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Theory of multiphoton ionization: Near-resonance effects in two-photon ionization

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I present a perturbation theory of multiphoton ionization based on the resolvent operator. The theory is applied to a detailed study of two-photon ionization under near-resonance conditions. It is shown that a distinction must be made between linear level shifts and widths, and resonance shifts and widths which appear in the transition probability. The resonance shifts and widths exhibit saturation effects and their values tend to be much smaller than those of the linear level shifts and widths. Using numerical examples corresponding to tunable dye lasers and alkali-metal atoms, we show that the above shifts can have a dramatic effect on the ionization rate even when the laser is not in exact resonance with the intermediate level. The question of "one-step" vs "two-step" two-photon ionization is also discussed. It is shown that exact resonance does not necessarily imply a two-step process. In fact, in most cases it is quite the opposite. A quantitative criterion for this distinction is established. Finally, a distinction is made between instrumental saturation and saturation of the transition probability. The two are shown to be of different nature. Further extensions of the work are also discussed.

I. INTRODUCTION

Multiphoton ionization has received renewed attention in the last two years or so. A number of interesting experimental results have been reported[1-11] and new theoretical work[12-25] has revealed new facets of the process. At the same time, advances in tunable, narrow-linewidth lasers have opened possibilities for further quantitative experiments dealing with some of its subtler aspects. In addition to their importance in understanding the process itself, many of these aspects are of central import to possible applications of multiphoton ionization, such as producing spin-polarized photoelectrons,[16] isotope separation, etc.

Several of the above-mentioned experiments[1-11] involved at least one resonance (or near resonance) with an atomic state. Most previous theoretical work has given only cursory attention to the details of resonance effects on multiphoton processes with intense lasers. That such details can be significant and surprising is *a priori* expected in view of the high light intensity and the narrow linewidth. But it is also indicated by a number of unusual features observed in experiments. Some of these features can be explained, at least qualitatively, by using relatively straightforward expressions for shifts of atomic levels under an external electromagnetic field. However, in many important cases a variety of effects come into play and considerable care is required. Otherwise, one may commit serious errors in calculating, for example, a transition rate.

Resonance multiphoton processes have often been discussed as if they were inherently different from off-resonance processes. As a consequence, terms such as "one-step" and "two-step" processes have been used, the latter referring to a resonance process, and the implication being that the second step is independent (has no memory) of the first step. Physically pleasing as this picture may be, it is not necessarily correct. As we show in this paper, resonance alone does not imply a two-step process. It is also the light intensity that determines whether the second step can be considered independent of the first, even at resonance. And more often than not this is not the case. As discussed in detail in Sec. VI, a necessary condition for the two-step picture to be meaningful is that the lifetime of the intermediate state be determined by spontaneous emission. Thus, whether resonant two-photon ionization in a given experimental situation is indeed a two-step process can be decided only after careful consideration of the induced radiative lifetime of the intermediate state.

In any case, such a separation of resonant from off-resonant multiphoton processes is rather artificial. From a fundamental viewpoint, one should be able to so formulate the problem as to obtain the resonant as well as the off-resonant processes as special cases. In doing so, one would account for radiative shifts and widths of intermediate states. When the laser frequency is tuned sufficiently far from resonance, such shifts and widths

would become small compared to the detuning and the off-resonance case would be obtained. This was in effect pointed out several years ago by Bebb and Gold,[26] who were the first to present quantitative calculations of multiphoton ionization rates for atoms other than hydrogen. But somehow their message seems to have been overlooked, although their calculations have been quoted widely. Bebb and Gold, however, did not consider the details of the process near resonance.

It is the purpose of this paper to present a systematic formulation of the problem. The method is based on the resolvent operator, which has been used successfully in a variety of problems.[27-29] The resolvent-operator technique has been discussed repeatedly in the literature. Its mathematical aspects were explored in considerable detail more than 20 years ago by Schönberg.[30] A brief discussion in a form useful to atomic physics problems has been given by Messiah.[31] The most complete and self-contained exposition of the method, as applied to quantum mechanics, is that of Goldberger and Watson.[32] It is their development, but without the use of projection operators, that is followed in this paper. Actually, the way it is employed here is related somewhat to Heitler's damping theory.[33] In addition to the references quoted above, the technique has been applied quite extensively to optical-pumping problems by Cohen-Tannoudji, Haroche, and co-workers.[34,35] It has also been generalized by the author[36] to the solution of the Liouville equation obeyed by the density matrix, and applied to a problem related somewhat to the subject of this paper.

The present paper is mainly concerned with the formal solution of the problem and its application to two-photon ionization. Actually, the results are applicable to N-photon ionization as long as it is only the first transition that is resonant. We are here particularly interested in the types of situations that are apt to arise in high-resolution experiments with tunable dye lasers. We study in considerable detail the shifts and widths of the intermediate, as well as the initial, atomic state, and their effects on the transition rate. One of the interesting results is that the shifts can be quite significant and can have a dramatic effect on the ionization rate even when the intermediate state is well outside the laser line, i.e., relatively far from resonance. This provides one illustration of the artificiality in the distinction between resonant and off-resonant processes. The effects discussed herein can have a significant influence on the spin polarization of the photoelectron. Previously reported results[16,17] should then be modified accordingly. This will be discussed in a subsequent publication. Several of the above effects have most recently been observed in three-photon near-resonance ionization of atomic sodium.[37]

Resonance effects in multiphoton ionization have very recently also been discussed by Gontier and Trahin,[19] and Chang and Stehle.[22] The present work differs from these papers both in the approach and the applications. For example, unlike Gontier and Trahin,[19] we find it necessary to take full consideration of the shift of the intermediate as well as the initial state. One of the reasons may be that we are here considering a single-photon resonance which connects the initial and intermediate states.

It has occasionally been claimed (most recently by Rachman, Laplanche, and Jaouen[38]) that some of the experimental results[1-11] for near-resonance multiphoton ionization suggest the breakdown of perturbation theory. The implication is that perturbation theory cannot predict "irregular" behavior such as that observed. That this is not the case is amply demonstrated by these results as well as those of Refs. 19 and 22. Moreover, it should be noted that the suggested alternative interpretations[38] are rather dubious, as the method[39] employed does not account for any resonance effects whatsoever, not to mention the fact that the related calculations are performed for the hydrogen atom while the experiments have been conducted on more complicated atoms. Also, the light intensities used in the experiments have in most cases been well below the commonly accepted limits[39] for the breakdown of perturbation theory. It is not my intention to imply that perturbation theory would not eventually break down for sufficiently high light intensity. I simply wish to caution against premature postulation of such breakdown when perturbation theory can account for the observed behavior. Furthermore, whatever nonperturbative method one attempts to use for the interpretation of the above experiments, it should account for resonance effects, at least in the low-intensity limit.

Section II is devoted to a more or less self-contained introduction to the resolvent operator as employed in this paper. Sections III–V deal with its application to two-photon ionization and a detailed study of shifts, widths, and the transition probability near resonance. In Secs. VI and VII, a quantitative study of these quantities for a model problem is presented, and in Sec. VIII, some generalizations and directions for further research are discussed.

II. FORMAL THEORY

We shall be concerned with a quantum-mechanical system whose Hamiltonian can be written as

$$H = H^0 + V, \tag{2.1}$$

where H^0 is the unperturbed part with eigenstates assumed to be known. Throughout this paper, all Hamiltonians are understood to have been divided by $\hbar$; thus all energies will be denoted by ω's and measured in $\sec^{-1}$. Let $|a\rangle, |b\rangle, |c\rangle, \ldots$ be the eigenstates of H^0 with respective energies $\omega_a, \omega_b, \omega_c, \ldots$. It is further assumed that H^0 can be written as

$$H^0 = H^A + H^R, \tag{2.2}$$

where H^A is the Hamiltonian of the free atom and H^R the Hamiltonian of the free radiation field; V will be the interaction between the two.

At $t=0$ the system is assumed to be in one of the eigenstates of H^0. We shall reserve the symbol $|a\rangle$ for the initial state; i.e., $\Psi(t=0) \equiv |a\rangle$. Since the total Hamiltonian H is time independent (no coupling to other systems), the total wave function of the system at a later time t is

$$\Psi(t) = e^{-iHt}\Psi(0) \equiv U(t)|a\rangle, \tag{2.3}$$

which defines the time-evolution operator $U(t)$. The rate of a particular process can be calculated from the matrix element

$$\langle f|U(t)|a\rangle \equiv U_{fa}(t), \tag{2.4}$$

where $|f\rangle$ is the appropriate final state to which the process under consideration leads.

The operator $U(t)$ can be obtained from the resolvent operator[31,32]

$$G(z) = 1/(z - H) \tag{2.5}$$

through the inversion integral

$$U(t) = \frac{1}{2\pi i}\int_C e^{-izt} G(z)\, dz, \tag{2.6}$$

where z is a complex number. The appropriate contour (C) of integration is shown in Fig. 1. Each matrix element of U can be obtained from the corresponding matrix element of G through Eq. (2.6). The problem is then reduced to calculating matrix elements of G. We are interested in matrix elements of G in the representation that diagonalizes H^0 because we are dealing with processes that can be described as transitions between eigenstates of H^0.

To set up the equations from which the necessary matrix elements of G may be obtained to the desired degree of approximation, one starts with Eq. (2.5) written as

$$(z - H^0 - V)G(z) = 1. \tag{2.7}$$

It is convenient to separate the diagonal from the off-diagonal matrix elements of G. This is accomplished by introducing two new operators $F(z)$ and $\mathcal{G}(z)$ such that $\mathcal{G}$ has only diagonal matrix elements that are equal to those of G. That is, we define

$$\mathcal{G}_{ba}(z) \equiv \mathcal{G}_{aa}(z)\delta_{ba} \equiv G_{aa}(z)\delta_{ba}, \tag{2.8}$$

which implies that, by definition, $\mathcal{G}_{aa} = G_{aa}$. Having $\mathcal{G}$ so defined, we now define $F(z)$ through the equation

$$G(z) \equiv F(z)\mathcal{G}(z), \tag{2.9}$$

which, owing to the diagonality of $\mathcal{G}$, leads to

$$G_{ba} = F_{ba}\mathcal{G}_{aa} = F_{ba}G_{aa}. \tag{2.10}$$

This equation obviously imposes a consistency condition on F, namely,

$$F_{aa} \equiv 1. \tag{2.11}$$

Thus the off-diagonal matrix element G_{ba} is expressed in terms of F_{ba} and the diagonal matrix element G_{aa}. The reason we are particularly interested in matrix elements of the form G_{ba} is that our initial state is $|a\rangle$ and we wish to calculate transitions from that state to others.

Substituting Eq. (2.9) into Eq. (2.7) we obtain

$$(z - H^0)F\mathcal{G} = 1 + VF\mathcal{G}. \tag{2.12}$$

Taking the aa matrix elements of both sides, and making use of the previous equations, we find

$$(z - \omega_a)\mathcal{G}_{aa} = 1 + (VF)_{aa}\mathcal{G}_{aa}. \tag{2.13}$$

Introducing the operator

$$R(z) \equiv VF(z), \tag{2.14}$$

and solving for $\mathcal{G}_{aa}$, we obtain

$$\mathcal{G}_{aa}(z) = G_{aa}(Z) = \frac{1}{z - \omega_a - R_{aa}(z)}, \tag{2.15}$$

which is a formal but exact expression for G_{aa}.

Taking the off-diagonal matrix element ba of

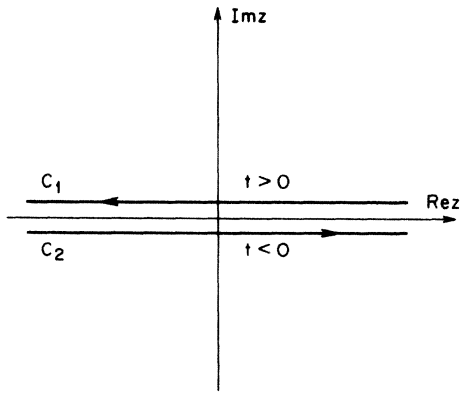

FIG. 1. Contours of integration for the inversion integral as given by Eq. (2.6). Contour C_1 applies for $t>0$ and C_2 for $t<0$.

Eq. (2.12), we find

$$(z-\omega_b)F_{ba}\mathcal{G}_{aa}=(VF)_{ba}\mathcal{G}_{aa}, \tag{2.16}$$

from which it follows that

$$(z-\omega_b)F_{ba}=\sum_c V_{bc}F_{ca} \tag{2.17a}$$

or

$$(z-\omega_b)F_{ba}=V_{ba}+\sum_{c\neq a}V_{bc}F_{ca}, \tag{2.17b}$$

where $b\neq a$. This clearly indicates that all (infinitely many, in general) matrix elements of F are coupled through a set of as many equations, which are integral equations when the spectrum of H^0 (or part of it) is continuous. In the latter case, the summations are replaced by integrations over the continuous part of the spectrum (see Sec. V). Depending on the particular problem to which this method is applied, one either truncates the set of equations retaining only a finite number of them on the basis of physical arguments, or one retains only a finite number of matrix elements thereby rendering the set of equations finite. It is in the first case that this method is particularly useful.

By combining Eqs. (2.14)–(2.16) and (2.10) we can also obtain a formal solution for G_{ba}, namely,

$$G_{ba}(z)=\frac{1}{z-\omega_b}R_{ba}(z)\frac{1}{z-\omega_a-R_{aa}(z)}. \tag{2.18}$$

The formal solutions (2.15) and (2.18) are very useful in studying the general properties of the matrix elements of $G(z)$. But for the actual calculation of such matrix elements one usually resorts to some approximate calculation of the matrix elements of $R(z)$. Then it is more convenient to work with Eqs. (2.17). From Eq. (2.16) it is clear that

$$(z-\omega_b)F_{ba}=R_{ba}, \tag{2.19}$$

which shows that there is a one-to-one correspondence between F_{ba} and R_{ba}. Knowing one, the other can be obtained from Eq. (2.19). The same is not true for the aa matrix element, because $F_{aa}=1$, while from Eq. (2.14) we have

$$R_{aa}(z)=\sum_d V_{ad}F_{da}, \tag{2.20}$$

which shows that R_{aa} depends on all off-diagonal matrix elements of F.

The program carried out in the following sections consists of obtaining and solving approximate equations which, to the desired degree of accuracy, describe the process under consideration. Our iteration and approximation procedure will be based on Eqs. (2.17).

In calculating the inversion integral of Eq. (2.6), it is useful to note the following property of $G(z)$. For positive values of t (which is what interests us here), one can replace z by $x+i\eta$, carry out the integration over the real variable x from $-\infty$ to $+\infty$, and then take the limit for $\eta\to+0$. The result is the same as if one integrated on the contour of Fig. 1. This is a general property of the resolvent operator[31,32] and we shall use it in subsequent sections. In denominators that contain nonvanishing imaginary parts, η can obviously be omitted and z simply replaced by x; otherwise η must be carried through and the limit taken (see Secs. IV and V).

We have here given a brief introduction to the theory of the resolvent operator which should enable even the unfamiliar reader to follow the development of the subsequent sections. For further details the reader is referred to Goldberger and Watson's exposition.[32]

III. APPLICATION TO TWO-PHOTON IONIZATION

The nonrelativistic unperturbed Hamiltonian H^0 of the problem under consideration consists of two parts: the atomic Hamiltonian H^A and the Hamiltonian H^R of the radiation field. The eigenstates of H^A will be denoted by $|1\rangle, |2\rangle, |3\rangle, \ldots$, with respective energies $\omega_1, \omega_2, \omega_3, \ldots$. Thus $H^A|1\rangle=\omega_1|1\rangle$, etc. The Hamiltonian H^R will be written in the second-quantization formalism, i.e.,

$$H^R=\sum_{\vec{k}\lambda}(a^\dagger_{\vec{k}\lambda}a_{\vec{k}\lambda}+\tfrac{1}{2})\omega_k, \tag{3.1}$$

where $\vec{k}$ is the wave vector and λ the polarization index of the $(\vec{k}\lambda)$th photon mode, $a^\dagger_{\vec{k}\lambda}$ and $a_{\vec{k}\lambda}$ the usual creation and annihilation operators, and ω_k the frequency of the $(\vec{k}\lambda)$th mode $(\omega_k=ck)$. We describe the incident light beam by a superposition of free space modes with the appropriate spectral and angular distributions. The modes appearing in Eq. (3.1) are the modes of a large box of linear dimension L with periodic boundary conditions and are therefore discrete. Of course a laser beam has a continuous, albeit narrow, spectrum. The transition from the discrete to the continuous is accomplished by letting $L\to\infty$ at the appropriate point in the calculation (see Sec. V).

The eigenstates of H^R are of the form $|\ldots, n(\vec{k}_1\lambda_1), n(\vec{k}_2\lambda_2), \ldots\rangle$, for which we will also use the symbol $|\{n(\vec{k}\lambda)\}\rangle$. For such a state we have

$$H^R|\{n(\vec{k}\lambda)\}\rangle=\left(\sum_{\vec{k}\lambda}[n(\vec{k}\lambda)+\tfrac{1}{2}]\omega_k\right)|\{n(\vec{k}\lambda)\}\rangle, \tag{3.2}$$

where the term $\frac{1}{2}$ leads to the well-known infinite part of the energy of the field.[33] We will omit it

from further considerations since it cancels out when one calculates transitions. Also, we shall omit the polarization index λ in order to compress notation. It will be assumed included in $\vec{k}$ but it will be taken explicitly into account whenever necessary. For the initial state of the system atom plus field, we take

$$|a\rangle \equiv |1\rangle|\ldots, n(\vec{k}_1), n(\vec{k}_2), n(\vec{k}_3), \ldots\rangle, \tag{3.3}$$

where $|1\rangle$ will be the ground state of the atom, unless otherwise stated. With this initial state, the final state of the system for two-photon ionization must be of the form

$$|f\rangle \equiv |3\rangle|\ldots, n(\vec{k}_1)-1, n(\vec{k}_2)-1, n(\vec{k}_3), \ldots\rangle, \tag{3.4}$$

where two photons have been removed from two arbitrary modes and the atom is in state $|3\rangle$, which is assumed to be in the continuum. For each such state $|f\rangle$, we have a matrix element $U_{fa}(t)$. But there are infinitely many possible final states, because the two photons may be absorbed from any two modes. Of course energy conservation imposes restrictions as to which modes can participate but this will show up later in the calculation. The probability that at time $t>0$ the atom has undergone two-photon ionization (i.e., it is in some state of the form of $|f\rangle$) is given by

$$\sum_{\vec{k}_1}\sum_{\vec{k}_2} |U_{fa}(t)|^2. \tag{3.5}$$

If there are contributions from more than one atomic ground state (or initial state, in general) the above expression will have to be averaged over such initial states. Moreover, the state of the incoming radiation field is not a pure number state $|\{n(\vec{k})\}\rangle$ but a superposition of such states. This means that expression (3.5) must also be averaged over initial photon states, which leads to well-known photon correlation effects.[40] We shall not consider such effects here in order not to obscure the main aspects of the present study.

The basic quantity therefore is U_{fa}, which can be obtained from G_{fa}, and which shifts the importance of the calculation to G_{fa}. For this we also need to specify the interaction V, which can be written[31-33] as

$$V = i\beta L^{-3/2}\sum_{\vec{k}} \omega_k^{1/2}[(\vec{r}\cdot\vec{\epsilon}_{\vec{k}})a_{\vec{k}} - (\vec{r}\cdot\vec{\epsilon}^{*}_{\vec{k}})a^{\dagger}_{\vec{k}}], \tag{3.6a}$$

where

$$\beta \equiv (2\pi e^2/\hbar)^{1/2}, \tag{3.6b}$$

and $\vec{r}$ is the position operator of the electron undergoing the transition, $\vec{\epsilon}_{\vec{k}}$ the polarization vector of the $\vec{k}$ photon mode, and L the linear dimension of the quantization cube. In this paper we are considering a one-electron model of the atom. In writing Eq. (3.6a), we have made the dipole approximation, and have used the $\vec{r}\cdot\vec{\mathcal{E}}$ form of the interaction[41] ($\vec{\mathcal{E}}$ being the electric field) in which the $\vec{A}^2$ term does not appear. Thus V has nonvanishing matrix elements only between field states differing by one photon in one mode.

From Eq. (2.10), we have

$$G_{fa} = F_{fa}\, G_{aa}. \tag{3.7}$$

Then we need F_{fa} and G_{aa}, and for the latter we need R_{aa}. From Eq. (2.20) we have

$$R_{aa} = \sum_b V_{ab} F_{ba} = \sum_b V^{*}_{ba} F_{ba}. \tag{3.8}$$

Given that $|a\rangle$ has the form of Eq. (3.3), V_{ba} is different from zero only for states $|b\rangle$ of the form

$$|b^{\pm}(\vec{k})\rangle \equiv |m\rangle|\ldots, n(\vec{k})\pm 1, n(\vec{k}'), \ldots\rangle, \tag{3.9}$$

where $|m\rangle$ is any atomic state, and one photon is either added to or subtracted from one arbitrary mode, while the number of photons in all other modes remain as in $|a\rangle$. Since $|m\rangle$ and $\vec{k}$ are arbitrary we have

$$R_{aa} = \sum_m \sum_{\vec{k}} (V^{*}_{b^{+}(\vec{k})a} F_{b^{+}(\vec{k})a} + V^{*}_{b^{-}(\vec{k})a} F_{b^{-}(\vec{k})a}). \tag{3.10}$$

For near-resonance two-photon ionization, there is one particular atomic state (to be denoted by $|2\rangle$) via which the transition proceeds. Under the assumption that all other atomic states are sufficiently outside the linewidth of the light, we need consider only the $m=2$ term in the above sum. If $|1\rangle$ is the ground state (as is assumed here), then the $b^{+}(\vec{k})$, terms will lead to antiresonant contributions because a ground state can only emit photons in virtual transitions; that is, it must reabsorb what it emits. This means that the $b^{+}(\vec{k})$ terms will make a contribution to the vacuum (Lamb) shift[42] of ω_1. Vacuum shifts do not interest us here, and will be understood to be incorporated in the atomic level energies. Thus ω_a is assumed to contain that part of R_{aa} that leads to a vacuum shift. As will be seen later there is also a part of the $b^{-}(\vec{k})$ terms that contributes to the vacuum shift. That too will be included in ω_1. Consequently, it is only states of the form

$$|b(\vec{k})\rangle \equiv |2\rangle|\ldots, n(\vec{k})-1, \ldots\rangle \tag{3.11}$$

that contribute, and R_{aa} becomes

$$R_{aa} = \sum_{\vec{k}} V^{*}_{b(\vec{k})a} F_{b(\vec{k})a}. \tag{3.12}$$

Now we need $F_{b(\vec{k})a}$, for which Eq. (2.17b) gives

$$(z-\omega_{b(\vec{k})})F_{b(\vec{k})a}=V_{b(\vec{k})a}+\sum_{c\neq a}V^{*}_{cb(\vec{k})}F_{ca}. \quad (3.13)$$

Again, given the form of $|b(\vec{k})\rangle$ and V, it is only states $|c\rangle$ of the form

$$|c^{\pm}(\vec{k}',m)\rangle=|m\rangle|\ldots,n(\vec{k})-1,\ldots,n(\vec{k}')\pm1,\ldots\rangle \quad (3.14)$$

that give nonvanishing contributions. Let us assume for the moment that there are no atomic states below $|2\rangle$ to which it can decay, except the ground state $|1\rangle$. In Sec. VIII we remove this restriction and show how the results are modified. Under the above assumption, there are two kinds of states $|c\rangle$ that give nonvanishing contributions: states of the form

$$|c^{+}(\vec{k}')\rangle\equiv|1\rangle|\ldots,n(\vec{k})-1,\ldots,n(\vec{k}')+1,\ldots\rangle, \quad (3.15)$$

where we must have $\vec{k}'\neq\vec{k}$, owing to the restriction $c\neq a$ in Eq. (3.13), and states of the form

$$|c^{-}(\vec{k}')\rangle\equiv|3\rangle|\ldots,n(\vec{k})-1,\ldots,n(\vec{k}')-1,\ldots\rangle, \quad (3.16)$$

where, according to our convention adopted in Eq. (3.4), $|3\rangle$ is assumed to be in the continuum. The selection of the above two forms of states simply reflects the fact that when only three atomic states are important, the intermediate excited state can either decay back down to the ground state or be ionized. Thus Eq. (3.13) becomes

$$(z-\omega_{b(\vec{k})})F_{b(\vec{k})a}=V_{b(\vec{k})a}+\sum_{\vec{k}'\neq\vec{k}}V^{*}_{c^{+}(\vec{k}')b(\vec{k})}F_{c^{+}(\vec{k}')a}+\sum_{\vec{k}'}V^{*}_{c^{-}(\vec{k}')b(\vec{k})}F_{c^{-}(\vec{k}')a}. \quad (3.17)$$

As will be seen later, restrictions of the form $\vec{k}'\neq\vec{k}$ are inconsequential when the transition to the continuum is made, but we shall carry them along for the sake of consistency.

Carrying the iteration one step further, we consider the equations for $F_{c^{+}(\vec{k}')a}$ and $F_{c^{-}(\vec{k}')a}$. For the first we have

$$(z-\omega_{c^{+}(\vec{k}')})F_{c^{+}(\vec{k}')a}=V_{c^{+}(\vec{k}')a}+\sum_{d\neq a}V^{*}_{dc^{+}(\vec{k}')}F_{da}. \quad (3.18)$$

From the form of $|a\rangle$ and $|c^{+}(\vec{k}')\rangle$ it is obvious that $V_{c^{+}(\vec{k}')}=0$. One of the states $|d\rangle$ for which $V_{dc^{+}(\vec{k}')}$ is nonzero is the state $|b(\vec{k})\rangle$. We now write

$$(z-\omega_{c^{+}(\vec{k}')})F_{c^{+}(\vec{k}')a}=V^{*}_{b(\vec{k})c^{+}(\vec{k}')}F_{b(\vec{k})a}+\sum_{d\neq a,b(\vec{k})}V^{*}_{dc^{+}(\vec{k}')}F_{da}. \quad (3.19)$$

Obviously there is a whole set of other states $|d\rangle$ that makes a nonvanishing contribution (of higher order) to the sum on the right side of Eq. (3.19). For our purposes, however, we may neglect the sum completely and take

$$F_{c^{+}(\vec{k}')a}\cong(z-\omega_{c^{+}(\vec{k}')})^{-1}V^{*}_{b(\vec{k})c^{+}(\vec{k}')}F_{b(\vec{k})a}. \quad (3.20)$$

The same procedure and reasoning as above, and the same approximation, lead to

$$F_{c^{-}(\vec{k}')a}\cong(z-\omega_{c^{-}(\vec{k}')})^{-1}V^{*}_{b(\vec{k})c^{-}(\vec{k}')}F_{b(\vec{k})a}. \quad (3.21)$$

The significance and motivation for the approximation employed will be discussed somewhat later (see Sec. VII).

Substituting Eqs. (3.20) and (3.21) into Eq. (3.17) we obtain

$$(z-\omega_{b(\vec{k})})F_{b(\vec{k})a}=V_{b(\vec{k})a}+\left(\sum_{\vec{k}'\neq\vec{k}}\frac{|\langle c^{+}(\vec{k}')|V|b(\vec{k})\rangle|^{2}}{z-\omega_{c^{+}(\vec{k}')}}+\sum_{\vec{k}'}\frac{|\langle c^{-}(\vec{k}')|V|b(\vec{k})\rangle|^{2}}{z-\omega_{c^{-}(\vec{k}')}}\right)F_{b(\vec{k})a}. \quad (3.22)$$

Introducing

$$D_{b(\vec{k})a}(z)\equiv\sum_{\vec{k}'\neq\vec{k}}\frac{|\langle c^{+}(\vec{k}')|V|b(\vec{k})\rangle|^{2}}{z-\omega_{c^{+}(\vec{k}')}}+\sum_{\vec{k}'}\frac{|\langle c^{-}(\vec{k}')|V|b(\vec{k})\rangle|^{2}}{z-\omega_{c^{-}(\vec{k}')}}, \quad (3.23)$$

and solving for $F_{b(\vec{k})a}$, we find

$$F_{b(\vec{k})a}(z)=\frac{\langle b(\vec{k})|V|a\rangle}{z-\omega_{b(\vec{k})}-D_{b(\vec{k})a}(z)}, \quad (3.24)$$

which is an approximate expression sufficient for our purposes. (We have been using both notations, V_{ab} and $\langle a|V|b\rangle$, for matrix elements, and we will continue doing so in order to avoid confusion of the various levels of subscripts in the more complicated formulas.)

Using Eq. (3.24) for $F_{b(\vec{k})a}$, Eq. (3.12) gives

$$R_{aa}(z)=\sum_{\vec{k}}\frac{|\langle b(\vec{k})|V|a\rangle|^{2}}{z-\omega_{b(\vec{k})}-D_{b(\vec{k})a}(z)}. \quad (3.25)$$

We now turn to the evaluation of F_{fa}. Again the

starting point is Eq. (2.17b), which gives

$$(z-\omega_f)F_{fa}=\sum_{d\neq a}V_{fd}F_{da}, \tag{3.26}$$

because the term V_{fa} vanishes. There are two particular states d that we will separate out. We call them $|b_1\rangle$ and $|b_2\rangle$, and they are

$$|b_1\rangle\equiv|2\rangle|\ldots,n(\vec{k}_1)-1,n(\vec{k}_2),n(\vec{k}_3),\ldots\rangle \tag{3.27a}$$

and

$$|b_2\rangle\equiv|2\rangle|\ldots,n(\vec{k}_1),n(\vec{k}_2)-1,n(\vec{k}_3),\ldots\rangle. \tag{3.27b}$$

Clearly these are the two intermediate states that lead from $|a\rangle$ to $|f\rangle$ via a two-photon transition. We write Eq. (3.26) in the form

$$(z-\omega_f)F_{fa}=V_{fb_1}F_{b_1a}+V_{fb_2}F_{b_2a}+\sum_{d\neq a,b_1,b_2}V_{fd}F_{da}. \tag{3.28}$$

The remaining sum now contributes to higher-order transitions from $|a\rangle$ to $|f\rangle$ as well as to the shift width of the final state. Since this state is in the continuum, we do not worry about such effects in this paper (they come in at much higher light intensities) and we take

$$(z-\omega_f)F_{fa}=V_{fb_1}F_{b_1a}+V_{fb_2}F_{b_2a}. \tag{3.29}$$

The problem now is to evaluate F_{b_1a} and F_{b_2a}. This proceeds along the same lines as the evaluation of $F_{b(\vec{k})a}$, except that now the iteration will be carried one step further. This is to be expected because R_{aa} is a correction to the amplitude G_{aa}, while F_{b_1a} itself is an amplitude and, therefore, to obtain approximations of the same order the iteration of F_{b_1a} and F_{b_2a} should be carried one step further. The main steps of the calculation are given in the Appendix. The result is

$$F_{b_ja}(z)=\frac{V_{b_ja}}{z-\omega_{b_j}-D_{b_ja}(z)}, \quad j=1,2. \tag{3.30}$$

Expressions for D_{b_1a} and D_{b_2a} are given in the Appendix.

Now we are in the position to write down an expression for G_{fa}. Combining Eqs. (3.30), (3.29), (3.7), and (2.15), we find

$$G_{fa}(z)=\frac{1}{(z-\omega_f)[z-\omega_a-R_{aa}(z)]}\times\left(\frac{V_{fb_1}V_{b_1a}}{z-\omega_{b_1}-D_{b_1a}(z)}+\frac{V_{fb_2}V_{b_2a}}{z-\omega_{b_2}-D_{b_2a}(z)}\right), \tag{3.31}$$

which is a formal, approximate expression for the amplitude of the resolvent operator. The approximate expressions for R_{aa} and D_{b_ja} are given in Eqs. (3.25) and (A17). The series of approximations made were dictated by the physical process (two-photon ionization) under consideration. In principle, substitution of this expression into the inversion integral (2.6) yields the transition amplitude $U_{fa}(t)$. But the above expression for G_{fa} is still too complex for the inversion integration to be performed. Further approximations, again based on the physics of the process, will be necessary. This is the subject of Sec. IV.

IV. TRANSITION PROBABILITY–FORMAL EXPRESSIONS

The complexity of $G_{fa}(z)$ arises from the fact that $R_{aa}(z)$ and $D_{b_ja}(z)$ are rather complicated functions of z. To invert the integral exactly, one must first find the roots of the equations $z-\omega_a-R_{aa}(z)=0$ and $z-\omega_{b_j}-D_{b_ja}(z)=0$, $j=1,2$. These roots constitute poles of the integrand and the integral can be calculated by a straightforward application of the Cauchy theorem. The solution of the above equations is a complicated task and in most cases must be done numerically. It turns out, however, that this is not always necessary. In fact, in many applications it is sufficient to approximate $R_{aa}(z)$ and $D_{b_ja}(z)$ by appropriately chosen constants.

Consider R_{aa} first. If the inequality $|R_{aa}(z)|\ll\omega_a$ is satisfied, and it certainly is in our case, R_{aa} is important only for values of z near ω_a. Then $R_{aa}(z)$ may be replaced by its value at $z=\omega_a$, if it is also true that it varies sufficiently slowly in the vicinity of ω_a, which will usually be the case. If this variation is not sufficiently slow, one can use higher terms of the Taylor expansion of $R_{aa}(z)$ around $z=\omega_a+i\eta$. With the above conditions in mind, we would replace $R_{aa}(z)$ by $R_{aa}(\omega_a)$. But $R_{aa}(z)$ itself has a resonance structure as shown by Eq. (3.25). The same reasoning leads to the replacement of $D_{b(\vec{k})a}(z)$ in that equation by $D_{b(\vec{k})a}(\omega_{b(\vec{k})})$. Therefore we replace $R_{aa}(z)$ in Eq. (3.31) by

$$R_a\equiv\sum_{\vec{k}}\frac{|\langle b(\vec{k})|V|a\rangle|^2}{\omega_a-\omega_{b(\vec{k})}-D_{b(\vec{k})}}, \tag{4.1a}$$

where

$$D_{b(\vec{k})}\equiv D_{b(\vec{k})a}(\omega_{b(\vec{k})})=\sum_{\vec{k}'\neq\vec{k}}\frac{|\langle c^+(\vec{k}')|V|b(\vec{k})\rangle|^2}{\omega_{b(\vec{k})}-\omega_{c^+(\vec{k}')}+i\eta}+\sum_{\vec{k}'}\frac{|\langle c^-(\vec{k}')|V|b(\vec{k})\rangle|^2}{\omega_{b(\vec{k})}-\omega_{c^-(\vec{k}')}+i\eta}, \tag{4.1b}$$

and $|b(\vec{k})\rangle, |c^+(\vec{k}')\rangle, |c^-(\vec{k}')\rangle$ are given by Eqs.

(3.11), (3.15), and (3.16).

Considering now $D_{b_1 a}(z)$, we proceed in an identical fashion. In the expression for $D_{b_1 a}(z)$ [Eq. (A17)], $D_{c^+(\vec{k})a}(z)$ is replaced by its value at $z = \omega_{c^+(\vec{k}')}$, and then $D_{b_1 a}(z)$ is replaced by

$$D_{b_1} \equiv D_{b_1 a}(\omega_{b_1}) = \sum_{\vec{k}' \neq \vec{k}_1} \frac{|\langle c^+(\vec{k}')|V|b_1\rangle|^2}{\omega_{b_1} - \omega_{c^+(\vec{k}')} - D_{c^+(\vec{k}')}} + \sum_{\vec{k}'} \frac{|\langle c^-(\vec{k}')|V|b_1\rangle|^2}{\omega_{b_1} - \omega_{c^-(\vec{k}')} + i\eta}, \tag{4.2a}$$

where

$$D_{c^+(\vec{k}')} \equiv \sum_{\vec{k}'' \neq \vec{k}'} \frac{|\langle d(\vec{k}'')|V|c^+(\vec{k}')\rangle|^2}{\omega_{c^+(\vec{k}')} - \omega_{d(\vec{k}'')} + i\eta}, \tag{4.2b}$$

and $|c^+(\vec{k}')\rangle$, $|c^-(\vec{k}')\rangle$, and $|d(\vec{k}'')\rangle$ are now given by Eqs. (A2), (A3), and (A8). And as before, D_{b_2} is obtained from D_{b_1} by replacing b_1 and $\vec{k}_1$ by b_2 and $\vec{k}_2$, respectively.

The z-independent quantities R_a, D_{b_1}, and D_{b_2} are in general complex. We introduce the definitions

$$R_a \equiv S_a - i\Gamma_a \tag{4.3a}$$

and

$$D_{b_j} \equiv S_{b_j} - i\Gamma_{b_j}, \quad j = 1, 2 \tag{4.3b}$$

where S and $-\Gamma$ are the real and imaginary parts. It should be clear by now that R_{aa} and $D_{b_j a}$ are the shift-width functions of the states $|a\rangle$ and $|b_j\rangle$, respectively. It is a general result of the theory[32] of the resolvent operator that Γ_a and Γ_{b_j} are nonnegative quantities. In our case, they are positive because they represent the transition probabilities out of the initial and intermediate states, respectively, and in the presence of a near-resonant field these transitions obviously have a nonzero probability. One does not have to use the general theorem about the Γ's but can proceed to calculate them and find that they are indeed positive. This property is important in calculating the transition probability.

Thus the matrix element G_{fa} becomes

$$G_{fa}(z) = \frac{1}{(z - \omega_f)(z - \omega_a - S_a + i\Gamma_a)} \left[\frac{V_{fb_1} V_{b_1 a}}{z - \omega_{b_1} - S_{b_1} + i\Gamma_{b_1}} + \frac{V_{fb_2} V_{b_2 a}}{z - \omega_{b_2} - S_{b_2} + i\Gamma_{b_2}} \right]. \tag{4.4}$$

The evaluation of $U_{fa}(t)$ is now straightforward. The integrand of the inversion integral has three simple poles. Each such pole gives rise to an exponential, and thus we obtain

$$U_{fa}(t) = \sum_{j=1,2} \left[\frac{e^{-i\omega_f t} V_{fb_j} V_{b_j a}}{(\omega_f - \omega_a - S_a + i\Gamma_a)(\omega_f - \omega_{b_j} - S_{b_j} + i\Gamma_{b_j})} + \frac{e^{-i(\omega_a + S_a)t - \Gamma_a t} V_{fb_j} V_{b_j a}}{(\omega_a + S_a - i\Gamma_a - \omega_f)(\omega_a + S_a - i\Gamma_a - \omega_{b_j} - S_{b_j} + i\Gamma_{b_j})} + \frac{e^{-i(\omega_{b_j} + S_{b_j})t - \Gamma_{b_j} t} V_{fb_j} V_{b_j a}}{(\omega_{b_j} + S_{b_j} - i\Gamma_{b_j} - \omega_f)(\omega_{b_j} + S_{b_j} - i\Gamma_{b_j} - \omega_a - S_a + i\Gamma_a)} \right]. \tag{4.5}$$

From this expression, and using a well-known procedure,[32] one can obtain the transition probability per unit time. Briefly, one calculates $|U_{fa}(t)|^2$ retaining only the nondecaying contributions, and then one integrates over all final energies. The result, which still depends on the photoelectron direction of propagation, is given by

$$dW_{fa} = 2\pi\rho(\omega_a) \left| \frac{V_{fb_1} V_{b_1 a}}{\omega_a + S_a - \omega_{b_1} - S_{b_1} + i\Gamma_{b_1}} + \frac{V_{fb_2} V_{b_2 a}}{\omega_a - S_a - \omega_{b_2} - S_{b_2} + i\Gamma_{b_2}} \right|^2. \tag{4.6}$$

Recalling that $|f\rangle$ is a pure state of the form $|3\rangle|\ldots, n(\vec{k}_1) - 1, \ldots, n(\vec{k}_2) - 1, \ldots\rangle$, where $|3\rangle$ is in the continuum, it is evident that the total transition probability per unit time for two-photon ionization is

$$W_K^{(2)} = \int_{\Omega_{\vec{K}}} d\Omega_{\vec{K}} \sum_{\vec{k}_1} \sum_{\vec{k}_2} dW_{fa}, \tag{4.7}$$

where $\vec{K}$ is the wave vector of the photoelectron, and $d\Omega_{\vec{K}}$ its direction of propagation. To proceed further, we need explicit expressions for shifts, widths, and matrix elements which are obtained in the following section.

V. TRANSITION PROBABILITY – EXPLICIT EXPRESSIONS

In multiphoton processes the polarization of the incident light is quite important because even total cross sections depend on it.[1,12] We shall therefore always assume that the light is polarized, the exact polarization to be specified whenever necessary. Another reason for this assumption is that multiphoton experiments are generally performed with polarized light. Thus we take

$$V = i(2\pi e^2/\hbar)^{1/2} L^{-3/2} \sum_{\vec{k}} \omega_k^{1/2} (\vec{r}^{\lambda} a_{\vec{k}\lambda} - \vec{r}^{\lambda *} a_{\vec{k}\lambda}^{\dagger}), \tag{5.1}$$

where $\vec{r}^{\lambda} \equiv \vec{r} \cdot \vec{\epsilon}_{\vec{k}\lambda}$ denotes the projection of $\vec{r}$ on the λ polarization vector, and $\vec{r}^{\lambda *}$ the complex conjugate. From the definition of the states $|a\rangle$, $|b\rangle$, and $|f\rangle$, we have

$$V_{b_j a} = i(2\pi e^2/\hbar)^{1/2} L^{-3/2} \omega_{k_j}^{1/2} \vec{r}_{21}^{\lambda} [n(\vec{k}_j)]^{1/2}, \quad j = 1, 2 \tag{5.2a}$$

and

$$V_{f b_j} = i(2\pi e^2/\hbar)^{1/2} L^{-3/2} \omega_{k_{j'}}^{1/2} \vec{r}_{32}^{\lambda} [n(\vec{k}_{j'})]^{1/2}, \quad j' = 1, 2 \tag{5.2b}$$

where $j' \neq j$, and $\vec{r}_{21}^{\lambda}, \vec{r}_{32}^{\lambda}$ are now atomic matrix elements. For the energy differences, we have

$$\omega_f - \omega_a = \omega_3 - \omega_1 - \omega_{k_1} - \omega_{k_2} = -(\omega_{k_1} + \omega_{k_2} - \omega_{31}), \tag{5.3a}$$

$$\omega_f - \omega_{b_1} = \omega_3 - \omega_2 - \omega_{k_2} = -(\omega_{k_2} - \omega_{32}), \tag{5.3b}$$

$$\omega_f - \omega_{b_2} = \omega_3 - \omega_2 - \omega_{k_1} = -(\omega_{k_1} - \omega_{32}), \tag{5.3c}$$

where $\omega_{nm} \equiv \omega_n - \omega_m$.

Consider now R_a as given by Eq. (4.1a), which involves $D_{b(\vec{k})}$ in its denominator. Calculating the matrix elements $\langle c^+(\vec{k}')|V|b(\vec{k})\rangle$ and $\langle c^-(\vec{k}')|V|b(\vec{k})\rangle$, and the energy differences as we did above, Eq. (4.1b) gives

$$D_{b(\vec{k})} = \sum_{\vec{k}' \neq \vec{k}} \frac{2\pi e^2}{\hbar} L^{-3} \omega_{k'} \frac{|\vec{r}_{12}^{\lambda *}|^2 (n(\vec{k}') + 1)}{\omega_{21} - \omega_{k'} + i\eta} + \sum_{\vec{k}'} \frac{2\pi e^2}{\hbar} L^{-3} \omega_{k'} \frac{|\vec{r}_{32}^{\lambda}|^2 n(\vec{k}')}{\omega_{23} + \omega_{k'} + i\eta}. \tag{5.4}$$

Now take the limit as $\eta \to +0$, using the identity[31,32]

$$\lim_{\eta \to +0} \frac{1}{x + i\eta} = \frac{\mathcal{P}}{x} - i\pi\delta(x), \tag{5.5}$$

where $\mathcal{P}$ denotes the Cauchy principal value and $\delta(x)$ is the δ function; also replace the summation over $\vec{k}'$ by integration using the usual formula[33]

$$\sum_{\vec{k}} \to \frac{L^3}{8\pi^3 c^3} \int_0^{\infty} \omega_k^2 \, d\omega_k \int_{\Omega_{\vec{k}}} d\Omega_{\vec{k}}, \tag{5.6}$$

where $\Omega_{\vec{k}}$ is the direction of propagation of the $\vec{k}$ photon. It is evident now that the restriction $\vec{k}' \neq \vec{k}$ in the sum has no effect on the integral. Denoting by s_2 and γ_2 the real and imaginary parts of $D_{b(\vec{k})}$, we obtain

$$D_{b(\vec{k})} \equiv s_2 - i\gamma_2, \tag{5.7a}$$

where

$$s_2 = \frac{2\pi e^2}{\hbar 8\pi^3 c^3} \left[|\vec{r}_{12}^{\lambda *}|^2 \mathcal{P} \int_0^{\infty} \omega_{k'}^3 \, d\omega_{k'} \int_{\Omega_{\vec{k}'}} \frac{(n(\vec{k}') + 1) \, d\Omega_{\vec{k}'}}{\omega_{21} - \omega_{k'}} + \mathcal{P} \int_0^{\infty} |\vec{r}_{32}^{\lambda}|^2 \, \omega_{k'}^3 \, d\omega_{k'} \int_{\Omega_{\vec{k}'}} \frac{n(\vec{k}') \, d\Omega_{\vec{k}'}}{\omega_{k'} - \omega_{32}} \right] \tag{5.7b}$$

and

$$\gamma_2 = \frac{2\pi e^2}{\hbar 8\pi^3 c^3} \left[|\vec{r}_{12}^{\lambda *}|^2 \int_0^{\infty} \omega_{k'}^3 \, d\omega_{k'} \int_{\Omega_{\vec{k}'}} (n(\vec{k}') + 1) \delta(\omega_{21} - \omega_{k'}) \, d\Omega_{\vec{k}'} + \int_0^{\infty} |\vec{r}_{32}^{\lambda}|^2 \, \omega_{k'}^3 \, d\omega_{k'} \int_{\Omega_{\vec{k}'}} n(\vec{k}') \delta(\omega_{k'} - \omega_{32}) \, d\Omega_{\vec{k}'} \right]. \tag{5.7c}$$

The quantities s_2 and γ_2 represent shifts and widths of the state $|b(\vec{k})\rangle$. In the expression for s_2 we shall neglect 1 from the factor $(n(\vec{k}') + 1)$ because it represents a contribution to the vacuum shift. We shall retain 1, however, in the expression for γ_2 because it represents the spontaneous decay of the intermediate atomic state $|2\rangle$. It is more convenient to express the light intensity in terms of the photon flux through the equation[33]

$$I(\omega_k) = \frac{\omega_k^2}{8\pi^3 c^2} \int_{\Omega_{\vec{k}}} n(\vec{k}) \, d\Omega_{\vec{k}}, \tag{5.8}$$

where $I(\omega_k)$ is expressed in number of photons per cm^2 per second per unit frequency. More generally, one can introduce the quantity $dI(\omega_k, \Omega_{\vec{k}})/d\Omega_{\vec{k}}$, which also involves the angular dependence of the photon flux. But for most cases of experimental interest one can assume a reasonably uniform angular dependence, and therefore work with $I(\omega_k)$.

Note that the matrix elements $|\vec{r}_{32}^{\lambda}|^2$ have been left under the integral over $\omega_{k'}$. The reason is that $|3\rangle$ is in the continuum and as a result the matrix element depends on $\omega_{k'}$. This dependence, however, will not be terribly important in most cases owing to the narrow linewidth of laser light. The terms involving $|\vec{r}_{32}^{\lambda}|^2$ must be multiplied by the density of final states of the outgoing electron since the continuum states have a δ-function normalization.[26] If the wave vector of the photoelectron is $\vec{K}$, its energy is

$$\omega_K = \hbar K^2/2m, \tag{5.9}$$

while the density of final states[26] is

$$\rho(\omega_K) = (mK/8\pi^3\hbar)\, d\Omega_{\vec{K}}, \tag{5.10}$$

where $\Omega_{\vec{K}}$ is the direction of $\vec{K}$. If the ionization energy of the atom from its ground state is ω_I, then

$$\omega_3 = \omega_I + \omega_K, \tag{5.11a}$$

which implies

$$\omega_{32} = \omega_K + \omega_I - \omega_2 = \omega_K + \omega_{I2}, \tag{5.11b}$$

where ω_{I2} gives the energy of ionization from the excited state $|2\rangle$. The state $|3\rangle$ will be characterized by the wave vector $\vec{K}$, i.e., $|3\rangle = |\vec{K}\rangle$, and the matrix element $\vec{r}_{32}^{\,\lambda}$ will be also denoted by $\vec{r}_{\vec{K}2}$. Noting further that $e^2/\hbar c \equiv \alpha$ is the fine-structure constant, we can write

$$s_2 \equiv s_{2(1)} + s_{2(K)}, \tag{5.12a}$$

where

$$s_{2(1)} \equiv 2\pi\alpha |\vec{r}_{12}^{\,\lambda *}|^2 \mathcal{P} \int_0^\infty \frac{\omega I(\omega)\, d\omega}{\omega_{21} - \omega}, \tag{5.12b}$$

$$s_{2(K)} \equiv 2\pi\alpha \mathcal{P} \int_0^\infty d\omega \int_0^\infty d\omega_K |\vec{r}'^{\,\lambda}_{K2}|^2 \frac{\omega I(\omega)}{\omega - (\omega_K + \omega_{I2})}, \tag{5.12c}$$

and

$$|\vec{r}'^{\,\lambda}_{K2}|^2 \equiv \int_{\Omega_{\vec{K}}} \frac{mK |\vec{r}^{\,\lambda}_{\vec{K}2}|^2}{8\pi^3\hbar}\, d\Omega_{\vec{K}}, \tag{5.12d}$$

the last integration being over all directions of propagation of the photoelectron. Now r'_{K2} has the same dimensions as r_{12}. Similarly, we write

$$\gamma_2 \equiv \gamma_{2(0)} + \gamma_{2(1)} + \gamma_{2(K)}, \tag{5.13a}$$

where

$$\gamma_{2(0)} \equiv \tfrac{2}{3}(\alpha/c^2)\, \omega_{21}^3 |\vec{r}_{12}|^2, \tag{5.13b}$$

$$\gamma_{2(1)} \equiv 2\pi^2\alpha |\vec{r}_{12}^{\,\lambda *}|^2 \omega_{21} I(\omega_{21}), \tag{5.13c}$$

and

$$\gamma_{2(K)} \equiv 2\pi^2\alpha \int_0^\infty \omega I(\omega) |\vec{r}'^{\,\lambda}_{K2}|^2\, d\omega. \tag{5.13d}$$

In the last equation, $r'^{\,\lambda}_{\vec{K}2}$ is to be evaluated at $\omega_K = \omega - \omega_{I2}$ owing to the presence of the δ function $\delta(\omega_{k'} - \omega_{32}) = \delta[\omega_K - (\omega_{k'} - \omega_{I2})]$. In all of the above equations, $\omega_{k'}$, which is a dummy variable, has been replaced by ω, and the δ functions in the expression for γ_2 have been used in performing some of the integrations. The remaining integrations require specification of the light spectrum $I(\omega)$ and knowledge of the functional dependence of r'_{K2} on ω_K. This dependence is due to the presence of K [which from Eq. (5.9) is $(m\omega_K/\hbar)^{1/2}$] in Eq. (5.12d), and also to the fact that the matrix element $\vec{r}_{K2}$ itself depends on the energy of the outgoing electron. With the narrow spectral widths of lasers, however, this dependence is not very significant. To obtain $\gamma_{2(0)}$, we sum over all possible light polarizations because the spontaneous emission is unaffected by the polarization of the exciting light. It is evident now that $s_{2(1)}$ and $\gamma_{2(1)}$ are the induced shift and width of the state $|2\rangle$ due to resonant transitions to the ground state, while $s_{2(K)}$ and $\gamma_{2(K)}$ are the corresponding quantities due to transitions to the continuum. These quantities are further discussed in Sec. VI.

Having obtained explicit expressions for $D_{b(\vec{k})}$, we now turn to the calculation of R_a itself. The matrix element $\langle b(\vec{k})|V|a\rangle$ is

$$V_{b(\vec{k})a} = i(2\pi e^2/\hbar)^{1/2} L^{-3/2} \omega_k^{1/2} r_{21}^{\lambda} [n(\vec{k})]^{1/2}, \tag{5.14}$$

while

$$\omega_a - \omega_{b(\vec{k})} = \omega_1 - (\omega_2 - \omega_k) = \omega_k - \omega_{21}. \tag{5.15}$$

Using now $s_2 - i\gamma_2$ for $D_{b(\vec{k})}$, Eq. (4.1a) gives

$$R_a = \frac{2\pi e^2}{\hbar} L^{-3} \sum_{\vec{k}} |r_{21}^{\lambda}|^2 \frac{\omega_k n(\vec{k})}{\omega_k - \omega_{21} - s_2 + i\gamma_2}. \tag{5.16}$$

Replacing as before the summation over $\vec{k}$ by integration, and separating the real and imaginary parts of R_a, we obtain

$$R_a = S_a - i\Gamma_a, \tag{5.17a}$$

where

$$S_a \equiv 2\pi\alpha |\vec{r}_{21}^{\,\lambda}|^2 \int_0^\infty \frac{\omega(\omega - \omega_{21} - s_2) I(\omega)\, d\omega}{(\omega - \omega_{21} - s_2)^2 + \gamma_2^2} \tag{5.17b}$$

and

$$\Gamma_a \equiv 2\pi\alpha |\vec{r}_{21}^{\,\lambda}|^2 \int_0^\infty \frac{\gamma_2 \omega I(\omega)\, d\omega}{(\omega - \omega_{21} - s_2)^2 + \gamma_2^2}, \tag{5.17c}$$

and where the quantities s_2 and γ_2 depend on the intensity and spectral shape of the incident light [Eqs. (5.12) and (5.13)].

The calculation of D_{b_1} and D_{b_2} proceeds in a similar fashion. One calculates $D_{c^+(\vec{k})}$ first [see Eq. (4.2b)]. Using the definitions of the Appendix and the explicit form of V, and carrying out the mathematical manipulations, we obtain

$$D_{c^+(\vec{k}')} \equiv s_1 - i\gamma_1, \tag{5.18a}$$

where

$$s_1 \equiv 2\pi\alpha |\vec{r}_{21}^{\,\lambda}|^2 \mathcal{P} \int_0^\infty \frac{\omega I(\omega)\, d\omega}{\omega - \omega_{21}} \tag{5.18b}$$

and

$$\gamma_1 = 2\pi^2\alpha|\vec{r}_{21}^{\lambda}|^2\omega_{21}I(\omega_{21}). \tag{5.18c}$$

Now s_1 and γ_1 represent the shift and width of the state $c^+(\vec{k}')$, which involves the ground atomic state. For this reason there is no vacuum-field contribution to γ_1 since the ground state can only make a transition by absorbing photons.

Using now these expressions for $D_{c^+(\vec{k}')}$ in Eq. (4.2a) in combination with the explicit expressions for the matrix elements and the energies, we obtain

$$D_{b_1} = S_{b_1} - i\Gamma_{b_1} \tag{5.19a}$$

and

$$S_{b_1} = -2\pi\alpha|\vec{r}_{12}^{\lambda *}|^2\int_0^\infty \frac{(\omega-\omega_{21}+s_1)\omega I(\omega)\,d\omega}{(\omega-\omega_{21}+s_1)^2+\gamma_1^2} + 2\pi\alpha\mathcal{P}\int_0^\infty d\omega\int_0^\infty d\omega_K|\vec{r}_{K2}'^{\lambda}|^2\frac{\omega I(\omega)}{\omega-(\omega_K+\omega_{I2})} \tag{5.19b}$$

and

$$\Gamma_{b_1} = \frac{2}{3}\frac{\alpha}{c^2}\omega_{21}^3|\vec{r}_{12}|^2 + 2\pi^2\alpha|\vec{r}_{12}^{\lambda *}|^2\int_0^\infty \frac{\gamma_1\omega I(\omega)\,d\omega}{(\omega-\omega_{21}+s_1)^2+\gamma_1^2} + 2\pi^2\alpha\int_0^\infty \omega I(\omega)|\vec{r}_{K2}'^{\lambda}|^2\,d\omega, \tag{5.19c}$$

where we have again omitted contributions to the vacuum shift. Proceeding in the same fashion we find that $D_{b_1} = D_{b_2}$. This should have been expected because the states $|b_1\rangle$ and $|b_2\rangle$ differ simply in the number of photons of the two modes, and since D_{b_1} and D_{b_2} involve integration over all modes, the difference disappears. Physically, D_{b_1} represents the shift and width of the state of the whole system (atom plus field) in which one photon has been absorbed and the atom is in the excited state $|2\rangle$. Owing to the large number of photons present it does not make any difference from which mode the photon has been absorbed. Mathematically this is taken into account when we replace $n(\vec{k}')$ by the laser spectrum $I(\omega)$. Therefore we should have $D_{b_1} = D_{b_2}$. From here on we shall denote both by $D_b \equiv S_b - i\Gamma_b$.

The quantities S_a, Γ_a, S_b, and Γ_b are now constants which, however, depend on the incident light spectrum and polarization. Using now the explicit expressions for the matrix elements V_{fb_j} and $V_{b_j a}(j=1,2)$, and for the energies, Eq. (4.6) gives

$$dW_{fa} = 2\pi\left(\frac{mK}{8\pi^3\hbar}\right)d\Omega_{\vec{K}}\left(\frac{2\pi e^2}{\hbar}\right)^2\omega_{k_1}\omega_{k_2}n(k_1)n(k_2)L^{-6}|\vec{r}_{32}^{\lambda}|^2|\vec{r}_{21}^{\lambda}|^2\left|\frac{1}{\omega_{k_1}-\omega_{21}+S_{ab}+i\Gamma_b}+\frac{1}{\omega_{k_2}-\omega_{21}+S_{ab}+i\Gamma_b}\right|^2, \tag{5.20}$$

where

$$S_{ab} \equiv S_a - S_b, \tag{5.21}$$

and K is to be evaluated at

$$K = [(2m/\hbar)(\omega_{k_1}+\omega_{k_2}-\omega_I)]^{1/2}. \tag{5.22}$$

Summing over all photon modes, integrating over photoelectron directions, using Eq. (5.12d), and replacing summations over $\vec{k}$ by integrations, we obtain

$$W_K^{(2)} = 8\pi^3\alpha^2\int_0^\infty d\omega\int_0^\infty d\omega'\,|\vec{r}_{K2}'^{\lambda}|^2|\vec{r}_{21}^{\lambda}|^2\omega\omega' I(\omega)I(\omega')\left|\frac{1}{\omega-\omega_{21}+S_{ab}+i\Gamma_b}+\frac{1}{\omega'-\omega_{21}+S_{ab}+i\Gamma_b}\right|^2, \tag{5.23}$$

where for simplicity we have now replaced ω_{k_1} and ω_{k_2} by ω and ω' since they are dummy variables. This is the total transition probability per unit time for two-photon ionization. The photoelectron angular distribution is $dW_K^{(2)}/d\Omega_{\vec{K}}$ and is obtained from the above expression by replacing $|\vec{r}_{K2}'^{\lambda}|^2$ with $(mK/8\pi^3\hbar)|\vec{r}_{\vec{K}2}^{\lambda}|^2$. As expected, the angular distribution is determined by the dipole matrix elements of the transition.

If we neglect shifts and widths in Eq. (5.23), and replace the light spectrum by a δ function, we obtain the usually quoted formula for $W_K^{(2)}$, except for a factor of 4, which has been neglected in previous treatments. It is evident now that the general equation, with all intermediate states taken into account, is

$$W_K^{(2)} = 8\pi^3\alpha^2 \int_{\Omega_{\vec{K}}} d\Omega_{\vec{K}} \frac{mK}{8\pi^3\hbar} \int_0^\infty d\omega \int_0^\infty d\omega'\, \omega\omega' I(\omega)$$

$$\times I(\omega') \left| \sum_m \left[\frac{\vec{r}^{\lambda}_{\vec{K}m} \vec{r}^{\lambda}_{m1}}{\omega - \omega_{m1} + S_{ab_m} + i\Gamma_{b_m}} + \frac{\vec{r}^{\lambda}_{\vec{K}m} \vec{r}^{\lambda}_{m1}}{\omega' - \omega_{m1} + S_{ab_m} + i\Gamma_{b_m}} \right] \right|^2 , \tag{5.24}$$

where the summation is over all atomic states m. This is obtained by going back to Eq. (3.10) and proceeding from there as we have done, but carrying along the summation over m. For a narrow-width light source whose center frequency is many linewidths away from any ω_{m1}, the shifts and widths can be neglected. Then we obtain the usual form of the off-resonance two-photon ionization rate. If, however, one or more atomic states lie near or within the light-source linewidth, shifts and widths will generally be important and must be included. In case the center frequency of the light is very near one particular atomic level while all other atomic levels are far away, then one can adequately describe the process by retaining only one term of the sum over m. Strictly speaking, even then the sum gives a background contribution which should be included, but in many cases of interest this background is several orders of magnitude smaller around the resonance. The background becomes important in the case of near resonance with two closely spaced levels. Then at some point between the levels, interference between the two amplitudes can cause the cross section to drop to very low values, in which case the main contribution may come from the background. Whether this happens depends on how narrow the light source is.

For off-resonance processes the shape and width of the light source is not important and the total flux is all that matters. This is obvious from Eq. (5.24) if one replaces $I(\omega)$ by a δ function and neglects the widths and shifts. But for near-resonance processes, the details about $I(\omega)$ can be important not only because $W_K^{(2)}$ involves integrations over the spectrum but also because shifts and widths depend on it. In Sec. VI, we study this case in some detail.

It is in going from Eq. (5.20) to Eq. (5.23) that photon-correlation effects would enter the expression for the transition probability. If Eq. (5.20) is averaged over all possible field states the resulting equation for the transition probability $W_K^{(2)}$ would involve a second-order field correlation function instead of $I(\omega)I(\omega')$. Since otherwise the results would be the same (and since photon-correlation effects have been discussed elsewhere[40]) we do not consider this question any further.

In the most general case, Eqs. (5.23) and (5.24) should contain the step function $\Theta(\omega+\omega'-\omega_I)$ under the integrand, where $\Theta(x)=1$ for $x\geq 0$ and zero otherwise. However, for a single laser beam centered at ω_0 with width $2\Delta_L$ such that $2\omega_0 - 2\Delta_L > \omega_I$, the step function becomes redundant and as a result we have not included it in the equations of this paper. For near-threshold two-photon ionization it would have to be included.

VI. APPLICATION TO A MODEL PROBLEM

We are now in the position to explore some of the details of resonant and near-resonant two-photon ionization on the basis of Eq. (5.23). As a model, let us consider a one-electron (alkali) atom and a laser with a linewidth of the order of a few wave numbers. It is with such lasers that most present day high-resolution multiphoton ionization experiments are performed. The laser line shape usually looks like a triangle. It turns out, however, that a square line shape gives most of the essential features of the process while at the same time it yields easily tractable analytical results. Thus we take

$$I(\omega) = I_0 \quad \text{for } \omega_0 - \Delta_L \leq \omega \leq \omega_0 + \Delta_L \tag{6.1}$$
$$= 0 \quad \text{otherwise},$$

where ω_0 is the laser center frequency and $2\Delta_L$ its linewidth.

Over linewidths of the order of a few cm^{-1} or smaller, the matrix element $\vec{r}^{\lambda}_{K2}$ is essentially constant. Also K, as given by Eq. (5.22), is an extremely slowly varying function of energy over the range $2\Delta_L$. We can therefore take $|\vec{r}'^{\lambda}_{K2}|^2$ outside of the integral, replacing it by its value at

$$K_0 \equiv [(2m/\hbar)(2\omega_0 - \omega_I)]^{1/2} . \tag{6.2}$$

Denoting that value by $|\vec{r}'^{\lambda}_{K_0 2}|^2$, we can write

$$W_K^{(2)} = 8\pi^3\alpha^2 |\vec{r}'^{\lambda}_{K_0 2}|^2 |\vec{r}^{\lambda}_{21}|^2 \omega_0^2 Q , \tag{6.3a}$$

where

$$Q \equiv \int_{\omega_0-\Delta_L}^{\omega_0+\Delta_L} d\omega \int_{\omega_0-\Delta_L}^{\omega_0+\Delta_L} d\omega' I_0^2 \frac{(\omega+\omega'-2\bar{\omega}_{21})^2 + 4\Gamma_b^2}{[(\omega-\bar{\omega}_{21})^2+\Gamma_b^2][(\omega'-\bar{\omega}_{21})^2+\Gamma_b^2]} \tag{6.3b}$$

and where

$$\bar{\omega}_{21} \equiv \omega_{21} - S_{ab} . \tag{6.3c}$$

We have also replaced $\omega\omega'$ by ω_0^2 as $\omega\omega'$ varies insignificantly over $2\Delta_L$. It is Q that now contains all the resonance and line-shape effects. Performing the integrations, we obtain

$$Q = I_0^2(\tfrac{1}{2} g_1^2 + (4\Delta_L/\Gamma_b)g_2 + 2g_2^2), \tag{6.4a}$$

where

$$g_1 \equiv \ln \frac{(\omega_0 - \bar{\omega}_{21} + \Delta_L)^2 + \Gamma_b^2}{(\omega_0 - \bar{\omega}_{21} - \Delta_L)^2 + \Gamma_b^2} \tag{6.4b}$$

and

$$g_2 \equiv \arctan \frac{2\Delta_L \Gamma_b}{(\omega_0 - \bar{\omega}_{21})^2 + \Gamma_b^2 - \Delta_L^2} . \tag{6.4c}$$

Note that the total light flux I in photons per cm^2 per second is

$$I = I_0 2\Delta_L . \tag{6.5}$$

The shifts and widths also depend on the light spectrum. The formulas obtained in Sec. V applied to the case of square line shape give

$$\Gamma_b \equiv \Gamma_{2(0)} + \Gamma_{2(K)} + \Gamma_{2(1)}, \tag{6.6a}$$

where

$$\Gamma_{2(0)} = \gamma_{2(0)} = \tfrac{2}{3}(\alpha/c^2)\omega_{21}^3 |\vec{r}_{12}|^2 , \tag{6.6b}$$

$$\Gamma_{2(K)} = \gamma_{2(K)} = 2\pi^2 \alpha |\vec{r}'^{\lambda}_{K_0 2}|^2 \omega_0 I \tag{6.6c}$$

and

$$\Gamma_{2(1)} = 2\pi\alpha |\vec{r}_{12}^{\lambda *}|^2 I_0 \left(\tfrac{1}{2}\gamma_1 \ln \frac{\gamma_1^2 + (\omega_0 - \omega_{21} + s_1 + \Delta_L)^2}{\gamma_1^2 + (\omega_0 - \omega_{21} + s_1 - \Delta_L)^2} + (\omega_{21} - s_1) \arctan \frac{2\Delta_L \gamma_1}{(\omega_0 - \omega_{21} + s_1)^2 + \gamma_1^2 - \Delta_L^2} \right) . \tag{6.6d}$$

The quantities γ_1 and s_1 are

$$\gamma_1 = 2\pi^2 \alpha |\vec{r}_{21}^{\lambda}|^2 \omega_{21} I_0 \quad \text{if } |\omega_0 - \omega_{21}| < \Delta_L$$
$$= 0 \qquad\qquad\qquad \text{if } |\omega_0 - \omega_{21}| > \Delta_L \tag{6.7a}$$

and

$$s_1 = 2\pi\alpha |\vec{r}_{21}^{\lambda}|^2 I \left(1 + \frac{\omega_{21}}{2\Delta_L} \ln \frac{|\omega_0 - \omega_{21} + \Delta_L|}{|\omega_0 - \omega_{21} - \Delta_L|} \right) . \tag{6.7b}$$

The shift S_b is given by

$$S_b = S_{2(K)} + S_{2(1)}, \tag{6.8a}$$

where

$$S_{2(K)} = 2\pi\alpha |\vec{r}'^{\lambda}_{K_0 2}|^2 I \Delta_L \tag{6.8b}$$

and

$$S_{2(1)} = -2\pi\alpha |\vec{r}_{12}^{\lambda *}|^2 I \left(1 - \frac{\gamma_1}{2\Delta_L} \arctan \frac{\gamma_1 2\Delta_L}{(\omega_0 - \omega_{21} + s_1)^2 + \gamma_1^2 - \Delta_L^2} + \frac{\omega_{21} - s_1}{4\Delta_L} \ln \frac{(\omega_0 - \omega_{21} + s_1 + \Delta_L)^2 + \gamma_1^2}{(\omega_0 - \omega_{21} + s_1 - \Delta_L)^2 + \gamma_1^2} \right) . \tag{6.8c}$$

S_a is given by

$$S_a = 2\pi\alpha |\vec{r}_{21}^{\lambda}|^2 I \left(1 - \frac{\gamma_2}{2\Delta_L} \arctan \frac{\gamma_2 2\Delta_L}{(\omega_0 - \omega_{21} - s_2)^2 + \gamma_2^2 - \Delta_L^2} + \frac{\omega_{21} + s_2}{4\Delta_L} \ln \frac{(\omega_0 - \omega_{21} - s_2 + \Delta_L)^2 + \gamma_2^2}{(\omega_0 - \omega_{21} - s_2 - \Delta_L)^2 + \gamma_2^2} \right) , \tag{6.9a}$$

where

$$s_2 = s_{2(1)} + s_{2(K)} = -s_1 + S_{2(K)} \tag{6.9b}$$

(where we have used the relations $s_{2(1)} = -s_1$ and $s_{2(K)} = S_{2(K)}$), and

$$\gamma_2 = \gamma_{2(0)} + \gamma_{2(K)} + 2\pi^2 \alpha |\vec{r}_{12}^{\lambda *}|^2 \omega_{21} I_0 \quad \text{if } |\omega_0 - \omega_{21}| < \Delta_L$$
$$= \gamma_{2(0)} + \gamma_{2(K)} \quad \text{if } |\omega_0 - \omega_{21}| > \Delta_L , \tag{6.9c}$$

and where $S_{2(K)}$, $\gamma_{2(0)}$, and $\gamma_{2(K)}$ have been calculated above. The sequence of equations (6.3)–(6.9) shows that given the atom (i.e., the matrix elements of $\vec{r}^{\lambda}$) and the characteristics of the laser (i.e., I_0, Δ_L, and the polarization λ), we must first calculate γ_1, s_1, γ_2, and s_2, then use their values to calculate S_a, S_b, and Γ_b, and finally calculate the transition probability $W_K^{(2)}$. The quantities γ_1 and s_1 are, respectively, the width and shift of the initial atomic state $|1\rangle$ under the influence of the incident light. Except for the vacuum shift which is contained in ω_1, there are no other significant contributions[43] to either γ_1 or s_1 because $|1\rangle$ has been assumed to be the ground state. Thus $1/2\gamma_1$ is the lifetime of $|1\rangle$ in the presence of the light. Similarly, γ_2 and s_2 are the width and shift of the atomic state $|2\rangle$ in the presence of the light. Note that γ_2 contains three terms: $\gamma_{2(0)}$, which is the natural width of $|2\rangle$; $\gamma_{2(K)}$, which is the width due to the probability that the excited state $|2\rangle$ may make a transition to the continuum; and $\gamma_{2(1)} = 2\pi^2\alpha \times |\vec{r}_{12}^{\lambda *}|^2 \omega_{21} I_0$ due to the probability that the atom may make a transition back down to the ground state under the influence of the exciting light. The last part is the resonant contribution and vanishes if the excited state is not inside the linewidth of the light. In other words this is the induced-emission

part and is equal to γ_1, as it should be, because absorption and induced emission have the same probability. The lifetime of $|2\rangle$ then is $1/2\gamma_2$. The shift s_2 also contains two parts (the third part, the vacuum shift, is included in ω_2): $-s_1$, which is the resonant contribution and is the opposite of s_1; and $S_{2(K)}=s_{2(K)}$, which is due to the possibility of a transition to the continuum. Both $-s_1$ and $S_{2(K)}$ are due to induced processes and vanish in the absence of the light. The induced shifts of $|1\rangle$ and $|2\rangle$ are finite and do not present the well-known divergence of the vacuum shift.[42] The reason is that the spectrum of the light has a cutoff and therefore the integral is finite. The divergence of the vacuum shift in the nonrelativistic approximation arises from the fact that the integration over ω is from 0 to ∞ and one must impose a cutoff in order to obtain a finite result. As the above equations show, the induced shifts and widths depend linearly on the light intensity, which should be expected since they are due to linear processes—absorption or emission.

The transition probability $W_K^{(2)}$ has a resonance structure, but the shifts S_a and S_b, and the width Γ_b appearing in Eq. (6.3b), are not the shifts and width of levels $|1\rangle$ and $|2\rangle$ discussed above. Consider Γ_b first. It contains three contributions, as γ_2 did. The natural (spontaneous) decay and the continuum contributions are the same as in γ_2. But the resonance contribution is much more complicated and certainly is not linear in light intensity [see Eq. (6.6d), and note that s_1 and γ_1 depend on I]. As we shall see later on, $\Gamma_{2(1)}$ reduces to $\gamma_{2(1)}$ for sufficiently low intensity. Thus, in general, the width of the resonance is Γ_b, which is not the width of the intermediate state. Similarly, the shifts S_a and S_b occurring in the expression for $W_K^{(2)}$ are not the shifts of the atomic states $|1\rangle$ and $|2\rangle$, although they do reduce to s_1 and s_2 for low intensity.

The difference between level shifts and widths, and the shifts and widths appearing in the transition probability, occurs in the resonant contributions, i.e., in the contributions due to transitions between $|1\rangle$ and $|2\rangle$. As we shall show subsequently, for relatively low light intensity, the lifetime (and hence the width) of the intermediate state $|2\rangle$ is determined by spontaneous emission. Then Γ_b is equal to $\gamma_{2(0)}$. With increasing intensity, however, it is the induced process (and particularly induced emission to $|1\rangle$) that dominates. As the intensity keeps increasing the lifetime of $|2\rangle$ becomes shorter and shorter and hence the width γ_2 increases linearly with light intensity. But the width Γ_b of the transition probability eventually saturates to approximately the width of the laser. Physically, this is simply due to the fact that induced transitions must take place within the linewidth of the laser since there are no photons outside it to stimulate transitions. Similar considerations apply to the shifts.

Let us now discuss our results in a more quantitative manner. First consider the ratio of the stimulated-emission width $\gamma_{2(1)}$ of $|2\rangle$ to the spontaneous width $\gamma_{2(0)}$. From Eqs. (6.6b) and (6.9c) we have

$$\frac{\gamma_{2(1)}}{\gamma_{2(0)}}=\pi^2\left(\frac{c}{\omega_{21}}\right)^2\frac{3|\vec{r}_{12}^{\,\lambda *}|^2}{|\vec{r}_{12}|^2}I_0 . \tag{6.10}$$

For optical frequencies, and as an order of magnitude calculation, we can take $\omega_{21}\simeq 10^{15}$ sec^{-1}. The ratio of the radial matrix elements depends on the particular polarization λ, but multiplied by 3, as in Eq. (6.10), it will not be much different from unity. Then we can write

$$\frac{\gamma_{2(1)}}{\gamma_{2(0)}}\sim 10^{-9}I_0=10^{-9}\frac{I}{2\Delta_L} . \tag{6.11}$$

If, for example, we have $2\Delta_L\sim 5$ cm^{-1}, it is equivalent to $\Delta\omega=9\times10^{11}$ sec^{-1}. Thus, if I is larger than 10^{21} photons/cm^{2}sec, $\gamma_{2(1)}$ will be larger than $\gamma_{2(0)}$. Usually two-photon ionization requires intensities of 10^{25} photons/cm^{2}sec or more. For such intensities $\gamma_{2(1)}\gg\gamma_{2(0)}$, and this is true in most cases of interest. It also turns out that $\gamma_{2(1)}$ is much larger than $\gamma_{2(K)}$, at least for the low-lying excited states of the alkalies. But this must be verified in each particular case. The same is true for the shifts. Consequently, for light intensities such that two-photon ionization is observable under typical experimental conditions, we can take

$$\gamma_2\cong\gamma_{2(1)}=2\pi^2\alpha|\vec{r}_{12}^{\,\lambda *}|^2\omega_{21}I_0 \tag{6.12a}$$

and

$$s_2\cong -s_1 , \tag{6.12b}$$

with s_1 as given by Eq. (6.7b).

Again, for an order of magnitude estimate, let us take $|\vec{r}_{12}^{\,\lambda *}|^2\simeq 10^{-17}$ cm^2, which is a typical matrix element for some of the excited levels of the alkalies. Then, using $\omega_{21}\simeq 10^{15}$, we have

$$\gamma_{2(1)}\cong(0.14\times10^{-2})I/2\Delta_L . \tag{6.13}$$

If we take $I=10^{25}$ photons/cm^{2}sec, and again a linewidth of 5 cm^{-1} [the linewidth in ω units ($\omega=2\pi\nu$) is $2\Delta_L=2\pi\times5\times3\times10^{10}\cong 9.42\times10^{11}$sec^{-1}], Eq. (6.13) gives $\gamma_{2(1)}\cong 1.5\times10^{10}$ sec^{-1}, which is almost two orders of magnitude larger than the natural width $\gamma_{2(0)}$. Suppose furthermore that ω_0 is chosen so that $\omega_0-\omega_{21}=0$. From Eq. (6.7b) we obtain $s_1\cong 0.45\times10^7$ sec^{-1}, which is totally insignificant compared to either ω_{21} or Δ_L. Under these conditions Eq. (6.6d) gives

$$\Gamma_{2(1)} = 2\pi\alpha|\vec{r}^{\lambda *}_{12}|^2 I_0 \omega_{21} \arctan(-2\gamma_1/\Delta_L)$$
$$\cong 2\pi^2\alpha|\vec{r}^{\lambda *}_{12}|^2 I_0 \omega_{21} = \gamma_{2(1)}, \quad (6.14)$$

where we have used the fact that $\gamma_1 = \gamma_{2(1)}$ and that $\arctan(-2\gamma_1/\Delta_L) \cong \pi$ when $2\gamma_1/\Delta_L \ll 1$, as is the case here. This proves an assertion we made earlier, namely, that $\Gamma_b \cong \Gamma_{2(1)} \cong \gamma_{2(1)}$ for sufficiently low intensity. Of course how low is "sufficiently low" depends on the radial matrix elements, transition frequencies, etc. Similarly, we find that $S_a = -S_b \cong s_1$, which as we saw above is negligible.

We have a situation in which the shifts are negligible and $\Gamma_b \ll \Delta_L$. Then Eqs. (6.4b) and (6.4c) give $g_1 \cong 0$ and $g_2 \cong \pi$, which substituted into Eq. (6.4a) yield $Q = I_0^2 2\pi(2\Delta_L/\Gamma_b + \pi)$. With the numbers of our present numerical example, we can take $Q \cong I_0^2 2\pi 2\Delta_L/\Gamma_b$, which can also be written $Q \cong 2\pi I^2/\Gamma_b 2\Delta_L$. Substituting into Eq. (6.3a) we find

$$W_K^{(2)} = 16\pi^4\alpha^2 \frac{|\vec{r}'^{\lambda}_{K_0 2}|^2 |\vec{r}^{\lambda}_{21}|^2 \omega_0^2}{\Gamma_b 2\Delta_L} I^2 . \quad (6.15)$$

The first thing to be noted in this result is that the denominator contains the product $\Gamma_b 2\Delta_L$, which in our numerical example is equal to $\gamma_{2(1)} 2\Delta_L$. This is to be contrasted to what we would have obtained if we had taken the off-resonance formula and intuitively inserted an imaginary part to represent the width of the intermediate state. Then the denominator would have been $\gamma_{2(1)}^2$, which is almost two orders of magnitude smaller than $\gamma_{2(1)} 2\Delta_L$. Second, this particular result for the denominator is due to the assumed specific form of the line shape of the laser. For a different line shape, but the same width, the denominator will in general turn out to be $\gamma_{2(1)} \mu 2\Delta_L$, where the coefficient μ depends on the detailed shape of the spectrum. Usually we will have $\mu \leq 1$. Third, if we recall that in this case

$$\Gamma_b = \gamma_{2(1)} = 2\pi^2\alpha|\vec{r}^{\lambda *}_{12}|^2 \omega_{21} I_0$$
$$= 2\pi^2\alpha|\vec{r}^{\lambda}_{21}|^2 \omega_{21}(I/2\Delta_L),$$

we obtain from Eq. (6.15)

$$W_K^{(2)} = 8\pi^2\alpha|\vec{r}'^{\lambda}_{K_0 2}|^2 \omega_0 I , \quad (6.16)$$

which means that at this value of I partial saturation has set in and the rate depends linearly on the light intensity. Such effects have been repeatedly observed in multiphoton ionization. This comes about, in the present case, when the intensity is such that the stimulated deexcitation of $|2\rangle$ is much more probable than the spontaneous decay. For much lower intensity, such that $\Gamma_b \cong \gamma_{2(0)} \gg \gamma_{2(1)}$, the rate would be proportional to I^2 because $\gamma_{2(0)}$ is independent of I. In most cases, however, this situation is of little practical interest because for such low intensities two-photon ionization would probably be unobservable. Off resonance of course the process does go like I^2 even for high I.

At first sight, one might be tempted to infer that Eq. (6.15) represents a "two-step" process. Indeed $W_K^{(2)}$ is proprotional to the product of the squares of the matrix elements for the transitions $|1\rangle \rightarrow |2\rangle$ and $|2\rangle \rightarrow |\vec{K}\rangle$ multiplied by the lifetime $(2\gamma_{2(1)})^{-1}$ of the intermediate state. This, however, does not mean that we have a "two-step" process, in the sense that the second transition retains no memory of the first transition. On the contrary, the lifetime of the intermediate state is determined by the exciting field and there is a definite correlation between the first and second transitions. The process must be treated as a single transition between an initial and final state. That the two "steps" are not independent is readily seen if one recognizes that the polarization of the light determines which magnetic substates of $|2\rangle$ are excited, and only such substates participate in the ionization process. A case in which the process could be truly considered as a two-step process is when the incident light is unpolarized and its intensity is such that $\Gamma_b = \gamma_{2(0)}$. Then it can be considered as two step because it would be the same even if the intermediate state had been excited by any other means, say collisions.

Another circumstance in which a two-step picture is meaningful is when the atoms also interact with a third system (or with each other if the pressure is sufficiently high), and as a result transitions between magnetic substates take place without deexciting the intermediate state. This has recently been discussed by Lambropoulos and Berry.[25] In that case, one must make sure that the collisional relaxation is faster than the dominant radiative lifetime of $|2\rangle$ and not just the natural lifetime. In an experiment with a single laser beam, in most circumstances it will be the stimulated lifetime that dominates. And as we saw earlier, under typical experimental conditions this lifetime is of the order of 3×10^{-11} sec or shorter, i.e., several orders of magnitude shorter than the spontaneous lifetime. From an experimental standpoint it is perhaps preferable to use two light beams of different frequencies. By keeping the intensity of the beam with the resonance frequency low enough, one may be able to achieve a radiative lifetime comparable to the collisional lifetime, assuming the latter can be made shorter than the natural lifetime. The resultant loss of intensity can then be made up by increasing the intensity of the second beam which is not in resonance with the transition $|1\rangle \rightarrow |2\rangle$, again assuming that the resulting lifetime $(2\gamma_{2(K)})^{-1}$ due to ionization from

$|2\rangle$ can be kept longer than the collisional relaxation. (See also Sec. VIII for further discussion of two-photon ionization with two laser beams.)

In connection with the question of two-step versus one-step processes it is often said that when the linewidth of the exciting light is larger than the width of the intermediate state, then we have a two-step process; i.e. the emission is independent of the absorption. This is usually based on a discussion of resonance fluorescence (which is a two-photon process) presented by Heitler in his classic book on the quantum theory of radiation.[33] One must be very careful in extrapolating that statement because Heitler explicitly considers the weak-field case in which the natural decay is the dominant mode of deexcitation of $|2\rangle$. As we saw above, when the field is intense the stimulated lifetime dominates, and Heitler's statement is no longer applicable. Moreover, even in Heitler's example, if the exciting light is polarized, albeit broadband, only certain magnetic substates of $|2\rangle$ are excited and this, strictly speaking, is not a two-step process. Again to make it a true two-step process either the light must be unpolarized or else there must be collisional relaxation of the magnetic substates. Heitler constructs a single-step process by taking the linewidth of the light source to be much smaller than the linewidth of the intermediate state. In the intense-field regime, however, we have a single-step process even when $2\Delta_L \gg \gamma_2$.

To look at the other extreme case, let us assume that the total photon flux is much larger than before, say, $I = 10^{29}$ photons/cm^2 sec, while the linewidth $2\Delta_L$ remains the same. Also assume that we are still on resonance, i.e., $\omega_0 = \omega_{21}$. We state without proof at this point that the shifts are small compared to Δ_L and we shall neglect them for the moment (see also Sec. VIII and Table I). Now the width of $|2\rangle$ is $\gamma_2 \cong \gamma_{2(1)} \cong 1.5\times10^{14}$ sec^{-1}, which is two orders of magnitude larger than the laser width. Since we have $\gamma_1 = \gamma_{2(1)} \gg \Delta_L$, from Eqs. (6.6) we find

$$\Gamma_b \cong \Gamma_{2(1)} \cong 2\Delta_L/\pi, \tag{6.17}$$

which proves what we had asserted earlier; namely, that although the width of the state $|2\rangle$ keeps increasing linearly with I, the width Γ_b which appears in the transition probability eventually saturates to a value of the order of the laser width. The exact saturation value depends on the detailed laser line shape. Here it is $2\Delta_L/\pi$ because of the chosen square line shape.

Substituting now into Eqs. (6.4) and noting that $g_1 \cong 0$ and $g_2 \cong 0.639\pi$, after some algebraic manipulations we obtain $Q \cong 20 I_0^2$, and from Eq. (6.3a),

$$W_K^{(2)} \cong 160\pi^3\alpha^2 |\vec{r}'^{\lambda}_{K_02}|^2 |\vec{r}^{\lambda}_{21}|^2 \omega_0^2 I_0^2, \tag{6.18}$$

which shows that the transition probability now is proportional to I_0^2 or, equivalently, to $(I/2\Delta_L)^2$.

The transition probability for resonance two-photon ionization for low I is, as we saw earlier, proportional to I^2. As the intensity increases and the stimulated-emission width of the intermediate state starts to dominate the natural width, the process becomes proportional to I. Finally, as the intensity increases further, γ_2 keeps increasing but Γ_b eventually saturates to a value of the order of Δ_L. Then the rate of two-photon ionization again becomes proportional to I^2.

It should be noted that in an actual experimental situation, the observed quantity, i.e., the number of photoelectrons per laser pulse, is given by

$$N = W_K^{(2)} \tau \rho v, \tag{6.19}$$

where τ is either the laser-pulse duration or the time the atoms spend in the light field (whichever is smaller), ρ the density of atoms in the interaction volume, and v the interaction volume. It may happen that $W_K^{(2)}\tau = 1$ for some intensity I. Further increase of the intensity will produce no increase of the signal because all atoms in the interaction volume are ionized. This in fact happens quite often in multiphoton ionization experiments,[44] and it is a saturation effect quite different from the ef-

TABLE I. Level shift (s_1), resonance shift (S_{ab}), and resonance width (Γ_b) as functions of detuning $\delta = (\omega_0 - \omega_{21})/\Delta_L$. ($\omega_0$ is the laser center frequency, ω_{21} the frequency of the atomic transition, and Δ_L the laser line half-width. For the parameters used in the calculation, see Sec. VII.)

δ	$2s_1/\Delta_L$	S_{ab}/Δ_L	Γ_b/Δ_L
4.0	1.158	0.879	0.0
3.0	1.571	1.226	0.0
2.0	2.490	1.444	0.0
1.5	3.648	1.407	0.0
1.4	4.061	1.361	0.0
1.3	4.617	1.290	0.0
1.2	5.435	1.183	0.0
1.1	6.901	1.013	0.0
1.05	8.417	0.899	0.0
0.95	8.304	0.595	0.211
0.9	6.674	0.622	0.266
0.8	4.980	0.624	0.347
0.7	3.932	0.595	0.410
0.6	3.142	0.545	0.465
0.5	2.490	0.480	0.510
0.4	1.921	0.401	0.550
0.3	1.403	0.311	0.580
0.2	0.919	0.212	0.603
0.1	0.455	0.108	0.617
0.0	2.038×10^{-3}	0.389×10^{-3}	0.661

fects discussed above. It is, so to speak, an instrumental effect and can occur in any of the intensity regimes discussed above. At what intensity it will occur in a given experiment depends on the particular atom (i.e., the matrix elements) and the time τ. It can, for example, be avoided by reducing the time the atom spends in the field, while the broadening and saturation effects discussed earlier are inherent in $W_K^{(2)}$, depend on I, and cannot be altered by changing the time the atom spends in the field.

VII. SATURATION EFFECTS

As in Sec. VI, we shall again consider a square laser line shape. The main contribution to the level shifts will generally be the resonant contribution $s_{2(1)} = -s_1$. Using as an illustration the parameters $\omega_{21} = 10^{15}$ sec^{-1}, $|\vec{r}_{21}^{\lambda}|^2 = 10^{-15}$ cm^2, and $2\Delta_L = 9\times 10^{11}$ sec^{-1}, which correspond to some of the first few excited states of the alkalies, we consider first Eq. (6.7b). It is evident that if the laser is tuned exactly on resonance (i.e., $\omega_0 = \omega_{21}$), the shift s_1 is $2\pi\alpha|\vec{r}_{21}^{\lambda}|^2 I$, which even for I as high as 10^{27} will be $\sim 5\times 10^{10}$ sec^{-1}. This is about one order of magnitude smaller than $2\Delta_L$. Of course, if I were larger and/or $2\Delta_L$ smaller, s_1 would be significant even on resonance. This is discussed later in this section, but for the moment we continue with the above numbers. The point to be made here is that exactly on resonance, the logarithm in Eq. (6.7b) vanishes because $\omega_0 - \omega_{21} = 0$. Slightly off-resonance, however, the logarithm will make the dominant contribution since it is multiplied by $\omega_{21}/2\Delta_L$, which is much larger than unity (typically of the order of 10^3). The logarithmic term dominates when the absolute value of the logarithm is larger than 10^{-3} in our numerical example, or more generally larger than $2\Delta_L/\omega_{21}$. Clearly, the logarithm is a large positive number if $\omega_0 - \omega_{21}$ is near Δ_L, and a negative number with large absolute value if $\omega_0 - \omega_{21} \simeq -\Delta_L$. The fact that s_1 diverges for $\omega_0 - \omega_{21} = \pm\Delta_L$ is simply an artifact of the jump discontinuity in the assumed laser line shape. In reality, the intensity in the wings of a laser line drops to zero in a continuous fashion and the divergence does not arise, and this divergence certainly has nothing to do with the well-known vacuum-shift[42] divergences.

Despite the somewhat special laser line shape, the emerging conclusion is basically correct; namely, as the laser line approaches the excited level, the shift $s_{2(1)}$ increases. Its value remains high as long as the intermediate level is near the edge of (just inside or just outside) the laser line. Obviously, the more abruptly the line shape drops to zero, the larger the shift will be, other things being equal. In other words, the level shifts s_1 and s_2 can become very large when a very narrow laser line is near the level, without being centered exactly on it.

However, it is not s_2 and s_1 but S_b and S_a that appear in the transition probability. In S_b, as in s_2, the dominant contribution will usually come from the resonant term $S_{2(1)}$; thus for near-resonance conditions, we have $S_b \cong S_{2(1)} = -S_a$. The quantity $S_{ab} = S_a - S_b$, which appears in Eqs. (6.3) and (6.4) for the transition probability, will then be equal to $2S_a$. As it turns out, S_a does not reach high values as s_1 does. To see the mathematical reason for this, let us introduce the abbreviations

$$\Delta_0 \equiv \omega_0 - \omega_{21} \tag{7.1}$$

and

$$\delta \equiv \Delta_0/\Delta_L \,. \tag{7.2}$$

As long as the intermediate level is outside the laser line, the widths are negligible and we can take

$$s_1 = -s_2 \cong 2\pi\alpha|\vec{r}_{21}^{\lambda}|^2 I \,\frac{\omega_{21}}{2\Delta_L} \ln\left|\frac{\delta+1}{\delta-1}\right| \tag{7.3}$$

and

$$S_a = -S_b = 2\pi\alpha|\vec{r}_{21}^{\lambda}|^2 I \,\frac{\omega_{21}+s_2}{2\Delta_L} \ln\left|\frac{\delta+1-s_2/\Delta_L}{\delta-1-s_2/\Delta_L}\right| . \tag{7.4}$$

As discussed above, s_1 and s_2 become large when $\delta \to \pm 1$, but this does not occur in S_a owing to the presence of s_2/Δ_L in the argument of the logarithm in Eq. (7.4). When $\delta \to +1$, the shift s_2 is positive, thus preventing the argument of the logarithm from attaining large values, and similarly for $\delta \to -1$ because s_2 is then negative. This is essentially a saturation effect and it was already apparent in the equations for Γ_a, Γ_b, S_a, and S_b derived in Sec. V. It is very similar to the situation which occurs in calculating a usual transition probability of resonance absorption or emission[33] of photons. In that case, the probability diverges as the resonance is approached. If the level widths are included, however, the result is finite. In the present case, the shifts S_a and S_b also have a resonance structure. Their values saturate when higher-order corrections are taken into account. These corrections are significant when the level shifts s_1 and s_2 become larger than the laser width $2\Delta_L$, which often does happen at the light intensities used in multiphoton transition experiments.

The above discussion was based on Eq. (7.4), which is applicable as long as the intermediate level is outside the laser line. When it is inside, the widths are not negligible any longer and the full

equations for S_a, S_b, Γ_a, and Γ_b must be used. These equations are more complicated and the saturation effect is not obvious from their analytical structure. The effect is present nevertheless as one would have expected on the basis of the more formal results of Sec. V.

As an example, we have calculated shifts and widths for various values of δ using the parameters of our numerical example and $I = 10^{25}$. Recall that when $\delta = n$, the center of the laser line is n laser half-widths away from the transition frequency ω_{21}. The results are given in Table I. As these results show, when the laser is tuned a few half-widths (Δ_L) away from ω_{21}, the shifts $2s_1$ and S_{ab} are approximately equal. As the laser is tuned closer to ω_{21}, the level shift s_1 increases rather rapidly, whereas S_{ab} increases at first, reaches a peak rather quickly, and then begins to decrease again. After ω_{21} enters the laser line, s_1 also begins to decrease, while S_{ab} begins to increase again, but after a small peak it resumes decreasing. When ω_0 is exactly equal to ω_{21}, both s_1 and S_{ab} obtain rather small values. Similarly Γ_b changes as ω_0 approaches ω_{21}, reaching a maximum at $\omega_0 = \omega_{21}$ ($\delta = 0$), whereas γ_1 and $\gamma_{2(1)}$ remain constant owing to the special laser line shape. The general trend indicated by Table I is to some extent independent of the exact laser line shape. However, the detailed behavior of shifts and widths as functions of δ does depend on the details of the laser spectrum. For example, exactly where S_{ab} and Γ_b peak, or how many peaks they exhibit, and so on, is determined to a considerable extent by the form of the laser line. This is important to keep in mind, since often the laser spectrum itself has more than one peak and is not a simple function of frequency. One of the interesting results emerging from Table I is that shifts and widths do exhibit a rather complicated behavior even when the light spectrum has a very simple structure.

In view of the above results, one would expect shifts and widths to have a significant effect on the transition rate. This is indeed borne out by the calculation of the rate using the same parameters as in the calculations of Table I. As shown by Eqs. (6.3) and (6.4), the transition rate is proportional to the quantity

$$q \equiv \tfrac{1}{2} g_1^2 + (4\Delta_L/\Gamma_b) g_2 + 2g_2^2, \tag{7.5}$$

which contains the dependence on δ, and where g_1 and g_2 are given by Eqs. (6.4b) and (6.4c). In Fig. 2, q is shown as a function of δ. If we use a line not with a jump discontinuity but with a finite slope at the edge, and then take the limit as the slope goes to infinity, we find that q follows the dashed line around $\delta = 1$. Thus, although s_1 diverges at that point, the transition probability is finite. The first interesting feature in Fig. 2 is that the rate does not have the usual simple Lorentzian shape normally found in broadened lines of single-photon processes. Not only is q depressed exactly on resonance (which is a typical saturation effect) but it also exhibits a second small peak in the wing. What is perhaps more remarkable is the effect illustrated by curve B of Fig. 2. This curve represents the transition rate when the intermediate level is outside the laser line but with shifts ignored completely; the widths in this case are zero because the level is outside the laser line. Then q varies according to $(\omega_0 - \omega_{21})^{-2}$, which is the usual off-resonance formula for two-photon ionization. Since ω_{21} is outside the laser line, the difference between curves A and B is due solely to the shifts. Clearly, the shifts have a significant effect on the rate even when ω_0 is several laser linewidths away from resonance. This effect becomes more pronounced as the light intensity per unit frequency ($I_0 = I/2\Delta_L$) increases, which is illustrated in Table II. This calculation has been performed with the same parameters as in Fig. 2 except for $2\Delta_L$, which now has been taken one order of magnitude smaller; thus I_0 is one order of magnitude larger. It is interesting to compare $2s_1$ with S_{ab} (recall that in the present case $S_{ab} = 2S_a$). The level shift s_1 is larger than S_a, and for certain

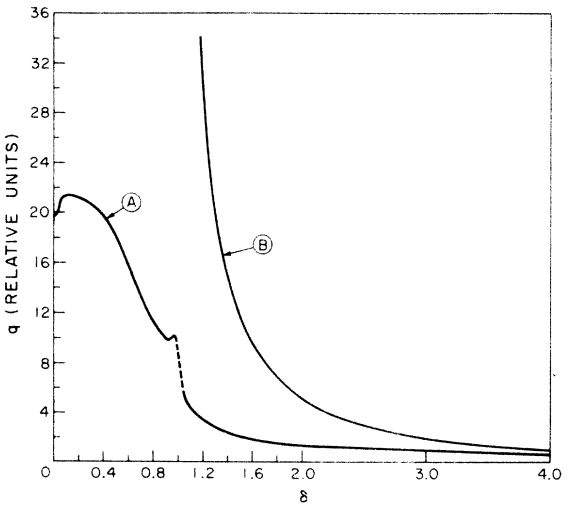

FIG. 2. Transition probability (in relative units) for two-photon ionization around a resonance with an intermediate state. Curve A represents the transition probability with all saturation effects included. Curve B has been obtained using the off-resonance formula with all shifts neglected. The quantity δ is defined by $\delta = (\omega_0 - \omega_{21})/\Delta_L$, where ω_0 is the laser center frequency, ω_{21} the frequency of the atomic transition in resonance with the laser, and Δ_L the laser line half-width. For the relation of q to the absolute magnitude of the transition probability see Eqs. (7.5), (6.4a), and (6.3a).

values of δ, s_1 is two orders of magnitude larger than S_a. If the formal treatment of Sec. III had been truncated one step earlier, the resulting expression for the transition rate would contain $2s_1$ instead of $2S_a$. In view of the above differences between s_1 and S_a, the resulting numerical values for the rate would be expected to be much different. This is also illustrated in Table II, where we list the values of Q (denoted by Q'') obtained by using $2s_1$ instead of S_{ab}. Obviously, for certain values of δ, there is a very large difference between Q and Q''. For example, for $\delta = 1.5$, Q'' is almost three and a half orders of magnitude smaller than Q. Even more important, Q'' decreases significantly as the laser line is tuned closer to the level. Similarly large discrepancies are also found when the intermediate level is inside the laser line, in which case the widths must also be included. For example, if we calculate Q with the parameters of Fig. 1 but using s_1 and γ_1 in place of S_a and Γ_a, we find that exactly on resonance ($\delta = 0$) Q assumes a value 20 times smaller than that plotted in Fig. 2.

These effects are very pronounced in the process discussed in this paper because the resonance transition between $|1\rangle$ and $|2\rangle$ is a single-photon transition and the related probability can be very high. In higher-order multiphoton processes, one can also have higher-order resonances. For example, in three-photon ionization, absorption of two photons can lead to an intermediate state which may happen to be in resonance. In that case, we would have a two-photon resonance which is a weaker process. Then, saturation will in general not be as significant as in the present case, unless the intensity becomes much larger. As a result, the shifts s_1 and s_2 may be satisfactory approximations. But these would contain only nonresonant contributions to lowest order and a resonant contribution of higher order. The details of this case will be discussed in a subsequent paper. For the moment, however, we wish to point out that one must be very cautious in invoking shifts nonlinear in the photon flux I for any arbitrary multiphoton process.

TABLE II. Shifts and transition probabilities as functions of detuning $\delta = (\omega_0 - \omega_{21})/\Delta_L$. [The parameters used in this calculation are the same as in Table I except for the laser linewidth, which has here been taken one order of magnitude smaller ($2\Delta_L = 0.4775\ \mathrm{cm}^{-1}$). For the other parameters see Sec. VII. The calculation of Q has included all saturation effects; for Q' all shifts have been neglected; for Q'' the linear approximation ($2s_1$) for the resonance shift (S_{ab}) has been used. For the relation of Q to the transition probability, see Eqs. (6.3a) and (6.4a).]

δ	$2s_1/\Delta_L$	S_{ab}/Δ_L	$10^{-27}Q$	$10^{-27}Q'$	$10^{-27}Q''$
20.0	22.69	14.80	0.17	0.49	0.11
10.0	45.49	13.84	0.35	1.99	0.064
7.5	60.81	11.95	0.52	3.57	0.042
5.0	91.91	8.88	1.03	8.17	0.021
4.0	115.79	7.31	1.56	13.03	0.014
3.0	157.11	5.54	2.74	24.21	0.0077
2.0	249.02	3.56	6.56	62.73	0.0031
1.5	364.81	2.45	10.86	143.01	0.0015

VIII. CONCLUDING REMARKS

The main purpose of this paper was to show how the resolvent operator can be used to develop a systematic theory of multiphoton ionization. This technique lends itself to adaptation to a large variety of situations that can occur in near-resonance processes. The exact, formal equations for the matrix elements of the resolvent operator can be replaced by approximate equations appropriate to a given process.

In the present paper, attention was focused on two-photon near-resonance ionization. The approximation procedure was guided by the fact that in this case, not only the transition probability, but also shifts and widths do in general exhibit a resonance structure. Thus the iteration of the equations was continued to higher orders until the dominant contributions to saturation effects were included. The resulting expressions essentially constitute a continued-fraction expansion of shifts and widths. For relatively lower light intensities, the shifts and widths assume the more familiar expressions[45] which are linear in the light intensity.

Although we have considered only one light beam, the generalization to the case of two light beams with different frequencies is self-evident. Then, in Eq. (5.23), only one of the two terms makes the dominant contribution, namely, the term for which the photon frequency is approximately equal to ω_{21}. The double integration over ω and ω' is over the line shapes of the two light beams. Finally, in Eqs. (6.3), ω_0^2 is replaced by the product of the frequencies of the two beams; I_0^2 is replaced by the product of the two intensities divided by the respective linewidths; and the integrand of Eq. (6.3b) is simplified to

$$\frac{1}{(\omega - \bar{\omega}_{21})^2 + \Gamma_b^2}, \tag{8.1}$$

where ω varies over the spectrum of the one beam which is in near resonance with ω_{21}. The integration over ω' is then trivial as the integrand's dependence on ω' comes only through $I(\omega')$. The expressions for resonance shifts and widths of course will only involve that light beam which is in near

resonance.

Similarly, it is easy to treat the case in which there are other states, besides $|1\rangle$, below $|2\rangle$. If $|2\rangle$ can decay to such states, and the light is still in resonance with ω_{21}, then Γ_b should also contain the sum of the spontaneous decay widths of $|2\rangle$ to all states below it. The shift S_b should also contain similar contributions which, however, are vacuum contributions and as such have already been assumed included in ω_2.

The near-resonance effects studied in this paper result from the influence of the laser light on a single atomic state. Thus the dips in Fig. 2 are not due to any interference between the amplitudes of adjacent levels. These dips therefore are of an origin different from that of a similar dip in the Chang and Stehle paper,[22] which is the result of interference between the resonant and nonresonant amplitudes. To be sure, such interference does occur, but the point to be made here is that the shift and broadening effects alone can create very unusual line shapes in multiphoton processes. Such effects can in practice be even more pronounced than indicated by our results because even a fairly monochromatic tunable dye laser may have more than one narrow peak inside its linewidth. It is then conceivable that one of these peaks, being even narrower than the over-all beam, will shift the level much more than anticipated. Preliminary calculations tend to support this prediction.

In considering higher-order processes in combination with light and photoelectron polarization effects, one is faced with a plethora of phenomena that require an even more detailed analysis. There are cases of multiple resonance with the associated saturation effects. The problem of partially (or elliptically) polarized light presents an entirely new facet because both polarization components can lead to resonance effects with different hyperfine structure levels. These problems will be discussed in forthcoming papers.

APPENDIX

From Eq. (2.17b) we have

$$(z-\omega_{b_1})F_{b_1a}=V_{b_1a}+\sum_{c\neq a}V^*_{cb_1}F_{ca}\,. \tag{A1}$$

Given the form of $|b_1\rangle$ and V, the matrix element $V^*_{cb_1}$ is different from zero for $|c\rangle$ of the form

$$|c^+(\vec{k}')\rangle\equiv|1\rangle|\ldots,n(\vec{k}_1)-1,\ldots,n(\vec{k}')+1,\ldots\rangle,\qquad \vec{k}'\neq\vec{k}_1 \tag{A2}$$

or

$$|c^-(\vec{k}')\rangle\equiv|3\rangle|\ldots,n(\vec{k}_1)-1,\ldots,n(\vec{k}')-1,\ldots\rangle. \tag{A3}$$

Thus we have

$$(z-\omega_{b_1})F_{b_1a}=V_{b_1a}+\sum_{\vec{k}'\neq\vec{k}_1}V^*_{c^+(\vec{k}')b_1}F_{c^+(\vec{k}')a}+\sum_{\vec{k}'}V^*_{c^-(\vec{k}')b_1}F_{c^-(\vec{k}')a}\,. \tag{A4}$$

For $F_{c^-(\vec{k}')a}$, it suffices to use the same approximation as in Eq. (3.21), the reason being that the free-electron state $|3\rangle$ does not "decay" back to a bound state. Therefore

$$F_{c^-(\vec{k}')a}\cong(z-\omega_{c^-(\vec{k}')})^{-1}V^*_{b_1c^-(\vec{k}')}F_{b_1a}\,. \tag{A5}$$

For $F_{c^+(\vec{k}')a}$, consider the equation

$$(z-\omega_{c^+(\vec{k}')})F_{c^+(\vec{k}')a}=\sum_{d\neq a}V^*_{dc^+(\vec{k}')}F_{da}\,, \tag{A6}$$

where we have used $V_{c^+(\vec{k}')a}=0$. This can be written

$$(z-\omega_{c^+(\vec{k}')})F_{c^+(\vec{k}')a}=V^*_{b_1c^+(\vec{k}')}F_{b_1a}+\sum_{d\neq a,b_1}V^*_{dc^+(\vec{k}')}F_{da}\,. \tag{A7}$$

Given the form of $|c^+(\vec{k}')\rangle$ as in Eq. (A2), we see that $V^*_{dc^+(\vec{k}')}$ is nonvanishing if $|d\rangle$ is of the form

$$|d(\vec{k}'')\rangle\equiv|2\rangle|\ldots,n(\vec{k}_1)-1,\ldots,n(\vec{k}')+1,\ldots,n(\vec{k}'')-1,\ldots\rangle,\qquad \vec{k}''\neq\vec{k}' \tag{A8}$$

where again we disregard vacuum-shift contributions. Then we obtain

$$(z-\omega_{c^+(\vec{k}')})F_{c^+(\vec{k}')a}=V^*_{b_1c^+(\vec{k}')}F_{b_1a}+\sum_{\vec{k}''\neq\vec{k}'}V^*_{d(\vec{k}'')c^+(\vec{k}')}F_{d(\vec{k}'')a}\,. \tag{A9}$$

Writing now an equation for $F_{d(\vec{k}'')a}$, we have

$$(z-\omega_{d(\vec{k}'')})F_{d(\vec{k}'')a}=\sum_{j\neq a}V^*_{jd(\vec{k}'')}F_{ja}\,, \tag{A10}$$

where we have used $V_{d(\vec{k}'')a}=0$. Separating out the $j=c^+(\vec{k}')$ term we write

$$(z-\omega_{d(\vec{k}'')})F_{d(\vec{k}'')a}=V_{d(\vec{k}'')c^+(\vec{k}')}F_{c^+(\vec{k}')a}+\sum_{j\neq a,c^+(\vec{k}')}V^*_{jd(\vec{k}'')}F_{ja}\,. \tag{A11}$$

Now we are ready to drop the sum and take

$$F_{d(\vec{k}'')a}\cong(z-\omega_{d(\vec{k}'')})^{-1}V_{d(\vec{k}'')c^+(\vec{k}')}F_{c^+(\vec{k}')a}\,, \tag{A12}$$

which substituted into Eq. (A9) gives

$$\left(z-\omega_{c^+(\vec{k}')}-\sum_{\vec{k}''\neq\vec{k}'}\frac{|\langle d(\vec{k}'')|V|c^+(\vec{k}')\rangle|^2}{z-\omega_{d(\vec{k}'')}}\right)F_{c^+(\vec{k}')a}=V^*_{b_1c^+(\vec{k}')}F_{b_1a}\,. \tag{A13}$$

Introducing

$$D_{c^+(\vec{k}')a}(z)=\sum_{\vec{k}''\neq\vec{k}'}\frac{|\langle d(\vec{k}'')|V|c^+(\vec{k}')\rangle|^2}{z-\omega_{d(\vec{k}'')}} \tag{A14}$$

and solving for $F_{c^+(\vec{k}')a}$ we obtain

$$F_{c^+(\vec{k}')a}=\frac{\langle c^+(\vec{k}')|V|b_1\rangle}{z-\omega_{c^+(\vec{k}')}-D_{c^+(\vec{k}')a}(z)}F_{b_1a}\,. \tag{A15}$$

Substituting this and Eq. (A5) into Eq. (A4) we find

$$(z-\omega_{b_1})F_{b_1a}=V_{b_1a}+\sum_{\vec{k}'\neq\vec{k}_1}\frac{|\langle c^+(\vec{k}')|V|b_1\rangle|^2}{z-\omega_{c^+(\vec{k}')}-D_{c^+(\vec{k}')a}(z)}F_{b_1a}+\sum_{\vec{k}'}\frac{|\langle c^-(\vec{k}')|V|b_1\rangle|^2}{z-\omega_{c^-(\vec{k}')}}F_{b_1a}\,. \tag{A16}$$

Introducing now

$$D_{b_1a}(z)\equiv\sum_{\vec{k}'\neq\vec{k}_1}\frac{|\langle c^+(\vec{k}')|V|b_1\rangle|^2}{z-\omega_{c^+(\vec{k}')}-D_{c^+(\vec{k}')a}(z)}+\sum_{\vec{k}'}\frac{|\langle c^-(\vec{k}')|V|b_1\rangle|^2}{z-\omega_{c^-(\vec{k}')}}, \tag{A17}$$

and solving Eq. (A16) for F_{b_1a} we obtain

$$F_{b_1a}(z)=\frac{V_{b_1a}}{z-\omega_{b_1}-D_{b_1a}(z)}\,. \tag{A18}$$

Obviously, F_{b_2a} is given by an expression similar to the above with b_1 replaced by b_2, and in the expression for D_{b_1a} as well as in the previous equations, $\vec{k}_1$ replaced by $\vec{k}_2$.

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