# Electron energy spectrum in low-energy collisions of negative ions and atoms

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The theory for electron detachment in low-energy collisions of negative ions and atoms and experimental methods for studying this detachment are reviewed. Theory and experiment are compared, particularly with regard to the energy spectra of the emitted electrons. The relationship between electron detachment and nonequilibrium processes in plasmas is discussed, as is the relationship between detachment and the occupation of highly excited states of the colliding particles. The typical parameters of the process, the possibility of extracting them from theory and experiment, and the various theoretical methods and models for detachment and ionization are all discussed. The excitation and decay of approximately stationary states (autoionization and autodetachment states) of quasimolecules and also of isolated atoms and negative ions are discussed. Isotopic effects and the corresponding theory are discussed. Information on the behavior of unstable terms of the colliding atomic particles and of the widths of these terms cannot be obtained by other methods, so that this branch of the physics of atomic collisions may be singled out for separate discussion as the "electron spectroscopy of unstable quasimolecular states."

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## INTRODUCTION

The importance of the processes which occur in low-energy collisions of atoms and ions and their typical general properties were recently discussed in this journal by Nikitin and Smirnov.[1]

In the present review we are interested in collisions which are accompanied by the detachment of an electron from a negative ion or atom. Such collisions involve a change in the charge state of atomic particles, and free electrons appear. These events are particularly important in a study of the behavior of plasmas in constant and varying external electromagnetic fields, for a study of plasma conductivity, etc., and also under very nonequilibrium conditions (in shock tubes, during the deceleration of high-speed objects in the upper atmosphere) when the plasma is far from equilibrium, and the parameters of the elementary processes must be known. In collisions of unexcited atoms, in contrast with electron collisions, ionization begins only when the kinetic energy of the colliding particles is several times (on occasion, many times) higher than the ionization potential of the isolated atom. During rapid nonequilibrium heating we then deal with the problem of the "first electron," which is accelerated by the external field and begins to act as a "sledgehammer," generating avalanche ionization and thermalization of the plasma.[1)]

The electrons emitted in low-energy collisions of atoms usually have energies of the order of 1 eV, and sometimes as much as several electron volts; i.e., the electrons are moving much faster than the atoms. We thus have an effective mechanism for the exchange of kinetic energy between atoms and electrons with energies below the excitation threshold of the atoms. Ordinary elastic scattering—which is the only binary process which occurs in this energy range—requires many thousands of collisions for such exchange.

All these circumstances make it extremely urgent to study the energy spectra of the electrons emitted in

[1)] After this paper has been prepared for publication, a review by Smirnov[96] appeared with a discussion of Penning ionization in thermal collisions of excited atoms. The present review deals with higher energies, at which electron detachment occurs at the expense of the kinetic energy of the relative motion of the atoms.

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atomic collisions. Research in this field, both theoretical and experimental, was taken up only in the mid-1960s and required the development of new measurement and calculation methods.

From the theoretical standpoint, any process which has three or more particles before or after the collision ($2-3, 3-2$) is qualitatively more complicated than ordinary ($2-2$) processes. It becomes very important to find an approximation which would make it possible to simplify the study and to distinguish a group of phenomena which are important for applications and accessible for experimental study, while at the same time amenable to a comparatively simple theoretical interpretation. Among such phenomena are collisions which are accompanied by the detachment of a low-energy electron, whose wavelength $\lambda$ is appreciably larger than the dimension ($R_0$) of the colliding system of atoms or ions, i.e., the quasimolecule. Under this condition it is possible to work out some comparatively simple and general calculation methods which become asymptotically exact as the parameter $\lambda/R_0$ goes to infinity.

Such a theory is particularly applicable to low-energy collisions involving negative ions, since the electron affinity is always several times lower than the energy required to detach the second and subsequent electrons. As a result, the one-electron approximation works quite well. Furthermore, a neutral atom is left after the electron is removed. Since this atom experiences a long-range Coulomb interaction with another atom, the theory is simplified even more, making it possible to use such a simple approximation as the approximation of zero-range potentials to describe the emitted electrons.

At the same time, both theory and experiment show that in all electron-detachment events the emission of a low-energy electron is either predominant or at least comparable to the emission of electrons with energies of several electron volts. The latter electrons are usually associated with the autoionization of atomic particles which have already separated. The energy spectrum of this group of electrons is usually complex, cannot be derived theoretically in its general form, and depends strongly on the individual characteristics of the colliding particles (the energies and widths of the maxima) as well as on the properties of the complex which is formed during the collision (the intensity of the maxima).

From the experimental standpoint, electron detachment can be observed most easily by detecting as many as possible of the electrons which are produced during a collision, i.e., by measuring the cross section $\sigma^-$ and its energy dependence. The next step—analyzing the energy of the emitted electrons—was begun in a study by one of the present authors.[2,3] This analysis has now become a rapidly developing field. The results of these measurements agree satisfactorily with the theory, whose initial version was proposed slightly earlier. Subsequent development of theory and experiment has confirmed the basic assumptions, and at this point the general picture of the electron-detachment process may be regarded as understood guite reliably.

## 1. BASIC STAGES IN THE DEVELOPMENT OF EXPERIMENTAL AND THEORETICAL WORK

### a) Cross sections

The cross section for electron detachment in collisions of negative halogen ions with inert gas atoms was first measured by Dukel'skiĭ and Zandberg[4] over the energy interval from $10^2$ to $10^3$ eV. Detachment cross sections were also studied by Hasted[5,6] in connection with the satisfaction of the Massey adiabatic criterion. The first calculations were carried out by Sida[7] in the Born approximation, but there is no justification for applying this approximation to low-energy collisions.

In a series of papers[4,8] by Zandberg, Bydin, and Dukel'skiĭ experimental results on electron detachment in collisions of halogen ions with inert gas atoms were used to introduce a concept of importance to an understanding of the mechanism for the process: the concept of a critical distance $R=R_0$ between the colliding particles, $A^-$ and B. Specifically, at $R>R_0$ the $AB^-$ system is stable, but at $R<R_0$ the weakly bound electron is "ejected" into the continuum and is rapidly detached. Fite's measurements[9] for the simplest pair, $H^-+H$, in crossed beams confirmed the concept of a critical distance for this system and showed that there is no energy threshold in this case because of the possibility of associative detachment ($H^-+H \rightarrow H_2+e$). Firsov and Smirnov[10] proposed a simple model for calculating $R_0$, which Bydin[11] used to discuss experiments on the detachment of electrons from negative ions of alkali metals. Further measurements of the cross sections have been carried out by several investigators (see the review by Risley[12]).

### b) Energy distribution of the emitted electrons

In 1964–1965 Demkov proposed a theory for the energy distribution of the low-energy electrons which appear in collisions of negative ions with atoms, working in the approximation of zero-range potentials.[13,14] In 1967 Bydin carried out the first measurements for halogen and inert-gas ions, confirming the basic theoretical conclusions and also discovering monoenergetic groups of electrons associated with the decay of quasistationary states of the negative ions (autodetachment). Smirnov[15] also derived a theory for the energy spectra of the electrons, examining the decay of an autodetachment state of a quasimolecule near the boundary of the continuum. For ionization during collisions of neutral atoms, the first measurements of the electron energy spectra were carried out by Berry.[16] He also discovered monoenergetic groups of electrons for the cases of Ar and He.

Demkov and Komarov[17] were successful in deriving a theory for the ionization of atoms during collisions only after the original theory for negative ions was generalized to the case of the interaction of an isolated state of a quasimolecule with an arbitrary system of noninteracting parallel terms.[18] The difficulty here was in incorporating the long-range Coulomb forces which act on the emitted electron. Measurements by Bydin and Ogurtsov[19] confirmed the basic theoretical conclusions

and made it possible to determine empirically the basic parameter of the theory. Specific subsequent ionization calculation were carried out by Olson.[20] Further applications of the zero-range potential theory were reported by Esaulov and Gauyacq.[21,22] Devdariani,[23] Bazylev, and Zhevago,[24] and Herzenberg and Ojha[25] have recently extended the theory to incorporate the dynamic effects responsible for the increase in the cross section with increasing energy which has been observed in several experiments. In addition, several recent studies[26,27] have been reported on the interactions between unstable quasimolecular states: their pseudocrossings, etc. The corresponding equations for bound states can in this case be modified by including in these expressions complex energies and a nonzero width: the imaginary part of the energy $\Gamma(R)$. As experimental results have shown, this interaction of terms may give rise to a filling of those terms which transform into autodetachment states (in the case of negative ions)[2,3] and autoionization states (for atoms)[16] as the particles fly apart.

The groups of electrons associated with the decay of autodetachment states were subsequently studied in a series of papers by Geballe, Risley, *et al.*, with a high energy resolution (see the review by Risley[28]), and this work gave rise to a new research direction in collisional spectroscopy: the study of the energy spectra of the electrons detached from negative ions. After the conversion of the stationary state of an electron shell of a quasimolecule into a quasistationary state, the subsequent evolution of the system involves the emission of electrons. The time evolution of the system thus ceases to be "invisible": The details of the evolution are reflected in the shape of the energy distribution, and we can "see" the width of the term, $\Gamma(R)$, its interaction with other terms, the various interference patterns which can give rise to oscillations in the spectrum, the occupation of autodetachment and autoionization states, etc. It is for this reason that a study of the electron spectra in low-energy atomic collisions can yield the most-detailed information about the time evolution of the collision, about the shape of the unstable terms, and about their widths. In other words, such studies can yield some absolutely new information, unobtainable by other methods.

## 2. EXPERIMENTAL PROCEDURE

The experimental procedure involves producing a beam of "projectile" particles (in this case negative ions or neutral atoms) with the appropriate energy. These projectile particles enter a collision chamber where they interact with the particles of a gaseous target; alternatively, a beam of projectile particles intersects a beam of target particles. An electron spectrometer is used to study the energy distributions of the electrons emitted during the collisions.

### a) Production of beams of projectile particles

1) Several types of ion sources have been used to produce beams of negative ions. Gas-discharge sources of the well-known type proposed by Nier, with discharges in the vapor of an alkali halide salt (to produce negative halogen ions), have been used.[4,8] Several more recent studies have used duoplasmatrons.[29-36] Certain ions are produced by discharges in an auxiliary "buffer" gas, into which the working medium is injected (for example, an alkali halide salt for producing negative halogen ions or $CH_4$ for producing $C^-$ ions[30]). Surface-ionization sources are also coming into widespread use.[37,38]

The negative ions leaving the source are accelerated to the desired energy (between a few tens of electron volts and a few thousand). The ions of interest are selected by a mass spectrometer (ordinarily, a sector magnetic mass spectrometer[3,30-36] or a Wien filter[45]), and the necessary focusing of the ion beam is carried out.

2) The following methods have been used to produce beams of fast neutral atoms.

Charge exchange of positive ions,

$$\vec{A}^+ + B \to \vec{A} + B^+ \tag{2.1}$$

(an arrow designates a fast particle). In several cases it is convenient to use charge exchange in "the same gas," e.g.,

$$\vec{A}^+ + A \to \vec{A} + A^+. \tag{2.2}$$

Electron detachment in a collision of a negative ion with a heavy particle, e.g.,

$$\vec{A}^- + B \to \vec{A} + B + e. \tag{2.3}$$

Photodetachment,

$$\vec{A}^- + h\nu \to \vec{A} + e. \tag{2.4}$$

(Fast H and D atoms were produced in Ref. 39 by arranging the intersection of beams of negative $H^-$ and $D^-$ ions with laser beams.)

When charge-exchange or electron-detachment methods are used to arrange neutralization, an auxiliary collision chamber is placed in the beam path. Those particles of the primary beam which have retained their charge are then deflected (usually with an electron static deflection system) and do not reach the rest of the apparatus. The current drawn by a Faraday cup at the exit from the chamber is used to monitor the intensity of the primary beam in experiments with ions. In experiments with accelerated neutral atoms, the flux density of the atoms is monitored by measuring the current of secondary-emission electrons from a collector in the path of the atom, but when this method is used with beams of different energies (in measurements of excitation functions, for example), the change in the secondary-emission yield with the energy of the neutral particles must be taken into account. Another possibility is to measure the current of the secondary particles produced upon neutralization in reactions (2.1)–(2.3): ions and electrons, respectively. In Ref. 40, the current of the beam of primary $A^+$ ions was taken as a measure of the flux density of neutral particles, and a correction was made for the change in the effective cross section for the charge exchange in (2.2) as a function of the energy of the beam particles.

### b) Research on the energy distributions

Several types of electron spectrometers have been used to study the electron energy distributions. The field of electron spectroscopy has been reviewed in detail in several monographs (see Refs. 41–44, for example).

The very first experiments[2,3] showed, and subsequent work verified (see Refs. 34 and 45, for example), that the energy distributions of the electrons emitted in collisions of negative ions[2)] include a group of comparatively low-energy electrons, with energies ranging from zero to several electron volts, and also some monoenergetic groups of electrons, which have been shown to result from autodetachment processes (here we are adopting the terminology used in the Russian translation of Massey's monograph[46]) and autoionization. Each part of the distribution is of independent interest, and a study of the entire distribution requires the use of several different methods. In this review we will be focusing on the groups of relatively low-energy electrons which constitute most of the distribution. Some mutually complementary methods have been used for direct study of energy distributions: the retarding-potential method and the method of transverse-field analyzers, which is being developed rapidly by several investigators in extensive parallel studies of collisions of positive ions. A time-of-flight method for studying the distributions is in an early stage of development.

There are several experimental difficulties and factors which must be taken into account in studying the energy distributions of electrons, *especially low-energy electrons*, and some precautionary measures must be taken to ensure correct measurements.

1. The paths traced out by the electrons, particularly low-energy electrons, are subject to the influence of magnetic fields (in particular, it is necessary to consider the fringing magnetic field in the measurement region when a magnetic mass spectrometer is used to select the ions of interest). The corresponding measures are to arrange a thorough shielding or to carefully cancel the fringing magnetic fields. In addition, the geometric parameters of the analyzer are chosen such that the Larmor radius of the lowest-energy electron is quite large in comparison with the characteristic parameters of the electron trajectories. The magnetic-field methods used in the early work carried out to analyze the electron energy distributions in atomic collisions[16] have not been pursued because of the difficulties in localizing these magnetic fields.

2. The electron paths are subject to the influence of contact potential differences (if they exist) between various parts of the energy analyzer.

3. A possible effect of surface charge on various parts of the apparatus must be taken into account.

4. The results may be affected by the emission of secondary electrons from surfaces under the influence of electrons and of the electromagnetic radiation emitted in the atomic collision.

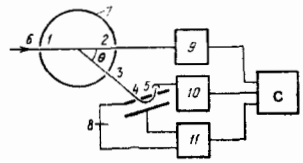


FIG. 1. Block diagram of the apparatus used to study the electron energy distributions in collisions of negative ions and atoms.[36] 1, 2—Diaphragms allowing passage of the ion beam; 3–5—diaphragms allowing passage of the electrons; 6—direction in which the ions are moving; 7—chamber with gaseous target; 8—electron energy analyzer ($\theta$ is the observation angle); 9—system for detecting the primary ion beam; 10—system for detecting electrons subjected to energy analysis; 11—system for unfolding the electron energy spectrum; C—computer.

The harmful effects in items 3 and 4 are combatted by covering the various parts of the analyzers and the collision chamber with an antiemission coating ("gold black," soot, etc.), which also eliminates or weakens the role of contact potential differences. The guiding electrodes of the analyzers are made of high-transparency grids, and auxiliary fields are used to confine secondary electrons. For a correct determination of the position of the monoenergetic groups on the energy scale, these positions are compared in the course of an experiment with the positions of peaks whose energies are well known from independent experiments carried out by a different procedure.

5. It is necessary to test the degree of isotropy in the emission-angle distribution of the emitted electrons. Here one can make use of studies of the energy distributions of electrons measured at various angles with respect to the beam of primary particles.

6. If the emission of the electron occurs *after* a collision, it becomes necessary to consider the influence of the Doppler effect on the measured energy of an electron emitted by a moving particle. For this purpose, in studies of the energy distributions a correction is introduced in accordance with[3)] (Ref. 47)

$$E = E_{\text{obs}} + \frac{m}{M} T + 2\sqrt{\frac{m}{M} T E_{\text{obs}}} \cos\theta.$$

Here $E$ is the energy of the electron with respect to the atom or ion from which it is emitted, $E_{\text{obs}}$ is the "observable energy," $T$ is the beam energy, $m/M$ is the mass ratio of the electron and the beam particle, and $\theta$ is the observation angle, reckoned from the direction in which the beam particles are moving (Fig. 1). In these cases, an autoionization state of the atom (or an autodetachment state of a negative ion) is formed, and the Doppler effect provides a way for experimentally determining from which particle (the projectile or target) the electron was emitted.

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[2)] There is a corresponding picture in collisions involving neutral particles.

[3)] Gordeev and Orgurtsov[48] have analyzed a more complex case. They studied the effect of the scattering of particles in atomic collisions on the electron energies being measured.

7. In high-precision measurements, a possible effect of the space charge of the particles on the measured electron energies is taken into account.

8. The electron-energy dependence of the "transparency" of the analyzer with respect to the electrons must be taken into account.

Some compromise is made among these somewhat contradictory requirements to suit the particular purposes of the measurements, since there are limitations on the sensitivity of the apparatus, the intensity of the primary beams which can be produced at a given collision energy, and so forth. Several methods are used to conduct the investigations.

In the earliest studies[2,3] of the energy distributions of the electrons detached in collisions of negative ions with atoms, a retarding-potential method was used (the analysis was carried out in a longitudinal electric field). A potential barrier was produced in the path of the particles to be analyzed, and only those particles whose energy was greater than the barrier height on the energy scale could overcome this barrier. The results of these measurements were "retardation curves" which reflected the integral energy distribution

$$\omega(E)=\int_{E}^{\infty}\rho(E')\,dE' \qquad (2.5)$$

and which could be compared directly with the theoretical conclusions. The retarding-potential method was used in two modifications:

a) A first modification was used in experiments on the electron energies during the photoionization of a gas with an analyzer of the Lozier-capacitor type,[49,50] with some refinements. Annular diaphragms (5 in Fig. 2) singled out electrons moving at an angle of $90°\pm10°$ with respect to the ion beam.

b) A second modification used a highly sensitive scintillation detector for electrons, operated in the particle-counting mode. Schematic diagrams of these analyzers are shown in Figs. 2 and 3 for a study of electrons moving in the direction perpendicular to the primary beam.

An advantage of the retarding-potential method is that it can be used to study rather low-energy electrons, since the path traversed by the low-energy electrons in the analyzer can be made quite short in comparison with the Larmor radius of these particles in the residual magnetic field. This method has made it possible (a) to obtain general information about the electron energy distributions in the cases studied and on the behavior of the distribution as a function of the collision energy, (b) to obtain data for comparison with theory, and (c) to discover that monoenergetic groups of electrons are excited in collisions of negative ions with atoms and to distinguish the relative contribution of these monoenergetic groups to the distribution. These results were subsequently supplemented with measurements taken with a transverse-field electrostatic analyzer.

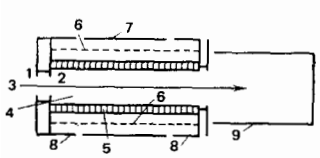



FIG. 2. System for analyzing the electron energy distributions by the retarding-potential method. 1, 2—Apertures for the ion beam (or for the beam of fast atoms); 3—direction in which the primary beam of ions or fast atoms is moving; 4—collision chamber; 5—diaphragms for selecting the electrons moving perpendicular to the beam; 6—analyzing grid; 7—cylindrical collector for the analyzed electrons; 8—guard electrodes; 9—Faraday cup.

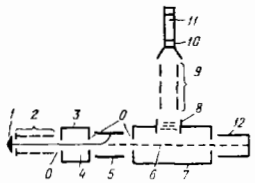



FIG. 3. Apparatus for studying the electron energy distributions with a scintillation detector. 1—Surface-ionization source of positive alkali-metal ions; 2—system for forming and accelerating the ion beam; 3—neutralization chamber; 4—ion beam; 5—ion deflection system; 6—beam of fast neutral atoms (dashed line); 7—collision chambers; 8—system of grids for the retarding-potential energy analysis of the electrons; 9—system for accelerating and focusing the analyzed electrons; 10—scintillator; 11—photomultiplier; 12—neutral-atom detector; 0—apertures for the particle beams.

Some new possibilities for studying the low-energy part of the electron distribution were used in Ref. 45, where a time-of-flight electron spectrometer[43,51,52] was connected to a collision chamber (Fig. 4). The procedure here was to measure the time which an electron with a given energy took to traverse a certain fixed distance. This method has the advantage that the accuracy with which the energy is determined increases as the electron energy decreases, since the transit time increases. The difficulties which must be overcome in the use of this method stem from the fact that with a long drift volume (50 cm in Ref. 45) the electron tra-

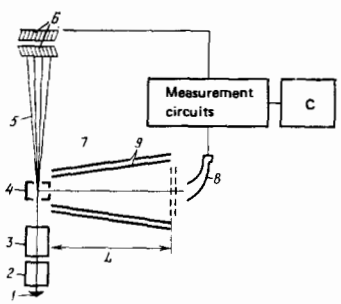



FIG. 4. Apparatus with a time-of-flight electron energy analyzer and a position-sensitive detector for detecting scattered heavy particles. 1—Surface-ionization source; 2—acceleration and focusing system; 3—mass analyzer and Wien filter; 4—collision chamber; 5—scattered heavy particles; 6—position-sensitive detector using microchannel plates; 7—time-of-flight electron energy analyzer ($L$ is the baseline); 8—electron detector (channel electron multiplier); 9—magnetic shields; C—computer.

jectories are strongly influenced by parasitic magnetic and electric fields. Their harmful effects may include not only a distortion of the measured energy but also a change in the "luminosity" of the analyzer. In the same apparatus provision was made for studying the scattering of a beam of heavy particles through small angles (0–3°). For this purpose, the primary ion beam was focused through the collision chamber onto a position-sensitive detector made from a microchannel matrix. The procedure for studying scattering by means of such detectors is discussed in the review by Leonas[53] and in the original papers of Refs. 37, 38.

After the monoenergetic groups of electrons were discovered,[2,3] they were studied in a series of experiments[29-36] through the use of an electron spectrometer having a transverse electric field. Cylindrical-capacitor analyzers and plane-electron-mirror analyzers were used. Figure 1 is a schematic diagram of a typical arrangement.[36] Detection of the electrons moving at various angles with respect to the velocity of the primary particle beam makes it possible to determine the degree of isotropy of the distribution. When the monoenergetic groups are identified, it then becomes possible to distinguish between the electrons produced by the fast particles and those produced by the target particles.

In studies[30,34] of the collisions of the negative ions $Br^-$ and $C^-$ with gas atoms, a control experiment was carried out to allow for a possible contribution to the energy distribution of those electrons which might arise from collisions of secondary neutral Br (or C) atoms produced in the reaction (2.3) with the gaseous target. For this purpose an auxiliary "neutralization chamber" was used for parallel experiments on the collisions of neutral Br or C atoms with the gaseous target.

The sensitivity and resolution $E/\Delta E_{min}$ of the apparatus have both improved as the experiments have continued, reflecting a general progress in experimental apparatus. In the early studies the resolution $E/\Delta E_{min}$ was 10, later 15, and the part of the distribution ranging from an electron energy of 0.5 eV and up could be detected reliably. In more recent studies,[4)] e.g., in Refs. 29–36 $E/\Delta E_{min}$ has reached 100–500, and the positions of the monoenergetic peaks can be determined within 0.05–0.8 eV. In a study of low-energy electrons by De Vreugd,[45] the energies of these electrons were determined within ~0.03–0.05 eV over the range ~0.2–4 eV.

In summary, it may be stated that the data on the energy distributions obtained from different studies are in general agreement, within the reported measurement errors.

## 3. BASIC THEORY

If we compare the theoretical description of electron detachment with that for charge exchange, excitation, excitation transfer, etc., we find that the main distinction is that these other processes can usually be described by considering a finite number of discrete states of a quasimolecule: a system of two colliding particles. In the course of the collision, the distance between the nuclei, $R$, varies over time; it first falls to a certain $R_{min}$ and then increases to infinity. The energies of these states—the terms $E_n(R)$—are functions of $R$, and the processes are described by working from a diagram of the terms which are important for the given process. The value of $R$ is specified at each time, and the state of the system may be thought of as a superposition of the given quasimolecular states. In other words, each term is assigned a certain amplitude $C_n$, and the sum of the square moduli of these amplitudes is one. If the terms are far apart, the system evolves adiabatically, and each amplitude remains constant in modulus, undergoing only a change in phase, described by

$$\arg C_n = -\frac{1}{\hbar}\int E_n\,dt.$$

A change in the modulus of $C_n$ occurs only when terms move close together. This closing of terms is described by the classical Landau-Zener approximation.[1] It is important to note that transitions of this type occur only in small neighborhoods of certain values of $R$, at so-called term pseudocrossings, while outside these regions, i.e., over the greater part of the collision time, nonadiabatic transitions do not occur. In all these cases the mathematical problem which describes the collision process reduces to a system of a few differential equations (in accordance with the number of states considered). These are either first-order differential equations, in the case of fast collisions, in which the motion of the nuclei can be treated classically, or they are of second order, in the case of slow collisions, when the motion of the nuclei is analyzed by quantum mechanics.

When we look at electron-detachment processes from the same standpoint, we see a much more complicated problem. The energy of the emitted electron has a continuous distribution, and each energy value corresponds to a wave function of the quasimolecule, so that a description of the process will require incorporating the interaction of an infinite number of states. In other words, an infinite system of equations must be solved. The usual procedure is to replace this system by a partial differential equation. It may therefore be expected that even the very simplest models for electron detachment must be constructed from partial differential equations, for which exact solutions are rare exceptions.

Models and solutions of this type have, nevertheless been found, and it has thus been possible to simplify the problem once again, while still retaining the impor-

[4)] In principle, data on the energy distributions of the emitted electrons can be extracted from measurements of the double differential cross sections $\sigma(\theta, \Delta E)$ where $\theta$ is the scattering angle, and $\Delta E$ is the energy lost by the fast particle (this loss can be measured by a time-of-flight method, as Esaulov, *et al.*[54] have done). The resolution of that method, however, is not yet very high; in measurements of the energy of the neutral atoms formed during the detachment of an electron in reaction (2.3), the resolution was $\Delta E \sim 0.4$ and 2 eV at primary-particle energies of 160 eV and 1 keV, respectively.

tant features of the process. The description of the detachment of an electron with a low energy which has been constructed is now just as complete as that for the interaction of two terms in the Landau-Zener model.[1] The system of models which has been constructed corresponds to the most important case, in which the term corresponding to the initial bound state at $R=R_0$ crosses the continuum boundary (i.e., a term of that system which has one fewer electron than the initial system), and the system becomes unstable and decays, emitting an electron.

In sufficiently slow collisions the decay occurs near the continuum boundary; here the electron wave functions have special properties which permit the introduction of models for the problem, and the problem can be reduced to an exactly soluable limiting case.

At positive energies, far from the continuum boundary, we can again use the representation of energy terms, term pseudocrossings, nonadiabatic transitions, etc., but the electron states of the quasimolecule are no longer stable and are described by a generally complex energy,

$$\mathscr{E}(R)=E(R)-\frac{i}{2}\Gamma(R),$$

where $\Gamma$ is a measure of the rate of the decay of the system accompanied by the emission of an electron. The adiabatic approximation, which deals with the time evolution of the system, is naturally generalized to this case: The probability ($\omega$) for the "survival" of the system as it evolves along one unstable term is given by

$$\omega=\exp\left(-\frac{1}{\hbar}\int\Gamma\,dt\right). \tag{4.1}$$

The fact that the terms become complex at real values of $R$ naturally means that the function $\mathscr{E}(R)$ must be investigated over the entire complex $R$ plane. The simplest case which can be dealt with in this way is the collision of a negative ion with an atom.

### a) Collision of a negative ion with an atom (the simplest approximation)

1) *Effective cross section.* In this case the electron detachment causes the system of colliding particles to become neutral, and the slowly decreasing Coulomb interaction is removed from the interaction of the electron with the quasimolecule. Figure 5 shows a typical system of terms for this case; we have plotted the real and imaginary parts of the energy along different axes. A term of the AB system plays the role of the continuum boundary for the $AB^-$ system. A term of the $AB^-$ system sometimes lies below the AB term for all $R$; there is no crossing point $R_0$; and the negative ion exists even in the limit of a combined atom (at $R=0$). The probability for electron detachment is thus exponentially small at low velocities. The simplest example of this type is a collision of an $I^-$ ion with an Ne atom, as can be seen from both the energy dependence of the cross section and the energy distribution of the emitted electrons.[38,45] A more common case is that in which terms of the AB and $AB^-$ systems coincide at some $R=R_0$, and at $R<R_0$ the $AB^-$ system has no bound state.

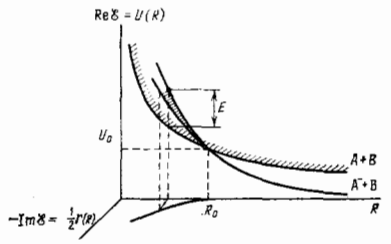



FIG. 5. Sketch of the terms of the system of $AB^-$ (solid curve) and AB (curve with hatching on top) the continuum boundary for $AB^-$. At $R<R_0$ the $AB^-$ term is complex; its imaginary part is plotted along the third axis. Also shown here is the projection $-\mathrm{Im}\mathscr{E}(R)=\Gamma(R)/2$.

The simplest assumption which can be made in this case is that the system is stable as long as the condition $R>R_0$ holds, while at $R<R_0$ it slowly decays. In this case all collisions for which the distance of closest approach satisfies $R_{min}>R_0$ do not lead to decay, while at $R_{min}<R_0$ the decay probability is one. Afterwards, if the trajectory can be assumed rectilinear, the electron detachment cross sections $\sigma_d$ will be constant, equal to $\sigma_d=\pi R_0^2$. If curvature of the trajectory is taken into account, on the other hand, i.e., if the condition $E_0=E_{AB^-}(R_0)\neq 0$ is considered [with $E_{AB^-}(\infty)=0$], then at $E_0>0$ (Fig. 5) the following result is found from conservation of angular momentum[8]:

$$\sigma_d=\pi R_0^2\left(1-\frac{E_0}{E}\right). \tag{4.2}$$

The experimental data, for the cases of $Br^-$ with He and $I^-$ with He, for example, agree with this dependence.[15] Obviously, in the case $E<E_0$ the region $R<R_0$ is never reached, and the cross section is zero in this approximation.

If $E_0<0$, the cross section increases with decreasing energy because of the focusing property of the attractive potential, according to (4.2).

A determination of $R_0$ requires detailed quantum-mechanical calculations; so far, these calculations have been carried out accurately only for the $H_2^-$ system. Smirnov and Firsov[10] have proposed a simple method for determining this quantity by working in the zero-range approximation for the electron-atom interaction. The interaction of an electron with atoms A and B is characterized exclusively by the scattering lengths $a_A$ and $a_B$ for the scattering of an electron by these atoms; these lengths are determined from the scattering cross section at zero energy or from the electron affinity. Analysis of the behavior of an electron term in the field of the two atoms in this approximation easily reveals that if both $a_A$ and $a_B$ are positive then one of the terms merges with the continuum at $R_0=\sqrt{a_A a_B}$, and the detachment cross section is given approximately by

$$\sigma_d=\pi a_A a_B.$$

It should be kept in mind that this cross section is found only when the negative ion has an electron affinity lower than that of the particle with which it collides ($A^-$ + B if $a_A>a_B>0$). If the electron affinities of the two atoms are very nearly equal, or if an ion and an atom

of the same element collide, it may be presumed that both states will be populated equally from the very beginning; alternatively, the states will mix as the particles close on each other, and the states will be populated equally even at rather large values of $R$, greater than $R_0$. In this case we have

$$a_A \approx a_B \approx a, \quad \sigma_d = \frac{\pi a^2}{2}.$$

A difference between the detachment cross sections should arise only at low energies. In principle, this difference could be used to determine the difference between the electron affinities of different atoms. If the colliding atoms have a spin $S \neq 0$ there will be two scattering lengths, with total spins $S + \frac{1}{2}$ and $S - \frac{1}{2}$, and several potential curves will arise for the AB and $AB^-$ systems. The theory of short-range potentials was generalized to this case back in the original paper by Smirnov and Firsov, and also in Refs. 57–63. For the $H_2^-$ system, for example, the points at which the continuum is entered for the $\Sigma_u$ and $\Sigma_g$ terms turn out to be (in atomic units)

$$R_{0u} = 3.5, \quad R_{0g} = 4.9,$$

while numerical calculations yield $R_{0u} = 3.2$ and $R_{0g} = 6.2$. In view of the simplicity of the approximation, this agreement should be judged satisfactory. A further improvement of this approximation depends on the fact that the detachment probability does not immediately reach a value of one at $R_{min} < R_0$, and at $R_{min} > R_0$ it does not immediately drop to zero; instead, there is a transition region at $R_{min} \neq R_0$, whose width increases with increasing collision energy. It has been shown[23,24] that this "blurring" of the target causes an increase in the effective cross section at high energies.

2. *Energy spectrum of the emitted electrons.* In order to construct a simple but realistic model for electron detachment we must analyze the dynamic behavior of the system of colliding particles at $R \approx R_0$. At $R \geq R_0$, $R - R_0$, the electron affinity approaches zero; the single potential well which the two colliding atoms represent for a weakly bound electron becomes too shallow; and the bound state disappears. Over distances much larger than the size of the region occupied by the atoms, the electron wave function becomes approximately the same as that in a centrally symmetric field, despite the asymmetry of the overall potential well. The simplest case is that in which this state asymptotically becomes a spherically symmetric $S$ state. On this basis, the field of the two atoms was replaced by a single potential well of zero range in Ref. 13, and the motion of the atoms was replaced by a change in the well depth. In this approximation the problem was reduced to a time-dependent radial Schrödinger equation for a free particle,

$$\left(-\frac{1}{2}\frac{\partial^2}{\partial r^2} - i\frac{\partial}{\partial t}\right)\psi = 0, \tag{4.3}$$

with the boundary condition

$$\left(\frac{1}{\psi}\frac{\partial \psi}{\partial r}\right)_{r=0} = f(t) \tag{4.4}$$

at $r = 0$. Equation (4.3) with boundary condition (4.4) is a model partial differential equation which can be used

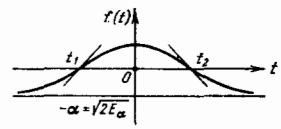



FIG. 6. Time dependence of boundary conditions (4.4), which simulates the electron detachment process. The change in the sign of $f$ at the points $t_1$ and $t_2$ corresponds to the attainment of the term $R = R_0$ as the particles close and move apart. A linear approximation for $f$ is shown for $t \approx t_1$ and $t \approx t_2$; also shown is the tendency toward $-\alpha$ in the limit $t \to \infty$, which corresponds to a free negative ion.

to describe the interaction of an infinite number of states. Negative values $f = -\alpha = \text{const}$ correspond to a stationary bound state

$$\exp\left(-\alpha r + \frac{i\alpha^2 t}{2}\right)$$

with an energy $E_\alpha = -\alpha^2/2$. As the atoms close to a distance $R = R_0$, $f(t)$ drops to zero; for motion in the region $R < R_0$, we have $f(t) > 0$. The overall collision is thus described by the behavior of the function $f(t)$, which is shown in Fig. 6. The critical regions near $t = t_1$ and $t = t_2$ describe the evolution of the system at $R \approx R_0$. In this region it is natural to replace the function $f(t)$ by a linear function of $t$, by setting $f(t) = \beta(t - t_2)$ and $f(t) = \beta(t - t_2)$. The linear approximation of the function $f(t)$ is based on the fact that this quantity, the reciprocal of the scattering length, crosses zero smoothly, changing from negative values to positive, if the depth of a potential well of the general type is gradually reduced (for long-range forces), so that the bound state disappears.

For the linear approximation of $f$ the problem can be solved exactly by Laplace contour integrals. It is convenient to replace the electron energy distribution by the resultant probability $\omega(E)$ for finding an electron with an energy higher than $E$ (in measurements of the energy of the emitted electrons by the retarding-potential method, it is this quantity which is measured). This quantity may be regarded as the probability for the "survival" of the ion $AB^-$ in the bound state all the way to the corresponding value $R < R_0$ for which $U_{AB^-} - U_{AB} = E$ (Fig. 5). Finally, we find the characteristic dependence

$$\omega(E) = \exp\left(-\frac{4\sqrt{2}}{3}\beta^{-1}E^{3/2}\right). \tag{4.5}$$

We can also evaluate the probability ($\omega$) that electron detachment will not occur, despite the fact that the system spends a time $t_d = t_2 - t_1$ in the region $R < R_0$. In this region the electron wave function is a wave packet composed of continuum states and which has correspondingly spread out. The part of the packet remaining after the spreading is again captured in the potential well as the atoms move apart and the critical point $R = R_0$ is reached. If this probability for a return capture is low, then an estimate yields

$$w = \frac{2\pi}{\beta^2 t_d^3}$$

as a dependence characteristic of the spreading of the wave packet. The parameter $\beta$ can be related to the

behavior of the terms of the system near $R=R_0$. In this region the electron affinity depends quadratically on $R-R_0$ and $t-t_1$:

$$E_a = -\frac{\beta^2 (t-t_1)^2}{2} = -c\frac{(R-R_0)^2}{2},$$
$$c = \left|\frac{d^2E_a}{dR}\right|_{R=R_0}.$$

Hence

$$\beta = v_0 \sqrt{\left|\frac{d^2E_a}{dR^2}\right|_{R=R_0}}, \tag{4.6}$$

where $v_0 = \left|dR/dt\right|_{R=R_0}$ is the velocity at which the atoms close or move apart in the critical region. To determine the constant $c$ theoretically, i.e., to calculate the terms near $R=R_0$, is a complicated problem even for the simplest system, $H_2^-$, but this is the only parameter in this very simple theory, and it can be determined from experimental data.

### b) Further development and refinement of the theory

This approximation was later generalized in several directions. First, the problem can be solved in the model of one short-range well [Eqs. (4.3) and (4.4)] by adopting as the function $f(t)$ one which would describe not only the crossing of the critical region, $R=R_0$, but also the overall collision. The most natural approximation in this case is the quadratic approximation:

$$f(t) = -\alpha t^2 + \gamma, \quad \alpha > 0.$$

The tendency of $f(t)$ toward $-\infty$ in the limits $t \to \pm\infty$ corresponds to an unbounded growth of the electron binding energy, i.e., to a rapid descent of the term of the $AB^-$ system in the limit $R \to \infty$. Although this property of the model does not correspond to the actual behavior of the term, it could not significantly affect the spectrum of emitted electrons, since in both the model problem and the real problem the probability for detachment tends rapidly toward zero in the limits $t \to \pm\infty$.

At large positive values of $\gamma$, the regions $t \approx t_1$ and $t \approx t_2$ are separated substantially by a region of large positive values of $f(t)$, in which the electron is free [the usual condition, $\psi(0)=0$, is satisfied for the radial wave function of the free electron; i.e., the case discussed above holds]. At negative values of $\gamma$, the function $f(t)$ is less than zero everywhere, and the bound state does not disappear in the course of the collision; this case was treated by Chaplik.[66] As we have already mentioned, the electron-detachment probability is exponentially small.

In the case $\gamma=0$ the problem can be solved exactly.[55] The detachment probability $w_d$ and the function $\omega(E)$, which is a measure of the electron energy distribution, are

$$\omega(E) = H_{2/5}^{(1)\prime}(z)\,H_{2/5}^{(2)}(z^*) - H_{2/5}^{(2)\prime}(z^*)\,H_{2/5}^{(1)}(z),$$
$$z = \frac{2}{5\sqrt{\alpha}}(2E)^{5/4}e^{i\pi/4}, \quad w_d = \frac{\sin(\pi/5)}{\sin(2\pi/5)} \approx 0.62,$$

where $H^{(1,2)}$ are the Hankel functions of the first and second kinds. This intermediate case corresponds to a trajectory of the particles during the collision such that the distance of closest approach, $R_{min}$, is equal to $R_0$. The problem cannot be solved analytically for arbitrary values of $\alpha$ and $\gamma$. A numerical solution of this problem is reported in Ref. 56, where some limiting cases are also studied.

The smooth decay of the electron-detachment probability with increasing impact parameter causes a general increase in the cross section with increasing velocity. The reason is that the decrease in the cross section which occurs in the region $R<R_0$ is overlapped by an increase in the cross section at $R>R_0$, because of the slower decay of the detachment probability at high velocities. The application of these arguments to the case of electron detachment in the collision $H^- + He$ has made it possible to achieve a satisfactory agreement in terms of the energy dependence of the detachment cross section.[23] An approximation which is actually very similar to that described above, and in which a deviation from the Born-Oppenheimer approximation for the quasimolecule is considered near the critical point $R=R_0$, was studied by Herzenberg and Ojha.[25] They derived similar results for the same case.

Another direction in which this approximation has been generalized has been to incorporate the finite dimensions and asymmetry of the resultant potential well of the two colliding atoms. In Ref. 14 the two atoms were replaced by two zero-range wells, separated by a distance $R_0$, and the motion of the atoms was replaced by a change in the depth of the well, in such a manner that the energy levels varied correctly with the time in the region near the critical region. For two identical wells this approach made it possible to examine both the symmetric state (g) and the antisymmetric state (u), which converts into a $p$ state at large values of $r$ in the limit $E_a \to 0$ and has a nodal plane which runs perpendicular to the axis connecting the nuclei of the atoms. It turns out that the finite dimensions of the effective potential well did not cause any great changes in the emitted-electron spectrum, and the zero-range approximation, used in the derivation of Eq. (4.5), is quite accurate.

The antisymmetric state, which converts into a $p$ state in the limit $R \to R_0$, $r \to \infty$, and also the other states of the $AB^-$ system, which convert into states with high values of $l$ at the continuum boundary (for example, the $\Pi_u$, $\Pi_g$, $\Delta_g$, and $\Delta_u$ terms convert into states with $l=1,2,3$, respectively), are quite different from the $\Sigma_u$ and $\Sigma_g$ states in that there is an effective centrifugal potential barrier which prevents the emission of low-energy electrons. As a result, an approximately stationary state is formed immediately after emission into the continuum; $\Gamma$ increases with increasing real part of the energy, more slowly the larger the effective value of $l$. For all these cases the derivative $E_0'$ of the electron affinity $E_a(R)$ with respect to $R$ at the point $R_0$ does not vanish, in contrast with the $\Sigma$ and $\Sigma_g$ terms. It is this parameter which characterizes the spectrum of low-energy electrons, produced during the decay of $u$ states:

$$\omega(E) = \exp\left(-\frac{(2E)^{3/2}}{15\,(E_0')^{4/3}v_0}\right).$$

It has been shown[15,59] that in the general case of the de-

cay of states with large limiting values of $l$ the following expression holds:

$$\omega(E) = \exp\left(-\frac{A_l E^{l+(3/2)}}{v_0}\right), \tag{4.7}$$

where $A_l$ is a constant determined by the behavior of the terms near the point $R_0$. If follows that with increasing $l$ the centrifugal barrier becomes a progressively greater hindrance to the emission of low-energy electrons, and the average energy of the emitted electrons increases.

The Smirnov-Firsov model of two zero-range wells yields, in the case of two identical wells, a point $R_0$ (of entrance into the continuum) only for the antisymmetric $\Sigma_u$ state. In this model it is a simple matter to calculate the level width $\Gamma(R)$ for all values of $R$ small than $R_0$. It is thus possible to use expression (4.1) for the survival probability and to take into account the fact that the system does not necessarily decay at $R_{min} < R_0$. The result is a decrease in the decay cross section with increasing velocity of the colliding particles. Calculations of this type were carried out for the $H_2^-$ system in Ref. 60; the results are in satisfactory agreement with experiment. The existence of several problems involving electron detachment which can be solved exactly makes it possible to formulate a time-varying general problem,[18] which is apparently the greatest possible generalization of the Landau-Zener approximation.[1] This generalization may be outlined as follows: There is a system of normalized, orthogonal (i.e., noninteracting), unperturbed states which do not depend on the time. In addition, there is a time-varying perturbation, which is the operator which performs a projection onto some specified function $\varphi$ and which depends linearly on the time. Geometrically, the system may be described as a system of "diabatic" horizontal terms and one inclined rectilinear term, which intersects all the others (Fig. 7). The interaction of each of the horizontal terms and the inclined term is assumed to be constant. If this interaction is small in comparison with the distance between the levels, the problem decays into a system of Landau-Zener pseudocrossings, greatly separated from each other, and the probability for a transition from any initial state to any final state can be calculated as the product of elementary Landau-Zener probabilities. Analysis of the exact solution of this problem shows, however, that this method for calculating the probability is correct even when the interaction is comparable to or large in comparison with the distance between levels, so that the interaction regions overlap. We can thus take the limit of going to a continuum, by reducing the distance between levels to zero. In this case we find precisely that case which holds during electron detachment when a bound state of a quantum system goes into the continuum, converting into an approximately stationary state with a definite width (the imaginary part of the energy) $i\Gamma/2$, and the spectrum of emitted electrons is found as a consequence of this decay at various times. It should be emphasized that this approximation permits an arbitrary interaction between the inclined level and the continuum; in other words, the width $\Gamma$ can vary in an arbitrary manner over time. In precisely the same manner, the state density in the continuum can be arbitrary—we may allow states to concentrate around certain values of the energy (i.e., we may allow approximately stationary states in the unperturbed continuum) and thereby describe the Landau-Zener interaction of approximately stationary states, etc.

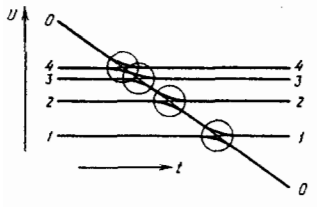



FIG. 7. Discrete system of adiabatic (heavy lines) and diabatic (light lines) terms for the generalized Landau-Zener approximation. These regions may overlap. The diabatic states are numbered at $\pm\infty$. A transition between an arbitrary initial state and a final state can occur only along a single chain of pseudocrossings, and the probability is found as the simple product of the elementary probabilities.

It can thus be seen that this class of problems is extremely broad, and by choosing the free parameters appropriately we can generate approximate descriptions of not only actual electron-detachment processes but also other physical processes. In particular, it may be suggested that this approximation can be used in the electron theory of the solid state, when there is a local energy level which goes from the energy gap into an allowed band upon a change in some slowly varying parameter.[5)]

In this approximation, the time-dependent energy operator of the system $H(t)$ is mathematically the sum of a time-independent operator $H_0$, which describes the horizontal system of terms, and an operator $V(t)$ (a linear function of the time), which performs a projection onto some specified function $\varphi$:

$$H = H_0 + |\varphi\rangle \beta t \langle\varphi|.$$

The general solution of the Schrödinger equation can then be written as the contour integral

$$|\psi\rangle = N \int_c \frac{\langle (H_0 - E)^{-1} | \varphi\rangle}{\langle \varphi | (H_0 - E)^{-1} | \varphi\rangle} \exp\left(-\frac{i}{\beta}\int^E \frac{dE'}{\langle \varphi | (H_0 - E)^{-1} | \varphi\rangle} - iEt\right) dE, \tag{4.8}$$

where the integration contour is determined by the initial condition, as it ordinarily is in the Laplace method. For a purely discrete spectrum in the natural representation, the operator $H$ is

$$H = \begin{pmatrix} \beta t & h_1 & h_2 & h_3 \dots \\ h_1 & \lambda_1 & 0 & 0 \dots \\ h_2 & 0 & \lambda_2 & 0 \dots \\ \dots & \dots & \dots & \dots \end{pmatrix},$$

where the parameters $\lambda$ characterize the horizontal (diabatic) terms, while the parameters $h_i$ characterize the interaction of these terms with the diabatic term $E = \beta t$ (Fig. 7).

[5)] The abstracts of the last International Conference on the Physics of Electronic and Atomic Collisions[97] contain a description of a theoretical approach similar to that taken here and apparently slightly more general.

The argument of the exponential function [Eq. (4.6)] may be regarded as an integral of the complex energy which has been integrated by parts:

$$\int E(t)\,dt = -\int_{E_0}^{E} t(E)\,dE,$$

where $t(E)$ is the inverse of the function $E(t)$. After this transformation, the spectrum of emitted electrons is no longer described by the expression

$$\omega(E) = \int_{E}^{\infty} \exp\left(-\frac{1}{\hbar}\int_{-\infty}^{t(E)} \Gamma(t')\,dt'\right) dE,$$

which holds only at small values of $\Gamma$; it is now described by

$$\omega(E) = \exp\left(-\frac{1}{\hbar}\int_{E_0}^{E} \operatorname{Im} t(E')\,dE'\right),$$

which holds for arbitrary relationships between $E$ and $\Gamma$ (aside from the case $E = \text{const}$, which gives us an ordinary dispersion distribution only in the case of some particular limit).[61,71] In the simplest of the cases discussed above, we have

$$E = -\frac{\beta^2 t^2}{2}, \quad t = \beta^{-1}\sqrt{-2E}, \quad \omega(E) = \exp\left(-\frac{4\sqrt{2}}{3\beta}E^{3/2}\right).$$

It is a simple matter to derive in a similar way Eq. (4.7) in the case $l \neq 0$. The spectrum of low-energy electrons near the continuum boundary is thus found from some extremely simple formulas describing the behavior of the complex energy as a function of the time. The problem of finding an effective approximate method in the electron-detachment problem essentially reduces to the search for an approximate quantum model in which the complex energies of the approximately stationary states (the poles of a Green's function) near the origin on the energy plane depend on the time in the same manner as for a real system of colliding particles. The behavior of the poles far from the origin is inconsequential for the low-energy part of the electron spectrum.

The general approach outlined above for dealing with processes involving the interaction of a single state and of a system of noninteracting states has made it possible to derive a general theory for ionization in slow collisions of atoms when the energy of the emitted electron is low.[17] In this case the unperturbed operator $H_0$ describing the noninteracting system of terms must be chosen to be the energy of the electron in the Coulomb field of the quasimolecular ion which remains after the ionization. Another natural suggestion, which holds in the case of a low electron energy, is that in the well, far from the turning point, all the hydrogen-like wave functions of both the discrete and continuous spectra differ by only a coefficient, for a given value of $l$, and can be expressed approximately in terms of Bessel functions (at zero energy, this expression becomes exact). Figure 8 shows a general picture of the continuum, of the Rydberg levels, and of a term which has interacted with them. This theory describes the interaction in the vicinity of $R \approx R_0$, where the diabatic term (indicated by the dashed line) goes into the continuum. An infinite series of Landau-Zener pseudocrossings

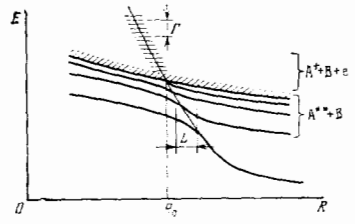



FIG. 8. Sketch of the adiabatic (heavy curves) and diabatic terms in the case of ionization. An infinite system of pseudocrossings with a Rydberg series of high-energy states of the AB molecule is shown. In the continuum, $R < R_0$, the width $\Gamma$ does not tend toward zero in the limit $R \to R_0$. The parameter $L$ is the interval over which the principal number (the quantum defect) changes by 1/2, the same for all pseudocrossings.

arises in this region. It can be seen from Fig. 8 that as R changes, and the region of $R_0$ is crossed along the adiabatic term, the effective quantum number, a measure of the binding energy $[E = -(1/2)n^2]$, changes by one. Denoting by $L$ the interval in which $n$ changes by one half, we find an expression for the integrated electron spectrum in the final state:

$$\omega = \omega_0 \exp\left(-\frac{LE}{\hbar v}\right), \tag{4.9}$$

where $\omega_0$ is the probability for the system to reach the energy $E = 0$ in the course of motion along the inclined term, and $v$ is the radial velocity of the colliding particles in the vicinity of $R \approx R_0$. This expression also holds at negative energies, as long as the Rydberg levels lie close to each other, and the stepped nature of the integrated spectrum in the discrete region is not obvious. In this approximation we can clearly see the characteristic "blurring" of the boundary between the discrete and continuous spectra, caused by the attractive Coulomb field.

Along with the time-varying problems involving the interaction of one term with a system of terms or with a continuum, in which the energy operator depends explicitly on the time, the approximation described above can also be used to treat the relative motion of the atoms from the quantum-mechanical standpoint.[18] This approach becomes necessary if the energy of the colliding particles is comparable to the energy of the emitted electrons, so that energy conservation and the boundedness of the electron spectrum must be taken into account. In the time-varying approximation, there is no high-energy bound on the electron spectrum.

Corresponding results for the spectrum of emitted electrons were reported in Ref. 58. So far, however, we have no experimental data on the electron distributions in this range, and we will not discuss these calculations here. In the high-energy limit they predict the same spectra as are predicted by the time-varying approximation in which the distance between the nuclei, $R$, is treated as a classical time-dependent parameter.

## 4. COMPARISON OF THEORY AND EXPERIMENT

The major region in which theory can be compared with experiment is the low-energy part of the electron

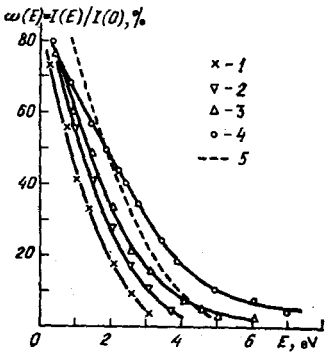



FIG. 9. Integral electron spectra[3] $\omega(E)$ for $Cl^-$, He. 1—$T=300$ eV; 2—500; 3—1000; 4—2750; 5—experimental results[45] for $T=2000$ eV.

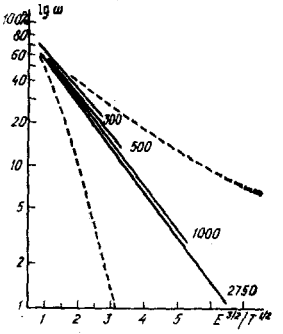



FIG. 11. The same as in Fig. 10, but here the abscissa scale is proportional to $E^{3/2}/(T_0/T)^{1/2}$. $T_0=1000$ eV. According to the theory, all the lines should coincide. Shown for comparison, by the dashed curves, are results obtained for $T=T_0$ when the abscissa scales are $E^1$ and $E^2$. There is a clear deviation of the dashed curves from the straight lines, confirming the power $E^{3/2}$ in the argument of the exponential function.

spectrum. It is there that the wave functions and the complex energies have their simplest time dependence, although the theory does not allow us to derive rigorously, from general considerations, the interval of electron energies in which the basic equations are applicable. We may nevertheless expect that the equations for the low-energy part of the spectrum, which includes a large fraction of the emitted electrons, are applicable over the energy interval from zero up to a value of the order of the electron affinity for the negative ion. From this point of view, the range of applicability is broader for the detachment of an electron from the halogen ions $F^-$, $Cl^-$, $Br^-$, and $I^-$ than from, for example, the ions of alkali metals, for which the electron affinities are a few tenths of an electron volt. The primary theoretical dependence to be tested is the dependence of the integrated spectrum on the energy and velocity of the collision. Using (4.5) and (4.6), we find that if we plot the electron energy, raised to the three halves power and divided by the collision velocity, along the abscissa, and if we plot the logarithm of the intensity of the integrated spectrum along the ordinate, we find a universal straight line which holds for all collision energies. This dependence holds very well in several cases. Figure 9 shows, in ordinary scale, the integrated spectra (retardation curves) for $Cl^-$ + He collisions at three collision energies. Figure 10 shows the same results, but as a plot of $\ln\omega(E)$ against $E^{3/2}$. Finally, the quantity plotted along the abscissa in Fig. 11 is $E^{3/2}(T_0/T^{1/2})$. We see that the change in scale which we made in going from Fig. 9 to Fig. 10 caused the curves to straighten out, and in going from Fig. 10 to Fig. 11 all the curves came to conform to a common straight line, within an error comparable to the experimental error. In order to show that the energy exponent of 3/2 actually follows from the experimental data, we have plotted results for a collision energy $T=2750$ eV for three abscissa scales in Fig. 11: $E^1$, $E^{3/2}$, and $E^2$. The $E^1$ and $E^2$ scales result in a substantial deviation of the experimental curve from a straight line. Figure 12 is a corresponding plot for $Br^-$ + He collisions.

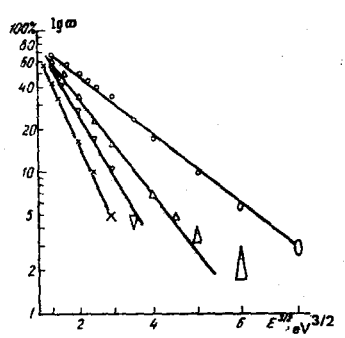



FIG. 10. The same as in Fig. 9, but here the abscissa scale is proportional to $E^{3/2}$ and the ordinate scale to $\log\omega$. The theory predicts a linear dependence. The "sizes" of the experimental points approximately reflect the error due to the change in scale.

The real situation, we might note, is generally much more complicated than the approximate calculations of this section of the paper. For a collision of a negative halogen ion with an inert gas, for example, the halogen is left in a $p$ state after electron detachment. There are accordingly two terms in the neutral quasimolecule ($\Sigma_1$ and $\Pi$ terms), two continuum boundaries, two critical points ($R_0'$ and $R_0''$), and two possible decay modes of a quasimolecular ion in the $\Sigma$ state. The angular momentum of a weakly bound electron is zero for one mode ($\Sigma-\Sigma$) and unity for the other ($\Sigma-\Pi$). Comparison with

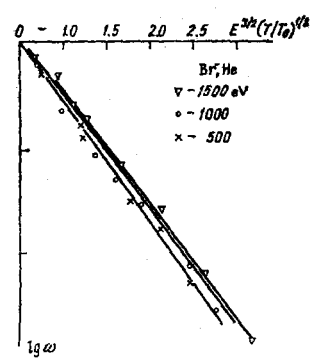



FIG. 12. The same as in Fig. 10, but for the pair $Br^-$, He.

experiment shows that for $Cl^- + He$ collisions the interaction of the term of the molecular ion with the $\Pi$ term is weak, while that with the $\Sigma$ term is strong. To the best of our knowledge, no corresponding theoretical calculations have been carried out. In principle, there might be a superposition of two electron spectra with comparable interactions, or there might be a nearly pure $\Sigma-\Pi$ interaction, with a corresponding spectral shift toward higher energies.

In collisions of the $A^- + A$ type there are equal probabilities for the occupation of two terms of a quasimolecule: terms which are symmetric and antisymmetric with respect to the plane passing halfway between the atoms. Correspondingly, two critical term-crossing points appear. For the $H^- + H$ system we must consider the two terms $\Sigma_g$ and $\Sigma_u$ and two states of the neutral system, $\Sigma^1$ and $\Sigma^3$, with a zero total spin (the ground-state term of the molecule, $\Sigma^1$) and with a unit total spin (the repulsive triplet term, $\Sigma^3$). The simple relationship $\Gamma \sim E^{l+(3/2)}$ holds (for $l \neq 0$) in all cases at sufficiently small values of $E$ near the critical point. From this standpoint, the expressions in (4.5) and (4.7) are also universal expressions at sufficiently small values of $E$. As mentioned earlier, however, it is difficult to evaluate the range of applicability of this dependence, and at the present stage of the relationship between theory and experiment it would be most natural to determine this region empirically. In general, the increase in $\Gamma$ slows with increasing $E$, and in the limit $R \to 0$, as the system approaches a spherically symmetric combined atom, we can expect a decrease in $\Gamma$ due to an increase in the overall symmetry of the system.

These arguments can be used to analyze the differential electron-detachment spectra found in Ref. 45. Figure 13 compares the spectrum of electrons emitted at an angle of 90° from the direction of the incident beam with the theoretical curve for $Cl^- + He$ collisions.

The slight oscillations in the experimental distribution apparently could result from interference effects averaged over the impact parameter. These oscillations should be seen most clearly in the "triple" differential cross section, for which the scattering angle of the heavy particles, the electron emission, and the electron emission angle are all fixed. In other words, we are approaching a "complete" experiment: an exact specification of the initial and final states of the system.

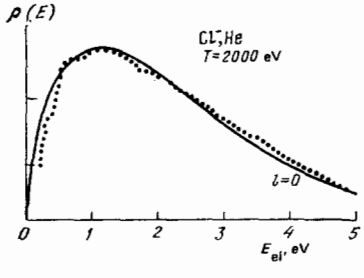



FIG. 13. Comparison of the theoretical results (4, 7), with $l=0$, with experimental results[45] for the pair $Cl^-$, He. $T=2000$ eV. The decaying low-energy part of the spectrum predicted by the theory is clearly shown. The experimental data are shown in arbitrary units. The theoretical and experimental curves were drawn to coincide at the peak.

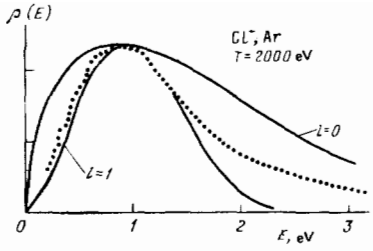



FIG. 14. The same as in Fig. 13, but for the pair $Cl^-$, Ar. $T=2000$ eV. The theoretical curves are drawn for $l=0$ and $l=1$ [Eq. (4.7)].

tem. The agreement with the results found previously by Bydin[3] can be judged on the basis of the figure. The cross section for electron emission integrated over emission angle will contain no traces of interference effects and should be described better by Eqs. (4.5) and (4.7). In this case we can achieve a satisfactory agreement between the theoretical expression and experiment by adjusting a single parameter, which determines the position of the maximum. Unfortunately, no spectra are given in Ref. 45 for other collision energies; the theory unambiguously predicts a change in the spectrum in this case. For some other pairs, $Cl^- + Ar$ and $Cl^- + Kr$, the spectral shape is described more poorly by Eq. (4.5), apparently because the two decay modes corresponding to $l=0$ and $l=1$ make comparable contributions. The rising part of the spectrum shows that the case $Cl^- + Ar$ (Fig. 14) is described better by (4.7) with $l=1$, while the case $Cl^- + Kr$ in fact corresponds better to $l=2$ (Fig. 15). The theoretical formulas predict a faster decay of the spectrum at high electron energies, which clearly indicates a slowing of the increase in the level width in comparison with the low-energy dependence $\Gamma \sim E^{l+(3/2)}$.

The basic distinction between the spectra of electrons emitted in collisions of neutral atoms or positive ions is that the argument of the exponential function always contains the energy raised to the first power. In contrast with the case of negative ions, therefore, the differential energy spectrum does not tend toward zero as the electron energy does. The reason is that in the absence of a long-range Coulomb interaction between the emitted electron and the quasimolecule the state density of the continuum tends toward zero at low energies (the more rapidly, the larger is $l$), while in the case of a long-range Coulomb interaction the continuum boundary becomes "smeared" (as mentioned earlier), and the in-

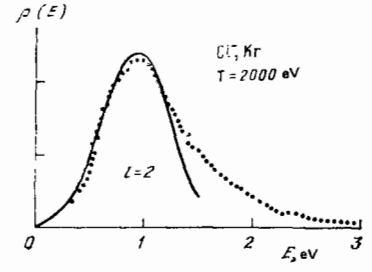



FIG. 15. The same as in Figs. 13 and 14, but for the pair $Cl^-$, Kr. $T=2000$ eV. The theoretical curve is drawn for $l=2$ [Eq. (4.7)].

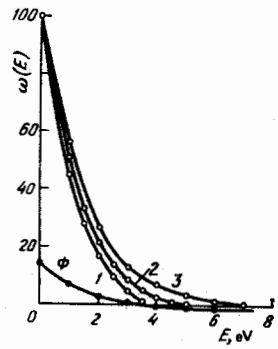



FIG. 16. Experimental results on the integral spectrum $\omega(E)$ in the K, Ne ionization. 1—$T$ = 700 eV; 2—1260; 3—2350. The background current is shown for the energy $T$ = 2350 eV.

teraction of the bound state with the continuum does not weaken in the limit $E \to 0$. Figure 16 shows integrated electron spectra for K+Ne collisions at various energies.[19] If these experimental points are plotted as the logarithm of the intensity against the electron energy, divided by the square root of the collision energy, we find the result shown in Fig. 17, i.e., a universal straight line, within the experimental errors.

Although this good agreement between theory and experiment is observed for only a few pairs of colliding atoms, the very fact that these "pure" cases exist is important. In all other cases (see Fig. 22 below) there is an initial (low-energy) descending part of the spectrum, where the theory applies, while the subsequent deviations occur because other decay channels come into play, because the increase in $\Gamma(R)$ slows down, because of an interaction with other autoionization states, etc.

## 5. AUTOIONIZATION STATES AND THEIR EXCITATION; MONOENERGETIC GROUPS OF ELECTRONS

Excitation of autoionization states plays an important role in atomic collisions and has been the subject of many studies. The results of these studies are periodically summarized in specialized reviews (Ref. 28 and 73–76, respectively).

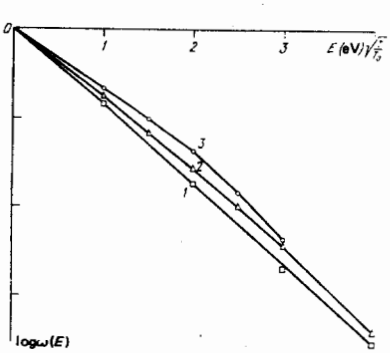



FIG. 17. Comparison of the data of Fig. 16 with the theory. The quantity $E\sqrt{I/I_0}$ is plotted along the abscissa for $T_0$ = 1260 eV; the quantity $\log\omega(E)$ is plotted along the ordinate. The theory predicts that all the data should conform to a common curve.

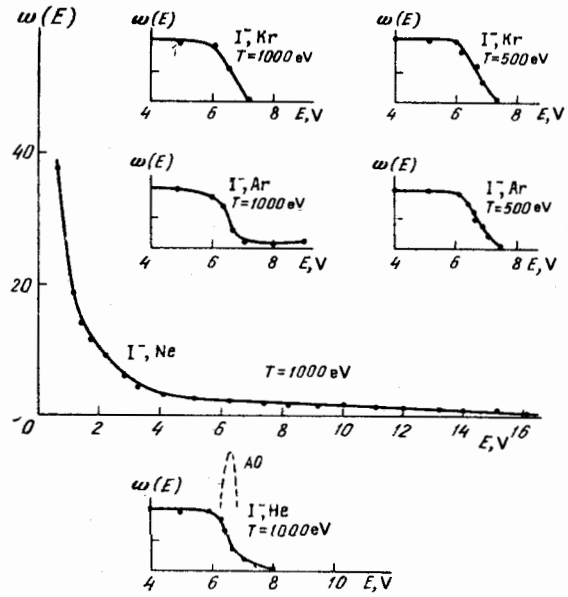



FIG. 18. The integral spectrum[3] $\omega(E)$ for $I^-$, Ne at an energy $T$ = 1000 eV and the "high-energy" parts of $\omega(E)$ for $I^-$, He at $T$ = 1000 eV and for $I^-$, Ar and $I^-$ Kr. The retarding potential $E$, in volts, is plotted along the abscissa; the ordinate scale is arbitrary. The stably descending high-energy parts of the curves indicate excitation of autodetachment states. AO (dashed curve)—position of the monoenergetic peak observed in the differential distribution in Ref. 3, associated with the excitation of an autodetachment state of the $I^-$ ion.

The first experimental indication of the excitation of autodetachment states of negative ions in collisions with atoms[6] came from Ref. 3. For collisions of the negative ions $I^-$ with He, Ar, Kr atoms, a monoenergetic group of electrons with an energy in the interval 6–7 eV was observed. These electrons were a consequence of the excitation of autodetachment states[7] of $I^-$ ions (Fig. 18). The intensity of this monoenergetic group increased with increasing collision energy (Fig. 19). Bydin[3] also observed that the conditions for the excitation of this monoenergetic group and its intensity were not determined exclusively by the kinetic energy of the relative motion of the two particles. There is a certain selectivity in the excitation: a dependence on the particular properties of the colliding particles and on the particular combination of particles.[8] In this sequential

[6] The excitation of autoionization states in collisions of neutral particles was first observed in a study[16] of the collisions of inert gas atoms.

[7] In one of the recent papers[35] devoted to autodetachment states of negative ions, a careful study was made of this energy range for this case, and a tentative identification of autodetachment states was offered (Fig. 20).

[8] It is interesting to note the anomalous features in the dependence of the conditions for the excitation of the monoenergetic groups on the nature of the particular particles involved, as observed in Ref. 34 for collisions of $Br^-$ ions with He and Ar. In the $Br^-$, He case, monoenergetic groups were detected which corresponded to both autodetachment states of $Br^-$ and autoionization states of the neutral Br atoms. In the $Br^-$, Ar case, on the other hand, only the $Br^-$ autodetachment peaks were observed. As mentioned in Ref. 28, this fact has yet to be explained satisfactorily.

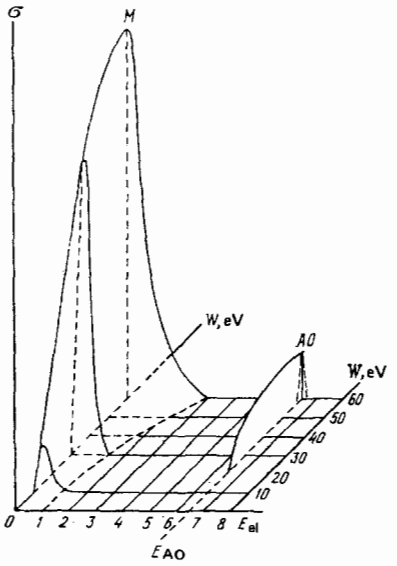



FIG. 19. Sketch of the formation of the electron energy distribution with a change in the energy of the relative motion, $W$ (electron volts). $I^-$ ions in He; the $\delta$ cross section in arbitrary units. AO—Excitation function of the monoenergetic electron group at $E = 6.41$ eV, associated with the excitation of an autodetachment state of the $I^-$ ion. The large "sail" characterizes the dependence of the spectrum of the monoenergetic electron group on the energy of the colliding particles. The small "sail" corresponds to the excitation of a monoenergetic electron group.

transition from the $I^-$, He pair to the cases of heavier inert gases, for example, this group *was essentially not observed* for the $I^-$, Ne pair; it reappeared again in the $I^-$, Ar and $I^-$, Kr cases. The first indication of this manifestation of the individual properties of the colliding particles in collisions of a negative ion with an atom came from Ref. 8, where an anomalous magnitude and an anomalous behavior were observed for the total electron-detachment cross sections for $I^-$, Ne collisions[9] (Fig. 21). Some recent measurements[45,77] of the differential cross sections for collisions, carried out with a position-sensitive detector, also revealed some anomalous results for the $I^-$, Ne pair. The investigators ascribed the anomalous results to the lack of a crossing of the potential curves for $I^- + Ne\ X^1\Sigma$ and $I + NeX^2\Sigma$.

In a subsequent series of studies,[29-36] the primary purpose was to learn more about the autodetachment states by observing and identifying these monoenergetic groups.

The results was the appearance of a new research field: the collisional spectroscopy of negative ions.

Table I, from Ref. 28, shows some data on the autodetachment states which have been observed.

With regard to the nature of these states, it was stated in Ref. 28–36 that they can be classified as

[9] Several anomalous features have also been observed in the detachment of electrons in collisions of negative alkali-metal ions with inerg-gas atoms, e.g., for the pairs $Li^-$, He and $Na^-$, Ne (Ref. 11).

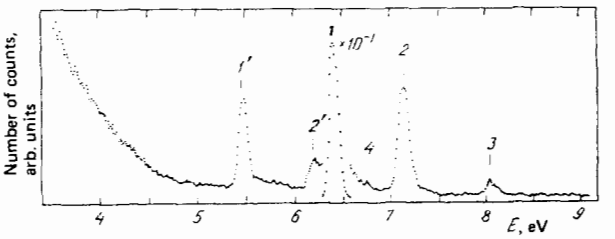



FIG. 20. Part of the energy distribution of the electrons emitted in $I^-$, He collisions according to the measurements of Ref. 35 with a high energy resolution. The energy of the beam ions is $T = 2$ keV. The intensity of the main peak (1), observed in Refs. 2 and 3, is reduced by a factor of ten. A tentative identification of the initial and final states of $I^-$ and I is offered in Ref. 35.

doubly excited states with predominant *nlnl* configurations (for a positively charged core). The most intense line usually corresponds to the lowest possible state, $ns^2$. An exceptional case is the excitation of various states of the $2s2p^6$ subshell for $O^-$. Many of the states listed in Table I have been independently determined theoretically for $C^-$, $O^-$, and $Cl^-$, and they have also been determined experimentally by other methods (the $H^-$-electron resonance).

It has thus proved possible to use collisions of heavy particles as a convenient method for exciting autodetachment states of negative ions. As shown in Ref. 28, several systems which could not be studied by the electron-resonance technique turned out to be amenable to study by this method.

Since the data in Table I were found from experiments which have so far been carried out for a comparatively few negative ions and over a rather narrow interval of collision energies, there is the hope that the collision method will make it possible to observe many other autodetachment states for various negative ions.

In collisions of fast neutral atoms with atoms, there is the possibility that monoenergetic groups of electrons will be excited, in addition to the group of "slow electrons," with energies ranging from zero to several electron volts (and whose formation was discussed in the preceding section of this paper). Study of the electron spectra in collisions of neutral atoms was begun in Ref. 16, which we have already mentioned. The approach there was to study the collisions of the pairs (He, He), (Ne, Ne), (Ar, Ar), (Kr, Kr), and (Xe, Xe) over the energy range from 300 to 3000 eV in the laboratory

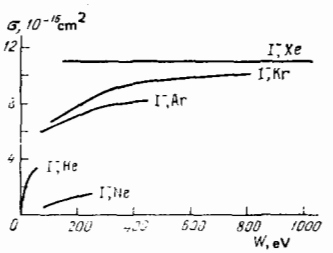



FIG. 21. "Anomalously" small detachment cross section for the $I^-$, Ne Pair, in comparison with the corresponding cross sections for $I^-$, He; $I^-$, Ar; and $I^-$, Kr.

TABLE I. Autodetachment states of negative ions observed by the excitation method during collisions.

| Ion | State energy, eV | Reference | Ion | State energy, eV | Reference | Ion | State energy, eV | Reference |
|---|---|---|---|---|---|---|---|---|
| $H^-$ | 9.59±0.03 | 26 | $F^-$ | 14.85±0.04 | 32 | $I^-$ | 6.41±0.06 | 35 |
| | 9.76±0.03 | | $Cl^-$ | 8.53±0.05 | 33 | | 6.75±0.06 | |
| $C^-$ | 7.44±0.07 | 36 | | 9.15±0.05 | | | 7.15±0.06 | |
| $O^-$ | 9.50±0.02 | 31, 36 | | 9.97±0.04 | | | 8.06±0.06 | |
| | 10.11±0.02 | | | 12.09±0.06 | | | | |
| | 10.87±0.02 | | $Br^-$ | 7.39±0.06 | 34 | | | |
| | 12.12±0.02 | | | 7.84±0.06 | | | | |
| | 13.71±0.02 | | | 8.85±0.06 | | | | |

frame. The low resolution of the apparatus, however, made it difficult to interpret the results. Systematic study of the electron spectra in collisions of the alkali metal atoms Na, K, Rb, Cs (which have low ionization potentials[10]) with inert-gas atoms was begun in Ref. 19 and continued in Refs. 78–82. Study of the electron spectra in collisions of neutral particles was continued in later papers by several investigators. As a result of this work it became possible to link the appearance of the monoenergetic groups with the excitation of autoionization states of the projectile and target particles. The major thrust of these studies was an effort to identify the autoionization states. It should be noted that there is a selectivity in the excitation of monoenergetic groups, which was followed in a study of collisions involving alkali metal atoms. This selectivity—a dependence of the excitation conditions on the particular properties of the colliding particles—can be illustrated by Fig. 22, which shows integral electron spectra for collisions of an alkali metal atom with an inert-gas atom. We see that the excitation conditions are determined by not only the kinetic energy of the relative motion but also the particular combination of particles. This selectivity of the excitation process may apparently be characteristic of collisions of heavy particles at comparatively low energies, at which only the outer shells of the particles are involved in their interactions.[11]

In some cases, over the ranges of conditions studied, it has been found that the number of particles in the monoenergetic groups can be a large fraction of the total number of emitted electrons (40%, for example, for the case of Rb, He at an energy $T = 3$ keV).

The appearance of monoenergetic groups can also be linked with a peculiar process observed[80] for the Rb, Ar case. This process is a close analog of Penning ionization [the excitation of one particle (Ar) to a state below the ionization limit and the "Penning ionization" of the other particle (an Rb atom), accompanied by the emission of monoenergetic electrons (Fig. 22)]. The appearance of a group of electrons with an energy of about 7 eV (7.2 eV according to a later study[84]) has been ascribed to this process. This process has also been observed for other pairs of particles, e.g., He, He and Ar, Ar (Ref. 85).

The study of the excitation functions of the monoenergetic groups in collisions of neutral particles is complicated by the difficulties in accurately measuring the intensity of the primary beam of fast atoms. An excitation function of a monoenergetic group observed for the Ar, Ar pair by Gerber *et al.*[86] corresponds to the Landau-Zener model [for the transition $Ar(3s, 3p^6, 4s)^1S \rightarrow Ar^*(3s^2, 3p^5) + e^-$ the energy of the electrons in the group is $E = 9.4$ eV]. Many of the observed excitation functions, however, are not consistent with this model and are more complex; they may become the subject of future research.

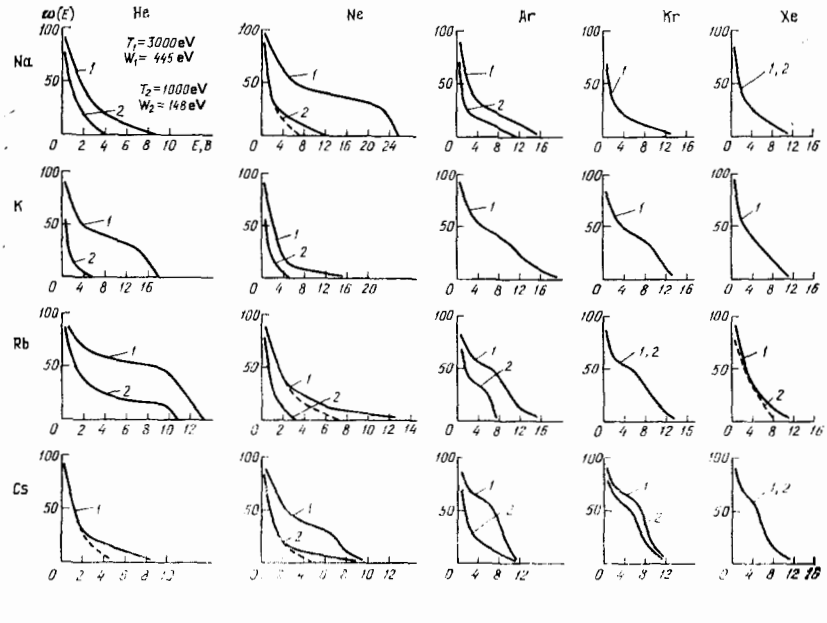
As has been mentioned in several papers (Ref. 28, for example), study of the electron spectra in collisions involving heavy particles is becoming a convenient tool for purely spectroscopic research. This method presents the experimentalist some opportunities not available in methods based on electron-atom collisions and studies of photoabsorption. By using projectile particles with various atomic-core configurations and with various spins, and by making use of the selectivity of the excitation process, it becomes possible to "turn on" or "off" the excitation of certain particular levels, which can be chosen by the experimentalist [the primary limitation in this approach in collisional spectroscopy is the limited energy resolution, associated with the kinematics of the collision (see the section "Experimental Procedure"), primarily the Doppler broading]. On the whole, study of the monoenergetic groups, identification of these groups, study of the angular dependences, and measurements of the peak widths have become a rapidly growing field of activity in the physics of atomic collisions.

From the theoretical standpoint, the excitation of autoionization and autodetachment states results from a crossing or pseudocrossing of two or several unstable states far from the continuum boundary. The theory for such crossings is a natural generalization of the Landau-Zener theory for bound states and also other cases: the Nikitin case,[87] the Nikitin-Demkov case (Ref. 88), transitions resulting from a rotation of the axis connecting the nuclei, etc.[1,89] For unstable states of a quasimolecule, it may be possible to derive a theory of transitions completely analogous to the theory for bound states. From the experimental standpoint, these transitions are in fact "more observable," since even the motion of the system along a single quasistationary term is reflected in the electron spectrum. At the term crossing points, structure may be observed in the spectrum; there may be an interference of electron spectra; etc. One example of this interference was observed in Ref. 90 for two groups of autoionization peaks in $K^* + Ar$ collisions. Both groups oscillated, out of phase, as functions of the collision energy (Fig. 23), proving that the oscillations are of an interference nature.

The correlation between the structure in the differential and total scattering cross sections, on the one hand, and the beginning of the excitation of some elec-

[10] This case corresponds better to the assumptions embodied in the theory of Ref. 17.

[11] Anomalies observed in studying cross sections for ionization of alkali atoms colliding with inert gas atoms are correlated with the selectivity of the process of excitation of autoionization states.




| | He | Ne | Ar | Kr | Xe |
|---|---|---|---|---|---|
| Na | $T_1$ = 3000<br>$W_1$ = 445<br>$T_2$ = 1000<br>$W_2$ = 148 | $T_1$ = 500<br>$W_1$ = 223<br>$T_2$ = 200<br>$W_2$ = 93 | $T_1$ = 2530<br>$W_1$ = 1604<br>$T_2$ = 600<br>$W_2$ = 380 | $T_1$ = 1200<br>$W_1$ = 948 | $T_1$ = 1200<br>$W_1$ = 1020<br>$T_2$ = 600<br>$W_2$ = 510 |
| K | $T_1$ = 2200<br>$W_1$ = 204<br>$T_2$ = 280<br>$W_2$ = 24 | $T_1$ = 2200<br>$W_1$ = 740<br>$T_2$ = 260<br>$W_2$ = 88 | $T_1$ = 1000<br>$W_1$ = 505 | $T_1$ = 1000<br>$W_1$ = 680 | $T_1$ = 1000<br>$W_1$ = 770 |
| Rb | $T_1$ = 3000<br>$W_1$ = 135<br>$T_2$ = 1560<br>$W_2$ = 67,5 | $T_1$ = 3000<br>$W_1$ = 570<br>$T_2$ = 500<br>$W_2$ = 95 | $T_1$ = 3000<br>$W_1$ = 954<br>$T_2$ = 200<br>$W_2$ = 63 | $T_1$ = 3000<br>$W_1$ = 1500<br>$T_2$ = 300<br>$W_2$ = 150 | $T_1$ = 3000<br>$W_1$ = 1815<br>$T_2$ = 200<br>$W_2$ = 120 |
| Cs | $T_1$ = 3000<br>$W_1$ = 87,5 | $T_1$ = 2950<br>$W_1$ = 386<br>$T_2$ = 1500<br>$W_2$ = 196 | $T_1$ = 600<br>$W_1$ = 138<br>$T_2$ = 300<br>$W_2$ = 69 | $T_1$ = 600<br>$W_1$ = 230<br>$T_2$ = 300<br>$W_2$ = 115 | $T_1$ = 600<br>$W_1$ = 297<br>$T_2$ = 300<br>$W_2$ = 148 |

FIG. 22. Integral spectra[82] $\omega(E)$ for collisions of alkali metal atoms with inert gas atoms for various energies in the laboratory frame ($T$, electron volts) and in the c.m. frame ($W$, electron volts). The retardation potential, $E$ in volts, is plotted along the abscissa. The ordinate scales are the same for all curves [$\omega(0) = 100\%$].

tron energy groups, on the other hand, indicates that these phenomena have a common cause: the beginning of an overlap of electron shells, which gives rise to a change in the behavior of the terms and to a crossing of the terms at strictly determined distances between the nuclei, $R$.

Along with the electron spectra which have a clearly defined low-energy part, in agreement with the theory in Section 3, or which have clearly defined autodetachment monoenergetic groups, there are a few ion-atom and atom-atom pairs whose spectra have a high-energy part which decays anomalously slowly; some examples are $I^-$, Ne; Rb, Ne; and K, Ne. These anomalous spectral features are accompanied by anomalous features in the total cross sections; for $I^-$, Ne, for example, the cross section at a given energy is roughly an order of magnitude lower than that for other inert gases. For $I^-$, Ne there is reason to believe that the $I^-$, Ne and I, Ne terms do not cross at all, so that the excitation of unstable quasimolecular states occurs with a lower probability.

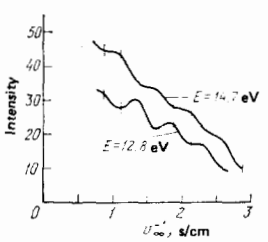



FIG. 23. Oscillations of the excitation functions (in arbitrary units) of the groups of electrons with the energies $E = 14.7$ eV (upper curve) and $E = 12.8$ eV (lower curve). The independent variable is the reciprocal of the collision velocity. The equidistant rule holds, and the oscillations are out of phase (the pair $K^+$, Ar).

The high-energy part of the electron spectrum may be a consequence of the survival and stabilization of molecular orbitals as the atomic particles close on each other. The conversion of a comparatively large fraction of the kinetic energy of the colliding particles into electron-excitation energy becomes a significant possibility. This type of energy conversion is usually greatly hindered by the large mass ratio of the electrons and atoms, and a search for processes which effectively populate the highly excited unstable states may be of definite practical interest. The stretching out of the high-energy part of the spectrum may be a consequence of a pseudocrossing of an unstable ground term with another, more stable, term. The interaction between these terms is such that there is a significant probability for the system to transfer to this term and to survive down to smaller values of $R$, where this term becomes prominent, and higher-energy electrons are emitted. (If this term is extremely narrow, the quasimolecule will survive until the particles fly apart, and autoionization peaks will appear in the spectrum.) Dalidchik and Ivanov[62] have offered a corresponding explanation for anomalous spectra.

## 6. ISOTOPIC EFFECT

When we turn to collisions of atoms, ions, and molecules which differ only in isotopic composition, we find that all the potential curves, pseudocrossings, critical distances, widths of autoionization states and autodetachment states, etc., remain the same for the different isotopes. All the differences in the effective cross sections and the spectra of the emitted electrons stem from the dynamics of the relative motion of the nuclei of different masses, without changes in the electron terms. We can therefore draw certain qualitative conclusions even when the quantitative behavior of the

terms is not known—solely on the basis of the isotopic effect.

An isotopic effect for the total ionization cross sections was discovered in Ref. 91 and observed later in Ref. 39. Specific measurements of the effect for the spectra of electrons emitted in collisions of alkali metal atoms with $H_2$ and $D_2$ molecules were carried out in Ref. 92. The combination of a heavy projectile (an alkali atom) with a light target (K, Rb, Cs; $H_2$, $D_2$) made it possible to attain a rather low collision energy in the c.m. frame (10–20 eV) and permitted accurate measurements of the threshold region for a rather high energy of the alkali metal atoms (250–500 eV).

There are two possible limiting cases for the dependence of the cross section and spectra of the emitted electrons on the isotopic composition. The simplest limit is that of fast collisions, where at all values of the impact parameter pertinent to the process the trajectories of the projectile particle are nearly rectilinear. We are also assuming that the target particle (atom or molecule) remains essentially fixed during the collision. It is then obvious that all the electron transitions, including the detachment of an electron or ionization, will go identically at given velocities of the projectile particle, regardless of the isotopic composition of the projectile and the target. It is also obvious that we must regard as inconsequential those collisions which are nearly head-on collisions, in which the trajectory is noticeably distorted (and differently for nuclei of different masses). In other words, this range of impact parameters, which narrows with increasing energy, must make a negligibly small contribution.

On the other hand, at low energies, near the threshold, where detachment or ionization requires that the system evolve along a nonstationary repulsive term of the quasimolecule, the emission of an electron with a given energy $E$ occurs only when a critical internuclear distance $R_0$ is reached. Near the threshold, this distance can be attained only in nearly head-on collisions, in which nearly all the energy of the relative motion of the nuclei, $W$, is converted into the potential energy of the electron term and of the Coulomb repulsion of the nuclei at the instant of closest approach. The position of the threshold in the effective cross section for a given energy of the emitted electrons therefore depends only on $W$, not on the isotopic composition. With increasing distance from the threshold, only the radial part of the energy $W$ can convert into potential energy; the relative importance of nearly head-on collisions falls off; and there is a gradual transition to a dependence of the cross section only on the velocity $v$.

The ionization cross section measurements of Ref. 91 yield values of the order of $10^{-17}$ cm$^2$, which are small

TABLE II.

| Pair | $T_{th}$, eV | $W$, eV | $V_i$, eV | Pair | $T_{th}$, eV | $W$, eV | $V_i$, eV |
|---|---|---|---|---|---|---|---|
| Cs, $H_2$ | 740 | 11.0 | 3.89 | Rb, $H_2$ | 490 | 11.2 | 4.18 |
| Cs, $D_2$ | 360 | 10.5 | 3.89 | Rb, $D_2$ | 280 | 12.5 | 4.18 |

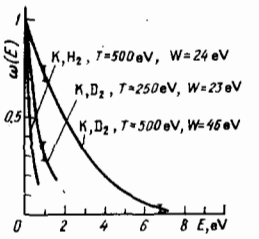



FIG. 24. Isotopic effect in the electron energy distribution.

in comparison with the sizes of atoms. There are two ways to interpret this result: Either the process goes with a low probability over a broad range of impact parameters ("a big but transparent target"), or it goes with a high probability in a narrow interval of impact parameters ("a small but dense target"). In the first case the cross sections and spectra must have been identical for identical velocities of the colliding particles, regardless of the isotopic composition. In the second case, we must be more or less approaching a case in which the cross sections (especially the thresholds in the cross sections) depend on $W$ alone. Table II shows that the thresholds $T_{th}$ (the "practical" thresholds, where the cross section, falling off sharply with the energy, becomes comparable to the experimental error) for two atom-molecule pairs for which measurements were made are in fact nearly the same for $H_2$ and $D_2$. The last column of this table shows the ionization potential of the alkali metal, i.e., the theoretical threshold for the process, which lies well below the practical threshold.

The electron spectra for K, $H_2$ and K, $D_2$ (Fig. 24) agree better with each other at a given value of $W$ than at given values of $v$ (or $T$). Measurements for a given projectile-target pair thus directly indicate the second possibility: a short critical distance and a "small but dense target" for the ionization (Fig. 25).

The measurements of Ref. 91 and 92 were carried out in an energy range where the cross section is increasing with the energy and has not reached the maximum, in which case we could expect the cross section to depend only on the velocity. For the pair K, $H_2$, however, the measurements were pursued to the point at

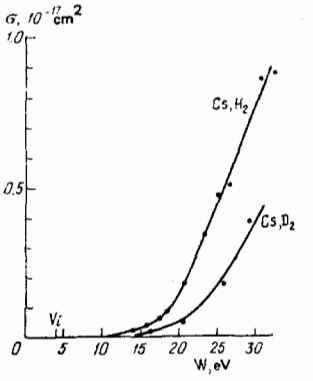



FIG. 25. Isotopic effect for the ionization cross sections; behavior near the threshold.

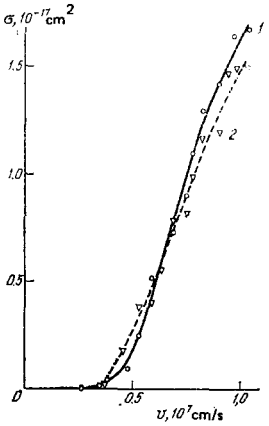



FIG. 26. Isotopic effect for the ionization cross sections. 1—K, $H_2$; 2—K, $D_2$.

which a transition to a maximum or at least to a slower increase in the cross section was found (Fig. 26). It is important to note that this bending of the curve occurs at the same velocity for $H_2$ and $D_2$, again in confirmation of the theory. Strictly speaking, the cross sections should have become identical in this case. It may be that a small absolute error was made in the measurements, in the determination of the pressure of the target gas ($H_2$ or $D_2$) and that the cross sections for $v > 1 \cdot 10^7$ cm/s are in fact more nearly equal.

Finally, we note that the isotopic effect is seen most clearly in the resonant dissociative capture of an electron:

$$(0)\ e + AB \to AB^- \begin{cases} \to AB \text{ (vibrational excitation)} + e, & (1) \\ \to A + B + e, & (2) \\ \to A^- + B, & (3) \end{cases}$$

where the $0 \to 1$, $0 \to 2$, and $0 \to 3$ processes are competing.

During the breakup of the unstable quasimolecule $AB^-$, the inverse decay occurs, and if the probability for the process $0 \to 3$ is small in comparison with those for $0 \to 2$ and $0 \to 1$ then $\int \Gamma dt$ depends strongly on the breakup time and correspondingly on the reduced mass of the colliding particles, i.e., on the isotopic composition. This effect was predicted theoretically[93] and observed experimentally[94] almost simultaneously for the collisions $e + H_2$ and $e + D_2$; the cross section for $D_2$ is much smaller than that for $H_2$. A large isotopic effect of the same nature has been observed for various simple organic and deuterated molecules.[95] The process under consideration here differs only in the initial and final channels ($1 \to 2$), goes through the same intermediate state, and is thus closely related to resonant dissociative capture.

## CONCLUSION

It can be concluded from the results covered in this review that a study of the spectra of the electrons emitted in collisions of atoms and ions yields information about the interactions of atomic systems which cannot be obtained by other methods. These spectra actually make it possible to study quasimolecular terms which are unstable with respect to electron detachment both at the boundary between the discrete and continuous spectra and also well into the continuous spectrum.

Near the continuum boundary the theory can be worked out in more detail, the spectra have a small number of effective parameters, and the agreement of theory and experiment is completely satisfactory. For negative ions, this circumstance is possible because the electron affinities of most negative ions are less than 1 eV (Ref. 98). This circumstance and also the comparatively rapid decrease in the electron-atom interaction force with the distance make it possible to use the boundary-condition method of Ref. 99 for a description of the system. The quantum-defect method is a corresponding method for atoms in this energy range (Rydberg states).[100]

It is interesting to note that this region forms an extremely distinctive class of quantum-mechanics problems, with distinctive methods and characteristic approximations, some of which were known previously, for example, in the theory of nuclear interactions (the method of zero-range potentials), while others were developed especially for this class of problems. Apparently, however, the latter methods can also be applied to other physical processes (the interaction of one term with a system of terms), so that this class of problems is important from the general theoretical standpoint.

Calculations for approximately stationary states of a system of colliding particles (a quasimolecule) are extremely complicated; the corresponding methods for many-electron systems are still being worked out. We will probably first see an accumulation of experimental data and theoretical analysis of these data with the goal of extracting the behavior of the terms and their widths as functions of the distance between the nuclei, $R$.

Experiments in which the scattering angle of the heavy particles and the energy and direction of the emitted electron are detected simultaneously are extremely important for further experimental progress. Here we can expect to find rapidly oscillating distributions, which would be a particularly rich store of information about the terms. It would clearly be of interest to carry out a systematic study of the various $A^- + B$ and $A + B$ pairs and to search for monoenergetic groups of electrons, i.e., for the excitation of autodetachment and autoionization states of atoms and ions. It is extremely important to study the inverse process, dissociative capture, about which we have said almost nothing here but which is intimately related to detachment. The theory makes quite definite predictions regarding the electron spectra in low-energy collisions near the threshold, and experimental data here would be extremely desirable.

The basic idea of the explanation of the spectrum of emitted electrons in terms of a "promotion" of a quasimolecular bound state into the continuum and the conversion of this state into an approximately stationary state is analogous to the concept of the promotion of terms corresponding to inner shells, which leads to the formation of vacancies in the inner shells of atoms and

ions. This idea was proposed in an effort to explain the discrete inelastic loss[101,64] in collisions of atoms and ions with energies of tens of keV and up. In this case we run into an unusual "self-preserving" property of the atoms: With increasing interaction energy, the same theoretical arguments turn out to be applicable to progressively deeper atomic shells.

The mechanisms for electron detachment in ion-atom collisions which we have discussed here may find significant use in describing the interaction of ions and atoms with solid surfaces. This is particularly true of the interaction of incident particles with atoms adsorbed on a surface, which are interacting only weakly with the crystal lattice. In many cases, however, the interaction of the incident atomic particle with the lattice may be regarded as a sequence of binary interactions with lattice atoms,[102-105] so that the methods of the *theory of atomic collisions are completely applicable.* Ion Auger spectroscopy is now being used quite widely [Ref. 105; the present state of this method was discussed in papers presented at the Sixth (and most recent) All-Union Conference on the Interaction of Atomic Particles with Solids[106]]. The formation of vacancies in inner shells of atomic particles is used in this method. As we go to slower incident ions we can expect that the general theory described in Section 3 of this review, for the interaction of one level with a group of levels, can be used to describe the emission of an electron either out of a crystal or into a vacant band—the conduction band. As we move to slower incident particles, we will find less damage to the object being analyzed. Many of the results discussed in this review can be used to study the spectrum of electrons emitted in collisions of slow ions or atoms with surfaces, so that this approach can be used as an effective method for studying surface properties. In particular, a study of the low-energy part of the electron spectrum, from a fraction of an electron volt to about 10–20 eV, and a search for monoenergetic electrons associated with the formation of free atoms and ions in ionization states may prove to be a unique method for studying the band structure of the outermost layers of a crystal, surface bands, etc. The general method for describing the interaction of a nonstationary level with the continuum (in particular, with an electron band) which was discussed in Section 3 can apparently be used for a theoretical analysis of the low-energy part of the spectrum of electrons emitted during the bombardment of a surface by atoms or ions. Finally, the presence of monoenergetic groups of electrons which are characteristic of the given colliding particles and which are selectively excited, depending on the particular combination of particles, makes it possible to study the outermost layers of a crystal without causing any important damage to the crystal. From this standpoint, low-energy ions and the processes which they initiate (including internal and external electron emission during bombardment by such ions) represent an important tool for surface research.

The electron-emission processes during slow atomic collisions which we have discussed here are intimately *related to other processes*, e.g., the associative detachment of an electron (and the inverse process, dissociative capture). In this case the emitted electron carries off so much energy that the colliding atomic particles are left in a bound state, and the electron spectrum during associative detachment correspondingly reflects the distribution of the resulting molecule over rotational and vibrational states.

From the general theoretical standpoint it would be important to study the widths of the unstable quasimolecular terms at small distances between nuclei, toward the limit of the combined atom. As has already been mentioned, there is reason to believe that as the quasimolecule approaches a spherically symmetric shape ($R \to 0$) the term widths should decrease substantially. A general theoretical or experimental confirmation of this possibility would be extremely interesting.

It can be seen from this review that research on the spectra of electrons emitted in low-energy collisions of atoms and ions is intimately related to many other fields of physics, is important for several practical applications, and can furnish unique types of information about unstable quasimolecular terms.

The overall program of research on unstable molecular terms is a field of activity no smaller in scope than research on the stable terms by optical and collisional methods.

The effective method described here for studying these terms, by means of electron spectra, may be called the "electronspectroscopy of time-varying molecular states."


[1]E. E. Nikitin and B. M. Smirnov, Usp. Fiz. Nauk **124**, 201 (1978) [Sov. Phys. Usp. **21**, 95 (1978)].
[2]Yu. F. Bydin, in: Abstracts of Papers of the Fifth International Conference on the Physics of Electronic and Atomic Collisions, Nauka, Leningrad, 1967, p. 218.
[3]Yu. F. Bydin, Pis'ma Zh. Eksp. Teor. Fiz. **6**, 827 (1967) [JETP Lett. (*sic*)].
[4]V. M. Dukel'skiĭ and É. Ya. Zandberg, Zh. Eksp. Teor. Fiz. **21**, 1270 (1951).
[5]J. B. Hasted and D. Phil, Proc. R. Soc. Ser. A **212**, 235 (1952); **222**, 74 (1954).
[6]J. B. Hasted and J. B. H. Stedeford, Proc. R. Soc. Ser. A **227**, 466 (1955).
[7]D. W. Sida, Proc. R. Soc. London, Ser. A **68**, 240 (1955).
[8]Yu. F. Bydin and V. M. Dukel'skiĭ, Zh. Eksp. Teor. Fiz. **31**, 569 (1956) [Sov. Phys. JETP **4**, 474 (1957)].
[9]D. G. Hummer, R. F. Stebbings, W. L. Fite, and L. M. Branscomb, Phys. Rev. **119**, 668 (1960).
[10]B. M. Smirnov and O. B. Firsov, Zh. Eksp. Teor. Fiz. **47**, 232 (1964) [Sov. Phys. JETP **20**, 156 (1965)].
[11]Yu. F. Bydin, Zh. Eksp. Teor. Fiz. **50**, 35 (1966) [Sov. Phys. JETP **23**, 23 (1966)].
[12]J. Risley, in: Proceedings of the Eleventh ICPEAC, Invited Papers and Progress Reports, North-Holland, Amsterdam, 1980, p. 619.
[13]Yu. N. Demkov, Zh. Eksp. Teor. Fiz. **46**, 1126 (1964) [Sov. Phys. JETP **19**, 762 (1964)].
[14]Yu. N. Demkov, Zh. Eksp. Teor. Fiz. **49**, 885 (1966) [Sov. Phys. JETP **22**, 615 (1966)].
[15]B. M. Smirnov, Atomnye stolknoveniya i élementarnye protsessy v plazme (Atomic Collisions and Elementary Processes in Plasmas), Atomizdat, Moscow, 1968.
[16]H. W. Berry, Phys. Rev. **121**, 1714 (1961); **127**, 1634 (1962).

[17]Yu. N. Demkov and I. V. Komarov, Zh. Eksp. Teor. Fiz. **50**, 286 (1966) [Sov. Phys. JETP **23**, 189 (1966)].
[18]Yu. N. Demkov and V. I. Osherov, Zh. Eksp. Teor. Fiz. **53**, 1589 (1967) [Sov. Phys. JETP **26**, 916 (1968)].
[19]Yu. F. Bydin and V. I. Ogurtsov, in: Abstracts of Papers of Fifth ICPEAC, Nauka, Leningrad, 1967, p. 220; V. I. Ogurtsov and Yu. F. Bydin, Zh. Eksp. Teor. Fiz. **57**, 1908 (1969) [Sov. Phys. JETP **30**, 1032 (1970)].
[20]R. E. Olson and B. Liu, Phys. Rev. **A20**, 1344 (1979).
[21]J. P. Gauyacq, J. Phys. B **20**, 1344 (1979).
[22]J. P. Gauyacq and V. Esaulov, cited in Ref. 12, p. 665.
[23]A. Z. Devdariani, Zh. Tekh. Fiz. **43**, 399 (1973) [Sov. Phys. Tech. Phys. **18**, 255 (1973)].
[24]V. A. Bazylev and H. K. Zhevago, Zh. Eksp. Teor. Fiz. **69**, 853 (1975) [Sov. Phys. JETP **42**, 436 (1975)].
[25]A. Herzenberg and P. Ojha, Phys. Rev. **A20**, 1905 (1979).
[26]A. Z. Devdariani, V. N. Ostrovskiĭ, and Yu. N. Sebyakin, Zh. Eksp. Teor. Fiz. **71**, 909 (1976) [Sov. Phys. JETP **44**, 477 (1976)]; **73**, 412, 1984 (1977) [Sov. Phys. JETP **46**, 215 (1977)]; **76**, 529 (1979) [Sov. Phys. JETP **49**, 266 (1979)]; see also Pis'ma Zh. Eksp. Teor. Fiz. **3**, 873 (1977) [JETP Lett. (*sic*)].
[27]V. A. Bazylev, N. K. Zhevago, and M. I. Chibisov, Zh. Eksp. Teor. Fiz. **71**, 1285 (1976) [Sov. Phys. JETP **44**, 671 (1976)].
[28]J. Risley, in: Proceedings of the Sixth International Conference on Atomic Physics, Zinatne, Riga, 1979, p. 223.
[29]J. S. Risley, A. K. Edwards, and R. Geballe, Phys. Rev. A **9**, 1115 (1974); R. Geballe and J. S. Risley, in: Eighth ICPEAC, Abstracts of Papers, Vol. 2, Belgrade, 1973, p. 834.
[30]N. Lee and A. K. Edwards, Phys. Rev. A **11**, 1768 (1975).
[31]A. K. Edwards, J. S. Risley, and R. Geballe, Phys. Rev. A **3**, 583 (1971).
[32]A. K. Edwards and D. L. Cunningham, Phys. Rev. A **9**, 1011 (1974).
[33]D. L. Cunningham and A. K. Edwards, Phys. Rev. A **8**, 2960 (1973).
[34]A. K. Edwards and D. L. Cunningham, Phys. Rev. A **10**, 448 (1974).
[35]D. L. Cunningham and A. K. Edwards, Phys. Rev. Lett. **32**, 915 (1974).
[36]A. K. Edwards and D. L. Cunningham, Phys. Rev. A **8**, 168 (1973).
[37]R. W. Wijnaendts van Resandt, H. C. den Harink, and J. Los. J. Phys. E **9**, 507 (1976).
[38]R. W. Wijnaendts van Resandt, R. L. Champion, and J. Los, Chem. Phys. **20**, 107 (1977).
[39]W. Aberle, J. Grosser, and W. Krüger, Chem. Phys. **41**, 245 (1979).
[40]G. Gerber, R. Morgenstern, and A. Niehaus, J. Phys. B **6**, 493 (1972).
[41]K. Siegbahn *et al.*, ESCA; Atomic, Molecular, and Solid State Structures Studied by Means of Electron Spectroscopy, Almqvist & Wiksells, Uppsala (1967).
[42]V. P. Afanas'ev and S. Ya. Yavor, Élektrostaticheskie analizatory dlya puchkov zaryazhennykh chastits (Electrostatic Analyzers for Charged-Particle Beams), Nauka, Moscow, 1978.
[43]S. A. Fridrikhov, Énergoanalizatory i monokhromatory dlya élektronnoĭ spektroskopii (Electron Analyzers and Monochromators for Electron Spectroscopy), Izd. LGU, Leningrad, 1978.
[44]I. G. Kozlov, Sovremennye problemy élektronnoĭ spektroskopii (Modern Problems in Electron Spectroscopy), Atomizdat, Moscow, 1973.
[45]C. De Vreugd, Electron Detachment in Ion Atom Collisions: Thesis, FOM Institute, Amsterdam (1980).
[46]H. Massey, Negative Ions, Cambridge Univ. Press (1976).
[47]M. E. Rudd, T. Jorgensen, and D. Volz, Phys. Rev. **151**, 28 (1966).
[48]Yu. S. Gordeev and G. N. Ogurtsov, Zh. Eksp. Teor. Fiz. **60**, 2051 (1971) [Sov. Phys. JETP **33**, 1105 (1971)].
[49]W. W. Lozier, Phys. Rev. **36**, 1285 (1930).
[50]F. I. Vilesov, B. L. Kurbatov, and A. N. Terenin, Dokl. Akad. Nauk SSSR **138**, 1329 (1961) [Sov. Phys. Dokl. **6**, 490 (1961)].
[51]G. G. Baldwin, Bull. Am. Phys. Soc. **9**, 53 (1964).
[52]G. G. Baldwin and S. I. Friedman, Rev. Sci. Instrum. **38**, 519 (1967).
[53]V. B. Leonas, Usp. Fiz. Nauk **127**, 319 (1979) [Sov. Phys. Usp. **22**, 109 (1979)].
[54]V. E. Esaulov, Dhuicq, and J. P. Gauyacq, J. Phys. B **11**, 1049 (1978).
[55]A. Z. Devdariani and Yu. N. Demkov, Vestn. Leningr. Univ. No. 16, 23 (1971).
[56]A. Z. Devdariani, Teor. Mat. Fiz. **11**, 213 (1972).
[57]Yu. N. Demkov, G. F. Drukarev, and V. V. Kuchinskiĭ, Zh. Eksp. Teor. Fiz. **58**, 944 (1970) [Sov. Phys. JETP **31**, 509 (1970)].
[58]A. Z. Devdariani and Yu. N. Demkov, Teor. Mat. Fiz. **21**, 74 (1964).
[59]Yu. N. Demkov and G. F. Drukarev, Zh. Eksp. Teor. Fiz. **49**, 691 (1965) [Sov. Phys. JETP **22**, 479 (1965)].
[60]Yu. N. Demkov and V. V. Kuchinskiĭ, Opt. Spektrosk. **35**, 804 (1973) [Opt. Spectrosc. (USSR) **35**, 467 (1973)].
[61]Yu. N. Demkov and V. N. Ostrovskiĭ, Zh. Eksp. Teor. Fiz. **59**, 1765 (1970) [Sov. Phys. JETP **31**, 959 (1971)]; in: Problemy teoreticheskoĭ fiziki (Problems of Theoretical Physics), Izd. Leningr. Univ., Leningrad, 1973, p. 279.
[62]F. I. Dalidchik and G. K. Ivanov, Opt. Spektrosk. **38**, 633 (1975) [Opt. Spectrosc. (USSR) **28**, 633 (1975)].
[63]G. B. Lopantseva and O. B. Firsov, Zh. Eksp. Teor. Fiz. **50**, 975 (1966) [Sov. Phys. JETP **23**, 648 (1966)].
[64]W. Lichten, Phys. Rev. A **164**, 131 (1967); U. Fano and W. Lichten, Phys. Rev. Lett. **14**, 627 (1965); W. Lichten, J. Phys. Chem. **84**, 2102 (1980).
[65]M. Born and V. Fock, Z. Phys. **51**, 165 (1928).
[66]A. V. Chaplik, Zh. Eksp. Teor. Foz. **45**, 1518 (1963) [Sov. Phys. JETP **18**, 1046 (1964)].
[67]V. M. Borodin, Vestn. Leningr. Univ. No. 16, 18 (1978).
[68]V. M. Borodin, Vestn. Leningr. Univ. No. 22, 47 (1978).
[69]Yu. N. Demkov and V. N. Ostrovskiĭ, in: Metod potentsialov nulevogo radiusa v atomnoĭ fizike (The Method of Zero-Range Potentials in Atomic Physics), Izd. Lening. Univ., Leningrad, 1975.
[70]Yu. N. Demkov, Cited in Ref. 12, p. 645.
[71]E. A. Solov'ev, Zh. Eksp. Teor. Fiz. **70**, 572 (1976) [Sov. Phys. JETP (*sic*)].
[72]Yu. N. Demkov, in: Problemy teorii atomnykh stolknoveniĭ (Problems of the Theory of Atomic Collisions), Izd. Lening. Univ., Leningrad, 1975.
[73]G. N. Ogurtsov, Rev. Mod. Phys. **44**, 1 (1972).
[74]A. K. Edwards, in: Proceedings of the Ninth ICPEAC, Invited Lectures, Review, Papers and Progress Reports, Seattle, 1976, p. 790; R. Morgenstern, p. 345.
[75]G. J. Schulz, Rev. Mod. Phys. **45**, 423 (1973).
[76]Yu. F. Bydin, in: Sbornik po fizike élektronnykh i atomnykh stolknoveniĭ: Materialy 2-ĭ Vsesoyuznoĭ shkoly (Collected Papers on the Physics of Electronic and Atomic Collisions). Proceedings of the Second All-Union School, Leningrad, 1973, p. 99.
[77]C. De Vreugd, R. W. Wijnaendts van Resandt, and J. Los, Chem. Phys. Lett. **64**, 175 (1979).
[78]V. I. Ogurtsov and Yu. F. Bydin, Pis'ma Zh. Eksp. Teor. Fiz. **10**, 134 (1969) [JETP Lett. **10**, 85 (1969)].
[79]V. I. Ogurtsov and Ju. F. Bydin, in: Proceedings of the Sixth ICPEAC, Boston, 1969, p. 475.
[80]Yu. F. Bydin, V. I. Ogurtsov, and V. S. Sirazetdinov, Pis'ma Zh. Eksp. Teor. Fiz. **13**, 340 (1971) [JETP Lett. **13**, 240 (1971)].
[81]Yu. F. Bydin and V. I. Ogrutsov, Astron. Vestn. **5**, 98

(1971).
[82]Yu. F. Bydin and V. I. Ogurtsov, in: Tezisy 5-ĭ Vsesoyuznoĭ konferentsii po fizike élektronno-atomnykh stolknoveniĭ (Abstracts, Fifth All-Union Conference on the Physics of Electron–Atom Collisions) Uzhgorod, 1972, p. 123.
[83]V. M. Dukelsky, Yu. F. Bydin, and A. M. Bukteev, in: Proceedings of the Fourth International Conference on Ionization Phenomena in Gases, Uppsala, 1960, North-Holland, Amsterdam, 1960, p. 165.
[84]R. Morgenstern and M. Trainer, Cited in Ref. 74, p. 872.
[85]G. Gerber, R. Morgenstern, and A. Niehaus, J. Phys. B **5**, 1396 (1972).
[86]G. Gerber, R. Morgenstern, and A. Niehaus, J. Phys. B 6, 493 (1972).
[87]E. E. Nikitin, Opt. Spektrosk. **6**, 761 (1962) [Opt. Spectrosc. (USSR) **13**, 431 (1962)]; Izv. Akad. Nauk, SSSR, Ser. Fiz. **8**, 996 (1963).
[88]Yu. N. Demkov, Zh. Eksp. Teor. Fiz. **45**, 195 (1963) [Sov. Phys. JETP **18**, 138 (1964)].
[89]D. R. Bates and D. A. Williams, Proc. Phys. Soc., London **83**, 425 (1964); Yu. N. Demkov, C. V. Kunasz, and V. N. Ostrovsky, Phys. Rev. **A18**, 2097 (1978).
[90]Yu. F. Bydin, S. S. Godakov, and V. M. Lavrov, in: Tenth ICPEAC, Abstracts of Papers, Vol. 2, p. 966; Yu. F. Bydin, V. A. Vol'pyas, and S. S. Godakov, Phys. Lett. **50**, 2399 (1974).
[91]Yu. F. Bydin and A. M. Bukhteev, Zh. Eksp. Teor. Fiz. **30**, 546 (1960) [Sov. Phys. JETP (*sic*)].
[92]Yu. F. Bydin, V. I. Ogurtsov, and V. S. Sirazetdinov, in: Seventh ICPEAC. Abstracts of Papers, Amsterdam, 1971, p. 1133.
[93]Yu. N. Demkov, Vestn. Leningr. Univ. **15**, No. 11, 150 (1965); Phys. Lett. **15**, 235 (1965).
[94]D. Rapp, T. E. Sharp, and D. D. Briglia, Phys. Rev. Lett. **14**, 533 (1965).
[95]V. I. Khvostenko, I. I. Furleĭ, I. Kh. Aminev, and V. A. Mazunov, Khim. Vys. Energiĭ **7**, 537 (1978).
[96]B. M. Smirnov, Usp. Fiz. Nauk **133**, 569 (1981) [Sov. Phys. Usp. **24**, 251 (1981)].
[97]R. D. Taylor, J. B. Delos, and T. S. Wang, in: Twelfth ICPEAC. Abstracts of Contributed Papers, Gatlinburg, Tennessee, Vol. 1, 1981, p. 527.
[98]V. M. Dukel'skiĭ, in: Problemy sovremennoĭ fiziki: Sbornik stateĭ k 100-letiyu so dnya rozhdeniya A. F. Ioffe (Problems of Modern Physics. Collection Dedicated to the 100th Anniversary of the Birth of A. F. Ioffe), Nauka, Leningrad, 1980, p. 473.
[99]B. M. Smirnov, Otritsatel'nye iony (Negative Ions), Atomizdat, 1978.
[100]A. Burgess and M. J. Seaton, Rev. Mod. Phys. **30**, 992 (1958).
[101]V. V. Afrosimov, Yu. S. Gordeev, M. N. Panov, and N. V. Fedorenko, Zh. Tekh. Fiz. **34**, 1624 (1964) [Sov. Phys. Tech. Phys. **9**, 1256 (1965)]; **36**, 123 (1966) [Sov. Phys. Tech. Phys. **11**, 89 (1966)].
[102]I. A. Abroyan, M. A. Eremeev, and N. N. Petrov, Usp. Fiz. Nauk **92**, 105 (1967) [Sov. Phys. Usp. **10**, 332 (1967)].
[103]U. A. Arifov, in: Vzaimodeĭstvie atomnykh chastits s poverkhnost'yu tverdogo tela (Interaction of Atomic Particles with Solid Surfaces), Nauka, Moscow, 1968.
[104]Yu. F. Bydin and V. A. Vol'pyas, in: Vtoroĭ Vsesoyuznyĭ simpozium po vzaimodeĭstviyu atomnykh chastits s tverdym telom (Second All-Union Symposium on the Interaction of Atomic Particles with Solids), Moscow, 1972, p. 17.
[105]N. N. Petrov and I. A. Abroyan, Diagnostika poverkhnosti s pomoshch'yu ionnykh puchkov (Diagnostics of Surfaces with Ion Beams), Izd. Leningr. Univ., Leningrad, 1977.
[106]A. A. Dorozhkin and A. A. Petrov, in: Materialy 6-ĭ Vsesoyuznoĭ konferentsii po vzaimodeĭstviyu atomnykh chastits s tverdym telom (Proceedings of the Sixth All-Union Conference on the Interaction of Atomic Particles with Solids Solids), Part 1, Minsk, 1981, p. 193; A. A. Dorozhkin, N. N. Petrov, and Yu. P. Sin'kov, *ibid.*, p. 196.

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