Dynamics of Resonances Rapidly Shifting under Short Laser Pulses

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We present a theoretical analysis of multiphonon ionization through intermediate states shifted through resonance during a short intense pulse. The dynamical behavior is described in terms of a density matrix evolving under a realistic temporal and spatial pulse shape. Our results, on atoms and with realistic parameters, show structure similar to that observed in recent experiments and suggest further interesting phenomena.

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Recent experiments[1,2] on multiphoton ionization (MPI) in connection with above-threshold ionization (ATI) have revealed new structure in the photoelectron energy spectra. It has appeared in experiments with short (subpicosecond) pulses of relatively high intensity (up to about 4×10^{14} W/cm^2) and of wavelengths in the range of $\sim$620 nm. In short, the first (closest to threshold) peak of the photoelectron energy (under higher resolution) exhibits a number of spikes which become more pronounced as the duration of the pulse becomes shorter, with its total energy held constant; which implies increasing intensity. Freeman *et al.*[1] have proposed a most interesting interpretation which relies on the idea that bound states of the atom shift into resonance under the large (mostly ponderomotive) shift which can be of the order of 2 eV at these intensities and wavelengths. The proposed interpretation appears to be qualitatively compatible with the observations, especially after the distribution of the laser intensity in the interaction volume is taken into consideration.[3]

These elegant experiments pose a number of interesting questions in connection with resonantly enhanced multiphoton ionization (REMPI). We have thus undertaken a quantitative theoretical analysis of this phenomenon and it is our purpose here to report some of our results which shed light, and to a large extent, support the basic idea of Freeman *et al.*[1] At the same time, a number of other interesting and at first sight surprising effects emerge, suggesting an unsuspected further variety of possible structure.

We consider here a system (atom) sufficiently simple to allow quantitative calculations, and sufficiently complicated to contain the main features of the phenomenon under study. Our system has a ground state $|0\rangle$, two intermediate bound states $|1\rangle$ and $|2\rangle$ of the same parity, an ionization potential, and infinitely many other states which contribute a nonresonant MPI background. The energy of $|j\rangle$ is denoted by $\hbar\omega_j$. We study the behavior of this system under conditions such that the two excited states shift in and out of resonance with a certain number of photons (to be specified in each case). We will use the abbreviated standard terminology $(m+n)$-REMPI, when m photons are necessary to reach near resonance with the states $|1\rangle$ and $|2\rangle$, and n photons to ionize from there. Realistic numbers corresponding to real atoms (specified below) are employed in all of our calculations.

At each position in the interaction volume (which is determined by the light-focusing system), the atoms see a pulse of a certain duration and temporal shape whose peak value is maximum at the center of the focal region and decreases outwards. Thus for a pulse of Fourier-limited bandwidth and frequency ω, the field amplitude can be written as $\mathcal{E}(\mathbf{R},t)$ where the indicated time variation is much slower than $2\pi/\omega$, being of the order of 200 fs or longer, in the present context.

A system of density matrix equations governing the dynamical behavior of the atom at a (macroscopic) space-time point $(\mathbf{R},t)$ can be derived, within the constraints of our model. The derivation parallels that of an earlier paper[4] in which a precursor to the present phenomenon was studied. The resulting differential equations (in a most compact form) for the slowly varying density matrix elements σ_{kj} are the following:

$$\frac{d}{dt}\sigma_{00}=\mathrm{Im}(\Omega_{01}\sigma_{10}+\Omega_{02}\sigma_{20})-\Gamma_0\sigma_{00}\,, \tag{1}$$

$$\frac{d}{dt}\sigma_{jj}=-\Gamma_j\sigma_{jj}-\mathrm{Im}(\Omega_{0j}\sigma_{j0})+\mathrm{Im}C_{jj},\quad j=1,2\,, \tag{2}$$

$$\left[\frac{d}{dt}-i\Delta_j+\tfrac{1}{2}\Gamma\right]\sigma_{j0}=\tfrac{1}{2}i\Omega_{j0}(\sigma_{jj}-\sigma_{00})-\tfrac{1}{2}i\Omega_{jj'}\sigma_{j'0}+\tfrac{1}{2}i\Omega_{j'0}\sigma_{jj'},\quad j,j'=1,2\ (j\neq j')\,, \tag{3}$$

$$\left[\frac{d}{dt}+i\bar{\omega}_{12}+\tfrac{1}{2}(\Gamma_1+\Gamma_2)\right]\sigma_{12}=-\tfrac{1}{2}i\Omega_{10}\sigma_{02}+\tfrac{1}{2}i\Omega_{02}\sigma_{10}+\tfrac{1}{2}i(\Omega_{12}^{*}\sigma_{11}-\Omega_{12}\sigma_{22})\,, \tag{4}$$

where $C_{11}=\Omega_{12}^{*}\sigma_{12}$ and $C_{22}=-\Omega_{12}\sigma_{12}$. Ω_{0j} is the m-photon Rabi frequency coupling the states $|0\rangle$ and $|j\rangle$, and is

given by $\mathcal{E}^m \mu_{0j}^{(m)}$ with $\mu_{0j}^{(m)}$ being the corresponding m-photon dipole matrix element. Γ_j is the ionization width of state $|j\rangle$, given by the product $\hat{\sigma}_n F^n$ of the respective multiphoton ionization generalized cross section $\hat{\sigma}_n$ and the photon flux F. The detuning from resonance with the intermediate state is $\Delta_j = m\omega - \bar{\omega}_{j0}$ where all atomic energy differences (in units of rad/s of the type $\bar{\omega}_{j0} = \bar{\omega}_j - \bar{\omega}_0$ and $\bar{\omega}_{12} = \bar{\omega}_1 - \bar{\omega}_2$ bear a horizontal bar to indicate that the ac Stark shift S_j has been added to the respective free-atom energy. These shifts S_j are proportional to the laser intensity I (W/cm^2) and approach the ponderomotive shift ($e^2\mathcal{E}^2/4m\omega^2$) as the excited state approaches the ionization threshold. The complex quantity Ω_{12} is proportional to $\mathcal{E}^2$ and to a two-photon matrix element connecting the excited states $|1\rangle$ and $|2\rangle$. It is complex whenever the energy $\bar{\omega}_{j+\omega}$ falls above the ionization threshold (see Ref. 4 for details). All of the above atomic parameters, Ω_{0j}, Γ_j, Δ_j, and Ω_{12}, are time dependent on a time scale over which the amplitude $\mathcal{E}(t)$ varies. As a consequence, the differential equations (1)–(4) have time-dependent coefficients.

The matrix elements $\sigma_{jk}(t)$ are slowly varying in the sense that the transformations $\sigma_{0j}(t) = \rho_{0j}(t)e^{-im\omega t}$ have removed the rapid (resonant) variation of the primary off-diagonal density matrix elements $\rho_{0j}(t)$. Our equations are therefore valid as long as the envelope amplitude of the pulse does not vary significantly over a time of order $2\pi/\omega$.

The ponderomotive shift causes the ionization potential E_∞ to shift upward, thus becoming time dependent as the pulse intensity rises and falls. The kinetic energy E_k of the ejected photoelectrons will therefore vary during the pulse, obeying the equation $E_k(t) = E_0 + S_0 + (m+n)\hbar\omega - E_\infty(t)$.

The dynamical equations enable us to calculate the angle-integrated photoionization signal P_{ion} through the relation $P_{\text{ion}}(t) = 1 - \sigma_{00}(t) - \sigma_{11}(t) - \sigma_{22}(t)$. The number of photoelectrons generated between t and $t+\Delta t$ is proportional to $\Delta P_t = P(t+\Delta t) - P(t)$ which represents the number of photoelectrons of energy $E_k(t)$. Our calculation is implemented essentially as described above, with the additional integration over the interaction volume using a Gaussian form. We can thus calculate the total number of photoelectrons of energy E_k generated anywhere in the interaction volume at the end of the pulse. The temporal pulse shape has also been taken to be Gaussian.

Before embarking upon the solution of the dynamical equations (1)–(4), we must calculate all relevant atomic parameters such as Ω_{ij}, Γ_j, and S_j. In each case, we have performed such calculations quite accurately employing multiphoton techniques[5] based on quantum-defect theory. For excited states not very close to the ionization threshold, the shift often differs somewhat from the ponderomotive shift. In our calculations, we have always included the actual shift of the state obtained with the same wave functions and techniques that yield the other parameters.

Here are the questions we propose to explore: If this system with its known and calculable structure and dynamics is exposed to a short intense laser pulse, will its photoelectron spectrum exhibit peaks? Will they correlate with the bound states having shifted into resonance? What other features could be expected, and under what conditions would they be observable?

We consider first 4+1 ionization in Na with $|0\rangle = |3s\rangle$, $|1\rangle = |7s\rangle$, $|2\rangle = |6d\rangle$, and radiation of frequency $\hbar\omega = 9625$ cm^{-1}. The relevant parameters (all in rad/s) are the following: $\Omega_{01} = 2.4\times10^{-11}I^2$, $\Omega_{02} = 3.6\times10^{-11}I^2$, $\Gamma_1 = 0.65I$, $\Gamma_2 = 22.6I$, $S_1 = 200I$, $S_2 = 150I$, $S_0 = -58I$, with I in units of W/cm^2. The ponderomotive shift is $S_p = 8$ cm^{-1} per 10^{10} W/cm^2. As in all cases considered here, we choose the frequency such that, at zero field, both excited states lie below $4\hbar\omega$, the idea being to examine the structure of the photoelectron spectra as these states shift into and away from resonance during the pulse. The result for a pulse of 1 ps and peak intensi-

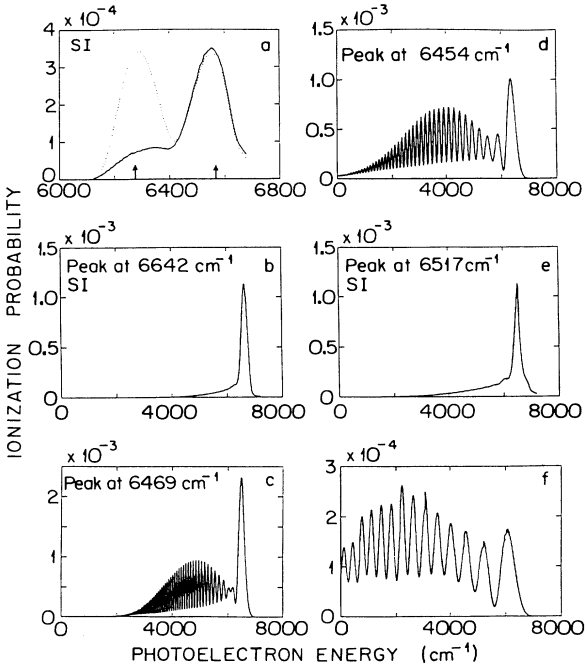

FIG. 1. Examples of photoelectron spectra at various pulse durations τ_L, photon frequencies ω, and intensities I, for a 4+1 process in Na. Photon frequency: $\omega = 9625$ cm^{-1} for (a) and 9725 cm^{-1} for (b)–(f). Peak intensity: $I = 5\times10^{11}$ W/cm^2 for (a), $I = 5\times10^{12}$ W/cm^2 for (b) and (c), $I = 10^{13}$ W/cm^2 for (d) and (e), and $I = 2.5\times10^{13}$ W/cm^2 for (f). Pulse duration: $\tau_L = 1$ ps for (a)–(c), $\tau_L = 0.5$ ps for (d) and (e), and $\tau_L = 0.2$ ps for (f). State $|1\rangle$ is in resonance at 6656 cm^{-1} for (b)–(f) and state $|2\rangle$ is in resonance at 6454 cm^{-1} also for (b)–(f). SI indicates signal integrated over space coordinates.

ty 5×10^{11} W/cm^2 is shown in Fig. 1(a) where one quite pronounced peak appears very close to the photoelectron energy corresponding to the $6d$ having shifted into resonance. The peak does in fact appear 23 cm^{-1} (in electron energy) after $6d$ has gone through resonance. No peak, however, appears when the $7s$ goes through resonance. Inspection of the ionization widths shows that only the state with the larger ionization width produces a peak. This may at first seem contrary to conventional rules of thumb about resonance ionization where states with larger ionization rates appear with broader profiles, when the frequency is scanned. The important difference here lies in that the frequency is not scanned but the state goes through resonance rather quickly and it requires a certain rate of ionization in order to produce signal significantly above the nonresonant background.

Equally important in shaping this behavior is the magnitude of Γ_j relative to Ω_{0j}. From the photoelectron energy corresponding to the peak, we infer that most of the signal comes from a region of the interaction volume of peak intensity around 2×10^{11} W/cm^2. At this intensity $\Omega_{01}/\Gamma_1\simeq8$ while $\Omega_{02}/\Gamma_2\leqq1$. Thus for the state $7s$, the Rabi oscillations being much faster than Γ_1^{-1} prevent efficient ionization, while for the state $6d$, Ω_{02} and Γ_2 are better matched.

To test the validity of this interpretation we have repeated the calculation leaving all parameters unchanged, except for the width of $7s$ which was set equal to that of $6d$. Two essentially identical peaks, one for each state almost on resonance, have now appeared [dotted line in Fig. 1(a)]. It is important to note here that a pulse of 1 ps at 5×10^{11} W/cm^2 does not cause saturation in this case. The total amount of ionization at the end of the pulse integrated over the interaction volume is 9%. The saturation intensity in this case is $\sim10^{12}$ W/cm^2.

We change now the photon frequency to 9725 cm^{-1} leaving the pulse duration the same (1 ps). The atomic parameters also remain practically unchanged. What is different now is that the states must shift by an extra 400 cm^{-1} for substantial ionization to occur, which means that the majority of ionization takes place at a slightly higher intensity region, but still below saturation, if the intensity were the same as before (5×10^{11} W/cm^2). A plot of the results (not shown here) looks much like Fig. 1(a). In fact, the broad hump is hardly present because the second state does not have the chance to come near resonance.

Let us now increase the peak intensity to 5×10^{12} W/cm^2 (which is slightly above the saturation intensity) leaving everything else unchanged. The resulting photoelectron spectrum is shown in Fig. 1(b). Only one peak has emerged, but both intermediate states have coalesced under the same peak; one having come into resonance 25 cm^{-1} before and the other 75 cm^{-1} after the photoelectron peak. When we reran the calculation with the ionization widths equal to each other, the plot looked practically the same; no particular sensitivity to the ionization rates in this case. The reason can be traced to the fact that, owing to the higher intensity, the states shift through resonance rather quickly and their contributions to the main ionization peak overlap. Moreover, most of the ionization is now produced at higher intensity than it was in Fig. 1(a).

Further insight into the physics of this behavior can be gained by examining this photoelectron spectrum before the integration over space is performed. This, of course, cannot be done experimentally, but the theoretical analysis has that flexibility. A sequence of results is shown in Figs. 1(c)–1(e). The first of these [Fig. 1(c)] corresponds to conditions identical to those of Fig. 1(b). The oscillatory structure following the main peak represents Rabi oscillations with a rapidly changing generalized Rabi frequency $(\Omega^2+\Delta^2)^{1/2}$ as the states shift away from resonance. If we decrease the pulse duration to 0.5 ps (with a corresponding increase in the intensity so as to keep the pulse energy constant), we can cause these oscillations to become more pronounced, as shown in Fig. 1(d). In fact, the prominence of the main peak of Fig. 1(c) is now somewhat deemphasized, as more signal is contained under the oscillatory structure. Would any of this structure survive the integration over the interaction volume? The answer is given in Fig. 1(e) where only a slight hump can be discerned to the left of the main peak. The rest of the structure has been smoothed out by the integration thus becoming inaccessible to experiment.

To illustrate this behavior further, we have performed a calculation at an even higher intensity and correspondingly shorter duration, with the result shown in Fig. 1(f) (before integration over space). The spectrum is now dominated by the structure of Rabi oscillations which would not be smoothed out completely by space integration. Having made this point, we should caution the reader that this result is correct within the model, but unrealistic for the real atom (Na) and the states we have

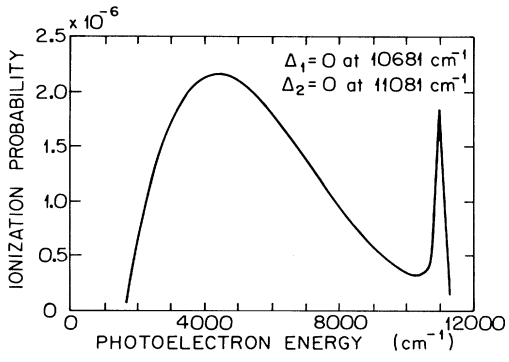

FIG. 2. Photoelectron spectrum for a 6+1 process in H. Photon frequency $\omega=17367$ cm^{-1}, pulse duration $\tau_L=1$ ps, peak intensity $I=4\times10^{13}$ W/cm^2, and the peaks at 10981 and 4565 cm^{-1}. The signal has been integrated over space coordinates.

chosen. The reason is that other states, such as $5g$, $5d$, $6s$, $4d$, $5s$, will shift into resonance just as the second peak begins developing, thus complicating but most probably not obliterating the structure. Only the signal for the initial part of the pulse is shown in Fig. 1(f). Because of the large intensity, a long spectrum of photoelectron energies results. At the point marked 0, the threshold has shifted by ~ 1.2 eV, the energy of one photon. From there on, it takes six photons to ionize the atom. Our calculation would be closer to reality if the two excited states were the two lowest ones.

We have examined a variety of other processes with overall similar results. Space permits to briefly quote 6+1 ionization in H, with $\hbar\omega = 17367$ cm^{-1}, $|1\rangle = |4s\rangle$, and $|2\rangle = |4d\rangle$. A new twist appears in this case. Although these two states are practically degenerate at zero field, they are about 1200 cm^{-1} apart at 10^{13} W/cm^2; because their shifts are $S_1 = 72I$, $S_2 = 50.5I$, and $S_0 = -1.8I$, all in rad/s. In the same units, the rest of the parameters are the following: $\Omega_{01} = -6.2\times 10^{-30} I^3$, $\Omega_{02} = 4.3\times 10^{-28} I^3$, $\Gamma_1 = 15.8I$, $\Gamma_2 = 8.8I$, and $S_p = 2.5$ cm^{-1} per 10^{10} W/cm^2. After integration over space (for 1 ps and peak intensity 4×10^{13} W/cm^2 which is well below the saturation intensity), we obtain the result of Fig. 2. The two states have come into resonance around the narrow peak. The broad peak reflects the fact that most of the ionization, in this case, comes from a region around the center of the interaction volume and at the peak intensity.

Having run out of space, we summarize the main conclusions emerging from our studies. The conjecture of Freeman *et al.*[1] is basically valid, in that states shifting through resonance are apt to produce structure. Integration over the interaction volume has a decisive effect on the structure, which looks significantly different below than it does above saturation. It appears that both experiments[1,2] so far were performed below saturation. The Rabi oscillations structure will appear only above saturation but in almost all cases it will be washed out because of spatial effects. Our analysis has shown that the relation between experimental peaks and resonant states is rather subtle and, in general, not a one to one. Not every shifting state produces a peak and vice versa. From extensive calculations on a number of atoms, we can say that the shifts of many excited states differ from the ponderomotive shift significantly, so that we cannot expect uniform and systematic shifting of all states. The shifts as well as the dynamical behavior will also exhibit some dependence on photon frequency. Moreover, the relation between Rabi frequencies and ionization widths will also influence the observed structure. At larger intensities, a larger set of states must be included, but in any case realistic calculations for the atom and process under consideration are indispensable to a quantitative interpretation of experiments.

The structures we have seen in our calculations reveal an intriguing variety which can be investigated with presently available sources in a number of atoms. Depending on the atom and the order of the process they could be observed under rather modest intensities (10^{11}–10^{13} W/cm^2) and in processes of low order such as 4+1, 5+2, 6+1, etc.

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