

Dynamic polarizability of highly excited atomic states

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Analytic expressions are derived for the dynamic polarizability of highly excited hydrogen-like atomic states. It is shown that a strong cancellation of the terms of the composite matrix element determines the dynamic polarizability. This makes the dynamic polarizability quasiclassically small compared to the individual terms of the composite matrix. It is concluded that the resonant behavior of the dynamic polarizability of highly excited states differs significantly from the resonant behavior of the polarizability in the ground and low-lying atomic states. The static limit and high-frequency limit of an electromagnetic field are considered.

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The properties of dynamic polarizability of atomic states are described in detail in the literature (see, e.g., Refs. 1 and 2). This quantity is the proportionality coefficient in the dependence of the shift δE_k of an atomic level, following application of a monochromatic electromagnetic field $\mathcal{E} \cos \omega t$, on the square of the intensity of this field:

$$\delta E_k = -\alpha_k \mathcal{E}^2 / 4.$$

Such a dependence is realized for an isolated nondegenerate state k and for external-field frequencies ω that are not at resonance with the frequencies of the atomic transitions.

For the ground and low-excited atomic states, the value of α_k can be calculated only by numerical methods. There are no simple analytic formulas for the matrix elements and the frequencies of the atomic transitions, which determine the dynamic polarizability (see Eq. (1) below).

In the present paper we calculate the dynamic polarizability of highly excited atomic states, when the principal quantum number n of the considered state k is large compared with unity: $n \gg 1$. It is known that for such states the wave functions and the energies are hydrogen-like, so that analytic expressions can be obtained for the dynamic polarizability.

We assume first that the electromagnetic wave, with frequency ω , is linearly polarized along the z axis. In the general case, the dynamic polarizability takes then the form

$$\alpha_{nlm} = 2 \sum_{n'l'} \frac{\omega_{nn'}}{\omega^2 - \omega_{nn'}^2} |z_{n'l'm}^{n'l'm}|^2. \quad (1)$$

Here, n , l , and m are the principal, orbital, and magnetic quantum numbers of the hydrogen-like states, $\omega_{nn'}$ are the frequencies of the corresponding atomic transitions, $z_{n'l'm}^{n'l'm}$ are the dipole matrix elements. Here and elsewhere we use the atomic system of units, in which $e = \hbar = M_e = 1$.

In accordance with the foregoing, we have for highly excited hydrogen-like states ($n, n' \gg 1$)

$$\omega_{nn'} = (2n'^2)^{-1} - (2n^2)^{-1}.$$

The quantity $z_{n'l'm}^{n'l'm}$ is a dipole matrix element of the operator z between the Coulomb wave functions.

We separate first in (1) the dependence on the magnetic quantum number m , which is a conserved quantity because

of the assumed linear polarization of the field. This is done on the basis of Eq. (29.7) of the book by Landau and Lifshitz.³ As a result we obtain from (1) (with allowance for the fact that l' takes on values $l' = l \pm 1$)

$$\alpha_{nlm} = \sum_{n'} \frac{2\omega_{nn'}}{\omega^2 - \omega_{nn'}^2} \left\{ \frac{l^2 - m^2}{(2l+1)(2l-1)} \times |R_{nl}^{n'l-1}|^2 + \frac{(l+1)^2 - m^2}{(2l+1)(2l+3)} |R_{nl}^{n'l+1}|^2 \right\}. \quad (2)$$

The quantities

$$R_{nl}^{n'l\pm 1} = \int_0^\infty R_{nl}(r) R_{n'l\pm 1}(r) r^3 dr \quad (3)$$

constitute here radial Coulomb dipole matrix elements ($R_{nl}(r)$ are radial Coulomb wave functions).

Thus, to solve the problem we must sum in (2) over the principal quantum numbers n' of the intermediate states (including integration over the states of the continuous spectrum). We note that, as can be seen from (2), there is no diagonal term (with $n' = n$) in such a summation. The summation problem breaks up into two: 1) summation over n' far from n , i.e., when $|n' - n| \sim n, n'$; 2) summation over n' close to n , i.e., when $|n' - n| \ll n, n'$.

We consider first the allowance for remote n' . In this case the quasiclassical equations obtained in Ref. 4 are valid for the matrix elements (3). Substituting these equations in (2) and replacing the quasiclassical summation over n' by integration, on the basis of the rule

$$\sum_{n'} \frac{1}{n'^3} (\dots) = \int_{-\infty}^{\infty} d\omega_{nn'} (\dots),$$

we can easily verify that the corresponding contribution to the polarizability (1) vanishes because the integrand is even in the variable $\omega_{nn'}$. This is explained by the quasiclassical character of the spectrum of the highly excited states and the ensuing symmetry of the summation over n' relative to n .

We note that for states with $n \sim 1$ the foregoing statement is certainly incorrect, since $\omega_{nn'} > 0$ and the summation over n' is substantially asymmetrical with respect to n .

Thus, the sum in (2) is determined only by states with n' close to n , when it is incorrect to replace the sum over n' by an integral, since an important role in this sum is played by a

relatively small number of terms. Since the terms of the sum with $n' > n$ cancel to a considerable degree the sums with $n' < n$, the quasiclassical radial dipole matrix elements (3) with $|n' - n| \ll n$, n' must be substituted with account taken of the next order, above the lowest one, in the parameter $1/n$ of the quasiclassical theory. We use for this purpose the result of Ref. 5:

$$R_{n'l}^{n'l \pm 1} = \frac{n_c^2}{s} \left[\pm J_s'(s\varepsilon) + \frac{(1-\varepsilon^2)^{1/2}}{\varepsilon} J_s(s\varepsilon) \right]. \quad (4)$$

Here $J_s(z)$ is a Bessel function, and we put

$$s = n' - n, \\ n_c = \frac{n(n+s)}{n+s/2}, \quad \varepsilon = \left[1 - \left(\frac{l}{n_c} \right)^2 \right]^{1/2}.$$

The substitution $n_c \rightarrow n$ results in quasiclassical matrix elements that do not take into account the next order in the quasiclassical approach. They were obtained in Ref. 6.

It is similarly necessary to write for $\omega_{n'n}$ an expansion in $s = n' - n$ accurate to terms of order s^2 inclusive. From the expression given above for $\omega_{n'n}$ we easily obtain

$$\omega_{n'n} = s/n^3 - 3s^2/2n^4. \quad (5)$$

Substituting (4) and (5) in (2) we obtain

$$\alpha_{n'lm} = 2n^6 \sum_{s=1}^{\infty} \frac{7s^2 - (\omega n^3)^2}{[s^2 - (\omega n^3)^2]^2} \left\{ \frac{l^2 - m^2}{(2l+1)(2l-1)} \left[-J_s'(s\varepsilon) + \frac{(1-\varepsilon^2)^{1/2}}{\varepsilon} J_s(s\varepsilon) \right]^2 + \frac{(l+1)^2 - m^2}{(2l+1)(2l+3)} \right. \\ \left. \times \left[J_s'(s\varepsilon) + \frac{(1-\varepsilon^2)^{1/2}}{\varepsilon} J_s(s\varepsilon) \right]^2 \right\}. \quad (6)$$

It is seen from (6) that

$$\alpha_{n'lm} \sim n^6,$$

only if we are not close to resonance with discrete levels in the vicinity of the n -th level, where the dynamic polarizability increases sharply. These resonances are determined by the obvious conditions

$$\omega = s/n^3.$$

It can be seen from (6) that in the vicinity of each of the resonances the quantity $\alpha_{n'lm}$ becomes infinite without reversing sign and stays positive. Thus, the resonant behavior of the dynamic polarizability of highly excited states differs qualitatively from the resonant behavior of $\alpha_{n'lm}$ for ground and low excited states, when the polarizability reverses sign on passing through resonance (see Figs. 8.1 and 8.2 of Ref. 1). The reason for this difference is that in the case considered here the resonances superimposed are in states that are higher and lower than n , whereas at $n \sim 1$ there is resonance with one discrete atomic level that is definite for a given frequency.

We discuss now the behavior of the dynamic polarizability in the intervals between the resonances. It is known (see, e.g., Fig. 8.1 of Ref. 1) that for the ground states of atoms (in this case, $n = 1$) the dynamic polarizability vanishes in each interval between resonances. For excited low-lying

states ($n \sim 1$) the dependence has a different character, inasmuch as with increasing frequency resonances with both high-lying and low-lying states can set in. In particular, it is possible for the dynamic polarizability not to vanish in the intervals between resonances (but it can reverse sign on passing through each resonance). In our case of highly excited states ($n \gg 1$) the dynamic polarizability, being a resonantly large positive quantity in the vicinity of the resonant frequencies, can take on negative values in the intervals between the resonances on account of the large negative term in the sum of (6) with $s = 1$ at frequencies $\omega > \sqrt{7}/n^3$. In this case it vanishes twice in the interval between the resonances.

We note the following important circumstance: the dynamic polarizability (6) is smaller by a factor $\sim n$ than each of the terms of the sum in (2), which are the order of n^7 , inasmuch as according to (4) the matrix element $R_{n'l \pm 1} \sim n^2$, and

$$\omega_{n'n'} / (\omega^2 - \omega_{n'n'}^2) \sim 1/\omega_{n'n'} \sim n^3.$$

This fact is a consequence of the already mentioned cancellation of the terms with $n' > n$ and $n' < n$.

In the static case $\omega n^3 \ll 1$ it follows from (6) that the dynamic polarizability is positive. This agrees with the known statement that terms of the hydrogen atom are always shifted downward because of the quadratic Stark effect [see p. 339 (Russian original) of Ref. 3]. Indeed, the transition from the spherical to the parabolic cases, in which the static shifts of the terms of the hydrogen atom are expressed, can be reached by multiplication by the squares of the corresponding Clebsch-Gordan coefficients.

A special case arises in the asymptotic limit of high frequencies, when $\omega n^3 \gg 1$. In this case, as can be seen from (6), the dynamic polarizability becomes quite small and negative, and is of the order of

$$\alpha_{n'lm} \sim -\omega^{-2}. \quad (7)$$

This expression, as expected, corresponds to the polarizability of a free electron oscillating in the field of a linearly polarized wave. The resultant numerical factor in (7) is due to separation, from the wave function of the free electron with specified momentum \mathbf{p} (plane wave $\exp(i\mathbf{p}\cdot\mathbf{r})$), of a state with a definite angular momentum l and its projection m .

It can be seen from (6) that the coefficient of n^6 in the expression for the dynamic polarizability depends on the quantities l , m , l/n , and ωn^3 . The dependence on ωn^3 is shown qualitatively in Fig. 1. It takes into account the dynamic-polarizability singularities considered above.

We turn now to various particular cases of the general expression (6), when this expression becomes greatly simplified. A definite simplification is reached in the case $l \gg 1$. We then obtain from (6)

$$\alpha_{n'lm} = 2n^6 \left(1 - \frac{m^2}{l^2} \right) \sum_{s=1}^{\infty} \frac{7s^2 - (\omega n^3)^2}{[s^2 - (\omega n^3)^2]^2} \times \left[J_s'(s\varepsilon) + \frac{1-\varepsilon^2}{\varepsilon} J_s^2(s\varepsilon) \right]. \quad (8)$$

We have separated here the universal dependence on the

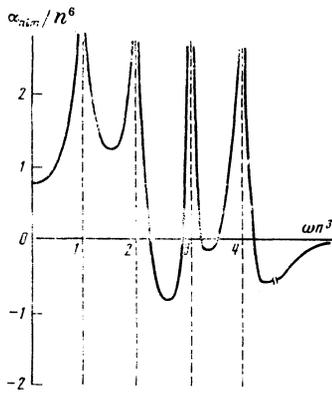


FIG. 1. Qualitative illustration of the character of the dependence of the dynamic polarizability of a highly excited hydrogenlike state (in relative units) on the frequency of the external field.

magnetic quantum number m :

$$\alpha_{nlm} \sim 1 - m^2/l^2.$$

In particular, for the static polarizability ($\omega n^3 \ll 1$) we have from (8)

$$\alpha_{nlm} = 14n^6 \left(1 - \frac{m^2}{l^2} \right) \times \sum_{s=1}^{\infty} \frac{1}{s^2} \left[J_s'^2(s\varepsilon) + \frac{1-\varepsilon^2}{\varepsilon^2} J_s^2(s\varepsilon) \right]. \quad (9)$$

As already noted, this result can be obtained also from the known expression for the polarizability of the hydrogen atom in a state with definite parabolic quantum numbers (see p. 339 of Ref. 3) by multiplication by the squared Clebsch-Gordan coefficients corresponding to transformation from parabolic quantum numbers (nn_1n_2) to spherical (nlm), and taking the limit $n \gg 1$.

We turn now to a particular case of the general formula (6), corresponding to $l = m = 0$. We obtain

$$\alpha_{n00} = \frac{2}{3} n^6 \sum_{s=1}^{\infty} \frac{7s^2 - (\omega n^3)^2}{[s^2 - (\omega n^3)^2]^2} J_s'^2(s). \quad (10)$$

In particular, for the static polarizability we form from (10)

$$\alpha_{n00} = \frac{14}{3} n^6 \sum_{s=1}^{\infty} \frac{1}{s^2} J_s'^2(s) \approx 0.6n^6. \quad (11)$$

In the opposite case of high frequencies ($\omega n^3 \gg 1$) we obtain from (10), using the theorem for sums of Bessel functions

$$\alpha_{n00} = -1/3 \omega^{-2}. \quad (12)$$

The numerical factor in (12) is connected with separation, from the plane wave, of the spherically symmetrical state with $l = m = 0$: this corresponds to averaging over the solid angle:

$$\overline{\cos^2 \theta_{pg}} = 1/3.$$

For the obtained expressions to be applicable it is necessary that the next higher orders of perturbation theory in the electric field intensity be small compared with the quadratic ones. This takes place if $\mathcal{E} \ll n^{-4}$ (Ref. 7). In addition, we

have neglected in our analysis the linear Stark shifts, which takes place in the case of a constant field for degenerate states. In the case of an alternate field, however, in accordance with the general theory (see, e.g., Refs. 1 and 2) we can neglect the onset of quasienergy states that imitate a linear Stark shift, subject to satisfaction of the condition

$$n^2 \mathcal{E} / \omega \ll 1, \quad (13)$$

which imposes an upper bound on the electric field intensity of the wave, and a lower bound on its frequency. In the derivation of the criterion (13) we used the fact that the characteristic dipole matrix elements (3) between the highly excited states are of the order of n^2 .

We note in conclusion that the results do not change on going from the purely hydrogenlike states considered above to highly excited state of complex atoms, if we are dealing with orbital angular momenta $l > 2$ of the considered states. In this case the quantum defect is negligibly small. For states with $l = 0, 1$, and 2 , however, the presence of the quantum defect prevents cancellation of the terms with $n' > n$ and $n' < n$, in view of the difference between the energies of the corresponding states. As a result, the dynamic polarizability increases abruptly and becomes of the order of n^7 . We then find ourselves within the framework of applicability of Eq. (2), in which we must substitute the frequencies of the atomic transitions with allowance for the quantum defect, whereas the dipole matrix elements can be substituted in the lowest order of the quasiclassical approximation.⁶ In particular, the states with $n' = n$ now no longer fail to make a zero contribution but, conversely, make a definite contribution to (2), since the corresponding quasiclassical matrix radial elements (3) turn out to be maximal.⁸ For example, for the S state we obtain from (2), confining ourselves in the sum over n' only to the term with $n' = n$,

$$\alpha_{n00} = 3/2 n^7 \delta / [\delta^2 - (\omega n^3)^2]. \quad (14)$$

We have used here the known expression of the matrix element R_{n0}^{n1} (see, e.g., Eq. (52.6) of Ref. 9). Next, $\delta = \delta_1 - \delta_0 > 0$, where δ_0 and δ_1 are the quantum defects of states with $l = 0$ and 1 , respectively, for the considered atom.

Of course, expression (14) has limited validity, only from the static limit to the vicinity of the resonance with the intermediate level $n, l = 1$. At higher frequencies ω , other resonant terms will predominate in the sum (2). Numerical calculations of α_{nlm} were carried out in Ref. 10, using matrix elements of the type (4), for a number of alkali atoms.

As noted at the very beginning of the article, we have considered the case of linear polarization of the wave field. Circular polarization of the electromagnetic field introduces no fundamental changes in the result, for all that changes in the initial formula (2) are the factors in front of the summation sign over n' , which depend on m and l . The sums over n' themselves are not changed. The same remarks hold also for the general case of elliptic polarization of the electromagnetic field.

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