RAPID COMMUNICATIONS

PHYSICAL REVIEW A VOLUME 58, NUMBER 6 DECEMBER 1998

Time-delay spectroscopy of autoionizing resonances

Stefano Cavalieri and Roberto Eramo
Istituto Nazionale di Fisica della Materia, Unità di Firenze, Dipartimento di Fisica and European Laboratory for Non-Linear Spectroscopy (LENS), Università di Firenze, Largo E. Fermi 2, I-50125 Firenze, Italy

(Received 15 June 1998)

The approach of time-delay spectroscopy is proposed as a tool for the study of high-lying autoionizing states through fast laser sources. [S1050-2947(98)50212-0]

PACS number(s): 32.80.Dz, 32.80.Qk

For years, the use of short pulse lasers has been devoted to the temporal analysis of fast relaxation phenomena in several fields of research, ranging from solid-state studies, to liquid-phase studies, and to high intense field processes in isolated atoms and molecules [1–4]. Recently, a temporal technique involving two delayed short laser pulses in resonance with a transition of the physical system (time delay spectroscopy, TDS) has been introduced for extracting spectral information [5–10]. A short pulse induces a coherence in a two-level system, creating a polarization in the medium. The induced polarization will oscillate at the transition frequency with decreasing amplitude during the dephasing time. The second pulse, depending on the phase of the polarization oscillations, can enhance or destroy the residual polarization and the population of the upper level. As a result, the radiative decay, at the end of the second pulse, exhibits interference fringes vs the delay between the two pulses. Information on the energy differences between nearby states in the atom and the dephasing time of the polarization, i.e., the line shape of the transition, are extracted from the time modulation of the fringe patterns [8]. This method, which can be thought as a variation of the Ramsey fringe experiments [11], may be very useful for the high-resolution spectroscopy of high-lying states with short laser pulses. In fact, the high peak intensity of many pulsed laser sources opens many possibilities for multiphoton spectroscopy, as well as single-photon spectroscopy in the far uv, where the laser field generates the probing radiation through high-order harmonic processes. Moreover, the spectral resolution of TDS is not limited by the time duration of the pulse. TDS has been recently used to investigate the coherent superposition states of several excited discrete states [12,13].

Up to now TDS has been used for the study of bound-bound transitions. In this paper we present its possibilities in the study of structured continua, namely, autoionizing states. We will show that the information extracted allows the determination of the important parameters of the continuum resonance: energy, decay time, and Fano parameter. This method appears to be an alternative to the synchrotron sources in one-photon spectroscopy of highly energetic states embedded into the continuum; it can be also considered a complementary spectroscopic tool, as it allows multiphoton transitions to probe the structured continua.

The coupling scheme is depicted in Fig. 1. The ground state is coupled to the autoionizing state $|e\rangle$ by means of the laser at frequency ω_p. We start from the atomic state vector expansion

$$|\Psi\rangle = c_g(t)|g\rangle + c_e(t)|e\rangle + \int d\omega c_\omega|\omega\rangle \tag{1}$$

in terms of the bound and continuum states. We work in the interaction picture, and use the rotating-wave approximation and the usual procedures of Markov elimination for the continuum amplitude, to get

$$\left(\frac{d}{dt} + \frac{\Gamma_g}{2}\right) c_g = \frac{i\gamma}{2}(-q+i)e^{i\Delta t}c_e, \tag{2}$$

$$\left(\frac{d}{dt} + \frac{\Gamma_e}{2}\right) c_e = \frac{i\gamma}{2}(-q+i)e^{-i\Delta t}c_g. \tag{3}$$

In these equations the notations

$$\Gamma_g = \left(\pi \frac{\Omega_{g\omega}\Omega_{\omega g}}{2}\right)_{\omega=\omega_0}, \quad \Gamma_e = 2\pi[T_{e\omega}T_{\omega e}]_{\omega=\omega_0},$$
$$\gamma = \pi(\Omega_{g\omega}T_{\omega e})_{\omega=\omega_0} = \sqrt{\Gamma_g\Gamma_e}, \tag{4}$$

$$q = \frac{P\int d\omega \dfrac{\Omega_{g\omega}T_{\omega e}}{\omega_0-\omega} + \Omega_{ge}}{\pi(\Omega_{g\omega}T_{\omega e})_{\omega=\omega_0}}, \quad \Delta = \omega_g + \omega_p - \omega_e \tag{5}$$

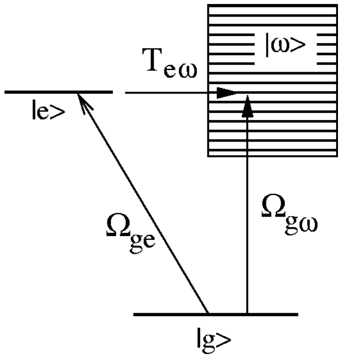

FIG. 1. Laser-induced autoionization process. Ω_{ge} is the Rabi frequency for the coupling between the ground state $|g\rangle$ and the autoionizing state $|e\rangle$; $\Omega_{g\omega}$ is the analogue for the continuum states $|\omega\rangle$. The coupling between the autoionizing state and the continuum, due to an intra-atomic interaction, has been denoted by $T_{e\omega}$.

1050-2947/98/58(6)/4263(4)/$15.00

have been used for the decay constants Γ_g and Γ_e, the coupling constants γ, the Fano parameter q, and the detuning Δ. In these definitions $\omega_0 = \omega_g + \omega_p \approx \omega_e$ is the frequency in the continuum where the laser is tuned,

$$\Omega_{\omega k} = E_p \langle \omega | \mathbf{d} \cdot \hat{\mathbf{e}} | k \rangle / \hbar \quad (k = g, e) \tag{6}$$

are the Rabi frequencies,

$$\mathbf{E} = \mathbf{E}_p \hat{\mathbf{e}} \cos \omega_p t \tag{7}$$

is the (linearly polarized) probe field, and $T_{\omega k}$ are the matrix elements of the autoionizing interaction. In Eqs. (2) and (3), the dynamic and static Stark shifts $\delta\omega_g$ and $\delta\omega_e$ have been included in the detuning; nevertheless, as will be shown in the following, they are irrelevant for the determination of the autoionizing state parameters. Equations (2) and (3) are relative to the field (7); if we had assumed a nonvanishing phase ϕ, i.e., $\mathbf{E} = \mathbf{E}_p \hat{\mathbf{e}} \cos(\omega_p t - \phi)$, instead of Eq. (7), we would have obtained the same Eqs. (2) and (3), with the amplitude c_e replaced by

$$c'_e = c_e e^{-i\phi}. \tag{8}$$

The effect on the dynamics caused by the relative phase ϕ between the two pulses can easily be seen in the perturbative case where $c_g \approx 1$. For the case of two pulses, Eq. (3), integrated over the duration of the first pulse, directly gives the value of the amplitude $c_e(\tau)$ at the end of the initial pulse. The same evolution happens during the second pulse, except for the the phase factor $\exp\{i(\phi - \Delta T)\}$, which is due both to delay and to the phase difference between the two pulses. The phase factor can thus give rise to a destructive or a constructive interference in the excitation of the atomic system. There are two main cases:

(i) In the case of TDS, the system interacts with two laser pulses, where the second pulse is a replica of the first one delayed by T; in this case, the interaction with the second pulse includes the phase factor $\phi = \omega_p T$ and the fringe exponential factor is $\exp\{-i(\phi - \Delta T)\} = \exp[-i\omega_{eg} T]$.

(ii) Another possibility is that the system interacts with the same wave field in two different instants. This is the analogue of Ramsey spectroscopy, where the time delay introduced by the flight time of the atoms is substituted by two amplified sections of a cw field [10]. In this case $\phi = 0$ and the fringe exponential factor is $\exp\{i\Delta T\}$.

Here we will study the time-delay spectroscopy. By using the dressed-states formalism, it is possible to find an exact, analytical and reasonably simple solution for the case of flat pulses. We prefer, anyhow, to present an analytical solution that is valid for an arbitrary pulse shape by using a perturbative approach in the probe field-atom interaction. In fact, this approach takes into account the effects of the pulse shape emitted by real laser systems. Furthermore, as the method is based on probing the residual excitation on a time scale that is necessarily greater than the pulse duration, it is not interesting to investigate a strong-probe-field regime, when the ionization probability during the pulse approaches unity.

We solve Eqs. (2) and (3) perturbatively with two well-separated pulses of duration τ and separation T (which represents the time between the beginnings of the two identical pulses). We do not consider the case of the two overlapping pulses, because our aim is to extract spectroscopic information from the quantum interferences; the passage from two overlapping pulses to the separated case is indeed the passage from optical interferences to quantum interferences, as shown in Ref. [14].

In order to study pulse shape effects we solve perturbatively Eqs. (2) and (3) for $\Delta\tau = 0$. By denoting with $c_g^{(k)}$ and $c_e^{(k)}$ the parts of the amplitudes that are of the order of $(\sqrt{\Gamma_g})^k$, that is, of the order of the Rabi frequency $(\Omega_{g\omega})^k$, we find, to second order, at the end of the first pulse, and using the notation $\tilde{\gamma} = (-q + i)\gamma$,

$$\begin{aligned} c_g(\tau) &= 1 + c_g^{(2)}(\tau) \\ &= 1 - \frac{1}{2} \int_0^\tau dt' \Gamma_g(t') \\ &\quad - \frac{1}{4} \int_0^\tau dt' \tilde{\gamma}(t') \int_0^{t'} dt'' \tilde{\gamma}(t'') e^{-\Gamma_e (t' - t'')/2}, \end{aligned} \tag{9}$$

$$c_e(\tau) = c_e^{(1)}(\tau) = \frac{i}{2} \int_0^\tau dt' \tilde{\gamma}(t') e^{-\Gamma_e(\tau - t')/2}. \tag{10}$$

The evolution between the two pulses is given simply by

$$c_g(T) = c_g(\tau), \quad c_e(T) = c_e(\tau) e^{-\Gamma_e(T - \tau)/2}. \tag{11}$$

Finally, at the end of the second pulse we find

$$\begin{aligned} c_g(T+\tau) &= 1 + c_g^{(2)}(t) \\ &= 1 - \frac{1}{2} \int_T^{T+\tau} dt' \Gamma_g(t') - \frac{1}{4} \int_T^{T+\tau} dt' \tilde{\gamma}(t') \\ &\quad \times \int_T^{t'} dt'' \tilde{\gamma}(t'') e^{-\Gamma_e(t' - t'')/2} \\ &\quad + \frac{i e^{-i\omega_{eg} T} c_e^{(1)}(\tau)}{2} e^{-\Gamma_e(T - \tau)/2} \\ &\quad \times \int_T^{T+\tau} dt' \tilde{\gamma}(t') e^{-\Gamma_e(t' - T)/2} + c_g^{(2)}(\tau), \end{aligned} \tag{12}$$

$$\begin{aligned} c_e(T+\tau) &= c_e^{(1)}(T+\tau) \\ &= \frac{i e^{i\omega_{eg} T}}{2} \int_T^{T+\tau} dt' \tilde{\gamma}(t') e^{-\Gamma_e(t - t')/2} + c_e^{(1)} \\ &\quad \times (\tau) e^{-\Gamma_e(t - \tau)/2}. \end{aligned} \tag{13}$$

The extremes of the integrals can be shifted by $-T$, as we suppose that the two pulses are identical and well separated [i.e., $\tilde{\gamma}(t+T) = \tilde{\gamma}(t)$, whenever $0 < t < \tau$]. At the end of the pulse, when $t = T + \tau$, the first row in Eq. (12) is equal to the last term $c_g^{(2)}(\tau)$, as given by Eq. (9), giving

$$\begin{aligned} c_g(T+\tau) &= 1 + 2c_g^{(2)}(\tau) + \frac{i e^{-i\omega egT} c_e(\tau)}{2} e^{-\Gamma_e(T - \tau)/2} \\ &\quad \times \int_0^\tau dt' \tilde{\gamma}(t') e^{-\Gamma_e t'/2}. \end{aligned} \tag{14}$$

The ionization probability, $I=1-|c_g(T+\tau)|^2$, is thus given by

$$I=2I_1+[q^2+1]I_f e^{-\Gamma_e(T-\tau)/2}\cos(\nu+\omega_{eg}T), \tag{15}$$

where

$$\tan\nu=\frac{2q}{q^2-1},$$
$$I_f=\frac{1}{2}\int_0^\tau dt'\,\gamma(t')e^{-\Gamma_e(\tau-t')/2}\int_0^\tau dt'\,\gamma(t')e^{-\Gamma_e t'/2} \tag{16}$$

and I_1 is the ionization probability characteristic of just one pulse:

$$\begin{aligned}I_1&=1-|c_g(\tau)|^2\\&=\int_0^\tau dt'\Gamma_g(t')+\frac{q^2-1}{2}\int_0^\tau dt'\,\gamma(t')\\&\quad\times\int_0^{t'}dt''\gamma(t'')e^{-\Gamma_e(t'-t'')/2}.\end{aligned} \tag{17}$$

In the limit $T\rightarrow\infty$, we recognize from Eq. (15) the ionization probability of the single pulse doubled. The novelties introduced by the coupling to the continuum are important in determining the structure of the interference fringes, which, compared to the discrete state case, are shifted by the phase ν. In the limit $q\gg1$, when the dynamics of the autoionizing state is nearly the same as that of a discrete state, Eq. (15) shows the discrete-state result, which is obtained, for example, when studying a discrete transition by observing the fluorescence with the time-delay technique. From Eq. (15) we can obtain the the result of Ref. [10] by substituting $q^2\Gamma_e\Gamma_g$ with the Rabi frequency Ω_{ge}^2, and considering that the ionization yield I corresponds, in that paper, to the fluorescence yield. As expected, the peculiarity of the autoionizing state interaction appears in the case where $|q|$ approaches unity or zero. In fact, for $|q|\approx1$, the ν shift becomes important. For $q=0$, this shift is absent but the cosine term has the sign opposite that expected from the discrete case. In principle, Eq. (16) provides a measure of q, which is based on the fringe phase extrapolated at $T=0$. From an experimental point of view this is quite difficult, as it involves a measurement of the origin of the time scale that is accurate to within λ/c and the monitor of this origin during the whole time-delay measurement.

From the fringe period of the ionization profile vs T it is possible to measure the autoionization energy $\hbar\omega_{eg}$, which is unaffected by ac-Stark shifts. This method of measurement is accurate, provided that the delay line allows delays of the order $1/\Gamma_e$. From the expression of the ionization probability we can see that it is not necessary to perform an interferometric measurement of the fringe profile in order to derive the resonance parameters q and Γ_e from the two-pulse response. In fact, by fitting the envelope of $I-2I_1$ [for example, the upper envelope, corresponding to $\cos(\omega_{eg}T+\nu)\rightarrow1$ in Eq. (15)] to an exponential, we find the excited-state width Γ_e. The q value can be determined by subtracting the term $I_{off}=2\int_0^\tau dt'\Gamma_g(t')$, which can be determined from an off-resonance measurement, from the mean value $2I_1$ of Eq. (17). Obviously, in order to obtain the Fano parameter value from $I_1-\int_0^\tau dt'\Gamma_g(t')$, it is necessary to know the temporal shape of the pulses. This knowledge is not necessary if we suppose that the autoionization probability is negligible during the pulse: $\Gamma_e\tau\ll1$. In this case, the second integral in Eq. (17) is equal to I_f, and the off-resonance measurement, together with the fit of the fringe envelope, directly gives Γ_e and $(q^2-1)/(q^2+1)$, as can be explicitly shown by the following formula:

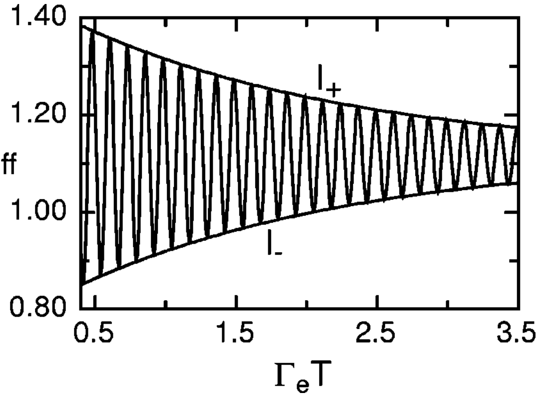

FIG. 2. Time-delay ionization fringes. The ionization probability [see Eq. (15)], normalized by the value off resonance, is plotted against the time delay. We suppose flat pulses with $\Gamma_e\tau=0.4$ and $q=1.5$. For graphical purposes, in the plot we chose $\omega_{ge}/\Gamma_e=50$. Also indicated are the envelopes $I_\pm$ that, as discussed in the text, can be used to obtain q^2 and Γ_e when the experimental conditions prevent reliable detection of the fringe structure.

$$\rho(t)=\frac{I_+-I_-}{I_++I_--2I_{off}}=\frac{q^2+1}{q^2-1}e^{-\Gamma_e(T-\tau)/2}, \tag{18}$$

where I_+ and I_- are the two branches of the envelope of Eq. (15):

$$I_\pm=2I_1\pm(q^2+1)I_f e^{-\Gamma_e(T-\tau)/2}. \tag{19}$$

When $\Gamma_e\tau$ is of the order of unity, the factor multiplying the exponential in $\rho(t)$ is no longer a function of the q parameter alone, as the ratio between I_f and the corresponding integral in Eq. (17) depends upon the pulse shape. In the case of flat pulses, one obtains

$$\rho(t)=\frac{q^2+1}{q^2-1}\frac{\mu^2}{1-\mu}\frac{\Gamma_e\tau}{4}e^{-\Gamma_e(T-\tau)/2}, \tag{20}$$

where $\mu=2(1-e^{-\Gamma_e\tau/2})/\Gamma_e\tau$, which reduces to $\mu\approx1-\Gamma_e\tau/4$ in the limit $\Gamma_e\tau\ll1$. In Fig. 2 we report a ionization profile $I(t)$ normalized to the off-resonance ionization yield I_{off}.

The results obtained here are valid for one-photon excitation. The extension to multiphoton excitation is straightforward, at least for the case in which the intermediate levels are nonresonant. For instance, for the case of three-photon excitation, the formal results are the same as the preceding one-photon ionization, provided that the ground-state Rabi frequency and the detuning are changed according to the following prescriptions:

$$\Omega_{\omega g} \to \frac{1}{4} \sum_{\alpha\beta} \frac{\Omega_{\omega\alpha}\Omega_{\alpha\beta}\Omega_{\beta g}}{(\omega_{\alpha g} - 2\omega_p)(\omega_{\beta g} - \omega_p)}, \qquad \Delta \to \omega_g + 3\omega_p - \omega_e, \tag{21}$$

where α and β are two indices running over the intermediate states.

In conclusion, we have presented a method for the study of autoionizing states using two-pulse time-delay spectroscopy. With the high power provided by short-pulse laser sources, we have shown that the method is suitable for the study of high-lying autoionizing states, either through multiphoton excitation of the structured continua or by the use of a one-photon transition with a high harmonic of the laser field. In comparison with synchrotron source experiments, the method might be a complement for multiphoton excitation or an alternative to the one-photon case.

[1] *Chemical Applications of Ultrafast Spectroscopy*, edited by G. R. Fleming (Oxford University Press, Oxford, 1986).

[2] *Atoms in Intense Laser Fields*, edited by Mihai Gavrila (Academic Press, San Diego, 1992).

[3] M. Saeed, B. Yang, X. Tang, and L. F. DiMauro, Phys. Rev. Lett. **68**, 3519 (1992).

[4] R. Righini, Science **262**, 1386 (1993).

[5] A. P. Heberle, J. J. Baumberg, and K. Kohler, Phys. Rev. Lett. **75**, 2598 (1995).

[6] P. C. M. Planken, P. C. van Son, J. N. Hovenier, T. O. Klaassen, W. Th. Wenckebach, B. N. Murdin, and G. M. H. Knippels, Phys. Rev. B **51**, 9643 (1995).

[7] S. Ceccherini, F. Bogani, M. Gurioli, and M. Colocci, Opt. Commun. **132**, 77 (1996).

[8] J. T. Fourkas, W. L. Wilson, G. Wackerle, A. E. Frost, and M. D. Fayer, J. Opt. Soc. Am. B **6**, 1905 (1989).

[9] M. Bellini, A. Bartoli, and T. W. Hansch, Opt. Lett. **22**, 540 (1997).

[10] M. M. Salour, Rev. Mod. Phys. **50**, 667 (1978).

[11] N. Ramsey, Phys. Rev. **76**, 996 (1949).

[12] R. R. Jones, Phys. Rev. Lett. **75**, 1491 (1995).

[13] R. R. Jones, C. S. Raman, D. W. Schumaker, and P. H. Bucksbaum, Phys. Rev. Lett. **71**, 2575 (1993).

[14] V. Blanchet, C. Nicole, M. Bouchene, and B. Girard, Phys. Rev. Lett. **78**, 2716 (1997).