Revisiting photon-statistics effects on multiphoton ionization

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We present a detailed analysis of the effects of photon statistics on multiphoton ionization. Through a detailed study of the role of intermediate states, we evaluate the conditions under which the premise of nonresonant processes is valid. The limitations of its validity are manifested in the dependence of the process on the stochastic properties of the radiation and found to be quite sensitive to the intensity. The results are quantified through detailed calculations for coherent, chaotic, and squeezed vacuum radiation. Their significance in the context of recent developments in radiation sources such as the short-wavelength free-electron laser and squeezed vacuum radiation is also discussed.

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I. INTRODUCTION

It has been known since the late 1960s that any nonlinear interaction of radiation with electrons depends on the quantum statistical properties of the radiation [1–15]. In particular, a transition from a bound state to a continuum, such as ionization, offers the simplest and most directly observable process in which intensity correlation functions of the radiation are involved. A standard derivation of the transition probability per unit time (rate) for N-photon ionization leads to a rate that is proportional to some effective N-photon matrix element multiplied by the Nth-order intensity correlation function. However, any N-photon transition from the ground state to the continuum inevitably involves transition amplitudes through virtual or real bound atomic intermediate states. Strictly speaking, the above statement on the dependence of the process on the Nth-order intensity correlation function is valid as long as the intermediate states can be assumed to be sufficiently far from resonance so that they can be eliminated adiabatically, which leads to the effective N-photon matrix element.

To make further discussion more concrete, we consider for the moment two-photon ionization, whose rate would be proportional to the second-order intensity correlation function. The transition amplitude for the first photon involves all nonvanishing matrix elements between the ground and excited states. A closely related problem, namely, the strong driving between two bound states by stochastic radiation, represents a very fascinating problem, which cannot be treated in terms of a single transition probability per unit time. That problem has received considerable attention in the past [16,17] and can be considered, for all practical purposes, solved. In what follows, we will be concerned with nonresonant two-photon ionization. We shall assume that the chosen photon frequency is far from resonance with the nearest allowable intermediate state; an assumption to be qualified later on. More precisely, we assume that the laser bandwidth is much smaller than the detuning from the nearest state. Taking this formally to a limiting case, we shall cast this discussion in terms of a monochromatic source, which implies zero bandwidth.

For the sake of simplicity, which does not entail a significant limitation of generality, we stay with the assumption that initially the electron is in the ground state. The two-photon transition amplitude involves a summation over the complete manifold of intermediate states connected to the ground state with nonvanishing matrix elements. In the limit of small intensity, the transition probability per unit time is indeed proportional to the second-order intensity correlation function multiplied by an effective two-photon matrix element in which all intermediate states are the bare atomic states [8]. To the extent that the above condition is satisfied, the rate of ionization is simply proportional to the second-order intensity correlation function, which for a chaotic state is larger by a factor of 2 than that for a coherent state. For an N-photon process, the ratio is $N!$, which hereafter shall be referred to as the chaotic state enhancement. It bears emphasizing at this point that the above analysis is valid only within perturbation theory, in the form of Fermi's golden rule, describing the two-photon transition in terms of a single rate from the ground state to the continuum. Modifications to that simple case are discussed in the sections that follow.

However, for two-photon ionization (or any nonlinear process for that matter) to be observable, the laser intensity cannot be too low. As a consequence, even if the photon frequency is sufficiently far from resonance with the nearest intermediate state, as the intensity rises, the Rabi frequency connecting that state to the ground state may reach a value for which the nonresonant condition is no longer valid; this will occur when the Rabi frequency becomes comparable to the detuning from that state. Obviously, this implies that the validity of the nonresonant condition, which is the basis for the adiabatic elimination of the intermediate states, is not independent of the intensity. When that condition is violated, the simple dependence of the process on the second-order correlation function becomes, at best, questionable. It therefore becomes

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necessary to examine the possible modification of the role of photon statistics as a function of the intensity.

One can explore the issue starting from the other end by considering two-photon ionization in the presence of one or even two nearby intermediate resonances, which has in fact been addressed quite some time ago [18–22]. As one might have expected, the simple proportionality of the rate to the second-order intensity correlation function was found to be modified significantly. Further richness was found in the vicinity of two neighboring intermediate states. Aiming at the generalization of that exploration by including a squeezed state, we consider two-photon and three-photon ionization as a function of intensity, at various detunings from the intermediate resonances. We focus, in particular, on the role of photon correlations as the Rabi frequency becomes comparable to the detuning.

The initial motivation for this work seemed academic, aiming at the calibration of the possibility of using nonlinear photoabsorption to obtain information on the photon statistics of squeezed light sources and its role on nonlinear photoabsorption [23–30]. This led us to the reexamination of that issue in the context of standard sources, such as coherent and chaotic, in the process of which we realized that certain assumptions, taken until now for granted, are highly questionable. As discussed in detail later on, it turns out that in practical terms, the notion of nonresonant few-photon ionization is an abstraction that is difficult, if possible at all, to implement in an experiment. This may explain why, over the last 40 years or so, there are hardly any definitive experimental data exhibiting the chaotic field enhancement, even in the simple case of two-photon ionization. In the few existing experimental data, the observed enhancement factor for chaotic light, in most cases, has been less than the expected factor of 2 [9–12]. The relevance of this work to present-day possibilities, as far as squeezed radiation is concerned, has been underscored by very recent experimental results on the effect of squeezed light on harmonic generation [31]; albeit at quite low intensities, a limitation which may be lifted in the future.

The theoretical problem can be cast in terms of the time-dependent wave function or the density matrix. If the quantity we need is the rate (transition probability per unit time), depending on the values of the parameters, the time-dependent wave function may exhibit rapid oscillations. Although they can be eliminated through suitable approximations, their meaning tends to be somewhat opaque, even with extensive discussion [18]. The density matrix, on the other hand, lends itself to the derivation of rate equations which are free of such oscillations, although their validity may become questionable, for certain values of parameters that will be discussed in detail.

The chief reason for using both approaches needs to be made clear at the outset. As already pointed out and demonstrated formally in the following section, for nonresonant processes, the dependence of the yield on field correlations is contained in the intensity correlation function. The only approximation involved in this case comes for the accuracy in the calculation of the N-photon matrix element, which multiplies the correlation function, thus affecting only the amount of ionization and not its dependence on field correlations. As it will become clear in the sections that follow, however, when near resonance is involved, atomic parameters and field properties do not factorize. As a consequence, the calculation depends on a number of inevitable approximations, the most demanding of which has to do with the summation over the photon-number distribution. Since no approach can provide an exact result, each of the two approaches described above is expected to provide more reliable results in different combinations of parameters, discussed in the appropriate sections of the paper. The extent to which the results of the two approaches lead to similar conclusions provides an indirect test of their validity.

II. GENERAL THEORETICAL BACKGROUND

A. Nonresonant multiphoton ionization rate

Let $|g\rangle$ be the ground state of an atom, coupled to a monochromatic radiation field. Assume that upon the absorption of N photons of frequency ω, the atom is ionized, ejecting one electron. Denoting the final continuum state by $|f\rangle$ and the sets of intermediate states required for the absorption of the N photons by $|a_i\rangle$, the transition probability per unit time describing the N-photon process is known to be of the form [8]

$$W_{fg}^{(N)} = \hat{\sigma}_N G_N, \tag{1}$$

where $\hat{\sigma}_N$ is a generalized cross section given by

$$\hat{\sigma}_N = \frac{(2\pi\alpha)^N}{4\pi^2}\frac{mK}{\hbar}\omega^N \int \left|\mathrm{M}_{fg}^{(N)}\right|^2 d\Omega_{\mathbf{K}}, \tag{2}$$

and G_N is the Nth-order intensity correlation function, which contains information about the coherence properties of the radiation field [23]. As usual, α is the fine-structure constant, m is the mass of the outgoing electron, and $\mathbf{K}$ is its wave vector. The total generalized cross section is obtained by integration of the differential generalized cross section $\frac{d\hat{\sigma}_N}{d\Omega_{\mathbf{K}}}$ over all possible directions $\Omega_{\mathbf{K}}$ of the ejected electron. As discussed in the sections that follow, this expression for the transition probability per unit time is valid only in the off-resonance, weak-field limit, where the intermediate states enter as virtual states, implying that they acquire no population during the process. If this condition is not satisfied, the process is not describable in terms of a single rate as in Eq. (1) and a time-dependent approach is necessary. The matrix elements $M_{fg}^{(N)}$ contain all of the information about the atomic structure and are defined via

$$M_{fg}^{(N)} = \sum_{a_{N-1}\ldots a_1} \frac{\langle f|r^{(\lambda)}|a_{N-1}\rangle \cdots \langle a_1|r^{(\lambda)}|g\rangle}{\left[\omega_{a_{N-1}} - \omega_g - (N-1)\omega\right] \cdots \left(\omega_{a_1} - \omega_g - \omega\right)}, \tag{3}$$

where $r^{(\lambda)}$ is the projection of $\mathbf{r}$ on the polarization vector of the field, and $\mathbf{r}$ is the position operator of the electron.

As long as the off-resonance condition is satisfied, the only other quantity we need, in addition to the above N-photon matrix element, is the Nth-order intensity correlation function, which is determined by the stochastic properties of the field. These properties depend on the physical processes within the source that produces the radiation, resulting in the particular photon probability distribution characterizing the source and its effect on nonlinear processes. A brief summary of the photon probability distributions for the three types of sources, namely, the coherent, the chaotic, and the squeezed state, that are of interest in this paper, is given in the following section.

B. Photon probability distributions

1. Coherent state

The coherent state is the eigenstate of the annihilation operator $\hat{a}$; therefore, by definition, it satisfies the equation

$$\hat{a}|a\rangle = a|a\rangle, \tag{4}$$

where the eigenvalue a can be any complex number. Expanding the coherent state in the orthonormal set of eigenstates of the number operator (Fock states), the probability of finding n photons in the field is

$$P_{\rm coh}(n) = |\langle n \mid a\rangle|^2 = e^{-|a|^2}\frac{|a|^{2n}}{n!}. \tag{5}$$

The average photon number is given by $\bar{n} = \sum_{n=0}^{\infty} n P_{\rm coh}(n) = |a|^2$, in terms of which the photon probability distribution assumes the form

$$P_{\rm coh}(n) = e^{-\bar{n}}\frac{\bar{n}^n}{n!}, \tag{6}$$

which is the well-known Poisson distribution.

2. Chaotic state

The chaotic state, which represents the equilibrium state of a boson field at temperature T, is a mixed state whose density operator has only diagonal matrix elements in the number basis. The average number of photons is given by $\bar{n} = \sum_{n=0}^{\infty} n P_{\rm chao}(n) = \frac{1}{e^{\hbar\omega/k_B T}-1}$ in terms of which the photon probability distribution for the chaotic state is

$$P_{\rm chao}(n) = \frac{1}{1+\bar{n}}\left(\frac{\bar{n}}{1+\bar{n}}\right)^n = \frac{\bar{n}^n}{(1+\bar{n})^{n+1}}. \tag{7}$$

3. Squeezed vacuum state

Since the properties of squeezed radiation and especially its photon-number distribution are not as commonly found in the literature, in this section we provide a somewhat extended summary of its properties. A squeezed state is a state with phase-sensitive quantum fluctuations, which at certain phase angles are less than those of a coherent or the vacuum field. Squeezed states of a radiation field are generated in nonlinear processes in which an electromagnetic field drives a nonlinear medium. In such a medium, pairs of correlated photons of the same frequency are generated. In the interaction picture, this process can be described by the effective Hamiltonian [32,33]

$$\hat{H}_I = \varepsilon(\hat{\alpha}^\dagger)^2 + \varepsilon^*\hat{\alpha}^2. \tag{8}$$

This Hamiltonian describes how a pump field is down-converted to its subharmonics at half the driving frequency, with the parameter ε containing the amplitude of the driving field and the second-order susceptibility for the down-conversion. Since the total Hamiltonian is time independent, the time evolution operator (also called squeeze operator) is

$$\hat{U}(t) = \exp\left(-\frac{i\hat{H}t}{\hbar}\right) = \exp\left[\xi\frac{(\hat{\alpha}^\dagger)^2}{2} - \xi^*\frac{\hat{\alpha}^2}{2}\right] \equiv S(\xi), \tag{9}$$

where $\xi = -\frac{i\varepsilon t}{\hbar}$ is the so-called squeezing parameter, which can also be written as $\xi = r\exp(i\varphi)$. The squeezing parameter characterizes the degree of squeezing and depends on the amplitude of the driving field and the interaction time, i.e., the time that it takes for light to travel via the nonlinear medium.

The action of the squeeze operator on the vacuum state $|0\rangle$ results in the so-called squeezed vacuum state, denoted by

$$|\xi\rangle \equiv S(\xi)|0\rangle. \tag{10}$$

In order to obtain the photon-number probability distribution of the squeezed vacuum state [32,33], we decompose $|\xi\rangle$ in the Fock basis,

$$|\xi\rangle = \sum_{n=0}^{\infty} C_n|n\rangle, \tag{11}$$

and seek an expression for the relevant coefficients. Starting with the vacuum state, which satisfies the relation

$$\hat{a}|0\rangle = 0, \tag{12}$$

we multiply by $\hat{S}(\xi)$ from the left and use the fact that $\hat{S}(\xi)$ is unitary to obtain

$$\hat{S}(\xi)\hat{a}\hat{S}^\dagger(\xi)\hat{S}(\xi)|0\rangle = 0 \Leftrightarrow \hat{S}(\xi)\hat{a}\hat{S}^\dagger(\xi)|\xi\rangle = 0. \tag{13}$$

By the definition of ξ, we find that

$$\hat{S}(\xi)\hat{a}\hat{S}^\dagger(\xi) = \hat{a}\cosh r + e^{i\theta}\hat{a}^\dagger\sinh r. \tag{14}$$

In view of Eq. (13), Eq. (14) becomes

$$(\hat{a}\cosh r + \hat{a}^\dagger e^{i\theta}\sinh r)|\xi\rangle = 0. \tag{15}$$

By substituting Eq. (11) in Eq. (15), we obtain a recursion relation for the coefficients C_n:

$$C_{n+1} = -e^{i\theta}\tanh r\left(\frac{n}{n+1}\right)^{1/2} C_{n-1}, \tag{16}$$

whose solution is

$$C_{2n} = (-1)^n(e^{i\theta}\tanh r)^n\left[\frac{(2n-1)!!}{(2n)!!}\right]^{1/2} C_0. \tag{17}$$

If we demand from C_{2n} to satisfy the normalization condition $\sum_{n=0}^{\infty}|C_{2n}|^2 = 1$, we obtain

$$|C_0|^2\left[1 + \sum_{n=0}^{\infty}\frac{(\tanh r)^{2n}(2n-1)!!}{(2n)!!}\right] = 1. \tag{18}$$

Using the identity

$$1 + \sum_{n=0}^{\infty} z^n\left[\frac{(2n-1)!!}{(2n)!!}\right] = (1-z)^{-1/2}, \tag{19}$$

Eq. (18) reduces to $C_0 = \sqrt{\cosh r}$. Finally, in view of the following two identities:

$$(2n)!! = 2^n n!, \tag{20}$$

$$(2n-1)!! = \frac{1}{2^n}\frac{(2n)!}{n!}, \tag{21}$$

one obtains the final expression for the coefficients,

$$C_{2n} = (-1)^n\frac{\sqrt{(2n)!}}{2^n n!}\frac{(e^{i\theta}\tanh r)^n}{\sqrt{\cosh r}}. \tag{22}$$

Substitution of Eq. (22) back into Eq. (11) gives the decomposition of the squeezed vacuum state in the Fock basis,

$$|\xi\rangle = \frac{1}{\sqrt{\cosh r}} \sum_{n=0}^{\infty} (-1)^n \frac{\sqrt{(2n)!}}{2^n n!} e^{in\theta} (\tanh r)^n |2n\rangle. \quad (23)$$

The probability of detecting $2n$ photons in the field is

$$P_{2n} = |\langle 2n \mid \xi\rangle|^2 = \frac{(2n)!}{2^{2n}(n!)^2} \frac{(\tanh r)^{2n}}{\cosh r}, \quad (24)$$

and the probability of the detection of $2n+1$ photons is

$$P_{2n+1} = |\langle 2n+1 \mid \xi\rangle|^2 = 0. \quad (25)$$

Equations (24) and (25) indicate that the photon probability distribution of a squeezed vacuum state is oscillatory, with the probability for all odd photon numbers to be zero. The probability can also be expressed in terms of the mean photon number, $\bar{n} = \sum_{n=0}^{\infty} P_{2n}(2n) = \sinh^2 r$, as

$$P_{2n} = \frac{1}{\sqrt{1+\bar{n}}} \frac{(2n)!}{(n!)^2 2^{2n}} \left(\frac{\bar{n}}{1+\bar{n}}\right)^n. \quad (26)$$

III. PHOTON CORRELATION EFFECTS IN NEAR-RESONANT TWO-PHOTON IONIZATION

In this section, we present a self-contained formulation and discussion of the effect of photon statistics on two-photon ionization, with emphasis on the near-resonant process. It is useful to solve the problem assuming that the field is initially prepared in a number state and then use the photon probability distributions derived in the previous section to obtain results for the cases of coherent, chaotic, or squeezed vacuum radiation. For reasons discussed in Sec. I, we have approached the problem through two different formulations: specifically, the resolvent operator and the density matrix.

A. Resolvent-operator formalism

Consider the atom initially in its ground state $|g\rangle$, in the presence of an external field in a Fock state $|n\rangle$. The initial state of the compound system (atom + field) is $|I\rangle = |g\rangle|n\rangle$. The initial atomic state is connected to an intermediate atomic state $|a\rangle$ via a single-photon electric dipole transition of frequency ω (Fig. 1), which brings the compound system to the intermediate state $|A\rangle = |a\rangle|n-1\rangle$. The absorption of a second photon takes the atom to the final continuum state $|f\rangle$. Therefore, the final state of the compound system is $|F\rangle = |f\rangle|n-2\rangle$. The energies of the above three system states are $\omega_I = \omega_g + n\omega$, $\omega_A = \omega_a + (n-1)\omega$, and $\omega_F = \omega_f + (n-2)\omega$. All energies are measured in units of frequency, as all Hamiltonians are assumed divided by $\hbar$. The detuning from the intermediate resonance is $\Delta = \omega - \omega_{ag} = \omega - (\omega_a - \omega_g)$. The Hamiltonian H of the system is the sum of the unperturbed Hamiltonian H^0 and the field-atom interaction Hamiltonian V. The wave function of the system at times $t > 0$ is given by $|\Psi(t)\rangle = U(t)|I\rangle$, where $U(t)$ is the time evolution operator.

In order to obtain the probability of ionization as a function of the time t, we need the equations of motion of the matrix elements U_{II} and U_{AI} or U_{FI} of the time evolution operator,

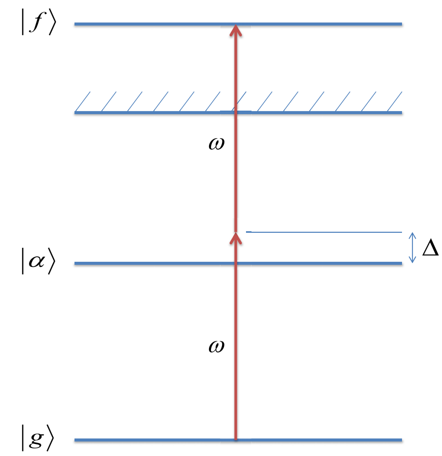

FIG. 1. Ionization via two single-photon electric dipole transitions.

in terms of which the ionization probability is expressed as

$$P_{\text{ion}}(t) = \int d\omega_F |U_{FI}(t)|^2 = 1 - |U_{AI}(t)|^2 - |U_{II}(t)|^2. \quad (27)$$

This equation, based on the conservation of probability, simply states that what is missing from the two bound states is in the continuum. The time evolution of these matrix elements can be obtained analytically with the help of the resolvent operator $G(z) \equiv (z - H)^{-1}$, which is the Laplace transform of $U(t)$. The procedure involves finding the equations that govern the time evolution of the matrix elements G_{II}, G_{AI}, and G_{FI} of the resolvent operator, from which the respective matrix elements of the time evolution operator are obtained through the inverse Laplace transform. The relevant mathematical details of this procedure are summarized in the Appendix.

The matrix element $2V_{AI}$ reflects the Rabi frequency of the $|g\rangle \leftrightarrow |a\rangle$ transition,

$$\Omega = 2V_{AI}, \quad (28)$$

while V_{FA} is related to the rate of ionization of the intermediate state Γ_A as

$$\Gamma_A = 2\pi|V_{FA}|^2. \quad (29)$$

Note that for Eq. (27) to represent the probability of ionization, the spontaneous decay of the intermediate state has to be negligible compared to the ionization width. Since we are working in the number state representation, we can express the Rabi frequency and the ionization rate in terms of the number of photons of the states $|I\rangle$ and $|A\rangle$ as

$$\Omega = \mu\sqrt{n}, \quad (30)$$

$$\Gamma_a = \sigma(n-1), \quad (31)$$

where μ is the single-photon dipole matrix element of the $|g\rangle \leftrightarrow |a\rangle$ transition and σ is the cross section associated with the ionization of $|a\rangle$.

To account for the effects of photon statistics, we average the ionization probability over the photon probability distributions of a coherent, a chaotic, and a squeezed vacuum state,

$$P_{\rm coh}(t) = \sum_{n=2}^{\infty} P_{\rm coh}(n,\langle n\rangle)P_{\rm ion}(t,n), \tag{32}$$

$$P_{\rm chao}(t) = \sum_{n=2}^{\infty} P_{\rm chao}(n,\langle n\rangle)P_{\rm ion}(t,n), \tag{33}$$

$$P_{\rm SV}(t) = \sum_{n=1}^{\infty} P_{\rm SV}(2n,\langle n\rangle)P_{\rm ion}(t,2n). \tag{34}$$

Notice that in Eqs. (32) and (33) the summation begins from $n = 2$ since it is the lowest number of photons necessary for the process to be completed. In Eq. (34), the summation begins from $n = 1$ since the argument of the squeezed vacuum distribution is $2n$.

We are interested in the behavior of the ratios $P_{\rm chao}(T)/P_{\rm coh}(T)$ and $P_{\rm SV}(T)/P_{\rm coh}(T)$ as a function of the mean photon number for various detunings, where T is a time sufficiently larger than the time it takes for the atom to get ionized. The results are presented and discussed in Sec. V.

B. Density matrix formalism

The density matrix describing resonant two-photon ionization is essentially the density matrix of a two-level system [8] with the addition of a relaxation for the upper state due to ionization. This is accomplished through the introduction of an ionization rate $\Gamma_{\rm ion}$ describing the transfer of population from the excited state to the continuum. Neglecting the spontaneous decay of the excited state, which in the present context is much smaller than the ionization rate, the density matrix rate equations governing the time evolution of the ground and the excited atomic state (denoted by $|g\rangle$ and $|a\rangle$, respectively), are

$$\frac{\partial}{\partial t}\rho_{gg}(t) = R[\rho_{aa}(t) - \rho_{gg}(t)], \tag{35}$$

$$\frac{\partial}{\partial t}\rho_{aa}(t) = -\Gamma_{\rm ion}\rho_{aa}(t) - R[\rho_{aa}(t) - \rho_{gg}(t)], \tag{36}$$

where

$$R = \frac{\Gamma_{\rm ion}|\Omega|^2}{\Delta^2 + \frac{\Gamma_{\rm ion}{}^2}{4}} \tag{37}$$

is the rate of the process, while ρ_{gg} and ρ_{aa} indicate the populations of the ground and the excited state, respectively. Note that since we neglected the spontaneous decay of the excited state and have no additional relaxation mechanism, the off-diagonal relaxation rate is $\gamma_{\alpha g} = \frac{\Gamma_{\rm ion}}{2}$.

In view of Eqs. (30) and (31) that relate the Rabi frequency and the ionization width to the number of photons, the rate is expressed in terms of the photon number n as

$$R = \frac{\sigma\mu^2 n(n-1)}{\Delta^2 + \frac{\sigma^2}{4}(n-1)^2} \equiv W(n). \tag{38}$$

Again, to obtain the effects of photon correlations, we average Eq. (38) over the photon probability distribution of the respective field state, as described in the previous section.

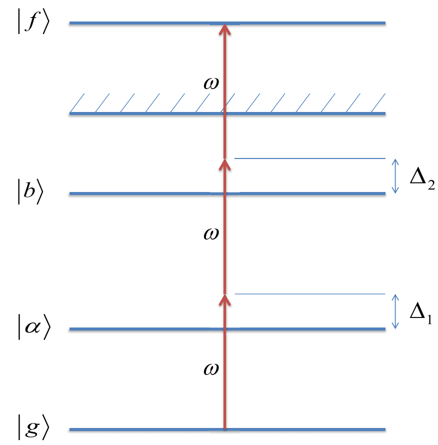

FIG. 2. Ionization via three single-photon electric dipole transitions.

IV. PHOTON CORRELATION EFFECTS IN NEAR-RESONANT THREE-PHOTON IONIZATION

A. Resolvent-operator formalism

Using the notation introduced in the previous section, we denote the states of the compound system (atom + radiation field) as $|I\rangle = |g\rangle|n\rangle, |A\rangle = |a\rangle|n-1\rangle, |B\rangle = |b\rangle|n-2\rangle, |F\rangle = |f\rangle|n-3\rangle$, where $|g\rangle$ is the initial atomic state, $|a\rangle$ and $|b\rangle$ are the two intermediate states, and $|f\rangle$ is the final atomic state that belongs to the continuum. Every state is coupled to its lower one via a single-photon electric dipole transition in the presence of a driving field with frequency ω (Fig. 2). The respective energies of the compound states are $\omega_I = \omega_g + n\omega$, $\omega_{\rm A} = \omega_a + (n-1)\omega$, $\omega_{\rm B} = \omega_b + (n-2)\omega$, and $\omega_F = \omega_f + (n-3)\omega$. We introduce the two detunings from the intermediate resonances as $\Delta_1 = \omega - \omega_{ag} = \omega - \omega_\alpha + \omega_g$ and $\Delta_2 = 2\omega - \omega_{bg} = 2\omega - \omega_b + \omega_g$.

We choose the energies of the atomic states and the driving frequency such that they result in a detuning Δ_1 sufficiently larger than the energy difference ω_{ag}, i.e., $\Delta_1 \gg \omega_{ag}$, implying that the first transition is off resonant, focusing on the problem for various detunings from the second resonance. The equations of motion of the resolvent operator's matrix elements are now four, but can be reduced to three after eliminating the continuum, as described in the Appendix. The coupling of $|b\rangle$ to $|f\rangle$ leads to an ionization rate Γ_b and a shift which, for the sake of simplicity, is neglected as it does not contribute to the issues of interest in this paper. Noting again that spontaneous decays of the intermediate states are negligible, the ionization probability at times $t > 0$ is given by

$$P_{\rm ion}(t) = 1 - |U_{II}(t)|^2 - |U_{AI}(t)|^2 - |U_{BI}(t)|^2, \tag{39}$$

where $U_{ii}, i = I$, and A,B are the matrix elements of the time evolution operator between the states of the compound system considered in our problem. It should be evident that the two-photon resonant, three-photon ionization problem is formally similar to the two-photon ionization case, with the only difference being that the two-photon Rabi frequency to the resonant state is now proportional to the intensity rather than the field amplitude. As a consequence, the Rabi frequency and the ionization rate of the excited state have the same dependence on the intensity.

The matrix elements $2V_{GA} \equiv \Omega_1$ and $2V_{AB} \equiv \Omega_2$ reflect the Rabi frequencies of the two transitions, while the ionization rate is equal to $\Gamma_b = 2\pi|V_{FB}|^2$. Since we are working in the number state representation, we express the two Rabi frequencies and the ionization rate in terms of the number of photons of the states $|I\rangle$, $|A\rangle$, and $|B\rangle$, i.e.,

$$\Omega_1 = \mu_1\sqrt{n}, \quad (40)$$

$$\Omega_2 = \mu_2\sqrt{n-1}, \quad (41)$$

$$\Gamma_b = \sigma(n-2), \quad (42)$$

where μ_1, μ_2 are the single-photon dipole matrix elements of the transitions $|g\rangle \leftrightarrow |a\rangle$ and $|a\rangle \leftrightarrow |b\rangle$, respectively, while σ is the ionization cross section of state $|b\rangle$.

We now average the ionization probability over the photon distributions of the field states, starting the sums from the least number of photons needed for the process to occur. Note that in the squeezed vacuum average, the argument of the ionization probability is $2n$ and the sum begins from $n = 2$ since the squeezed vacuum photon probability distribution is zero for odd number of photons,

$$P_{\text{coh}} = \sum_{n=3}^{\infty} P_{\text{coh}}(n,\langle n\rangle)P_{\text{ion}}(n), \quad (43)$$

$$P_{\text{chao}} = \sum_{n=3}^{\infty} P_{\text{chao}}(n,\langle n\rangle)P_{\text{ion}}(n), \quad (44)$$

$$P_{\text{SV}} = \sum_{n=2}^{\infty} P_{\text{SV}}(2n,\langle n\rangle)P_{\text{ion}}(2n). \quad (45)$$

In Sec. V, we plot the ratios $P_{\text{chao}}/P_{\text{coh}}$ and $P_{\text{SV}}/P_{\text{coh}}$ as a function of the mean number of photons for various detunings from the second resonance.

B. Density matrix formalism

As in the previous section, we choose the frequencies of the atomic states and the external frequency such that the condition $\Delta_1 \gg \omega_{ag}$ is satisfied. Since the first transition is off resonance, as noted in the previous section, the overall three-photon process is formally similar to the two-photon case, with the resonant transition driven by an effective two-photon Rabi frequency Ω_{eff}. This allows us to use the rate derived for the two-photon case, with the effective Rabi frequency and the ionization rate now given by

$$\Omega_{\text{eff}} = \mu^{(2)}\sqrt{n(n-1)}, \quad (46)$$

$$\Gamma_{\text{ion}} = \sigma(n-2), \quad (47)$$

where σ is the ionization cross section and $\mu^{(2)}$ is the effective two-photon dipole matrix element.

The resulting expression for the rate of ionization now is

$$R = \frac{\Gamma_{\text{ion}}|\Omega_{\text{eff}}|^2}{\Delta^2 + \frac{\Gamma_{\text{ion}}^2}{4}} = \frac{\sigma(\mu^{(2)})^2 n(n-1)(n-2)}{\Delta^2 + \frac{\sigma^2(n-2)^2}{4}} \equiv W(n). \quad (48)$$

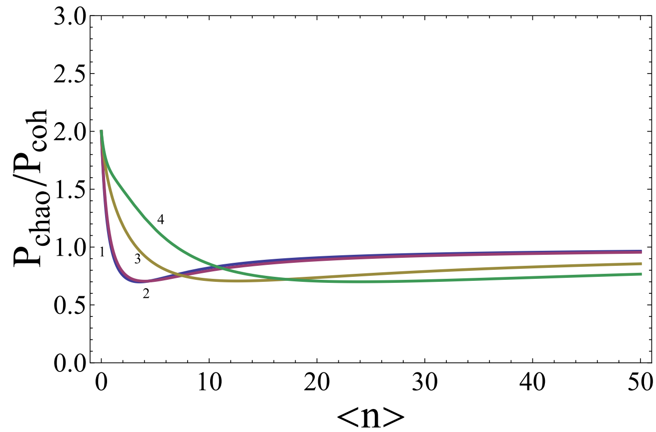

FIG. 3. Ratio of chaotic over coherent two-photon ionization probability as a function of the mean photon number for various detunings from the intermediate resonance. The values of the dipole matrix element and the cross section used are $\mu = \sigma = 0.0003$ a.u. (1) Blue line: $\Delta/\omega_\alpha = 0.0001$; (2) red line: $\Delta/\omega_\alpha = 0.01$; (3) olive line: $\Delta/\omega_\alpha = 0.05$; and (4) green line: $\Delta/\omega_\alpha = 0.1$. The blue and red lines coincide.

As in the previous sections, the effect of field correlations on the overall process is obtained through averaging the above rate over the appropriate photon-number distribution.

V. RESULTS AND DISCUSSION

Having established the formal aspects of the problem, in this part, we present and discuss a collection of results with an interpretation of the underlying physics. Although the basic physics is common to both cases, we discuss the two- and three-photon cases separately, as there are some differences in the details. In the plots that follow, we show ionization yields or transition rates as a function of intensity for different quantum states of the driving field. In order to assess and illustrate the enhancement due to bunching, we plot the ratio of the yield for either a chaotic or squeezed vacuum state to that for a coherent state, as a function of the intensity. The respective ionization probabilities are denoted by the self-evident notation P_{coh}, P_{chao}, and P_{SV} and the respective transition rates by W_{coh}, W_{chao}, and W_{SV}.

A. Two-photon results and discussion

In Fig. 3, we have chosen the dipole matrix element coupling to the intermediate state and the ionization cross section so that they result in the Rabi frequency equal to the ionization rate Γ, for small mean photon numbers. This picture changes with increasing intensity because the Rabi frequency is proportional to the square root of intensity, while the ionization rate scales linearly with intensity. Note that in the single-mode approximation, the mean photon number is approximately related to the average intensity I via $\langle n\rangle = (8\pi^3c^2/\omega^2)(I/\Delta\omega)$ [8], where $\Delta\omega$ is the bandwidth of the source.

At low intensities, the ratio $P_{\text{chao}}/P_{\text{coh}}$ is equal to 2, in agreement with the expected enhancement factor due to the linear dependence of the ionization on the second-order correlation function, which is 2 for the chaotic field. As the intensity

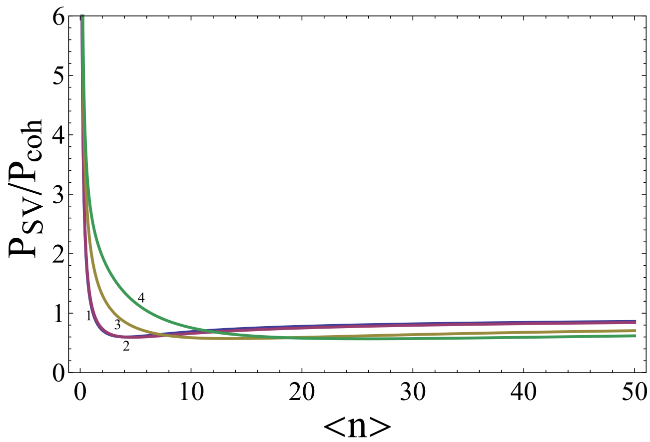

FIG. 4. Ratio of squeezed vacuum over coherent two-photon ionization probability as a function of the mean photon number for various detunings from the intermediate resonance. The values of the dipole matrix element and the cross section used are $\mu = \sigma = 0.0003$ a.u. (1) Blue line: $\Delta/\omega_\alpha = 0.0001$; (2) red line: $\Delta/\omega_\alpha = 0.01$; (3) olive line: $\Delta/\omega_\alpha = 0.05$; (4) green line: $\Delta/\omega_\alpha = 0.1$. The blue and red lines coincide.

increases, however, we notice a rapid decrease of the ratio below the value of 2. This decrease from 2 can be attributed to the fact that with saturation approaching, the ionization yield begins depending on all higher-order correlation functions and not only on the second-order one. As a result, we observe a drastic change of the ratio.

The different curves in Fig. 3 correspond to different values of the detuning from the intermediate resonance. In the limit of large intensities, all curves end up to unity as expected due to saturation, but the decrease of the ratio below the $N!$ factor is faster when the external frequency is tuned on resonance with the $|a\rangle \leftrightarrow |g\rangle$ transition because that is when the validity of the nonresonant scheme breaks down faster with increasing intensity. It is interesting to note that there is a rather broad regime of mean photon numbers for which the ratio drops below unity. Evidently, for that range of intensities, chaotic radiation is less effective in two-photon ionization than coherent radiation, which is a rather surprising result. Actually, these results are in agreement with those of an earlier work by one of the authors on saturation in atomic transitions [16,17], where it was shown that the initially observed monotonical decrease of the ratio to unity was due to the assumption of a chaotic field within the decorrelation approximation (DA). When the DA is adopted to the case of an N-photon transition, it results in equations of motion that contain information only about the Nth-order correlation function. Therefore, for low intensities where the process depends only on the Nth-order correlation function, the DA is valid. However, for stronger fields, the simple proportionality of the process to the Nth-order correlation function breaks down since higher-order correlation functions come into play, at which point the DA can lead to false predictions.

In Fig. 4, we plot the ratio of the two-photon ionization probability for squeezed vacuum over coherent as a function of the mean photon number, again for different values of the detuning from the intermediate resonance. Although the overall behavior of the ratios, as depicted in those curves, appears similar to those of Fig. 3 , an important difference arises at small mean photon numbers for which the ratio diverges. This is compatible with the fact that at weak fields, the process should depend linearly on the second-order field correlation function, which in the case of a squeezed vacuum field is equal to $\langle n\rangle^2(3 + \frac{1}{\langle n\rangle})$. This result can be obtained by averaging the second-order correlation function of a field in a Fock state, i.e., $G_2^{\rm Fock} = n(n-1)$, over the squeezed vacuum photon probability distribution given by Eq. (46). The ratio of the squeezed vacuum over coherent second-order correlation functions would then be equal to $3 + \frac{1}{\langle n\rangle}$, which apparently diverges when $\langle n\rangle \to 0$. Be that as it may, a nonlinear process, such as a two-photon transition, becomes meaningless in the limit of zero intensity.

In the strong-field limit as expected, owing to saturation, all curves approach unity, reaching that value at approximately $\langle n\rangle \simeq 200$. As in the case of a chaotic field, there is a broad region of intensities between the weak field and the saturation limits, where the ratio drops below unity. Therefore, in two-photon near-resonant ionization, squeezed vacuum radiation is more effective than coherent radiation only in the vicinity of small mean photon numbers. For the parameters used in the problem at hand, in view of the relation between the mean photon number and the intensity shown above, the notion of "small mean photon numbers" corresponds to field intensities in the vicinity of $I = 10^5$ W/cm^2. Although the loss of the enhancement due to chaotic radiation, in a certain range of intensities, had been noted in earlier works [16,17], finding the same behavior for superbunched squeezed radiation could not have been anticipated.

Before continuing with the rate equations' results, we need to clarify the issue regarding the possible efficiency of squeezed vacuum radiation, in near-resonant few-photon ionization. It is known that the Nth-order correlation function of a field in a strongly squeezed vacuum state is equal to $(2N-1)!!\langle n\rangle^N$ [34]. For $N = 2$, this is equal to $3\langle n\rangle^2$. One might be tempted to infer that the strongly squeezed vacuum light is three times more efficient than coherent light in two-photon ionization. We should, however, keep in mind that the notion of strongly squeezed vacuum refers to a squeezed vacuum state with a high squeezing parameter r and therefore a high mean photon number, according to $\langle n\rangle = (\sinh r)^2$ [35]. In fact, the enhancement factor 3 can also be seen by considering $\langle n\rangle \gg 1$ in the two-photon squeezed vacuum correlation function $G_2^{\rm SV} = \langle n\rangle^2(3 + \frac{1}{\langle n\rangle})$. Due to the exponential character of the $\sinh r$ function, small changes of the squeezing parameter are equivalent to large changes in the mean photon number. For example, an increase of r from 1 to 2 is equivalent to an increase of the mean photon number from about 1.4 to 13.2. Therefore, in view of the results of Fig. 4, we should not expect to observe the $(2N-1)!!$ enhancement in near-resonant ionization due to the rapid approach to the saturation limit. In others words, the $(2N-1)!!$ enhancement requires intensities in the range where the simple dependence of the process on the Nth-order intensity correlation function has already become invalid near resonance. However, the near-resonant process may be enhanced significantly if the atom is exposed to weak squeezed vacuum radiation, assuming observability is feasible.

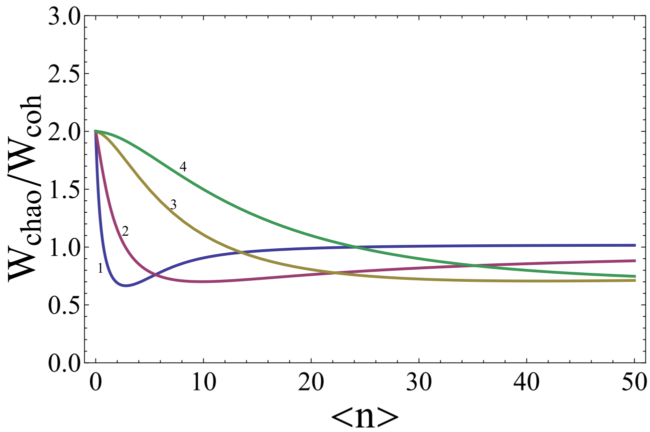

FIG. 5. Ratio of chaotic over coherent two-photon ionization rate as a function of the mean photon number, for various detunings from the intermediate resonance. The values of the dipole matrix element and the cross section used are $\mu = \sigma = 0.0003$ a.u. (1) Blue line: $\Delta/\omega_\alpha = 0.0001$; (2) red line: $\Delta/\omega_\alpha = 0.01$; (3) olive line: $\Delta/\omega_\alpha = 0.05$; (4) green line: $\Delta/\omega_\alpha = 0.1$.

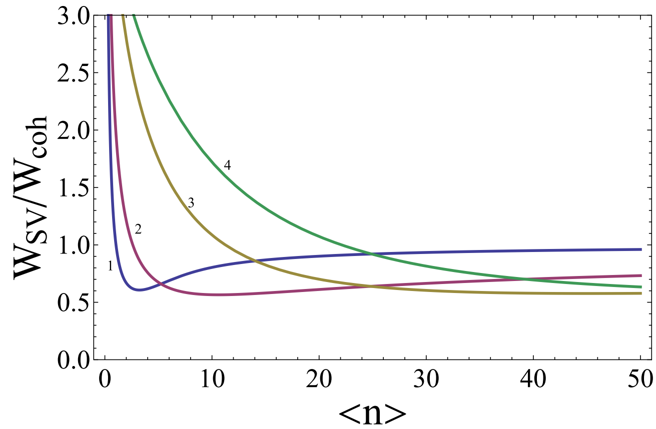

FIG. 6. Ratio of squeezed vacuum over coherent two-photon ionization rate as a function of the mean photon number, for various detunings from the intermediate resonance. The values of the dipole matrix element and the cross section used are $\mu = \sigma = 0.0003$ a.u. (1) Blue line: $\Delta/\omega_\alpha = 0.0001$; (2) red line: $\Delta/\omega_\alpha = 0.01$; (3) olive line: $\Delta/\omega_\alpha = 0.05$; (4) green line: $\Delta/\omega_\alpha = 0.1$.

As discussed in the previous sections, apart from the ionization probability using the time-dependent wave function, a transition probability (rate) can also be derived with the help of the density matrix equations. A sample of the results is shown in Fig. 5, with parameters identical to those of Fig. 3.

The behavior of the various curves of Fig. 5 is in overall agreement with the respective behavior of the curves of Fig. 3, eventually reaching the value of unity. A difference can be noticed, however, in that all curves, with the exception of the blue one corresponding to detuning 0.0001 times the frequency of the intermediate state, now will reach unity at much higher mean photon numbers ($\langle n\rangle \simeq 800$), which has been verified numerically, although not shown in the figure; a result that should be viewed with precaution because the derivation of the two-photon rate is based on the assumption of a Rabi frequency not much larger than the ionization rate Γ and/or the detuning from the intermediate resonance. However, owing to the linear dependence of the ionization rate on the photon number, it increases much faster than the Rabi frequency, which is proportional to the square root of the photon number. Therefore, even if they are comparable for small mean photon numbers, the necessary condition $\Omega < \Gamma$ can be reached fairly quickly, as the intensity rises. However, since the detuning is fixed, for large mean photon numbers the Rabi frequency will eventually become larger than the detuning, with the validity of the rate approximation breaking down.

In Fig. 6, we present results on the ratio $W_{\mathrm{SV}}/W_{\mathrm{coh}}$ as a function of the mean photon number as obtained through the rate equations. Comparing the results of this figure to those of Fig. 4, we note that now the ratio of the rates is more sensitive to detuning than the ratio of the ionization probabilities. This is reflected in the startling difference between the blue and red lines (which in Fig. 4 are indistinguishable), as well as in the different behavior of the green and olive lines, with increasing intensity. Still, the overall trend of the curves in the two figures is similar. We should point out that owing to the specific form of Eq. (38), in averaging over a photon probability distribution, the dipole matrix element and the ionization cross section appearing in the numerator of (38) are factored out and cancel when the ratios are taken. This leads to ratios that depend only on the detuning and the cross section appearing in the denominator of (38). As a result, changes in the dipole matrix element will not affect the ratio of the rates. But since the derivation of the rate equations is based on the approximation discussed above, the results would be meaningful only when the intensities are such that they conform to a Rabi frequency within the limits of the approximation. It is very interesting to notice that Eq. (38) within the limit $\Delta \gg \frac{\sigma}{2}(n-1)$ reduces to the second-order correlation function of a field in a number state, multiplied by the factor $\frac{\sigma\mu^2}{\Delta^2}$. This suggests that the $(2N-1)!!$ enhancement of the two-photon ionization under squeezed vacuum radiation, over that under coherent, would appear when the above condition is satisfied, according to the ratio of the respective correlation functions. But we must keep in mind that the summations over a photon probability distribution include photon numbers up to infinity. Even if the high photon number terms enter with less weight, when high mean photon numbers are considered, the condition $\Delta \gg \frac{\sigma}{2}(n-1)$ would no longer be satisfied. This actually is another way to see why the simple proportionality of an N-photon process to the field Nth-order correlation field will eventually break down with increasing intensity.

B. Three-photon results and discussion

In three-photon near-resonant ionization, there are two intermediate states, which means a double near-resonance is possible. In this work, we have chosen the photon frequency so that the detuning $\Delta_1 \gg \omega_{ag}$ of the first transition is sufficiently large for the two-photon transition to the second intermediate state to satisfy the nonresonant condition for all intensities employed in the calculations. The reason is that we wanted to explore the role of the nonlinearity in the bound-bound transition, in contrast to the two-photon case where the bound-bound transition depends linearly on the radiation. Thus we have only one near-resonance state to study.

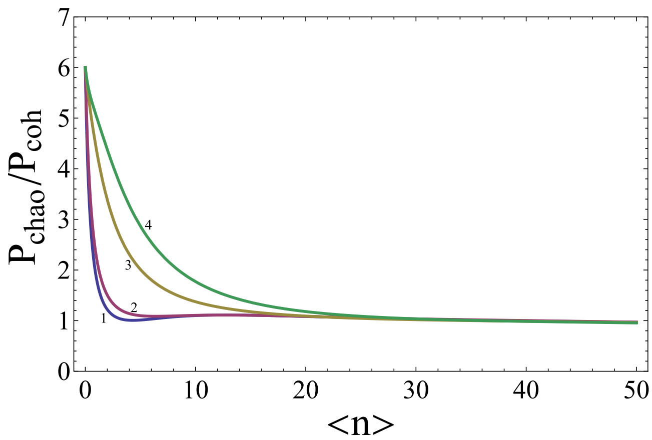

FIG. 7. Ratio of chaotic over coherent three-photon ionization probability as a function of the mean photon number, for various detunings from the second intermediate resonance. The values of the dipole matrix elements and the cross section used are $\mu_1 = \mu_2 = 0.0004$ a.u. and $\sigma = 0.0008$ a.u. (1) Blue line: $\Delta_2/\omega_b = 0.0001$; (2) red line: $\Delta_2/\omega_b = 0.01$; (3) olive line: $\Delta_2/\omega_b = 0.05$; (4) green line: $\Delta_2/\omega_b = 0.1$.

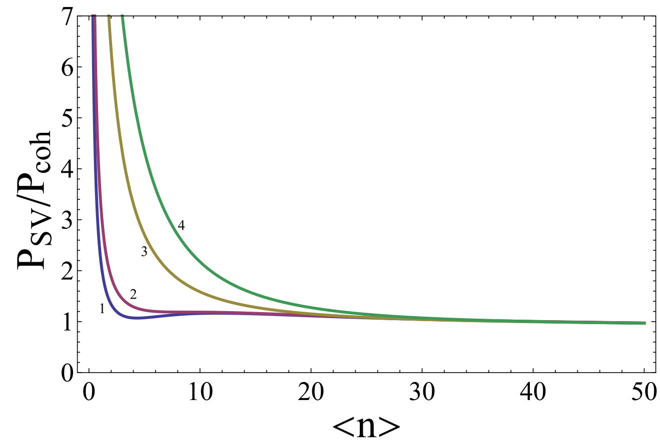

FIG. 8. Ratio of squeezed vacuum over coherent three-photon ionization probability as a function of the mean photon number, for various detunings from the second intermediate resonance. The values of the dipole matrix elements and the cross section used are $\mu_1 = \mu_2 = 0.0004$ a.u. and $\sigma = 0.0008$ a.u. (1) Blue line: $\Delta_2/\omega_b = 0.0001$; (2) red line: $\Delta_2/\omega_b = 0.01$; (3) olive line: $\Delta_2/\omega_b = 0.05$; (4) green line: $\Delta_2/\omega_b = 0.1$.

In direct analogy with the two-photon case, we have a Rabi frequency coupling the bound states and an ionization cross section. For the results of Fig. 7, we have chosen a cross section $\sigma = 0.0008$ a.u. that is two times higher (expressed in atomic units) than the dipole matrix elements $\mu_1,\mu_2 = 0.0004$ a.u. of the transitions $|g\rangle \leftrightarrow |a\rangle$ and $|a\rangle \leftrightarrow |b\rangle$, respectively. At low intensities, the ratio of chaotic over coherent ionization transition probabilities is equal to 6, which is compatible with the expected weak-field $N!$ enhancement for $N = 3$, arising from the ratios of the respective correlation functions. With increasing intensity, the ratio drops below $N!$ rather rapidly, approaching unity, as expected. The approach to unity turns out to be faster, as the photon frequency is tuned closer to resonance with the second transition. In contrast to the two-photon case, the ratio does not drop below unity at any intensity. It appears that the nonlinearity in the two-photon Rabi frequency, in this case, is responsible for this behavior. Recall that now both Rabi frequency and ionization rate have the same dependence on intensity.

As in the two-photon case, the squeezed vacuum over coherent ratio of ionization transition probabilities (Fig. 8) exhibits a behavior similar to that of the chaotic over coherent ratio, with the exception of the divergence for weak fields noted also for two-photon ionization. Again, this is connected to the form of the squeezed vacuum third-order correlation function $G_3^{\mathrm{SV}} = \langle n\rangle^3(15 + \frac{9}{\langle n\rangle})$, which diverges in the vicinity of $\langle n\rangle = 0$ when divided by the coherent third-order correlation function $G_3^{\mathrm{coh}} = \langle n\rangle^3$. For high mean photon numbers, the correlation function is equal to $15\langle n\rangle^3$, capturing the $(2N - 1)!!$ strongly squeezed vacuum enhancement factor for $N = 3$. However, if tuned near resonance, saturation is approached much faster, with the observation of the expected enhancement being problematic.

In order to illustrate cases that are in contrast to the above results, in Figs. 9 and 10 we show the behavior for the relatively large detuning of $\Delta_2/\omega_b = 0.5$ from two-photon resonance. These results have been obtained through the rate equations by taking averages of Eq. (48) over the respective photon probability distributions. Although a detuning of this magnitude may be a bit too large, within the constraints of our model, let us nevertheless examine the dependence of ionization as a function of intensity.

For $\sigma = 0.0003$ a.u. corresponding approximately to a cross section about 10^{-20} cm^2, the ratios tend to stabilize to values with the enhancements factors 6 and 15, reflecting the chaotic and squeezed vacuum correlation functions, respectively. Eventually, even the off-resonant curves will fall to unity, but much more slowly than the near-resonant ones. As in the two-photon case, the specific form of the three-photon ionization rate (48) implies that the ratios will only depend

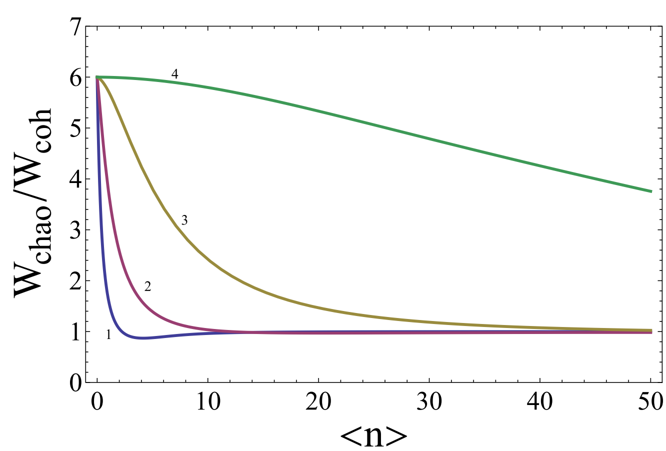

FIG. 9. Ratio of chaotic over coherent three-photon ionization rate as a function of the mean photon number, for various detunings from the second intermediate resonance. The value of the cross section used is $\sigma = 0.0003$ a.u. (1) Blue line: $\Delta_2/\omega_b = 0.0001$; (2) red line: $\Delta_2/\omega_b = 0.01$; (3) olive line: $\Delta_2/\omega_b = 0.05$; (4) green line: $\Delta_2/\omega_b = 0.5$.

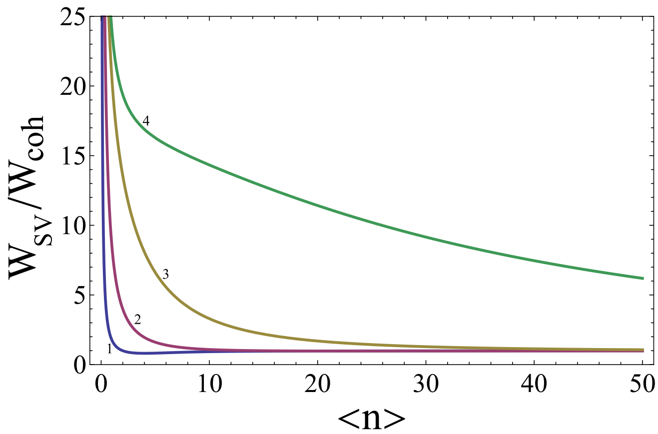

FIG. 10. Ratio of squeezed vacuum over coherent three-photon ionization rate as a function of the mean photon number, for various detunings from the second intermediate resonance. The value of the cross section used is $\sigma = 0.0003$ a.u. (1) Blue line: $\Delta_2/\omega_b = 0.0001$; (2) red line: $\Delta_2/\omega_b = 0.01$; (3) olive line: $\Delta_2/\omega_b = 0.05$; (4) green line: $\Delta_2/\omega_b = 0.5$.

on σ and Δ_2. The effective two-photon dipole matrix element $\mu^{(2)}$ does not appear in the ratios, but has to be such that it does not invalidate the rate approximation. If the cross section σ is chosen, for example, one order of magnitude larger than 0.0003 a.u., even the green curves approach unity very rapidly. But for cross sections smaller than 0.0003 a.u., the ratios do indeed stabilize to the theoretical enhancement factors for a broad range of intensities in the nonresonant limit. Since the values of the parameters we have chosen in the above illustrations are not unphysical, the message that emerges is that the conditions satisfying the nonresonant assumption are quite sensitive to the interplay between intensity and parameters.

VI. CONCLUSION AND CLOSING REMARKS

An N-photon transition from a bound state to a continuum, such as ionization, involves summation over intermediate states. As long as it may be justified to assume that all of them are "sufficiently" far from resonance with the absorption of one or more photons, a transition probability proportional to the Nth-order intensity correlation function is meaningful. Theoretically, the matter stops there, as has been the case with much of the related literature [1–6,19,25]. Given, however, that any nonlinear process is observable only if the intensity is sufficiently strong, the nonresonant condition cannot be taken for granted beyond a theoretical academic exercise or, at best, proof of principle.

A two- or three-photon process should be optimal for nonresonant ionization, as it may be possible to select the photon frequency so as to satisfy the nonresonant requirement, up to some intensity enabling observability. For four- or higher-order processes, it is practically impossible to avoid near resonance with intermediate states because, with increasing energy, their spacing becomes progressively denser. As we have shown in this paper, however, even for two- and three-photon ionization, it is only at quite low intensity that the condition of nonresonance can be taken for granted. As a consequence, the enhancement expected for chaotic or squeezed radiation will more often than not be smaller than predicted on the basis of the relevant intensity correlation function. This may well be the reason that over the 50 years or so that have elapsed since the first predictions of the chaotic enhancement [1–6], even for two-photon ionization a definitive enhancement by the expected factor of 2 has been very difficult to observe, let alone for order of three or higher. There is, of course, always the nagging issue of whether the radiation is truly chaotic or truly coherent [10–12], which in the light of our results poses a dilemma. On the one hand, an N-photon process would be an ideal tool for the measurement of an Nth-order intensity correlation function. On the other hand, the possible influence of intermediate near resonances are apt to be misleading as to the underlying reason for departure from the expected enhancement factor. It seems to us that given the specific atomic system employed in an experiment, only the quantitative evaluation of the role of intermediate states can offer a way out of the dilemma.

The very recent achievement in measuring the enhancement in harmonic generation due to superbunched squeezed radiation reported by Spasibko *et al.* [31] appears to be in contrast to the above dilemma. Actually, for two reasons, the contrast may be only apparent. First, owing to the long wavelength of the radiation in that experiment, the few-photon absorption was within the bound spectrum, satisfying the nonresonant condition. Second, the intensity was quite low; too low to induce a Rabi frequency comparable to the detuning. And the observation of up to the fourth harmonic at such low intensity attests to the elegance of that experiment. Actually, in the medium of that experiment, even the absorption of four photons was energetically well below the first possible resonance. Considering therefore the intensities and structure of the medium, there is no contradiction with our results. On the other hand, even in harmonic generation, at shorter wavelengths reaching into the continuum [36], the issue of intermediate states is of extreme importance. Hoping that it will eventually be possible to explore the effect of superbunching on nonlinear processes at shorter wavelengths and higher intensities, our results can serve as a guide to the planning of relevant experiments.

Departing for the moment from transitions to a continuum, the effect of superbunching on a strongly driven two-photon bound-bound transition, i.e., an extension of its single-photon counterpart solved quite some time ago by Ritsch and Zoller [28,29], poses a daunting theoretical challenge. In early work [16,17], it has been found that in contrast to bound-continuum transitions, chaotic radiation is less effective than coherent radiation in saturating a two-photon bound-bound transition. Would superbunched squeezed radiation be even less effective in that situation? It may well be that squeezed light at wavelengths and intensities appropriate for the strong driving of a bound-bound two-photon transition may be available not too long from now.

Finally, aside from using multiphoton ionization as a "detector" of an intensity correlation function, from the standpoint of enhancing the process induced by bunched radiation, the exact factor of enhancement may not be as important, especially for higher-order processes. Regarding that aspect, the results by Lecompte *et al.*, reported quite some time ago [15], may well be the most dramatic example on record in which, and in line with our analysis, the enhancement was not exactly 11. Still, it was less than two orders of magnitude lower. The enhancement of multiphoton ionization under chaotic radiation has reemerged during the last ten years or so for systems driven by free-electron-laser sources, which are known to exhibit strong intensity fluctuations, similar to those of chaotic radiation [37], and references therein]. The theoretical problem, using realistic simulation of the free-electron-laser (FEL) radiation, has been addressed to some extent [38]. Given that in several experiments fairly high-order ionization processes have been observed [38, and references therein], the intensity fluctuations must surely have played a very significant role. Up to this point, however, there has not been any systematic investigation aiming at the quantification of the effect on experimental data.

ACKNOWLEDGMENTS

The work on this paper was motivated by questions posed to one of us (P.L.) by Dr. Gerd Leuchs. For this as well as occasional useful discussions, we are very grateful. As always, discussions with Dr. George Nikolopoulos have been quite helpful during our work. In addition, we gratefully acknowledge communication with Dr. Chekhova, after submission of our manuscript, which provided very useful information concerning the compatibility of our results with their data.

APPENDIX: TWO- AND THREE-PHOTON IONIZATION RESOLVENT-OPERATOR FORMALISM

In this Appendix, we present the procedure by which the two- and three-photon ionization probability can be obtained in terms of the resolvent operator.

The resolvent operator is defined via $G(z) \equiv (z - H)^{-1}$, where H is the system Hamiltonian. For two-photon ionization (Sec. III), the equations of motion of the relative resolvent operator matrix elements are

$$(z - \omega_I)G_{II} = 1 + V_{IA}G_{AI}, \tag{A1}$$

$$(z - \omega_\mathrm{A})G_{AI} = V_{AI}G_{II} + \sum_F V_{AF}G_{FI}, \tag{A2}$$

$$(z - \omega_F)G_{FI} = V_{FA}G_{AI}. \tag{A3}$$

We could have taken into account that the intermediate state has a spontaneous decay rate γ_a by making the substitution $\omega_A \to \tilde{\omega}_A = \omega_A - i\gamma_a$; however, such a substitution does not account for the repopulation of $|g\rangle$. In fact, the only way to properly describe the spontaneous decay of excited states is via a theoretical formulation in terms of the density operator. Therefore, in this approach, we neglect the spontaneous decay in the sense that it is negligible compared to the ionization rate for the combination of parameters considered in our problem.

Solving Eq. (A3) for G_{FI} and substituting back to Eq. (A2) yields

$$\left(z - \omega_A - \sum_F \frac{|V_{FA}|^2}{(z - \omega_F)}\right)G_{AI} = V_{AI}G_{II}. \tag{A4}$$

If the continuum of states is smooth, z can be replaced by ω_A in the denominator of $\frac{|V_{FA}|^2}{(z-\omega_F)}$, in the sense that this term is a slowly varying function of z and its value is significant only for $z \simeq \omega_A$. After some standard algebra [20,21], one finds that the sum over all final states is reduced to a complex number whose real and imaginary parts represent the shift and the width of state $|a\rangle$ due to its coupling with the continuum, respectively. For the sake of simplicity, we neglect the effect of the shift and focus on the width introduced, which is related to the coupling of the discrete state to the continuum via

$$\Gamma_A = 2\pi |V_{FA}|^2. \tag{A5}$$

In view of the above, the system of equations can be written as

$$(z - \omega_I)G_{II} = 1 + V_{IA}G_{AI}, \tag{A6}$$

$$(z - \omega_A + i\Gamma_A)G_{AI} = V_{AI}G_{II}, \tag{A7}$$

$$(z - \omega_F)G_{FI} = V_{FA}G_{AI}, \tag{A8}$$

whose solution is

$$G_{II} = \frac{z - \omega_A + i\Gamma_A}{(z - \omega_I)(z - \omega_A + i\Gamma_A) - |V_{AI}|^2}, \tag{A9}$$

$$G_{AI} = \frac{V_{AI}}{(z - \omega_I)(z - \omega_A + i\Gamma_A) - |V_{AI}|^2}, \tag{A10}$$

$$G_{FI} = \frac{V_{FA}V_{AI}}{(z - \omega_F)[(z - \omega_I)(z - \omega_A + i\Gamma_A) - |V_{AI}|^2]}. \tag{A11}$$

The denominator in the equation can be factorized as follows:

$$(z - \omega_I)(z - \omega_A + i\Gamma_A) - |V_{AI}|^2 = (z - z_1)(z - z_2), \tag{A12}$$

with

$$z_{1,2} = \tfrac{1}{2}\{(\omega_I + \omega_A - i\Gamma_A) \pm [(\Delta + i\Gamma_A)^2 + 4|V_{AI}|^2]^{1/2}\}. \tag{A13}$$

Therefore, G_{FI} can be written as

$$G_{FI} = \frac{V_{FA}V_{AI}}{(z - \omega_F)(z - z_1)(z - z_2)}. \tag{A14}$$

The matrix elements $U_{ij}(t)$ of the time evolution operator are related to the respective resolvent operator's matrix elements via

$$U_{ij}(t) = -\frac{1}{2\pi i}\int_{-\infty}^{+\infty} e^{-ixt}G_{ij}(x^+)dx, \tag{A15}$$

where $x^+ = x + i\eta$, with $\eta \to 0^+$.

In view of Eq. (A15), it is easy to show that the matrix element of the time evolution operator between the initial and final state of the system is

$$U_{FI}(t) = V_{FA}V_{AI}\left[\frac{\exp(-i\omega_F t)}{(\omega_F - z_1)(\omega_F - z_2)} + \frac{\exp(-iz_1 t)}{(z_1 - \omega_F)(z_1 - z_2)} + \frac{\exp(-iz_2 t)}{(z_2 - \omega_F)(z_2 - z_1)}\right]. \tag{A16}$$

Similar expressions can also be found for $U_{AI}(t)$ and $U_{II}(t)$ using the same procedure. The probability of ionization at times $t > 0$ is

$$P_{\text{ion}}(t) = \int d\omega_F |U_{FI}(t)|^2 = 1 - |U_{AI}(t)|^2 - |U_{II}(t)|^2. \tag{A17}$$

In the case of three-photon ionization (Sec. IV), the equations of motion of the resolvent operator's matrix elements are four, but using the same procedure as described before, the elimination of the continuum leads to the following set of equations:

$$(z - \omega_I)G_{II} = 1 + V_{IA}G_{AI}, \tag{A18}$$

$$(z - \omega_A)G_{AI} = V_{AI}G_{II} + V_{AB}G_{BI}, \tag{A19}$$

$$(z - \tilde{\omega}_B)G_{BI} = V_{BA}G_{AI}, \tag{A20}$$

where $\tilde{\omega}_{\text{B}} = \omega_{\text{B}} - i\Gamma_b$, and Γ_b is the ionization width. Note that the spontaneous decay of the intermediate states has been neglected.

Solving for G_{BI}, one gets

$$G_{BI} = \frac{V_{BA}V_{AI}}{(z - \tilde{\omega}_B)(z - \omega_A)(z - \omega_I) - |V_{AI}|^2(z - \tilde{\omega}_B) - |V_{BA}|^2(z - \omega_I)}. \tag{A21}$$

If z_1, z_2, z_3 are the three roots of the denominator,

$$(z - z_1)(z - z_2)(z - z_3) \equiv (z - \tilde{\omega}_B)(z - \omega_A)(z - \omega_I) - |V_{AI}|^2(z - \tilde{\omega}_B) - |V_{BA}|^2(z - \omega_I), \tag{A22}$$

we can express G_{BI} as

$$G_{BI} = \frac{V_{BA}V_{AI}}{(z - z_1)(z - z_2)(z - z_3)}. \tag{A23}$$

Inversion of resolvent transformation using Eq. (A15) leads to the transition amplitude,

$$U_{BI}(t) = V_{BA}V_{AI}\left[\frac{e^{-iz_1t}}{(z_1 - z_2)(z_1 - z_3)} + \frac{e^{-iz_2t}}{(z_2 - z_1)(z_2 - z_3)} + \frac{e^{-iz_3t}}{(z_3 - z_1)(z_3 - z_2)}\right]. \tag{A24}$$

The same procedure leads to the corresponding expressions for the amplitudes $U_{AI}(t)$ and $U_{II}(t)$. The probability of ionization at times $t > 0$ is given by

$$P_{\text{ion}}(t) = 1 - |U_{II}(t)|^2 - |U_{AI}(t)|^2 - |U_{BI}(t)|^2. \tag{A25}$$

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