

# AC Stark shift of atomic energy levels

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**Abstract.** Calculated and experimental data on the AC Stark shift of atomic levels in an external, subatomic-strength variable field are considered. Theoretical predictions concerning the disturbance of atomic spectra by fields of atomic and superatomic strength are discussed. The limiting value of the atomic AC Stark shift in a light-frequency radiation field is estimated.

## 1. Introduction

This review is devoted to the problem of the disturbance of atomic levels by the electromagnetic field of laser radiation. The shift of levels in a static electric field is known as the *DC Stark shift*, while the shift of levels in a variable monochromatic electromagnetic field is referred to as the *AC Stark shift*.

The DC Stark shift of atomic levels was discovered by J Stark in 1913. Up to the middle of the 20th century, both the experimental and theoretical research of the effect was limited to the case of a dc electric field. Only in the 1960s the development of lasers stimulated research in the disturbance

(shift and splitting) of atomic levels initiated by variable electromagnetic fields, primarily the radiation field from lasers. This research became a constituent part of the general problem of the interaction between matter and a strong radiation field. Thus, the domain of physics to which this review is devoted is fairly new. For instance, the first observation of the AC Stark effect initiated by the laser radiation field was carried out by Bonch-Bruevich and co-workers in 1969 [1].

The experimental and theoretical research conducted over the last three decades provides a detailed picture of the AC Stark effect in atoms, generated by the electromagnetic field of laser radiation. This picture will be a major focus of interest in our review.

Several reviews on this topic have been published [2–4], and it has also been discussed in a number of monographs [5–9]. However, only in Refs [4] and [7, 8] the material is discussed in detail. Unfortunately, these sources are almost inaccessible to most physicists. This fact and the desire to generalize the material as fully as possible has prompted us to write this review.

Before we begin the detailed description of the physics underlying the process of the disturbance of atomic levels we would like to note that the Stark effect in a variable field differs dramatically from the analogous effect in a stationary electric field.

The first distinction is that while in a static field the perturbation of a nondegenerate bound atomic state reduces to a shift in the energy of that state (in other words, to a Stark shift of the atomic level), in a monochromatic electromagnetic field the initial nondegenerate state is transformed into an assembly of quasi-energy states with the distance between the

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adjacent quasi-levels equal to the energy of the photon of the radiation field. More than that, the entire quasi-energy spectrum is shifted in relation to the initial unperturbed level. In a few cases (see below) only one quasi-level is effectively populated, which just corresponds to the AC Stark shift of that particular atomic level.

The second qualitative distinction is that at a certain frequency of the electromagnetic field the resonance may occur when this frequency is close to the frequency of an atomic transition from this level to another bound state. If this happens, even in a weak electromagnetic field the resonance level may really become populated (the saturation effect) and this is accompanied by the splitting of both the initial level and the resonance level into two quasi-energy levels each (the Rabi effect). The resonance case is described in monographs [5, 7], so that in the present review we limit ourselves to the nonresonant Stark effect.

The other distinctions are of a quantitative nature but they lead to qualitative distinctions of the Stark effect in dc and variable fields.

One such distinction lies in the fact that in laboratory conditions the attainable limiting strength of a dc electric field is about  $10^5 \text{ V cm}^{-1}$ , while the strength of a variable laser radiation field can be of the order of the atomic field strength ( $10^9 \text{ V cm}^{-1}$ ) and higher. Thus, in a dc electric field, the Stark shift always constitutes a small correction to the value of the initial energy and can always be calculated employing perturbation theory. By contrast, in a variable laser radiation field, the disturbance of an atomic system can be enormous, exceeding even the unperturbed energy, although the broadening of the level will remain small (otherwise the very concepts of a bound state and its Stark shift lose all meaning).

When intense laser radiation interacts with an atom, the so-called *dynamic* one- or multiphoton resonances induced by this light may emerge (there can be no such resonances in an unperturbed atom or in a weak field [8]). This changes the degree of nonlinearity of the multiphoton ionization process in the atom. The shift of the ground state also changes the tunneling ionization rate and the threshold of the atomic barrier-suppression decay [10].

Worth noting is one more important distinction which is related to the experimental method. High and ultrahigh laser fields are realized by reducing the length of the laser pulses to values on the order of one period of the laser radiation ( $10^{-15} \text{ s}$  in the frequency range of a visible light). In such conditions, the concept of quasi-energy levels, which stems from the monochromatism of the radiation, lose all meaning (and so does the concept of a Stark shift).

All these distinctions will become very noticeable in our detailed discussion of the AC Stark effect in the present review.

## 2. The DC Stark effect

There are two reasons why the Stark effect in a dc electric field is of interest in relation to the main theme of the present review.

Firstly, in the various stages of studying the AC Stark effect it is instructive to compare the results with those for the case of a dc field.

Secondly, a static electric field is obviously the limiting case of a low-frequency variable field. Knowing this limit is extremely important in interpreting the experimental data. Since variable laser field can be extremely strong, of special

interest are the data on the Stark effect in strong dc fields. At present such data can be obtained only theoretically.

In accordance with what we have just said, the present section is a brief exposition of the basic data on the Stark effect in a weak constant field (in comparison to the characteristic strength of an atomic field); these data have been discussed far more thoroughly in the references cited below. After that we shall describe in detail the relatively new theoretical data for the case of a strong static electric field with strengths comparable to the strength of an atomic field.

### 2.1 A weak stationary electric field

The Stark effect in a weak dc electric field has been thoroughly studied both experimentally and theoretically. The theory of the effect is expounded in any standard course of quantum mechanics. A general exposition of the results of theoretical and experimental studies on this topic can be found in the monographs by El'yashevich [11] and Frish [12] and in Bonch-Bruевич and Khodovoi's review [13]. Below is an overview of the main results of these studies.

When an external dc electric field of strength  $F$  is switched on, an electron bound in an atom and having a negative energy  $E_n$  acquires an additional energy  $\delta E_n(F)$ , since the atom becomes polarized in the field.

If the state in question is not degenerate, its energy in the external field is given by

$$E_n(F) = E_n + \delta E_n(F). \quad (1)$$

A degenerate state with an energy  $E_{nm}$ , where  $m$  is the magnetic quantum number, experiences splitting in the electric field into  $2l + 1$  components, since the sublevels corresponding to different values of  $m$  acquire different additional energies  $\delta E_{nm}(F)$  in the field. In particular, what J Stark observed was the splitting of the Balmer  $H_\alpha$  line in the spectrum of the hydrogen atom initiated by a dc electric field.

The hydrogen atom (except for its ground state) and highly excited hydrogen-like (Rydberg) states of many-electron atoms have additional degeneracy in the orbital quantum number  $l$ , which is removed by an electric field. In the absence of this field, such an atom possesses a constant dipole moment  $d$ . The additional energy acquired by an atom with a constant dipole moment in an external electric field is

$$\delta E_{nm} = -d_{nm}F. \quad (2)$$

Here  $n_1$  is the parabolic quantum number characterizing the split sublevel. From Eqns (1) and (2) it follows that in this case the variation in the energy is proportional to the first power of the field strength. This is what is known as the *linear DC Stark effect*.

Multielectron atoms that are in the ground or low-lying excited states exhibit a zero constant dipole moment, but an external electric field induces in them a dipole moment

$$d_{nlm} = \alpha_{nlm}F. \quad (3)$$

Here  $\alpha_{nlm}$  presents the static polarizability of the atom in the state with the given quantum numbers. From formulas (1)–(3) it follows that the additional atomic energy in this case takes the form

$$\delta E_{nlm}(F) = -\frac{1}{2}\alpha_{nlm}F^2. \quad (4)$$

The main goal of the theory in describing the DC Stark effect in a constant electric field is the calculation of the static polarizabilities for different states of various atoms. When the external field is weak, i.e. the field strength is small compared to the characteristic atomic field strength, expansions in a perturbation series are employed. The number of such calculations is very large and their results are compiled in various summary tables. The data on the ground states of most atoms can be found in Radtsig and Smirnov's reference book [14].

The relatively small value of the electric field strength that can be realized in experiments (not larger than  $10^5$  V cm<sup>-1</sup>) is the reason for the relatively small values of the shifts and splittings of the atomic levels established experimentally. The values of these quantities usually do not exceed 1 cm<sup>-1</sup> ( $10^{-4}$  eV). Of course, these values are much larger than the natural width of atomic levels (of order  $10^{-3}$ – $10^{-4}$  cm<sup>-1</sup>) and the Doppler spectral linewidth at room temperature (of order 0.1 cm<sup>-1</sup>). However, observations of the Stark effect in a dc electric field are fraught with difficulties and require complicated and precision experiments [13]. Accordingly, it is prevalent to interpret the Stark effect in a dc electric field as small corrections to the initial values of the unperturbed energies in the spectrum of the atom. This statement becomes invalid only for very highly excited Rydberg states, for which the distances between the adjacent unperturbed levels are extremely small.

The experimental data are described very accurately by perturbation-theory calculations with allowance for only the first term in the expansion of the static dipole moment in powers of the field strength.

Using the Wigner–Eckart theorem, we can easily obtain an analytical expression for the dependence of the DC Stark shift on the magnetic quantum number  $m$  from the general formula derived in the second order of quantum-mechanical perturbation theory, or

$$\delta E_i(F) = F^2 \sum_{k \neq i} \frac{|z_{ik}|^2}{\omega_{ik}}. \quad (5)$$

Here  $z_{ik}$  and  $\omega_{ik} = E_i - E_k$  are the matrix element of the coordinate and the difference of the unperturbed energies, respectively. The expression sought is given by

$$\delta E_i(F) = -\frac{1}{2} \left[ \alpha_S^{nl} + \alpha_t^{nl} \frac{3m^2 - j(j+1)}{j(2j-1)} \right] F^2. \quad (6)$$

Here  $\alpha_S$  and  $\alpha_t$  are the scalar and tensor static polarizabilities, respectively, and  $j$  is the angular momentum of the state  $i$  under examination. It can be seen that the contribution of the tensor polarizability disappears as a result of averaging over the magnetic quantum number of the level considered.

For arbitrary states of the hydrogen atom with given parabolic quantum numbers, both the linear and the quadratic DC Stark shifts are well known, and we will not discuss them here.

For arbitrary states of the hydrogen atom with a given orbital quantum number, the linear shift goes to zero, while for the quadratic DC Stark shift the scalar part of the static polarizability has the simple form [14]

$$\alpha_S^{nl} = n^6 + \frac{7}{4} n^4 (l^2 + l + 2) \text{ a.u.} \quad (7)$$

Here  $n$  and  $l$  are the principal and orbital quantum numbers of the state. In particular, for the ground state we arrive at the

well-known result  $\alpha_S^{10} = 9/2$ . For excited states Eqn (7) yields the simple formula  $\alpha_S^{n0} = n^6 + (7/2)n^4$ .

The formula for the tensor part of static polarizability of the excited states of the hydrogen atom is somewhat more complicated [15]:

$$\alpha_t^{nl} = -\frac{l}{4(2l+3)} n^4 (3n^2 + 11l^2 + 11l - 9). \quad (8)$$

The magnitude of this quantity is of the same order as that of the scalar part. According to Eqn (8), for states with  $l = 0$  the tensor part is zero.

## 2.2 A strong stationary electric field

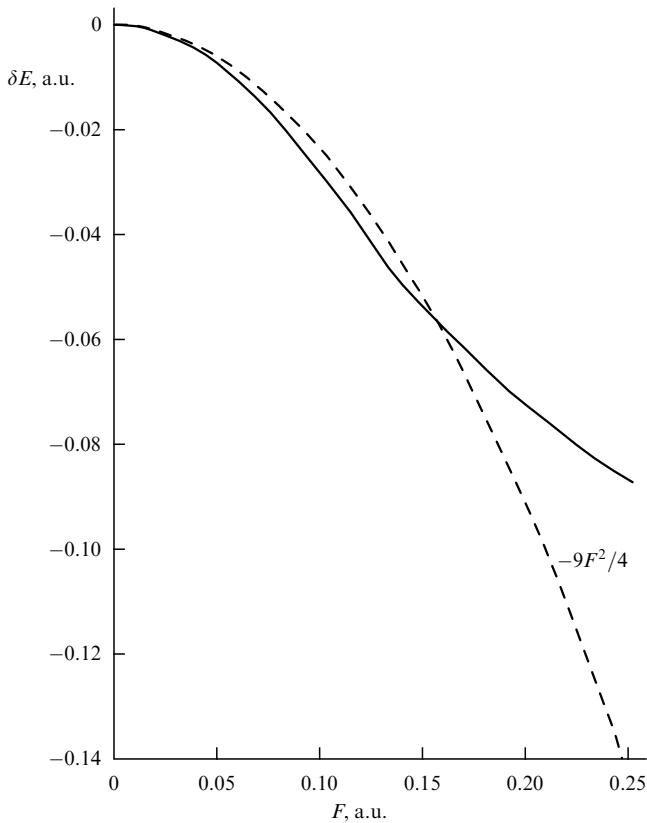
Calculations of shifts and splittings of atomic levels in a strong dc electric field, for which perturbation theory breaks down, have been carried out only for the hydrogen atom. Analytical expressions for arbitrary states of this atom becomes extremely complicated as the order of perturbation theory increases. Alliluev and Malkin [16] arrived at exact results for excited states of the hydrogen atom up to the fourth order of perturbation theory (the states are characterized by parabolic quantum numbers). Bekenstein and Krieger [17] used the semiclassical Bohr–Sommerfeld quantization rule to find the DC Stark shifts. Numerical calculations of the DC Stark shift of the ground state of the hydrogen atom in the constant electric field have been carried out by Silverman and Nicolaides [18], Franceschini et al. [19], Maquet et al. [20], Benassi and Grecchi [21], and Mur and Popov [22] using various methods (all computations yield results that are very close, differing only by several percent). Table 1 lists the results of these calculations. We see that already at  $F = 0.2$  a.u. the exact value of the DC Stark shift differs significantly from the result obtained in second-order perturbation theory. The data from Table 1 are also presented diagrammatically in Fig. 1.

**Table 1.** DC Stark shift of the ground state of the hydrogen atom as a function of the electric field strength.

Field strength $F$ , a.u.	Exact value of shift, a.u.	Perturbation theory, $-9F^2/4$ , a.u.
0.025	-0.00143	-0.00141
0.030	-0.00207	-0.00202
0.050	-0.00610	-0.00562
0.100	-0.0274	-0.0225
0.200	-0.0705	-0.0900
0.250	-0.086	-0.141
0.500	-0.120	-0.562
1.000	-0.124	-2.25

Table 1 also shows that the DC Stark shift in a weak field proves to be somewhat larger than that predicted in the lowest (second) order of perturbation theory, while in a stronger field it becomes much smaller than the result predicted by a second-order perturbation theory.

It should also be noted that the level width (whose magnitude is not given here; see Ref. [22]) becomes comparable to the DC Stark shift of the level for a field strength  $F \approx 0.25$  a.u. If the field intensity is increased still further, the level width exceeds the DC Stark shift, so that the concept of shift of atomic levels loses all physical meaning (however, in Table 1 we also list the corresponding values for large field strengths obtained purely mathematically by solving the Schrödinger equation).



**Figure 1.** DC Stark shift of the ground state of the hydrogen atom as a function of the electric field strength. The solid curve represents the results of numerical calculations, and the dashed curve the results of the lowest-order perturbation-theory calculations.

If the strength of the dc electric field is small compared to the characteristic atomic value, the size of the DC Stark shift substantially exceeds the ionization width (the imaginary part of the energy is small compared to the variation of the real part). But if the external field strength is of the order of, or larger than, the characteristic atomic value (here the atomic value stands for the strength of the field at which the energy of the level in question is equal to the energy at the top of the effective potential barrier), the energy shift proves to be of the same order of magnitude as the imaginary part of the energy. However, the problem of calculating the level shift is still meaningful, although the concept of discreteness of an atomic spectrum breaks down. In scattering problems such levels act as resonances in the scattering cross section, with the width of the resonance corresponding to the imaginary part of the energy, and the position of the maximum to the real part.

The strength of a constant electric field at which the level energy  $E_n$  in the Coulomb field of an ion with charge  $Z$  is equal to the energy at the top of the effective potential barrier is well known [23]:

$$F_{an} = \frac{E_n^2}{4Z} = \frac{Z^3}{16n^4}. \quad (9)$$

Of course, Eqn (9) bears a semiquantitative character since it was obtained by employing the one-dimensional ionization model. The atomic field strengths for highly excited states of the hydrogen atom were found numerically by Popov et al. [24]. These values depend not only on the

principal quantum number but also on the parabolic quantum numbers of the level. Table 2 lists the values of the classical ionization threshold for the case of highly excited states of the hydrogen atom with  $n = 16$ . We see that the atomic field strength is much larger than the estimate provided by Eqn (9), i.e.  $1/16n^4$ .

**Table 2.** Values of the classical ionization threshold for several parabolic states of the hydrogen atom with the principal quantum number  $n = 16$  and  $m = 0$  (in units of  $1/n^4$ ) [24].

$n_1$	$n_2$	$F_a$
15	0	0.308
13	2	0.233
12	3	0.214
11	4	0.200

The expansion in a perturbation series for the Stark shift in a dc electric field is asymptotic and the series diverges no matter how small the electric field strength is. The terms of the series first decrease but then increase without bound. Summation is done up to the smallest term in the series.

An analytical asymptotic expression for the coefficients of the perturbation-series expansion of the ground-state energy of the hydrogen atom for  $k \gg 1$  is also known [25]:

$$E_{1s}(F) = -0,5 - \sum_{k=1}^{\infty} \alpha_k F^{2k},$$

$$\alpha_{2k} = \frac{6}{\pi} \left(\frac{3}{2}\right)^{2k} \Gamma(2k+1) \left(1 - \frac{107}{36k}\right). \quad (10)$$

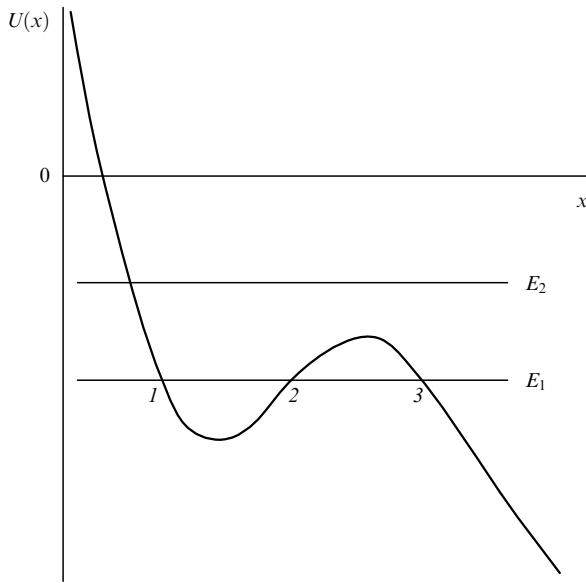
One can see that these coefficients rapidly increase with their number  $k$ . Notice that although all the terms in the series (10) are negative, the DC Stark shift in a strong field may be positive as well (this is a property of asymptotic series, in contrast to convergent series).

We would like to stress the fact that, according to Mur and Popov's calculations [22], even for the relatively small electric field strength  $F = 0.1$  a.u. no less than 20 terms of the perturbative series are required if we wish to pass from the simple second-order perturbation-series result,  $-0.0225$  a.u., to the exact value,  $-0.0274$  a.u. (see Table 1).

In Ref. [22], the DC Stark shift of arbitrary hydrogen-atom states was studied by the fairly accurate  $1/n$ -expansion method as a function of the field strength. The paper presents the results for states with the parabolic quantum numbers

$$n_1 = n - 1, \quad n_2 = m = 0 \quad \text{and} \quad n_2 = n - 1, \quad n_1 = m = 0.$$

They constitute the extreme components of the multiplet with a given principal quantum number  $n$ . The range of electric field strengths extended to 1 a.u., and the range of the principal quantum numbers began at two and extended to infinity. The scale of the field strengths for different principal quantum numbers was  $1/n^4$ , since it is well known that the value of the field strength at which the level with the principal quantum number  $n$  becomes higher than the effective potential barrier is  $1/16n^4$  a.u. The results of numerical calculations show that even up to the field strengths of order  $1/2n^4$  a.u. the DC Stark shift is approximately a linear function of the field strength (as in the weak-field limit): the first extreme component points upward, and the second extreme component downward (the other components of the



**Figure 2.** A schematic sketch of the effective potential energy  $U(x)$ . Here 1, 2, and 3 are the classical turning points; the energy  $E_1$  corresponds to a subbarrier state (tunneling), and the energy  $E_2$  to an overbarrier state.

multiplet lie between these extreme components). As for larger values of the field strength, the results have hardly any meaning since the width of the split sublevels becomes of order of the distance between them on the energy scale.

If the external field strength is smaller than the atomic field strength, the DC Stark shift can be determined from the Bohr–Sommerfeld quantization rule applied to the classical region of the particle motion between the turning points 1 and 2 (see Fig. 2). The extreme right turning point 3 corresponds to the outer part of the effective potential barrier, with the probability that a particle from the inner part of the potential well will appear on the external side being exponentially small.

As the electric field strength approaches the atomic value, points 2 and 3 move closer to each other and the Bohr–Sommerfeld quantization rule breaks down,

If the field strength exceeds the value given by Eqn (9), the turning points 2 and 3 become complex conjugate to each other and the Bohr–Sommerfeld quantization rule turns valid anew. Mur and Popov [26] found that to determine the DC Stark shift and the imaginary part of the energy one can use the analytic continuation of the Bohr–Sommerfeld quantization rule to the overbarrier region:

$$\frac{1}{2\pi} \oint_C \sqrt{2m[E_n - U(x)]} dx = \left(n + \frac{1}{2}\right) \hbar, \quad (11)$$

with the integration contour  $C$  encompassing the complex turning points 1 and 3. Equation (11) is much simpler from the computational viewpoint than other (numerical) methods of finding the real and imaginary parts of the energy in the case of overbarrier resonances. The next correction in the degree of quasi-classicality is also simple: in the integrand in Eqn (11) one should do the following substitution

$$p \rightarrow p + \frac{1}{24} \frac{U''}{p^3}.$$

This analytic-continuation approach was used in Ref. [26] in the case of highly excited states of the hydrogen atom with a

zero magnetic quantum number. The results for the real part of the energy of the overbarrier resonance are listed in Table 3 for the same values of the quantum numbers as in Table 2 and for an electric field strength  $F = 16.8 \text{ kV cm}^{-1}$  (which corresponds to 0.214 in units of  $1/n^4$ ). In accordance with data from Table 2, this value shows evidence of being subbarrier for the first two states, and overbarrier for the last two. Table 3 also presents the experimental values taken from Ref. [27]. Clearly, there is good agreement between the experimental and theoretical findings.

**Table 3.** Position of some of the Stark sublevels (in units of  $\text{cm}^{-1}$ ) for the hydrogen-atom multiplet with  $n = 16$  in an electric field of strength  $F = 16.8 \text{ kV cm}^{-1}$ .

$n_1$	$n_2$	$-E$ , theory [26]	$-E$ , experiment [27]
15	0	196.5	198.5
13	2	273.6	275.8
12	3	313.3	314.8
11	4	353.8	351.4

Thus, for a constant electric field, the theory in hand provides a fairly complete answer, and the results are in good agreement with the experimental data in a weak-field range.

### 3. Specific features of the Stark effect in a variable field

A dc electric field shifts the atomic energy levels. As is known, the law of conservation of energy is valid only in a dc field, i.e. the energy is not conserved in a time-dependent field. Under certain conditions we can speak about the Stark shift of an energy level only in the case of an external monochromatic field (this fact was briefly outlined in the Introduction). The initial relationship that allows for this leans upon the Floquet theorem.

#### 3.1 The Floquet theorem and the quasi-energy spectrum

According to the Floquet theorem [28] on the solution of a linear homogeneous differential equation with periodic coefficients, we must represent the wave function of a system placed in an external monochromatic field as follows

$$\Psi(\mathbf{r}, t) = \exp(-iE_a t) \varphi(\mathbf{r}, t), \quad (12)$$

where the periodic function  $\varphi(\mathbf{r}, t) = \varphi(\mathbf{r}, t + 2\pi/\omega)$  can be expanded in a Fourier series in time, so that

$$\Psi(\mathbf{r}, t) = \exp(-iE_a t) \sum_{k=-\infty}^{k=\infty} C_k(\mathbf{r}) \exp(-ik\omega t). \quad (13)$$

The wave function is thus seen to be a superposition of a number of stationary states with energies  $E_a + k\omega$ . Such a superposition is called a *quasi-energy state*, with  $E_a$  the *quasi-energy*. The notion of quasi-energy was introduced by Nikishov and Ritus [29]. The approach to solving the problem of the Stark shift, based on the quasi-energy concept, was developed by Ritus [30] in his theory of the AC Stark shift of atomic levels. The number of quasi-energies is equal to the number of unperturbed states of the system, and the spectrum of values of  $E_a + k\omega$  is called the *spectrum of quasi-harmonics* (see B Zel'dovich's review [31]).

The spectrum of quasi-harmonics represents the spectrum of states for a new quantum system 'atom + field'. This system, often named as a 'dressed atom', has become the universally adopted model in the physics of laser radiation

interaction with the atomic and molecular objects (see, for example, Ref. [5]).

From the material presented in the next section it follows that the results of experiments are in good agreement, both qualitatively and quantitatively, with the above predictions concerning the emergence of a spectrum of quasi-harmonics in a quantum system consisting of an atom and a field. There we will also show that there is one case, important from the practical viewpoint, where in the entire spectrum of quasi-harmonics only a single quasi-harmonic (the zeroth quasi-harmonic) is populated, which corresponds to a shift of an atomic level by  $E_a(F) - E_a(0)$ , in the same way as this occurs in a dc electric field.

### 3.2 The relationship between the external field frequency and the transition frequency in the atomic spectrum

It is well known that the energy separation between the neighboring levels in the assembly of bound atomic states rapidly decreases with increasing the principal quantum number  $n$ , e.g. for Rydberg states it is proportional to  $n^{-3}$ . Hence, for the standard laser frequency ( $\omega$ ) range of interest to us from  $\approx 0.1$  eV (the carbon dioxide laser) to  $\approx 5$  eV (excimer lasers), both cases,  $\omega < n^{-3}$  and  $\omega > n^{-3}$ , can occur in the atomic spectrum. The first inequality corresponds to the ground and first excited states, while the second inequality corresponds to highly excited (Rydberg) states. Consequently, each specific case, with the exception of disturbance of the ground and Rydberg states, requires special analysis.

Indeed, with the rare exception of alkali atoms and light from excimer lasers, the frequency of the transition from the ground state (0) to the first excited state (1) is higher than  $\omega$  ( $\omega_{10} > \omega$ ), i.e. in relation to the perturbation of the ground states of atoms the laser radiation field is *low-frequency*. On the other hand, at values of the principal quantum number  $n \sim 10$  the distance between the neighboring levels is already about 0.01 eV, which is smaller than the energy of a photon even from a carbon dioxide laser, and so practically any laser radiation is *high-frequency* in relation to the Rydberg atomic states.

Since all the experiments measure not the perturbation of an isolated atomic state (i.e. not the Stark shift of the given level) but the variation of the energy of the transition from one state (the initial state) to another state, a typical situation in the interaction of laser radiation and atom is the one in which the overall effect of the disturbance of the ground state by a low-frequency field and the disturbance of a Rydberg state by a high-frequency field is observed. We will discuss just such cases in Section 4.

### 3.3 The time constant characterizing the nonresonant AC Stark effect and the laser radiation field of action

It is often said that the nonresonant Stark effect demonstrates no inertial properties, but actually such a statement is not rigorous. The thing is that the time constant characterizing the nonresonant AC Stark effect is given by the energy – time uncertainty relation  $\Delta E \Delta t \geq \hbar$ . Here  $\Delta E$  is the detuning from resonance (the energy defect) in the transition of an electron (that has absorbed one photon from the external field) to the nearest real bound state with allowance for the dipole selection rules, i.e.  $\Delta E = |\omega - \omega_{nm}|$ . The quantity  $\Delta t$  is the lower bound of the time constant for the emergence of the level disturbance, i.e. in general the time it takes an unperturbed atom to become a dressed atom; in particular, it is the time it takes the level  $n$  under consideration to shift.

The minimum value of  $\Delta E$  and the maximum value of  $\Delta t$  correspond to the case where a one-photon resonance emerges. Here the value of  $\Delta E$  is equal to the natural width of the atomic level, and the value of  $\Delta t$  is equal to the spontaneous (radiative) lifetime of the atomic electron in a given state  $n$ , exceeding  $10^{-8}$  s. On the other hand, the maximum value of  $\Delta E$  is of order 10 eV, and hence the minimum value of  $\Delta t$  is of order  $10^{-17}$  s. Depending on the specific situation, the value of  $\Delta t$  we are interested in lies between these limits.

Experiments in observing and measuring the atomic AC Stark effect are carried out in the radiation fields generated by  $Q$ -switched pulsed lasers with pulse lengths ranging from several nanoseconds to several tens of femtoseconds. These figures suggest that up to very large values of the principal quantum number  $n \gg 10$ , the typical detunings  $\Delta E$  from resonance are so large that they correspond to time constants smaller than the laser pulse length. This means that the magnitude of the Stark disturbance is determined by the ‘instantaneous’ intensity of the laser radiation field. The level shifts at the laser pulse front, the shift reaches its maximum value at the peak of the pulse, decreases on the pulse trailing edge, and the level returns to its initial unperturbed value as the pulse vanishes. Thus, the integral effect that emerges in the course of the action of the pulse amounts to a broadening of the observed line in the absorption spectrum of the auxiliary light. Here the magnitude of the broadening is of order of the maximum shift of the level at the pulse peak. Just such broadening was observed by Bonch-Bruевич et al. [1] in the first experimental study of the atomic Stark effect in the laser radiation field.

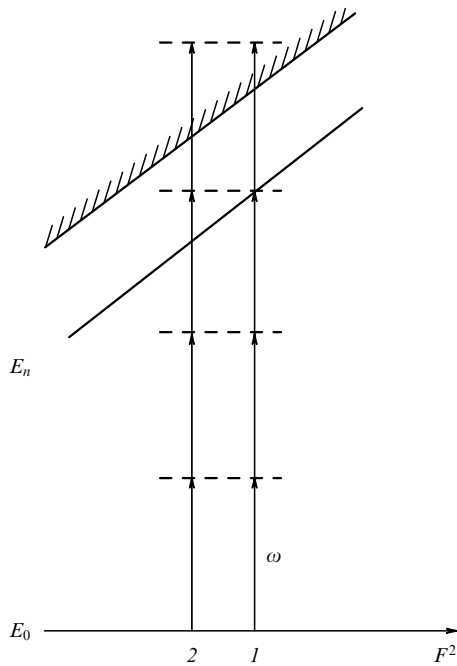
### 3.4 Experimental methods for measuring the AC Stark effect in a laser radiation field

In this section we briefly discuss the experimental methods used to study the Stark effect in the most important case where the field-produced perturbation reduces to a shift of the initial atomic level.

Various classical spectral methods may be used in studies. Among these are the absorption of auxiliary radiation, two-photon spectroscopy, double radio-optical resonance, and the use of a polarized light. The review article [2] briefly discusses these methods, so that there is no need to discuss them here. The thing is that practically all experimenters who observed large AC Stark shifts of atomic levels in a laser radiation field used another technique, namely, the multiphoton ionization spectroscopy [32].

The latter approach is based on observing the process of multiphoton ionization of an atom in the presence of an intermediate multiphoton resonance with the level under investigation. What is registered is the number of photoelectrons, which resonantly increases when the intermediate resonance emerges. As the intensity of an ionizing radiation is increased, the atomic level shifts and the position of the fixed resonance level changes in relation to the ground level. Changing the radiation frequency makes it possible to compensate for this change in energy and once again attain an intermediate multiphoton resonance and observe the resonant increase in the electron yield. Knowing this change in frequency, we can extract the necessary data on the AC Stark shift of the level. Figure 3 illustrates the method discussed.

Since  $\omega$  is usually much smaller than  $\omega_{10}$ , i.e.  $\omega \ll \omega_{10}$ , where  $\omega_{10}$  is the frequency of the transition from the ground



**Figure 3.** Three-photon resonance (1) and nonresonance (2) excitations of a Rydberg state of an atom with an energy  $E_n$ . Here  $E_0$  is the ground-state energy; the energies are depicted as functions of the square of the field strength  $F$ , and the hatched area stands for the continuum boundary.

state (0) to the first excited state (1), then for the ground state the radiation of the frequency considered here is low-frequency and the AC Stark shift of the ground state coincides, to an adequate accuracy, with the level shift in a dc electric field. The corresponding static polarizability of the atomic ground states is well known (e.g., see Radtsig and Smirnov's reference book [14]), and this makes it possible to allow for the contribution of the ground state to the measured overall effect of variation of the transition energy from the ground state (0) to the fixed excited resonance state (1) and in this way to determine the shift of the excited energy level.

Specific examples of using the method of multiphoton ionization spectroscopy are given in the next section.

### 4. The general case

In the general case of real atoms having an infinite number of bound states, the problem of perturbation of certain states can be solved only numerically and approximately, with allowance for only a finite number of states. For an example of such calculations we may cite the paper by Crance [33] who did them for the hydrogen atom. This approach is not only too complicated but has also little potential, since it does not make it possible to draw general conclusions about the perturbation of the atomic spectrum in a variable field. Consequently, we turn to the solution of model problems, which have a very definite range of applicability.

#### 4.1 One-level atom

An analytic solution for the problem of the population of quasi-energy states can be obtained in a quantum-mechanical model containing only one level. We denote by  $d$  the constant dipole moment of the particle residing at the level. Then the energy of interaction between a monochromatic variable field and this dipole moment has the simple form,  $-dF \cos \omega t$ . We

also assume that the particle possesses the polarizability  $\alpha$  induced by the field. The interaction energy associated with this polarizability has the well-known form

$$-\frac{1}{2}\alpha(F \cos \omega t)^2.$$

If we denote the total interaction by  $V(t)$ , the time-dependent Schrödinger equation for this system may be written as

$$i \frac{da}{dt} = V(t)a,$$

or

$$i \frac{da}{dt} = \left( -dF \cos \omega t - \frac{1}{2}\alpha F^2 \cos^2 \omega t \right) a. \tag{14}$$

Here  $a$  is the quantum-mechanical amplitude of this state; the absolute value of this amplitude is unity since there are no other states in the given model with a single level.

The solution of Eqn (14) has the simple form

$$a(t) = \exp \left[ -i \int_0^t V(t') dt' \right]. \tag{15}$$

Expanding the exponential in a Fourier series, we find that the solution (15) has the form of (13), as the Floquet theorem predicts, with the AC Stark shift of the energy level being

$$E_a(F) = -\frac{1}{4}\alpha F^2, \tag{16}$$

and the population amplitudes of the quasi-energy harmonics are

$$C_k = \sum_{S=-\infty}^{\infty} (-1)^k J_S \left( \frac{\alpha F^2}{8\omega} \right) J_{k+2S} \left( \frac{dF}{\omega} \right). \tag{17}$$

Here the  $J_S$  are Bessel functions.

In the general case, a wide diversity of quasi-energy harmonics are populated. Here we examine three limiting cases.

(a) *The case of a weak high-frequency field.* The following inequalities hold in this instance:

$$dF \ll \omega, \quad \alpha F^2 \ll \omega. \tag{18}$$

Then the arguments of all the Bessel functions in Eqn (17) are small, with the result that the only term in (13) with  $k = S = 0$  differs essentially from zero. Thus, the quasi-harmonics are not populated and the perturbation reduces to the quadratic AC Stark shift (16) of the level in question.

(b) *The case of a strong low-frequency field.* The following inequalities hold in this situation:

$$dF \gg \omega, \quad \alpha F^2 \ll \omega. \tag{19}$$

Then the properties of the Bessel functions imply that the only quasi-energy harmonics that are populated are those with numbers  $S = 0$  and  $k = \pm dF/\omega$  (and the neighboring harmonics). From Eqn (13) we find that the energies of these quasi-harmonics are  $E_a(F) = \pm dF$ . Thus, there emerges a linear Stark shift in a variable field, which differs from the linear Stark shift in a dc electric field in that the initial level splits into two symmetrically arranged sublevels with equal populations. Note that a similar splitting occurs in

a two-level system when there is exact resonance with a monochromatic field (the so-called Rabi splitting; see Section 3.1 of our book [5]).

For an example we can take the Rydberg states of atoms (with the exception of states with small orbital quantum numbers, for which a finite quantum defect leads to a zero constant dipole moment). Using the estimates  $d \propto n^2$  and  $\alpha \propto n^6$  [see Eqn (7)] and inequalities (19), we arrive at the conditions under which a *linear* AC Stark shift occurs in Rydberg atoms with the principal quantum number  $n$ :

$$n^2 F \gg \omega, \quad n^6 F^2 \ll \omega \quad (20)$$

(all quantities are expressed in atomic units). Here the frequency of the external field must be small compared to the distance between neighboring Rydberg shells for the single-level model to be valid, i.e.  $\omega \ll n^{-3}$ . Actually this case requires the use of a microwave electromagnetic field.

(c) *The case of a very strong field with a very low frequency.* The following inequalities, which are the opposites of Eqn (18), hold in this instance:

$$dF \gg \omega, \quad \alpha F^2 \gg \omega. \quad (21)$$

Then the expansion (17) implies that the only quasi-energy harmonics that are populated are those with the numbers

$$k = \pm \frac{dF}{\omega} \pm \frac{\alpha F^2}{4\omega} \quad (22)$$

and the neighboring harmonics. Here the energies of the shifted and split sublevels have the form

$$E_a(F) = \pm dF \pm \frac{\alpha F^2}{4} - \frac{\alpha F^2}{4}. \quad (23)$$

Hence, in all three cases the perturbation reduces to an AC Stark shift of the atomic level. However, in the general case, where the parameters of the atomic system are related to those of the electromagnetic field in an arbitrary manner, many quasi-energy states are excited and the very notion of a Stark shift disappears.

#### 4.2 The Blokhintsev formula

The example of the above section can serve only as an illustrative model. It can be related to an AC Stark shift of the excited states of the hydrogen atom due to the degeneracy of these states (for more details see our book [5]). The simplest situation emerges in the case of a field of moderate intensity, where the states with a given quantum number  $n$  do not mix with states with other principal quantum numbers.

If we can limit ourselves to the states belonging only to a single shell with a given principal quantum number, then, since the matrix element of the coordinate  $z$  is diagonal in the representation that leans upon parabolic quantum numbers  $(n, n_1, n_2)$ , the constant dipole moment of the atom can be written as

$$d = \frac{3}{2} n(n_1 - n_2). \quad (24)$$

Substituting this into (17) and ignoring the polarizability  $\alpha$ , we find that  $S = 0$  and the populations of the quasi-harmonics take the form (this is what is known as the

*Blokhintsev formula*; for more details see our book [5]):

$$C_k^2 = J_k^2 \left[ \frac{3n(n_1 - n_2)}{2\omega} F \right]. \quad (25)$$

We see that any state with fixed parabolic quantum numbers in an external monochromatic field constitutes a superposition of a large number of quasi-energy harmonics.

Equation (25) is applicable if the condition  $\alpha F^2 \ll \omega_{n, n \pm 1}$  is met. Estimating on quasi-classical grounds the right-hand side of this inequality as  $n^{-3}$  and the polarizability as  $\alpha \sim n^6$  [see Eqn (7)], we arrive at a quasi-classical restriction on the field strength at which the Blokhintsev formula is valid:

$$F \ll \frac{F_a}{n^{4.5}}. \quad (26)$$

Here  $F_a$  is the atomic field strength. If condition (26) is not met, the Blokhintsev formula becomes invalid and we must allow for the contribution of the neighboring shells with respect to the principal quantum number (this cannot be done analytically). In the latter case the problem makes sense, since the field strength at which the concept of a level with a given principal quantum number  $n$  (with  $n \gg 1$ ) loses all meaning is much larger than specified by Eqn (26); more precisely, the field strength is given by the expression [5]

$$F_{an} = \frac{F_a}{16n^4}. \quad (27)$$

We now examine the limit of formula (25) in the case of a field so strong that  $n(n_1 - n_2)F \gg \omega$ . As mentioned in the previous section, the properties of the Bessel functions imply that the quasi-energy harmonics becoming substantially populated are only those with numbers

$$k = \pm n(n_1 - n_2) \frac{3F}{2\omega} \quad (28)$$

and the neighboring harmonics. The population of such harmonics corresponds to a linear Stark shift of excited states of the hydrogen atom in a dc electric field whose strength is  $F$  or  $-F$ :

$$\Delta E(n, n_1, n_2) = \pm \frac{3}{2} n(n_1 - n_2) F. \quad (29)$$

This result agrees with Eqn (23).

#### 4.3 Experimental data

Koch [34] was the first to observe quasi-energy states with energies  $E_n(F) + k\omega$ , when a strong low-frequency field was applied to highly excited states of the hydrogen atom. However, Bayfield et al. [35] conducted a much more thorough experimental investigation of the problem. Let us discuss their experiment.

Hydrogen atoms in highly excited states with principal quantum numbers  $n$  of about 45 were prepared by charge-exchange of 10-keV protons in a gas consisting of argon atoms. Excited states of hydrogen atoms with different principal quantum numbers  $n$  form in the proton charge-exchange process. The probability of excitation to these states depends on  $n$  as  $n^{-3}$  (see Smirnov's book [36]). In this way a beam of excited atoms in different states is formed. The light beam from a carbon dioxide laser with a photon energy of about 0.1 eV is directed along the axis of the atomic beam. The photon energy is approximately equal to the energy of electron transition in the hydrogen spectrum from a state with



$n = 10$  to a highly excited state with  $n = 44$ . The exact tuning to resonance with the transition to a specific highly excited state was done by varying the proton energy via the Doppler effect. Then the beam of excited atoms landed in a region with a dc electric field with a controlled strength. The fraction of atoms for which the field strength was larger than the critical strength became ionized. The value of this critical field intensity is [see Eqn (27)]

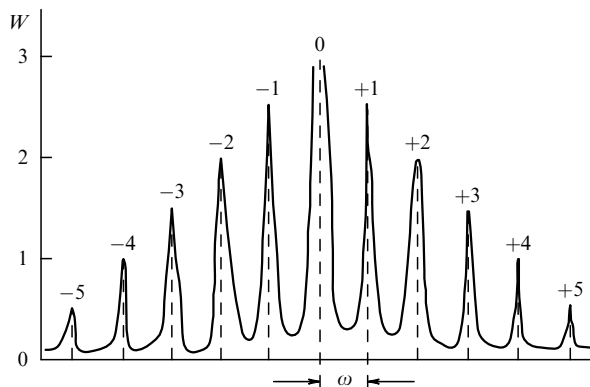
$$F_c = \frac{C(n_1/n, n_2/n)}{n^4} F_a. \quad (30)$$

The constant in this expression has been calculated numerically (see Smirnov's book [36]). The particles registered in the experiment were protons. By varying the strength of the static electric field and using the difference effect, atoms with definite values of the principal quantum number can be separated. The situation with parabolic quantum numbers proved to be more complicated, and fixed values of these numbers have yet to be established.

This method makes it possible to produce beams of hydrogen atoms excited to definite states with  $n$  amounting to about 45 with an efficiency and selectivity sufficiently large for the various experiments to be conducted (see the review articles [37, 38]).

The experiment of Bayfield et al. [35] consisted in observing the effect of a microwave field with a frequency  $\omega$  small compared to the frequency (proportional to  $n^{-3}$ ) of the transition to neighboring shells with respect to the principal quantum number and a strength such that the condition  $n^2 F \gg \omega$  was met [see Eqn (20)]. The microwave field was generated in a cavity through which the beam of the excited atoms travelled.

The main result of this experiment is depicted in Fig. 4. The excited states were those with a principal quantum number  $n = 44$  in the presence (or absence) of a microwave field with a frequency  $\omega = 8$  GHz and a maximum value of the field strength  $F = 30$  V cm $^{-1}$ . In the absence of a microwave field only the central resonance peak corresponding to the excitation of the unperturbed state with  $n = 44$  was observed. But when the microwave field was switched on, in addition to the central resonance peak there was a spectrum of satellites with energies  $\pm k\omega$  with respect to the energy of the central peak. Satellites with  $k = 1-5$  have been detected.



**Figure 4.** Probability of exciting (in relative units) the multiplet of hydrogen-atom states with the principal quantum number  $n = 44$  in the experiment conducted by Bayfield et al. [35]. The number placed above each satellite is  $k$ , the number of absorbed or emitted photons of the microwave field.

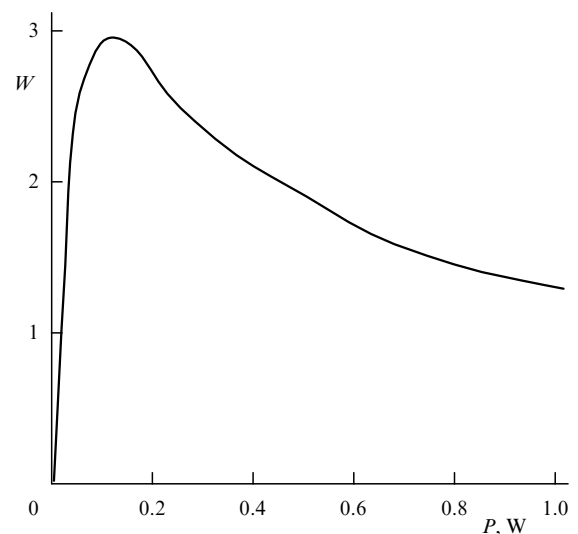
Clearly, in this case the earlier requirements that the frequency must be low and the field strength large were met. For instance, for the above values of the strength and frequency of the field, the ratio  $n^2 F/\omega$  ranges from 5 to 10. Under these conditions, the contribution of the polarizability  $\alpha$  can be ignored. However, no linear AC Stark effect was observed in this experiment and the population maximum fell on the central peak with  $k = 0$  rather than on side satellites with  $k = 5-10$ , as Blokhintsev's theory predicts. The reason was the mixing of states with different parabolic quantum numbers in the process of excitation. Such mixing led to a situation in which the states with a large difference of the parabolic quantum numbers,  $n_1 - n_2 \propto n$ , provided a small contribution to the satellite population.

Thus, this experiment has clearly demonstrated that when the frequency of the field is small and the field strength is relatively large, the perturbation of the highly excited states of the hydrogen atom consists in emerging a spectrum of quasi-energy states for each set of the parabolic quantum numbers.

Another parameter measured in this experiment was the population dependence of the quasi-energy state with  $k = -1$  on the power of the microwave field (see Fig. 5). This dependence is qualitatively described by an expression that follows from the Blokhintsev formula (25):

$$|C_1|^2 \propto J_1^2\left(\frac{dF}{\omega}\right). \quad (31)$$

Unfortunately, there is not much more that can be definitely said about this dependence since the value of the constant dipole moment  $d$  is not well-defined (this fact has been mentioned earlier). The experimental data have been described in greater detail by Bersons [39] who also derived a quasi-classical expression for the wave function in the case where the frequency of the electromagnetic field is comparable to the energy separation between neighboring shells with respect to the principal quantum number. Also calculated were the probabilities of radiative transitions between Rydberg states of atoms in the presence of a strong microwave field.



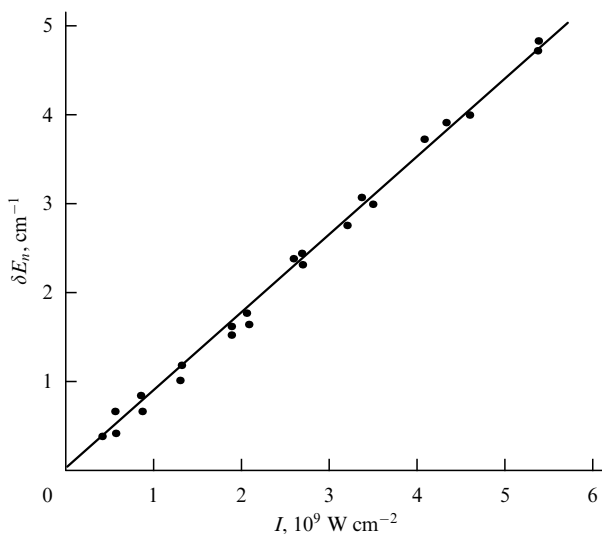
**Figure 5.** Probability of satellite excitation (in relative units) with  $n = 44$  and  $k = -1$  (see Fig. 4) as a function of the power  $P$  of the microwave field [35].

Let us now turn to the other limit — a weak high-frequency field. The work done by O'Brian et al. [40] can be cited as an example of such an experiment. The researchers observed the disturbance of the excited states of the xenon atom with values of the principal quantum number ranging from 10 to 15. The energy of a photon of the laser radiation was  $\omega \approx 1.2$  eV. For the excited states in question such radiation is of the high-frequency type. Indeed, not only the condition  $\omega \gg \omega_{n,n\pm 1}$  is met for these states but also  $\omega \gg E_n$ , where  $E_n$  is the binding energy (the ionization potential) for these excited states. At the same time, in relation to the ground state this radiation is of the low-frequency type, since  $\omega \ll \omega_{01}$ , where the quantity on the right-hand side of the inequality is the frequency of the transition from the ground state (0) to the first excited state (1). Accordingly, we can replace, to a satisfactory accuracy, the dynamic polarizability of the ground state by its static polarizability, which has been tabulated in Radtsig and Smirnov's reference book [14].

The static polarizability of noble-gas atoms is relatively small compared to the factor  $1/\omega^2$  in Eqn (16) at a frequency  $\omega \sim 1$  eV. This makes it possible, when measuring the variation in the frequency of the transition from the ground state to excited states with values of the principal quantum number  $n$  ranging from 10 to 15, to ignore variations in the ground-state energy and ascribe the entire effect to the excited state.

O'Brian et al. [40] used the UV radiation of a dye laser to excite xenon atoms from the ground state to Rydberg states with  $n = 10-15$ . The excited atoms which form as a result of a two-photon absorption of the UV radiation, were ionized in the field of IR radiation with a frequency  $\omega \approx 1.2$  eV. The same field perturbed the atomic spectrum. The variations in the energies of the ground state and various excited states were specified by the resonance increase in the ion yield when the radiation-field frequency was varied. The data on the frequency variations made it possible to determine the change in the transition energy.

The results of this experiment are depicted in Fig. 6. Clearly, in the case at hand the perturbation reduces to a



**Figure 6.** AC Stark shift of Rydberg p-states of the xenon atom with principal quantum numbers  $n = 10-15$  as a function of the intensity of the laser radiation [40].

change in the energy of the excited states and this perturbation is, to a good accuracy, proportional to the power of the radiation (i.e. to the square of the radiation-field strength). The quantitative data of Fig. 6 show that the experiment was carried out at an electric field strength

$$F = 2.5 \times 10^6 \text{ V cm}^{-1} < 10^{-3} F_a,$$

i.e. the radiation field was weak. Here, the dynamic polarizability is numerically equal to  $-1/\omega^2$ , and the change in energy is  $\delta E_n(F) = F^2/(4\omega^2) = E_{\text{vib}}$ , where  $E_{\text{vib}}$  is the vibrational energy of a free electron in the field of a linearly polarized electromagnetic wave.

In conclusion of this section we would like to note that the results of the experiments of Bayfield et al. [35] and O'Brian et al. [40] suggest that they confirm, both qualitatively and quantitatively, the main inferences following from the theoretical analysis of the one-level model system.

## 5. A weak variable field

### 5.1 Scalar, tensor and axial polarizabilities

The theoretical description of the AC Stark shift in a weak electromagnetic field for nondegenerate atomic states is based on the time-dependent second-order perturbation theory. The problem gets simpler if we employ the basis of quasi-energy states of the system consisting of an atom and a field (see Section 3.1). Then we can use the well-known result for the energy level shift in a dc field

$$\delta E_n = \sum_{m \neq n} \frac{|z_{nm} F|^2}{E_n - E_m}, \quad (32)$$

but instead of the unperturbed energies of the intermediate states of the atom we use the energies  $E_m + \omega$  and  $E_m - \omega$  of the system consisting of the atom and the field. These two energies are related to the absorption and emission of a single photon in the transition from the initial state to an intermediate state over which the summation in (32) is performed (higher orders of the perturbation theory correspond to absorption and emission of a larger number of photons). Thus, Eqn (32) becomes

$$\delta E_n = \sum_{m \neq n} \left| \frac{z_{nm} F}{2} \right|^2 \left( \frac{1}{E_n - E_m - \omega} + \frac{1}{E_n - E_m + \omega} \right). \quad (33)$$

The additional multiplier  $1/2$  reflects the fact that the variable field strength is represented in the form

$$F(t) = F \cos \omega t = \frac{F}{2} [\exp(i\omega t) + \exp(-i\omega t)].$$

From Eqn (33) we finally get

$$\delta E_n = -\frac{\alpha_n(\omega) F^2}{4} = \frac{F^2}{2} \sum_m \frac{\omega_{nm} |z_{nm}|^2}{\omega_{nm}^2 - \omega^2}. \quad (34)$$

Here  $\omega_{nm} = E_n - E_m$  is the difference of the unperturbed energies (the frequency of transition from the initial state to an intermediate state), and  $\alpha_n(\omega)$  is known as the *dynamic polarizability* of the given state  $n$ . For the sake of simplicity we assume that the field is linearly polarized. The quantity  $z_{nm}$  is the dipole matrix element.

The condition for the applicability of second-order perturbation theory is written as

$$z_{mn}F \ll |\omega - \omega_{mn}|,$$

which actually reduces to one of the following inequalities

$$z_{mn}F \ll \omega \quad \text{or} \quad z_{mn}F \ll \omega_{mn}.$$

The first inequality coincides with the corresponding inequality in Eqn (18), obtained in the single-level model. The second inequality states that the perturbation must not exceed the distance to the neighboring energy levels.

Notice that the sum over the intermediate states in Eqn (34) includes both the states of the discrete spectrum and those of the continuous spectrum. In the next order of the perturbation theory there appears what is known as hyperpolarizability (see Section 5.5 and our book [7], Section 7.2.2).

The dynamic polarizability of a given state depends on its magnetic quantum number. This dependence can be specified analytically since the magnetic quantum numbers enter only into the well-known spherical functions, which in turn enter into the total wave functions of stationary states and do not enter into the radial components of the wave functions. For a linearly polarized field, using the Wigner–Eckart theorem for the angular parts of the dipole matrix element, we obtain [a similar expression in the static limit has been given earlier, see Eqn (6)]

$$\alpha^{njM}(\omega) = \alpha_S^{nj} + \alpha_t^{nj} \frac{3M^2 - j(j+1)}{j(2j-1)}. \quad (35)$$

Here  $j$  is the angular momentum of the given state. The quantity  $\alpha_S$  is known as the *scalar polarizability*, and the quantity  $\alpha_t$  the *tensor polarizability*. The degeneracy that remains is that with respect to the sign of the magnetic quantum number  $M$ . In accordance with Eqn (35), the tensor part is responsible for the AC Stark splitting of a level in the magnetic quantum number. Here averaging over  $M$ , according to (35), nullifies the contribution of the tensor part of the polarizability.

Equation (35) shows that the tensor polarizability is zero for states with  $j = 0, 1/2$ . For states with other angular momenta, the magnitude of the tensor polarizability is generally comparable to the magnitude of the scalar polarizability. The ratio of the two polarizabilities depends on the frequency of the electromagnetic field. At frequencies exceeding the binding energy of the level in question, the scalar part of the polarizability rapidly tends to the asymptotic value

$$\alpha_S^n(\omega > E_n) \rightarrow -\frac{1}{\omega^2}, \quad (36)$$

which corresponds to vibrations of a free electron in the field of a linearly polarized wave. Here, the scalar polarizability does not depend on the atomic state. The tensor part of the polarizability decreases as  $\omega^{-4}$  and proves to be much smaller than the scalar part.

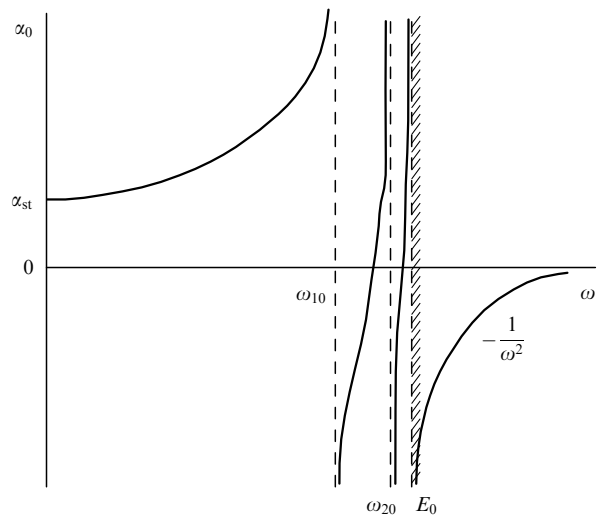
In the case of circular polarization, the use of the Wigner–Eckart theorem leads to the following explicit dependence of the dynamic polarizability on the magnetic quantum number  $M$ :

$$\alpha^{njM}(\omega) = \alpha_S^{nj} \pm \alpha_a^{nj} \frac{M}{2j} - \alpha_t^{nj} \frac{3M^2 - j(j+1)}{2j(2j-1)}. \quad (37)$$

The quantity  $\alpha_a$  is known as the *axial (asymmetric) polarizability*. The sign  $\pm$  in formula (37) corresponds to the right- or left-hand circular polarization, respectively. The quantity  $M$  is the projection of the angular momentum on the direction of propagation of the electromagnetic wave. The axial polarizability is zero for states with  $j = 0$ . Such states are only shifted by the radiation field and are unaffected by splitting.

The axial polarizability changes sign under time reversal [in accordance with Eqn (37), both the axial polarizability and the magnetic quantum number change signs under time reversal, but their product does not change sign, of course, and this leads to a sizable shift of the energy level, which may not depend on the direction of time]. Hence, in the static limit ( $\omega \rightarrow 0$ ) the axial polarizability always vanishes for all atomic states. In the high-frequency limit, the axial polarizability decreases as  $\omega^{-k}$ , with the value of  $k > 2$  depending on the quantum numbers of the state in question, in contrast to the tensor part (see below). Thus, in this limit the axial polarizability is also small compared to the asymptotic scalar part of the polarizability (36) (e.g., for hydrogen-atom states with orbital (angular) momentum larger than two the value of  $k$  is seven [41]; see the next section for more details).

A typical frequency dependence of the dynamic polarizability of the atomic ground state is depicted in Fig. 7. The dynamic polarizability tends to infinity, changing sign when the radiation frequency coincides with the frequencies of allowed dipole transitions to excited states of this atom. With  $\omega \rightarrow \infty$  it tends to zero by the law (36).



**Figure 7.** Typical frequency dependence of the dynamic polarizability of the ground atomic state (0). The excited states (1 and 2) into which allowed dipole one-photon transitions occur, are indicated.

### 5.2 Limiting analytical expressions for the hydrogen atom

If the field frequency is small compared to the energy of the level in question, then, as noted earlier, the dynamic polarizability reduces to static polarizability. Simple analytical expressions can be obtained only for arbitrary states of the hydrogen atom. The scalar and tensor parts have been discussed earlier, when we examined the case of a dc electric field [see Eqns (7) and (8)].

As for the axial polarizability, it vanishes in the static limit, as mentioned in the previous section. At low frequencies

it is proportional to the frequency, and the analytical expression in the low-frequency limit is [15]

$$\alpha_a^{nl}(\omega \ll E_n) = -\frac{1}{8}n^6 l \omega (55n^2 + 26l^2 + 26l + 149). \quad (38)$$

Now we turn to the opposite, high-frequency, limit, where the inequality  $\omega \gg E_n$  holds (actually, this limit is reached very fast). As noted in the previous section, in this case the scalar part of the polarizability is predominant, and for all atoms the expression for it has the simple form (36), which is independent of the state in question. Here we are interested in the other parts of the polarizability and in the correction to the scalar part that depends on the quantum numbers of the given state. The expression for this correction depends on the value of the orbital quantum number [30, 42]:

$$\begin{aligned} \alpha_S(n, l = 0) &= -\frac{1}{\omega^2} - \frac{4}{3n^3 \omega^4}, \\ \alpha_S(n, l = 1) &= -\frac{1}{\omega^2} - \frac{2\sqrt{2}(n^2 - 1)}{9n^5 \omega^{11/2}}, \\ \alpha_S(n, l \geq 2) &= -\frac{1}{\omega^2} - \frac{2}{\omega^6} \langle r^{-6} \rangle. \end{aligned} \quad (39)$$

We see that the correction terms rapidly decrease with increasing principal quantum number (the transition to the Rydberg states) or with increasing frequency of the external field.

The high-frequency dependence of the tensor polarizability has the following form [30, 42] (the reader will recall that for s-states the tensor polarizability is zero):

$$\begin{aligned} \alpha_t(n, l = 1) &= \frac{4}{15n^3 \omega^4}, \\ \alpha_t(n, l \geq 2) &= -\frac{4}{n^7(l+1)(2l+1)(2l+3)\omega^4}. \end{aligned} \quad (40)$$

Finally, the asymptotic expression for the axial polarizability at a frequency that exceeds the energy of the excited hydrogen-atom state under consideration takes the form [42]

$$\begin{aligned} \alpha_a(n, l = 1) &= -\frac{2\sqrt{2}(n^2 - 1)}{9n^5 \omega^{11/2}}, \\ \alpha_a(n, l \geq 2) &\propto \frac{1}{\omega^7} \langle r^{-8} \rangle. \end{aligned} \quad (41)$$

In the paper by Beigman et al. [43] one can find expressions for the dynamic polarizability of Rydberg states of the hydrogen atom, averaged over the orbital and magnetic quantum numbers (actually, this is the scalar part of the polarizability averaged over the orbital quantum number at a fixed value of the principal quantum number).

An analytical expression for the scalar part of the dynamic polarizability of Rydberg states of the hydrogen atom for arbitrary values of the external field frequency was derived in Ref. [44]. As the frequency varies, both limits, the static and the high-frequency, can be reached by this expression. More than that, it contains resonances when the field frequency coincides with the frequencies of transitions from the given state to other Rydberg states.

### 5.3 Stark splitting of Rydberg states of the hydrogen atom

As is known, the unperturbed Rydberg states of the hydrogen atom are degenerate in the orbital and magnetic quantum

numbers. In a dc electric field this degeneracy is removed, the split levels being characterized by parabolic quantum numbers. However, in the variable field of laser radiation, a Rydberg state is excited via step-by-step photon absorption. Thus, there occurs excitation of a state with fixed values of the orbital and magnetic quantum numbers through the action of dipole selection rules in the absorption of photons and the fact that the initial state of the atom is characterized by a conserved value of the orbital angular momentum. The higher the frequency of the radiation, the better the orbital quantum number is conserved with the passage of time and the smaller the mixing of the degenerate states with each other.

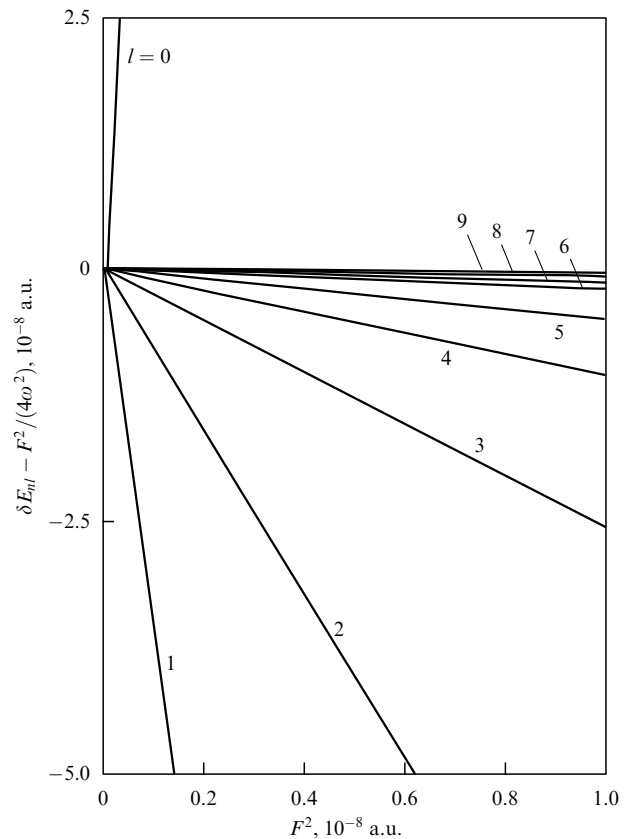
The aforesaid also refers in a straightforward manner to Rydberg states of many-electron atoms with orbital quantum numbers  $l \geq 3$ .

In accordance with the formulas of the previous section, the AC Stark shift and the Stark splitting of Rydberg states at a frequency  $\omega \gg E_n$  are described within the scope of the first nonvanishing order of perturbation theory by the expression

$$\delta E_n = \frac{F^2}{4\omega^2} \left( 1 + \frac{A_{nlm}}{\omega^2} \right), \quad (42)$$

where  $A_{nlm}$  is a complicated function of all the quantum numbers, being given in the previous section. Figure 8 depicts the results of calculations done by this formula for the Rydberg state of the hydrogen atom with  $n = 10$  and  $m = 0$  at  $\omega = 0.03$  a.u. (an Nd:glass laser).

Since the splitting energy is small compared to the energy of a level shift [according to the first formula in Eqn (39), the



**Figure 8.** Stark splitting of the Rydberg state of the hydrogen atom with  $n = 10$  and  $m = 0$  in the high-frequency limit  $\omega > E_n$  for different values of the orbital quantum number  $l = 0-9$  [6].

difference of the AC Stark shift and the vibrational energy decreases as  $n^{-3}$ ], in Fig. 8 we show only the above-mentioned difference, which characterizes only the level splitting. We see that this difference depends strongly and nonuniformly on the orbital quantum number. A similar pattern is observed for states with nonzero values of the magnetic quantum number.

The formulas of the previous section that describe the energy values of AC Stark shifts and level splittings can be used as long as the outermost components of the neighboring Stark multiplets do not intersect. The estimate of the critical field strength (see Eqn (9.11) in our book [7]) in this case is given by the formula

$$F_c = \frac{\omega^{2/3}}{7n^2} \text{ a.u.} \quad (43)$$

For the example shown in Fig. 8 this value is equal approximately to  $10^{-4}$  a.u. Then the distance between the outermost components of the multiplet is  $F^2/(3\omega^4n^3) = 1.5 \text{ cm}^{-1}$ .

But if the state excited in the experiment is a Rydberg state with a fixed orbital quantum number  $l$ , then according to the second formula in Eqn (40) the distance between the outermost components of its multiplet in the magnetic quantum number ( $m = l$  and  $m = 0$ ) takes the form

$$\frac{F^2}{2\omega^4n^7} \frac{3l}{(l+1)(2l+3)(4l^2-1)}.$$

In particular, for  $l = 4$ ,  $n = 10$ , and  $F = F_c$  we get a distance of order  $0.01 \text{ cm}^{-1}$ .

The absolute magnitude of the splitting energy is in this case an extremely important parameter: when it is larger than the width of the laser radiation spectrum, there can be no mixing of states with different values of the orbital and magnetic quantum numbers.

Thus, for each value of the field strength there exists a 'fine-tooth comb' of split Rydberg levels. As the value of the principal quantum number increases, the Stark splitting energy decreases. If the width of the spectrum of the ionizing radiation exceeds the size of the Stark splitting, some of the Stark components undergo coherent excitation. The wave packet formed in this manner oscillates in time.

The mixing of Stark components explains the suppression effect of photoionization established experimentally by Jones and Bucksbaum [45]. A barium atom was successively excited to Rydberg states with principal quantum numbers  $n = 25$  and 35. In the same region of space where excitation took place there was a dc electric field whose strength amounted to  $100 \text{ V cm}^{-1}$ . In this field the Rydberg levels split into Stark multiplets, and the splitting was linear in the field strength. By irradiating the region with high-power laser light whose frequency was much larger than the electron binding energy in these Rydberg states, photoionization from the Stark components was initiated. The experiment revealed that the probability of photoionization from the components of the state with  $n = 25$  is lower than that from the components of the state with  $n = 35$ .

This result can be explained by the above model of mixing of Stark components in an ionizing field. The length of the ionizing pulse was 70 ps, and the width of the radiation spectrum  $1 \text{ cm}^{-1}$ . Many Stark components that were coherently excited land in the band of the spectrum of the

ionizing radiation. This leads to the formation of a wave packet that oscillates in the external dc electric field. Since the distance between the outermost components of a single multiplet is  $3Fn$ , the time of oscillations of the wave packet with coherent population of all the states of the multiplet is  $t_0 = 2\pi/(3Fn)$ . At  $n = 25$  this time is 75 ps, which is longer than the laser pulse length. i.e. actually there are no oscillations at all. In other words, there is no mixing in the orbital quantum number and states with small values of  $l$  do not occur. The photoionization effect is suppressed in this case since only the probability of photoionization from Rydberg states with a small value of the orbital quantum number is high. The opposite situation occurs for the Stark multiplet with  $n = 35$ , which explains the result of the experiment.

#### 5.4 Rydberg states of complex atoms

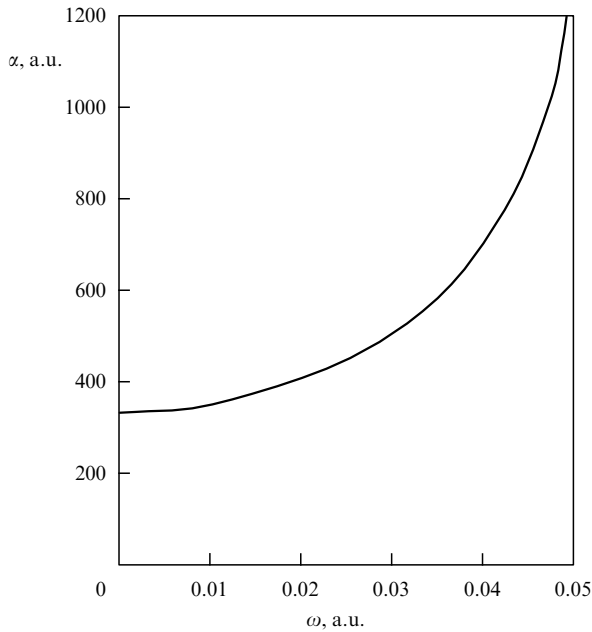
The case of Rydberg states of complex atoms is similar to the situation for states of the hydrogen atom with an orbital quantum number  $l > 2$ . The quantum defect for such states is negligible. However, for states with  $l = 0, 1, 2$ , due to the large quantum defect, there is no degeneracy in the orbital quantum number, with the result that the contributions to the sum in Eqn (34) from states above and below the given state do not balance each other. Hence, the dynamic polarizability increases substantially and its value (for frequencies of the laser radiation that are not too high) can be estimated at  $n^7$  [instead of  $n^6$ , see Eqn (7)]. More than that, in this case the dynamic polarizability is determined only by the contributions from the two Rydberg states closest to the given state.

Huillier et al. [46] used the method of the multichannel quantum defect to do the numerical calculations of the dynamic polarizability of complex atoms.

The work by Marinescu et al. [47] can be cited as an example of numerical calculations of the dynamic polarizability in the intermediate case, where the polarizability can be reduced neither to the static limit nor to the high-frequency limit. The researchers calculated the dynamic polarizability of the ground state of the rubidium atom as a function of the field's frequency by using the wave functions of the model-potential problem, in which the potential was chosen such that the low-lying energy levels coincided with the experimental ones. The results are depicted in Fig. 9 (for frequencies ranging from zero to the first resonance inclusive). In particular, the value of the dynamic polarizability for a Nd:glass laser (wavelength equal to 1064 nm) was found to be 711 a.u., which is in good agreement with the experimental result of  $769 \pm 61$  a.u. obtained by Bonin and Kadar-Kallen [48].

The literature on the experimental findings referring to the perturbation of excited atomic states by high-frequency radiation is vast. Some of the data was obtained at relatively small field strengths, for instance, the data of O'Brian et al. [40] (see Section 4.3). A large body of data has been gathered for fields of subatomic strength [49–55].

In Refs [49–55], the data on the perturbation of excited atomic states have been gathered by the method of multiphoton ionization spectroscopy (see Section 3.4). In these experiments, the frequency of the laser radiation was about 2 eV (with the exception of the work by Perry et al. [55], where it amounted to 4 eV). The polarization of the laser light was linear, with the exception of the work by Agostini et al. [50] where circularly polarized light was used. The field strength of



**Figure 9.** Dynamic polarizability of the ground state of the rubidium atom below the first p-resonance as a function of the electric field frequency (according to the calculations done by Huillier et al. [47]).

the radiation varied in the range from 0.05 to 0.1 of the atomic field strength. The perturbed excited states studied in these experiments were those of xenon [49–53], krypton [54], and helium [55]. The values of the principal quantum number ranged from four to ten. In all cases the laser radiation frequency was either larger or much larger than the distance between the neighboring energy levels, or even comparable to the magnitude of the binding energy of the excited state of the atom.

The results of this research amount to the following:

(a) the variation in the energy of the excited states in question is quadratic in the electric field strength;

(b) the absolute value of the energy variation is equal to the vibrational energy of a free electron in the field of the electromagnetic wave, and the maximum variation in energy is of order 1 eV;

(c) the largest energy variation is observed for states 2p and 3d in the helium atom and may run as high as 3.5 eV;

(d) the observed variations in the energy of the excited states are not only much larger than the distance between neighboring levels but they also exceed both the energy of the laser photon and the electron binding energy of a given excited state.

Unfortunately, no data for other radiation frequency ranges and other atoms are presently available.

### 5.5 Dynamic hyperpolarizability

Third-order perturbation theory with respect to the electric field strength contributes nothing to the AC Stark shift of energy levels (in the absence of degeneracy of the states). The fourth-order contribution can be found fairly easily by using the result of time-independent perturbation theory and the quasi-energy approach described above. The resulting formula is cumbersome and can be found, for example, in our book [5]. The hyperpolarizability defined in this manner is a tensor of rank four.

A comparison of polarizability and hyperpolarizability readily shows that the analytical criterion for smallness of hyperpolarizability amounts to the requirement that the perturbation produced by the field be small compared to the characteristic frequencies of the atomic transitions. However, the calculations done by Davydkin et al. [56] for the ground states of atoms of the alkali metals evidence that in the absence of resonances the contribution of hyperpolarizability becomes comparable to the contribution of polarizability already at field strengths of order  $10^6 \text{ V cm}^{-1} \ll F_a$ . More than that, at such field strengths all the terms in the power series in the electric field intensity have the same order of magnitude, i.e. the perturbative series diverges (for alkali atoms).

Actually, hyperpolarizability provides a correct value for the AC Stark shift of atomic energy levels only in the regions of anomalously small values of dynamic polarizability in interresonance intervals or when the frequency of an atomic transition is close to the *double* frequency of the laser radiation. In the latter case hyperpolarizability undergoes a resonant increase, in contrast to the behavior of ordinary polarizability.

## 6. Laser radiation of superatomic intensity

Above we used perturbation-theory techniques to study the case of a weak disturbing field. When the field is strong, one theoretical method that can be used leans upon the Floquet theory. In recent years many theoretical papers have appeared that study one more method of investigating the effect of a strong field on atomic systems, namely, the Kramers–Henneberger method. We will discuss this approach in the present section.

### 6.1 Ultrastrong high-frequency fields

During recent years extensive research has been in progress concerning one of the most effective approximate methods used in studying the dynamics of quantum systems placed in ultrastrong high-frequency field, to be exact, the Kramers–Henneberger method. The latter is based on switching to the oscillating reference frame in which the electron found in an external electromagnetic field is at rest (a complete description of this method can be found in Section 4 of our review [57]). The transfer to this reference frame is achieved with the aid of the time-dependent unitary transformation

$$\Psi_{\text{KH}} = \exp\left(i\frac{\mathbf{r}\mathbf{F}}{\omega} \sin \omega t\right) \Psi. \quad (44)$$

The equation for the wave function in the oscillating reference frame (which became known as the Kramers reference frame) has the form [ $U(r)$  is the potential of the atomic core]

$$i\frac{\partial \Psi_{\text{KH}}}{\partial t} = -\frac{1}{2}\Delta \Psi_{\text{KH}} + U\left(\mathbf{r} + \frac{\mathbf{F}}{\omega^2} \cos \omega t\right) \Psi_{\text{KH}}. \quad (45)$$

This is an exact equation (the case of linear polarization is examined). In the high-frequency approximation, where the frequency of the laser radiation is large compared to the unperturbed binding energy of the system under investigation, this equation can be made simpler — it can be reduced to the time-independent Schrödinger equation with a potential that is the zeroth Fourier harmonic of the above

potential, i.e.

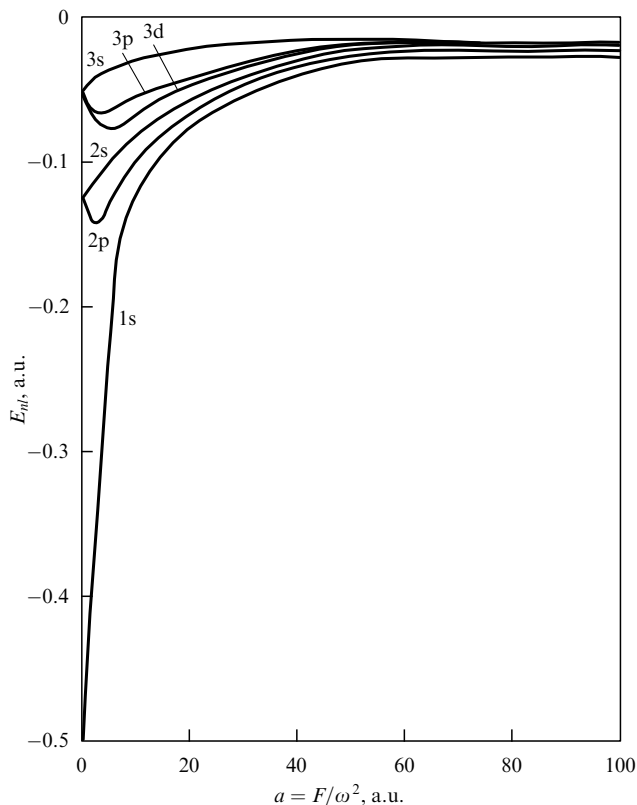
$$U_0(\mathbf{r}) = \frac{1}{2\pi} \int_0^{2\pi} U\left(\mathbf{r} + \frac{\mathbf{F}}{\omega^2} \cos \omega t\right) d(\omega t). \quad (46)$$

The wave function of a level consists of two probability clouds separated by a distance of  $2a = 2F/\omega^2$  (this is known as the *dichotomy*), where  $a$  is the amplitude of electron vibrations in the field of the wave.

At present the results obtained by the Kramers–Henneberger method have been corroborated in the experiments conducted by de Boer et al. [58]. These researchers discovered the effect of adiabatic stabilization of the neon atom, predicted by the Kramers–Henneberger model.

Pont and Gavrilu [59] used the Kramers–Henneberger method to study the AC Stark shifts of the levels of the hydrogen atom. In the presence of a (linearly polarized) high-frequency field, the levels with the same principal quantum number were found to be split in the orbital quantum number. The parameter  $a = F/\omega^2$  was varied from 0 to 100 (in the system of atomic units). The nonmonotone dependence was to be replaced by a monotonic increase of the energies of all levels up to a value equal to the vibrational energy (this limit equals zero in the oscillating Kramers reference frame). Here the ways in which the position of each level approaches the vibrational energy are different for various levels (Fig. 10). Thus, the theory predicts the collapse of the atomic spectrum at large values of the parameter  $a$ .

Similar results have been obtained by Pont et al. [60] for the case of a circularly polarized field. Here, however, in



**Figure 10.** Dependence of the energies of the hydrogen-atom levels with principal quantum numbers  $n = 1-3$  on the amplitude  $a$  of electron vibrations in the oscillating Kramers reference frame according to the calculations done by Pont and Gavrilu [59]. The field is linearly polarized.

contrast to the case of a linearly polarized field, all the Stark levels were found to merge into a single level when  $a > 100$ . Pont [61] derived an analytical formula for the energy of any level of the hydrogen atom in the ultrastrong high-frequency field of a circularly polarized wave, valid for  $F/\omega^2 \gg 1$ :

$$E_{nl}(F) = \frac{F^2}{2\omega^2} - \frac{\omega^2}{2\pi F} \ln \frac{F}{\omega^2}. \quad (47)$$

Volkova et al. [62] used the method of direct numerical integration of the time-dependent Schrödinger equation to study the dynamics of a one-dimensional quantum system with a short-range potential, placed in a high-frequency electromagnetic field of superatomic strength and a low-frequency probe field (the intensity of the probe field is low). The researchers found that steady states form in the Kramers–Henneberger potential describing the atom in an ultrastrong high-frequency field. These states differ substantially from the initial atomic states and constitute a set of basis states that actually exist during the time that a laser pulse acts on the system (they replace the initial unperturbed atomic states). The energies of the Kramers–Henneberger states differ substantially from the unperturbed energies. In particular, as the intensity of the high-frequency field increases, all these energies tend to zero (this corresponds to the energy in the laboratory reference frame being equal to the vibrational energy of a free electron; see the above discussion).

The fact that the Kramers–Henneberger approximation breaks down when the low frequency of the laser radiation is smaller than the ionization potential of the atom was corroborated again by the numerical calculations of Volkova et al. [63]. An exception is the case where the intensity of the laser radiation exceeds the above-barrier value (the barrier-suppression ionization threshold corresponds to an ionization regime in which the time it takes the electron to leave the atom is shorter than the optical-cycle period) [64]. Here, the Kramers–Henneberger approximation works. This condition is more stringent than the one adopted by Gavrilu and Kaminski [65] who suggested that the frequency of the laser radiation field must exceed the electron binding energy in the Kramers–Henneberger potential rather than in the initial potential.

Fearnside et al. [66] arrived at new results concerning the light-induced bound states of the hydrogen atom (states that do not appear if there is no laser field). These states emerge from the continuum at certain values of the light intensity, go deeper into the discrete spectrum, and then approach again the edge of the continuum in an ultrastrong field. However, the width of the light-induced levels amounts to several electronvolts, so that such levels have yet to be observed in experiments.

The case of complex atoms was studied by Rapoport [67] who used the example of a circularly polarized field. A model pseudopotential was taken for the potential of the atomic core. The researcher set up, in the high-frequency limit, a system of analytic functions of the discrete and continuous spectra in the rotating Kramers reference frame.

Before long, this approach was generalized by Rapoport et al. [68] who took a Hartree–Fock self-consistent potential for that of the atomic core. Numerical calculations of the dynamic polarizability were carried out for neon, krypton, and argon atoms in the high-frequency limit. The researchers derived a simple formula for the high-frequency dynamic

polarizability of an atom with the atomic number  $Z$  (the number of electrons in the atom):

$$\alpha(\omega \gg 1) = -\frac{Z}{\omega^2} - \frac{2,7Z^4}{\omega^4} \text{ a.u.} \quad (48)$$

The second term on the right-hand side reflects the deviation from the vibrational energy of a free electron in the field of a circularly polarized wave. The last formula can be used if  $F/\omega^2 \ll 1$ , which is the opposite of the condition for the validity of formula (47).

Concluding this section, we note that the Kramers–Henneberger atom, which is a steady-state system in a double-well potential, furnishes a real example of a dressed atom.

## 6.2 AC Stark shift in negative ions

The negative atomic ions constitute weakly bound electronic states with orbital quantum numbers 0 or 1. Such states can be studied within the framework of the model of a short-range potential. We denote the radius of such a potential by  $r_0$ . For negative ions one finds  $k_i r_0 \ll 1$ , with  $k_i = \sqrt{2E_i}$ , where  $E_i$  is the unperturbed ground state energy of the ion being considered. If the radius of the potential is zero, there can be only one bound state in such a potential (its orbital quantum number is zero). If the potential radius is finite, then a bound state with  $l = 1$  is a possibility. The value of  $r_0$  is of order of the neutral atomic core radius for the given negative ion.

The problem in question is simpler for the case of a circularly polarized field, which we will consider below. The time-dependent Schrödinger equation describing the interaction between a system with a short-range potential and a circularly polarized electromagnetic wave reduces to a stationary Schrödinger equation if we transfer to a reference frame rotating with the frequency of the external field about the direction of propagation of the electromagnetic wave. In the system of atomic units, the time-independent Hamiltonian written in the rotating (noninertial) reference frame takes the form

$$\hat{H} = -\frac{1}{2}\Delta + U(r) - \omega\hat{L}_z + Fx. \quad (49)$$

Here  $F$  is the amplitude of the electric field strength in the electromagnetic wave,  $\omega$  is the field's frequency, the  $z$  axis points in the direction of wave propagation, and  $U(r)$  is the short-range potential of the atomic core.

We begin with the state with  $l = 0$  and consider distances satisfying the following inequalities:  $r_0 \ll r \ll k_i^{-1}$ . On the one hand, at such distances the wave function has an asymptotic shape that follows from the effective-radius theory:

$$\psi_E(r) \propto \frac{1}{r} - k_i + r_0 E \quad (50)$$

(here  $E$  is the perturbed energy). On the other hand, we can use the expression for the wave function of a free electron in the field of the electromagnetic wave at distances that are small compared to the de Broglie wavelength:

$$\psi_E(r) \propto \frac{1}{r} + \frac{1}{\sqrt{2\pi i}} \int_0^\infty \frac{1}{t^{3/2}} \{\exp[iEt + i\varphi(t)] - 1\} dt. \quad (51)$$

Here we have introduced the notation

$$\varphi(t) \equiv \left[ 1 - \cos \omega t - \frac{1}{2}(\omega t)^2 \right] \frac{F^2}{\omega^4 t}. \quad (52)$$

We equate expression (51) to (50) and arrive at an equation for finding the complex-valued energy  $E$  [69, 70]. Its real part determines the AC Stark shift of the level in a radiation field of arbitrary intensity, while the imaginary part determines the width of the level. Actually, we have solved the problem, although analytical results can be obtained only in limiting cases. In the weak-field limit, the AC Stark shift of the level is proportional to the square of the field strength, as expected (the formula is not given here; see our book [8]).

In the opposite limit of an ultrastrong radiation field, the energy of the level increases to infinity [71] (irrespective of the field's frequency and the value of the unperturbed energy of the level) according to the law

$$E = 0.175F^{2/3} \text{ a.u.} \quad (53)$$

The level width rapidly increases by the same law. Calculations for the intermediate case were done numerically by Kraĭnov and Mulyukov [72] in the low-frequency limit. The results show that first the energy of the level decreases in accordance with the law of the quadratic Stark effect, reaches its minimum at a field strength  $F = 2(2E_i)^{3/2}$ , and then begins to increase.

Notice that a law of type (53) is fairly general. It also holds for the ground state of the hydrogen atom in an ultrastrong electric field [25] (although it does contain corrections logarithmic in the field strength).

Andreev et al. [73] found the low-frequency AC Stark shift of the atomic level for the case where the orbital angular momentum is unity. Here, the limit of an ultrastrong field is of special interest, since the presence of a centrifugal barrier prevents the electron from leaving the negative ion very fast. The value of the AC Stark shift of the level is much larger than the value of the unperturbed binding energy, while the lifetime of the level is much longer than the period of the laser radiation. The dependence of the AC Stark shift on the strength of the field of a circularly polarized wave has the form

$$E \propto F^{4/3}. \quad (54)$$

More than that, Andreev et al. [73] found that  $(2E_i)^{3/2}$  is the atomic field strength only for states in a short-range potential with  $l = 0$ . For states with  $l = 1$ , the atomic field strength is much larger and is estimated at  $(1/r_0)^3$ .

Trainham et al. [74] were the first to observe the AC Stark shift of the level in the negative ion  $\text{Cl}^-$ . Using the same type of ion, Davidson et al. [75] showed that the AC Stark shift of the continuum boundary in the field of the linearly polarized IR radiation emitted by a Nd:glass laser (with a photon energy of 1 eV) is equal to the vibrational energy of the electron in the field of the electromagnetic wave. The binding energy of the electron in this negative ion (the electron affinity) is about 3.6 eV, and the AC Stark shift of this level is small compared to the shift of the continuum boundary.

## 7. Conclusions

At the end of our review of the studies on the AC Stark effect in atoms we would like to formulate the most important results.

Generally, for arbitrary values of the frequency  $\omega$  and the strength  $F$  of the external variable field, the perturbation of an isolated atomic bound state consists in the formation of quasi-energy states with energies  $E_n(F) \pm k\omega$ , states in which



the quasi-energy  $E_n(F)$  is shifted in relation to the energy  $E_n(0)$  of the initial state, with the spectrum of quasi-energy harmonics  $\pm k\omega$  containing a large number of components. Clearly, there is a dramatic difference between the nature of the perturbation of the atomic spectrum in a variable electromagnetic field and that in a dc electric field.

In the particular case of a high-frequency ( $\omega \gg \omega_{n,n\pm 1}$ ) and weak ( $F \ll F_a$ ) field, only one state ( $k = 0$ ) proves to be populated in the spectrum of the quasi-energy harmonics, so that the perturbation results only in a change in position (shift) of the atomic level. This shift is proportional to the square of the field strength and numerically is equal to the vibrational energy of a free electron in the field of the electromagnetic wave:

$$\delta E_n(F) = \frac{F^2}{4\omega^2} \quad (55)$$

(for the field of a linearly polarized wave). We see that in this particular case there is perfect analogy between the nature of perturbations in variable and static fields.

In the typical case of bound states of atoms in the field of laser radiation of the visible spectrum, the perturbation of highly excited states corresponds to the above particular case at subatomic field strengths. The shift of the ground state, for which this radiation is low-frequency, is similar to the static polarization of an atom — it is negative. Thus, the ionization potential of a dressed atom is higher than the ionization potential of the unperturbed atom (see Fig. 11).

These most important conclusions follow from the results of theoretical and experimental investigations, which are in good agreement both qualitatively and quantitatively.

Now we turn to several aspects that so far have received little attention and require further investigation.

Of primary interest is the problem of observing the collapse of an atomic spectrum, which according to theoretical predictions must occur at a frequency and strength of the radiation field where the amplitude  $a = F/\omega^2$  of the oscillations of a free electron in the field of the electromagnetic wave

is much larger than the size of the atom. The discovery of spectrum collapse in experiments will serve as convincing proof that there is indeed such an object as a Kramers–Henneberger atom that goes to work as a model of a dressed atom in fields of atomic and superatomic strengths. However, the possibility of conducting such an experiment is highly problematic. The thing is that in realizing the inequalities  $a \gg 1$  and  $\omega > E_n(F)$ , where  $E_n(F)$  is the binding energy of the electron in the dressed atom, required by the theory, the photoionization of the atom may prove to be the dominating factor, and it is in such cases that stabilization of the atom [57], a process that has yet to be thoroughly studied, plays an important role.

It goes without saying that the studies on the process of the disturbance of an atom in a low-frequency field must be continued. The thing is that so far we know of only two experiments in which the process of formation of quasi-energy harmonics has been observed [34, 35], and the results of the experiment conducted by Bayfield et al. [35] do not agree well with theoretical predictions (see Section 4.3).

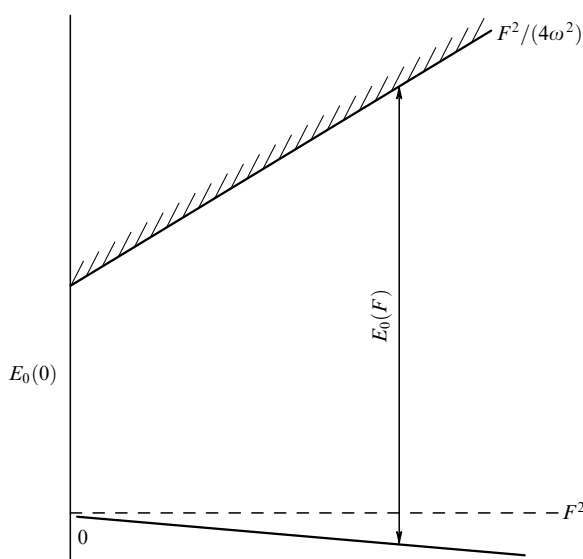
Obviously, it would be interesting to gather more experimental data on perturbations in a weak high-frequency field. We are speaking about observations of the quadratic shift of the initial energy of the bound electron by the value of the vibrational energy of a free electron in the radiation field of the wave for other atoms, in addition to noble-gas atoms, and at other frequencies, in addition to the visible-light spectrum. Although there is now no reason to believe that the general relationships (see Section 5.4) will break down, it is desirable to gather such data and make the picture complete.

Another interesting question that requires an exhaustive answer is: What is the maximum value of the AC Stark shift of an atomic level in the field produced by visible radiation? The answer to this question requires the use of data on nonlinear ionization of an atom in a light field.

From the general theory of nonlinear ionization developed by Keldysh [76] it follows that if the adiabaticity parameter

$$\gamma = \frac{\omega\sqrt{2E_n}}{F} \approx \frac{\omega}{F} \quad (56)$$

is of order unity, the nature of the ionization process changes dramatically. When  $\gamma^2 \gg 1$ , ionization is a multiphoton process, and when  $\gamma^2 \ll 1$ , it is a tunneling process. This conclusion is well corroborated for atoms by a number of numerical calculations (e.g., see the paper by Dörr et al. [77]) and by experiments (see the paper by Mevel et al. [78]). In the case of tunneling ionization, the electron from the initial (ground) state does not land in the energy range corresponding to highly excited states; it tunnels through the effective potential barrier. This means that for  $\gamma^2 < 1$  the perturbation reduces to that of only the ground state of the atom. As noted earlier (see Section 3.4), in the field induced by visible radiation the energy shift of the ground state is small and even negligible compared to the shift of a highly excited state. Thus, the condition  $\gamma^2 < 1$  limits the range of variation of the field strength within which the quadratic shift of the excited states is realized. If we compare expression (56) for the adiabaticity parameter and expression (55) for the electron vibrational energy, we will see that the maximum shift, which occurs when  $\gamma^2 \sim 1$ , amounts to  $1/4$  a.u.  $\approx 7$  eV (in the field of a linearly polarized wave). This estimate is in satisfactory



**Figure 11.** Ionization potential  $E_0(F)$  of a dressed atom and the unperturbed ionization potential  $E_0(0)$ . The hatched area stands for the continuum boundary.

agreement with the maximum value of the AC Stark shift of 3.5 eV, observed in the helium atom by Perry et al. [55].

Finally, we would like to stress that the AC Stark shift plays an important role in various processes that emerge in the interaction between highly intense laser light and atoms.

The first effect that we mention once more is the increase in the ionization potential of a dressed atom in comparison to the ionization potential of an unperturbed atom. When the field is strong, the increase may be as large as the energy of a photon from the external field or even exceed it. This can lead to an increase in the degree of nonlinearity of the process (the multiphotonicity of the process, so to say) from the initial value  $K(0) = [E_n(0)/\omega + 1]$  realized in a weak field to the large value  $K(F) = [E_n(F)/\omega + 1]$  corresponding to a strong field (the square brackets indicate here the integral part of the number inside them).

The second effect is the emergence of dynamic resonances (including multiphoton resonances) when the atomic levels get shifted by the time-dependent field of the laser pulse. This leads to alternation of the direct (in the absence of resonances) and resonant ionization processes at the front and trailing edge of a single laser pulse. Only in a weak field, where the AC Stark shift of the level is small, we can speak of a single process, direct or resonant. The criterion of smallness is obvious:  $\delta E_n(F) \leq \Gamma$ , where  $\Gamma$  is the maximum width among all widths of the specific experiment (the Doppler width, the width of the laser spectrum, etc.).

AC Stark effect influences not only the ionization process in the multiphoton limit but also in the opposite tunneling limit. The shift of the energy of an atomic ground state must be taken into account in calculations of the tunneling ionization probability [79] and in calculations of the threshold radiation intensity at which there is barrier-suppression decay of the atom [80]. Note that the shift of the ground state energy of the atom in a low-frequency field (estimated by the static polarizability) differs essentially for different atoms. It is smallest for noble-gas atoms and largest for alkali atoms.

Finally, at large intensities of the laser field, the full ionization of the target atoms is achieved already at the front of the laser pulse, so that at the pulse peak and the trailing edge the radiation is already interacting with a plasma. Here, a new realm of phenomena emerges, which must be treated separately, however. Of particular interest is the disturbance that is generated by two fields — a variable electromagnetic field and a dc electric field. These topics are discussed in detail in Bureeva and Lisitsa's book [9].

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