Quasimolecules

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Studies of quasimolecular states and transitions in atomic collisions are reviewed. The statistical theories of the quasimolecule based on the Thomas-Fermi model and the statistical approach to the process of ionization in collision of heavy atoms are discussed. A quantum theory of the quasimolecule is presented. Mechanism of ionization in a quasimolecule and the properties of quasimolecular autoionization states are discussed. Some exotic quasimolecules are described: superheavy, which are formed in the collision of heavy atoms (up to uranium); mesoquasimolecules, which arise in the collision of an atom and a mesonic atom; and quasimolecules formed by fission fragments. The fundamental properties of radiation from quasimolecules and the mechanisms of generating it are presented. In closing we indicate the prospects for applying quasimolecular effects in different fields of physics.

1. Introduction. The term "quasimolecule" denotes a system of two atoms that approach and separate in the process of collision. Apart from extremely rare cases of orbiting, the lifetime of a quasimolecule equals the mutual time of transit of the atoms. For energies of 0.1–100 keV this amounts to 10^{-15} to 10^{-16} s. Within this time the axis of the quasimolecule rotates by an angle equal to $\pi - \theta$ (θ is the scattering angle). In contrast to ordinary molecules, quasimolecules do not constitute stable structures, even when the latter exist for a given pair of atoms. The minimum internuclear distance—the distance of closest approach in the collision—is much smaller than the dimensions of ordinary molecules. It can be smaller than the dimensions of the inner electron shells, which enables one to speak of the "limit of fused nuclei" in describing a quasimolecule.

The introduction of concepts of quasimolecules, and quasimolecular states and transitions is based on the adiabatic principle, according to which the electrons move much faster than the nuclei and form orbitals that correspond to stationary nuclei. The deeper the electron shell is, the better this principle is fulfilled.

The concepts of molecular orbitals, which were proposed as early as 1928 by R. S. Mulliken,[1] were first applied to atomic collisions in 1932 by W. Weizel and O. Beeck.[2] They also adduced Mulliken's idea of the promotion of terms as the atoms approach to explain the high ionization threshold in atomic collisions. Interestingly, even then they pointed out the Auger effect as a mechanism of irreversible restructuring of an excited shell, and the crossing of terms as a cause of transitions between them. In the same year E. C. Stückelberg,[3] L. D. Landau,[4] and C. Zener[5] studied the problem of crossing an psuedocrossing of terms, which then were applied for many decades to describe charge transfer in atomic collisions.

The second birth of interest in quasimolecules and the onset of vigorous development of studies in this field occurred from the late fifties to the middle sixties, when simultaneously E. Everhart and his associates in the USA[6] and N. V. Fedorenko and V. V. Afrosimov and their associates[7] in the USSR experimentally discovered an unusually high intensity of ionization in the collision of heavy atoms of medium energy and concomitant characteristic energy losses involving the formation of vacancies in the inner shells of the colliding atoms.

It was found that, immediately above the ionization threshold at velocities of $5 \times 10^6 - 10^7$ cm/s, long before the velocity of the ions becomes comparable with the orbital velocity of the electrons, the ionization cross sections sharply increase and exceed by 14 orders of magnitude the values calculated in the Born approximation according to the mechanism of impact Coulomb ionizatin (!).

Such a strong excitation of the electron shells in slow collisions, when by the adiabatic hypothesis the electrons must still follow the motion of the nuclei, indicated the existence of some special mechanism of excitation.

It proved to be what was subsequently called "Pauli excitation"[8]: in close approach of the atoms there is simply no space for the doubled number of electrons in levels of the same type in the "united atom." Consequently a regrouping of states, promotion and lowering of terms, and exchange of electrons and vacancies occur between the crossing terms (Figs. 1–3). Here the velocity of the colliding atoms plays no essential role, merely enabling the attainment of the needed internuclear distances.[9]

To explain two of the three characteristic energy losses in the experiments,[6,7] U. Fano and W. Lichten[10] associated them with the removal of one or two electrons from the L shell of argon owing to transitions between terms of the quasimolecule Ar_2^+. The third characteristic loss (50 eV) was explained[11] by formation of vacancies in the outer shells, where the number of vacancies exceeds by a factor of about two the number of emitted Auger electrons, while the characteristic energy losses are 2–3 times as great as the ionization energy. V. K. Nikulin[12] associated this characteristic loss with an autoionization state of the Kr^+ ion, which is the united-atoms limit for the Ar_2^+ quasimolecule.

Generally atomic collisions are characterized by the excitation of quasimolecular autoionization states owing to formation of inner vacancies upon crossing of terms. The decay of such states is the source of a considerable fraction of the emitted electrons. This circumstance was far from being immediately understood. An objection was raised to the autoionization mechanism, based on the long lifetime of atomic autoionization states ($10^{-14} - 10^{-15}$ s) as compared *with the time of collision. Moreover the autoionization state* that arises at small interatomic distances is not always conserved after their separation. However, B. M. Smirnov[13] called attention to the fact that the long lifetimes of autoion-
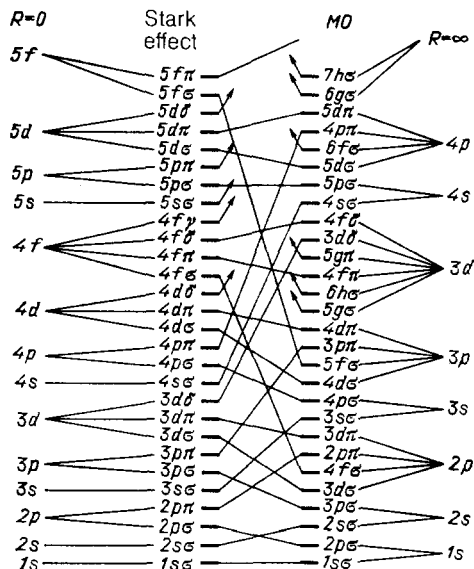
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FIG. 1. Correlation diagram for the terms of a homonuclear one-electron quasimolecule.[23]

ization states in atoms are caused by their spherical symmetry, which is absent in a quasimolecule.

Direct calculation of the rate of decay of quasimolecular autoionization states as a function of the distance between the nuclei showed a sharp increase in the region of 0.5 Å, where it reaches a magnitude comparable with, and even exceeding, the reciprocal time of passage of the atoms. This circumstance, which implies that electron emission can occur even during the collision process, has played the decisive role in confirming the autoionization mechanisms of ionization in atomic collisions. The cited calculation was the first one that treated a quasimolecule formed by an atom and
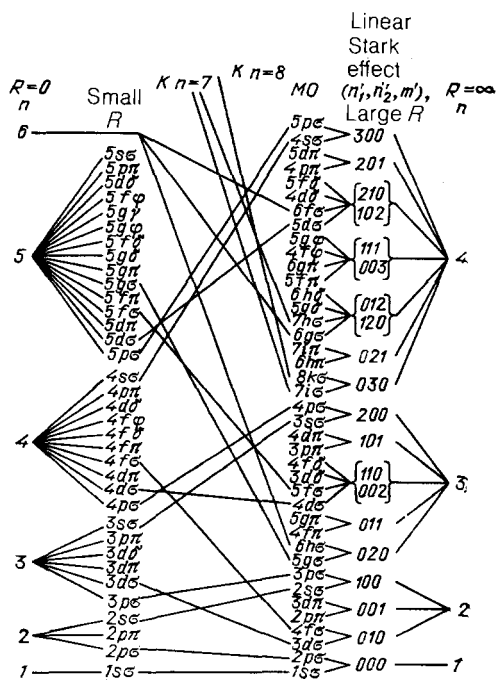
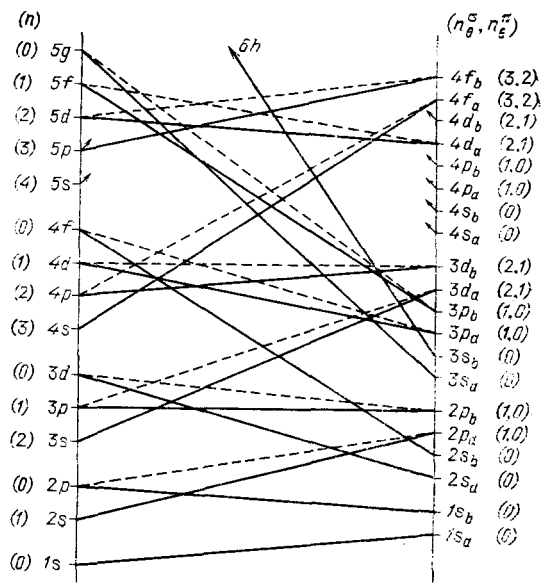FIG. 2. Diabatic one-electron correlation diagram of a homonuclear multielectron quasimolecule.[23]

FIG. 3. Schematic diabatic correlation diagram for a slightly asymmetric system.[23] The solid line denote σ-orbitals, the dotted lines π-orbitals. The numbers in parentheses represent the radial quantum number for the united atom (left) and the angular quantum number for the separated atoms (right).

multiply charged ions, and also studied the interatomic Auger effect and introduced the term "Auger ionization."

A feature of quasimolecules is the continuous variation of the interatomic distance during the entire lifetime, and with it all the quantities that depend on the distance–wave functions, terms, rates of decay, population of levels. This feature, as well as the dynamic theory constructed by Yu. N. Demkov[15] of promotion of terms into the continuous spectrum and his formulation of certain general questions of the theory have given rise to intensive experimental studies of a typically quasimolecular effect–the appearance of a continuous component in the energy distribution of the electrons emitted in the collision. Experiments have been set up in a coincidence scheme, in which the decay of quasimolecular autoionization states was traced at fixed impact parameters.[16]

In 1972 the same R. S. Mulliken performed a computer experiment[17] in which he calculated the electronic terms of two nitrogen atoms as a function of the distance between the nuclei. He found that at small distances the energies of the molecular obitals go over into the levels of a silicon atom. The computer program that R. S. Mulliken used was called ALCHEMY, while the calculation was based on the idea that, if one brings together atoms of lighter elements to small internuclear distances, one can briefly obtain heavy atoms and study their electronic levels. A similar 20th-Century alchemy was achieved in Ref. 18 by using heavy-ion accelerators. It was of special interest to obtain quasiatoms of the superheavy transuranium elements, which do not exist (or have not yet been discovered) in nature. One can study in this way the electronic terms of atoms without possessing them: by selecting pairs for which the total $Z = Z_1 + Z_2 > 173$, one can observe the creation of positrons. This effect is also of quasimolecular character, since at internuclear distances smaller than a critical value, the energy of the lowest orbitals, e.g., $1s\sigma$, becomes larger in modulus

than $2mc^2$. When a vacancy exists in this orbital, it can be filled by an electron from the Dirac continuum—or positron creation occurs.

The discovery in 1972, which won the Röntgen prize, of continuous x-ray emission of quasimolecular origin—the so-called molecular-orbital radiation[19]—made it possible directly to "see" a quasimolecule. It can emit during collision if the lifetime of the excited quasimolecular states is of the order of the time of collision. The lifetime of vacancies in the inner shells is comparable with the time of collision of heavy fast ions with an energy in the hundreds of kiloelectron-volts, while the high fluorescence yield close to unity for atomic numbers corresponding to fused nuclei makes possible the decay of vacancies, not only by emission of Auger electrons, but also by x-ray emission. In constrast to the characteristic emission usually observed in atomic collisions, this emisison has a continuous spectrum owing to the dependence of the quantum energy on the continuously varying internuclear distance.

At present quasimolecules—these "temporary molecules"—are found and play a substantial role in a broad set of physical processes involving current problems of the action of beams of accelerated heavy ions on matter, the design of x-ray lasers, and the development of reactors for controlled thermonuclear fusion.

2. Statistical theories.

The pattern of approach, crossing, and separation of terms, as well as the formation of vacancies in the collision of multielectron atoms, is so complex that an exact and detailed calculation of them by the methods of quantum mechanics was at first (and still remains) difficult.

The strong interaction of the large number of electrons, the close arrangement of the terms, the formation of intermediate multivacancy autoionization quasimolecular states, and also the fast variation of the entire pattern with varying internuclear distance do not allow one, on the one hand, to apply without qualification any of the known methods of quantum mechanics. On the other hand, they offer grounds for using statistical methods.

2.1 The Firsov potential.

One of the first applications of statistical physics to calculations of quasimolecules was the study of O. B. Firsov,[20] in which the energy of the electron shell of a quasimolecule was calculated as a function of the internuclear distance by the Thomas-Fermi model.

Minimal and maximal principles were introduced. By using them, the energy of the electron shell calculated by the variation method is bracketed between lower and upper bounds, which can be brought together until the needed accuracy is attained.

In the adiabatic theory the energy of the electrons, which depends on internuclear distance, contributes to the interatomic potential so as to cause it to differ from the Coulomb potential. It has the form

$$V(R) = Z_1 Z_2 e^2 \chi \left[(Z_1^{1/2} + Z_2^{1/2})^{2/3} \frac{R}{a} \right] R^{-1}, \qquad (2.1)$$

Here R is the internuclear distance, Z_1 and Z_2 are the atomic numbers, χ is the Thomas-Fermi screening function, $a = 0.855a_0$ is the Thomas-Fermi parameter, and a_0 is the Bohr radius.

The screened Coulomb potential of Firsov was the first potential calculated on the basis of a rigorous quasimolecu-

lar approach. It has already been used for 30 years for calculating scattering cross sections of atoms in gases and solids.

Further refinements of the potential performed by Abrahamson and by Firsov himself[20] are based on applying the Thomas-Fermi-Dirac model.

2.2. Semiclassical ionization theory.

In 1959 O. B. Firsov proposed a semiclassical model of excitation of electrons in atomic collisions by internal friction of the electron shells of the colliding atoms.[21] The calculation also employed the quasimolecular Thomas-Fermi model. However, the exchange of energy between the electrons of the fast and slow atoms was calculated classically, as a transport phenomenon in gases.

The mean momentum of translational motion acquired by an electron in one of the atoms is transferred through the surface S separating the region of action of the two atoms in the quasimolecule. The total energy of excitation of the electrons of the quasimolecule is

$$E = 2m \int_{R_0}^{\infty} dR \frac{dR}{dt} \int_S dS \frac{nv}{4}, \qquad (2.2)$$

Here m is the mass of an electon, R_0 is the distance of closest approach,

$$n = 2^{3/2} (me\varphi)^{3/2} (3\pi^2 \hbar^3)^{-1}, \quad v = 3 (3\pi^2)^{1/3} \hbar n^{1/3} (4m)^{-1} \qquad (2.3)$$

are the density of the electron shell and the velocity of the electrons according to the Thomas-Fermi model, and ϕ is the potential at the surface S:

$$\varphi = 2 (Z_1 + Z_2) e\chi \left[0,565 (Z_1 + Z_2)^{1/3} \frac{R}{a_0} \right] R^{-1}. \qquad (2.4)$$

Subsequently the Firsov model has been refined by more rigorous definition of the form and position of the surface S, by taking account of the curvature of the trajectories of the atoms, of their charges, and of shell effects by the Slater method or on the basis of Rutan-Hartree-Fock wave functions, and also by taking account of the time spent in exchange of electrons and the rate of decay of the autoionization states.[21]

By using the Firsov model and its modifications, the inelastic energy losses and ionization and stripping cross sections in atomic collisions have been successfully calculated, along with the coefficients of ion-electron emission and the degree of ionization of atoms scattered by the surface of a solid.

2.3. Statistical model.

A. Russek[22] has developed a somewhat different approach based on a purely statistical treatment of the process of excitation of electrons in atomic collisions. He studied in detail the heating of the electrons and their vaporization leading to ionization. He introduced a combinatorics of the apportionment of the excitation energy among the electrons of the colliding atoms and obtained a sequence of maxima and crossing points of the curves of the charge distribution of the ions after collision. However, the process itself of transfer of the energy of translational motion of the atoms by the electrons of the quasimolecule was simply postulated, while the magnitude of the transferred energy was taken from experiment.

3. Quantum theory of quasimolecules.

The basis of the quasimolecular description of atomic collisions is the Born-

Oppenheimer approximation, in which the electronic and nuclear components of the total Hamiltonian are separated into subsystems, while their interaction is taken into account according to perturbation theory in the parameter m/M. We shall not deal with the problems involving the motion of the nuclei and the nonadiabatic effects that arise from the electronic-nuclear interaction, which are presented exhaustively in the monograph of Ref. 23.

We shall take up the description of the electronic subsystem, which is more dynamic than the nuclear subsystem, and which undergoes substantial changes in the collision process. To do this we must know the wave functions and energies of the electronic terms as functions of the internuclear distance, the matrix elements of the internuclear interaction, and the association of the terms of the quasimolecule with the terms of the atoms that form it.

In this section we shall treat the fundamental methods of calculating the electronic terms and wave functions, as well as the methods of establishing the correspondence between the quantum numbers of the united atom and the separated atoms.

3.1 Molecular orbitals (MOs).

This approximation is equivalent to the self-consistent-field method in the theory of atoms.[23] One assumes that each electron moves independently in a certain static effective potential $V(\mathbf{r},R)$ created by the field of the nuclei and all the other electrons. It is assumed concerning the properties of the potential that it has the molecular symmetry, allows separation of variables (e.g., in spheriodal coordinates), and depends on R as a parameter. The MO approximation allows one to introduce the concept of the energy and quantum numbers of an individual electron in the molecule and their dependences on the internuclear distance.

Although distinct quantitative criteria for the applicability of the MO method are currently lacking, we can consider it suitable for describing the electrons in light quasimolecules, and also for the inner shells of medium and heavy systems,[23,24] i.e., in the cases in which the Coulomb interaction of the electrons with the nuclei is much greater that their interaction with one another. As the internuclear distance varies, the MO approximation is valid from the limit of the united atoms (UA) up to values of R such that the MO levels are close to the one-electron levels of the separated atoms.[23]

3.2 Quasimolecular wave functions.

Two methods exist for obtaining the one-electron wave functions of a quasimolecule: the historically earlier and widespread expansion in the atomic wave functions, and the direct use of molecular functions.

In the former case the one-electron quasimolecular function is expanded in a basis set composed of atomic orbitals centered at each nucleus or at their center of mass. An extensive bibliography devoted to these functions is collected in the books of Refs. 23 and 25.

The molecular or two-center wave functions are obtained directly by solving the Schrödinger equation for an electron in the field of two Coulomb centers having charges Z_1 and Z_2 lying at a distance R apart:

$$\left(-\frac{\Delta_r}{2} - \frac{Z_1}{r_1} - \frac{Z_2}{r_2} \right) \Phi(\mathbf{r}, R) = E\Phi(\mathbf{r}, R). \qquad (3.1)$$

Equation (3.1) allows separation of the variables in the prolate spheroidal coordinates ξ, η, and ϕ:

$$\xi = \frac{r_1 + r_2}{R}, \quad |\eta| = \frac{r_1 - r_2}{R}, \quad \varphi = \arctan\frac{y}{x}. \qquad (3.2)$$

$\Phi(\mathbf{r},R)$ is called the spheroidal Coulomb function. An exhaustive presentation of the theory of spheroidal functions, algorithms of calculation, applications of them in different fields, and also an extensive bibliography are collected in Ref. 26. Among the later studies devoted to calculating two-center functions, we can mention Refs. 27 and 28. The use of two-center functions has become widespread in recent years, when the appearance of commercial computers has enabled calculating them rapidly and with high accuracy for any arbitrary ratio of the nuclear charges Z_2/Z_1 and over a broad range of R. Moreover, the Coulomb spheroidal functions directly correspond to the symmetry of the molecule. Ultimately this considerably decreases the length of the basis expansions in these functions.

As regards the wave functions of the continuous spectrum in a quasimolecule, either ordinary atomic Coulomb functions of the continuum are used in this role, centered in some way, or two-center wave functions that satisfy (3.1) with an energy $E \geqslant 0$.[26]

Great interest has been aroused in Refs. 29–32. Here, in calculating the terms of the one-electron two-center problem for complex values of R, heretofore unknown diabatic bound states,[29–31] and virtual and quasistationary states[32] were found. A remarkable property of a bound term is that it crosses the Rydberg crowding of levels and escapes into the continuous spectrum. Its continuation in the continuum is a quasistationary level. The existence of such levels indicates the possibility of direct ionization of a quasimolecule from a bound state, and enables calculating cross section and energy spectrum of the electrons.[29,32]

All that we have said above pertains to a quasimolecule with one electron. To calculate multielectron systems one applies different variants of the self-consistent-field method and the ideology of the effective potential. The one-electron functions and energies of a set of homo- and heteronuclear quasimolecules, both neutral and ionized, were calculated[33–39] by using the self-consistent-field method.

In the studies devoted to the effective potential, the interaction of the given electron with the nuclei and with the other electrons is described by a parametric one-particle potential. The methods used differ only in the procedure for determining the parameters of the potential. Most of the studies have used potentials that allow separation of the spheroidal coordinates, and this considerably simplifies the numerical calculations. The general form of such a potential in spheriodal coordinates is[26]

$$V(\xi, \eta, \varphi, R) = -\frac{2}{R^2}\left[\frac{a(\xi) + b(\eta)}{\xi^2 - \eta^2} + \frac{c(\varphi)}{(\xi^2 - 1)(1 - \eta^2)} \right], \qquad (3.3)$$

Here $a(\xi)$, $b(\eta)$, and $c(\phi)$ are polynomials in ξ, η, and ϕ. A potential of the type of (3.3) was first sued to calculate the ground state of the H_2 molecule.[40] There $c(\phi)$ was assumed to be zero, $a(\xi) = R(a_0 + a_1\xi)$, and $b(\eta) = Rb_2\eta^2$. The parameters a_0, a_1, and b_2 are found from the condition of coincidence of the potential of (3.3) as $R \to 0$ with the potential of the united atom, and as $R \to \infty$ with the potential for a hydrogen atoms in the field of a distanc Coulomb center. In Refs. 41 and 42 this method was generalized to the case of heteronuclear quasimolecules with two and more electrons. The

function $a(\xi)$ is given by

$$a\ (\xi)\ =\ R\ (a_0\ +\ a_1\xi\ +\ a_2\xi^2),\quad b\ (\eta)\ =\ R\ (b_1\eta\ +\ b_2\eta^2),$$

a_i and b_i were chosen both as constant and as dependent on R. In this case a variational procedure was used. The calculated energy of the ground state and the equilibrium position for the quasimolecules H_2, He_2^+ and HeH^+ agree well with the Hartree-Fock calculations. As was indicated,[40] a calculation of the electronic states with an effective potential of the tupe of (3.3) with parameters determined by the variational method is equivalent in a sense to the self-consistent-field method. The Thomas-Fermi potential was used in a number of studies[43–46] as the effective potential. The one-electron states were calculated by this method for a large number of homo- and heteronuclear quasimolecules $N + N^{n+}$ ($n = 0,1,2$). $Ne + Ne''^+$ ($n = 0,2,4$), $Ar + Ar$, $Kr + Kr$, $Xe + Xe$, $Ne + Ar$, $Ar + Xe$, $Kr + Xe$. The effective-potential method was further developed in Refs. 47–50, where a potential $V_{eff}(\xi,\eta,\phi,R)$ of the type of (3.3) was proposed, which took account of the splitting of terms having the different l values in the united-atom limit:

$$V_{eff}\ (\xi,\ \eta,\ \varphi,\ R) = -\frac{2}{R\,(\xi^2-\eta^2)}\ [(Z_1 + Z_2 - a_1)\,\xi R$$
$$+ (Z_2 - Z_1 - b_1)\ R\eta$$
$$- a_0 R - \tilde{a}_1 - b_2 R\eta^2],$$
$$(3.4)$$

Here Z_1 and Z_2 are the charges of the nuclei corresponding to the distances r_1 and r_2. For a homonuclear system we have the parameter $b_1 = 0$ owing to the symmetry of the Hamiltonian, while the parameter $\tilde{a}_1$ gives the splitting of the energy levels having different l values for a given n in the limit of the united atom. The parameter a_1 and $\tilde{a}_1$ for a given molecular oribital are determined by comparing the energies and the mean value of the potential of (3.4) for $R = 0$ with these same values obtained from atomic calculations, e.g., by the self-consistent-field method. The parameters a_0, b_1, or b_2 are determined analogously. The one-electron energies of the quasimolecules He_2^+, Ne_2^{+g} ($g = 1,2,4$), Kr_2^+, etc., were calculated by this method. A merit of this method is that it correctly takes account of the splitting of terms having a given n for $R = 0$, together with the simplicity of the algorithms of calculation, which involves the fact that the potential of (3.4) is separated in spheriodial coordinates and reduced to the well known problem of the quasimolecule H_2^+. Comparison of the calculations[47–50] with others performed by more cumbersome methods, e.g., variable screening,[43,45,46] shows good agreement. Moreover, in this method both the ground and excited states are obtained equally rapidly and accurately, which is difficult in the self-consistent-field methods.

Calculations are lacking at present for the continous spectrum, both in the effective-potential framework and in the Hartree-Fock method. Most studies[51–54] have used one-center Coulomb functions or Bessel functions as the wave function of the continuum. The most general approach was developed in Ref. 55. The exact wave function of the continuum with account taken of the interaction with the other electron in the final discrete state (a two-electron quasimolecule was treated) is the solution of the integrodifferential equation having a molecular potential

$$-\frac{\Delta_r}{2} - \frac{Z_1}{r_1} - \frac{Z_2}{r_2} + \int\ |\ \psi_j\ (\mathbf{r}_0,\ R)\ |^2\ r_{01}^{-1}\ \psi_c\ (\mathbf{r}_1,\ R)\ d\tau_0$$
$$= E\psi_c\ (\mathbf{r}_1,\ R) - \int\ \psi_j\ (\mathbf{r}_1,\ R)\ \psi_c\ (\mathbf{r}_0,\ R)\ r_{01}^{-1}\ d\tau_0.\quad (3.5)$$

The function $\psi_j\ (\mathbf{r},R)$ describes the electron in the final discrete state. Equation (3.5) was solved numerically, both directly and without taking account of the exchange term on the right-hand side. Moreover, solutions of (3.5) were studied without taking account of the integral terms, corresponding to indentical screening of the charges Z_1 and Z_2 of the nuclei. Unfortunately, even a numerical solution of (3.5) is a difficult problem. In this regard a method was proposed[56] of variable screening of the charges of the nuclei Z_1 and Z_2 that considerably simplified the solution of (3.5). The calculations[55,56] were performed by different systems, and it is difficult to compare the results for estimating the applicability of the approximations used for the continuum functions.

3.3. One-electron correlation rules.

Even for a one-electron quasimolecule the terms for arbitrary R can be calculated only numerically.[26] Therefore the problem arises of obtaining qualitative rules of correspondence of the electron levels from the separated-atom limit to the united-atom limit. The basis for constructing such rules, also called correlation diagrams (CDs), is the molecular-orbital (MO) approximation. Substantial restrictions on the mutual arrangement of the electronic terms of the quasimolecule are imposed by the non-crossing theorem.[57,58] According to this theorem, as a parameter is continuously varied, the eigenvalues of the Hamiltonian $H(R)$ pertaining to different irreducible representations of the total symmetry group of this Hamiltonian can coincide. Eigenvalues pertaining to identical irreducible representations cannot coincide. The separation of the variables in spheriodal coordinates of a one-electron diatomic molecule indicates the existence of an additional symmetry differing from the geometrical symmetry.[59,60] Actually, along with the projection of the angular momentum l_z of the electron, an integral of motion is the operator for the separation constant, which in spheroidal coordinates has the form[60–62]

$$\Lambda = -\frac{1}{\xi^2-\eta^2}\ \left[(1-\eta^2)\ \frac{\partial}{\partial\xi}\ (\xi^2-1)\ \frac{\partial}{\partial\xi}\right.$$
$$\left. - (\xi^2-1)\ \frac{\partial}{\partial\eta}\ (1-\eta^2)\ \frac{\partial}{\partial\eta}\right]$$
$$+ \left(\frac{1}{\xi^2-1} - \frac{1}{1-\eta^2}\right)\ \frac{\partial^2}{\partial\varphi^2} + RZ_1\ \frac{\xi\eta+1}{\xi+\eta} - RZ_2\ \frac{\xi\eta-1}{\xi-\eta},$$
$$(3.6)$$

Here Z_1 and Z_2 are the charges of the nuclei.

The one-electron two-center system is the only one for which one can establish exact correlation rules for the terms.[63,64] There results rest on the theorem of conservation of the number of zeros of the solution of the Sturm-Liouville problem, which depends on the parameter R. However, the correlation rules alone[64] do not suffice for constructing the CD, since these rules do not establish the sequential order of the terms. To do this one must establish the position of the terms in the limits $R \to 0$ and $R \to \infty$. For small R the one-electron energy $E(R)$ has the form[26]

$$E\ (R) = -\frac{Z^2}{2n^2}\cdot$$
$$- 2Z_1 Z_2\ [l\ (l+1) - 3m^2]\ \frac{(ZR)^2}{n^3 l\ (l+1)\ (4l^2-1)\ (2l+3)},$$
$$(3.7)$$

Here $Z = Z_1 + Z_2$. We see from (3.7) that the terms with smaller m lie lower for a given n and l, while for n and $m = $ const the lowest level is that with $l = 1$, and the highest that with $l = 0$. For large R, e.g., for the Z_1 terms,[26] we have

$$E\,(R) = -\frac{Z_1^2}{2n^2} - \frac{Z_2}{R} + \frac{3Z_2 n\,(n_1 - n_2)}{2R^2 Z_1}\,. \tag{3.8}$$

Here the terms lie lower with larger n_2 for a given n. The correlation diagram thus obtained for the σ-terms of a one-electron homonuclear molecule is shown in Fig. 1.[65] We can easily see that, in going from the separated-atom (SA) limit to the united-atom (UA) limit, the principal quantum number generally increases. The phenomenon has been called the promotion of electronic levels.[1]

For multielectron quasimolecules the correlation rules[64] are inapplicable. This involves the impossibility of separating the variables in parabolic coordinates in the limit of separated atoms. The following rules were proposed in Refs. 10, 65, and 66:

$$n_r^{UA} = n_r^{SA}. \tag{3.9}$$

Here n_r is the number of zeros of the solution of the radial function $(n_r = n - l - 1)$. Here, for a given n^{SA}, the sublevel is promoted least that lies lowest. An example of the CD of a homonuclear system is shown in Fig. 2.[22]

A number of studies have calculated the one-electron wave functions and energies of different homo- and heteronuclear quasimolecules over a broad interval of R by using the Hartree-Fock method[33,34,36,67–72] and the Thomas-Fermi method.[43–45,73–76] In calculating these diagrams quasicrossings of terms were found that contradict the rules (3.9). In this regard new correlation rules were proposed[45] instead of (3.9):

$$n_r^{UA} = n_\theta^{SA} = (l - m)^{SA}. \tag{3.10}$$

Here n_θ is the number of zeros of the angular function. In contradiction to (3.9) correlation is established between the sublevels that maximally undergo promotion and demotion within the limits of a given shell. A schematic diagram using the rules of (3.10) is shown in Fig. 3. In Ref. 77, owing to introduction of a new region of crossings at large R, an attempt is made to improve the rules of (3.9). Correlation diagrams were obtained in Ref. 48 that do not agree with the rules of (3.10). The authors of Ref. 48 associate this fact with the identical screening of all orbitals applied in Refs. 43–45, and they propose selecting the parameters of the effective potential individually for each state. As was pointed out in Ref. 78, the rules of (3.9) and (3.10) are empirical; using them to obtain correlation diagrams requires additional assumptions. Here rigorous correlation diagrams were derived under the assumption that each MO having a certain principal quantum number can be constructed from Coulomb MOs having the same n:

$$n_r^{UA} = n_r^{SA}, n_\theta^{UA} = 2n_\theta^{SA} \quad \text{for} \quad \text{symmetric orbitals,}$$

$$= 2n_\theta^{SA} + 1 \quad \text{for} \quad \text{antisymmetric orbitals.} \tag{3.11}$$

We note that the first equation in (3.11) coincides with (3.9). The formula (3.11) was derived without taking account of the behavior of the terms upon varying R. The Stark effect leads to quasicrossings that change the order of the terms. In this case the MOs are correlated whose quantum numbers satisfy the relationships

$$n_r^{UA} = n_\theta^{SA}, n_\theta^{UA} = 2n_r^{SA} \quad \text{for} \quad \text{symmetric orbitals,}$$

$$= 2n_r^{SA} + 1 \quad \text{for} \quad \text{antisymmetric orbitals.} \tag{3.12}$$

The first of the conditions of (3.12) coincides with (3.10). The correlations for heteronuclear systems are constructed analogously.

The construction of correlation diagrams for multielectron systems and their application to atomic-collision problems is closely associated with the concepts of adiabatic and diabatic behavior of colliding system.[23,79] Owing to the vanishing of the radial nonadiabatic coupling between diabatic terms of identical symmetry, the probability of transition between these terms is small at high velocities, whereas for the diabatic terms it is small at small velocities. The separation of the diabatic Hamiltonian H_{diab} from the total adiabatic Hamiltonian H enables one to simplify the procedure of constructing the terms and establishing the correlation rules, and also to construct a basis convenient for treating collisions at high energies.[23] The reviews of Refs. 80–83 have also been devoted to these problems. The correlation rules (3.9)–(3.12) can be tested experimentally by studying the decay of vacancies in inner shells formed in atomic collisions.[80,81] In particular, the data obtained in collisions of symmetric atoms[64] indicate the validity of the rules (3.9), while for asymmetric systems they confirm the rules (3.10).

4. Autoionization of quasimolecules. The emission of an electron is associated both with direct transitions to the continous spectrum from the discrete levels of the quasimolecule, and with formation and subsequent decay of autoionization states. Autionization states involve vacancies in the inner shells that arise in the interaction of atoms with multiply charged ions or in the process of promotion of levels. An autoionization state is characterized by the energy E and rate of decay per unit time W (and width ΔE), which in a quasimolecule depend on R. Knowledge of $E(R)$ and $W(R)$ makes it possible to calculate the energy spectra of the electrons and the ionization cross sections, which can be compared with the experimental data. Recently it has become possible to extract the $E(R)$ and $W(R)$ relationships directly from experiment.

This section will discuss a model of direct ionization owing to escape into the continuum of a diabatic term, and will discuss the different methods of formation and methods of calculation of quasimolecular autoionization states, as well as radiationless and radiative channels of their decay.

4.1 Transitions to the continuous spectrum. In treating the energy terms E of quasimolecules, a situation can occur in which a discrete term at a certain $R = R_0$ will cross the boundary of the continuous spectrum. This means that, when $R \leqslant R_0$ the bound state is absent in the system, the term becomes quasistationary, and ionization can occur. Adiabatic terms of this type exist in quasimolecules formed in collisions of negative ions with atoms. A detailed review of the theoretical and experimental studies ionionization in slow collisions of negative ions with atoms is contained in Ref. 85.

In the interaction of positive ions with atoms the existence of the Coulomb crowding of levels near the boundary of the continuous spectrum makes it impossible for an adiabatic term to escape into the continuum. In this regard it is of great interest to seek diabatic terms that cross the Coulomb crowding and escape into continuous spectrum. The general problem of crossing by a diabatic term of the system of terms

for a one-electron system with two Coulomb centers was solved in Ref. 86. However, until recently such terms had not been discovered in real quasimolecules. Such terms were first obtained in Ref. 29. Here the terms were calculated of a one-electron, two-center problem for complex values of the internuclear distance R. Pairwise crossings of the adiabatic terms E_{Nlm} and $E_{N+1,lm}$ were obtained successively for all values of $N \geqslant l + 1$. These crossings exist for all values of the nuclear changes Z_1 and Z_2. When R is small, the crossing points lie near the real axis, and infinite series of quasicrossings arise on it. The obtained crossing points R_{Nlm} with differing N and fixed l and m form an infinite sequence localized in a small region of the complex plane and converging to a certain limit point

$$R_{lm} = \lim_{N \to \infty} R_{Nlm}. \tag{4.1}$$

In this region the terms of the series with a given l and m are described by the approximate formula

$$E_{lm}(R) = -(Z_1 + Z_2)^2 \left(2 \left| \ln \frac{R - R_{lm}}{2\pi i} \right|^2 \right)^{-1}. \tag{4.2}$$

In passing around a crossing point, a transition occurs from one term to a term having a different N for the given l and m.

We can consider the existence of the infinite series of quasicrossings as the interaction of the diabatic term escaping into the continuous spectrum with an infinite Rydberg series.[87] Since the region of crossings is small, the diabatic terms escapes steeply upward. Figure 4 shows the adiabatic and diabatic terms obtained for H_2 quasimolecules. The existence of the quasicrossings that draw the diabatic term into the continuum, as is assumed in Ref. 29, involves the redistribution of the potential in going from the two-center problem to the one-center problem as $R \to 0$. Here initially the lowest levels in the given l, m series are redistributed, while the corresponding adiabatic terms are bent upward with decreasing R and are reflected from the overlying adiabatic term. Thus an infinite chain of quasicrossings arises. The expression obtained from this qualitative treatment for the point of escape of the term into the continuous spectrum (for $m = 0$) is

$$R_l = l(l + 1)(Z_1 + Z_2)^{-1} \tag{4.3}$$

This agrees well with the results of numerical calculation.

The existence of singular points in the complex region enabled solving in unitary fashion questions in the two-cen-
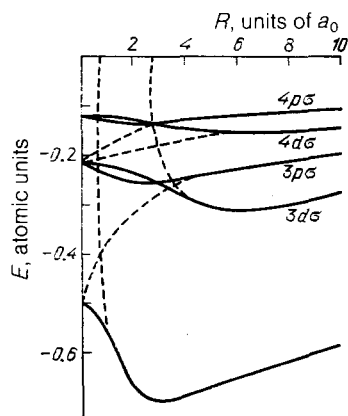
ter problem, such as differing radius of convergence of the expansions for the energies of states for small R and the existence of minima in the terms for which the condition is satisfied that $l(l + 1) > 3m^2$. Upon using the results of Ref. 29 for the probability of ionization due to quasicrossings, a formula was derived for the cross section for direct ionization from the term Nlm:

$$\sigma = \pi v N^2 \mid R_{Nlm} \mid^2 \exp \left(-\frac{2Zl}{vN^2} \right)$$

$$\left(1 - \exp \left[-\frac{l^3(l+1)^2}{vN^2Z \mid R_{Nlm} \mid^2} \right] (Zl)^{-1} \right), \tag{4.4}$$

Here we have $Z = Z_1 + Z_2$. Comparison with experiment on the ionization of hydrogen by protons showed that the cross section of (4.4) is several times lower, which is explained by the contribution to the cross section of the process of resonance charge transfer with subsequent shaking off of electrons into the continuum. A comparison must be made for systems in which resonance charge transfer is absent, e.g., HeH^+.

Quasistationary and virtual levels have been discovered[32] by this same method in the two-center Coulomb problem involving escape into the continuum of a diabatic term. The data on the dependence of the energy of the quasistationary term E on R make it possible to calculate the energy spectrum of the electrons in ionization from a diabatic term being promoted. In Ref. 88 the spectrum of electrons in the direct ionization by protons of the helium atom was experimentally measured in the keV energy range, while this same spectrum was calculated by the formulas of Ref. 29. The agreement of the two spectra serves to confirm the mechanism treated in Refs. 29 and 32 of direct ionization.

Reference 89 proposed a model of direct ionization into the continuum from a strongly promoted discrete term owing to nonadiabatic transitions. The experiments[90,91] show that this mechanism is valid in the keV energy range of colliding atoms.

4.2 Autoionization states of quasimolecules. Three mechanisms are known for formation of autoionization states in the process of atomic collisions. One is the collision of excited atoms or of atoms in the ground and excited states, called the Penning process.[92] In this case ionization occurs owing to the total energy of excitation upon transfer of excitation to the lighter atom being ionized. The second mechanism involves collisions with participation of multiply charged ions, in which a quasimolecule is formed with a large number of inner vacancies, or free levels of the ion. The filling of these vacancies leads to multiple ionization. This process has been called Auger ionization.[93] Finally, it has been shown[10,66,65] from considering the correlation diagrams for the levels in a quasimolecule that the promotion of levels in the process of approach of the atoms leads to crossing of terms and formation of vacancies in the inner and the unfilled shells. Subsequent decay of the vacancies leads to ionization. This mechanism is realized mainly in multielectron quasimolecules.

One of the fundamental methods of studying autoionization states of quasimolecules is to describe them as resonances in the scattering of electrons by the quasimolecule. The phase shift in scattering near a resonance depends on the energy and the width of the level. Thus, for calculating the

FIG. 4. Adiabatic (solid lines) and diabatic (dash lines) terms for the H_2 quasimolecule.[29]

257   Sov. Phys. Usp. **32** (3), March 1989

B. G. Krakov and É. S. Parilis   257

energies and widths of resonances for scattering of an electron by H_2^+, a parametric formula has been used for the dependence of the phase shift on the energy and the width of the level[94,95]:

$$\eta_{lm} = ak(R) + b + \sum_{i=1}^{N} \text{arctg} \frac{\Gamma_i(R)}{(k_i^2(R)/2) - E_i(R)}, \quad (4.5)$$

Here k is the momentum of the scattered electron, a and b are adjustment parameters, and $\Gamma_i(R)$ and $E_i(R)$ are the width and energy of the ith resonance. To calculate the phase shift, the Kohn variation principle was used with test functions in spheriodal coordinates. In Ref. 96 the energy E_0 of an autoionization state also was found from the scattering phase $\delta_l(E_0)$,

$$\delta_l(E_0) = \pi\left(n + \frac{1}{2}\right), \quad \frac{\partial}{\partial E}\delta_l(E)\Big|_{E=E_0} > 0, \quad (4.6)$$

Here $n = 0.1,\ldots$, while the width of the level is determined from the asymptotic behavior of the solution of the Schrödinger equation for scattering $\chi(x) \sim \sin[kx - (l\pi/2) + \delta_l(E)]$

$$\Gamma \approx K\left(M\int_0^{x_0} \chi^2(x)\,dx\right)^{-1}; \quad (4.7)$$

Here M is the reduced mass, and x_0 is the first zero of $\chi(x)$ outside the region of action of the potential. The method, which is allied to the method of strong coupling of channels, was developed in Refs. 97 and 98, where the system of coupled integrodifferential equations is replaced by a system of algebraic equations upon replacing the integrals containing the unknown function with quadrature formulas of the Gauss type. As the basis functions one-center functions of the self-consistent-field method were used. Exchange terms were taken into account in the calculation.

The method of complex scale transformation proposed in Ref. 99 determines the energy and width of an autoionization state as the real and imaginary components of the complex eigenvalue of the Hamiltonian obtained by scale transformation of the electronic coordinates $r \to \eta r$, where $\eta = a\exp(i\theta)$. This methd has been applied for calculating autoionization in molecules.[100,101] In these studies only the coordinates of the electron in the quasimolecule are transformed. That is, at first one uses the Born-Oppenheimer approximation, and then transforms to complex coordinates. To identify autoionization states one uses the complex virial theorem.[102] In practice one seeks the singular points as functions of the eigenvalues of the complex Hamiltonian in the parameter θ. The position of a singular point yields the sought value of the energy and the width of the level. Gaussian orbitals were used as the basis functions.

4.3 Auger decay of autoionization states. Using the methods discussed above for calculating concrete quasimolecular systems is a rather complicated problem that requires very laborious numerical calculations. Only with the spread of high-power computers did it become possible to perform detailed calculations of the energies and decay rates of low-lying autoionization states, and that only for the simplest two- and three-electron systems. The study of such quasimolecules as the homonuclear H_2, He_2^+, and the heteronuclear HeH^+, etc., corresponds in meaning to the calculations of the lower autoionization states in the helium

atom, since it allows one to evaluate the different approximations of the theory without the influence of extraneous factors. Moreover, for these quasimolecules the design of the experiment and the interpretation of the results are facilitated.

The decay of an autoionization state in a quasimolecule at large internuclear distances R has been treated in Ref. 54. The interaction potential leading to decay is taken to be dipole-dipole. Ionization is treated as a two-stage process: emission of a photon with subsequent photoionization. This yields the following formula for the width $\Gamma(R)$ of the level:

$$\Gamma(R) = c\,[(d_x)_{ik}^2\,\sigma_\Phi^x + (d_y)_{ik}^2\,\sigma_\Phi^y + 4\,(d_z)_{ik}^2\sigma_\Phi^z]\,(2\pi\Delta ER^6)^{-1}, \quad (4.8)$$

Here ΔE is the energy of the transition, the $(d_j)_{ik}$ are the matrix elements of the dipole moment, the σ_Φ^j are the photoionization cross sections, and c is the velocity of light.

A simple method has been proposed[103-105] for calculating the energies of two-electron quasimolecules, including autoionization states. One uses the single-configuration wave function $\Phi(1,2)$ composed of the symmetric product of one-electron, two-center functions multiplied by the function $E(g_l r_{12})$, which explicitly contains the coordinates r_{12} of their relative motion. Here g_l is an effective parameter; $g_l = 1$ for singlet states, $g_l = 0.5$ for triplet states. As the function $E(g_l r_{12})$ one uses a modified Clifford-Bessel function calculated in first-order perturbation theory. A simple method of calculating the resonances in scattering has been proposed in Refs. 106-108. Its advantages include the use of only functions of the discrete spectrum for calculations of the energy and widths of autoionization states and the uncomplicated way of revealing the resonances on the background of other states. To do this, one calculates the eigenvalues of the Hamiltonian for a variable number of basis functions. The eigenvalues are treated as functions of the number of basis configurations. If the energy is "stabilized", i.e., it does not depend on the dimension of the basis, then it corresponds to a resonance state. References 109–111 developed a diagonalization method of configurational interaction based on the formalism of projection operators.[112-114] This method at present has become most widespread in calculation of autoionization states, including those in quasimolecules. In the diagonalization method autoionization states are treated as being stationary, while their coupling with the continuum is taken into account approximately in the first order of perturbation theory. The partial rate of decay $W_g(S,R)$ has the form

$$W_g(S, R) = 2\pi\,|\,\langle\psi_a(S, R)\,|\,V\,|\,\psi_E^g(S, R)\rangle\,|^2; \quad (4.9)$$

Here $\psi_E^g(S,R)$ is the wave function of the final state with the index g describing the system after decay when one of the electrons lies in the continuous spectrum. If decay can occur to different final states, then the overall rate $W(S,R)$ equals the sum of the partial rates of (4.9). The functions $\psi_a(S,R)$ are expressed in terms of the symmetrized products of the one-electron functions of the discrete spectrum. Here, following Ref. 109, one omits from this set the functions of the discrete spectrum that describe the final state of the system.

The calculations of autoionization in atoms showed[111] that the diagonalization method yields the same accuracy of approximation to experiment as the more fundamental yet far more cumbersome methods: strong coupling[115,116] and

258   Sov. Phys. Usp. 32 (3), March 1989

B. G. Krakov and É. S. Parilis   258

the Fano method.[117,118] The method allows one to use the final number to test the set of approximations that it is based upon. The merits of the diagonalization method and its perspicuity, simplicity of the formulas of calculation, ease of numerical realization on a computer, control of the contributions of the individual basis configurations ϕ_n (Λ,S) to the total wave function, the energy, and the probability of decay of the autoionization state. However, attainment of high accuracy requires taking account in the expansion of a large number of configurations, especially for highly excited states. This leads to the need to diagonalize matrices of high dimensionality.

The initial calculations of autoionization in quasimolecules were devoted to the second[14] and first[51,119,120] mechanisms. Despite the imperfection of the methodology, even the early study[14] obtained such essential features of autoionization in quasimolecules as the sharp increase in the probability of Auger transitions as compared with the united-atom limit; the correlation of the probability maximum of the transition with the minimum of the energy of the escaping Auger electron; the existence of three possible channels of Auger ionization; and the possibility of observing Auger ionization at the very lowest velocities of the ions.

Fundamental attention is paid in the calculations to the very simple homonuclear systems H_2 and He_2^{2+}. The quasimolecule H_2 has become the proving ground for testing different methods of calculating autoionization states. As a rule, the lower autoionization states of different symmetries are studied as the simplest identifiable and well-marked terms on the background of the higher-lying terms. The diagonalization method was used in Refs. 121–126. Another group is comprised of Refs. 95, 98, 127, 128, which consider the autoionization states as resonances in the scattering of an electron by the quasimolecules H_2^+, the method of complex scale transformation,[100] and perturbation theory.[104] The calculations for H_2^+ have been conducted mainly by the diagonalization method[49,126,129–132] and by perturbation theory.[102] Figures 5 and 6 show the energies of a set of the lower autoionization states of the quasimolecules H_2 and H_2^{2+}. We
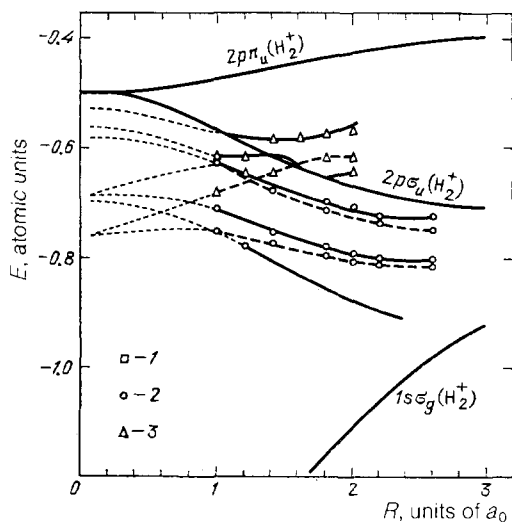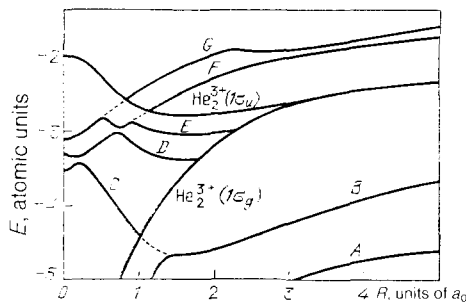

FIG. 6. Electron terms for $^1\Sigma_g$ states of He_2^{3+}.[55] A, B—singly excited states, C, D, E,F, G—autoionization states.[55]

FIG. 5. Energies of autoionization states of differing symmetry for H_2.[95] 1—Σ_g, 2—Σ_u, 3—Π_u. Solid lines—singlet states; dash lines—triplet states.

can see well the characteristic regions of quasicrossings of terms characterized by a sharp drawing closer together of the energy curves. The crossing of the autoionization levels of the one-electron ground state of the quasimolecule has the result that decay becomes impossible. Figure 7 shows the energy of the lowest $^1\Sigma_g^+$ autoionization state of the H_2 quasimolecule calculated by different methods. We see that the calculations performed by different methods agree well over a broad range of variation of R. The pattern differs somewhat for the decay rates. Figures 8 shows the decay-rate curves for the same state as obtained in these same calculations. For $R < 1.6\ a_0$ all the calculations mainly agree well with one another. In the region $R > 1.6\ a_0$ the data are classified into two groups, within which good agreement again exists. One group is composed of the calculations performed by the diagonalization method, and the other by the methods of scattering theory. The data of Refs. 97 and 121 differ sharply from one another and from the data of other studies. Thus, the $W(R)$ relationship obtained in Ref. 121 has a maximum of $R \approx 1.8\ a_0$ and declines toward the stabilization point.

On the other hand, for the He_2^{2+} quasimolecule the dependence of the decay rate $W(R)$ on the internuclear distance R was also calculated for the lowest $^1\Sigma_g^+$ autoionization state.[131] The function and the energies of the one-electron quasimolecules having the same ratio $Z_2/Z_1 = k$ are related by the scale transformation[26]

$$R' = \frac{R}{n}, \qquad \psi_i'(R') = \psi_i\left(\frac{R}{n}\right), \qquad E_i' = n^2 E_i. \qquad (4.10)$$

For the He_2^{2+} and H_2 quasimolecules we have $n = 2$. Taking account of the interaction of the electrons in calculating the energies of the autoionization terms breaks down the simple
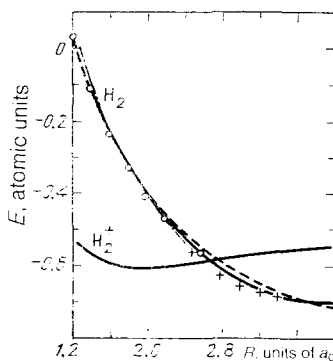

FIG. 7. Energy of the lowest $^1\Sigma_g$ autoionization state of the H_2 quasimolecule calculated by different methods.[125]
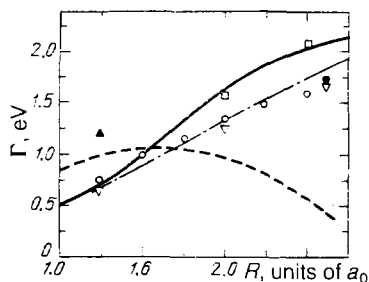
FIG. 8. Width of the level of the lowest $^1\Sigma_g^1$ state obtained by different methods.[125]

FIG. 9. Matrix element of the Auger transition I_l (R) to an l state of the continuous spectrum as a function of R and l.

scale law (4.10), but a comparison of the results of Refs. 131, 95 with account taken of scaling yields a good agreement. If we compare from this same standpoint the data of calculations of the rates of decay of the terms, then the results of Ref. 131 agree better with the results of Ref. 121, albeit qualitatively. The positions of the maxima of $W(R)$ match, as well as the decline toward the stabilization point. Quantitatively the results strongly differ, although in an atom, e.g., the probability of Auger decay depends weakly on the charge of the nucleus. In Ref. 133 the energy and decay rate of an autoionization state were obtained as functions of R from the experimental data on the spectra of electrons emitted in He$^+$ + He collisions, while using the Airy approximation[134] to describe the spectrum. The results that were obtained agree well with the data of Ref. 129. The authors of Ref. 133 point out that this indicates the applicability of the Airy approximation[134] to describe autoionization spectra in collisions of light atoms.

Heteronuclear systems have been investigated in not such a great number of studies, although the spectrum of studied systems is broader. These are the quasimolecules HeH$^+$,[56,135] HeH,[136,137] HeLi^{3+},[138] HeBe^{4+},[139] and HeC^{6+}.[140] The dependence of the probability of an Auger transition on the partial state of the electron in the continuum was studied in Ref. 137. Figure 9 shows the matrix elements for Auger transition I_l (R) to an l state of the con-
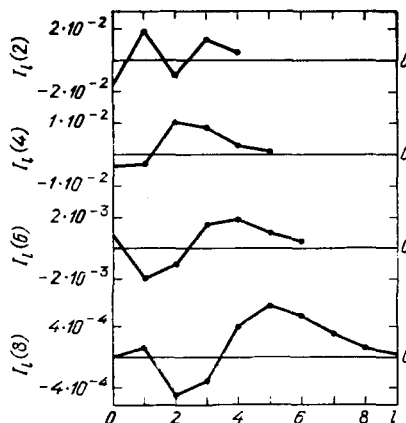
tinuous spectrum for different values of R over a broad interval of l values. For fixed R, I_l is an oscillatory function of l, while for fixed l, I_l (R) oscillates with R. I_l (R) has a maximum in l and R are associated with the equation of the turning point

$$E_c = -\frac{1}{R} + \frac{l_{max}^2}{2R^2}, \quad l_{max} = (2E_cR^2 + 2R)^{1/2}. \quad (4.11)$$

When $l < l_{max}$, I_l (R) oscillates as a function of l, while when $l > l_{max}$, I_l (R) declines exponentially. We see from (4.17) that the number of states of the continuous spectrum to which an Auger transition occurs increases with increasing R. In the studies on the HeH$^+$ quasimolecule the effects of configuration interaction and their influence on the energies and decay rates of the autoionization states were studied within the framework of the diagonalization method. The calculations show that the total wave function is characterized by a predominant contribution from a certain configuration outside the region of quasicrossings of the adiabatic terms. In the region of quasicrossings the contributions of
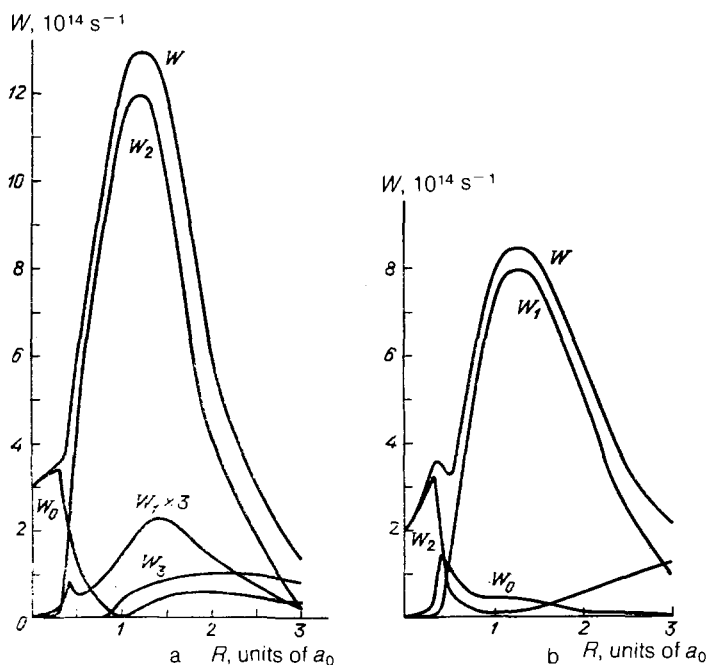

FIG. 10. Total $W(R)$ and partial W_g (R) rates of Auger transitions for the lowest I(a) and II(b) $^1\Sigma^+$ autoionization states of the HeH$^+$ quasimolecule.[56]

two or more configurations become comparable, and the coefficients c_n of the expansion change sign. The quasicrossing of terms also affects the dependence on R of the total rates $W(R)$ and partial rates $W_g(R)$ of Auger transitions. Figure 10 shows the total and partial rates of Auger transitions for the autoionization states $1^1\Sigma^+$ and $2^1\Sigma^1$. In the quasicrossing region oscillations occur as a function of R in the partial rates $W_g(R)$ when $R \approx 0.35$ a_0 for $1^1\Sigma^+$ and when 0.4 $a_0 < R < 0.5a_0$ for $2^1\Sigma^+$. These are manifested also in the total rates $W(R)$. These features, in contrast to the oscillations obtained in Ref. 137, involve the fact that states are crossing whose decay rates depend in different ways on R. We must note that, if taking account of configuration interaction leads to a relative energy change by $\Delta E / E = \varepsilon = 0.03$–$0.05$, then the relative change in the rate of Auger decay now amounts to $\Delta W / W \approx \varepsilon^{1/2} \approx 0.2$. The sharp decline of $W(R)$ when $R > 1.5$ a_0 involves the fact that the wave function of the autoionization state is localized at the light nucleus H^+, which involves the predominant contribution of the configuration $(2p\sigma)^2$, whereas the vacancy in the $1s\sigma$ orbital at large R belongs to the heavy nucleus He. The increase in the barrier between the nuclei with increasing R leads to an exponential decline in $W(R)$. A comparison with allowance for the scale transformation (4.10) of the calculations for the quasimolecules HeH^+ and $HeBe^{4+}$, for which $n = 2$, indicates good agreement. However, we note that, owing to the decrease in the relative magnitude of the perturbation $1/r_{12}$, with increasing n the configuration interaction declines and the probability of Auger transition increases.

Upon going to more asymmetric systems with $k = 3$, e.g., HeC^{6+}, the features noted above of quasimolecular autoionization states are conserved. However, new interesting properties are manifested here, which must be noted.[141] In the system HeC^{6+} the wave functions of the electrons in the initial state and in the bound state after transition for large R are localized at the heavy C nucleus. That is, even after separation the autoionization state is conserved. This has the result that the region of decline in $W(R)$ goes over at $R > 1.5$ a_0 into a region in which the rate of decay begins to rise. The asymptotic behavior of $W(R)$ as $R \to \infty$ involves the problem of what atomic states the given quasimolecular autoionization states transform into, and what their rates of decay are. As $R \to \infty$, the presence of the He^{2+} ion is reduced to the appearance of an external electric field. A similar problem of the decay of an autoionization state in the field of an ion has been treated in Ref. 142.

It is of interest to compare the calulcations of the lower autoionization states $^1\Sigma^+$ for a series of homo- and heteronuclear quasimolecules.[141] Figure 11 shows the curves $W(R^*)$ for the lowest adiabatic states of the quasimolecules H_2, He_2^+, HeH^+, $HeBe^{4+}$, and HeC^{6+}. The generalized internuclear distance is $R^* = (Z_1 + Z_2)$ $R/3$. All these states are characterized by a predominant contribution of the configuration $(2p\sigma)^2$ to the total wave function. Characteristically, the maxima of the frequencies of the terms lie approximately at the same value $R^* \approx 1.2a_0$. All the magnitudes of W_{max} (R^*) exceed 10^{15} s^{-1}, although they are distinguished by a strong scatter. All of this allows us to conclude that the behavior of $W(R^*)$ in the region $R^* \lesssim R^*_{max}$ and $R^* \gtrsim R^*_{max}$ is determined by the properties of the configuration $(2p\sigma)^2$ in the united potential well with $Z = Z_1 + Z_2$. The behavior of $W(R^*)$ in the asymptotic re-
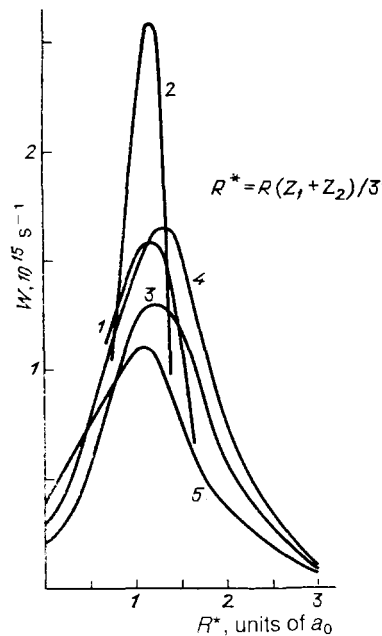

$R^* = R(Z_1 + Z_2)/3$

FIG. 11. Rates of Auger transitions for the lowest $^1\Sigma^+$ adiabatic states of two-electron quasimolecules.[141] 1—H_2, 2—He_2^+, 3—HeH^+, 4—$HeBe^{4+}$, 5—HeC^{6+}.

R^*, units of a_0

gion of R^* depends on the degree k of the system. For symmetric quasimolecules at a certain finite R^*_f the term of the autoionization state crosses the term of the singly ionized quasimolecule, and Auger decay becomes energetically forbidden. In the case $1 < k < 3$ the wave function of the initial state is localized at the lighter nucleus, while the vacancy belongs to the heavier nucleus. Then we have $W(R^*) \sim \exp(-\alpha R^*)$ owing to the need of tunnelling through the potential barrier. When $k \geqslant 3$ in the region of large R^*, the lower quasimolecular autoionization state transforms into the same state at the heavy nucleus plus the electric field of the light nucleus. In this case the probability of Auger transition reaches a constant value. These three cases exhaust the possible types of behavior of $W(R^*)$ as $R^* \to \infty$.

In multielectron quasimolecules, as we have already noted above, an autoionization state can be formed by the mechanism of promotion of levels and formation of vacancies in the inner shells. The decay of such autoionization states has been studied experimentally in Refs. 143 and 144, where estimates of the probability of Auger transitions to the falling $4p\pi$ orbital for the Kr_2^+ quasimolecule and the $2p\pi$ orbital for the Ne_2^+ and O_2^+ quasimolecules were obtained by analyzing the energy spectra of the emitted electrons within the framework of the Airy approximation.[134] They respectively amount to values of the order of 10^{16} and 10^{15} s^{-1}. Reference 145 treated autoionization with participation of multiply charged ions. For the system $HeXe^{2+}$ a reciprocal power-law dependence of the probability $W(R)$ on R was obtained from the measured differential ionization cross sections. Here $W(R)$ attains values $> 10^{15}$ s^{-1}. Unfortunately the retrieval of the $W(R)$ relationship from the experimental data involves certain a priori assumptions on the behavior of the energies and decay rates as functions of R that are not always justified. There are extremely few theoretical studies as a result of the great laboriousness of these calculations.

There are studies on Penning ionization.[146,147] References 141 and 148 undertook an attempt to use the effective-potential wave functions[47,50] that have proved successful in calculating the energies of the discrete quasimolecular states, and the screened functions of the continuous spectrum[56] for calculating the decay probability of the $2p\pi$ vacancy in the Ne_2^+ quasimolecule. This is the first attempt directly to obtain $W(R)$ in a multielectron system. The total probability of filling the vacancy owing to the transitions treated in the study reaches a value of 10^{15} s^{-1} at the maximum, which agrees with the estimates of Ref. 144. With increasing R, $W(R)$ obeys the rule for symmetric systems: the autoionization state vanishes.

The obtained values of $W(R)$ exceed by severalfold the values of W in the united-atom limit, as has been observed also in calculations for the simplest quasimolecules. This confirms the conclusion that such an increase in $W(R)$ is a typical quasimolecular effect.

4.4. Auger transitions in quasimolecules formed by multiply charged ions.

At present low-energy beams of highly charged ions have been obtained, down to completely stripped nuclei. As a slow, highly charged ion approaches a multielectron atom, a quasimolecule is formed in which an inverted population of the levels by electrons exists from the very onset. Such a system must relax rapidly by Auger transitions whose probability depends on the internuclear distance.

A possibility exists of decay of such an inverted-population quasimolecule with emission of high-energy electrons by multielectron "fractional" Auger transitions,[149] and first of all, by the three-electron semi-Auger effect,[150] in which two or more vacancies are filled simultaneously, while the entire energy is transferred to a smaller number of electrons or even to a single Auger electron. A theory of the semi-Auger effect in a quasimolecule has been constructed in Ref. 151.

To calculate the probability of the semi-Auger effect one can use the shake-up approximation. In this approximation the probability $W(R)$ of the three-electron transition has the form

$$W (R) = 2\pi \mid \langle f \mid V \mid i \rangle \mid^2$$
$$= W_A (R) \int \varphi_g^* \varphi_m \, d\tau = W_A (R) \, W_S (R), \quad (4.12)$$

Here f and i are the total wave functions of the final and initial states, v is the perturbation operator, ϕ_m and ϕ_g are the initial and final functions of the electron undergoing shake-up. $W_A (R)$ is the probability of an oridinary Auger transition, $W_S (R)$ is the probability shake-up, and R is the internuclear distance. The calculations of the electron wave functions and matrix elements entering into (4.12) were performed using the model of two Coulomb centers.

As a very simple example we can treat the collision of a bare C^{+6} nucleus with the three-electron Li atom. The initial configuration of the LiC^{+6} quasimolecule that is formed has the form $(2p\sigma)^2 4d\sigma$, the ground state is $(1s\sigma)^2$. Using Eq. (4.12) calculations were made of the shake-up probability W_S, of Auger transition probability W_A, and of the total probability W of three-electron transition to the ground-state $(1s\sigma)^2$ as functions of the internuclear distance R.

The increase of $W(R)$ with varying R is caused by the increase of both the probability of the ordinary Auger transi-

tion and the probability of shake-up in the quasimolecule owing to the decrease in the energy of the Auger electron, the weakening of the selection rules, and the increased overlap of the wave functions. Both W_A and W_S pass through a maximum at $R \approx 0.6a_0$. Here $W_S (R)$ reaches 10^{-2}, in contrast to the analogous quantity in an atom, where it is of the order of 10^{-4}.[150] At large R, since the wave functions of the ground and excited states are localized at different nuclei, we have $W(R) \rightarrow 0$.

The energy spectrum of the Auger electrons $d\sigma/dE$ is calculated by the formula[137]

$$\frac{d\sigma}{dE} = 4\pi R_E^2 W \; (R_E) \left| \frac{dE}{dR} \right|^{-1} \left(1 - \frac{u_0 (R_E)}{E_0} \right)^{1/2} v_0^{-1}, \quad (4.13)$$

Here v_0 is the relative velocity of collision, E_0 is the energy in the system of the center of inertia, $u_0(R)$ is the interaction potential of the atom and the ion, and R_E is the internuclear distance at which an electron is emitted with the energy E. Figure 12 shows the spectra of electrons for the semi-Auger process, and for comparison, for the ordinary Auger process from the same autoionization state for the two initial energies $E_0 = -0.5$ and 2 keV.

We see that the semi-Auger effect yields a high-energy peak at the energy $E \approx 490$ eV, which practically does not overlap the spectrum of the ordinary Auger effect, and differs in intensity by two orders of magnitude in all. At such initial ion energies one cannot obtain a similar electronic effect owing to other processes, e. g., impact ionization. If we take as the target an atom with a large number of electrons, then, owing to the increased number of possible electronic transitions, the role of the semi-Auger effect increases in comparison with the oridinary Auger process. Actually, in a quasimolecule with N outer electrons and M inner vacancies, the probability of a three-electron transition is $W \sim N(N-1)(N-2)M(M-1)$, while that of an ordinary Auger transition is $W_A \sim N(N-1)M$. Then the relative probability of the semi-Auger effect is $W_S = W/W_A \sim (N-2)(M-1)$.

The cross sections σ of the Auger effect was calculated by the formula

$$\sigma = \frac{4\pi}{v_0} \int_{R_m}^{\infty} R^2 W \; (R) \left(1 - \frac{u_0 (R)}{E_0} \right)^{1/2} dR, \quad (4.14)$$

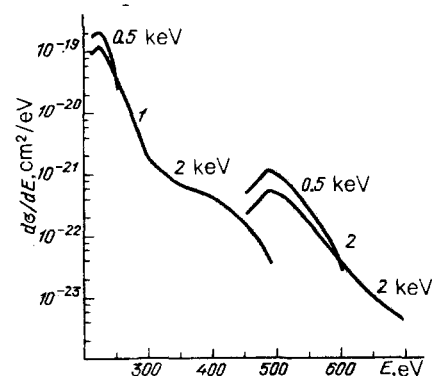Here R_m is the distance of closest approach of the nuclei in

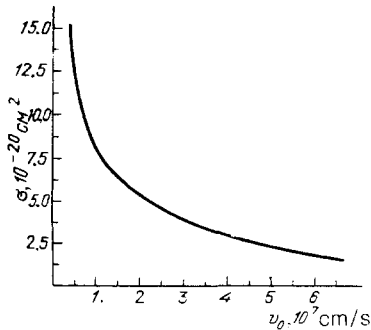FIG. 12. Energy spectra of Auger electrons. *1*—Auger effect; *2*—semi-Auger effect.[151]

FIG. 13. Dependence of the cross section of the semi-Auger effect on the relative velocity of collision of a multiply charged ion with an atom.[151]

FIG. 14. Total rates of radiative decay $W_R(R)$ and of Auger decay $W_A(R)$ (in units of 10^{-14} s) in HeH^+.[156] 1—$W_R(1\ ^1\Sigma^+)$; 2—$W_R(2\ ^1\Sigma^+)$; 3—$W_A(1\ ^1\Sigma^+)$; 4—$W_A(2\ ^1\Sigma^+)$.

head-on collision. Figure 13 shows the dependence of the cross section σ on the velocity v_0. We see that the cross-section σ varies as $1/v_0$. This involves the fact that the integral in (4.14) varies weakly as a function of the velocity (only R_m depends on the velocity). The cross section is rather large throughout the entire range of velocities and attains values of the order of 10^{-19} cm^2. In Ref. 152, where a three-electron Auger transition was found experimentally in an atom in high-energy hard atomic collisions in which the necessary divacancy in the L-shell is formed, the cross section of the transition proved to be of the order of 10^{-21} cm^2. This magnitude arises from the small value of the cross section for formation of two inner vacancies in a single collision, which amounts to 10^{-18} cm^2, and from the relative probability of the semi-Auger effect in the atom, which amounts to $\sim 10^{-4}$.

The considerably larger magnitude of the cross-section of the semi-Auger effect involving multiply charged ions, 10^{-19} cm^2, arises not only from the elevated value of its relative probability in the quasimolecule (at the peak up to 10^{-2}), but also from the existence of a large number of ready vacancies in the inner shells.

As regards Auger transitions of higher multiplicity, which should be expected for highly charged ions, they will lead to appearance in the energy spectrum of peaks declined in intensity with energeies that are approximate multiples of the energy of an ordinary Auger transition. Thus, in the collision of slow (10^{-6}–10^{-7} cm/s) multiply charged ions, e.g., bare nuclei with multiply charged atoms, we should expect the appearance with cross sections up to 10^{-18} cm^2 of high-energy Auger electrons with energies of several keV and even tens of kiloelectron-volts.

4.5 Radiative decay of autoionization states. Besides Auger transitions, autioionization states can decay by emission of radiation. The probability of radiative transitions increases sharply with increasing energy of the emitted radiation and charges of the nuclei. In this regard radiative transitions are characteristic of medium and heavy quasimolecules and inner shells.[153]

For the spectroscopy of quasimolecular autoionization states, data are needed on the dependence of the energy E of the radiation and the rate of radiative decay W_R on the internuclear distance R. Quasimolecular radiation will be discussed in more detail in Sec. 6. Here we shall take up the calculations of $W_R(R)$. The energy $E(R)$ of the emitted radiation is calculated simply as the difference of the terms of the initial and final states.

Radiative decay of autoionization states arise mainly from the electronic dipole moment $\mathbf{p}_e = -(\mathbf{r}_1 + \mathbf{r}_2)\,e$. The
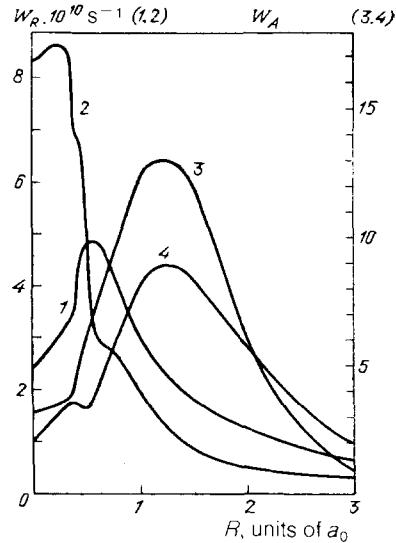
rates of radiative transitions in a quasimolecule, just like the rates of Auger transitions, are functions of the internuclear distance. For a fixed distance R between the nuclei of the quasimolecule, the rate of radiative decay has the form[154]

$$W_R(R) = 4E_{if}^3(R)\,|\langle i\,|\mathbf{p}_e|f\rangle|^2\,(3\hbar c^3)^{-1}; \qquad (4.15)$$

Here $E_{if}(R) = E_i(R) - E_f(R)$ is the energy of the photon.

Despite the fact that the calculation of $W_R(R)$ is far simpler than that of the probability $W_A(R)$ of an Auger transition, there are very few studies devoted to calculating $W_R(R)$. Reference 155 treated the transition $1\pi_g$–$1\sigma_g$ in the N_2 quasimolecule, while Ref. 156 treated the radiative decay of $^1\Sigma^+$ autoionization adiabatic states of the HeH^+ quasimolecule. Here a comparison was made with the rates $W_A(R)$ of Auger transitions from these same autoionization states. Figure 14 shows the overall rates of radiative decay $W_R(R)$ and of Auger decay $W_A(R)$ of the two lower $^1\Sigma^+$ autoionization states of the HeH^+ quasimolecule.[156] As was pointed out in Sec. 4.3, the quasicrossing of adiabatic autoionization states leads to features in the dependence of $W_A(R)$ on R. We see from Fig. 14 that the features in $W_R(R)$ have the same nature.

Characteristically, the strength of the line $S_{ij}(R) = |\langle i|\mathbf{P}_e|f\rangle|^2$ has a maximum in approximately the same region of R as $W_A(R)$ does. The displacement of the maximum of $W_R(R)$ into the region of small R, which was found also in Ref. 155, involves the sharp decline of the energy $E_{ij}(R)$ of the radiation as the nuclei are separated. The rates $W_R(R)$ in HeH^+ attain values of the order of 10^{10}–10^{11} s^{-1}, and in N_2 of as much as 10^{12}–10^{13} s^{-1}, which confirms the strong dependence of W_R on the charges of the nuclei of the quasimolecule.

5. Exotic quasimolecules.

5.1. Superheavy systems and generation of positrons. Great interest has been aroused in studying superheavy atoms with $Z\alpha > 1$. Superheavy atoms enable one to study the properties of electrons in strong electric fields produced by nuclei and to establish the stability limits of nuclei with a large number of protons and neutrons, in particular the is-

lands of nuclear stability for the magic nuclei.

Upon increase of the nuclear charge Z to the so-called critical value Z_c, the energy of the lowest levels decreases so much that the 1s level passes over the boundary of the continuum of negative energies and the bound state 1s disappears. Here the energy of the level is $E_{1s} < -2mc^2$, where m is the mass of the electron, and $Z_c \gtrsim 170$. Physically this means that in such a strong electric field the vacuum becomes unstable with respect to creation of electron-positron pairs. If a vacancy in the K shell exists in such an atom, then one or two positrons can be generated, depending on the number of vacancies. The review of Ref. 157 discussed in detail the properties of the vacuum and the electron shells of nuclei for $Z_c \alpha \gtrsim 1$ and studied the different mechanisms of pair generation and the energy spectrum and probability of positron emission. Modern nuclear physics has no possibility for creating such nuclei. An original solution of this problem, which uses a quasimolecule mechanism, was proposed in Ref. 158. Upon approach of two bare nuclei, e.g., uranium nuclei, when R is not too small, the Coulomb field becomes so strong that the lower $1s\sigma_{1/2}$ level of the quasimolecule "dives" into the continuum. This situation corresponds to the fused-atom approximation, in which the electrons in the quasimolecule feel the field of the total charge $Z = Z_1 + Z_2$. We should note that this idea is the basis of all the subsequent studies on phenomena in strong fields.

It was shown[159] that pair formation is also possible under less rigid restrictions, e.g., in the collision of a bare nucleus Z_2 with an atom Z_1 under the condition $Z_2 > Z_1$. In this case the lower $1s\sigma$ level is formed from the unfilled K shell of the heavy nucleus. In connection with the quasimolecule method of obtaining Z_c, the problem arises of solving the relativistic two-center Coulomb problem, i.e., obtaining the energy terms of an electron in the field of the two nuclei with charges Z_1 and Z_2 as a function of the internuclear distance. The dependence of the energy of R makes it possible for a given pair Z_1 and Z_2 to determine the R_c at which the level enters the continuum. References 159–166 were devoted to calculating R_c as a function of the nuclear charges for the different electronic levels. Figure 15 shows the energy levels of an electron in the field of two centers with three combinations of the nuclear charges Z_1 and Z_2. We see that, for $Z_1 = Z_2 = 98$, not only the lowest level $1s\sigma$ reaches the continuum, but also the $2p\sigma_{1/2}$ level. In Fig. 16 the dependence of R_c on the charge Z is constructed for symmetric collisions for the $1s\sigma$ state. The calculations indicate an almost linear dependence of R_c on Z, with the data of the variational calculations[159-164] systematically exceeding the data obtained
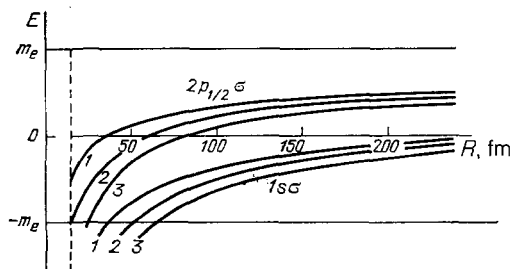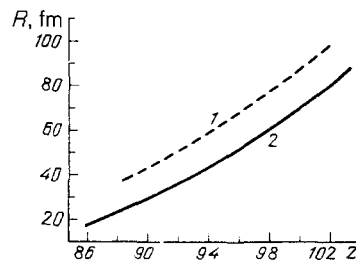

FIG. 16. Dependence of R_c on the charge Z of the colliding nuclei for symmetric systems.[180] 1—variational calculations; 2—numerical integration.

by direct numerical integration of the Dirac equation.[165,166]

The mechanism discussed above of spontaneous pair creation owing to attaining a critical field does not depend in principle on the velocity of the colliding particles and can occur at very low energies provided that the nuclei can approach to a distance $R \leqslant R_c$. In the region of nonadiabaticity positrons can be generated owing to the variation of the Coulomb field of the nuclei in the collision process.[167-175] Here pair formation can occur before the submersion of the level into the continuum. The processes of spontaneous and stimulated positron creation are coherent. In this regard it was proposed[170,171] to treat them as a unitary phenomenon.

In studying the energy spectrum of positrons generated in heavy quasimolecules, peaks were found[176] that could not be explained within the framework of vacuum decay, spontaneous or stimulated by the variation of the field. The spontaneous mechanism leads to a very narrow positron spectrum.[177,178] Owing to stimulated decay, the spectrum strongly heightens and broadens.[167,169] The peak found in Ref. 176 lies at higher energies but is less intense. To explain these experiments a new mechanism of positron generation was proposed,[179] analogous to autoionization in a quasimolecule in the presence of vacancies in the inner shells. Two vacancies in the $1s\sigma$ shell are filled with an electron from a higher level, e.g., $2s\sigma$, and an electron from the continuum. Here a positron is also created. The process is energetically allowed if

$$E_{2s\sigma}(R) - 2mc^2 - E_{(1s\sigma)^2}(R) \geqslant 0. \tag{5.1}$$

Analysis of the relativistic correlation diagrams shows that the condition (5.1) is fulfilled at not too small values of R. The probability of such an autoionization creation of a positron amounts to 25% of the probability of direct transition from the continuum.[179]

In the low-energy part of the positron spectrum a narrow peak was found whose width does not agree with the uncertainty relationship if we take the peak width as ΔE and the time of existence of the $1s\sigma$ orbital in the energy region below $E_{1s\sigma} - mc^2$ as Δt.

Reference 235 proposed an explanation of this involving the formation of a peculiar positron quasimolecule in which the time of the existence of the positron (if it survives to reach this state) is increased. The positron seemingly becomes "stuck" for some time between the two repulsive centers, just as radiation is trapped between two mirrors. Another possible explanation is the creation and subsequent decay in such collisions of a new elementary particle—the "axion."[180]

The phenomena in strong fields are presented in detail in the reviews of Refs. 181, 182.

5.2. **Mesoquasimolecules.** Recently the interest has

FIG. 15. Quasimolecular correlation diagram for different supercritical quasimolecules.[180] 1—U-U; 2—U-Cf; 3—Cf-Cf.

sharply arisen in studying mesoatomic and mesomolecular processes. This involves the prediction[183] and experimental discovery[184] of a highly excited bound state in the mesomolecules $dd\mu$ and $dt\mu$. The rate of resonance formation of the mesomolecule $dt\mu$, $\lambda_{dt\mu} \approx 10^8$ s^{-1} is such that one μ meson can effect the catalysis of the order of a hundred fusion reactions of the deuterium and tritium nuclei. The studies on meson catalysis have been reviewed in detail in Ref. 185.

For the dynamics of the catalysis we much know the capture time of the meson and the discrete spectrum and time of decay to the ground state. It is commonly taken that a free, thermalized μ meson is captured into highly excited levels of deuterium with the principal quantum number $n = 14$. As a result of a cascade of Auger and radiative transitions it reaches the ground state. Here interaction with neighboring atoms causes a Stark mixing of the levels of the mesoatom, which increases the rate of radiative transitions and external Auger transition. Calculations of the cascade time in mesoatoms have been performed in Refs. 186 and 187. At the same time experimental data exist[188] that capture of a meson into the ground state and transitions in the outer shells occur in the quasimolecule. In this regard it is of interest to study the influence of quasimolecular effects on the mesonic transitions. The first attempt was undertaken in Ref. 189, where the Auger transitions were calculated in a quasimolecule consisting of two deuterons at a distance R from one another, a meson in a highly excited state with $n = 14$ and an electron in the ground state $1s\sigma$. A transition is energetically allowed from this state to a level with $n = 7$, and with increased R, also to $n = 8$. Figure 17 shows the $W(R)$ dependence for the transitions $n = 14 \rightarrow n = 7(1)$ and $n = 14 \rightarrow n = 8(2)$. The strong dependence on R indicates the importance of taking account of transitions in the quasimolecule. Reference 189 treated only the initial stage of the cascade. It seems pertinent within the framework of the quasimolecular approach to study the entire process of capture and deexcitation of the meson.

5.3. **Quasimolecules and nuclear fission**. The quasimolecular approach finds application even in such a seemingly remote field as nuclear fission. In the study of "instantaneous" fission of a nucleus of a mesoatom by a muon undergoing a 2p–1s transition the question arises: what is the probability of finding the muon on the light or heavy fragment[190]? This typically quasimolecular problem is solved by using the Demkov formula.[15] It turns out that it remains in the ground state of the heavy fragment with a probability of 99%.

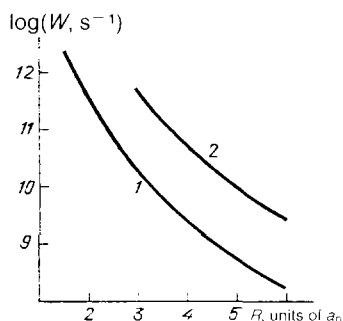In nuclear fission, which can be considered as a "half-

collision," the problem arises of the charge composition of the fragments, which amount to 20–22-fold charged ions. Since the velocity of the fragments is small in comparison with the velocity of the inner electrons, the problem is treated within the framework of the quasimolecular approximation. In Refs. 191 and 192 the charge composition was treated in the "sudden shakeup" approximation, which was based on the assumption that the electrons in the original uranium nucleus whose orbital velocities v_U^{el} are smaller than the velocity of the heavy fragment v_{heavy} are completely stripped off in nuclear fission. However, this approach does not consider the inner shell, and the degree of ionization remains too low.

To solve this problem Ref. 194 used a diabatic correlation diagram for the quasimolecule Sr + Xe (the most probable fission products of the ^{235}U nucleus). An examination of the diagram implied that part of the electrons for which $v_U^{el} > v_{heavy}$ also is stripped off, since their terms are correlated with highly excited states of the fragments for which $v_{light,heavy}^{el} \ll v_{light,heavy}$. The total charge of the fragments $g = 46$ agrees well with the experimental value $g \approx 42$.[195] Analysis of the correlation diagram enables one to conclude that the probability of forming two vacancies in the M shell of the heavy fragment is almost unity, and 50% for formation of a vacancy in the L shell of the light fragment. Detection of x-rays from the M shell would be an experimental confirmation of the quasimolecular mechanism of vacancy formation in nuclear fission.

In collisions at large energies in the region of predominance of the nuclear forces, nuclear molecules are formed.[196,197] These short-lived states lead to formation of characteristic resonances in the collision cross sections. It would be interesting to study also this type of quasimolecule.

6. **Quasimolecular emission of radiation**. In 1972 in studying[19] photon spectra obtained in slow Ar$^+$–Ar collisions, a continuous x-ray band was found that did not coincide with the positions of the characteristic atomic spectra. Even in this first study the authors indicated a quasimolecule as the source of formation of the continuous spectrum, and adduced correlation diagrams and a mechanism of double collision to explain the properties of the observed radiation. The interest in the quasimolecular x-ray emission involves the possibility of obtaining information on the energy levels of the inner shells of heavy and superheavy quasimolecules and quasiatoms. Intensive development of this field of study has been facilitated by the construction of the heavy-ion accelerators at the Joint Institute for Nuclear Research at Dubna and the GSI, where total charges of the colliding nuclei $Z = Z_1 + Z_2 \gtrsim 100$ have been attained. A number of reviews[153,198–200] is devoted to different aspects of the continuous x-ray emission.

6.1. **Inner-shell vacancies**. As was pointed out above, the quasimolecular mechanism of excitation leads to formation of vacancies in the inner shells. These vacancies are filled by radiationless transitions of the Auger type and radiative transitions. The former predominate for light systems and outer shells. The occurrence of emission of radiation requires that the time of collision should be comparable with or greater than the lifetime of the vacancy with respect to radiative transition. Therefore we can expect quasimolecular emission of radiation for collisions of medium and heavy atoms with excitation of the inner shells,[153]

log(W, s^{-1})

FIG. 17. Rates of Auger transitions from highly excited states of the ($dd e\mu$) quasimolecule.[189] 3—$n = 14 \rightarrow n \rightarrow = 7$; 2—$n = 14 \rightarrow n = 8$.

since the probability of emission of radiation increases rapidly with increasing charges of the nuclei and energy of the radiation.

In a number of references[19,201,202] that studied quasimolecular emission of radiation in the bombardment of heavy targets, a dependence was found of the emission cross section on the density of the target. To explain this dependence a mechanism was proposed of double collision—a "carom shot."[19] The impinging atom in the first collision acquires a vacancy in an inner shell, which then decays in the process of the second collision. The fraction f of ions having a vacancy, e.g., in the L shell, is equal in the solid to

$$f = \sigma_L d v \tau_L \ (\mathrm{AM})^{-1}, \tag{6.1}$$

Here σ_L is the cross section for forming an L vacancy, AM is the number of atoms of the target per unit volume, v is the velocity of the ion, and τ_L is the lifetime of the L vacancy in the bombarding particle. This fraction can be rather large. Estimates[153] show that 10–20% of the ions (at 200 keV) have a vacancy in the L shell after passing through a thin film. The double-collision mechanism is effective for vacancies whose lifetimes with respect to radiative transitions exceed the time of collision. As was pointed out in Ref. 153, the double-collision mechanism predominates for the elements of the first row of the periodic table in emission from the K shell. For elements of the second, and possibly the third row, K–MO emission takes place for collisions involving recoil atoms. For heavier systems the double-collision mechanism is characteristic of L- and M–MO emission. A theory of quasimolecular emission of radiation based on this mechanism is presented in Refs. 155 and 203.

With increasing charges of the nuclei Z_1 and Z_2 of the colliding atoms, the lifetime of vacancies in the inner shells decreases. This time becomes comparable with the time of collision. For such systems the single-collision mechanism is applicable, in which the vacancy decays during the same collision in which it is created. Reference 204 states that the single-collision mechanism is applicable for strongly asymmetric quasimolecules and for collisions of heavy atoms (Z_1, $Z_2 > 50$). A theory of this mechanism was developed in Ref. 205.

6.2. **Emission spectrum.** Quasimolecular emission of radiation is observed in the form of a continuous band in the energy spectrum of photons (Fig. 18).[153] This involves the continuous variation of the energy of the radiation with the distance between the colliding atoms. If the collision time is
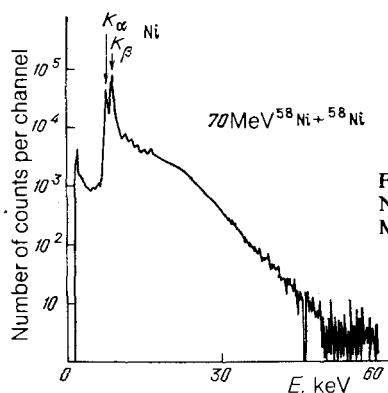
great enough in comparison with the time of radiation decay of a vacancy, then emission of radiation can occur for any internuclear distance R. In the quasistatic approximation the energy of quasimolecular emission $E(R)$ is simply equal to the energy difference between the terms of the initial and final states at the given R. Analysis of the correlation diagrams enables one to distinquish characteristic regions of the spectrum. Thus, we should expect the greatest emission energies at small R in the united-atom limit. References 201, 206, and 207 observed a shift of the spectrum to higher energies with increasing velocity of collision. The correlation diagrams used for calculating the emission spectra were obtained in Refs. 43, 45, 208, and 209. Within the framework of the double-collision mechanism of formation of quasimolecular emission, the following expression for the spectrum was derived[155]:

$$\frac{d\sigma}{dE} = 4\pi R_0^2 \left(\frac{dE}{dR} \right)^{-1} \Big|_{R=R_0} \left(1 - \frac{U(R_0)}{T} \right)^{1/2} (v\tau_R(R_0))^{-1}, \tag{6.2}$$

Here R_0 is the distance corresponding to the energy E, v is the velocity of the ion, $U(R_0)$ is the interaction potential at R_0, T is the energy of the ion, and τ_R is the radiative lifetime of the vacancy. Hence we see that the spectrum has singularities at $dE/dR \approx 0$, i.e., for transition energies that depend weakly on R. The spectrum drops off steeply toward larger E at the turning point (at $U(R) = T$). The real spectrum is broadened in the classically forbidden region owing to the dynamics of the collision. This phenomenon—the effect of collisional broadening—will be treated below. The Airy approximation was used to calculate the spectrum in the classically forbidden region.[199,210] The form of the spectrum has been calculated within the framework of the single-collision mechanism in Refs. 204, 205, and 211.

In addition to quasimolecular emission proper, processes of electronic and nuclear bremsstrahlung, radiative electron capture, and radiative ionization contribute to the continuous component. These effects must be taken into account for a correct comparison of the theoretical and experimental data. Figure 19 shows the experimental data on the emission yield in Pb-Pb collisions for 4.2 MeV/nucleon[212,213] and the theoretical curves[214] with account taken of the contribution of nuclear-nuclear bremsstrahlung. The
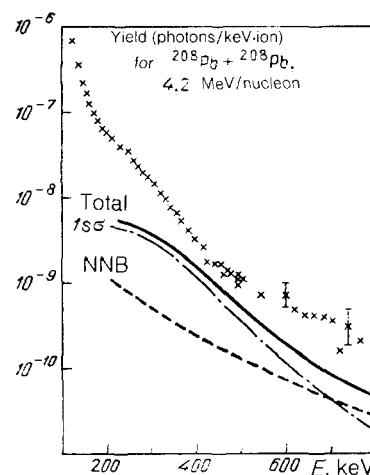

FIG. 18. Emission spectrum for Ni-Ni collisions at energy 70 MeV.[153]

FIG. 19. Emission yield of ^{208}Pb–^{208}Pb collisions for 4.2 MeV/nucleon. Symbols—experiment,[212] lines—theory,[214] including excitation of the $1s\sigma$ orbital and nuclear-nuclear bremsstrahlung (NNB).
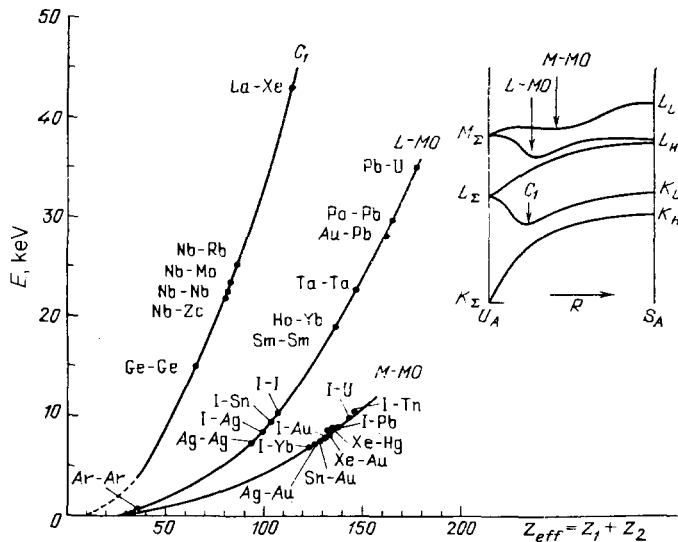
FIG. 20. Energy of characteristic structures in the quasimolecular emission spectrum as a function of the total charge of the nuclei Z_{eff}.[153]

influence of this effect increases with increasing quantum energy.

As was pointed out in the discussion of Eq. (6.2), the weak dependence of the transition energy E on R leads to the existence of a peak-shaped structure in the spectrum. Examination of the correlation diagrams shows that such a situation can occur in the region of small R. If the radius of the electron shell n in the united atom $r_n \gtrsim 2R$, then for the electrons of this and the subsequent shells in the quasimolecule the quasiatomic approximation is applicable, i.e., these shells are considered in the united atom having the charge $Z = Z_1 + Z_2$. The conditions for formation of quasiatoms impose restrictions on the velocity v of collision[153]:

$$0.02 \lesssim \frac{v}{v_n} \lesssim 0.16, \qquad (6.3)$$

Here v_n is the orbital velocity in the nth shell of the united atom. The quasiatomic emission yields information on the levels of superheavy atoms, including those not existing in nature. Figure 20 (from Ref. 153) shows the energies of the characteristic structures in the quasimolecular emission as a function of the total charge Z_{eff} of the colliding atoms. The existing data are classified into groups corresponding to transition to a defined shell. This indicates that the features in the spectrum involve the dependence of the energy of a given shell, common for all Z, on R. The most explicit quasiatomic spectra are characteristic of transitions to the M shell.[201,208,215,216] For quasiatomic emission, the collision time $\tau_{\text{coll}} \sim r_n/v$ is large near the threshold. Therefore the quasiatomic peaks in the spectrum increase with decreasing energy of collision.[217]

The strong dependence of the energy of the $1s\sigma$ level $E_{1s\sigma}$ on R and the effect of collisional broadening do not allow one to extract data on it from the spectra. However, a possibility exists of determining $E_{1s\sigma}(R)$ from data on the probability of exciting the $1s\sigma$ level in collision with a fixed impact parameter.[200]

6.3. **Anisotropy of emission.** In Refs. 218–221 an angular anisotropy of quasimolecular emission was found. Figure 21 (Ref. 153) shows data on the angular dependence of the emission intensity. The intensity maximum corresponds to a direction perpendicular to the axis of the ion beam. For all

angles the maximum anisotropy lies near the energy of a transition in the united atom.[218] This makes it possible to extract data on the levels of superheavy atoms from measurements of the anisotropy of emission of the different shells of the quasimolecule.[214,222–224]

A large number of studies[223–231] are devoted to the theory of the angular dependence of the emission. It was assumed in Refs. 223–225 that the anisotropy involves induced radiative transitions[201] that arise from rotation of the internuclear axis during the collision. The authors of Refs. 226–231 consider the strong Coriolis interaction between the σ and π orbitals that causes a differing population of the electron subshells that contribute to the radiative collisions. Both mechanisms agree with the experimental data,[153] but it is not yet clear which of them to favor.

6.4. **Collisional broadening.** As was pointed out above, Eq. (6.2) predicts a steep decline of the spectrum for $E > E(R_0)$. However, in experiments one observes a "tail" of the distribution that declines exponentially with increasing E. It has been called collisional broadening. The appearance of photons with an energy larger than the classically allowed value involves the fact that the emission occurs in the process of collision. Owing to the Heisenberg uncertainty principle, the emission energy depends on the velocity of collision. The effect of collisional broadening makes it impossible to extract data on the energies of the $1s$ level of the united atom with $Z = Z_1 + Z_2$ from the spectra.[153] The collisional broadening is commonly characterized by the half-width of
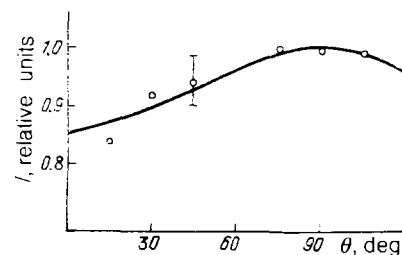

FIG. 21. Angular dependence of the quasimolecular emission intensity for the M shell in I-Au collisions at 11-MeV energy.[153] The curve is described by the formula $I(\theta) = 0.85 + 0.15 \sin^2\theta$.[153]

267   Sov. Phys. Usp. 32 (3), March 1989

B. G. Krakov and É. S. Parilis   267

the high-energy part of the emission distribution H. If the spectrum in the forbidden region is represented in the form[232,233]

$$\frac{d\sigma}{dE} \sim Ee^{-E/2\Gamma},\qquad(6.4)$$

then H has the form

$$H = (2\ln 2)\,\Gamma.\qquad(6.5)$$

It is of great interest to study the dependence of H on the velocity of collision v. The obtained results are described by the general formula

$$H \sim v^{a}.\qquad(6.6)$$

The value of a differs in different studies: $a = 1/2$,[203] 1,[232] $2/3$,[234] and 0.59 ± 0.03.[233] This result was obtained by analyzing the experimental data. In Ref. 199 $a = 0.66$ was obtained with a different processing method, which agrees with Ref. 234.

7. Conclusion. The brief review presented above of development of the views on quasimolecules and quasimolecular processes, and their applications in different problems shows that this new, rapidly developing field in atomic physics is very fruitful.

The quasimolecular treatment has proved not only useful, but is the only possible one in the vigorously expanding field of studies of the interaction of multiply charged ions with matter. It is very necessary in radiation physics, hotatom chemistry, and radiation biophysics, where the interaction of slow, multiply charged recoil atoms with atoms and molecules is decisive.

Quasimolecular effects are manifested in the passage of ions through a solid and along its surface, in channeling phenomena, ion implantation, sputtering of solids and their breakdown by heavy ions and nuclear-fission fragments, in beam-foil spectroscopy, and in ion Auger spectroscopy.

We stand at the threshold of studying phenomena caused by slow, highly charged ions—nuclei have been obtained of krypton, xenon, and even uranium fully stripped of electrons, and with energies not exceeding 100 eV per unit charge. The as-yet unstudied interaction of such ions with atoms of matter must be substantially quasimolecular.

On the agenda are the study of multielectron quasimolecular effects and multiparticle quasimolecular fractional Auger transitions, multiatomic quasimolecules, the study of the properties of transuranium atoms by formation of superheavy quasimolecules, and the study of processes in the electron shells of nuclei undergoing fission.

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269   Sov. Phys. Usp. 32 (3), March 1989

B. G. Krakov and É. S. Parilis   269

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