Nonlinear susceptibilities of atoms at frequencies above the ionization threshold

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The first correct calculation is reported of the third-harmonic generation coefficients β and of the hyperpolarizabilities γ of the ground and excited states of hydrogen atoms in alkali metals at above-threshold frequencies. The physical interpretation of the susceptibility due to atomic ionization in an optical field is discussed. A rapid decrease of β and γ at high frequencies is noted. The corrections that must be introduced in the strong-field photoeffect to account for the imaginary part of γ are analyzed. It is shown that an approximate calculation method based on discarding the contribution of the intermediate continuum states to the composite matrix elements of perturbation theory is inadequate even for estimating the nonlinear susceptibilities.

§1. INTRODUCTION

Nonlinear susceptibilities are defined as the coefficients of the expansion of a dipole moment $P(t)$ in powers of the external fields that induce this moment in an atom. They are very important microscopic properties of the atom, and their values determine the feasibility of observing in practice various nonlinear optical phenomena in an atomic gas. We calculate here the simplest nonlinear susceptibilities that determine the dipole interaction of an atom with the electric field of a monochromatic light wave:

$$F(t) = \text{Re}\,[F \exp(-i\omega t)]. \tag{1}$$

The expansion of $P(t)$ in such a field is of the form (summation over repeated indices is implied)

$$P_j(t) = \text{Re}\,\{\alpha_{jk}(\omega)F_k e^{-i\omega t} + \beta_{jklm}(\omega)F_k F_l F_m e^{-3i\omega t}$$
$$+ \gamma_{jklm}(\omega)F_k^* F_l F_m e^{-i\omega t} + O(F^5)\}, \quad j,k,l,m = x,y,z. \tag{2}$$

For an isolated atom, the individual terms in (2) determine the elementary processes that occur when a quantum system interacts with radiation: $\alpha(\omega)$ (dynamic polarization) determines the Rayleigh scattering of the light, $\beta(\omega)$ determines third-harmonic scattering of the incident radiation (three-photon coalescence), and $\gamma(\omega)$ determines the corrections, linear in intensity, to the cross section for Rayleigh scattering, particularly to the degree of polarization and to the angular distribution of the scattered radiation (see §3). In addition, β and γ determine (accurate to F^2 and F^4, respectively) the shift, splitting, and ionization broadening in a field $F(t)$ (at frequencies exceeding the one-photon ionization threshold (it will be shown in §3 that it is incorrect to retain the term with γ in the expansion (2), for in this case γ describes only a property of the atomic level and is not a correction to the dipole moment of the atom). For an atomic gas, the nonlinear susceptibilities β and γ determine coherent nonlinear optical phenomena due to specific elementary processes. Namely, β yields the third-harmonic-generation amplitude and γ the corrections, linear in the light-wave intensity, to the refractive index of the medium. These corrections lead, in particular, to self-focusing and to self-induced rotation of the polarization ellipse of the propagating wave (see Ref. 1).

It should also be noted that γ is in fact a perturbative correction one order higher than the polarizability α. Comparison of α and γ permits therefore a definite estimate of the field intensities that limits the use of perturbation theory to describe nonlinear optical phenomena or to calculate the restructuring of atomic levels in a laser field.

In practice computations of nonlinear susceptibilities entail calculation of composite matrix elements of higher-order perturbation theory. Thus, the tensors β_{jklm}, γ_{jklm} for an atom in a state $|n\rangle$ and having an energy E_n are expressed in terms of linear combinations of matrix elements such as

$$T_{jklm}(\omega_1, \omega_2, \omega_3) = \langle n | d_j G_{E_n+\hbar\omega_1}^{(+)} d_k G_{E_n+\hbar\omega_2}^{(+)} d_l G_{E_n+\hbar\omega_3}^{(+)} d_m | n \rangle, \tag{3}$$

where d_i is the atom-dipole-moment projection operator, and

$$G_E^{(\pm)} = \mathbf{S}_{n'} \frac{|n'\rangle\langle n'|}{E_{n'}-(E\pm i0)} \tag{4}$$

is a Green's function. S denotes here summation over the discrete spectrum ($E_{n'} < 0$) and integration over the continuum ($E_{n'} > 0$) of the atomic states $|n'\rangle$. Note that the choice (discussed below) of the imaginary increment in the denominator of (4) is significant only for $E > 0$, when the integral over the continuum has a pole in terms of the variable $E_{n'}$ which must be enclosed in a specified manner.

In calculations of composite matrix elements it is customary to use only the one-electron approximation, in which the operators d and G in (3) pertain only to the optical electron of the atom. Even in this approximation, however, well-developed calculation methods exist only for the case when all $E_\mu \equiv E_n + \hbar\omega_\mu$ ($\mu = 1,2,3$) in (3) are negative. (This means physically that the frequency ω and its harmonics, which are accounted for in this process, are below the ionization threshold $|E_n|/\hbar$.) One of the most effective calculation methods is to use in (3) for the one-electron Green's function

$$G_E^{(+)}(\mathbf{r},\mathbf{r}') = \sum_{L=0}^{\infty}\sum_{M=-L}^{L} g_L(E;r,r')\,Y_{LM}(\mathbf{r}/r)\,Y_{LM}^*(\mathbf{r}'/r') \quad (5)$$

the Sturm expansion of the radial parts of $g_L(E;r,r')$.[2] This reduces the calculation of the composite matrix elements to a numerical summation of rapidly converging series of hypergeometric polynomials (which we call Sturm series). This was precisely the method used in the first correct calculation of the nonlinear susceptibilities for hydrogen[3,4] and to obtain extensive information on the character of the dispersion relation and on the nonlinear susceptibilities of various atoms.[2]

Data for the $E_\mu < 0$ region alone, however, are insufficient for many vital problems. The study of nonlinear susceptibilities at frequencies above threshold, when ω or its harmonics exceed the ionization threshold, is of interest, particularly when gaseous media are used to generate ultraviolet or soft x rays,[5,6] in planning of experiments on above-threshold ionization of atoms,[7,8] and also in investigations of excited atoms by methods of nonlinear laser spectroscopy.[9] In the latter case the energy of even one optical photon can exceed the binding energy of the state in question.

The Sturm-expansion technique is not directly transferable to the $E_\mu > 0$ region, where the Sturm series diverge. At present, therefore, there are no correct calculations of the nonlinear susceptibilities at frequencies above threshold even in the simplest case of the hydrogen atom. (An attempt to calculate the hyperpolarizability of hydrogen[10] by using directly the spectral expansion (4) did not yield correct results because of the technical difficulty of carrying out multiple integration over continuum states; a recent paper[11] reports calculations, by the Padé-approximant method, of sums of divergent Sturm series, but no results are cited for frequencies above threshold.)

It is important to note that the estimates frequently employed for the susceptibility, with only a small number of discrete-spectrum states taken into account in the spectral expansion (4), are also valid only at $E_\mu < 0$ in quasiresonant situation, when the E_μ are close to the energies of certain bound states. Attempts to refine these estimates, however, which require allowance for a large number of discrete states and discarding the continuum contribution (see, e.g., Refs. 12–14), are utterly unfounded. We show in the Appendix that the separate contributions of the matrix elements (3) by the discrete and continuous spectrum states diverge,[1]) and only the sum is finite. It is clear therefore that at $E_\mu > 0$ one can use only methods that permit account to be taken of the entire intermediate-states spectrum.

We have previously obtained[15] for the Green's functions g_L a Sturm-expansion generalization applicable, in the model-potential approximation, both to a Coulomb potential and to a non-hydrogenic atom.[2] A feature of this expansion is the presence in it of a free parameter α. A suitable choice of α ensures convergence of the Sturm series even at $E_\mu > 0$ (with α dependent on E_μ). The new expansion thus permits extension of the Sturm technique of calculating nonlinear susceptibilities to include the case $E_\mu < 0$. This approach is used in the present paper to calculate the tensors β (§2) and γ (§3) in the hydrogen atom and in alkali atoms. In §4 we discuss nonlinear corrections, determined by the hyperpolarizability $\gamma(\omega)$, to the level shift and to the photoeffect.

§2. THIRD-HARMONIC GENERATION

Expressions for the nonlinear susceptibilities are derived (in the form of expansions in powers of F) by calculating the mean value $\langle\psi|d_j|\psi\rangle$ of the dipole moment in the state $|\psi\rangle$ obtained from the initial state $|n\rangle$ under the action of the field $\mathbf{F}(t)$. The choice between the Green's functions $G^{(+)}$ and $G^{(-)}$ [see Eq. (4)] is determined by the fact that at frequencies above threshold the function $|\psi\rangle$ describes a decay state (called quasistationary quasienergy state).[10,16] The perturbation-theory expansion of $|\psi\rangle$ then contains only the Green's functions $G^{(+)}$ having a divergent-wave asymptote corresponding to decay, while the expansion of $\langle\psi|$ contains the functions $G^{(-)}$. If, however, the frequency ω is regarded as positive, the use of $G^{(-)}$ in the expressions for the susceptibilities is frequently unnecessary. Thus, the expression for the tensor β_{jklm} in terms of the matrix elements (3) is

$$\beta_{jklm} = {}^1\!/_4 S_{klm}\{T_{jklm}(3\omega, 2\omega, \omega)$$
$$+ T_{kjlm}(-\omega, 2\omega, \omega) + T_{kljm}(-\omega, -2\omega, \omega)$$
$$+ T_{klmj}(-\omega, -2\omega, -3\omega)\}, \quad (6)$$

where S_{klm} denotes symmetrization of the expression in the curly brackets with respect to the indices k, l, and m. The Green's functions to the left of the operator d_j in each matrix element must formally be $G^{(-)}$. Just these Green's functions, however, definitely have a negative energy E at $\omega > 0$. $G^{(-)}$ and $G^{(+)}$ are then equal, so that Eq. (6) can be expressed in terms of the matrix elements (3) that contain only $G^{(+)}$ (cf. the analogous discussion of the polarizability tensor α_{jk} in §59 of Ref. 17).

For a nondegenerate initial state $|n\rangle$, the tensor β_{jklm} is expressed in terms of only one atomic parameter $\beta(\omega) \equiv \beta_{zzzz}(\omega)$, and the polarization vector (2) at the frequency 3ω is[18]

$$\mathbf{P}(t) = \mathrm{Re}\{\mathbf{P}(3\omega)e^{-3i\omega t}\}, \quad \mathbf{P}(3\omega) = l\beta(\omega)|\mathbf{F}|^2\mathbf{F}, \quad (7)$$

where $l = |\mathbf{F}^2|/|\mathbf{F}|^2$ is the degree of linear polarization of the wave.

Following integration over the angular and radial variables and the use of expansion (5) and the Sturm expansion of g_L (Ref. 15), the calculation of the matrix elements T in Eq. (6) reduces to summation of series made up of polynomials that can be conveniently expressed in terms of the Appel hypergeometric function F_2. The values of the complex parameters α for each of the three Green's functions in T depend on ω and are chosen by the procedures indicated in Ref. 15. The calculations are more complicated for $E_\mu > 0$ than for $E_\mu < 0$. To obtain a result with three of four significant figures it is necessary to take into account several dozen terms in each series made up of the polynomials F_2. The accuracy required in the calculation of high-power polynomials is ensured by using a set of recurrence relations for the function F_2, and the appropriate relations for the various parameter values are chosen by using an asymptotic expression for F_2 (Ref. 15).
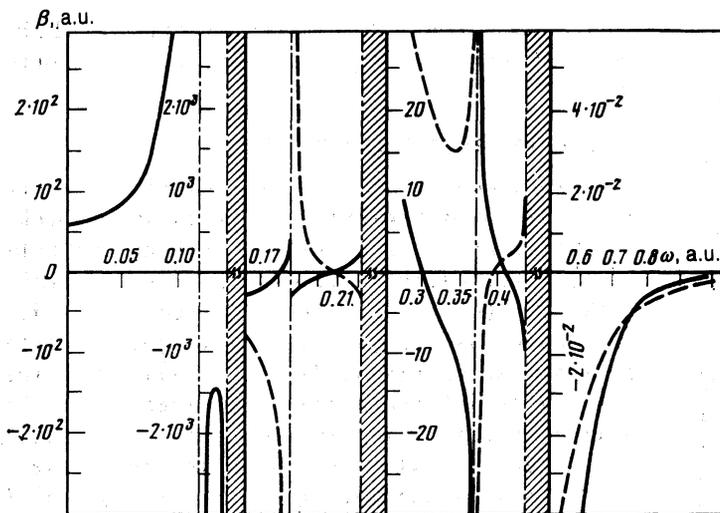
FIG. 1. Dispersion dependences of real (solid line) and imaginary (dashed) parts of the third-harmonic-generation coefficient β for the $1s$ level of hydrogen. The solid and dash-dot vertical lines denote respectively the threshold and resonance frequencies. The near-threshold frequency regions where β has condensing resonances are shaded. The scale along the β axis for different regions of ω are shown in the figure. The ω-axis scale (uniform in each interval) changes on going through the threshold frequencies.

The calculated susceptibility $\beta_{1s}(\omega)$ for the $1s$ state of hydrogen is shown in Fig. 1. The dispersion relation has a large number of singularities, viz., one-, two-, and three-photon resonances, as well as thresholds of one-, two-, and three-photon ionization. So complicated a dependence prevents the characteristic values of β from being specified by only one or two parameters in a wide frequency range. At $\hbar\omega > |E_{1s}|$ the dependence of β_{1s} on ω becomes continuous. In the limit $\hbar\omega \gg |E_{1s}|$ it is possible to obtain the asymptotic expression (in atomic units)

$$\beta_{1s}(\omega) \approx [(1-i)/45\omega^{7,5}][(^2/_3)^{1/2}+2^{1/2}-2]. \tag{8}$$

We note that the numerical coefficient in (8) is small and the asymptotic value is reached at very high frequencies. Therefore, in particular, Fig. 1 should show one more reversal of the sign of $\mathrm{Re}\,\beta_{1s}$ at $\omega > 1$ a.u. Test calculations have shown that $\mathrm{Re}\,\beta_{1s}$ does indeed reverse sign at $\hbar\omega \approx 6|E_{1s}|$. At $\hbar\omega = 20|E_{1s}|$ $\mathrm{Re}\,\beta_{1s}$ and $\mathrm{Im}\,\beta_{1s}$ reach respectively 30% and 85% of their asymptotic value (8).

With increasing principal quantum number n, the asymptotic value of $\beta(\omega)$ decreases:

$$\beta_{ns}(\omega) = n^{-3}\beta_{1s}(\omega), \quad \omega \to \infty.$$

At the same time, the static susceptibilities are known to increase rapidly with increasing n. This dependence on n is preserved also at not-too-high frequencies. Thus, typical values of $\beta_{2s}(\omega)$ at frequencies up to the first threshold ($\hbar\omega < |E_{2s}|/3 = 0.042$ a.u.) are 10^6–10^7 a.u. The values of β_2 for certain frequencies above threshold are given in Table I.

It is also of interest to compare $\beta_{1s}(\omega)$ with the third-harmonic-generation coefficient $\beta^{(\delta)}(\omega)$ for a particle in a short-range potential (δ-well) with binding energy $|E_{1s}|$. The calculation for a δ potential is similar to the calculation of γ in Ref. 10. $\beta^{(\delta)}(\omega)$ has square-root singularities at the ionization thresholds $\omega = \frac{1}{2}$, $2\omega = \frac{1}{2}$, $3\omega = \frac{1}{2}$. In the atom, however, $\beta(\omega)$ tends to a finite limit when ω approaches the threshold frequency from above, and has an infinite number of poles is the threshold is approached from below. This behavior accords with the general theory of threshold singularities for Coulomb and short-range potentials.[19]

The static susceptibilities in a short-range potential are

ω	α	β	γ_l	γ_c	Γ_{2l}	Γ_{2c}
0,043	181	$(3+2i)\cdot 10^8$	$5.69\cdot 10^5$	$4.69\cdot 10^6$	–	–
0,066	980	$(-2.18+6.88i)\cdot 10^4$	$(-19.1+2.59i)\cdot 10^7$	$(-19.7+3.58i)\cdot 10^7$	–	–
0,086	−58,8	$(3.14+6.81i)\cdot 10^3$	$(-6.46+1.52i)\cdot 10^5$	$(-6.12+2.27i)\cdot 10^5$	–	–
0,170	−35.8+17,6i	$-13.4+628i$	$(-2.55+1.89i)\cdot 10^3$	$(-0.46+1.35i)\cdot 10^3$	$3.73\cdot 10^3$	$4.31\cdot 10^3$
0,200	−26.4+10.4i	$22.6-346i$	$368+496i$	$279+385i$	$1.22\cdot 10^3$	$1.39\cdot 10^3$
0,375	−7.62+1.27i	$0.105-0.595i$	$-12.9+1.62i$	$-10.7+1.89i$	14.4	15.4

TABLE II. Nonlinear susceptibilities of 6s level of cesium.

ω	α	β	γ_l	γ_c
0.043	1076	$-5.8\cdot10^6$	$-3.9\cdot10^8$	$-1.2\cdot10^8$
0.066	-539	–	$1.0\cdot10^7$	$1.2\cdot10^7$
0.170	$-38+0.63i$	$-344-19i$	$7080+57i$	$5290-443i$
0.200	$-26+0.15i$	$-168-8i$	$3090+64i$	$2180-67i$

always smaller than in the "looser" Coulomb potential.[20] Thus, as $\omega \to 0$ the polarizability ratio is

$$\alpha_{1s}/\alpha^{(\delta)}=18.$$

The difference increases for susceptibilities of higher order:

$$\beta_{1s}(\omega\to0)/\beta^{(\delta)}(\omega\to0)=74^1/_{16}. \qquad (9)$$

In the high-frequency region, however, the situation changes radically. Whereas the polarizability $\alpha(\omega\to\infty)$ $= -e^2/m\omega^2$ does not depend at all on the form of the potential and is determined by the free-electron oscillations in the wave field, the susceptibility $\beta^{(\delta)}(\omega\to\infty)\sim\omega^{-5,5}$ decreases with increasing ω much more slowly than β_{1s} in (8). The slow decrease of $\beta^{(\delta)}$ arises because the δ-potential is more singular than a Coulomb potential as $r\to0$ ($\beta(\omega\to\infty)\sim\omega^{-8}$ for a particle with a smooth potential).

In non-hydrogenic atoms the qualitative singularities of the dispersion dependence of $\beta(\omega)$ are the same as those of β_{1s} (Fig. 1). By way of example, Table II lists the values of β calculated for the ground state of the Cs atom in the model-potential approximation. Just as in the case of hydrogen, the value of β decreases abruptly beyond the ionization threshold ($|E_6^{(Cs)}| = 0.143$ a.u.). Thus, the quantity $|\beta|^2$, which determines the cross section for third-harmonic generation at the neodymium-laser frequency ω_N, exceeds by almost 10 orders of magnitude the value of $|\beta|^2$ at the frequency $5\omega_N$ (150% of the ionization potential of Cs). At frequencies above threshold, the generation efficiency is decreased not only by the competing ionization, but also by the appreciable decrease of β itself. This can decrease substantially the yield of the harmonics of hard ultraviolet radiation in atomic gases compared with those of optical frequencies.

§3. DYNAMIC HYPERPOLARIZABILITY

The expression for γ (see, e.g., Ref. 2) contains, besides the composite matrix elements (3), also "non-diagrammatic" terms such as

$$T_{jm}^{(N)}(\omega)=\langle n|d_j[G_{E_n+\hbar\omega}^{(+)}]^N d_m|n\rangle, \qquad N=1,2. \qquad (10)$$

For the s state, the dependence of γ on the tensor indices is determined by two atomic parameters, viz, the hyperpolarizabilities $\gamma = \gamma_{zzzz}$ and $\gamma_c = 2\gamma_{zxzx}$ (Ref. 1):

$$\gamma_{jklm}=(\gamma_l-\gamma_c)\delta_{jk}\delta_{lm}+^1/_2\gamma_c(\delta_{jl}\delta_{km}+\delta_{jm}\delta_{kl}). \qquad (11)$$

According to (2), the polarization vector at the frequency ω takes the form

$$\mathbf{P}(t)=\mathrm{Re}\,\{\mathbf{P}(\omega)e^{-i\omega t}\}, \quad P(\omega)=\alpha\mathbf{F}+\{l\gamma_l\mathbf{F}^*+iA\gamma_c[\mathbf{nF}]\}|\mathbf{F}|^2 \qquad (12)$$

(where $\mathbf{n}$ is the unit vector in the wave-propagation direction, $A = i\mathbf{n}[\mathbf{FF}^*]/|\mathbf{F}|^2$ is the degree of circular polarization of the field, and $A^2 + l^2 = 1$). It is recognized here that $\alpha_{jk} = \alpha\delta_{jk}$, while the phase of the complex vector $\mathbf{F}$ is chosen such that $\mathbf{F}^2 = |\mathbf{F}^2|$.

Let us examine the physical meaning and the validity of the expansion (12) in various frequency intervals. At frequencies below threshold, $\hbar\omega < \frac{1}{2}|E_n|$, the susceptibilities α, γ_l, and γ_c are real and the vectors $\mathbf{P}(t)$ and $\mathbf{F}(t)$ oscillate in phase. On going through the two-photon ionization threshold ($\frac{1}{2}|E_n| < \hbar\omega < |E_n|$), Eqs. (12) describe the dipole-moment oscillations of an atom no longer in a bound but in a quasistationary state (see 2). The imaginary parts of the hyperpolarizabilities γ_l and γ_c determine the lag of the $\mathbf{P}(t)$ oscillations behind those of $\mathbf{F}(t)$, a lag due to light-energy absorption caused by the two-photon ionization. At $\hbar\omega > |E_n|$, an imaginary part is acquired also by α and yields the one-photon ionization cross section. It can be shown in this case that allowance for perturbation-theory terms $\propto F^3$, besides yielding more accurate values of the cross section, leads to a new effect, whereby the ionization-photocurrent density acquires an oscillatory component of frequency ω. Examining the variation of the ionization with time, we see that with increasing "size" $R \approx vt$ of the photoelectron wave function ($v = [2(E_n + \hbar\omega)/m]^{1/2}$) the dipole-moment component at the frequency ω also increases: $P(\omega) \propto R^2$. Thus, at $\hbar\omega > |E_n|$, the electric properties of an atom in an strong field are qualitatively altered at the frequency ω: the amplitude of the $\mathbf{P}(t)$ oscillations remains constant only to first order in $\mathbf{F}$, while the terms containing γ in (12) are no longer correct. This is formally manifested in the fact that in some of the composite matrix elements the susceptibility γ acquires Green's functions $G_{E_\mu}^{(-)}$ with positive energy $E = W_n + \hbar\omega$ (we note for the sake of comparison that no such Green's functions occur in expression (6) for β at any $\omega > 0$). The matrix elements

$$\langle n|d_kG_{E_n+\hbar\omega}^{(-)} d_jG_E^{(\pm)} d_lG_{E_n+\hbar\omega}^{(+)} d_m|n\rangle,$$

which contain $G_{E_\mu}^{(+)}$ and $G_{E_\mu}^{(-)}$ of like energy $E_\mu > 0$, simultaneously then diverge, meaning that $P(\omega) \propto R^2$ increases without limit.

It is easy to verify that divergences of the same type appear in the calculation of the corrections to susceptibilities $\chi(-\omega_N, \omega_{N-1}, ..., \omega_1)$ of general form, if the expression for χ contains Green's functions G_{E_μ} with $E_\mu > 0$. For example, allowance for the terms $\sim F^5 \exp(-3i\omega t)$ in the expansion (2), which give the corrections to the third-harmonic-generation coefficient β, is no longer valid (leads to divergences) at $\hbar\omega > \frac{1}{3}|E_n|$, whereas the terms $\sim F^5$
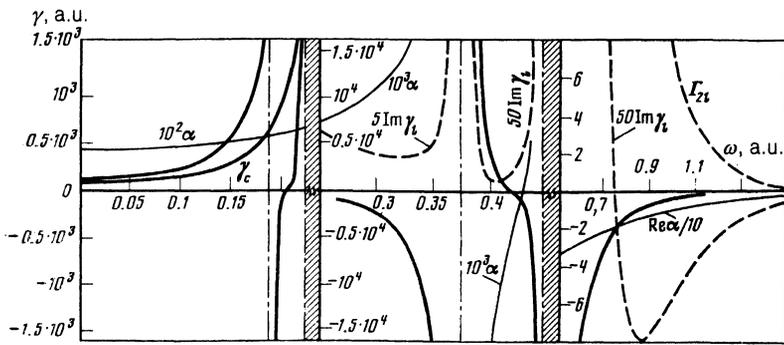
FIG. 2. Real (solid line) and imaginary (dashed) parts of the polarizability γ_l for the $1s$ level of hydrogen in a linearly polarized field (in atomic units). The real part of the polarizability $\alpha(\omega)$ (thin line) and the hyperpolarizability γ_c in a circularfield at below-threshold energies are shown for comparison. At $\omega < 0.25$ the difference between γ_l and γ_c is negligible. The contribution of the two-photon ionization Γ_{2l} to Im γ_L is also shown.

$\exp(-5i\omega t)$ which determine $P(5\omega)$ in the first nonvanishing order, are valid for all ω.

We assume hereafter [in accord with (3)] that γ in all the matrix elements contain only the Green's functions $G^{(+)}$. The tensor γ remains therefore finite also at $\hbar\omega > |E_n|$. Although it does not describe the atom's dipole moment in this case, it is only when so defined that this tensor retains the meaning of a quasistationary-level property (see §4). The numerical values of γ were calculated by the procedure used for β in §2. Figure 2 shows experimental plots of the real and imaginary parts of γ_l for the $1s$ state of hydrogen. Just as β, the hyperpolarizability contains pole and threshold singularities, and only one- and two-photon resonances are possible (on the p- and s-, d-levels, respectively). The hyperpolarizability decreases rapidly in the frequency region $\hbar\omega > |E_{1s}|$. The asymptotic behavior of $\gamma_{l,c}$ at $\hbar\omega \gg |E_n|$

$$\gamma_{l,c} = a_{l,c} \frac{2(2^{1/2}-1)(1-i)}{15\omega^{7,5}}, \qquad a_l = 3, \qquad a_c = 2,$$

is similar to (8), i.e., the real and imaginary parts of γ are of equal magnitude and decrease in proportion to $\omega^{-7.5}$. Just as in the case of β, the asymptote is reached quite far beyond the threshold. Results similar to those of §2 are also obtained by comparison of the hyperpolarizability of the $1s$ state with the hyperpolarizability γ investigated in Ref. 10 for the case of a δ potential. The behavior of the hyperpolarizabilities of the excited states in nonhydrogenic atoms is illustrated by the data of Table I and II. We present also the values of α and γ for the excited $7s$ state of cesium at the second neodymium-laser harmonic $2\omega_N > |E_{7s}^{(Cs)}|$:

$$\alpha = -620 + 72i, \quad \gamma_l = (2,5 - 0,5i)\cdot 10^7, \quad \gamma_c = 0,95\gamma_l.$$

In most cases, the parameters $\gamma_{l,c}$ contribute corrections $\propto F^2$ to effects, determined by the polarizability α, of first order in perturbation theory. Thus, for the cross section of Rayleigh scattering of light we get from (12)

$$\sigma = \sigma_0 \left[1 + \frac{2|F|^2}{\alpha} \mathrm{Re}\,(l^2\gamma_l + A^2\gamma_c) \right], \qquad \sigma_0 = \frac{8\pi}{3c^4}\alpha^2\omega^4.$$

The very same combination $l^2\gamma_l + A^2\gamma_c$ determines also the corrections to the s-level shift (see §4). Of primary interest in such cases is a comparison of α and γ, from which we can assess the extent to which perturbation theory is valid for the description of an atom in an intense field (most instructive in this respect is Fig. 2, which shows that $|\mathrm{Re}\,\gamma| \gg |\alpha|$, if $\hbar\omega < |E_n|$ and that $|\mathrm{Re}\,\gamma| \ll |\mathrm{Re}\,\alpha|$ at frequencies above

threshold). The presence of "anisotropy" in (12), however, also gives rise to new effects. Rewriting the expression for $P(\omega)$ in the form

$$P(\omega) = (\alpha + \gamma_c|F|^2)F + (\gamma_l - \gamma_c)l|F|^2F^*,$$

we see that the difference between γ_l and γ_c leads to a difference between the polarizations of the vector P and the pump F (these two coincide, however, in the important cases of linear and circular wave polarization). The degree of ellipticity ε $(2\varepsilon/(1 + \varepsilon^2) = A)$ of the scattered radiation is also changed. For forward scattering, the polarization change $\Delta\varepsilon = \varepsilon_{scat} - \varepsilon$ takes the simple form

$$\Delta\varepsilon = 2\varepsilon l \frac{\gamma_c - \gamma_l}{\alpha}|F|^2.$$

For intense light propagating in the medium, this effect leads to self-induced light-polarization-ellipse rotation through an angle proportional to the difference $\gamma_l - \gamma_c$ (Ref. 1). It can be seen from the data of Table II that the polarization of the scattered light can change noticeably in alkali-metal laser fields. The difference $\gamma_l - \gamma_c$ is largest in the vicinity of two-photon resonances of on s levels, since γ_c has no such resonances in view of the dipole selection rules. Linear and circular light propagates through the medium without change of polarization. In this case the parameter γ_l or γ_c determines the self-focusing of a spatially confined beam.[21] An interesting effect can be observed if γ_l and γ_c are of opposite sign (see Fig. 2), so that the beam becomes focused or defocused, depending on the polarization of the light.

We consider now the hyperpolarizabilities of degenerate states. In our case, the calculation of γ calls for prior diagonalization of the polarizability matrix of the sublevels $|nLM\rangle$ of the nL level, something impossible in general form.[2] The situation is simplified in the case of linear and circular polarizations of $F(t)$. In these cases, the moment induced in the atom at the frequency ω is

$$P_{l,c}(\omega) = \alpha_{l,c}F + \gamma_{l,c}|F|^2F. \qquad (13)$$

We assume that the linear and circular fields are polarized along the z axis (atomic quantization axis) and in the xy plane, respectively. It is then convenient to represent the dependence of γ on the magnetic quantum number of p-states in a form similar to the expression of $\alpha_{l,c}$ in terms of the scalar (α^s), vector (α^v), and tensor (α^t) components of the polarizability tensor α_{jk} (Ref. 22):

TABLE III. Nonlinear susceptibilities of $2p$ level of hydrogen. The parameters $\Gamma_{2l,2c}^{(s,v,t)}$, which give the dependence of Γ_2 on the magnetic quantum number, were determined in analogy with Eq. (14).

ω	0.016	0.066	0.170	0.450
$\alpha^{(s)}$	185	1570	$-50.8+11.9i$	$-3.75+0.179i$
$\alpha^{(v)}$	-1180	-2340	$-41.8-15.9i$	$-3.77-0.216i$
$\alpha^{t)}$	-20.7	-184	$7.2-1.6i$	$-1.51-0.028i$
$\gamma_l^{(s)}$	$3.47\cdot10^5$	$(-46.8+2.68i)\cdot10^7$	$(-4.76-32.7i)\cdot10^2$	$-1.11+6.15i$
$\gamma_l^{(t)}$	$5.63\cdot10^5$	$(-9.6-5.01i)\cdot10^7$	$(-7.49+21.8i)\cdot10^2$	$1.30-7.52i$
$\gamma_c^{(s)}$	$2.28\cdot10^5$	$(-62.1+3.86i)\cdot10^7$	$(-2.68-51.3i)\cdot10^2$	$-4.36+10.86i$
$\gamma_c^{(v)}$	$45.74\cdot10^5$	$(68.2-3.64i)\cdot10^7$	$(-4.61+73.6i)\cdot10^2$	$6.23-16.88i$
$\gamma_c^{(t)}$	$-1.72\cdot10^5$	$(-12.1+0.58i)\cdot10^7$	$(4.11-20.9i)\cdot10^2$	$-2.27+6.03i$
$\Gamma_{2l}^{(s)}$	–	–	$16.6\cdot10^2$	0.47
$\Gamma_{2l}^{(t)}$	–	–	$-4.3\cdot10^2$	-0.16
$\Gamma_{2c}^{(s)}$	–	–	$20.9\cdot10^2$	0.57
$\Gamma_{2c}^{(v)}$	–	–	$-14.7\cdot10^2$	0.12
$\Gamma_{2c}^{(t)}$	—	–	$3.9\cdot10^2$	0.15

$$\gamma_l=\gamma_l^{(s)}+\gamma_l^{(t)}(3M^2-2),\quad \gamma_c=\gamma_c^{(s)}-\gamma_c^{(v)}AM+\gamma_c(3M^2-2) \tag{14}$$

(at $L>1$ the expansion of γ also contains terms with M^3 and M^4, so that the number of independent atomic parameters is increased). In nonlinear-optics applications, principal interest attaches to the scalar parts $\alpha^{(s)}$ and $\gamma_{l,c}^{(s)}$, that determine the value of the vector $\mathbf{P}(\omega)$ averaged over the magnetic sublevels (as well as the shift of the "centroid" of the nL level in the optical field).

The dispersion relations for the quantities $\gamma_{l,c}^{(s,v,t)}$ are similar to those shown in Fig. 2. In view of the large number of the parameters γ for excited levels Table III lists the values of $\gamma_{l,c}^{(s,v,t)}$ for the hydrogen $2p$-level only for a few selected characteristic frequencies (near the midpoints of the principal intervals between resonances and thresholds). Inasmuch as in the case of excited states there is insufficient information even on the polarizabilities, Table III also includes the values of $\alpha^{(s,v,t)}$. The limited set of frequencies notwithstanding, Table III indicates order-of-magnitude values of α and γ for excited states. At frequencies up to the first threshold (two-photon ionization), the parameters γ increase rapidly with increasing level number n ($\gamma \propto n^{14}$ in the static case). At frequencies above threshold, this difference vanishes. The values of γ are considerably smaller at $\hbar\omega > |E_n|$ that at $\hbar\omega < |E_n|$, and decrease rapidly ($\propto \omega^{-8}$) with increasing ω.

§4. LEVEL SHIFT AND PHOTOEFFECT IN A STRONG LIGHT FIELD

The connection

$$\partial E/\partial\mathbf{F}^*=-\mathbf{P}(\omega)/4 \tag{15}$$

between the dipole-moment component at the frequency of the external field $\mathbf{P}(\omega)$ and the quasilevels E of the atomic level is a generalization of the existing relations for a system in a static field. Using (12), we have hence for the shift of the s level in a light field

$$\Delta E=-{}^1\!/_4\alpha|\mathbf{F}|^2-{}^1\!/_8(l^2\gamma_l+A^2\gamma_c)|\mathbf{F}|^4. \tag{16}$$

For degenerate states in a linear or circular field we obtain from (13) a similar relation

$$\Delta E_{l,\,c}=-{}^1\!/_4\alpha_{l,\,c}|\mathbf{F}|^2-{}^1\!/_8\gamma_{l,\,c}|\mathbf{F}|^4, \tag{17}$$

that describes not only the shift but also the splitting of the level (as a result of the dependences of α and γ on M).

From the numerical results of §3 it follows that the level splitting and shift are of the same order of magnitude and depend substantially on the radiation frequency. At frequencies near resonances we have $|\gamma|\gg|\alpha|$, so that the corrections $\propto F^4$ are significant in fields F that are much weaker than the atomic field $F_0 = 5\cdot10^9$ V/cm. At $\hbar\omega > |E_n|$ these corrections are unimportant and the level position is determined with good accuracy by the quadratic Stark effect. At frequencies above threshold, however, interest attaches to the imaginary parts of α and γ, which determine the ionization broadening Γ of the $|nLM\rangle$ level:

$$\Gamma=-2\,\mathrm{Im}\,\Delta E$$

[it is important that expressions (16) and (17) are valid at all frequencies, including at $\hbar\omega > |E_n|$ (Ref. 10), when it is no longer correct to allow for the term with γ in the expansion (2) of $\mathbf{P}(\omega)$]. At $\frac{1}{2}|E_n| < \hbar\omega < |E_n|$ the polarizability α is real, and $\mathrm{Im}\,\Delta E$ is determined only by the imaginary part of γ, which yields in this frequency interval simply the two-photon ionization probability $W_2 = \Gamma/\hbar$ of the atomic state considered. For degenerate states, the total probability of the nL-level ionization is determined only by the scalar part of the hyperpolarizability. The values of W_2 for atoms have been calculated by many authors (see Ref. 2). Some idea of polarization and dispersion dependences of W_2 for hydrogen and cesium atoms can be gained from the data of Tables I–III and of Fig. 2.

At $\hbar\omega > |E_n|$ the dominant atom-decay channel in a field is the photoeffect, and its total probability for the nL level is

$$W_1^{(nL)} = \frac{1}{2\hbar} \operatorname{Im} \alpha^{(s)} |\mathbf{F}|^2.$$

In this case $\operatorname{Im} \gamma$ introduces in W_1 corrections proportional to the wave intensity and dependent on both the frequency and the polarization of the light (W_1 does not depend on the type of polarization). Actually $\frac{1}{2} \operatorname{Im} \gamma |\mathbf{F}|^2$ is the "induced" radiative correction to the photoeffect cross section and stems, in contrast to the usual radiative corrections, from interaction with real photons. Analysis[10] shows that $\operatorname{Im} \gamma$ is a sum of two parts: $\operatorname{Im} \gamma = \Gamma_2 + \Gamma_{1-3}$. One of them, Γ_2, yields the probability of the two-photon above-threshold ionization that alters the energy spectrum of the photoelectrons ($E_f = E_n + 2\hbar\omega$). This part (which is by its very meaning positive at all $\hbar\omega > |E_n|$) is given in Tables I and III and in Fig. 2. The other part, Γ_{1-3}, is determined by the interference between the amplitudes of the ordinary photoeffect and of the three-photon process of one-photon ionization with photon re-emission (in accordance with the scheme $E_n + 2\hbar\omega - \hbar\omega = E_n + \hbar\omega$), and includes also the "nondiagrammatic" components that stem from the terms $T^{(1,2)}$ of Eq. (10). In contrast to Γ_2, the corrections connected with re-emission can be positive as well as negative, depending on ω. The total correction to the photoeffect, as can be seen from the numerical data, has a rather complicated behavior.

Thus, fourth-order effects can either increase or decrease the ionization width of a level. For degenerate states, the signs of the corrections are found in a number of cases to be different for different sublevels. Effects of this kind may turn out to be substantial in resonant ionization of atoms, when one-photon ionization from a resonant level is possible. At frequencies not much higher than the ionization threshold, the ratio $|\operatorname{Im} \gamma/\operatorname{Im} \alpha|$ for excited states reaches quite high values $|\operatorname{Im} \gamma/\operatorname{Im} \alpha| \sim 10^4$ for the $3p$ state of hydrogen), so that fourth-order effects become significant even in laser fields of strength $F \sim 10^6$ V/cm. In the $\hbar\omega \gg |E_n|$ region, however, the photoeffect probability $W_1 \sim \omega^{-(L+4.5)}$ decreases more slowly (for states with small L) than $\operatorname{Im} \gamma$, and the corrections $\propto F^4$ become insignificant.

APPENDIX

Contribution of intermediate states of the discrete atomic spectrum to the composite perturbation-theory matrix elements

To calculate composite matrix elements it is necessary to determine correction functions of the form

$$\Psi(\mathbf{r}) = \int d\mathbf{r}' \, G_E(\mathbf{r}, \mathbf{r}') V(\mathbf{r}') \Phi(\mathbf{r}'), \qquad (A.1)$$

where $\Phi(\mathbf{r})$ is a function that attenuates exponentially at infinity (e.g., the bound-state function). Note that at $E < 0$ the function $\Psi(\mathbf{r})$ also decreases exponentially with increasing r. If the spectral expansion (4) is used for the Green's function G_E, the function $\Psi(\mathbf{r})$ breaks up naturally into two components, one belonging to the subspace of the discrete-spectrum functions, and the other to the continuum:

$$\Psi(\mathbf{r}) = \Psi_1(\mathbf{r}) + \Psi_2(\mathbf{r}), \qquad \Psi_1 = \hat{P}_1 \Psi, \qquad \Psi_2 = \hat{P}_2 \Psi,$$

$$\hat{P}_1 + \hat{P}_2 = \hat{I}, \qquad \hat{P}_1 \hat{P}_2 = 0. \qquad (A.2)$$

This is followed by considering, for simplicity, functions $\Psi(r)$ of a single variable, which describe radial motion with a definite angular momentum L. $\hat{P}_1$ and $\hat{P}_2$ are then the operators for projection on the subspace of the radial functions:

$$\langle r | \hat{P}_1 | r' \rangle = \sum_{n=L+1}^{\infty} \Phi_{nL}(r) \Phi_{nL}(r'),$$

$$\langle r | \hat{P}_2 | r' \rangle = \int_0^{\infty} dE \, \Phi_{EL}(r) \Phi_{EL}(r'); \qquad (A.3)$$

Φ_{nL} and Φ_{EL} are the Coulomb radial functions of the discrete and continuous spectra. Let us find the asymptotic form of $\Psi_2(r)$ and $r \to \infty$. From (A.2) and (A.3) we have

$$\Psi_2(r) = \int_0^{\infty} dE \, \Phi_{EL}(r) \langle EL | \Psi \rangle. \qquad (A.4)$$

As $r \to \infty$, $\Phi_{EL}(r)$ is a rapidly oscillating function of the energy E, and the main contribution to the integral is made by the vicinity of the point $E = 0$. Substituting the integral representation[23] of Φ_{EL} in (A.4) and an estimate by the stationary-phase method yield (in atomic units)

$$\Psi_2(r \to \infty) \approx 3(2\pi^2 r^9)^{-1/4} \cos[(8r)^{1/2} - L\pi - \pi/4] \langle E=0, L | \Psi \rangle. \qquad (A.5)$$

We see that the behavior of $\Psi_2(r)$ as $r \to \infty$ is similar to the behavior of a Coulomb wave function with zero energy. In particular, $\Psi_2(r)$ falls off at infinity according to a power law, not exponentially. Obviously, the asymptote of $\Psi_1(r)$ differs from (A.5) only in sign, since the sum $\Psi_1 + \Psi_2 = \Psi(r)$ is a rapidly decreasing function.

This yields a somewhat unexpected result. The functions Ψ_1 and Ψ_2 have a finite norm and, as is clear from (A.2),

$$\langle \Psi_1 | \Psi_1 \rangle + \langle \Psi_2 | \Psi_2 \rangle = \langle \Psi | \Psi \rangle.$$

The functions $r\Psi_1$ and $r\Psi_2$, however, are already unnormalizable, i.e., the integrals

$$\int_0^{\infty} dr \, r^2 (r\Psi_1)^2, \qquad \int_0^{\infty} dr \, r^2 (r\Psi_2)^2,$$

diverge, as follows from (A.5). At the same time, the sum $r\Psi_1 + r\Psi_2 = r\Psi$ remains normalizable in view of the rapid decrease of $\Psi(r)$.

The functions $\Psi_1 = \hat{P}_1 \Psi$ always appear (explicitly or implicitly) in the calculations of expressions such as (A.1), when only the sum over the discrete spectrum is retained in the spectral expansion. Calculation of matrix elements with several Green's functions is then equivalent to calculation of integrals of slowly decreasing or even increasing functions, and, generally speaking, leads to divergences.

Thus, in the case of the dipole interaction $V = -\mathbf{F} \cdot \mathbf{r}$, divergences appear in the composite matrix element starting with fourth order, and in the presence of multipole perturbations $V \propto r^k$ with $k > 1$ they appear also in third-order elements. In these cases the calculations of the nonlinear susceptibilities, with allowance for a large number of discrete

levels in the expansion of G and with the contribution of the continuum discarded, can yield results with arbitrarily large deviations from the correct ones.

[1]N. Bloembergen, *Nonlinear Optics*, Benjamin, 1965, Chap. 5.
[2]L. P. Rapoport, B. A. Zon, and N. L. Manakov, Theory of Multiphoton Processes in Atoms [in Russian], Atomizdat, 1978.
[3]J. Mizuno, J. Phys. **B5**, 1149 (1972).
[4]N. L. Manakov, M. A. Preobrazhenskii, and L. P. Rapoport, Opt. Spektrosk. **35**, 24 (1973).
[5]J. Reintjes, C. Y. She, R. C. Eckardt *et al.*, Appl. Phys. Lett. **39**, 480 (1977).
[6]R. Wallenstein, Laser and Optoelektron. **14**, 29 (1982).
[7]P. Kruit, J. Mikkan, H. G. Muller, and M. J. van der Weil, Phys. Rev. **A28**, 248 (1983).
[8]F. Fabre, G. Petite, P. Agostini, and M. Clement, J. Phys. **B15**, 1353 (1982).
[9]N. B. Delone, V. P. Kraĭnov, and D. L. Shepelyanskiĭ, Usp. Fiz. Nauk **140**, 355 (1983) [Sov. Phys. Usp. **26**, 551 (1983)].
[10]N. L. Manakov, M. A. Preobrazhenskiĭ, L. P. Rapoport, and A. G. Fainshteĭn, Zh. Eksp. Teor. Fiz. **75**, 1243 (1978) [Sov. Phys. JETP **48**, 626 (1978)].
[11]E. Arnous, J. Bastian, and A. Maquet, Phys. Rev. **A27**, 977 (1983).
[12]R. B. Miles and S. E. Harris, IEEE **QE-9**, 470 (1973).
[13]H. Eicher, *ibid.* **QE-11**, 121 (1975).
[14]G. V. Al'tshuler, E. G. Dul'neva, K. I. Krylov *et al.*, Opt. Spektr. **54**, 408 (1983).
[15]N. L. Manakov, S. I. Marmo, and A. G. Fainshteĭn, Teor. Mat. Fiz. **59**, 49 (1984).
[16]N. L. Manakov, L. P. Rapoport, and A. G. Fainshteĭn, Izv. AN SSSR, Ser. Fiz. **45**, 2401 (1981).
[17]V. B. Berestetskii, E. M. Lifshitz, and L. P. Pitaevskii, *Quantum Electrodynamics*, Pergamon, Oxford (1982).
[18]N. L. Manakov and V. D. Ovsyannikov, Zh. Eksp. Teor. Fiz. **79**, 1769 (1980).
[19]A. I. Baz', Ya. B. Zel'dovich, and A. M. Perelomov, *Scattering, Reactions, and Decay in Nonrelativistic Quantum Mechanics*, Wiley, 1969.
[20]Yu. N. Demkov and V. N. Ostrovskii, Method of Zero-Radius Potential in Atomic Physics [in Russian], Leningrad, Univ. Press, 1975.
[21]L. D. Landau and E. M. Lifshitz, *Electrodynamics of Continuous Media*, Pergamon, 1984.
[22]N. L. Manakov and V. D. Ovsyannikov, Zh. Eksp. Teor. Fiz. **75**, 803 (1978) [Sov. Phys. JETP **48**, 406 (1978)].
[23]A. Erdelyi, ed., Higher Transcendental Functions, McGraw, 1953, Vol. 1.

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