The Threshold Law for Single Ionization of Atoms or Ions by Electrons

GREGORY H. WANNIER
Bell Telephone Laboratories, Murray Hill, New Jersey
(Received February 3, 1953)

When an electron hits an atom or ion, it may knock off an electron. This process is fundamental in almost all types of gas discharge. The reaction is endothermic; hence there is a threshold value in the electron energy below which it does not occur. In this paper, the dependence of the yield on the energy just above this threshold is derived. The derivation is not rigorous because it circumvents some of the difficulties of the three-body problem by applying ergodicity, albeit in a weakened form. The result is that, for atoms, the yield rises as the 1.127th power of the energy excess. For ions the exponent lies between this number and unity.

I. INTRODUCTION

IN almost all forms of electric discharge through a gas the ionization of neutral molecules by electrons is a fundamental process. General ideas about the efficiency of this process can be gained from the discharge process; on the other hand, an accurate determination of ion yield as a function of the energy of the bombarding electron is still an object of research. Results obtained to date are not in disagreement with the hypothesis that near an energy threshold the yield varies linearly with the energy excess.[1,2] It is hard however to settle such a question from experiment alone; therefore it seems desirable to take it up from the theoretical side.

Accounting theoretically for detailed observations on reactions or transmutations is difficult; the reactants usually pass through an intermediate state in which all constituents are tightly coupled. It has been pointed out by Wigner,[3] however, that it is a relatively easier problem to derive the "threshold law," that is, the dependence of the yield on the energy in the neighborhood of the energy threshold. In such a derivation the final escape of the reaction products may be separated from the reaction proper which is confined to a small "reaction zone." It is then shown that the threshold arises (generally) from a feature of the escape process, namely, lack of kinetic energy for complete escape. This feature is amenable to calculation even when the reaction proper is not.

Wigner has applied his idea to all relevant cases in which the reaction product consists of two particles escaping from each other. In the ionization process which is under study here the final number of particles is three: two electrons and a positive ion. This produces obstacles, both technical and conceptual, if an extension of Wigner's theory is attempted. The removal of the technical obstacles occupies Sec. II, and of the conceptual ones Sec. III; Sec. IV contains the derivation of the law itself.

[1] Fox, Hickam, Kjeldaas, and Grave, Phys. Rev. 84, 859 (1951).
[2] F. T. McClure, private communications.
[3] Eugene P. Wigner, Phys. Rev. 73, 1002 (1948).

II. MECHANICS OF THREE-BODY MOTION

The technical obstacle which we face in the problem of ionization by electrons is the fact that we deal with a three-body problem. It is true that if Wigner's basic idea is to be used, no description of the ionization process in the reaction zone is required. However even in the outside space we are still faced with three particles linked to each other by inverse square law forces; a correct treatment of this feature is essential if we are to end up with the right answer for the threshold law.

The problem of three particles linked by inverse square central forces is known mainly from celestial mechanics as the "problem of three bodies." The present problem is a specialization of the general case because two of the bodies are identical. However even with this restriction a full quantum-mechanical description of all possible final states is hardly possible. Fortunately this is not needed. We can get along with incomplete information about states satisfying special conditions, and still get the final answer. This information will be collected in the following paragraphs.

Let the charge of an electron be $-e$ and the mass m. Let the charge of the ion after ionization be Ze. The ion is sufficiently heavy so that it may be considered at rest during the reaction. The connection of symmetry and spin will be passed over at this time and will be taken up later in an appropriate connection. On the other hand, the orbital angular momentum needs full discussion. Among the angular momenta contained in the plane wave representing the incoming electron, the s part couples most strongly with an atomic system. In the same way an S state for the two outgoing electrons is favored over other angular momenta if it is consistent with the angular momentum change taking place within the ion. We conclude from this that, in general, the probability of reaction into an S state has a threshold at least as favorable as the probability of reacting into higher angular momentum states. This reasoning is confirmed by the explicit results of the Tables I, II, and III of reference 3. The threshold law for reaction into an S state for the electron pair will therefore be worked out in the belief that it will generally yield the true threshold law.

The assumption of zero angular momentum simplifies

the Hamiltonian greatly. In general, our problem would require for description six coordinates: the two distances r_1 and r_2 of the electrons from the ion, and four angles. With zero angular momentum, the motion becomes confined to a fixed plane, and the angles are reduced from four to two. The condition of zero angular momentum in the plane permits elimination of one more angle. The one remaining angle is preferably taken as the angle γ between the two vectors $\mathbf{r}_1$ and $\mathbf{r}_2$. In terms of the three coordinates r_1, r_2, γ and the conjugate momenta p_1, p_2, p_γ, the Hamiltonian of the system outside the reaction zone takes the form

$$\mathcal{H}=\frac{1}{2m}(p_1^2+p_2^2)+\frac{1}{2m}\left(\frac{1}{r_1^2}+\frac{1}{r_2^2}\right)p_\gamma^2 - e^2\left[\frac{Z}{r_1}+\frac{Z}{r_2}-\frac{1}{(r_1^2+r_2^2-2r_1r_2\cos\gamma)^{\frac{1}{2}}}\right]. \quad (1)$$

A more convenient coordinate system is obtained by setting

$$r_1=r\cos\tfrac{1}{2}\chi, \quad (2a)$$

$$r_2=r\sin\tfrac{1}{2}\chi, \quad (2b)$$

$$0\leqq\chi\leqq\pi. \quad (2c)$$

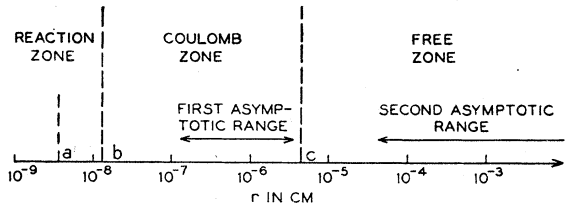

FIG. 1. Qualitative picture of the zones of behavior of r; $r=(r_1^2+r_2^2)^{\frac{1}{2}}$.

This puts (1) in the form

$$\mathcal{H}=\frac{1}{2m}\left[p_r^2+\frac{4}{r^2}p_\chi^2+\frac{4}{r^2\sin^2\chi}p_\gamma^2\right] - \frac{Ze^2}{r}\left[\frac{1}{\cos\frac{1}{2}\chi}+\frac{1}{\sin\frac{1}{2}\chi}-\frac{1/Z}{(1-\sin\chi\cos\gamma)^{\frac{1}{2}}}\right]. \quad (3)$$

In Eq. (3) the symmetry in the two electrons has become a symmetry in the variable χ about the value $\chi=\pi/2$.

One advantage of the form (3) is to make the variable r appear. We shall take as the boundary between the reaction zone and the outside space the hypersphere

$$r=b, \quad (4)$$

where b may be assumed of the order of magnitude of the Bohr radius a.

A second subdivision in the radial coordinate plays a role in the following work. It is implicit in our problem that the total energy ϵ of our system must be taken as positive and small. We may make this more precise by demanding that $\epsilon b/Ze^2$ be small compared to unity. In this case a second boundary radius, $r=c$, makes its appearance, separating the region in which the kinetic energy is essentially equal to ϵ from an inner one in which it essentially cancels the (negative) potential energy. For reasons of convenience we define c precisely as

$$c=e^2(4Z-1)/\sqrt{2}\epsilon. \quad (5)$$

We shall call the region between the two boundaries the Coulomb zone, and the region beyond c the free zone. A qualitative picture of these zones is shown in Fig. 1. The great width of the Coulomb zone will be seen to have the consequence that the motion falls into a first asymptotic pattern in the outer part of this zone. This behavior gets disturbed near the zone boundary c; a second, different asymptotic pattern then arises after the free zone is well penetrated. A passage to the limit in ϵ implies a sweep of the zone boundary c to infinity; the first asymptotic behavior is thus the true one for orbits of zero energy. It should be observed, as a restriction to this reasoning, that the zone boundary c loses its meaning when χ lies very close to 0 or π, that is, when one electron stays far behind the other one.

In either one of the outer zones the *motion of the electrons is essentially classical.* This is seen as follows. If we neglect the interaction between the two electrons, then ionization requires that the kinetic energy of either be larger than the negative of its potential energy:

$$\tfrac{1}{2}mv^2\geqq Ze^2/r. \quad (6)$$

Equation (6) entails a constraint on the de Broglie wavelength λ which reads

$$2\pi\lambda/r\leqq(a/Zr)^{\frac{1}{2}}. \quad (7)$$

Outside the reaction zone the right-hand side is small; hence wave packets can be constructed for each electron and classical mechanics employed. The introduction of an electron-electron interaction disturbs this argument in two ways. In the first place it permits transfer of energy so that (6) breaks down for one of the electrons, but not the other. It will be seen in the course of the argument that for the important orbits the difference between the speeds is always small compared to the speed itself, hence the inequalities (6) and (7) cannot be violated seriously for this reason. The second effect of the interaction is the addition of a negative term to the right-hand side of (6). Configurations in which this term is important must be reached against the repulsion of the two electrons; the tendency of the two electrons to avoid each other will therefore limit the term and effectively preserve the inequality (7). It will be seen, in fact, that for the orbits of importance for ionization the angle γ approaches asymptotically the value π. Furthermore, if there is any serious difficulty about making the right-hand side of (7) small, then we are

still free to use a radius $r=b$ which is larger than the Bohr radius a.

These preliminary considerations reduce the general quantum problem of three bodies to a *classical analysis of the Hamiltonian* (3), *with particular emphasis upon asymptotic properties of orbits* of small positive energy ϵ which arise from a small reaction zone at the origin.

The equations of motion for the Hamiltonian (3) read

$$m\ddot{r}=\tfrac{1}{4}mr\dot{\chi}^2+\tfrac{1}{4}mr\sin^2\chi\dot{\gamma}^2-(Ze^2/r^2)B(\chi,\gamma), \quad (8)$$

$$\frac{d}{dt}(\tfrac{1}{4}mr^2\dot{\chi})=\tfrac{1}{4}mr^2\sin\chi\cos\chi\dot{\gamma}^2+\frac{Ze^2}{r}\frac{\partial B(\chi,\gamma)}{\partial\chi}, \quad (9)$$

$$\frac{d}{dt}(\tfrac{1}{4}mr^2\sin^2\chi\dot{\gamma})=\frac{Ze^2}{r}\frac{\partial B(\chi,\gamma)}{\partial\gamma}, \quad (10)$$

where $B(\chi,\gamma)$ is an abbreviation for

$$B(\chi,\gamma)=\frac{1}{\cos\frac{1}{2}\chi}+\frac{1}{\sin\frac{1}{2}\chi}-\frac{1/Z}{(1-\sin\chi\cos\gamma)^{\frac{1}{2}}}. \quad (11)$$

The equations possess an energy integral which will be assumed zero or positive and small,

$$\epsilon=\tfrac{1}{2}m\dot{r}^2+\tfrac{1}{8}mr^2\dot{\chi}^2+\tfrac{1}{8}mr^2\sin^2\chi\dot{\gamma}^2-(Ze^2/r)B(\chi,\gamma). \quad (12)$$

A number of properties of the equation system (8)–(10) will now be enumerated and some limiting cases worked out. The results obtained will find their application in Sec. IV.

We observe first that the equations obey a *similarity principle*, that is, they are invariant under the substitutions,

$$r\to\alpha r, \quad (13a)$$

$$\chi\to\chi, \quad (13b)$$

$$\gamma\to\gamma, \quad (13c)$$

$$t\to\alpha^{\frac{3}{2}}t, \quad (13d)$$

$$\epsilon\to\alpha^{-1}\epsilon. \quad (13e)$$

The principle gains its full effectiveness if it is put to a double use: In the first place, the entire pattern of orbits expands but remains similar to itself as ϵ is reduced; in addition, at a fixed but small energy the orbits in the reaction and Coulomb zones consist of families of similar orbits.

The special position of the coordinate r is brought out by the theorem that in any orbit r *has one single minimum and no maximum.* We prove this by combining (8) and (12) in the form

$$m\dot{r}\ddot{r}=-\tfrac{1}{2}m\dot{r}^2+\tfrac{1}{8}mr^2\dot{\chi}^2+\tfrac{1}{8}mr^2\dot{\gamma}^2\sin^2\chi+\epsilon. \quad (14)$$

At a stationary radius r, the velocity $\dot{r}$ vanishes; $\ddot{r}$ is then a sum of positive terms and is itself positive; hence $\dot{r}$ is increasing, and r has a minimum. In the special case of zero energy the possibility arises that all velocities vanish simultaneously; at such a point $\ddot{r}$ is also zero, and higher derivatives must be brought in. We observe first from (12) that B is also zero, and then from (11) that $\partial B/\partial\chi$ and $\partial B/\partial\gamma$ cannot vanish simultaneously with B (unless $Z=\frac{1}{4}$ which is physically impossible); hence, from (9) and (10), the second derivatives of χ and γ cannot both be zero. The first nontrivial equation results then from (14) by differentiating twice. We find

$$\dot{r}=0, \quad \ddot{r}=0, \quad \dddot{r}=0, \quad \ddddot{r}>0.$$

$\dot{r}$ is thus again increasing as in the general case preceding. The theorem makes the concept of "outgoing orbits" a rigorous one, permits measuring flux along a surface $r=\text{const}$, and suggests the use of r as independent variable in the place of t if we wish to discuss the nature of the orbits.

The two properties just proved yield, when combined, the fact that *all orbits initially symmetric in the two electrons lead to the escape of both particles* (*double escape*). This is a consequence of the fact that the equations,

$$\chi=\pi/2, \quad (15a)$$

$$\dot{\chi}=0, \quad (15b)$$

$$\dot{r}>0, \quad (15c)$$

are preserved in time.

In the work to follow we are only interested in the outgoing orbits. To discuss their shape we follow up the idea expressed above. We use as independent variable the quantity

$$r=be^q, \quad (16)$$

and eliminate the time by a standard procedure of mechanics. We find

$$\frac{\chi''-\gamma'^2\sin\chi\cos\chi}{1+\frac{1}{4}\chi'^2+\frac{1}{4}\gamma'^2\sin^2\chi}+\chi'=\frac{2\partial\ln B(\chi,\gamma)/\partial\chi+\frac{1}{2}\chi'}{1+[\epsilon be^q/Ze^2B(\chi,\gamma)]}, \quad (17)$$

$$\frac{\gamma''+2\chi'\gamma'\cot\chi}{1+\frac{1}{4}\chi'^2+\frac{1}{4}\gamma'^2\sin^2\chi}+\gamma'=\frac{2\csc^2\chi\partial\ln B(\chi,\gamma)/\partial\gamma+\frac{1}{2}\gamma'}{1+[\epsilon be^q/Ze^2B(\chi,\gamma)]}. \quad (18)$$

Here the primes denote differentiation with respect to q.

Before discussing orbits in general it is useful to treat first the case of *zero energy*. The first theorem to be proved for this case is that *almost all orbits end up asymptotically at* $\chi=0$ *or* $\chi=\pi$ and that *all these orbits lead to single escape only*. A quick feeling for this statement can be gained by "switching off" temporarily the interaction of the two electrons. In the orbits leading to double escape the electrons then describe congruent parabolas in the same plane so as to cancel each other's angular momentum, and the energy of each electron is zero separately. However, it is infinitely more probable that the electrons have equal energies of

opposite sign. One electron then describes a hyperbola, the other an ellipse; because of (2), χ then approaches either 0 or π; double escape is not accomplished.

In the presence of interaction between the two electrons the establishment of the theorem becomes very much more difficult, although it is intuitively just as reasonable. We start out from (17) and (18), with the denominator on the right-hand side equal to unity. The independent variable does not then occur explicitly in the equations, in accordance with the similarity principle. This means first that the orbits arising from the reaction zone differ from the generality of orbits only in a scale factor and thus share proportionately in all types of asymptotic behavior. Second, Eqs. (17) and (18) become the equations of a simulated mechanical system in which q is the simulated time and which possesses a simulated energy relation. This relation is seen to be

$$(d/dq)[\ln(1+\tfrac{1}{4}\chi'^2+\tfrac{1}{4}\gamma'^2\sin^2\chi)-\ln B(\chi,\gamma)] = -\tfrac{1}{4}(\chi'^2+\gamma'^2\sin^2\chi). \quad (19)$$

The equation is one of a dissipative mechanical system. The geometry corresponds to the surface of a sphere on which χ is the pole distance and γ the azimuth. The potential energy on this surface equals $-\ln B(\chi,\gamma)$, it is shown in Fig. 2 in stereographic projection; the hemisphere not shown is identical with the one shown. The figure is drawn for the case of atoms that is $Z=1$; however the picture remains qualitatively the same as long as $Z>\frac{1}{4}$. We see at the bottom an inaccessible domain, surrounded by an infinite potential wall; this is the region where the true potential, $-e^2B/r$, is positive. Within the accessible area no stable minimum exists. The lowest regions are two infinitely deep troughs at $\chi=0$ and $\chi=\pi$. These features together with the dissipative structure of (19) prove that χ must almost always end up in one of them; this is the first half of the theorem. The second half is proved by analyzing the asymptotic behavior of χ near one of the troughs, say $\chi=0$. In this limit, the potential term in Eq. (17) becomes positive and very large. Neither a term in χ'' nor one in χ' can balance it in the mean, although they may make contributions of this order during certain periods. The reason is that χ becomes small by assumption and hence χ' and χ'' are either small themselves or, if they are large, they necessarily oscillate in sign to keep χ converging to zero. The balance must therefore be provided in the mean by the second term on the left;[4] this equivalence reads $\chi\gamma'^2/(1+\frac{1}{4}\chi'^2+\frac{1}{4}\chi^2\gamma'^2) \approx 2/\chi$. Multiplying up with χ and adding a term on each side we get it in the form $(\chi'^2+\chi^2\gamma'^2)/(1+\frac{1}{4}\chi'^2+\frac{1}{4}\chi^2\gamma'^2)\approx 2+\chi'^2/(1+\frac{1}{4}\chi'^2+\frac{1}{4}\chi^2\gamma'^2)$, or $(\chi'^2+\chi^2\gamma'^2)/(1+\frac{1}{4}\chi'^2+\frac{1}{4}\chi^2\gamma'^2)\gtrsim 2$. This yields finally $\chi'^2+\chi^2\gamma'^2\gtrsim 4$. We now apply this result to Eq. (19). The kinetic energy term is then seen to be completely negligible; the remainder becomes $\chi^{-1}d\chi/dq\lesssim -1$, and finally $\chi\lesssim Ae^{-q}$, or, with (16), $\chi\cdot r\lesssim Ab$. This is the desired result which proves the theorem.

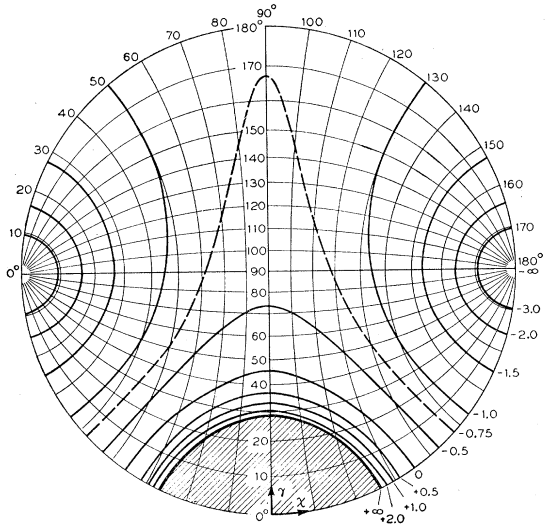

FIG. 2. Plot in stereographic projection of the simulated potential $-\ln B(\chi,\gamma)$. The second hemisphere is a mirror image of the one shown.

In looking for *orbits leading to double escape at zero energy* we look for a manifold whose *dimension is lower than the total.* This manifold is represented by unstable ridges or points in the simulated potential diagram of Fig. 2. There is one unstable equilibrium point at $\chi=\pi/2$, $\gamma=\pi$. For this point the equations for the orbit vanish identically; physically this means that the symmetric escape of two electrons in opposite directions retains this character in future times. Connected with this point in Fig. 2 there is an unstable ridge $\chi=\pi/2$. This is the set of symmetric orbits. We have already shown that all of them lead to double escape; Fig. 2 permits us now to describe their behavior in γ. The potential in γ has a stable minimum at $\gamma=\pi$ flanked by inaccessible towers near $\gamma=0$ and $\gamma=2\pi$. The motion is therefore oscillatory about $\gamma=\pi$ with gradually decreasing amplitude because of the dissipation feature of Eq. (18).

The symmetric orbits are lower by two dimensions than the total set of orbits. This may be seen from (15). However, *at zero energy the total set of orbits leading to double escape has only one less dimension than all orbits; all these orbits approach asymptotically the point* $\chi=\pi/2$, $\gamma=\pi$. It is again useful to check this theorem in a preliminary way for the case with "switched off" electron-electron interaction. The case discussed here is the one where the electrons run in congruent parabolas in the same plane, but with a difference in their timing. The asymptotic behavior in these parabolas is $r_1 \sim A(t-t_1)^{\frac{2}{3}}$, $r_2\sim A(t-t_2)^{\frac{2}{3}}$. With the definition (2) of r and χ this yields easily

$$\chi-\pi/2\sim(t_1-t_2)(A/r)^{\frac{3}{2}}. \quad (20)$$

[4] The ambiguous language used here arises from the fact that we must average over several cycles of the quasi-elliptic motion of the electron staying behind; I was unable to find a rigorous averaging process accomplishing this.

Equation (20) not only proves the theorem for the case $Z=\infty$ (except for the γ-part of it which is not true in this limit) but also exhibits the manner in which the limit is reached. We now are to explore this behavior for Z general. In Fig. 2 this means that we must analyze the orbits which start out away from the ridge $\chi=\pi/2$ but for which χ and χ' are just balanced so that χ' vanishes asymptotically as $\chi\to\pi/2$. The existence of such orbits is made abundantly clear by Fig. 3. The figure shows this exceptional curve $\chi(q)$ which results from numerical integration of (17) in the particular case $\gamma=\pi$ (which is a stable valley). Usually we have a doubly asymptotic behavior around $\chi=\pi/2$ and $\gamma=\pi$ which is handled conveniently by linearizing (17) and (18) around this point. For this purpose the function $B(\chi,\gamma)$ defined by (11) is to be replaced by the expansion

$$B(\chi,\gamma)=2\sqrt{2}-\frac{1}{2}\sqrt{2}\frac{1}{Z}+\frac{1}{2}\left(\frac{3}{2}\sqrt{2}-\frac{1}{8}\sqrt{2}\frac{1}{Z}\right)\left(\chi-\frac{\pi}{2}\right)^2$$
$$-\frac{1}{2}\frac{1}{8}\sqrt{2}\frac{1}{Z}(\gamma-\pi)^2. \tag{21}$$

Equations (17) and (18) then read,

$$\chi''+\frac{1}{2}\chi'-\frac{12Z-1}{8Z-2}\left(\chi-\frac{\pi}{2}\right)=0, \tag{22}$$

$$\gamma''+\frac{1}{2}\gamma'+\frac{1}{8Z-2}(\gamma-\pi)=0. \tag{23}$$

The asymptotic motion in χ separates from the one in γ. The general solution is

$$\chi-\pi/2=e^{-\frac{1}{4}q}(C_1e^{-\frac{1}{2}\mu q}+C_2e^{+\frac{1}{2}\mu q}) \tag{24}$$

$$\gamma-\pi=C_3e^{-\frac{1}{4}q}\cos(\tfrac{1}{2}\rho q+C_4). \tag{25}$$

Here we have set for brevity

$$\mu=\tfrac{1}{2}[(100Z-9)/(4Z-1)]^{\frac{1}{2}}, \tag{26}$$

$$\rho=\tfrac{1}{2}[(9-4Z)/(4Z-1)]^{\frac{1}{2}}. \tag{27}$$

The solutions form a four-dimensional manifold among which the symmetric subset is selected by the two constraints: $C_1=0$, $C_2=0$. Because of the inequality,

$$\mu\geqq 5/2, \tag{28}$$

the solution will diverge from the ridge $\chi=\pi/2$ unless $C_2=0$. Thus the total set leading to double escape is obtained by this one constraint. Thus the theorem is proved, and the exact asymptotic behavior,

$$\chi-\pi/2\approx C_1(b/r)^{\frac{1}{2}\mu+\frac{1}{4}}, \tag{29}$$

is derived. The formula agrees with (20) in the appropriate limiting case. It should be observed before leaving this subject that the solutions (24) and (25) satisfy the similarity principle in its stringent form. We accomplish

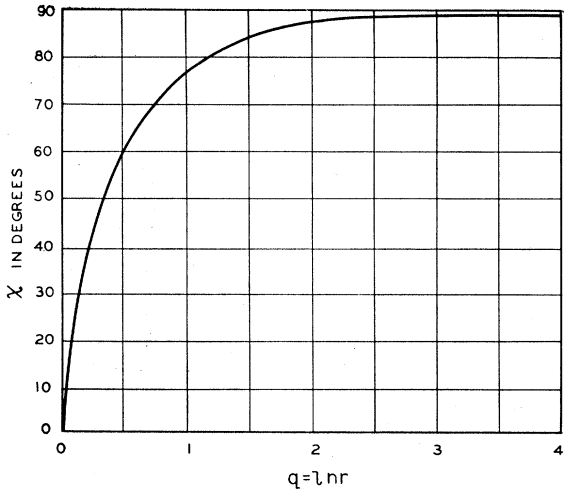

FIG. 3. Orbit leading to double escape along the "valley" $\gamma=\pi$. Abscissa origin is arbitrary. This is to exhibit that orbits leading to double escape generally start from asymmetric initial conditions.

the similarity transformation (13) by the substitution

$$C_1\to\alpha^{-\frac{1}{4}-\frac{1}{2}\mu}C_1, \tag{30a}$$

$$C_2\to\alpha^{-\frac{1}{4}+\frac{1}{2}\mu}C_2, \tag{30b}$$

$$C_3\to\alpha^{-\frac{1}{4}}C_3, \tag{30c}$$

$$C_4\to C_4+\tfrac{1}{2}\rho\ln\alpha. \tag{30d}$$

In view of the factor b included in the definition (16) this means that an orbit belongs to those emerging from reaction zone if $|C_1|$, $|C_2|$, and C_3 are below certain numerical limiting values; these values are complicated functions of each other and of C_4.

We now pass to the *discussion of the orbits of finite energy* ϵ. The physical idea followed in their treatment is extremely simple and requires no computation. An easy presentation can be given which does, however, leave unproved several important features. A logically complete discussion of these orbits can be given instead, in which we find the basic reasoning obscured by analytic details. The first type of reasoning will be given now, and the second will be found in the appendix.

In this *semi-intuitive approach to orbits of finite* ϵ we first observe by inspection of (17) and (18) that there is no difference between the orbits of zero energy and of small energy in the reaction and Coulomb zones Hence an identification of the two orbits can be made It is then intuitively reasonable that all orbits which led to double escape at zero energy will continue to do so at finite ϵ. This means, as previously, that the set selected in the first asymptotic range by setting C_2 in (24) equal to zero and leaving C_1, C_3, and C_4 arbitrary still leads to double escape. However, because the energy is finite, other orbits will also be possible now, and thus the possible range of C_2 is presumably widened. The way in which this widening takes place is the

central piece of information to be transferred to Sec. IV. From the similarity law (13) and the definition (5) it follows that at fixed energy ϵ the surface separating double from single escape can depend on r and ϵ only through the combination r/c or ϵr. Now the divergent solution in (24) has the form

$$\chi-\pi/2\approx C_2(r/b)^{\frac{1}{2}\mu-\frac{1}{4}}. \tag{31a}$$

To make r/c appear we substitute

$$C_2=D(b/c)^{\frac{1}{2}\mu-\frac{1}{4}}. \tag{31b}$$

The selection of possible values of D leading to double escape cannot be dependent on energy. It is reasonable, and is proved in the appendix, that small values of D indeed do lead to double escape. Hence there must be some maximum value $D_{\max}$, where double escape ceases. Through (31b), this imposes in turn a limitation on C_2.

$$(C_2)_{\max}=D_{\max}(b/c)^{\frac{1}{2}\mu-\frac{1}{4}}, \tag{32}$$

or with (5)

$$(C_2)_{\max}\propto\epsilon^{\frac{1}{2}\mu-\frac{1}{4}}. \tag{33}$$

Equation (33) is the desired relation between the range of C_2 and the energy.

III. THE QUASI-ERGODIC ASSUMPTION

We now come to the difficulty of principle mentioned before, which arises when one attempts to extend Wigner's method[3] without modification to reactions involving three particles.

In the problems discussed in Wigner's paper it is always true that if the particles come out of the reaction zone with sufficient energy to escape each other they will finally succeed, the only question being the rate at which this will occur. The reason for this is that the wave function for the two-body problem is completely specified by the magnitude of the conserved quantities: momentum, angular momentum, energy, and the specification of the sense in which the motion proceeds. In the three-body problem the same information still leaves us with an infinity of solutions.

In the case under discussion, this indeterminacy shows up as follows: Suppose we know that two electrons recede from an ion with zero angular momentum and fixed energy. Their wave function must then be an outgoing wave in the coordinate r. But its dependence on χ and γ is fixed by continuity requirements with the reaction zone and cannot be known without a closer knowledge of the ionization process. If we are to determine a threshold law without knowledge of the reaction mechanism, then we must try to do it without such detailed information.

I propose to derive in the following the rate of ionization by computing the volume in phase which escapes per second from the reaction zone and which is subtended by orbits leading to double escape; this volume will shrink as the energy excess above threshold is reduced; this shrinkage I presume to be the variation of the cross section with the energy because all other features of a complete calculation do not vary critically with the energy. The easiest way to justify this procedure is to make an ergodic assumption for all redundant degrees of freedom, that is, by assuming that in the neighborhood of the reaction zone the density of representative points of the system in phase space is constant in the mean.

Proceeding with the derivation on the basis of this ergodic hypothesis would be logically clear and unambiguous, but it would leave the result open to criticism which is generally not justified. It is therefore worth while at this point to investigate how serious a departure from ergodicity is needed to make the proposed calculation wrong. In the first place we may replace the uniform distribution by a variable one, which has no zeros or infinities. In other words we can allow nonergodic, but smooth nonvanishing distributions of energy between the two particles, or in the angle γ. For γ we can go even farther; because of the decoupling of the motions in γ and χ exhibited in Eqs. (22) and (23) or (a) and (b) of the Appendix, we may allow any distribution in γ whatever provided only that the probability for $\gamma=0$ is of measure zero compared to all other angles. For χ we cannot go quite so far, but we can allow zeros in the distribution if only the dimensionality in phase space of the zero is less than that of the double escaping pencil at zero energy.

The case for χ just discussed actually arises in connection with spin. The two electrons can come out in either a singlet or a triplet state. In the former case the coordinate wave function is symmetric, in the latter case antisymmetric. This means that the entire symmetric subset of orbits discussed in Sec. II is wiped out for the triplet state. This will affect the probability in its factor but not in the threshold law, because the symmetric orbits are in relation to all double-escape orbits at zero energy as a single point on a line, and hence not sufficiently numerous to produce a change of dimension in the limiting probability. In consequence we would predict that the triplet and singlet configurations have the same threshold law but that the ratio 3:1 in the factors may very well be reduced by the exclusion principle.

We conclude therefore that, while the correctness of the proposed procedure cannot be proved, it can be made plausible beyond reasonable doubt. An extremely strong selectivity would be required in the ionization process to make the result wrong.

IV. DERIVATION OF THE THRESHOLD LAW

The quantity to compute in the following is the number of representative points in six-dimensional phase space which, at fixed density, leave the reaction zone per unit time along orbits leading to double escape. If the number for such orbits were divided by the same number for all orbits, then the probability of ionization would result. However, the latter quantity is certainly

not critical in the energy, so that the division is not necessary for the purpose at hand.

The way the computation will be carried out is to define all but one of the integration variables in such a way that in the limit of zero energy these variables have a finite range within the manifold leading to double escape. The last variable (together with the Jacobian) will then be predetermined by what we mean by phase space, and the result of this last integration as a function of the energy excess will yield the threshold law.

The volume Ω of a portion of phase space is given by the formula

$$\Omega=\int\int\int\int\int\int dr dp_r d\gamma dp_\gamma d\chi dp_\chi. \tag{34}$$

We are working in the intersection of this volume with a hypersurface of constant energy; this demands that we introduce ϵ as one of the variables of integration into (34). If we substitute ϵ for p_r from (12), we get

$$\Omega=m\int\int\int\int\int\int\frac{dr d\epsilon d\gamma dp_\gamma d\chi dp_\chi}{p_r(r,\epsilon,\gamma,p_\gamma,\chi,p_\chi)},$$

and for the intersection of Ω with a surface of constant energy ϵ

$$\Omega_\epsilon=m\int\int\int\int\int\frac{dr d\gamma dp_\gamma d\chi dp_\chi}{p_r(r,\epsilon,\gamma,p_\gamma,\chi,p_\chi)}. \tag{35}$$

Actually we want not a volume but a volume flux, that is, the volume swept out by a set of points in a very small time dt, divided by dt. If we choose as reference hypersurface a hypersphere, then the integration over dr is to be omitted, and we find

$$\left(\frac{d\Omega_\epsilon}{dt}\right)_{r=R}=m\int\int\int\int\frac{(dr/dt)d\gamma dp_\gamma d\chi dp_\chi}{p_r}.$$

The two factors under the integral sign cancel each other, and we end up with

$$d\Omega_\epsilon/dt=\int\int\int\int d\gamma dp_\gamma d\chi dp_\chi. \tag{36}$$

The integration is to be taken over the four-dimensional hypersurface cut out of phase space by the conditions $\epsilon=$ const and $r=$ const. In principle, this second constant can be given any fixed value we please. In practice however we must place the integration into a region where the behavior of the orbits is well understood. This is the first asymptotic range. In this domain q is large compared to unity because of (16) and the constant C_2 is small because of (j). Hence all terms in (24) and (25) are small, and the use of the linearized equations is *ex post facto* justified. It is therefore possible to transform the fourfold integral (36) into one over C_1, C_2, C_3, and C_4. The first steps are

$$\begin{aligned}d\gamma dp_\gamma d\chi dp_\chi&=r^4 d\gamma d\dot\gamma d\chi d\dot\chi\\&=m^2r^2\dot r^2 d\gamma d\gamma' d\chi d\chi'\\&=\sqrt{2}me^2(4Z-1)r d\gamma d\gamma' d\chi d\chi'.\end{aligned}$$

Here the primes denote differentiation with respect to q. Use has been made of the fact that the orbits cluster around $\chi=\pi/2$, $\gamma=\pi$ and that factors can be evaluated as of this point. The factor showing above does not contain ϵ. We now find easily from (24) and (25)

$$\partial(\gamma,\gamma',\chi,\chi')/\partial(C_1,C_2,C_3,C_4)=\tfrac{1}{2}\rho\mu C_3 e^{-q}=\tfrac{1}{2}\rho\mu C_3 b/r,$$

and hence

$$\frac{d\Omega_\epsilon}{dt}=\frac{1}{\sqrt{2}}me^2(4Z-1)\mu b\rho\int\int\int\int C_3 dC_1 dC_2 dC_3 dC_4. \tag{37}$$

It is to be observed that (37) contains an incidental check on the calculation, namely, the disappearance of

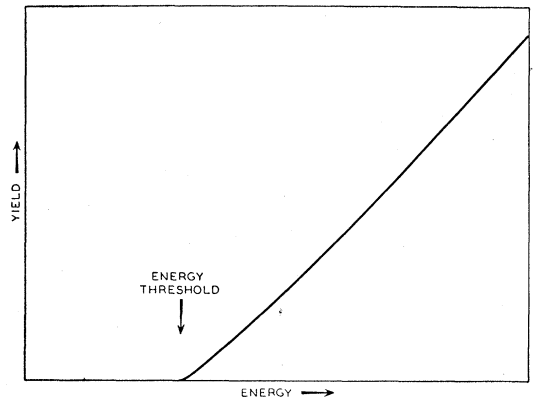

FIG. 4. Theoretical yield *versus* energy curve for single ionization of atoms by electrons. To produce a straight line the 0.8874th power of the yield should be plotted against energy.

r from the integral: $d\Omega_\epsilon/dt$ comes out independent of the position of the hypersphere as it should. The part under the integral breaks up as desired. From the discussion in Sec. II and the Appendix it follows that C_1, C_3, and C_4 have finite ranges, while C_2 is limited by (33) or (l) if we are to stay within the pencil leading to double escape. Hence the integral is limited in the same way, and we get

$$d\Omega_\epsilon/dt\propto\epsilon^{\frac{1}{2}\mu-\frac{1}{4}}. \tag{38}$$

This is the looked-for threshold law. By the arguments given the yield and the cross section are expected to vary in the same manner. For the important case of atoms when $Z=1$ we get from (26)

$$d\Omega_\epsilon/dt\propto\epsilon^{1.12689}. \tag{39}$$

Figure 4 shows the variation of yield *versus* energy predicted from Eq. (39). The line appears almost straight, with a slight upward bend; its main distinction

is that the threshold is entered with zero slope. The curves resulting from (38) for the ionization of ions, that is $Z>1$, are qualitatively similar. The resemblance to a straight line is more marked because the exponent is much closer to unity than in the case (39).

V. CONCLUDING REMARKS

Bates, Fundaminsky, Massey, and Leech[5] have discussed among other things ionization by electrons, making use of the Born approximation. In Table III of their paper they give the threshold laws obtained from their calculation and find for the process discussed here a variation with the first power of the energy excess. They indicate that this is the right answer, because the Born approximation is known to give correct threshold laws, as pointed out by Wigner.[3] It should be remembered however that this is true only if the correct wave function is used for the final state. Their heading indicates that they used a Coulomb wave function for one escaping electron and a plane wave for the other. This would indeed be a very poor choice. I have checked this point and find that their heading is probably accidentally labelled incorrectly. The result which they state arises if both electrons are given Coulomb wave functions; this is the most reasonable simple choice one can make. It is discussed in this paper as the case of "switched off" electron-electron interaction or $Z\to\infty$. For this case, I find exactly the same answer as they do, and this should strengthen the confidence in the calculation method used here. However, their answer is not really correct; the Coulomb functions are the best ones we can think of, but they are not right. The correct functions are the quantum solutions of the three-body problem. These have been discussed by Gronwall[6] and Bartlett,[7] but nobody has been able so far to make use of them in a wider context. The present quasi-statistical derivation is therefore the only one which takes into account the specific three-body feature of the problem. I believe that its non-rigorous features are justified and that the answer (39) is the right one. This implies the belief that Bates and his co-workers would have found this same answer if they had used the correct three-body wave function for the final state.

In conclusion, I want to express my thanks to Dr. C. Herring and Professor E. Wigner who have helped me in clarifying the ideas which underlie this derivation.

APPENDIX

In the text a derivation of Eq. (33) was presented which made no use of any property of the orbits of finite ϵ except the similarity law. It did however make certain assumptions about them which appeared intuitively reasonable. These assumptions will now be investigated, and it will be found that we arrive at the same conclusions.

The essential requirement is the possibility of following the solutions (24) and (25) from the first into the second asymptotic range. This can indeed be accomplished. We start over again from (17) and (18), keeping the denominator on the right this time. Linearization around $\chi=\pi/2$, $\gamma=\pi$ proceeds as before via Eq. (21); we find the following generalizations of (22) and (23):

$$\chi''+\chi'=\left[\frac{1}{2}\chi'+\frac{12Z-1}{2(4Z-1)}\left(\chi-\frac{\pi}{2}\right)\right]\Big/\left(1+\frac{b}{c}e^{q}\right), \quad \text{(a)}$$

$$\gamma''+\gamma'=\left[\frac{1}{2}\gamma'-\frac{1}{2(4Z-1)}(\gamma-\pi)\right]\Big/\left(1+\frac{b}{c}e_{q}\right). \quad \text{(b)}$$

These equations are explicitly soluble in terms of Legendre functions. Setting

$$z=[1+(b/c)e^{q}]^{\frac{1}{2}}=(1+r/c)^{\frac{1}{2}}, \quad \text{(c)}$$

we find

$$\chi-\pi/2=(z^2-1)^{-\frac{1}{4}}[D_1Q_{\frac{1}{2}}^{\mu}(z)+D_2P_{\frac{1}{2}}^{\mu}(z)], \quad \text{(d)}$$

$$\gamma-\pi=(z^2-1)^{-\frac{1}{4}}[(D_3+iD_4)P_{\frac{1}{2}}^{i\rho}(z)+(D_3-iD_4)P_{\frac{1}{2}}^{-i\rho}(z)]. \quad \text{(e)}$$

The solutions contain r only in the combination r/c as required by the similarity principle. Inspection of (c) shows that the first asymptotic range discussed previously lies near $z=1$; the second asymptotic range is reached for large z. Consideration of the subset $C_2=0$, which is known to produce double escape for zero energy, requires analysis of Eq. (d). $Q_{\frac{1}{2}}^{\mu}(z)$ is a solution which vanishes at infinity as $z^{-\frac{1}{2}}$; hence it is rigorously true that the solutions $D_2=0$ lead to double escape in which $\chi\to\pi/2$. However, small values of D_2 will also lead to double escape because $P_{\frac{1}{2}}^{\mu}(z)$ diverges as $z^{+\frac{1}{2}}$ and $\chi-\pi/2$ approaches thus a finite value of the order of D_2. For large D_2 the linearization procedure breaks down, but the quantities D can still be defined as the multipliers of the first term in a perturbation treatment of (17) and (18), starting from (a) and (b). The similarity principle then demands that there be some positive $D_{\max}$ and some negative $-D_{\min}$ which separates for each triple D_1, D_3, D_4 the values of D_2 leading to double from those leading to single escape,

$$-D_{\min}<D_2<D_{\max}, \quad \text{(f)}$$

$$0<D_{\min}=D_{\min}(D_1, D_3, D_4), \quad \text{(g)}$$

$$0<D_{\max}=D_{\max}(D_1, D_3, D_4). \quad \text{(h)}$$

The important point is that because of the similarity principle these relations *cannot* contain the energy ϵ explicitly, even outside the linear range. To compare the C's defined in the text and the D's defined here, the expansions of the Legendre functions around $z=1$ are needed. If we complete the definition of $P_{\frac{1}{2}}^{\mu}(z)$ by

[5] Bates, Fundaminsky, Massey, and Leech, Trans. Roy. Soc. (London) **243**, 93 (1950).
[6] T. H. Gronwall, Phys. Rev. **51**, 655 (1937).
[7] J. H. Bartlett, Phys. Rev. **51**, 661 (1937).

demanding that it vanish at $z=1$ and compare the expression (d) with (24), we get

$$C_1=A_1(c/b)^{\frac{1}{4}+\frac{1}{2}\mu}D_1, \quad \text{(i)}$$

$$C_2=A_2(b/c)^{-\frac{1}{4}+\frac{1}{2}\mu}D_2+A_3(b/c)^{\mu}C_1. \quad \text{(j)}$$

Here A_1, A_2, A_3 are numbers. These equations show that as D_1, D_3, D_4 vary over their range and D_2 is zero, C_1, C_3, C_4 do likewise, while C_2 takes a finite value linked to C_1. However for small ϵ, that is small b/c, this value is very much smaller than C_1 which itself is limited by the size of the reaction zone. Now as D_2 passes through its finite range allowed by (f), C_2 varies independently of C_1 within a small range; this range is given by

$$\Delta C_2=A_2(b/c)^{\frac{1}{2}\mu-\frac{1}{4}}(D_{\min}+D_{\max}), \quad \text{(k)}$$

and hence

$$\Delta C_2 \propto \epsilon^{\frac{1}{2}\mu-\frac{1}{4}}. \quad \text{(l)}$$

The relation (k) is equivalent to (32), and (l) to (33); thus the simple reasoning yielding (33) is justified.

PHYSICAL REVIEW VOLUME 90, NUMBER 5 JUNE 1, 1953

The Stopping of Heavy Ions in Gases

G. E. Evans, P. M. Stier, and C. F. Barnett
Oak Ridge National Laboratory, Oak Ridge, Tennessee

(Received October 6, 1952)

The extrapolated ionization range for the ions He^+, N^+, Ne^+, and A^+ in the stopping gases He, N_2, air, and A has been determined as a function of energy in the energy range from *ca* 20 kev to *ca* 250 kev, using monoenergetic heavy ions produced in a Cockcroft-Walton accelerator. A collimated beam of heavy ions is admitted to the range chamber via a three-stage differential pumping system so as to avoid the use of foil windows. The range was determined using a parallel plate ionization chamber mounted so as to permit translation parallel to the axis of the beam. It has been found that the range as measured at a pressure P is not inversely proportional to P, and an interpretation of this pressure effect has been given in terms of large angle scattering of the ions into regions outside of the volume swept out by the ionization chamber. A method of correcting for this pressure effect has been developed and applied to the data to yield range-energy curves which are independent of the ionization chamber size. The space distribution of ionization produced in a gas by a collimated beam of heavy ions has been determined for the same combinations of incident ion, stopping gas, and energy as above. The attenuation of the beam of ions is found to be approximately exponential in the axial direction and approximately Gaussian in the lateral direction. A method has been developed for computing the shape and size of a given ionization density contour at a given pressure if it is known at another pressure and the same energy.

I. INTRODUCTION

THE problem of determining the rate and mechanism of energy loss of high energy charged particles in matter has received a large amount of attention, both experimentally and theoretically, during the past few decades. The range, specific ionization, scattering, and straggling of protons, deuterons, and alpha-particles have been determined over wide energy intervals by various investigators and comprehensive summary reports have been published.[1] The theory of the mechanism of energy loss by these light particles is sufficiently well understood to allow a quantitative description of the processes of elastic and inelastic scattering in terms of simple classical or quantum-mechanical models, and the criteria for the validity of the models have been determined.[2] A much smaller amount of experimental work has been done on the range and specific ionization of fission fragments, yet even in this much more complex problem, qualitative agreement between theory and experiment has been achieved.[3]

In almost all of the research done in this field in the past, the velocity of the incident ion has been large compared to the velocity of its outermost electrons. Furthermore, in a majority of the previous research, the mass of the incident ion has been small compared to the atomic mass of the stopping material. There remains a large and practically unexplored field of penetration phenomena in which the velocity of the ion is of the same order of magnitude or smaller than the velocity of its outermost electrons, and in which the mass of the incident ion is allowed to vary over wide limits. Work within this latter field has been limited because of the major difficulties in theoretical interpretation of results[4] and because the experimental

[1] H. A. Bethe, Atomic Energy Commission Report AECU 347 (BNL-T-7); Aron, Hoffman, and Williams, Atomic Energy Commission Report AECU 103 (UCRL 121 rev, 2nd ed.) (unpublished).

[2] See, e.g., H. A. Bethe, Revs. Modern Phys. **22**, 213 (1950); M. S. Livingston and H. A. Bethe, Revs. Modern Phys. **9**, 245 (1937); E. J. Williams, Revs. Modern Phys. **17**, 217 (1945).

[3] Katcoff, Miskel, and Stanley, Phys. Rev. **74**, 631 (1948); N. O. Lassen, Kgl. Danske Videnskab. Selskab, Mat.-fys. Medd. **25**, No. 11 (1949).

[4] N. Bohr, Kgl. Danske Videnskab. Selskab, Mat.-fys. Medd. **18**, No. 8 (1948).