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Abstract
We present a self-consistent theory and analytical results for the three-photon–one-photon coherent control of ionization in an optically dense autoionizing medium. We show that for an optically thick medium, over a short scaled propagation distance, the phase and amplitude of the harmonic field settle to values that are fully determined by the atomic and fundamental field parameters and are completely independent of the initial relative phase between the two fields, thus preventing efficient phase control of the autoionization and its products. Control of the autoionization and the branching ratio of its products is still feasible, however, through the variation of the detuning of the fundamental field from the atomic transition resonance.

1. Introduction

In recent work [1], we have addressed the issue of the effect of propagation on the control of photoabsorption through external control of the relative phase between a pump field and its third harmonic. We did so, in the simplest system employed in relevant theoretical as well as experimental studies [2–5], namely the excitation of a bound–bound transition by the superposition of the above-mentioned combination of fields. We found that the effects of propagation are indeed significant, as the relative phase, after a rather short scaled distance of propagation, settles to a value that cancels any transition by the combination of the two fields. The issue is of course important from the point of view of possible applications of such schemes to the control of photobreakup products on a large scale.

However, photobreakup products will at some stage involve transitions into a continuum and preferably to discrete states embedded in continua, as in autoionization [6,7]. In fact, some of the experimental investigations of these schemes have involved autoionizing states [8]. As in

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the case of bound–bound transitions, the processes are fairly well understood at the single-atom (molecule) level, even in the presence of autoionization [8–10]. The effect of propagation, however, remains an open question in that context. One might expect similarities with the corresponding behaviour in bound–bound transitions, but continua are different, and more so when autoionization is involved. We have thus undertaken the task of investigating the effect of propagation on coherent control through the phase of the fields, in the context of autoionization. Anticipating the discussion and results in the sections that follow, we find that again the effects are significant essentially to the same degree.

In section 2 we set up and discuss the issue in the context of one discrete state embedded in a single continuum, so that we can establish the basic propagation behaviour in such a system. However, control of photobreakup products must involve, at least, two continua. This case, formally more complex but necessary, is taken up in section 3. In both cases, we are able to produce analytical results, although those in section 3 result in rather complicated, but nevertheless, useful expressions. Our conclusions are summarized in section 4.

2. Autoionizing state coupled to a single continuum

2.1. System description

Consider the stationary propagation of a bichromatic electromagnetic field E through an optically dense medium. This field is a function of time t and space coordinate z and is composed of the fundamental and its third harmonic modes that have the same (linear) polarization and angular frequencies ω_f and $\omega_h = 3\omega_f$, respectively. It can be expressed as

$$E(z, t) = \tfrac{1}{2} \left[E_f \mathrm{e}^{\mathrm{i}(k_f z - \omega_f t)} + E_h \mathrm{e}^{\mathrm{i}(k_h z - \omega_h t)} + \text{c.c.} \right] \tag{2.1}$$

where $E_j = |E_j| \mathrm{e}^{-\mathrm{i}\phi_j}$, $j = f, h$, is the complex amplitude of the corresponding field which is slowly varying in time and space, and $k_j = \omega_j n_j c^{-1}$, with n_j the refractive index at frequency ω_j, which accounts for the contribution of the host medium (if any) as well as all non-resonant polarization effects of the active medium itself. The relative phase θ between the two fields is given by $\theta(z) = (\phi_h - 3\phi_f) - \delta k z$, where $\delta k = k_h - 3k_f$ is the phase mismatch over a unit distance of propagation. At the entrance to the medium ($z = 0$), the relative phase has a definite value which can be controlled externally, while its evolution during the course of the propagation of the fields inside the medium is fully determined by the medium response described by the polarization

$$P(z, t) = \tfrac{1}{2} \left[P_f \mathrm{e}^{\mathrm{i}(k_f z - \omega_f t)} + P_h \mathrm{e}^{\mathrm{i}(k_h z - \omega_h t)} + \text{c.c.} \right] \tag{2.2}$$

where $P_{f,h}$ is the field-induced polarization at the corresponding frequency which is slowly varying in time and space.

The medium is represented by a vapour of atoms (or molecules) that involve a ground state $|1\rangle$ and a discrete state $|2\rangle$ with opposite parity (figure 1). The excitation of $|2\rangle$ is accomplished by the simultaneous action of the fundamental and harmonic fields through the near-resonant three- and one-photon transitions from the ground state, respectively. The discrete state is embedded into a single continuum $|c\rangle$ and coupled to it via configuration interaction V which causes the autoionization. Using the standard procedure, whose detailed description can be found, for example, in [9], we obtain the following set of equations for the three main elements $\sigma_{nk} \equiv \langle n| \sigma |k\rangle$, $n, k = 1, 2$, of the atomic density matrix σ transformed to the frame rotating at $(\omega_h t - k_h z)$:

$$\partial_t \sigma_{11} = -\gamma \sigma_{11} - 2 \operatorname{Im} \left\{ \left[M_{12} \left(1 - \frac{\mathrm{i}}{q} \right) E_h^* + M_{12}^{(3)} \left(1 - \frac{\mathrm{i}}{q^{(3)}} \right) E_f^{*3} \mathrm{e}^{\mathrm{i}\delta k z} \right] \sigma_{21} \right\} \tag{2.3}$$
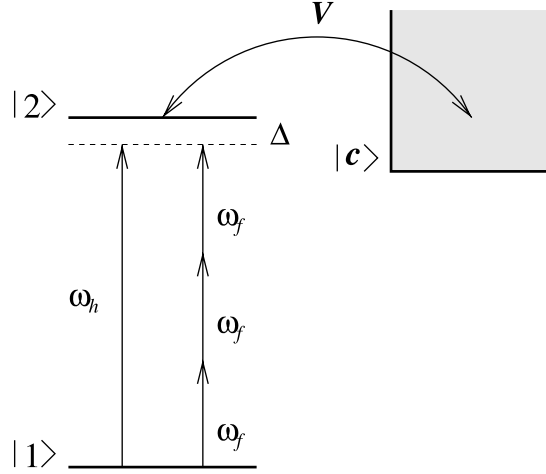
Figure 1. Energy levels of an atom interacting with two electromagnetic fields. The autoionizing state $|2\rangle$ decays into the single continuum $|c\rangle$.

$$\partial_t \sigma_{22} = -\Gamma \sigma_{22} + 2 \operatorname{Im} \left\{ \left[M_{12} \left(1 + \frac{i}{q} \right) E_h^* + M_{12}^{(3)} \left(1 + \frac{i}{q^{(3)}} \right) E_f^{*3} e^{i\delta kz} \right] \sigma_{21} \right\} \tag{2.4}$$

$$\left[\partial_t + i\tilde{\Delta} + \tfrac{1}{2}(\gamma + \Gamma) \right] \sigma_{21} = i \left[M_{21} \left(1 - \frac{i}{q} \right) E_h + M_{21}^{(3)} \left(1 - \frac{i}{q^{(3)}} \right) E_f^3 e^{-i\delta kz} \right] \sigma_{11}$$

$$- i \left[M_{21} \left(1 + \frac{i}{q} \right) E_h + M_{21}^{(3)} \left(1 + \frac{i}{q^{(3)}} \right) E_f^3 e^{-i\delta kz} \right] \sigma_{22} \tag{2.5}$$

where M_{12} and $M_{12}^{(3)}$ are the one- and three-photon transition matrix elements between the ground state and the autoionizing state modified by an admixture of states of the continuum [6]; q and $q^{(3)}$ are the corresponding asymmetry (Fano) parameters; γ is the ionization width of the ground state $|1\rangle$ directly into the continuum, and Γ is the autoionization width of state $|2\rangle$; $\tilde{\Delta}$ is the detuning of both fields from resonance with the atomic transition $|1\rangle \rightarrow |2\rangle$, modified by the AC Stark shift. (Detailed definition of these quantities is given in the appendix.) In a similar manner, the ionization rate R into the continuum $|c\rangle$ can be calculated through the integration of $\partial_t \sigma_{cc}$, where $\sigma_{cc} \equiv \langle c| \sigma |c\rangle$, over the continuum states, with the result

$$R = \int \partial_t \sigma_{cc} \, dc = \gamma \sigma_{11} + \Gamma \sigma_{22} - 2 \operatorname{Im} \left\{ 2i \left[m E_h^* + m^{(3)} E_f^{*3} e^{i\delta kz} \right] \sigma_{21} \right\} \tag{2.6}$$

where $m = M_{12}/q$ and $m^{(3)} = M_{12}^{(3)}/q^{(3)}$ are the effective one- and three-photon matrix elements of the indirect transition $|1\rangle \rightarrow |c\rangle \rightarrow |2\rangle$ from the ground state to the autoionizing state via the continuum (see the appendix). Using equations (2.3) and (2.4), it is easy to verify that $R = -(\partial_t \sigma_{11} + \partial_t \sigma_{22})$, as it should.

Let us turn now to the equations describing the evolution of the field. In the following, the depletion of the fundamental field will be neglected since it is assumed to be significantly strong to sustain the three-photon transition amplitude so that it has appreciable magnitude which is comparable to the single-photon one. The polarization of the medium at the frequency of the harmonic field is given by the equation

$$P_h = 2N \left(\mu_{12} \sigma_{21} + \int \mu_{1c} \sigma_{c1} \, dc \right) \tag{2.7}$$

where N is the density of atoms and $\mu_{1n} \equiv \langle 1| e\vec{r} |n\rangle$, $n = 2, c$, is the matrix element of the electric dipole operator $e\vec{r}$. From (2.7), after adiabatic elimination of σ_{c1}, we obtain

$$P_h = 4N\hbar \left[M_{12}\left(1 - \frac{i}{q}\right)\sigma_{21} + i\frac{m}{\bar{\Gamma}}\left(mE_h + m^{(3)}E_f^3 e^{-i\delta kz}\right)\sigma_{11} + \left(s^{(1)}E_h + s^{(13)}E_f^3 e^{-i\delta kz}\right)\sigma_{11} \right] \tag{2.8}$$

where $\bar{\Gamma} \equiv \Gamma/2$ is the autoionization half-width. Finally, the stationary propagation of the harmonic field is governed by the reduced wave equation

$$\partial_z E_h = i\frac{\omega_h}{2c\epsilon_0 n_h} P_h \tag{2.9}$$

which, together with the polarization (2.8) and the density matrix equations (2.3)–(2.5), provide a complete self-consistent description of the system.

2.2. Analytic solution

To present analytical results on the behaviour of the system, we make the rate approximation which is valid in the weak-field limit, when the configuration interaction is stronger than the fundamental and harmonic field induced dipole interactions

$$\Gamma \gg \gamma^{(1)}, \gamma^{(3)}, \Omega_h, \Omega_f^{(3)} \tag{2.10}$$

where $\gamma^{(1)}$ and $\gamma^{(3)}$ are, respectively, the single- and three-photon direct ionization widths from $|1\rangle$ to $|c\rangle$ (see the appendix), and $\Omega_h = M_{12}|E_h|$ and $\Omega_f^{(3)} = M_{12}^{(3)}|E_f|^3$ are the Rabi frequencies of the corresponding fields. To estimate the range of intensities for which the rate approximation approach is adequate, consider a typical atomic system, e.g. Ca, involving ground state $|1\rangle \equiv |4s^2(^1S_0)\rangle$, autoionizing state $|2\rangle \equiv |3d5p(^1P_1)\rangle$ and continuum $|c\rangle \equiv |4s\epsilon p\rangle$. The three-photon transition matrix element of Ca is highly enhanced due to the $|4s5s(^1S_0)\rangle$ state which is near-resonant with the two-photon transition from the ground state. The following atomic parameters are relevant here: $\Gamma \simeq 1.2 \times 10^{14}$ s^{-1}, $\gamma^{(1)} \simeq 3.5\,I_h$ s^{-1}, $\gamma^{(3)} \simeq 4.4 \times 10^{-21}\,I_f^3$ s^{-1}, $\Omega_h \simeq 4.5 \times 10^7\,I_h^{1/2}$ s^{-1} and $\Omega_f^{(3)} \simeq 2.7 \times 10^{-4}\,I_f^{3/2}$ s^{-1}, where the intensities of the harmonic and fundamental fields, I_h and I_f, are in units of W cm^{-2} [11]. The comparison of these numbers with (2.10) gives a restriction on the intensity of the fundamental: $I_f \ll 3 \times 10^{11}$ W cm^{-2}. Taking, for safety, $10^8 \leqslant I_f \leqslant 10^{10}$ W cm^{-2}, and requiring that $\Omega_h \sim \Omega_f^{(3)}$ which leads to $I_h \sim 4 \times 10^{-23}\,I_f^3$, we obtain that $40 \leqslant I_h \leqslant 4 \times 10^7$ W cm^{-2}.

It is important to mention that in the case of pulsed fields, condition (2.10) should be supplemented by yet another condition which implies that the rate of change of the field amplitude (Rabi frequency) is smaller than the autoionization width Γ. However, taking into account the value of Γ listed above, one can see that for optical fields this condition is almost always satisfied unless femtosecond pulses are used. We note that the pulsed nature of the fields can influence the system dynamics through the time-dependent Stark shift [1]. This effect is, however, unimportant in the weak-field limit when the width of the atomic resonance dominates over the AC Stark shift.

In the rate approximation, the equations for the ionization rate as well as for the evolution of the harmonic field are found by assuming that $\sigma_{11} \sim 1 \gg \sigma_{22}$ and $\partial_t \sigma_{21} = \partial_t \sigma_{22} = 0$, which leads to

$$\sigma_{21} \simeq \frac{1}{\bar{\Delta} - i\bar{\Gamma}} \left[M_{21}\left(1 - \frac{i}{q}\right)E_h + M_{21}^{(3)}\left(1 - \frac{i}{q^{(3)}}\right)E_f^3 e^{-i\delta kz} \right] \tag{2.11}$$

$$\sigma_{22} \simeq \frac{1}{\bar{\Gamma}} \text{Im}\left\{ \left[M_{12}\left(1 + \frac{i}{q}\right)E_h^* + M_{12}^{(3)}\left(1 + \frac{i}{q^{(3)}}\right)E_f^{*3} e^{i\delta kz} \right]\sigma_{21} \right\}. \tag{2.12}$$

Substituting this into (2.6) and (2.8), after some algebra, we obtain

$$R = -\partial_t \sigma_{11} = \frac{2}{\bar{\Gamma}(\epsilon^2 + 1)} \left| m(\epsilon - q)E_h + m^{(3)}(\epsilon - q^{(3)})E_f^3 e^{-\mathrm{i}\delta kz} \right|^2 \tag{2.13}$$

$$P_h = \mathrm{i}\frac{4N\hbar m}{\bar{\Gamma}(\epsilon - \mathrm{i})} \left[m\left(\epsilon - 2q - \mathrm{i}q^2\right)E_h + m^{(3)}\left(\epsilon - q^{(3)} - q - \mathrm{i}qq^{(3)}\right)E_f^3 e^{-\mathrm{i}\delta kz} \right] \tag{2.14}$$

where $\epsilon = \tilde{\Delta}/\bar{\Gamma}$ is the detuning normalized by the autoionization halfwidth. In (2.14), we have, for simplicity, dropped the terms proportional to the polarizabilities $s^{(1)}$ and $s^{(13)}$ and responsible for the phase shift of the harmonic field, assuming that their contribution is incorporated in δk. Now equation (2.9) can be solved analytically with the result

$$E_h(z) = E_h(0)\,\mathrm{e}^{\mathrm{i}\alpha_h z} + \frac{\alpha_f}{\delta k + \alpha_h} E_f^3 (\mathrm{e}^{\mathrm{i}\alpha_h z} - \mathrm{e}^{-\mathrm{i}\delta kz}) \tag{2.15}$$

where

$$\alpha_h = a\,\frac{(\epsilon q^2 - \epsilon + 2q) + \mathrm{i}(\epsilon - q)^2}{\epsilon^2 + 1}$$

$$\alpha_f = a^{(3)}\,\frac{(\epsilon q q^{(3)} - \epsilon + q + q^{(3)}) + \mathrm{i}(\epsilon - q)(\epsilon - q^{(3)})}{\epsilon^2 + 1}$$

and

$$a = \frac{2N\hbar\omega_h M_{12}^2}{c\epsilon_0 n_h \bar{\Gamma}q^2} \qquad a^{(3)} = a\,\frac{q}{M_{21}}\frac{M_{21}^{(3)}}{q^{(3)}}.$$

One could think of α_h as a complex absorption coefficient.

(a) Consider first the trivial case $E_f = 0$, i.e. only the harmonic field is present. Then

$$E_h(z) = E_h(0)\,\mathrm{e}^{\mathrm{i}\alpha_h z} \tag{2.16}$$

or

$$|E_h(z)| = |E_h(0)|\exp\left[-a\frac{(\epsilon - q)^2}{\epsilon^2 + 1}z\right] \tag{2.17}$$

$$\phi_h(z) = \phi_h(0) - a\,\frac{\epsilon q^2 - \epsilon + 2q}{\epsilon^2 + 1}\,z \tag{2.18}$$

that is, as z increases, the real amplitude of the harmonic field decays according to the exponential Beer's law, while its phase experiences a shift. Meanwhile, the ionization rate is given by the familiar single-field formula [6, 7]

$$R(z) = \frac{2m^2}{\bar{\Gamma}}\frac{(\epsilon - q)^2}{(\epsilon^2 + 1)}|E_h(z)|^2 = \gamma^{(1)}(z)\frac{(\epsilon - q)^2}{(\epsilon^2 + 1)} \tag{2.19}$$

where

$$\gamma^{(1)}(z) = \gamma^{(1)}(0)\exp\left[-2a\frac{(\epsilon - q)^2}{\epsilon^2 + 1}z\right].$$

At $\epsilon = q$, the ionization vanishes and, consequently, the field amplitude remains unchanged during the course of the propagation, while the phase shift is given by $\phi_h(z) = \phi_h(0) - aqz$.

(b) The other special case which needs to be considered separately, is when $\epsilon = q$ but $E_f \neq 0$. Then $\alpha_h = aq$ and $\alpha_f = a^{(3)}q^{(3)}$ are both purely real and, as is apparent from equation (2.13), the harmonic field does not contribute to the ionization

$$R = \frac{2m^{(3)2}}{\bar{\Gamma}} \frac{(q - q^{(3)})^2}{(q^2 + 1)} |E_f|^6 = \gamma^{(3)} \frac{(q - q^{(3)})^2}{(q^2 + 1)} \tag{2.20}$$

while its evolution is given by

$$E_h(z) \simeq E_h(0)\, e^{iaqz} + \frac{M_{21}^{(3)}}{M_{21}} E_f^3 (e^{iaqz} - 1). \tag{2.21}$$

(c) Finally, let us examine the general situation $\epsilon \neq q$ and $E_f \neq 0$. For the distances of propagation

$$z \gg \frac{1}{\text{Im}[\alpha_h]} = \frac{\epsilon^2 + 1}{a(\epsilon - q)^2} = \zeta \tag{2.22}$$

the terms proportional to the exponent $e^{i\alpha_h z}$ in (2.15) are totally damped away and we are left with a simple expression,

$$E_h(z) \simeq -\frac{q}{M_{21}} \frac{M_{21}^{(3)}}{q^{(3)}} \frac{\epsilon - q^{(3)} - q - iqq^{(3)}}{\epsilon - 2q - iq^2} E_f^3 e^{-i\delta kz}. \tag{2.23}$$

Substituting this into (2.13), after some algebra, we obtain

$$R = \frac{2m^{(3)2}}{\bar{\Gamma}} \frac{q^2(q - q^{(3)})^2}{(\epsilon - 2q)^2 + q^4} |E_f|^6 = \gamma^{(3)} \frac{q^2(q - q^{(3)})^2}{(\epsilon - 2q)^2 + q^4}. \tag{2.24}$$

Thus, the ionization rate is expressed through the atomic parameters, detuning ϵ and the cube of the intensity of the fundamental field, whereas it does not contain in any way the relative phase between the two fields, since, independently of the initial amplitude and phase, over a distance of propagation of several ζ, the harmonic field acquires the amplitude given by (2.23). With the parameters for Ca listed above, an estimate for ζ at resonance $\epsilon \sim 0$ gives $\zeta \sim 3 \times 10^{16} N^{-1}$ cm, where N is measured in cm^{-3}. For an atom with a narrower autoionizing state, ζ would be smaller. In figure 2 we plot the Rabi frequency of the harmonic field Ω_h and the ionization rate R as a function of ϵ for several different values of the asymmetry parameters q and $q^{(3)}$. The dependence of the ionization rate on the detuning is given by the Lorentzian (2.24) with the maximum $R_{\text{max}} = \gamma^{(3)}(1 - q^{(3)}/q)^2$ at $\epsilon = 2q$. In the case of $q = 0$, both the harmonic field amplitude and the ionization rate vanish for all $\epsilon \neq 0$. At $\epsilon = 0$ we have $\Omega_h = \Omega_f^{(3)}/2$, $\theta = \pi$, and $R = \gamma^{(3)}q^{(3)2}/4$. The more interesting situation, however, is realized when either the detuning is very large, $\epsilon \gg q, q^{(3)}$, or the two asymmetry parameters are equal $q = q^{(3)}$. Then the ionization vanishes, $R = 0$, while the harmonic field amplitude and phase settle to the values

$$\Omega_h = \Omega_f^{(3)} \qquad \theta = \pi \tag{2.25}$$

for all ϵ. Thus, in this limiting case the autoionizing resonance behaves completely analogously to the bound–bound resonance [1]. An apparent curiosity worth noting is that, if we *formally* set $\epsilon = q$ (which was excluded at the beginning of this paragraph since it would mean that $\text{Im}[\alpha_h] = 0$), equation (2.24) turns into equation (2.20) which is a rather unexpected result, since in that case equation (2.23) is invalid. This is, however, a consequence of the form of equation (2.13), which eliminates the contribution of E_h when $\epsilon = q$.
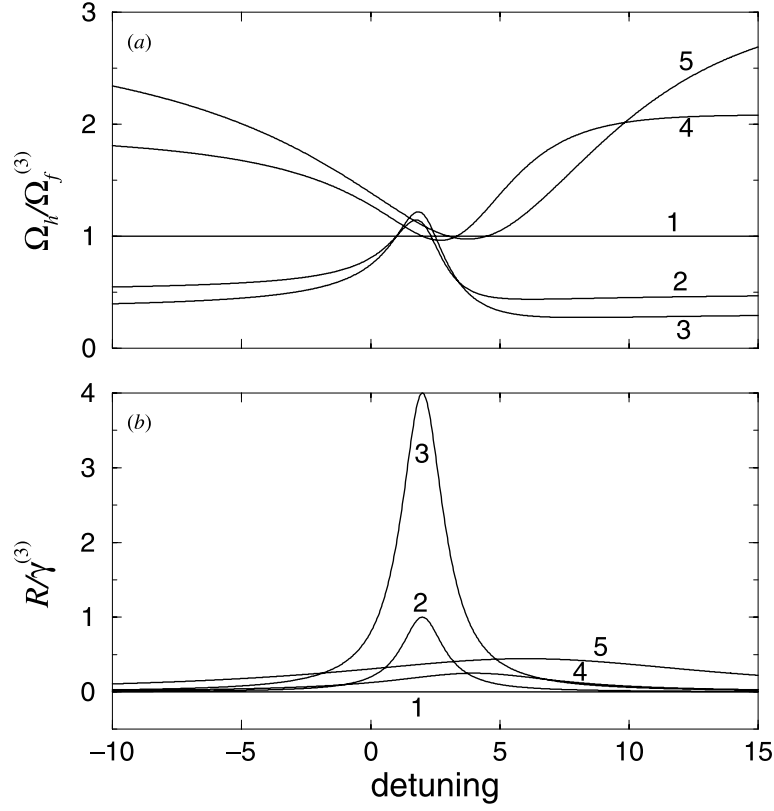
Figure 2. (a) Rabi frequency of the harmonic field Ω_h (normalized by $\Omega_f^{(3)}$) and (b) ionization rate R (normalized by $\gamma^{(3)}$) versus detuning ϵ for $q = q^{(3)} = 1$ (curve 1); $q = 1, q^{(3)} = 2$ (curve 2); $q = 1, q^{(3)} = 3$ (curve 3); $q = 2, q^{(3)} = 1$ (curve 4); $q = 3, q^{(3)} = 1$ (curve 5).

3. Two continua coupled to the autoionizing state

3.1. System description

In this section, we consider the more general situation when the autoionizing state $|2\rangle$ is embedded into two different continua $|c_1\rangle$ and $|c_2\rangle$ (figure 3). Now, the equations for the density matrix elements can be expressed as

$$\partial_t \sigma_{11} = -\sum_l \gamma_l \sigma_{11} - 2\,\mathrm{Im} \left\{ \left[M_{12} \left(1 - \frac{\mathrm{i}}{q} \right) E_h^* + M_{12}^{(3)} \left(1 - \frac{\mathrm{i}}{q^{(3)}} \right) E_f^{*3} \mathrm{e}^{\mathrm{i}\delta kz} \right] \sigma_{21} \right\} \tag{3.1}$$

$$\partial_t \sigma_{22} = -\sum_l \Gamma_l \sigma_{22} + 2\,\mathrm{Im} \left\{ \left[M_{12} \left(1 + \frac{\mathrm{i}}{q} \right) E_h^* + M_{12}^{(3)} \left(1 + \frac{\mathrm{i}}{q^{(3)}} \right) E_f^{*3} \mathrm{e}^{\mathrm{i}\delta kz} \right] \sigma_{21} \right\} \tag{3.2}$$

$$\left[\partial_t + \mathrm{i}\tilde{\Delta} + \frac{1}{2} \sum_l (\gamma_l + \Gamma_l) \right] \sigma_{21} = \mathrm{i} \left[M_{21} \left(1 - \frac{\mathrm{i}}{q} \right) E_h + M_{21}^{(3)} \left(1 - \frac{\mathrm{i}}{q^{(3)}} \right) E_f^3 \mathrm{e}^{-\mathrm{i}\delta kz} \right] \sigma_{11}$$

$$- \mathrm{i} \left[M_{21} \left(1 + \frac{\mathrm{i}}{q} \right) E_h + M_{21}^{(3)} \left(1 + \frac{\mathrm{i}}{q^{(3)}} \right) E_f^3 \mathrm{e}^{-\mathrm{i}\delta kz} \right] \sigma_{22} \tag{3.3}$$
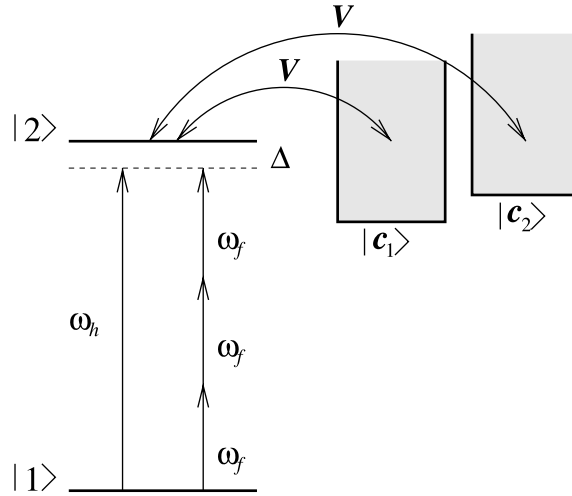
Figure 3. Autoionizing state $|2\rangle$ decays into two different continua $|c_1\rangle$ and $|c_2\rangle$.

where γ_l is the ionization width of ground state $|1\rangle$ directly into continuum $|c_l\rangle$, $l = 1, 2$, and Γ_l is the partial autoionization width of $|2\rangle$ into $|c_l\rangle$. Similarly to (2.6), the rate of ionization R_l into continuum $|c_l\rangle$ is given by

$$R_l = \int \partial_t \sigma_{c_l c_l} \, dc_l = \gamma_l \sigma_{11} + \Gamma_l \sigma_{22} - 2 \, \mathrm{Im} \left\{ 2\mathrm{i} \left[m_l E_h^* + m_l^{(3)} E_f^{*3} \mathrm{e}^{\mathrm{i}\delta kz} \right] \sigma_{21} \right\} \tag{3.4}$$

from where it follows that the total ionization rate $R \equiv \sum_l R_l = -(\partial_t \sigma_{11} + \partial_t \sigma_{22})$. Finally, the polarization P_h for the harmonic field is given by the equation

$$P_h = 4N\hbar \left[M_{12} \left(1 - \frac{\mathrm{i}}{q} \right) \sigma_{21} + \mathrm{i} \sum_l \frac{2m_l}{\Gamma_l} \left(m_l E_h + m_l^{(3)} E_f^3 \mathrm{e}^{-\mathrm{i}\delta kz} \right) \sigma_{11} \right.$$

$$\left. + \sum_l \left(s_l^{(1)} E_h + s_l^{(13)} E_f^3 \mathrm{e}^{-\mathrm{i}\delta kz} \right) \sigma_{11} \right]. \tag{3.5}$$

Thus, the formalism of this section is a generalization of that of the previous section to the system with multiple continua. Consequently, all of the results of section 2 can be derived from the solution presented below in the special case of a single continuum.

3.2. Analytic solution

The validity of the rate approximation for the present situation again is based on the weak-field limit condition

$$\bar{\Gamma} \equiv \tfrac{1}{2} \sum_l \Gamma_l \gg \gamma_l^{(1)}, \gamma_l^{(3)}, \Omega_h, \Omega_f^{(3)} \tag{3.6}$$

where $\gamma_l^{(1)}$ and $\gamma_l^{(3)}$ are, respectively, the single- and three-photon direct ionization widths from $|1\rangle$ to $|c_l\rangle$, $l = 1, 2$ (see the appendix). Following the same procedure as in the derivation of equations (2.13) and (2.14), for the rate of ionization into continuum $|c_l\rangle$ and polarization P_h,

we obtain

$$R_l = \frac{2}{\bar{\Gamma}(\epsilon^2 + 1)} \left| \sqrt{\frac{2\bar{\Gamma}}{\Gamma_l}} \left(m_l E_h + m_l^{(3)} E_f^3 e^{-i\delta kz} \right) (\epsilon + i) \right.$$

$$\left. - \sqrt{\frac{\Gamma_l}{2\bar{\Gamma}}} \left[M_{21} \left(1 + \frac{i}{q} \right) E_h + M_{21}^{(3)} \left(1 + \frac{i}{q^{(3)}} \right) E_f^3 e^{-i\delta kz} \right] \right|^2 \tag{3.7}$$

$$P_h = i \frac{4N\hbar M_{12}}{\bar{\Gamma}(\epsilon - i)q} \left\{ \frac{M_{21}}{q} \left[\epsilon(1 + g^2) - 2q - i(q^2 + g^2) \right] E_h \right.$$

$$\left. + \frac{M_{21}^{(3)}}{q^{(3)}} \left[\epsilon(1 + gg^{(3)}) - q^{(3)} - q - i(qq^{(3)} + gg^{(3)}) \right] E_f^3 e^{-i\delta kz} \right\} \tag{3.8}$$

where g and $g^{(3)}$ are the one- and three-photon correlation coefficients which are derived in the appendix. As in the single continuum case, we have dropped in (3.8) the terms proportional to the polarizabilities $s_l^{(1)}$ and $s_l^{(13)}$ which are assumed to be effectively incorporated in δk. Equation (3.8) is now used to solve equation (2.9) analytically, which yields formally the same result as (2.15) where the coefficients α_h and α_f are, however, slightly different

$$\alpha_h = a \frac{(\epsilon q^2 - \epsilon + 2q) + i[(\epsilon - q)^2 + g^2(\epsilon^2 + 1)]}{\epsilon^2 + 1}$$

$$\alpha_f = a^{(3)} \frac{(\epsilon qq^{(3)} - \epsilon + q + q^{(3)}) + i[(\epsilon - q)(\epsilon - q^{(3)}) + gg^{(3)}(\epsilon^2 + 1)]}{\epsilon^2 + 1}.$$

(a) Consider again the case $E_f = 0$, when the harmonic field propagates alone in the medium. Then we have

$$|E_h(z)| = |E_h(0)| \exp \left\{ -a \left[\frac{(\epsilon - q)^2}{\epsilon^2 + 1} + g^2 \right] z \right\} \tag{3.9}$$

$$\phi_h(z) = \phi_h(0) - a \frac{\epsilon q^2 - \epsilon + 2q}{\epsilon^2 + 1} z \tag{3.10}$$

that is, the phase shift is given by the same formula as in the single continuum case. Also the real amplitude of the field decays according to Beer's law with, however, a different absorption coefficient which now contains an additional (detuning-independent) correlation term g^2. The presence of such a term in the multiple continua case is essential since it leads to the conclusion that the absorption does not vanish for any detuning ϵ. Only if $g = 0$, that is $\mu_{1c_1}/V_{c_12} = \mu_{1c_2}/V_{c_22}$ (see the appendix), which need not be the case for an arbitrary atom, the absorption vanishes at $\epsilon = q$, as in the single-continuum case. This can also be seen from the equations for the ionization rate showing that the ionization is present at any detuning ϵ unless $g = 0$:

$$R_l(z) = \frac{2}{\bar{\Gamma}(\epsilon^2 + 1)} \left[\left(\epsilon m_l - M_{12} \frac{\Gamma_l}{2\bar{\Gamma}} \right)^2 \frac{2\bar{\Gamma}}{\Gamma_l} + g^2 \frac{M_{12}^2}{q^2} \frac{\Gamma_{l'}}{2\bar{\Gamma}} \right] |E_h(z)|^2$$

$$= \frac{\bar{\gamma}^{(1)}(z)}{(\epsilon^2 + 1)} \left[q^2 \left(\epsilon \frac{m_l}{M_{12}} - \frac{\Gamma_l}{2\bar{\Gamma}} \right)^2 \frac{2\bar{\Gamma}}{\Gamma_l} + g^2 \frac{\Gamma_{l'}}{2\bar{\Gamma}} \right] \tag{3.11}$$

$$R(z) = R_1 + R_2 = \frac{2M_{12}^2}{\bar{\Gamma}q^2} \left[\frac{(\epsilon - q)^2}{(\epsilon^2 + 1)} + g^2 \right] |E_h(z)|^2 = \bar{\gamma}^{(1)}(z) \left[\frac{(\epsilon - q)^2}{(\epsilon^2 + 1)} + g^2 \right] \tag{3.12}$$

where $l, l' = 1, 2, l \neq l'$, and

$$\bar{\gamma}^{(1)} = \frac{2(m_1 + m_2)^2}{\bar{\Gamma}} |E_h|^2 = \frac{2\Omega_h^2}{\bar{\Gamma}q^2}$$

is the single-photon direct ionization width of the ground state $|1\rangle$ weighted by the configuration interaction (obviously $\bar{\gamma}^{(1)} = \gamma^{(1)}$ in the single continuum case). Thus, the correlation term g^2, being essentially detuning-independent, contributes to an additional background in the ionization spectrum of an atom with multiple continua. In the case of $g = 0$, equation (3.12) eventually turns into equation (2.19) with vanishing ionization at $\epsilon = q$. The branching ratio of the two products of ionization

$$B = \frac{R_1}{R_2} = \frac{\Gamma_2}{\Gamma_1} \frac{q^2(2\epsilon m_1 \bar{\Gamma} - M_{12}\Gamma_1)^2 + g^2 M_{12}^2 \Gamma_2 \Gamma_1}{q^2(2\epsilon m_2 \bar{\Gamma} - M_{12}\Gamma_2)^2 + g^2 M_{12}^2 \Gamma_1 \Gamma_2} \tag{3.13}$$

is constant throughout the propagation distance z since it does not contain the harmonic field intensity and depends only on the atomic parameters and detuning ϵ, through which it can be controlled.

(b) Finally, we consider the general situation when both fields are present ($E_h \neq 0$, $E_f \neq 0$). Similarly to the single continuum case, for the distances of propagation

$$z \gg \frac{1}{\text{Im}[\alpha_h]} = \frac{\epsilon^2 + 1}{a[(\epsilon - q)^2 + g^2(\epsilon^2 + 1)]} = \zeta \tag{3.14}$$

the terms with $e^{i\alpha_h z}$ in (2.15) are totally damped away and we obtain

$$E_h(z) \simeq -\frac{q}{M_{21}} \frac{M_{21}^{(3)}}{q^{(3)}} \frac{\epsilon(1 + gg^{(3)}) - q^{(3)} - q - i(qq^{(3)} + gg^{(3)})}{\epsilon(1 + g^2) - 2q - i(q^2 + g^2)} E_f^3 e^{-i\delta kz}. \tag{3.15}$$

Note that due to the presence of g^2 in the denominator of condition (3.14), the case $\epsilon = q$ need not be considered separately. Substituting (3.15) into (3.7), for the partial ionization rate R_l we obtain a rather cumbersome nevertheless illustrative result:

$$R_l = \frac{\bar{\gamma}^{(3)}}{(\epsilon^2 + 1)(X^2 + S^2)} \left\{ \left(Y_l^2 \frac{2\bar{\Gamma}}{\Gamma_l} + g^2 \frac{\Gamma_{l'}}{2\bar{\Gamma}} \right) \left(X^{(3)2} + S^{(3)2} \right) \right.$$

$$+ \left(Y_l^{(3)2} \frac{2\bar{\Gamma}}{\Gamma_l} + g^{(3)2} \frac{\Gamma_{l'}}{2\bar{\Gamma}} \right) (X^2 + S^2)$$

$$- 2 \left[\left(Y_l Y_l^{(3)} \frac{2\bar{\Gamma}}{\Gamma_l} + gg^{(3)} \frac{\Gamma_{l'}}{2\bar{\Gamma}} \right) (XX^{(3)} + SS^{(3)}) \right.$$

$$\left. \left. + (-1)^{l'} \sqrt{\frac{\Gamma_{l'}}{\Gamma_l}} \left(g^{(3)} Y_l - g Y_l^{(3)} \right) (X^{(3)} S - XS^{(3)}) \right] \right\} \tag{3.16}$$

where $l, l' = 1, 2, l \neq l'$,

$$\bar{\gamma}^{(3)} = \frac{2(m_1^{(3)} + m_2^{(3)})^2}{\bar{\Gamma}} |E_f|^6 = \frac{2\Omega_f^{(3)2}}{\bar{\Gamma}q^{(3)2}}$$
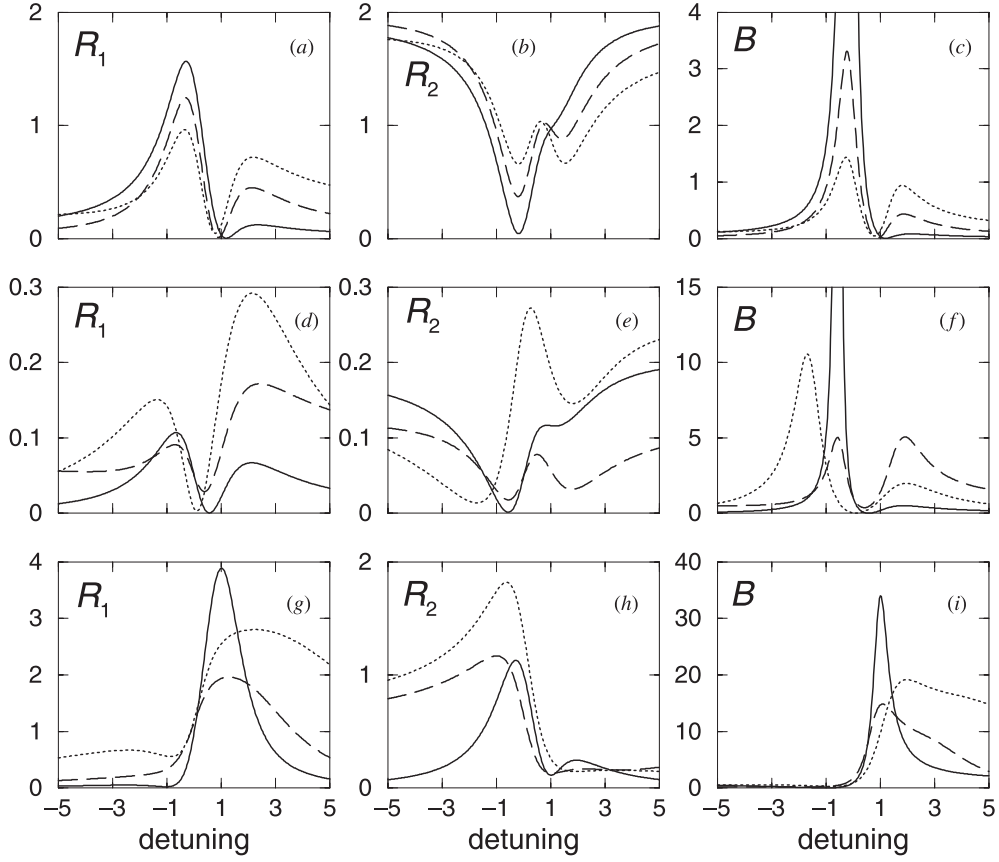
Figure 4. (a) Partial ionization rates R_1 and R_2 (normalized by $\bar{\gamma}^{(3)}$) and branching ratio $B = R_1/R_2$ versus detuning ϵ. For (a)–(c), $q = 1$, $q^{(3)} = 2$, $g = 1$, $g^{(3)} = 3$; $\Gamma_1/\Gamma_2 = 0.5$ (full curves), $\Gamma_1/\Gamma_2 = 2$ (broken curves), $\Gamma_1/\Gamma_2 = 5$ (dotted curves). For (d)–(f), $q^{(3)} = 1$, $g = 2$, $g^{(3)} = 1$; $q = 2$, $\Gamma_1/\Gamma_2 = 0.5$ (full curves), $q = 2$, $\Gamma_1/\Gamma_2 = 5$ (broken curves), $q = 3$, $\Gamma_1/\Gamma_2 = 0.5$ (dotted curves). For (g)–(i), $g = 1$, $\Gamma_1/\Gamma_2 = 0.5$; $q = 1$, $q^{(3)} = 3$, $g^{(3)} = 1$ (full curves), $q = 2$, $q^{(3)} = 1$, $g^{(3)} = 2$ (broken curves), $q = 3$, $q^{(3)} = 1$, $g^{(3)} = 2$ (dotted curves).

is the three-photon direct ionization width of the ground state $|1\rangle$ weighted by the configuration interaction (obviously $\bar{\gamma}^{(3)} = \gamma^{(3)}$ in the single continuum case), and

$$X = \epsilon(1 + g^2) - 2q \qquad X^{(3)} = \epsilon(1 + gg^{(3)}) - q - q^{(3)}$$

$$Y_l = q\left(\epsilon\frac{m_l}{M_{12}} - \frac{\Gamma_l}{2\bar{\Gamma}}\right) \qquad Y_l^{(3)} = q^{(3)}\left(\epsilon\frac{m_l^{(3)}}{M_{12}^{(3)}} - \frac{\Gamma_l}{2\bar{\Gamma}}\right)$$

$$S = q^2 + g^2 \qquad S^{(3)} = qq^{(3)} + gg^{(3)}.$$

The branching ratio $B = R_1/R_2$, which we plot in figure 4 for several different values of the parameters q, $q^{(3)}$, g, $g^{(3)}$ and Γ_1/Γ_2 (or, equivalently, q, $q^{(3)}$, m_1/m_2, $m_1^{(3)}/m_2^{(3)}$ and Γ_1/Γ_2), again does not depend on the harmonic field intensity and the relative phase of
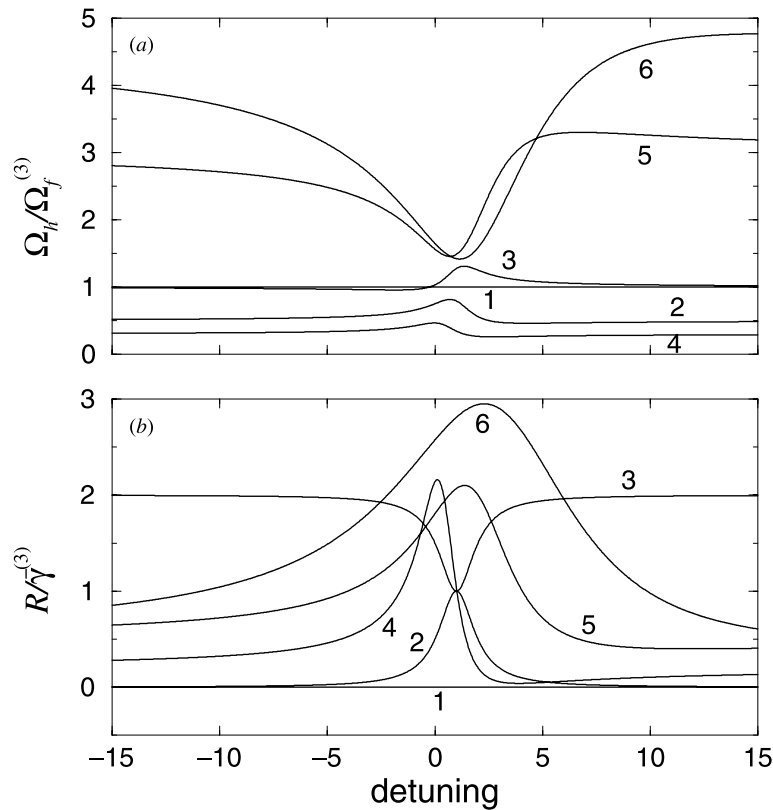
Figure 5. (a) Rabi frequency of the harmonic field Ω_h (normalized by $\Omega_f^{(3)}$) and (b) ionization rate R (normalized by $\bar{\gamma}^{(3)}$) versus detuning ϵ for $q = q^{(3)} = 1$, $g = g^{(3)} = 2$ (curve 1); $q = 1$, $q^{(3)} = 2$, $g = g^{(3)} = 1$ (curve 2); $q = 1$, $q^{(3)} = 2$, $g = 1$, $g^{(3)} = 3$ (curve 3); $q = 1$, $q^{(3)} = 2$, $g = 2$, $g^{(3)} = 1$ (curve 4); $q = 2$, $q^{(3)} = 1$, $g = 1$, $g^{(3)} = 2$ (curve 5); $q = 3$, $q^{(3)} = 1$, $g = 1$, $g^{(3)} = 2$ (curve 6).

the two fields. The equation for the total ionization rate has a more compact form

$$R = \frac{\bar{\gamma}^{(3)}}{\left[\epsilon(1 + g^2) - 2q\right]^2 + \left[q^2 + g^2\right]^2} \left\{ q^2(q - q^{(3)})^2 + q^2(g^{(3)}q - gq^{(3)})^2 \right.$$

$$+ g^2\left[\epsilon(g - g^{(3)}) + (g^{(3)}q - gq^{(3)})\right]^2$$

$$\left. + \left[(\epsilon - q)(g - g^{(3)}) + (g^{(3)}q - gq^{(3)})\right]^2 \right\} \tag{3.17}$$

and, as in the single continuum case, R is expressed through the atomic parameters, detuning ϵ and the cube of the intensity of the fundamental field. In figure 5 we plot the Rabi frequency of the harmonic field Ω_h and the ionization rate R as a function of ϵ for several different values of the parameters q, $q^{(3)}$, g and $g^{(3)}$. Now the situation is analogous to bound–bound resonance [1], when $R = 0$, $\Omega_h = \Omega_f^{(3)}$ and $\theta = \pi$, is realized only if $q = q^{(3)}$ and $g = g^{(3)}$. It is easy to verify that if the correlation coefficients g and $g^{(3)}$ are set to zero, only the first term in curly braces of (3.17) survives which leads to (2.24).

4. Conclusions

To summarize, we have presented a detailed theoretical investigation of the propagation of pump fundamental and its third harmonic fields through an optically dense autoionizing medium. Two cases of atomic systems were considered. In the first case, the single autoionizing state is embedded in a single continuum, while the second system involves two different continua. At the entrance to the medium, the two fields have a preselected relative phase, which, as was shown by the previous works, allows for an efficient phase control of the photoionization and the branching ratio of its products of a single atom (molecule). We have found, however, that the situation changes dramatically if the propagation effects are properly taken into account, since over a short scaled propagation distance, the phase and amplitude of the harmonic field settle to values that are determined only by the atomic and fundamental field parameters and are completely independent of the initial relative phase between the two fields, thus preventing the large-scale efficient phase control of the autoionization and its products. The parameters of the fundamental, through which the control of photoabsorption is still achievable, are the intensity and, most notably, the detuning from the autoionizing resonance. It is worth stressing here the presence of the correlation coefficients in the multiple continua case, which effectively contribute to an additional detuning-independent background in the ionization spectrum of an atom. We have shown that the expressions for the field evolution and for the rate of ionization obtained for the multiple continua case turn into the corresponding expressions for the single continuum case, if the correlation coefficients are set to zero.

Finally, we would like to note that since the output harmonic field is determined only by the atomic and fundamental field parameters (figures 2(a) and 5(a)), the results of this paper can also be treated from the point of view of third harmonic generation in autoionizing media.

Appendix

Here we define the atomic parameters used in the main text. These definitions correspond to the general case of an atom with multiple continua $|c_l\rangle$, $l = 1, 2, \ldots$ (figure 3). The same parameters for the atom with single continuum $|c\rangle$ (figure 1) are simply obtained by dropping everywhere the subscript l and summation $\sum$.

One- and three-photon transition matrix elements between the ground state $|1\rangle$ and autoionizing state $|2\rangle$:

$$M_{12} = \frac{\mu_{12}}{2\hbar} - \sum_l \mathcal{P} \int \frac{\mathrm{d}c_l}{\omega_{c_l 1} - \omega_h} \frac{\mu_{1c_l} V_{c_l 2}}{2\hbar^2} \tag{A.1}$$

$$M_{12}^{(3)} = \frac{\mu_{12}^{(3)}}{2\hbar} - \sum_l \mathcal{P} \int \frac{\mathrm{d}c_l}{\omega_{c_l 1} - \omega_h} \frac{\mu_{1c_l}^{(3)} V_{c_l 2}}{2\hbar^2} \tag{A.2}$$

where $\mathcal{P}$ denotes the principal value part of the integral.

One- and three-photon asymmetry parameters:

$$q = \frac{M_{12}}{\sum_l m_l} \qquad\qquad m_l = \pi \frac{\mu_{1c_l} V_{c_l 2}}{2\hbar^2} \tag{A.3}$$

$$q^{(3)} = \frac{M_{12}^{(3)}}{\sum_l m_l^{(3)}} \qquad m_l^{(3)} = \pi \frac{\mu_{1c_l}^{(3)} V_{c_l 2}}{2\hbar^2}. \tag{A.4}$$

Ionization width of ground state $|1\rangle$ directly into the continuum $|c_l\rangle$:

$$\gamma_l = 2\pi \left| \frac{\mu_{1c_l}}{2\hbar} E_h^* + \frac{\mu_{1c_l}^{(3)}}{2\hbar} E_f^{*3} \mathrm{e}^{\mathrm{i}\delta kz} \right|^2. \tag{A.5}$$

Alternatively, the ionization γ_l from the ground state can be written as a sum of ionizations due to each field separately and an interference term:

$$\gamma_l = \gamma_l^{(1)} + \gamma_l^{(3)} + 2\cos\theta \sqrt{\gamma_l^{(1)} \gamma_l^{(3)}} \tag{A.6}$$

where the expressions for $\gamma_l^{(1)}$ and $\gamma_l^{(3)}$ are easily obtained from the comparison of (A.5) and (A.6):

$$\gamma_l^{(1)} = \pi \frac{|\mu_{1c_l}|^2}{2\hbar^2} |E_h|^2 \qquad \gamma_l^{(3)} = \pi \frac{|\mu_{1c_l}^{(3)}|^2}{2\hbar^2} |E_f|^6.$$

Autoionization width of state $|2\rangle$ into continuum $|c_l\rangle$:

$$\Gamma_l = 2\pi \frac{|V_{2c_l}|^2}{\hbar^2}. \tag{A.7}$$

Detuning of both fields from the (modified) atomic transition resonance:

$$\tilde{\Delta} = \Delta + \sum_l (s_l - S_l) \tag{A.8}$$

where

$$s_l = \mathcal{P} \int \frac{\mathrm{d}c_l}{\omega_{c_l 1} - \omega_h} \left| \frac{\mu_{1c_l}}{2\hbar} E_h^* + \frac{\mu_{1c_l}^{(3)}}{2\hbar} E_f^{*3} \mathrm{e}^{\mathrm{i}\delta kz} \right|^2 \tag{A.9}$$

$$S_l = \mathcal{P} \int \frac{\mathrm{d}c_l}{\omega_{c_l 1} - \omega_h} \left| \frac{V_{2c_l}}{\hbar} \right|^2 \tag{A.10}$$

are the AC Stark shifts of the states $|1\rangle$ and $|2\rangle$, respectively, due to the interaction with continuum $|c_l\rangle$. Alternatively, the AC Stark shift s_l of the ground state can be written as a sum of the Stark shifts due to each field separately and a cross term:

$$s_l = s_l^{(1)} |E_h|^2 + s_l^{(3)} |E_f|^6 + 2\cos\theta \, s_l^{(13)} |E_h||E_f|^3 \tag{A.11}$$

where the coefficients $s_l^{(1)}$, $s_l^{(3)}$ and $s_l^{(13)}$ (polarizabilities) are easily obtained from the comparison of (A.9) and (A.11).

Correlation coefficients for an atom with two continua:

$$g = \frac{\mu_{1c_1} V_{c_2 2} - \mu_{1c_2} V_{c_1 2}}{\mu_{1c_1} V_{c_1 2} + \mu_{1c_2} V_{c_2 2}} = \frac{\pi}{2\hbar^2} \frac{\mu_{1c_1} V_{c_2 2} - \mu_{1c_2} V_{c_1 2}}{m_1 + m_2} \tag{A.12}$$

$$g^{(3)} = \frac{\mu_{1c_1}^{(3)} V_{c_2 2} - \mu_{1c_2}^{(3)} V_{c_1 2}}{\mu_{1c_1}^{(3)} V_{c_1 2} + \mu_{1c_2}^{(3)} V_{c_2 2}} = \frac{\pi}{2\hbar^2} \frac{\mu_{1c_1}^{(3)} V_{c_2 2} - \mu_{1c_2}^{(3)} V_{c_1 2}}{m_1^{(3)} + m_2^{(3)}}. \tag{A.13}$$

Obviously, in the case of a single continuum, these coefficients vanish: $g = g^{(3)} = 0$.

In the above definitions, μ_{1n} and $\mu_{1n}^{(3)}$ are the one- and three-photon dipole matrix elements for the harmonic and fundamental fields, respectively, on transition $|1\rangle \rightarrow |n\rangle$, $n = 2, c_l$; $V_{2c_l} \equiv \langle 2| V |c_l\rangle$ is the configuration-interaction matrix element; ω_{n1} is the $|1\rangle \rightarrow |n\rangle$ transition resonance frequency.

References

[1] Petrosyan D and Lambropoulos P 2000 *Phys. Rev. Lett.* **85** 1843
Petrosyan D and Lambropoulos P 2001 *Phys. Rev.* A **63** 043417

[2] Shapiro M, Hepburn J W and Brumer P 1988 *Chem. Phys. Lett.* **149** 451
Chan C K, Brumer P and Shapiro M 1991 *J. Chem. Phys.* **94** 2688

[3] Camparo J C and Lambropoulos P 1997 *Phys. Rev.* A **55** 552
Camparo J C and Lambropoulos P 1999 *Phys. Rev.* A **59** 2515

[4] Chen C, Yin Y and Elliott D S 1990 *Phys. Rev. Lett.* **64** 507
Chen C and Elliott D S 1990 *Phys. Rev. Lett.* **65** 1737

[5] Karapanagioti N E, Xenakis D, Charalambidis D and Fotakis C 1996 *J. Phys. B: At. Mol. Opt. Phys.* **29** 3599

[6] Fano U 1961 *Phys. Rev.* **124** 1866

[7] Lambropoulos P and Zoller P 1981 *Phys. Rev.* A **24** 379

[8] Zhu L, Suto K, Fiss J A, Wada R, Seideman T and Gordon R J 1997 *Phys. Rev. Lett.* **79** 4108
Zhu L, Kleiman V, Li X, Lu S, Trentelman K and Gordon R J 1995 *Science* **270** 77

[9] Nakajima T and Lambropoulos P 1993 *Phys. Rev. Lett.* **70** 1081
Nakajima T and Lambropoulos P 1994 *Phys. Rev.* A **50** 595

[10] Nakajima T, Zhang J and Lambropoulos P 1997 *J. Phys. B: At. Mol. Opt. Phys.* **30** 1077
Lambropoulos P and Nakajima T 1999 *Phys. Rev. Lett.* **82** 2266

[11] Zhang J 1991 Laser-induced continuum structure and third harmonic generation in one- and two-valence-electron atoms *PhD Dissertation* University of Southern California, Los Angeles
Lambropoulos P, Zhang J and Tang X 1992 *Coherence Phenomena in Atoms and Molecules in Laser Fields* (New York: Plenum)