Highly Accurate Theoretical Simulation of the Resonant Multiphoton Ionization Processes With Simplest Atoms

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Abstract. We present an advanced theoretical approach enabling highly accurate studies of a wide class of resonant $2+1$ photoionization processes involving hydrogeic levels to be carried out. AC-Stark shifts, non-zero ionization rates of all states involved are naturally incorporated into the theoretical setup developed, together with spatial and temporal inhomogeneities of the laser signal, fine structure contributions, as well as second order Doppler shifts. In contrast with the usual perturbative technique, the time evolution of the atomic states is described by direct numerically solving a coupled system of time-dependent differential relativisitic equations. Particular numerical simulations have been carried out to model two-step 3-photon ionization process in muonium, $1S \xrightarrow{2\hbar\omega} 2S \xrightarrow{\hbar\omega} \varepsilon P$, induced by a CW laser signal of high intensity.

1 Introduction

Multiphoton resonant processes with simplest fundamental quantum systems exposed to sufficiently strong laser fields attracted conspicuous attention over last years. Currently, this interest is being especially strongly stimulated by dramatic improvements in the precision of measurements presently attainable in spectroscopic experimental studies of hydrogenic and few-particle atoms. Using methods of ultra high precision Doppler-free spectroscopy, particularly impressive results have been recently obtained in studies of fundamental bounded systems such as *hydrogen* (H) and its *natural* isotopes deuterium (D) and tritium (T) [1,2,3,4,5,6,7], *positronium* [8,9], denoted Ps $= (e^+ - e^-)$, *muonium* [10,11,9,12,13,14,15], denoted (M $= \mu^+ - e^-$), and the helium atom (He) [16] [1]. With these systems the dominant electromagnetic part of the atomic binding energy can be calculated to a very high precision, which, in combination with appropriate results of highly accurate measurements, enables the fundamental constants like, e.g., particle masses or the fine structure constant α to be extracted [17]. Furthermore, the influences of other interactions, particularly strong and weak, along with possible contributions from yet unknown forces, can be investigated as well. In the latter case, either new effects beyond the standard theory may be discovered or respective speculative theoretical models can

[1] See also the respective contributions in this volume for a more extended list of references and as yet unpublished results

be restricted with respect to their parameters. A very high precision appears, apparently, to be a basic requirement with any measurements aimed at achieving either of these goals. This demands at the same time that systematic spurious effects introduced in the course of experimental procedures be understood at a level where they might not mimic essential physical contributions. In the past, the interaction of atoms with electromagnetic radiation was usually treated in optical spectroscopy using idealized assumptions regarding temporal and spatial properties of radiation. It can be foreseen, therefore, that somewhat more accurate methods will be needed with many forthcoming high-precision spectroscopy projects. This has been demonstrated in the case of muonium laser spectroscopy [14,18,19], where a relevant accuracy could be attained only using a numerical approach based on density matrix formalism and measured properties of the laser light.

It has been recognized already a long time ago (see [20,21] for a more detailed discussion) that the $1S-2S$ transition offers unique opportunities for high precision spectroscopy due to the narrow natural line width, $\Gamma_{2s}^{(\mathrm{nat})}$, of the $2S$-state. Experimentally, the $1S-2S$ transition can be induced Doppler-free by absorbing two photons from two identical counter-propagating laser beams being generated by either a sufficiently powerful *pulsed* laser (as with muonium [14]) or a *continuous* laser (as with hydrogen [5,6]). In the latter case, for example, where $\Gamma_{2s}^{(\mathrm{nat})} \approx 1.3$ Hz, the quality factor of $\delta\nu/\nu \simeq 10^{-15}$ has already been achieved today [6] by accurately measuring the radiation resulting from the two-photon quenching of the $2S$-state: $2S \xrightarrow{2\hbar\omega} 1S$. Unlike the hydrogenic case, it appears to be technically difficult to observe the $1S-2S$ transition in muonium by detecting the radiation due to the $2S$-state deexcitation. This is because of the fact that appropriate line intensities in this atom happen to be by several orders of magnitude weaker than in hydrogen, owing to much lower densities at which muonium atoms can be produced. This necessitates in turn that laser sources of much higher intensity (by a factor of 10^4, at least) must be employed to generate a detectable signal. The $2S$-state of muonium is observed, therefore, via its photoionization by the third photon absorbed from one of the laser beams: $1S \xrightarrow{2\hbar\omega} 2S \xrightarrow{\hbar\omega} \varepsilon P$. The use of this scheme in the new experimental study recently finalized at the Rutherford Appleton Laboratory has enabled the $1S-2S$ energy interval in muonium to be determined to as yet unbeatable for this system accuracy of 9.8 MHz [14]. This uncertainty was solely due to some lack of statistics and as well because of inaccuracy (≈ 0.85 MHz for muonium and ≈ 8.5 MHz for deuterium) of the laser frequency standard available at that time. The measured data have already allowed to deduce a new value for the muon mass and to establish a new limitation on the muon-electron charge equality [14]. The scheme of the study in question is presented in Fig. 1(a) where $\hbar\omega_{\mathrm{L}} \approx 3/16$ *a.u.* stands for the resonant photon energy of the 2-photon $1S \to 2S$ transition. Experimental results for muonium and deuterium are shown in Figs. 2 and 3 together with the appropriate theoretical expectations based on our past work [19].

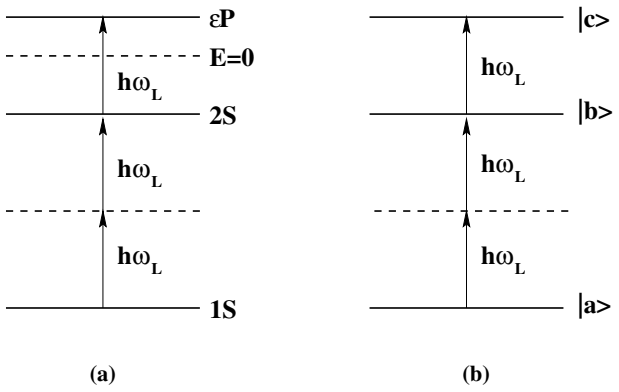

Fig. 1. (**a**) – The scheme of the new 1S-2S experiment in muonium. (**b**) – The set of states to model the stepwise 3-photon ionization

In this paper we present a highly accurate *ab initio* theoretical study to simulate, under most general condition, ionization probabilities and line profiles for two-photon resonant excitation, $|a\rangle \xrightarrow{2\hbar\omega} |b\rangle$, possibly followed by one-photon ionization, $|b\rangle \xrightarrow{\hbar\omega} |c\rangle$, occurring with any hydrogen-like levels. Our present investigation can be viewed, therefore, as an extension of our past work [19], and it is intended primarily to account for a wider class of most important systematic spurious contributions to the energy intervals that make their appearance whenever an atom is subject to laser radiation of arbitrary intensity. As an illustration of our approach, particular numerical simulation has been carried out for the $2 + 1$ resonant photoionization of the ground state in muonium. Unlike our former calculations (see Fig.4) this transition was now assumed to be induced by a continuous rather than pulsed laser light. Appropriate results can be considered, therefore, as a precise theoretical prediction which may be of great interest

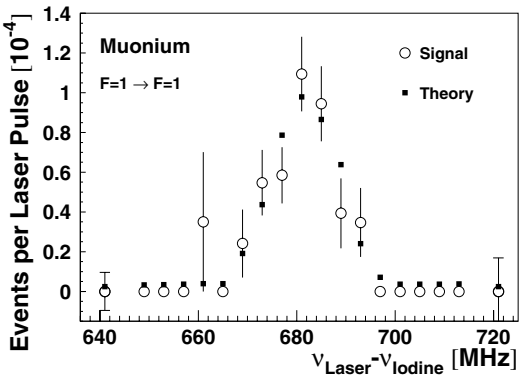

Fig. 2. Muonium 1s-2s signal [14]. The solid squares represent the theoretical expectations based on measured laser parameters and our theory [19]

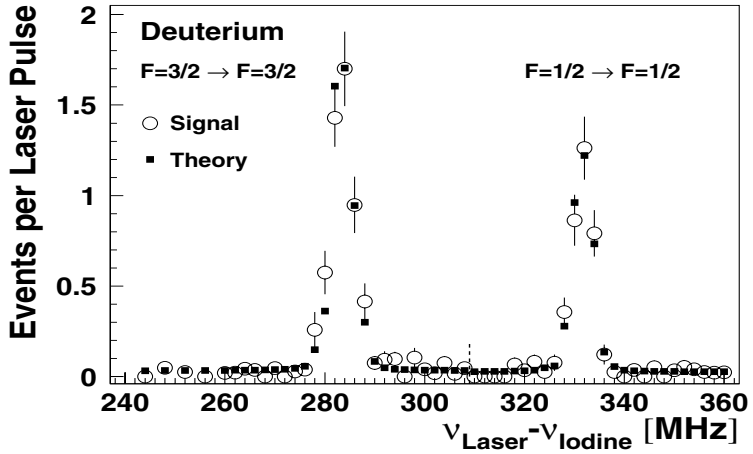

Fig. 3. Deuterium $1S-2S$ signal [14]. The solid squares represent the theoretical expectations based on shot by shot measured pulsed laser parameters and our theory [19]

and relevance in the forthcoming experimental investigations of the muonium atom by means of CW laser radiation of high intensity. Additional motivations of this study are discussed in more detail in [14,19].

Our current theoretical model constitutes a significant improvement upon our obsolete scheme [19] which has been stringently verified recently (to the accuracy of about $\simeq 2$ MHz) for the deuterium $1S-2S$ transition [14] driven by a high-power pulsed laser [22,23] with an rms chirp of 2.3 MHz (see Figs. 2 and 4). These improvements have resulted eventually in by a factor $\simeq 10$ higher overall accuracy (now, $\leq$ 100kHz) as well as in a wider scope of physical pro-

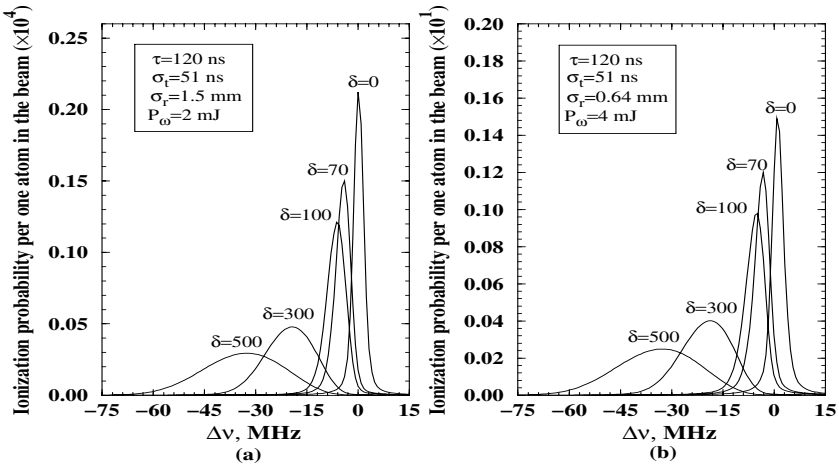

Fig. 4. The shift and broadening of the muonium 1s-2s line is simulated in (**a**) and (**a**) for various values of power P_ω, size σ_r, pulse length τ and laser chirp δ

cesses which are presently incorporated systematically into the model on the equal footing. Without imposing any restriction on the strength of the laser field, the theoretical framework developed is currently capable of accounting for its arbitrary spatial and temporary inhomogeneities, non-zero ionization rates of intermediate atomic relay levels, along with Stark shifts and appropriate exact fine structure contributions. It should be emphasized that the case of light fields with time-varying amplitudes and frequencies is also covered by our rigorous approach. Even with CW laser sources, time dependencies of the laser light's electric field and phase may arise as a result of intensity fluctuations and/or refractive index changes in any optical component along laser beam paths. Furthermore, curved wave fronts may also cause effective chirps, as seen by an atom in its rest frame moving with an average velocity v in the laboratory system. Presently, our model is capable of allowing for this movement to order $(v/c)^2$, i.e. takes into account the *second order* Doppler shifts as well. The latter feature appears to be essential for a proper interpretation of most highly accurate experimental data available now-a-days. Indeed, under common experimental conditions, the *second* order Doppler shift at the photon frequency $\omega_0 = |\mathbf{k}_0|c$, $\delta\omega = \omega - \omega_0 \simeq (v/c)^2\omega_0 \simeq 10^{-4}\omega_0$ can be of the same order of magnitude as, or even larger than, the leading Dirac α^2-corrections to the nonrelativistic energy intervals between levels i and j: $\varepsilon_i - \varepsilon_j = \varepsilon_i^{(0)} - \varepsilon_j^{(0)} + a_{ij}\alpha^2$. Here, c is the speed of light and $\alpha \approx 1/137$ is the fine structure constant. This requires that corrections to atomic energies and wave functions of order α^2 be taken into account on the same footing as those $\propto (v/c)^2$ due to the second order Doppler shifts. To incorporate naturally both corrections into our theoretical setup, the time evolution of all atomic states involved was simulated in this work by direct numerically solving a coupled system of relativistic time-dependent inhomogeneous differential equations. In regard to somewhat unique combination of the aforementioned features and the overall precision achieved thereby, our current simulations surpass most similar type of calculations performed so far [20,21,24,25,26,27,28,29,30,31,4]. This enables the model developed to be efficiently employed for a highly accurate analysis of either 2- or 3-photon resonant phenomena with few-particle systems, which are induced by either pulsed or continuous sources of laser radiation. Although technically difficult to construct, high-power continuous CW lasers offer nowadays a number of inviting and unique opportunities for ultra high precision spectroscopy with simplest atoms, especially those containing $\mu^{\pm}$-muons. This makes the current work of relevance and use both for current and future highly precise studies with various fundamental quantum systems.

2 Underlying Theory

In this section we outline a theoretical framework enabling the $2 + 1$ resonant photoionization of a hydrogenic atom to be analyzed. Generally, the process is assumed to be induced by a non-monochromatic laser field with a time-dependent amplitude and taking place in the presence of intermediate resonance. It is shown

that the phenomenon in question can be described by a coupled system of non-linear equations (7)–(9) derived upon most general conditions, without specifying particular functional forms of the laser frequency and intensity.

To model the physical situation of interest we consider, following [19], a set of three hydrogen-like levels, $|a\rangle$, $|b\rangle$ and $|c\rangle$, of an atom with the charge Z of its nucleus and the reduced mass m^*, such that their energies satisfy the inequality: $\varepsilon_a < \varepsilon_b < \varepsilon_c$; this rather general setup is shown in Fig. 1(b). It is assumed that the given 3-level system is exposed to two counter-propagating (along the z-axis) laser waves with equal time-dependent circular frequencies $\omega(t) \equiv \omega_{\rm L} + \phi(t)/t$, polarizations vectors $\boldsymbol{\epsilon}$, and wave vectors $\boldsymbol{k}_1(t) = -\boldsymbol{k}_2(t) \equiv \boldsymbol{k}(t) \parallel \boldsymbol{n}_z$, $|\boldsymbol{k}(t)| = \omega(t)/c$, with c being the speed of light. The stationary part $\omega_{\rm L}$ of the field frequency $\omega(t)$ is assumed to be such that it is in the 2- and 1-photon resonances with two pairs of states, ($|a\rangle$, $|b\rangle$) and ($|b\rangle$, $|c\rangle$). This implies that $2\pi\nu_{\rm L} \equiv \omega_{\rm L} = \omega_{b,a}/2\hbar = \omega_{c,b}$ with $\omega_{j,i} \equiv \varepsilon_j - \varepsilon_i$, $(i,j = a,b,c)$ being the energy differences. In addition, it is supposed that the $E1$-transition is forbidden between $|a\rangle$ and $|b\rangle$ and is allowed between $|b\rangle$ and $|c\rangle$.

The electric field of the laser signal with polarization ϵ can be taken in the form (the reduced atomic system of units, $\hbar = e^2 = m^* = 1$, is used throughout the paper):

$$\boldsymbol{E}_{1,2}(\boldsymbol{r},t) = \frac{1}{2}\boldsymbol{\epsilon}E_{1,2}(t)U_{1,2}(\boldsymbol{r})\exp\left\{\mathrm{i}\left(\boldsymbol{k}_{1,2}(t)\boldsymbol{r} - \omega(t)t\right)\right\} + c.c.\,, \tag{1}$$

where $U_1(\boldsymbol{r}) = U_2(\boldsymbol{r}) \equiv U(\boldsymbol{r})$ and $E_1(t) = E_2(t) \equiv E_0(t)$ denote the spatial inhomogeneity of the laser field and its time-dependent amplitude. These quantities are directly related to the laser intensity $I(\boldsymbol{r},t) = cE^2(t)U^2(\boldsymbol{r})/8\pi$ which, along with the chirped circular laser frequency $\omega(t)$, is obtainable from measurements. As usually happens in most practical situations, both the amplitude $E(t)$ and the frequency $\omega(t)$ are slow-varying functions of time, such that the magnitude of the chirp, $|\dot{\omega}(t)|$, is normally small compared with the frequency $\omega_{\rm L}$. Thus, we assume that $\omega(t)$ and $E(t)$ are subject to the following conditions [32,33]:

$$|t\dot{\omega}(t)| \ll |\omega(t) - \omega_{\rm L}| \equiv \left|\frac{1}{t}\phi(t)\right| \approx |\dot{\phi}(t)| \ll \omega_{\rm L}\,; \tag{2}$$

$$\left|\dot{E}(t)\right| \ll |\omega_{\rm L}E(t)|\ . \tag{3}$$

In the dipole approximation which happens to be accurate enough for our purposes, an *effective two-photon* operator $\widehat{Q}^{(2)}(E)$ acting on the states $|a\rangle$, $|b\rangle$ and $|c\rangle$ is defined as

$$\widehat{Q}^{(2)}(E) \equiv \boldsymbol{\epsilon}^*\cdot\boldsymbol{\alpha}\frac{1}{E - \widehat{H}_0}\boldsymbol{\epsilon}\cdot\boldsymbol{\alpha}\ . \tag{4}$$

Here, $\boldsymbol{\alpha}$ is the Dirac matrix, E is a certain energy parameter, and $\widehat{H}_0$ is the Hamiltonian of an isolated atom whose eigenvalues are denoted by ε_r: $\widehat{H}_0|r\rangle = \varepsilon_r|r\rangle$. Equation (4) can be readily inferred (see paper of V. Yakhontov in this volume) by taking into account the relativistic "atom–photon field" interaction

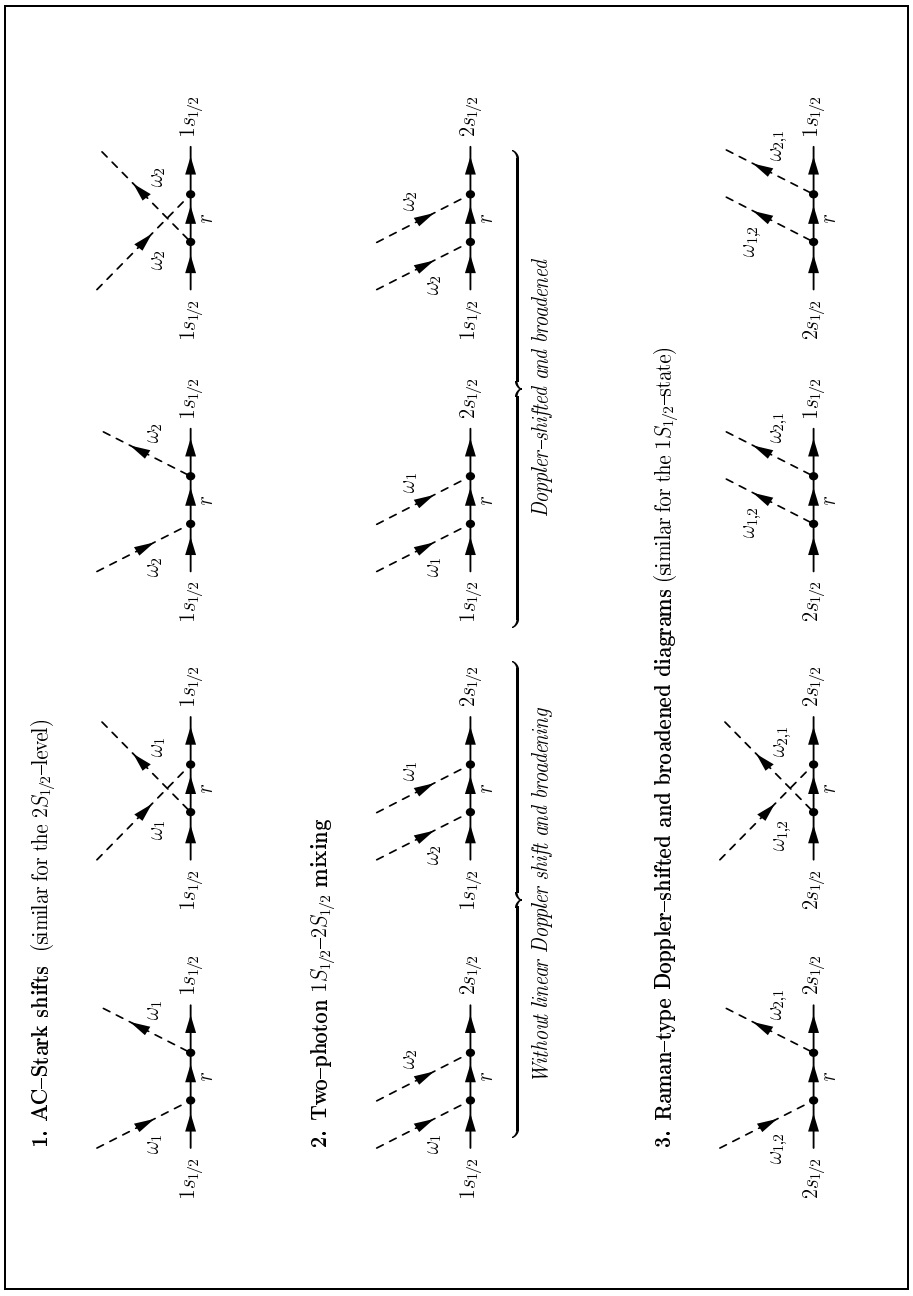

Fig. 5. Diagrams contributing to the AC Stark-shifts and mixing of the $1S_{1/2}$- and $2S_{1/2}$-levels of a hydrogen-like atom under the action of two laser waves of the frequency $\omega_{\rm L}$, counter-propagating in the direction $\boldsymbol{n}_z$. As seen by an atom in its rest frame moving with the velocity $\mathbf{v} = v\boldsymbol{n}$ relative to the laboratory system, appropriate Doppler-shifted frequencies are determined as $\omega_{1,2} = \omega_{\rm L}(1 \pm v\boldsymbol{n}\cdot\boldsymbol{n}_z/c)/\sqrt{1-(v/c)^2}$

$\widehat{V}(\boldsymbol{r},t)$ (cf. [34]),

$$\widehat{V}(\boldsymbol{r},t) = \mathrm{i}\frac{c}{2\omega_{\mathrm{r}}(t)}E_{\mathrm{r}}(t)U(\boldsymbol{r})\boldsymbol{\alpha}\cdot\boldsymbol{\epsilon}e^{\mathrm{i}\omega_{\mathrm{r}}(t)t} + c.c.\ , \tag{5}$$

in the second order of the conventional time-dependent perturbation theory [34]. Here, $E_{\mathrm{r}}(t)$ and $\omega_{\mathrm{r}}(t)$ denote the electric component (cf. (1)) and the (time-dependent) frequency of the light field as seen by the atom *in its rest frame*.

For laser parameters of interest, the validity of (5) follows from the estimate: $|\nabla U(\boldsymbol{r})| \simeq 1/\sigma_{\mathrm{r}} \approx 10^{-7} \ll |\boldsymbol{k}(t)\cdot\boldsymbol{r}| \simeq 2\pi/\lambda_{\mathrm{L}} \approx 10^{-3}$. This implies that the contribution of the quadrupole terms $\propto E_{\mathrm{r}}(t)(\nabla U(\boldsymbol{r})\cdot\boldsymbol{\alpha})$, which originate from the spatial *macroscopic* inhomogeneity of $\boldsymbol{E}(\boldsymbol{r},t)$, is expected to be a factor 10^{-7} smaller than the dipole contribution. The similar estimate holds also for corrections due to the quadrupole component $\propto E_{\mathrm{r}}(t)U(\boldsymbol{r})|\boldsymbol{k}(t)|(\boldsymbol{\epsilon}\cdot\boldsymbol{\alpha})^2$ of the field. Appropriate $E2$-contributions appear to be suppressed, therefore, by a factor 10^{-8}, at least, as compared with the dipole ones in all practically interesting situations.

The time evolution of the levels $|a\rangle$, $|b\rangle$ and $|c\rangle$ under the action of the light field can be described by a standard coupled system of time-dependent equations of the conventional perturbation theory [34] for the state amplitudes $c_{a,a}(t)$, $c_{b,b}(t)$, $c_{c,c}(t)$. The effects which are being taken thereby into account comprise the AC-Stark shifts of all levels involved, their two-photon mixing, as well as all conceivable Raman-type processes of absorption and scattering. For the particular case of $|a\rangle = |1s_{1/2}\rangle$ and $|b\rangle = |2s_{1/2}\rangle$, these are shown diagrammatically in Fig. 5. For an atom moving with the velocity $\boldsymbol{v} = v\boldsymbol{n}$ in the laboratory system, the laser frequency $\omega(t)$ undergoes a Doppler shift in the atomic rest frame. Depending on which of two counterpropagating laser beams the moving atom interacts with, two appropriate Doppler-shifted frequencies are denoted in Fig. 5 as

$$\omega_{1,2} = \gamma\omega_{\mathrm{L}}\left(1 \pm \frac{v}{c}\boldsymbol{n}\cdot\boldsymbol{n}_z\right)\ , \qquad \gamma = \frac{1}{\sqrt{1-(v/c)^2}}\ , \tag{6}$$

so that $\omega_1+\omega_2 = 2\gamma\omega_{\mathrm{L}}$. The fact that for $v \neq 0$ these two frequency are unequal makes the scope of the processes involved much more diverse compared to the case of a single monochromatic photon usually considered in QED. Furthermore, if the laser frequency ω_{L} is a slowly varying function of time in the laboratory frame, then ω_{L} has to be generally replaced in (6) by $\omega(t)$.

Analysis shows that the system of equations, which governs the time evolution of the given 3-level system under the action of the laser field with a time-dependent amplitude and frequency, resembles its nonrelativistic counterpart [19] and has the form:

$$\dot{C}(t) = -\mathrm{i}D_{b,a} + \mathrm{i}D_{a,b}C^2(t) + \mathrm{i}\Big(D_{a,a} - D_{b,b} + 4\pi\Delta\nu + 2\dot{\phi}(t)\Big)C(t)\ , \tag{7}$$

$$\dot{\eta}(t) = D_{a,a} + D_{a,b}C(t)\ , \tag{8}$$

$$\dot{W}_c(t) = I(\boldsymbol{r},t)\,|C(t)|^2\left(\frac{\sigma_b^{(\gamma)}(\omega_1)}{\omega_1} + \frac{\sigma_b^{(\gamma)}(\omega_2)}{\omega_2}\right)\exp\left(2\Im\eta(t)\right)\ . \tag{9}$$

Here, the auxiliary functions $\eta(t)$ and $C(t)$ are related to the true state amplitudes $c_{a,a}(t)$ and $c_{b,b}(t)$ as:

$$c_{a,a}(t) \equiv e^{-\mathrm{i}\eta(t)}, \tag{10a}$$

$$c_{b,a}(t) \equiv C(t)\exp\left\{-\mathrm{i}\left[2\left(\gamma\omega_{\mathrm{L}} - \frac{\omega_{b,a}}{2}\right)t + \eta(t) + 2\phi(t)\right]\right\}, \tag{10b}$$

where $2\pi\Delta\nu \equiv \gamma\omega_{\mathrm{L}} - \omega_{b,a}/2$ stands for the time-independent frequency detuning off the resonance, $\sigma_b^{(\gamma)}(\omega)$ denotes the total photoionization cross section of the state $|b\rangle$ at the frequency ω, $W_c(t) \propto |c_{c,c}|^2$ is the probability for an atom to be ionized by the time t via absorption of 3 photons from the laser beam of the intensity $I(\boldsymbol{r},t)$. Finally, $D_{j,i},\ j,i = \{a,b\}$ denote the $\omega_{1,2}$-dependent effective two-photon dipole matrix elements between the states $|a\rangle$, $|b\rangle$; $D_{j,i}$ are given by the following expressions:

$$\begin{aligned} D_{ba} = -\frac{2\pi}{c\omega_1\omega_2} I(\boldsymbol{r},t)\Big[&\widehat{Q}^{(2)}_{b,a}(\varepsilon_a+\omega_1) + \widehat{Q}^{(2)}_{b,a}(\varepsilon_a+\omega_2) \\ &+\frac{\omega_2}{\omega_1}\widehat{Q}^{(2)}_{b,a}(\varepsilon_a+\omega_2)e^{\mathrm{i}\Delta\omega t} + \frac{\omega_1}{\omega_2}\widehat{Q}^{(2)}_{b,a}(\varepsilon_a+\omega_2)e^{-\mathrm{i}\Delta\omega t}\Big], \end{aligned} \tag{11}$$

$$\begin{aligned} D_{aa} = &\frac{2\pi}{c\omega_1^2} I(\boldsymbol{r},t)\left[\widehat{Q}^{(2)}_{a,a}(\varepsilon_a-\omega_1) + \widehat{Q}^{(2)}_{a,a}(\varepsilon_a+\omega_1)\right] \\ &+\frac{2\pi}{c\omega_2^2} I(\boldsymbol{r},t)\left[\widehat{Q}^{(2)}_{a,a}(\varepsilon_a-\omega_2) + \widehat{Q}^{(2)}_{a,a}(\varepsilon_a+\omega_2)\right] \\ &+\frac{2\pi}{c\omega_1\omega_2} I(\boldsymbol{r},t)\left[\widehat{Q}^{(2)}_{a,a}(\varepsilon_a-\omega_1) + \widehat{Q}^{(2)}_{a,a}(\varepsilon_a+\omega_2)\right]e^{-\mathrm{i}\Delta\omega t} \\ &+\frac{2\pi}{c\omega_1\omega_2} I(\boldsymbol{r},t)\left[\widehat{Q}^{(2)}_{a,a}(\varepsilon_a+\omega_1) + \widehat{Q}^{(2)}_{a,a}(\varepsilon_a-\omega_2)\right]e^{\mathrm{i}\Delta\omega t}, \end{aligned} \tag{12}$$

where

$$\omega_{1,2} = \gamma\omega_{\mathrm{L}}(1 \pm v_z/c) + \phi(t)/t\,, \quad \Delta\omega = \omega_1 - \omega_2 \equiv 2\gamma v_z/c\,;$$

D_{bb} and D_{ab} are obtainable from (11)–(12) using the replacement $a \leftrightarrow b$.

The matrix elements $\widehat{Q}^{(2)}_{b,a}(\varepsilon_a \pm \omega_{1,2})$ entering (12)–(11) are given explicitly by the following expression:

$$\widehat{Q}^{(2)}_{b,a}(\varepsilon_a \pm \omega_{1,2}) = \sum\!\!\!\!\!\!\int_r \frac{\langle b|\boldsymbol{\epsilon}^*\cdot\boldsymbol{\alpha}|r\rangle\langle r|\boldsymbol{\epsilon}\cdot\boldsymbol{\alpha}|a\rangle}{\varepsilon_a - \varepsilon_r \pm \gamma(\omega_{\mathrm{L}} \pm v_z/c)}\,, \tag{13}$$

where the summation spans all Coulomb eigenstates of the Hamiltonian $\widehat{H}_0$ which are allowed by the selection rules, including those belonging to the positive ($\varepsilon_r > mc^2$) and negative ($\varepsilon_r < -mc^2$) continuum. Usually, there remains a formidable practical problem of accurately evaluating (13) numerically for arbitrary ε_a, ω_{L}, and v_z. This difficulty can be overcome, however, by using exact closed-form analytic formulas for this type of complicated sums (see paper by V.

Yakhontov in this volume). The analytic relations obtained in the latter work admit error-free numerical evaluation at values of $\omega_{\rm L}$ lying both below and above respective ionization thresholds. Note that in the latter case $\widehat{Q}^{(2)}_{b,a}(\varepsilon_a \pm \omega_{1,2})$ becomes complex-valued, with its imaginary part being proportional to the width of the state due to the one-photon ionization.

Under typical experimental conditions, the states $|a\rangle$, $|b\rangle$ are usually prepared before the very process of the excitation/ionization. The initial populations of these levels, which are proportional to $|c_{a,a}|^2 \equiv \exp\{2\Im\eta(t)\}$ and $|c_{b,b}|^2$, can be modeled by choosing appropriately the values for $C(-\infty)$, $\eta(-\infty)$. Thus, the system (7)–(9) is to be solved subject to the following general initial conditions:

$$C(-\infty) = C_0, \qquad \eta(-\infty) = \eta_0, \qquad W_c(-\infty) = 0\,, \tag{14}$$

which determine all three function uniquely at all times t. In particular, $W_c(t = +\infty, \Delta\nu, r, v)$ describes the 3-photon resonant ionization probability of an atom at infinitely large positive times, i.e. when the interaction between the laser signal and the atomic system has already ceased and/or an equilibrium population of the levels is reached. As a function of the laser frequency detuning $\Delta\nu$, $W_c(t = +\infty, \Delta\nu, r, v)$ determines, after averaging over spatial variables and appropriate velocity distribution, the 3-photon ionization line profile. Similarly, $C(+\infty)$ and $\eta(+\infty)$ describe in turn the equilibrium final populations of the appropriate bounded states.

3 Results

Equations (7)–(9) are well suited for numerical evaluation with arbitrary functions defining the spatial and temporal distributions of the laser pulse. In addition, the system (7)–(9) is rather convenient for analytical treatment. In particular, one can develop further perturbative expansion of (7)–(8) in terms of the fine structure constant α. In the leading order, this yields nonrelativistic formulas which agree with those formerly derived by us in [19]. For unchirped laser signals (i.e., $\dot{\phi}(t) = 0$) these reduce further to the result of [31] by expanding all quantities in powers of the laser intensity $I(\boldsymbol{r}, t)$. Extensive numerical tests carried out by us for various forms of the chirp $\phi(t)$, pulse envelopes $E_0(t)$, and spatial distributions $U(\boldsymbol{r})$ show that (7)–(9) are capable of producing all essential details of the process in question, including Doppler and power shifts and broadenings. A detailed description of our numerical procedure will be published elsewhere. To illustrate the efficiency of the method, however, we present the results of calculations carried out for the $2+1$ resonant ionization process, $1S_{1/2} \xrightarrow{2\hbar\omega} 2S_{1/2} \xrightarrow{\hbar\omega} \varepsilon P_{1/2}$, with muonium where $m^* = m_e/(1 + m_e/m_\mu) \approx (1.00484)^{-1}\, m_e$. Here, the value for the electron to μ^- mass ratio, $m_\mu/m_e = 206.768262$, was used. Furthermore, we assumed that the ionization is being induced by the unchirped CW laser signal of the power $P = 10\,\mathrm{kW}$ and the Gaussian spatial form of the intensity $I(\boldsymbol{r}, \boldsymbol{v}, t)$:

$$I(\boldsymbol{r}, \boldsymbol{v}, t) = \frac{P}{2\pi\sigma_r} \exp\left(-\frac{(x - v_x t)^2 + (y - v_y t)^2 + z^2}{2\sigma_r^2}\right)\,, \tag{15}$$

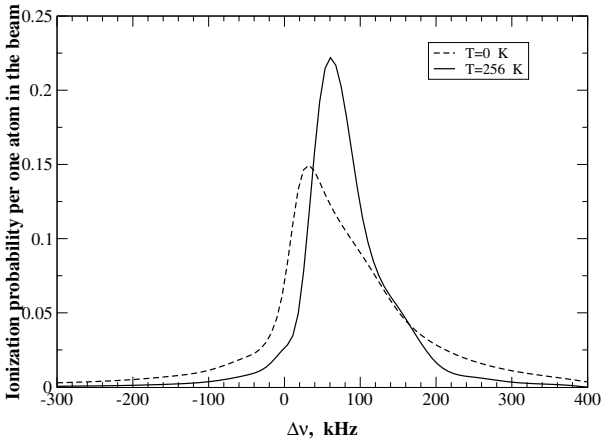

Fig. 6. 3-photon resonant ionization $1S \xrightarrow{3\hbar\omega} \varepsilon P$ lines in muonium, induced by the unchirped CW laser signal at $P = 10\,\mathrm{kW}$ and $\sigma_r = 2\,\mathrm{mm}$, are calculated for two gas temperatures $T = 0\,\mathrm{K}$ and $T = 256\,\mathrm{K}$ (this work)

where $\sigma_r = 2\mathrm{mm}$ is the dispersion of the beam in the XY-plane perpendicular to the direction of the light propagation. The dependence on the atoms's velocity $\boldsymbol{v}_\perp = (v_x, v_y, 0)$ has been introduced in (15) so as to take into account a so-called "finite-time-of-flight" effect [20,21,31]. The latter allows for the fact that the laser field of a beam of a finite geometric size becomes time-dependent in the rest frame of the atom with $\boldsymbol{v}_\perp \neq 0$ (in the laboratory system), even though this field is stationary in the laboratory system. Apparently, this effects vanishes completely only for a particle strictly at rest ($\boldsymbol{v} = 0$) and/or for a homogeneous beam of infinite dimensions in the plane perpendicular to the direction of its propagations. Generally, neither of these conditions are supposed to be satisfied.

Two 3-photon ionization line shapes shown in Fig.6 are calculated by numerically solving (7)–(9) and finally averaging the solutions over Maxwellian distribution at two different temperatures: $T = 0\,\mathrm{K}$ and $T = 256\,\mathrm{K}$. These correspond to the following values for the mean velocity $\langle v\rangle = 2\sqrt{2kT/\pi m^*}$: $\langle v\rangle = 0$ and $\langle v\rangle = 7.415\,\mathrm{mm}/\mu s$. Two curves clearly exhibit typical features inherent to the process under consideration, such as shifts, asymmetries and broadening of the lines. The latter includes also a wide and well-pronounced Doppler background due to the 2-photon absorption from each of the laser beams. This enables us to expect that particular results presented here for $1S-$, $2S-$ and εP-states im muonium can be readily obtained for arbitrary hydrogenic levels $|a\rangle$, $|b\rangle$, $|c\rangle$ of fundamental atoms, including exotic ones. Low-lying excited states in positronium and muonium, as well excited $ns-$levels, $2 \leq n \leq 5$, in hydrogen are of particular current interest for ultra high precision laser spectroscopy. We consider therefore the study of such states in these atoms as a promising subject for our work in future.

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References

1. F. Nez, M.D. Plimmer and S. Bourzeix et al.: Europhys. Lett. **24**, 635 (1993)
2. S. Bourzeix et al.: Phys. Rev. Lett. **76**, 384 (1996)
3. D. Berkeland, M.D. Boshier and E. Hinds: Phys. Rev. Lett. **75**, 2470 (1995)
4. F. Schmidt-Kaler, D. Leibfried, S. Seel et al.: Phys. Rev. A **51** 2789 (1995)
5. Th. Udem, A. Huber, B. Gross et al.: Phys. Rev. Lett. **79**, 2646 (1997)
6. M. Niering, R. Holzwarth, J. Reichert et al.: Phys. Rev. Lett. (2000) in press
7. A. Huber, Th. Udem, B. Gross et al.: Phys. Rev. Lett., **80**, 468 (1998)
8. M.S. Fee, S. Chu, A.P. Mills et al.: Phys. Rev. A **48**, 192 (1993)
9. A.P. Mills, Jr.: Hyperfine Interactions **76**, 233 (1993)
10. F.E. Maas, B. Braun, H. Geerds et al.: Phys. Lett. **A187**, 247 (1994)
11. K. Jungmann: Physikalische Blätter **51**, 1167 (1995)
12. G. zu Putlitz: Hyperfine Interactions **103**, 103 (1996)
13. M.G. Boshier, V.W. Hughes, K. Jungmann and G. zu Putlitz: Comments Atom. Mol. Phys. **33**, 17 (1996)
14. V. Meyer, S.N. Bagaev, P.E.G. Baird et al.: Phys. Rev. Lett. **84**, 1136 (2000)
15. K. Jungmann: *this edition*, pp. 81–102
16. K.S. Eikema, U. Ubachs, W. Vassen and W. Hogervorst: Phys. Rev. A **55** 1866 (1997); Phys. Rev. Lett. **71**, 1690 (1997)
17. P. J. Mohr and B. N. Taylor: Rev.Mod. Phys. **72**, 351 (2000); see also P. Mohr and B. N. Taylor: *this edition*, pp. 145–156
18. V. Meyer et al., Hyperfine Interactions **127**, 197 (2000)
19. V. Yakhontov, R. Santra and K. Jungmann: J. Phys. B: Atom. Mol. Opt. Phys. **32** 1615 (1999)
20. V.S. Letokhov and V.P. Chebotaev: *Nonlinear Laser Spectroscopy*, Springer Series in Optical Sciences (Springer, Berlin, Heidelberg, New York 1977)
21. E. Giacobino and B. Cagnac. In: *Progress in Optics XVII* ed. by E. Wolf (Amsterdam, North-Holland 1980) pp. 86-161
22. I. Reinhard, M. Gabrysch, B. Fischer von Weikerstahl et al.: Applied Physics B **63** 467 (1996)
23. P. Bakule et al.: Appl. Phys. B**71**, 11 (2000)
24. N.B. Delone and V.P. Krainov: *Multiphoton Processes in Atoms* (Berlin: Springer 1994)
25. L.P. Rapoport, B.A. Zon and N.L. Manakov: *Theory of Multiphoton Processes in Atoms* (Atomizdat, Moscow 1978) (in Russian)
26. B.A. Zon: Opt. Spectrosc. **36** 838 (1974)
27. B.A. Zon and B.G. Katsnel'son: Sov. Phys. JETP **65**, 947 (1973)

28. B.A. Zon, N.L. Manakov and L.P. Rappoport: Opt. Spectrosc. **38** 6 (1975)
29. F. Bassani, J.J. Forney and A. Quattropani: Phys. Rev. Lett. **39**, 1070 (1977)
30. B. Cagnac, M.D. Plimmer, L. Julien, and F. Biraben: Rep. Prog. Phys., **57**, 853 (1994)
31. G.R. Beausoleil and T.W. Hänsch: Phys. Rev., A **33**, 1661 (1986)
32. C. Cohen-Tannoudji, J. Dudpont-Roc, G. Grynberg: *Atom–photon interactions: basic processes and applications* Vol. 2 (Weiley Interscience, New York 1998)
33. M. D. Levinson: *Introduction to Nonlinear Spectroscopy* (Academic, New York, 1982)
34. V.B. Berestetskii, E.M. Lifshitz and L.P. Pitaevskii: *Quantum Electrodynamics. Landau and Lifshitz Course of Theoretical Physics*, Vol.4, 2nd edn. (Oxford, Butterworth-Heinemann, 1996)