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Quantum beats in photoionization from a coherent superposition of fine-structure levels

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We present a theory of quantum beats in photoionization from a coherent superposition of $D_{3/2,5/2}$ levels in alkali-metal atoms. The semiclassical density-matrix formalism is used to describe both the excitation of the $D_{3/2,5/2}$ levels by a two-photon resonant pulse and the subsequent photoionization by a delayed probe pulse. Quantum beats occur in the ionization signal as a function of the delay of the probe pulse. The depth of modulation is determined for different light polarizations.

I. INTRODUCTION

Quantum beats in a variety of contexts have been discussed in a number of papers during the last few years.[1-8] Reported observations have dealt with beats in spontaneous light emission[1-3] and resonant absorption[4] from a coherent superposition of fine- or hyperfine-structure atomic levels, as well as in quasimolecular electron emission from coherently excited autoionizing states.[7] Most recently the observation of beats in dc-field ionization of highly excited D states of Na has also been reported.[5] In addition to its intrinsic interest, the subject of quantum beats presents interest as a tool for the measurement of level splittings.

In this paper we present a theory of quantum beats in photoionization from a coherent superposition of bound fine-structure D levels of alkali-metal atoms excited by two photon absorption. This process can be viewed in some sense as a special case of two-photon-resonant three-photon ionization executed under conditions that maximize the manifestation of beats in the ionization signal. For light linearly polarized, one-photon ionization from a $D_{3/2}$ level leads to $P_{1/2,3/2}$ and $F_{5/2}$ continuum states; while ionization from a $D_{5/2}$ level leads to $P_{3/2}$ and $F_{5/2,7/2}$ continuum states. Interference occurs between the amplitudes from the two D states to the same continuum state. In this case we have separate interferences to the $P_{3/2}$ and $F_{5/2}$ channels. If the two D levels ($D_{3/2}$ and $D_{5/2}$) have been excited in a coherent superposition, this interference gives rise to a modulation of the photoelectron current or the total ionization signal at the frequency of the spin-orbit splitting. The depth of modulation will depend on the polarization of the light and the relative magnitude of the amplitudes leading to the P and F partial waves.

Photoionization appears, at least theoretically, to have advantages in certain cases over fluorescent and resonant absorption spectroscopy. High Rydberg states may be a case in point since their radiative decay is very weak and no optical transitions to higher bound states exist. Although their ionization cross sections are small, one can easily compensate by increasing the light intensity. Moreover, there are circumstances under which the detection of an ionization signal may be more efficient than the detection of photons.

In the experiment by Ducas *et al.*,[4] where quantum beats were observed in resonant absorption from the $3P_{1/2}$ hyperfine components of atomic Na to the $20S_{1/2}$ level, dc-field ionization was employed to measure the population of $20S_{1/2}$. Although the quantum beats were observed in the ionization signal, the quantum interference occured in a bound-bound and not in a bound-free transition which is the case in the present paper. Quantum beats in bound-free transitions observed in dc-field ionization of the $22D_{3/2,5/2}$ levels of the Na have been recently reported by Leuchs and Walther.[5] The D levels were excited by two-photon stepwise absorption from the ground state. Even the above process is in general different from the one discussed herein. Depending on the intensity of the applied dc field, the ionization of a highly excited state—proceeding via tunneling as it does in that case—is considerably more complicated and only partially understood. Consequently the interpretation of quantum beats in such experiments is only qualitatively understood at this time.

Photoionization and resonant absorption are stimulated processes. Unlike the case of quantum beats in fluorescence, the theory of quantum beats in stimulated transitions does not require the quantization of the radiation field. In this paper, we treat the problem in a semiclassical density-matrix formalism. The theory describes the excitation of the $D_{3/2,5/2}$ levels in a coherent superposition by a two-photon-resonant pulse and the sub-

sequent photoionization by a delayed probe pulse. The beats can be observed either in the ionization current or in the total collected charge as a function of the time delay of the probe pulse. However, if the beats are to correspond to the unperturbed fine-structure splitting, the intensity of the probe pulse must be below a certain maximum value as discussed in Sec. II.

II. THEORY OF QUANTUM BEATS IN PHOTOIONIZATION

We consider an alkali-metal atom modeled by the system shown in Fig. 1. Level $|1\rangle$ represents the $S_{1/2}$ ground level, $|2\rangle$ and $|3\rangle$ a $D_{3/2,5/2}$ doublet and the set $\{|l\rangle\}$ stands for all $P_{1/2,3/2}$ and $F_{5/2,7/2}$ levels, bound or free. To observe quantum beats in the photoionization from the $D_{3/2,5/2}$ levels the atom is first excited in a superposition of these two levels by two-photon absorption. At time $t=0$ the atom in the ground state is irradiated by an optical pulse

$$\vec{E}_a(t)=\hat{e}_a[\epsilon_a(t)e^{i\omega_a t}+\epsilon_a^*(t)e^{-i\omega_a t}], \tag{1}$$

where $\hat{e}_a$ is the polarization unit vector, $\epsilon_a(t)$ the complex amplitude which is nonzero only in the time interval $0<t<t_a$, and ω_a the center frequency of the field which is chosen such that $2\omega_a \simeq \omega_{21} + \frac{1}{2}\omega_{32} = \omega_{31} - \frac{1}{2}\omega_{32}$.

The atom-field interaction is described by the equation of motion for the density matrix ρ

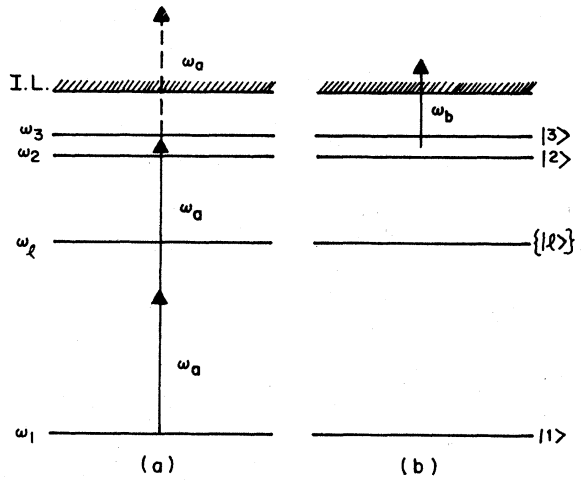

FIG. 1. Schematic diagram for observation of quantum beats in photoionization from a coherent superposition of levels $|2\rangle$ and $|3\rangle$ carried out in two steps: (a) Two-photon excitation from the ground level $|1\rangle$. $\{|l\rangle\}$ is the set of all levels with allowed dipole transitions to levels $|1\rangle$, $|2\rangle$, and $|3\rangle$. The dotted arrow indicates ionization during the excitation step. (b) Ionization by a delayed probe pulse.

$$i\hbar\frac{\partial\rho}{\partial t}=[H_a+H'(t),\rho], \tag{2}$$

where H_a is the unperturbed atomic Hamiltonian and $H'(t)=-\vec{\mu}\cdot\vec{E}_a(t)$ the electric dipole ($\vec{\mu}$) interaction. Making the rotating wave-approximation, i.e., $\rho_{12}(t)=\sigma_{12}(t)e^{i2\omega_a t}$, $\rho_{13}(t)=\sigma_{13}(t)e^{i2\omega_a t}$, $\rho_{23}(t)=\sigma_{23}(t)$, and $\rho_{ii}(t)=\sigma_{ii}(t)$, $i=1,2,3$ and eliminating adiabatically the intermediate bound levels and the ionization continuum,[9] we obtain the following set of equations:

$$\left(\frac{d}{dt}+i(2\omega_a-\omega_{21}-\delta\omega_{21})+\tfrac{1}{2}(\Gamma_2+\gamma_2)\right)\sigma_{12} = i\hbar^{-2}\gamma_{12}\epsilon_a^2(\sigma_{22}-\sigma_{11})-i\hbar^{-2}q_{32}|\epsilon_a|^2\sigma_{13} + i\hbar^{-2}\gamma_{13}\epsilon_a^2\sigma_{23}^*, \tag{3}$$

$$\left(\frac{d}{dt}+i(2\omega_a-\omega_{31}-\delta\omega_{31})+\tfrac{1}{2}(\Gamma_3+\gamma_3)\right)\sigma_{13} = i\hbar^{-2}\gamma_{13}\epsilon_a^2(\sigma_{33}-\sigma_{11})-i\hbar^{-2}q_{32}|\epsilon_a|^2\sigma_{12} + i\hbar^{-2}\gamma_{12}\epsilon_a^2\sigma_{23}, \tag{4}$$

$$\left(\frac{d}{dt}+i(\omega_{23}+\delta\omega_{23})+\tfrac{1}{2}(\Gamma_2+\Gamma_3+\gamma_2+\gamma_3)\right)\sigma_{23} = i\hbar^{-2}|\epsilon_a|^2(q_{32}^*\sigma_{33}-q_{32}\sigma_{22}) - i\hbar^{-2}(\gamma_{13}\epsilon_a^2\sigma_{12}^*-\gamma_{12}\epsilon_a^{*2}\sigma_{13}), \tag{5}$$

$$\frac{d}{dt}\sigma_{11}=\Gamma_2\sigma_{22}+\Gamma_3\sigma_{33} + 2\hbar^{-2}\mathrm{Im}(\gamma_{12}\epsilon_a^{*2}\sigma_{12}+\gamma_{13}\epsilon_a^{*2}\sigma_{13}), \tag{6}$$

$$\left(\frac{d}{dt}+\Gamma_2+\gamma_2\right)\sigma_{22} = -2\hbar^{-2}\mathrm{Im}(\gamma_{12}\epsilon_a^{*2}\sigma_{12}-q_{32}|\epsilon_a|^2\sigma_{23}), \tag{7}$$

$$\left(\frac{d}{dt}+\Gamma_3+\gamma_3\right)\sigma_{33} = -2\hbar^{-2}\mathrm{Im}(\gamma_{13}\epsilon_a^{*2}\sigma_{13}+q_{32}^*|\epsilon_a|^2\sigma_{23}). \tag{8}$$

In the equations above, the parameters γ_{12} and γ_{13} are composite matrix elements for the two-photon transitions $|1\rangle \leftrightarrow |2\rangle$ and $|1\rangle \leftrightarrow |3\rangle$, respectively, and are given by

$$\gamma_{1k}(\omega_a)=\sum_{l\neq k}\frac{\mu_{1l}\mu_{lk}}{\omega_{lk}+\omega_a}, \quad k=2,3 \tag{9}$$

with $\mu=\vec{\mu}\cdot\hat{e}_a$ and the summation being over all virtual intermediate states, bound or free. The parameter q_{32} is a composite matrix element for the two-photon transition $|2\rangle \leftrightarrow |3\rangle$ and is given by

$$q_{32}(\omega_a) = q'_{32}(\omega_a) - iq''_{32}(\omega_a)$$

$$= \sum_l \left(\frac{\mu_{3l}\mu_{l2}}{\omega_{l2} - \omega_a} + \frac{\mu_{3l}\mu_{l2}}{\omega_{l2} + \omega_a} \right), \tag{10}$$

where the imaginary part $q''_{32}(\omega_a)$ arises from the pole in the ionization continuum at $\omega_l = 3\omega_a \simeq \omega_2 + \omega_a$. The optical Stark shifts $\delta\omega_{21}$, $\delta\omega_{31}$, and $\delta\omega_{32}$ can be expressed in terms of the real parts of the polarizabilities

$$\delta\omega_{jk} = \hbar^{-1}[\alpha'_k(\omega_a) - \alpha'_j(\omega_a)]\,|\epsilon_a(t)|^2, \tag{11}$$

where the polarizabilities are given by

$$\alpha_k(\omega_a) = \alpha'_k(\omega_a) - i\alpha''_k(\omega_a) = \hbar^{-1} \sum_l \left(\frac{|\mu_{kl}|^2}{\omega_{lk} - \omega_a} + \frac{|\mu_{kl}|^2}{\omega_{lk} + \omega_a} \right). \tag{12}$$

For $k = 2, 3$ the imaginary part of the polarizability arises from the pole at $\omega_l = \omega_k + \omega_a$ in the ionization continuum. For $k = 1$ the imaginary part is zero because the photon energy $\hbar\omega_a$ is not sufficient to ionize the ground state. The parameters γ_2 and γ_3 are one-photon ionization rates from levels $|2\rangle$ and $|3\rangle$, respectively, and can be expressed in terms of the imaginary parts of the polarizabilities as

$$\gamma_k = 2\hbar^{-1}\alpha''_k(\omega_a)\,|\epsilon_a(t)|^2, \quad k = 2, 3 \tag{13}$$

which is equal to the one-photon ionization cross section multiplied by the photon flux. Finally, we have introduced the spontaneous decay rates Γ_2 and Γ_3 from levels $|2\rangle$ and $|3\rangle$ to intermediate levels $|l\rangle$. For simplicity we have here assumed that from the intermediate levels the atom returns to the ground level in a time shorter than $1/\Gamma_2$ or $1/\Gamma_3$. Note that here we have $\Gamma_2 = \Gamma_3$.

Equations (3)–(8) describe the preparation of the atom in a superposition of the $D_{3/2}$ and $D_{5/2}$ levels taking into account the effects of Stark shifts, ionization, and saturation.[10] If the exciting pulse is not Fourier limited, the amplitude $\epsilon_a(t)$ can be considered as a stochastic process. The equations for the density-matrix elements can then be averaged statistically to account also for the incoherence of the exciting pulse.[11] As we will see later on, for maximum depth of modulation in the quantum beat signal the pulse must leave the atom excited in a coherent state such that $\sigma_{22}(t_a) = \sigma_{33}(t_a) = |\sigma_{23}(t_a)|$. For a large ionization signal we must also have a large two-photon excitation $[\sigma_{22}(t_a) \to \frac{1}{2}]$. To achieve these conditions the intensity, center frequency ω_a, and duration of the exciting pulse must be chosen appropriately. The optimum values for these parameters of the exciting pulse depend on the particular atomic system and on whether or not the pulse is Fourier limited. For coherent excitation by Fourier-limited pulses the analysis is too complicated and requires numerical solution of the density-matrix equations. The optimum pulse for this type of excitation would be nearly a two-photon π pulse. For weak two-photon excitation with a broadband laser the density-matrix equations can be reduced to simple rate equations and the analysis is simplified. In that case one finds[3] that the pulse duration must satisfy the condition $t_a \ll |\omega_{32}|^{-1}$ in order for $|\sigma_{23}(t_a)|$ to be comparable to $\sigma_{22}(t_a)$ and $\sigma_{33}(t_a)$. In what follows we assume that the exciting pulse has left a large number of atoms in a coherent superposition of the $D_{3/2}$ and $D_{5/2}$ levels.

After the end of the $\vec{E}_a(t)$ pulse, the atomic system evolves freely with the excited $D_{3/2,5/2}$ levels decaying spontaneously. At time $t_0 = t_a + t_d$ the density-matrix elements σ_{22}, σ_{33}, and σ_{23} are given by

$$\sigma_{22}(t_0) = \sigma_{22}(t_a)e^{-\Gamma_2 t_d}, \tag{14}$$

$$\sigma_{33}(t_0) = \sigma_{33}(t_a)e^{-\Gamma_3 t_d}, \tag{15}$$

$$\sigma_{23}(t_0) = \sigma_{23}(t_a)\exp\{[i\omega_{32} - \tfrac{1}{2}(\Gamma_2 + \Gamma_3)]t_d\}. \tag{16}$$

The off-diagonal matrix element σ_{23} precesses at the frequency of the fine-structure splitting ω_{32}. To observe this precession in the photoionization current, the atom is irradiated again by a probe pulse

$$\vec{E}_b(t) = \hat{e}_b[\epsilon_b(t)e^{i\omega_b t} + \epsilon_b^*(t)e^{-i\omega_b t}], \tag{17}$$

where $\hat{e}_b$ is the polarization unit vector, and $\epsilon_b(t)$ the complex amplitude which is nonzero only in the interval $t_0 < t < t_0 + t_b$. The center frequency ω_b is chosen such that atoms in the excited $D_{3/2,5/2}$ levels can be ionized by absorption of a single photon. We also require that ω_b be such that the probe does not couple resonantly the $D_{3/2,5/2}$ levels with any other bound level of the atom. Under these conditions the equations for the density-matrix elements σ_{22}, σ_{33}, and σ_{23} are

$$\left(\frac{d}{dt} + i(\omega_{23} + \delta\omega_{23}) + \tfrac{1}{2}(\Gamma_2 + \Gamma_3 + \gamma_2 + \gamma_3)\right)\sigma_{23} = i\hbar^{-2}|\epsilon_b|^2(q^*_{32}\sigma_{33} - q_{32}\sigma_{22}), \tag{18}$$

$$\left(\frac{d}{dt} + \Gamma_2 + \gamma_2\right)\sigma_{22} = 2\hbar^{-2}|\epsilon_b|^2\,\mathrm{Im}(q_{32}\sigma_{23}), \tag{19}$$

$$\left(\frac{d}{dt} + \Gamma_3 + \gamma_3\right)\sigma_{33} = -2\hbar^{-2}|\epsilon_b|^2\,\mathrm{Im}(q^*_{32}\sigma_{23}), \tag{20}$$

where $\delta\omega_{23}$, q_{32}, γ_2, and γ_3 are evaluated at the frequency and the field strength of the probe.

The probability current for photoionization is given by

$$\frac{dP_{\mathrm{ion}}}{dt} = -\frac{d}{dt}\sum_i \sigma_{ii} = \gamma_2(t)\sigma_{22}(t) + \gamma_3(t)\sigma_{33}(t) + 2\gamma_{23}(t)\,\mathrm{Re}[\sigma_{23}(t)], \tag{21}$$

where $\gamma_{23}=2\hbar^{-2}q''_{32}|\epsilon_b(t)|^2$. The first two terms correspond to direct ionization from levels $|2\rangle$ and $|3\rangle$, while the third term corresponds to quantum interference in the ionization from the two D levels to the same final free-electron states. Solving Eqs. (18)–(20) to lowest order in $|\epsilon_b(t)|^2$, we obtain

$$\sigma_{22}(t)=\sigma_{22}(t_a)e^{-\Gamma_2 t_d}\exp\left(-\int_{t_0}^{t}[\Gamma_2+\gamma_2(t')]dt'\right), \tag{22}$$

$$\sigma_{33}(t)=\sigma_{33}(t_a)e^{-\Gamma_3 t_d}\exp\left(-\int_{t_0}^{t}[\Gamma_3+\gamma_3(t')]dt'\right), \tag{23}$$

$$\sigma_{23}(t)=\sigma_{23}(t_a)\exp\{[i\omega_{32}-\tfrac{1}{2}(\Gamma_2+\Gamma_3)]t_d\}\times\exp\left(\int_{t_0}^{t}\{i[\omega_{32}+\delta\omega_{32}(t')]-\tfrac{1}{2}[\Gamma_2+\Gamma_3+\gamma_2(t')+\gamma_3(t')]\}dt'\right). \tag{24}$$

This approximation is valid provided that

$$2\hbar^{-2}|q_{32}(\omega_b)||\epsilon_b(t)|^2\ll|\omega_{32}+\overline{\delta\omega}_{32}|,$$

where $\overline{\delta\omega}_{32}$ is the average value of the relative Stark shift during the pulse. This condition implies that (a) the probe pulse causes no significant population redistribution between levels $|2\rangle$ and $|3\rangle$, and (b) the interference in the ionization probability has negligible effect on the evolution of the atomic system. The population redistribution is associated with the real part of q_{32} while interference in ionization is associated with the imaginary part of q_{32}. Note that the upper limit on the intensity of the probe imposed by the above condition could be increased by decreasing the magnitude of the real part of $q_{32}(\omega_b)$. This could be achieved by tuning ω_b so that there is destructive interference between the contributions from the different bound states and the continuum. If the real part of q_{32} is made smaller than the imaginary part, then the above condition reduces to $\gamma_{23}\ll|\omega_{32}+\overline{\delta\omega}_{32}|$. Since $\gamma_{23}\ll\gamma_2\simeq\gamma_3$ (see Sec. III), this last condition can also be written as $\gamma_2\lesssim|\omega_{32}+\overline{\delta\omega}_{32}|$. If $|\omega_{32}|\gg|\overline{\delta\omega}_{32}|$, the maximum allowable ionization rate is equal to the natural level splitting. If $|\overline{\delta\omega}_{32}|\gg|\omega_{32}|$, then the maximum allowable ionization rate can be greater than the natural level splitting.

Substituting Eqs. (22)–(24) into Eq. (21) we obtain

$$\frac{dP_{\rm ion}}{dt}=\gamma_2(t)\sigma_{22}(t_a)e^{-\Gamma_2 t_d}\exp\left(-\int_{t_0}^{t}[\Gamma_2+\gamma_2(t')]dt'\right)+\gamma_3(t)\sigma_{33}(t_a)e^{-\Gamma_3 t_d}\exp\left(-\int_{t_0}^{t}[\Gamma_3+\gamma_3(t')]dt'\right)$$
$$+2\gamma_{23}(t)|\sigma_{23}(t_a)|\cos(\omega_{32}t_d+\theta)e^{-(\Gamma_2+\Gamma_3)t_d/2}\exp\left(-\frac{1}{2}\int_{t_0}^{t}[\Gamma_2+\Gamma_3+\gamma_2(t')+\gamma_3(t')]dt'\right), \tag{25}$$

where θ is defined by $\sigma_{23}(t_a)=|\sigma_{23}(t_a)|e^{i\theta}$ and we have assumed that the pulse duration (t_b) is such that

$$\int_{t_0}^{t_0+t_b}[\omega_{32}+\delta\omega_{32}(t)]dt\ll 1.$$

This restriction on the pulse duration is imposed so that $\cos(\omega_{32}t_d+\theta)$ is the only oscillatory factor in the ionization signal. As we can see, the (peak) ionization current as a function of the delay time t_d exhibits a sinusoidal modulation with frequency ω_{32}. This modulation is also exhibited in the total probability of ionization by the probe pulse

$$\Delta P_{\rm ion}=\int_{t_0}^{t_0+t_b}\frac{dP_{\rm ion}}{dt}\,dt. \tag{26}$$

III. DEPTH OF MODULATION AND ITS DEPENDENCE ON POLARIZATION

If we assume that $\sigma_{22}(t_a)\simeq\sigma_{33}(t_a)\simeq|\sigma_{23}(t_a)|$ then, since $\Gamma_2=\Gamma_3$ and $\gamma_2\simeq\gamma_3$, the depth of modulation in the probability current as a function of the delay time t_d is given by

$$M=2|\gamma_{23}|/(\gamma_2+\gamma_3). \tag{27}$$

The value of M depends on the polarization of the fields $\vec{E}_a(t)$ and $\vec{E}_b(t)$ and also on the relative magnitude of the P and F free-electron partial waves. Consideration of the dipole-transition selection rules shows that the depth of modulation is larger when the field $\vec{E}_a(t)$ exciting the two-photon transition is linearly polarized. Figure 2(a) gives the angular factors of the $D\rightarrow P$ and $D\rightarrow F$ bound-free

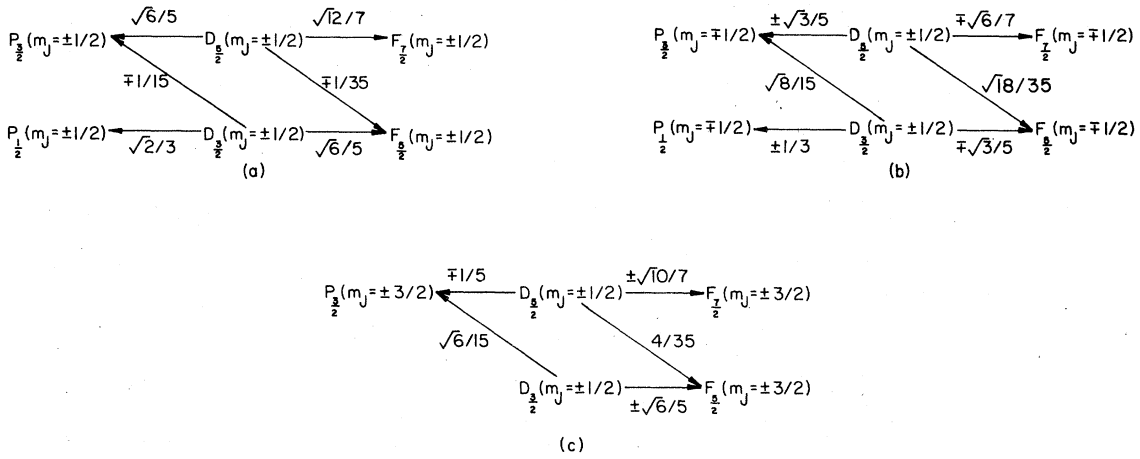

FIG. 2. Angular factors of the $D \rightarrow P$ and $D \rightarrow F$ electric dipole matrix elements.

dipole matrix elements for the case in which $\vec{E}_b(t)$ is linearly polarized in the same direction as $\vec{E}_a(t)$ ($\hat{e}_a = \hat{e}_b$). The two different initial states ($m_j = \pm\frac{1}{2}$) lead to opposite signs for γ_{23}. However, the same is true for the sign of r_{12} and hence σ_{23}. Therefore, in this case the modulations in the $m_j = +\frac{1}{2}$ and $m_j = -\frac{1}{2}$ photoelectrons are in phase. Using Fig. 2(a) we find

$$M = 2\frac{\frac{1}{5}\sqrt{6}(\frac{1}{15})r_P^2 + \frac{1}{5}\sqrt{6}(\frac{1}{35})r_F^2}{[(\frac{1}{5}\sqrt{6})^2 + (\frac{1}{15})^2 + (\frac{1}{3}\sqrt{2})^2]r_P^2 + [(\frac{1}{7}\sqrt{12})^2 + (\frac{1}{35})^2 + (\frac{1}{5}\sqrt{6})^2]r_F^2} = 2\frac{\frac{1}{15}\sqrt{6}\,r_P^2 + \frac{1}{35}\sqrt{6}\,r_F^2}{\frac{7}{3}r_P^2 + \frac{17}{7}r_F^2}, \tag{28}$$

where r_P and r_F are the $D \rightarrow P$ and $D \rightarrow F$ bound-free radial dipole matrix elements. If the P wave dominates ($r_P^2 \gg r_F^2$) $M = \frac{2}{35}\sqrt{6} \simeq 0.14$, while if the F wave dominates $M = \frac{2}{85}\sqrt{6} \simeq 0.06$. Usually, the lower-angular-momentum photoelectron partial wave dominates very near the ionization threshold, but as the energy of the photoelectron increases, the higher-angular-momentum partial wave takes over. Therefore, large depth of modulation can be obtained if ω_b is such that $2\omega_a + \omega_b$ lies just above the ionization limit.

A larger depth of modulation is obtained if the probe field $\vec{E}_b(t)$ is circularly polarized relative to the linearly polarized $\vec{E}_a(t)$ field. Figures 2(b) and 2(c) give the angular factors of the $D \rightarrow P$ and $D \rightarrow F$ bound-free dipole matrix elements for this combination of field polarizations. It is evident that for each of the two initial states, the interference in the $P_{3/2}$ and $F_{5/2}$ photoelectron partial waves subtract thus reducing the depth of modulation in the total electron current. Moreover, in this case the modulation in the $m_j = \pm\frac{3}{2}$ and $m_j = \pm\frac{1}{2}$ photoelectrons are 180° out phase and the depth of modulation in the total current is reduced further. Using Figs. 2(b) and 2(c) we find

$$M = 2\,\frac{[(\frac{1}{5}\sqrt{3})(\frac{1}{15}\sqrt{8}) - \frac{1}{5}(\frac{1}{15}\sqrt{6})]r_P^2 + [(-\frac{1}{5}\sqrt{3})(\frac{1}{35}\sqrt{18}) - (-\frac{1}{5}\sqrt{6})(\frac{4}{35})]r_F^2}{[(\frac{1}{3})^2 + (\frac{1}{5}\sqrt{3})^2 + (\frac{1}{15}\sqrt{8})^2 + (\frac{1}{5})^2 + (\frac{1}{15}\sqrt{6})^2]r_P^2 + [(\frac{1}{5}\sqrt{3})^2 + (\frac{1}{35}\sqrt{18})^2 + (\frac{1}{7}\sqrt{6})^2 + (\frac{4}{35})^2 + (\frac{1}{7}\sqrt{10})^2]r_F^2}$$

$$= 2\,\frac{\frac{1}{75}\sqrt{6}\,r_P^2 + \frac{1}{175}\sqrt{6}\,r_F^2}{\frac{1}{3}r_P^2 + \frac{35}{49}r_F^2}. \tag{29}$$

If the P wave dominates $M = \frac{6}{75} \simeq 0.2$, while if the F wave dominates $M = \frac{2}{125}\sqrt{6} \simeq 0.04$. The modulations in the total electron current obtained with right- and left-hand circularly polarized $\vec{E}_b(t)$ are 180° out of phase. Subtracting the signals for right- and left-hand circular polarization the dc component is removed and errors owing to fluctuations can be reduced.[4]

In the discussion above, we considered the depth of modulation in the ionization probability current integrated

over the direction of electron emission. The angular distribution of the ionization probability current is given by

$$\frac{d}{d\Omega_{\vec{K}}}\left(\frac{dP_{\rm ion}}{dt}\right)=\frac{d\gamma_2}{d\Omega_{\vec{K}}}\sigma_{22}+\frac{d\gamma_3}{d\Omega_{\vec{K}}}\sigma_{33}+2\frac{d\gamma_{23}}{d\Omega_{\vec{K}}}Re(\sigma_{23}) \tag{30}$$

with $d\Omega_{\vec{K}}$ being a differential solid angle in the direction of the wave vector $\vec{K}$ of the free electron,

$$\frac{d\gamma_2}{d\Omega_{\vec{K}}}=2\hbar^{-1}e^2|\epsilon_b(t)|^2\mathrm{Re}\Bigg(\sum_{l=1,3}\sum_{l'=1,3}\sum_{m_l=-l}^{l}\sum_{m_l'=-l}^{l'}\sum_{j=l-1/2}^{l+1/2}\sum_{j'=l'-1/2}^{l'+1/2} i^l(-i)^{l'}e^{-i(\delta_l-\delta_{l'})}(lsm_lm_s|lsjm_j)(l'sm'_lm_s|l'sj'm'_j)^*$$
$$\times\langle 2|\vec{r}|E_k;ljm_j\rangle\langle 2|\vec{r}|E_k;l'j'm'_j\rangle^*$$
$$\times Y^*_{lm}(\theta_k,\phi_k)Y_{l'm'}(\theta_k,\phi_k)\Bigg) \tag{31}$$

and similar expressions for $d\gamma_3/d\Omega_{\vec{k}}$ and $d\gamma_{23}/d\Omega_{\vec{k}}$. In Eq. (31) e is the electronic charge, δ_l the phase shift of the partial wave with angular momentum l, $(lsm_lm_s|lsjm_j)$ a Clebsch-Gordan coefficient, $\langle 2|\vec{r}|E_K=\hbar(\omega_2+\omega);ljm_j\rangle$ the bound-free matrix element of the position vector $\vec{r}$, and $Y_{lm}(\theta_k,\phi_k)$ a spherical harmonic. Because of the different angular dependence of $d\gamma_2/d\Omega_{\vec{k}}$, $d\gamma_3/d\Omega_{\vec{k}}$, and $d\gamma_{23}/d\Omega_{\vec{k}}$, a larger depth of modulation could be attained by collecting only those electrons which are emitted within a particular solid angle for which

$$2\frac{d|\gamma_{23}|/d\Omega_{\vec{k}}}{d(\gamma_2+\gamma_3)/d\Omega_{\vec{k}}}>\frac{2|\gamma_{23}|}{\gamma_2+\gamma_3}.$$

The specific direction (θ_k,ϕ_k) for which the depth of modulation is maximum is determined by the relative magnitudes of the dipole matrix elements and the phase shifts of the partial waves. These quantities can be easily calculated to a satisfactory approximation using quantum-defect theory. This optimum direction will in general depend on the particular atom, the D state and the photon energy $\hbar\omega_b$.

IV. CONCLUDING REMARKS

The interest in quantum beats in ionization from coherently excited atomic states is relatively recent. To our knowledge the first observations are due to Leuchs and Walther[5] who observed ionization by a dc field. Beats in photoionization do not seem to have been observed yet but we are aware of two experiments presently in progress. One of the main reasons for the interest in these processes is their possible usefulness in measuring fine- or hyperfine-structure splittings of highly excited states. For a realistic assessment of their merits one should wait until further experience is gained from experiments. At this point, a few comments on the general features of beats in fluorescence and ionization are perhaps pertinent.

The expression for quantum beats in the photoionization current [Eq. (25)] is similar to that for quantum beats in the intensity of fluorescence.[3] In the latter case the signal is proportional to the spontaneous decay rate, which for Rydberg states decreases as n^{-3} with increasing principal quantum number and as a consequence the detection becomes increasingly difficult. The photoionization current, however, is intensity dependent and can be made detectable by increasing the intensity of the laser probe. According to our theory, the maximum allowable laser intensity for observation of quantum beats corresponds to the photoionization rate being equal to the fine-structure splitting. Similarly, in the case of dc-field ionization one would expect that the ionization rate can be made as large as the fine-structure splitting. Using dc-field ionization, Leuchs and Walther[5] were able to measure the fine-structure splitting of the 21D to 31D states of sodium. The fine-structure splitting of the 31D state of sodium is about 3 MHz. Therefore, the maximum ionization rate for measuring that splitting is $6\pi\times10^6$ sec^{-1}. In contrast, the spontaneous decay rate of the 31D state is less than 10^4 sec^{-1}, which is more than three orders of magnitude smaller than the ionization rate. Measuring the fine-structure splitting of the 31D state of sodium by observing quantum beats in fluorescence would be a difficult task. In fact, Fabre *et al.*[1] who used that technique to measure fine-structure splittings of D states in sodium were able to measure only up to the 16D state. For higher states the signal-to-noise ratio was too small for reliable measurements. The method of observing quantum beats as a function of the delay time of a probe pulse adds another advantage to photoionization over fluorescence. In the case of photoionization, the quantum beats can be observed in the total number of photoelectrons produced by the probe pulse [Eq. (26)]. Their detection does not require a fast detector. In the case of fluorescence, how-

ever, quantum beats cannot be observed in the total number of photons emitted. The quantum beats are observed in the intensity of fluorescence (photon flux) and the detection system must have a rise time shorter than the period of the beats. This sets an upper limit on the modulation frequency which can be detected with available detection systems.

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