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Penning ionization by nonmetastable atoms

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Penning ionization by highly excited atoms is considered. The asymptotic two-center electron wave function is set up for an arbitrary ion+atom system. This function is needed for the solution of many atomic-collision-theory problems involving nonresonant transitions of the electron from one center to another. The results of the calculations are applied to the case of ionization of noble-gas atoms and hydrogen molecules by highly excited helium atoms. It is shown that the process proceeds mainly via the exchange channel. The conclusions of the theory are in good agreement with the experimental results.

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1. INTRODUCTION FORMULATION OF PROBLEM

In gas-discharge physics, besides the Penning ionization process^[1] (ionization by metastable atoms), great interest attaches also to ionization by more strongly excited atoms. In experiments with ionization chambers,^[2-5] for example, an increase of the ionization current due to one fast α particle was observed in gas mixtures in which ionization by metastable atoms is energywise impossible in one collision (He+Ne, Ar+Xe etc.). To produce a gas laser in a recombining plasma^[6] it is important to know the cross sections for the ionization of the impurity gas atoms by the excited helium atoms. Results of the direct measurements of the cross section for the ionization of Ne, Ar, Kr, Xe atoms by He ($3'P$, 3^3P , 3^3S , $3'S$) atoms at a collision energy

600 °K were recently reported.^[7]

We consider processes of the type



the excitation energy of the atom A^* being larger than the ionization potential J_X of the atom X. When such particles approach each other, an autoionization state is produced, the decay of which leads to reaction (1). The magnitude of the decay width and the potential energy of the interaction of the produced state depend strongly on the excitation number of the atom A^* , so that the cross sections of the reactions (1) can differ significantly in absolute magnitude and in the character of the dependence on the collision energy for the different excited

states of the atom A.

Getting ahead of ourselves, we can state that ionization by strongly excited atoms differs significantly from ionization by metastable atoms. The reason for the difference is the following: Owing to the rapid decrease of the decay width with increasing distance between atoms, the characteristic radius of the reaction (1) turns out to be much smaller than the dimension of the orbit of the strongly excited states, so that decay takes place deep inside the orbit of the excited electron. The ionized atom then interacts principally with the core of the ionizing atom, i. e., with the ion A^+ . This circumstance increases the decay probability for two reasons. First, the polarization attraction decreases the distance between the particles, making thereby the decay more effective. Second, owing to the attraction by the Coulomb field of the ions, the probability that the electrons of the atom X will stay near A^+ increases, thereby increasing the role of the exchange channel of the reaction.

The decay can proceed via two channels. In the first channel the excited electron of the atom A^* drops to the ground state of the atom A, and the electron of the atom X becomes ionized. The decay width corresponding to this channel is given by (we use the atomic system of units)

$$\gamma_{dd} = 2\pi \left| \left\langle \psi_{n_l}(r_1) \psi_X(r_2) \left| \frac{1}{r_{12}} \right| \psi_E(r_2) \psi_0(r_1) \right\rangle \right|^2 \quad (2)$$

and has been calculated in^[8-12] for the case when a dipole transition from the excited state ψ_{n_l} of the atom A to the ground state ψ_0 of the atom A is allowed (ψ_E is the wave function of the continuous spectrum and ψ_X is the wave function of the atom X). The ionization cross section, without allowance for the exchange channel, can then be expressed in terms of the photoionization cross section of the atom X, if the decay manages to occur at large interatomic distances. In the second, exchange, channel the electron of the atom X goes over to the ground state of the atom A, and the excited electron of the atom A^* is ionized. The decay width is in this case

$$\gamma_{\text{exch}} = 2\pi \sum_{l'} \left| \left\langle \psi_{n_l}(r_1) \psi_X(r_2) \left| \frac{1}{r_{12}} \right| \psi_0(r_2) \psi_{E l'}(r_1) \right\rangle \right|^2 \quad (3)$$

The matrix element (3), in contrast to (2), is determined by the region of the electron coordinates when the second electron is near the atom A, since ψ_0 is a more strongly bound state than ψ_X .

We investigate in this paper the decay of strongly excited atoms A^* via the exchange channel. In this case, as already noted, the decay takes place mainly within distances much smaller than the radius $1/J^*$ of the region in which the excited electron is distributed

$$R \ll 1/J^*, \quad (4)$$

where J^* is the ionization potential of the excited atom.

The matrix element (3) is determined by the region $r_1 \sim 1/J^*$, $r_2 \ll 1/J^*$, so that in the calculation of (3) we can use the expansion

$$\frac{1}{r_{12}} \approx \frac{1}{r_1} + \frac{r_1 r_2}{r_1^3} + \dots, \quad r_1 \gg r_2, \quad (5)$$

where r_1 and r_2 are the distances of the electrons from the nucleus of the atom A. Using this expansion, the orthogonality of the functions of the initial and final states, and (5) we obtain

$$\gamma_{\text{exch}} = 2\pi M_1^2 M_2^2, \quad M_1^2 = \sum_{l'} \left| \left\langle \psi_{n_l}(r_1) \left| \frac{r_1 r_2}{r_1^3} \right| \psi_{E l'}(r_1) \right\rangle \right|^2, \quad |k|=1, \quad (6)$$

$$M_2^2 = |\langle \psi_X(r_2) | r_2 | \psi_0(r_2) \rangle|^2.$$

The emitted electron interacts both with the ion X^+ and with the atom A. The field of the atom A can be neglected as being much weaker. The function ψ_{n_l} of the excited state of the atom A^* , if the condition

$$R_0/\lambda \ll 1 \quad (4a)$$

is satisfied, can be regarded as centered at X. More accurately speaking, when this condition is satisfied it does not matter at which of the centers the excitation is located. Here R_0 is the characteristic radius of the reaction (1) and λ is the wave length of the electron in the excited state, i. e., the dimension of the inhomogeneity of the function ψ_{n_l} . If (4) is satisfied, the distance r_1 in (5) can be regarded as measured from X. Then, using the Ehrenfest theorem operators, we reduce M_1^2 to the form

$$M_1^2 = \omega^4 \sum_{l'} \left| \langle \psi_{n_l}(r_1) | r_1 k | \psi_{E l'}(r_1) \rangle \right|^2, \quad (7)$$

$\omega = E_f - E_i - J_A - J_X$ at $R \gg 1$, and the summation is carried out here over all states to which a dipole transition is allowed.

The exchange decay channel, just as the direct channel,^[8-12] turns out to be connected with the characteristics of the photoionization process. The dipole matrix element (7) between hydrogen functions was tabulated in^[13]. The exchange decay channel is due to symmetrization of the total wave function of the system of two colliding atoms with respect to permutation of all the electrons. In the case of ionization of atoms with filled shells, we obtain formula (3) after integrating over the electrons that do not change their states. For the case considered by us, that of ionization by an excited helium atom, we have neglected here the other exchange amplitude: the electron of the atom X ends up at the ground state of the helium atom together with the exciting electron, and the core electron of the helium goes off to the continuous spectrum. The amplitude of this transition has an additional smallness in comparison with the transition taken into account in (3), since it describes a simultaneous transition of three electrons.

The asymptotic expansion which will be obtained below for the two-center wave function makes it possible to consider only those states of the electrons of the atom X which have a zero projection of the orbital angular momentum on the axis joining the nuclei. The contribution made to the decay probability by states with non-zero projection is small in comparison with the contribution of the electrons, and for its determination it is

necessary, strictly speaking, to evaluate the succeeding terms of the asymptotic expansion of the wave function. We neglect the contribution of the higher projections in this paper.

In the calculation of the matrix element M_2 we encounter an additional difficulty: it is necessary to know the wave function ψ_X of the electron of the atom X in the region far below the barrier—near the ion A^+ , where it is strongly perturbed by this ion. We therefore proceed now to the construction of this function.

2. TWO-CENTER SINGLE-ELECTRON WAVE FUNCTION FOR A COULOMB POTENTIAL WITH A CORE

A characteristic feature of the considered reaction (1) is the difference between the properties of the atoms A and X. In particular, the difference between the ionization potentials of these atoms is of the order of the ionization potentials themselves. Consequently, the electron of the atom X interacts with the ion A^+ under non-resonant conditions: the probability of observing it near A^+ is exponentially small at all distances R . The interaction with the excited electron can be neglected if the condition (5) is satisfied, so that the problem reduces to a solution of the single-electron Schrödinger equation

$$[-\Delta/2 + V_A(r_A) + V_X(r_X) - E]\psi_X = 0 \quad (8)$$

with the boundary condition

$$\psi_X \rightarrow \psi_X^{(0)}, \quad r_X \ll R. \quad (9)$$

where $\psi^{(0)}$ is the electron wave function of the isolated atom X; $r_{A,X}$ is the distance of the electron to the nuclei of the atom A and X, while $V_{A,X}$ are the interaction potentials of the electron with A^+ and X^+ . It is required to determine ψ near A^+ , i. e., at $r_A \sim 1$.

Using the Green's function for the field of the ion A^+ , we rewrite (8) in integral form:

$$\psi_X(r_X) = - \int G_A(E, r_A, r_A') V_X(r_X') \psi_X(r_X') d'r_X'. \quad (10)$$

The construction of this equation is such that our problem is solved already after the first iteration, if we substitute in the right-hand side the X-atom function that takes into account the influence of the Coulomb part of the potential V_A [14-16].

$$\psi_X = \left(\frac{R}{r_A}\right)^n a r_X^{n-1} \exp\left(-\frac{r_X}{n}\right) Y_{LM}(\theta_X, \varphi_X), \quad (11)$$

$$r_X \sim r_A \sim R, \quad E = -1/2n^2 = -1/2n_0^2 - 1/R.$$

The coefficient a is determined here by matching with the numerical wave functions of the atom X at $r_X \sim 1$ [16]; L and M are the quantum numbers of the electrons in the atom X.

Since G_A decreases exponentially with increasing distance from the point to the nucleus A, while ψ_X decreases exponentially (with practically the same exponent) with increasing distance from the nucleus X, the main contribution to the integral (10) is made by a

cylindrical region of length R and radius $\sim R^{1/2}$ near the internuclear axis. The regions near each of the nuclei where (11) does not hold make a contribution of the next order of smallness in R^{-1} to the integral of (10) in comparison with the main contribution. A similar situation takes place also in resonant single-electron exchange.

We consider the case when A^+ is a pure Coulomb center, i. e., $V_A = -1/r_A$. The analytic expression for the Green's function takes in this case the form [17]

$$G_A = \frac{\Gamma(1-n)n}{2\pi|r_A-r_A'|} \left(\frac{\partial}{\partial y} - \frac{\partial}{\partial x}\right) W_{n,1/2}\left(\frac{x}{n}\right) M_{n,1/2}\left(\frac{y}{n}\right), \quad (12)$$

$$x = r_A + r_A' + |r_A - r_A'|, \quad y = r_A + r_A' - |r_A - r_A'|.$$

Here W and M are Whittaker functions. [18]

In our case, when $r_A \sim 1$ and $r_A' \sim R$, we obtain

$$x \approx 2r_A' + r_A - \kappa r_A, \quad y = r_A + \kappa r_A. \quad (13)$$

Here κ is a unit vector in the direction from the atom A to X. Using the asymptotic behavior of $W(\xi)$ at large ξ and expressing M in terms of a confluent hypergeometric function, [18] we find that the Green's function (12) takes in the coordinate region of interest to use the form

$$G_A \approx \frac{\Gamma(1-n)}{2\pi n} 2^n \left(\frac{r_A}{n}\right)^{n-1} \exp\left(-\frac{r_A+r_A'}{n}\right) F\left(1-n; 1; \frac{r_A+\kappa r_A}{n}\right), \quad (14)$$

$$r_A' \sim R \gg r_A.$$

The integral in (10) is calculated, taking (11) and (14) into account, by first integrating over a plane perpendicular to the internuclear axis, and then integrating with respect to r_A' from 0 to R . After integration we obtain

$$\psi_X \approx D(R) \exp\left(-\frac{r_A}{n}\right) F\left(1-n; 1; \frac{r_A+\kappa r_A}{n}\right), \quad (15)$$

$$D(R) = a\Gamma(1-n) \left(\frac{2R}{ne}\right)^{n_0} R^{n-1} \exp\left(-\frac{R}{n_0}\right) Y_{LM}(0),$$

which agrees with the known result, [19,20] obtained by matching solutions that are valid in different coordinate regions. The use of an integral equation in place of a differential equation has greatly simplified the problem: the solution has reduced to evaluation of a trivial integral. The integral equation automatically matches the wave functions of the different regions.

The function (15) can be applied to the reaction (1) only in the case of ionization by an excited hydrogen atom. Of greater practical interest is ionization by excited helium atoms, etc., for which it is necessary to take the core into account. In this case we use the series representation of the Green's function [21]

$$G_A = - \frac{2}{r_A r_A'} \sum_{l,m} g_l(r_A, r_A') Y_{lm}(\theta, \varphi) Y_{lm}(\theta', \varphi'), \quad (16)$$

where the radial Green's functions are equal to

$$g_l = w^{-1} f_1(r_<) f_2(r_>), \quad r_{\geq} = \max\{r_A, r_A'\}, \quad (17)$$

$$w = [f_1 f_2' - f_1' f_2] |_{r_A = r_A'} = \text{const};$$

$$\left[-\frac{d^2}{dr_A^2} + 2V_A + \frac{l(l+1)}{r_A^2} + \frac{1}{r^2} \right] f_l = 0. \quad (17a)$$

Here f_1 is finite at zero, and f_2 at infinity is equal to $f_2 \sim r_A^n e^{-r/n}$. The eigenvalues of (17a) do not coincide with n^2 .

Substituting (16) in (10), we obtain

$$\psi_X(r_X) = \sum_{l=0}^{\infty} D_l(R) \frac{f_{li}(r_A)}{r_A} P_l^{(0)}(\theta_A, \varphi_A), \quad (18)$$

$$D_l(R) = a \left(\frac{2L+1}{4\pi} \right)^{1/2} \left(\frac{2L+1}{w} \right) R^{2n_0-1} e^{-R/n}. \quad (18a)$$

This expression for the wave function is practically the final answer, since the selection rules for the matrix element M_1 automatically select from the sum (18) only one or two terms, depending on the angular momentum of the ground state in the field $V_A(r_A)$.

The partial functions (18) are orthogonal to all the eigenfunctions in the field V_A that have a binding energy larger than J_X . For this reason, the constructed complete two-electron functions of the initial and final states are orthogonal to one another. For the levels in the well V_A lying above $-J_X$ the overlap integral with the function (18) is determined by the region near the X nucleus.

The result (18a) is valid, generally speaking, only for small angular momenta satisfying the condition $l^2 < R$ (in dimensionless atomic units!). Under this condition the centrifugal energy in (17a) is small, and we can use for the functions f_{2l} a Coulomb asymptotic form of the type (11).

The electron wave function constructed here is needed for many problems in the physics of atomic collisions. In addition to the problem considered here, this function is essential for the ionization processes considered in^[19], for two-electron charge exchange, etc. To make further progress, we shall specify below more concretely the type of the potential V_A , since it is impossible to connect in simple and reliable manner the matrix element M_2 with the characteristics of the isolated atom A.

3. CALCULATION OF THE DECAY WIDTH AND OF THE REACTION CROSS SECTION

We consider a model potential

$$V_A = -1/r_A + B/r_A^2, \quad (19)$$

in which the parameter B is chosen such that the ground level in this potential coincides with the observed binding energy of the atom A. The energy levels in this potential are known exactly, and the wave functions are expressed in terms of a confluent hypergeometric function.^[15] Calculation of the matrix elements with these functions and with the function (18) for the same potential reduces to a calculation of a tabulated integral. Omitting the simple manipulations, we present only the final result (for the final ground state without the angular momentum):

$$M_2(R) = CR^{2n_0-1} \exp\left(-\frac{R}{n_0}\right);$$

$$C = a(2L+1)^{1/2} \left(\frac{2}{n_0 e}\right)^{n_0} \frac{2^{2n_0} n_0^{2.5} (2n_0 v^{-1})^{s_0+1.5} \Gamma(s_0+1-n_0) \Gamma(s_0+s_1+4)}{(1+n_0 v^{-1})^{s_0+s_1+4} \Gamma(2s_0+2) \Gamma^2(2s_0+3)} \times {}_2F_1\left(s_0+1-n_0, s_0+s_1+4; 2s_0+2; \frac{2v}{v+n_0}\right); \quad (20)$$

$$s_0 = [(l+1/2)^2 + v(v-1)]^{1/2} - 1/2, \quad v = (2J_A)^{-1/2}.$$

It is assumed that the electron of the X atom has a zero projection of the angular momentum on the internuclear axis.

For the pure Coulomb case (ionization by an excited hydrogen atom), when $B=0$, Eq. (20) is transformed into

$$C(B=0) = 8a(2L+1)^{1/2} \left(\frac{2}{n_0 e}\right)^{n_0} \left(\frac{n_0}{n_0+1}\right)^5 \left(\frac{n_0-1}{n_0+1}\right)^{n_0-2} \Gamma(1-n_0). \quad (20a)$$

We write down the decay width in the form

$$\gamma_{\text{exch}}(R) = \gamma_0 R^{4n_0-2} \exp(-2R/n_0), \quad \gamma_0 = 2\pi M_1^2 C^2. \quad (21)$$

The constants that characterize the exchange width (21) are listed in Table I. The amplitudes a were determined by matching the asymptotic form (11) with the Hartree-Fock wave functions.^[22] These amplitudes are overestimated in^[16], since only one term of the asymptotic expansion (11) is taken into account; in our calcu-

TABLE I. Parameters characterizing the exchange width of the decay of the initial state, M_1^2 is averaged over the direction of the internuclear axis \times (all the quantities are given in atomic units, and in the case of Li averaging was carried out over the possible spin states).

	He	Ne	Ar	Kr	Xe	H ₂	Li	Mg
n_0	0.744	0.794	0.929	0.986	1.059	0.939	1.589	1.334
a	2.23±0.10	1.5±0.05	2.07±0.02	2.12±0.03	2.15±0.05	2.64	0.84±0.01	2.00±0.2
α_X	1.39	2.76	11.1	16.8	27.2	2.52	165	120
	C	171.0	18.6	11.8	7.41	12.3	0.450	1.431
He(3 ² S)	M_1^2	1.48·10 ⁻³	2.45·10 ⁻³	2.65·10 ⁻³	2.82·10 ⁻³	2.50·10 ⁻³	7.63·10 ⁻³	4.50·10 ⁻³
	γ_0	272.0	5.33	2.32	0.973	2.38	9.69·10 ⁻³	6.28·10 ⁻²
He(3 ¹ S)	M_1^2	1.18·10 ⁻³	2.26·10 ⁻³	2.48·10 ⁻³	2.67·10 ⁻³	2.30·10 ⁻³	7.58·10 ⁻³	4.47·10 ⁻³
	γ_0	217.0	4.91	2.17	0.921	2.19	9.63·10 ⁻³	6.24·10 ⁻²
He(3 ² P)	M_1^2	7.97·10 ⁻⁴	7.73·10 ⁻⁴	7.34·10 ⁻⁴	6.97·10 ⁻⁴	7.73·10 ⁻⁴	—	—
	γ_0	146.0	1.68	0.630	0.241	0.703	—	—
He(3 ¹ P)	M_1^2	7.20·10 ⁻⁴	7.43·10 ⁻⁴	7.10·10 ⁻⁴	7.81·10 ⁻⁴	7.37·10 ⁻⁴	—	—
	γ_0	132.0	1.615	0.621	0.232	0.701	—	—
He(4 ² S)	M_1^2	5.05·10 ⁻⁴	9.38·10 ⁻⁴	1.03·10 ⁻³	1.11·10 ⁻³	9.57·10 ⁻⁴	—	—
	γ_0	92.8	2.04	0.901	0.383	0.910	—	—
He(4 ¹ S)	M_1^2	4.60·10 ⁻⁴	9.10·10 ⁻⁴	1.00·10 ⁻³	1.08·10 ⁻³	9.28·10 ⁻⁴	—	—
	γ_0	84.5	1.98	0.875	0.373	0.882	—	—
He(4 ² P)	M_1^2	8.65·10 ⁻⁴	9.46·10 ⁻⁴	8.99·10 ⁻⁴	8.65·10 ⁻⁴	9.42·10 ⁻⁴	—	—
	γ_0	159.0	2.06	0.786	0.298	0.895	—	—
He(4 ¹ P)	M_1^2	8.64·10 ⁻⁴	9.34·10 ⁻⁴	8.98·10 ⁻⁴	8.56·10 ⁻⁴	9.23·10 ⁻⁴	—	—
	γ_0	159.0	2.03	0.786	0.295	0.877	—	—

TABLE II. Comparison of the dipole-dipole^[6] width and the exchange width given by^[21].

R, au	He(3P)+Ar		He(3P)+Xe		He(3P)+Li	He(3P)+Mg
	γ_{dd}^* , eV	γ_{exch} , eV	γ_{dd}^* , eV	γ_{exch} , eV	γ_{exch} , eV	γ_{exch} , eV
3	0.106	0.460	0.072	0.253	—	—
4	0.019	0.087	0.013	0.073	—	—
5	0.005	0.015	0.003	0.018	0.539	0.189
6	0.002	0.003	0.001	0.004	0.339	0.077
8	—	—	—	—	0.096	0.010
10	—	—	—	—	0.020	0.002
12	—	—	—	—	0.002	—

* $\gamma_{dd} = 8\pi\mu_{He}^2\mu_X^2R^{-6}$; $\mu_{He}^2(3P) = 0.0433$ is the square of the matrix element of the dipole transition $He(3P) \rightarrow He(1S)$, μ_X^2 is the same for the photoionization of the atoms X.^[7]

lations we choose five terms of the asymptotic expansion. The mean-square value of this amplitude, averaged over the orientations of the molecule axis is given for the hydrogen molecule in^[23]. The excited-state photoionization matrix element M_1 is taken from the calculation in^[13]. The analytic expressions for this matrix element as functions of the excitation number are quite complicated. For very high excitations we can use the Kramers average quasi-classical limit (see below).

Table II shows a comparison of the exchange width calculated here with the dipole-dipole width.^[6] It is seen that even for resonant states in the working region of internuclear distances, the exchange width is larger than the dipole width. In addition, any of the excited states of helium can decay via the exchange channel regardless of the angular momentum or the spin. The dispersion decay channel should prevail in the case of collision of heavier atoms, when the collision velocities are relatively small and the working distances turn out to be the relatively larger interatomic distances.

To calculate the reaction cross section we describe the motion of the nuclei with the aid of classical trajectories. The ionization probability for a trajectory with impact parameter ρ is equal to^[8]

$$P(\rho) = 1 - \exp\left[-\frac{2}{v_0} \int_{R_0}^{\infty} \frac{\gamma(R) dR}{(1 - \rho^2/R^2 - U(R)/\epsilon)^{1/2}}\right]; \quad (22)$$

where $U(R)$ is the interaction potential of the atoms, R_0 is the closest-approach distance of the atoms, and $\epsilon = \mu v_0^2/2$ is the relative collision energy. Allowance is made here for the fact that each attainable distance R is negotiated twice in one collision.

We introduce the quantity $P(\rho, R_1)$, which is the probability of ionization when the particles approach to within a distance R_1 for the given trajectory. Since we have determined only the principal term of the asymptotic expansion of the width γ in the reciprocal powers of R , we are justified in integrating only the exponential in (22). We then have

$$P(\rho, R_1) = 1 - \exp\left[-\frac{n_0\gamma(R_1)}{v(R_1)}\right], \quad v(R_1) = v_0 \left(1 - \frac{\rho^2}{R_1^2} - \frac{U(R_1)}{\epsilon}\right)^{1/2}. \quad (23)$$

The interaction between the particles constitutes polarization attraction of the atom X to the ion A^+ :

$$U(R) = -\alpha_X/2R^4,$$

where α_X is the polarizability of the atom X. In this potential as is well known,^[24] there are two classes of trajectories. At $\rho > \rho_0 = (4\alpha_X/\mu v_0^2)^{1/4}$ the trajectories are practically straight lines, with $R_0 \approx \rho_0$. At thermal collision energies, the probability of ionization on these trajectories is negligibly small. On trajectories with impact parameters $\rho \leq \rho_0$, the particles come very close together and the decay is more effective. The cross section of reaction (1) can then be expressed in the form

$$\sigma = P_n \sigma_{capt} \quad \sigma_{capt} = \pi(2\alpha_X/\epsilon)^{1/2}, \quad (24)$$

where P_n is the ionization probability and is the same for all the capture trajectories (n is the excitation number of the atom A^*). For thermal energies $\epsilon < 1$ eV, this quantity is also independent of the collision energy, inasmuch as in the closest-approach region the velocity of the atoms is determined by a relatively large interaction; $U(R \sim 1) \gg \epsilon$. For ionization of noble-gas atoms by helium atoms excited to states $n=3$ and $n=4$, it is easy to ascertain with the aid of formula (20) and the data of Table I that the ionization probability $P(\rho, R)$ becomes equal to unity at $R \sim 5$, where the foregoing asymptotic expansion is valid. For these cases, the ionization probability P_n in formula (24) is equal to unity, and the cross section of the reaction coincides with the polarization-capture cross section.

Table III shows a comparison of the theoretical and experimental^[7] cross sections. The latter are on the average 1.5–2 times smaller than the theoretical ones. The discrepancy is apparently due to the unaccounted-for interaction between the atom X and the excited electron prior to penetration into the interior of its orbit. This interaction is most readily of the repulsion type (notwithstanding the fact that the lengths for the scattering of electrons by the noble-gas atoms Ar, Kr, and Xe are negative). The theoretical cross section must therefore be multiplied by the penetrability of the barrier at the given temperature. It can be concluded from a comparison of the theoretical and experimental cross sections that for He^* ($n=3$) this quantity is ~ 0.2 – 0.8 . For the ionization of the atoms He^* ($n=4$), this interaction is much weaker, and the cross sections of this reaction (1) should be closer to the theoretical ones given in Table III (at the same collision energy).

To analyze the reaction (1) with more highly excited helium atoms it is necessary to examine the behavior of the terms of the systems $He^* + X$ at short distances and, in particular, at $R=0$. The wave function of the electron of the atom X has an additional nodal surface near the ion A^+ , since the ionization potential is $J_X < J_{He}$.^[20] This

TABLE III Comparison of the theoretical and experimental^[7] ionization cross section (\AA^2).

	Ne	Ar	Kr	Xe	H ₂
σ from (24) with $P_n=1$	38.7	77.5	95.4	121	54.7
He(3P)	28±4	56±10	50±8	73±12	—
He(3P)	24±4	25±6	22±3	64±10	—
He(3S)	24±4	23±4	24±6	49±9	—
He(3S)	21±3	14±3	16±4	61±10	—

means that in the compound-nucleus limits one of the electrons of the atom X goes over into a state in which it has larger quantum number than in the atom X (i. e., this electron is excited). The produced vacancy is filled by the ground-state electron of He^+ . Thus, the electron shell of the $\text{He}^+ + \text{X}$ system turns out to be excited in the $R=0$ limit. For example, for the $\text{He}^+ + \text{Ne}$ system one of $2p$ electrons of Ne should go over to the $3p$ state of the compound excited ion $\text{Mg}^+(1s^2; 2s^2; 2p^6; 3p)$. If we now recall the presence of a highly-excited electron, then we obtain a two-electron-excited (i. e., autoionization) state of the compound atom. It is natural to assume next that the behavior of the electron energy with the additional nodal surface as a function of R is similar to the behavior of the energy of the $1\sigma_u$ electron in the H_2^+ ion. This assumption is supported by a comparison of the terms $E_{1\sigma_u}(R)$ of the H_2^+ ion^[25] and $E_{\text{He}^+ + \text{H}}$.^[26,27] From this comparison we can conclude that at distances $(2-3)a_0$ the $\text{He}^+ + \text{X}$ terms are "repulsive" so that the distance between the atoms at thermal energies is apparently not smaller than $R \sim 3a_0$. At low energies, consequently, the effective region of the internuclear distances is the asymptotic one.

For ionization by strongly excited atoms it is possible to use the Kramers classical limit^[28] for the photoionization probability, according to which $M_1^2 \approx 0.123n^{-5}$. Using this result and the data of Table I, we can write down the cross sections for the ionization by an atom in any excited state, in the form

$$\sigma = P_n \pi \left(\frac{2\alpha_X}{\varepsilon} \right)^{1/2}, \quad P_n = \begin{cases} 1, & n_0 \geq n \geq 3 \\ (n_0/n)^2, & n \geq n_0 \end{cases}, \quad (25)$$

where $n_0 \sim 4$ for ionization of noble-gas atoms, and $n_0 \sim 5-6$ for such relatively weakly bound and strongly polarizable atoms as Li and Mg.

At $n \sim 1/V_0$, ionization of the excited electron as a result of elastic scattering by the atom X is possible. At such large n , however, the cross sections of the two processes are small and vary independently.

For collision energies of the order of and larger than several dozen electron volts, the ionization is the result of the decay of the compound atom (i. e., at $R \sim a_0$) and can be estimated at $\sigma \sim \pi a_0^2 (a_0/v_0\tau_0)$, where τ_0 is the lifetime of the autoionization state of the compound atom and a_0 is the Bohr radius.

Notwithstanding the expectations,^[1,6,29] the cross sections of Penning ionization by a helium atom excited to the level $n=3$ turn out at thermal energies to be larger by 1.5-2 times than the corresponding cross sections for the state $n=2$.^[1,7] This circumstance is an additional obstacle to population inversion.

We note in conclusion that the results obtained here (particularly formula (25)) are valid for ionization by

any strongly excited atom having an excitation energy larger than the ionization potential of the atom X.

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