

## CONTINUOUS SPECTRA OF ATOMIC GASES AND PLASMA

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Usp. Fiz. Nauk 91, 193-246 (February, 1967)

## INTRODUCTION

THE most complete exposition of the theoretical and experimental results on continuous spectra is contained in the article by Finkelnburg and Peters<sup>[1]</sup>. We confine ourselves in this review to a narrower group of problems, connected with the continuous spectra of a low-temperature plasma and atomic gases; we shall consider only multi-electron atomic systems\*; principal attention will be paid to the near infrared, the visible, and the ultraviolet bands. These questions are of interest in themselves and essentially new physical results were obtained for them since the publication of<sup>[1]</sup>. Let us list the radiative processes that will be considered in the present review.

The electron can be in a bound state (in which case its energy is negative and assumes a discrete set of values) or free (positive energy, which can vary continuously). Continuous absorption and emission spectra are the result of the transitions of the electron from the bound state to the free one and vice-versa (bound-free and free-bound transitions) and as a result of free-free transitions. Bound electrons can be situated in an atom, a positive ion, or a negative ion; a free electron can travel through the field of an atom or an ion. Accordingly, a distinction is made between two types of free-bound transitions in the case of the emission of radiation: in the field of the ion-recombination radiation ( $A^+ + e \rightarrow A + h\nu$ ,  $A^{++} + e \rightarrow A^+ + h\nu$ , etc.), and in the field of the atom-radiative adhesion ( $A + e \rightarrow A^- + h\nu$ ), and between two types of free-free transitions: bremsstrahlung in the field of the ion or the atom ( $A + e(v_1) \rightarrow A + e(v_2) + h\nu$ , where  $(mv_1^2/2) - (mv_2^2/2) = h\nu$ , etc.). In the case of absorption, a distinction is made between bound-free transition in the field of the ion (photoionization of atoms and ions:  $A + h\nu + A^+ + e$ ,  $A^+ + h\nu \rightarrow A^{++} + e$ , etc.) and in the field of the atom (photodetachment from negative ions:  $A^- + h\nu \rightarrow A + e$ ) and free-free transitions in the field of the atom and ion.

We shall also discuss the formation of the continuous spectrum as a result of coalescence and the

vanishing of discrete levels at the boundaries of the series. We shall not consider absorption and emission of light by electrons situated in a field produced to an equal degree by several particles.

As a rule, the resultant continuous spectra are superpositions of several continua that are due to individual transitions. The number of such superimposed continua may turn out to be quite appreciable, in which connection the determination, and particularly the analysis, of the resultant spectrum may turn out to be a far from trivial problem.

In Secs. I and III we describe methods of calculating the probabilities of individual transitions. We present a summary of theoretical and experimental results and discuss possible causes of the existing discrepancies. In Secs. II and IV we consider the spectra resulting from the superposition of a considerable number of continua. The measurement results are compared with the predictions of the theory. In Sec. V we discuss the possibility of using the described results for the analysis of spectra of non-equilibrium gases and plasma; we consider also multiphoton processes.

## I. PHOTOIONIZATION CROSS SECTIONS

## 1.1 Calculation of Cross Sections

The theory of photoionization is considered in detail in<sup>[2,7-10]</sup>. We present some general results. In the single-electron approximation, the expression for the cross section is of the form

$$\sigma = C_1 E \mathfrak{S} \sum_{l'=l+1}^{\infty} Q_{ll'} \left| \int_0^{\infty} R_{nl}(r) R_{kl'}(r) r dr \right|^2, \quad (1.1)$$

where  $(1/r)R_{nl}(r)$  and  $(1/r)R_{kl'}(r)$  are the radial wave functions of the active electron in the initial and final states,  $n$  is the principal quantum number,  $l$  and  $l'$  are the orbital quantum numbers; the energy of the absorbed photon is  $E = |E_{nl}| + k^2$ , and  $E_{nl}$  and  $k^2$  are the electron energies in the initial and final states, expressed in Rydberg units; the factor  $\mathfrak{S}$  takes into account the role of the passive electrons<sup>[8,9]</sup>, and usually  $\mathfrak{S} \cong 1$ ;  $Q_{ll'}$  is a numerical coefficient that depends on the spectroscopic type of the initial and final states<sup>[8-10,72,91]</sup>;  $C_1 = 4\pi\alpha_0^2 a/3 = 8.56 \times 10^{-19}$ ; the wave function of the free electron is so normalized that when  $r \rightarrow \infty$  we get

\*The spectra of single-electron atomic systems are covered quite fully in the literature<sup>[1-5]</sup>. On the other hand, molecular spectra could serve as a subject of a separate review (photoionization of simple molecules was considered in<sup>[6]</sup> and of complex ones in<sup>[7]</sup>).

$$R_{kl}(r) \rightarrow k^{-1/2} \sin \left[ kr - \frac{\pi}{2} l' + \frac{Z}{k} \ln 2kr \right. \\ \left. + \arg \Gamma \left( l' + 1 - i \frac{Z}{k} \right) + \delta_{l'}(k) \right], \quad (1.2)$$

$Z$  is the charge of the residual ion, and the phase  $\delta_{l'}(k)$  is due to the non-Coulomb nature of the potential at small  $r$ .

Expression (1.1) is derived by using the matrix element of the radius vector. The cross section can also be expressed in terms of the matrix elements of the velocity (momentum) and acceleration<sup>[2,11]</sup>. The main contribution to different matrix elements is made by different distances from the nucleus. The wave functions are known only approximately, and their use may, depending on the methods used to derive them, turn out to be more reliable far from the nucleus, or near it, or in an intermediate region. This determines the most advantageous choice of the form of the matrix element. On the other hand, agreement between results obtained for different types of matrix elements is an indirect criterion of the quality of the approximate wave function as a whole.

A widely used method for finding the wave functions is that of the self-consistent field (the Hartree-Fock method), which is described in detail in a number of references (see, for example, <sup>[10,12]</sup>). Let us consider in greater detail the sources of errors in the photoionization cross sections calculated with the aid of self-consistent wave functions.

The Hartree-Fock method is approximate even in its most general formulation. In addition, owing to the large computational difficulties, additional approximations and simplifications are used in determining the wave functions for concrete atomic systems. These approximations affect both fundamental problems (for example, allowance for exchange), and methods of solving the equations. Consequently, the calculations of the wave functions (and accordingly of the photoionization cross sections) for concrete atomic systems are periodically under revision. It is essential that the calculated cross sections are quite sensitive to refinements in the wave functions.

The self-consistent field method makes it possible, generally speaking, to obtain only the wave functions of bound states. It has not yet been consistently extended to include a system with a free electron, owing to the fundamental difficulties that arise when attempts are made to take polarization into account, i.e., to allow for the influence of the free electron on the ion. Therefore the wave function of the free state is calculated for an electron situated in the static self-consistent field of the ion (exchange effects can be taken into account). Sometimes this field is assumed for simplicity to be the same as the self-consistent field acting on the bound optical electron prior to ionization.

In order to make some allowance for the influence of the free electron on the ion, a polarization potential  $V(r) \rightarrow \alpha/2r^4$  as  $r \rightarrow \infty$ , where  $\alpha$  is the polarizability of

the residual ion, is added to the static self-consistent field of the ion in some calculations. Such an allowance for the polarization is not consistent and requires, in particular, knowledge of the value of  $\alpha$ . In addition, the polarization potential cannot be introduced uniquely, owing to the arbitrariness in the definition of the potential at small distances.\* Nonetheless, such an allowance for the polarization makes it possible to improve the results greatly in certain cases.

The sensitivity of the cross section to the choice of the wave function (both free and bound) is due to the fact that the wave functions obtained with the aid of the Hartree-Fock method are the best approximate wave functions for the determination of the energies of the bound states, but are not the best approximate wave functions for the calculation of the cross sections. Therefore a refinement of the wave functions which results in small corrections to the values of the energy can greatly change the photoionization cross sections. Thus, the cross sections obtained with the aid of the available approximate functions may be subject to appreciable error.

It would be more consistent to use a variational principle formulated directly for the matrix element. However, work in this direction has only recently begun<sup>[14-17]</sup> and has not yet been applied to a concrete calculation of photoionization. A variational principle for the matrix element will apparently lead to equations that are more complicated than the Hartree-Fock equations.

Returning to the Hartree-Fock method, we emphasize that an improvement of this method cannot be the end purpose of the construction of a theory of many-electron atoms. The point is that the self-consistent field approximation is best for single-electron approximations. Therefore, the obtained wave functions take very little account of the correlation between particles. In order to improve the results, a dependence of the wave function of the system on the interatomic distance is postulated in the theory of two-electron systems; the calculations are carried out without separating the variables<sup>[2]</sup>. This procedure is hardly realistic for atoms with a large number of electrons. Another way is to consider the self-consistent field in the many-configuration approximation.

A promising approach may be the use of modern methods of many-particle theory. In these methods, the self-consistent functions are used as a zeroth approximation<sup>[19]</sup>. The first attempt in this direction, as applied to photoionization, were made in<sup>[20-22]</sup>. In<sup>[21]</sup> the theory was developed far enough to permit calculation of the cross sections. It was not the purpose of the authors of<sup>[21]</sup> to obtain reliable cross sections, since this entails both fundamental and computational difficulties. However, using alkali-earth atoms as an example, they

\*The introduction of the polarization potential in the Hartree-Fock method is considered, for example, in<sup>[13]</sup>.

Table I. Calculation of photoionization cross sections

Atom*	Method	Atom*	Method	Atom*	Method
He	D 27, 28	Li	B 37	Hg	D 22
B	B 29 **		A 38	Li <sup>+</sup>	D 27
C	B 29, 30		D 39	N <sup>+</sup>	B 43
N	B 29-31	Na	A 34	Mg <sup>+</sup>	C 44
O	B 31-33		B 40	Si <sup>+</sup>	C 44
F	B 29		B 41	K <sup>+</sup>	C 45
Ne	A 34	K	B, C 42	Ca <sup>+</sup>	A 46, 47 (See also 40)
	B 35	Be	D 21	Cu <sup>+</sup>	A 34
Ar	A 34, 36	Mg	D 21	Ag <sup>+</sup>	A 34
	D 22	Ca	D 21	N <sup>+4</sup>	A 48
Kr	A 34	Sr	D 21	O <sup>+5</sup>	A 48
Xe	A 36				

A and B – calculations with self-consistent wave functions (A – wave function of the free state is calculated in the same field as for the bound state, B – in the field of the unperturbed residual ion), C – a polarization potential is added to the self-consistent potential in calculating the wave function, D – an attempt is made to take account of correlation in some manner.

\*The calculation for Li was made for the first six excited states, [38], for Mg<sup>+</sup> – for the states 3<sup>2</sup>S, 2<sup>2</sup>P, and 2<sup>2</sup>D, for Si<sup>+</sup> – 4<sup>2</sup>S, 2<sup>2</sup>P, 3<sup>2</sup>P, and 3<sup>2</sup>D, for Ca<sup>+</sup> – 4<sup>2</sup>S, 2<sup>2</sup>P, and 3<sup>2</sup>D, for N<sup>+4</sup> and O<sup>+5</sup> – 2, 3, 5<sup>2</sup>S, 2<sup>2</sup>P; only the photoionization cross sections of the ground states were calculated for the remaining atoms and ions.

\*\*In [29], the calculated cross sections were approximated by means of simple analytic formulas: In addition to the atoms B, C, N, O, F, and Ne, they present cross sections for the following iso-electronic ions: C<sup>+</sup>, N<sup>+</sup>, O<sup>+</sup>, F<sup>+</sup>, Ne<sup>+</sup>, Na<sup>+</sup>, N<sup>+2</sup>, O<sup>+2</sup>, F<sup>+2</sup>, Ne<sup>+2</sup>, Na<sup>+2</sup>, Mg<sup>+2</sup>, O<sup>+3</sup>, F<sup>+3</sup>, Ne<sup>+3</sup>, Na<sup>+3</sup>, Mg<sup>+3</sup>, Al<sup>+3</sup>, F<sup>+4</sup>, Ne<sup>+4</sup>, Na<sup>+4</sup>, Mg<sup>+4</sup>, Al<sup>+4</sup>, and Si<sup>+4</sup>.

have shown that allowance for the correlation can radically change the calculated cross section. It is essential that similar refinements have a rather slight effect on the eigenvalues of the energy, thus emphasizing once more the specific feature of the Hartree-Fock functions. It is therefore possible that when a more rigorous theory is constructed it will be more convenient to choose as the zeroth approximation the single-electron functions which are best in the sense of the matrix element.

Attention should be called also to the choice of the type of coupling. In determining the wave functions, the type of coupling (usually LS) is postulated prior to the solution. But deviations from LS coupling may be significant even for light elements, especially for excited and free states; this will be discussed in the next section.

Summarizing, we can state that the approach towards a consistent theoretical determination of the photoionization cross sections is already being indicated at the present. However, by virtue of the arising difficulties, the now available methods (principally the Hartree-Fock method) contain such assumptions and approximations (not only simplifying the calculations but having also a fundamental character), that the methods themselves lose their consistent theoretical character, and the results obtained by them cannot claim to be the most accurate. In the earlier literature (see [8]), when only the Hartree-Fock functions were used, it was assumed that the result can be regarded as reliable, provided the "quenching" is weak, i.e., the calculated radial interval in (1.1) is not too small. There are no grounds for being certain of this. Therefore the discrepancies between the calculations and the measurements, for example those in the case of Ca [23], are not at all surprising.

In view of all these factors, an extensive literature has been devoted to the calculation of the wave functions and energies of bound states\* and to the improvement of the Hartree-Fock method and other variational methods, and the number of papers in which the photoionization cross sections are calculated is much smaller. In Table I we summarize the calculated photoionization cross sections, including the most recent published data on each atom or ion (references to earlier calculations can be found in the papers referred to in the table, and also in the reviews [7-9, 25, 26]).

### 1.2 Semiempirical Methods of Calculating the Cross Sections

The fundamental and computational difficulties connected with consistent theoretical methods of cross-section calculation make it necessary to resort to semiempirical methods. The most widespread method is one using asymptotic wave functions determined from semi-empirical considerations. For the calculation of the photoionization cross sections of complex atoms, such a method was proposed by Burgess and Seaton [49, 26], who used the quantum-defect method [50] to determine the wave function of an electron in a Coulomb field.

The quantum-defect method deals with a two-body system consisting of an external (optical) electron and a residual positive ion. Account is taken of the fact that the radial part of the wave function of the optical electron satisfies a Schrödinger equation with a Coulomb potential in the entire region of space outside the core.

\*We call attention to [24], where a many-configuration approximation, which takes into account an admixture of free states, is developed for the calculation of the energy of the bound states.

For the bound state we have

$$\left[ \frac{d^2}{dr^2} + E_{nl} + \frac{2Z}{r} - \frac{l(l+1)}{r^2} \right] R_{nl}(r) = 0. \quad (1.3)$$

Using the experimentally obtained value of  $E_{nl}$ , we can solve (1.3) and thus obtain the wave function outside the core<sup>[51]</sup>.  $R_{nl}(r)$  is expressed in terms of the Whittaker function

$$R_{nl}(r) = [n_l^* \Gamma(n_l^* + l + 1) \Gamma(n_l^* - l)]^{-1/2} W_{n_l^*, l + \frac{1}{2}} \left( \frac{2Zr}{n_l^*} \right), \quad (1.4)$$

where the effective quantum number is determined by the relation

$$E_{nl} = -Z/n_l^*. \quad (1.5)$$

The determination of the radial function of the free state is a more complicated matter. The point is that the general solution of (1.3) is written in the form of a linear combination of two linearly independent solutions. In the case of bound states, one of the solutions diverges when  $r \rightarrow \infty$ , and must therefore be discarded. But in the case of free states, a linear combination of both solutions must be taken into account, since both are finite at infinity. Therefore to determine the radial function it is necessary to obtain additionally the coefficient in this linear combination or, what is the same, to find the phase shift  $\delta_l(k^2)$ . A method for determining  $\delta_l(k^2)$  was proposed by Seaton<sup>[52, 50]</sup>, and consists in the following: Let us consider a sequence of terms that differ only in the principal quantum number. We define for each term the quantum defect  $\mu_{nl}^*$

$$\mu_{nl} = n - n_l^*. \quad (1.6)$$

The points  $\mu_{nl}$  lie on some continuous curve corresponding to the function  $\mu_l(E_{nl})$ , which depends little on the energy  $E_{nl}$ . If we extrapolate the thus-obtained function  $\mu_l(E_{nl})$  to positive values of the energy  $k^2$ , we get the function  $\mu_l(k^2)$ . It turns out that the sought function  $\delta_l(k^2)$  and the obtained function  $\mu_l(k^2)$  are connected by the simple relation

$$\delta_l(k^2) = \pi \mu_l(k^2). \quad (1.7)$$

This result of Seaton's is very important and is widely used, but the proof proposed for it in<sup>[50]</sup> cannot be regarded as fully satisfactory<sup>[53]</sup>. It turns out, however, that if we use the theory of elastic scattering for small energies (the effective-radius theory<sup>[54-57]</sup>) for an attractive Coulomb field, and then go over from positive energies (continuous spectrum) to negative ones (discrete spectrum), then we obtain a connection between the eigenvalues of the energy and the phases of the wave functions in the continuous spectrum, i.e., between  $\mu_l(E_{nl})$  and  $\delta_l(k^2)$ . This connection justifies the extrapolation of  $\mu_l(E_{nl})$ . Thus, the quantum-defect method is a consequence of the theory of elastic scat-

\* $\mu_{nl}$  can depend also on other quantum numbers besides  $n$  and  $l$ ; for the sake of brevity we shall not indicate this dependence here and below.

tering by a force center. This question was considered in<sup>[53]</sup> and somewhat later in<sup>[58]</sup>.

Using Coulomb radial function, Burgess and Seaton<sup>[49, 26]</sup> obtained approximate formulas and compiled tables which make it possible to calculate the photoionization cross sections of atoms and ions of different elements in arbitrary states. In<sup>[26]</sup>, the photoionization cross section  $\sigma_{nl}(\nu)$  is given in the form

$$\sigma_{nl}(\nu) = C_l E E_{nl}^{-2} \sum_{l'=\pm 1} Q_{ll'} g_{ll'}^2(n_l^*, \epsilon),$$

$$g_{ll'}(n_l^*, \epsilon) = G_{ll'}(n_l^*) \zeta^{-1/2}(n_l^*) (\epsilon_{nl}/\epsilon)^{\gamma_{ll'}(n_l^*)} \cos \pi [n_l^* + \mu_{l'}(k^2)$$

$$+ \chi_{ll'}(n_l^*, \epsilon)], \quad (1.8)$$

where  $\epsilon_{nl} = n_l^{*-2}$  and  $\epsilon = Z^{-2}E$ ;  $n_l^*$  is the effective quantum number of the initial state;  $\mu_{l'}(k^2)$  is the extrapolated quantum defect of the levels  $l'$ . The quantities  $G_{ll'}(n_l^*)$ ,  $\gamma_{ll'}(n_l^*)$ , and  $\chi_{ll'}(n_l^*, \epsilon)$  are obtained with the aid of the tables given in<sup>[26]</sup>.

Let us consider the factor  $\zeta_l(n_l^*)$ , which was not considered in<sup>[49, 51]</sup>. Its appearance is due to the correction of the normalization of the functions (1.4), as given in<sup>[50]</sup>. The normalization factor in (1.4) was chosen in analogy with hydrogen ( $n$  was replaced by  $n_l^*$ ), since it was impossible to calculate directly the normalization integral. To get around this difficulty, a special procedure<sup>[50]</sup> was used in<sup>[50]</sup>, whereby the integral over the volume was replaced by an integral over an infinitely remote surface. The latter integral can already be calculated using asymptotic values. It has turned out that it is necessary to introduce in (1.4) a factor  $\zeta_l^{-1/2}(n_l^*)$  given by

$$\zeta_l(n_l^*) = 1 + \partial \mu_l / \partial n_l^* = 1 + 2n_l^{*-3} \frac{\partial}{\partial E_{nl}} \mu_l(E_{nl}). \quad (1.9)$$

For the upper excited states  $\zeta_l(n_l^*) \cong 1$ , and for the ground and several other states, at which  $n_l^*$  is small, account must be taken of  $\zeta_l(n_l^*)$ . If  $n_l^*$  is close to  $l$ , a simple formula can be obtained for  $\zeta_l(n_l^*)$ . If  $n_l^* \rightarrow l$ , then  $\mu_l(E_{nl}) \rightarrow n - l$ , since  $\mu_l(E_{nl})$  is a slowly varying function, we get in the linear approximation  $\mu_l(E_{nl}) = n - l - b_l (l^{-2} - n_l^{*-2})$ . Taking (1.5) into account we get  $b_l = n_l^{*2} l^2 (n_l^* + l)^{-1}$ . Substituting the obtained value in (1.9) we get

$$\zeta_l(n_l^*) = 1 - 2n_l^{*-3} b_l = (n_l^* - l) (n_l^* + 2l) n_l^{*-1} (n_l^* + 1)^{-1}. \quad (1.10)$$

When  $l = 1$ , Eq. (1.10) coincides with a formula presented without proof in<sup>[50]</sup>.

In calculating the photoionization cross section for values of  $n_l^*$  close to  $l$ , account must be taken of the fact that  $\zeta_l^{-1/2}(n_l^*) \rightarrow \infty$ , and the quantity  $G_{ll'}(n_l^*)$ , which contains the factor  $\Gamma^{-1/2}(n_l^* - l)$ , vanishes. It is therefore necessary to use the finite quantities  $\zeta_l(n_l^*) (n_l^* - l)^{-1}$  and  $G_{ll'}(n_l^*) (n_l^* - l)^{-1/2}$ ; the latter is also tabulated in<sup>[26]</sup>.

The Burgess-Seaton formulas are universal and are

widely used in the literature. The cross sections of different states of C<sup>[60,61]\*</sup>, N<sup>[60,62,63]</sup>, O<sup>[62,63]</sup>, of the alkali metals<sup>[64,65]</sup>, Mg<sup>[62]</sup>, Xe<sup>[66]</sup>, and others were calculated on their basis; they served as the basis of obtaining approximate expressions which will be discussed in Sec. II below. The Burgess-Seaton procedure is also used to calculate photo-ionization from the internal shells (the K shell of Li, Be, and other light metals<sup>[67-69]</sup>, of the L-shell of Ne<sup>[70]</sup>); in these cases, it is necessary to obtain the quantum defects in a suitable genealogical scheme for each transition<sup>[67,60]</sup>. Let us consider the limits of applicability and the possible causes of errors, as well as ways of improving the Burgess-Seaton formulas.

The radial functions and the method of extrapolating  $\delta_l(k^2)$  were determined within the framework of a simple Coulomb model. Therefore, many effects (which will be discussed later) were not taken into consideration. At the same time, the extrapolation involved experimental values of the quantum defects, i.e., "effectively" all the subtle moments were taken into account in some manner or another. It must also be stated that certain errors become manifest in similar fashion in both the free and bound wave functions, and are thus partially offset in the radial integral. Nevertheless, in some cases formula (1.8) gives erroneous results.

The Coulomb interaction is only the strongest but not the sole long-range potential. There exist beside it the polarization potential proportional to  $r^{-4}$ , the spin-orbit interaction proportional to  $r^{-3}$ , etc. In addition to forces having a central character, an interaction without spherical symmetry may also be significant, for example one due to multipole (primarily quadrupole) moments of the charge system of the residual ion. This interaction, as is well known, causes splitting of terms belonging to one configuration. The solution of the problem with due allowance for additional potentials entails considerable mathematical difficulties. An attempt to refine the effective-radius theory with allowance for additional long-range potentials (particularly  $r^{-4}$ ) has been made in<sup>[71]</sup>.

Polarization becomes manifest not only in the fact that a long-range potential proportional to  $r^{-4}$  appears, but also in the deformation of the short-range potential, which becomes different from the potential of the unperturbed core. This deformation can depend on the energy. Thus, the dependence of the potential on the energy (nonadiabaticity) must be taken into account in the effective-radius theory.

Elimination of the foregoing errors makes the computable cross section more accurate and the extrapolation of  $\delta_l(k^2)$  more reliable (see also p. 77), but it can hardly lead to a radical change in the results. Of greater importance may be the errors that are connected

directly with the many-electron character of the problem and are due to the type of coupling and the superposition of the configurations.

Following<sup>[26]</sup>, formula (1.8) is customarily used as applied to the LS coupling. Substituting the corresponding value of  $Q_{ll'}$ , this formula can also be used for other types of coupling (the values of  $Q_{ll'}$  for different transitions are considered in<sup>[72]</sup>). The relative magnitudes of the photoionization cross sections for the terms of one multiplet are then altered. It is essential, however, that the type of coupling changes not only from atom to atom, but also from state to state in one and the same atom. In particular, on approaching the limit of the series, the coupling becomes intermediate, close to jj<sup>[73,74]</sup>, and this should remain in force also for the adjacent spectrum of the free states. The selection rules depend on the type of coupling that describes the upper states. At the same time, the quantum defects of different series belonging to the same value of  $l$  differ among themselves for many atoms, both in absolute magnitude and in energy dependence. Therefore a refinement of the type of coupling can lead, compared with the LS approximation, to a change in the quantum defects of the free state, which must be taken into account for the calculation of photoionization from a given level. Finally, the type of coupling between the free electron and the ion can change with electron energy, and this leads to an energy dependence of the "effective"  $Q_{ll'}$ . An investigation of all these questions has been made difficult so far by the limited available information on the splitting of the highly-excited terms. The determination of the type of coupling from the splitting of the terms is considered in<sup>[73,75,76]</sup>.

The quantum-defect method and the Burgess-Seaton formula are valid within the framework of the one-electron approximation. In atomic spectra, however, a large role is frequently played by the configuration interaction. It is shown in<sup>[77]</sup>, using the bound-bound transitions  $s^2p^n - s^2p^{n-1}s$  as an example, how great an influence can be exerted on the transition probability by the perturbing action of another configuration ( $sp^{n+1}$ ) in the upper state. The matrix element becomes the algebraic sum of terms corresponding to single-electron transitions  $s^2p^n - s^2p^{n-1}s$  and  $s^2p^n - sp^{n+1}$ . It is possible to have both an increase in the resultant transition probability and a unique "quenching"—mutual cancellation of the terms, even though each of the single-electron matrix elements may be large. To consider these effects one must have semiempirical methods of determining the configuration admixtures (including allowance for autoionization in the continuous spectrum) and a refinement of the calculations of  $n_l^*$  and  $\mu_l$  in the case of perturbations.

To take into account the configuration interaction, it is necessary to develop a multichannel quantum-defect method<sup>[78]</sup>. The general theory is developed in<sup>[78-81]</sup>. It is used in<sup>[82,83]</sup> to consider the determination of the scattering phases of an electron in the field of He<sup>+</sup> and

\*Formula (18) was not used in that reference, in the matrix elements were calculated directly, with wave functions determined by the quantum-defect method.

other single-electron ions, and in<sup>[84]</sup> to determine the perturbation of the series and autoionization for calcium. Related problems of the theory are touched upon in<sup>[85]</sup>.

The last error that should be mentioned is due to the unknown contribution of small values of  $r$  to the radial integral. It is apparently of little importance. This error can appear most noticeably either for states with low energy or for states, transitions from which correspond to near-zero radial integrals ("quenching"—mutual cancellation of the contributions of different intervals in  $r$  to the radial integral). In these cases, however, the errors discussed above may turn out to be more important. The presence of "quenching" can be deduced from the small value of the cosine in (1.8)<sup>[26]</sup>.

Summarizing, it can be stated that the main criterion for a reliable application of the semiempirical procedure is the presence of the required experimental data on the term scheme, and also the possibility of extracting from it all the information (not only concerning the radial asymptotic values, but also concerning the type of coupling and the configuration admixtures). Even formal application of expression (1.8) is presently sometimes impossible because of lack of data or the irregular behavior of the quantum defects.

It is of interest to compare the results for the cross sections and oscillator strengths obtained by the quantum-defect method and in the self-consistent-field approximation. Experience with such comparisons<sup>[26,86]</sup> indicates that the agreement is satisfactory; in the worst case the possible difference is less than by a factor of two. We note that the greater part of these comparisons pertains to the ground states, i.e., to the case when the contribution of small  $r$  is the largest.

A comparison made over a wide range of energies is given in<sup>[43]</sup>: Figure 1 shows the results for  $N^+$ . The quantum-defect method and the Hartree-Fock approximation give nearly equal results within the limits  $k^2 < Z^2$ , which agrees with the theoretical estimates<sup>[26]</sup>.\* At high energies, the Born approximation gives good results; it is shown in<sup>[43]</sup> that it is necessary in this case to use the acceleration matrix element, since it is equivalent to the velocity matrix element calculated using the next order of the Born approximation.

### 1.3 Autoionization

In the case of complex atoms, a discrete spectrum, corresponding to excitation of two (and more) electrons

\*In many cases the condition  $k^2 < Z^2$  overestimates the region of applicability of (1.8). Formula (1.8) has been obtained by approximately calculating the radial integrals, and therefore does not give a perfectly accurate result even for hydrogen. For frequencies far from threshold, the discrepancy with the exact hydrogen results may turn out to be appreciable<sup>[63,87-89]</sup>. Formula (1.8) is corrected for large  $k^2$  in<sup>[63,89]</sup>. However, the application of the obtained expressions to complex atoms cannot be reliable, since it requires a relatively remote extrapolation of the quantum defects.

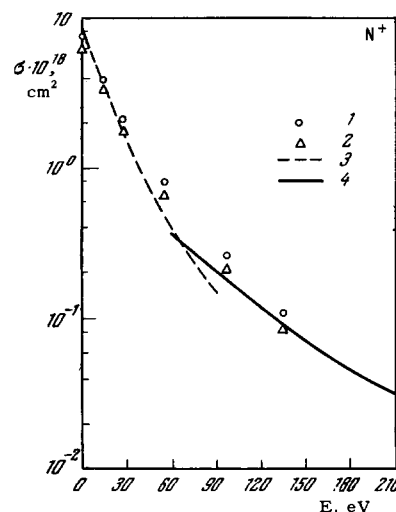


FIG. 1. Calculated cross sections for the photoionization of  $N^+$  ( $2p^2 \ ^3P \rightarrow 2pk^2d, \ ^3P \ ^3D$ )<sup>[43]</sup> as functions of the energy of the detached electron. 1 and 2 – Hartree-Fock (using the matrix elements of the radius  $-1$  and of the velocity  $-2$ ), 3 – Burgess-Seaton, 4 – Born approximation (with acceleration matrix element).

or to the excitation of the internal shell, is superimposed on the continuous spectrum. The states of the discrete spectrum can interact with the continuum, and this determines the possibility of nonradiative transition of the optical electron to the continuous spectrum (autoionization) or the inverse (dielectronic recombination).

If we neglect the interaction, then the spectrum of absorption from some lower state is a simple superposition of the spectral line on the continuum. Taking the interaction into account, we obtain an isolated absorption spectrum, separation of which into lines and continuum is arbitrary: A region of relatively sharp variation of the absorption coefficient can be regarded as a line, and the region of slow variation as the continuum. As a result of autoionization, the line turns out to be strongly broadened. It must be emphasized that, as will be shown later, the perturbation can also noticeably influence the photoionization cross section in the regions adjacent to the line.

In calculation methods considered in Secs. 1.1 and 1.2, autoionization was not taken into account. At the same time, for many atoms it is impossible to obtain satisfactory theoretical photo-ionization cross sections without taking autoionization into account. At the present time the theory of autoionization is not yet at the stage where methods are available for calculating the absorption spectra. However, in recent years much progress was made, in which an important role was played by the paper of Fano<sup>[90]</sup>, who explained the main laws of autoionization spectra. According to<sup>[90]</sup>, the ratio of the photoionization  $\sigma$ , obtained with account of the configuration interaction, to the cross section  $\sigma_0$  calculated in the zeroth approximation can be approximately described by the simple function

$$\sigma/\sigma_0 = (q+x)^2(1+x^2)^{-1}, \quad (1.11)$$

where  $x = 2(h\nu - E_1)\Gamma^{-1}$ , with  $E_1$  the position of the perturbing level with allowance for the configuration interaction and  $\Gamma$  the width of the perturbing level, due to the autoionization ( $\Gamma = 2\pi|V|^2$ , where  $V$  is the matrix element of the configuration interaction). The parameter  $q = M_1/\pi VM$ , where  $M_1$  and  $M$  are the matrix elements characterizing the probability of the direct transitions from the lower state to the discrete level and to the continuum. It must be emphasized that the probabilities of transitions to the discrete level and to the continuum, when taken separately, have no physical meaning in the presence of interaction. The probability of photoionization is determined not by the sum of these probabilities, but by the square of the sum of the corresponding matrix elements, taken with the coefficient  $-(\pi V^*)^{-1} \tan \Delta$  (where  $\Delta = \tan^{-1}[\Gamma/2(E_1 - h\nu)]$ ), which depends on the energy and takes on positive and negative values. We note that  $\Delta$  is the additional increment in the phase of the asymptotic value of the wave function (1.2). In the perturbation region, the phase changes smoothly by an amount equal to  $\pi$ . Far from the perturbing level,  $\Delta \rightarrow 0$  on one side and  $\Delta \rightarrow \pi$  on the other.\*

Figure 2 shows a family of curves corresponding to (1.11). The cross section consists of a peak (corresponding to the line), which goes over rapidly on one side to a zero minimum. Depending on the sign of  $q$ , the minimum can be on the left or on the right of the peak. In the side opposite to the minimum, the function drops off to unity slowly and monotonically. A similar slow character is possessed by the increase in the function to unity after passing through the minimum. Thus, the region in which the perturbation appears is much

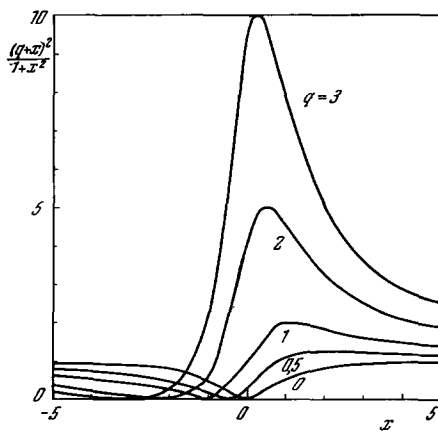


FIG. 2. The Beutler-Fano profile. The curves for  $q < 0$  symmetrical to the curve  $q > 0$  about the line  $x = 0$ .

\*Fano considered also the perturbation of a sequence of discrete terms by a superimposed level and obtained the empirically known result [91] that the quantum defect of this sequence changes by unity in the perturbation region. The expression for the change in the quantum defect is similar to the expression for  $\Delta/\pi$ .

larger than the spectral section occupied by the "line." Thus, when  $q = 3$  the half-width of the line is  $\Delta x_\Gamma = 2.5$ , whereas the distance between the points corresponding to  $\sigma/\sigma_0 = 2$  and  $\sigma/\sigma_0 = 1/2$  is  $\Delta x_\sigma \approx 17$ . With increasing  $q$ , this situation becomes aggravated, since  $\Delta x_\Gamma \rightarrow 2$  and  $\Delta x_\sigma \rightarrow 5.8q$ .

The characteristic asymmetrical profile shown in Fig. 2 is frequently called the Beutler-Fano profile; it is interesting that at values of  $q$  close to zero, the perturbing level becomes manifest only as an absorption minimum. With respect to the value of the cross section at the minimum, it must be stated that photoionization from a given state usually corresponds to transitions to several continua. Autoionization perturbs only part of these continua. Therefore the real minimum of the photoionization cross section is equal not to zero but to the cross section  $\sigma_1$  corresponding to the unperturbed transitions.

The problem is solved in [90] by directly considering the superposition of bound and free configurations, and the method of solution is adapted from the discrete spectrum. The Beutler-Fano profile was subsequently obtained in [92, 93]. In [92] the atom is regarded as a set of classical oscillators (which is valid in the near-threshold region), and account is taken of the fact that the oscillators are coupled to one another (the equivalent of configuration interaction). In [93], the theory of resonant nuclear reactions is used for the analysis of atomic phenomena. We note that the presence of maximum and of a deep minimum can be obtained also from formula (1.8) by introducing the phase  $\Delta$  and taking into account its energy dependence.

Fano [90] considers essentially the very simple case, when one discrete level is superimposed on one continuum. The results are generalized also to include the case of one discrete level superimposed on several continua, and of several discrete levels superimposed on a single continuum. These questions are considered in greater detail in [94], which contains also a preliminary discussion of the Rydberg series of perturbing levels. The corresponding continuum begins at the limit of such a series, and therefore the photoionization cross section experiences here a sharp change. In [94] is proposed an approximate expression for the jump  $\Delta\sigma$  of the cross section at the limit of the autoionization series

$$\Delta\sigma = \sigma - (\sigma_0 + \sigma_1) = \frac{\pi}{2} \bar{\Gamma} (\bar{q}^2 - 1) \sigma_0, \quad (1.12)$$

where  $\sigma$  is the cross section after the jump,  $\sigma_0 + \sigma_1$  is the cross section ahead of the jump (in the intervals between the autoionization lines), the distinction between  $\sigma_0$  and  $\sigma_1$  was explained before, and  $\bar{\Gamma}$  and  $\bar{q}$  are the mean values for the series,  $\bar{\Gamma}$  being the reduced width (the ratio of the width of the level to the distance between the neighboring levels). If  $\bar{q}^2 < 1$ , then  $\Delta\sigma < 0$ . Indeed, at small values of  $q$  the perturbing level appears only as a "window" in the absorption spectrum (Fig. 2). It is therefore obvious that at the limit of a series of

such "windows" the absorption coefficient should become smaller than between the "windows."

The papers discussed above explain the main qualitative laws governing the influence of autoionization on the photoionization spectra. However, a reliable calculation of the values of  $q$ ,  $\Gamma$ , the level shift, and the oscillator strengths is still difficult. Some estimates are given in<sup>[94]</sup>. The angle parts of the matrix elements of the configuration interaction are calculated in<sup>[95,96]</sup>. The calculation of the width of the autoionization levels is the subject of<sup>[97]</sup>.

The most complete calculations were made for He. In<sup>[98-100,28]</sup>, in the strong-coupling approximation, are considered the scattering of an electron by an He<sup>+</sup> ion, and the position, half-width, and probability of autoionization of the discrete levels of an He atom in the continuum are determined; the mixing of the discrete states with the continuum is taken into account from the very outset in the calculation of the wave functions. The He levels are calculated also in<sup>[93]</sup>; a classification of these levels is given in<sup>[101,102]</sup>. As mentioned in Sec. 1.2, calculations were also made for He with the aid of the multichannel quantum defect method<sup>[82,83]</sup>, the de-

velopment of which will prove quite useful for the analysis of autoionization<sup>[78-85]</sup>.

Estimates were made of the autoionization probabilities of He, Li, Be<sup>+</sup><sup>[103-105]</sup>, and He<sup>[106]</sup>, the energy levels of Li<sup>[107]</sup>, the oscillator strength of NeIs<sup>2p<sup>6</sup> - sp<sup>6</sup>mp<sup>[108]</sup></sup> and AlIs<sup>2p<sup>2</sup>P - sp<sup>2</sup>2S<sup>[109]</sup></sup>; the wave functions in these papers were calculated without account of the interaction between the discrete levels and the continuum. A paper paying principal attention to predissociation—a phenomenon which is related to autoionization—may be of interest.<sup>[110]</sup>

#### 1.4 Measurement Results; Comparison with Calculations

The work done on the experimental determination of the photoionization cross sections is summarized in Table II for the ground states and in Table III for the excited states. Table II gives only the latest measurements for each given element; where possible, work performed in parallel in different laboratories is cited. References to earlier work, in which certain cross sections were measured for the first time (He, Ne, Ar, Kr,

Table II. Measurements of the photoionization cross sections of ground states

Atom, threshold (Å)	Method	Measurement range (Å)	Atom, threshold (Å)	Method	Measurement range (Å)
H, 911	I 113	851	Xe, 1022	II 140	923—280
He, 504	I 114	504—200	I 118	I 118	250—23
	II 115	504—280	I 141	I 141	275—80
	IV 116	504	I 135	I 135	1010—600
	IV 117	504—230	III 142	III 142	1022—860
	I 118	250—44	I 136	I 136	44—7
	I 119	250—100	I 143	I 143	2300—1450
	I 120	240—180	I 144	I 144	2300—1150
	II 121	504—300	I 145	I 145	280—80
Ne, 575	II 122	500—300	I 146	I 146	2412—1000
	I 123	575—80	I 147	I 147	1100—600
	III 124	575—280	I 148	I 148	2856—1150
	II 125	575—300	III 7	III 7	2972—2400
	II 126	575—200	I 7	I 7	3185—2000
Ar, 787	III 127 *	790—400	Mg, 1622	I 149	1622—1450
	II 128	500—400	Ca, 2028	I 150	2028—1080
	I 129	787—600	Sr, 2177	I 151	2177
	I 130	250—23		I 152	2177
	II 131	790—280		V 153	appr. 2177
	I 132	790—170	Ba, 2379	I 154 **	appr. 2379
	I 133	790—400		I 155 **	appr. 2379
	III 124	575—280		I 156	2379—1700
	I 134	300—100	Mg, 1622	I 149	1622—1450
	II 122	780—300	Cd, 1379	I 157	1379—1150
	I 135	790—600	Hg, 1188	I 159	1188
	I 136	44—7	Al, 2060	I 158	2060—1700
Kr, 886	I 137	886—600		V 153	appr. 2060
	II 128	560—400	Ga, 2070	V 153	appr. 2070
	I 138	845—230	In, 2220	I 159	2220—1700
	I 118	250—23		V 153	appr. 2220
	I 135	886—600	Tl, 2030	I 160 ***	2030—1450
Xe, 1022	I 139	900—450	N, 852	III 162	725—400
	I 129	1022—600	O, 910	I 163	910—500
	I 138	923—230	Xe <sup>+</sup> , 585	I 164	700—450

I — absorption method, II — double ion chamber method, III — ion current method, IV — electron impact method, V — extrapolation estimate.

Investigations devoted to autoionization lines only are not mentioned in the table; reference to these investigations is made in p. 63.

\*Relative measurements.  
 \*\*Qualitative study of the spectrum.  
 \*\*\*Results of [160] as refined in [161].



Table III. Measurements of the photoionization cross sections of excited states

Atom	State*	Reference**	$\lambda, \mu$	Agreement with (1.8)***	Agreement with $\sigma(\nu_{mn})$ ****
C	(3s) (3p 1P, 3D) (3p 3P, 3S) 2p 3 3D <sup>0</sup>	201	0.28—0.58	satisf. 201 poor 201	
N	3p 2S, 4P, 4S, 2D 3p 4D, 2P	202	0.43—0.63	satisf. 62 poor 62	
O	3p 3P, 5P	203	0.43—0.63	satisf. 62,153	satisf. 153
Mg	3p 3P	204	0.24—0.27	poor 62,153	poor 153
Cl *****	(4s) (4p)	205	0.28—0.54	poor	
Ar	(4s)	206	0.25—0.35	satisf. 153	satisf. 153
Ca	4p 3P, 3d 3D	207	0.285—0.355	poor 153	satisf. 153
Cs	6p 2P, 5d 2D	65, 208	0.4—0.6	satisf. 65	satisf. 65

\*The multiplet structure was not resolved in the measurements for Cl and Ar and in some measurements for C.  
\*\*All the results were obtained from measurements of the intensity of the recombination spectra.  
\*\*\*Apart from the use of formula (1.8), no other calculations were made so far for these cross sections.  
\*\*\*\*For N and Cl, there are not enough known oscillator strengths to construct the  $\sigma(\nu_{mn})$  by means of formula (1.13).  
\*\*\*\*\*The experiments in [205] are subject to certain doubts (see p. 81), and calculation by means of formulas (1.8) is difficult because of the incompleteness of the term scheme and a strong "quenching."

alkali metals, Ca) can be found in the cited papers, and also in the reviews<sup>[7,9,111,112]</sup>. Before discussing the results let us dwell briefly in the basic measurement methods.

Absorption method<sup>[7,9]</sup>. Measurements are made of the intensities  $I_0$  and  $I_1$  of a nearly monochromatic beam of light incident on a layer of thickness  $l$  of the investigated gas, and passing through this layer. The spectral absorption coefficient is

$$k_\nu = l^{-1} \ln(I_0/I_1).$$

The photoionization cross section can be readily obtained if one knows, besides  $k_\nu$ , the concentration of the absorbing particles. It is seen that relative measurements of  $I_0$  and  $I_1$  are sufficient. The method is the most widely used, and its various modifications are also described in the papers cited in Table II.

Ion-current method<sup>[7,9]</sup>. One measures the absolute values of  $I_0$  and of the current  $i$  of the ions produced as a result of the photoionization

$$k_\nu = -l^{-1} \ln[1 - (ih\nu/eI_0)].$$

The required kind of ion can be separated with a mass spectrometer.

Double ion chamber method<sup>[165]</sup>. One measures the ion currents  $i_1$  and  $i_2$  produced in two neighboring layers of gas of equal thickness  $d$ :

$$k_\nu = d^{-1} \ln(i_1/i_2).$$

The measurements are made simultaneously, making it possible to get rid of the errors due to fluctuations of  $I_0$ .

Observation of recombination spectra<sup>[166]</sup>. One measures the spectral brightness of the continuum and also the temperature and composition of the gas (the

gas must be heated, so as to produce sufficient ionization). These data can be used to calculate the recombination cross section, and consequently the photoionization cross section. Usually several recombination continua become superimposed (other processes also contribute; see Sec. IV), and therefore the value of the individual cross section can be determined directly only in the vicinity of the jump.

Electron impact method<sup>[167,168]</sup>. One investigates inelastic collisions at high electron energies and at small scattering angles. Under these conditions, the Bethe-Born approximation, which makes it possible to determine the corresponding cross section of the optical transition from the cross section of the inelastic collisions, is valid. The final results are obtained by slightly extrapolating the experimental data to the limiting conditions, when the Bethe-Born formula becomes exact.

In addition to direct measurements of the cross section, an extrapolation estimate<sup>[153]</sup> is possible if the oscillator strengths of the lines of the corresponding spectral series are known from experiment. We shall arbitrarily define as the photoexcitation cross section the quantity  $\sigma_m(\nu_{mn})$ , which is proportional to the "smeared" density of the oscillator strengths:

$$\begin{aligned} \sigma_m(\nu_{mn}) &= C_2 df/d\varepsilon \cong C_2 f_{mn}/\Delta\varepsilon_n \\ &\cong C_2 n_n^{*3} f_{mn}/2; \quad C_2 = 8.07 \cdot 10^{-18} \text{ cm}^2. \end{aligned} \quad (1.13)$$

where  $\nu_{mn}$  and  $f_{mn}$  are the frequencies and oscillator strengths of the lines corresponding to transitions from the  $m$ -th state to different  $n$ -th states,  $\Delta\varepsilon_n = 2n_n^{*3}$  is the "smearing" interval of the individual oscillator strengths, and  $n_n^*$  is the effective quantum number of

the  $n$ -th level. The cross section  $\sigma_m(\nu)$  for the photoionization of an atom from the  $m$ -th state can be obtained in the near-threshold region, by extrapolating with respect to frequency the quantity  $\sigma_m(\nu_{mn})$ . But if the photoionization cross section is known, then the relative correspondence between the measured cross section and the density of the experimental oscillator strengths is an additional criterion for the reliability of the experimental results<sup>[26,153]</sup> (the theoretical quantities can be verified in the same manner<sup>[169]</sup>).

### Ground States

**Hydrogen.** In view of the experimental difficulties, the first measurements were made only recently<sup>[113]</sup>. There is good agreement between the results and the predictions of the theory.

**Inert gases.** The results are most complete. Agreement exists between the cross sections obtained in different laboratories. Different series of measurements yielded reliable data in a wide wavelength interval (with the exception of the structure of certain autoionization lines). Recent results (especially for Ar) differ from those obtained earlier and given, for example, in<sup>[7,9]</sup>.

The ratio of the photoionization cross sections corresponding to the formation of ions in the states  $^2P_{1/2}$  and  $^2P_{3/2}$  was measured in<sup>[170]</sup> for Ar, Kr, and Xe in a wide range of wavelengths.

Different calculations are compared with the experimental data in Fig. 3, with Ne as an example. Calculation with self-consistent wave functions by method B<sup>[35]</sup> (see Table I) turned out to be more successful than that by method A<sup>[34]</sup>. Agreement with the measured oscillator strength of the resonance line is obtained. The Burgess-Seaton Coulomb approximation also gives satisfactory results, although the excellent agreement between the data of<sup>[70]</sup> and the experimental points beyond the L-threshold is apparently accidental.

Both detailed calculations and the quantum-defect method agree well with the measurement for He<sup>[26,43]</sup>. Calculations<sup>[34]</sup> for Ar and Kr deviate from the experimental data both in the frequency dependence and in absolute magnitude (by a factor 2–3). Calculation by means of (1.8) apparently gives better accuracy in the near-threshold region.

**Alkali metals.** In view of the chemical activity of the vapors, a special measurement procedure was developed<sup>[9]</sup>. The cross sections are small and have a deep minimum directly beyond the threshold. To obtain reliable results in the region of the minimum, it is necessary to separate more precisely the contributions of the atomic and molecular components of the vapors to the absorption coefficient<sup>[146]</sup>.

The agreement between different calculations and the experimental data is shown in Fig. 4 with Na as an example. We see that none of the calculations gives good agreement in the entire measurement range. The

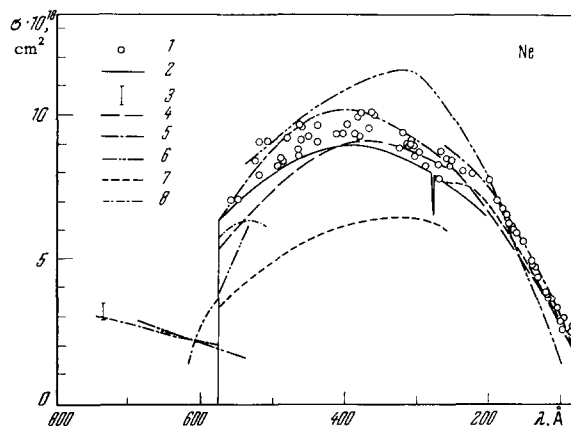


FIG. 3. Photoionization cross section of neon. Experimental data: 1 – <sup>[23]</sup>, 2 – <sup>[26]</sup>, 3 – photoexcitation cross section point corresponding to the oscillator strength of the resonance line <sup>[71]</sup>. Calculation results: 4,5 – <sup>[35]</sup> (calculations made with velocity matrix element –4 and radius matrix element –5). 6 – <sup>[34]</sup> (the photoexcitations are also shown separately for the  $p \rightarrow s$  and  $p \rightarrow d$  transitions; we note that the wavelengths of the lines and the ionization potentials in <sup>[34]</sup> were calculated, and the results differed somewhat from the true ones, and therefore the corresponding curves in the figure are shifted), 7 – <sup>[70]</sup> – calculation by the quantum-defect method (details unknown), 8 – formula (1.8) (the photoexcitation cross sections are also indicated separately for  $p \rightarrow s$  and  $p \rightarrow d$  transitions).

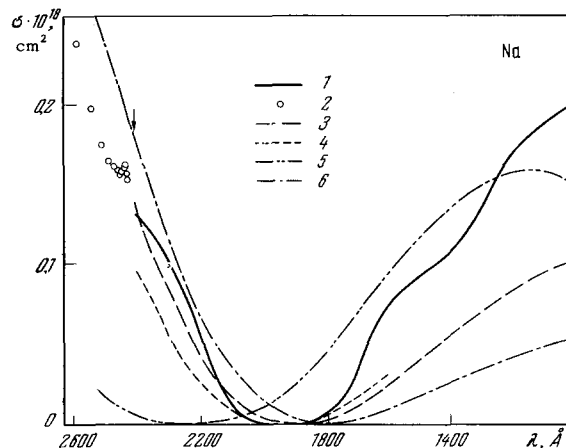


FIG. 4. Photoionization and photoexcitation cross sections for sodium. Experimental data: 1 – <sup>[146]</sup>, 2 – points for the photoexcitation cross section corresponding to oscillator strengths from <sup>[172,173]</sup>. Calculation results: 3 – <sup>[41]</sup>, 4 – <sup>[40]</sup>, 5 – <sup>[34]</sup> (a calculated ionization potential somewhat different from the true one was used in <sup>[34]</sup>), 6 – formula (1.8).

best agreement is attained for method C, but the polarizability  $\alpha = 1.85 \times 10^{-25} \text{ cm}^3$  used in<sup>[41]</sup> differs from the values  $1.31 \times 10^{-25}$  and  $1.48 \times 10^{-25}$  used in<sup>[174]</sup> and<sup>[175]</sup> respectively and obtained from the energies of the hydrogenlike levels of Na. Formula (1.8) gives satisfactory results near threshold; it is difficult to obtain a reliable cross section at lower wavelengths, owing to the very strong “extinction.”

The calculations for Li exhibit a noticeable scatter, in spite of the relative simplicity of this atom<sup>[144]</sup>; good results are obtained with (1.8). Calculations for potassium were made by method C<sup>[42]</sup> at several values of  $\alpha$  for  $K^+$  from 0 to  $2 \times 10^{-24}$ . The agreement with experiment turns out to be best for  $\alpha = 1.55 \times 10^{-24}$ .<sup>[148]</sup> It was found in<sup>[42]</sup> that the cross section is quite sensitive to the choice of the value of  $\alpha$ ; the curve corresponding to the value  $\alpha = 0.811 \times 10^{-24}$  obtained in<sup>[174]</sup> has nothing in common with the experimental cross section. This may be connected with the fact that the bound wave function was calculated in<sup>[42]</sup> with allowance for exchange and without allowance for polarization, whereas the free function was calculated with allowance for polarization but without allowance for exchange, i.e., under different approximations. In addition, the method for taking polarization into account can itself be regarded as doubtful. Unsatisfactory results for K are obtained also with the Burgess-Seaton formula.

The deviation of  $\sigma_{\min}$  from zero is explained by the fact that actually there are two transitions:  $ns^2S \rightarrow k^2p^2P_{1/2}$  and  $^2P_{3/2}$ , the corresponding cross sections going through zero at some different wavelengths, so that  $\sigma_{\min} > 0$  for the total cross section<sup>[40]</sup>. The calculations for Na, K, Rb, and Cs yielded  $\sigma_{\min} \times 10^{20} = 0.001, 0.03, 0.4,$  and  $3$ , while the experimental values were  $< 0.3, < 0.4, 0.4,$  and  $6$  respectively. It is noted in<sup>[40]</sup> that a nonzero minimum is obtained also when quadrupole transitions are taken into account.

**Rare-earth metals.** The available experimental data are quite limited (with the exception of Ca) and pertain to the near-threshold region. For the elements of this group, as shown with Ca as an example<sup>[150,176,177]</sup>, an important role is played by the autoionization lines.

The correspondence between different calculations and the experimental data is illustrated in Fig. 5, with Sr as the example. The cross sections obtained with self-consistent wave functions, both without and with account of correlation, do not duplicate the characteristic variation of the experimental data. Formula (1.8) gives better results. A similar picture takes place for Ca and Mg<sup>[21,62,150]</sup>. A minimum near threshold is apparently observed for all elements. It would be of interest to investigate  $\sigma_{\min}$ .

**Elements of Al group.** A specially important role is played for these elements by the superposition of configurations in the discrete and in the continuous spectrum.

By way of an example, Fig. 6 shows the cross section of Tl, the experimental data for which are most complete. The autoionization line  $^2P_{1/2}^0 - ^4P_{3/2}$  perturbs a relatively narrow spectral interval. Outside this interval, the photoexcitation and photoionization cross sections correspond well to each other, and the autoionization minimum corresponds to the cross section of the ps transition, which is not perturbed by this line. The appearance of the  $^2P_{1/2}^0 - ^4P_{3/2}$  line and the fact

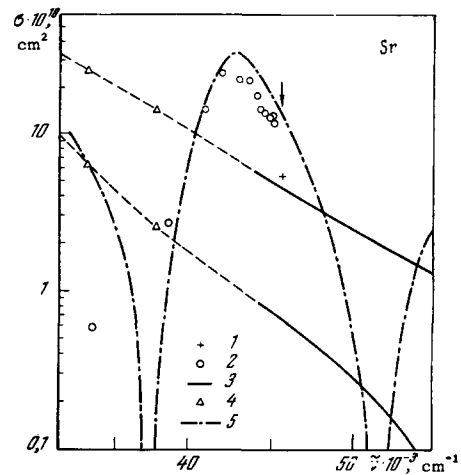


FIG. 5. Photoionization and photoexcitation cross sections for strontium. Experimental data: 1 - <sup>[151]</sup>, 2 - photoexcitation cross section determined using oscillator strengths from <sup>[176]</sup>. Calculation results: 3,4 - <sup>[21]</sup> (3 - photoionization cross section, 4 - points for the photoexcitation cross section corresponding to oscillator strengths of two lines; we note that the calculated values used in <sup>[21]</sup> for the line wavelengths and for the excitation potential differs somewhat from the true ones; the dashed lines show the interpolated photoexcitation cross section. Two calculations were made in <sup>[21]</sup>: the lower curve corresponds to results obtained without account of correlation, and the upper one with account of correlation), 5 - formula (1.8). The arrow denotes the position of the threshold.

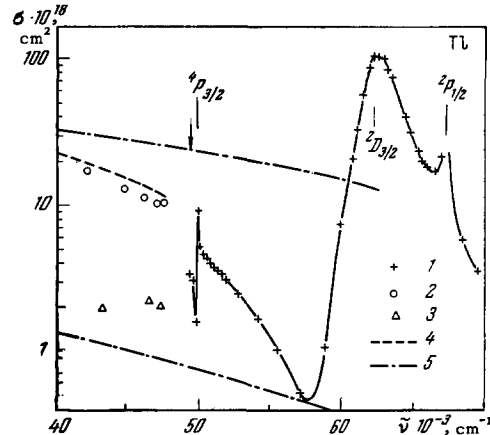


FIG. 6. Photoionization and photoexcitation cross sections for thallium. Experimental data: 1 - <sup>[160,161]</sup>, 2,3,4 - photoexcitation cross section determined using oscillator strengths from <sup>[179]</sup> (2 -  $p \rightarrow d$  transition, 3 -  $p \rightarrow s$  transition, 4 - sum). Calculation results: 5 - formula (1.8) (the small contribution of the  $p \rightarrow s$  transition is indicated). The arrow denotes the position of the threshold.

that it perturbs the  $^2D_{3/2}$  continuum point to a deviation from LS coupling.

The  $^2P_{1/2}^0 - ^2D_{3/2}$  line is very strong ( $f = 0.5$ ), and, in addition, the perturbation of the spectrum is allowed in the LS-coupling scheme. It is seen from Fig. 6 that the cross section given by (1.8) can be interpreted approximately as being  $\sigma_0$  of expression of (1.11). Then

Fig. 6 is an illustration of the fact that the strong autoionization line can perturb a very broad spectral interval, including also the discrete spectrum of the corresponding series (the processing<sup>[161]</sup> of the cross section of Tl with the aid of formula (1.11) also shows that the perturbation encompasses a very broad interval, although no account was taken in<sup>[161]</sup> of the possibility of perturbing indiscrete spectrum). Obviously, an inverse situation is also possible, in which the strong interaction of the configuration in the discrete spectrum affects the threshold region of the photoionization. The lines  ${}^2P_{1/2}^0 - {}^4P_{3/2}$ ,  ${}^2D_{3/2}$  have a characteristic Beutler-Fano profile. The level  ${}^2P_{1/2}$  cannot perturb the d-continuum; the corresponding line is additively superimposed on the background and has apparently a symmetrical profile.

The  ${}^2D_{3/2}$  level of Ga and In is closer to the ionization boundary and the absorption minimum appears in the region of the threshold<sup>[153, 180]</sup>. Assuming that the cross sections of Ga and In are similar to the cross sections of Tl, but are shifted in frequency, and using the available information for individual spectral intervals<sup>[153, 180, 159, 181]</sup>, we can approximately construct the cross section in a sufficiently broad interval. The cross section of Al has an absorption maximum near the threshold and the minimum is shifted even farther in the region of the photoexcitation cross section<sup>[153]</sup>. Thus, with decreasing number of electrons, the  ${}^2D_{3/2}$  level approaches the ionization boundary, causing a nonmonotonic change in the value of the cross section at threshold.

Formula (1.8) is not suitable for elements of this group. The cross sections obtained turn out to be close for all the atoms:  $\sim 2 \times 10^{-17}$  cm<sup>2</sup> at threshold<sup>[153]</sup>. On the other hand, the experimental data differ both in frequency dependence and in absolute magnitude (within two orders of magnitude). The error is due not only to the upper but also to the lower states, where there is also an admixture of the  $sp^2$  configuration.

**Nitrogen and oxygen.** The photoionization cross section of O is shown in Fig. 7. Formula (1.8) gives good results in the near-threshold region; a reliable comparison for the other succeeding threshold regions is made difficult by the lack of the required quantum defects and the need for extrapolating the tabulated Burgess-Seaton data, since the tables are limited to  $n_p^* \geq 1$ , and  $n_p^* < 1$  is required. For short wavelengths, calculations using the self-consistent functions give better results than (1.8). The data are less complete for nitrogen, but a similar agreement between theory and experiment can be expected.

**Autoionization.** Extensive measurements were made in inert gases. The level positions for He were determined in<sup>[184, 188, 117]</sup>, and the line profiles and the photoionization cross section in the region of the lines were measured in<sup>[120]</sup>. The structure of the photoionization cross section, the line profiles, and the position of the levels between the first and the second ionization thresh-

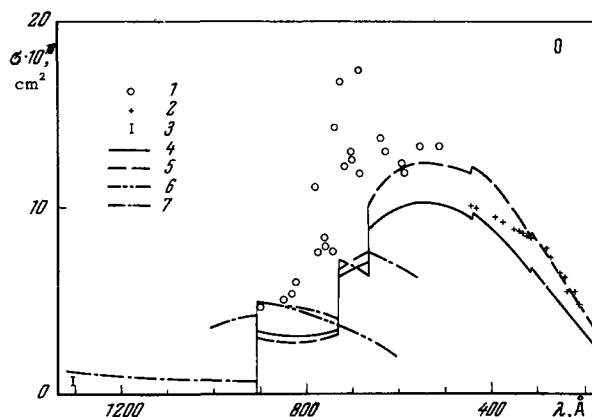


FIG. 7. Photoionization cross section of atomic oxygen. Experimental data: 1 - photoionization cross section of atomic oxygen<sup>[163]</sup>, 2 - half of the photoionization cross section of O<sub>2</sub>,<sup>[163]</sup> 3 - point for the photoexcitation cross section of O, corresponding to the oscillator strength of the resonance line<sup>[182, 183]</sup>. Calculation results: 4, 5 - [33] (4 - calculations with velocity matrix element, 5 - with radius element), 6 - [31] (calculated only for the process  $O2p^4 \ {}^3P \rightarrow O^+2p^3 \ {}^4S$ ), 7 - formula (1.8) (the photoexcitation cross sections are also indicated separately for  $p \rightarrow s$  and  $p \rightarrow d$  transitions).

holds ( ${}^2P_{1/2}$  and  ${}^2P_{3/2}$ ) were measured for Ar<sup>[129, 135]</sup>, Kr<sup>[137, 135]</sup>, and Xe<sup>[129, 189, 135, 142]</sup>. Similar measurements for the lines  $s^2p^6 - sp^6mp$  were made in<sup>[128]</sup> for Ar and Kr; measurements limited to the wavelengths of such lines are reported for Ne and Ar in<sup>[194, 187, 188]</sup> and for Kr and Xe in<sup>[190, 191, 187]</sup>. The positions of the levels corresponding to the excitation of the d-electron were determined in<sup>[192, 193]</sup> for Kr and in<sup>[192-194]</sup> for Xe. The simultaneous excitation of the d and p electron in Kr and Xe is investigated in<sup>[195]</sup>. Excitation of the internal shell  $4p^6$  of xenon was observed in<sup>[192, 195]</sup>.

As to the other elements, as already mentioned, investigations were made on Ca<sup>[150, 176, 177]</sup> and Tl<sup>[160, 161]</sup>. The profile and the oscillator strengths of the components of the doublet AlI  $s^2p \ {}^2P^0 - sp^2 \ {}^2S$  were determined in<sup>[196]</sup> and those of InI  $s^2p \ {}^2P - sp^2 \ {}^2S$  and  ${}^2P$  in<sup>[181]</sup>. An investigation was made of the  $p^2 \ {}^3P$  level of cadmium<sup>[197]</sup>. Autoionization of these elements, as well as of Ga, Sr, Ba, Pb, and a few others, is discussed in<sup>[180]</sup>. Levels of Li, K, and Rb, lying between the first and second ionization thresholds, were observed in<sup>[198]</sup>.

The main features of the observed autoionization lines and of the adjacent regions of the photoionization cross sections agree with the qualitative predictions of the theory. An analysis made in<sup>[90, 94, 120, 161, 181]</sup> shows that the parameters  $q$  and  $\Gamma$  can be so chosen (of course, separately for each line) that formula (1.11) agrees well with the observed profile. Besides the asymmetrical lines, "windows" in absorption, corresponding to  $q \approx 0$  were also observed (Fig. 2). Observations made of series of autoionization lines have shown that, in accord with (1.12), the jump in the photoionization can have positive, negative, or zero values<sup>[94]</sup>.

**Positive ions.** Experiments are made difficult by the fact that it is necessary to work with a plasma and to carry out the measurements in the ultraviolet. The only paper published thus far<sup>[164]</sup> deals with the  $\text{Xe}^+$  ion. The absorption cell was a shock tube. Autoionization phenomena were also observed for ions. Characteristic asymmetrical lines were observed in the spectrum of OIII.<sup>[199]</sup> Processes due to autoionization of inert-gas ions were investigated in<sup>[200]</sup>. The methods used to calculate the cross sections for positive ions are the same as for atoms, and there are no grounds for assuming that any peculiar difficulties will arise in the future when comparison is made with the measurement results.

### Excited States

As seen from Table III, the number of investigated individual cross sections is small. Attention is called to the sharp divergence from the Burgess-Seaton formulas in half the cases, the reliability of the measurements being confirmed by agreement with the photoexcitation cross sections (Fig. 8a shows by way of an example the cross section of  $\text{Ca } 3^3\text{D}$ ). Thus, the approximate character of the existing variant of the quantum-defect method becomes evident for both ground states and excited ones. This confirms the opinion advanced in 1.2 that the reliability of formula (1.8) is connected essentially not with the degree of excitation of the considered states, but with the degree of manifestation of the interaction of the configurations and the deviations from LS coupling.

The role of the configuration interaction is confirmed also in measurements<sup>[201]</sup> that have revealed that the first threshold of the photo-ionization of the carbon atoms from the state  $2s^3 3^3\text{D}^0$  corresponds to the formation of a carbon ion in the state  $2s^2 p$ . This can be explained as meaning that the term identified as  $2s^3 3^3\text{D}^0$  has actually an admixture of  $2s^2 p 3^3\text{D}^0$ . This opinion is confirmed also by the observation of a strong  $2s^2 p^4 p^3\text{P} - 2s^3 3^3\text{D}^0$  line.

An interesting picture is obtained for  $\text{Mg } 3^3\text{P}^0$  (Fig. 8b). The discrepancy between the photoionization and photoexcitation cross sections becomes even larger if account is taken of the fact that what was actually meas-

ured in<sup>[204]</sup> was the ratio of the photoionization cross section to the oscillator strength of the transition  $3^3\text{P}^0 - 5^3\text{S}$ , the value of which was taken from the theory and turned out to be 2–4 times lower than the values obtained in later measurements. Unless subsequent experiments change this situation, the observed picture can be attributed to the fact that a perturbing level is located in the  $38\,000\text{ cm}^{-1}$  region, and thus the Beutler-Fano profile connects the regions of photoexcitation and photoionization.

The discussion presented for the ground and excited states shows that deviations of the calculated curves from the experimental ones can have a nonmonotonic local character and in this case they are due to perturbation of the upper states. Other deviations are monotonic and encompass a broad spectral interval, and in this case they are due to the crudeness of the analysis of the lower states or to a smooth variation of the character of the upper state (for example, change in the type of coupling). In semiempirical calculations, one can attempt to use several experimental points as reference points for the reconstruction of the entire curve.

### 1.5 Verification with the Aid of Sum Rules

The experimental and theoretical cross sections can sometimes be verified with the aid of sum rules<sup>[209-211]</sup>. The sums

$$S(k) = \sum_n f_{mn} (E_n - E_m)^k \quad (1.14)$$

are expressed in terms of quantities that characterize only the  $m$ -th state. These quantities can be obtained from measurements or calculated quite accurately (if one knows the wave function  $\psi_m$ ; the wave functions  $\psi_n$  are no longer required here). Expression (1.14) is a sum taken over all the discrete states plus an integral over the continuum. The most useful are the sum rules<sup>[209,210]</sup>

$$S(-2k) = \beta_k, \quad k = 2, 3, 4, \dots, \quad (1.15)$$

$$S(-2) = \frac{\alpha_m}{4}, \quad (1.16)$$

$$S(-1) = \frac{1}{3} \langle m | \left( \sum_i r_i \right)^2 | m \rangle, \quad (1.17)$$

$$S(0) = N, \quad (1.18)$$

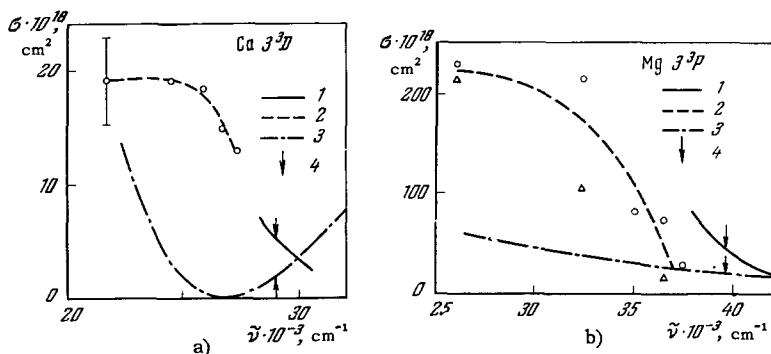


FIG. 8. Photoionization and photoexcitation cross sections of  $\text{Ca } 3^3\text{D}$  (a) and  $\text{Mg } 3^3\text{P}$  (b)<sup>[153]</sup>. 1 – measured photoionization cross section<sup>[204,207]</sup>; 2 – photoexcitation cross section drawn through the experimental points (the points for Mg were obtained by different workers); 3 – calculation according to (1.8); 4 – limit of spectral series.

**Table IV.** Contributions of different parts of the spectrum to the sums  $S(k)$  for  $\text{Ne}^*$ 

Processes**	Spectral interval, Ry	$S(-4)$ $Ry^{-4}$	$S(-2)$ $Ry^{-2}$	$S(-1)$ $Ry^{-1}$	$S(0)$	$S(1)$ $Ry$	$S(2)$ $10^4 Ry^2$
1	1,24	0.068	0.104	0.13	0.16	0.2	—
2	1.45—1.58	0.027	0.060	0.09	0.13	0.2	—
3	1.58—3.56	0.077	0.357	0.84	2.02	5.5	—
4	~3.4	—	0.004	0.01	0.04	0.1	—
5	3.56—13.0	0.006	0.146	0.78	4.57	32.7	0.03
6	13.0—63.7	—	0.004	0.07	1.36	31.4	0.10
	63.5	—	—	—	0.02	1.1	0.01
7	63.7—227.8	—	—	0.02	1.63	167.0	1.96
	227.8—911.3	—	—	—	0.17	64.5	2.68
	911.3—7353	—	—	—	0.01	16.7	3.19
	7353— $\infty$	—	—	—	—	1.4	3.20
Sum		0.178	0.675	1.94	10.1	321	11.2
$S(k)$		0.18	0.671	2.22	10	293.7	10.4

\*The last line of the table contains the results of direct measurements or calculations of the values of  $S(k)$ , taken from [215] and, for the case  $k = -4$ , from [210].

\*\*1 — resonance line; oscillator strength taken from measurements [171]; 2 — remaining  $2p \rightarrow ns$  and d lines; summary oscillator strengths determined by interpolation of the photoexcitation cross section; 3 — continuum between  $L_{2,3}$  and  $L_1$  thresholds; photoionization cross section taken from measurements [126]; 4, 6 — lines  $2s - np$  and  $1s - np$  respectively; spectral interval chosen to equal 0.34 Ry in analogy with transitions from the 2p shell; oscillator strengths determined from the extrapolated photo excitation cross section; 5, 7 — continua between  $L_1$  and K thresholds and beyond the K threshold, respectively; results taken from [215], where the existing calculated and experimental data are used.

$$S(1) = \frac{4}{3} \left\{ E_m + \frac{1}{2} \sum_{i \neq j} \langle m | \mathbf{p}_i \mathbf{p}_j | m \rangle \right\}, \quad (1.19)$$

$$S(2) = \frac{16}{3} \pi Z \sum_i \langle m | \delta(\mathbf{r}_i) | m \rangle, * \quad (1.20)$$

where  $\alpha_m$  is the polarizability of the atom,  $E_m$  the binding energy,  $\mathbf{p}_i$  and  $\mathbf{r}_i$  the momentum and radius vector of the  $i$ -th electron; all the quantities are expressed in atomic units and the energy in Rydberg units;  $N$  is the number of electrons. The quantities  $\beta_k$  can be obtained from the values of the Verdet constant or the refractive index [210]. The quantity  $S(-1)$  can be related with the diamagnetic susceptibility  $\chi$  as follows:

$$\chi = -7.9 \cdot 10^{-7} [3S(-1) - \sum_{i \neq j} \langle m | \mathbf{r}_i \mathbf{r}_j | m \rangle].$$

The Van der Waals forces acting between the atoms are expressed in terms of the quantities  $S(k)$ . [211, 213, 214]

The spectral region making the main contribution to  $S(k)$  varies as a function of  $k$  (this is illustrated in Tables IV and V with Ne and Li as examples). This determines the efficacy of choosing any particular sum rule to verify the cross section in a definite spectral interval. We see that for Ne the calculation of the quantities  $S(-4)$ ,  $S(-2)$ ,  $S(-1)$ , and  $S(0)$  is a good check on the cross section in the spectral interval of interest to us. For Li, on the other hand, the main contribution to all  $S(k)$  is made either by the resonance line or by the photoionization from the K shell. We therefore cannot verify in this manner the reliability of the photoionization cross section of Li in the ultraviolet region. A similar situation obtains also for the re-

**Table V.** Contributions of different parts of the spectrum to the sums  $S(k)$  for Li

Processes	Spectral interval, A	$S(-2)$ $Ry^{-2}$	$S(-1)$ $Ry^{-1}$	$S(0)$	$S(1)$ $Ry$
1	6710	40.8	5.53	0.750	0.102
2	3230—2300	0.19	0.06	0.020	0.007
3	2300—1150	0.27	0.15	0.083	0.049
4	280—80	0.04	0.23	1.35	8.84
Sum	—	41.3	5.97	2.20	9.00
$S(k)$		$38 \pm 4$		3	

1 — Resonance line,  $f$  taken from [216]; remaining lines of the  $2s - np$  series,  $f$  taken from [216] and partially interpolated; some uncertainty exists in connection with the insufficiently good agreement between the photoionization and photoexcitation cross sections; 3 — photoionization  $2s - k^2p$ , cross section taken from [144]; 4 — photoionization from K shell, cross section taken from [145], where measurements were made for a metallic lithium film.

maining alkali metals. Thus, the sum rules cannot be used for verification of any arbitrary cross section.

The sums  $S(k)$  were calculated in detail for He in [217], and the results were in good agreement with direct calculations or measurements of  $S(k)$ . Calculated sums ( $k = 0, -1, -2, -4, -6$ ) are given [213] for all inert gases; we note the good satisfaction of the rule (1.18).

Let us apply the sum rules to the hydrogen atom. There is noticeable disparity between the experimental and theoretical photoionization cross sections (see Fig. 7). We are interested in the ultraviolet band, therefore (in analogy with Ne) to clarify the reliability of the cross sections we shall calculate  $S(-2)$ . The contribution of the experimental cross section is 1.0

\*The sum rule introduced in [212] actually coincides with (1.20).

and that of the theoretical one<sup>[33]</sup> 0.677. Recognizing that the contribution of the resonance line is 0.068 and of the remaining lines 0.094, we find that the polarizability corresponding to S(-2) is  $\alpha = 7 \times 10^{-25} \text{ cm}^3$  if we assume the experimental cross section and  $\alpha = 5 \times 10^{-25} \text{ cm}^3$  if we assume the cross section calculated in<sup>[33]</sup>. On the other hand, a direct determination of the polarizability yields  $7.7 \times 10^{-25} \text{ cm}^3$  (measurement) and  $8.9 \times 10^{-25} \text{ cm}^3$  (theory)<sup>[218]</sup>. Thus, the cross section measured in<sup>[163]</sup> turned out to be more reliable than that calculated in<sup>[33]</sup>.

In calculating the sums, some of the missing transition probabilities can be estimated by interpolating and extrapolating the cross sections<sup>[169,153]</sup>. An important contribution is made in some cases by autoionization lines. The values of the directly measured or calculated polarizabilities are given in<sup>[218,219]</sup>. Approximate sum rules may be useful; for example, the rule (1.18) is approximately satisfied for individual shells, such 1s<sup>2</sup> and 2s of Li, and 1s<sup>2</sup> and 2s<sup>2</sup>p<sup>6</sup> of Ne, but it is already impossible to separate the 2s<sup>2</sup> and p<sup>6</sup> shells of Ne (see Tables IV and V).

### 1.6 Shift of Photoionization Threshold in a Plasma

In a real plasma, the atoms, ions, and electrons interact with one another. These phenomena may exert an influence on the continuous spectra, the degree of ionization, and other plasma properties. At the present time these effects have not yet been sufficiently investigated. Let us examine qualitatively their influence on the photoionization cross section.

The interaction prevents realization of the higher discrete levels (this consideration, as is well known, is used to cut off the partition function). In addition, the uppermost realized levels, can, generally speaking, overlap as a result of broadening. These two phenomena modify the level scheme of the atom, causing an actual reduction in the ionization potential and, furthermore, the coalescence of the upper level leads to an apparent reduction. The end point of the continuous spectrum shifts towards lower frequencies. In the spectrograms, the role of these phenomena is indistinguishable, and no corresponding theory has been developed so far. We shall therefore combine them and, bearing both phenomena in mind, we shall talk of the transformation of the lines into a continuous spectrum. The resultant shift of the threshold frequency will be denoted  $\Delta\nu$ .

For an approximate account of the shift of the photoionization threshold, we can assume that the influence of the interaction on the continuous spectra reduces only to transformation of the upper terms of the spectral series into a continuous spectrum in accord with the unperturbed density of their oscillator strengths. Thus, the photoexcitation cross section (1.13) gives us the form of the photoionization cross section in a plasma for frequencies lower than the ideal threshold

frequency. For higher frequencies, the photoionization cross section is assumed invariant. Such assumption constitute the extension of the principle of spectroscopic stability on the upper terms of the spectral series and a continuous spectrum, which is not sufficiently justified. However, there are certain experimental data confirming these assumptions<sup>[153]</sup>.

Generally speaking, it is necessary to compare the following quantities: the oscillator strength density and the photoionization cross section, both measured for an isolated atom, and the photoionization cross sections measured at different ever increasing shifts  $\Delta\nu$ . However, there is no set of such measurements for any of the cross sections. The most complete results can be obtained for the photoionization of oxygen from the state 3<sup>5</sup>P and argon from 4s and s'. For transitions from these levels there exist oscillator strengths which make it possible to obtain at two points the summary cross section  $\sigma(\nu_{mn})$ . The photoionization cross sections under plasma conditions were also measured (Fig. 9). The latter can be separated from the spectra<sup>[203,206]</sup> formed by certain superimposed continua. It is therefore possible to determine reliably only the threshold cross sections.

It is seen from Fig. 9 that the obtained values agree

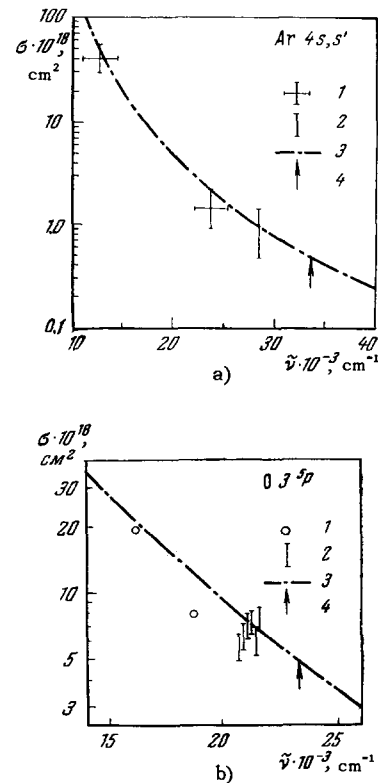


FIG. 9. Photoionization and photoexcitation cross sections of Ar 4s, s' (a) and O 3<sup>5</sup>P (b) <sup>[153]</sup>. 1 - Experimental points for the photoexcitation cross section; 2 - threshold values of the photoionization cross section, measured in <sup>[203,206]</sup>; 3 - calculation in accord with (1.8); 4 - limit of the series of the isolated atom.

well with the points for the photoexcitation cross sections.

For oxygen, the measurements were made at several temperatures, corresponding to different values of the shift  $\Delta\nu$ , so that the threshold value of the cross section can be determined for several values of the frequency. Unfortunately, the obtained points exhibit a strong scatter. The frequency dependence can nevertheless be roughly estimated by separating at one temperature the contribution of the individual continuum from the data of<sup>[203]</sup> in a certain interval beyond the threshold. The obtained dependence (decrease with increasing frequency) also agrees with the variation of the photoexcitation cross section.

The experimental points agree with the theoretical curve constructed after Bates-Damgard-Burgess-Seaton. Therefore it is possible to assume that the theoretical curve can serve as a real photoionization and photoexcitation cross section for the isolated atom.

Figure 9 demonstrates that the assumed spectroscopic stability of the higher terms of the spectral series as they are transformed into a continuous spectrum is reasonable. The cross section of Ca (see Fig. 8) was also obtained under conditions when the photoionization threshold was shifted. In this case, too, the cross section turned out to be continued in the direction towards the available points for the photoexcitation cross section. The sharp frequency dependence of the cross sections for O, Ar, and Ca makes any other interpretation difficult. Additional experimental confirmations will be obtained in Sec. IV in the analysis of the summary spectra.

In the theoretical calculation, the variation of the cross section in the region adjacent to the threshold is determined by the Burgess-Seaton formulas (or some other formulas for the photoionization cross sections), by analytically continuing them to negative values of  $k^2$ .

The value of  $\Delta\nu$  can be approximately determined by the Inglis-Teller formula<sup>[220]</sup>. The validity of this formula was recently confirmed by the reduction of the results of<sup>[202, 203]</sup> in<sup>[221]</sup>. It should be recalled at the same time that the Inglis-Teller formula was obtained for hydrogen and does not take into account the peculiarities of complex atoms. Estimates show that even for the upper non-hydrogenlike excited levels of complex atoms the broadening mechanism may differ from that for hydrogen. For hydrogenlike levels, on the other hand (i.e., those with near zero quantum defect), the following may be significant: a) the incomplete degeneracy in  $l$ , which leads to a decrease in the number of the Stark components; b) the larger number of levels with identical  $n$  and  $l$ , due to the multiplet nature; c) the role of the non-hydrogenlike lower level, which becomes manifest in the fact that the intensities and the number of the Stark components of the corresponding lines may differ from the hydrogenlike levels (this circumstance pertains to lines corresponding to transitions from non-hydrogenlike upper levels). These

misgivings are confirmed by measurement results<sup>[196]</sup> in which the values of the numbers  $m$  turned out to be different for simultaneously observed series Ca I  $4s^2\ ^1S_0 - 4smp\ ^1P^0$  and Al I  $3s^2p\ ^2P^0 - 3s^2md\ ^2D$  (13 and 9 respectively).

In conclusion we mention the phenomenon of forced autoionization<sup>[222]</sup>, which appears when the continuous spectrum produced as a result of lowering of the ionization potential is superimposed on a discrete level situated below the ionization potential of the isolated atom. The corresponding line broadens and acquires a characteristic asymmetry. This phenomenon was apparently also observed in<sup>[199]</sup>.

## II. RESULTANT RECOMBINATION AND BREMS-STRAHLUNG SPECTRA

In some regions of the spectrum, the absorption is due to photoionization from different excited states. The total absorption coefficient  $\kappa_{bf}(\nu, T)$  can be obtained by calculating the cross sections, multiply them by the corresponding concentrations, and summing over all the states from which the photoeffect is possible upon irradiation at frequency  $\nu$ :

$$\kappa_{bf}(\nu, T) = N_a \sum_{n, l} \frac{\omega_l}{\Sigma_0} \exp(u_{nl} - u_l) \sigma_{nl}(\nu), \quad (2.1)$$

where  $\omega_l$  is the statistical weight of the excited state, a Boltzmann distribution of the atoms over the state is assumed,  $\Sigma_0$  is the partition function of the atom,  $u_{nl} = |E_{nl}|/kT$  ( $u_l$ —value of  $u_{nl}$  for the ground state),  $T$  is the temperature, and  $N_a$  is the concentration of the atoms.

In 1938, when there could be no talk of any rigorous calculation of  $\kappa_{bf}(\nu, T)$ , Unsold<sup>[223]</sup> proposed an approximate formula, extending to many-electron atoms the resultant expression for absorption coefficient valid for hydrogen and obtained after replacing the summation over the excited states by integration. The singularities of the structure of complex atoms were taken into account by introducing an effective charge  $Z^*$  and a factor  $\Gamma$  that took into account the multiplet nature of the terms of the complex atom. Unsold included in his analysis also free-free transitions, using for them the same effective charge  $Z^*$  as for photoionization. As a result it was possible to obtain a single general formula accounting for both bound-free and free-free transitions:

$$\kappa(\nu, T) = C_3 \Gamma Z^{*2} \exp(-u_l + u + \Delta u) \nu^{-3} N_a, \quad (2.2)$$

where  $C_3$  is a constant,  $u = h\nu/kT$ ,  $\Delta u = h\Delta\nu/kT$ . It was noted subsequently that (2.2) can be used when  $\nu \leq \nu_g$ ; when  $\nu > \nu_g$  the argument of the exponential does not change and  $\kappa(\nu, T)$  decreases like  $\nu^{-3}$ ; the value of the end-point frequency  $\nu_g$  is determined by the lower excited state<sup>[224, 1]</sup>. A review of investigations in which formula (2.2) was used is given in<sup>[87]</sup>, where it is shown that the published recommendations on the



choice of  $Z^*$  and  $\Gamma$  have neither theoretical nor experimental justification and contradict each other.

The recently developed methods of calculating the cross sections have made a direct calculation of expression (2.1) more realistic. However, in view of the complexity of the calculations of the cross sections and the large number of levels which must be taken into account in the summation, the calculation by means of formula (2.1) is in the general case a laborious problem. In addition, it must be recalled that the theoretical cross sections are approximate in character. In this connection, direct summation is in most cases an unjustified procedure.

Expression (2.1) and the Burgess-Seaton formulas were used in<sup>[225]</sup> as the basis for obtaining a number of simplifying assumptions, valid for all atoms, and a general formula, which is theoretically justified and suitable for practical use, was obtained for  $\kappa_{bf}^H(\nu, T)$ . Further analysis is presented in<sup>[226,87]</sup>.

The entire energy level scheme of the atom is broken up into two parts A and B. Group A comprises the levels which have an appreciable quantum defect; the levels of group B have practically no quantum defects. Group A includes levels with small  $l$  (usually  $l \leq 2$ ). This makes it possible to use as the basis the value  $\kappa_{bf}^H(\nu, T)$  for hydrogen, by introducing a factor  $\xi(\nu)$ ,\* which takes into account these peculiarities of the cross sections of the group A levels. The summation over the levels is replaced by integration. To determine  $\kappa_{bf}^H(\nu, T)$ , use is made of a well known expression that follows from the Kramers formulas. In calculating  $\xi(\nu)$  it turns out to be possible to employ a number of approximations which greatly simplify the use of the parameters tabulated by Burgess and Seaton.

For atoms with several valence electrons, the sum (2.1) should be taken not only over the quantum numbers  $n$  and  $l$ , but also over the values of the total spin  $S$ , the total orbital angular momentum  $L$  of the initial state, and the angular momentum  $L'$  of the final state, and, in general, over the values of the total angular momenta  $j$  and  $j'$ . In many cases, the energies and the quantum defects of states with identical  $n$  and  $l$  differ little. It is then possible to separate the summation over  $n$  and  $l$  and to carry out the summation over the remaining quantum numbers. In the formula for  $\kappa_{bf}^H(\nu, T)$ , there appears an additional factor  $\gamma$ , equal to the statistical weight of the parent term of the atom under consideration. This result, obtained for LS coupling, remains in force also for other types of coupling, since the summary line strength (so long as we have unified all the levels with given  $n$  and  $l$ ) does not depend on the quantum numbers used to describe the separate levels. To take into account photoionization from the shifted terms, the quantity  $\gamma$  must be replaced by the partition function of the residual ion  $\Sigma_1$ .

\*It will be shown that  $\xi(\nu)$  is as a rule practically independent of  $T$ , and this is a very interesting and useful result.

Until recently, free-free transitions of an electron in the field of a positive ion were assumed to be hydrogenlike or calculated with the aid of (2.2). A quantum mechanical analysis is presented in<sup>[87,88]</sup>. The matrix elements were obtained by extrapolating the bound-free transition matrix elements calculated by Burgess and Seaton. Direct extrapolation was made difficult by the fact that it turned out that the Burgess-Seaton formulas are unsuitable for calculation of the photoionization cross sections (at constant  $\nu$ ) of the upper excited states. To carry out the extrapolation it was therefore necessary to modify the parameters tabulated by Burgess and Seaton, correcting them with the aid of exact expressions known for hydrogen. The expression obtained for the matrix elements takes into account the specific nature of the free-free transitions in the field of the ion, compared with the transitions in the field of the proton (or nucleus).

To find the absorption coefficient  $\kappa_{ff}(\nu, T)$  due to the free-free transitions, derivations were used similar to those employed in the analysis of the photoionization absorption. The free states, in accordance with their quantum defects, were separated into groups A and B. The Kramers formula was used to determine  $\kappa_{ff}^H(\nu, T)$  and the function  $\xi(\nu)$  was introduced. The electron velocity distribution was assumed Maxwellian.

The resultant absorption coefficient  $\kappa(\nu, T)$  is equal to the sum of  $\kappa_{bf}^H(\nu, T)$  and  $\kappa_{ff}(\nu, T)$ . Inasmuch as integration over the electron energies was used in the calculation of both terms, it becomes possible to combine both terms in one expression and to use a common function  $\xi(\nu)$ . The final formula for the frequencies below the end-point frequency  $\nu_g$  is

$$\kappa(\nu, T) = C_3 \left( 2 \sum_1 / \sum_0 \right) T \exp[-u_1 + u + (h\nu/kT)] Z^2 \xi(\nu) \nu^{-3} N_a, \\ C_3 = 16\pi^2 k e^6 (3 \sqrt{3} e h^4)^{-1} = 0.89 \cdot 10^{24}, \quad (2.3a)$$

and for  $\nu > \nu_g$

$$\kappa(\nu, T) = \kappa(\nu_g, T) \xi^{-1}(\nu_g) \xi(\nu) (\nu_g/\nu)^3 + \sum \kappa_{nl}(\nu, T), \quad (2.3b)$$

where  $u_g = h\nu_g/kT$ . The end-point frequency is equal to the maximum threshold frequency of the photoeffect for the excited states taken into account in integral fashion. However, as a rule, there are also several levels in isolated positions, the photoionization from which must be taken into account individually. Consequently one introduces in (2.3b) the sum of the photoabsorption indices for states whose threshold frequency is larger than  $\nu_g$  but smaller than the considered frequency  $\nu$ . As a rule, the number of such levels is small and this does not complicate the calculation.

We note that for  $\nu < \nu_g$  the ratio of the contributions of the bound-free and free-free transitions is approximately  $(e^u - 1):1$ , so that the contribution of the free-free transitions becomes predominant when  $h\nu < 0.7 kT$ . If  $h\nu_g < 0.7 kT$ , then the contribution of the free-free transitions prevails in the entire region of frequencies up to the thresholds of the isolated

levels. A considerable fraction of the atoms has quantum defects, which can be approximately assumed independent of the energy for a given  $l$ . Then

$$\xi(\nu) = 1 + \sum_{l=0}^{l_1} K_{ll'} e^{m_{ll'}} \{ \cos^2 \pi [\chi_{ll'}(\epsilon) + \mu_{l'} - \mu_l] - \cos^2 \pi \chi_{ll'}(\epsilon) \},$$

where  $l_1$  is the largest value of  $l$  for states of group A;  $K_{01} = 0.75$ ,  $K_{12} = 2.3$ ,  $K_{23} = 6$ ,  $m_{01} = m_{12} = 0.82$ ,  $m_{23} = 0.90$ ,  $l' = l + 1$  (the contribution of the  $l' = l - 1$  transitions is neglected as small),  $\chi_{ll'}(\epsilon) = a_{ll'} + b_{ll'} \sqrt{\epsilon} + c_{ll'} \epsilon$  if  $\nu < \nu_g$  and  $\chi_{ll'}(\epsilon) = \chi_{ll'}(n_g^*, \epsilon)$  if  $\nu > \nu_g$ , the coefficients  $a_{ll'}$ ,  $b_{ll'}$ , and  $c_{ll'}$  are given in [49, 26], with  $n_g^*$  corresponding to  $\nu_g$ , and  $\mu_l$  and  $\mu_{l'}$  are the quantum defects of the levels  $l$  and  $l'$ . In most remaining cases the dependence of the quantum defects on the energy is linear. An analytic expression for the function  $\xi(\nu)$ , [87] which in this case can depend on  $T$ , was also obtained in the case of such a dependence.

Using Kirchhoff's law, we can obtain formulas for the radiation brightness  $\epsilon(\nu, T)$ :

$$\epsilon(\nu, T) \begin{cases} C_4 (2 \sum_1 / \sum_0) \exp[-u_1 + (h\Delta\nu/kT)] Z^2 \xi(\nu) kTN_a, & \text{if } \nu \leq \nu_g, \\ \epsilon(\nu_g, T) \xi^{-1}(\nu_g) \xi(\nu) \exp(u_g - u) + \sum \epsilon_{nl}(\nu, T), & \text{if } \nu > \nu_g, \end{cases} \quad (2.4a)$$

$$C_4 = 32\pi^2 e^6 (3 \sqrt{3} h^3 c^3)^{-1} = 0.95 \cdot 10^{-7}. \quad (2.4b)$$

The quantity  $\epsilon(\nu, T)$  is given for a thickness of 1 cm in units of  $\text{erg}\cdot\text{sec}^{-1}\text{cm}^{-3}\text{sr}^{-1}(\text{sec}^{-1})^{-1}$ . If we express  $N_a$  in (2.3a) and (2.4a) by means of the Saha formula in terms of  $N_e$  and  $N_i$ , we obtain respectively

$$\kappa(\nu, T) = C_5 N_e N_i (kT)^{-1/2} \exp[(h\Delta\nu - e\Delta I)/kT] Z^2 \xi(\nu) e^{u\nu^{-3}}, \quad (2.5)$$

$$C_5 = 8e^6 \sqrt{\pi} (3 \sqrt{6} m h c m)^{-1} = 4.3,$$

$$\epsilon(\nu, T) = C_6 N_e N_i (kT)^{-1/2} \exp[(h\Delta\nu - e\Delta I)/kT] Z^2 \xi(\nu), \quad (2.6)$$

$$C_6 = 8 \sqrt{2\pi} e^6 (3 \sqrt{3} m m c^3)^{-1} = 6.36 \cdot 10^{-47},$$

where  $\Delta I$  is the lowering of the ionization potential in the Saha formula. It is customarily assumed that  $h\Delta\nu$  is much larger than  $e\Delta I$  [227].

Let us explain the appearance of  $\Delta\nu$  in formulas (2.3)–(2.6). Under the assumptions made in 1.6 with respect to the photoionization cross sections under plasma conditions, the summation (2.1) should be extended over all levels for which  $\nu_{nl}^0 - \Delta\nu < \nu$ , where  $\nu_{nl}^0$  is the threshold frequency for the isolated atom. All the subsequent derivations given in [87] remain unchanged and now give formulas (2.3)–(2.6). The formulas for  $\xi(\nu)$  remain unchanged.  $\nu_g = \nu_g^0 - \Delta\nu$ , where  $\nu_g^0$  is determined from the term scheme of the isolated atom.

The spectroscopic-stability principle was applied also to the transformation of bound-free transitions

into free-free transitions. Under this assumption, the formulas obtained after replacing the summation by integration are not changed at all. The role of the shift of the threshold is manifest only in the formal delineation between the contributions made to the general expression by the bound-free and the free-free transitions.

Formulas (2.3)–(2.6) can be easily generalized when the plasma consists of different chemical elements and contains ions of different multiplicity. For example, (2.6) takes the form ( $\nu < \nu_{gtz}$  for all  $Z$  and  $t$ ):

$$\epsilon(\nu, T) = C_6 N_e (kT)^{-1/2} \sum_{Z,t} \exp[(h\Delta\nu_Z - e\Delta I_Z)/kT] Z_i^2 N_{it} \xi_{it}(\nu), \quad (2.7)$$

where  $t$  is the index of the chemical element of the mixture, and the summation is carried out over  $t$  and  $Z$ . The quantities  $N_i$ ,  $\nu_g$ , and  $\xi(\nu)$  depend on  $t$  and  $Z$ , while  $\Delta\nu$  and  $\Delta I$  are assumed to depend on  $Z$  only.

In the derivation of (2.3)–(2.7) we used for  $\kappa_{bf}^H(\nu, T)$  and  $\kappa_{ff}^H(\nu, T)$  expressions that followed from the Kramers formulas. In the infrared region it is necessary in some cases to take into account the Gaunt factor  $\bar{g}(\nu, T)$  [3, 4, 228] for free-free transitions. Then, for example, we obtain in lieu of (2.3a) and (2.6)

$$\kappa(\nu, T) = C_3 \left( 2 \sum_1 / \sum_0 \right) T \exp(-u_1) \left[ \exp\left(u + \frac{h\Delta\nu}{kT}\right) - 1 + \bar{g}(\nu, T) \right] Z^2 \xi(\nu) \nu^{-3} N_a, \quad (2.8)$$

$$\epsilon(\nu, T) = C_6 N_e N_i (kT)^{-1/2} \left[ \exp \frac{h\Delta\nu}{kT} - e^{-u} + e^{-u} \bar{g}(\nu, T) \right] \times \exp\left(-\frac{e\Delta I}{kT}\right) Z^2 \xi(\nu). \quad (2.9)$$

Formulas (2.8) and (2.9) are customarily useful at frequencies such that the peculiarities of the ions do not appear in practice. Therefore, the factor  $\xi(\nu) \cong 1$  has been introduced only for a smooth transition in (2.3a) and (2.6) (otherwise the Gaunt factor would have to be taken into account also in the derivation of  $\xi(\nu)$ ).

Expressions (2.3)–(2.6) differ formally from those of Unsold in the fact that the constant factor  $(Z^*/Z)^2$  is replaced by the function  $\xi(\nu)$  and the factor  $\Gamma$  (in the expression for  $\kappa(\nu, T)$ ) is replaced by double the ratio of the partition functions. Plots of  $\xi(\nu)$  are given in Fig. 10. A temperature-dependent value for  $\xi(\nu)$  is given in [87]. The obtained functions  $\xi(\nu)$  have as a rule a strong frequency dependence. As  $\nu \rightarrow 0$  we get  $\xi(\nu) \rightarrow 1$  as a result of the predominance of group-B levels. However, even in the visible range  $\xi(\nu)$  can be several times larger or smaller than unity. The latter is of particular interest, since the value of  $(Z^*/Z)^2$  was always chosen in the literature to be larger than unity for all atoms.

Arguments are advanced in [226, 87] to facilitate an estimate of  $\xi(\nu)$  for a number of elements for which no calculations were made, by comparing the quantum defects. In particular, it is indicated that for alkali metals  $\xi(\nu)$  should be close to the  $\xi(\nu)$  of inert gases,

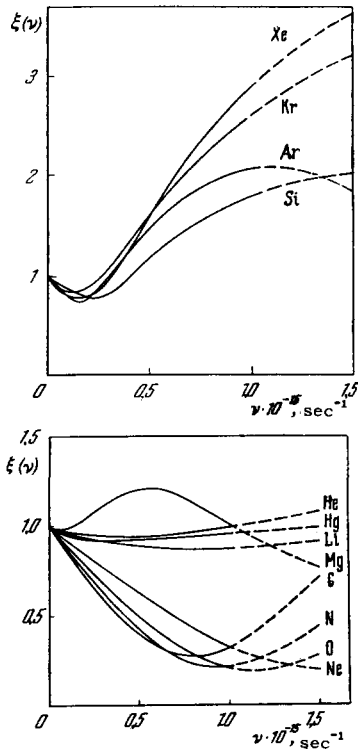


FIG. 10. Plots of the function  $\xi(\nu)$  for different atoms. The dashed lines show the less reliable values.

something subsequently confirmed by direct calculations<sup>[64]</sup> (Fig. 11).

In a number of cases it is necessary to know  $\xi(\nu)$  for heavy elements (Fe and others). The calculations are made difficult by the lack of data on the term energies, and also because of the strong manifestation of the configuration interaction (the latter lead, in particular, to an uncertainty in the photoionization thresholds). So far, only rough estimates under the assumption  $\xi(\nu) \cong 1$ , or the determination of  $\xi(\nu)$  from the experimental data, have been useful.

Figure 12 shows, with oxygen as an example, the functions  $\xi(\nu)$  for ions of the same element but with different ionization multiplicity. With increasing  $Z$ , the system becomes more hydrogenlike, i.e.,  $\xi(\nu) \rightarrow 1$ . Then  $\xi(\nu)$  no longer tends to unity monotonically (with  $\nu/Z^2$  constant), but experiences a number of oscillations.

Formulas (2.3)–(2.6) are universal, but have an integral character and were obtained with the aid of a number of simplifying assumptions. Figure 13 shows a comparison with the results of a direct summation of the Burgess-Seaton cross sections. On the whole, the agreement is satisfactory (levels with equal  $n$  and  $l$  were unified in<sup>[66]</sup> so that the curves of<sup>[66]</sup> have sharper jumps than actually exist). An attempt<sup>[229]</sup> to correct the functions  $\xi(\nu)$  for Ar, such as to take into

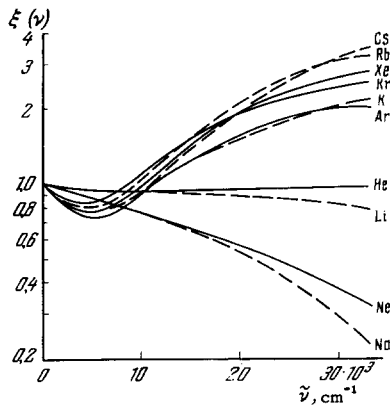


FIG. 11. Comparison of the functions  $\xi(\nu)$  obtained for inert gases (solid lines) and for alkali metals (dashed).

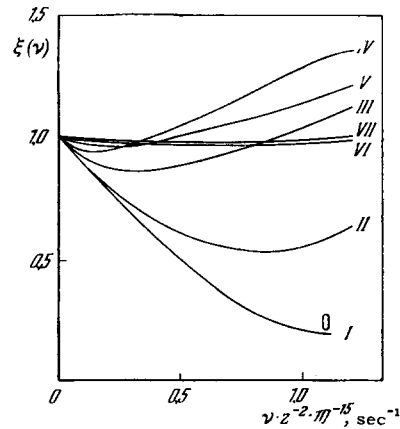


FIG. 12. Plots of  $\xi(\nu)$  for oxygen ions.

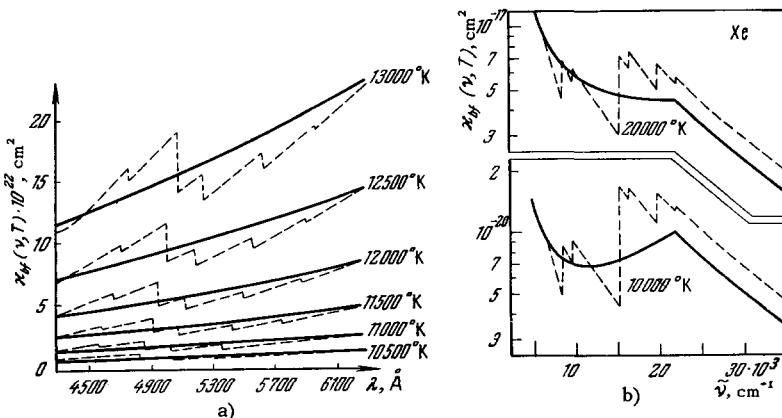


FIG. 13. Comparison of the absorption coefficients obtained by direct summation<sup>[62,66]</sup> (dashed) with those calculated by means of (2.3) (solid lines); a – nitrogen, b – xenon ( $\Sigma_1 = 9$  for N and  $\Sigma_0 = 1$  for Xe, free-free transitions disregarded).

account the real arrangement of the levels, led to an error.

The coefficients of photoionization absorption of Ne, Ar, Kr, and Xe were recently calculated<sup>[230]</sup> by direct summation, and agreement with the integral formula (2.3) was likewise obtained. The individual sections were calculated in<sup>[230]</sup> not with the aid of (1.8), but by direct calculation of radial integrals with Coulomb functions. This was due to a criticism expressed in<sup>[89]</sup>. However, the results differed only slightly from (1.8).

We note the arbitrariness of the choice of  $\nu_g$  in formulas (2.3)–(2.6). It must be remembered, however, that individual cross sections sometimes do not correspond to the Burgess-Seaton formulas (see 1.4); the summed results are apparently more reliable than the individual cross sections. The choice of  $\nu_g$  affects  $\xi(\nu)$  (via  $\chi_{II'}(\epsilon)$ ); however, the possible changes are small as was verified by direct calculations in<sup>[64]</sup>.

An estimate of the free-free transitions in the field of the  $O^+$  ion, carried out in<sup>[31]</sup> by the Hartree-Fock method, agrees qualitatively with  $\xi(\nu)$ . A recent paper<sup>[231]</sup> gives detailed calculations of the matrix elements of free-free transitions using wave functions obtained by the quantum-defect method<sup>[26, 50]</sup>. There is still no Maxwellian averaging in<sup>[231]</sup>, nor are results given for the absorption coefficients due to the sum of all  $II'$  transitions. It is therefore not clear whether the results of<sup>[231]</sup> are a noticeable improvement on the results of<sup>[88]</sup>. We note that, in accord with<sup>[88]</sup>, it is found in<sup>[231]</sup> that the results of<sup>[26]</sup> for bound-free transitions cannot be directly extrapolated to free-free transitions.

The analysis presented in this section is valid for frequencies higher than the plasma frequency. Problems in the theory of radiation in the region of the plasma frequency are investigated, for example, in<sup>[232]</sup>.

### III. ELECTRON TRANSITIONS IN THE FIELD OF A NEUTRAL ATOM

#### 3.1 Photodetachment

The photodetachment cross sections were calculated by formula (1.1) in the same manner as the photoionization cross sections, but the requirements imposed on the methods of calculating the wave functions turn out to be somewhat different. The point is that whereas in photoionization the influence of the external electron on the core is a correction to the Coulomb interaction, in photodetachment this influence is the sole cause of the long-range interaction between the atom and the external electron (whether in the bound or in the free state). Therefore the effects of polarization, distortion, correlation, etc. can be much more significant in calculations for photodetachment.

The most thoroughly investigated was photodetachment from the hydrogen ion  $H^-$ . The relative simplicity

of the two-electron system makes it possible to employ in this case high-precision methods of calculating the wave functions and to obtain good agreement with the available experimental data. A review of the results for  $H^-$  is given in<sup>[233]</sup>, and in addition we refer to<sup>[234–236]</sup>. So far, similar calculation methods cannot be applied to more complex ions.

The most approximate calculations of photodetachment are made with wave functions obtained for a static central self-consistent potential of the unperturbed neutral atom. These calculations are highly unreliable: the results of the calculations for  $C^-$ <sup>[237]</sup> exceeded the subsequently obtained experimental data<sup>[238]</sup> by one order of magnitude. A discrepancy by one order of magnitude (but in the opposite direction) between the calculation<sup>[239]</sup> and the subsequent experiments<sup>[233]</sup> was obtained also for  $O^-$ . The corrected calculations performed later on give more successful results: for  $C^-$ , the calculations of<sup>[240]</sup> are already much closer to the experimental curve, although they still deviate greatly from it in the near-threshold region.

It was proposed in<sup>[241]</sup> to take into account the polarization potential in the calculation of the photodetachment of  $O^-$ . This was done in more consistent fashion in<sup>[242]</sup>. The results of<sup>[242]</sup> were extended and somewhat improved in<sup>[243]</sup>, where the cross sections were also obtained for  $C^-$ ,  $F^-$ , and  $Cl^-$ . The gist of the procedure is as follows: a) The self-consistent potential  $V(r)$  of the unperturbed atomic core is obtained. b) The radial Schrödinger equation for the bound state

$$\left[ \frac{d^2}{dr^2} - 2V(r) + \frac{\alpha}{(r^2 + r_p^2)^2} - \frac{l(l+1)}{r^2} - \beta^2 \right] R_{\beta l}(r) = 0, \quad (3.1)$$

is solved; the bound-state energy  $\beta^2$  is obtained here from experiment or from other calculations,  $r_p$  is chosen equal to the average distance from the nucleus to the outer electrons of the unperturbed atomic core, and the polarizability  $\alpha$  is determined as the eigenvalue of Eq. (3.1) together with the wave function  $R_{\beta l}(r)$ . c) The free wave functions  $R_{kl}(r)$  are obtained using the already known value of  $\alpha$  from (3.1) and replacing  $(-\beta^2)$  by  $k^2$ . The obtained wave functions are most reliable for large distances, so that the radius matrix element is used in calculating the photodetachment cross section.

The effects of exchange, correlation, etc., are taken into account in (3.1) indirectly, since an experimental value is used for  $\beta^2$ . Therefore the value of  $\alpha$  determined from (3.1) need not agree with the polarizability of the atomic core. Calculations<sup>[242, 243]</sup> show, however, that the difference is very negligible (14% for C, 9% for O, and 0.7% for F). This gives reason for hoping that the indirectly allowed-for factors play a much smaller role than the potential  $\alpha/2r^4$ . These effects, however, can be different in the bound and in the free states.

An attempt to take into account the correlation in the free state was made in<sup>[244]</sup> with  $C^-$  as an example, by introducing into the wave function the dependence

on the interelectron distance of the free  $s$ - and bound  $p$ -electron. The analytic form of this dependence was determined by the boundary conditions and by intuition, while the parameters were determined from the Hulthen variational principle. The agreement obtained in<sup>[244]</sup> between the velocity and radius matrix elements is much better than in the model of the rigid self-consistent potential with exchange<sup>[240]</sup>, but the deviation from experiment was much greater than in<sup>[240]</sup>.

In<sup>[245]</sup>, which so far is only of methodological interest, an attempt was made (with  $O^-$  as an example) to use the analytic properties of the amplitude of scattering of an electron by a neutral atom (the bound wave function is not investigated here). The obtained cross section turns out to be closer to experiment than that calculated in the Born approximation.

An attempt to calculate the photodetachment of  $H^-$  and  $Li^-$  was made in<sup>[18]</sup>. It was proposed that each of the two  $s$ -electrons, which do not interact with each other, moves in a model potential  $V(r) = r_0^{-1} - r^{-1}$  if  $r \leq r_0$  and  $V(r) = 0$  if  $r \geq r_0$  (the  $1s^2$  shell of  $Li^-$  is combined together with the nucleus). The parameter  $r_0$  is determined beforehand from the condition that the potential  $V(r)$  correspond to only bound state and that the energy of this state be equal to the affinity energy of the atom under consideration. Inasmuch as the Schrödinger equation is solved for the chosen  $V(r)$  exactly, this ensures the equality of the three forms of the matrix elements and the satisfaction of the sum rules (1.17) and (1.18)\*; this, however, is not a sufficient criterion for the accuracy of the calculated cross section. The calculation made in<sup>[18]</sup> for  $H^-$  agrees well with the variational calculations, and the cross section for photodetachment of  $Li^-$  was calculated by assuming that the affinity energy is 0.384 eV. A calculation for  $Li^-$  was repeated by the same procedure in<sup>[246]</sup> for an affinity energy 0.8 eV, and the form of the curve as well as the absolute magnitude at the maximum changed insignificantly, but the position of the maximum shifted by 0.4 eV. This allows us to assume that the affinity energy can be deduced from the position of the maximum. A model calculation for  $O^-$  using an ineffective procedure is given<sup>[247]</sup>.

Of use in simplifying the numerical calculations made with the results of<sup>[248,249]</sup> (and of the later<sup>[250]</sup>), in which analytic expressions for the photodetachment cross sections are proposed. They use for the free functions Eq. (3.5) with published data for the phase<sup>[248]</sup> or a plane wave<sup>[249]</sup>, and for the bound states the published self-consistent functions approximated by linear combination of exponentials. Thus, the main task, that

of calculating the bound and free wave functions, is not considered in<sup>[248,249]</sup>. It must also be recalled that the self-consistent functions can lead to significant errors in the photodetachment cross section, all the more since approximation formulas for the wave functions have in<sup>[248-250]</sup> an asymptotic behavior which does not agree with (3.10). The assumption  $\delta_p = 0$  made in the calculations for  $Li^-$ ,  $Na^-$ , and  $K^-$ <sup>[249]</sup> is doubtful. Cross sections for  $C^-$ ,  $O^-$ ,  $N^-(^3P)$ ,  $Cl^-$ , and  $F^-$  are also calculated in<sup>[248,249]</sup>.

Let us consider the measurements of the photodetachment cross sections. In the crossed-beam method<sup>[233]</sup> the photodetachment cross section is determined from the small current of free electrons produced in a high vacuum when two mutually perpendicular beams cross, one containing negative ions separated by a mass analyzer, and the other in intense beam of visible light from a light filter. The relative frequency dependence of the photodetachment cross section is measured. The absolute values are obtained by measuring the integral cross section or by comparison with the already known cross section for another ion.

Vapor emission and absorption cross sections were investigated in<sup>[251-255]</sup>. Salts were evaporated by passage of a shock wave in a shock tube filled with an inert gas. The choice of the salt was determined by the requirement of obtaining a sufficient concentration of negative ions at relatively low temperature, so that the photodetachment be strong and the only source of absorption<sup>[251,252,254]</sup> (halides of alkali metals were used in the investigation of the halogen ions). For the emission spectra<sup>[253,255]</sup> it was accordingly necessary to obtain a sufficient concentration of electrons and of the corresponding atoms at a moderate temperature, so as to make the radiation adhesion strong and the only source of radiation ( $K_2O_2$  and  $Rb_2O$  were used for the investigation of  $O^-$ ). The photographic method ensures high resolution, and is therefore advisable for the investigation of the fine structure of the spectrum, particularly the behavior of the cross sections at threshold; measurement of photodetachment in the ultraviolet became possible for the first time. Measurements using this procedure yielded reliable relative results; the error in the absolute values is still large, since no reliable control over the establishment of thermodynamic equilibrium has been exercised.

Radiative adhesion spectra at relatively high temperatures were investigated in discharges<sup>[202,203,256-258]</sup> and in shock tubes<sup>[259-262]</sup>. Other radiative processes play an important role under these conditions, so that the reliability with which the contribution of the radiative adhesion is determined depends on the extent to which the other processes can be calculated (see Sec. IV).

The measurements are summarized in Table VI. We see that the number of investigated ions is small, and the spectral intervals of the measurements are

\*The rule (1.17) is satisfied<sup>[18]</sup> if model wave functions are also substituted in the right side of this equation. On the other hand, to check the approximate cross sections, it is necessary to calculate the right-side of (1.17) with exact wave functions. The rule (1.18) is rigorously satisfied in the model analysis<sup>[18]</sup> only for  $H^-$ .

Table VI. Measurements of the photodetachment cross sections

Ion, threshold $\text{\AA}$	Method	Measurement range ( $\text{\AA}$ )	Ion, threshold $\text{\AA}$	Method	Measurement range ( $\text{\AA}$ )			
$\text{H}^-$ , 16 439	A 233	13000—4000	$\text{O}^-$ , 8386 $\pm$ 6	B 257	Thresh- 3100 old			
	B 260	6000—4000		A 263				
	B 261	6000—4000		A 264				
$\text{C}^-$ , 10 000 $\pm$ 250 $\text{N}^-$ , ?	B 262	8000—3000	$\text{S}^-$ , 6000 $\pm$ 200	C 252	Near threshold			
	A 238	Thresh- 4000 old				$\text{F}^-$ , 3595 $\pm$ 5	B 258 *)	Near threshold3000
	B 202	6300—4300	Cl $^-$ , 3427 $\pm$ 4	C 251, 253, 254	Near threshold			
	B 256	7500—2700				Br $^-$ , 3688 $\pm$ 4	C 251, 253, 254	Near threshold
	B 259	5000						
B 257	Thresh- old 4000	C 251, 253, 254	Near threshold					
A 233	6300—4300							
$\text{O}^-$ , 8386 $\pm$ 6	B 203	6300—4300						
	C 255	Near threshold						

A — method of cross beams, B — measurement of plasma emission spectra, C — measurement of vapor emission and absorption spectra.

\*Qualitative study of the spectrum.

small. Therefore no extensive comparison of experiments with calculation can be made. The following was found for individual ions: For  $\text{H}^-$ , as indicated above, the agreement is good. The calculations for  $\text{O}^-$  and  $\text{C}^-$  could in general be satisfactorily reconciled<sup>[243]</sup>; we note only that the maxima of the experimental curves are closer to the threshold than those of the theoretical ones. Tentative data for  $\text{F}^-$  and  $\text{Cl}^-$  do not contradict the calculations<sup>[243, 249]</sup>.

Two photodetachment thresholds corresponding to two states of the produced atom,  $\text{X}^- (^1\text{S}_0) - \text{X} (^2\text{P}_{1/2}$  and  $^2\text{P}_{3/2})$  were observed for halogens<sup>[251-253, 266, 268]</sup>. The threshold structure, which is due also to the splitting of the level of the most negative ion, was investigated for oxygen:  $\text{O}^- (^2\text{P}_{3/2}$  and  $^2\text{P}_{1/2}) \rightarrow \text{O} (^3\text{P}_2, ^3\text{P}_1, ^3\text{P}_0)$ <sup>[255]</sup>. For  $\text{O}^-$  there was observed also a threshold corresponding to the formation of an atom in the first excited state:  $\text{O}^- ^2\text{P} \rightarrow \text{O} ^1\text{D}$ <sup>[263]</sup>. Photodetachment from the excited state of a negative ion was registered for  $\text{C}^-$ <sup>[238]</sup>.

To check on the experimental and theoretical cross sections, one can use sum rules, which are more useful in the case of photodetachment than in the case of photoionization, since the spectrum consists of a continuum only. A reliable comparison has been made so far only for  $\text{H}^-$ <sup>[235]</sup>. For the remaining ions, the analysis is made difficult by the fact that the cross sections have not been obtained in a sufficiently broad interval<sup>[233]</sup>. The rule (1.16), which requires a relatively narrow interval, can very rarely be used because of the lack or unreliability of the values of  $\alpha$ . Data are available for  $\text{F}^-$  ( $\alpha = (0.8 - 1.2) \times 10^{-24}$ <sup>[218, 267]</sup> and  $1.8 \times 10^{-24} \text{ cm}^3$ <sup>[219]</sup>) and for  $\text{Cl}^-$  ( $(3 - 3.5) \times 10^{-24}$ <sup>[218]</sup> and  $6.2 \times 10^{-24} \text{ cm}^3$ <sup>[219]</sup>). Calculations by integration of the calculated cross sections yield  $2.2 \times 10^{-24}$  ( $\text{F}^-$ ) and  $5.4 \times 10^{-24}$  ( $\text{Cl}^-$ ); the cross sections obtained in<sup>[243]</sup> are thus apparently too high.

In the study of photodetachment it is necessary to know the values of the affinity energies. A review of

the experimental and theoretical values is given in<sup>[268]</sup>\*. Under plasma conditions, a decrease in the affinity energy may be observed<sup>[272]</sup>. Unlike the drop in the ionization potential, this effect becomes manifest in pure form and no strong lines are superimposed on it. For ions with low affinity energy, the perturbing action of the surrounding particles may lead to the absence of such ions even at not too dense a plasma. Under plasma conditions, a change may also occur in the photodetachment cross section, but this question has not yet been investigated.

So far we have spoken of stable negative ions. Recently, unstable excited states of negative ions have been under persistent study<sup>[93, 273-277]</sup>. The existence of such ions and their energy levels were established from the appearance of the resonances in the scattering of electrons by atoms. The number of such states turns out to be quite appreciable. Their influence on the absorption and emission spectra has so far not been considered. Unstable ions, if they play any role at all, can appear primarily in the emission spectra, since the brightness due to radiative adhesion is proportional to the concentration of the electrons and atoms and does not depend on the ion concentration.

### 3.2 Free-free Transitions

The transitions investigated in greatest detail were those in the field of the hydrogen atom. The first calculations were made in the Born approximation and, as shown by subsequent calculations, gave values that differed from the true ones by one or two orders of magnitude. This was followed by a number of investigations in which account was taken of all the main effects, which were made more precise. Of all the investigations aimed at independently determining and

\*See also <sup>[233, 269]</sup>. Data for  $\text{Li}^-$ ,  $\text{Na}^-$ , and  $\text{K}^-$  are gathered in <sup>[249]</sup>. Measurements for  $\text{K}^-$ ,  $\text{Rb}^-$ , and  $\text{Cs}^-$  were made in <sup>[270]</sup>. The ions  $\text{Al}^-$ ,  $\text{Ga}^-$ ,  $\text{In}^-$ , and  $\text{Tl}^-$  were observed in <sup>[271]</sup>.

refining more accurately the wave functions, followed by direct calculation of the matrix element, the greatest accuracy was attained in<sup>[278-280]</sup>.

Free-free transitions in the field of multielectron atoms were investigated numerically using nitrogen and oxygen as examples, in the series of papers<sup>[281-284]</sup>. The first calculations<sup>[281,282]</sup> were made for the self-consistent field of the unperturbed atom. This was followed<sup>[283,284]</sup> by investigation of exchange and polarization effects. The polarization was taken into account by perturbation theory. So far there are no sufficiently well developed consistent methods for taking polarization into account, so that one cannot expect the results of<sup>[283,284]</sup> to be perfectly reliable, all the more since the allowance for the polarization leads to a decrease in the order of magnitude of the bremsstrahlung intensity. The role of exchange is much weaker<sup>[283]</sup>.

In<sup>[285]</sup>, three calculations were made for nitrogen: for the field of the unperturbed atom and for the potential used in (3.1), using two pairs of not greatly differing values of  $\alpha$  and  $r_p$ . The results have shown that allowance for the polarization potential reduces the absorption coefficient by almost two orders of magnitude, and that even small changes in the parameters greatly influence the result.

These estimates show that the calculations are highly sensitive, so that calculations<sup>[286]</sup> for crude model potentials are hardly meaningful.

A variational principle was used directly in<sup>[287]</sup> for the matrix element (as applied to the hydrogen atom). The calculations were made with two- and four-parameter wave functions. The accuracy attained was the same as in calculations with ordinary variational principles carried out with a large number of parameters. Reference<sup>[287]</sup> is in practice a continuation of the general variational principles formulated in<sup>[14]</sup>. We note that the asymptotic form used in both<sup>[287]</sup> and<sup>[14]</sup> for the wave functions neglects the polarization potential and other long-range potentials.

In a group of papers, the probability of the free-free transitions is related to the cross section  $\sigma_{el}$  for the elastic scattering of an electron by an atom. Such a connection was first established with the aid of asymptotic wave functions (see Sec. 3.3). In<sup>[288]</sup> is given a simplified method using the classical expression for the energy  $d\epsilon_\nu$  radiated in the spectral interval from  $\nu$  to  $\nu + d\nu$  upon collision of an electron with an atom ( $2\pi\nu\tau \ll 1$ ),  $d\epsilon_\nu = (4/3)(e^2/c^3)(\Delta v)^2 d\nu$ , where  $\Delta v$  is the change in the velocity vector upon collision, and  $\tau$  is the collision time. If  $h\nu \ll E_0 = mv^2/2$ , then averaging over the scattering angle yields  $(\Delta v)^2 = 2v^2(1 - \cos \theta)$ , and the differential effective emission cross section is

$$d\sigma_\nu = \sigma_{el} \overline{d\epsilon_\nu/h\nu} = (8e^2v^2/3c^3h\nu) \sigma_{tr} d\nu, \quad (3.2)$$

where  $\sigma_{tr} = \sigma_{el}(1 - \overline{\cos \theta})$  is the transport cross section. Equation (3.2) differs from (3.16) only in the ab-

sence of factors which have little effect when  $h\nu \ll E_0$ , and in the fact that  $\sigma_{tr}$  is preferable to  $\sigma_{el}$ .

An attempt to relate free-free transitions with scattering in general form was made in<sup>[298]</sup>. A diagram technique developed for this purpose has made it possible to present lucidly the structure of the processes and to write down both general expressions and the contributions in any order of perturbation theory. The sum of all the diagrams of the perturbation theory can be represented in the form of six diagrams (Fig. 14). The free electron corresponds here to a thin line, the atom to a heavy one, the photon to a dashed line, and the sum of all diagrams describing the scattering of an electron is denoted by a shaded rectangle, which can include thus also inelastic processes.

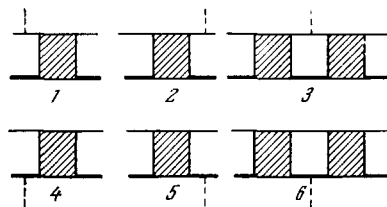


FIG. 14. Diagrams corresponding to free-free transitions.

It is seen from Fig. 14 that free-free transitions are actually connected with the scattering process, but it is necessary to know the scattering amplitudes off the energy shell, and not the amplitudes of the real scattering. Diagrams 1-3 correspond to electron radiation, diagrams 4-6 to atom radiation. Assumptions concerning the possible role of the atom radiation were advanced earlier, and the results of<sup>[289]</sup> make it possible to estimate these effects quantitatively.

Equating the scattering amplitude to its value on the energy shell (this can be done when  $h\nu \ll E_0$ , and apparently also when the cross section depends weakly on the energy), the authors of<sup>[289]</sup> found that the contribution of diagrams 3-6 can be neglected, and diagrams 1-2 yield an expression that differs from (3.2) only by the factor  $(1 - h\nu/E_0)^{1/2}$ . We note that this factor, which is not important when  $h\nu \ll E_0$ , describes correctly the vanishing of the cross section as  $h\nu \rightarrow E_0$ . In the approximation of one partial wave (but not necessarily the s-wave), diagrams 1 and 2 yield (3.16). Averaging over a Maxwellian distribution, the authors of<sup>[289]</sup> obtained

$$\kappa(\nu, T) = C_7 N_e N_a (kT)^{-1/2} \overline{\sigma_{el}} \nu^{-2} \exp(h\nu/2kT) K_2(h\nu/2kT),$$

$$C_7 = 2e^2 h (3\pi m c \sqrt{2\pi m})^{-1}, \quad (3.3)$$

where  $K_2(x)$  is a Bessel function of imaginary argument.

A rough experimental verification of the connection between the radiation intensity and the elastic-scattering cross section was made in<sup>[290]</sup>. The results of the measurements ( $T = 6000-9000^\circ\text{K}$ ,  $\lambda = 2-8 \mu$ ) were ap-

proximated by the Kramers formula, from which the value of  $Z^2$  was obtained. As seen from the table, a correlation exists between  $Z^2$  and  $\sigma_{el}$ . We note that the Kramers formula is physically meaningless here,

	$Z^2 \cdot 10^2$	$\bar{\sigma}_{el} \cdot 10^{16}$
O	0.2	0.2
N	0.9	0.5
N <sub>2</sub>	2.2	2

so that its use in a wide interval of  $\lambda$  and  $T$  can lead to an appreciable error. In particular, from (3.3) in the limit  $h\nu/2kT \ll 1$  we have

$$Z^2 = (2\sqrt{3}/\pi^2 e^4) \sigma_{el}(T) (kT)^2; \quad (3.4)$$

at large frequencies,  $Z^2$  depends also on  $\nu$ :  $Z^2 = (\sqrt{3}/4\pi e^4 \sqrt{\pi}) \bar{\sigma}_{el}(T, \nu) (h\nu)^{3/2} (kT)^{1/2}$  if  $h\nu/2kT \gg 1$ .

The simple connection with the scattering cross section has a very limited region of validity. In particular, nothing definite can be said so far for atoms with large polarizability and for atoms with the Ramsauer effect. One can, however, expect for them a greater role of the radiation from the atoms themselves.

### 3.3 Calculations with Asymptotic Wave Functions

In the simplest approximation, one neglects the long-range forces acting between the electron and the atom. Then the radial function of the free electron outside the atomic core takes the form<sup>[291]</sup>:

$$R_{kl}(r) = (-1)^l \sqrt{\frac{2}{\pi}} \frac{r^{l+1}}{k^l} \left( \frac{d}{r dr} \right)^l \frac{\sin [kr + \delta_l(k)]}{r}, \quad (3.5)$$

with

$$R_{kl}(r) \xrightarrow{r \rightarrow \infty} \sqrt{2/\pi} \sin \left[ kr - \frac{\pi}{2} l + \delta_l(k) \right] \quad (3.6)$$

(formulas (3.5) and (3.6) coincide for the s-wave). The phase shift  $\delta_l(k)$  is due to the potential of the atomic core. It is significant, however, that the analytic form of the dependence of  $\delta_l(k)$  on  $k$  at low energies is universal. The quantity

$$f_l(k^2) = k^{2l+1} \operatorname{ctg} \delta_l(k) \quad (3.7)$$

can be expressed at small values of  $k$  by an approximation linear in  $k^2$ :

$$f_l(k^2) = -a_l^{-1} + \frac{1}{2} r_{0l} k^2 \quad (3.8)$$

(it is sometimes useful to expand the inverse  $f_l^{-1}(k^2) = -a_l - (1/2) a_l^2 r_{0l} k^2$ ). The distinguishing features of the short-range potential become manifest only in the values of the constants  $a_l$  and  $r_{0l}$ <sup>[54-57]</sup>.

The function  $f_l(k^2)$  can be continued analytically to negative energies. It is necessary then to make the substitutions  $k \rightarrow i\beta$  and  $\cot \delta_l(k) \rightarrow i$ <sup>[54]</sup>. We obtain a

connection between  $a_l$  and  $r_{0l}$  and the eigenvalues  $\beta$ <sup>[54,292,293]</sup>:

$$(-1)^l \beta^{2l+1} = a_l^{-1} + \frac{1}{2} r_{0l} \beta^2 \quad \text{or} \quad (-1)^l \beta^{-2l-1} = a_l - \frac{1}{2} a_l^2 r_{0l} \beta^2. \quad (3.9)$$

We note that inasmuch as  $\beta > 0$  and the second term of the expansion is smaller than the first, the equations of (3.9) can hold only at a definite sign of the scattering length. An opposite sign of the scattering length indicates that it is impossible to produce a bound state<sup>[54]</sup>.

For the bound state we have outside the core

$$R_{\beta l}(r) = N r^{l+1} \left( -\frac{1}{\beta r} \frac{d}{dr} \right)^l \frac{e^{-\beta r}}{r}. \quad (3.10)$$

With the aid of the procedure indicated in the derivation of (1.10) we get

$$N^{-2} = (2\beta)^{-1} [1 + 2l - (-1)^l r_{0l} \beta^{1-2l}]. \quad (3.11)$$

The same result is obtained also from an analysis of the meaning of the constant  $r_{0l}$ <sup>[294]</sup>.

The obtained wave functions make it possible to determine the character of the behavior of the photodetachment cross section at the threshold<sup>[295,296]</sup>

$$\sigma \sim k^{2l_m+1} [1 + O(k^2)], \quad (3.12)$$

where  $l_m$  is the smallest value of the number  $l$  for the free states at which the dipole transition is allowed. Thus, for  $H^-$  and alkali-metal ions  $\sigma \sim k^3$ , and the cross section starts out from the threshold with a zero slope, while for  $O^-$ ,  $C^-$ , etc.,  $\sigma \sim k$  and the cross section (as a function of the energy, frequency, or wavelength) increases vertically upward from the threshold.

The asymptotic functions (and the radius matrix element) can be used also for a complete determination of the transition probabilities, the result being given in analytic form. For the photodetachment cross section this was proposed in<sup>[242]</sup> with  $O^-$  as an example ( $p \rightarrow s, d$ -transitions). The constant  $N$  and the phase  $\delta_s$  were obtained by numerically solving Schrödinger's equations (see p. 71). Photodetachment of  $H^-$  ( $s \rightarrow p$  transition) was considered in<sup>[292]</sup> under the assumption that  $\delta_p = 0$ . The obtained

$$\sigma_{sp}^0 = \frac{64}{3} \pi^2 \alpha_0 a_0^2 N^2 k^3 E^{-3}. \quad (3.13)$$

The value of  $N$  was determined from (3.9) and (3.11). The results of<sup>[242,292]</sup> are in satisfactory agreement with the experimental data. Allowance for the phase shift  $\delta_p$  has been made for  $H^-$  in<sup>[297]</sup>; they obtained

$$\sigma_{sp} = \sigma_{sp}^0 \left[ \cos \delta_p + \frac{1}{2} (\beta^2 + 3k^2) \beta k^{-3} \sin \delta_p \right]^2. \quad (3.14)$$

The cross section determined under the assumption  $\sin \delta_p = \tan \delta_p = a_p k^3$  yields no better agreement with the experimental data in the short-wave part of the measurement range than the assumption  $\delta_p = 0$ . Good agreement is attained by putting  $\sin \delta_p = \tan \delta_p = a_p k^3 (\beta^2 - k^2) (\beta^2 + 3k^2)^{-1}$ .<sup>[297,298]</sup>



The use of asymptotic wave functions for the calculation of the matrix elements of free-free transitions was proposed in<sup>[299]</sup> and later in<sup>[300]</sup>. In these papers, only  $s \rightarrow p$  and  $p \rightarrow s$  transitions are considered. The wave functions are taken in the form (3.5), but the phase shift  $\delta_p$  is assumed equal to zero. The expression obtained for the matrix element is

$$\frac{1}{2} k_1^2 \sin \delta_s(k_0^2). \quad (3.15)$$

Calculation with the aid of (3.15), besides its simplicity, has, compared with direct calculations of the matrix elements, the advantage that the usual variational principles give the values of the phase much more accurately than the values of the wave functions; the phase can also be determined from the experimental data (see below).

Calculations were made in<sup>[299]</sup> for hydrogen and repeated and expanded later in<sup>[301,302]</sup> with account taken of new values of  $\delta_s(k)$ . Calculations for He are given in<sup>[303]</sup> and for the  $H_2$  molecule in<sup>[304]</sup>. Formula (3.15) is used also in<sup>[283,284]</sup> for O and N.

Expression (3.15) takes into account only  $\delta_s(k)$ . Extension to the case  $\delta_p(k) \neq 0$  entails no fundamental difficulty. One can also consider the transitions  $p \rightarrow d$ ,  $d \rightarrow p$ ,  $d \rightarrow f$ , etc. The obtained expressions are more complicated and include (to eliminate divergences) a small cutoff radius corresponding to the dimension of the atomic core.

Expression (3.15) makes it possible to connect the probability of the free-free transitions with the cross section for elastic scattering of slow electrons (for which experimental data are frequently available), inasmuch as  $\sigma_{el} \equiv \sigma_{tr} \sim \sin^2 \delta_s$  when the higher phases are neglected. The expression obtained for the photon emission cross section<sup>[300]</sup> ( $mv^2/2 = E_0 - h\nu$ ) is

$$d\sigma_v = (4e^2v^2/3c^3h\nu) \sqrt{1 - hv/E_0} [\sigma(v') + \sigma(v) - (hv/E_0) \sigma(v)] dv \\ \cong (4e^2v^2/3c^3h\nu) \sqrt{1 - hv/E_0} (2 - hv/E_0) \bar{\sigma} dv. \quad (3.16)$$

No such simple connection is obtained when  $\delta_p$  is taken into account. In<sup>[305]</sup>, using transitions in the argon field as an example, results of cross sections calculated by different formulas are compared. It was found that certain approximations, particularly (3.16), can lead to significant errors.

When using the asymptotic wave functions to calculate photoionization and free-free transitions in the ion field, we had at our disposal also the quantum-defect method, which afforded a semi-empirical method of determining the phases. There is no semi-empirical method as yet for determining  $\delta_l(k^2)$  (or the parameters  $a_l$  and  $r_{0l}$ ) in calculations for photodetachment and free-free transitions. This greatly decreases the usefulness of such formulas as (3.13)–(3.15). Some way out is provided by the use of experimental elastic-scattering cross sections directly via (3.16), and also by reconstructing the values of all the partial phases

from the cross section and substituting them in expressions of the type (3.14) and (3.15).

Another possibility is indicated in<sup>[306]</sup>. With the aid of the quantum-defect method we can calculate the phases of the wave functions of the electron in the field of ions of an iso-electron series, and then attempt to extrapolate these data in order to find the phases for the neutral atom. For example, from the phases for the ions  $Na^+$ ,  $Mg^{++}$ ,  $Al^{+++}$ , etc. one can determine the phases for the Ne atom. A method of such an extrapolation is proposed in<sup>[306]</sup> for  $\delta_s(k)$ . Development of the extrapolation procedure, and also its extension to  $l > a$ , will make it possible to obtain data for the calculation of photodetachment and free-free transitions.

Another important shortcoming of formulas (3.13)–(3.15), etc. is the fact that they do not take into account (or can take into account only partially) polarization and similar long-range forces between the electron and the atomic core; nor is account taken of possible effects due to the multi-electron nature of the problem (all this has much in common with the discussion presented in pp. 56 and 57).

The behavior of the wave functions in a field ( $-\alpha r^{-4}/2$ ) is considered in<sup>[293,307]</sup>. The wave function outside the atomic core is expressed in terms of a Mathieu function, and at large distances the normalized function differs from (3.6) by an additional factor that depends on  $k$  (see<sup>[308]</sup>). The expansion (3.8) is obtained, but the analytic dependence of  $f_l(k^2)$  on  $\delta_l(k)$  turns out to be more complicated than (3.7).<sup>\*</sup> For comparison with the earlier expansion, one can separate  $\tan \delta_l$ . The result obtained for the s-wave is<sup>[293,307]</sup> ( $\gamma^2 = \alpha/a_0$ )

$$k^{-1} \operatorname{tg} \delta_s(k) = -a_s - \frac{\pi}{3} \gamma^2 k - \frac{4}{3} a_s \gamma^2 k^2 \ln 1.23 \gamma k \\ - a_s^2 \left( \frac{1}{2} r_{0s} + \frac{\pi}{3} \gamma - \pi \gamma^3 / 3 a_s^2 \right) k^2 + \frac{\pi}{3} \gamma^2 k^3 \left( a_s^2 + \frac{7}{117} \gamma^2 \right) + \dots \quad (3.17)$$

The results for  $l > 0$  were  $\delta_l \sim k^{2[291]}$  and the expansions<sup>[293,307]</sup>

$$\operatorname{tg} \delta_p(k) = \pi \gamma^2 k^2 / 15 - \gamma^2 k^3 a_p / 9 + O(k^4), \\ \operatorname{tg} \delta_l(k) = \pi \gamma^2 k^2 / (2l+3)(2l+1)(2l-1) + O(k^4), \quad l > 1. \quad (3.7')$$

These expressions were used in<sup>[310]</sup> to determine  $a_s$ ,  $r_{0s}$ , and  $a_p$  of inert gases from the experimental cross sections  $\sigma_{el}$  and the known polarizability  $\alpha$ .

The expansions (3.17) etc. are valid in a relatively narrow region of small energies, while the expansion

<sup>\*</sup>The behavior of the phase  $\delta_s(k)$  in a field ( $-\alpha r^{-4}/2$ ) was considered also in<sup>[309]</sup>. The Schrödinger equation was solved approximately, making it possible to construct from  $\tan \delta_s(k)$ , the polarizability, and from  $k$  an expression which actually corresponds to  $f_s(k^2)$ , but which is assumed constant in<sup>[309]</sup>. Thus, the dependence of the phase  $\delta_s(k)$  on  $k$  was determined in<sup>[309]</sup> under the assumption  $r_{0s} = 0$ . As in<sup>[293]</sup> it is indicated in<sup>[309]</sup> that the affinity energy can be used to determine  $\delta_s(k)$ .

Table VII. Measurements of the summary spectra

Gas	Method	$\lambda$ , $\mu\text{m}$	$T$ , $10^3$ °K	Remarks
Hydrogen	B <sub>1</sub> <sup>262</sup>	0.3—0.8	11—18	$N_e = 0.3 - 1.1 \cdot 10^{17}$
Carbon	A <sup>201</sup>	0.28—0.58	12.5—14.5	$p = 1$ atm
C+H	D <sup>314</sup>	0.22—0.7	39	$p = 120$ and $500$ atm
C+N+O	A <sup>224</sup>	0.23—0.65	10.9	$p = 1$ atm
Nitrogen	A <sup>202</sup>	0.43—0.63	10.5—13	$p = 1$ atm
	B <sub>2</sub> <sup>315, 317</sup>	2—6	8	$Q/Q_0 = 0.8$
		3	6.5—9	$p_1 = 1$ mm Hg
	B <sub>1</sub> <sup>259</sup>	0.5	9.25	$Q/Q_0 = 0.2 - 2 \cdot 10^{-2}$
	A <sup>256</sup>	0.25—0.75	11 and 12	$p = 1$ atm
		4.4	12	
	0.5	9.3—11.6		
	B <sup>316</sup>	0.25—0.55	40—50	$N_e \approx 10^{18}$
Oxygen	A <sup>203</sup>	0.43—0.63	10.5—13	$p = 1$ atm
	B <sub>1</sub> <sup>318</sup>	0.5	9—12	$p_1 = 1$ mm Hg
	A <sup>319</sup>	0.3—2.5	9—14	$p = 1$ atm
Air	B <sub>2</sub> <sup>320</sup>	1—4.8	8	$Q/Q_0 = 0.85$
		2—8	8	$Q/Q_0 = 0.9$
		2.4 and 3.9	6—8	$p_1 = 1$ mm Hg
	B <sub>1</sub> <sup>321</sup>	0.25—2	9.65	$p_1 = 0.1$ mm Hg
	B <sub>1</sub> <sup>322</sup>	0.5	9.65	$p_1 = 0.1 - 1$ mm Hg
		0.5—1.3	10.5	$p_1 = 1$ mm Hg
	B <sub>2</sub> <sup>323</sup>	0.2—1	7—11	$p = 0.1 - 1$ atm
	B <sub>1</sub> <sup>317</sup>	0.2—2.8	9.65	$p_1 = 0.1$ mm Hg
	B <sub>1,2</sub> <sup>318</sup>	0.51	9.65	$Q/Q_0 = 10^{-3} - 0.1$
	B <sub>1</sub> <sup>318</sup>	6	8—12	$p_1 = 0.1$ mm Hg
	C <sup>316</sup>	0.25—0.55	40—50	$N_e = 10^{18}$
	C <sup>324</sup>	0.4—0.48	~35	$N_e = 10^{16} - 10^{17}$
	Argon	B <sub>1</sub> <sup>325</sup>	0.42—0.58	10—13
A <sup>326</sup>		0.3—1	16	$p = 1.1$ atm
B <sub>2</sub> <sup>327</sup>		0.48*	10.5	$N_e = 10^{16}$
		0.4—0.7	10.5—13	$p = 1$ atm
		0.4—2.4	11—11.7	
A <sup>206</sup>		0.25—0.75	12	$p = 1$ atm
B <sub>1</sub> <sup>329</sup>		0.41 and 0.45	~10	$p \approx 1$ atm **
B <sub>1</sub> <sup>330</sup>		0.4—0.6	30	$p_1 = 1$ atm
		0.45	24	
B <sub>2</sub> <sup>331</sup>		0.4—0.6	~12	$p = 6$ atm
A <sup>332</sup>		0.4	12	$p = 1$ atm
A <sup>359</sup>		0.35—0.6	~13	$p = 1$ atm
A <sup>333</sup>		0.35—0.8		$p = 5 - 50$ torr
Krypton	B <sub>2</sub> <sup>327</sup>	0.34—0.48*	10.5	$N_e \approx 3 \cdot 10^{16}$
	B <sub>1</sub> <sup>334</sup>	0.43		
		and 0.55***	9—11	$N_e = 0.2 - 1.2 \cdot 10^{17}$
	B <sub>1</sub> <sup>329</sup>	0.43 and 0.49	~10	$p = 1$ atm **
	B <sub>1</sub> <sup>330</sup>	0.45	~38	$p_1 = 1$ atm
	B <sub>2</sub> <sup>331</sup>	0.4—0.6	~13	$p \approx 13$ atm
Kr + H	B <sub>2</sub> <sup>260</sup>	0.4—0.6	11	$p \approx 40$ atm
	B <sub>2</sub> <sup>261</sup>	0.4—0.6	8	$p \approx 40$ atm
Xenon	A <sup>335 ****</sup>	0.2—1.9	8—10	$p \approx 25$ atm
	B <sub>2</sub> <sup>327</sup>	0.48*	10.5	$N_e = 10^{17}$
	B <sub>1</sub> <sup>334</sup>	0.55***	9—11	$N_e = 0.6 - 2 \cdot 10^{17}$
	B <sub>1</sub> <sup>329</sup>	0.43	~10	$p \approx 1$ atm **
	B <sub>2</sub> <sup>331</sup>	0.4—0.6	~13	$p \approx 20$ atm
Chlorine	A <sup>205</sup>	0.28—0.54	10.5—12	$p = 1$ atm
CHCl <sub>3</sub>	A <sup>336</sup>	0.4—0.6	11.2 and 11.5	$p = 1$ atm
Iron	A <sup>337</sup>	0.3—0.5	6.3	$N_e = 3 \cdot 10^{16}$
Mercury	A <sup>338</sup>	0.2—3	~6	$p = 1.6$ atm
	A <sup>339</sup>	1.1—1.6	7.3	$p = 35$ atm
	A <sup>340</sup>	0.28—0.65	7.8	$p = 60$ atm

A — arc discharge, B<sub>1</sub> — incident shock wave, B<sub>2</sub> — reflected shock wave, C — spark, D — capillary discharge, p — pressure in plasma, p<sub>1</sub> — pressure of cold gas ahead of the shock wave front, N<sub>e</sub> — electron density in plasma,  $\rho/\rho_0$  — relative plasma density ( $\rho_0$  — normal density).

\*The relative measurements were made in the range  $\lambda = 0.24 - 0.48 \mu$ .  $T = 7.15 - 12 \times 10^3$  K,  $N_e = 10^{15} - 10^{18}$ .

\*\*Only relative measurements were made; the parameter ranges are:  $N_e^2(kT)^{-1/2} = 10^{31} - 3 \times 10^{34}$  (Ar);  $3 \times 10^{30} - 3 \times 10^{33}$  (Kr);  $10^{29} - 10^{32}$  (Xe).

\*\*\*Relative measurements were made in the range  $\lambda = 0.3 - 0.6 \mu$ .

\*\*\*\*Review of work on xenon high-pressure arcs.

for  $f_l(k^2)$  or  $f_l^{-1}(k^2)$  is apparently applicable in a wider interval. In<sup>[311]</sup> attempts were made to find an expansion that is valid in a wide energy range.

All the results of<sup>[293,307]</sup> were obtained from exact solutions of the Schrödinger equation, which were available for the potential  $(-\alpha r^{-4}/2)$ . An analysis method which does not require knowledge of the exact solution was proposed in<sup>[312]</sup> and used subsequently<sup>[313,308]</sup> for scattering in the field of a quadrupole potential (we recall that this potential is non-central). An expansion was obtained for  $\tan \delta_l$  under the simultaneous action of a quadrupole and polarization potential.

The influence of the nonadiabaticity of the polarization on the character of the dependence of the phase on the energy is considered in<sup>[311]</sup>.

The more accurate values of  $\delta_l(k^2)$  can be used in formulas of the type (3.14) and (3.15). It is not clear, however, whether it is necessary to recalculate anew the matrix elements with the more correct asymptotic functions. It is obvious that the functions (3.5) and (3.6) must be used with a more accurate normalization factor; for the threshold behavior of the photodetachment cross section this has yielded<sup>[308]</sup>

$$\sigma \sim k^{2l_m+1} [1 - Ck^2 \ln k + O(k^2)], \quad (3.18)$$

where the constant C is determined by the polarizability, the quadrupole moment, and  $l_m$ .

The behavior of the cross section at the threshold is investigated in the measurements of<sup>[253-255]</sup>. The results point to the validity of (3.12) for all the investigated ions, although for  $\text{Br}^-$  and  $\text{I}^-$  resonance maxima were observed near threshold<sup>[254]</sup>. These peaks apparently do not pertain to photodetachment proper, although the possibility of autodetachment is not excluded (a phenomenon analogous to autoionization). In<sup>[254]</sup> an attempt was made to verify formula (3.18), but the insufficient accuracy has not made it possible to conclude that (3.18) agrees with the experimental data better than (3.12).

#### IV. SUMMARY SPECTRA

There are now a large number of papers reporting measurements of the spectra of hot gas or plasma. The spectra determined are for the most part those of emission. The absorption coefficient is determined in<sup>[314,330]</sup> (from the change in brightness with increasing layer thickness<sup>[314,330]</sup> and directly, from the attenuation of the transmitted beam<sup>[314]</sup>).\*

The observed spectra are produced as a rule as a result of superposition of spectra due to several elementary processes. The existing theoretical and experimental data on the individual processes considered in the preceding sections make it possible to interpret

\*A new method of measuring the absorption coefficient is considered in<sup>[341]</sup>.

the observed spectra. To this end, however, it is necessary that a complete set of parameters (temperature, pressure, chemical composition, etc.) be determined in the measurements. A summary of the experiments which satisfy to some degree or another this requirement is given in Table VII.

An analysis of the experimental data shows that on the whole the results of the calculations and the measurements for the summary spectra are in satisfactory agreement. Examples of the comparison is shown in Figs. 15–20, under conditions for which different processes predominate. Let us discuss the results of the comparison of the measured and calculated spectra.

We note first that in the interpretation of the continuous spectra it is necessary sometimes to take the role of the molecules into account, even if they are present in small concentrations (for example, in Fig. 19 the concentration of NO is 1/40 that of the atoms). The molecules make a contribution to the continuous spectrum via the same processes as the atoms (recombination radiation and bremsstrahlung, radiative adhesion, etc.), and also via distinct molecular processes (for example, photodissociation). In addition, the analog of spectral line in molecular spectra are bands which, under conditions of increased pressure, mutual superposition, and insufficient resolution, can be taken to be sections of a continuous spectrum.

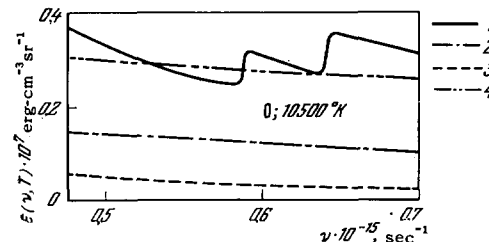


FIG. 15. Radiation brightness of oxygen plasma (10 500°K, 1 atm.). Measurement results: 1 – <sup>[203]</sup>. Calculation results: 2 – recombination radiation and bremsstrahlung (2.6), 3 – bremsstrahlung of O atoms (3.3), 4 – sum, including  $\text{O}^-$  radiative adhesion.

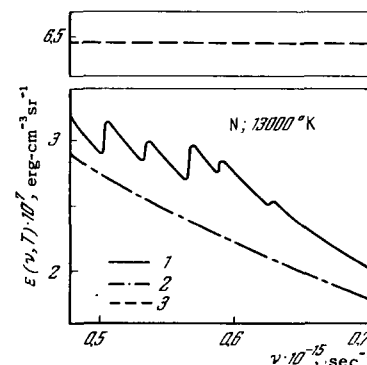


FIG. 16. Radiation brightness of nitrogen plasma (13 000°K, 1 atm.). 1 – Measurement results <sup>[202]</sup>, 2 – recombination radiation and bremsstrahlung calculated in accordance with (2.6), 3 – calculation in accordance with (2.2) at minimum value  $Z^{*2} = 1$ .

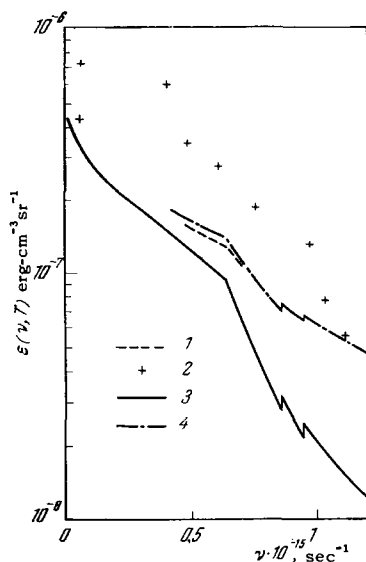


FIG. 17. Radiation brightness of a nitrogen plasma (12 000°K, 1 atm.). Measurement results: 1 - [202], 2 - [256]. Calculation results: 3 - formulas (2.6) and (2.9) (the levels  $3s^2P$  and  $4^1P$  have been separated, the level  $2p^4\ ^4P$  was not taken into account), 4 - the brightness of radiative adhesion of  $N^-$ , estimated under the assumption that the photodetachment cross section is constant at  $10^{-16}$  cm<sup>2</sup> and the affinity energy is 1 eV, has been added to the brightness given by curve 3.

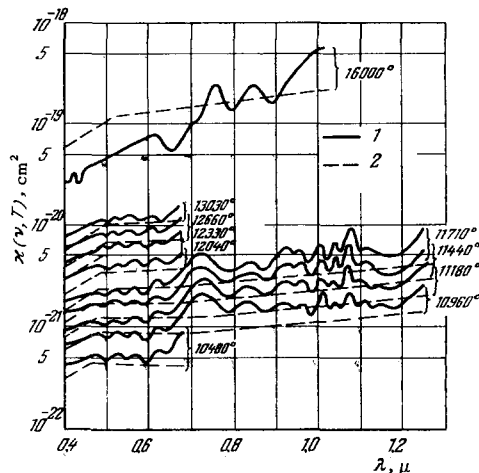


FIG. 18. Absorption coefficient of argon plasma. 1 - Experimental results [328] (for 16 000°K we give the curve calculated in [328] from data of [326]). 2 - calculation according to (2.3).

**Recombination radiation and bremsstrahlung (with ions).** Formulas (2.3)–(2.9) describe satisfactorily the available experimental data. The agreement is both in absolute magnitude and in the frequency and temperature dependences. Cases of  $\xi(\nu) > 1$  as well as  $\xi(\nu) < 1$  are included. The frequency dependence of  $\epsilon(\nu, T)$  when  $\nu < \nu_g$  was experimentally confirmed.

The functions  $\xi(\nu)$  are different for ions of the same chemical element but of different ionization multiplicity. With increasing  $Z$ , they tend to unity. Thus,  $\xi(\nu) \approx 1$  for O III and N III. In [316], the emission spec-

tra of air were actually found to be independent of the frequency under conditions when these ions predominate. We note that for ions the deviation of  $\xi(\nu)$  from unity becomes manifest with increasing  $Z$  at ever increasing frequencies. For an experimental observation of the frequency dependence of  $\xi(\nu)$  it is necessary to carry out measurements in a frequency interval proportional to  $Z^2$ .

At small values of  $\nu$ , when free-free transitions predominate (formula (2.9)),  $\epsilon(\nu, T)$  depends also on  $\nu$  (see Fig. 17), this being due to the deviation of the Gaunt factor from unity. Expression (2.9) is valid up to the plasma frequency near which a sharp decrease of glow is observed [343, 359]. Another possible limitation on the applicability of (2.9), on the low-frequency side, is due to the appearance of reabsorption: with further decrease in frequency, the brightness decreases in accordance with the black-body formula [344, 345].

The agreement between theory and experiment is better for the summary recombination spectra than for the individual cross sections discussed in Sec. 1.4. The reason is that some of the errors which appear in (1.8) for individual cross sections (see Sec. 1.2) cancel each other upon summation.

The levels of the real atom are not uniformly distributed, so that the experimental spectra can have certain nonmonotonic deviations from the smooth curves given by (2.3)–(2.7) (see Fig. 18). Direct summation over all the levels does not always improve the situation markedly, since all the errors of formula (1.8) come into play here. This is confirmed by direct calculations for nitrogen [62].

In comparing theory with experiment, account was taken of the displacement of the photoionization threshold. The value of the factor  $\exp(h\Delta\nu/kT)$  did not differ greatly from unity and amounted to 1.25–1.5. This factor could therefore not influence noticeably the results of the comparison of theory with experiment. At the same time, the factor  $\exp(h\Delta\nu/kT)$  improved in all cases the agreement between theory and experiment, thus demonstrating that the assumptions made in the approximate allowance of the role of the interaction effects are reasonable.

Usually the measurements are made at pressures on the order of 1 atm (several dozen atmospheres for xenon arcs). In [314] the measurements were made in a capillary discharge at pressures 120 and 500 atm. Allowance for  $\exp(h\Delta\nu/kT)$  leads to good agreement between theory and experiment at 120 atm. At 500 atm, however, this factor leads to theoretical brightnesses which are high compared with experiment. Thus, at high pressures, factors that attenuate the intensity of the continuous spectrum come into play, and in particular, the section of the trajectory on which the electron interacts with the individual ion becomes shorter. The creation and investigation of a dense plasma entails considerable difficulties; in [330, 346] attempts were made to carry out measure-

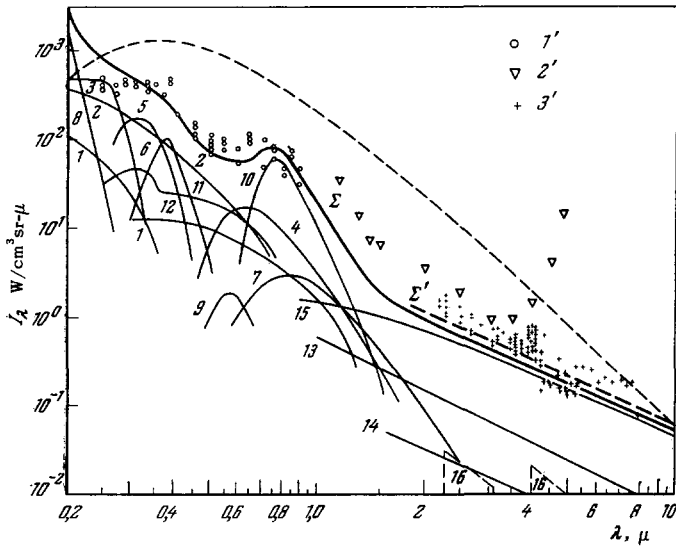


FIG. 19. Spectral intensity of radiation from air (8000°K, 35 atm, layer thickness 1 cm) [342]. Experimental values: 1' - [358], 2' - [320], 3' - [315] ( $p = 38$  atm). Calculated contributions of individual processes: 1 -  $O_2$  bands; 2,3,8,9,10,16 - NO bands; 4,5 -  $N_2$  bands; 6,7 -  $N_2^+$  bands; 11 -  $O^-$  radiative adhesion; 12 -  $N^-$  radiative adhesion; 13 - bremsstrahlung and recombination radiation of electrons in  $NO^+$  field; 14 - the same for the ions  $N^+$  and  $O^+$ ; 15 - bremsstrahlung of electrons in fields of neutral particles (essentially  $N_2$ ),  $\Sigma$  - summary calculated intensity of radiation;  $\Sigma'$  - the same for  $p = 38$  atm. The thin dashed line corresponds to 0.1 of the intensity of the black-body radiation.

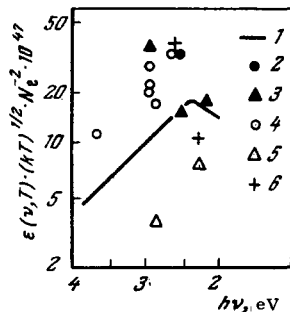


FIG. 20. Radiation brightness of inert gases heated by a strong shock wave. 1) Theoretical curve (some differences between the results for Ar, Kr, and Xe are disregarded); Experimental points: 2) Ar [237], 3) points obtained in [327] from the results of [325]; 4) Kr [327], 5) Kr [334], 6) Xe (upper point from [327], lower from [334]).

ments for a gas heated and compressed by a shock wave produced by an explosion (the initial gas pressure is atmospheric).

**Radiative adhesion.** The photodetachment cross sections measured by direct methods agree well with the observed summary spectra (see Fig. 15). For  $N^-$  there are no direct measurements, but since the existence of this ion has been established, the excess of the observed glow [202, 256, 259] can be attributed to radiative adhesion. Subtracting from the measured brightness the calculated brightness due to recombination and bremsstrahlung processes, we can estimate the

photodetachment cross section\*; the obtained value can then be used to determine the range of  $p$  and  $T$  at which  $N^-$  plays an important role [347]. At 1 atm and 13 000°K, such an estimate shows that the contribution of the radiative adhesion is small and, indeed, experiment agrees with theory without involving  $N^-$  (see Fig. 16).

The recombination continuum has a different temperature and pressure dependence than the continuum due to radiative adhesion. Therefore measurement of such dependences for the summary continuum will help identify the nature of the observed spectrum [259], and also make it possible to separate approximately the continua due to different processes, without resorting to direct calculations of individual contributions [203, 257]. This separation is facilitated by the fact that the temperature dependence has an analytic form not only for the continuum of the radiative adhesion, but also for the recombination-bremsstrahlung continuum, since the graphically specified function  $\xi(\nu)$  is practically independent of  $T$ .

**Bremsstrahlung processes (with atoms).** The scanty available experimental data agree with the theoretical estimates. For comparatively simple systems, we can present a quantitative comparison (see Fig. 19) by using (3.3). From (3.4) follows an approximate general criterion for the predominance of bremsstrahlung processes with atoms over bremsstrahlung processes with ions [300]:

$$N_i/N_a \ll 10^{-3} \bar{\sigma}(T) T^2, \quad (4.1)$$

where  $\bar{\sigma}(T)$  is expressed in units of  $\pi a_0^2$  and  $T$  in electron volts. Under the conditions of [339], at which the spectral brightness of the mercury arc was measured, the inequality (4.1) is satisfied and the measured value is actually one order of magnitude higher than that given by formula (2.6). Equation (4.1) was not satisfied in [328] for argon, and the measurements agreed with the value given by (2.6).

**Existing discrepancies.** One group of experiments [259, 318] reveals that the measurement results are somewhat higher than the calculated data and the results of other experiments. These measurements, however, were made with shock tubes without direct measurements of  $T_e$  and  $N_e$ . In such cases it is difficult to expect high accuracy. Figure 20 shows the results of similar measurements for inert gases. It is stipulated in [327] that the absolute measurements are accurate within a factor 2-3, and that the accuracy of the results of [325] is not higher. The reliability of the measurements in [334] is also estimated to be of this order.

Cooling, possibility of deviation from equilibrium, non-ideal nature of the reflection of the shock-wave,

\*In view of the uncertainty in the binding energy, it is in fact more convenient to estimate the brightness of the radiation emitted in radiative adhesion, as well as the absorption coefficient, calculated in terms of one electron and one atom.

errors in the calculation of the temperature, etc. make it difficult to compare the measurement results with theory when the calculated parameters of the shock waves are used. Comprehensive measurements yielded results which agreed well with theory<sup>[262]</sup>.

Let us evaluate the results obtained in<sup>[205]</sup> for the emission of a chlorine plasma in a discharge. Measurements at different temperatures made it possible to separate the recombination continuum. It was found to comprise the smaller part of the observed brightness. Direct calculation by means of (2.6) also shows that recombination processes cannot explain the entire observed emission (the value of  $\xi(\nu)$  was assumed, from considerations of similarity of the quantum defects<sup>[87]</sup>, the same as for K and Ar). The emission excess cannot be attributed to  $\text{Cl}^-$ , whose affinity energy is 3.6 eV (we note that the edge of the spectral interval in<sup>[205]</sup> overlapped the threshold of  $\text{Cl}^-$ , but no corresponding continuum was observed). To identify the excess emission with bremsstrahlung transitions in the fields of the atoms it is necessary to have, in accordance with (4.1),  $\bar{\sigma} \gg 10^2 \pi a_0^2$ , which is not very likely, all the more since we can expect the presence of the Ramsauer effect in the case of Cl. The emission from the plasma of chloroform ( $\text{CHCl}_3$ ), due essentially to the chlorine, was measured in<sup>[336]</sup>. The results of<sup>[336]</sup> are half as large as those of<sup>[205]</sup> (when referred to one chlorine atom). This decrease, however, still does not eliminate the question of excess emission.

It is of interest to measure in greater detail the temperature dependence of the recombination emission. The results of<sup>[202,256]</sup> for nitrogen are somewhat contradictory, and there is also a certain discrepancy between the measurements of<sup>[256,201]</sup> and the predictions of the theory. On the other hand, agreement between experiment and calculation for the relative temperature dependence should be much better than for the absolute values. Thus, when T changes from 10 480 to 13 030°K, the absorption coefficient of Ar ( $\lambda = 0.4 \mu$ ) changes by a factor of 18.4 (calculation) and 18.0 (measurement) (Fig. 18).

An unidentified maximum is observed in the spectrum of carbon<sup>[201]</sup>.

Integral measurements. There is a number of investigations in which an attempt was made to measure the integral radiant fluxes of different gases (in a larger or smaller region of the spectrum); data on the radiated energy can be obtained from an analysis of arc balance<sup>[348]</sup> or shock-wave cooling<sup>[350]</sup>. These results also afford a certain possibility of verifying the theoretical calculations of the continuous spectra. It must be recognized, however, that besides the continuous spectrum, the spectral lines also make an important and sometimes the main contribution to the energy radiated by a low-temperature plasma, as shown in<sup>[349-351]</sup>.

Use for diagnostics. Experimental and theoretical investigations of the continuous spectra have made it

possible to obtain in a number of cases sufficiently reliable results for the absolute values of the brightness and for the spectral and temperature dependences. Therefore the use of the analysis of continuous spectra for plasma diagnostics is at present much more justified (see, for example,<sup>[352-354]</sup>).

## V. SOME ADDITIONAL QUESTIONS

Nonequilibrium conditions. In the derivation of the expressions for the summary coefficients of absorption or emission, it was assumed above that local thermodynamic equilibrium obtains. We can consider in exactly the same manner the radiation of a nonequilibrium gas; it is necessary then to use the corresponding distributions of the atoms and ions with respect to the excited states, and those of the electrons with respect to the velocities. The situation becomes simpler if the state of the gas is such that it is possible to introduce an electron temperature  $T_e$  and an excitation temperature. Then a number of the formulas obtained above can be used directly.

In finding the resultant photoionization-absorption index it was assumed only that a Boltzmann distribution obtains with respect to the excited states. Therefore the result can be used also in those nonequilibrium cases, when the excitation temperature differs from the kinetic temperature. All that matters is that the distribution of the excited atoms be describable by the Boltzmann formula. This is the temperature that must be used in the resultant expressions for the absorption index.

Sometimes the populations of the excited states and the electron density differ from the equilibrium values to an equal degree<sup>[355]</sup>. The relative distribution with respect to the excited states is characterized by  $T_e$ . In this case one introduces into the expression for the absorption index both  $T_e$  and a coefficient that takes into account the common measure of deviation from equilibrium. It must be indicated that the deviation from equilibrium may have also a more complicated character, as shown experimentally in<sup>[352]</sup> and theoretically in<sup>[356]</sup>.

Analogously, the formulas for the brightness of the recombination and bremsstrahlung emission (in the field of ions or atoms) are valid in all those cases when the velocity distribution of the electrons is Maxwellian.  $T_e$  can differ from the temperature of the heavy particles. In such cases it is necessary to use in (2.6) and (3.3) the quantity  $T_e$  and the actual values of  $N_e$  and  $N_a$  (the same considerations hold also for absorption due to free-free transitions). In spite of the self evident nature of these considerations, the discussion of this question in the literature is not perfectly clear. This is correctly indicated in<sup>[357]</sup>, where measurements are reported, showing the applicability of expression (2.6) under conditions when a Maxwellian distribution is realized and there is a strong deviation from the Saha formula.

The functions  $\xi(\nu)$  in themselves still have an even wider range of applicability under nonequilibrium conditions. The point is that in the derivation of the formula for  $\xi(\nu)$  it is in fact not necessary to have the explicit distributions of the atoms with respect to the excited states. We can assume this distribution to be arbitrary (the only limitation is that for levels with identical energy the populations must be proportional to the statistical weights, i.e., the distribution is of the form  $(\omega_l/\Sigma_0)f_t(E_{nl})$ , where the parameters characterizing the distribution are denoted by the symbol  $t$ ). The entire derivation is carried out in perfect analogy, and we obtain  $\kappa(\nu, t) = \kappa_H(\nu, t)\xi(\nu)$ ,

$$\kappa_H(\nu, T) = \sum n^2 f_t(E_{nl}) \sigma_{nl}(\nu) \cong \int f_t(E_{nl}) \frac{1}{2} Z^{-2} n^5 \sigma_{nl}(\nu) dE_{nl},$$

obtaining for  $\xi(\nu)$  the same formula as before. This result is valid in the case of quantum defects that do not depend on the energy; inasmuch as we have seen that even for linear quantum defects the functions  $\xi(\nu, T)$  depend little on the temperature, then it is evident that the average value  $\xi(\nu) = \overline{\xi(\nu, T)}$  can also be applied to a gas with other than Boltzmann distribution. Allowance for the multiplicity and extension to include free-free transitions are carried out in perfect analogy and introduce no new features whatever.

**Multiphoton processes.** A general analysis is presented in<sup>[360]</sup>. We confine ourselves to a discussion of only a few questions connected with two-photon absorption and emission. Let us write the Hamiltonian of the interaction of the radiation field with the charges, confining ourselves for simplicity to examination of one electron. In the standard notation

$$H_i = - (e/mc) \hat{A} \hat{p} + (e^2/2mc^2) \hat{A}^2. \quad (5.1)$$

The operator  $\hat{A} \hat{p}$  describes single-photon processes in first-order perturbation theory, and a group of two-photon absorption and emission processes in second order; the latter can be treated as transitions from the initial state to the final state via an aggregate of virtual states. It is then necessary that the photon frequencies  $\omega_\alpha$  and  $\omega_\beta$  correspond to the condition

$$E_2 - E_1 = \hbar\omega_\alpha + \hbar\omega_\beta, \quad (5.2)$$

and the initial and final states have equal parity.

The operator  $\hat{A}^2$  leads to two-photon processes even in first order of perturbation theory. This process goes without participation of virtual states. The condition (5.2) is necessary, as before, but the parities of the initial and final states should be different, making it possible to consider the two aforementioned groups of two-photon processes independently. Let us note some qualitative singularities of two-photon processes.

The absorption probability of two photons is proportional to  $n_{\omega_\alpha} \cdot n_{\omega_\beta}$ —the product of the concentrations of the photons of the corresponding frequen-

cies<sup>[361]</sup>. Analogously, the probability of emission of two photons is proportional to

$$(n_{\omega_\alpha} + 1)(n_{\omega_\beta} + 1) = n_{\omega_\alpha} n_{\omega_\beta} + n_{\omega_\alpha} + n_{\omega_\beta} + 1. \quad (5.3)$$

The first term in the right side of (5.3) represents stimulated emission of two photons, and the latter spontaneous emission. The second and third terms represent a radiative process which has no analog in the group of single-photon processes, and which can be treated in the following manner: an excited atom emits under the influence of photons of any particular frequency ( $\omega_\alpha$  or  $\omega_\beta$ ) two photons ( $\omega_\alpha$  and  $\omega_\beta$ ). It can be shown that one of them is identical in its characteristics to the photons causing the transition. The only condition imposed on the second photon is the one determining its frequency in accordance with (5.2). It is appropriate to call this process stimulated-spontaneous emission<sup>[362]</sup>.

An equilibrium between the radiation field and matter in the presence of two-photon absorption and emission processes can be obtained only when the stimulated-spontaneous emission is taken into account. Detailed balancing should take place separately for the processes due to the first and second terms of the Hamiltonian (5.1). This yields the connection between the probabilities of all four processes of each group<sup>[362]</sup>.

Unlike the single-photon processes, the two-photon processes lead to the appearance of continuous spectrum even in the case of transitions between discrete states (see (5.2)). In the case of two-photon ionization, the continuous spectrum is produced in a region of frequencies below the limits of the photoeffect.

The number of known published papers reporting observation of two-photon absorption by gases in the optical range is quite limited. Thus, two-photon absorption of emission from a ruby laser by cesium vapor was first observed in<sup>[363]</sup>. The transition produced there was 6S – 9D, as evidenced by the appearance of emission of the Cs 5847 Å line (transition from 9D<sub>3/2</sub> to the intermediate level 6P<sub>3/2</sub>). The absorption probability was calculated. The result of the calculation was used to estimate the intensity of  $\lambda$  5847 Å, which turned out to be two orders of magnitude higher than the measured value. The author of<sup>[363]</sup> proposes that the discrepancy is connected with the quenching of the 9D<sub>3/2</sub> state by interatomic collisions.

Two-photon absorption in potassium vapor, causing transition between the discrete levels 4S – 6S, was observed in<sup>[364]</sup>. The potassium atoms were subjected to the action of two light flashes, one from a powerful ruby laser and the other resulting from Raman scattering of the laser beam. The presence of two-photon absorption was revealed by the appearance of the potassium lines corresponding to the transitions from the 6S level.

In<sup>[365]</sup>, where the method of crossed beams was

used, two-photon detachment from I was observed (the photon energy in the laser beam was 1.785 eV, and the affinity energy of iodine is 3.076 V). Calculation of the photodetachment probability is relatively easy, since there are only two states (the ground state of the ion and the continuum). The probability  $W_2$  of two-photon detachment, calculated per negative ion and per second, is equal to  $W_2 = \delta F^2$ , where  $F$  is the photon flux (in  $\text{cm}^{-2}\text{sec}^{-1}$ ). It was found<sup>[366]</sup> that  $\delta = 5 \times 10^{-51}$  (for  $\text{I}^-$ ),  $1.2 \times 10^{-51}$  ( $\text{Br}^-$ ), or  $0.3 \times 10^{-51}$  ( $\text{F}^-$ ). Experiment<sup>[365]</sup>, however, yields  $\delta = 180 \times 10^{-51}$  ( $\text{I}^-$ ). The authors of<sup>[365]</sup> propose that the discrepancy is due to the fact that in calculating the matrix elements in<sup>[366]</sup>, the wave function of the free electron was chosen to be plane. The discrepancy may possibly also be due to the fact that only the term  $\hat{A}\hat{p}$  of the Hamiltonian was taken into account in<sup>[366]</sup>. Allowance for the term  $A^2$  (in the plane-wave approximation) leads to  $\delta = 20 \times 10^{-51}$ <sup>[367]</sup>. Since the negative ion does not have excited discrete states, the probabilities of the single-photon and two-photon photodetachments can be related with each other. In<sup>[367]</sup>, using the known cross section of single-photon photodetachment, a value  $\delta = 410 \times 10^{-51}$  was obtained for the two-photon photodetachment. The role of the first and second term in the interaction Hamiltonian is also discussed in<sup>[368-369]</sup>.

Zernik<sup>[370]</sup> developed a theory of two-photon ionization of hydrogenlike states. He took into account the first term of the Hamiltonian. To calculate the sum of the second-order matrix elements he used a method proposed in<sup>[371]</sup>. The results were extended in<sup>[372]</sup>. Assume that both single-photon and two-photon ionization are energetically feasible; the summary cross section of the photoionization is equal to

$$\sigma_n(\lambda) = 1.045 \cdot 10^{-2} Z^4 n^{-5} \lambda^3 [g_1 + g_2 (I/I_0) (\lambda/\lambda_0)^3],$$

where  $g_1$  is the Gaunt factor,  $g_2$  a quantity close to unity and weakly dependent on  $\lambda$  and  $n$ ,  $I_0 = 7.019 \times 10^{16} \text{ W/cm}^2$ , and  $\lambda_0 = 455.88 \text{ \AA}$ . For wavelengths larger than the red edge of the photoeffect, when only two-photon ionization is possible,  $\sigma_n(\lambda)$  oscillates strongly with variation of the wavelength, increasing on the average with increasing  $\lambda$  (at a fixed energy density of the incident radiation).

Rand<sup>[373]</sup> considered free-free single-photon and two-photon absorption occurring upon irradiation of an electron moving in the Coulomb field of an ion. The result was strongly dependent on the parameter  $e^2 E^2 / m \hbar \omega^3$ , where  $E$  is the intensity of the incident field and  $\omega$  its frequency. It was shown that whereas for small values of the parameter the cross section varies like  $\omega^{-7/2}$ , at large values it varies like  $\omega$ .

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Note added in proof. We call attention to a number of papers published after this article went to press.

Photoionization. Calculations were made of the cross sections of He<sup>[1]</sup>, N, and O<sup>+[2]</sup>\* from the ground states and Cs<sup>[3]</sup> for a number of states. Measurements were made for the ground states of the atoms H<sup>[4]</sup> (840 and 826 Å; an unexpected deviation from theory is observed), Ar<sup>[5]</sup> (550 – 350 Å), O<sup>[6]</sup> (refinements for individual wavelengths), Ca<sup>[32]</sup> (2028 – 1660 Å), Al and Tl<sup>[7]</sup> (2100 – 1500 Å), Ga and In<sup>[8]</sup> (2500 – 1500 Å), and the states 2p<sup>3</sup> 2D<sup>0</sup> and 2P<sup>0</sup> of the nitrogen atom<sup>[9]</sup> (near threshold). Autoionization calculations were made for He<sup>[1,10]</sup>, and autoionization lines were investigated experimentally for Ar<sup>[5]</sup> (350 – 550 Å) and He<sup>[33]</sup>.

Photodetachment. The cross sections were calculated for H<sup>-[11,12]</sup>, C<sup>-[2]</sup>, and O<sup>-[13]</sup>. The continuum of radiative adhesion, due to the formation of N<sup>-</sup>, was measured in<sup>[14,15,16]</sup>; the results confirm the very large value of the photodetachment cross section. The forbidden continuum 1s → k<sup>2</sup>s of the ion H<sup>-</sup> (and of alkali ions) is considered theoretically in<sup>[17]</sup>; this continuum can appear in a plasma because of the presence of micropoles, and make a dominating contribution in the near-threshold region, inasmuch as the

corresponding cross section of photodetachment increases like k, whereas for the allowed transition 1s – k<sup>2</sup>p the cross section is proportional to k<sup>3</sup>.

Bremsstrahlung processes on neutral particles. Free-free transitions of an electron in the field of the H atom were calculated in<sup>[12,18]</sup>. Calculations were made also for He<sup>[19]</sup>, C<sup>[20]</sup>, N and O<sup>[21]</sup>, H, He, N, O, Ne, H<sub>2</sub>, N<sub>2</sub>, and O<sub>2</sub><sup>[22]</sup>, and Cl<sup>[34]</sup>. The influence of resonances in elastic scattering on bremsstrahlung transitions is considered in<sup>[23]</sup>.

Summary spectra. The absorption coefficients of hot air is calculated in<sup>[24]</sup>, and the photoionization spectra in<sup>[25]</sup> for N<sup>4+</sup> and O<sup>5+</sup> and in<sup>[26]</sup> for N, O, N<sup>+</sup> and O<sup>+</sup>. Plasma radiation cross sections were measured for oxygen and nitrogen<sup>[14,15,36]</sup>, air<sup>[16,36]</sup>, xenon<sup>[35]</sup>, and absorption was measured in inert gases<sup>[27]</sup>. The measurements in<sup>[14]</sup> were made only for individual wavelengths, but in a wide interval of T (9500 – 13 500°K). To interpret their results, the authors of<sup>[14]</sup> use the theoretically-known relative temperature dependences of the radiative-adhesion and recombination continua, and, by choosing normalization factors, good agreement is obtained between the calculated and measured values in the entire interval of T. Thus, the absolute values of the contributions of each of the continua were determined in<sup>[14]</sup> for oxygen and nitrogen. The obtained values of ξ(ν) turned out to be somewhat higher than those obtained in the earlier approximate calculations (see Sec. II). The theory of photoionization and photodissociation spectra of diatomic molecules at high temperatures is considered in<sup>[28]</sup>. Continuous molecular emission of inert-gas plasma was measured in<sup>[29]</sup>, and the theory of this process was discussed in<sup>[30]</sup>.

Multiphoton ionization. The theory is considered in<sup>[31]</sup>.

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Translated by J. G. Adashko