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Ionization Produced by High-Energy Atomic Collisions*

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A statistical theory, developed earlier, to account for the ionization produced by violent collisions between two many-electron atoms is here re-examined in the light of recent experimental results. It is found that the statistical theory is consistent with the concept of an autoionization transition. This transition, which occurs after the collision is over, is between an initial state in the discrete spectrum of the atom and a final continuum state at the same energy. The statistical distributions introduced in the earlier papers are intimately related to the density of final states $\rho(E_f)$ in the standard formula for the transition probability between a discrete level and a continuum: $w=(2\pi/\hbar)|H_{fi}'|^2\rho(E_f)$. In addition to reinterpreting the previous results, the statistical theory is here extended and improved, and simple algebraic expressions are obtained for the ionization probabilities. Finally, the ionization process is considered in detail, and a theory for the ionization energies appropriate to violent collisions is presented. It is shown that the appropriate ionization energies increase monotonically with the excitation energy of the autoionizing level and are always larger than the ionization energies as determined spectroscopically.

I. INTRODUCTION

DURING the past several years, a considerable body of experimental data has been accumulated on the ionization produced by violent ion-atom collisions as functions of the collision parameters. In particular, the differential measurements reported by Everhart and his collaborators[1–4] and Federenko and his collaborators[5–7] are sufficiently comprehensive so as to make possible a detailed theoretical investigation of the processes which occur in a collision between two many-electron atoms. Initially, the experimental data gave the probabilities that a projectile ion would become n-fold ionized, as the result of a collision with a target atom, as functions of the incident ion energy and the angle of scattering. During the time that the initial data was being collected, an attempt was made by the present author, in collaboration with Thomas and Bulman, to formulate a phenomenological theory of the collision process to account for the behavior of the observed ionization probabilities. This work is described in a series of papers,[8–10] hereinafter called I, II, and III. The present work has, as its purpose, an extension and modification of that first theoretical attempt in the light of illuminating results which have since become available.

Briefly, in its original form the theory held that the collision leaves each of the colliding atoms with a substantial excitation energy which is a function of the collision parameters and that, *upon separation*, this excitation energy is statistically distributed among the electrons in the outer shell. These statistical aspects of the theory were successful in accounting for much of the behavior of the ionization probabilities as functions of the collision parameters. In this paper, the statistical aspects of the theory are improved and made much more comprehensive. It is shown that the statistical aspects of the ionization probabilities are consistent with the concept of an autoionization transition.

Despite the success of the original theory, the mechanism proposed in I for the production of the excitation energy now appears to be incorrect. In I, it was assumed that the excitation was due to a friction-like mechanism, resulting from random electron-electron collisions as the two electronic distributions swept through each other. At that time, the only direct measurements on the inelastic energies were fragmentary,[7] so that no direct confrontation with experiment of the excitation mechanism therein proposed was possible.

Recently, two papers have appeared which shed important light both on the nature of the excitation mechanism and the reasons for the statistical distribution of this excitation energy. Berry[11] has made measurements on the energy distribution of electrons from ion-atom collisions, and finds evidence for the production of discrete intermediate atomic states, excited by the collision, which later decay by autoionization transitions. Particularly in the case of He$^+$ on He, the energy spectrum of He being well understood, it is even possible to identify the excited state and to obtain theoretical estimates on the autoionization lifetimes of that state. The results indicate that for collisions that take place at

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[10] J. B. Bulman and A. Russek, Phys. Rev. **122**, 506 (1961), Paper III.

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energies in which we are interested, there is ample time for complete electronic separation of the colliding atoms before the autoionization transition occurs.

Morgan and Everhart[12] have measured the inelastic energies associated with high-energy Ar^+ on Ar collisions as functions of the collision parameters. These measurements indicate that the excitation energies are almost completely insensitive to the relative velocities of the nuclei and depend only on the distance of closest approach. The dependence on this variable indicates very large abrupt increases in the excitation energy when the L shells of the two colliding atoms just begin to overlap and again when the K shells just begin to overlap. This behavior sheds considerable light on the nature of the excitation mechanism, which is discussed in Sec. II. In that section, also, the basic assumptions of the statistical aspects are restated more precisely in terms of an autoionization transition.

This paper also reports a considerable improvement in the calculation of the ionization probabilities. The numerical procedures, described in I, II, and III, involved in the calculation of the ionization probabilities have now been carried out in closed analytic form. As a result, analytic expressions for the ionization probabilities have been obtained not only for the uniform ionization energy case required by the assumptions of I, but also when the ionization energies vary with the number of electrons escaping. The details of these calculations are presented in the Appendix, but the major results are also stated in Sec. II. With these improvements, it is now possible to consider the previously anomalous case of Ne^+ on Ne and as well, shed light on the mechanism of the ionization process itself. Section III treats in detail the theory of the ionization energies which, in I, was merely stated in the form of an empirical assumption, i.e., a constant ionization energy. It is found that the ionization energies vary as functions of the excitation energy and, to a lesser extent, on the number of electrons escaping. Section IV compares the theory with experiment.

II. EXTENSION OF THE EVAPORATION MODEL

Four assumptions which constitute the evaporation model were stated in I; but a better understanding brought about by additional evidence makes it possible to restate them simply and more precisely.

A. The Assumptions

(1) (a) When two atoms or an atom and an ion suffer a violent atomic collision, each atom or ion receives an excitation energy which is a reasonably well defined function of the collision parameters. (b) This excitation energy is initially an excitation to one of the discrete energy levels in the energy spectrum of the atom or ion.

(2) After, or nearly after, complete separation of the colliding atoms, each undergoes an autoionization transition from the discrete level to a continuum state at the same energy.

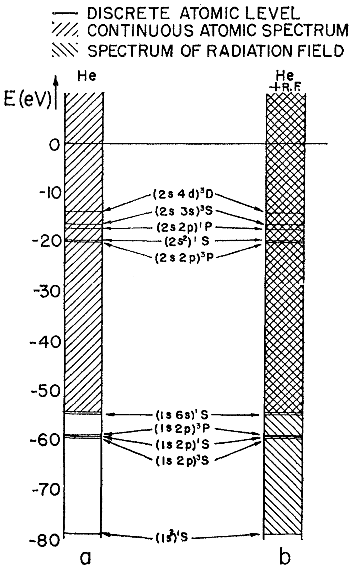

FIG. 1. The energy spectrum of helium. Discrete energy levels, a representative sampling of which are shown, are indicated by lines. Continuous portions of the spectra are indicated by hatched regions. Part (a) shows the continuous spectrum of the particle Hamiltonian only (or, rather, of a suitable unperturbed part thereof), while part (b) also shows the continuous spectrum of the radiation field. The overlap of the two continua is the region where autoionization and spectral emission are competitive.

B. Discussions of the Assumptions

The four assumptions of I have here been condensed to two. The first deals with the excitation mechanism, which was incorrectly conceived in I. A discussion of this assumption, with a possible explanation for the initial excitation to a discrete energy level is presented later in this section. The statistical aspects of the original presentation will here be shown to be a consequence of the second assumption. In particular, they follow from the density of states ρ that appears in the formula for the transition probability from a discrete state to a continuum. This connection will be demonstrated immediately. Finally, a refined treatment of the ionization process, presented in Sec. III eliminates the need for a separate assumption concerning the ionization energies.

As is well known, when a many-electron atom is excited to an energy level above the first ionization energy, the processes of autoionization and de-excitation by photon emission are competitive. Below this energy, only the latter process is possible. Figure 1(a) shows, for purposes of illustration, the energy spectrum of helium, although we are primarily interested in atoms with many more electrons. However, calculations of the highly excited states of such atoms have not been made, whereas the calculations have been made in the case of helium. A few of these states are illustrated in the diagram. This is but one example of a discrete energy spectrum embedded in a continuum. A much more familiar example of a discrete spectrum embedded in a continuum is the quantum mechanical system which consists of an atom *plus the radiation field*. In this

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[12] G. H. Morgan and E. Everhart, Phys. Rev. **128**, 667 (1962).

example [Fig. 1(b)] the radiation field supplies the continuous part of the spectrum and one of the most elementary problems of the quantum theory of radiation is to calculate the transition probability from a state in the discrete spectrum (atom in excited state, no energy in the radiation field) to a state in the continuous spectrum at the same energy (atom in ground state, a photon present in the radiation field).

For these excited states with excitation energies higher than the first ionization energy, the autoionization process competes with photon emission. Wentzel[13] discussed this problem as early as 1928, and calculations were carried out by Kreisler,[14] Kiang, Ma, and Wu,[15,16] Wu,[17] and Bransden and Dalgarno[18] on autoionization transitions in neutral helium atoms. Bransden and Dalgarno point out that the discrete and continuous states involved in the transitions under discussion cannot be eigenstates of the total particle Hamiltonian

$$H_p=\sum_i\{p_i^2/2m-Ze^2/r_i+\sum_{j<i} e^2/r_{ij}\},$$

but of some "unperturbed" Hamiltonian H_{0p}, the remainder of H_p being the perturbation responsible for the transitions. Bransden and Dalgarno conclude that for those excited states in helium for which autoionization is not forbidden, autoionization is the predominant process over photon emission by a factor of the order of 10^6.

Thus, Assumption (1) states that a violent collision between many-electron atoms leaves each of the colliding atoms excited to one of the discrete energy levels embedded in the continuum. Assumption (2) then holds, in extension of the conclusions reached for helium by Bransden and Dalgarno, that the probability of de-excitation by photon emission can be neglected. The autoionization transition should distribute the excitation energy among only the outer shell of electrons. This is justified on the basis that the most violent collisions observed by Morgan and Everhart[12] involved excitations of about 600 eV per atom in Ar^+ on Ar which appear to be excitations of the L shell. This is barely enough to remove two electrons from the L shell and that only if all of the energy is somehow transferred to just these two electrons. Thus, the predominant event in this case is a transition which involves de-excitation of the L shell transferring the energy to the outer electrons only (i.e., an Auger transition). For the lowest excitation energies observed by Morgan and Everhart, even the initial discrete excitation undoubtedly involved M-shell electrons only, inasmuch as the entire excitation energy was not sufficient even to excite a single L-shell electron.

Finally, the autoionization process proceeds by a statistical distribution of the excitation energy among the outer electrons. This follows once the idea of an autoionization transition is accepted. The general formula for the transition probability when the initial state is in the discrete spectrum and the final state is in the continuum is given by (see, e.g., Schiff[19])

$$w=(2\pi/\hbar)|H_{if}'|^2\rho,$$

where w is the transition probability per unit time, H_{if}' is the matrix element of the interaction term in the Hamiltonian between the initial discrete state ψ_i and a final continuum state ψ_f with $E_i=E_f$ and ρ gives the density of states in the vicinity of ψ_f. For a nondegenerate continuous spectrum with the states normalized to a delta function,

$$(\psi_E,\psi_{E'})=\delta(E-E'), \tag{1}$$

then ρ is unity, i.e., "one state" per unit energy range or, otherwise stated, one state per energy cell of unit size. On the other hand, if the spectrum, at the energy in question is ν-fold degenerate with equal matrix elements to all members of the degenerate set, then additivity of the transition probability demands that $\rho=\nu$.

Consider, now, multiple ionization of a many-electron atom resulting from an autoionization process. To make the problem tractable, it is necessary to assume that all those matrix elements which do not vanish are, *on the average*, equal. Those matrix elements which do vanish determine the "selection rules," e.g., conservation of angular momentum, etc. Let $w_{\mathrm{tot}}^{(N)}$ be the total autoionization transition probability for an outer shell containing N electrons. Further, let $w_n^{(N)}$ be the sum of the transition probabilities to all final states in which n electrons are ionized from the outer shell. Thus,

$$w_{\mathrm{tot}}^{(N)}=\sum_{n=0}^{N} w_n^{(N)}. \tag{2}$$

Note here that the bound-energy region (i.e., the energy of a given electron is lower than the ionization energy) is also considered to be a continuum. Thus, there is a possibility that the excitation energy can be distributed among the outer electrons so that none have sufficient energy to escape. This implies that there also exist continuum states which are fully bound, or at least that the data conspires to make it appear that these states exist. This question was considered in I and it was there concluded that agreement between theory and experiment requires this assumption.

According to the above discussion, it follows that

$$w_{\mathrm{tot}}^{(N)}(E_T)=\frac{2\pi}{\hbar}|M|^2\frac{K_N([E_T/\epsilon])}{\epsilon^{N-1}}f. \tag{3}$$

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[18] B. H. Bransden and A. Dalgarno, Proc. Phys. Soc. (London) **A66**, 904 (1953).

[19] L. I. Schiff, *Quantum Mechanics* (McGraw-Hill Book Company, Inc., New York, 1949), p. 193.

Here, E_T is the excitation energy, ϵ is the size of the energy cell, $[E_T/\epsilon]$ is the integral part of E_T/ϵ (e.g., $[2.4]=2$), M is the mean value of the nonvanishing matrix elements and $K_N(m)$ is the number of ways of expressing m as the sum of N nonnegative integers, i.e., the number of ways of dividing the energy $E_T=m\epsilon$ among N electrons. The factor f is the number of different final state angular momentum combinations for which the matrix element M is not small. In this connection, it should be noted that the matrix element is required to vanish completely only when angular momentum between initial and final states is not conserved. However, if, as is reasonable, the autoionization process is primarily a radial explosion, then all matrix elements would be small for which the angular momentum of any individual electron is substantially changed in the process. This would have the effect of making f have a value close to unity. At any rate, the factor $K_N f/\epsilon^{N-1}$ in Eq. (3) is just the degeneracy mentioned previously or, as otherwise termed, the "number" of final states at the given energy. Thus,

$$\rho = K_N([E_T/\epsilon]) f/\epsilon^{N-1}. \tag{4}$$

If the final states are now classified according to the ionization state and $P_n^{(N)}$ is defined to be that fraction of the total number of final states which are n-fold ionized, then these are just the ionization probabilities whereby theory and experiment are compared:

$$w_n^{(N)}(E_T) = w_{\text{tot}}^{(N)}(E_T) P_n^{(N)}(E_T). \tag{5}$$

Assuming that f is not a function of the number of electrons escaping (even if it is not exactly equal to unity), $P_n^{(N)}$ is, then, the number of ways in which the energy $E_T=m\epsilon$ can be divided among N electrons such that n and only n have more then the ionization energy $E_{\text{ion}}=r\epsilon$, divided by the total number of ways in which the energy $m\epsilon$ can be divided among N electrons. Mathematical expressions will be obtained below for these ionization probabilities, but at this point, the mechanism for the initial discrete excitation will be considered.

In the collisions which are being discussed, projectiles such as Ne^+ and Ar^+ are incident at energies up to 100 keV. At these energies the projectiles are moving with velocities comparable to those at which electrons would move with kinetic energies of the order of 0.7 to 1.4 eV. Thus, even the most violent of the collisions considered are proceeding slowly when compared with even the lowest energy orbital motions. It might be expected, therefore, that these collisions would be adiabatic. Figure 2, reproduced from Fig. 7 of Morgan and Everhart, shows, however, that this is far from the case. On the basis of the results shown in Fig. 2, the following excitation mechanism is now proposed.

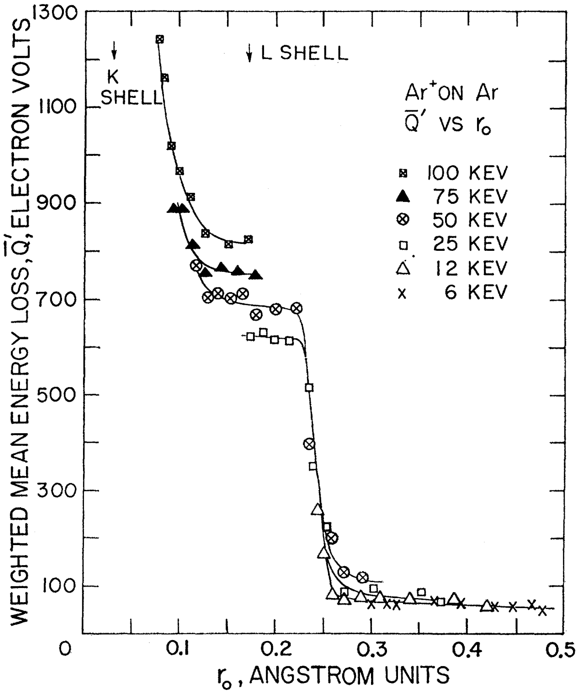

FIG. 2. Experimental values for the inelastic energy as a function of the collision parameters for Ar^+ on Ar. This figure is reproduced from Morgan and Everhart.[12] The ordinate in this figure is $\bar{Q}'$, the mean inelastic energy, excluding the neutrals, the energy of which could not be determined. $\bar{Q}'$ is the inelastic energy, which is shared by both participants in the collision. The excitation energy E_T for one of the atoms is assumed to be half of $\bar{Q}'$, on the average.

As the two colliding atoms approach, diatomic molecular orbitals begin to form in an *almost* adiabatic way. However, it will be remembered that the static molecular orbitals are referred to a z axis which is the internuclear axis. The internuclear axis is here rotating, as is illustrated in Fig. 3. Thus, superimposed on all the molecular orbital motion is the rotary motion of the internuclear axis. For purposes of illustration the case of Ar on Ar will be considered and attention restricted to the L-shell orbitals for the case in which the projectile energy is 25 keV and the internuclear separation at closest approach is approximately twice the radius of the L shell. Note that this is where the very steep rise in excitation energy occurs in Fig. 2. Assuming that the diatomic molecular orbitals have formed, each of the 16 electrons (8 from each atom) has superimposed on its

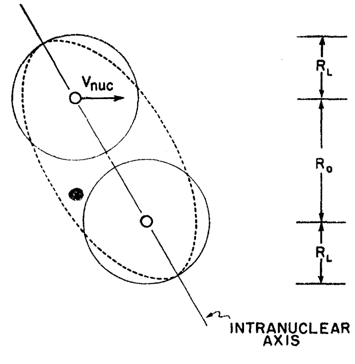

FIG. 3. Rotation of the internuclear axis. The circles represent the mean radius of the L shell of argon. The dashed ellipse represents, schematically, a molecular orbital trajectory.

orbital motion a velocity v_{nuc} given by

$$v_{\text{nuc}}=(2E_{\text{inc}}/M)^{1/2}=3.5\times10^{7}\text{ cm/sec},$$

where E_{inc} is the incident ion energy and M the mass of the argon nucleus. This will give each electron an extra angular momentum l' which is roughly equal to (see Fig. 3)

$$l'=mv_{\text{nuc}}(r_0+2r_L)=0.19\times10^{-27}\text{ g cm}^2/\text{sec}=0.18\hbar,$$

where r_0 is the nuclear separation at closest approach, r_L is the radius of the L shell and m the electronic mass. For the case under consideration $E_{\text{inc}}=25$ keV, $r_0=0.25\times10^{-8}$ cm, $2r_L=0.35\times10^{-8}$ cm. Thus, the nuclear motion would give each electron 0.18 quantum units of angular momentum relative to its frame of reference, were the electron capable of accepting that much. However, each L shell contains eight electrons and, therefore, receives 1.4 units of angular momentum due to the nuclear motion, in this simple classical model. If, as is reasonable, quantum mechanics roughly reflects the classical analogy, then it is expected that the collision will leave the L shell of each atom with a unit of angular momentum. Being a full shell, it cannot accept this angular momentum without an excitation energy of about 250 eV (at least enough to raise one of the electrons out of the L shell to one of the higher orbitals, so that the resultant state can be one of angular momentum other than zero). Moreover, since the classical picture leaves each electron with only a fraction of a unit of angular momentum, it is reasonable to expect that the excited state is one in which not merely a single electron is excited to a higher orbital, but is a collective excitation of the entire shell, in which all electrons share the additional angular momentum.

Since there is more than enough angular momentum, on the basis of the classical picture, to force whatever excitation is achieved, it is reasonable to expect that the excitation energy is *not* a function of the incident ion energy, but rather a function of the minimum internuclear separation. This, of course, is suggested by the results of Morgan and Everhart, which also shows a similar phenomenon occurring for the two K shells. The small excitation energies at large impact parameters is undoubtedly a similar result for the M shells. As a final point, it must be remembered, in referring to the work of Morgan and Everhart, that they measure the total excitation energy for the entire process whereas we are considering the excitation energy per atom. Therefore, the energies in Fig. 2 should be divided by 2.

C. The Ionization Probabilities

Let $P_n^{(N)}(E_T)$ be the probability that when excitation energy E_T is statistically distributed among N electrons in the outer shell, n and only n will have enough energy to escape. On the basis of the discussion in paragraph B, this is given by the limit, as $\epsilon\to0$, of the number of of ways in which E_T/ϵ units of energy can be distributed among N electrons such that n and only n electrons have enough energy to escape, divided by the total number of ways in which E_T/ϵ units of energy can be distributed among the N electrons. In order to achieve continuity in the presentation of the physical aspects of the theory, the final results will here merely be stated, with the proofs relegated to the Appendix, where the countings, followed by the limiting process $\epsilon\to0$, are carried out in detail.

1. *The Uniform Ionization Energy Case*

If the ionization energy is independent of the number of electrons escaping, it is shown in the Appendix that

$$P_n^{(N)}(E_T/E^{\text{ion}})=\binom{N}{n}\sum_{i=0}^{k}(-1)^i\binom{N-n}{i}\left(1-\frac{n+i}{E_T/E^{\text{ion}}}\right)^{N-1},\qquad(6)$$
$$\text{for}\quad n+k\leq E_T/E^{\text{ion}}\leq n+k+1,$$

where E^{ion} is the ionization energy. Note that the ionization probabilities are given by different functional forms in each integral range of E_T/E^{ion}. Inasmuch as all the counting and limiting processes are carried out for a fixed value of E_T/E^{ion}, the result given by Eq. (6) remains valid if E^{ion} is a function of the excitation energy E_T. There is good reason for believing that such is the case, as will be shown later.

2. *The Staggered Ionization Energy Case*

In the case in which the ionization energy depends on the number of electrons escaping, let E_n^{ion} denote the energy needed *per electron* when the total number of escaping electrons is n. Note that E_n^{ion} is *not* the nth ionization energy, but the minimum energy needed to remove all n electrons divided by n. In this case, it has not been possible to derive exact expressions for the ionization probabilities, but reasonably good approximate expressions have been obtained:

$$P_n^{(N)}(E_T)\simeq\binom{N}{n}\sum_{i=0}^{k}(-1)^i\binom{N-n}{i}\times\left(1-\frac{nE_n^{\text{ion}}+iE_{n+1}^{\text{ion}}}{E_T}\right)^{N-1},\qquad(7)$$
$$\text{for}\quad k\leq E_T/E_{n+1}^{\text{ion}}-nE_n^{\text{ion}}/E_{n+1}^{\text{ion}}\leq k+1.$$

As before, the ionization energies can, and will, be functions of the excitation energy. The results expressed by Eq. (7) reduce to those given by Eq. (6) in the event that all the ionization energies are equal, and in that event, the expression is exact. When the ionization energies are staggered, however, the expressions given by Eq. (7) are all slightly too large, as is pointed out in the derivation in the Appendix. For the cases of interest, the sum of all the errors is of the order of a few percent and is, therefore, inconsequential.

D. Ion-Atom Collisions

So far, the ionization probabilities have been considered that result when a neutral atom has excitation energy E_T statistically distributed among the electrons in its outer shell. However, the experimental data which has been obtained are for collisions of projectile ions on target atoms. In this case, the probability $\tilde{P}_n$ that the projectile is n-fold ionized is given by

$$\tilde{P}_n = aP_n{}^{(N)} + (1-a)P_{n-1}{}^{(N-1)}\,, \tag{8}$$

where a is the electron capture probability, which is a function of the collision parameters. This equation was postulated in III, but because of the better understanding of the physical processes involved, the result now makes more sense. The evaporation process is now regarded as an autoionization transition which occurs after separation of the two atoms, that is, after the probability of further electron exchange is negligible. Therefore, it is, indeed, reasonable to introduce a capture probability and to write the over-all ionization probability in the form given by Eq. (8).

III. THE IONIZATION ENERGIES

A. General Theory

In the previous section expressions were obtained for the ionization probabilities in terms of the ionization energies. This section will be concerned with a rather crude determination of the ionization energy as a function of the number of electrons escaping and of the excitation energy of the electronic shell. Also, inasmuch as the notion of ionization energy which is suitable for spectroscopic studies is not suitable for the study of collision ionization, this quantity must be redefined for the present purposes.

In the crude calculation of the ionization energies which follows, the relatively small effects such as the fact that a $2s$ electron is bound somewhat more strongly than a $2p$ electron will be neglected. Rather, only the gross electrostatic effect will be considered which makes the nth electron removed from an atom require approximately n times as much energy as did the first, because it has to be separated from a core that has n times the charge of the core from which the first electron is separated.[20,21] Let $\mathcal{E}_{n,}{}^{\text{sp}}$ be the nth spectroscopic ionization energy. This is the energy needed to remove the nth electron, if electrons are removed one at a time, while leaving all other electrons that remain in the atom unexcited. Then, the total energy needed to remove n electrons is, in the present approximation,

$$\sum_{r=1}^{n} \mathcal{E}_r{}^{\text{sp}} = \sum_{r=1}^{n} r\mathcal{E}_1{}^{\text{sp}} = \tfrac{1}{2}n(n+1)\mathcal{E}_1{}^{\text{sp}}\,. \tag{9}$$

Table I. Average ionization energies for neon and argon.

n	$E_n{}^{\text{ion,sp}}$ for neon Experimental	 Theoretical	$E_n{}^{\text{ion,sp}}$ for argon Experimental	 Theoretical
1	21.6	26.5	15.8	16.0
2	31.4	39.8	21.7	24.0
3	42.4	53.0	28.1	32.1
4	55.8	66.3	36.0	40.1
5	69.9	79.5	43.8	48.1
6	84.6	92.8	51.7	56.1
7	102.1	106.0	62.5	64.3
8	119.2	119.2	72.3	72.3

Now, denote by W the ground-state energy of *the outer shell*, and by N the number of electrons in the outer shell. Since W is defined to be the energy needed to remove all N electrons,

$$W = \tfrac{1}{2}N(N+1)\mathcal{E}_1{}^{\text{sp}}\,. \tag{10}$$

Eliminating $\mathcal{E}_{1,}{}^{\text{p}}$ from Eq. (9), yields

$$\sum_{r=1}^{n} \mathcal{E}_r{}^{\text{sp}} = \frac{n(n+1)}{N(N+1)}W\,. \tag{11}$$

Remembering, now, that in the autoionization process all the electrons which escape come out simultaneously, and they will, therefore, all require the same ionization energy. This is given by the average of the first n spectroscopic ionization energies as customarily defined, since when n electrons escape, they will need the same total energy to do so, regardless of whether they leave simultaneously or one at a time.

$$E_n{}^{\text{ion,sp}} = \frac{1}{n}\sum_{r=1}^{n} \mathcal{E}_r{}^{\text{sp}} = \frac{n+1}{N(N+1)}W\,. \tag{12}$$

Thus, $E_n{}^{\text{ion,sp}}$ is the energy needed by *each* electron which escapes.

Crude as the approximation made above may be, it nevertheless yields quite good results as can be seen in Table I, which compares $E_n{}^{\text{ion,sp}}$ as computed from Eq. (12) with the experimental values.

Here, n is the number of electrons escaping and $E_n{}^{\text{ion,sp}}$ is the mean ionization energy per electron when n electrons escape. The theoretical values are calculated from Eq. (12).

In Eq. (12) the designation $E_n{}^{\text{ion,sp}}$ indicates that this ionization energy is, in some sense, a spectroscopic limit. Notwithstanding the fact that the electrons are now considered to come off simultaneously, Eq. (12) has been derived under the implicit assumption that those electrons which remain behind are unexcited. This is the important characteristic of the spectroscopic case. On the other hand, in the high-energy autoionization transitions under consideration, even the electrons which remain in the atom are excited and this, as will now be shown, affects the ionization energies of those electrons which do escape.

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[20] A. Russek, in *Second International Conference on the Physics of Electronic and Atomic Collisions* (W. A. Benjamin, Inc., New York, 1961), p. 45.

[21] A. Russek, Trans. N. Y. Acad. Sci. **23**, 681 (1961).

The quantity W is defined to be the binding energy of the outer shell in its ground state. Suppose, for heuristic purposes, the whole outer shell is excited, giving *each* electron an energy $\bar{E}$ which is insufficient to ionize it. The total binding energy w of the outer shell would now be reduced;

$$w = W - N\bar{E}. \tag{13}$$

In the ordinary sense, the ionization energies e_n for an atom so excited would be, by analogy with Eq. (12),

$$e_n = \frac{n+1}{N(N+1)} w. \tag{14}$$

However, it must be remembered that the evaporation theory of the preceding paragraphs has implicitly included $\bar{E}$ in the definition of the ionization energy, for, the ionization energy is the energy needed to remove an electron which is initially in the ground state. Therefore,

$$E_n^{\mathrm{ion}} = \bar{E} + \frac{n+1}{N(N+1)} w. \tag{15}$$

Defining, now, $\bar{E}_R$ as the excitation energy which remains with the electrons which do *not* escape,

$$\bar{E}_R = (N-n)\bar{E}. \tag{16}$$

This is the excitation state of the residual shell after the ionization has taken place. Since

$$w = W - N\bar{E} = W - \frac{N}{N-n}\bar{E}_R,$$

Eq. (15) becomes

$$E_n^{\mathrm{ion}} = \frac{\bar{E}_R}{N-n} + \frac{n+1}{N(N+1)}\left(W - \frac{N}{N-n}\bar{E}_R\right)$$

$$= \frac{n+1}{N(N+1)} W - \frac{\bar{E}_R}{N+1},$$

and, finally, after regrouping in a somewhat peculiar way:

$$E_n^{\mathrm{ion}} = \frac{(n+1)[W/N(N+1)]}{1-(1/N+1)(\bar{E}_R/E_n^{\mathrm{ion}})}$$

$$= \frac{E_n^{\mathrm{ion,sp}}}{1-(1/N+1)(\bar{E}_R/E_n^{\mathrm{ion}})}, \tag{17}$$

where Eq. (12) has been used to simplify the final expression. Here, E_n^{ion} is expressed in terms of $\bar{E}_R/E_n^{\mathrm{ion}}$ because the evaporation theory itself can supply the values of this latter quantity just as well as it yields the ionization probabilities.

It is clear from Eq. (17) that in the limit in which the electrons which remain in the atom are unexcited (i.e., $\bar{E}_R = 0$), the nth ionization energy is just that given by the spectroscopic limit $E_n^{\mathrm{ion,sp}}$, thus, justifying the notation. It is also clear that as the residual excitation increases, each of the ionization energies also increase.

B. The Self-Consistent Ionization Theory

It is now possible to derive, without further assumption, the ionization energies appropriate to violent collisions. (It will be recalled that, in I, the spectroscopic ionization energies were found not to be consistent with the data and a special assumption, the uniform ionization energy assumption was there postulated to achieve agreement with the data.)

Consider an autoionization transition at excitation energy E_T and suppose that, as a result, n electrons escape. The remaining $N-n$ electrons will, in all probability, be excited, and the total excitation of these remaining electrons will be denoted by E_R and called the residual excitation energy. Now, even with n and E_T given, there is not a single residual excitation energy associated with the collision. Rather, there is a distribution of residual excitation energies, denoted by $T(n,E_T;E_R)$, just as there is a distribution of kinetic energies carried off by the escaping electrons. It is shown, in Appendix III, that this distribution function (not normalized) is given by

$$T(n,E_T;E_R) = (E_T - nE_n^{\mathrm{ion}} - E_R)^{n-1}$$
$$\times \sum_{i=0}^{[E_R/E_{n+1}^{\mathrm{ion}}]} \frac{(-1)^i}{i!(N-n-i)!}\left\{\frac{E_R}{E_{n+1}^{\mathrm{ion}}} - i\right\}^{N-n-1}, \tag{18}$$

where $[E_R/E_{n+1}^{\mathrm{ion}}]$ is the integral part of $E_R/E_{n+1}^{\mathrm{ion}}$. A few typical distribution functions are shown in Fig. 4, and it can there be seen that the peaks in these distributions are sufficiently sharp so that the *most probable*

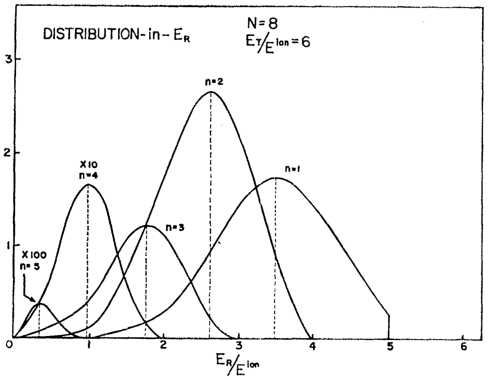

FIG. 4. Typical distribution functions for the residual excitation energy E_R, which remains with the electrons that are not ionized. The curves shown here are computed from Eq. (18) for the particular case of the uniform ionization energy, with excitation energy $E_T = 6E^{\mathrm{ion}}$. Although the curves are not normalized, the ratios of areas under them are equal to the ratios of the corresponding ionization probabilities. The values of E_R at which the peaks of the distribution functions occur are indicated by vertical dashed lines. These are the most probable values of E_R, and are denoted by $\bar{E}_R$.

TABLE II. Self-consistency check of the uniform-ionization energy theory at excitation energy $E_T/E^{\text{ion}}=6$.

n	$\bar{E}_R/E^{\text{ion}}$	$E_n^{\text{ion}}/E_1^{\text{ion,sp}}$	$E_n^{\text{ion}}/E_1^{\text{ion}}$
1	3.50	1.64	1.00
2	2.60	2.11	1.29
3	1.77	2.49	1.52
4	1.00	2.81	1.71
5	0.33	3.11	1.90
6	0.00	3.50	2.14

value of E_R may be taken as *the* value of E_R in the collision. Thus, as is illustrated in Fig. 4, an effective value of E_R/E_n^{ion} can be associated with each collision. Denoted by $\bar{E}_R/E_n^{\text{ion}}$, it is a function of E_T and n, and, as can be seen from Eq. (18), it also depends on the ratio $E_n^{\text{ion}}/E_{n+1}^{\text{ion}}$. This value for $\bar{E}_R/E_n^{\text{ion}}$ can then be substituted into Eq. (17) and the value of E_n^{ion} is then predicted by the theory of the ionization energies given in paragraph A. These calculated ionization energies ought to be consistent with the ionization energies which were assumed at the outset. When this condition is fulfilled, the ionization energies are termed the *self-consistent ionization energies.*

Before attempting to obtain the self-consistent ionization energies, it is useful to first investigate how close to being self-consistent is the uniform ionization energy (which was assumed without theoretical justification in I, II, and III).

Figure 4 gives, for a typical excitation energy $E_T/E^{\text{ion}}=6$, the distribution functions $T(n,E_T;E_R)$ of residual excitation energies E_R which follow from the uniform ionization theory. These have been computed from Eq. (18), where all the ionization energies have been set equal to each other, and consequently the subscript n has been dropped. Table II lists, for this excitation energy E_T, the most probable residual excitation energy $\bar{E}_R/E^{\text{ion}}$, for each value of n which is indicated on the abscissa of Fig. 4. Substituting these values into Eq. (17) yields the ionization energies which follows from the statistics of the uniform ionization energy theory. These, too, are listed in Table II, and it can be seen that the uniform ionization energy theory is not consistent with itself. It predicts that the ionization energies shall vary as a function of the number n of electrons escaping.

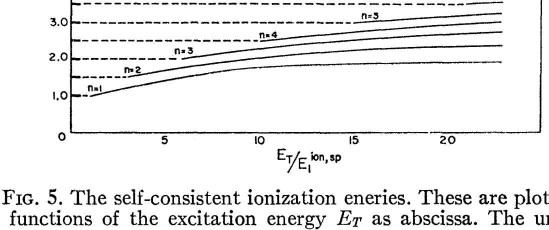

FIG. 5. The self-consistent ionization eneries. These are plotted as functions of the excitation energy E_T as abscissa. The units here used are absolute energy units; namely, the first *spectroscopic* ionization energy (e.g., 15.8 eV for argon).

TABLE III. The self-consistent ionization energies compared with the spectroscopic ionization energies.

E_T/E_1^{ion}	n	$E_n^{\text{ion}}/E_1^{\text{ion,sp}}$	$E_n^{\text{ion}}/E_1^{\text{ion}}$	$E_n^{\text{ion,sp}}/E_1^{\text{ion,sp}}$
1.00	1	1.00	1.00	1.00
2.00	1	1.12	1.00	1.00
3.00	1	1.28	1.00	1.00
	2	1.56	1.22	1.50
4.00	1	1.49	1.00	1.00
	2	1.73	1.16	1.50
5.00	1	1.76	1.00	1.00
	2	1.94	1.10	1.50
	3	2.17	1.23	2.00
6.00	1	1.80	1.00	1.00
	2	2.07	1.15	1.50
	3	2.29	1.28	2.00
	4	2.53	1.41	2.50
8.00	1	1.87	1.00	1.00
	2	2.23	1.20	1.50
	3	2.50	1.34	2.00
	4	2.72	1.46	2.50
10.00	1	1.89	1.00	1.00
	2	2.31	1.22	1.50
	3	2.64	1.39	2.00
	4	2.90	1.53	2.50
	5	3.12	1.65	3.00
12.00	1	1.91	1.00	1.00
	2	2.36	1.24	1.50
	3	2.73	1.43	2.00
	4	3.02	1.58	2.50
	5	3.25	1.70	3.00
	6	3.53	1.85	3.50

The self-consistent ionization energies are then obtained by inserting the ionization energies just calculated into Eq. (18) and starting all over again. As is the usual procedure for getting any self-consistent results, the iteration process is repeated until the output ionization energies finally agree with the input ionization energies. The self-consistent ionization energies thus obtained are listed in Table III and also plotted in Fig. 5. It should be noted that in Table III the excitation energies are given in terms of E_T/E_1^{ion}, while the abscissa of Fig. 5 is given in terms of $E_T/E_1^{\text{ion,sp}}$.

In Table III, the first column gives the excitation energy (in units of the first ionization energy), and the second column gives the ionization state. The third column gives the nth self-consistent ionization energy in terms of the first *spectroscopic* ionization energy (e.g., 15.8 eV for argon), and it can there be seen that the self-consistent ionization energies increase as the excitation energy increases. The fourth column gives the ratio of the nth self-consistent ionization energy to the first self-consistent ionization energy, while the fifth column gives, for comparison purposes, the corresponding ratio

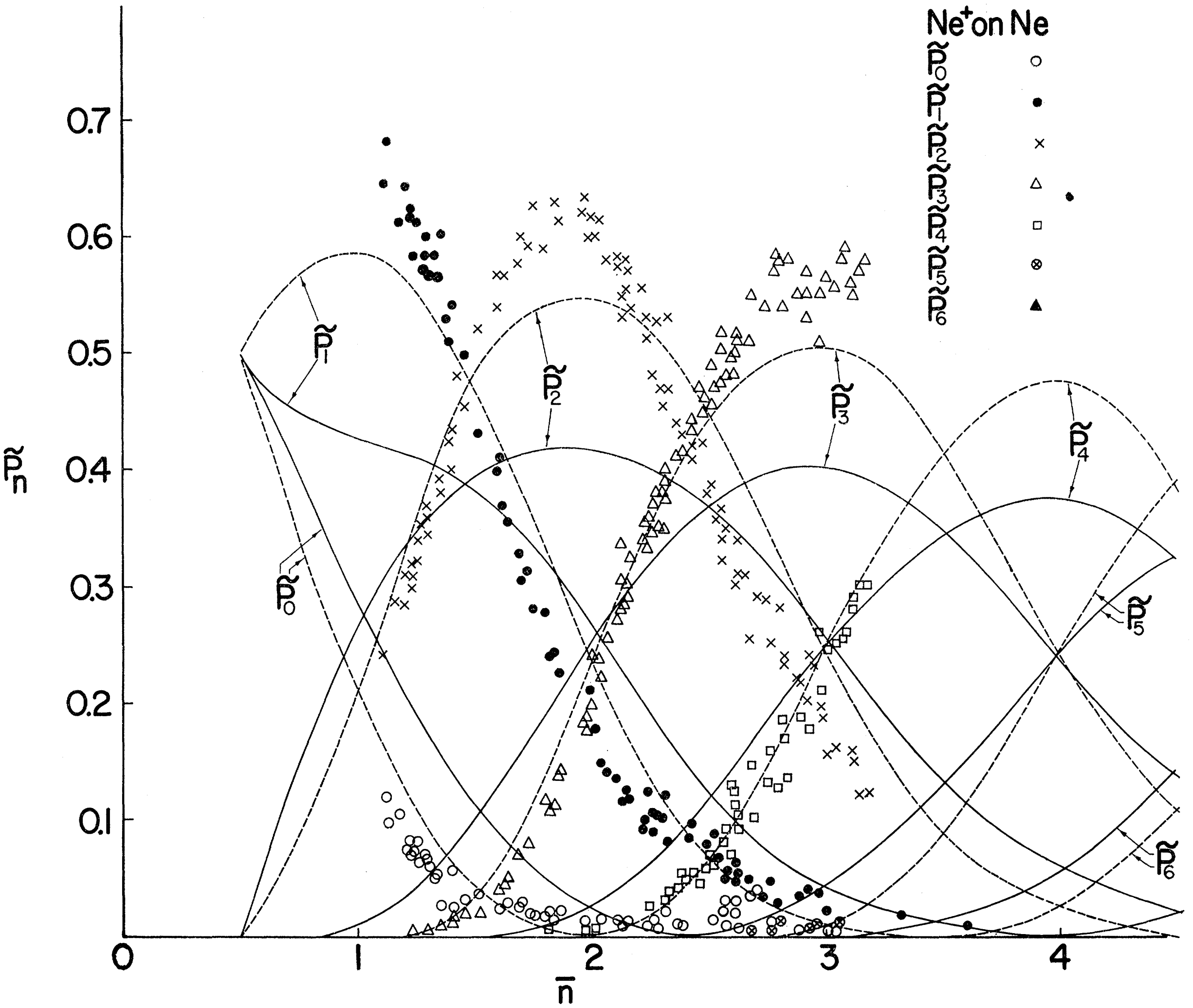

FIG. 6. The ionization probabilities for Ne^+ on Ne. The points show the experimental data. The solid curves are the theoretical ones which follow from the uniform ionization energy assumption and a capture probability of one half. The dashed curves follow from the self-consistent ionization energy assumption, also with a capture probability of one half.

for the spectroscopic ionization energies. A comparison of column four and column five shows that the self-consistent ionization energies are, indeed, considerably closer to the uniform ionization energy limit than they are to the spectroscopic ionization energy limit. This, to a great extent, justifies the uniform ionization assumption of I. Nevertheless, as can be seen in Figs. 6–8, the differences between the ionization probabilities which follow from the two assumptions considered here, concerning the ionization energies, are considerably greater than the experimental inaccuracies involved. There is no doubt that the case of Ar^+ on Ar follows the uniform ionization limit rather than the self-consistent limit. It is also clear that Ne^+ on Ne agrees much better with the self-consistent limit and that Ne^+ on Ar lies part way between the two. These points will be taken up in greater detail in the next section.

IV. COMPARISON WITH EXPERIMENT

In this section, the predictions of the theory are compared with the experimental results. In doing so, however, it must be remembered that the data thus far obtained related to ion-atom collisions. Therefore, according to Eq. (8), one would expect that the dependence of the capture probability on the collision parameters would have to be empirically fitted before a comparison could be made. In an attempt to avoid this empirical aspect and thereby achieve a direct comparison of the ionization and statistical aspects of the theory with experiment *without benefit of any empirical adjustment whatever*, the ionization probabilities are here plotted as functions of $\bar{n}$, the mean ionization state of the scattered projectile. The reasoning behind this is as follows. The excitation energy, as pointed out previously, depends principally on the distance of closest approach,

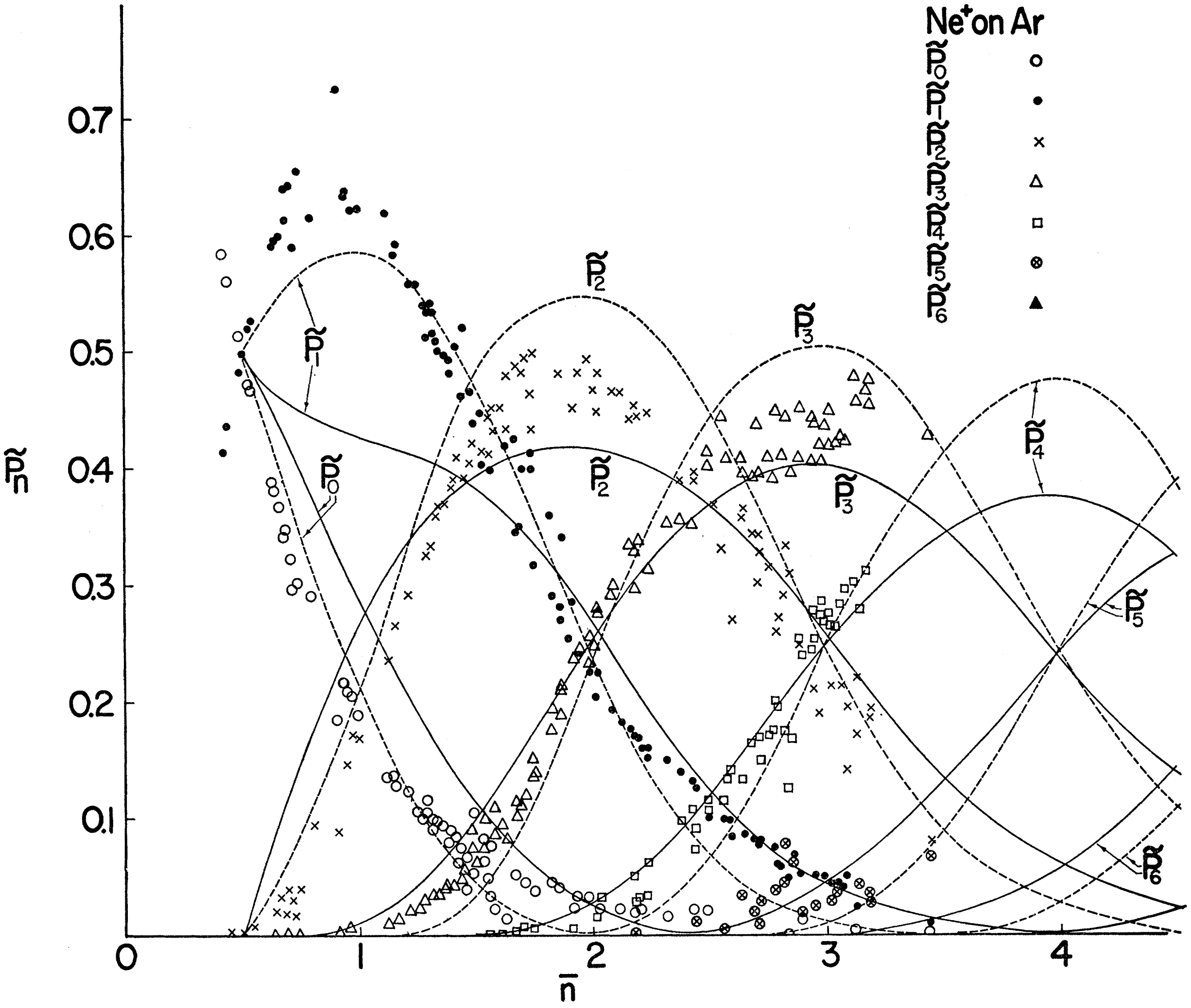

FIG. 7. The ionization probabilities for Ne^+ on Ar. The points show the experimental data. The solid curves are the theoretical ones which follow from the uniform ionization energy assumption and a capture probabliity of one half. The dashed curves follow from the self-consistent ionization energy assumption, also with a capture of one half.

whereas the capture probability depends principally on the time of collision which, in turn, depends (for a given projectile) only on the incident projectile energy. Thus, the various combinations of impact parameter and incident projectile energy which result in a given distance of closest approach will result in different capture probabilities. Consequently, plotting the ionization probabilities as functions of $\bar{n}$ will tend to average out the capture probability. This average capture probability should be one half, for collisions in which projectiles and target are of the same species. On the other hand, for cases in which projectile and target are not of the same species (e.g., Ne^+ on Ar), the average capture probability should not be expected, on *a priori* grounds, to be equal to one half. Nevertheless, in the comparison of theory and experiment which follows, a capture probability of one half will be consistently assumed.

Caution must be exercised in interpreting the comparison with experiment, made in this manner, for small values of $\bar{n}$. Values of $\bar{n}$ less than one half are clearly quite forbidden, unless the capture probability is greater than one half. By the same token, values of $\bar{n}$ which are close to one half undoubtedly select out from the data those combinations of the collision prameters which lead to higher-than-average capture probabilities followed by relatively little excitation-induced ionization. For this reason, all discrepancies between theory and experiment at values of $\bar{n}$ less than unity will be ignored, even though some of the discrepancy might be very real indeed.

In Figs. 6–8, the experimental ionization probabilities are plotted as functions of $\bar{n}$ for the cases of Ne^+ on Ne, Ne^+ on Ar, and Ar^+ on Ar, respectively. Shown also, in each of these figures, are the theoretical curves which

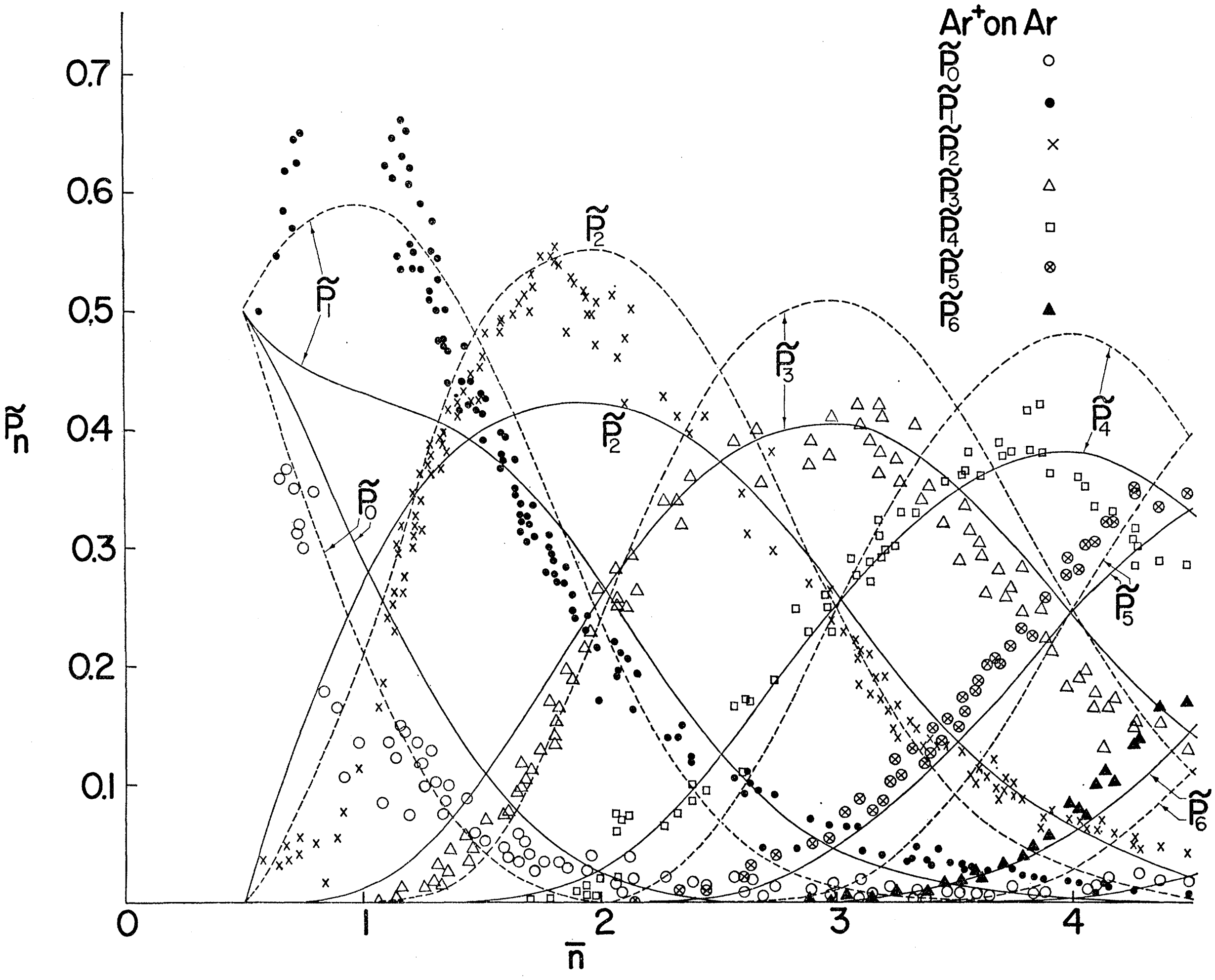

FIG. 8. The ionization probabilities for Ar$^+$ on Ar. The points show the experimental data. The solid curves are the theoretical ones which follow from the uniform ionization energy assumption and a capture probability of one half. The dashed curves follow from the self-consistent ionization energy assumption, also with a capture probability of one half.

follow from the self-consistent ionization limit, drawn as the dashed curves, and the uniform ionization energy limit, drawn as the solid curves. Both sets of theoretical curves have been plotted with the average capture probability assumed to be one-half. The theoretical curves are determined using Eq. (8) (with $a=\frac{1}{2}$) together with either Eq. (6), for the uniform ionization energy case, or Eq. (7), for the self-consistent ionization energy case. This, of course, yields the $\tilde{P}_n$ as functions of the excitation energy. For each excitation energy, $\bar{n}$ is then obtained, using the definition,

$$\bar{n}=\sum_{n=0}^{N} n\tilde{P}_n/\sum_{n=0}^{N} \tilde{P}_n.$$

Figure 9 shows, for example, the dependence of $\bar{n}$ on $E_T/E_1{}^{\mathrm{ion,sp}}$ for the self-consistent ionization energy case. With this dependence, the abscissa for the $\tilde{P}_n$ curves can be re-expressed in terms of $\bar{n}$. The experimental curves are handled in the same way; for each set of collision parameters, $\bar{n}$ is determined. In this way, both theoretical and experimental values for the $\tilde{P}_n$ can be plotted as functions of $\bar{n}$, despite the fact that the theoretical values are initially determined as functions of the excitation energy, while the experimental values are determined in terms of the collision parameters, usually the angle of scattering and incident energy of the projectile ion.

When considering the discrepancies, apparent in Figs. 6–8, between theory and experiment, it should be borne in mind that the agreement therein contained has been achieved without benefit of any empirical adjustment whatever, and, considering all the semiclassical approximations and simplifying assumptions made in the derivations of the preceeding sections, both sets of theoretical curves may well be considered as fitting the data as closely as one would have the right to expect.

Nevertheless, a discussion of the discrepancies will be attempted.

First, consider the differences between the Ne$^+$ on Ne and Ne$^+$ on Ar data, as shown in Figs. 6 and 7. Here, it should be noted that the theory holds that the ionization probabilities observed in a given species (Ne in this case) should depend only on the excitation energy. The ionization probabilities should, therefore, be independent of the target atom except, possibly, for a difference in capture probability. To this end, it was assumed that the Ne$^+$ on Ne data were due to a capture probability of one half; and indeed, the Ne$^+$ on Ne data lies closest to the self-consistent ionization energy curves with capture probability one half. The capture probability was then varied on either side of one half, in hopes that a difference in capture probability could explain the difference in the ionization probabilities when Ar was used as a target instead of Ne. The results proved negative. A variation of capture probability on *either* side one half made the peak heights of the theoretical curves *go up, instead of down.* In other words, the heights of the peaks of the $\tilde{P}_n$ curves are minimum for a capture probability of one half. This negative result was not unexpected, inasmuch as good agreement was achieved in III for Ne$^+$ on Ar by starting with the uniform ionization energy curves and adjusting the capture probability.

Thus, it seems that the target atom has some effect on the ionization energies, and argon as target seems to cause the ionization energies to be independent of the number of electrons escaping. As has been pointed out, this effect does not lie within the framework of the present theory. As a matter of fact, since only the self-consistent ioization energies have been justified *a priori*, the fact that the Ar$^+$ on Ar data follows the uniform ionization energy curves should also be considered as anomolous. Possible explanations for this behavior are

(1) The possibility that the distribution-in-E_T (as distinct from the distribution of E_T among the outer electrons) is dependent on the target atom. A wider half-width in the distribution-in-E_T tends to lower peak heights. In this connection, see Table I of II (Ref. 9), where the effect of a distribution-in-E_T was considered. This effect is in the right direction and of the right magnitude to make the self-consistent ionization energy curves look like the uniform ionization energy curves. The results obtained in II should, however, be regarded as only qualitative, inasmuch as the distribution-in-E_T was there derived on the assumption that the excitation energy was due to electron-electron collisions.

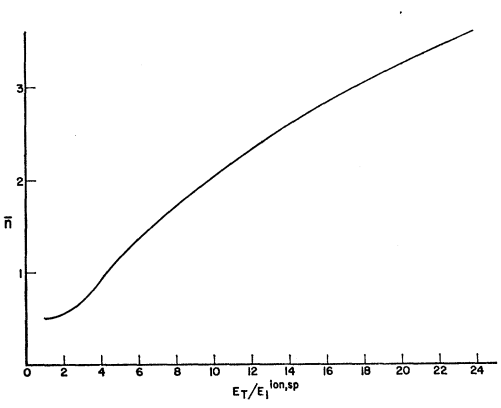

FIG. 9. The mean ionization state $\bar{n}$ is here plotted as a function of the excitation energy E_T in units of the first spectroscopic ionization energy. This dependence follows from the self-consistent ionization energy theory with capture probability one half.

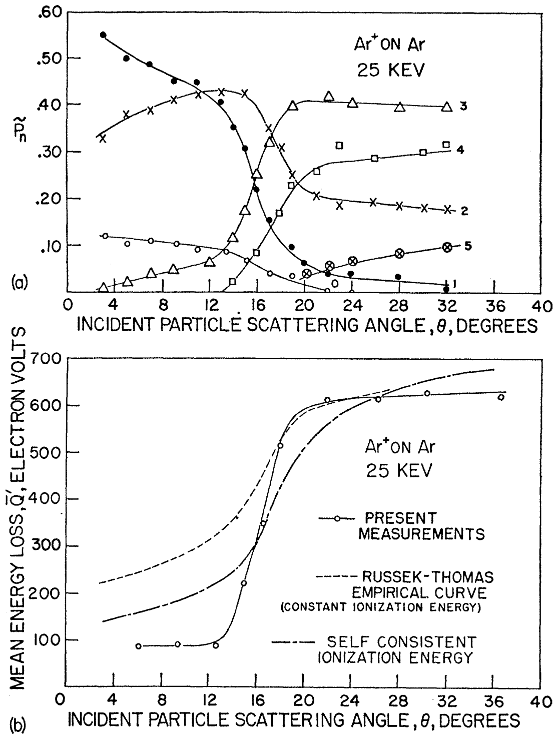

FIG. 10. (a) The experimental ionization probabilities $\tilde{P}_n$ of the scattered incident particles are plotted vs the scattered incident angle for 25 keV Ar$^+$ on Ar collisions. This data is reproduced from Fuls *et al.*[2] (b) The mean inelastic energy $\bar{Q}'$ measured by Morgan and Everhart (Ref. 12) is plotted for this same case. The circles show the experimental data and the solid curve is drawn through them. The dashed curve shows the theoretical results which follow from I assuming a constant ionization energy (independent of n and E_T) which is adjusted to force agreement at large values of θ. Finally, the broken curve shows the results of the self-consistent ionization energy theory, with *no adjustment whatever.*

(2) A proximity effect. That is, there may be an appreciable effect on the ionization energies if another atomic system is nearby at the time of the autoionization transition.

(3) The possibility that the division of excitation energy between projectile and target may depend on whether or not electron capture has taken place.

As a final comparison of the theory with experiment, Fig. 10 shows the inelastic energy for Ar$^+$ on Ar collisions which follows from the present theory. This is compared with the experimental results of Morgan and Everhart.[12] For each value of θ, $\bar{n}$ was determined from the experimental values for $\tilde{P}_n$, shown in part *a* of Fig. 10. With this, the excitation energy of the observed projectile can be read off from Fig. 9, taking $E_1^{\text{ion,sp}}$, the first spectroscopic ionization energy for argon, to be 15.8 eV. This excitation energy is then doubled to obtain the over-all inelastic energy for the entire collision, which is shown as the broken line in Fig. 10(b). Also shown are the experimental curve (the solid line) and, for comparison, the empirical fit obtained in I (the dashed line), assuming a constant ionization energy which was adjusted so as to fit the inelastic-energy data at large values. It should be mentioned, in this respect, that the present agreement, shown by the broken line, was obtained without empirical adjustment. It should also be mentioned, however, that the self-consistent ionization energy case was used in comparing the Ar$^+$ on Ar data which, as has been mentioned, follows the uniform ionization energy curves. This was done because, as mentioned previously, no theoretical justification has been given for the uniform ionization energy limit. One cannot, therefore, be sure of the exact values of this ionization energy, other than that it would not be expected to differ greatly from the self-consistent ionization energies. Thus, this uniform ionization energy has been taken to be equal to E_1^{ion} of the self-consistent ionization energy theory. The closeness of the theoretical to the experimental curve bears this out.

ACKNOWLEDGMENTS

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APPENDIX I

In Sec. II, $P_n^{(N)}(E_T)$ was defined to be the probability that when excitation energy E_T is statistically distributed among the N electrons in the outer shell, n will have enough energy to escape. This is given by the limit, as $\epsilon\rightarrow 0$, of number of ways in which E_T/ϵ units of energy can be divided among N electrons such that n, and only n, have enough energy to escape, divided by the total number of ways in which E_T/ϵ units of energy can be divided among the N electrons.

To facilitate the counting, two quantities are introduced, one of which was defined in I, and the other of which is a generalization of a definition given in I. First, $K_n(m)$ is the number of ways of expressing the integer m as a sum of n nonnegative integers (where $1+2+3$ and $1+3+2$ are counted as two different ways of writing 6 as the sum of three integers.) As pointed out in I, K_n satisfies the recursion relationships

$$K_{n+1}(m)=\sum_{i=0}^{m} K_n(m-i)\,, \qquad \text{(A1)}$$

the solutions of which are given by

$$K_n(m)=0 \quad \text{for} \quad m<0,$$

$$K_n(m)=\prod_{i=1}^{n-1}(m+i)/(n-1)!=\binom{m+n-1}{m} \quad \text{for} \quad m\geq 0, \qquad \text{(A2)}$$

where $\binom{m+n-1}{m}$ is the binomial coefficient. Second, $Q_n^r(m)$ is defined to be the number of ways of expressing the integer m as a sum of n nonnegative integers, *all less than r*. This satisfies the recursion relationship

$$Q_{n+1}^r(m)=\sum_{j=0}^{r-1} Q_n^r(m-j)\,, \qquad \text{(A3)}$$

since taking the $n+1$st integer to be j (which takes on values in turn from zero to $r-1$), the remaining n integers must add up to $m-j$. To start off the recursion relationship, it is clear that

$$\begin{aligned} Q_1^r(m)&=1 \quad \text{for} \quad 0\leq m\leq r-1 \\ &=0 \quad \text{for} \quad m\geq r, \end{aligned} \qquad \text{(A4)}$$

since there is only one way of expressing an integer as the sum of but one integer, and, if that integer is r or greater, the defining condition is violated. This recursion relation is solved by the following expression:

$$Q_n^r(m)=\sum_{i=0}^{[m/r]}(-1)^i\binom{n}{i}K_n(m-ir)\,, \qquad \text{(A5)}$$

which is proven by induction in Appendix II.

Inasmuch as it will be necessary to go to the limit of very small cell size, the limiting expressions for m, $r\gg n$ will also be given:

$$K_n(m)\rightarrow m^{n-1}/(n-1)! \quad \text{for} \quad m\gg n, \qquad \text{(A6)}$$

$$Q_n^r(m)\rightarrow nr^{n-1}\sum_{i=0}^{[m/r]}(-1)^i\frac{((m/r)-i)^{n-1}}{i!(n-i)!} \quad \text{for} \quad m,\, r\gg n. \qquad \text{(A7)}$$

It is now possible to obtain the ionization probabilities $P_n^{(N)}$, first treating the "uniform ionization energy" in which the energy needed by a given electron to escape is independent of the number of electrons which escape.

After this, the results will be generated to the case in which the ionization energy is a function also of the number of escaping electrons. This latter has been referred to as the "staggered ionization energy" case.

1. The Uniform Ionization Energy Case

Let the ionization energy, which, in this case, is independent of the number of electrons escaping, be given by

$$E^{\text{ion}}=r\epsilon. \qquad \text{(A8)}$$

Also let

$$E_T = m\epsilon. \tag{A9}$$

Then, by a simple generalization of the result given in III, the probability that m units of energy statistically distributed among N electrons will result in n electrons having greater than or equal to the ionization energy is given by

$$P_n^{(N)}(m) = \binom{N}{n} \sum_{j=0}^{m-rn} K_n(j) Q_{N-n}{}^r(m-rn-j)/K_N(m). \tag{A10}$$

The expression given by (A10) is easily interpreted. The denominator $K_N(m)$ is the total number of ways in which the energy $E_T = m\epsilon$ can be distributed among the N electrons. Clearly, the numerator must be the number of ways in which n, and only n, electrons have energy $\geqslant r\epsilon$. This is expressed as a product, one factor of which is the binomial coefficient, which gives the number of ways that the n electrons which escape can be chosen from among N electrons. In the sum which this binomial coefficient multiplies, $K_n(j)$ is the number of ways that the kinetic energy $j\epsilon$, which is carried off by the escaping electrons, can be distributed among them. This multiplies $Q_{N-n}{}^r(m-rn-j)$, which is the number of ways in which the energy which remains with the $N-n$ electrons which stay being can be distributed among them, remembering that all these electrons must have energies $\leqslant r\epsilon$. The energy which these electrons share is the excitation energy $m\epsilon$ minus the energy $nr\epsilon$ needed just to free n electrons and minus also the excess energy $j\epsilon$ given them in the form of kinetic energy. The sum, taken over all possible excess energies, adds up the number of ways associated with each of the latter.

Going now to the limit $\epsilon \to 0$, the sum in Eq. (A10) becomes an integral and, using the limiting expressions given by Eqs. (A6) and (A7), the following result is obtained:

$$P_n^{(N)}(\mu) = \binom{N}{n} \frac{(N-1)!}{\mu^{N-1}} \int_0^{\mu-n} \frac{x^{n-1}}{(n-1)!} \times \sum_{i=0}^{[\mu-n-x]} (N-n)(-1)^i \frac{(\mu-n-x-i)^{N-n-1}}{i!(N-n-i)!} dx, \tag{A11}$$

where

$$\mu = m/r = E_T/E^{\text{ion}}, \quad x = j/r = \text{excess kinetic energy}/E^{\text{ion}}. \tag{A12}$$

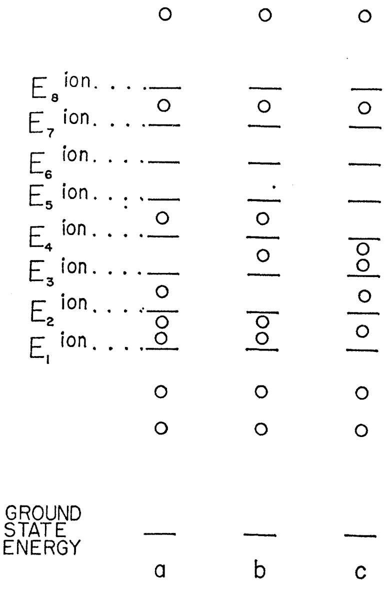

FIG. 11. Distributions which contribute to P_3.

These are clearly the quantities of physical interest. Note that the upper limit of the summation in the integral depends on the variable of integration x. This makes the integrand change discontinuously as $\mu-n-x$ passes through integral values. The functions $P_n^{(N)}$ will, however, be continuous functions of μ, although the slopes will change discontinuously at integral values of μ. (Since, of course, $\mu-n$ will be an integer whenever μ is.) Equation (A11) can be simplified somewhat to

$$P_n^{(N)}(\mu) = \binom{N}{n} \frac{(N-1)!}{(n-1)!} \frac{N-n}{\mu^{N-1}} \times \int_0^{\mu-n} \sum_{i=0}^{[\mu-n-x]} \frac{(-1)^i}{i!(N-n-i)!} \times x^{n-1}(\mu-n-x-i)^{N-n-1} dx. \tag{A13}$$

The integrals in (A13) can all be evaluated using the standard formula,

$$\int_0^a x^n (a-x)^m dx = \frac{n!m!}{(m+n+1)!} a^{n+m+1}, \tag{A14}$$

to give, after a little regrouping and canceling, the final expression for $P_n^{(N)}$:

$$P_n^{(N)}(E_T/E^{\text{ion}}) = \binom{N}{n} \sum_{i=0}^{k} (-1)^i \binom{N-n}{i} \left(1 - \frac{n+i}{E_T/E^{\text{ion}}}\right)^{N-1} \tag{A15}$$

$$\text{for} \quad n+k \leq E_T/E^{\text{ion}} \leqslant n+k+1,$$

which is Eq. (6) in the text. Note that Eq. (A15) yields a different functional form for $P_n^{(N)}$ in each integral range of E_T/E^{ion}.

2. The Staggered Ionization Energy Case

Consider, now, the case in which the ionization energy is a function of the number of electrons escaping. Denote by E_n^{ion} the ionization energy when n electrons escape. Note that E_n^{ion} is *not* the energy needed to remove the nth electron. It is the energy *per electron* needed to remove n electrons. Before a mathematical expression can be obtained for $P_n^{(N)}$ in this case, it is necessary to first decide which distributions will lead to the various ionization states. This is by no means an easy classification to make. To make the calculations tractable, the distributions are classified as follows: *A given distribution will lead to the loss of n electrons if n electrons have energy* $\geqslant E_n^{\text{ion}}$ *while the remaining* $N-n$ *have energy* $\leqslant E_{n+1}^{\text{ion}}$. That this classification is reasonable, but not exactly correct can be seen by reference to the illustration Fig. 11. Parts (a) and (b) of this figure clearly are distributions that contribute to P_3. Case *a* leads to no difficulty at all. Three electrons have energy greater than E_3^{ion} while all the rest have energy less than E_3^{ion}. Case (b) requires a bit more consideration, for here, four electrons have energy greater than E_3^{ion}. However, before all four electrons could escape, they would all need more than E_4^{ion}. Hence, the electron with energy $E_3^{\text{ion}}<E<E_4^{\text{ion}}$ will have to remain behind. (Obviously, if all four cannot escape, the one with the least energy will remain behind.) Case c, however, points up the inexactness of the classification scheme. Here, again, four electrons have energy greater than E_3^{ion}. Two of these four have energy $E_3^{\text{ion}}<E<E_4^{\text{ion}}$ and one of these must be considered to be one of the three electrons with energy greater than E_3^{ion} (and, therefore, to escape), while the other must be considered to be the one with energy less than E_4^{ion} (and, therefore, remain behind). Clearly, the one with greater energy will actually escape and the other will remain behind. Nevertheless, according to the criterion just defined, the roles of these two electrons can be interchanged and the requirements still satisfied (i.e., the electron with the smaller energy can be one of the three which escape). Therefore, among distributions of this type, the number of ways of achieving threefold ionization is overcounted by a factor of two. It would, at this stage, be too difficult to employ a condition which would not overcount and, fortunately, the number of distributions which present this problem constitute only a small percentage of the total.

Now, the fraction of the total number of ways of dividing up m units of energy such that n have energy $\geqslant E_n^{\text{ion}}=r_n\epsilon$ while $N-n$ have energy $\leqslant E_{n+1}^{\text{ion}}=r_{n+1}\epsilon$ is, by analogy with the uniform-ionization energy case,

$$P_n^{(N)}=\binom{N}{n}\sum_{j=0}^{m-nr_n}K_n(j)\times Q_{N-n}^{r_{n+1}}(m-nr_n-j)/K_N(m). \qquad \text{(A16)}$$

The superscript r_{n+1} on the Q allows each of the $N-n$ electrons which stay being to have energy $\leqslant E_{n+1}^{\text{ion}}$, as required.

Defining

$$\mu_n=m/r_n,\quad x=j/r_n,\quad R_n=r_n/r_{n+1}, \qquad \text{(A17)}$$

and going on to the limit $\epsilon\rightarrow 0$:

$$P_n^{(N)}=\binom{N}{n}\{\mu_n^{N-1}/(N-1)!\}^{-1}R_n^{n+1-N}\times\int_0^{\mu_n-n}\frac{x^{n-1}}{(n-1)!}\sum_{i=0}^{[(\mu_n-n-x)R_n]}(-1)^i\binom{N-n}{i}\times\{(\mu_n-n-x)R_n-i\}^{N-n-1}dx \qquad \text{(A18)}$$

and

$$\mu_n=E_T/E_n^{\text{ion}},\quad R_n=E_n^{\text{ion}}/E_{n+1}^{\text{ion}}, \qquad \text{(A19)}$$

carrying out the indicated integrals, using Eq. (A14), and simplifying, yields

$$P_n^{(N)}=\binom{N}{n}\sum_{i=0}^{k}(-1)^i\binom{N-n}{i}\times\left(1-\frac{nE_n^{\text{ion}}+iE_{n+1}^{\text{ion}}}{E_T}\right)^{N-1}$$

$$\text{for}\quad k\leqslant(E_T-nE_n^{\text{ion}})/E_{n+1}^{\text{ion}}\leqslant k+1, \qquad \text{(A20)}$$

which is Eq. (7) in the text.

APPENDIX II

Here, Eq. (A5) is proved by induction. Assume that for some n, Eq. (A5) is true; then, by the recursion relationship Eq. (A3),

$$\begin{aligned} Q_{n+1}^r(m)&=\sum_{j=0}^{r-1}Q_n^r(m-j)\\ &=\sum_{j=0}^{r-1}\sum_{i=0}^{[m/r]}(-1)^i\binom{n}{i}K_n(m-ir-j)\\ &=\sum_{i=0}^{[m/r]}(-1)^i\binom{n}{i}\sum_{j=0}^{r-1}K_n(m-ir-j), \end{aligned} \qquad \text{(A21)}$$

$$Q_{n+1}^r(m)=\sum_{i=0}^{[m/r]}(-1)^i\binom{n}{i}\{\sum_{j=0}^{m-ir}K_n(m-ir-j)-\sum_{j=r}^{m-ir}K_n(m-ir-j)\}. \qquad \text{(A22)}$$

So far, the order of summation has been interchanged and a sum over the range zero to $r-1$ expressed as a sum from zero to $m-ir$ minus the sum form r to $m-ir$. Using, now, the recursion relationship Eq. (A1), which defines the K's to simplify the first term in brackets on the right-hand side of Eq. (A22), and redefining the variable of summation in the second, it is seen that

$$Q_{n+1}{}^{r}(m)=\sum_{i=0}^{[m/r]}(-1)^{i}\binom{n}{i}\Big\{K_{n+1}(m-ir)-\sum_{j=0}^{m-(i+1)r}K_{n}(n-(i+1)r-j)\Big\}$$

$$=\sum_{i=0}^{[m/r]}(-1)^{i}\binom{n}{i}\{K_{n+1}(m-ir)-K_{n+1}(m-(i+1)r)\},$$

$$Q_{n+1}{}^{r}(m)=\sum_{i=0}^{[m/r]}(-1)^{i}\binom{n}{i}K_{n+1}(m-ir)-\sum_{i=1}^{[m/r]+1}(-1)^{i}\binom{n}{i-1}K_{n+1}(m-ir),\quad\text{(A23)}$$

$$Q_{n+1}{}^{r}(m)=(-1)^{0}\binom{n}{0}K_{n+1}(m)+\sum_{i=1}^{[m/r]}(-1)^{i}\left\{\binom{n}{i}-\binom{n}{i-1}\right\}K_{n+1}(m-ir)-(-1)^{[m/r]+1}\binom{n}{[m/r]}\times K_{n+1}(m-[m/r]r-r).\quad\text{(A24)}$$

The first term in (A24) is just that term of the first sum of (A23) for which $i=0$. The second term in (A24) contains all terms in both sums of (A23) for which i varies from 1 to $[m/r]$. Finally, the last term in (A24) is just that term of the second sum for which $i=[m/r]+1$.

Now, $m-[m/r]r-r$ is always less than zero, so that the last term of (A24) vanishes [see Eq. (A2)]. Also, by a little algebraic manipulation, it is seen that

$$\binom{n}{i}-\binom{n}{i-1}=\binom{n+1}{i},$$

$$\binom{n}{0}=1=\binom{n+1}{0}.$$

Therefore, Eq. (A24) reduces to

$$Q_{n+1}{}^{r}(m)=\sum_{i=0}^{[m/r]}(-1)^{i}\binom{n+1}{i}K_{n+1}(m-ir),\quad\text{(A25)}$$

which proves the theorem for $n+1$.

APPENDIX III

Consider, now, the distribution of residual excitation energy E_R, which resides with the electrons that are not ionized, as a function of the over-all excitation energy E_T and the number of electrons which are ionized. According to Eq. (A16) and the discussion which follows Eq. (A10), the number of ways of distributing the energy $E_T=m\epsilon$ among N electrons such that n electrons escape is

$$\binom{N}{n}\sum_{j=0}^{m-rn}K_{n}(j)Q_{N-n}{}^{rn+1}(m-nr_{n}-j).$$

The factor $\binom{N}{n}$ gives the number of ways in which the n electrons which escape can be chosen from among the N electrons in the shell. The factor $K_n(j)$ gives the number of ways in which the excess kinetic energy j can be distributed among the n electrons which escape, and the factor $Q_{N-n}{}^{rn+1}(m-nr_n-j)$ gives the number of ways in which the residual excitation energy can be distributed among the $N-n$ which remain behind, with the requirement, of course, that all have less than the $(n+1)$st ionization energy $E_{n+1}{}^{\text{ion}}=(r+1)\epsilon$. The residual excitation energy,

$$E_R=(m-nr_n-j)\epsilon,$$

is the difference between the over-all excitation energy E_T and the energy $(nr_n-j)\epsilon$ carried off by the n escaping electrons. This latter energy is the sum of the kinetic energy $j\epsilon$ shared by these n electrons and the energy $nE_n{}^{\text{ion}}=nr_n\epsilon$ needed just to ionize them.

The product of these three factors, $\binom{N}{n}K_n(j)$ $Q_{N-n}{}^{rn+1}(m-nr_n-j)$, is then the number of ways of distributing energy $E_T=m\epsilon$ among N electrons such that n electrons escape and the remaining $N-n$ share the energy $E_R=(m-nr_n-j)\epsilon$. The summation in Eq. (A16) is a sum over all possible divisions of energy between the two groups of electrons, in order to obtain all possible distributions in which n electrons escape. [The denominator $K_N(m)$ in Eq. (A16) is the total number of ways, without restriction, of distributing the energy E_T so that the ratio is that fraction of the total number of ways in which n electrons escape, i.e., the ionization probability $P_n{}^{(N)}(m)$.] From the above discussion, it follows that when energy E_T is distributed among N electrons and n electrons are ionized, the relative probability that the remaining electrons will share the residual excitation energy E_R is given by

$$K_n(j)Q_{N-n}{}^{rn+1}(m-nr_n-j).$$

This is the distribution-in-E. The factors $\binom{N}{n}$ and $K_N(m)$ have here been omitted since only the unnormalized distribution-in-E_R are desired. Substituting in the limiting expressions Eqs. (A6) and (A7) for the two factors yields

$$T(n,E_T;E_R)=(E_T-nE_n{}^{\text{ion}}-E_R)^{n-1}\times\sum_{i=0}^{[E_R/E_{n+1}{}^{\text{ion}}]}\frac{(-1)^{i}}{i!(N-n-i)!}\left(\frac{E_R}{E_{n+1}{}^{\text{ion}}}-i\right)^{N-n-1},\quad\text{(A26)}$$

where again factors have been omitted which multiply the entire distribution as a scale factor. This is Eq. (18) of the text.