# Dynamic polarizability and scattering of hf radiation by hydrogenic atoms

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Expansions of the amplitudes of the elastic and inelastic scattering of light by hydrogenic atoms and of the dynamic polarizabilities in terms of powers of the reciprocal of the frequency $\omega$ are derived. It is shown that these expansions include terms with half-integral power exponents of $\omega$, which are associated with the singular nature of the Coulomb potential. An analysis is made of the conditions of validity of these approximations.

## 1. INTRODUCTION

Atoms in highly excited (Rydberg) states and their interaction with external fields are currently the subject of many experimental and theoretical investigations (see, for example, Ref. 1). The low energies of the Rydberg states make it possible to calculate the interaction of a Rydberg atom with optical-frequency radiation by means of simple expressions derived for a number of atomic characteristics in the form of expansions in terms of a small parameter $\Omega^{-1} = z^2\mathrm{Ry}/\hbar\omega$, where $z$ is the charge of the atomic core. We shall derive such expressions for the light-scattering tensor and for the dynamic polarizabilities, because rigorous calculations of these quantities meet with considerable difficulties. A highly excited electron will be described by a potential $U(r)$, which is created by the nucleus and the core, and in some cases (particularly in the case of the states with a large orbital momentum $l$) this potential can be quite acurately regarded as of the Coulomb type.

We shall assume that $\omega$, $\mathbf{e}$ and $\omega'$, $\mathbf{e}'$ are the frequencies and the polarization vectors of the incident and scattered photons. The scattering tensor for a transition of an optical electron from a state $|1\rangle \equiv |nlm\rangle$ to a state $|2\rangle \equiv |n'l'm'\rangle$ is of the familiar form (see 59 in Ref. 2):

$$(c_{ik})_{21} = \langle 2|d_i G_{E_n+\hbar\omega} d_k + d_k G_{E_n-\hbar\omega'} d_i|1\rangle, \quad i, k = x, y, z, \quad (1)$$

where

$$G_E = \sum_{nlm} \frac{|nlm\rangle\langle nlm|}{E_{nl}-E} + \sum_{lm} \int_0^\infty dE' \frac{|E'lm\rangle\langle E'lm|}{E'-E-i0}$$

$$\equiv [\hat{H} - E - i0]^{-1} \quad (2)$$

is a Green function which contains summation over discrete ($E_{nl}$) and integration over continuous ($E'$) spectra of the states of an optical electron; $d_{i,k}$ are the components of the dipole moment of an electron. For $|1\rangle \equiv |2\rangle$ and $\omega = \omega'$ the tensor $c_{ik}$ is identical with the tensor $\alpha_{ik}(\omega)$, representing the dynamic polarizability. In addition to the coherent (Rayleigh) scattering tensor $\alpha_{ik}(\omega)$, we shall find also the shift, splitting, and ionization broadening of a level $|nlm\rangle$ in a monochromatic field $\mathbf{F}(t) = F\,\mathrm{Re}\{\mathbf{e}e^{-i\omega t}\}$, which are quadratic functions of the amplitude $F$. Analytic expressions for $\alpha_{ik}$ and $c_{ik}$ can be obtained only for the hydrogen atom, but even in this case the results for the states with $n = 2$ contain cumbersome combinations of hypergeometric functions ${}_2F_1$ (Refs. 3 and 4). In the case of many-electron atoms the values of $\alpha_{ik}$ and $c_{ik}$ are found by numerical calculations.

Equation (1) simplifies greatly in the limiting case of high frequencies. (It is assumed then that $\hbar\omega$ remains small compared with the excitation energy of the inner electrons.) Thus, at frequencies $\omega$ exceeding considerably the binding energy of an optical electron, we have (see Ref. 2)

$$(c_{ik})_{21} \approx -\frac{e^2}{m\omega^2}\delta_{ik}\delta_{21}. \quad (3)$$

This expression is independent of the quantum numbers and describes the shift of all the energy levels by an amount equal to the average vibrational energy of atomic electrons in the field of a wave; in the language used for the scattering cross sections, this expression describes the classical (Thomson) cross section for scattering by free electrons. The inelastic scattering effects (in the case when $|1\rangle \neq |2|\rangle$) and the dependence $(c_{ik})_{21}$ on the quantum characteristics of the states $|1\rangle$ and $|2\rangle$ appear in the next orders in $\omega^{-1}$. Terms proportional to $\omega^{-4}$ in the expansion for the polarizability have been considered by several authors.[3-7] However, the method used then is inapplicable in the case of terms of higher order (see Sec. 2), but these terms are essential for estimating the precision of the results and also for finding the antisymmetric parts of the tensors $\alpha_{ik}$ and $c_{ik}$ which—as established by numerical calculations in Ref. 8—contain half-integral powers of $\omega$ already in the main term of the asymptote. A correct expansion has been obtained only for the polarizability $\alpha_{1s}(\omega)$ of the ground state of a hydrogenic ion with a charge $z$ and this has been done using an expression for $\alpha_{1s}$ in terms of a hypergeometric function[9]:

$$\alpha_{1s}(\omega) = -\frac{4a^3}{z^4\Omega^2}\left\{1 + \frac{16}{3}\Omega^{-2} - \frac{32(1+i)}{3\Omega^{7/2}} + \frac{32i\pi}{3\Omega^3} + O(\Omega^{-7/2})\right\}, \quad (4)$$

where $a$ is the Bohr radius. We can show that the expansion of Eq. (4) has the following structure:

$$\sum_k \Omega^{-k/2}\{\beta_k + \gamma_k \ln \Omega\},$$

where the series in terms of half-integral powers of $\Omega$ converge when $\Omega > 2$. (The coefficients $\gamma_k$ differ from zero for $k \geqslant 12$.)

In Sec. 2 below we shall investigate the formal expansion of the tensor $c_{ik}$ as a series in integral powers of $\omega^{-1}$ and describe a method for calculating the terms containing half-

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integral powers of the frequency. In the next two sections (Secs. 3 and 4) we shall give for the scattering cross sections and the polarizability tensor final results which are valid irrespective of the values of the principal quantum numbers $n$ and $n'$. Finally (Sec. 5) we shall consider the conditions of validity of our results.

## 2. EXPANSION OF THE SCATTERING TENSOR IN RECIPROCAL POWERS OF THE FREQUENCY

At high frequencies characterized by $\hbar\omega$, $\hbar\omega' \gg |E_n|$, $|E_{n'}|$ we can rewrite Eq. (1) conveniently in terms of matrix elements of the derivatives of the potential $U(r)$ using the familiar expression

$$\langle f|\mathbf{r}|i\rangle = -\frac{\hbar^2}{m\omega_{fi}^2}\langle f|\nabla U|i\rangle, \tag{5}$$

representing the operator of the interaction with the field in the form of "acceleration."[10] Transformation carried out using Eq. (5) in $(c_{ik})_{21}$ separates explicitly terms of the orders of $\omega^{-2}$ and $\omega^{-4}$:

$$(c_{ik})_{21} = -\frac{e^2}{m\omega\omega'}\delta_{ik}\delta_{21} - \frac{e^2}{m^2\omega^2\omega'^2}\left\langle 2\left|\frac{\partial^2 U}{\partial x_i \partial x_k}\right|1\right\rangle + \frac{e^2}{m^2\omega^2\omega'^2}\left\langle 2\left|\frac{\partial U}{\partial x_i}G_{E_n+\hbar\omega}\frac{\partial U}{\partial x_k} + \frac{\partial U}{\partial x_k}G_{E_{n'}-\hbar\omega}\frac{\partial U}{\partial x_i}\right|1\right\rangle. \tag{6}$$

Expanding now $G_{E_{n,n'}\pm\hbar\omega}$ formally in powers of $\omega^{-1}$

$$G_{E_n+\hbar\omega} = [\hat{H} - E_n - \hbar\omega - i0]^{-1} \tag{7a}$$

$$= -\frac{1}{\hbar\omega}\sum_{p=0}^{\infty}\left[\frac{\hat{H}-E_n}{\hbar\omega}\right]^p \tag{7b}$$

and using the commutation relationships for the operators $H$ and $U$, we obtain a series in powers of $\omega^{-1}$ for the scattering tensor:

$$(c_{ik})_{21} = -\frac{e^2}{m\omega^2}\delta_{ik}\delta_{21} - \frac{e^2}{m^2\omega^4}\left\{\sum_{\gamma=0}^{3}\left[\frac{E_{n'}-E_n}{\hbar\omega}\right]^\gamma(\gamma+1)\right\} \times \left\langle 2\left|\frac{\partial^2 U}{\partial x_i \partial x_k}\right|1\right\rangle - \frac{e^2}{m^3\omega^6}\left\{\sum_{\gamma=0}^{1}\left[\frac{E_{n'}-E_n}{\hbar\omega}\right]^\gamma(\gamma+1)\right\} \times \sum_{j=x,y,z}\left\langle 2\left|\frac{\partial^2 U}{\partial x_i \partial x_j}\frac{\partial^2 U}{\partial x_j \partial x_k}\right|1\right\rangle + \frac{ie^2}{m^4\omega^7}\sum_{f=x,y,z}\left\langle 2\left|\left[\frac{\partial}{\partial r}\left(\frac{1}{r}\frac{\partial U}{\partial r}\right)\right]^2\hat{l}_f\right|1\right\rangle e_{ikf} + O(\omega^{-8}). \tag{8}$$

Here, $e_{ikf}$ is a unit antisymmetric tensor of rank three, $\hat{l}_f$ is the operator of the $f$th projection of the angular momentum, and the quantity $\omega'$ is expressed in terms of $\omega$ in accordance with the law of conservation of energy $E_n + \hbar\omega = E_{n'} + \hbar\omega'$, so that the sums over $\gamma$ appear simply in the expansion of $(\omega')^{-2}$ in powers of $\omega^{-1}$.

The first term in Eq. (8) differs from zero only in the case of elastic scattering and it is identical with Eq. (3); the other terms are determined by the form of the potential $U(r)$.

We shall now discuss the general nature of expansions of the type given by Eq. (8). When the infinite sum of Eq. (7b) is substituted in Eq. (6) for a matrix element containing a Green function and this is followed by integration term by term, the result is a series in powers of $\omega^{-1}$. In general, this series is asymptotic[1)] and it can be used to estimate the matrix element, but it is unsuitable for calculating the effects that decrease exponentially on increase in $\omega$. However, in the case of the potential which has a cubic singularity in the limit $r\to 0$ the nature of the expansion changes. For example, in the first three matrix elements $\langle 2|...|1\rangle$ in Eq. (8) the operators considered in the limit $r\to 0$ have, respectively, a singularity $r^{-3}$, $r^{-6}$, and $r^{-8}$. The degree of singularity rises for the last terms of the expansion. If we bear in mind that $\psi_{nlm}(r\to 0) \propto r^l$, we find that the radial integrals in the matrix elements of Eq. (8) converge respectively for $l + l' \geqslant 1$, $l + l' \geqslant 4$, $l + l' \geqslant 6$. Therefore, only a certain number $s$ of the first terms in the expansion (8) is finite ($s$ increases on increase in $l + l'$) and then a divergence appears in the radial integrals. This divergence means that in the case of the Coulomb potential the nature of the functional dependence on $\omega$ changes in the higher terms of the expansion [for example, Eq. (4) contains terms with $\omega^{-(k+1/2)}$].

It should be noted that if in the course of substitution of Eq. (7) into Eq. (6) we employ the spectral expansion of Eq. (2) for Eq. (7b), we obtain in particular the following integrals for a continuous spectrum:

$$\int_0^\infty dE\left[\frac{E_n - E}{\hbar\omega}\right]^p\left\langle 2\left|\frac{\partial U}{\partial x_i}\right|El_0m_0\right\rangle\left\langle El_0m_0\left|\frac{\partial U}{\partial x_k}\right|1\right\rangle, \quad p = 1, 2, \ldots \tag{9}$$

Here, the matrix elements $\partial U/\partial r_i$ are finite for all values of $l$ and $l'$ and the divergence can appear only in the upper limit of the integrals in Eq. (9) (the sums over a discrete spectrum show no divergences). In the case of a potential with the Coulomb asymptote $U(r) \propto -z/r$ in the limit $r\to 0$ we can obtain an estimate of the radial matrix element $\langle nl|\partial U/\partial r|El_0\rangle$ for $E\to\infty$. We can do this by replacing $\langle r|El_0\rangle$ with a function representing free motion and estimating both $\langle r|nl\rangle$ and $\partial U/\partial r$ in the limit $r\to 0$ (it is the vicinity of the point $r = 0$ that dominates the contribution to the integral with a rapidly oscillating function $\langle r|El_0\rangle$):

$$\partial U/\partial r \approx z/r^2, \qquad \langle r|nl\rangle \approx N_{nl}(r/a)^l.$$

As a result, we obtain

$$\left\langle nl\left|\frac{\partial U}{\partial r}\right|El_0\right\rangle \underset{E\to\infty}{\approx} 2^{(2l-1)/5}\frac{\Gamma((l_0+l+1)/2)}{\Gamma((l_0-l+2)/2)}z \times\left[\frac{ma}{\pi\hbar^2}\right]^{1/2} N_{nl}\left(\frac{E}{2Ryz^2}\right)^{-(2l+1)/4} \tag{10}$$

In the case of a smooth potential a matrix element decreases exponentially on increase in $E$:

$$\langle nl|\partial U/\partial r|El_0\rangle \propto \exp\{-kE^{1/2}\}, \qquad k>0.$$

Therefore, the integral in Eq. (9) for a smooth potential $U$ converges for all values of $p$ and if the potential is of the Coulomb type, it converges only for $2p < l + l' - 1$.

We shall show that the first "incorrect" term of the asymptote for the Coulomb case contains $\omega$ with a half-integral power exponent. We shall calculate the relevant term using the identity

$$G_{E_n+\hbar\omega} = -\frac{1}{\hbar\omega} - \frac{H-E_n}{(\hbar\omega)^2} - \ldots - \frac{(H-E_n)^{s-1}}{(\hbar\omega)^s} - \left(\frac{H-E_n}{\hbar\omega}\right)^s G_{E_n+\hbar\omega}, \qquad (11)$$

which gives the following expression for the matrix element

$$M_{21} = \left\langle 2\left|\frac{\partial U}{\partial x_i} G_{E_n+\hbar\omega} \frac{\partial U}{\partial x_k}\right|1\right\rangle = \sum_{p=0}^{s} \frac{\varkappa_p}{\omega^p} + M_{21}'(\omega), \qquad (12)$$

where $s = (l + l')/2$ ($l + l'$ is always even, see Sec. 3) is the largest number such that all the coefficients in Eq. (12) are finite. Then, the term of interest to us is obtained from an estimate of $M_{21}'(\omega)$:

$$M_{21}'(\omega) \approx \frac{1}{\hbar\omega} \sum_{l_0 m_0} \int_A^\infty dE \frac{\langle 2|\partial U/\partial x_i|El_0m_0\rangle\langle El_0m_0|\partial U/\partial x_k|1\rangle}{E-E_n-\hbar\omega-i0} \times (E_n-E)^{(l+l')/2}, \quad z^2\,\mathrm{Ry} \ll A \ll \hbar|\omega|, \qquad (13)$$

where we have retained only the integral over a continuous spectrum, which dominates $M_{21}'$ in the limit $\omega \to \infty$ [the rejected contribution of a discrete spectrum and of the low-energy part of a continuous spectrum is $\sim \omega^{-(s+1)}$ and it is of higher order of smallness in Eq. (13)]. Since $E \gg z^2\mathrm{Ry}$, in the integrand in Eq. (13), we have to drop $E_n$ and in the calculation of the matrix elements we should use Eq. (10) and then assume that $A = 0$. Consequently, the integral with respect to $E$ in Eq. (13) becomes

$$\int_0^\infty \frac{dE}{E^{1/2}(E-\hbar\omega-i0)} = \begin{cases} i\pi/(\hbar\omega)^{1/2}, & \omega>0 \\ \pi/(|\hbar\omega|)^{1/2}, & \omega<0 \end{cases}. \qquad (14)$$

Therefore, $M_{21}'$ in Eq. (12) behaves as $\omega^{-(s+1/2)}$. It should be noted that if $\omega > 0$, the integral of Eq. (14) is determined entirely by the correction $i0$ in the denominator [which is lost if we use the expansion of Eq. (7b)]. This technique was used by us to calculate $c_{ik}$ ($\omega \to \infty$) in the Coulomb case. The results of the calculation are summarized below.

## 3. ASYMPTOTIC EXPRESSIONS FOR THE SCATTERING CROSS SECTION

Expanding the tensor $c_{ik}$ into scalar, antisymmetric, and symmetric parts $c_{ik}^0$, $c_{ik}^a$, and $c_{ik}^s$ (Ref. 2), we find the scattering cross section $d\sigma/d\Omega'$ averaged over $m$ and summed over the projections of the momentum $m'$:

$$\frac{d\sigma}{d\Omega'} = \frac{\omega\omega'^3}{c^4}\Big\{|f_0|^2|\mathbf{ee}'^*|^2 + \frac{1}{2}|f_1|^2(1-|\mathbf{ee}'|^2) + \frac{3}{10}|f_2|^2\Big(1+|\mathbf{ee}'|^2-\frac{2}{3}|\mathbf{ee}'^*|^2\Big)\Big\}, \qquad (15)$$

where the amplitudes $f_0, f_1$, and $f_2$ are expressed in terms of $c_{ik}^0$, $c_{ik}^a$, and $c_{ik}^s$, respectively. The actual expressions linking $f$ and $c$ depend on the momenta of the initial and final states $l$ and $l'$. Asymptotic expansions of the amplitudes $f_p(\omega)$ are obtained from expansions of $c_{ik}$. We shall give the results for the pure Coulomb potential $U(r) = -ze/r$. In the case of a potential other than that of the Coulomb type, it should be noted that $n$ and $n'$ should be replaced with $z\nu$ and $z\nu'$, where $\nu$ and $\nu'$ are the effective principal quantum numbers ($\nu = (-\mathrm{Ry}/E_n)^{-1/2}$), and also in terms with the half-integral powers of $\Omega$ we have to introduce a factor $\varkappa_{nl}^2\varkappa_{n'l'}^2$ which allows for the difference in the normalization of the radial wave function at the origin of the coordinate system:

$$\varkappa_{nl} = \frac{\psi_{nl}(r)}{\psi_{nl}^{\mathrm{Coul}}(r)}\bigg|_{r=0}. \qquad (16)$$

As pointed out already, for arbitrary values of $n$ and $n'$ the results are different for different $l$ and $l'$, so that we shall consider separately three cases.

### A. Scattering accompanied by a change in $l$: $|nl\rangle \to |n'l'=l\pm 2\rangle$

For a transition characterized by $l = 0 \to l' = 2$, we have

$$|f_2|^2 = \frac{2^9a^6}{3z^8\Omega^4}\Big\{\frac{3}{\Omega^4}[(r^{-3})_{21}]^2\Big(\frac{a}{z}\Big)^6\Big\{1-\frac{4(n'^2-n^2)}{\Omega(nn')^2}\Big\} - \frac{16}{15}\frac{[nn'(n'^2-1)(n'^2-4)]^{1/2}}{n^2n'^4\Omega^{5.5}}(r^{-3})_{21}\Big(\frac{a}{z}\Big)^3 + O(\Omega^{-6})\Big\}, \qquad (17)$$

whereas for transitions with $l \to l+2$ with $l \geqslant 1$, the corresponding expression is

$$|f_2|^2 = \frac{2^8\cdot 3(l+1)(l+2)a^6}{(2l+1)(2l+3)z^8\Omega^4}\Big\{\frac{[(r^{-3})_{21}]^2}{\Omega^4}\Big(\frac{a}{z}\Big)^6 \times\Big\{1-\frac{4(n'^2-n^2)}{\Omega(nn')^2}\Big\} + O(\Omega^{-6})\Big\}. \qquad (18)$$

where $(r^{-3})_{21}$ are radial matrix elements described by very cumbersome expressions in the general case of arbitrary values of $n$ and $n'$. In the case of $l = 0 \to l' = 2$ transitions and lower states, we have

$$(r^{-3})_{1s;3d} = \frac{1}{18\sqrt{30}}\Big(\frac{z}{a}\Big)^3, \qquad (r^{-3})_{2s;3d} = -\frac{8}{9\cdot 125\sqrt{15}}\Big(\frac{z}{a}\Big)^3,$$

$$(r^{-3})_{3s;3d} = 0.$$

For states with high values of the principal quantum numbers, using the method proposed in Ref. 11, we can obtain approximate expressions for the matrix elements $(r^{-3})_{n'l\pm 2;nl}$:

$$(r^{-3})_{n'l-2;\,nl} \approx (n^2-n'^2)/3(nn')^{1/2}, \qquad (r^{-3})_{n'l+2;\,nl} \approx 0, \qquad (19)$$

where $n > n'$, $n,n',n - n' \gg 1$, $l \ll n'^{2/3}$. It is interesting to note that in the case of $|nl\rangle \to |n,l\pm 2\rangle$ transitions in the Coulomb potential without a change in the principal number, we find that

$$(r^{-3})_{nl;\,nl\pm 2}=0 \tag{20}$$

for all values of $n$ and this specific selection rule was established in Ref. 12 for the hydrogen states. Such transitions are characterized by

$$|f_2|^2_{ns;nd}=\frac{2^{15}}{25\cdot 81}\frac{a^6(n^2-1)(n^2-4)}{z^8n^{10}\Omega^{11}},$$

$$|f_2|^2_{nl;nl+2}=\frac{3\cdot 2^{12}(l+1)(l+2)a^6}{(2l+1)(2l+3)z^{10}\Omega^{12}}[(r^{-6})_{21}]^2\left(\frac{a}{z}\right)^{12} \tag{21}$$

and the cross section is supplemented, compared with Eqs. (17) and (18), by additional small terms $\Omega^{-3}$ and $\Omega^{-4}$.

### B. Raman scattering without a change in $l$: $|nl\rangle \to |n'l\rangle$

The scattering cross section for transitions between the $S$ states contains only the scalar part

$$|f_0|^2_{l=0;\,l'=0}=\frac{2^{12}a^6}{9z^8\Omega^4}\{(nn')^{-3}\Omega^{-4}-4(nn')^{-3}\Omega^{-4,5}+O(\Omega^{-5})\}.$$

If $l=l'\geqslant 1$, the main contribution to $d\sigma/d\Omega'$ comes from the symmetric scattering process

$$|f_2|^2=\frac{2^9l(l+1)a^{12}}{(2l+3)(2l-1)z^{14}\Omega^8}[(r^{-3})_{21}]^2\left\{1-\frac{4(n'^2-n^2)}{\Omega(nn')^2}\right\}, \tag{22}$$

and $f_0$ and $f_1$ are of higher orders of smallness in $\Omega^{-1}$. In particular, if $l=1$, then

$$|f_0|^2=\frac{2^{15}a^6}{3^4z^8\Omega^{11}}\frac{(n^2-1)(n'^2-1)}{(nn')^5},\qquad |f_1|^2=\frac{1}{3}|f_0|^2; \tag{23}$$

for $l=2$, we have

$$|f_0|^2=\frac{2^{14}a^6}{z^8\Omega^{12}}\left\{[(r^{-6})_{21}]^2\left(\frac{a}{z}\right)^{12}\right.$$

$$\left.-\frac{4}{5\cdot 27}\frac{[nn'(n^2-1)(n^2-4)(n'^2-1)(n'^2-4)]^{1/2}}{(nn')^4\Omega^{1/2}}(r^{-6})_{21}\left(\frac{a}{z}\right)^6\right\},$$

$$|f_1|^2=\frac{2^{15}a^6}{9\cdot 5^4z^8\Omega^{13}}\frac{(n^2-1)(n^2-4)(n'^2-1)(n'^2-4)}{(nn')^7}.$$

As in case $A$, the cross sections are expressed in terms of the matrix elements in powers of the reciprocals of $r$. In the case of high values of $n$ and $n'$ we can use an expression obtained by analogy with Eq. (19):

$$(r^{-3})_{n'l;\,nl}\approx l^{-3}(nn')^{-3/2}.$$

### C. Rayleigh scattering: $|nl\rangle \to |nl\rangle$

In this case the matrix elements $(r^{-k})_{nl;nl}$ have the simple form

$$(r^{-3})_{nl;\,nl}=(z/a)^3[n^3(l+1/2)B]^{-1},$$

$$(r^{-6})_{nl;nl}=\left(\frac{z}{a}\right)^6\frac{35n^4+5n^2[5-6B]+3B[B-2]}{n^7(l+1/2)B[B-2][2B-3/2][4B-15]}, \tag{24}$$

where $B\equiv l(l+1)$, which makes it possible to analyze the dependence of $d\sigma/d\Omega'$ on both $n$ and $l$. The antisymmetric and symmetric parts of the Rayleigh scattering cross section are given by Eqs. (22) and (23) with $n=n'$. The scalar part differs from Eq. (23) and in the limit of high frequencies the principal term is identical with the Thomson scattering cross section

$$\frac{\omega^4}{c^4}|f_T|^2|\mathbf{ee}'^*|^2,\qquad f_T=-\frac{4a^3}{z^4\Omega^2}.$$

The corrections to the term $|f_T|^2$ in the scalar scattering cross section are readily obtained from the expressions for $\alpha_0$ [see Eq. (30)]. We can see that for fixed values of $n$ and $\Omega$ the corrections to the Thomson cross section decrease rapidly on increase in $l$ (for $l\geqslant 2$), which corresponds to states which are more semiclassical and have a larger orbital momentum. This accounts also for the rapid fall of the Raman scattering cross sections on increase in $l$ (cases $A$ and $B$) and this fall disappears in the classical limit.

The results of the present section can be used also to estimate the Rayleigh scattering cross sections for nonhydrogenic atoms, when terms proportional to $\Omega^{-4}$ in $c_{ik}$ can be described for $(r^{-3})_{nl;nl}$ by an approximate expression used widely in calculations of the spin–orbit splitting constant (see Sec. 19 in Ref. 10):

$$(r^{-3})_{nl;\,nl}=z^2z_i/a^3\nu^3l(l+1/2)(l+1). \tag{25}$$

Here the charge $z$ of the atomic core is unity for a neutral atom and $z_i$ is the effective charge dependent on $l$, selected as described in Ref. 10.

## 4. DYNAMIC POLARIZABILITY AND CHANGES IN THE SPECTRUM OF AN ATOM IN A HIGH-FREQUENCY FIELD

A change in the quasienergy $\varepsilon_{nlm}$ of the $|nlm\rangle$ state in a monochromatic field

$$\mathbf{F}(t)=F\,\mathrm{Re}\{\mathbf{e}e^{-i\omega t}\}$$

in the lowest order of perturbation theories quadratic in $F$ and depend strongly not only on the frequency, but also on the polarization of the field $\mathbf{F}(t)$. The expression for $\Delta\varepsilon_{nlm}=\varepsilon_{nlm}-E_{nl}$ can be analyzed conveniently by introducing a scalar polarizability $\alpha^0_{nl}(\omega)$, as well as antisymmetric (vector) $\alpha^a_{nl}(\omega)$ and tensor $\alpha^s_{nl}(\omega)$ polarizabilities related to the Rayleigh scattering tensor $c_{ik}$ by[3,4]

$$(c_{ik}{}^0)_{11}=\delta_{ik}\alpha_{nl}{}^0(\omega),\qquad (c_{ik}{}^a)_{11}=\frac{i}{2l}e_{ikj}\langle nlm|\hat{l}_j|nlm\rangle\alpha_{nl}{}^a(\omega),$$

$$(c_{ik}{}^s)_{11}=-\frac{3}{4}\frac{\left\langle nlm\left|\hat{l}_i\hat{l}_k+\hat{l}_k\hat{l}_i-\frac{2}{3}\delta_{ik}\hat{l}^2\right|nlm\right\rangle}{l(2l-1)}\alpha_{nl}{}^s(\omega). \tag{26}$$

When this definition is used, both $\alpha^0_{nl}(\omega=0)$ and $\alpha^s_{nl}(\omega=0)$ are identical with the corresponding polarizabilities in a static electric field, whereas $\alpha^a_{nl}(\omega=0)=0$. In the general case of an elliptic polarization $\mathbf{F}(t)$ the states $|nlm\rangle$ characterized by different values of $m=-l,\dots,l$ are mixed by the field and $\Delta\varepsilon_{nl}$ are found by diagonalization of a matrix of rank $(2l+1)$; the nondiagonal elements of the matrix then contain only the tensor polarizability $\alpha^s_{nl}(\omega)$ (Ref. 3).

In the case of linear and circular polarizations of the field $\mathbf{F}(t)$ the projection $m$ is conserved along, respectively, the direction of polarization and the direction of propagation of the wave. Then, $\Delta\varepsilon_{nlm}$ is of the form

$$\Delta\varepsilon_{nlm}=-\frac{F^2}{4}\left[\alpha_{nl}{}^0(\omega)+\alpha_{nl}{}^s(\omega)\frac{3m^2-l(l+1)}{l(2l-1)}\right] \tag{27}$$

for the linear polarization of the wave and

$$\Delta\varepsilon_{nlm}=-\frac{F^2}{4}\left[\alpha_{nl}{}^0(\omega)+A\alpha_{nl}{}^a(\omega)\frac{m}{2l}-\alpha_{nl}{}^s(\omega)\frac{3m^2-l(l+1)}{2l(2l-1)}\right] \tag{28}$$

for the circular polarization where $A=+1$ or $-1$ for the right-and left-handed polarizations of $\mathbf{F}(t)$, respectively.

The asymptotic (in the $\Omega\gg1$ case) expressions for the polarizabilities are obtained by expanding the amplitudes $f_p$ in accordance with the results of Secs. 2 and 3. We must bear in mind that in Eqs. (27) and (28) the state is assumed to be nondegenerate in $l$. In the hydrogenic atom the field mixes also the states with different values of $l$ for given $n$ and $m$, and in general $\Delta\varepsilon_{nm}$ is obtained by diagonalization of a matrix of rank $n-|m|$ (Refs. 5 and 13). The diagonal elements $W_{l,l}$ of the matrix contain the right-hand sides of Eqs. (27) and (28) [for the cases of the linear and circular polarizations of $\mathbf{F}(t)$, respectively] and the off-diagonal elements $W_{l,l\pm2}$ are expressed in terms of the scattering amplitudes $(f_2)_{nl;nl\pm2}$ of Eq. (21). As pointed out already in Sec. 3B (see also Ref. 12), it follows from the relationship (20) that the high-frequency expansions of these amplitudes begin only with the terms proportional to $\Omega^{-6}$, whereas the differences between the diagonal elements begin with the terms proportional to $\Omega^{-4}$. Including the off-diagonal terms by means of perturbation theory, we can readily see that their contribution to $\Delta\varepsilon_n$ if of the order of $\Omega^{-8}$. Therefore, to within an error smaller than $\Omega^{-8}$, the orbital momentum $l$ remains a good quantum number and $\Delta\varepsilon_{nlm}$ are given by Eqs. (27) and (28) also in the case of hydrogenic levels [the exception are the states with $l=0$ or 2, because according to Eq. (21) we have $W_{0,2}\propto\Omega^{-5.5}$ and approximate diagonalization is possible only to a precision worse than $\Omega^{-7}$].

In the case of the $ns$ states, the polarizability is

$$\alpha_{ns}{}^0(\omega)=-\frac{4a^3}{z^4}\left\{\Omega^{-2}+\frac{16}{3}n^{-3}\Omega^{-4}-\frac{32}{3}\frac{1+i}{n^3\Omega^{4,5}}\right\}, \tag{29}$$

which is identical with the expansion of Eq. (4) in the case of the ground state. The expressions for the polarizabilities of the states with $l\geqslant1$ are

$$\alpha^0_{n,l=1}(\omega)=-\frac{4a^3}{z^4}\left\{\Omega^{-2}+\frac{32}{9}\frac{(n^2-1)(1-i)}{n^5\Omega^{5,5}}\right\},$$

$$\alpha^0_{n,l\geqslant2}(\omega)=-\frac{4a^3}{z^4}\left\{\Omega^{-2}+\frac{32}{\Omega^6}(r^{-6})_{11}\left(\frac{a}{z}\right)^6\right\};$$

$$\alpha^a_{n,l=1}(\omega)=-\frac{2^7a^3(n^2-1)(1+i)}{9z^4\Omega^{5,5}n^5},$$

$$\alpha^a_{n,l=2}(\omega)=\frac{2^8a^3}{75z^4\Omega^{6,5}}\frac{(n^2-1)(n^2-4)(1-i)}{n^7};$$

$$\alpha^s_{n,l=1}(\omega)=\frac{2^6a^3}{15z^4}\left\{n^{-3}\Omega^{-4}-\frac{4(n^2-1)(1-i)}{n^5\Omega^{5,5}}\right\}$$

$$\alpha^s_{n,l\geqslant2}(\omega)=-\frac{64la^3}{(2l+3)z^4\Omega^4}\left\{(r^{-3})_{11}\left(\frac{a}{z}\right)^3-\frac{4}{\Omega^2}(r^{-6})_{11}\left(\frac{a}{z}\right)^6\right\}. \tag{30}$$

It follows from the system (30) that the vector polarizability $\alpha^a_{nl}$ is small compared with $\alpha^{0,s}_{nl}$. Hence, the splitting of the levels in a circular field expressed bearing in mind the sign of $m$ [see Eq. (28)] is considerably less than the splitting expressed in terms of $|m|$. It is interesting to note that if $\Omega\ll1$, then $\alpha^a_{nl}\propto\Omega$ and it is also small compared with the static values $\alpha^{0,s}_{nl}(0)$, although for $\Omega\sim1$ all the polarizabilities are of the same order of magnitude. It is worth noting also the rapid decrease of the polarizabilities on increase in $l$, so that the effect of the field is strongest on the states with small orbital momenta.

The imaginary part of the polarizability governs the broadening of a level due to photoionization. In the expansion of Eq. (8) there are no imaginary parts. They appear precisely in those orders in $\Omega^{-1}$ which cannot be calculated by means of Eq. (8). We find from Eqs. (6), (7a), and (10) that in the case of a state with a momentum $l$ the imaginary parts of the polarizabilities at high values of $\Omega$ are of the order of $\Omega^{-l-9/2}$ (exactly as the first term of the asymptote $\text{Re}\,\alpha_{nl}$, containing half-integral powers of the frequency). This behavior of $\text{Im}\,\alpha_{nl}$ is in agreement with the familiar asymptotic behavior $\sigma_{nl}(\omega)\propto\omega^{-l-7/2}$ of the photoionization cross section[14] related to $\text{Im}\,\alpha_{nl}(\omega)$ by the optical theorem

$$\sigma_{nl}(\omega)=\frac{4\pi\omega}{c(2l+1)}\,\text{Im}\,\alpha_{nl}(\omega).$$

It is clear from Eq. (30) that calculations of the terms proportional to $\Omega^{-4}$ in the expansion of $\Delta\varepsilon_{nl}$, carried out earlier in Refs. 5 and 7, gives only the main term of the asymptote of the tensor polarizability $\alpha^s_{nl}$ and is insufficient to find $\alpha^a_{nl}$ and $\alpha^0_{nl}$ (with the exception of the trivial term $4a^3/z^4\Omega^2=e^2/m\omega^2$) or the widths of the levels.

## 5. RANGE OF VALIDITY OF THE RESULTS

The expressions obtained can be used for the pure Coulomb potential $-ze/r$ and also in the more general case of a model potential with the Coulomb asymptote in the limit $r\to0$. In the case of transitions between low-lying states $|1\rangle$ and $|2\rangle$ (when $n\sim1$ and $n'\sim1$) the only expansion parameter is $\Omega^{-1}$ so that expansions of $|f|^2$ and $\alpha$ are valid when $\Omega\gg1$. However, when $n\gg1$ and $n'\gg1$, the parameter of the expansion depends on the relationships between $n$, $n'$ and $l,l'$. For lack of space, we shall consider only the case when $n\sim n'$ and $l\sim l'$. If $l\ll n$, then allowing for the dependence of the radial matrix elements on $n$

$$|\langle1|r^{-m}|2\rangle|\propto(nn')^{-3/2}(z/a)^m,\quad m\geqslant3,$$

we can easily see that the expansion for $f$ and $\alpha$ deduced from Secs. 3 and 4 are

$$\alpha(n,\omega)=n^{-3}F_\alpha(\Omega),\qquad f(n,\omega)=n^{-3}F_f(\Omega), \tag{31}$$

so that the condition of validity of the expansion is in fact

$\Omega \gg 1$. It should be noted that the scalar part of the amplitude $f_0$ of the elastic ($n = n', l = l'$,) scattering and of the polarizability $\alpha^0$ includes not only terms of the type given by Eq. (31), but also the Thomson term $f_T = -4a^3/z^4\Omega^2$, which does not contain a small term proportional to $n^{-3}$. However, if we consider transitions between states with large values of $l \sim n$, we find that

$$|\langle 1|r^{-m}|2\rangle| \sim (nn')^{-m}(z/a)^m$$

and the expansion parameter is $[n^3\Omega]^{-1}$. In this case both $f$ and $\alpha$ have a structure (including $f_0$ and $\alpha^0$)

$$[an^2/z]^3F(n^3\Omega).$$

Here, $an^2$ is the radius of the $n$th Bohr orbit and the characteristic frequency $z^2\mathrm{Ry}/n^3$ is governed by the energy of a transition to the nearest $|nl\rangle$ levels. Therefore, at high values of $l$ the asymptotic expansion begins to operate already at frequencies less than the ionization threshold $z^2\mathrm{Ry}/n^2$ (contrary to what we would expect). This demonstrates in particular the smallness of the residues at the poles of $f$ and $\alpha$, corresponding to the excitation to states with the principal quantum number $n'' \gg n, n'$.

A rigorous numerical calculation of the change in the hydrogen spectrum is made in Ref. 13 allowing for mixing of $l$ in the case of states with $n = 1$–$6$ at frequencies of ruby ($\hbar\omega_R = 1.785$ eV $= 0.1312$ Ry) and neodymium ($\hbar\omega_N = 1.16$ eV $= 0.086$ Ry) lasers. A calculation of $\Delta\varepsilon_{nlm}$ for $n = 6$ and $\omega = \omega_R$ ($n^3\Omega \approx 28$) based on Eqs. (27)–(30) ensures a satisfactory agreement with the exact results. However, if $\omega = \omega_N$ the results are close only for the states with $l = 4$ or 5. The reason for the discrepancy for the states with $l \leqslant 3$ is related not to the smallness of $n^3\Omega \approx 18$ but to the proximity of $\hbar\omega_N$ to a "downward" resonance with the $n = 3$ level ($\Delta E_{6-3} = 0.0834$ Ry). (The states with $l = 4$ or 5 are not mixed by the dipole interaction with $n = 3$ levels.)

We shall conclude by pointing out that the results obtained allow us to analyze completely the change in the spectrum of an atom in a field and also the polarization dependence of the cross sections for the scattering of hf light by atoms.

[1)]The asymptotic nature of the series follows already from the fact that the expansion represented by Eq. (7b) loses the information on the anti-Hermitian part of $G$, which is governed by the term $i0$ in the denominator of Eq. (7a). [The effects associated with the anti-Hermitian part of $G$ were indeed exponentially small in the case of a smooth potential $U(r)$.]


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