# *IONIZATION IN ATOMIC COLLISIONS*

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Ionization processes in atomic and ionic collisions are considered. The collision of two helium atoms is investigated. It is shown that for helium atoms whose electron configuration at large internuclear distances corresponds to two atoms in the ground state, the configuration for sufficiently small distances between the atoms corresponds to an auto-ionization state of the quasimolecule. The internuclear distance at which the electronic term of the quasimolecule $He_2$ composed of atoms in the ground state pseudo-crosses the nearest electron term, is estimated, as well as the separation of the terms at the pseudocrossing point. The degree of excitation of the electron shell of the colliding atoms, which occurs irreversibly as a result of the motion of the nuclei at the instant of overlap of the electron shells of the atoms, is estimated. These estimates lead to the conclusion that in the case when two helium atoms in the ground state collide, the ionization occurs when the atoms move apart, since transitions occur to the state of the $He_2$ quasimolecule. In the case of infinite distance between nuclei, the transitions correspond to two atoms in the excited state and therefore become auto-ionization transitions when the atoms are moved sufficiently far apart. The decay of these auto-ionization states causes the release of the electrons. The spectrum of the electrons released in the case of single and multiple ionization is explained on the basis of the auto-ionization mechanism of ionization of colliding atoms.

1. A number of recent experiments make it possible to study different aspects of the ionization produced when atomic particles collide at velocities lower than the velocities of the valence electrons. Such experiments include measurement of the inelastic energy loss in collisions of atoms[1-10], the determination of the spectra of the electrons released upon ionization,[11-19] the determination of the ionization cross sections for a given colliding-particle scattering angle,[20] and measurement of the partial cross sections of multiple ionization in collisions of atomic particles.[21]

The information obtained from these experiments makes it possible to describe certain details of the mechanism of atom ionization by collision.

As to the theory, there exists at present two models for the description of the ionization of colliding atoms. In the first, the classical Firsov model,[22] it is assumed that the excitation of the atomic electrons is effected continuously by inelastic transfer of energy from the moving nuclei. Such an approach is valid so long as the distances between the nuclei are not too large.[23] In the second model[24, 25] it is assumed that the electronic term of the considered state of the quasimolecule, made up of the colliding atoms, crosses the boundary of the continuous spectrum at a certain distance between the nuclei. The resultant autoionization state of the quasimolecule decays, and this leads to a release of the electrons. The inelastic transitions between the states of the quasimolecule do not play an important role. Such a model is known to be applicable to the case of collision between an atom and an ion of the same element.[24] The electronic term corresponding to the odd state of the quasimolecule made up of these particles crosses the boundary of the continuous spectrum.

We must ascertain which of the foregoing models[1)] describing the ionization mechanism is the more acceptable. This is one of the questions considered in the present paper. In addition, we clarify a number of details of the ionization of the colliding atomic particles. Most results were obtained here for the case of collision of two helium atoms, since the mathematical treatment employed in this case is the simplest. We can see, however, that many of the qualitative conclusions obtained in this manner are general.

2. If we assume that the electronic term of a quasimolecule made up of two atoms in the ground state does not cross other terms, then we find, in accordance with the Massey criterion, that the ionization has an adiabatically low probability when the collision between these atoms is slow. However, numerous experimental data on the ionization cross sections of atoms[30] offer evidence that at not too low collision velocities the ionization cross section turns out to be of atomic order of magnitude. Moreover, in many cases it was observed[31] that the ionization cross section of atoms, even near the ionization threshold, depends on the atom collision velocity not in accordance with a power law, but exponentially. We can therefore conclude that in most cases when the atoms come close together, the quasimolecule term corresponding to the ground state of the atom crosses other electron terms, and possibly crosses the boundary of the continuous spectrum. We shall show that in the case of two helium atoms the electron term of the quasimolecule corresponding to the ground state of the atoms crosses the boundary of the continuous spectrum.

Let us investigate the behavior of the terms of a quasimolecule made up of two helium atoms when these atoms come close together. If the two atoms are in the ground state, then a quasimolecule with an electron shell of $He_2(1\sigma_g^2\, 1\sigma_u^2)$ is produced when the atoms come close together. The lowest state of the beryllium atom which has such a symmetry and is produced when the helium atoms combine is the electron-shell state of

[1)]We do not stop to discuss here the phenomenological approach [26–29], which has no clear physical basis, so that it is hardly reasonable to use it in the study of details of the ionization process.

$Be(1s^2 2p^2)^1S$. Thus, the ground state of the two helium atoms goes over into the excited state of beryllium, if we neglect the small splitting between the two pseudocrossing terms and regard this splitting as a crossing. We shall show that the indicated state of the beryllium is an auto-ionization state. The energy of excitation of one of the electrons in the beryllium atom with transition from the ground state $(1s^2 2s^2)$ into the state $(1s^2 2s2p)$ is 5.3 eV. The excitation energy of the 2s electron in the 2p state should be larger, since this electron is situated in a field of the charge of the atomic core, which is not screened by another electron, and is therefore more strongly coupled than the electron in the first case. The energy necessary to excite the beryllium atom to the state $(1s^2 2p^2)$ is therefore, at any rate, not smaller than 10.6 eV, which exceeds the ionization energy of the beryllium atom, 9.32 eV.

Another approach makes it possible to estimate more accurately the excitation energy of the $Be(1s^2 2p^2)^1S$ state. Since the 2p electrons are located far from the atomic core and their penetration into the $1s^2$ shell can be neglected, the binding energy of these electrons coincides with the binding energy of the electrons in the He atom with similar shell $(2p^2)^1S$, which is equal to[32] 16.12 eV. This corresponds to the excitation energy of the $(1s^2 2p^2)^1S$ state, which is equal to 11.4 eV. Thus, both estimates show that the term of the electronic state, which corresponds in the case of a large distance between nuclei to two atoms in the ground state, crosses the boundary of the continuous spectrum when the atoms come closer together.

Let us trace the behavior of the term of the helium quasimolecule produced when the atoms come close together, when one electron in each of the atoms is in the 1s state, and the second electron of one of the atoms is in the 2s state. Let us consider an even state of the quasimolecule, in which the wave function of the electrons does not reverse sign upon reflection of the electrons relative to the symmetry plane; this plane is perpendicular to the line joining the nuclei and bisects it. In this state of the quasimolecule, three electrons, two of which correspond to the helium atom in the ground state and the third to 2s electron in the second helium atom, form the configuration $1\sigma_g^2 2\sigma_g$. This electron configuration corresponds to the electron shell of the beryllium ion in the ground state, which is obtained when the helium nuclei are combined. Thus, if the fourth electron is placed in the excited helium atom in any state, then combining the nuclei results in an excited beryllium atom with an unexcited atomic core. This means that when the helium atoms come closer together the term corresponding to the ground state of the two helium atoms crosses a large number of terms corresponding, in the case of large distances between the nuclei, to both atoms being in the excited state. In particular, the ground state of beryllium is produced by combining the nuclei of helium atoms which are in the metastable $(1s2s)^1S$ or $(1s2s)^3S$ state.

Thus, we have found that when the helium atoms come close together the term of the quasimolecule corresponding to helium atoms in the ground state crosses the boundary of the continuous spectrum[2)] and the large number of terms situated near the boundary and corresponding, in the case of large distances between the nuclei, to one atom in the ground state and one atom in the auto-ionization state.

3. Let us estimate the distance $r_0$ between two helium atoms, at which the electron terms of the state $^1S(1\sigma_g^2 1\sigma_u^2)$ and $^1S(1\sigma_g^2 2\sigma_g^2)$ cross. If the distance of closest approach of the colliding helium atoms is smaller than $r_0$, then the atoms can become ionized as a result of such a collision, since the electron shell is excited continuously, starting with internuclear distances close to $r_0$. To estimate $r_0$ we shall assume that this distance is smaller than the dimension of the electron orbit of the valence electrons. The Hamiltonian of the system of electrons has, in the case of small distances between the helium nuclei, the form

$$\hat{H} = \hat{H}_0 + \sum_i \left( \frac{2Z}{r_i} - \frac{Z}{|\mathbf{r}_i - \mathbf{R}/2|} - \frac{Z}{|\mathbf{r}_i + \mathbf{R}/2|} \right). \qquad (1)$$

here $\hat{H}_0$ is the Hamiltonian of the system of electrons in the case when the nuclei are joined together, $Z = 2$ is the charge of the nuclei, $\mathbf{r}_i$ is the coordinate of the electron, and $\mathbf{R}$ is the distance between nuclei. Unless specially stipulated, we shall use a system of atomic units $\hbar = m = e^2 = 1$. When $R \to 0$ we get, accurate to the first terms of the expansion in $R$

$$\hat{H}(R) = \hat{H}_0 + \sum_i \left( \frac{2Z}{r_i} - \frac{4Z}{R} \right), \quad r_i < \frac{R}{2}. \qquad (2)$$

The difference between the terms of the states under consideration is determined by the valence electrons, since the internal electrons influence in the same manner the course of the terms of the states under consideration. For this reason, the dimension of the orbit of the internal electrons can be arbitrarily related to the distance between the nuclei. Using the single-electron approximation, we obtain for the term shift due to the change in the interaction of the i-th electron with the atomic cores:

$$V_i(R) = \int_0^{R/2} \left( \frac{2Z_a}{r_i} - \frac{4Z_a}{R} \right) |\psi_i(r_i)|^2 r_i^2 dr_i = \frac{Z_a}{12} R^2 |\psi_i^2(0)|.$$

Here $\psi_i$ is the radial wave function of the i-th valence electron and $Z_a = 1$ is the charge of the atomic core.

Recognizing that the radial wave function of the 2p electron located near the nucleus equals zero, we obtain for the difference of the electron terms of the considered states of the quasimolecule made up of the two helium atoms

$$E_1(R) - E_2(R) = \frac{Z_a}{6} R^2 |\psi_{2s}(0)|^2 = \frac{Z_a Z_{ef}^3}{12} R^2. \qquad (3)$$

Here $Z_{eff}$ is the effective charge of the atomic cores and determines the behavior of the wave function of the electron near these cores. We assume $Z_{eff} = 27/16$, and

[2)] It is even easier to prove that a term of a quasimolecule can cross the boundary of the continuous spectrum in the case when an ion comes close to its own atom [24]. When an ion comes close to its own atom in the ground state, the energy level splits into two, odd and even. The term corresponding to the odd state, at which repulsion of the atoms takes place, crosses the boundary of the continuous spectrum. But in this case the possiblity of crossing is connected with the degeneracy of the energy at large distances between the nuclei. On the other hand, in the case of two helium atoms considered here, the crossing of the term of the quasimolecule with the boundary of the continuous spectrum is due to the overlap of the electron shells of the atoms, something which takes place in the general case.

choose for the excitation energy of the $(1s^2 2p^2)^1S$ state of the beryllium atom the previously obtained value 11.4 eV. We then obtain for the internuclear distance at which the quasimolecule electron terms under consideration cross the value $r_0 \approx 1$. This result can be used as an estimate, since at such distances the second term on the expansion of the term difference

$$E_1(R) - E_2(R) = \frac{Z_a R^2}{6} |\psi_{2s}(0)|^2 + \frac{Z_a R^3}{24} \frac{d}{dr} |\psi_{2s}(r)|^2 \Big|_{r=0} \tag{4}$$

is larger than the first. Since the second term of the expansion of the term difference differs in sign from the first term, we can expect the true value of $r_0$ to exceed the obtained estimate.

The obtained estimate agrees with the result of Leonas,[20] according to which the ionization in the collision of two helium atoms occurs at closest-approach distances smaller than unity.

4. In fact, when two terms of like symmetry approach each other, a pseudocrossing takes place, and not a crossing of these terms. When collisions of atoms are considered, these terms can be regarded as crossing if the separation of the terms in the pseudocrossing region turns out to be small at the collision velocity under consideration. For this reason it is of interest to determine the separation of the pseudocrossing terms.

Let us estimate the separation of the terms between the states $(1\sigma_g^2 1\sigma_u^2)^1S$ and $(1\sigma_g^2 2\sigma_g^2)^1S$ of a quasimolecule made up of two helium atoms. We assume that the pseudocrossing of these terms occurs at small distances between the nuclei compared with the dimension of the orbit of the valence electron. In both states under consideration, the internal shell $1\sigma_g^2$ is the same, so that the pseudocrossing is determined by the valence electrons and its magnitude can be represented in the form $\Delta = 2\langle 2p, 2p | r_{12}^{-1} | 2s, 2s \rangle$, where $r_{12}$ is the distance between the valence electrons, and 2p and 2s correspond to the states of these electrons in the beryllium atom. The term separation turns out to be $\Delta = 0.057 = 1.5$ eV. When the nuclei approach each other with a velocity v, the configuration of the electron shell can change in the vicinity of the crossing point, and in the case of a single passage through the pseudocrossing point this probability is equal to[33] $\pi\Delta^2/2Fv$, where $F = dE/dR|_{r_0}$ is the derivative of the difference of the unperturbed terms at the pseudocrossing point.

If we use formula (3) for the difference of the terms of the states under consideration, we get $F \approx 0.8 r_0 \approx 0.8$. Therefore, in a single passage through the pseudocrossing point in the case of a collision of two helium atoms the transition probability is $0.4 v_i/v$, where $v_i = \sqrt{2I/M}$ is the collision velocity at the ionization threshold, and M and I are the mass of the nucleus and the ionization potential of the helium atom.

We thus found that the separation of the electron terms is not much smaller than the energy difference between the electron states in the atom. Nonetheless, the probability of a transition with a change of the electron configuration of the quasimolecule is small, owing to the peculiarities of the transition in the Landau–Zener case. Inasmuch as the separation of the terms is not small, multiple pseudocrossing of the terms is also possible, so that the eigenstate of the quasimolecule turns out to be a combination of several configurations of electron shells. In this case the picture becomes more complicated and our conclusion that the change of the electron configuration has a low probability no longer holds.

5. Let us assess the role played in the ionization process by the excitation of the electron shell, corresponding to transfer of energy from moving nuclei to electrons. Such a process proceeds continuously at small distances between the nuclei, when the terms of the quasimolecule have come sufficiently close together. This method of excitation corresponds to the first of the models considered for the description of the ionization of the colliding atoms. We shall estimate the energy interval for the quasimolecule states between which nonadiabatic transitions take place, and also the electron-shell excitation energy corresponding to the mechanism under consideration.

Let us determine the quantity $\Delta E^2 = \langle \hat{H}^2 \rangle - \langle \hat{H} \rangle^2$, when the uncertainty of the energy of the quasimolecule state corresponds to motion of the nuclei. This quantity is equal to[23]

$$\Delta E^2 = \sum_i (\mathbf{v}_1 - \mathbf{v}_i)^2 \left\langle \frac{p_i^2}{2} \right\rangle + \sum_k (\mathbf{v}_2 - \mathbf{v}_k)^2 \left\langle \frac{p_k^2}{2} \right\rangle, \tag{5}$$

where $\mathbf{v}_i$ and $\mathbf{v}_k$ are the average velocity of the given electron, the k electrons being connected essentially with the first nucleus, and the i electrons with the second. In the case of helium in the region where the terms of the quasimolecule cross, the distance between nuclei is smaller than the dimension of the orbit of the valence electrons, so that $\mathbf{v}_{i,k} = 0$ and $\mathbf{v}_1 = -\mathbf{v}_2 = \mathbf{v}/2$, where $\mathbf{v} = \mathbf{v}_1 - \mathbf{v}_2$ is the relative velocity of the nuclear collision. We obtain

$$\Delta E^2 = \frac{v^2}{2} \sum_i \left\langle \frac{p_i^2}{2} \right\rangle \approx v^2 \varepsilon_b, \tag{6}$$

where $\varepsilon_b$ is the binding energy of the valence electrons. The quantity $\Delta E$ characterizes the region of the quasimolecule states between which transitions occur effectively. Namely, in the case of helium this energy interval for states between which non-adiabatic transitions take place amounts to

$$\omega \sim \sqrt{\overline{\Delta E^2}} = v\sqrt{\varepsilon_b} \tag{7}$$

and can be quite broad.

Let us estimate the energy going over into excitation of the valence electrons as a result of the motion of the nuclei. We shall use here the classical theory of excitation of atoms,[22] assuming the valence electrons to be classical. Then the change in the energy of the valence electrons when the distances between the nuclei are smaller than the orbits of the valence electrons is

$$\frac{dE}{dt} = v^2 \sum_i \int \frac{v_i}{4} dS,$$

where i is the number of the valence electron and the surface S is perpendicular to the axis joining the nuclei and bisects it. In the case of collision of like atoms we get

$$dE/dt \approx v^2 N \bar{v}_v / 4\bar{r}_v, \quad E_{exc} \sim N v \bar{v}_v, \tag{8}$$

where N is the number of valence electrons, $\bar{v}_v$ is the average velocity of the valence electrons, $\bar{r}_v$ is the dimension of their orbit, and $E_{exc}$ is the inelastic energy transferred during the entire collision act (the time during which energy is transferred to the electrons is $\sim \bar{r}_v/v$). The inelastic energy transfer $E_{exc}$ is proportional to the velocity of the nuclei and contains, in addition, a small numerical coefficient which we could not obtain by means of our estimating method. Therefore in the case of a small number of valence electrons the excitation of the quasimolecule due to the motion of the nuclei plays a minor role. Such a situation takes place in the case of collision of two helium atoms.

In the case of collision of heavy atoms, the inelastic transfer of energy from the nuclei to the electrons can play a certain role, since the electron shells contain many electrons. Even in this case, however, the ionization mechanism is determined by the behavior of the electronic terms of the molecule if the atom collision velocity is small compared with the characteristic atomic velocities.

6. We have thus found that the electronic term of a quasimolecule made up of two atoms in the ground state crosses other electronic terms and possibly the boundary of the continuous spectrum. This occurs at internuclear distances at which the electron shells of the atoms overlap. Transitions between the quasimolecule electronic states with close energies occur freely when atoms collide in this region of distances. When the nuclei come closer together, or, to the contrary, when they move apart, some of these electronic states of the quasimolecule become auto-ionization states. It is the decay of these auto-ionization states which leads to the ionization of the quasimolecule.

Let us examine the proposed point of view, using as an example the collision between two helium atoms. It was shown that the electron configuration of a quasimolecule made up of helium atoms, which corresponded in the case of large distances between the nuclei to two atoms in the ground state, corresponds in the case of small distances between nuclei to the auto-ionization state. Therefore one of the reaction channels leading to the ionization of the atoms, can be connected with the decay of the auto-ionization state of the quasimolecule at small distances between the nuclei. In our opinion, the more probable reaction channel is the one corresponding at large distances between nuclei to decay of the auto-ionization state. Assume that the helium atoms have come sufficiently close together during the collision. The configuration of the electron shell of the beryllium atom produced when the nuclei combine, corresponding at large distances between the nuclei to two helium atoms in the ground state, is of the form $Be(1s^2 2p^2)^1S$. In the collision process, transitions to other states of the quasimolecule are possible, and the most probable of them correspond to a change of the angular momentum or of the projection of the angular momentum of the electron with conservation of the principal quantum number. Therefore the motion of the nuclei leads, in the case of small distances between the nuclei, to the formation of one of the configurations of the electron shell, $(1s^2 2s^2)^1S$, $(1s^2 2s2p)^1P$, or $(1s^2 2p^2)^1S$, $^1D$. The table shows a comparison of the terms of the quasimolecule at large and small distances R between the nuclei, corresponding to the given electron configuration in the case when the nuclei are combined. The

Comparison of electronic terms of a quasimolecule made up of two helium atoms, at small and large distances between nuclei

| $R \to 0$ | $R \to \infty$ |
|---|---|
| Be $(1s^2\ 2s^2)$ | 2He $(2^1S)$; 2He $(2^3S)$ |
| Be $(1s^2\ 2p^2)$ | 2He $(1^1S)$; 2He $(2^1P)$; 2He $(2^3P)$ |
| Be $(1s^2\ 2s\ 2p)$ | He $(2^1S)$ + He $(1^1S)$; He $(2^1S)$ + He $(2^1P)$; He $(2^3S)$ + He $(2^3P)$ |

spin of the electron shell is in this case equal to zero.

As seen from the table, at large distances between the nuclei most transitions in the quasimolecule lead to the formation of two excited atoms. The corresponding state of the quasimolecule becomes an auto-ionization state when the distances between nuclei exceed a certain value. The decay of auto-ionization states of this kind during the atom-collision process leads to the ionization of the atoms.

There is a serious objection to the auto-ionization mechanism of ionization of the colliding atoms. The lifetimes of the auto-ionization states of the atoms is quite large. For example, the width of the level of the auto-ionization state $(2s^2)^1S$ of helium is 0.2 eV,[32, 34] that of the $(2s2p)^1P$ level is 0.04 eV,[34] and for other states this width is even smaller. If the width of the auto-ionization states of the quasimolecule is just as small, then these states do not have time to decay during the time of the collision of the atoms, and their formation does not influence the ionization process. The small width of the auto-ionization levels of the atoms is apparently connected with the spherical symmetry of the system, which leads to a weak correlation between the electrons. In the case of a quasimolecule this symmetry disappears, so that we can expect a large width of the auto-ionization state of the quasimolecule if the distance between its nuclei is of the order of atomic dimensions.

This can be shown by using data on the ionization of slow atoms, such that the excitation energy of one of them exceeds the ionization potential of the other. In this case, the state of the quasimolecule is auto-ionization from the very beginning, but the width of the level decreases rapidly with increasing distance between nuclei. Thus, the cross section of the process $2He(2\,^3S) \to He^+ \to He(1\,^1S)$ amounts to $10^{-14}$ cm$^2$ at thermal collision energies.[35] This process corresponds to transfer of one of the valence electrons from one atomic core to the other, and to the release of the second valence electron. For this reason, the width of the auto-ionization state $2He(2\,^3S)$ decreases exponentially as large distances between the nuclei, and so large a value of the cross section of the process is evidence that the width of the level of the auto-ionization state of the quasimolecule is of atomic order of magnitude in the region of atomic distances between nuclei. The same conclusion can be drawn also for the case of a quasimolecule made up of an atom in a resonantly excited state and an atom with a small ionization potential.[36, 37] If we extrapolate the width of the auto-ionization level of the quasimolecule, obtained for large distances between nuclei, to the region of atomic distances, we find that at these distances the width of the auto-ionization level is of atomic order of magnitude.

7. Starting from the auto-ionization mechanism of ionization of colliding atoms, let us determine the spectrum of the electrons released thereby. To determine the spectrum of the ionization electrons it is necessary to find the dependence of the line width of the auto-ionization on the energy $\varepsilon_a$ by which the energy level of the auto-ionization state exceeds the boundary of the continuous spectrum. Let us determine this dependence in the case when the energy of the released electrons is small. The width of the level of the auto-ionization state is

$$\Gamma = 2\pi \int |\langle \Psi | V | \psi_+ \psi_q \rangle|^2 \delta\left(\varepsilon_a - \frac{q^2}{2}\right) dq, \quad (9)$$

where $\Psi$ is the exact function of the quasimolecule, $\psi_+$ and $\psi_q$ are the wave functions of the ion and free electron, $q$ is the momentum of the released electron, and $V$ is the interaction that leads to the decay of the auto-ionization state. Since $\psi_q$ is normalized to $\delta(q - q')$, we have $\psi_q \sim 1/\sqrt{q}$ for small values of q. In addition, the wave function $\Psi$ does not depend on q at small values of q. It follows therefore that at small values of the released-electron energy the width of the auto-ionization level $\Gamma$ does not depend on the energy $\varepsilon_a$ of the released electron.[3)] If n electrons are produced in the decay of the auto-ionization state, then the width of the auto-ionization level relative to such a decay is

$$\Gamma = 2\pi \int \left| \left\langle \Psi | V | \psi_{n+} \prod_{i=1}^{n} \psi_{q_i} \right\rangle \right|^2 \delta\left(\varepsilon_a - \sum_{i=1}^{n} \frac{q_i^2}{2}\right) \prod_{i=1}^{n} dq_i \sim \varepsilon_a^{n-1},$$

where $\varepsilon_a$ is the sum of kinetic energies of the emitted electrons.

The decay probability $1 - w$ of the auto-ionization state of the quasimolecule, with emission of an electron satisfies at a given instant of time t the equation

$$dw / dt = -\Gamma w. \quad (10)$$

In the case when one electron is released, $\Gamma$ does not depend on the energy of the released electron, so that $w = e^{-\Gamma t}$, where the time t is reckoned from the instant when the auto-ionization level of the quasimolecule is reached. Since $t = \varepsilon/(d\varepsilon/dR)|_{r_0} |v_R$, we have

$$\frac{dP}{d\varepsilon} d\varepsilon = \left| \frac{dw}{dt} \right| dt = \frac{a}{v_R} \exp\left[-\frac{a\varepsilon}{v_R}\right], \quad (11)$$

where $a = \Gamma \left.\frac{d\varepsilon}{dR}\right|_{r_0}$, $P(\varepsilon)$ is the relative probability of emission of an electron with energy $\varepsilon$, $\varepsilon$ is the energy of the released electron, and the radial component of the relative velocity $v_R$ of the atom collision and the derivative $d\varepsilon/dR$ of the term difference between the auto-ionization state and the boundary of the continuous spectrum are taken at the point where the term under consideration crosses the boundary of the continuous spectrum. The resultant spectrum of the electrons, in the case of single ionization (11), coincides with the result of Demkov, and Komarov,[25] obtained by a more complicated method using several model assumptions.

Let us consider the case of n-fold ionization of a quasimolecule. The probability of decay of the auto-ionization state with release of n electrons, $1 - w_n$, is given in lieu of (10) by the equation

$$dw_n/dt = -\Gamma_n w_1,$$

since $w_1 \gg w_n$. Hence

$$\frac{dP_n}{d\varepsilon} d\varepsilon \sim \varepsilon^{n-1} e^{-a\varepsilon/v_R} d\varepsilon. \quad (12)$$

Let us estimate the relative probability of the release of n electrons compared with single ionization for a given impact parameter of the atom collision. For the probability of single ionization we have

$$\int_0^T e^{-\Gamma t} dt \sim \frac{1}{\Gamma}(1 - e^{-aE/v_R}),$$

where E is the maximum value of the energy of the auto-ionization state, which can be attained at the collision impact parameter under consideration. The total probability of n-fold ionization of the quasimolecule is determined by the solution of (12) and is equal to

$$w_n = \int_0^T \Gamma_n w_1 dt \sim \int_0^E \frac{\varepsilon^{n-1}}{v_R} d\varepsilon \exp\left(-\frac{a\varepsilon}{v_R}\right).$$

It follows therefore that the relative probability of n-fold ionization at a given collision parameter increases with increasing particle collision velocity $v_R$ to atomic velocities, and ceases to depend on the velocity starting with atomic velocities. This conclusion can be extended also to the ratio of the cross sections of n-fold and single ionizations. It must be taken into account here that when the collision velocity is increased, an increasing role is assumed by single ionization in collisions at which the quasimolecule level under consideration has not yet reached the limit of the continuous spectrum. For this reason, the ratio of the cross section of the n-fold ionization of the quasimolecule to the cross section of single ionization will decrease at large velocities. Thus, the ratio of these cross sections as a function of the collision velocity has a maximum at collision velocities on the order of atomic velocities. This fact, which seems strange at first glance, was experimentally established by Afrosimov et al.[21] This result was obtained by us on the basis of formula (10), which was assumed to be valid at all collision velocities. At low collision velocities this formula corresponds to the auto-ionization mechanism of quasimolecule decay, and at large velocities it corresponds to the Born approximation in the description of inelastic transitions. This confirms the correctness of the result.

8. The considerations presented in this paper allow us to advance the following point of view with respect to the ionization mechanism in atomic collisions. When atoms collide at interatomic distances corresponding to the overlap of the electron shells, transitions are possible between quasimolecule electronic configurations of nearly equal energy. This leads in final analysis to the formation of a quasimolecule in the auto-ionization state, and the decay of the auto-ionization state corresponds to ionization of the atoms.

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[3)]It is necessary to have here $\Gamma \ll \mathcal{E}_a$, otherwise the level width becomes meaningless.

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