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Resonant multiphoton ionization via the Fano autoionization formalism

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We introduce an analogy between the theory of autoionizing states as described by Fano and the theory of certain states ("pseudo-autoionizing states") of an irradiated atom. These "pseudo-autoionizing states" are used to obtain a number of qualitative results concerning resonant multiphoton ionization probabilities for several experimental arrangements. This method makes clear the importance of nonresonant processes in determining resonant multiphoton ionization line shapes.

I. INTRODUCTION

Multiphoton ionization has received a great deal of attention in recent years from both experimentalists[1] and theoreticians.[2] This interest has been fueled by the advent of high-powered tunable lasers which make possible ionization measurements as functions of both the power and the frequency of the incident light.

Most of the calculations of multiphoton ionization processes reported thus far have been numerical in character, and have therefore been restricted to specific atoms—generally hydrogen or the alkali metals. Because these calculations have as a goal the quantitative numerical description of the multiphoton ionization process for specific atoms, no effort has been made to determine which features of the results depend on general qualitative behavior of the process and which features depend on the specific atom involved. For example, as we change from one atomic species to another, what are the important atomic parameters whose change causes the observed differences in experimental profiles? As the techniques previously reported were chosen for purposes of numerical convenience, their complex nature seems ill-suited to the discussion of this and other qualitatively oriented questions. Thus, although a great deal of information is available about line shapes for specific multiphoton processes at specific wavelengths and intensities, very little appears to be known as to what kinds of line shapes are potentially possible. This is evidenced by the fact that experimental results and theoretical calculations are very seldom expressed in parametrized form, being presented instead in a completely numerical fashion. (The effective order of the process is of course an exception.)

In this article we develop an analogy between autoionization and certain types of resonant multiphoton ionization processes. Since the Fano formulation[3] of autoionization is well known to many atomic physicists, this analogy provides a convenient and easy method of studying the qualitative aspects of multiphoton ionization.[4] The probability of multiphoton ionization can immediately be expressed in a form which clearly indicates which aspects result from peculiarities of the specific atom being considered, and which aspects are of a more general nature. The simplicity of the results obtained allow, we feel, a greater physical insight into multiphoton ionization than is generally obtained from the more complicated quantitative calculations. In addition, the results focus attention on those parameters of the atom which need to be numerically calculated in order to explain the process quantitatively.

The Fano[3] formalism for autoionizing states is reviewed in Sec. II. Section III is devoted to their irradiated-atom analog, "pseudo-autoionizing states." A resonant two-photon ionization line shape is derived in Sec. IV A using these states, while the generalization to an n-photon process is discussed in Sec. IV B. Section V discusses a more complicated situation in which an additional intermediate resonance is considered. A brief summary is then given in Sec. VI.

II. AUTOIONIZING STATE

We first briefly review the theory of autoionizing states as given by Fano.[3] It is assumed that the atomic Hamiltonian H_A has, in the zeroth approximation, a discrete eigenstate $|\varphi)$ which is imbedded in a continuum of eigenstates $|\alpha E)$, where α is a label which removes the degeneracy of all possible states of energy E. With respect to these states, the matrix elements of H_A are assumed to be of the form

$$(\varphi|H_A|\varphi)=E_\varphi,$$
$$(\beta E|H_A|\varphi)=V_E\delta_{\alpha\beta}, \tag{1}$$
$$(\alpha E|H_A|\beta E')=\delta_{\alpha\beta}\delta(E-E')E.$$

For simplicity, we assume here and below that the phases of the states have been chosen so that all matrix elements are real.

The wave function which diagonalizes H_A with eigenvalue E within the manifold of states $|\varphi)$ and $|\alpha E)$ can be written as

$$|\Psi_E)=a(E)|\varphi)+\int b_{E'}(E)|\alpha E')\,dE'$$
$$=\frac{\sin\Delta}{\pi V_E}|\Phi)-\cos\Delta|\alpha E), \tag{2}$$

where

$$|\Phi)=|\varphi)+\mathcal{P}\int\frac{dE'\,V_{E'}|\alpha E')}{E-E'} \tag{3}$$

is the bound state "clothed" by the continuum ($\mathcal{P}$ indicates principal-part integration), and

$$\tan\Delta=-\pi V_E^2/[E-E_\varphi-F(E)]. \tag{4}$$

The quantity $F(E)$ is a shift in the energy of $|\varphi)$ due to the interaction with the continuum:

$$F(E)=\mathcal{P}\int\frac{|V_{E'}|^2dE'}{E-E'}. \tag{5}$$

The probability of a transition from a ground state $|g)$ to the states $|\Psi_E)$ is, in lowest-order perturbation theory, proportional to

$$|(g|T|\Psi_E)|^2, \tag{6}$$

where T is the transition operator. Using Eq. (2), one finds

$$(g|T|\Psi_E)=\frac{1}{\pi V_E}(g|T|\Phi)\sin\Delta-(g|T|\alpha E)\cos\Delta. \tag{7}$$

We see from Eqs. (4) and (7) that there will be a resonance in the transition probability when $E=E_\varphi+F(E)$. On one side of the resonance, the contributions from $|\Phi)$ and $|\alpha E)$ will interfere constructively, while on the other side they will interfere destructively. This leads to the well-known asymmetric Fano profile for absorption. Using Eq. (7) in Eq. (6), we find

$$\frac{|(g|T|\Psi_E)|^2}{|(g|T|\alpha E)|^2}=\frac{(q+\epsilon)^2}{1+\epsilon^2}, \tag{8}$$

where

$$\epsilon=(E-E_\varphi-F)/\pi V_E^2, \tag{9}$$

and

$$q=\frac{(\Phi|T|g)}{\pi V_E(\alpha E|T|g)}. \tag{10}$$

In using Eq. (8) for analyzing experimental data, it is assumed that $F(E)$, V_E, and q vary slowly in the neighborhood of the resonance and hence may be replaced by constants. Note that Eq. (8) has a zero when $q=-\epsilon$. This zero is a direct consequence of the interaction between the discrete and continuum contributions to the transition probability.

III. PSEUDO-AUTOIONIZING STATES

"Pseudo-autoionizing states" are the irradiated-atom analogs of the autoionizing states of Sec. II. The atom is again described by the Hamiltonian H_A. We assume that the eigenstates of H_A are known (in this section and below we are interested in eigenstates of H_A which represent bound states and continuum eigenstates not near an autoionizing resonance, the autoionizing formalism of Sec. II being used only for the atom-field interaction). To introduce the radiation field into the problem, we must add the Hamiltonian of the free field, H_F, and the Hamiltonian of the interaction between the atom and field, H_{AF}. The total Hamiltonian H now becomes

$$H=H_A+H_F+H_{AF}. \tag{11}$$

The eigenstates of H_F are, of course, of the type $|n_1\omega_1,n_2\omega_2,\ldots)$, where

$$H_F|n_1\omega_1,\ n_2\omega_2,\ldots)$$
$$=(n_1\hbar\omega_1+n_2\hbar\omega_2+\ldots)|n_1\omega_1,n_2\omega_2,\ldots). \tag{12}$$

The usual electric-dipole approximation is taken for H_{AF}:

$$H_{AF}=i\left(\frac{2\pi e^2}{\hbar L^3}\right)^{1/2}\sum_{\omega,\epsilon}\omega[\vec{r}\cdot\hat{\epsilon}a_\omega-(\vec{r}\cdot\hat{\epsilon})^\dagger a_\omega^\dagger], \tag{13}$$

where $a_\omega^\dagger$ is a creation operator for a photon of frequency ω, polarization $\hat{\epsilon}$, and the remaining symbols have their usual meaning.

Suppose now that the eigenstates $|a,n\omega)$, $|E,(n-1)\omega)$ of H_A+H_F are known, where $|a)$ is a discrete atomic state, $|E)$ is a continuum atomic state, and $|n\omega)$ represents a field of n photons of frequency ω. We assume that the energy of the state $|a,n\omega)$, $E_a+n\hbar\omega$, lies in the continuum of energies $E+(n-1)\hbar\omega$ as shown in Fig. 1 (in all figures, the vertical axis is atomic energy); i.e., we assume that a photon of frequency ω can ionize an atom beginning in state $|a)$. If we now consider diagonalizing the Hamiltonian H, and restrict our attention to the manifold of states discussed above, then the problem is mathematically identical to that discussed in Sec. II. By restricting our attention to this particular manifold of states, we are

of course excluding certain parts of the general problem. We will discuss the implications of this restriction at the end of this section.

Using the results of the previous section, we can immediately write down the eigenfunctions of H:

$$H|\Psi_{\mathcal{E}}) = \mathcal{E}|\Psi_{\mathcal{E}}), \tag{14}$$

where

$$|\Psi_{\mathcal{E}}) = \frac{\sin\Delta}{\pi H_E}|\Phi_a) - \cos\Delta\,|E,(n-1)\omega),$$

with E being fixed by the condition

$$\mathcal{E} = E + (n-1)\hbar\omega$$

and

$$H_E = (a, n\omega|H_{AF}|E,(n-1)\omega),$$

$$\tan\Delta = \frac{-\pi H_E^2}{E - E_a - \hbar\omega - F(E)},$$

$$F(E) = \mathcal{P}\int \frac{|H_{E'}|^2 dE'}{E - E'},$$

$$|\Phi_a) = |a, n\omega) + \mathcal{P}\int \frac{dE' H_{E'}}{E - E'}|E',(n-1)\omega).$$

Consider now the probability of transition from a state $|b,(n-1)\omega,\omega')$ to the continuum of states $|\Psi_{\mathcal{E}})$, where $|b)$ is a bound state of the atom of the same parity as $|a)$ (Fig. 1). In lowest-order perturbation theory, this probability is proportional to the square of

$$(\Psi_{\mathcal{E}}|H_{AF}|b,(n-1)\omega,\omega') = \frac{\sin\Delta}{\pi H}\mathcal{P}\int \frac{H_{E'}(E',(n-1)\omega|H_{AF}|b,(n-1)\omega,\omega')}{E-E'}\,dE' - \cos\Delta(E,(n-1)\omega|H_{AF}|b,(n-1)\omega,\omega'), \tag{15}$$

where $\mathcal{E} = E_b + (n-1)\hbar\omega + \hbar\omega'$. The matrix element of Eq. (15) is similar to the matrix element of Eq. (7) which describes absorption by an autoionizing state. Using the same assumptions discussed in Sec. II, we may cast the result in the same form as Eq. (8). Note the parameter q for this process is given by the expression

$$q = \frac{\mathcal{P}\int \frac{H_{E'}(E',(n-1)\omega|H_{AF}|b,(n-1)\omega,\omega')}{E-E'}\,dE'}{\pi H_E(E,(n-1)\omega|H_{AF}|b,(n-1)\omega,\omega')}$$

and is independent of the intensity of the strong field $|n\omega)$, i.e., is a constant. At first sight this might seem to say that the Fano absorption profile persists even as $n \to 0$. However, for this case the energy parameter ϵ is given by

$$\epsilon = [\mathcal{E} - E_a - n\hbar\omega - F(E)]/\pi H_E^2,$$

which is inversely proportional to n. Using this fact, it readily follows that the profile given by Eq. (8) tends to one as $n \to 0$, as expected.

For moderately large n, this process shows a Fano profile with a resonance in the region $\omega' = (E_a + \hbar\omega - E_b)/\hbar$. In this case, the Fano profile is produced by the strong interaction between the discrete state $|a, n\omega)$ and the continuum of states $|E,(n-1)\omega)$. We therefore refer to $|a, n\omega)$ as a "pseudo-autoionizing state."

The situation discussed above can be easily realized experimentally. It corresponds, for example, to the case in which an atom is illuminated by two light sources with the longer-wavelength source having a very much higher power than the shorter-wavelength one. Thus, the long-wavelength source might be a high-power laser, and the short wavelength could be produced by synchrotron sources. The short wavelength should, of course, be of a frequency such that it can ionize the atom from the state in which it enters the interaction region (e.g., the ground state).

In the calculation above we have neglected certain matrix elements. First, we have neglected nonresonant bound-bound matrix elements. Customary physical insight tells us that if n is not too large, then these corresponding processes contribute at most a small shift to all the states involved. We are also assuming that no pair of atomic states

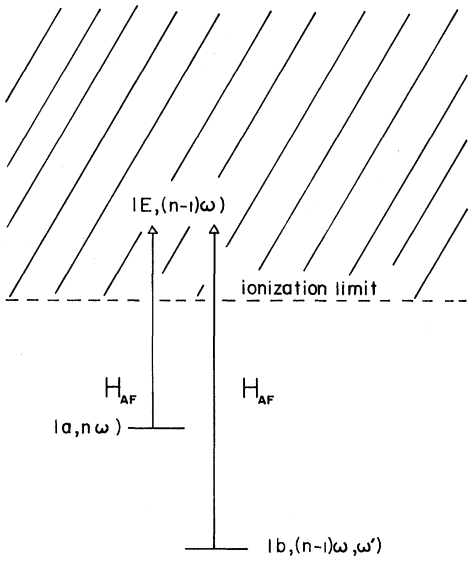

FIG. 1. "Pseudo-autoionizing state" $|a, n\omega)$.

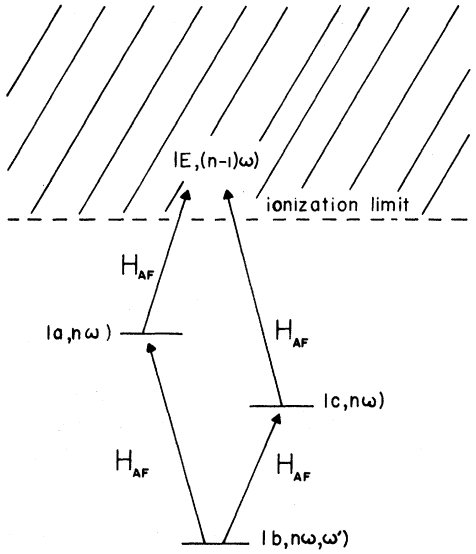

FIG. 2. Two-photon ionization involving a resonant intermediate state $|a,n\omega)$ and a nonresonant intermediate state $|c,n\omega)$.

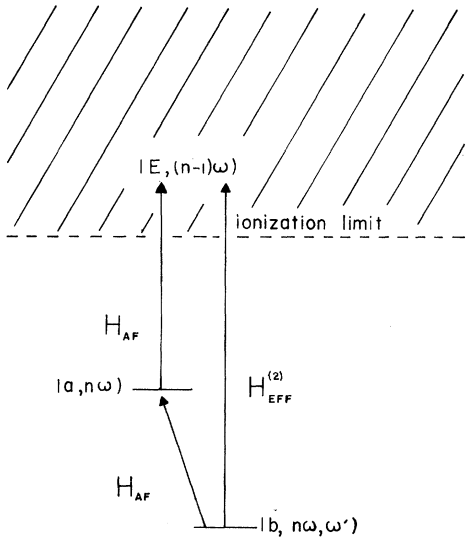

FIG. 3. Two-photon ionization in which the nonresonant process of Fig. 2 has been approximated by an effective Hamiltonian $H^{(2)}_{\text{eff}}$.

has an energy separation nearly equal to a multiple of $\hbar\omega$. We will consider in later sections situations where this assumption is no longer valid.

Secondly, we have neglected the spontaneous decay of the states. This is valid if n is sufficiently large, so that the stimulated processes dominate.

Finally, we have neglected the effect of free-free transition induced by the light of frequency ω. This seems reasonable because such processes are relatively structureless, at least over the energy range of interest in the experiment discussed above. Similar assumptions to the above will be made in future sections without further discussion.

IV. RESONANT MULTIPHOTON IONIZATION

A. Two-photon case

The situation described above becomes even more closely related to that of autoionizing states when the effects of other levels in the atom are considered. Consider the situation pictured in Fig. 2, where now $|b)$ is of the opposite parity to $|a)$. The weak light source is taken in this case to have a frequency

$$\omega' \approx (E_a - E_b)/\hbar$$

such that the process $|b,n\omega,\omega') \rightarrow |a,n\omega)$ is close to resonance. The atomic state $|c)$ has an energy such that the process

$$|b,n\omega,\omega') \rightarrow |c,n\omega)$$

is very nonresonant; the transitions

$$|b;n\omega,\omega') \rightarrow |c,n\omega) \rightarrow |E,(n-1)\omega)$$

are thus weak, and can be treated using the lowest-order nonvanishing perturbation theory.

We find that the nonresonant part of the interaction between $|b)$ and $|E)$ contains terms of the type

$$\sum_c \frac{(b,n\omega,\omega'|H_{AF}|c,n\omega)(c,n\omega|H_{AF}|E,(n-1)\omega)}{E_c - E_b - \hbar\omega'} \tag{16}$$

which, because of the nonresonant nature of the interaction, are roughly independent of ω'. Thus, to a very good approximation, we can simply replace Eq. (16) by

$$(b,n\omega,\omega'|H^{(2)}_{\text{eff}}|E,(n-1)\omega), \tag{17}$$

where $H^{(2)}_{\text{eff}}$ is an effective Hamiltonian (Fig. 3).

We once again calculate the first-order probability of a transition from the state $|b)$ into the continuum of states $|\Psi_g)$ of Eq. (14). This probability is, using Eq. (17), proportional to the square of

$$(\Psi_g|(H_{AF}+H^{(2)}_{\text{eff}})|b,n\omega,\omega') = \frac{\sin\Delta}{\pi H_E}(\Phi_a|(H_{AF}+H^{(2)}_{\text{eff}})|b,n\omega,\omega') - \cos\Delta(E,(n-1)\omega|H^{(2)}_{\text{eff}}|b,n\omega,\omega'), \tag{18}$$

where $\mathcal{E} = E_b + n\hbar\omega + \hbar\omega' = E + (n-1)\hbar\omega$. The Fano profile in this case is given by

$$\frac{|\langle\Psi_{\mathcal{E}}|(H_{AF}+H_{\rm eff}^{(2)})|b,n\omega,\omega'\rangle|^2}{|\langle E,(n-1)\omega|H_{\rm eff}^{(2)}|b,n\omega,\omega'\rangle|^2} = \frac{(q+\epsilon)^2}{1+\epsilon^2}, \tag{19}$$

where, in analogy to Eqs. (9) and (10),

$$\epsilon = [\mathcal{E} - E_a - n\hbar\omega - F(E)]/\pi H_E^2,$$

$$F(E) = \mathcal{P}\int \frac{|H_{E'}^2|}{E-E'}\,dE', \tag{20}$$

and

$$q = \frac{\langle\Phi_a|(H_{AF}+H_{\rm eff}^{(2)})|b,n\omega,\omega'\rangle}{\pi H_E\langle E,(n-1)\omega|H_{\rm eff}^{(2)}|b,n\omega,\omega'\rangle}. \tag{21}$$

Note that we can write q as

$$q = A + B/n,$$

where A and B are roughly constants; that is, $q \to$ constant for large n. Once again, we see that a Fano profile results, with a resonance in the region of

$$\omega' = (E_a - E_b)/\hbar.$$

The situation discussed here (Fig. 2) describes a special case of the two-photon ionization of an atom. From Eq. (18), we see that the Fano profile is produced, in this case, by the *nonresonant* processes. That is, if $H_{\rm eff}^{(2)}$ were zero, Eq. (18) would give simply a Lorentzian line shape. Thus, nonresonant processes are seen to be crucial in the calculation of line shapes in multiphoton ionization.

B. $p+r$—Photon resonant ionization

The methods of the previous section can be extended to study the process in which an atom is ionized by an $m = p + r$ photon absorption, enhanced because of a p-photon resonance with an intermediate state. The process is incorporated into the previous formalism by introducing the following effective Hamiltonians: $H_{\rm eff}^{(m)}$ for the m-photon direct transition from the ground state $|g\rangle$ to the continuum via nonresonant intermediate states (the equivalent of $H_{\rm eff}^{(2)}$ of Sec. IV A); $H_{\rm eff}^{(r)}$ for the r-photon mixing of the resonant intermediate state $|a\rangle$ into the continuum; and $H_{\rm eff}^{(p)}$ for the p-photon transition from the ground state $|g\rangle$ to the resonant intermediate state $|a\rangle$. These operators are defined as in the previous section by use of the first nonvanishing term in perturbation theory, the use of these expressions being justified in the same fashion. We again require that $H_{\rm eff}^{(m)}$ and $H_{\rm eff}^{(p)}$ be small, so that first-order perturbation theory for transition to the "pseudo-autoionizing state" is justified.

With the obvious substitutions, the process is again described by Eqs. (19)–(21) of Sec. IV A. It is easily verified that the parameter q has the form

$$q = A + B/n^r$$

where $n \gg 1$ is the number of photons in the field which couples the resonant intermediate state to the continuum via the r-photon process, and A and B are constants. As in the previous section, q tends to a constant for large intensity. The corresponding Fano profile is broadened and flattened as n increases.

It should further be mentioned that the requirement that $H_{\rm eff}^{(m)}$ and $H_{\rm eff}^{(p)}$ be small actually corresponds to many experimental situations and does not require that two separate lasers be used to drive the process. For moderate intensities, whenever $p > r$, both $H_{\rm eff}^{(m)}$ and $H_{\rm eff}^{(p)}$ will be small compared to $H_{\rm eff}^{(r)}$; under the same restrictions, whenever $p > 1$, then $H_{\rm eff}^{(p)}$ and $H_{\rm eff}^{(m)}$ will be absolutely (rather than comparatively) small. Both of these circumstances are those most commonly met in the laboratory.

V. THREE-PHOTON IONIZATION IN MUTILEVEL ATOMS

In the previous section we have only considered the case where a single intermediate-state resonance occurs. In actual experimental situations it may happen that additional resonances between intermediate bound states also occur. In this section we demonstrate how the Fano formalism may also be used to handle situations of this type. The results in this case are much more complicated than those of the previous section. However, the source of these complications can be traced because of the simplicity of the formalism.

As an example, we consider the three-photon ionization process depicted in Fig. 4, where

$$\omega' \approx E_d - E_b, \quad \omega \approx E_a - E_d.$$

We have once again introduced effective operators, as indicated in Fig. 4, to describe multiphoton processes proceeding via nonresonant intermediate states. In particular, the operator $H_{\rm eff}^{(2)}$ describes the two-photon transition

$$|b,n\omega,\omega'\rangle \to |a,(n-1)\omega\rangle,$$

$H_{\rm eff}^{(3)}$ describes the three-photon transition

$$|b,n\omega,\omega'\rangle \to |E,(n-2)\omega\rangle,$$

and $H_{\rm eff}^{(2)'}$ describes the two-photon transition involving only the strong field

$$|d,n\omega\rangle \to |E,(n-2)\omega\rangle.$$

Our first step is to take into account the effects

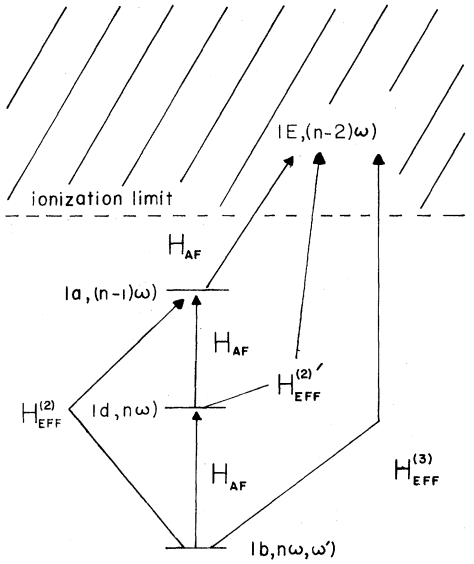

FIG. 4. Three-photon ionization involving a resonance between intermediate discrete states. Nonresonant processes have been approximated by effective Hamiltonians.

of the strong field by carrying out a diagonalization of H between the states $|d)$, $|a)$, and $|E)$. Following Fano again, we find that

$$(H+H_{\text{eff}}^{(2)\prime})|\Psi_{\mathcal{E}}) = \mathcal{E}|\Psi_{\mathcal{E}}), \tag{22}$$

where

$$|\Psi_{\mathcal{E}}) = \cos\Delta\left(\frac{\tan\Delta_1}{\pi H_{1E}}|1) + \frac{\tan\Delta_2}{\pi H_{2E}}|2) - |E,(n-2)\omega)\right),$$

E being fixed by the condition

$$\mathcal{E} = E + (n-2)\hbar\omega .$$

The wave functions $|1)$ and $|2)$ are defined by

$$\begin{aligned} |1) &= \alpha|d,n\omega) + \beta|a,(n-1)\omega) \\ &\quad + \mathcal{P}\int \frac{dE' H_{1E'}|E',(n-2)\omega)}{E-E'}, \\ |2) &= \beta|d,n\omega) - \alpha|a,(n-1)\omega) \\ &\quad + \mathcal{P}\int \frac{dE' H_{2E'}|E',(n-2)\omega)}{E-E'}, \end{aligned} \tag{23}$$

with

$$\begin{aligned} H_{1E} &= (1|(H_{AF}+H_{\text{eff}}^{(2)\prime})|E,(n-2)\omega) \\ &= \alpha(d,n\omega|H_{\text{eff}}^{(2)\prime}|E,(n-2)\omega) \\ &\quad + \beta(a,(n-1)\omega|H_{AF}|E,(n-2)\omega) \\ &\equiv \alpha H_{dE} + \beta H_{aE}, \\ H_{2E} &= \beta H_{dE} - \alpha H_{aE}, \end{aligned}$$

$$\alpha = \left(\frac{W-\delta}{2W}\right)^{1/2}, \quad \beta = \left(\frac{W+\delta}{2W}\right)^{1/2}, \quad \delta = E_a' - E_d',$$

$$E_a' = E_a + (n-1)\hbar\omega + \mathcal{P}\int \frac{H_{aE'}^2}{E-E'}dE',$$

$$E_d' = E_d + n\hbar\omega + \mathcal{P}\int \frac{H_{dE'}^2}{E-E'}dE',$$

$$\begin{aligned} W^2 &= \delta^2 + 4\left((d,n\omega|H_{AF}|a,(n-1)\omega)\right. \\ &\quad \left. + \mathcal{P}\int \frac{dE' H_{dE'}H_{E'a}}{E-E'}\right)^2 \\ &\equiv \delta^2 + 4H_{da}^2 . \end{aligned}$$

The states $|1)$ and $|2)$ can be recognized as the two states of the Autler-Townes[5] or ac-Stark doublet, "clothed" by the interaction with the continuum. The angles Δ_1 and Δ_2 corresponding to these states are defined by

$$\begin{aligned} \tan\Delta_1 &= -\pi H_{1E}^2/(\mathcal{E}-E_1), \\ \tan\Delta_2 &= -\pi H_{2E}^2/(\mathcal{E}-E_2), \end{aligned} \tag{24}$$

where

$$E_{1,2} = \tfrac{1}{2}(E_a'+E_d') \pm \tfrac{1}{2}W .$$

Finally, Δ is defined by

$$\tan\Delta = \tan\Delta_1 + \tan\Delta_2 .$$

The first-order probability of a transition from $|b,n\omega,\omega')$ to the states $|\Psi_{\mathcal{E}})$ is given by the square of the matrix element

$$(b,n\omega,\omega'|(H_{AF}+H_{\text{eff}}^{(2)}+H_{\text{eff}}^{(3)})|\Psi_{\mathcal{E}}) = \cos\Delta\left[\frac{\tan\Delta_1}{\pi H_{1E}}(b,n\omega,\omega'|(H_{AF}+H_{\text{eff}}^{(2)})|1) + \frac{\tan\Delta_2}{\pi H_{2E}}(b,n\omega,\omega'|(H_{AF}+H_{\text{eff}}^{(2)})|2) - (b,n\omega,\omega'|H_{\text{eff}}^{(3)}|E,(n-2)\omega)\right], \tag{26}$$

evaluated at

$$\mathcal{E} = E_b + n\hbar\omega + \hbar\omega' = E + (n-2)\hbar\omega .$$

As indicated by Eq. (26), the probability of absorption of a photon of frequency ω' is, in this case, a very complicated function of ω'. This complicated structure arises because of interference between the Fano and ac Stark effects. A number of very different absorption profiles can result in this case, depending on the exact values

of the various matrix elements involved. For example, if all the effective Hamiltonians are very small, the profile will be dominated by the usual ac Stark effect. Then, for $\delta = 0$, a single symmetric absorption will occur for small values of H_{ad}, splitting into two symmetric curves when H_{ad} becomes larger than the linewidth of the states. The linewidth in this case is related, of course, to the lifetime of the states with respect to decay into the continuum via absorption of another photon, since spontaneous lifetimes have not been included in our calculation.

Once the effective Hamiltonians become important, however, the absorption curve will become asymmetric, and can show as many as two zeros of intensity in addition to the relative minimum which occurs between the two maxima of the ac Stark profile. One zero of intensity will occur in the case that $H_{\text{eff}}^{(3)}$ is small, but either (or both) $H_{\text{eff}}^{(2)}$ or $H_{\text{eff}}^{(2)'}$ is large. It can easily be seen that the term in square brackets in Eq. (26) vanishes at one value of ω' for this case. The two zeros of probability will result whenever $H_{\text{eff}}^{(3)}$ becomes significantly large, as can be seen once again by reference to the term in square brackets in Eq. (26). When this occurs, the situation becomes very analogous to the case of two close-lying autoionizing states discussed by Fano.[3]

It is obvious from this brief discussion that the absorption curve can take on many different shapes when an additional resonance occurs between intermediate bound states. Because the features of the curve depend very critically on the relative strengths of the interactions a more complete general analysis of these profiles would be quite lengthy. Specific analyses, although useful, would take us beyond the scope of this paper. However, once again, we can easily see the extreme importance of nonresonant processes in determining the shape of the profile.

VI. SUMMARY AND DISCUSSION

In the preceding analysis, we have pointed out the analogy between certain states of an irradiated atom ("pseudo-autoionizing states") and autoionizing states of an atom in the absence of incident radiation. This analogy permitted the Fano[3] formalism for autoionizing states to be employed for treating certain resonant multiphoton ionization processes. Explicit discussions were presented for m-photon ionization, where a single intermediate state is resonant with the ground state plus $p<m$ photons (with the additional requirement that $p>m-p$), and for three-photon ionization, where an additional resonance occurs between two discrete states of the atom. In the former case, a Fano profile is predicted for the resonance, while the latter case shows complicated structure resulting from the interference of the Fano and ac Stark effects.

We have always assumed above that the transition out of the ground state involved a weak field. This was done so that first-order perturbation theory could be used to obtain the transition probability. If the first transition is also strong, the resulting calculation is much more tedious. Complications arising when this assumption is invalid will be discussed elsewhere.[6]

One strength of this approach is that it enables one to see the importance of nonresonant processes in determining the structure of the resonance profile. The characteristic Fano profile, in fact, arises from interference between these nonresonant terms and the resonant transition. The importance of the nonresonant terms becomes even more apparent for the case considered in Sec. V. Here, a large variety of profiles can result, depending on the relative magnitudes of the various nonresonant terms. The importance of these processes has not generally been emphasized in more quantitative calculations.

Another aspect of a more general approach such as the one described above is that it provides convenient equations for the parametrization of experimental data. Thus, just as autoionization data is presented by giving the parameters q and πH_E^2, so may multiphoton ionization data be concisely parametrized. This has the benefit that it focuses attention on the aspects of the data which are unique to a specific atom, thus simplifying the work of both experimentalist and theoretician.

We have attempted to demonstrate above how our method may be utilized to obtain qualitative information about multiphoton ionization processes. Our emphasis has been on the ease and simplicity with which such qualitative information can be obtained. No attempt has been made here to obtain quantitative information about specific profiles, although the method certainly allows such determination in principle. Of course, both the qualitative and quantitative information can be obtained by a variety of more commonly used techniques, e.g., the method of resolvents.[7] However, our method provides a different vantage point for these familiar calculations, and we think it serves to focus attention on those features of the process which are physically significant.

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