PHYSICAL REVIEW A VOLUME 12, NUMBER 6 DECEMBER 1975

Exact solution of a realistic model for two-photon ionization*

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(Received 30 June 1975)

A realistic model for resonant two-photon ionization of an atom is developed which can be solved exactly to give the ionization probability as a function of time, photon intensity, and a few atomic parameters. The exact solutions are compared to various commonly used perturbation results in order to ascertain the regions of validity of the perturbation calculations. It is shown that there are combinations of the parameters for which ionization rates cannot accurately describe the correct results, and that one commonly used perturbation development is not generally applicable to resonant two-photon ionization. Extension of the model to $(n+m)$-photon ionization having an m-photon resonance is discussed. The model is applied to two- and three-photon ionization in Cs.

I. INTRODUCTION

Resonant multiphoton ionization of atoms has received a great deal of attention of late, both theoretically[1] and experimentally.[2] Many formulations have appeared which attempt to explain the experimental results, usually by using some form of perturbation theory to calculate a multiphoton ionization rate in a manner which incorporates intensity-induced shifts and widths of the resonant intermediate states. While in many cases this seems very sensible, it is nonetheless not *a priori* clear that it is even possible to fit the experimental data with a single ionization rate, no matter how the rate is calculated.

It is the purpose of this article to explore the question: "When is it possible to describe a resonant multiphoton ionization experiment by a single ionization rate; what are the parameters which determine this region of applicability; and what does one do if a single rate model is not sufficient?" In order to resolve this question, we choose a particularly simple (although not unrealistic) model. Generalizations of this simple model can be made in a very straightforward manner. We assume that a single monochromatic beam of light of frequency ω is incident on a single atom; this light is approximately resonant with the energy separation between the ground state $|g)$ and a single excited state $|a)$, with no other nearby resonances. The frequency ω is sufficiently large that a two-photon ionization of the atom is possible. It is assumed that the interaction is turned on at $t=0$, and proceeds for a time T. We then compute the probability $P(T)$ that the atom has been ionized as of time T. [The quantity which a pulsed-laser ionization experiment measures is $N=N_0P(T)$, where N is the number of ions formed, N_0 is the number of atoms in the interaction region, and T is the length of the pulse.]

The sudden switching on and off of the photon field certainly does not correspond to the physical situation present in most, if not all, experiments. However, this field behavior is assumed for almost all of the perturbation-type calculations which have been made, and thus must be kept here if we are to ascertain the regions of applicability of these perturbation calculations within the model problem which they seek to solve. Further, if the region of transients which are introduced by this sudden switching can be identified from the calculation, and the interaction time is sufficiently large compared to this region, little error is expected as compared to a smoother switching procedure.

In Sec. II, we discuss the formalism used to solve the model problem, and the results obtained. In Sec. III, these results are considered in detail. Section IV contains an application of these results to two- and three-photon ionization of Cs. A brief resumé of the results is given and conclusions are drawn in Sec. V.

II. FORMALISM

The Hamiltonian H for the problem is taken in the usual form[3]

$$H=H_{\mathrm{A}}+H_{\mathrm{F}}+H_{\mathrm{AF}}\ ,$$

where H_{A} is the atomic Hamiltonian, H_{F} is the field Hamiltonian, and H_{AF} is the usual atom-field interaction in the position-space form of the dipole approximation (use of the dipole approximation is not essential to this calculation). The Hamiltonian H_{A} is assumed to have discrete eigenstates $|i)$ of energy E_i and a continuum of ionized eigenstates $|\alpha E)$ of energy E, where α is a label which removes all degeneracies for the continuum states. The continuum states are normalized such that $(\alpha E|\alpha E')=\delta(E-E')$. The Hamiltonian H_{F} has eigenstates $|n_1\omega_1, n_2\omega_2, \ldots)$ corresponding to n_1 photons of frequency ω_1, etc. The eigenstates of $H_A + H_F$, $|i, n\omega)$, etc., are assumed to be known.

We use the usual resolvent method[3] to evaluate $P(t)$, the probability that the atom, originally in the ground state $|g)$ at time $t=0$, is in some continuum eigenstate at a later time t, with two photons having been absorbed from the beam. As the use of resolvents in the calculation of the time evolution operator is straightforward and well known,[3] we shall not give the details of the calculation. However, in setting up the problem and obtaining our solutions, we make several simplifying assumptions which should be explicitly stated:

(a) The applied photon field is of the type $|n\omega)$, i.e., n photons of frequency ω in a single mode.

(b) The direct two-photon ionization of $|g)$ via nonresonant intermediate states is treated by using an effective Hamiltonian $H^{(2)}_{\text{eff}}$ which directly connects $|g)$ to the continuum of states $|\alpha E)$. We assume for simplicity that the matrix elements of $H^{(2)}_{\text{eff}}$ are those given by second-order perturbation theory:

$$(g, n\omega | H^{(2)}_{\text{eff}} | \alpha E, (n-2)\omega) \equiv \sum_{i \neq a} \frac{(g, n\omega | H_{\text{AF}} | i, (n-1)\omega)(i, (n-1)\omega | H_{\text{AF}} | \alpha E, (n-2)\omega)}{E_g - E_i - \omega}, \tag{1}$$

although a more accurate form, containing higher-order corrections to this expression, could easily be used. (Throughout this article, we take $\hbar = 1$.) Near resonance, the weak ω dependence of these matrix elements can be safely neglected.

(c) Free-free transitions are ignored. It is safe to assume (and model calculations verify this) that free-free transitions will only contribute significantly to the form of the energy distribution of the photoelectrons, and not to the probability that the atom will be ionized.

(d) In evaluating the Fourier transform of the resolvent by the method of residues, the usual approximation of spontaneous decay theory[3] is made; i.e., integrations over continuum states are evaluated at roughly the resonance energy, in this case $E_g + n\omega$. This approximation is quite good if the matrix elements involved are only weak functions of the photon energy over the range being considered, which is certainly the case here.

(e) The spontaneous decay of the intermediate resonant state $|a)$ has been ignored. For laser intensities customarily used, the probability that $|a)$ will be ionized is far greater than the spontaneous decay probability, so that this is an excellent approximation. In any event, it is not difficult to include this effect in any specific numerical treatment using the methods described here.

(f) Only a single continuum $|\alpha E)$ is considered. The generalization to several uncoupled continua is trivial.

(g) The usual rotating-wave approximation[4] is made.

With the above assumptions, the calculations of $P(t)$ is straightforward, and involves no further approximations. Using (1), the equation for the resolvent G takes the form

$$(z - H_A - H_F)G(z) = 1 + (H_{\text{AF}} + H^{(2)}_{\text{AF}})G(z) . \tag{2}$$

The states $|g, n\omega)$, $|a, (n-1)\omega)$, and $|\alpha E, (n-2)\omega)$ (all E) are connected to one another by this relation, and all other states are uncoupled from them. Taking matrix elements with respect to these states yields a set of algebraic equations which are easily solved. One finds, for instance, that

$$G_{gg} \equiv (g, n\omega | G | g, n\omega)$$

is given by

$$G_{gg}(z) = \frac{z - E'_a + \frac{1}{2} i \gamma_a}{(z - z_+)(z - z_-)}, \tag{3}$$

where

$$z_\pm = \tfrac{1}{2}\{E'_a + E'_g - \tfrac{1}{2} i \Gamma \pm [(\delta - \tfrac{1}{2} i \rho)^2 + \gamma_a \gamma_g (q - i)^2]^{1/2}\} , \tag{4}$$

and

$$\gamma_g = 2\pi |(g, n\omega | H^{(2)}_{\text{eff}} | \alpha E, (n-2)\omega)|^2 , \tag{5}$$

$$\gamma_a = 2\pi |(a, (n-1)\omega | H_{\text{AF}} | \alpha E, (n-2)\omega)|^2 \tag{6}$$

are the ionization decay widths of the $|g)$ and $|a)$. In these expressions, $E \simeq E_g + 2\omega \approx E_a + \omega$. For compactness of notation, we also introduce the related quantities $\Gamma = \gamma_a + \gamma_g$ and $\rho = \gamma_g - \gamma_a$. E'_a and E'_g are the bound-state energies shifted by the interaction with the continuum,

$$E'_g = E_g + n\omega + \Delta E_g, \quad E'_a = E_a + (n-1)\omega + \Delta E_a , \tag{7}$$

where

$$\Delta E_g = \text{P} \int \frac{|(g, n\omega | H^{(2)}_{\text{eff}} | \alpha E, (n-2)\omega)|^2 \, dE}{z - E - (n-2)\omega} , \tag{8}$$

$$\Delta E_a = \text{P} \int \frac{|(a, (n-1)\omega | H_{\text{AF}} | \alpha E, (n-2)\omega)|^2 \, dE}{z - E - (n-2)\omega} , \tag{9}$$

the principal-part integral being evaluated at $z = E_g + n\omega$. The quantity q is a measure of the interference between the resonant and nonresonant processes, and is given by

$$q=\frac{(g,n\omega|\left(H_{\mathrm{AF}}+\mathrm{P}\int dE\frac{H_{\mathrm{eff}}^{(2)}|\alpha E,(n-2)\omega)(\alpha E,(n-2)\omega|H_{\mathrm{AF}}}{z-E-(n-2)\omega}\right)|a,(n-1)\omega)}{\pi(g,n\omega|H_{\mathrm{eff}}^{(2)}|\alpha E,(n-2)\omega)(\alpha E,(n-2)\omega|H_{\mathrm{AF}}|a,(n-1)\omega)}$$

$$\equiv\frac{2H_{ga}}{(\gamma_a\gamma_g)^{1/2}}\ , \tag{10}$$

where the principal-value integral is again evaluated at resonance. The quantity q is similar to Fano's q value,[5] introduced in studies of autoionizing states, and has previously been shown to be of importance in understanding the shape of resonant multiphoton ionization profiles.[6] Note q must be real, and that by its definition H_{ga} contains the sign of q. The energy difference δ is defined by

$$\delta=E_g'-E_a'\ .$$

In terms of the same variables, G_{ag} is given by

$$G_{ag}=\frac{1}{2}\frac{(\gamma_a\gamma_g)^{1/2}(q-i)}{(z-z_+)(z-z_-)}\ . \tag{11}$$

The time translation operator $U(t)$ is the Fourier transform of $G(z)$.[3] Denoting matrix elements of $U(t)$ in the obvious fashion, it is easy to see that the probability of ionization $P(t)$ is given by

$$P(t)=1-|U_{gg}(t)|^2-|U_{ag}(t)|^2\ . \tag{12}$$

Evaluating the Fourier transforms by the usual method of residues gives

$$\begin{aligned}P(t)=1-\{&(\tfrac{1}{4}W^2+\tfrac{1}{16}\Gamma^2+\tfrac{1}{4}a^2+\tfrac{1}{2}\delta a\cos\varphi-\tfrac{1}{4}\rho a\sin\varphi)e^{-\Gamma_1 t}+(\tfrac{1}{4}W^2+\tfrac{1}{16}\Gamma^2+\tfrac{1}{4}a^2-\tfrac{1}{2}\delta a\cos\varphi+\tfrac{1}{4}\rho a\sin\varphi)e^{-\Gamma_2 t}\\&-2[(\tfrac{1}{4}W^2+\tfrac{1}{16}\Gamma^2-\tfrac{1}{4}a^2)\cos(ta\cos\varphi)+(\tfrac{1}{2}\delta a\sin\varphi+\tfrac{1}{4}a\rho\cos\varphi)\sin(ta\cos\varphi)]e^{-\Gamma t/2}\}/a^2\ ,\end{aligned} \tag{13}$$

where

$$\begin{aligned}&W=(\delta^2+q^2\gamma_a\gamma_g)^{1/2}=(\delta^2+4|H_{ga}|^2)^{1/2}\ ,\\&a^2=[(W^2-\tfrac{1}{4}\Gamma^2)^2+(\delta\rho+2q\gamma_a\gamma_g)^2]^{1/2}\ ,\\&\tan2\varphi=-(\delta\rho+2q\gamma_a\gamma_g)/(W^2-\tfrac{1}{4}\Gamma^2)\ ,\\&\Gamma_1=\tfrac{1}{2}\Gamma-a\sin\varphi,\quad\Gamma_2=\tfrac{1}{2}\Gamma+a\sin\varphi\ .\end{aligned} \tag{14}$$

It should be remarked that $P(t)$ can also be evaluated by computing $U_{Eg}(t)$, squaring, and integrating over all final states. Although the resulting expression appears remarkably different from Eq. (13), tedious algebraic manipulations show that the two expressions are identical.

The expression obtained above for $P(t)$ is obviously a very complicated function of time and the parameters γ_a, γ_g, δ, and q. In Sec. III, we discuss the properties of this function at some length.

III. DISCUSSION

The expression for $P(t)$ given above [Eq. (13)] has been obtained without assumptions concerning either the photon intensities involved or the relative magnitudes of the atomic matrix elements. Thus, $P(t)$ is exact within the model space used and provides a fixed standard to which perturbation calculations can be compared in order to evaluate their validity. As such, Eq. (13) is the key result of this paper.

As has already been noted, $P(t)$ is a function of γ_a, γ_g, q, and δ, as well as of the time t. Three of these parameters depend on the particular atomic species under investigation—q, γ_a, and γ_g. These three parameters are also intensity dependent: $\gamma_g=aI^2$, $\gamma_a=bI$, and $q=c+dI^{-1}$, with the coefficients of proportionality depending on the atomic species. Equation (13) then explicitly indicates that the atomic parameters which must be calculated in order to understand a resonant two-photon process are γ_a, γ_g, and q (or a, b, c, and d). We should also remark that the generalization of these results to an $(m+n)$-photon ionization having an m-photon resonant intermediate state is immediate; one need only replace H_{AF} by the appropriate m- and n-photon effective Hamiltonians.

For a fixed detuning δ and experimental time $t=T$, $P(T)$ has a very complicated intensity dependence, and no simple approximation is generally valid. For fixed intensity and time, the same may be said for the dispersion curve near resonance. In fact, for a general intensity, atomic system, detuning, and experimental time T, there is no simpler expression than Eq. (13) that can properly account for the ionization, nor is it generally possible to define an ionization probability per unit time (rate of ionization). This is not to say that for particular experiments simpler expressions are not possible. Regions of applicability of these simpler expressions will be discussed below.

The most convenient way in which to discuss the properties of $P(T)$ is to explore its δ and T dependence with the relative values of γ_a, γ_g, and H_{ga} (or equivalently, q) held fixed. This corresponds to fixing the atomic species and the photon intensity. This we do below, splitting the discussion into six regions depending on the relative values of γ_a, γ_g, and H_{ga}. Note that, because these three parameters depend differently on I, a change in I could change an experiment from one of these six regions to another, all other experimental parameters being held fixed.

Several comments are in order before discussing the individual regions explicitly. First, the shape of the dispersion curve is most strongly controlled by the value of q. As the other variables are changed, keeping q fixed, the dispersion shape is relatively constant, with only the scale of the δ variation changing. Second, each of the simplified expressions derived below occurs when two of the three parameters γ_a, γ_g, and H_{ga} are small compared to the third. This circumstance allows a Taylor expansion of the radical in Eq. (4), thus providing the simplification. When any two parameters are comparable, and greater than or comparable to the third, the Taylor expansion is no longer justified, and the entire radical must be retained. Finally, an estimate of the decay time of the species using ordinary perturbation theory very often does not provide a reasonable estimate of either transient or saturation times for experiments. Rather, it is often necessary to use the complete information developed below.

A. $\gamma_g \ll \gamma_a$

For photon intensities currently used, this will generally be the case.

1. $2|H_{ga}| \ll \frac{1}{2}\gamma_a$

In this region, essentially all the atoms which reach the intermediate state $|a)$ will be ionized immediately. Investigation of $P(t)$ in this limit shows that the coefficient of the first exponential term is very large (close to 1), and the quantity $(\frac{1}{2}\Gamma - a\sin\varphi)$ appearing in the exponent is relatively small compared to γ_a. The remaining three exponential terms have very small coefficients, and decay rapidly with a lifetime of the order of $1/\gamma_a$. Thus, $P(t)$ can be approximated by the expression

$$P_1^{(t)} = 1 - e^{-\gamma_1 t} \ , \tag{15}$$

where

$$\gamma_1 = \gamma_g \left(\frac{(2\delta + q\gamma_a)^2}{4\delta^2 + \gamma_a^2} \right) \tag{16}$$

is the first nonvanishing term in $(\frac{1}{2}\Gamma - a\sin\varphi)$. The quantity γ_1 is identical to the probability per unit time of ionization that we have previously obtained[6] using a simple perturbation argument. This expression can also be obtained directly from the Fourier integral of the resolvent when the poles are found using perturbation theory, with only the first nonvanishing shifts of the poles away from E_a' and E_g' being retained. Because this is the usual low-intensity approximation used in obtaining $U(t)$, γ_1 is the equivalent of most of the ionization rates obtained using perturbation theory, simplified somewhat because of our approximation of a single field mode and our treatment of nonresonant processes.

In order to evaluate the effects of the fast-decaying exponentials on the short-time behavior of $P(t)$, we compared curves of $P_1(t)$ vs δ with curves of $P(t)$ vs δ for various values of t, and for various values of H_{ga}, γ_g, and γ_a consistent with the limitations of this section. We find that, as might be expected, for times $t < 3/\gamma_a$, $P_1(t)$ and $P(t)$ are quite different, in both magnitude and over-all shape. For times $t > 3/\gamma_a$, the curves have very nearly the same shape but may differ somewhat in magnitude near $\delta = 0$ for fairly long periods of time.

The differences in the short-time region are, of course, due to the fast-decaying exponentials in $P(t)$. The differences in the longer-time region are due to the fact that, for given γ_g, γ_a, and H_{ga}, the coefficient of the first exponential in $P(t)$ is not exactly 1, but is a function of δ given approximately by

$$1 + \frac{3|H_{ga}|^2\gamma_a^2}{4(\delta^2 + \frac{1}{4}\gamma_a^2)^2} \equiv 1 + \alpha \ .$$

Comparison of $P_1(t)$ and the more correct value

$$P'(t) = 1 - (1+\alpha)e^{-\gamma_1 t}$$

shows that $P_1(t)$ and $P'(t)$ differ by more than 10% for times $t < t_0 \approx \alpha/(0.1+\alpha)\gamma_1$. Thus, if $\alpha = 0.04$, $P'(t)$ would be less than 90% of $P_1(t)$ for times less than $t_0 = 0.3(1/\gamma_1)$. For times $t > t_0$, $P_1(t)$ provides a very good approximation to $P(t)$.

2. $2|H_{ga}| \gg \frac{1}{2}\gamma_a$, $2|H_{ga}| \gtrsim \delta$

In this region, the strong driving field H_{ga} can roughly equilibrate the populations of $|a)$ and $|g)$; the decay into the continuum is only a perturbation of this process. In this limit, we can also obtain an approximate expression for $P(t)$. One finds that $a\cos\varphi \approx W$; thus, the last two terms in Eq. (13) contain $\cos Wt$ and $\sin Wt$, where $W \gg \gamma_a$. These two terms can therefore be expected to average to zero during an experiment, and can, to a good approximation, be dropped. In addition, $a\sin\varphi \cong (\gamma_a\gamma_g)^{1/2} \ll \Gamma$; therefore, the first two exponential terms in Eq. (13) have very nearly the same exponent. The coefficients of these two terms are also approximately the same magnitude. We can therefore approximate these two remaining terms by a single exponential if we set the oscillating terms in $P(t)$ equal to zero, and define

$$\left.\frac{dP(t)}{dt}\right|_{t=0} = \left.\frac{dP_2(t)}{dt}\right|_{t=0} ,$$

where (17)

$$P_2(t) = 1 - e^{-\gamma_2 t} .$$

We obtain in this manner by keeping the lowest nonvanishing contribution to $[dP(t)/dt]_{t=0}$,

$$\gamma_2 = \frac{\gamma_g}{2}\left(1 + \frac{(\delta + \gamma_a q)^2}{\delta^2 + 4|H_{ga}|^2}\right) , \qquad (18)$$

which had previously been obtained[7] using a straightforward perturbation approach.

We have compared curves of $P_2(t)$ vs δ and $P(t)$ vs δ for various values of t. Once again, we find great differences between the two for very short times, with the long-time behavior being essentially identical. In this case, the differences are caused primarily by the $\sin Wt$ and $\cos Wt$ terms which have been dropped in determining $P_2(t)$; the differences exist, therefore, only for a time $t \sim 1/W$. As δ increases in value, the situation described above no longer exists, and $P_2(t)$ ceases to be a good approximation to $P(t)$ over the entire range of t. It can be shown, however, that for $\delta \gg 2|H_{ga}|$, $P_2(t)$ and $P(t)$ agree extremely well for times $t \leqslant 1/2\gamma_a$.

3. $2|H_{ag}| \sim \frac{1}{2}\gamma_a$

This is the most interesting of the three regions considered thus far. In this region, an atom excited into state $|a)$ is equally likely to be ionized with lifetime $1/\gamma_a$ or to undergo a stimulated emission, returning to the ground state $|g)$. Under these conditions, there are no approximations to Eq. (13) which are satisfactory on any time scale. For short times, the damped transients dominate the process: for longer times, the oscillating terms become important. The latter occurs because $a\cos\varphi \approx \gamma_a$ in this case; thus the oscillating terms in (13) have periods of the order of the decay times, and are therefore quite important (see Fig. 1). It is obvious that, in this region, no transition rate can be defined either.

It is interesting that, in this case, both perturbation expressions, $P_1(t)$ and $P_2(t)$, quite significantly overestimate the rate of ionization near $\delta = 0$ for times almost up to saturation (see Fig. 2).

The wings of $P(t)$ are predicted well by $P_1(t)$ for most times, as might be expected, since a large δ is in many ways equivalent to a small H_{ga}. Near saturation, the center of the line is fitted very well by $P_2(t)$. This equality between $P_2(t)$ and $P(t)$ occurs at approximately $t = 2/|H_{ga}|$. However, this equality is at best very rough, since the value of $P(t)$ then oscillated above and below $P_2(t)$ because of the last two terms in Eq. (13).

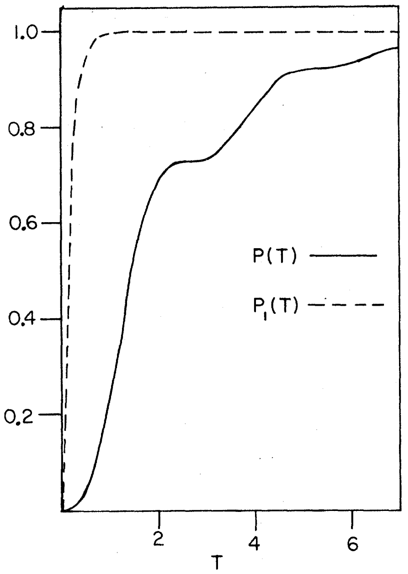

FIG. 1. Graph of the transition probability $P(t)$ [Eq. 13)] vs time T. T is measured in units of γ_a^{-1}. This curve was generated for the parameters $\gamma_g = 10^{-2}\gamma_a$, $q = 24$, and $\delta = 0$. The single-rate model of normal perturbation theory $P_1(T)$ [Eq. (15)] is plotted for comparison.

B. $\gamma_a \approx \gamma_g$

One very interesting aspect of Eq. (13) arises because there are values of H_{ag}, γ_a, γ_g, and δ

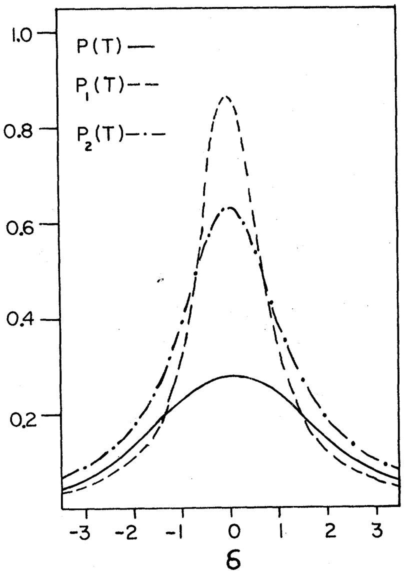

FIG. 2. Dispersion curves for $P(t)$ [Eq. (13)], $P_1(T)$ [Eq. (15)], and $P_2(T)$ [Eq. (17)] vs the energy difference δ. δ is measured in units of γ_a. These curves were generated for the parameters $T = 2\gamma_a^{-1}$, $\gamma_g = 10^{-4}\gamma_a$, and $q = 100$.

for which $|a \sin\varphi| = \frac{1}{2}\Gamma$. In this case, one of the first two exponentials simply becomes unity. If the coefficient of this term is not equal to zero, one obtains the rather surprising result that under these circumstances $P(t=\infty)$ will be less than unity. One can easily show that

$$|a \sin\varphi| = \tfrac{1}{2}\Gamma$$

is equivalent to the condition

$$(\delta\rho + 2q\gamma_a\gamma_g)^2 = (W\Gamma)^2 \ . \tag{19}$$

This equation is satisfied for

$$\delta = \tfrac{1}{2}q\rho \tag{20}$$

and corresponds to a value of

$$P(t=\infty) = \frac{\gamma_g}{\gamma_a + \gamma_g} \ . \tag{21}$$

The equations of Sec. III A are clearly consistent with this general result.

For $\gamma_a = \gamma_g$, condition (20) is satisfied at $\delta = 0$ for all values of H_{ga}, and

$$P(\infty) = \tfrac{1}{2} \ \text{ for } \delta = 0, \text{ all } H_{ga} \ .$$

Thus, for very long times, there will always be a "hole" in the ionization curve at $\delta = 0$ when $\gamma_a = \gamma_g$. Away from $\delta = 0$, the decay is dominated by γ_g; that is, the atom ionizes with lifetime $1/\gamma_g$ for δ fairly large, and the dispersion curve is very flat away from $\delta = 0$ for all values of H_{ga}.

As might be expected, in this region, neither perturbation expression given above is particularly useful, and the entire expression for $P(t)$ must be used. One finds that the effect of increasing $|H_{ga}|$ (i.e., increasing $|q|$) is, in this case, simply to make the hole in $P(t)$ wider and somewhat asymmetric in δ. Of course, as t increases, the hole gets narrower, since only at $\delta = 0$ does the probability of ionization not go to 1 as $t \to \infty$.

One very interesting aspect of the time development of $P(t)$ is that for $t < 1/\gamma_g$ the entire dispersion curve is very flat, showing almost no effect of the resonant process. For longer times, however, the region near $\delta = 0$ reaches its saturation value of $\frac{1}{2}$, and the "hole" is then formed as its sides rise toward their saturation value of 1. Thus, the effect of the resonant process would be unobservable in an experiment which did not run almost to complete saturation, i.e., until $T \sim 2 - 3(1/\gamma_g)$.

The result might have important implications for mathematically similar, or identical, processes, e.g., autoionization.[3,6] For autoionization, $|a)$ is an autoionizing state, $1/\gamma_a$ is the decay time of $|a)$ into the continuum via the Coulomb interaction, and $1/\gamma_g$ is the ionization time for the ground state via absorption of a photon. An absorption experiment to detect the autoionizing state under conditions such that $\gamma_a \approx \gamma_g$ would then produce no measurable results unless the atoms interacted with the photon beam for a time long compared to $1/\gamma_a$. This could be particularly difficult in the case of metastable autoionizing states, where $1/\gamma_a \approx 10^{-5}$ sec.

C. $\gamma_g \gg \gamma_a$

When $|H_{ga}| \ll \gamma_g$, the complete expression for $P(t)$ can, to a very good approximation, be replaced by

$$P_3(t) = 1 - e^{-\gamma_3 t} \ , \tag{22}$$

where

$$\gamma_3 = \gamma_g \left[1 + \gamma_a \frac{4\delta q - \gamma_g(q^2 - 1)}{4\delta^2 + \gamma_g^2} \right] \approx \gamma_g \ . \tag{23}$$

This result agrees with intuition, which would say that the strong direct process should almost completely mask the effect of the weak resonant process in this case. The present formalism is perhaps not well suited for calculations in this region, however, since perturbation theory was originally used to obtain the value of γ_g. In any case, as we show below, this region corresponds to presently unrealizable laser intensities, and thus is of little practical interest.

The case $|H_{ga}| \approx \gamma_g$ also does not occur except in unusual physical situations, and will not be discussed further, except to note that the complete expression for $P(t)$ must be used.

IV. APPLICATION: CESIUM

In order to obtain a better feel for the ranges of the parameters γ_a, γ_g, and H_{ga} which occur physically, we have explicitly estimated these parameters for two cases. The first is for a two-photon ionization of cesium when the $7p$ state is nearly resonant ($\lambda \approx 4590$ Å), while the second is of three-photon ionization of cesium when the $9d$ state is nearly two-photon resonant ($\lambda \approx 6920$ Å). In the latter case, the two-photon resonant transition is treated by introducing a two-photon effective Hamiltonian; the direct transition from the ground state into the continuum occurs, in this case, via a three-photon effective Hamiltonian. The decay parameters of Eqs. (5) and (6) were evaluated using effective Hamiltonian operators which were obtained in all cases from the lowest nonvanishing perturbation term [e.g., as shown by Eq. (1)]. The sums over intermediate states were truncated to four or five intermediate states, by which time the sums seemed to have converged to within roughly 10%. Experimental energies for the intermediate states were used to evaluate the energy denominators.

Bound-bound matrix elements were obtained from the oscillator strengths of Stone[8] and Warner,[9] while bound-free matrix elements were taken from Burgess and Seaton.[10] The principal-value integral occurring in H_{ga} was neglected, as it is expected to be small, and the spin-orbit doublet was treated as a single quasiresonant intermediate state. The calculation assumes linear polarization of light, and properly takes account of the presence of two final-state continua.

For the two-photon case with $\lambda \approx 4590$ Å, we find

$$\begin{aligned} \gamma_g^{(2)} &\approx 3\times10^{-24} I^2 \text{ cm}^{-1} , \\ \gamma_a^{(2)} &\approx 1\times10^{-9} I \text{ cm}^{-1} , \\ H_{ga}^{(2)} &\approx -2\times10^{-3} I^{1/2} \text{ cm}^{-1} , \end{aligned} \tag{24}$$

where I is measured in W/cm^2. For the three-photon case with $\lambda \approx 6920$ Å, we find

$$\begin{aligned} \gamma_g^{(3)} &\approx 3\times10^{-34} I^3 \text{ cm}^{-1} , \\ \gamma_a^{(3)} &\approx 5\times10^{-10} I \text{ cm}^{-1} , \\ H_{ga}^{(3)} &\approx 2\times10^{-9} I \text{ cm}^{-1} . \end{aligned}$$

Using the parameters of (24), we find that in the two-photon case, if $I \ll 8\times10^{12}$ W/cm^2, then $\frac{1}{2}\gamma_g^{(2)} \ll \frac{1}{2}\gamma_a^{(2)} \ll 2|H_{ga}^{(2)}|$, so that the approximate ionization probability given by Eq. (18) can be used. (We note again that this is not the result usually obtained in perturbation calculations.) For $I \gg 4\times10^{14}$ W/cm^2, $2|H_{ga}^{(2)}| \ll \frac{1}{2}\gamma_a^{(2)} \ll \frac{1}{2}\gamma_g^{(2)}$, so that the situation discussed in Sec. III C prevails. For values of I intermediate to these two limits, the full expression for $P(t)$ [Eq. (13)] must be used. Thus for all intensities of current experimental interest, the ionization probability is well represented by $P_2(t)$ [Eq. (18)].

For the three-photon case, we have that $2|H_{ga}^{(3)}| \approx 16(\frac{1}{2}\gamma_a^{(3)})$ for all intensities. For $I \ll 1\times10^{12}$ W/cm^2, $\frac{1}{2}\gamma_g^{(3)} \ll \gamma_a^{(3)} \approx \frac{1}{16} 2|H_{ga}^{(3)}|$, so that we are approximately in the region in which Eq. (18) applies once again. Because $\frac{1}{2}\gamma_a^{(3)}$ and $2|H_{ga}^{(3)}|$ are relatively close in value, however, deviations may be expected. Comparison of $P(t)$ [Eq. (13)] with the approximation $P_2(t)$ [Eq. (18)] for this case shows that the two equations predict very similar dispersion curves, with very close agreement near the maxima of the curves. However, the width of the resonance is overestimated by $P_2(t)$ by almost 30%. This indicates that transition regions such as this require the more correct formula if accurate values of the parameters are to be obtained from experiment. For $I \gg 4\times10^{12}$ W/cm^2, $\frac{1}{2}\gamma_g^{(3)} \gg |H_{ga}^{(3)}| \approx 16(\frac{1}{2}\gamma_a^{(3)})$ and we are once again in the situation described in Sec. III C. Intermediate values of I must be treated using the complete expression for the probability.

V. CONCLUSIONS

In the preceding sections we have considered the problem of two-photon resonant ionization of an atom. Under certain simplifying assumptions (which are not unrealistic), we have derived an expression for the probability of ionization $P(t)$ of the atom as a function of time [Eq. (13)]. This relation for $P(t)$ is a rather complicated function of the ionization widths γ_g and γ_a of the bound states, an interference parameter q, and the detuning δ, as well as being explicitly time dependent. An arbitrary experimental setup satisfying the model assumption requires this general expression for its description. Simplified expressions have been given whenever any one of the three parameters q, γ_g, and γ_a is large compared to the other two. Finally, explicit estimates of the three parameters γ_g, γ_a, and q were given for resonant two- and three-photon resonant ionization of cesium.

From this investigation we infer the following:

(1) The three parameters γ_g, γ_a, and q are the intensity-dependent atomic parameters necessary to describe the resonant multiphoton ionization process. They are also sufficient within the limits of our model.

(2) A simple rate model of the ionization process does not generally provide an adequate description, no matter how the rate is calculated.

(3) In those circumstances where a simple rate model is inapplicable, the expression given by Eq. (13) should provide an adequate description of the process. Note that this requires knowledge of the experimental pulse length T.

(4) In order to decide whether a simple rate model is applicable, all three of the parameters γ_g, γ_a, and q must be estimated. Such conclusions will depend on the intensity of the experimental beam, and may change as the intensity is varied.

(5) Even those circumstances where a single rate model is applicable are not necessarily best described by a simple addition of induced widths to the usual perturbation theory. Rather, an estimate of the three parameters γ_a, γ_g, and q is required to decide whether γ_1, γ_2, or γ_3 is to be used [Eqs. (16), (18), or (23)]. The values of γ_1, γ_2, and γ_3 given above are obtained by keeping only the first nonvanishing terms. As such, they could be improved upon somewhat by keeping higher-order terms. However, one cannot go from one region to another in this fashion (unless, of course, the expansions are carried out to infinite order), as there are intermediate regions in

which no rate equation is possible, i.e., $P(t)$ is not of the form $1-e^{-\gamma t}$.

(6) The intensity dependence of the ionization probability is very complicated in general. Because this intensity dependence can be so complicated depending on the values of the parameters, we have attempted to make no general statements concerning it. Rather, it is best to estimate the parameters, and use Eq. (13) (or one of its simplifications) to obtain this dependence for a particular species, duration of experiment, etc.

(7) For fixed intensity and atomic species, the shape of the dispersion curve in δ is determined primarily by q. For most values of the parameters, these curves are remarkably similar to simple Fano profiles.[5] However, we must emphasize that it is not correct to simply fit the data to a Fano profile and then interpret the resulting parameters in their usual fashion. This will lead to gross inaccuracies in the derived parameters, and even, in some cases, to incorrect identification of the parameters. The more complicated expression given by Eq. (13) or one of the simplifications is unfortunately required. Note that this requires knowledge of the experimental pulse time T for its application.

(8) Even in cases in which a transition rate can be defined, care must be taken that the experimental times are long compared to the transient times. Those transient times can be estimated by consideration of the complete expression for $P(t)$ [Eq. (13)], as was done in some detail in Sec. III A 1. For customary experimental pulse times, the condition seems well satisfied.

(9) Finally, any experiment designed to extract the parameters γ_g, γ_a, and q will probably require sweeping in both intensity and wavelength.

As indicated by the sample calculation of Sec. IV, this formalism can be applied directly to any $(m+n)$-photon ionization in which there is a single m-photon resonant intermediate state. Although we have found that $P_2(t)$ [Eq. (17)] is generally sufficient to describe two-photon ionization, we would expect all regions discussed above to be pertinent for some larger value of $m+n$. In particular, the region in which $2|H_{ga}|\sim\frac{1}{2}\gamma_a$, in which no rate equation is possible, should be reached for $m+n$ only slightly larger than 2, with $m>n$. The region in which $P_1(t)$ is valid should be reached for $m+n\gg 2$, $m\gg n$.

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*Work supported in part by the National Science Foundation.

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