Theory of resonant multiphoton processes*

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The present paper applies the method of high-intensity quantum electrodynamics developed earlier to several problems of current experimental interest. In this paper the intensity-dependent shifts and widths of atomic levels are calculated and applied to a given transition near resonance. The technique is demonstrated with three examples: the multiphoton ionization of atomic cesium and hydrogen in atomic beams and third-harmonic production in an atomic vapor. It is found that the multiphoton-ionization rate in a relatively weak laser beam (of order 10^8 W/cm^2) is determined by the intensity-dependent level width ($6f$ configuration) as well as the interference of the fine-structure states, and that the rates for hydrogen, in a much more intense beam (of order 10^{12} W/cm^2) are determined by both the intensity-dependent widths and shifts as well as the wave-function renormalization constants. The agreement of these two examples of calculations with the experiments done recently is satisfactory. For third-harmonic production the role of two-photon resonance is emphasized, and the dependence of the generated third-harmonic intensity on the intensity and frequency of the fundamental is discussed. Near resonance, the ratio of third-harmonic intensity to fundamental intensity saturates.

I. INTRODUCTION

Study of the interaction of high-intensity radiation with matter is of interest for its own sake and has possible applications in areas, such as laser-induced fusion, of the greatest possible practical importance. A complete understanding of the fundamental processes which occur when atoms are exposed to intense radiation at optical frequencies is therefore essential. The present paper gives an account of multiphoton ionization of atoms under circumstances when resonances can occur, and of the closely related topic of resonant harmonic production. The method used is based directly on established methods in quantum electrodynamics.

The essential idea in high-intensity quantum electrodynamics is to include the effect of forward scattering in the electron propagator.[1] This amounts to renormalizing the propagator in a way analogous to the renormalization produced by virtual photons.[2] but with two important differences. In high-intensity quantum electrodynamics the renormalization is finite, being done to only those modes present in the incident beam instead of arising from all the modes of the vacuum. Further, the distinction between "self-energy" processes (forward scattering with no intervening processes) and vertex parts becomes blurred, and to avoid overcounting of diagrams, it is necessary to renormalize the external electron lines also.

In Sec. II, four-photon resonant ionization of Cs atom is treated.[3] The asymmetry near resonance[4] is here found to be due to the interference of the $J=\frac{5}{2}$ and $J=\frac{7}{2}$ of the $6f$ configuration. Section III treats the six-photon ionization of the hydrogen atom.[5] Because of the high intensity encountered here, the renormalization effect causes the physical states to shift and to come into resonance with the laser radiation, and a large enhancement in the ionization probability is found. The results of Sec. II and III are consistent with the experimental reports.[4,5] In Sec. IV, we extend the analysis to the problem of optical third-harmonic production in alkali-metal vapors. Here we predict a large resonant enhancement of third-harmonic intensity, if one of the atomic states can be reached by two-photon absorption from the ground state. Finally, in Sec. V, we discuss the theoretical and experimental implications of the results.

II. FOUR-PHOTON RESONANT IONIZATION OF CESIUM ATOM

The experimental work has been reported recently,[4] using a tunable Nd:glass laser. The wavelength is about 1.06 μm. The half-width of the radiation is $\gamma_l \simeq 0.36$ cm^{-1}. The intensity I is about 10^8 W/cm^2. One of the experimental results is the asymmetry of ionization probability near resonance, which is found near the Cs $6f$ level. The off-resonance behavior has been treated earlier.[3] The present section will be devoted to the near-resonance situation.

To begin with, we write the s-photon absorption renormalized amplitude assuming the atom to be in a known initial state at time $t=0$ as

$$\tilde{A}_{fi}^{(s)}(t)=\int d^3r\, d^3r_1\cdots d^3r_s\, dt_1\cdots dt_s\,\Theta(t_s)\bar{\Psi}(\vec{r})\tilde{G}(\vec{r},\vec{r}_1;t-t_1)i\hat{e}\left(\frac{N}{2\omega V}\right)^{1/2}\hat{e}e^{i(\omega t_1-\vec{k}\cdot\vec{r}_1)}$$

$$\times\tilde{G}(\vec{r}_1,\vec{r}_2;t_1-t_2)i\hat{e}\left(\frac{N}{2\omega V}\right)^{1/2}\hat{e}e^{i(\omega t_2-\vec{k}\cdot\vec{r}_2)}\cdots\Psi_i(\vec{r}_s)e^{-i\tilde{E}_i t_s}\,, \tag{1}$$

where $\tilde{G}(\vec{r},\vec{r}';t-t')$ is the renormalized electron propagator taking into account the effect of forward scattering, $\Theta(t)$ is the unit step function, N/V is the photon density, and $\hat{e}=e_\mu\gamma^\mu$, e_μ being the laser photon polarization. The renormalized electron propagator has the form[1]

$$\tilde{G}(\vec{r},\vec{r}';t-t')=\sum_n\Psi_n(\vec{r})\bar{\Psi}_n(\vec{r}')\int_{-\infty}^{\infty}\frac{(d\Omega/2\pi i)e^{i\Omega(t-t')}}{\Omega+\tilde{E}_n+\tilde{H}_{n,n}(-\Omega)}\,, \tag{2}$$

where

$$\Psi_n(\vec{r})=Z_n^{-1/2}\psi_n(\vec{r})\,, \tag{4}$$

$$\tilde{E}_n=E_n+H'_{n,n}(\tilde{E}_n)\,, \tag{3}$$

$$Z_n=1+\frac{\partial H'_{n,n}(\tilde{E}_n)}{\partial(-\tilde{E}_n)}\,. \tag{5}$$

$H_{n,n}(-\Omega)$ and $H'_{n,n}(-\Omega)$ are the matrix elements of the forward-scattering mass operator for the resonant and nonresonant parts, respectively.

Applying (1) with $s=4$ and recognizing that the $6f$ fine-structure levels are the three-photon resonant states, we get

$$\tilde{A}(\tilde{E},t)=e^4I^2\sum_J A_J\langle\tilde{E}|\hat{r}|6\tilde{f},J\rangle\int_{-\infty}^{\infty}\frac{d\Omega}{2\pi i}e^{i\Omega t}\{(\tilde{E}+\Omega)(\tilde{E}_{6s}+4\omega+\Omega)[\tilde{E}_{6f,J}+\omega+\Omega+\tilde{H}^J_{6f,6f}(-\Omega-\omega)]\}^{-1}\,. \tag{6}$$

The nonresonant amplitudes have been omitted. The sum over J includes all relevant fine-structure levels coming from the $6f$ configuration because of spin-orbit coupling; it is necessary to include them individually because they are resonant at different, but not very different, energies. The intensity I equals $N\omega/V$. Then

$$A_J=\sum_{m,n}\langle 6\tilde{f},J|\hat{r}|\tilde{m}\rangle\langle\tilde{m}|\hat{r}|\tilde{n}\rangle\langle\tilde{n}|\hat{r}|6\tilde{s}\rangle \times[(\tilde{E}_m-2\omega-\tilde{E}_{6s})(\tilde{E}_n-\omega-\tilde{E}_{6s})]^{-1}\,. \tag{7}$$

The quantity $\tilde{H}^J_{6f,6f}$ is obtained from the forward-scattering process in which three photons are emitted from $|6f,J\rangle$ leading to $|6s\rangle$ and these three photons are absorbed returning to $|6f,J\rangle$:

$$\tilde{H}^J_{6f,6f}(-\Omega)=\frac{-e^6I^3|A_J|^2}{\tilde{E}_{6s}+3\omega+\Omega}\,. \tag{8}$$

The single-photon absorption from $|6f,J\rangle$ to continuum does not lead to singularity because the integration over the states in the continuum eliminates such a singularity. This behavior is quite different from the resonant denominator involving the transition between any two bound states. The shifted energy $\tilde{E}_{6f,J}$ can be written as

$$\tilde{E}_{6f,J}=\tilde{E}'_{6f,J}+i\gamma_{6f}\,, \tag{9}$$

where γ_{6f} is positive and comes from the imaginary part of the single forward-scattering process, $|6f\rangle+\omega\rightarrow|E\rangle+|6f\rangle+\omega$:

$$\gamma_{6f}=e^2\pi I[\rho(E)|\langle E|\hat{r}|6f\rangle|^2]_{E=E_{6f}+\omega}\,. \tag{10}$$

The dependence of γ_{6f} on J can be neglected, because the splitting is small. For the experiment of interest to us, we have

$$\gamma_{6f}/\gg 1,\quad \gamma_{6f}\gg e^3I^{3/2}|A_J|\,. \tag{11}$$

The ionization probability is given by

$$P(t)=\int d\tilde{E}\,\rho(\tilde{E})|A_{5/2}(\tilde{E},t)+A_{7/2}(\tilde{E},t)|^2\,. \tag{12}$$

With the approximations (11), we find the rate of ionization

$$f(x)=\frac{dP(t)}{dt}=e^6|A_{7/2}+A_{5/2}|^2\gamma_{6f}I^3\frac{[x+\epsilon\delta/(\epsilon+1)]^2+\gamma_{6f}^2}{(x^2+\gamma_{6f}^2)[(x+\delta)^2+\gamma_{6f}^2]}\,, \tag{13}$$

where[6]

$$\epsilon=A_{7/2}/A_{5/2}\approx-1.23\,. \tag{14}$$

In calculating (14), it is necessary to use the state $|nJLSM\rangle$ instead of $|nLSM_lM_s\rangle$; the latter level scheme is not desired because of L-S coupling. In (13), x and δ are defined as

$$x=\tilde{E}'_{6f,5/2}-\tilde{E}_{6s}-3\omega\,, \tag{15}$$

$$\delta=E_{6f,7/2}-E_{6f,5/2}=0.102\ \text{cm}^{-1}\,. \tag{16}$$

For $I\sim1.4\times10^8$ W/cm^2, γ_{6f} is found to be approximately 0.05 cm^{-1}. The maximum of (13) is

found at $x \approx -0.2\delta$. Thus the exponent of $f(x)$ at resonance is slightly less than 2. Let

$$x_0 = \frac{\epsilon\delta}{\epsilon+1} \approx 5.4\delta \approx \tfrac{3}{2}\gamma_l \ , \tag{17}$$

where γ_l is the laser width; then

$$f(x_0)/f(-x_0) \approx 240 \ . \tag{18}$$

This number agrees with the order of magnitude of the reported observation.[4] Thus, the asymmetry near resonance is due to the interference between the states $J = \frac{7}{2}$ and $J = \frac{5}{2}$ of the $6f$ configuration. The variation of the exponent defined by

$$K = \frac{\partial \ln f(x)}{\partial \ln I} \tag{19}$$

as function of the laser frequency near resonance can also be described. Here we note that x is a function of laser intensity I. The resulting curve is as given in an earlier publication,[3] and will not be repeated here.

The effect near resonance shown here demonstrates the importance of the spin-orbit coupling which determines the degree of asymmetry as observed. This coupling has also an effect on the polarization of the final electron ejected from the atom, as was described by Lambropoulos.[7]

III. SIX-PHOTON IONIZATION OF THE HYDROGEN ATOM

The method of Sec. II can be applied to the six-photon ionization of hydrogen atoms. This has been studied experimentally[5] using the second harmonic of a Nd:glass laser with $\omega = 2.343$ eV at power levels approximately 10^{12} W/cm^2. At these powers the atomic levels are shifted appreciably, an effect not important in the Cs experiments, and the resonance occurs between the shifted levels. The resonance exists, therefore, only for incident radiation of the proper range of intensity, the intensity needed depending on the incident frequency.

From (3) and (5), we have

$$\begin{aligned} \tilde{E}_a' &= E_a + \sum_{n=1}^{\infty} A_n(-E_a) I^n \ , \\ Z_a &= 1 + \sum_{n=1}^{\infty} \frac{\partial A_n(-E_a)}{\partial(-E_a)} I^n \ , \end{aligned} \tag{20}$$

where $\tilde{E}_a'$ is assumed to be real,

$$\tilde{E}_a = \tilde{E}_a' + i\gamma_a \tag{21}$$

as in (10). The first two terms in (20) are

$$A_1(-E_a) = -e^2 \sum_n |\langle n|\hat{r}|a\rangle|^2 \left(\frac{1}{E_n - E_a + \omega} + \frac{1}{E_n - E_a - \omega} \right),$$

$$A_2(-E_a) = e^4 \left\{ \sum_{j,k,l} \frac{\langle a|\hat{r}|j\rangle\langle j|\hat{r}|k\rangle\langle k|\hat{r}|l\rangle\langle l|\hat{r}|a\rangle}{(E_j - E_a + \omega)(E_k - E_a + 2\omega)(E_l - E_a + \omega)} + (\text{term with } \omega \to -\omega) \right\} . \tag{22}$$

A simple analysis of hydrogen energy levels indicates that $2s$ and $3p$ are of particular importance. Here we note that

$$\begin{aligned} E_{3p} - E_{1s} - 5\omega &= 0.37 \text{ eV} , \\ E_{2s} - E_{1s} - 4\omega &= 0.83 \text{ eV} . \end{aligned} \tag{23}$$

It is possible, when the laser intensity reaches certain levels, that the renormalized $3p$ state will be the five-photon resonant intermediate state, and that the renormalized $2s$ state will be the four-photon resonant intermediate state. The corresponding ionization widths of $3p$ and $2s$ are, respectively,

$$\gamma_{3p} = \pi e^2 I \left[\rho(E) |\langle E|\hat{r}|3p\rangle|^2 \right]_{E = E_{3p} + \omega} \ , \tag{24}$$

$$\gamma_{2s} = \pi e^4 I^2 \left[\left| \sum_n \frac{\langle 2s|\hat{r}|n\rangle\langle n|\hat{r}|E\rangle}{E_n - E_{2s} - \omega} \right|^2 \rho(E) \right]_{E = E_{2s} + 2\omega} \tag{25}$$

in complete analogy with (11).

A numerical calculation using the tables of Bethe and Salpeter[8] shows that

$$\Delta_5 = \tilde{E}_{3p}' - \tilde{E}_{1s} - 5\omega \approx 0, \quad I \approx 5 \times 10^{11} \text{ W/cm}^2 , \tag{26}$$

and

$$\Delta_4 = \tilde{E}_{2s}' - \tilde{E}_{1s} - 4\omega \approx 0, \quad I \approx 3 \times 10^{12} \text{ W/cm}^2 . \tag{27}$$

The situation is therefore similar to the resonant ionization described in Sec. II. We thus compute the ionization amplitude of (1) with $s = 6$, and compare the result with the simple perturbation calculations using the bare states. For this purpose, we introduce the following quantity

$$R_j = \frac{\text{(Ionization prob. using physical states)}}{\text{(Ionization prob. using bare states)}} \ . \tag{28}$$

The subscript j indicates the number of photons absorbed that will cause resonance in an intermediate physical state; $j = 5$ or 4 when (26) or (27) is satisfied, respectively.

At the intensity levels given in (26) and (27), one can verify the analogous conditions (11) are

satisfied in the present case as well. Thus, it is not hard to derive that

$$R_5 = \frac{(E_{3p} - E_{1s} - 5\omega)^2}{Z_{3p}^2(\Delta_5^2 + \gamma_{3p}^2)} \tag{29}$$

for the intensity near that given in (26), and

$$R_4 = \frac{(E_{2s} - E_{1s} - 4\omega)^2}{Z_{2s}^2(\Delta_4^2 + \gamma_{2s}^2)} \tag{30}$$

for the intensity near that given in (27). In the low-intensity limit, one gets $R_4 = R_5 = 1$, of course. The wave-function renormalization constants Z_{3p} and Z_{2s} are computed in accordance with (20).

A rough quantitative estimate of (29) and (30) can be made using the tables of Bethe and Salpeter.[8] When (26) is used, we find roughly $\gamma_{3p} \approx 100\ \mathrm{cm}^{-1}$, $Z_{3p} \approx 3$, and

$$R_5 \approx 100\,. \tag{31}$$

On the other hand, if (27) is applicable, we have $\gamma_{2s} \approx 30\ \mathrm{cm}^{-1}$, $Z_{2s} \approx 4$, and

$$R_4 \approx 2500\,. \tag{32}$$

The result (32) indeed agrees with the experimental order-of-magnitude report for the intensity level shown in (27). The two-order-of-magnitude increase of (31) at lower intensity can easily be tested experimentally.

The calculations demonstrated here result from the dynamical effect based on the principle of quantum electrodynamics. It is different from the 6! increase due to the "thermal" nature of laser radiation as has been suggested.[9] Whether the experimental results here considered are a dynamical effect or statistical effect of the laser can be easily determined by experiments of this kind without ambiquity. It is clear that the statistical consideration of a 6! increase at $I \approx 3\times10^{12}\ \mathrm{W/cm^2}$ will also result in the same 6! increase at $I \approx 5\times10^{11}\ \mathrm{W/cm^2}$, instead of the number given in (31). In my opinion, the dynamical effect that causes a large increase of the observed ionization probability at the indicated intensities, seems to be more important.

IV. OPTICAL THIRD-HARMONIC PRODUCTION IN ALKALI-METAL VAPORS

The resonant effect considered in Secs. II and III can also be applied to the case of harmonic production. Some suggestion of phase matching has been made recently.[10] However, harmonic production near resonance with an atomic intermediate state has not been explicitly carried out. In the following, we wish to calculate the third-harmonic intensity where the resonance occurs when two photons are absorbed. The situation where resonances occur either at one- or at three-photon absorption is less interesting from a practical point of view, because there exists a strong spatial attenuation as the radiation propagates.

Let the ground state be $|g\rangle$; it is an s state for alkali atoms. We denote the atomic position vector by $\vec{R}_j$. The transition amplitude for the third-harmonic production corresponds to the elementary process where three photons each having energy-momentum $(\omega, \vec{k})$ have been successively absorbed and then a photon $(\omega_3, \vec{k}_3)$ is emitted. The initial and final state of the atom are the same ground state $|g\rangle$. Applying a formula similar to (1), we have the following amplitude:

$$C_j^{(3)}(t) = e^4\left(\frac{N\omega}{2V}\right)^{3/2}\left(\frac{\omega_3}{2V}\right)^{1/2}\xi^*(\omega) \times \xi(3\omega)F(t)\exp[i(3\vec{k} - \vec{k}_3)\cdot\vec{R}_j]\,, \tag{33}$$

where

$$\xi(x) = \sum_n \frac{\langle\tilde{g}|\hat{r}|\tilde{n}\rangle\langle\tilde{n}|\hat{r}|\tilde{I}\rangle}{\tilde{E}_n - \tilde{E}_g - x}\,, \tag{34}$$

$$F(t) = \int_{-\infty}^{\infty}\frac{d\Omega}{2\pi i}\,e^{i\Omega t} \times\{(\Omega + \omega_3 - 3\omega + \tilde{E}_g - i0)[\tilde{E}_g + \Omega + \tilde{H}_{g,g}(-\Omega)] \times[\tilde{E}_I + \Omega - 2\omega + \tilde{H}_{I,I}(-\Omega + 2\omega)]\}^{-1}\,. \tag{35}$$

$|I\rangle$ is the resonant two-photon atomic intermediate state, which may be an S or D state depending on the polarization of the laser radiation. Here

$$\tilde{H}_{g,g}(-\Omega) = -e^4I^2|\xi(\omega)|^2/(\tilde{E}_I + \Omega - 2\omega)\,, \tag{36}$$

$$\tilde{H}_{I,I}(-\Omega) = -e^4I^2|\xi(\omega)|^2/(\tilde{E}_g + \Omega + 2\omega)\,. \tag{37}$$

For simplicity, we assume that the ionization energy of the atom is greater than 3ω but is less than 4ω. Further we may assume, for the sake of argument, that the four-photon ionization rate κ satisfies the condition

$$\kappa t \ll 1\,. \tag{38}$$

For the result to be established below, (38) is always satisfied. Thus $\tilde{E}_g$ is real and $\tilde{E}_I$ can be put into a form similar to (9) or (21) above,

$$\tilde{E}_I = \tilde{E}_I' + i\gamma_I\,, \tag{39}$$

where

$$\gamma_I = \pi e^4 I^2\left[\left|\sum_n \frac{\langle I|\hat{r}|n\rangle\langle n|\hat{r}|E\rangle}{E_n - E_I - \omega}\right|^2\rho(E)\right]_{E=E_I+2\omega} \tag{40}$$

is the two-photon ionization width of $|I\rangle$.

Let

$$\Delta_2 = \tilde{E}_I' - \tilde{E}_g - 2\omega , \tag{41}$$

$$z_\pm = \tfrac{1}{2}\{i\gamma_I - \Delta_2 \pm [(\Delta_2 - i\gamma_I)^2 + 4e^4 I^2 |\xi(\omega)|^2]^{1/2}\} , \tag{42}$$

then (35) becomes

$$F(t) = e^{-iE_6 t}\left[\frac{\partial}{\partial z_+}\left(e^{iz_+ t}\,\frac{z_+(z_+ + \Delta_2 - i\gamma_I)}{(z_+ - z_-)^2(z_+ - x)}\right) + \frac{\partial}{\partial z_-}\left(e^{iz_- t}\,\frac{z_-(z_- + \Delta_2 - i\gamma_I)}{(z_- - z_+)^2(z_- - x)}\right) + e^{ixt}\,\frac{x(x + \Delta_2 - i\gamma_I)}{(x - z_+)^2(x - z_-)^2}\right] , \tag{43}$$

where

$$x = \omega_3 - 3\omega . \tag{44}$$

Let N_A be the total number of atoms contained in a volume $V_A = lA$, where A is the cross section perpendicular to the direction of $\vec{k}$. The probability of the third-harmonic production is found by summing (33) over the position of atoms j, taking the absolute square of the resultant amplitude, and summing over the $(\omega_3, \vec{k}_3)$ photon final state:

$$P_3(t) = V(3\omega)^2 \int_{-\infty}^{\infty} dx \oint d\Omega_{\vec{k}_3} \left| \sum_{j=1}^{N_A} C_j^{(3)}(t) \right|^2 . \tag{45}$$

The third-harmonic intensity is given by

$$I_3 = \frac{3\omega}{A}\,\frac{dP_3(t)}{dt} . \tag{46}$$

Since γ_I is one order higher than $e^2 I|\xi(\omega)|$, one expects that $e^2 I|\xi(\omega)| \gg \gamma_I$, if I is not too big. Furthermore, if $e^2 I|\xi(\omega)|t \ll 1$, then (46) has the form

$$I_3 = 4\pi e^8 G(3\omega)^4 |\xi(\omega)\xi(3\omega)|^2 \left(\frac{I^3}{\Delta_2^2 + 4e^4 I^2 |\xi(\omega)|^2}\right) \times \left(1 + \frac{4e^8 I^4 |\xi(\omega)|^4}{[\Delta_2^2 + 4e^4 I^2 |\xi(\omega)|^2]^2}\right) , \tag{47}$$

where

$$G = \oint d\Omega_{\vec{k}_3} \left| \sum_{j=1}^{N_A} \exp[i(3\vec{k} - \vec{k}_3)\cdot \vec{R}_j] \right|^2 / A . \tag{48}$$

It must be pointed out that, in (45), the x integration is only effective in the integrand containing the function $|F(t)|^2$, which can be calculated from (43). This function is essentially proportional to $\delta(x)$ because of energy conservation. Thus the magnitude of $\vec{k}_3$ appearing in (48) is proportional to 3ω if a normal dispersion relation is used, which is applicable in the present case. The phase factor defined in (48) has a value appreciably different from zero only when a suitable phase matching is satisfied. A detailed quantitative analysis of such a phase-matching condition using a buffer gas has been given by Miles and Harris.[10]

The simple result (47) rests on the approximation which may be summarized as follows:

$$1 \gg e^2 I|\xi(\omega)|t \gg \gamma_I t \gg \kappa t . \tag{49}$$

Here we note that $\gamma_I \propto e^4 I^2$ and $\kappa \propto e^8 I^4$, as mentioned before. The last two inequalities of (49) are justifiable if I is not sufficiently large. The first inequality of (49) can be satisfied if the effective interaction time t is small. This means that a shorter pulse would be better.

We may study I_3 of (47) as a function of I and ω, the laser intensity and frequency. For a given intensity, the only sensitive frequency dependence is through Δ_2 defined in (41); the variation of $|\xi(\omega)|$ can be neglected when $\Delta_2 \simeq 0$. The maximum of I_3 is at exact resonance, namely $\Delta_2 = 0$. This situation can happen even when $E_I - E_g - 2\omega \neq 0$, for the intensity-dependent shift of E_I and E_g can make $\tilde{E}_I' - \tilde{E}_g - 2\omega \equiv \Delta_2 = 0$, with a certain range of I. We also find that at exact resonance, the third-harmonic intensity is linearly proportional to laser intensity instead of its cubic dependence. This situation is similar to the resonant ionization treated in Sec. II. In the semiclassical treatment of Bloembergen[11] a dependence of I^3 is always present. It is clear that near resonance, the Bloembergen method is inapplicable. Off-resonance and in the weak-field limit, (47) agrees with Bloembergen's approach[11] as expected. The resonance effect demonstrated here can be used as an effective method of producing the third-harmonic radiation where the incoming laser intensity can be relatively low. The experimental advantage is thus quite obvious, and need not be elaborated any further.

The situation involved in resonant third-harmonic production is similar to that in resonant multiphoton ionization; only the last step is different. Here, it is a spontaneous transition to the ground state; there, it was an induced transition to the continuum. The appearance of the phase-matching factor is important for the collective production of third harmonic by many atoms necessary for efficient conversion.[10] This factor contains $\vec{k}$ and $\vec{k}_3$. If there exists either a one-photon or a three-photon resonance, the propagation of the incident beam or of the third-harmonic beam will be attenuated, a large imaginary part of the index of refraction being present. In the case examined here, this does not happen because only many-photon resonances occur.

V. DISCUSSION

The work reported in this paper differs from other treatments of multiphoton ionization[12] and resonant harmonic production. In the Cs problem the renormalization of the electron propagator is important while the energy level shifts produced by the radiation field are not large at the intensities used. This renormalization has not been taken into account in any semiclassical calculation known to us. Also the effect of the fine structure on the symmetry of the resonance has not been appreciated in earlier work. The agreement between the asymmetry calculated on the basis of interference between the $J=\frac{5}{2}$ and $J=\frac{7}{2}$ resonances and the observations of Held *et al.*[4] is very satisfactory.

In the H-atom ionization problem the intensities used are high enough to produce significant level shifts, and the resonance occurs between shifted levels. The idea here is quite similar to that of Davydkin *et al.*,[13] who calculated the "quadratic Stark effect" on the atomic levels produced by the incident radiation. The actual calculation of the shifts is quite different, however, and here again the renormalization of the electron propagator plays an essential role. The experimental results[5] to date are not extensive enough to affirm or to contradict the predicted intensity dependence of the resonant effect. The existence of a maximum resonance effect for finite intensity is predicted, of course, by any theory involving an intensity dependence of the resonant level.

The question of the influence of the statistics of the radiation field on the transition probability is an involved one. In the simplest approximation the probability can be expressed as proportional to the sixth-order field correlation function[14]; and this can differ from the sixth power of the intensity by a factor as large as 6! if the light is Gaussian. When more accurate calculations are made, the simple proportion between the transition probability and the correlation function is no longer found. The intensity enters the level shifts and the renormalization constants, and any averaging over an ensemble must involve the entire expression for the transition probability, not just the factor I^6 appearing overall. The high-intensity peaks contributing so much to the correlation function for a Gaussian ensemble do not produce resonance of the intensity-dependent levels and do not, therefore, contribute as much to the transition probability as might have been expected if no resonances played an essential part. The same thing is true in the Cs case, although here only a factor of at most $4!=24$ is involved. Because the level shifts are not important, the high peaks contributing to I^4 will not cause detuning, but again at resonance the transition probability is proportional to I^2, and one should expect at most a factor $2!=2$ to appear if Gaussian light is used.

The harmonic generation calculated in Sec. IV involves features not present in the usual treatments.[11] The most striking difference with other calculations is the intensity dependence of the width term in (47). This has the important effect of producing saturation at high intensity wherever the Δ_2^2 in that expression is smaller than the width term. The closer one is to resonance, the lower the intensity required to produce saturation. If an intensity-independent width is used, the third-harmonic generation remains proportional to I^3, and the conversion efficiency proportional to I^2. In a related process involving parametric amplification via the third-order susceptibility, saturation has been observed.[14]

The resonance involved in (47) is described by the energy levels in the presence of the incident field; so the resonant frequency itself may be dependent on the intensity. In Cs this effect will be small, because the intensity used must be less than that which produces much four-photon ionization, and even in the calculation of this in Sec. II the energy shifts produced by the incident field are negligible.

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