Nonresonance perturbation of an atomic spectrum in a strong light field

N. B. Delone, B. A. Zon, V. P. Kraĭnov, and V. A. Khodovoĭ

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The phenomenon of nonresonance perturbation of an atomic spectrum in a light field is discussed. Experimental methods for investigating the perturbation are described. The role of the degeneracy of atomic levels and of the strength and elliptic polarization of the field is reviewed. The results of experiments and of calculations are reproduced for a number of different special cases. The range of validity of perturbation theory is considered.

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CONTENTS

I. INTRODUCTION

The different phenomena that arise during the interaction between light and an atom have been discussed by physicists since the beginning of this century. Until quite recently, most of this discussion was confined to processes in which the interaction between light and an atom could be reduced to absorption, scattering, or the emission of individual photons. This reflected the specific properties of noncoherent sources of light, the spectral density of which was restricted by the very principle upon which their operation was based. Whenever an external field had to be considered, this was usually a constant electric field or a constant magnetic field. The effects of such fields upon the atom were a shift and a splitting of the atomic levels because of the removal of degeneracy. Moreover, a constant electric field gave rise to an exponentially small subbarrier ionization of the atom (tunnel effect).

The advent of coherent sources, i.e., lasers, has enabled a new class of phenomena, occurring during the interaction between an atom and the light field, to be investigated. Modern lasers are capable of producing, at given wavelengths, fields of up to 100 $\mathscr{E}_{at}$, where $\mathscr{E}_{at}$ is the atomic field strength (10^9 V·cm^{-1}). Naturally, all the phenomena which we shall consider will take place for $\mathscr{E} \ll \mathscr{E}_{at}$ since, for $\mathscr{E} \sim \mathscr{E}_{at}$, the atom ceases to exist as a bound system in a time of the order of the atomic time ($\sim 10^{-17}$ sec).

In the case of variable electromagnetic fields, the character of the interaction becomes much more complicated because the field is then characterized by a large number of parameters. Apart from the field strength, these parameters include the frequency, polarization, frequency spread, and duration of interaction with the atom. When the field strength is not too high, we must take into account spontaneous effects but, as the field increases, stimulated effects occurring under the action of the field must also be included. (Of course, in some cases, only some of these parameters are important.)

If we now consider the character of the interaction between the light field and an atom, we can distinguish a number of different cases. Thus, the resulting problems can be subdivided into two classes, depending on whether we are dealing with resonance or nonresonance perturbing fields. By a *resonance field*, we understand the case where the energy of the original atomic state plus the energy of one or a few quanta of the electromagnetic field is comparable with the energy of another discrete atomic state. When a resonance field acts on the atom, the result is a resonance behavior of the various parameters characterizing the interaction.

A resonance field does not necessarily lead to a mixing of resonating states as a result of which the perturbed state consists of comparable fractions of unperturbed resonating states. Additional conditions must be satisfied if such mixing is to occur. Thus, firstly, the time of operation of the field must be long enough and, secondly, the possibility of achieving sufficiently precise resonance must be available.

We shall use the phrase *resonance perturbation* of an atom to describe the situation where there is a mixing of the resonating states and the phrase *nonresonance perturbation* when such mixing does not occur, independently of whether the field is a resonance or a nonresonance field.

The simplest illustration of these definitions is provided by the well-known example of a two-level system in a resonance field.[1] For mixing to occur, the time

τ of operation of the field must satisfy the condition $V_{0r}^{(1)}\tau \gtrsim 1$, where $V_{0r}^{(1)}$ is the matrix element of the interaction $\mathbf{d}\mathscr{E}$ between the system and the field (assumed to be of the dipole type), **d** is the dipole moment operator, and $\mathscr{E}$ is the field amplitude. If resonance occurs as a result of the absorption of a number of quanta, the matrix element $V_{0r}^{(1)}$ must be replaced by the multiphoton matrix element $V_{0r}^{(k)}$ (see[2,3] for its explicit form). We note that $V_{0r}^{(k)}(\mathscr{E}) \sim \mathscr{E}^k$. If we label the initial state of the atom with the index 0 and the resonating state with the index r we obtain the following condition for the time of operation of the field in the case of multiphoton resonance:

$$V_{0r}^{(k)}\tau \gg 1. \tag{1}$$

Moreover, for mixing to occur, we must also demand (again by analogy with the two-level system) that the detuning from resonance, $\Delta(\mathscr{E})$, must be small enough and that the broadening produced by the field must be greater than the spontaneous and ionization widths:

$$V_{0r}^{(k)}(\mathscr{E}) \gg \Delta(\mathscr{E}),\ \gamma_{0r},\ \Gamma_r(\mathscr{E}); \tag{2}$$

where $\Delta(\mathscr{E}) = E_r - E_0 - k\hbar\omega + \delta E_{0r}(\mathscr{E})$ is the detuning from resonance, $\Delta E_{0r}(\mathscr{E})$ is the change in the transition energy $E_r - E_0$ under the influence of the external field, γ_{0r} is the difference between the spontaneous widths of the resonance and initial states (the reason for the appearance of this difference is explained, for example, in[4]), and Γ_r is the ionization width of the level r.

Thus, the *resonance perturbation* of the atom occurs when both (1) and (2) are satisfied.

The object of the present review is to investigate the *nonresonance perturbation* of an atom by light, i.e., perturbations for which either the incident field is a nonresonance field or at least one of the conditions, (1) or (2), is not satisfied in a resonance field.

When we analyze the character of the nonresonance interaction between light and an atom, it is interesting to consider separately the data on the shifts and broadening of atomic levels in a variable electromagnetic field of arbitrary strength, the appearance of new states and new quantum numbers, the energy and populations of quasilevels, and so on. We note that the possibilities are very much more extensive in the case of a variable field than they are for a constant field. Thus, level shifts are then rapidly varying functions of the frequency of the incident light, they can vanish, or they can change sign. Level broadening may become large because of the large ionization (including multiphoton polarization) probability. The character of the ionization process may be different, depending on whether: 1) the electron passes through the potential barrier produced by the field,[5] 2) the electron absorbs a number of light quanta and then passes through a smaller barrier, and 3) the electron absorbs the number of quanta necessary to enable it to reach the continuous spectrum, and then passes over the barrier. The transition from the first to the third process is the transition from the tunnel to multiphoton ionization. For weak fields ($\mathscr{E} \ll \mathscr{E}_{at}$), the probability of ionization in the first case is proportional to $\exp(-C_1/\mathscr{E})$ and, in the third case, to $C_2\mathscr{E}^{2k}$.[6] The problem for both theory and experiment is to determine the coefficients C_1 and C_2 as functions of frequency, polarization of light, and the atomic spectrum, and to investigate the situation for stronger fields. Smaller fields are sufficient to take us outside the framework of perturbation theory in the case of atomic multiplets. This is, clearly, due to the fact that the energy intervals in the fine structure of the multiplet are small. The fact that the continuous spectrum need not be taken into account makes the solution of this problem much easier. The limiting case where the energy intervals between several levels are zero is realized in the hydrogen atom because of degeneracy with respect to the orbital angular momentum. When the field is turned on, the orbital angular momentum ceases to be a good quantum number, and this leads to a number of interesting consequences. Degeneracy in the magnetic quantum number is of interest in the case of elliptically polarized fields.

In this review, we shall confine our attention to the main phenomena that arise when an *isolated* atom interacts with a light field.

II. EXPERIMENTAL METHOD

1. General characterization of experimental conditions

As noted in the Introduction, we shall be concerned with changes in the spectrum of bound states of an electron in an atom, due to the incidence of high-intensity light. It is well known that bound-electron states in the unperturbed atomic spectrum are characterized by the binding energy, spontaneous width, and a set of quantum numbers (see, for example,[7]). An external field modifies the spherical symmetry of the atom so that, in some cases, some of the quantum numbers are no longer good quantum numbers. Moreover, the external field may modify the binding energy and the form of the atomic level, including its half-width. In what follows, we shall describe particular methods of investigation. It is important to note, however, that the problems which we shall encounter can be divided into two groups, namely, studies of ground and excited electronic states, respectively. The latter, in contrast to the ground states, have finite widths due to spontaneous relaxation to the ground state. The light field strength producing the observed perturbation of excited states must therefore be sufficiently large to ensure that the perturbation is at least comparable with the spontaneous width. In typical experiments, the measured quantities are the transition energies and probabilities between different states. Such measurements are characterized by a very broad range in which the measured quantities can lie and the necessity for relatively high experimental precision.

The problems that arise when perturbations of an atomic spectrum are investigated impose mutually contradictory requirements on the atomic target. Thus, there are a number of fundamental restrictions on the maximum and minimum possible number of atoms, i.e., their density in the target. Firstly, the atoms must be sufficiently isolated to ensure that there are no collisions between them, or with free electrons, during the operation of the perturbing field. It is only when this condition is satisfied that the observed perturbation of the atomic spectrum is due to the light field alone. A restriction on the total number of atoms in the target is also imposed by the requirement that the experimental conditions must be such that absorption of the perturbing light can be neglected. It is also important to take into account self-action effects which occur when high-intensity light passes through an atomic medium. These effects are particularly important in the case of resonance between the frequency of the incident radiation and the frequency of the atomic transitions. Finally, we note that atomic beams have great advantages as targets as compared with gas or vapor targets. The linear Doppler effect is absent when the atomic and light beams are perpendicular. Moreover, the Doppler broadening in a gas at room temperature may amount to $0.1\ \mathrm{cm}^{-1}$, which is several orders of magnitude greater than the width of the single-frequency laser line and therefore gives rise to a substantial deterioration in frequency resolution. However, it is also important to remember that the limiting density of atoms in atomic beams is $10^{12}-10^{14}\ \mathrm{cm}^{-3}$ for a beam diameter of the order of 1 mm, which corresponds to a total number of illuminated atoms of the order of 10^{10}. The corresponding figure in the case of a gas (vapor) is of the order of 10^{16} for a density of $10^{16}\ \mathrm{cm}^{-1}$ and characteristic linear dimensions of 1 cm. (We note that these figures are only very rough and depend on the particular experimental conditions.) The lower limit for the number of atoms in the target is dictated by the sensitivity of the measuring equipment. All the experiments involve the detection of light, either re-emitted or scattered by the atom, or of electrons (ions) released during the ionization process. Modern electron multipliers can record individual ions, i.e., the result of the interaction between the light field and an individual atom. The practical sensitivity limit exceeds this ideal limit by a moderate factor. The sensitivity of light detectors is much lower. Shot noise and the quantum yield of photocathodes determine the light detection threshold. Thus, for a quantum yield of about 1% and a signal-to-noise ratio of about 10, about 1000 photons must be recorded. The sensitivity of photographic materials is exceptionally low even in comparison with this figure. Thus, in the visible part of the spectrum, a photographic film requires an illumination of the order of 10^{12} photons/cm^2. These numbers determine the lower limit for the number of atoms in the target.

Let us now consider the sources of light. It is clear that the main requirement in the case of studies of perturbations of atomic spectra is that the light must be monochromatic and of high intensity. It is well known that, when noncoherent sources are employed, these two requirements are mutually contradictory. The maximum spectral brightness is produced by lamps using high-frequency discharges in atomic vapor. For a linewidth of about $0.1\ \mathrm{cm}^{-1}$, it is possible to achieve a spectral brightness of up to $0.1\ \mathrm{W}\cdot\mathrm{cm}^{-3}$, which corresponds to a field strength of about $1\ \mathrm{V}\cdot\mathrm{cm}^{-1}$.[1] The light field due to such sources cannot be represented by a monochromatic wave of constant amplitude but is, in fact, a random emission whose amplitude fluctuates in time with frequency determined by the spectrum width (i.e., in the above special cases, with frequency of the order of $10^{-9}\ \mathrm{sec}^{-1}$). Since, in the case of lamps, the time of observation is several orders of magnitude greater (usually a few seconds), one observes the average perturbation of the atomic spectrum. Finally, we recall that, in the case of noncoherent light sources, the brightness cannot be increased by focusing.[8]

It follows that the laser is the only source of light capable of producing the high intensities discussed in the Introduction. The limiting values of the parameters characterizing the various available lasers are exceedingly different from the lamp parameters. Modern pulsed lasers can produce field strengths exceeding the atomic field by two orders of magnitude (i.e., up to $10^{11}\ \mathrm{V}\cdot\mathrm{cm}^{-1}$). They can generate radiation practically throughout the visible range with continuously tunable frequency within a band of several hundred cm^{-1}, and produce light within the limits of generation linewidths down to $10^{-4}\ \mathrm{cm}^{-1}$. Lasers can work under different conditions, i.e., they are capable of continuous operation or they can produce pulses with pulse lengths of the order of 10^{-11} sec. Finally, the intensity of the laser radiation can be sharply increased by focusing, and the size of the focusing region can be reduced down to a length of the order of the wavelength of the radiation.[9] Unfortunately, the limiting figures mentioned above refer to lasers of different design, and operating under different conditions, so that the achievement of a particular desirable parameter value may involve the use of highly nonoptimal other parameters. However, for experiments concerned with perturbations of the atomic spectrum, the important point is that field strengths up to $10^5\ \mathrm{V}\cdot\mathrm{cm}^{-1}$ can currently be produced at practically any frequency in the wavelength band between 0.3 and 1.0 μ for pulse lengths of the order of 10^{-8} sec and spectrum width of the order of $10\ \mathrm{cm}^{-1}$. To achieve the field strengths indicated above, the laser radiation (divergence of the order of 0.001 rad) is focused down to a circle of 0.01–0.001 cm in diameter. All such lasers use complex organic molecules (dyes) as the working material. They are pumped by radiation from solid-state lasers, occasionally transformed to another frequency band by the methods of nonlinear optics. The exceptional advantages of the laser as compared with noncoherent (thermal) light sources are obvious. However, the radiation generated by pulsed lasers suffers from three important disadvantages which produce considerable complications in the interpretation of experiments in which they are used. The first difficulty is that, as a rule, the radiation of such lasers consists of many modes with different longitudi-

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[1] Of course, there are many different types of lamp capable of emitting radiation with much higher integrated brightness. However, the width of the radiated spectrum produced by such lamps is very large, so that the spectral brightness is much lower.

nal indices and randomly distributed phases.[2] The statistical properties of this radiation are close to those of narrow-band thermal sources.[10] Single-frequency generation (generation of one mode with fixed longitudinal and transverse indices) is possible only for individual lasers working at given wavelengths. The second disadvantage is that the radiation has a nonuniform distribution in time and, finally, the third disadvantage is that it has a nonuniform spatial distribution. The nonuniform character of these distributions can be taken into account, but the experimental procedure is then complex and laborious.

2. Absorption of auxiliary radiation

Let us suppose that the atom is in the ground state and receives a perturbing field of frequency ω. This frequency and its simple harmonics are not in resonance with any of the frequencies of the atomic transitions between discrete levels. To observe the perturbation of the atomic spectrum, the atom is illuminated by light of frequency ω_1 from an auxiliary source, and the corresponding absorption spectrum is investigated (Fig. 1). The perturbation of the atomic spectrum by the field of the auxiliary light should be weak. The criterion for this is the absence of shifts and broadening of lines in the absence of the perturbing field. When the absorption linewidth is determined by the Doppler effect in the case of optical transitions with oscillator strengths of the order of unity, this criterion is satisfied when the field strength in the monochromatic auxiliary radiation is less than 30 V · cm^{-1}. There are two ways in which the absorption spectrum can be observed. The first method is based on the use of monochromatic auxiliary light of frequency ω_1 which is varied continuously and observations are made of the intensity of light transmitted by the atomic target as a function of ω_1. In the second method, which is the more widely used, the auxiliary radiation has a broad spectrum and observations are made of changes in this spectrum after passage through the atomic gas under investigation. A certain definite optical density (product of absorption coefficient of the atomic target by the length of the absorbing layer) is necessary before the absorption of the auxiliary radiation can be detected. Thus, in the case of a transition with Doppler absorption-line broadening and oscillator strength of the order of unity, an optical density of saturated vapor of the order of unity is achieved for atom density of the order of 10^{10} cm^{-3} and path length of ~1 cm. This minimum necessary density increases linearly with decreasing oscillator strength and increasing linewidth (for example, due to ionization broadening by the perturbing light). The maximum density is restricted by the appearance of self-focusing of the perturbing light in the atomic target.[11]

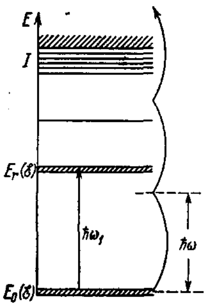

FIG. 1. Principle of the method based on absorption of auxiliary light. ω—frequency, $\mathscr{E}$—perturbing field, $E_0(\mathscr{E})$, $E_r(\mathscr{E})$—energy of ground (0) and excited (r) states of the atom in the field $\mathscr{E}$; I is the ionization energy of the atom in the field.

The main advantages of the method using absorption of auxiliary radiation is that the measurement results can be interpreted relatively simply, and the perturbing field can be varied in a broad range of values.

The observed shift of the center of gravity of an absorption line is determined by the shift of the two states—initial and excited—between which transitions involving absorption of the auxiliary radiation take place. When these levels are shifted in the same direction, the shift of the absorption line is equal to the difference between the level shifts; when the levels are shifted in opposite directions, the absorption-line shift is equal to their sum. The broadening of the absorption line corresponding to the auxiliary radiation is equal to the half-sum of the broadening of the ground and excited states.

The lower limit of the perturbing field strength corresponds to the minimum reliably detectable shift of the absorption line. In the case of the absorption lines of atomic vapors, the linewidth is determined by the Doppler effect and is of the order of 0.01 cm^{-1}. The field strength can be reduced if, instead of vapor, one uses atomic beams perpendicular to the direction of the auxiliary light beam so that there is no linear Doppler effect.

The perturbing field strength necessary for the realization of the auxiliary-light method can at present be achieved only by using lasers with pulse lengths of the order of 10^{-8} sec. For perturbations of such short duration, we have the problem of producing a sufficiently strong source of auxiliary radiation, enabling us to record the change in absorption during the time of a single laser pulse.[3] When the auxiliary radiation transmitted by the atomic vapor is recorded photoelectrically, the signal due to the change in absorption must exceed shot fluctuations in the photo-current within the transmission bandwidth of the recording circuitry, which is of the order of 10^{-3}–10^{-2} cm^{-1}. When unavoidable losses of auxiliary radiation associated with the elimination of the background due to scattered laser radiation are taken into account, the spectral density of the visible radiation produced by the strongest thermal sources is, as a rule, insufficient for reliable detection of the spectrum.[12] The most promising source of auxiliary light is, therefore, a low-intensity laser

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[2] This is called single-mode (one type of oscillation in the transverse indices) and multifrequency (large number of oscillations with different longitudinal indices) generation.

[3] It might be thought that the necessary intensity of the auxiliary source could be reduced by measuring the spectrum for a large number of laser pulses, but this is restricted by the low pulse repetition frequency (typically of the order of 1 pulse per minute).

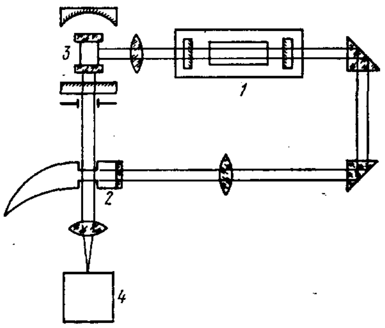


FIG. 2. Principle of the experiment[13] on the perturbation of the atomic spectrum of potassium, using the absorption of radiation from an auxiliary source. Radiation from laser 1 is directed into the vessel containing potassium vapor 2 and into the dye solution in the cell 3. The radiation from the dye laser has a spectral width of about 50 Å and is used as the auxiliary light, the absorption of which by potassium vapor is observed with spectrograph 4.

with spectral components covering the absorption line under investigation. An experiment of this kind on the shift of the D lines of the principal doublet of potassium atoms (7665 and 7699 Å) in the field of ruby-laser radiation is illustrated in Fig. 2.[13] To ensure maximum spatial homogeneity in the distribution of the ruby-laser radiation on the target, the laser had spherical mirrors and generated a large number of nonlocked transverse and longitudinal modes. This system has been used to measure shifts of the center of gravity of absorption lines of 0.02–2 cm^{-1}.

Another variant of these experiments may be more convenient for the investigation of ionization broadening of atomic levels. In this case, the main and the auxiliary light beams propagate in opposite directions. When the target length is small (of the order of 1 mm), and the diameter of the auxiliary beam is small in comparison with the diameter of the main beam, this approach may ensure high spatial uniformity in the distribution of the perturbing field over the target.

In conclusion of our survey of the auxiliary absorption method, we note its limitations and the associated difficulties. Among the more obvious limitations is the fact that this method cannot be used to investigate perturbations of atomic levels to which single-photon transitions from populated states (usually the ground state) are forbidden by the selection rules. The difficulties in applying this method increase when absorption lines are investigated in the ultraviolet and vacuum ultraviolet regions ($\lambda < 300$ nm) because of the difficulty of producing sufficiently strong auxiliary light of the necessary frequency. We note that, when very large absorption line broadening (up to 1 cm^{-1}) is investigated, so that the reduction in the absorption coefficient must be compensated by a substantial increase in the density of atoms, nonlinear phenomena such as parametrically stimulated electronic Raman scattering from excited levels populated by the auxiliary light become important. It has been shown[14,15] that these phenomena may lead to much more complicated perturbations of the energy spectrum. They can be eliminated by reducing the intensity of the auxiliary light. For high target densities, the criterion for small perturbation by the auxiliary light, given at the beginning of this section, may turn out to be insufficient.

3. Double radio-optical resonance

The double resonance method is a development of the absorption method described above. Let us suppose that the atom is in one of the sublevels of the ground state E_{01} (for example, a level in the hyperfine or Zeeman structure), and that it is illuminated by a field of frequency ω (Fig. 3). The frequency ω and its harmonics are not in resonance with any of the atomic transition frequencies. A measurement is made of the difference $E_{02} - E_{01}$ between the sublevels of the ground state, due to the field of frequency ω, by observing the change in the frequency ω_{12} corresponding to the transition between the two sublevels of the ground state. To detect the resonance transition frequency ω_{12}, the atom is exposed to two weak fields, namely, a monochromatic radiofrequency field, whose frequency ω_0 is varied, and an optical field with the frequency ω_1 of one of the optical transitions from the ground state. The width of the spectral line of the auxiliary optical radiation is much greater than the Doppler linewidth of the optical transition and the frequency ω_0, so that a change in ω_0 due to the perturbing optical field does not affect the absorption of the auxiliary optical radiation. The magnitude of this absorption depends on the population of the level E_{02} (in the limit, one transition at frequency ω_0 of the radiofrequency field produces a change in the auxiliary light flux by one photon). The resonance in the absorption of the radiofrequency field can be observed either through the resonance in the absorption of the auxiliary optical field or through the resonance in the intensity of resonance fluorescence from the level r. The difference between the ground-state sublevel populations exceeds by several orders of magnitude its value under thermodynamic equilibrium. The well-known optical orientation (or optical pumping) method is used to produce this difference. In this method, the atoms are excited by resonance radiation with the polarization or spectral composition necessary to ensure essentially different probabilities of excitation of atoms from the ground-state levels under investigation.[16,17] The magnitude of the population difference due to excitation and spontaneous decay depends on the ratio of the rates of excitation and relaxation of atoms to the equilibrium value. The necessary population difference

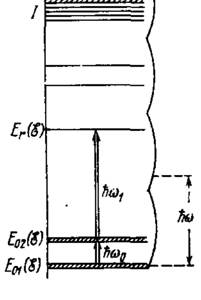


FIG. 3. Principle of the method of double resonance with optical pumping. $E_{01}(\mathscr{E})$, $E_{02}(\mathscr{E})$—sublevels of the ground state $E_0(\mathscr{E})$, ω—perturbing-field frequency, ω_0—alternative-field frequency in radioband, ω_1—light-field frequency; the fields of frequency ω_0 and ω_1 are auxiliary and are used for the diagnostics of the atomic spectrum.

(of the order of 1%) can at present be achieved only for a limited number of elements, the vapors of which are used in resonance emission lamps of sufficient intensity. These atoms are the alkali metals, Hg, Cd, He, Yb, Sr, and Ba. The frequency resolution of this method is determined by the linewidth of the radiofrequency transitions and is therefore exceptionally large in comparison with the standard resolution for optical fields. It is possible to detect a shift of the ground-state components by an amount of the order of 1 Hz (of the order of 10^{-11} cm^{-1}). The main disadvantage of the radio-optical double resonance method is that it can only be used for measuring the difference between the shifts of the ground-state sublevels. The shift of the center of gravity of the ground state cannot be measured. Moreover, the maximum observed shifts of the ground-state levels are restricted by the linewidth of the optical orientation sources (up to 10^{-1} cm^{-1}), since for large shifts the optical absorption line lies outside the limits of the orientation-source line, and orientation is not, in fact, produced.

4. Two-photon spectroscopy

This method is also a development of the absorption method. It is based on recording the transition from the ground to the excited state when light of frequency ω_1 and ω_2 is absorbed. The transition is observed through the resonance increase in the number of excited atoms when the sum of the photon energies is equal to the transition energy (Fig. 4). The change in the number of excited atoms is usually observed by measuring the change in the intensity of fluorescence at frequency ω_3 which is produced as a result of the spontaneous decay of the excited state.

A certain definite intensity of spontaneous emission is necessary before the two-photon resonance can be detected, and this, in turn, is found to be proportional to the concentration of atoms, the intensity of the exciting light, and the probability of spontaneous relaxation. Since the probability of two-photon transitions is small in comparison with, for example, the probability of single-photon transitions, two-photon spectroscopy requires greater perturbing-light intensities than the methods of single-photon spectroscopy. The probability of two-photon excitation can be increased by several orders of magnitude by using a resonance with an intermediate atomic level,[18-20] which can be achieved by using two perturbing fields with different frequencies. It is well known that two-photon transitions can occur between states with equal parities. Two-photon spectroscopy can therefore be used to investigate a whole class of transitions that are forbidden in single-photon spectroscopy. Two different perturbing fields with both different frequencies and different propagation and polarization vectors can be used in two-photon spectroscopy. The linear Doppler effect can be compensated for by using beams of light of equal frequency but traveling in opposite directions.[21] The condition for two-photon resonance in this case is

$$E_r - E_0 = \hbar\omega\left(1+\frac{v_z}{c}\right)+\hbar\omega\left(1-\frac{v_z}{c}\right),$$

where v_z is the component of the velocity of the atom along the direction of propagation of the light. However, when the frequency of light in both beams is the same, the absorption of photons from both beams will be accompanied by the absorption of two photons from either beam (right or left). For atoms absorbing two photons, the Doppler effect is not compensated. The fact that the signal due to atoms that absorb photons traveling in opposite directions can be separated out is due to the quadratic dependence of the probability of two-photon transition on the intensity (number of photons) and the fact that the number of photons traveling in opposite directions is twice as large as the number of photons from the right (left)-hand beam. The narrow resonance maximum that appears when the photons traveling in opposite directions are absorbed is located on a broad background due to the absorption of photons from the right (left)-hand beam. The effect-to-background ratio can be substantially increased by ensuring that the frequencies of the two beams traveling in opposite directions are different ($\omega_1 \neq \omega_2$) but the sum is, as before, equal to the transition frequency ($\omega_1 + \omega_2 = \omega_{0r}$). When $\omega_1 \neq \omega_2$, the compensation of the Doppler broadening will not be complete but may still be sufficient for $\omega_1 \approx \omega_2$. Thus, to reduce the width of the two-photon resonance in comparison with the Doppler broadening by a factor of 100, the difference between these frequencies must be such that $|\omega_1 - \omega_2| \lesssim 10^{-2}\omega_{1,2}$. A suitable choice of the degree of elliptical polarization can ensure that the transition under consideration will be allowed for photons from the opposing beams but forbidden for photons from one beam. When this is so, one can use radiation of one frequency, and completely compensate for the Doppler effect.

Finally, let us consider the difficulties and limitations of this method. It cannot be used in practice to investigate large ionization broadening of excited levels because of the reduced quantum yield of spontaneous emission. This is a characteristic feature of all methods involving the detection of the relaxation of excited states. Two-photon spectroscopy also has the disadvantage that the interpretation of the observed two-photon excitation spectra is relatively more complicated because these spectra depend on the interference between the probability amplitudes for two-photon transitions.[22] This feature of two-photon transitions is connected both with the fact that photon absorption sequences are indistinguishable, and the fact that events involving the absorption of photons through different intermediate states of the atom can take place even for a given absorption se-

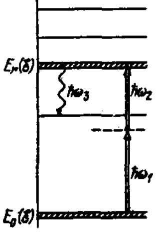


FIG. 4. Principle of the method of two-photon absorption. Photons of frequency ω_0 and ω_1 are absorbed and observations are made of the decay of the excited state r with the emission of light of frequency ω_3.

quence. When several intermediate states are available, it is the probability amplitudes for the various possible two-photon transition paths rather than the probabilities themselves that have to be added together. The sign of the probability amplitudes depends on the sign of the photon energy difference and the energies of the intermediate states, and the sum of the amplitudes may tend to zero under certain conditions. This may give rise to the appearance of sharp interference minima in the two-photon absorption spectrum with widths of the order of the atomic level width.[18] Finally, we note that, from the standpoint of the present review, i.e., nonresonance perturbation of atomic spectra, two-photon spectroscopy is also restricted to light field strengths below a certain maximum value. Thus, as the field strength increases, it is always possible to reach a situation where the probability of stimulated two-photon transition from the excited state to the ground state will be greater than the probability of spontaneous relaxation of the excited state to some other third state. The perturbation of the ground and excited states will then be of resonant character: they will be mixed by the perturbing field. (The analytic form of the conditions for resonance mixing is given in the Introduction.) The most promising modification of this method is, therefore, that in which the nonresonance field perturbing the atomic transition under investigation is large whilst the diagnostic fields with frequencies ω_1 and ω_2 are low enough not to produce an observable perturbation of the spectrum.

5. Observation of excited state relaxation

We assume in this method that the atom is in an excited state E_i and is illuminated by a field of frequency ω. The frequency ω and its simple harmonics are not in resonance with any of the atomic transition frequencies. To observe a perturbation of the atomic spectrum, one investigates the frequency shift and the broadening of the lines due to spontaneous emission from the level E_i (Fig. 5). The target is usually in the form of perturbed atoms in the plasma of a low-pressure (of the order of 1 Torr) discharge lamp. The spontaneous emission linewidth is then close to the Doppler width and is of the order of 0.01 cm^{-1}. The strength of the perturbing field that is necessary for the observation of a nonresonance shift of the spontaneous emission lines is of the order of 10^5 V/cm. As noted above, this figure can be reached only by using lasers producing pulse lengths of the order of 10^{-8} sec. An example of the application of the relaxation method is the work reported in[23,24] on the perturbation of the transitions $7^3S_1-6^3P_2$ and $7^3S_1-6^3P_1$ in the atomic spectrum of mercury. The 5461 Å and 4358 Å relaxation lines corresponding to these transitions were observed in the emission spectrum of a high-frequency discharge plasma in mercury vapor. The discharge lamp was illuminated by neodymium laser radiation having a wavelength of 1.06 μ (Fig. 6). The spectral profile of the emission lines was examined with a Fabry-Perot interferometer, the frequency band of which was divided into four zones of equal spectral width (0.05 Å). The emission in each zone was recorded by a separate photomultiplier. This meant that, instead of the integrated change in the spectrum, it was possible to observe the dynamics of changes in the emission lines during the development of the laser pulse (pulse length of the order of 10^{-8} sec). The above lines are the strongest mercury emission lines in the visible part of the spectrum, and this has facilitated the elimination of effects associated with the background due to other lines and to the laser emission.

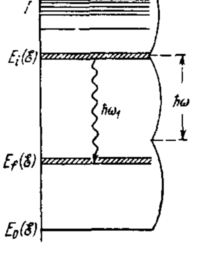


FIG. 5. Principle of the method based on the relaxation of an excited state i. The atom relaxes to state f with the emission of light of frequency ω_1. The frequency of the perturbing field is ω.

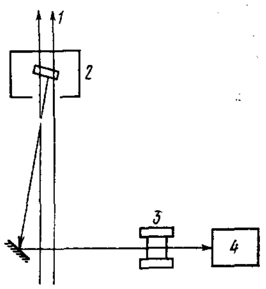


FIG. 6. Principle of the experiment on the perturbation of the spectrum of mercury by neodymium-laser radiation, using the relaxation of an excited state.[23] 1—laser beam, 2—mercury vapor, excited by hf discharge, 3—Fabry-Perot interferometer, 4—photomultiplier.

The method based on the observation of excited-state relaxation is attractive because of the simplicity of the experiment and of the interpretation of the final results. It is clear that experimental data on the perturbation of a single line will provide information on the change in transition energy and reduced width of the corresponding pair of states. By comparing the shift for a number of lines in the spontaneous emission spectrum associated with transitions from the same level, it is possible, at least in some cases, to separate out the effect due to a particular level and thus determine the magnitude of its level shift. An important advantage of this method is that it is possible to investigate shifts for levels from which transitions to the ground or metastable states are forbidden by selection rules and which cannot, therefore, be investigated by examining the absorption of auxiliary radiation.

The main difficulty in observing the relaxation of excited states is the production of a sufficiently large flux of recorded photons per laser pulse. Shot noise is always large, especially when the perturbing radiation is focused within a small volume in order to achieve high field strengths. When the laser pulse lengths are of the order of 10^{-8} sec, the relaxation method can be used to investigate the shift of only the strongest atomic lines. Moreover, the method is basically unsuitable for studies of the perturbation of highly excited states when the single-photon ionization channel is open and stimulated transitions to the continuum compete with relaxation.

6. Polarization methods

Polarization methods of investigating perturbations of the atomic spectrum involve measurements of the polarization of auxiliary light after passage through an atomic target exposed to a perturbing light. Methods of this kind are based on the appearance of the birefringence of the atomic medium near the absorption lines, which accompanies the splitting of levels participating in the atomic transitions by the light field.[25] The principle of the method can be understood by considering the splitting of one of the excited levels (Fig. 7). Suppose that a doubly degenerate level E_r splits into two sublevels $E_{r1}(\mathcal{E})$ and $E_{r2}(\mathcal{E})$ under the action of linearly polarized light, so that the absorption of auxiliary linearly polarized light of frequency ω involving the transition of the atom to the state $E_{r1}(\mathcal{E})$ is possible only for $\vec{\mathcal{E}}(\omega_1) \parallel \vec{\mathcal{E}}(\omega)$ whereas absorption involving transitions to $E_{r2}(\mathcal{E})$ is possible only for $\vec{\mathcal{E}}(\omega_1) \perp \vec{\mathcal{E}}(\omega)$. When the frequency ω_1 of the auxiliary radiation is arbitrary, the absorption coefficients for auxiliary-light components $\pi[\vec{\mathcal{E}}(\omega_1) \parallel \vec{\mathcal{E}}(\omega)]$ and $\sigma[\vec{\mathcal{E}}(\omega_1) \perp \vec{\mathcal{E}}(\omega)]$ will be different and, consequently, the refractive indices will also be different. The atomic medium will then become birefringent. When the electric-field vector in the auxiliary radiation is at an angle to the electric-field vector in the perturbing radiation, the change in the phases of the π and σ components of the auxiliary light will be different, and radiation which is linearly polarized at entry into the atomic target will be elliptically polarized when it leaves it. The degree of elliptical polarization will depend on the degree of splitting of the level E_r. By measuring the elliptical polarization and its dependence on ω_1, it is possible to investigate the perturbation of the level E_r.

We shall consider separately the cases of small splitting $\Delta\omega_r$ of an absorption line, when $\Delta\omega_r$ is much less than the linewidth Γ_r, and large splitting, when $\Delta\omega_r$ is much greater than Γ_r.

a) Small splitting: $\Delta\omega_r < \Gamma_r$. In this case, the difference $n_\pi(\omega_1) - n_\sigma(\omega_1)$ between the refractive indices is practically given by the derivative of the dispersion curve for the refractive index, and is proportional to the level splitting (Fig. 8a). By investigating the elliptic polarization, it is possible, at least in principle, to detect extremely small splitting, much less than the linewidth Γ_r, because the degree of elliptical polarization necessary for detection can be increased by increasing the concentration of atoms. At the same time, the use of this method for quantitative studies is difficult because it demands a knowledge of the concentration of atoms and the availability of a source with emission linewidth smaller than the absorption linewidth. Unless this condition is satisfied, measurements of the mean change in the elliptical polarization may give rise to considerable uncertainties in the amount of splitting when ω_1 is close to the absorption-line frequency.

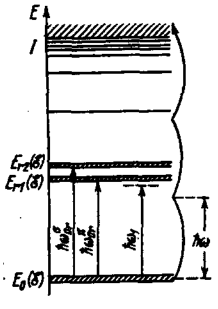


FIG. 7. The polarization method. The excited state $E_r(\mathcal{E})$ splits into $E_{r1}(\mathcal{E})$, $E_{r2}(\mathcal{E})$; ω—frequency of perturbing field, ω_1—frequency of auxiliary light, ω^π_{0r} and ω^σ_{0r}—frequencies at maximum absorption of auxiliary light (π and σ—plane of polarization of auxiliary light respectively parallel and perpendicular to the plane of polarization of perturbing light).

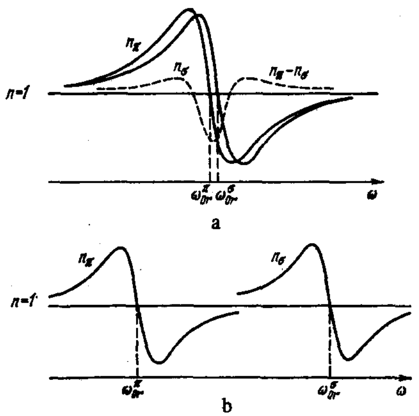


FIG. 8. Dispersion curves for a split line. n_π, n_σ—refractive indices; a—small splitting, b—large splitting.

The above version of the polarization method has been used to observe the splitting of the D_1 and D_2 lines of the principal doublet of potassium atoms in the field of ruby-laser radiation.[26,27] The auxiliary radiation was produced by a resonance potassium lamp working in conjunction with a monochromator which defined spectral bands of width 0.03 cm^{-1} near the potassium lines under investigation. Crossed polaroids were placed in the path of the auxiliary beam before and after the cell containing the potassium vapor. Under the action of the linearly polarized radiation from the ruby laser, the auxiliary beam became elliptically polarized and was transmitted by the crossed polaroids. Signals representing the change in polarization could be reliably recorded when the potassium level splitting was of the order of 10^{-4} cm^{-1} for a linewidth of the order of 0.01 cm^{-1}.

The main disadvantage of this variant of the polarization method is the difficulty (and, frequently, the impossibility) of reliable separation of contributions due to splitting and broadening of levels to the resultant effect associated with the change in the polarization of the auxiliary light. This basic difficulty can be removed in the case of large splitting ($\Delta\omega_r > \Gamma_r$) by measuring the change in the polarization of the auxiliary light as a function of frequency.

b) Large splitting of atomic levels: $\Delta\omega_r > \Gamma_r$. In this case, the dispersion profiles $n(\omega_1)$ are resolved (Fig. 8b); the line splitting can be obtained directly by measuring the difference between the frequencies ω_1 corresponding to the $n(\omega_1)=1$ points between the extrema of the dispersion profiles, and by measuring the distance between the extrema one can deduce the width of the components of the split line. The concentration of atoms need not be known, and the source of probing radiation can have a broad spectral line, overlapping the spectral region under investigation. The possibilities and restrictions of this variant are analogous to the situation in the case of the method involving the absorption of auxiliary light (Sec. 2). It is clear that studies based on the spectral dependence of the change in polarization in the case of two-photon excitation of atoms by elliptically polarized beams traveling in opposite directions are very promising. The presence of a sharp resonance, compensated for the Doppler width (see Sec. 4), leads to a corresponding sharp resonance in the rotation of the plane of polarization of the radiation.[28]

It is interesting to consider the possibilities of intraresonance methods for the analysis of the rotation of the plane of polarization (the cell containing the atomic vapor is placed inside the laser cavity) by which it is possible to measure rotations of the plane of polarization down to 10^{-6}–10^{-7} seconds of arc.

We end our survey of polarization methods by concluding that these methods can be used in qualitative studies of small amounts of splitting or broadening of levels, much smaller, in fact, than the linewidth. When the splitting is large, the possibilities of this method approach those of absorption methods.

7. Resonance multiphoton ionization

All the methods discussed above were based on the absorption or emission of photons from the atomic excited state under investigation. As already noted, ionization from the excited state restricts the applicability of these methods. The ionization process is a competing phenomenon in a large number of cases (when the strength of the perturbing field is large, or highly excited states are investigated), and this practically excludes methods based on the observation of the emission or absorption of light. However, the ionization process can itself be used for investigating the perturbation of an atomic spectrum. The point is that this can be done by multiphoton ionization of atoms.[29] It involves the detection of ions formed as a result of the multiphoton ionization of atoms, the change in the frequency and strength of the light field, and the resonance increase in the yield of ions connected with the intermediate resonance between the combined energy of a number of photons and the transition energy in the spectrum of the atom (Fig. 9). The condition for the realization of the resonance ionization process is

$$\Delta_{0r}(\mathscr{E}) = |\, E_r(\mathscr{E}) - E_0(\mathscr{E}) - k_{0r}\hbar\omega \,| \lesssim \Gamma_{0\,r}(\mathscr{E}), \tag{3}$$

where $\Gamma_{0,r}(\mathscr{E})$ are the widths of the ground and resonance states in the field, and k_{0r} is the nonlinearly of the $0r$ transition. If the transition $0r$ is allowed by the selection rules for multiphoton transitions, the ionization probability W_i, when (3) is satisfied, is much greater than when the inequality sign in (3) is reversed and there is no resonance. By varying the frequency and strength of the field and observing the resonance increase in the ionization probability for different values of these parameters, it is possible to obtain information on the perturbation of the atomic spectrum.

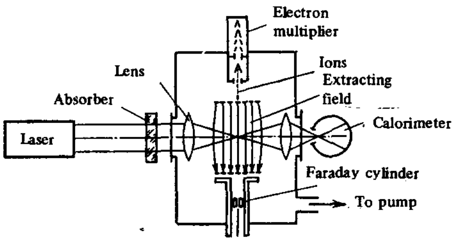


FIG. 9. Principle of the experiment on multiphonon ionization of an atom.

Since, in this method, the probing resonance field is also the perturbing field, the frequency, polarization, and strength of this field determine the nature of the perturbation of the resonance state 0 or r.

The nonresonance perturbation in which we are interested here is achieved when the ionization broadening of the resonance state r predominates over the field splitting due to the mixing of the states 0 and r.[30] This situation occurs when $2k_{rE} < k_{0r}$ where k_{rE} is the nonlinearity of the transition rE, and k_{0r} is the nonlinearity of the $0r$ transition. For single-photon ionization from excited states, which is the most interesting situation from the practical point of view, the degree of nonlinearity of the resonance transition should be $k_{0r} \geqslant 3$. When the above relationship between k_{0r} and k_{rE} is satisfied, the resonance ionization process assumes a cascade character and can be described as multiphoton excitation to the state r followed by ionization from this state.

For the cascade transition $0 \rightarrow r \rightarrow E$, the dependence of ionization probability on frequency and field strength is given by the Keldysh resonance formula[6]

$$W_{0E}^{(k_0)}(\mathscr{E},\, \omega) = \frac{V_{0r}^{(k)}(\mathscr{E})\,|^2}{[\Delta_{0r}(\mathscr{E})]^2 + [\hbar\Gamma_r(\mathscr{E})]^2}\, W_{rE}^{k_0-k}, \tag{4}$$

where the detuning from resonance is $\Delta_{0r}(\mathscr{E}) = |\, E_r(\mathscr{E}) - E_0(\mathscr{E}) - k\hbar\omega \,|$ and $\Gamma_r(\mathscr{E}) \equiv W_{rE}^{k_0-k}(\mathscr{E})$. In accordance with the conditions for the realization of this case, we neglect the field broadening of the ground state in comparison with the broadening of the resonance state in (4) (the field shift of the ground state cannot be neglected because the dynamic polarizability is a rapidly varying function of the frequency of light). The structure of (4) is analogous to the structure of the Weisskopf formula for resonance fluorescence.[31] The reason for this analogy is clear: in both cases, the transition proceeds through a quasidiscrete resonance level.[1,32] Moreover, (4) contains elements that are typical for multiphoton processes (matrix element of order k, where k is the photon resonance denominator) and for strong fields (field dependence of the energy of transition to the resonance state).

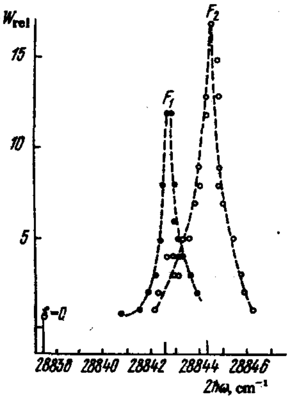


FIG. 10. Resonance increase in the probability of multiphonon ionization during the appearance of an intermediate resonance with an electronic bound state. Three-photon ionization of the metastable He 2^1S state by linearly polarized red light; the two-photon intermediate resonance with the 6^1S state is observed for two intensities with $F_2 > F_1$. In the absence of the field ($\mathscr{E}=0$), the resonance frequency for the 2^1S–6^1S transition is less than the resonance frequency in the field.

Measurements of the dependence of the $0r$ transition energy on the field strength can be performed by two different methods, i.e., by measuring the dependence of ionization probability on the frequency of light for a number of fixed values of the field strength, or by measuring the dependence of ionization probability on the field strength for several fixed values of frequency. It is important to note that, in many cases, useful information can be obtained by measuring the degree of nonlinearity $k = \partial \log W/\partial \log \mathscr{E}^2$ as a function of frequency. However, the quantity k itself is a dynamic characteristic of the ionization process and can be measured only for a varying light intensity. This method is therefore applicable only when the detuning from resonance undergoes a small change with field strength by the amount necessary for a sufficiently accurate determination of k.

We shall now consider the characteristic features of the method based on the dependence of ionization probability on frequency for fixed values of the field strength. Firstly, this method becomes much simpler when it is reduced to the measurement of the amplitude of the ion signal as a function of frequency, i.e., $A_i(\omega)$, instead of $W(\omega)$, and of the energy Q transmitted by the target instead of the radiation intensity F. The necessary condition for this is that the laser should generate one simple transverse mode. To achieve optimum resolution and frequency, the measurements must be performed so that the Doppler effect is unimportant (atomic-beam axis perpendicular to the light beam) and the width of the laser-beam spectrum is at a minimum (single frequency generation). The only instrumental factor which, in principle, cannot be eliminated is the nonuniform spatial and temporal distribution of radiation over the target. This nonuniformity has a complicated effect because the perturbation of atomic levels and the ion formation process are nonlinear in character, and the *integrated* ion yield is, in fact, measured. The presence of inhomogeneous broadening leads to two effects. Firstly, the integrated ion yield must be associated with some effective field strength which depends on the form of the spatial distribution of radiation over the target, the degree of nonlinearity of the transitions $0r$ and rE, and the presence or absence of saturation with respect to the transition rE, i.e., on the condition $\int_0^\tau W_{rE}\, dt \lesssim 1$, where τ is the laser pulse length. Secondly, the presence of inhomogeneous broadening leads to a broadening of $A_i(\omega)$ as compared with the function $W(\omega)$ in which we are interested. Effects associated with inhomogeneous broadening can be taken into account quantitatively with sufficient accuracy.[33] Figure 10 shows the results of a typical experiment[34] on three-photon ionization of helium in the presence of an intermediate two-photon resonance with the energy of the 2^1S–6^1S transition. We note that absolute measurements of perturbation require absolute measurements of radiation intensity. Such measurements can be carried out at present with an uncertainty of 30–40% by independent determinations of the spatial distribution of illuminance (using a photometric method) and the time distribution of intensity integrated over the beam cross section.[29]

The method of resonance multiphoton ionization suffers from two disadvantages. The first is typical for highly nonlinear processes. Thus, the method is applicable only in a very narrow range of variation of the field strength. The upper limit corresponds to the appearance of saturation in the multiphoton transition of the electron from the ground state to the continuum ($\int_0^\tau W_{0E}\, dt \sim 1$). A change in the laser pulse length cannot substantially alter this limit because the dependence on pulse length is linear whereas that on the field strength is strongly nonlinear. The second disadvantage is the small width of the perturbing-field spectrum for which experimental information can be obtained, since this requires resonance with the transition frequency. This is typical for all methods involving the absorption of light.

III. PERTURBATION OF ISOLATED ATOMIC STATES IN LINEARLY AND CIRCULARLY POLARIZED FIELDS

8. Perturbation theory

According to the fundamental principles of quantum mechanics, atoms located in variable external fields have no stationary states. Nevertheless, when the external field is not too strong, it is possible to construct long-lived quasistationary states that are not very different from the stationary states of the atom in zero external field.

In the case of light, the wavelength is much greater than the size of the atom. One can then use the dipole approximation and take into account the effect of only the electric field

$$\vec{\mathscr{E}}(t) = \mathrm{Re}\,[\vec{\mathscr{E}}_0(t)\, e^{-i\omega t}], \tag{5}$$

which is constant throughout the volume of the atom at each instant of time. Suppose that the amplitude $\mathscr{E}_0$ is a slowly-varying function of time, i.e., $d\mathscr{E}_0/dt \ll \omega \mathscr{E}_0$. We shall suppose that $\mathscr{E}_0 \to 0$ as $t \to \pm\infty$.

The solution of the time-dependent Schrödinger equation for an atom in the field will be sought in the form of an expansion in terms of the eigenfunctions of the Hamiltonian $\mathscr{H}_0$ for the free atom:

$$\psi(t)=\underset{n}{S}a_n(t)\,e^{-iE_nt/\hbar}|n\rangle,\quad \mathscr{H}_0|n\rangle=E_n|n\rangle, \tag{6}$$

where S represents summation over the discrete spectrum and integration over the continuous spectrum of the atom. The coefficients a_n satisfy the following set of equations

$$i\hbar\dot{a}_n=\underset{m}{S}V_{nm}(t)\,e^{i\omega_{nm}t}a_m(t),\ \omega_{nm}\equiv\frac{E_n-E_m}{\hbar},\qquad V_{nm}(t)=-\langle n|\mathbf{d}\vec{\mathscr{E}}(t)|m\rangle, \tag{7}$$

where d is the dipole moment operator for the atom.

If the atom is in the state $|0\rangle$ before the field is turned on, the largest coefficient in (6) is a_0. Moreover, in the coefficient a_0 itself, the low-frequency harmonic will have the largest weight (in comparison with ω and $\omega_{0n}\pm\omega$), since $a_0\to 1$ when the field is turned off. Let us take into account the admixture of states $|n\rangle\neq 0$ to the wave function (6) in accordance with perturbation theory. In first-order perturbation theory,

$$i\hbar\dot{a}_n=V_{n0}(t)\,e^{i\omega_{n0}t}a_0(t),\quad n\neq 0.$$

Integrating this equation with respect to time and recalling that, since a_0 and $\vec{\mathscr{E}}_0$ are slowly-varying functions of time [see (9)], they can be taken out from under the integral sign, we have finally

$$a_n(t)=\frac{a_0}{2\hbar}\left(\frac{\mathbf{d}_{n0}\vec{\mathscr{E}}_0}{\omega_{n0}-\omega-i\lambda}e^{i(\omega_{n0}-\omega)t}+\frac{\mathbf{d}_{n0}\vec{\mathscr{E}}_0^*}{\omega_{n0}+\omega-i\lambda}e^{i(\omega_{n0}+\omega)t}\right), \tag{8}$$

where $\lambda\to+0$ corresponds to an adiabatically slow introduction of the field. Substituting (8) in (7), and retaining only the slowly-varying terms, we obtain

$$a_0(t)=\exp\left[\frac{i}{4\pi}\alpha_{pq}\int_{-\infty}^{t}\mathscr{E}_{0p}^*(t')\,\mathscr{E}_{0q}(t')\,dt\right], \tag{9}$$

where

$$\alpha_{pq}(\omega)=\frac{1}{\hbar}\underset{n}{S}\left[\frac{(d_p)_{0n}(d_q)_{n0}}{\omega_{n0}-\omega-i\lambda}+\frac{(d_q)_{0n}(d_p)_{n0}}{\omega_{n0}+\omega-i\lambda}\right] \tag{10}$$

is the dynamic polarization tensor of the state $|0\rangle$ at the frequency ω [the summation is carried out over the repeated subscripts p and q in (10)].

Thus, in an external field, the wave function for the atom contains an additional phase gain which can be interpreted as a change in the level energy by the amount[7]

$$-\frac{1}{4}\alpha_{pq}\mathscr{E}_{0p}^*(t)\,\mathscr{E}_{0q}(t). \tag{11}$$

This energy change is sometimes referred to as the quadratic Stark effect in a variable field. This choice of terminology is not entirely successful because the phenomenon may be much more complicated in a varying field than in a constant field (this was mentioned in the Introduction). Moreover, there is no other analogy apart from the similarity in the analytic form of the dependence on the field strength.

Dynamic polarizability may turn out to be a complex quantity. In fact, when single-photon ionization from the state 0 is possible, the continuum spectrum will also include states for which $\omega_{n0}=\omega$. It is possible to separate the real and imaginary parts of the polarizability where

$$\operatorname{Im}\alpha_{pq}(\omega)=\pi S(d_p)_{0n}(d_q)_{n0}\delta|E_n-E_0-\omega|.$$

The states n satisfy the conservation of energy $E_n=E_0+\hbar\omega$.

The wave function is thus exponentially attenuated in time, and the attenuation constant is given by

$$\Gamma(t)=\frac{1}{4}\operatorname{Im}\alpha_{pq}\mathscr{E}_{0p}^*\mathscr{E}_{0q}=W_{0E}(t) \tag{12}$$

i.e., as can be seen, it is determined by the total probability of photoionization of the atom from the state 0 under the action of the external field. We note that $\Gamma(t)$ may be zero in first-order perturbation theory, in which we are interested here, if the ionization of the atom from the particular state by a single photon is impossible. The ionization width is then determined by the probability of multiphoton ionization from the given state.[29] The real part of the polarizability determines the change in the energy of the quasistationary state:

$$\Delta E(t)=\frac{1}{4}\operatorname{Re}\alpha_{pq}(\omega)\,\mathscr{E}_{0p}^*\mathscr{E}_{0q}, \tag{13}$$

where $\operatorname{Re}\alpha_{pq}$ can be found from (10).

The change in the energy of atomic levels is manifested spectroscopically by a change in the frequency of the absorption and emission lines of the atom, and possible decay of the levels is reflected in the broadening of these lines.

Let us consider the validity of (12) and (13).

Firstly, these expressions are not valid if the state 0 resonates at frequencies ω or $k\omega$ with the level r and, in particular, when $|\Delta E+i\Gamma|\gtrsim|\hbar(\omega_{r0}\pm k\omega)|$, $k=1, 2, \ldots$. The level r is then supposed to belong to the discrete spectrum.

Secondly, (13) is not valid if a level s lies near the level 0 in such a way that $|\Delta E|\gtrsim|\hbar\omega_{0s}|$. Transitions between the levels s and 0 are then possible. This means that, in addition to the coefficient a_0 in the wave function given by (6), there is another significant coefficient, namely, a_s, so that if the atom is initially in the state 0, it will subsequently occupy the state s for a considerable proportion of the time. We note that mixing occurs in relatively weak light fields in the hydrogen atom for $n\geq 3$ states, when the energy shift begins to exceed the fine splitting. Atomic levels with nonzero angular momentum J consist of a group of degenerate magnetic sublevels which can be mixed by the field. However, it is readily seen that, in linearly polarized light, the direction of polarization is a special direction, so that the component of J along this direction is conserved and the mixing of magnetic sublevels does not occur. In precisely the same way, in the case of circularly polarized fields, the special direction is

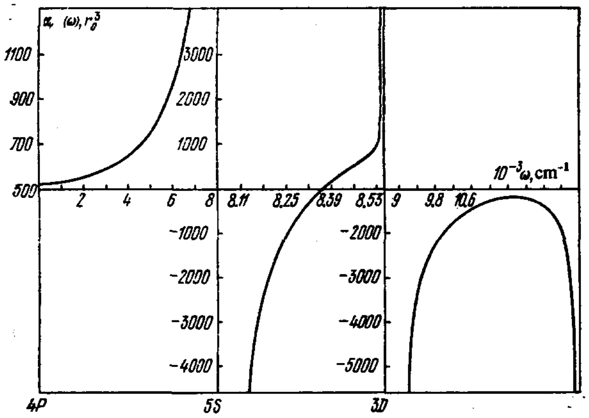


FIG. 11. Dynamic polarizability α_{pq} of the potassium atom in the first excited state $4^2P_{1/2}$ (r_0 is the Bohr radius).

the direction of propagation of the radiation, and the magnetic sublevels again are not mixed. We must now consider some of the features of dynamic polarizability as a function of field frequency ω, taking as an illustration the dynamic polarizability of the $4P$ state of potassium,[35] shown in Fig. 11.

The quantity $\alpha_{pq}(0)$ is the static polarizability because it determines the reaction of the atom to a constant electric field. As the frequency increases, the polarizability changes from its static value and, as ω approaches the resonance transition frequency corresponding to the nearest discrete level r, we have $\alpha_{pq}\to\infty$ for $\omega\to\omega_{r0}$ from the left (to be specific, we are assuming that $\omega_{r0}>0$, i.e., the level r lies above the level 0). In Fig. 11, this frequency is approximately 8000 cm^{-1} and corresponds to resonance between the $4P$ and $5S$ levels. The region $\omega\sim\omega_{r0}$ in which polarization undergoes a rapid change with frequency is called the region of anomalous dispersion because it is precisely in this region that the dispersive properties of the medium are very well defined. After passing through resonance, we have $\alpha_{pq}\to-\infty$ as $\omega\to\omega_{r0}$ from the right. Regions in which polarizability decreases with increasing frequency are commonly referred to as regions of negative dispersion.

Further increase in frequency is accompanied by an increase in polarizability, and the subsequent behavior is determined by the position of the next resonance. Two cases may arise:

a) The next resonance r' is also above the level 0. In the above example, this is the $3D$ state. Under these conditions, as $\omega\to\omega_{r'0}$ from the left, the polarizability assumes very large values, as before. However, for certain intermediate field frequencies, the polarizability should vanish at one or several points (in the case of nonmonotonic variation). At these frequencies ($\omega\approx8360$ cm^{-1} in Fig. 11), the atomic level is not shifted in the first nonvanishing order of perturbation theory. Since the dynamic polarizability tensor (10) is identical with the coherent scattering tensor for light of frequency ω from the state 0,[32] these points correspond to zero light scattering cross sections in the first nonvanishing approximation of perturbation theory. Such frequencies correspond to a kind of "transparency" of the medium.

b) The next resonance r' lies below the level 0. Here, as $\omega\to\omega_{0r'}$ from the left, we again have $\alpha_{pq}\to-\infty$, just as for $\omega\to\omega_{r0}$ from the right. Thus, in this particular frequency band, the polarizability passes through a maximum (or several maxima), and there are broad frequency bands in which dispersion is negative. In Fig. 11, this region corresponds to 11 500 cm^{-1} $\leqslant\omega\leqslant$ 13 000 cm^{-1}. Its appearance is connected with a resonance between the $4P$ level and the $4s$ ground state of the potassium atom.

After passing through the region of resonances with higher-lying levels (this region is determined by the ionization potential of the state 0) and the region of resonances with lower-lying levels, the polarizability becomes a smooth function of frequency. Its asymptotic behavior at frequencies much greater than the characteristic atomic parameters is given by the well-known formula[32]

$$\alpha_{pq}\approx-\frac{Ze^2}{m\omega^2}\delta_{pq}, \tag{14}$$

where Z is the number of optical electrons. The asymptotic behavior is reached almost immediately after the single-photon ionization channel becomes open. The frequency ω should then be much smaller than the characteristic frequencies for the excitation of the atomic core, so that its polarizability can be neglected.

As already noted, the formulas for the dynamic polarizability given in this section are valid for linearly and circularly polarized radiation when the mixing of magnetic sublevels by the field need not be taken into account. In this case, one can obtain the polarizability as a function of the magnetic quantum numbers, and thus determine the relative shifts and splitting of the magnetic sublevels in the field.

Consider, to begin with, a linearly polarized field defined by $\mathscr{E}_{0z}=\mathscr{E}^*_{0z}=\mathscr{E}_0$, $\mathscr{E}_{0x}=\mathscr{E}^*_{0x}=0$. In this case,

$$\alpha_{zz}^M(\omega)=u_J+J(J+1)w_J-2M^2w_J, \tag{15}$$

where

$$\left.\begin{aligned}&u_J=(J+2)P_{J+1}-P_J+(J-1)P_{J-1},\quad w_J=\frac{P_{J+1}}{J+1}+\frac{P_J}{J(J+1)}+\frac{P_{J-1}}{J},\\&P_{J+1}=\frac{D_{J+1}(\omega)+D_{J+1}(-\omega)}{2\sqrt{(2J+1)(2J+3)}},\qquad P_{J-1}=\frac{D_{J-1}(\omega)+D_{J-1}(-\omega)}{2\sqrt{(2J+1)(2J-1)}},\\&P_J=\frac{1}{2}[D_J(\omega)+D_J(-\omega)].\end{aligned}\right\} \tag{16}$$

The parameters $D_J(\pm\omega)$ can be expressed in terms of the reduced matrix element of the dipole moment operator for the atom, as follows:

$$D_J(\pm\omega)=\frac{1}{\hbar}\mathop{S}_{\nu_l}\frac{\langle\nu_0J\|d\|\nu_l\rangle\langle\nu_l\|d\|\nu_0J\rangle}{\omega_{\nu_0J,\nu_l}\pm\omega\pm i\lambda}. \tag{17}$$

It is clear from (15) that degeneracy with respect to the magnetic quantum number is not wholly removed in linearly polarized fields. States differing by the sign of M have the same polarizability. This is connected with the fact that the atom-plus-field system is invariant under time reversal. Since the component of the angular momentum is T-invariant, and, in the linearly polarized field, there are no other T-invariant, quantities, the spectrum can depend only on M^2.

Let us now consider a circularly polarized field. For right-handed polarization, $\vec{\mathscr{E}}_0 = \mathscr{E}_0(\mathbf{e}_x - i\mathbf{e}_y)/\sqrt{2}$. The energy shift is given by

$$\Delta E - i\Gamma = -\frac{\mathscr{E}_0^2}{4}[\alpha_{xx} + \alpha_{yy} + i(\alpha_{xy} - \alpha_{yx})]. \tag{18}$$

Simple calculations then yield

$$\Delta E_M - i\Gamma_M = \frac{\mathscr{E}_0^2}{4}(u_J - v_J M + w_J M^2), \tag{19}$$

where

$$v_J = \frac{2J+3}{2J+1} q_{J+1} + \frac{q_J}{J(J+1)} - \frac{2J-1}{J} q_{J-1}. \tag{20}$$

The quantities q_j differ from the P_j by the different sign in front of the parameters $D_j(-\omega)$. In a circularly polarized field, degeneracy with respect to the sign of M is removed because all the photons now have definite helicity.

9. Calculations of dynamic polarizability

As shown in the preceding section, the perturbation of an isolated atomic level in linearly and circularly polarized fields is determined by the dynamic polarizability tensor (10). Evaluation of the polarizability is therefore the fundamental problem for the theory. It is clear that, before the polarization can be calculated, we must know the matrix elements of the dipole-moment operator for the atom between the state 0 and all other states, including the continuous spectrum. These matrix elements must be summed over the discrete spectrum and integrated over the continuum, which is also not a simple problem by far. We note that the second difficulty is specific only for the real part of the polarizability, which determines the level shift, since calculation of the imaginary part which determines the broadening can , in view of (12), be reduced to the evaluation of the photoionization probability, i.e., only one matrix element. The summation problem remains even when one of the terms in (10) is much greater than all the others. This is possible when one of the energy denominators in (10) becomes small, i.e., when the frequency of the field becomes close to the atomic resonance frequency, but the detuning from resonance substantially exceeds the natural level widths. The sum of a large number of small terms may be of the same order of magnitude as one large term.

Thus, calculations of polarizability cannot, generally speaking, be confined to a finite number of intermediate states. Many theoretical methods for calculating atomic polarizabilities, which are not confined to the inclusion of a few intermediate states, have been put forward. It is important to note, however, that most theoretical papers have been devoted to the evaluation of static polarizabilities, and the dynamic case has been the concern of a much smaller number of publications. A review of theoretical work and experimental data on static polarizabilities is given in[36].

The dynamic polarizability can be calculated by carrying out an expansion in powers of ω near the point $\omega = 0$. The coefficients of this series are the static characteristics of the given atomic state and can be calculated by the same methods that are used for calculating static polarizability. It is clear that the static polarizability itself is the zero-order term, and the subsequent terms of the series contain the higher powers of the frequency differences in the denominators of the sums. This method of calculating the dynamic polarizability is called the method of moments in the literature. The precision of the method of moments is, of course, determined by the precision of the calculated static parameters of the atom, and both the upper and lower bounds for the remainder of the series can be estimated. A review of all the published work on the method of moments and the results of various calculations of the moments for the ground states of noble gas atoms is given in[37]. The method of moments has not been applied to excited atomic states.

Various variational methods for the calculation of dynamic polarizabilities have been put forward in the literature. In these methods, the sum (10) over an infinite set of eigenstates is replaced by a sum over a finite set of certain fictitious states for which the spectrum and the dipole matrix elements are obtained from a linear variational principle. This approach has been used to calculate the dynamic polarizabilities of certain atomic systems with a small number of electrons, including the ground[38–40] and excited[41] states of hydrogen, helium,[42–44] beryllium, and the ions Li^+ and H^-.[43]

An important simplification of the many-electron problem is the replacement of the exact many-particle problem, with complete inclusion of the interelectron interaction, by the single-particle Hartree-Fock approximation in which each atomic electron is assumed to move in the self-consistent potential due to all the other electrons. There is a large number of published papers on the self-consistent potential and simple analytic approximations to it that are convenient for applications. In the simplest variant, it is assumed that the self-consistent potential is not modified by the presence of the variable electric field (this is the so-called uncoupled Hartree-Fock approximation). This approach has been used to calculate the dynamic polarizabilities of helium,[45] beryllium,[46] and the ions Li^+ and Ne^+.[47] More accurate calculations allow for the change in the self-consistent potential in the presence of the variable field (this is the so-called coupled Hartree-Fock approximation). This method has been used to calculate the polarizabilities of helium, lithium, beryllium, and neon.[48–54] The results obtained by calculations based on various modifications of the Hartree-Fock approximation are compared in[49]. As already noted, interelectron correlations, the inclusion of which provides an improvement on the Hartree-Fock approximation, do result in an appreciable contribution to the dynamic polarizability of atoms containing two or more electrons in the outer shell. Partial inclusion of correlation effects in the case of the oxygen atom is reported in[55] and, in the case of noble-gas atoms, in[56].

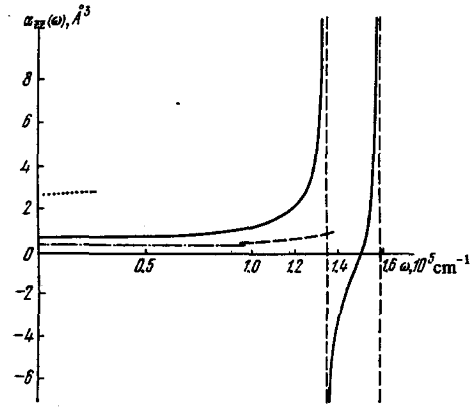


FIG. 12. Dynamic polarizability of neon in the ground state. Solid curve—pseudopotential method,[58] dashed curve—method of moments,[37] dot-dash curve—Hartree-Fock approximation with partial inclusion of correlation effects,[56] points—experimental data.[57]

All the calculations involving the above atoms except for hydrogen have been confined to the ground states.

Semiphenomenological methods have also been developed in recent years, i.e., the quantum defect and pseudopotential methods. Here, the spectrum of the atom is assumed to be known in advance (and this is the phenomenological essence of these methods), but knowledge of the real, experimentally established, spectrum enables some of the correlation effects to be taken into account. The quantum defect method has long been widely used in atomic physics for calculating the probabilities of ordinary electromagnetic transitions. It is based on the fact that the main contribution to the matrix elements of the electromagnetic interaction operator is due to regions located well away from the atomic core, where the effective, i.e., single-particle, potential in which the motion of the optical electron takes place can be looked upon as a purely Coulomb potential. This assumption turns out to be very satisfactory for the ground state of atoms with a single electron in the valence shell, and for the excited states of all other atoms. The dynamic polarizabilities of both the ground and the first excited states of alkali metal atoms were calculated in this approximation in[35]. In the pseudopotential method, the radial part of the potential for the optical electron is also assumed to be of the Coulomb type, and the constant in the centrifugal part is chosen by fitting the theoretical spectrum to experimental data. Calculations of the dynamic polarizabilities of noble-gas atoms based on this approach are reported in[58]. An undoubted advantage of semiphenomenological methods, which makes them useful in different applications, is that they can yield the polarizabilities of excited atoms. It is particularly important to emphasize that, computationally, these methods are also much simpler.

Figure 12 shows the dynamic polarizability of the neon atom calculated by the semiphenomenological pseudopotential method[58] (solid curve), the method of moments[37] (dashes), and the Hartree-Fock approximation, partially corrected for correlation effects[56] (dot-dash line). The vertical lines indicate the position of the resonance frequencies corresponding to the excited states $(2p)^5 3S$ and $(2p)^5 4S$ of the atom, respectively.

10. Effect of a nonmonochromatic perturbing field

The light fields used in studies of the perturbation of atomic spectra are never strictly monochromatic and always have a finite spectrum width. Even the radiation of a single-frequency cw laser has a width in excess of 1000 Hz, due to fluctuations in the cavity length. In the case of pulsed single-frequency lasers, the spectral linewidth is determined by the regular temporal variation in laser intensity, and is of the order of the reciprocal of the pulse length. In the absence of mode locking, the radiation generated by multimode lasers is a set of *harmonics in a narrow spectral interval with a* random phase distribution. When the number of modes is large, the statistical properties of this multimode radiation are close to the properties of narrow-band Gaussian noise.[10] The emission of resonance high-frequency discharge lamps, which provide the highest spectral brightness among nonlaser sources, has a spectral linewidth of the order of 0.01 cm^{-1}. The electric field strength associated with this radiation is subject to irregular temporal fluctuations with a characteristic period (correlation time) of the order of the reciprocal of the spectral linewidth, i.e., of the order of 10^{-9} sec.

Since the instantaneous values of the atomic-level shifts depend on the amplitude of the perturbing field, it follows that, when these amplitudes are functions of time, the level positions will also be functions of time. When perturbations of the atomic spectrum by nonmonochromatic fields are investigated, the time of observation becomes an important factor. In the case of multimode lasers, the time of observation is greater than, or of the order of, the reciprocal of the spectral linewidth of the perturbing radiation, so that the observed picture of the perturbed atomic spectrum is, in fact, the time average.

It is clear that the dynamics of the perturbed spectrum should be determined by the dynamics of the perturbing field. There are no general methods at present for calculating the nonresonance perturbation of an atomic spectrum for any arbitrary statistics of the perturbing field. Let us therefore consider a number of special cases.

The simplest calculation is that for a regular pulsed perturbation, for example, pulses from single-frequency lasers with lengths of the order of 10^{-8} sec. When the average change in the frequency of the atomic transition under consideration is much greater than the reciprocal of the pulse length of the perturbing radiation, the instantaneous change in the atomic-level energies involved in this transition can be looked upon as adiabatically slow, and can be calculated from (13):

$$\Delta E(t) = \frac{1}{4}\alpha_{pq}|\mathscr{E}_{0q}(t)|^2.$$

Theoretical analysis of the dynamics of the spectrum of two- and three-level systems for different shapes of the perturbing pulse is given in[59,60].

Analysis of the perturbation of an atomic spectrum by irregular optical radiation is much more complicated. A rigorous analysis is available only in the two-level approximation either for a field which is a random Markov process[61,62] or for a field with complex Gaussian statistics.[63,64] The perturbing field with Markov-type phase and frequency modulation is realized in the case of monochromatic perturbation of the spectrum of an atom undergoing a collision which instantaneously changes its direction of motion. For the interpretation of existing experiments, the most important is the analysis of the perturbation of the atomic spectrum by fields with complex Gaussian statistics (which is characteristic for the field of thermal and gas-discharge sources). The statistical properties of multimode (or multifrequency) laser radiation in the absence of mode locking are also close to this situation.

Since the state amplitudes cannot be averaged, the rigorous procedure for calculating the perturbed atomic spectrum is very complicated and involves the averaging of measured quantities over an ensemble of perturbing-field realizations. There is a great variety of methods for investigating perturbations of the atomic spectrum, but we shall confine our attention to the method involving the absorption of auxiliary radiation, which is particularly simple to interpret. A rigorous analysis of this problem is given in[63] in the two-level approximation.

We shall assume that the atom is in the nondegenerate ground state E_0 and that, from the time $t=0$ onward, it is illuminated by a strong, nonresonance, linearly polarized, field of mean frequency ω and spectral linewidth $\Delta\omega$. We shall investigate the absorption of a weak field of frequency ω_1 when the atom undergoes a transition to a nondegenerate excited state E_r which, in the absence of the strong perturbing field, will relax spontaneously to the ground state with probability 2γ (Fig. 1). The shape of the absorption line for the auxiliary light is, in this case, given by

$$h(\omega_1) \propto \left(\frac{\pi}{2}+\operatorname{arctg}\frac{\omega_1-\omega_{r0}}{\gamma}\right)\times\begin{cases}\exp\dfrac{\omega_{r0}-\omega_1}{\Delta_0}, & \omega_1>\omega_{r0},\\ 1, \quad \omega_1<\omega_{r0}.\end{cases} \tag{21}$$

The most important factor which determines the linewidth is the constant Δ_0 which is proportional to the radiation intensity. When $\Delta_0 \gg \Delta\omega$, the atom is, in effect, in a quasimonochromatic field with amplitude that varies slowly in comparison with the reciprocal of the mean line shift Δ_0. The field amplitude will continuously pass through all the possible values during an interval of time much greater than the correlation time $\tau_c=\Delta\omega^{-1}$ of the strong perturbing field, and the line shift will also assume all the corresponding possible values. This will show up as the inhomogeneous line broadening. At each instant of time, the line shift is proportional to the square of the field amplitude. For a complex Gaussian field, the distribution of the square of the amplitude is[65]

$$W(|\mathscr{E}|^2)=\frac{\pi}{2\overline{|\mathscr{E}|^2}}\exp\left(-\frac{|\mathscr{E}|^2}{\overline{|\mathscr{E}|^2}}\right).$$

The other limiting case corresponds to perturbation by a field with a broad spectrum, so that $\Delta_0 \ll \Delta\omega$. Physically, this corresponds to mean square perturbing fields for which the mean absorption line shift is much smaller than the width $\Delta\omega$ of the spectral line of the perturbing field. In this case, the line shift is proportional to the mean square of the perturbing field, and is equal to the shift of the absorption line in a monochromatic perturbing field with the same power density. The line broadening due to the perturbing field is

$$\gamma=\int \Delta E^2(t)\,dt \sim \frac{\Delta_0^2}{\Delta\omega},$$

from which it follows that, for broad perturbing-field spectral lines ($\Delta\omega \gg \Delta_0$), the absorption linewidth is less than the line shift by a factor of $\Delta\omega/\Delta_0$ and is proportional to the fourth power of the root mean square perturbing field. In the limiting case of small absorption line shifts, the field amplitude varies rapidly in comparison with the mean line shift, and we have an averaging of the instantaneous line positions relative to the mean shift Δ_0, which manifests itself as a small broadening. The effective averaging time is the period of the mean line shift Δ_0, i.e., the time necessary to ensure a frequency measurement to within Δ_0. It is clear that the degree of averaging of the instantaneous line shifts is determined by the ratio of the mean time for a change in the field amplitude $\tau_m=\Delta\omega^{-1}$ to the time for averaging Δ_0^{-1}, i.e., by the ratio $\Delta\omega/\Delta_0$.

Thus, the results obtained for the two limiting cases of perturbation of the atomic spectrum by radiation with broad and narrow spectral lines lead to the conclusion that the most important changes in the shape of lines in the atomic spectrum, i.e., saturation of the line shift and its broadening, become important when the center of gravity of the line is shifted by an amount that is of the order of, or greater than, the linewidth of the perturbing field. The change in the shape of atomic lines in the intermediate region, i.e., for shifts of the center of gravity of the order of the linewidth of the perturbing radiation, gives rise to the greatest difficulties for theoretical analysis although it is clear that the one limiting case must continuously go over to the other.

It should be noted particularly that the apparently obvious continuous transition from the nonmonochromatic to the monochromatic perturbation as the perturbation linewidth $\Delta\omega$ is reduced does not, in fact, occur. On the contrary, the perturbed spectrum for broad perturbing spectral lines is the closest in appearance to the spectrum for monochromatic perturbation. As the perturbation linewidth decreases at constant intensity, there is an increase in the difference between the spectra perturbed by nonmonochromatic and monochromatic radiation. The absence of a limiting transition from the Gaussian to the monochromatic field with reducing linewidth is due to the difference between their statistics. In the case of a Gaussian field, the amplitude is variable and runs through all the realizations during the time of detection of the perturbed spectrum $\Delta t \gg \Delta\omega^{-1}$. As the linewidth $\Delta\omega$ decreases, there is an increase in only the time necessary for the realization of all the

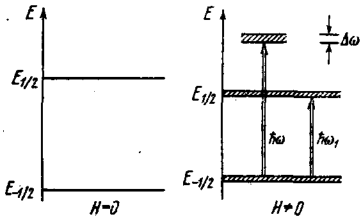


FIG. 13. Measurement of the change in the Zeeman absorption line for auxiliary radiation (ω_1) of cadmium in the presence of narrow-band noise field of frequency ω.[63]

values of the field amplitude. In the case of a monochromatic field, the amplitude remains constant throughout the time of recording of the spectrum.

Let us now consider experiments on the perturbation of the atomic spectrum, using Gaussian noise radiation in the radiofrequency band and designed to verify the theory in terms of the two-level model.[63] The method of double radio-optical resonance[66] was used in these experiments to investigate the change in the shape of the Zeeman line seen in absorption when weak auxiliary radiation of frequency ω_1 illuminated Cd^{113} atoms exposed to a narrow-band Gaussian noise field formed from white noise by linear rectangular filters (Fig. 13).

Figure 14 shows the measured absorption line shift Δ as a function of the square of the perturbing field strength. For small noise fields, the shift Δ is the same as for a monochromatic perturbing field. It was established that, under these conditions, the absorption line shape was not very different from the Lorentz profile (Fig. 15), and its broadening was proportional to the fourth power of the perturbing field strength, in accordance with the theoretical predictions [formula (21)]. However, the absorption-line shift saturates in high noise fields. Saturation becomes important for line shifts ΔE of the order of the spectral linewidth $\Delta\omega$ of the perturbing radiation. It was established that, when the shift ΔE reached saturation, the line shape became highly asymmetric (Fig. 16): it was exponential in the direction of the line shift, and the linewidth was proportional to the square of the perturbing field. The line profile is in agreement with (21) to within experimental error.

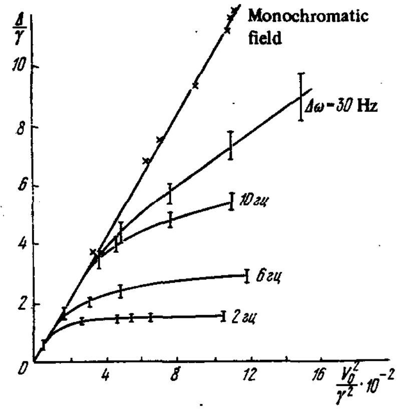


FIG. 14. Shift Δ of the maximum of the Zeeman absorption line as a function of the square of the perturbing field. The shift is in units of the half-width of the original line, and the square of the field is in units of $2\gamma^2/\pi^2\gamma_0^2$ where γ_0 is the paramagnetic ratio and $\Delta\omega$ the linewidth.

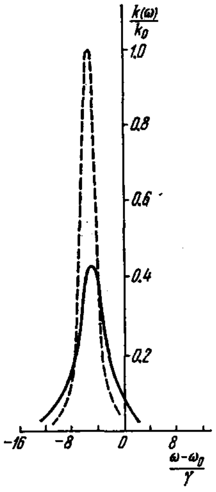


FIG. 15. Shape of absorption line. Solid line—observed for $\Delta\omega = 30$ Hz, $V_0^2/\gamma^2 = 500$, broken line—line shape observed in monochromatic perturbing field of the same power, K_0—absorption coefficient at line maximum in the absence of perturbation, V_0—mean matrix element of the perturbation.

The conclusion that we may draw from our review of experimental data is that they are in agreement with the theoretical predictions. The most important of these is that the line shift in the atomic spectrum saturates, and that the lines are broadened by a Gaussian field when the shift of the center of gravity of the lines is of the order of, or greater than, the linewidth of the perturbing radiation. Another interesting experimental result was the discovery of substantial fluctuations in the absorption coefficient for the auxiliary radiation, which are absent when a monochromatic perturbing field is used.[67–69]

11. Experimental results and comparison with theoretical calculations

The character of the weak perturbation of bound electronic states by linearly and circularly polarized light is qualitatively quite clear. Therefore, the main problem for experimental and theoretical calculations is to obtain quantitative data on dynamic polarizability. The differences between the spectra of particular atoms, the sharp dependence of polarizability on light frequen-

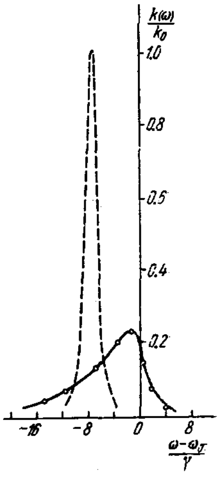


FIG. 16. Shape of absorption line. Solid curve—calculated from (9) (Sec. 8), open circles—experiment ($\Delta\omega = 2$ Hz, $V_0^2/\gamma^2 = 700$), dashed curve—same as in Fig. 15.

cy, and the large relative frequency changes, all demonstrate the difference between the resulting situation and the usual situation in a constant field. It is desirable to carry out calculations on dynamic polarizability as a function of frequency for different typical atomic configurations (one optical electron, closed shell, and so on) and to obtain experimental data at individual characteristic points (near the midresonance zero perturbation, near resonances, and so on), which could then be used in comparisons between measured and computed data. This should lead to optimum computational methods which can then be applied to other cases that can be regarded as analogous.

A useful procedure is to divide all the experimental data into three groups corresponding, respectively, to the perturbation of the ground, low excited, and high excited states. In contrast to the low excited states, the high excited states will be defined as those from which single-photon ionization can take place for a fixed frequency of the perturbing field.

a) Perturbations of ground states. The ground states of atoms have the smallest width and their shift can be detected for perturbing field strengths of the order of 1 V/cm. Such fields can be produced by continuous sources of radiation, so that it is much easier to ensure spatial uniformity of radiation over the target and a constant intensity.

The first group consists of experiments concerned with transitions between the sublevels of the ground state (Zeeman or hyperfine structure components). All that can be measured in these experiments is the difference between the shifts of two sublevels, but the shift of the center of gravity of the ground state can not be determined. The first experiments, performed by the method of double radio-optical resonance, showed qualitatively that shifts of the order of 1 Hz could be determined in the case of the magnetic sublevels of the ground state of the mercury atom.[70, 71] The dependence of the Zeeman splitting frequency on the presence of a perturbing optical radiation with two circular polarizations was investigated. The sign of the Zeeman frequency is different for different polarizations since, in the case of σ^+ polarization, the $m = -1/2$ sublevel is largely perturbed whereas, in the case of σ^-, this occurs for the $m = +1/2$ sublevel. The broadening of resonances was not observed, and this is in good agreement with calculations [see Sec. 10, Eq. (21)].

Quantitative data on the shift of atomic ground states by a light field were obtained in[72]. These experiments were also performed by the double radio-optical resonance method and were concerned with the shift of the 0–0 hyperfine transition frequency for the ground state of Rb^{87} atoms (Fig. 17). The frequency of the hyperfine transition was perturbed by radiation from a high-frequency rubidium lamp with spectral linewidth of the order of 0.01 cm^{-1} and mean frequency close to the frequencies of the resonance D_1 and D_2 absorption lines of the principal doublet of rubidium (frequency difference of the order of 0.01 cm^{-1}). The sublevels of the hyperfine states with $n=0$ are not shifted in a constant magnetic field (terrestrial and laboratory fields) and, therefore, the 0–0 transition line has the smallest width, amounting to about 100 Hz for concentrations of the order of 10^{10} cm^{-3}. Figure 17b shows the measured and calculated frequency shifts for the 0–0 hyperfine transition as functions of the intensity of the unpolarized perturbing radiation. In this calculation, the different magnitude of the departure from resonance of the frequencies of the perturbing radiation and the atomic D lines (the corresponding virtual transitions provide the main contribution to the shift of the ground-state levels) was taken into account by assuming that each of the harmonics shifted the ground state independently and the contributions of the different harmonics were summed with weights depending on the closeness to resonance and intensity. It is clear from Fig. 17b that the calculations satisfactorily reproduce the experimental dependence. This agreement demonstrates that a sufficiently precise calculation of the hyperfine transition shifts can be carried out on the basis of second-order perturbation theory by summing the contributions of the different harmonics to the level shift.

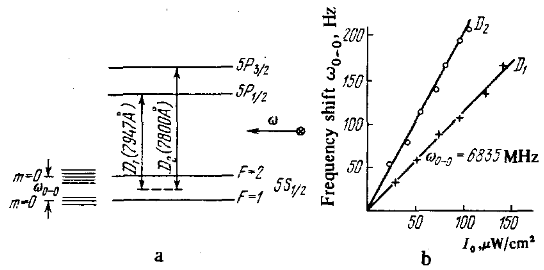


FIG. 17. Level scheme of Rb^{87} (a) and shift of the hyperfine transition frequency ω_{0-0} as a function of perturbing-light intensity (b).

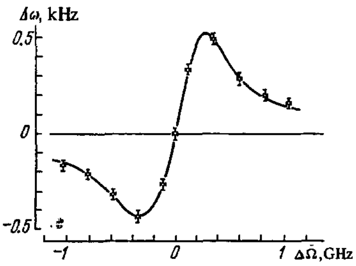


FIG. 18. Frequency shift $\Delta\omega$ of the 0–0 transition in cesium as a function of the frequency difference $\Delta\Omega$ between the laser and the absorption line.[73]

In a recent paper,[73] Arditi and Picoque investigated the shift of the 0–0 hyperfine transition frequency for the cesium atom ($\omega = 9192.63$ MHz) in the radiation field of a continuous GaAr laser with wavelength close to the D_2 absorption line of cesium (8521 Å). They found that, for small line shifts, the shape of the line was unaffected, whereas the sign and the dependence of the frequency shift $\Delta\omega$ on the frequency difference $\Delta\Omega = \omega_0 - \omega_{21}$ between the laser and the cesium absorption line were in good agreement with theoretical predictions (Fig. 18).

The above group of experiments is characterized by the fact that they were concerned with the difference between the shifts of two ground state levels. The method of two-photon spectroscopy, using beams traveling in opposite directions, has been used to investigate the shift of the ground state in the case of the sodium atom.[74] Two-photon excitation of the $3S_{1/2}$–$4D_{5/2}$

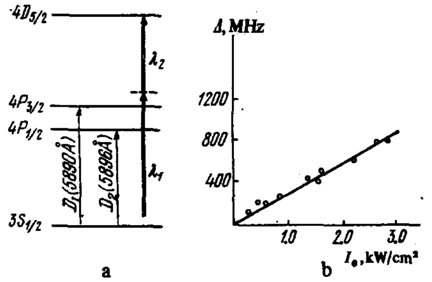


FIG. 19. Level scheme of sodium (a) and shift of the 3S ground-state level of sodium as a function of perturbing-light intensity (b).

transition was carried out in these experiments in the case of sodium vapor using opposing beams generated by two cw dye lasers with wavelength $\lambda = 589$ and 569 nm. The occurrence of two-photon transitions was monitored by recording the $4P$–$3S$ (330 nm) fluorescence produced as a result of the spontaneous relaxation of the $4D$ state (Fig. 19). The shift of the $3S_{1/2}$ ground state was induced mainly by the 589-nm radiation which was close to the wavelength of the $3S$–$4P$ transition. The shift of the ground state could therefore be investigated by ensuring that the intensity of the 589-nm exciting field was much greater than the intensity of the second field, and by measuring the change in the frequency of the two-photon excitation (Fig. 19). The observed shift of the $3S_{1/2}$ level was much smaller than the Doppler broadening; it could not be measured without using light beams traveling in opposite directions. The measured level shift was found to be satisfactorily described in terms of the two-level approximation.

In conclusion of our review of studies of the perturbation of the ground states of atoms, we note that all the experiments which we have discussed were performed under conditions where the main contribution to the perturbation of the ground state was due to a single virtual transition with well-known oscillator strength. It is too early to draw any general conclusions with regard to the validity of the calculations from the satisfactory agreement between the calculations and the experimental data because the volume of experimental results is still quite small.

b) Perturbations of low excited states. The characteristic feature of experiments on low excited states is the absence of one-photon ionization from the excited state. The relatively substantial natural width of the excited states (due to the spontaneous relaxation of these states) means that strong fields have to be used to produce perturbations exceeding this width. Thus, fields in excess of 10^4 V · cm^{-1} have to be used and can be produced only with the aid of laser radiation.

A polarization method was used in[26] to investigate the splitting of the D_1 and D_2 lines of the principal doublet of K^{39} ($4S_{1/2}$–$4P_{1/2}$ and $4S_{1/2}$–$4P_{3/2}$ transitions, respectively) in linearly and circularly polarized ruby laser radiation. The laser used in these experiments was operated under multimode generation conditions without mode locking. The total spectral linewidth was about 0.01 Å. The ruby-laser radiation had a wavelength close to the wavelength corresponding to the $4P_{3/2}$–$6P_{1/2}$ ($\lambda = 6939$ Å) transition, so that only the D_2 line was subject to splitting in the case of linear polarization of the laser radiation because of the shift of the $\pm 1/2$ sublevels of the $4P_{3/2}$ state (Fig. 20) whereas, in the case of circular polarization, both D_2 and D_1 were split. The latter splitting was expected to be much smaller, and this was, in fact, confirmed experimentally.

Quantitative studies of the D_1 and D_2 line shifts in the case of the potassium atom were investigated in[13] using absorption of auxiliary light. Linearly polarized radiation from a ruby laser ($\lambda = 9642.5$ Å) with a linewidth of about 0.01 Å was used as the perturbing field. The laser was operated under multimode conditions without phase locking in order to achieve maximum spatial uniformity in the intensity distribution. It was found that the shift of the center of gravity of these absorption lines was a quadratic function of the laser field up to $\mathscr{E} = 5 \times 10^5$ V/cm^{-1}, and the shift constants were found to be $\alpha(D_1) = (0.2 \pm 0.1) \times 10^{-11}$ cm^{-1}/V^2 cm^{-2} and $\alpha(D_2) = 1.0 \pm 0.5 \times 10^{-11}$ cm^{-1}/V^2 cm^{-2}. These constants are described by the calculations reported in[17] to within experimental error. These experiments have revealed a considerable broadening of the D lines as compared with their shift. At the same time, estimates based on the relationships given in Sec. 8 in the case of monochromatic fields indicate that the broadening should be smaller than the shift by at least two orders of magnitude. It is suggested in[75] that this broadening is due to the amplitude modulation of the perturbing field. This proposal was confirmed in[76] for the change in the shape of the D_2 line in the absorption spectrum of the rubidium atom (7800 Å) in the field of a multimode dye laser with a spectrum width of the order of 1 Å and wavelength close to the D_1 wavelength (7947 Å). It was found that the perturbing field produced a broadening of the D_2 line up to about 10 Å, and a similar shift of its center of gravity. We note that this large broadening cannot be due to the spatial and temporal nonuniformity in the distribution of the radiation.

Relaxation of excited states has been used to determine the shift of the resonance lines $\lambda = 5461$ Å (7^3S_1–6^3P_2) and $\lambda = 4358$ Å (7^3S_1–6^3P_1) of mercury in neodymium laser radiation ($\lambda = 1.06$ μ).[23,24] Multimode laser

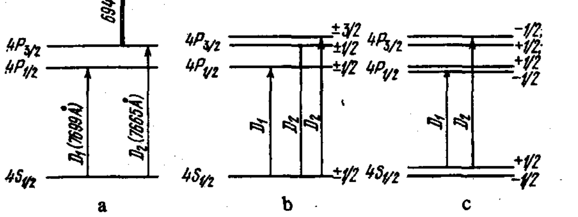


FIG. 20. Splitting of potassium levels in ruby-laser radiation. a—unperturbed level scheme, b—level scheme in linearly polarized laser field, c—in circularly polarized laser field.

TABLE I. Measured and calculated shifts of the 7^3S_1 state of mercury by 1.06-μ radiation.

Field, V cm^{-1}	ΔE_{exp}, cm^{-1}[23]	ΔE_{theor}, cm^{-1} [35]	Field, V cm^{-1}	ΔE_{exp}, cm^{-1}[23]	ΔE_{theor}, cm^{-1}[35]
$1.5\cdot10^5$	0.085	0.098	$4.3\cdot10^5$	0.44	0.65
$3.5\cdot10^5$	0.34	0.49	$6.0\cdot10^5$	0.88	1.3

radiation without mode locking was used with a spectral linewidth of about 10 Å and linear polarization. These lines correspond to transitions from the same state (7^3S_1; Fig. 21). It was established that the lines were shifted toward the short-wave region in proportion to the square of the light field strength, and the absolute magnitude of the shift was the same for both lines to within experimental error (approximately 15%). It was therefore concluded that the shift was connected mainly with the shift of the 7^3S_1 level. Calculations of the shift of the 5461-Å resonance line by the 1.06-μ radiation showed that the line shift was, in fact, determined by the shift of the upper 7^3S_1 level of mercury, the polarizability of which was higher by an order of magnitude than the polarizability of the lower 6^3P_2 level.[35] Comparison of observed and calculated shifts of the 5461-Å line (Table I) showed that the measured shifts were satisfactorily described by the calculations but were systematically somewhat lower than the theoretical values and this difference increased with increasing intensity of the perturbing laser radiation. A possible reason for this discrepancy may be line saturation due to the fact that the perturbing laser radiation was not monochromatic.

In conclusion of our review of studies of the lower excited states, we note the exceptionally small amount of available experimental data. Nevertheless, the results discussed above have broadly confirmed the validity of the methods employed and the high precision of the experimental data.

c) Perturbations of the upper excited states. In accordance with the above classification, the upper excited states are the electronic states for which the single-photon ionization channel is open for a given perturbing-field frequency. The high field strength necessary for the observation of perturbations of highly excited states is due to the short lifetime of these states for the ionization process. Hence, independently of the process responsible for the atom being in the excited state, the observation of this state through the absorption or emission of light is, in practice, quite difficult.

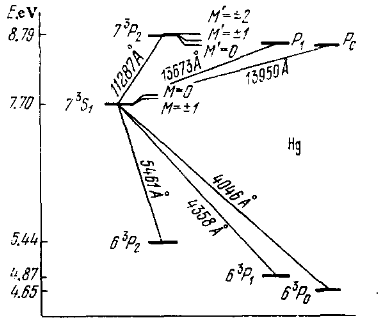


FIG. 21. Transitions in the mercury atom.

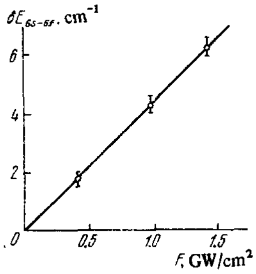


FIG. 22. 6S–6F transition energy in cesium as a function of intensity.[78]

However, it is possible to use resonance multiphoton ionization in this case.

Three measurements performed by this method have been reported in the literature[77–79] (Table II). The four-photon resonance in the case of five-photon ionization from the metastable 2^3S state of the helium atom has been observed by measuring the function $W(\mathscr{E})$ for a number of fixed radiation frequencies. The function $W(\omega)$ was measured in other cases for a number of fixed values of the field strength. All these experiments were performed with linearly polarized radiation.

Let us consider some of the properties of these transitions. A single-frequency laser was used in the experiment with the cesium atoms. The resonance $6F$ state of the cesium atom is the doublet $6F_{5/2}$, $6F_{7/2}$ which, in the absence of the external field, is known to have a splitting of about 0.1 cm^{-1}. In the case of the three-photon resonance in a field of 10^6 V · cm^{-1}, the interaction with the field is much greater than the spin-orbit coupling, so that the $6F$ doublet can be looked upon as a single level, the total angular momentum of which is equal to the orbital angular momentum. In a linearly polarized field, the $6F$ state should split into four components with magnetic quantum numbers $m=0$, 1, 2, 3, respectively. The three-photon transition from the initial $6S$ ($m=0$) state is allowed only to the resonance $6F$ ($m=0$) state, i.e., a single resonance maximum should be observed, and this is confirmed by experimental data. We also note that calculations[35] yield the following values for the real part of the dynamic polarizability: $\alpha(6S)=-350$ and $\alpha(6F)=625$ a.u., i.e., the main contribution to the resultant polarizability of the $6S$–$6F$ transition is the polarizability of the ground state. The measured dependence of the $6S$–$6F$ transition energy on the light intensity is shown in Fig. 22.

The data on the 2^3S–14^3D transition in the helium atom, shown in Table II, are the most reliable example among a large volume of data on four-photon transitions from the 2^3S state to the higher S and D states, reported in a series of experiments on the resonance five-photon ionization of metastable helium.[80] A multimode laser with spectrum width of the order of 3 cm^{-1} was employed.

TABLE II. Polarizability α_{0r} in linearly polarized field (experiment).

Atom	$0-r$	$\hbar\omega$, eV	$\sim\mathscr{E}$, V cm^{-1}	$\alpha_{0,r}$, at. units	Reference
He *	2^1S-6^1S	1.78	$5\cdot10^5$	5600	79
He *	2^3S-14^3S	1.17	10^6	~10 000	77
Cs	$6S-6F$	1.17	10^6	580	78

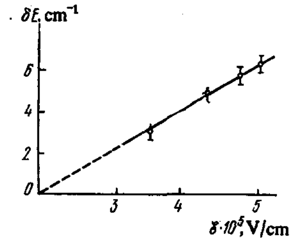


FIG. 23. 2^1S-6^1S transition energy in helium as a function of the intensity of red ruby-laser radiation.[79]

The experiment on three-photon ionization from the metastable singlet state of the helium atom by radiation from a multimode ruby laser ($\Delta\omega \approx 0.1$ cm^{-1}) in which intermediate photon resonance was produced[79] is the most difficult to interpret. As already noted, in this special case, the field dependence of resonance and nonresonance perturbations is the same ($\sim \mathscr{E}^2$), so that one cannot say *a priori* which effect will predominate. The change in the 2^1S-6^1S transition energy is proportional to the square of the field strength (Fig. 23), but the constant α is lower by an order of magnitude than predicted by perturbation-theory calculations.[35]

Only one experiment on the same $6S-6F$ transition in the cesium atom has been reported[81] in circularly polarized light. Resonance was observed for linearly and circularly polarized light with a fixed field strength of 10^6 V·cm^{-1} (Fig. 24). The observed change in transition energy was found to depend on the polarization. Experimental data for circularly polarized light (assuming that the perturbation is a quadratic function of the field) yield the following value for the dynamic polarizability: $\alpha(6S-6F) = (9.4 \pm 3.2) \times 10^2$ a.u. The $6F$ level splits into seven sublevels in a circularly polarized field (the spin-orbit interaction can be neglected in comparison with the interaction with the field), corresponding to the possible discrete values of the component of the total angular momentum along the direction of propagation of the wave ($m = 0, \pm 1, \pm 2, \pm 3$). The three-photon resonance transition ($\Delta m = \pm 1$) occurs from the ground state $6S$ ($m = 0$) to the $6F$ state ($m = \pm 3$) where the sign is determined by the sign (left or right) of the circular polarization of the field. Since the perturbation of the ground ($6S$) state is independent of the polarization of the field, the polarization dependence of the change in the $6S-6F$ transition energy is due to the difference between the polarizabilities of the $6F$ ($m = 0$) (linear field) and $6F$ ($m = \pm 3$) (circular field) sublevels.

We now return to Table I which summarizes all the quantitative results. Firstly, it is seen that the perturbation is proportional to the square of the field. Secondly, in the last two cases, where it is known *a priori* that the perturbation has a nonresonance character, the change in the transition energy is in satisfactory agreement with calculations.

d. Conclusions. We must now attempt to summarize all the data on perturbations of isolated atomic levels by a light field. The conclusions are as follows.

The first point that must be noted is that there is good qualitative and quantitative agreement between estimates and calculations, on the one hand, and practically all the available experimental data, on the other. It would, however, be an error to overestimate this optimistic situation because the second and undoubted point to note is that there is exceptionally little experimental material (only two or three examples in each case). It is very desirable to extend the experimental data, especially quantitative data on shifts, and data on broadening, which are totally absent. The third point concerns the importance of further studies of the effect of a nonmonochromatic perturbing field. Finally, we have so far totally ignored the limits of the perturbation amplitude, i.e., the field-strength range within which the perturbation of an isolated level can be described by the first (quadratic in the field) term of the expansion of the dynamic polarizability. This question is discussed in Chap. VI.

IV. ELLIPTICALLY POLARIZED FIELDS

12. Nonconservation of the *z*-component of orbital angular momentum. Kramers theorem for a variable field

When an atom is placed in an external field, the spherical symmetry of the atomic Hamiltonian is violated and the total angular momentum is not conserved. It is well known, for example, that, for a spin-orbit multiplet, an increasing magnetic field will break the LS coupling, and the Zeeman effect will go over to the Paschen-Back effect. This corresponds to the fact that the total angular momentum of an atom in a weak field can be approximately regarded as a good quantum number, and this approximation improves as the field becomes weaker. In a strong field, the total angular momentum of the atom is no longer conserved and the quasistationary states are superpositions of states with different angular momenta. The analogous transition from a weak constant electric field, for which the interaction energy is much smaller than the fine splitting energy, to a strong field, in which the opposite situation prevails, is seen in the Stark effect in the hydrogen atom as a transition from the quadratic to the linear effect.[82] However, in the case of constant fields—both electric and magnetic—the Hamiltonian exhibits a cylindrical symmetry associated with the direction of the external field. The component of the angular momentum along the axis of symmetry continues, therefore, to be conserved and the levels can be classified in terms of the magnetic quantum number for any field strength. This is well known in the theory of the Stark and Zeeman effects.[7,83]

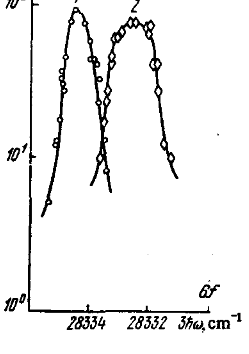


FIG. 24. Resonance increase in ion yield N_i in four-photon ionization of cesium during the appearance of an intermediate three-photon resonance between the $6S$ ground state and the $6F$ state in the field of linearly (1) and circularly (2) polarized radiation of fixed intensity. $6F$—transition frequency in zero field.

The essentially new point, specific for variable fields, is that it is possible to produce fields that do not have axial symmetry, namely, elliptically polarized fields. The quasistationary states of an atom in such fields are superpositions of states with different magnetic quantum numbers. Since, in the absence of the field, the magnetic sublevels are degenerate, it is, in principle, possible to observe the nonconservation of the z-component of angular momentum in fields as low as convenient. The only restrictions are those due to the capabilities of the experimental arrangement.

Let us begin by considering the nature of the splitting of levels in an elliptically polarized variable field. We recall that, in a constant electric field of arbitrary configuration, the well-known Kramers theorem tells us that all the quantum states of the system with an odd number of electrons are at least doubly degenerate.[1] When the variable field is linearly polarized, we still have doubly degenerate levels with respect to the z-component of the angular momentum except for the $M=0$ state which can occur in an atom with an even number of electrons whereas, in a circularly polarized field, the degeneracy is removed completely. We may generalize these results by saying that degeneracy is totally removed from an elliptically polarized field provided only the ellipse does not degenerate to a straight line because, when it does, the degree of circular polarization (a pseudoscalar) is not zero.[84] The Kramers theorem can thus be generalized to the case of a variable electromagnetic field as follows: "the quasistationary states of a quantum-mechanical system with an odd number of electrons are at least doubly degenerate in a variable electromagnetic field in the absence of circular polarization." This also follows immediately from the explicit form of the equations describing the behavior of atoms[85] and molecules[86] in elliptically polarized fields.

Despite the fact that a level with angular momentum J splits into $2J+1$ sublevels in both the elliptically polarized variable field and the constant magnetic field, there is an essential difference between these two fields insofar as the nature of the splitting is concerned. Thus, in a constant magnetic field, we have an equidistant separation between the sublevels which is determined by the g factor of the state[83] whereas, in the field due to a wave, the separation between the sublevels is not constant and the relative separation is a function of the degree of elliptic polarization. Unfortunately, the situation is similar to that prevailing in the case of a Zeeman multiplet in that the relative intensities of the components of a spontaneous emission line, or an absorption line for weak radiation, split by a strong wave field, cannot be predicted theoretically in a sufficiently general form. The calculations must be performed for each individual state of each atom, and the precision of such calculations is determined by the accuracy with which the corresponding dynamic polarizabilities can be calculated.

13. Quasistationary states

We now consider an atom in an elliptically polarized field. Let us take out from (7) the equations corresponding to a particular level with angular momentum J (the remaining quantum numbers of this level will, as before, be denoted by ν_0):

$$\begin{aligned} i\hbar\dot{a}_{\nu_0JM} &= \sum_{M'} V_{\nu_0JM,\,\nu_0JM'}(t)\,a_{\nu_0JM'} \\ &\quad + \mathop{S}_{\nu jm\neq\nu_0JM} V_{\nu_0JM,\,\nu jm}(t)\,e^{i\omega_{\nu_0J\nu j}t}a_{\nu jm}, \\ i\hbar\dot{a}_{\nu jm} &= \sum_{m} V_{\nu jm,\,\nu_0JM}(t)\,e^{i\omega_{\nu j,\,\nu_0J}t}a_{\nu_0JM} \\ &\quad + \mathop{S}_{\nu'j'm'} V_{\nu jm,\,\nu'j'm'}e^{i\omega_{\nu'j,\,\nu'j'}t}a_{\nu'j'm}, \end{aligned} \tag{22}$$

where ν, j, and m are the quantum numbers of the virtual states. It is clear from physical considerations that, if the atom is initially in the ν_0J state, which does not resonate at the frequencies ω and 2ω with other levels, all the remaining states other than ν_0J can be regarded as virtual and their contribution to the ν_0J state can be taken into account by perturbation theory. We therefore omit the second term on the right-hand side of the second equation in (22), and integrate the resulting equation with respect to time. The coefficients a_{ν_0JM} are slowly-varying functions of time [in comparison with $\exp(i\omega_{\nu_0J,\nu_j}\pm\omega)t$], and they can therefore be taken outside the integral. Substituting the results into the first equation in (22), and retaining only the slowly-varying functions of time in this equation, we obtain

$$\begin{aligned} \dot{a}_{\nu_0JM} = \frac{i}{4\hbar}\mathop{S}_{\nu jm,\,M'}\Bigg[&\frac{\langle\nu_0JM\,|\,\mathbf{d}\vec{\mathscr{E}}_0^*\,|\,\nu jm\rangle\langle\nu jm\,|\,\mathbf{d}\vec{\mathscr{E}}_0\,|\,\nu_0JM'\rangle}{\omega_{\nu j,\,\nu_0J}-\omega-i\lambda} \\ &+\frac{\langle\nu_0JM\,|\,\mathbf{d}\vec{\mathscr{E}}_0\,|\,\nu jm\rangle\langle\nu jm\,|\,\mathbf{d}\vec{\mathscr{E}}_0^*\,|\,\nu_0JM'\rangle}{\omega_{\nu j,\,\nu_0J}+\omega-i\lambda}\Bigg]a_{\nu_0JM'}. \end{aligned} \tag{23}$$

As can be seen, states with different components of the angular momentum of the atom are mixed in (22). If the usual polarizability (10) is given by the coherent part of the unshifted scattering tensor (22), which corresponds to the scattering of light without a change in the state of the atom ($M=M'$), the equations given by (22) will also contain the noncoherent part of the scattering tensor corresponding to the reorientation of the magnetic moment of the atom in space ($M\to M'\neq M$). This is the physical significance of the additional terms: scattering processes accompanied by a change in the direction of the magnetic moment of the atom participate in the formation of the quasistationary states of the atom in the field.

If we separate out the angular parts in (22), we can rewrite the equations in the matrix form as follows[85]

$$\dot{\hat{a}}=\frac{1}{4}EQ^{(J)}\hat{a}.\qquad \hat{a}=(a_{-J},\,\ldots,\,a_J),$$

$$Q^{(J)}_{MM}=u_J-v_JAM+w_JM^2,$$

$$Q^{(J)}_{M,\,M-2}=Q^{(J)}_{M-2,\,M}=-\frac{l}{2}w_J\sqrt{[J^2-(M-1)^2](J+M)(J+2-M)},$$

where $E=\mathscr{E}_0\mathscr{E}_0^*$ is the intensity of the radiation, the parameters u, w, v are defined in Sec. 8, and l and A are the degrees of linear and circular polarization of the wave, respectively; since the wave is assumed to be fully polarized, $l^2+A^2=1$. Right (left) circular polarization corresponds to $A=1$ (-1), $l=0$; linear polarization corresponds to $l=1$, $A=0$.

The solution of (23) can be written in terms of the eigenvectors of the matrix $\hat{Q}$

$$\hat{Q}\hat{f}^{(r)} = \alpha_r \hat{f}^{(r)}, \qquad r = 1, 2, \ldots, 2J+1, \tag{24}$$

in the following form:

$$\hat{a}(t) = \sum_{r=1}^{2J+1} C_r e^{\frac{1}{4} i\alpha_r Et} \hat{f}^{(r)}, \tag{25}$$

where C_r are constants determined by the initial conditions.

Substituting this in (23), we obtain the following expression for the atomic wave function:

$$\begin{gathered} \psi(t) = \sum_r C_r e^{i[E_{\nu_0 J} - (\alpha_r E/4)]} \Phi^{(r)}_{\nu_0 J}, \\ \Phi^{(r)}_{\nu_0 J} = \sum_M f^{(r)}_M |\nu_0 JM\rangle. \end{gathered} \tag{26}$$

The functions $\Phi^{(r)}_{\nu_0 J}$ are thus the wave functions for the required quasistationary states of the atom in the field, and the eigenvalues α_r of the matrix $\hat{Q}$ are the polarizabilities of these states. Thus, the determination of the spectrum of the atom in the field is reduced to the determination of the spectrum of the matrix $\hat{Q}$.

Let us consider some of the properties of this matrix. We note, *first of all*, that $\hat{Q}$ splits into a direct sum of two three-diagonal matrices, each of which mixes the states with $|\Delta M| = 2, 4, \ldots$. It is clear that this fact follows from the choice of the quantization axis which is taken to lie along the direction of propagation of the wave. The perturbation of the spectrum is determined by the virtual two-photon processes of the absorption-emission and emission-absorption type, where, after each such process, the quantum number M of the atom is either unchanged or changes by ± 2 since the wave contains only photons with angular momentum components of ± 1 along the axis. We note also that this property of the matrix can be associated with the remaining symmetry of the elliptically polarized field: rotation through 180° about the wave vector does not change the symmetry of the field. The effective Hamiltonian for the atom in the field, i.e., the matrix $\hat{Q}$, cannot therefore have nonzero matrix elements between states with $|\Delta M| = 1, 3, \ldots$ since rotation through 180° results in a change of sign of the matrix elements whereas the Hamiltonian should not change. The matrix $\hat{Q}$ is symmetric and, therefore, its eigenvectors are orthogonal: $\sum_M f^{(r)}_n f^{(r')}_M = S_{rr'}$. In certain special cases, therefore, the constants C_r can be found: if at the initial time the atom is in the state M_0, then $C_r = f^r_{M0}$. When the parameters u, v, w are real, the symmetry of the matrix $\hat{Q}$ ensures that it is self-adjoint, and the quasistationary states $\Phi^{(r)}$ are mutually orthogonal. On the other hand, we already know that these parameters are real when single-photon ionization of the atom from the states $\nu_0 J$ is impossible, i.e., when the quantity $i\lambda$ in the denominators in (23) can be omitted. If, on the other hand, the single-photon ionization channel is open, the parameters u, v, w become complex, the matrix Q ceases to be self-adjoint, and the quasistationary states of the atom in the field are no longer mutually orthogonal. This means that if, at the initial time t_1 the atom is in the state r_1, then for times $t_2 > t_1$ it can be found in a state $r_2 \neq r_1$.

In linearly or circularly polarized fields, both the bound state of the atom and the state in the continuum have been characterized by the quantum numbers M. A given quasistationary state with angular momentum component M could split after the absorption of a strong-field photon only into "its own" channel in which the states have angular momentum component M in the case of linear polarization and $M = \pm 1$ in the case right-handed (left-handed) polarization. The quasistationary states and states in the continuum were thus found to be in one-to-one correspondence. In an elliptically polarized field, where there are no selection rules for M, there is no one-to-one correspondence between the quasistationary states and the states in the continuum: different quasistationary states can decay into a given channel. If, on the other hand, two states r_1 and r_2 are not orthogonal to the same state in the continuum, they will not usually be orthogonal to one another. Nonorthogonal overlapping states have a number of interesting properties which can be seen in their decay and excitation, and in the resonance scattering by them.[87] In particular, the resonance scattering cross section can no longer be written as the sum of the resonance cross sections for each individual level. The resulting interference terms may even lead to zero cross section at a certain particular energy.

14. Results of calculations and experiments

For atomic levels with angular momenta $J = 0$, 1/2, there are *no nondiagonal* matrix elements of $\hat{Q}$ and, therefore, the eigenvalues of this matrix are equal to its diagonal elements. For levels with angular momenta 1 and 3/2, the determination of the spectrum reduces to the solution of simple quadratic equations. The corresponding formulas expressing the spectral and quasistationary states in terms of the parameters u, v, w are given in[85]. In the case of levels with large angular momenta, the spectrum and the quasistationary states can be found numerically. Figure 25 shows the behavior of the real parts of the polarizabilities of quasistationary sublevels of the $4f$ level of the potassium atom in the field of a neodymium-laser beam. The parameters u, v, w were calculated on the basis of the quantum defect model. The values $\theta = 0$, $\pi/2$ correspond to right-handed (left-handed) circular polarization. The component of the angular momentum in the direction of propagation of the wave is then conserved, and the corresponding values of M are given in the figure on the left and on the right. The value $\theta = \pi/4$ cor-

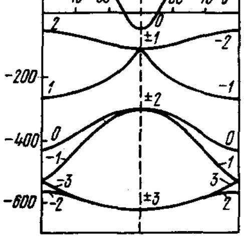


FIG. 25. Polarizability of the quasistationary sublevels of the $4f$ state of potassium in an elliptically polarized field. Linear and circular polarizations are expressed in terms of the angle θ as follows: $l = \sin\theta$, $A = \cos 2\theta$.

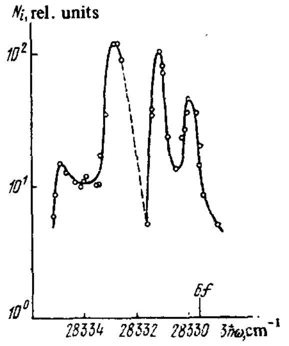


FIG. 26. Three-photon resonances with the sublevels of the 6*f* state of cesium perturbed by a polarized field.[88]

responds to linear polarization. In this case, the component of the angular momentum in the direction of polarization is conserved (broken line in the figure) and, moreover, all levels other than $M=0$ are doubly degenerate in the sign of M. One of the two submatrices into which the matrix $\hat{Q}$ divides mixes the three states $M=\pm 2$, 0, and the other the four states $M=\pm 1$, ± 3. In the case of linear polarization, the eigenvalues of different submatrices turn out to be equal.

The perturbation of an atomic spectrum in an elliptically polarized field was observed experimentally in[88] by the method of resonance multiphoton ionization. The four-photon ionization of the cesium atom by tunable neodymium–laser radiation was investigated. The degree of elliptical polarization was defined by the angle $\theta=32°$. Three-photon absorption by the cesium atom can be followed by resonances with the magnetic sublevels of the 6*f* level. Figure 26 shows the dispersion relation for the probability of four-photon ionization as a function of laser frequency. In general, the 6*f* state splits into $2J+1=7$ sublevels but, in accordance with general theory, only the four sublevels due to the mixing of the states $M=\pm 1$, ± 3 by the field are populated during the three-photon absorption. The $M=\pm 2$, 0 sublevels are mixed independently and are not populated in this process. This prediction is confirmed by the presence of the four resonances on the experimental dispersion curve.

If we know the electric field strength in the laser radiation field (in this particular experiment, it was 10^6 V·cm^{-1}), we can use the measured positions of the resonances to determine both the values of u, v, w for the 6*f* level and the polarization of the 6*f* ground state of the cesium atom. To do this, the eigenvalues of the matrix $\hat{Q}$ can be regarded as given, and the equations for these numbers are solved for u, v, and w which are present in the matrix elements. The observed positions of the resonances are also found to depend on the shift of the ground state of the atom, the polarization of which is thus also found to be mixed in the equations. The result of all this is that we have four equations (corresponding to the number of resonances) for the four unknown quantities. Table III shows the results of a numerical solution of these equations, and the theoretical predictions obtained by the quantum defect method. The agreement between theory and experiment may be regarded as satisfactory for all the quantities with the exception of w, for which the theoretical and experimental values differ by an order of magnitude. The results reported in[88] suggest that polarization experiments are promising because they can be used to obtain the maximum possible information on the matrix elements of the atoms, and to determine separately the polarizabilities of states between which the transition takes place.

V. PERTURBATION OF THE SPECTRUM OF A HYDROGEN-LIKE ATOM

15. Character of spectrum perturbation as a function of the field frequency and strength

The spectrum of the hydrogen atom in an alternating field has certain definite properties, the origin of which, i.e., degeneracy with respect to the orbital quantum number, is the same as that of the linear Stark effect in a constant field (in distinction to the quadratic effect in other atoms). However, the transition from the variable to the constant field is not trivial in this case.

Let us suppose that the interaction between the atom and the wave field is much greater than the spin-orbit splitting, so that the latter can be neglected. For the $n=2$ shell, the corresponding electric field amounts to about 10^5 V·cm^{-1} and falls rapidly with increasing n (approximately as n^{-3}). The field then mixes all the states belonging to the shell with principal quantum number n. The only states not mixed are those with different values of the magnetic quantum number, provided the field is neither linearly nor circularly polarized. Since the orbital angular momentum in the field is not conserved, the states of the hydrogen atom will, in general, have nonzero dipole moments, similarly to the states with definite parabolic quantum numbers in a constant field. The interaction of the atom with the field is thus characterized not only by the polarizability (as in the case of other atoms) but also by the dipole moment.

However, the part of the interaction Hamiltonian that corresponds to the constant dipole moment, i.e., $\vec{d}_0\cdot\mathscr{E}(t)$, varies rapidly in time with the field frequency ω, in contrast to the component of the Hamiltonian that is determined by the polarizability of the atom and is a quadratic function of the field strength, so that it contains terms that are slowly-varying functions of time. For this reason, the permanent dipole moment begins to have an effect only when the field frequency is not too high or, more specifically, when

$$|\mathrm{d}_0\vec{\mathscr{E}}| \gg \hbar\omega. \tag{27}$$

In the opposite case, when

$$|\mathrm{d}_0\vec{\mathscr{E}}| \ll \hbar\omega, \tag{28}$$

TABLE III. Polarizability α_{6S} of the ground state and values of u, v, and w characterizing the perturbation of the 6*f* state of cesium in an elliptically polarized field.

	α_{6S}, at. un.	u	v	w
Experiment[88]	1240	933	—540	199
Theory[85]	1500	674	—883	19

the permanent dipole moment can be neglected in comparison with the induced moment despite the fact that the latter is proportional to the external field strength which is always much smaller than the atomic field. Classically, this corresponds to the situation where the permanent dipole moment does not succeed in following the rapidly-varying external field, so that it provides no contribution to the energy after averaging with respect to time. A very strong field is necessary before dipole-moment corrections to the energy become important. Of course, these corrections become quadratic functions of the field as a result of this averaging.

In the optical band, where the field frequency is of the order of the frequencies of the Balmer lines, condition (27) can be satisfied only for field strengths of the order of the fields in the interior of atoms, and there is no point in considering quasistationary states of atoms in this case. The condition given by (27) can, in fact, be satisfied only in the infrared: $\hbar\omega \lesssim 0.1$ eV for $n=2$. As n increases, the upper frequency limit decreases as n^{-2}.

If, on the other hand, condition (27) is satisfied, the effect of the variable field on the atom leads not only to a level energy shift, but also to the appearance of admixtures in the wave functions which depend on time through the factors $\exp(\pm in\omega t)$, i.e., the so-called quasienergy harmonics.[89–91] The appearance of the harmonics is accompanied by the appearance of satellites in the emission and absorption spectra of the atom, which are separated from one another by the frequency ω. The number $N_{\max}$ of the harmonic with maximum weight in the wave function is then found to depend on the field strength. For very low frequencies, when (27) assumes the form

$$|\mathbf{d}_0\vec{\mathscr{E}}| \gg \hbar\omega, \tag{29}$$

the number $N_{\max}$ is a linear function of the field amplitude. It is clear that all these spectral manifestations of such states of the atom are as if the energy of the atomic state were a linear function of the field strength.

However, (29) is not a sufficient condition for the appearance of the linear effect. The further condition is that the corrections that are quadratic functions of the field should be small, i.e.,

$$|\mathbf{d}_0\vec{\mathscr{E}}| \gg \alpha\mathscr{E}^2; \tag{30}$$

where α is the dynamic polarizability of the atom at the particular frequency. We note parenthetically that condition (30) is analogous to the same condition for a constant magnetic field when it indicates that the quadratic Stark shift is small in comparison with the linear shift. However, in the case of a variable field, the fact that (30) is not satisfied, but (29) is, ensures that many ($\sim \alpha\mathscr{E}^2/\hbar\omega$) harmonics are present in the wave function with large weights and are separated from one another by $\hbar\omega$. The shift of the center of gravity of an atomic line is then a linear function of the field but, at the same time, the total width increases in proportion to the square of the field.[91]

Using the numerical values of the parameters for the hydrogen atom,[7,82] it can readily be shown that condition (30) is satisfied when $\mathscr{E} \ll 3\times10^8 n^{-4}$ V·cm^{-1}. It follows that the simultaneous application of (29) and (30), which will ensure an effect that is a linear function of the field, imposes relatively stringent restrictions on the field parameters. In the case of the CO_2 laser frequencies ($\hbar\omega \approx 0.1$ eV), the inequalities given by (29)–(30) are satisfied only for states in the $n=2$ shell for $\mathscr{E} \approx 5\times10^7$ V·cm^{-1}.

16. Properties of quasistationary states

Even when (28) is satisfied, so that the permanent dipole moment can be neglected, the difference between hydrogen and other atoms is still quite substantial. Thus, in the case of the hydrogen atom, we cannot use the isolated-level approximation because the field produces strong mixing of states with different orbital angular momenta, which are degenerate in the absence of the field. The consequence of the violation of the spherical symmetry of the original Hamiltonian is that certain superpositions of states with different orbital angular momenta are quasistationary. The situation is simplified somewhat when the field is either linearly or circularly polarized. Axial symmetry then remains and ensures that the z-component of the angular momentum is conserved. We shall confine our attention here to the case of linearly polarized fields, but this will, nevertheless, enable us to exhibit some of the features that are characteristic for hydrogen-like states.

A method completely analogous to that used in Sec. 13 can be employed to obtain the following set of differential equations for the coefficients a_l which define the admixture of the $|nlm\rangle$ state to the quasistationary wave function[89]:

$$\dot{a}_l = \frac{i}{4}\mathscr{E}_0^2 \sum_{l'} Q_{ll'} a_{l'},$$

$$Q_{ll'} = \frac{1}{\hbar} \mathop{S}_{NL} \frac{2\omega_{Nn}}{(\omega_{Nn} - l\lambda)^2 - \omega^2} \langle nlm | d_z | NLm \rangle \langle NLm | d_z | nl'm \rangle, \tag{31}$$

where $\mathscr{E}_0$ is the amplitude of the electric field of the wave which is parallel to the z axis. These equations contain terms that are not diagonal in l, l' and correspond to the contribution of scattering with a change in the orbital angular momentum of the atom to the formation of quasistationary states. The solution of (31) can be expressed in terms of the eigenvectors of the matrix Q through (23)–(25). Let us consider some of the properties of this matrix and the ensuing properties of the quasistationary states of the atom.

In accordance with the selection rules for electric dipole transitions, which are well known in spectroscopy, the operator d_z has nonzero matrix elements only between states with different parity. In the case of the hydrogen atom, the parity of a state is determined by the parity of the orbital angular momentum of the electron, so that the quantity L in (31) has the opposite parity to that of l and, therefore, l and l' have the same parity. The matrix $\hat{Q}$ therefore splits into the direct sum of two submatrices, each of which mixes states with only even or only odd orbital angular momenta. The state of the hydrogen atom in a variable field will, therefore, also be characterized by definite parity just as in the case of the free atom which has a fixed orbital angular momentum. We recall that the states of the free atom, characterized by parabolic quantum numbers, do not have definite parities. Of course, this property is a consequence of condition (28), which we have assumed. In particular, in the $n=2$ shell, the $2s$ and $2p$ states are not mixed by the variable field whereas, in the $n=3$ shell, the $3p$ state is not mixed with other states.

As already noted, in the case of mixing, the quasistationary states are superpositions of states with different orbital angular momenta. It follows that, if the lifetime for the radiative decay of a state with a given angular momentum is large, then when the strong field forces it into a state with a short lifetime, the atom will decay mainly from this state. Conversely, an atom occupying a state with a short lifetime, prior to the introduction of the field, will decay more slowly after the imposition of the field because of its transfer by the field to a relatively long-lived state. It is, however, clear from these considerations that the imposition of the field cannot lead to the formation of new metastable states of the atom. In particular, the width of the quasistationary state of the atom in the field cannot be less than the smallest of the widths of the free-atom states. Similarly, the lifetime of an atom for decay cannot be very sharply reduced: the width of the quasistationary state of an atom in a field cannot be greater than the largest of the free-atom widths.

Mixing does not change the individual mean width or the mean energy shift of levels of even or odd parity, as compared with values found without taking mixing into account. This follows from the invariance of the trace of the matrix under a diagonalizing transformation.

When the single-photon ionization channel for states in the shell n is open, the matrix $\hat{Q}$ is no longer self-adjoint and the quasistationary states of the hydrogen atom in the field become mutually nonorthogonal, just like the magnetic sublevels of any other atom in an elliptically polarized field.

Finally, we note an asymptotic property of the matrix $\hat{Q}$. When $\omega\to\infty$, the nondiagonal elements of the matrix tend to zero more rapidly than the diagonal elements. In the limit of high frequencies, therefore, the orbital angular momentum again becomes a good quantum number.

17. Numerical and experimental results

The evaluation of the matrix elements and the determination of the spectrum of eigenvalues of the matrix (31) were performed in[92] for ruby ($\hbar\omega = 14\,400$ cm^{-1}) and neodymium ($\hbar\omega = 9440$ cm^{-1}) laser radiation of linear and circular polarization and states belonging to the $n=1$–6 shells. The general result of these calculations is that the polarizabilities have the high-frequency asymptotic behavior predicted by (14) (this corresponds to the addition of the energy of a free electron in the wave field to the energy of the atomic level) almost immediately after the single-photon ionization channel for states in the given shell becomes open. This has a simple physical interpretation and indicates that the polarizability of states in the given shell is due to interaction with states in the nearest neighboring shells. It is clear, however, that the ionization potential of the given shell may be very different from the ground-state ionization potential, and the asymptotic behavior predicted by (14) is, strictly speaking, valid only when the energy of the field quantum exceeds the ground-state ionization potential.

The modification of the spectrum of the hydrogen atom by a variable field was investigated experimentally in[93]. The CO$_2$ laser ($\lambda = 10.6\ \mu$) was operated under continuous generation conditions, and the laser beam was focused on a target consisting of excited hydrogen atoms. The spontaneous emission of these atoms corresponding to the H_6 line ($n=6\to n=2$) was investigated. The laser produced 3–4 mW · cm^{-2} radiation power. The observed emission spectrum is shown in Fig. 27. The large peak on the right corresponds to the undisturbed H_6 line and is due to the emission of atoms outside the laser focus. The peak on the left is emitted from the focal region and, therefore, the corresponding wavelength is shifted.

Theoretical estimates of the shift of the H_6 line reported in[94,95] indicate a qualitative agreement with experiment.

Unfortunately, the experimental data available at present are clearly insufficient for a systematic comparison with theory. In particular, it would be very interesting to have observations of the field splitting of the hydrogen atom lines and of the appearance of forbidden lines which are predicted theoretically in[95].

VI. STRONG NONRESONANCE PERTURBATION OF THE ATOMIC SPECTRUM

18. Limits of validity of perturbation theory. Hyperpolarizability

Because of the large number of parameters that have to be included, there is no single criterion defining the limits of applicability of perturbation theory in the description of the perturbation of an atomic spectrum by a light field. In the case of single-photon ionization of a nondegenerate low-lying excited state, perturbation theory ceases to be valid for fields of the order of the atomic field; however, when this is so, the problem itself ceases to exist. In other cases, the number of absorbed quanta, or the quantum numbers of states, are the large parameters determining the range of values for the fields which are small in comparison with the atomic field but, at the same time, sufficiently large for perturbation theory to break down. The simplest example is provided by the two-level system in a low-

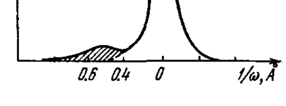


FIG. 27. The H_6 line of hydrogen in the absence of the perturbing field and in a field of 10^4 V · cm^{-1}. The shaded area is produced by the field.[93]

frequency field. It is shown in[96] that perturbation theory is violated for fields of the order of $\mathscr{E} \sim \sqrt{\omega \Delta E_{ij}}\mathscr{E}_{\text{at}}$, where ΔE_{ij} is the level separation.

The role of quantum numbers and numerical parameters can also be estimated for a low-frequency field. This can be done on the basis of well-known results for the hydrogen atom in a constant field, which can be used approximately for a low-frequency field. It is readily seen that perturbation theory is valid when $n^4 \mathscr{E} \ll 1$, where n is the principal quantum number of the particular state. It is clear that, even for small values of n, perturbation theory breaks down for field strengths much smaller than the atomic field.

The energy shift δE_0 of the ground state of the hydrogen atom in a constant field is given by the following approximate formula: $\delta E_0 \approx -\mathscr{E}^2 \sum_{n=0}^{\infty} C_n (10\mathscr{E})^{2n}$, where the coefficients C_n are of the order of unity (in particular, $C_0 \approx 2.25$, $C_1 \approx 0.55$, $C_2 \approx 0.49$, $C_3 \approx 0.79$, and $C_4 \approx 1.94$).[97] Thus, perturbation theory breaks down for fields that are lower by an order of magnitude than the atomic field. There are no symbolic parameters in this problem, but there is a numerical parameter which can be explained as follows. The expression for δE could have been obtained from the quasiclassical approximation, followed by an expansion in powers of $\mathscr{E}^2$. Of course, since the state which we are considering is the ground state, the well-known Bohr quantization rule is insufficient and must be augmented by first-order corrections with respect to the quasiclassical parameter.[98] The inclusion of these corrections results in a reasonably satisfactory expression. The quantization rule for δE contains the quantity πn and not n, so that the above criterion for the validity of perturbation theory is in fact $(\pi n)^4 \mathscr{E} \ll 1$, and this shows why the criterion takes the form $\mathscr{E} \ll (\pi)^{-4}\mathscr{E}_{\text{at}} \sim 10^{-2}\mathscr{E}_{\text{at}}$ even for $n \sim 1$.

The next term in the expansion of the dynamic polarizability of a given state in powers of the field strength can be used to describe moderate departures from lowest-order perturbation theory. This term is called the hyperpolarizability.

The difference between the hyperpolarizabilities of states 0 and r determines the correction to the change in the transition energy $\Delta E_{0r}(\mathscr{E})$ due to the inclusion of the next order following the lowest order of perturbation theory. As noted above, the introduction of hyperpolarizability is useful whenever the usual polarizability lies between the resonances in the frequency ω and becomes anomalously low. In the opposite case, we find that either the hyperpolarizability is small in comparison with polarizability, and need not be taken into account, or the two are of the same order, in which case the entire series in $\mathscr{E}$ must be taken into account.

The ground-state hyperpolarizability was calculated in[99] for hydrogen, the alkali elements, and the noble gases as a function of frequency and polarization of light. The results for the alkali atoms show that terms of the order of $\mathscr{E}^4$ are comparable with terms of the order of $\mathscr{E}^2$ even in fields of $10^6\ \text{V}\cdot\text{cm}^{-1}$. Since, in this case, terms of the order of $\mathscr{E}^2$ are not anomalously low (i.e., they do not lie in the gap between resonances), this range of values of the field does, in fact, define the limits of validity of perturbation theory. One would expect that, in such fields, all the terms in the expansion in $\mathscr{E}$ would be of the same order of magnitude. The reason why the limiting field is so low is, clearly, due to the large quantum numbers of the ground states of the alkali atoms and the numerical factor $1/\pi^4$, mentioned above.

Finally, we note that, when perturbation theory is substantially violated for a real atom, the very expansion of the solution into a series in $\mathscr{E}$ may be incorrect. This is so because perturbation theory series do not allow for tunneling transitions. From the mathematical point of view, tunneling means that the dynamic polarizability has an essential singularity at $\mathscr{E} = 0$. The tunneling transition channel predominates over the multiphoton transition channel (described by the perturbation theory series) whenever $E_{\text{col}} \lesssim E_r$. When this condition is satisfied before the above condition for the breakdown of perturbation theory in an increasing field, the introduction of higher-order corrections to the multiphoton transition probabilities will, in general, be quite pointless. If we consider only the transition frequency ω, we readily see that, as $\mathscr{E}$ increases, the condition $E_{\text{col}} \ll E_r$ is first violated and then the condition $\mathscr{E} \ll \sqrt{\omega/E_r}\,\mathscr{E}_{\text{at}}$ breaks down (in other words, tunneling begins to occur before higher-order corrections to the multiphoton transition probability become important). This is why, as a rule, there is little point in introducing these corrections. Nevertheless, this question must be investigated in each specific problem because the quantum numbers, the dipole matrix elements, and the numerical factors may turn out to be additional large parameters operating in either direction.

For a fixed value of the field strength, tunneling has a much smaller effect on the real part of hyperpolarizability than on the imaginary part, because the probability of the tunnel effect is exponentially small in $\mathscr{E}$ and the hyperpolarizability is proportional to $\mathscr{E}^4$.

19. Theoretical methods outside the framework of perturbation theory

The absence of sufficiently general criteria for the applicability of perturbation theory naturally draws attention to other methods of studying perturbations of an atomic spectrum by a light field. Among the various approaches to this problem, we shall select two, namely, the exact solution and the quasiclassical approximation. This choice is dictated by the importance and uniqueness of the results obtained by these methods. Other methods will be briefly mentioned in the Conclusion.

The main difficulty that arises in any attempt to obtain an exact general solution is connected with the fact that the spatial and temporal variables in the Schrödinger equation cannot be separated.

A very considerable simplification occurs when the external field is circularly polarized. The time-dependent Schrödinger equation can then be reduced to a time-independent form by a suitable transformation of the wave functions.[5] This approach has been used[100,101] to treat the behavior of a negative ion (in general, a particle in a short-range potential) in a circular field of arbitrary strength, including values comparable with the atomic field. Although the solution of this problem demands the use of a computer, it is incomparably simpler than the general case in which the temporal and spatial coordinates cannot be separated. The eigenvalues of the problem were obtained in[100,101] where it was found that the real part determined the energy shift in an arbitrary field, and the imaginary part determined the probability of nonresonance ionization. The results are valid for fields of arbitrary strength and frequency. In the case of weak low-frequency fields, the results obtained for the imaginary part of the dynamic polarizability (i.e., the imaginary part of the eigenvalues) become identical with the well-known results reported in[6] (or, more precisely, the results given in[102] where the case of circularly polarized fields was investigated). Even in the case of weak fields, the results reported in[100,101] are preferable to those in[102] because the level shift and the transition probabilities given in[100,101] are obtained as a result of a general solution of the problem, and the method used does not demand that the multiphoton condition $k = \langle \bar{I}/\hbar\omega + 1\rangle \gg 1$ should be satisfied. For example, for nondegenerate states in the limiting tunneling case ($\gamma = \omega\sqrt{E_0}/\mathscr{E} \gg 1$), the energy in the external field is, as expected,[101]

$$E(\mathscr{E}) = E_0 + C\mathscr{E}^2 + iC'e^{-C''/\mathscr{E}},$$

where $C = -1/32E_0^2$, $C' = -1/4\sqrt{2}E_0^{3/2}$, $C'' = (4\sqrt{2}/3)E_0^{3/2}$ are constants that depend on the unperturbed energy E_0. The real part of $E(\mathscr{E})$ thus determines the usual level shift, which is quadratic in the field, and the imaginary part determines the tunneling probability from the given state through the potential barrier. In the multiphoton case, when $\gamma \gg 1$, we have

$$E(\mathscr{E}) = E_0 + \mathscr{E}^2\left\{\frac{1}{2\omega^2} - \frac{2E_0^2}{3\omega^4}\left[\left(1+\frac{\omega}{E_0}\right)^{3/2} + \left(1-\frac{\omega}{E_0}\right)^{3/2} - 2\right]\right\}.$$

The imaginary part of this expression determines (for $\omega/E_0 > 1$) the probability of single-photon ionization from the particular level.

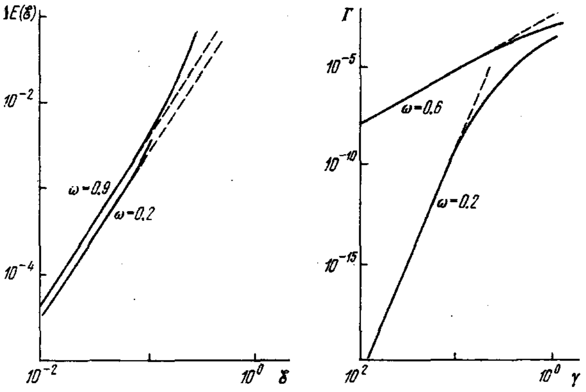
Figure 28 shows the results of exact calculations of the level shift and width. It is clear from these graphs where the departure from perturbation theory first sets in. The slower increase in the level width as the adiabatic parameter approaches unity can be qualitatively understood in terms of the results reported in[6]: for fixed I and ω, the increase in the probability for $\gamma \sim 1$ occurs more slowly than the power-type increase for $\gamma \gg 1$. The fact that the condition $k \gg 1$ is not used in these exact calculations enables us to compare them with experiments in which a transition from the excited state to the continuum occurs for $k \approx 1$.

The other method which takes us outside the framework of perturbation theory is the quasiclassical approximation. It can be applied to the present problem provided $\hbar\omega/(E_0 - E_r) \ll 1$, i.e., it is based on the multiphoton character of the transitions which we are considering. When the frequency of the external field is small in comparison with the atomic level separation, the external field is adiabatic and it is well known[1] that the adiabatic theory is mathematically equivalent to the quasiclassical approximation for the over-barrier reflection problem. All that is required is to replace the momentum by the energy, and the position coordinate by the time. To determine the perturbation of atomic states, we must first determine the adiabatic energies $E(t)$ of the levels as functions of t. When the atom is illuminated by a monochromatic field, the time t enters only through the electric field strength $\mathscr{E}\sin\omega t$. The main difficulty is therefore to determine the term energy in a static field of arbitrary amplitude. Perturbation theory is totally invalid in this case because the main interest is in the "turning points," i.e., fields for which these terms are found to cross. Perturbation of the term difference $\delta E_{0r}(\mathscr{E})$ by the field is determined by the root of the equation $E_0(\mathscr{E}^*) = E_r(\mathscr{E}^*)$ that is the closest to the t axis. In accordance with[103], we find that the perturbation of the levels 0 and r in the field $\mathscr{E}$ consists of the real part

$$\mathrm{Re}\,\delta E_{0r}(\mathscr{E}) = \frac{1}{4}\left(E_r''(0) - E_0''(0)\right)\mathscr{E}^2,$$

which is equal to half the quadratic static Stark effect (primes indicate derivatives of $E_{r,0}$ with respect to $\mathscr{E}$ for $\mathscr{E} = 0$), and the imaginary part Γ.

The general expression for the broadening Γ is different, depending on the magnitude of the adiabatic parameter. When $\gamma \gg 1$, ionization occurs by tunneling, and the probability of ionization is determined by the transmission of the barrier (apart from a pre-exponential factor): $\Gamma \sim \exp(-2\int_{r_1}^{r_2} |p|\, dr)$, where r_1 and r_2 are the classical turning points. When $\gamma \gg 1$, we have multiphoton ionization and $\Gamma \sim (\alpha\mathscr{E})^{2k}$, where k is the number of photons absorbed during the ionization process and the quantity α is determined only by the properties of the atomic spectrum. In this case, the expression for Γ is, in fact, the result of perturbation theory. The advantage of the semiclassical approach is that it yields a closed expression for α which does not contain sums



a b

FIG. 28. Exact calculations of $\Delta E + i\Gamma$ in a circularly polarized field.[100] $\mathscr{E}$, $\Delta E(\mathscr{E})$ are given in atomic units. Departures from perturbation theory (broken lines) set in for $\mathscr{E} \ll \mathscr{E}_{at}$ and $\gamma \gg 1$.

over the continuous spectrum. Within the framework of the quasiclassical approximation, departures from perturbation theory set in for fields $\mathscr{E}\sqrt{\Delta E/\omega}\gtrsim 1$, in which case $\gamma \gg 1$, i.e., transition to tunneling occurs before the first nonvanishing approximation of perturbation theory ceases to be valid. However, in real systems, the situation may be different for numerical reasons. In general, the quantity Γ is given by $\Gamma \sim (\alpha\mathscr{E})^{2k} e^{\beta k \mathscr{E}^2}$, where β, like α, is determined only by the properties of the system. For example, for the ground state of the hydrogen atom, the quantity β is of the order of 100,[103] so that perturbation theory breaks down very early on for numerical reasons. Tunneling can, therefore, predominate in the region where the departure from the first nonvanishing approximation takes place.

Let us consider in greater detail the criterion for the applicability of the adiabatic approximation $\omega \ll \Delta E_{ij}$. If we compare the perturbation of the term difference $\delta E_{r0}(\mathscr{E})$ (in the limiting case of weak fields, for simplicity) with the well-known expression given by the time-dependent perturbation theory, we find that, when the number of absorbed quanta is 1, 3, 5, ..., the ratio of transition probabilities differs from unity by 25, 11, and 5%, respectively.[103] The reason for this small difference is that the quasiclassical approximation is valid even for small quantum numbers for numerical reasons, as noted above.

Finally, we note one further widely discussed approach which takes us outside the framework of perturbation theory, namely, the so-called momentum translation approximation.[104] There has been much published work in recent years on calculations based on this method, including calculations concerned with bound electronic states. In this approach, the atomic wave function in an external field $\mathscr{E}\sin\omega t$ is written in the form

$$\psi = \psi_0 e^{-i(\mathscr{E}r/\omega)\cos\omega t},$$

where ψ_0 is the unperturbed wave function. This expression is exact when the electron is free. The basic assumption in this method is, therefore, that the above expression is a good approximation for a bound electron provided $\omega \ll \Delta E_r$. However, it is shown in[105–107] that this method is fundamentally incorrect. It is, in fact, incorrect both in the region in which perturbation theory is valid, where it yields an incorrect value for the numerical coefficients in the multiphoton transition probability, and in strong fields, where it results in an incorrect functional dependence on the field strength.

It may therefore be concluded that, in the case of strong perturbations of the atomic spectrum, the majority of the problems remain unsolved, as before.

VII. CONCLUSIONS

In concluding our review of perturbations of atomic spectra by light fields, we must consider two questions, namely, whether this is an opportune time for reviewing the subject and whether the review itself is complete enough.

It seems to us that there are two factors that are the most important in relation to the timing of this review. The most immediate impression that one gains by comparing the above material with the last review in this field[25] is that we now know much more than we did ten years ago when the last review was published. This is indicated both by the appearance of new techniques (photon spectroscopy and resonance ionization) and new fields of study (hydrogen atom, elliptical field, strong perturbation, and the effects of nonmonochromatic fields). It is also indicated by the Bibliography, which contains mainly papers published during the last ten years. However, the great lack of experimental data, which is in contrast to the volume of theoretical results, suggests that the answer to the second of the above two questions is negative. Our only justification is the hope that the present review will draw the attention of experimenters to the urgent necessity for an extensive program of measurements.

The question of the extent to which our review is complete is connected both with our frames of reference, defined in the Introduction (nonresonance perturbation of an isolated atom in a light field), and the depth and range of the review within this framework. The fact that we have been confined to this framework has meant that we have had to ignore many of the classical papers (for example, [108]), but, as a rule, there are good objective reasons for this.

The question of the depth and range of our discussion is more difficult. Insofar as experimental methods are concerned, we have not discussed the role of the statistical properties of multimode laser radiation, the duration of the perturbing field, or the saturation of individual transitions ($\int_0^\tau W dt \sim 1$). Insofar as the essence of the phenomena is concerned, we have not discussed the possibility of observing the degree of coherence of mixed atomic states through the relaxation of a number of excited states,[109] the effects associated with the re-emission of photons (resonance with the continuum), and studies of the phase coherence of atomic states. Finally, we have not treated at all the effect of the dynamic polarizability of the atomic core on transition probability. It is clear that the external field produces forced oscillations of the electron core; these oscillations in turn produce a time-dependent atomic field which, together with the external field, may eject a particular electron. It is possible that the role of the electron core in the variable field is small because the frequencies of the forced oscillations ($\omega \ll \Delta E_{\rm at}$) are small in comparison with the frequencies of natural oscillations of the core ($\omega_{\rm core} \sim Z\Delta E_{\rm at}$). This question will require careful investigation, especially since core polarization has an essential effect on the oscillator strength of nonresonance transitions in the discrete spectrum, at any rate in atoms with one external electron.[110]

We could continue listing many such questions. Most of them are of obvious interest but are characterized by the absence of experimental data. At the same time, it is the *physics* of the phenomena, i.e., the theoretically conceivable experimental material that is, in our view, of basic interest.

Fundamental problems in "pure" theory are, of course, of equal interest. Thus, for example, modern readers may be surprised by the absence of any mention of the method of quasienergy.[89,90] (It is well known that, according to the Floquet theorem, there are solutions of the Schrödinger equation for an atom in a periodic external field which can be expanded in terms of a set of stationary states with energies $E_i + k\hbar\omega$, where k is an integer.) The formalism of quasienergy states predicts the absorption, emission, and scattering spectra for light interacting with a quantum-mechanical system located in a strong field. There is no doubt that the method of quasienergy is very promising in those cases where the probability of finding a system in a state with nonzero harmonic ($K \neq 0$) is comparable with the probability of finding it in the zero harmonic ($K = 0$). Even the very early estimates[89] showed that, during the nonresonance perturbation of an isolated atomic level by a light field, the probabilities become of the same order of magnitude probably for field strengths comparable with the internal atomic field. The situation is quite different for infrared radiation[111] or for resonance perturbation.[2]

It is also important to note that our statement that the problem is incorrectly posed for $\mathscr{E} \sim \mathscr{E}_{\text{at}}$ is somewhat dogmatic. In actual fact, whereas this statement is obvious in the case of a constant field, the situation in which we are interested, i.e., tunneling through a rapidly-varying barrier, has not been adequately investigated. There are published papers dealing with an atom in a variable field of strength $\mathscr{E} \gtrsim \mathscr{E}_{\text{at}}$. The interaction of an atom with a field has been investigated[112,113] for $\mathscr{E} \gg \mathscr{E}_{\text{at}}$, $\mathscr{E}/\omega \gg \mathscr{E}_{\text{at}}/\Delta E_{ij}$, where ΔE_{ij} is a typical atomic level separation and ω is the frequency of the external field. When the external field $\mathscr{E}\sin\omega t$ is present, the electron executes forced oscillations about the nucleus with frequency ω. When the field is removed, the electron may turn out to be in one of the bound states, and it is required to determine the probability of this process. When the above conditions are satisfied, the atomic potential can be taken into account by perturbation theory. Since the wave function in the zero-order approximation which corresponds to a free electron in a periodic field has a well-known simple analytic form,[32] the inclusion of the atomic potential in the lowest-order perturbation theory is not a complicated problem. It has been found that the transition probability between states ij is, in this case, given by $W_{ij} = C_{ij}\omega^2/\mathscr{E} \ll 1$. It turns out that there is a finite probability for any external-field frequency ω, i.e., the external field is a nonresonance field. There is clear interest in further work in this field.

In quoting the various original papers, reviews, and monographs, we have not been concerned with questions of scientific priority, and it has not been our intention to list all the references known to us. Our aim was to extract the minimum amount of information necessary to deepen our knowledge of the subject under review.

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Gamma-resonance solid-state spectroscopy under high-frequency excitation conditions

E. F. Makarov and A. V. Mitin

Institute of Chemical Physics, USSR Academy of Sciences,
and Kazan' Physico-technical Institute, USSR Academy of Sciences

Usp. Fiz. Nauk **120**, 55–84 (September 1976)

Experimental and theoretical studies of high-frequency excitations in solids by γ-resonance spectroscopy are reviewed. Both the resonance-type and non-resonance-type alterations in Mössbauer spectra that are produced by high-frequency ac fields are elucidated. A considerable part of the review is devoted to problems of modulation of γ radiation by ultrasonic vibrations. Various mechanisms of exciting sound by a radiofrequency field are studied, in particular, magnetostriction in ferromagnets. A new effect found by γ-resonance spectroscopy is discussed: collapse of the hyperfine structure upon fast remagnetization of a ferromagnet. A number of new nonlinear resonance phenomena are discussed that amount to combining the Mössbauer effect with the methods of radiospectroscopy (NMR, EPR, etc.). The possibility is discussed of applying these phenomena for studying the properties of solids.

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CONTENTS

1. INTRODUCTION

Application of the Mössbauer effect in various fields of solid-state physics and chemistry has facilitated the rapid growth of γ-resonance spectroscopy (GRS). It has become most fruitful to use GRS to study the hyperfine interaction of Mössbauer nuclei in crystals. Owing to the high energy resolution of GRS, these investigations have become an effective way of studying solids. Methods have become widespread of studying the structures and properties of solids by applying static external perturbations, as well as of studying the relaxation processes that arise from the motion of nuclei, spins, or fast chemical reactions.

It has recently become possible to control dynamic