at a certain detuning from the central frequency are found to be particular simple examples for such dark pulses. Our theoretical predictions are confirmed by results of numerical calculations for the $4s \rightarrow 4d$ transition in the K atom.

APPENDIX: PERTURBATION THEORY IN THE FREQUENCY DOMAIN

Here we present a derivation of the transition amplitude to any order in the coupling of the electron to a short laser pulse using perturbation theory formulated in the frequency domain. The Schrödinger equation and the wave function $\psi(t)$ can be written using the time-dependent perturbation method as (see, e.g., Ref. [17], Sec. 35, [18], Chap. XIII):

$$i\dot{\psi}(t) = [H_0 + \lambda h(t) H_I]\psi(t), \tag{A1}$$

$$\psi(t) = \psi^{(0)}(t) + \lambda\psi^{(1)}(t) + \lambda^2\psi^{(2)}(t) + \cdots, \tag{A2}$$

where H_0 is the (e.g., atomic or molecular) reference Hamiltonian, λ is an expansion parameter, H_I is a constant matrix, and $h(t)$ is a real-valued time-dependent function (e.g., the electric field of the linearly polarized laser pulse). After standard steps one gets the following set of equations:

$$i\dot{\psi}^{(0)}(t) = H_0\psi^{(0)}(t), \tag{A3}$$

$$i\dot{\psi}^{(n)}(t) = H_0\psi^{(n)}(t) + h(t)H_I\psi^{(n-1)}(t), \quad n = 1,2, \ldots . \tag{A4}$$

The latter equation (A4) is a multidimensional complex harmonic oscillator equation for $\dot{\psi}^{(n)}(t)$ with the driving force $h(t)H_I\psi^{(n-1)}(t)$. Let us now switch to the frequency domain and denote the Fourier transforms of the wave function and $h(t)$ by $\tilde{\psi}(\omega)$ and $\tilde{h}(\omega)$, respectively. Using $|\psi(t)\rangle = \exp(-i\omega_g t)|g\rangle$ as the initial unperturbed solution, where $|g\rangle$ is, e.g., the ground state of the atom or molecule, we get as a recursive solution of the above equations by using the propagator of the harmonic oscillator with appropriate boundary conditions

$$|\tilde{\psi}^{(0)}(\omega)\rangle = \sqrt{2\pi}\delta(\omega - \omega_g)|g\rangle \tag{A5}$$

$$|\tilde{\psi}^{(n)}(\omega)\rangle = \frac{1}{\sqrt{2\pi}}\frac{1}{\omega - H_0 + i\epsilon}H_I \times \int_{-\infty}^{\infty}\tilde{h}(\omega')|\tilde{\psi}^{(n-1)}(\omega - \omega')\rangle d\omega'. \tag{A6}$$

The amplitude in nth order of finding the atom in a particular atomic eigenstate $|f\rangle$ after the interaction with the pulse can be obtained by projection followed either by Fourier transform of Eq. (A6) or by direct integration of Eq. (A4). It is given by

$$\langle f|\psi^{(n)}(t)\rangle = e^{-i\omega_f t}\langle f|H_I\int_{-\infty}^{\infty}\tilde{h}(\omega')|\tilde{\psi}^{(n-1)}(\omega_f - \omega')\rangle d\omega', \tag{A7}$$

where ω_f is the eigenfrequency of the state $|f\rangle$. Equation (1) of the present paper is the respective expression for $n=2$ and $t \rightarrow \infty$ given in the interaction picture.

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