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On the Theory of Ionization Yield of Radiations in Different Substances*

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The energy absorbed by a substance exposed to an ionizing radiation is used partly in ionization, partly in optical excitation. Arguments based on atomic mechanics are presented, to show that, the greater the ionization potential, the greater is the share of the absorbed energy which is actually spent in ionization. This explains why the ionization potential of a substance has little influence upon the amount of energy that must be absorbed by that substance per each pair of ions actually produced.

1. INTRODUCTION

THE over-all efficiency of a corpuscular or electromagnetic radiation in ionizing a gas is the reciprocal of the average energy spent by the radiation per ion pair produced:

$$\epsilon = V/J, \tag{1}$$

where V is the total amount of radiation energy absorbed by a volume of gas and J is the number of ion pairs produced within this volume.

While the absorption of ionizing radiations by matter starts a complicated chain of phenomena, there are only a few comparatively simple processes that play a central rôle in the mechanism of ionization. Positive ions arise from the stripping of an electron from a molecule; this is caused most frequently by the impact of a fast charged particle against the molecule, whether the primary radiation is corpuscular or electromagnetic. The formation of positive ions with release of electrons is the essential process from the standpoint of energy balance, as negative ions are then formed with a minor release of energy when the free electrons are eventually captured by other molecules.[1]

Experimental determination[2] of ϵ for a number of gases has not yielded very consistent results; but, taken as a whole, it indicates that:

(a) ϵ is largely independent of the characteristics of the primary ionizing radiation, and of the mass, charge, and velocity of the fast charged particles (primary or secondary) whose impact is the immediate cause of the ionization.

(b) While ϵ has a different value for different gases, this value is generally of the order of magnitude of 30 ev and shows no general correlation with the ionization potential of the gas—that is, with the energy actually required to tear off an electron from a gas molecule. (For instance, ϵ is especially small for the rare gases, whereas their ionization potential is especially great.)

(c) An experiment on liquid CS_2 indicates a basic similarity between the values of ϵ in gaseous and in condensed state.[3] This result is important with respect to the action of radiations on biological materials.

Of these results, (a) has been explained theoretically, and (c) is not so unexpected as to require particular investigation at this time. On the other hand, (b) is a remarkable fact, which has important applications and which is still unexplained. Theoretical calculation of ϵ is difficult, because it requires an evaluation of the number of further ionizations produced by the electron set free in each ionization. An early estimate,[4] and a later more complete calculation,[5] using quantum-mechanical methods, gave satisfactory estimates of the order of magnitude of ϵ in general, and of its value for atomic hydrogen in particular. These theories, however, incorrectly predicted a distinct positive correlation of ϵ with the ionization potential. The present

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[1] Radiation in the far ultraviolet is set apart from other ionizing radiations because it produces positive ions primarily by direct action on individual molecules. This radiation is of little practical interest, however, as it can be handled only in a vacuum; therefore it will not be considered in this paper.

[2] J. J. Thomson, *Conduction of Electricity through Gases* (1933), Vol. 2, pp. 103, 160, 237. Geiger-Scheel, *Handbuch der Physik* (1933), Vol. 22, No. 2, pp. 61, 217. W. Gerbes, Ann. d. Physik **30**, 169 (1937).

[3] F. Mohler and L. Taylor, J. Research Nat. Bur. Stand. **13**, 659 (1934).

[4] H. Bethe, Ann. d. Physik **5**, 325 (1930).

[5] E. Bagge, Ann. d. Physik **30**, 72 (1937).

paper is intended to explain this discrepancy between theory and experiment, and to show why, on the contrary, ϵ may be nearly independent of the ionization potential.

In Section 2 available theoretical data are taken as a clue to the observed behavior of ϵ. In Section 3 a discussion of earlier theories traces the cause of their shortcomings and leads to a more definite qualitative understanding of the behavior of ϵ. In Section 4 approximate expressions of ϵ are obtained in terms of optical constants. Substitution of theoretical values of these constants for H and He leads to satisfactory results; in particular, the results give a quantitative justification of the arguments used in Section 3.

2. INFORMATION OBTAINED FROM THE DISTRIBUTION OF OSCILLATOR STRENGTHS

The energy ϵ must be greater than the ionization potential I because a part of the energy absorbed by a substance is always spent for other purposes than ionization. Most of the energy thus "wasted" goes into excitation of optical levels and thus into the production of light. In order to explain how I can be especially large for a particular substance without bringing about a correspondingly large value of ϵ, it must be shown that the "wasted" energy $\epsilon-I$ is especially small in that substance.

Most of the energy of ionizing radiations is absorbed by molecules through induced dipole oscillations of their electronic charge. Lower frequency oscillations lead to excitation, those of higher frequency to ionization of the molecules. The behavior of a gas with reference to dipole oscillations is equivalent to the behavior of a mixture of different harmonic oscillators whose frequencies are the characteristic spectral absorption frequencies of the gas. All of these oscillators absorb approximately the same amount of energy under the influence of an ionizing radiation. The *proportion of oscillators* whose frequency corresponds to any particular process of energy absorption by the gas molecules is called the "oscillator strength" of that process. Therefore the sum of the oscillator strengths of all excitation processes in any substance is an index of the amount of energy spent in excitations, and may be expected to parallel the "waste" of energy incurred by radiation acting upon that substance. In the following table available theoretical information[6, 7] on the oscillator strengths of excitations is compared with the value of the ionization potential, for a series of three characteristic atoms (Table I). This shows a critical inverse correlation between the total oscillator strength of excitations and the ionization potential, suggesting that the "waste" of energy $\epsilon-I$ is actually an inverse function of I. In particular, the data in the table roughly account for the small value of ϵ observed for He. This indicates that theoretical methods should be available for an improved calculation of ϵ.

3. QUALITATIVE DISCUSSION

Arguments will be presented, in the various subdivisions of this section, which lead, respectively, to the following conclusions: (a) The simple "hydrogen-like" approximation of atomic mechanics implies a detailed similarity between different atoms and thus leads to the incorrect prediction of a positive correlation between ϵ and I. (b) Bagge's calculation of ϵ involves the same type of shortcoming as the simple hydrogen-like approximation. (c) Important departures from similarity between atoms act to suppress the correlation between ϵ and I. (d) A qualitative theory of the observed behavior of ϵ follows from a type of hydrogen-like approximation which takes into account the effect of outer screening.

(a)

Bethe's calculation[4] of ϵ is based upon his own theory of the excitation and ionization of molecules by fast charged particles. This theory, which applies primarily to atomic hydrogen, is adjusted for approximate application to other

TABLE I.

Substance	H	He	Li
I(ev)	13.5	24.5	5.4
Oscillator strength of all excitations	57%	21%	88%

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[6] Geiger-Scheel, *Handbuch der Physik* (1933), Vol. 24, No. 1, pp. 443, 467.

[7] J. A. Wheeler, Phys. Rev. **43**, 258 (1933).

molecules by treating each molecular electron as though it belonged to a hydrogen-like atom. In the application to He, for example, each of the two electrons is assumed to behave as though it belonged to a hydrogen-like atom of "effective atomic number" $\mathbf{Z}=1.35$. This value is so chosen that the ionization potential $I=\mathbf{Z}^2Ry$ ($Ry=$ Rydberg's energy $=13.5$ ev) will coincide with the experimental value 24.5 ev. The difference between the actual atomic number of He, $Z=2$, and the effective number $\mathbf{Z}=1.35$ is assumed to take care of the repulsion of the two atomic electrons.

A hydrogen atom and a hydrogen-like atom are thus treated as "dynamically similar" systems, in which all corresponding lengths (e.g., the atomic radii) are in a ratio of 1 to $1/\mathbf{Z}$ and all corresponding energies (e.g., the ionization potentials) are in a ratio of 1 to $\mathbf{Z}^2$. All dimensionless quantities, on the other hand, have the same value in two similar systems; such are the total oscillator strength of all excitations, the ratio of the cross sections for excitation and ionization of the atom by an impinging particle, and the ratio ϵ/I, which is the object of the present study. Bethe's theory is thus bound to yield equal values of all these quantities for all atoms and molecules; in particular, it yields a proportionality between ϵ and I. None of these results agrees with the experimental evidence. Indeed, the large difference between the theoretical values of the oscillator strengths exhibited in Section 2 shows that similarity is a characteristic of the hydrogen-like approximation which is not preserved by the more accurate methods.

(b)

Some comments may be added concerning Bagge's calculation of ϵ,[5] based on the Thomas-Fermi instead of the hydrogen-like model. Since the ionization potential given by the Thomas-Fermi model is a smooth function of the atomic number, a function which does not account for the individual properties of the elements, the theoretical ionization potential of each molecule is replaced in Bagge's calculation by the corresponding experimental value. This procedure is akin to the adjustment of the effective atomic number in the hydrogen-like approximation to yield the correct ionization potential, and therefore it leads to the same incorrect prediction, namely, a positive correlation between ϵ and I.

(c)

A comparison of the ground state and of the excited states of H and He shows a striking departure from dynamic similarity between the two atoms. The binding energies of the electron, as well as the atomic radii of H and He in excited states of equal quantum number, are very nearly equal, since the repulsion of the excited electron in He by the second electron, which remains in the ground state, offsets almost completely the greater attraction exerted by the double nuclear charge. In the ground state of He, on the contrary, the two electrons are, on the average, equally distant from the nucleus; hence their repulsion offsets only a small part of the double nuclear charge, so that the binding energy is far larger and the atomic radius far smaller than the corresponding quantities for H in the ground state.[8]

In general, the binding energy of an electron in an excited state and the radius of its orbit are smooth, slowly varying functions of the atomic number; while for outer electrons in the ground state the binding energy and the orbital radius undergo sharp variations, depending upon the number of electrons in the outermost shell of each atom. As the number of electrons in the outermost shell is increased, the binding energy of each of these electrons (i.e., the ionization potential of the atom) is increased and the radius of the whole atom in the ground state is decreased, but no correspondingly large variation is observed for the excited states.

In the hydrogen-like approximation, which preserves similarity, dimensionless quantities are independent of the ionization potential. Actually, the larger the ionization potential the larger is, in general, the ratio of the binding energy of the outermost electron in the ground state to its binding energy in the first excited state, and the

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[8] A fair description of the ground state of He uses for each electron a hydrogen-like wave function with $\mathbf{Z}=27/16=1.6875$ (compare with $\mathbf{Z}=1.35$ above), while $\mathbf{Z}=1$ should be taken for the wave function of an excited or ionized p electron. The use of different values of $\mathbf{Z}$ for the ground state and for the excited states of atoms has been suggested, for example, by D. R. Bates (Roy. Astronom. Soc. M. N. **100**, 23 (1939)) with reference to the photo-ionization of different gases.

smaller the ratio of the corresponding orbital radii. It may, then, be expected that this lack of similarity should also involve variations of those other dimensionless quantities that are important in the calculation of ϵ—namely, the total oscillator strength of all excitations, the ratio of the cross sections for excitation and for ionization of a molecule by an impinging particle, and the ratio ϵ/I itself. All these quantities are of course directly related to each other. Furthermore, it seems reasonable that they should also be directly related to the ratio of the atomic radii in the ground state and in the excited states. Hence, all of them should be inversely related to the ionization potential I. This conclusion explains qualitatively why the quantity $\epsilon = I \times (\epsilon/I)$ should be little affected by variations of I.

(d)

These general arguments will now be made a little more specific by using a form of hydrogen-like approximation which takes into account the lack of similarity between different atoms. In Bethe's treatment, the repulsion exerted on one electron (k) by all other electrons of the same atom was taken into account by replacing the actual atomic number Z, which characterizes the nuclear attraction, with a lower "effective number" $\mathbf{Z} = Z - s$. The number s is called "inner screening number." It represents the average effect of offsetting—or "screening"—of the nuclear charge by that part of the electronic cloud which is nearer to the nucleus than the electron k, and thus acts to keep k away from the nucleus. Taking into account the inner screening only, it is found that the binding energy of the electron k should be $\mathbf{Z}^2 Ry$; or, more generally,

$$\text{binding energy} = \mathbf{Z}^2 Ry/n^2, \tag{2}$$

if the electron is in a state of total quantum number n. Consideration will be given now to the "outer screening" effect due to that part of the electronic cloud which is farther away from the nucleus than the electron k. The average repulsion of this part of the cloud affects the electron k like an outer screening, i.e., like an outer electrically charged shell. Such a charged shell does not exert any electric force upon a charge in the interior of the shell, where the electron is, but establishes a negative potential difference of $-S$ volts between the interior of the shell and external points at infinite distance. The effect of this potential difference becomes apparent if one tries to remove the electron from the atom: as soon as the electron passes to the exterior of the outer screening shell the charge of this shell exerts a repulsive force and thus helps to remove the electron. This effect causes the binding energy of the electron to be reduced by the product of the potential difference S and of the electronic charge e. Hence (2) must be replaced by

$$\text{binding energy} = \mathbf{Z}^2 Ry/n^2 - eS. \tag{2'}$$

The outer screening effect upon an optical electron[9] is negligible in the case of alkali atoms. However, when there are many electrons in the outermost shell, they interact with one another partly by inner but also partly by outer screening. In this case the effect of outer screening (i.e., S) becomes comparatively large at the expense of the effect of inner screening (i.e., s); and so it happens that, as a rule, all three quantities—the ionization potential I, $\mathbf{Z} = Z - s$, and S—are directly related to each other. S varies even more sharply than I and $\mathbf{Z}$: it is more than half as large as I in the case of He, while it vanishes for H.

For qualitative purposes, the excitation or ionization of an atom or molecule may be resolved into two phases. In the first phase, an electron in the outer shell absorbs energy as if it belonged to a hydrogen-like atom with atomic number $\mathbf{Z} = Z - s$. The average energy absorbed by the electron under the impact of a charged particle is directly related to $\mathbf{Z}^2$; hence it is even greater when $\mathbf{Z}$ is related to the given binding energy I by formula (2′) than when it is related by formula (2). In the second phase, the electron uses its newly acquired energy to move farther away from the nucleus (or nuclei); energy absorptions that would only be sufficient to excite a hydrogen-like atom with atomic number $\mathbf{Z}$ may then result in ionizations, owing to the effect of outer screening which reduces the binding energy. The greater S, therefore, the greater will be the comparative frequency of ionizations.

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[9] Internal electrons are infrequently affected by the impact of fast charged particles and hence are not considered in this connection.

The behavior of ϵ as a function of the atomic number can thus roughly be described as follows. Within any single row of the periodic system, the number of electrons in the outermost shell increases from left to right; and thus, as indicated above, the ionization potential I and the corresponding value of S also increase at the same time. Hence the comparative frequency of excitations decreases with increasing I in such a way as to reduce the "waste" of energy. In the transition from one row to the next along the first column of the periodic system the ionization potential decreases; but at the same time the total quantum number increases, and this in turn is known[4] to increase the "waste" of energy. The variations of ionization potential and of energy waste appear thus to be generally correlated in such a way as to minimize the variations of ϵ.

4. APPROXIMATE CALCULATION OF ϵ

It is proposed here to calculate an approximate expression for ϵ suitable for a quantitative test of the qualitative considerations presented in the previous sections. The calculation will be conducted with particular reference to H and He but may be applicable, with suitable changes, to other substances as well. One basic assumption will be carried over from Bethe's theory:[4] namely, that particles of different charge, mass, and velocity are equally efficient in producing ionizations, provided that they are capable of ionizing at all. The accuracy of this assumption will be discussed on the basis of the results to be obtained.

The total cross section σ for inelastic impacts of a charged particle against an atom will be separated into three parts: (a) σ_e refers to inelastic impacts leading to excitation only; (b) σ_{i1} refers to impacts which lead to ionization and in which the residual energy of the ejected electron is less than the ionization potential I of the atom; and (c) σ_{i2} refers to impacts which lead to ionization and in which the residual energy of the ejected electron exceeds I. The average energy lost by the impinging particle in an impact type (a) or type (b) will be indicated by E_e or E_{i1}. The electron ejected in an impact of type (c) is capable of ionizing further atoms; moreover, according to the assumption made, its kinetic energy is used to produce ionizations with the same efficiency as the energy of the impinging particles. This kinetic energy ($E_{i2}-I$ on the average) is thus merely transferred from one particle to another, which makes little difference to the over-all production of ionizations. Hence the calculation of ϵ may be carried out *as though* the kinetic energy $E_{i2}-I$ were not lost by the impinging particle; that is, as though the impinging particle lost only the energy I in any impact of type (c). The energy ϵ absorbed per ion pair produced can then be expressed thus:

$$\epsilon=(\sigma_e E_e+\sigma_{i1}E_{i1}+\sigma_{i2}I)/(\sigma_{i1}+\sigma_{i2}). \tag{3}$$

In the case of atomic H, sufficient theoretical numerical data are available[10] for a quantitative evaluation of this result. One finds

$$\epsilon\sim 36 \text{ ev}$$

in the case of impinging electrons of 10 kv, and $\epsilon\sim 37$ ev for 100-kv electrons. Since experimental data are not available for atomic H, comparison is limited to observing that this value is near the experimental values of ϵ for most substances. It is also only 8 percent greater than Bagge's corresponding theoretical value.[5] The agreement is therefore not unsatisfactory.

In the case of substances other than H, it is not easy to apply the standard theory of inelastic impacts in sufficient detail to provide good numerical data for evaluating (3). It seems advisable, therefore, to simplify this theory in order to obtain more workable equations. Inelastic impacts of charged particles are conveniently classified according to the change of momentum (and hence the deflection) undergone by the particle. Impacts with a small momentum change are loosely identified with those in which the particle interacts with an atom while passing far outside of it ("grazing impacts"). In cases of extremely small change of momentum, the perturbation exerted by the particle on the atom consists of an electromagnetic pulse of short duration. It is therefore equivalent to the perturbation exerted by a continuous spectrum of electromagnetic radiation of uniform intensity (like a continuous x-ray spectrum), and hence it induces dipole oscillations within the atom.

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[10] Geiger-Scheel, *Handbuch der Physik* (1933), Vol. 24, No. 1, pp. 517 and 519.

Dipole oscillations seldom result in the ejection of an electron having great residual energy. Impacts with large changes of momentum are loosely identified with those in which the impinging particle passes very near to an atomic electron ("head-on impacts"). The atomic electron then acts much as if it were free, and usually receives a large amount of energy. The relative probability of different types of impacts is inversely related to the change of momentum involved: grazing impacts are much more probable, head-on impacts much less probable.

First Approximation

For purposes of orientation, a drastic simplification will be made by assuming that only the extreme type of grazing impacts (involving a very small change of momentum) occurs with any considerable frequency. The circumstance that some of these impacts result in the ejection of an electron with sufficient residual energy to produce further ionizations will be disregarded; that is, the entire cross section for ionization will be taken as σ_{i1}, and it will be assumed that $\sigma_{i2}=0$.[11]

The probability of transition of an atom from the ground (0th) state to the jth excited or ionized state is then proportional to the square of the dipole matrix element $x_{j0}=\int\psi_j x\psi_0 d\tau$ associated with this transition. This matrix element will be assumed, for simplicity, to be real and will be expressed in terms of the atomic unit $a=0.53\times10^{-8}$ cm. Hence,

$$\begin{aligned}\sigma_e&=\text{const. }\textstyle\sum_{ej}x_{j0}^2,\\ \sigma_{i1}&=\text{const. }\textstyle\sum_{ij}x_{j0}=\text{const.}\times x_i^2,\end{aligned}\tag{4'}$$

where the first sum is over excited states, the second over ionized states. The latter is actually an integration and its value is denoted by x_i^2. Moreover,

$$\begin{aligned}\sigma_eE_e+\sigma_{i1}E_{i1}&=\text{const. }\textstyle\sum_j h\nu_{j0}x_{j0}^2\\ &=\text{const. }h^2/8\pi^2ma^2\textstyle\sum_j f_{j0}\\ &=\text{const.}\times Ry.\end{aligned}\tag{4''}$$

(As usual, ν_{j0} and f_{j0} indicate, respectively, the oscillation frequency and the oscillator strength of the transition from 0 to j; $\sum_j f_{j0}=1$, according to Thomas-Kuhn's sum rule; and $Ry=h^2/8\pi^2ma^2$ is Rydberg's energy.) The first approximation for ϵ is then

$$\epsilon_1=(\sigma_eE_e+\sigma_{i1}E_{i1})/\sigma_{i1}=Ry/x_i^2.\tag{4}$$

For atomic H, $x_i^2=0.283$ [12] and hence $\epsilon_1=48$ ev, that is about 35 percent in excess of the value obtained above. Since the frequency of excitations, and hence the "waste" of energy, are comparatively greatest in the case of grazing impacts, it was expected that (4) would yield too great a value of ϵ_1. In general, all the errors involved in the assumption made tend to increase the resulting value of ϵ_1.

In the case of He, x_i^2 has been calculated by using hydrogen-like wave functions with $\mathbf{Z}=27/16$ for the ground state and $\mathbf{Z}=1$ for the excited and ionized states.[8] (This method involves the use of one-electron wave functions that do not belong to a single orthogonal system; this means disregarding the two-electron transitions which, however, are unimportant.)[13] The result is $x_i^2=0.256$, $\epsilon_1=53$ ev. The difference between these results and the ones obtained for H appears to be very small, considering that if the single value $\mathbf{Z}=1.35$ had been used for all states the results would have been $x_i^2=0.156$, $\epsilon_1=87$ ev. The inaccuracy of our method did not seem to warrant the use of better wave functions.

Since x_i^2 is the characteristic of an atom that determines the value of ϵ_1, we should supplement the qualitative considerations of Section 3 by investigating why the difference between the values of x_i^2 for H and for He is so small. x_i^2 was therefore calculated as a function of the parameter $\mathbf{Z}$ characterizing the ground state, while $\mathbf{Z}$ for the ionized states was kept equal to 1. The results are shown in Table II. The third line shows the ratio of $x_i^2=\sum_{ij}x_{j0}^2$ to $x^2_{\text{Av}}=\sum_j x_{j0}^2=1/\mathbf{Z}^2$. ($x^2_{\text{Av}}$ is the mean value of x^2 for an electron in the ground state.) This ratio represents the proportion of all inelastic impacts that produce ionizations; and it increases from 0 to 1 as $\mathbf{Z}$ increases from 0.5 to ∞. The total fre-

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[11] Actually, σ_{i2} should include about 14 percent of the cross section for ionization in the case of H, 24 percent in the case of He.

[12] Geiger-Scheel, *Handbuch der Physik* (1933), Vol. 24, No. 1, p. 442.

[13] J. P. Vinti, Phys. Rev. **42**, 632 (1932).

quency of inelastic impacts, proportional to x^2_{Av}, is steadily decreasing as $\mathbf{Z}$ increases. Therefore, the frequency of ionizations, proportional to x_i^2, shows a maximum which happens to occur at a value of $\mathbf{Z}$ intermediate between those corresponding to H and He. If a single value of $\mathbf{Z}$, determined on the basis of (2), were used for the ground state and the ionized states, the ratio would be fixed at .283, and both x_i^2 and x^2_{Av} would be inversely proportional to $\mathbf{Z}^2$, i.e., to I.

As a further supplement to the discussion at the end of Section 3, it should be noted that the average energy lost by the impinging particle in an inelastic impact is $Ry/x^2_{Av}=Ry\mathbf{Z}^2$ (cf. (4′) and (4″)), and is equal to I or $I+eS$, depending on whether $\mathbf{Z}^2$ is related to I by (2) or by (2′); note that $n=1$, in the case of He. Thus as a direct effect of the outer screening—i.e., of the energy term eS—the average energy lost in an impact becomes greater than the ionization potential; this clearly increases the comparative frequency of ionizations.

The value of $\mathbf{Z}$ to be entered in (2′), and hence the wave function to be used, can best be determined for the ground states of substances other than H and He on the basis of Slater's rules.[14] No similar rules seem to be available, however, for determining the wave functions of the ionized states.

Details of the calculation of dipole matrix elements are given in an appendix.

Second Approximation

Head-on inelastic impacts, in addition to grazing impacts, will now be taken into account; but every impact will be considered as belonging to one extreme type—i.e., as being either typically grazing or typically head-on. This approximation is still quite rough, but it yields values for the total cross sections for ionization or for excitation of H atoms that are close to those obtained by more accurate methods. Also, its results do not appear to depend critically upon the position of the boundary which must be assumed to separate grazing from head-on impacts. In this calculation it will be assumed that an impact is grazing or head-on, according to whether the change of momentum undergone by the impinging particle is smaller or greater than $(2mI)^{\frac{1}{2}}$. Furthermore, it will now be taken into account that $\sigma_{i2}\neq 0$ for grazing as well as for head-on impacts.

The cross section σ_{j0} for induced transition of an atom from the ground to the jth state is then separated into two parts, $\sigma_{j0}{}^{(g)}$ and $\sigma_{j0}{}^{(h)}$, corresponding to grazing or head-on impacts. On the basis of Born's approximation,[15] one finds approximately:

$$\sigma_{j0}{}^{(g)}=(kx_{j0}{}^2\log r)/Ry,\qquad \sigma_{j0}{}^{(h)}=k/(h\nu_{j0})^2, \tag{5′}$$

except that $\sigma_{j0}{}^{(h)}$ vanishes unless the jth state is ionized. In these formulae $k=2\pi z^2e^4/mv^2$ (e and m are charge and mass of an electron, ze and v are charge and velocity of the impinging particle), and $r=2mv^2/I$; r should depend on the index j, but this has been disregarded. On the basis of the analogy with (4′), it follows easily that:

$$\begin{gathered}\sigma_e{}^{(g)}E_e{}^{(g)}=kf_e\log r,\quad \sigma_{i1}{}^{(g)}E_{i1}{}^{(g)}=kf_{i1}\log r,\quad \sigma_{i2}{}^{(g)}I=k(I/Ry)x_{i2}{}^2\log r,\\ \sigma_e{}^{(h)}E_e{}^{(h)}=0,\quad \sigma_{i1}{}^{(h)}E_{i1}{}^{(h)}=k\log 2,\quad \sigma_{i2}{}^{(h)}I=k/2,\\ \sigma_{i1}{}^{(g)}+\sigma_{i2}{}^{(g)}=(kx_i{}^2\log r)/Ry,\quad \sigma_{i1}{}^{(h)}+\sigma_{i2}{}^{(h)}=k/I,\end{gathered} \tag{5″}$$

where the meaning of the indices (g), (h), e, $i1$, $i2$ is the same as used elsewhere in this section. According to (3), (4), (5′), and (5″), the second approximation to the value of ϵ can then be written as:

$$\begin{aligned}\epsilon_2&=\frac{kf_e\log r+kf_{i1}\log r+k\log 2+k(I/Ry)x_{i2}{}^2\log r+k/2}{kx_i{}^2\log r/Ry+k/I}\\ &=Ry/x_i{}^2\frac{(f_e+f_{i1}+x_{i2}{}^2I/Ry)\log r+1.2}{\log r+Ry/x_i{}^2I}=\epsilon_1\frac{1-(f_{i2}-x_{i2}{}^2I/Ry)+1.2/\log r}{1+\epsilon_1/I\log r}.\end{aligned} \tag{5}$$

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[14] J. C. Slater, Phys. Rev. **36**, 57 (1930).

[15] Geiger-Scheel, *Handbuch der Physik* (1933), Vol. 24, No. 1, pp. 493 ff.

Table II.

$\mathbf{Z}$	0.5	1.0	1.2	1.4	1.6	1.6875	1.8	2.0	$\gg 1$
x_i^2	0	0.283	0.313	0.299	0.271	0.256	0.238	0.207	$1/\mathbf{Z}^2$
x_i^2/x^2_{Av}	0	0.283	0.450	0.587	0.693	0.730	0.772	0.828	1

This formula includes two separate corrections to the first approximation: (a) The term in parentheses in the numerator of the final expression takes into account the fact that some of the electrons ejected through dipole oscillations are capable of further ionizing action. (b) The remaining part of the final expression indicates that ϵ_2 is the weighted mean of the quantity $\epsilon_1[1-(f_{i2}-x_{i2}^2 I/Ry)]$—the value of ϵ corresponding to grazing impacts only—and of the quantity $1.2I$—the value of ϵ corresponding to head-on impacts only; the "weights" of head-on and grazing impacts are in the ratio of their frequencies—namely, $\epsilon_1/I \log r$ to I. The following approximate numerical data may be used to calculate ϵ_2 in the case of 10 kv electrons impinging on H or He (relativistic corrections are required in the case of 100 kv electrons) (Table III). Correction (b) is less important for He than for H, because of the larger value of I; but at the same time the "outer screening" again becomes effective by greatly increasing the importance of correction (a).

Incidentally, formulae (4) and (5) show why ϵ is largely independent of the physical characteristics of the impinging particle. In the first approximation (grazing impacts only), the action of the particle is equivalent to the action of a continuous spectrum of electromagnetic radiation, and ϵ_1 is wholly independent of the mass, charge, and velocity of the particle. In the second approximation, the velocity of the particle determines the parameter r, which in turn affects, through a logarithmic factor only, the weight of correction (b). Formula (5) shows that this influence of the velocity is directed towards making ϵ_2 greater for faster particles. The ionizing secondary electrons (whose residual energy exceeds I) are generally not very fast, and hence they should be more efficient in ionizing than the primary particle. This consideration introduces a further corrective factor that cannot be easily calculated but must reduce ϵ to below ϵ_2. It must also be emphasized that our calculation has been based entirely on Born's approximation to the theory of inelastic impacts; this approximation is not accurate when applied to comparatively slow secondary ionizing electrons, so that any assumption as to the ionizing efficiency of secondary electrons is necessarily tentative.

The calculation shown in this section does not bring the theoretical value of ϵ for He into close agreement with its experimental value, which is less than 30 ev.[2] It indicates, however, that the effect of outer screening discussed in Section 2 is of sufficient importance to cancel the effect of the difference between the ionization potentials of H and of He. The rough simplifications introduced into the theory of inelastic impacts do not seem to have appreciably affected the result; since, in the case of 10 kv electrons impinging on H, the same result is found by using (5) as by evaluating (3) on the basis of Bethe's numerical data.

APPENDIX

The computation of dipole matrix elements, using hydrogen-like wave functions with different values of $\mathbf{Z}$ ($\mathbf{Z}_g$ and $\mathbf{Z}_e=\mathbf{Z}_g/\alpha$) for the ground state and for the excited states, can be easily carried out if the wave functions are expressed by means of the confluent hypergeometric function. The result for a $1s$ to np transition is:

$$x_{n1}^2=(1/\mathbf{Z}_e^2)(2^8/3)\alpha^3(2\alpha-1)n^7(n^2-1)$$
$$\times(n\alpha-1)^{2n-6}/(n\alpha+1)^{2n+6} \text{ atomic units.}$$

This formula was used in the computations for He with $\mathbf{Z}_e=1$, $\alpha=27/16$. The sum of the squares

Table III.

	H	He
f_{i2}	0.10	0.35
x_{i2}^2	0.04	0.06
I/Ry	1.0	1.81
$f_{i2}-x_{i2}^2 I/Ry$	0.06	0,24
$\log r$	8.0	7.4
ϵ_2	36 ev	38 ev

of the matrix elements for the ionized states of the p series is then given by:

$$(x^2)_{11}-\sum_{2}^{\infty}x_{n1}{}^2=1/\mathbf{Z}_g{}^2-\sum_{2}^{\infty}x_{n1}{}^2,$$

where the summation over n converges rapidly. The use of this formula relies on the fact that the set of p wave functions, considered as functions of the distance from the nucleus, forms a complete system.

A different method may be suggested here for calculating dipole matrix elements by means of properly adjusted hydrogen-like wave functions. For an electron in the region where the wave functions of the ground state and of the excited states overlap, the inner screening number s is likely to be nearly $Z-1$; therefore it should not be proper in this problem to use a value of $\mathbf{Z}(=Z-s)$ much different from 1. On the other hand, even with the restriction $\mathbf{Z}=1$, it is still possible to adjust the binding energies and the atomic radii for each state by introducing a suitable potential term A/r^2. Indicate, then, the ionization potential of an atom—i.e., the binding energy of an electron in the outermost shell—by $Ry/\mathbf{n}_g{}^2$, and the binding energy of an electron in the first excited state of a series of $Ry/\mathbf{n}_e{}^2$. Since the behavior of the wave functions in the interior of the atom is not very important for our purpose, it may be assumed that the radial parts of the wave functions of these states have no node. Hence the "effective total quantum number" $\mathbf{n}$ may be written in the form $l+\mathbf{l}+1$, where l is the actual azimuthal quantum number and $\mathbf{l}$ is an additional effective azimuthal quantum number which defines the additional potential term $(h^2/8\pi^2m)\mathbf{l}(\mathbf{l}+1)/r^2$. The binding energy of the $(p+1)$th term of the excited series is then $Ry/(\mathbf{n}_e+p)^2$. The square of the dipole matrix element for the transition from the ground state to this state is:

$$\begin{aligned}x_{\mathbf{n}_e+p,\,\mathbf{n}_g}{}^2=&\frac{l'}{2l_g+1}\,\frac{\Gamma(2\mathbf{n}_e+p)}{p!\Gamma(2\mathbf{n}_g)}\exp\{2(\mathbf{n}_g+\mathbf{n}_e)\log 2\\&-\log 3+2(\mathbf{n}_e+1)\log\mathbf{n}_g+2(\mathbf{n}_g+1)\log(\mathbf{n}_e+p)\\&-2(\mathbf{n}_g+\mathbf{n}_e+2)\log(\mathbf{n}_g+\mathbf{n}_e+p)\}\Bigg[\frac{\Gamma(\mathbf{n}_g+\mathbf{n}_e+2)}{\Gamma(2\mathbf{n}_e)}\\&\times F\left(-p,\,\mathbf{n}_g+\mathbf{n}_e+2,\,2\mathbf{n}_e,\,\frac{2\mathbf{n}_g}{\mathbf{n}_g+\mathbf{n}_e+2}\right)\Bigg]^2,\end{aligned}$$

where l' is equal to l_g or to l_e, whichever is larger and where F indicates the hypergeometric function. The factor in square brackets can be also indicated by:

$$\sum_{\nu}\binom{p}{\nu}(\Gamma(\mathbf{n}_g+\mathbf{n}_e+2+\nu)/\Gamma(2\mathbf{n}_e+\nu))\times(-2\mathbf{n}_g/(\mathbf{n}_g+\mathbf{n}_e+p))^{\nu}.$$

The sum of the squares of the matrix elements for the ionized states of the series is given by:

$$\begin{aligned}(l'/(2l_g+1))(x^2)_{\mathbf{n}_g\mathbf{n}_g}-\sum_{0}^{\infty}x_{\mathbf{n}_e+p,\,\mathbf{n}_g}{}^2\\=(l'/(2l_g+1))\mathbf{n}_g{}^2(\mathbf{n}_g+1/2)(\mathbf{n}_g+1)/3\\-\sum_{0}^{\infty}x_{\mathbf{n}_e+p,\,\mathbf{n}_g}{}^2.\end{aligned}$$