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FEBRUARY 1965

AIAA JOURNAL

VOL. 3, NO. 2

Inelastic Atomic Collisions in Plasmas

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Introduction

THE collision processes that play the greatest role in the L excitation and ionization state of a typical thermal plasma are excitation, ionization, charge transfer, and recombination of atoms, molecules, and ions. In this paper, we shall restrict the discussion to excitation and ionization collisions involving electrons, atoms, and ions at thermal and near thermal energies. Denoting an atom or ion by A, B and an electron by e, the processes are then

$$e + A(r, n) \rightarrow e + A(r, n')$$
 (1a)

$$e + A(r, n) \rightarrow (r' - r + 1)e + A(r', n')$$
 $r' > r$ (1b)

$$A(r, m) + B(s, n) \to A(r, m') + B(s, n')$$
 (2a)

$$A(r, m) + B(s, n) \rightarrow A(r', m') + B(s', n') +$$

$$(r' + s' - r - s)e \tag{2b}$$

$$r' \geq r$$
, $s' \geq s$, $r' + s' - r - s \geq 1$

 $r, s, r', s' = -1, 0, 1, 2 \dots =$ charge on atom or ion

m, n, m', n' =state of atom or ion

Although formally all of the foregoing processes are included under (2b), the differences between electron (1) and heavy particle (2) collisions, and between excitation (a) and ionization (b) collisions are large enough to require separate

Presented as Preprint 64-54 at the AIAA Aerospace Sciences Meeting, New York, January 20-22, 1964. This work was supported in part by NASA Contract NASw-894. I would like to thank M. J. Seaton for the preprint of the Heddle and Seaton paper, and Dr. Kunkel for a copy of the Robben paper. I also would like to express my appreciation to Joe Scanlon, Marcella Neuman, and Jack Graham and his staff for their extensive help in the preparation of this paper for publication.

discussions. It is also usual to distinguish the cases where at least one atom is neutral (r = 0 and/or s = 0) from the other cases.

Since "thermal" plasma temperatures are only some few electron volts, the collision cross sections are needed in energy ranges determined by Maxwell distributions which, in many cases, will be declining rapidly with energy at the threshold for excitation or ionization of the ground state of typical atoms. However, for excited states of the atoms, the threshold energies are smaller by factors of 10 to 1000, and it is now the atomic cross section that is declining in the region where the velocity distributions peak. These points are illustrated in Fig. 1. It can be seen that the only part of the ground state cross section which contributes appreciably to the excitation rate is the part just above threshold, whereas for an excited state, the region of the cross section above its maximum will be most important. As is well known, the current state of collision theory and experiment tends to give particularly poor accuracy for the threshold, so that much of our discussion will be concerned with the accuracy available for various cross sections in the threshold region.

We begin with a discussion of some of the collision parameters for a thermal plasma, with some asymptotic cross sections used to illustrate typical collision processes. The following two sections will treat firstly electron collisions with ground and excited states of hydrogen and then collisions with other atoms and ions. Finally, there will be a discussion of heavy particle collisions treated more briefly than the electron case because the collision rates involved are usually smaller and therefore play a smaller role in the state of the plasma.

Effective Cross Sections in a Thermal Plasma

For almost all plasmas of interest, the particle velocities in the plasma remain in equilibrium, obeying the Maxwell-

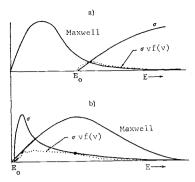


Fig. 1 Sketch of energy regions in which a) high threshold and b) low threshold cross sections contribute most to the effective cross section.

Boltzmann distribution, even when most other quantities, such as the radiation field, the numbers of atoms in various excited states, and the state of ionization, depart from thermodynamical equilibrium. Hence, under these conditions, the effective excitation and ionization collision cross sections are determined uniquely by the temperature of the exciting particles and the inelastic cross section for the $i \rightarrow j$ processes (including ionization); the effective cross section relevant to collision rates is expressed as an average over the Maxwellian velocity distribution f(v)dv:

$$\bar{\sigma}_{ij}(T) = \int_{v_0}^{\infty} \frac{v \sigma_{ij}(v) f(v) dv}{\bar{v}} = h(T) \int_{E_0}^{\infty} \sigma_{ij}(E) E e^{-E/kT} dE$$

$$\bar{v} = \int v f(v) dv \tag{3}$$

$$h(T) = (kT E_0 e^{-E_0/kT})^{-1}$$

where T is the temperature, v the velocity, E the energy, v_0 the velocity, E_0 the energy required for excitation of the transition $i \to j$, and σ_{ij} is the corresponding inelastic cross section.

To illustrate the way in which different energy regions of the cross sections become important, the two extremes of threshold energy, much greater or much smaller than the mean kinetic energies of the colliding particles, are investigated:

$$E_0\gg kT$$
 $\sigma_{ij}(T)\approx h(T)E_0\int_{E_0}^{E_0+\Delta E}\sigma_{ij}(E)e^{-E/kT}\,dE$ (4a)

$$E_0 \ll kT$$
 $\bar{\sigma}_{ij}(T) \approx h(T) \int_{E_0}^{\infty} E \sigma_{ij}(E \gg E_0) e^{-E/kT} dE$ (4b)

Considering first the large-threshold case (4a), we see that we require the value of the cross section only in the threshold region E_0 to $E_0 + \Delta E_0$. Now the cross section shape at threshold for excitation is known from Wigner's work¹ to have the form

$$\sigma_{ij}(E) = C_e(E - E_0)^{\alpha} \qquad E_0 \le E \le E_0 + \Delta E \quad (5)$$

where C_e is a constant, and $\alpha = \frac{1}{2}$, 0 for excitation of atoms and ions, respectively, and $\alpha = -\frac{1}{2}$, -1 for superelastic collisions with atoms and ions, respectively. Unfortunately, the value of the constant C_e is known only for one or two cases at present, and further, it is not known in general over what range of energies the threshold law is valid.* In fact, Seaton² has pointed out that in some cases the threshold law holds for such a small range of energy that the effective threshold law for atom excitation may be, e.g., $C(E-E_0)^{3/2}$ rather than $C(E-E_0)^{1/2}$.

The corresponding threshold law for multiple ionization of an atom or ion giving an ion of charge *ne* is believed to be³

$$\sigma_{ij}(E) = C_i(E - E_0)^n \qquad E_0 \le E \le E_0 + \Delta E \quad (6)$$

Now turning to the case of threshold energies that are small compared to kT, we require approximate cross sections at large energies. For allowed transitions, which certainly dominate the collisional transitions at these high energies, we have various forms of the Bethe cross section for atom and ion excitation and ionization

$$E \gg E_0 \qquad \sigma(E) \approx (C/E) \ln(DE)$$
 (7)

The cross-section approximations (5–7) enable the effective cross sections (4) to be evaluated for the large and small threshold limits. As examples we give some large threshold effective cross sections for $E_0 \gg kT$:

Atom Excitation

$$\alpha = \frac{1}{2}$$
 $\bar{\sigma} = \frac{1}{2} C_e (\pi k T)^{1/2}$ (8a)

Ion Excitation

$$\alpha = 0$$
 $\tilde{\sigma} = C_{\bullet}$ (8b)

Atom Superelastic

$$\alpha = -\frac{1}{2}$$
 $\bar{\sigma} = C(\pi/kT)^{1/2}$ (8c)

Ion Superelastic

$$\alpha = -1 \text{ diverges}$$
 (8d)

Ionization to Ion ne

$$\alpha = n \qquad \bar{\sigma} = C_i n! (kT)^n \tag{8e}$$

The divergence of the ion superelastic collision effective cross section follows from the Coulomb interaction and the $E_0=0$ condition. Some illustrative numerical values follow (adopting ev units for energy and temperature and expressing the cross sections in terms of $\pi a_0^2 = 0.88 \times 10^{-16}$ cm², where a_0 is the Bohr radius). For electron collisions with hydrogen $C_e \approx 0.25 \pi a_0^2 (\text{ev})^{-1/2}$ for 1s - 2p, $C_i \approx 0.078 \pi a_0^2 (\text{ev})^{-1}$ (adapted from Fite, et al.^{4, 5}), giving

$$\bar{\sigma}_e \approx 0.22(kT)^{1/2} \pi a_0^2$$
 (9a)

$$\bar{\sigma}_i \approx 0.078(kT) \pi a_0^2 \tag{9b}$$

Thus, even though the peak values of the cross sections are about πa_0^2 , it is seen that, at temperatures of 10^{-2} , 1, 4 ev, the effective excitation cross sections are only 0.02, 0.2, and 0.4 πa_0^2 , respectively, and the effective ionization values 0.001, 0.1, and $0.3 \pi a_0^2$, respectively, are even smaller. These results emphasize once again the importance of knowing the values of cross sections accurately at low energies.

Electron Collisions with Hydrogen Atoms

Our discussion is divided into three parts: an outline of the theory of electron collisions as a guide to various approximate atomic collision theories, the current situation for electron collisions with the ground state of hydrogen, and then the situation for excited states.

Theory

Electron collisions with atoms are less complicated than collisions of ions or atoms with atoms because there is no internal structure to add to the possible variety of reaction channels. In addition, since the validity of most approximations depends on the velocity rather than the energy, it is possible to calculate electron cross sections accurately down to energies some two or three orders of magnitude smaller than those for ion or atom cross sections, except for special cases.

^{*} I am indebted to Kazem Omidvar for reminding me that Wigner's threshold law was derived for short range forces and need not hold necessarily for atomic excitation just above the threshold; however, in a practical sense, the experimental threshold measurements will determine which law is valid. See the discussions by Omidvar⁹¹ and by Gailitis and Damburg.⁹²

Referring to the Appendix, we find that the type of collision theory most studied involves the solution of various approximations to an infinite set of coupled integrodifferential equations (A11), which for simplicity we can symbolize by

$$LF^{\pm}(n') = \sum_{n''} [V(n'n'') \pm W(n'n'')]F^{\pm}(n'')$$
 (10)

The scattering amplitudes, and therefore the cross sections, depend on the asymptotic (large electron-atom separation) forms of F^{\pm} . In (10) V and W are the direct and exchange-integral-operator interaction potentials. Massey⁸ has given a convenient classification of the approximations for the case where only the hydrogen states with the same principal quantum numbers as the initial and final states (n, n') are considered in (10). The approximations without exchange all have W=0: Born approximation has all V=0 except V(n'n)= small; distorted wave retains diagonal terms plus V(n'n); and close coupling retains all terms. The exchange approximations include the corresponding W terms. As an example, we write the close coupling with exchange equations:

$$LF^{\pm}(n) = [V(nn) \pm W(nn)]F^{\pm}(n) + [V(nn') \pm W(nn')]F^{\pm}(n')$$

$$LF^{\pm}(n') = [V(n'n) \pm W(n'n)]F^{\pm}(n) + [V(n'n') \pm W(n'n')]F^{\pm}(n')$$
(11)

In the case of 1s - 2p, excitation of hydrogen, when all the degenerate energy states belonging to n = 1 and n = 2 are included, i.e., 1s, m = 0; 2s, m = 0; 2p, m = -1, 0, +1, there are actually five coupled equations. With the advent of large computers, it has become possible to handle such large sets of integrodifferential equations and even add in some other states.

The most recent survey of electron atom collisions is the very useful one by Heddle and Seaton¹² in July 1963, and we have used this extensively. We refer the reader to their excellent bibliography for the period January 1960 to mid-1963; in the present paper we include some papers published since that date. We will not attempt to cover the other theoretical approaches to the scattering problem.^{10, 11, 24} A recent review of the experimental measurement of atomic cross sections has been given by Fite.²³

Ground State of Hydrogen

Despite the vast amount of theoretical work done on hydrogen atom collisions, at present it is not possible to calculate accurately excitations or ionizations from the ground state at energies below several times threshold. Since low energy collisions bring in most of the complexity of a threebody problem, it is not really surprising that no theoretical way has been found to surmount the low energy problem yet. Fortunately, there are good experimental measurements down to near threshold for some of the important transitions. In Fig. 2, from the paper by Burke, Schey, and Smith¹³ (see also similar work by Omidvar¹³), we see that the close coupling calculations, including the 1s-2s-2p states, when compared with the experimental values do not give much improvement over the Born approximation for the 1s-2p transition. In more recent work, Taylor and Burke¹⁴ have included the 1s-2s-2p-3s-3p states, but find only a small change in the results for 1s-2p (see also Ormonde and Smith³²). The results 13 for 1s-2s are given in Fig. 3 for 1s-2s-2p coupling; the addition of the 3s, 3p states, giving one cross section at 16.5 ev after about 10 hr of calculation on the Stretch computer, brought the 1s-2s result down to the Born value at

Since the 1s-2p experimental values are believed to be accurate, it is clear that the close coupling method is not accurate near threshold. Since the inclusion of some few discrete states and exchange terms does not adequately allow

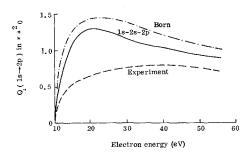


Fig. 2 Total 1s-2p excitation cross section as a function of incident electron energy as given by the Born approximation and by the calculation of Burke, Schey, and Smith.¹³ Experimental results are those of Fite and Brackmann, and of Fite, Stebbings, and Brackmann.

for the continuum, which almost certainly strongly influences the discrete state excitations, it might be expected that the method would fail. On the other hand, there is no other theoretical method at present which appears to be better for inelastic collisions; some of the other methods available for elastic scattering are difficult to extend to the inelastic case.

Thus, one adopts the Born approximation for high energies and the experimental values for low energies for 1s-2s, 15 , 16 1s-2p, 4 1s-3. For other states there do not appear to be experimental values available, so that we have accurate theoretical values at high energies from the Born 18 , 19 or other approximations, 12 , 20 but at lower energies the results are uncertain; hopefully they may not be wrong by more than a factor of 2 in the threshold region. It is tempting to scale down the Born calculations for 1s-n'l' transitions in the same ratio as the experimental to Born ratio for the 1s-2p transitions; however, there are dangers in such semiempirical tampering with a theoretical result; note, for example, that, as n' increases, the number of levels degenerate with any given l' sublevel increases as n', increasing the complexity to be considered.

There are experimental values for the ionization cross section down to threshold.^{21, 22} Heddle and Seaton¹² compare the adopted fit to the several experimental values with some of the theoretical values (Fig. 4). It is hoped that the error in the experimental curve is not more than about 10% even in the threshold region. Since the experiments are so satisfactory, theory^{25, 26, 36, 37} is mostly useful here for determining the applicability of theory to cases where experimental values are not available.

Excited States of Hydrogen

There are no experimental results. The basic problem experimentally is to be able to produce a reasonable concen-

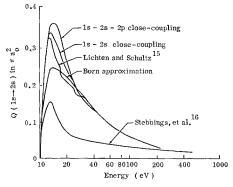


Fig. 3 Total 1s-2s excitation cross section as a function of incident electron energy as given by various calculations of Burke, Schey, and Smith¹³ and by two sets of experiments.

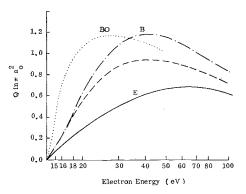


Fig. 4 Ionization of hydrogen atoms by electron impact, from Heddle and Seaton.¹²

tration of one excited state, without too much contamination by other states, and hold this concentration long enough to carry out slow speed collisions. There seem to be some hopes of achieving this soon for the metastable 2s state.

In the theoretical work, the basic problem is similar to the ground-state case. Except at high energies, the simple perturbation approximation cannot be rigorously justified, and more complicated types of traditional calculations suffer from the same defect as the ground-state calculations to date, namely, not properly allowing for the continuum. In the complete absence of experiments, we do not have any criteria to judge the accuracy of the excited state calculations at low energies other than ground-state experience and plausibility arguments. Some plausibility arguments about the accuracy of the Born approximation for excited states are as follows: 1) in terms of relative energy units, i.e., expressing the energy in terms of threshold energy units for the particular transition, we "expect" the cross section to peak at some few thresholds for excited states in the same way as for the ground states, and we hope that the accuracy of the theory will also be comparable at the same number of thresholds; 2) comparing the $n \to n+1$ and $1 \to 2$ transitions in threshold units, the other states $(\ldots n-2, n-1, n+2, n+3,$...) are much further away in energy for $n \to n+1$ than for $1 \rightarrow 2$ (for $1 \rightarrow 2$, all of the other states are nearer in energy to level 2 than level 1 is); in particular, in this sense, the continuum is relatively further away from n, n + 1 than from 1, 2; and 3) on the other hand, it can be argued²⁷ hat since a slow electron spends so much time traversing the large region "occupied" by the atom in a highly excited state n, and is there relatively unshielded from the nucleus, the perturbations of the electron wave will be much larger than for the ground-state case.

Many of the more important cross sections for $nl \to n'l'$, with n, n' in the range 1-13, are now available in the first Born approximation^{2s-31}; some of these have also been treated in more complicated approximations.³²⁻³⁴ In Fig.

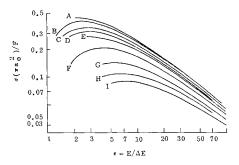


Fig. 5 Normalized Born cross section plotted against the energy expressed in threshold energy units. A, 1s-2p; B, 2p-3d; C, 3d-4f; D, 4f-5g; E, 5g-6h; F, 2s-3p; G, 3s-4p; H, 4s-5p; I, 5s-6p (McCoyd and Milford³¹).

 5^{31} we compare a number of the Born cross sections for allowed transitions. The cross sections are normalized to equal values at $E=\infty$ by dividing by

$$F = \frac{18.14}{E_0} \left(\frac{l+1}{2l+1} \right) \left| \frac{I(nl, n'l')}{a_0} \right|^2$$
 (12)

where I(nl, n'l') is the dipole radial integral.³¹ The large n Born cross sections are enormous, as illustrated in Fig. 6.

Similar remarks apply to ionization from excited states; recent calculations include modified Bethe³⁵ for n = 1-15, Born³⁶ for n = 1-5, and close coupling³⁷ for 2s and 2p.

In summary, the best that we can do at present is to hope that, for transitions with threshold energies in the range 0.001–0.1 ev, the cross sections will not be too inaccurate for energies in the 1–10 ev range.

Electron Collisions with Other Atoms and Ions

The many body nature of complex atoms and the importance of spin interactions makes theoretical calculations difficult in the general case. Simplified wave functions can be used, but the accuracy of the resulting cross sections is then difficult to assess. However, in some cases it is possible to make reasonably accurate approximate calculations. In general, where experimental values are available, it is probably best to use them directly if they are absolute measurements, or to use them after normalizing them to the high energy theoretical curves if the measurements are relative ones only. Many of the earlier results are quoted in Refs. 7, 10, 12, 23, and 56.

This section is divided in terms of various groups of atoms, with a final section on collisions with ions. Helium atoms are considered first. Extensive research has been done on helium atom collisions, because helium is monatomic and

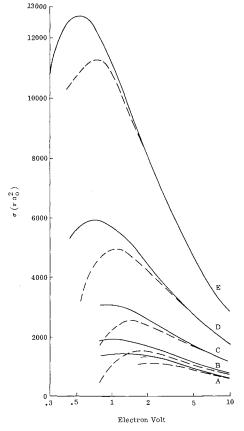


Fig. 6 Born (solid curves) and Bethe (broken curves) total cross sections for the 5-6 transitions of H atoms. A, 5s-6p; B, 5p-6d; C, 5d-6f; D, 5f-6g; E, 5g-6h. (Milford, Morrissey, and Scanlon³¹).

chemically inactive (easier for experiments than, e.g., hydrogen) and the atom has only two electrons (easier to treat theoretically than any atom except hydrogen).

Helium Atoms

Experimental cross sections are available for excitations to many levels and for ionization. Moreover, it has been possible to use the recently developed electron beams of high energy resolution, down to 0.06 ev half-width, in some of these experiments, and it is believed that the experimental results for helium are quite good even near threshold.

In order to illustrate the effect of improving the electron beam energy resolution, Heddle and Seaton¹² compare the results obtained with beams of different energy resolutions (Heddle and Lucas³⁸ and Yakhontova,³⁹ 0.8 ev resolution; Smit,⁴⁰ 0.4 ev resolution) for excitation of 4³S (Fig. 7). It is to be noted that the initial rise in the cross section, which occurs just before the threshold for excitation of the 4³S state, is a result of the unwanted spread in energy of the electron beam due to production by a hot cathode. To a considerable extent, the energy resolution of the beam can be inferred from this measured behavior at threshold and also by the sharpness of the peak.

Recent experimental inelastic results at low and medium energies are given in Refs. 12, 41, and 42. There are also recent measurements for collisions with excited states of helium, in which Robben⁴⁶ finds agreement with the excitation threshold law (5) for the cross sections σ_n , n+1 averaged over the levels with principal quantum numbers n and summed over the levels with principal quantum numbers n+1, in the region E_0 to $E_0+0.3$ ev:

$$\sigma_{2,3} = 110(E - E_0)^{1/2} \pi a_0^2 \tag{13a}$$

$$\sigma_{3,4} = 830(E - E_0)^{1/2}\pi a_0^2 \tag{13b}$$

$$\sigma_{4,5} = 4300(E - E_0)^{1/2}\pi a_0^2$$
 (13c)

(It should be noted that the cross sections are not measured directly, so that some intermediate steps are necessary.)

In general, theory seems to give more accurate results for helium than for hydrogen excitation, ^{10, 12, 34, 44} although there are discrepancies that may result partly from inaccurate wave functions as well as from collision theory approximations. Unlike the hydrogen case, a comparison between theory and experiment is possible for collisions with the excited helium states. Thus, Robben⁴⁶ compares his results [Eq. (13)] with Gryzinski's⁴⁷ classical cross sections and finds agreement within a factor of about 3 for the averaged cross sections. Earlier work^{10, 43, 45} indicated a factor of 5 between theory and experiment for the 2¹S-2³S transition.

There is some preliminary work on ionization from the excited 2^1S and 2^3S states, 50 as well as more detailed studies of the ground state (there is also work on simultaneous excitation and ionization, e.g., Ref. 51). Experimental ionization cross sections have now been measured in detail near threshold 49 , 54 ; these and earlier measurements by Fox 48 confirm that the linear threshold law for single ionization [Eq. (6) with n=1] appears to hold for several electron volts above threshold, and the quadratic $(E-E_0)^2$ law for double ionization [Eq. (6) with n=2] applies for about 20 ev above the threshold. 23 To date, there appear to be theoretical ionization cross sections for the ground state only.

Rare Gas Atoms

Recent experiments on excitation^{12, 42, 52} of the ground states include some measurements near threshold, but also show structure in the cross sections at energies above 500 ev when a resolution of 0.5 ev is employed.

For ionization from the ground state, a considerable amount of work^{23, 49, 53} suggests that the expected threshold behavior of $(E - E_0)^n$ for *n*-fold ionization [Eq. (6)] is followed, at

least approximately, up to about the threshold energy of the first excited state of the resulting ion. In fact, the experiments suggest that (6) may be valid up to n = 6. Of course, in this case the experiments give the shape of the curve resulting from the sum of ionization plus formation of excited ions, whereas in most plasma calculations we need the individual cross sections. The procedure is then to assume the nth power ionization behavior found just above threshold and subtract this from the sum to obtain the cross section for excitation of the first excited state of the ion, and so on. Actually, the measurements indicate a more complex behavior than just outlined; it is possible that autoionization and Auger transitions due to inner shell ionization may contribute to these complexities. The foregoing remarks refer to the shapes of the curves; the absolute magnitudes are not well known.

Alkali Metals Li, Na, K, Rb, Cs

Because of the single valence electron it is possible to treat these theoretically as hydrogen-like in a first approximation, although theoretical calculations of varying degrees of greater complexity have been carried out. In addition to earlier work, ^{12, 23} there have been recent calculations of Li ionization, ⁵⁵ Na 3s-3p excitation, ³⁴ experimental measurements of Li, Na, K, Rb relative ionization cross sections, ⁵⁷ and inelastic Cs cross sections. ⁵²

Of particular interest is the verification of the $(E - E_0)^n$ threshold ionization law for production of Na⁺, Na⁺⁺, and Na⁺⁺⁺ from Na over a considerable range of energy above the respective thresholds⁵⁸ (see Fig. 8); in this case the first excited states are far above the thresholds (e.g., 33 ev above threshold for Na⁺⁺).

The comparison of the lithium experimental relative ionization cross sections⁵⁷ and the Born-Coulomb calculations⁵⁵

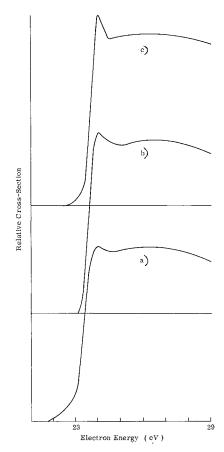


Fig. 7 Excitation functions by electrons for He $4^3S - 2^3P$ near threshold; a) Heddle and Lucas, 38 b) Yakhontova, 39 and c) Smit. 40 Adapted from Heddle and Seaton. 12

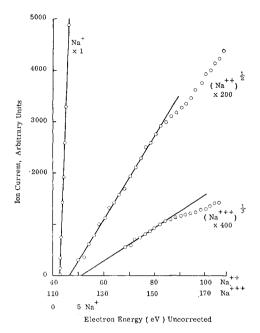


Fig. 8 Ionization probability curves for Na⁺⁺, Na⁺⁺, and Na⁺⁺⁺ ions. The first power, square root, and cube root of the respective ion currents are plotted against the uncorrected ionizing voltage (Dibeler and Reese⁵⁸).

gives moderate agreement in the threshold region, with differences of about a factor of 3 in the region between threshold and maximum.

Nitrogen and Oxygen

Because of their importance in atmospheric processes, it is gratifying that there are recent measurements of ionization cross sections for oxygen and nitrogen atoms.

The nitrogen absolute ionization cross sections have been measured from 25–750 ev⁵⁹ and at 2.5 kev,⁵³ for the sum of single and multiple ionizations; the multiple ionization is expected to be a very small fraction of the single ionization so that the total ionization curve can be compared with the theoretical (Bethe type) cross section for single ionization⁶⁰ (Fig. 9). The agreement is fair but for our present purposes we hope that the threshold region will be further studied, and also that the atomic nitrogen beams now available will be used for excitation measurements.

Oxygen ionization is currently being studied in the threshold region by Fite and Brackmann,⁵⁰ with their preliminary results shown in Fig. 10. There is a definite break in the ionization efficiency curves at 15.2 ev, but it is not yet clear whether this is associated with ionization of the ground (³P)

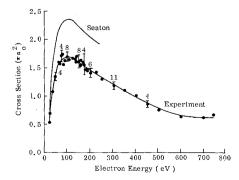


Fig. 9 Cross sections for ionization of atomic nitrogen by electron impact (Smith, Caplinger, Neynaber, Rothe, and Trujillo⁵⁹).

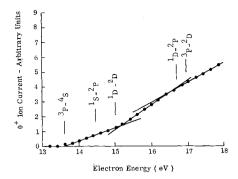


Fig. 10 Ionization efficiency for O^+ production using a gas discharge in pure O_2 , showing the well-defined break at 15.2 ev and a less well-defined downward break at about 16.6 ev. The known thresholds for ionization from given atom to given ion states falling within the energy range of the figure are indicated (Fite and Brackmann⁵⁰).

state or the lower metastable (¹D) state. In the latter case, the cross section measured would be for

$$e + 0({}^{1}D) \rightarrow 2e + 0 + ({}^{2}D)$$

Measurements²² at higher energies of the absolute cross section for ionization of the oxygen ground state are compared with theoretical values⁶⁰ in Fig. 11. It appears that we should have accurate, absolute, ionization cross sections at all energies in the very near future.

On the theoretical side, Seaton and others have studied transitions between the terms of the p^4 ground configuration of oxygen, etc.^{6, 7}

Other Atoms

These will not be discussed here. Recent work was summarized at the London and Paris Conferences. $^{12.~61-65}$

Collisions with Ions

Experimental difficulties are such that there are no measurements of the excitation of ions to date; however, in the last two years there have been measurements of the *ionization* cross sections^{66, 67} for He⁺, Ne⁺, and N⁺.

Fortunately, the theoretical calculations are more accurate for ions (at least for highly ionized ones) than for atoms because the Coulomb interaction dominates other perturbing potentials. (The same is true for inner-shell ionization of atoms.) In fact, for strictly hydrogenic ions, the Coulomb-Born-Oppenheimer approximation becomes exact as the nuclear charge $Z \to \infty$ for excitation as well as for ionization. Among recent calculations^{61, 62, 64, 65, 68–70} we

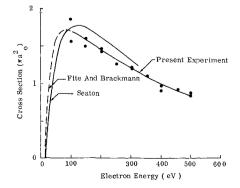


Fig. 11 Cross sections for ionization of atomic oxygen by electron impact (Rothe, Marino, Neynaber, and Trujillo²²).

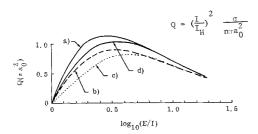


Fig. 12 a) C.B.O., z = 50; b) z = 2, experimental results (Dolder et al., 1961); c) z = 1, experimental results (Fite and Brackmann⁵); d) C.B.e, z = 2. Adapted from Burgess and Rudge.⁶⁸

give the results of Burgess and Rudge for ionization of hydrogenic positive ions in terms of scaled cross sections

$$Q = (I/I_H)^2(\sigma/n\pi a_0^2)$$

where I_H is the ionization energy of hydrogen, I the ionization energy of the ion, n the effective number of atomic electrons (n=1 here), and the energy units $E_0=I$ are used. In Fig. 12, adapted from their paper, ⁶⁸ it can be seen that the Coulomb-Born exchange results for He⁺, Z=2 are in excellent agreement with experiment; this is very pleasing for such a small Z value. The Z=1 (H atom) experimental and Z=2 (He⁺) experimental curves combined with the theoretical Z=50 curve give a progression that should enable interpolations to be made for other ions of different Z,I, and equivalent electrons n.

Similar remarks apply to interpolation of cross sections for the excitation of ions, except that the $Z=1,\,2,\,\ldots$ curves are all theoretical. ^{10, 12}

Thus, for large Z, and not many electrons (n small), the theoretical cross sections for excitation and ionization should be quite accurate even near threshold.

Heavy Particle Inelastic Collisions

Since most of the heavy particle collisions (we exclude charge transfer) do not contribute appreciably to the inelastic collision processes in a thermal plasma, our treatment of them is correspondingly reduced. The recent reviews by Dalgarno,⁷¹ Bates,⁷² Gerjuoy,²⁴ and Fite²³ consider various aspects of heavy particle collisions.

From the point of view of thermal plasmas, the major experimental difficulty arises from the fact that heavy particle cross sections reach their maxima at energies where their relative velocities are approximately equal to the corresponding electron collision velocities, so that the energies involved are of the order of tens of kilovolts, far from the thermal region of interest here. The result is that at 10 ev the cross section will be smaller by some orders of magnitude than at maximum, making it extremely difficult to measure it experimentally. Currently, however, with the improvement of experimental techniques, measurements are being extended down into the tens of electron volts region.

The theoretical situation is almost hopeless for the most general types of heavy particle collisions in the thermal region. There are many more possible scattering channels than in the electron case, particularly when the heavy particle is not a bare nucleus and can therefore undergo excitation or ionization itself. Perhaps even worse, from the viewpoint of thermal plasmas, is the fact that the validity of most approximations depends on the relative velocity between the colliding systems being large; a proton of energy 10 ev has the same velocity as an electron of energy about 5 mev. There are some particular types of inelastic collisions, such as heavy particle ionization of inner shells of atoms, where even the Born approximation gives accurate calculations down to the threshold region. Also, it has been found

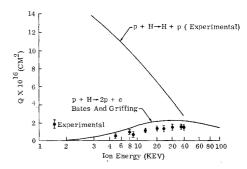


Fig. 13 Cross section for ionization of the hydrogen atom on proton impact, comparing the theoretical prediction of Bates and Griffing and the cross section for charge transfer (Fite, Stebbings, Hummer and Brackmann⁷⁷).

that the Born ionization law $\alpha \sim (1/E) \log E$ for high energies holds even at relatively "low" energies ($\sim 50 \text{ keV}$).

We consider heavy particle collisions with ground-state and excited hydrogen atoms, and with other atoms.

Heavy Particle Collisions with Hydrogen Atoms

Most of the numerous experimental measurements^{23, 73, 73, 80, 86, 87} are at much higher energies than thermal, and some of these are for molecular hydrogen. The lowest energies for which cross sections have been derived appear to be about 7 kev for ionization by protons⁷⁷; these results indicate that the theory probably overestimates the cross section in the few kev region, but it is not possible to make any definite statements about the threshold region yet.

There have been calculations for ionization⁷² and for excitation of various excited states of hydrogen by proton impact^{72, 81} and by hydrogen or other atom or ion impact.⁷²

Figures 13 (H atom)⁷⁷ and 14 (H molecule)⁸⁰ compare some of the experimental and theoretical ionization curves. It is not justified to interpolate between the threshold point and the low energy experimental points!

Heavy Particle Collisions with Excited Hydrogen Atoms

The only experiments⁸⁸ are the ones where a 10 mev beam of hydrogen atoms mostly in states n=5–9 is passed through a hydrogen gas cell; excitation cross sections for hydrogenexcited hydrogen collisions can be inferred for transitions such as 5–6, 5–7, . . . , 8–9, etc.

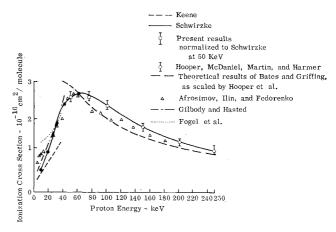


Fig. 14 Total ionization cross section for protons in hydrogen gas. The cross sections obtained in the Kuyatt and Jorgensen work are used to connect the low-energy results of Schwirzke and the high-energy results of Hooper et al. Results of other experiments and theory are shown for comparison (Kuyatt and Jorgensen⁸⁰).

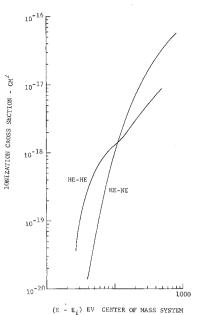


Fig. 15 He-He and He-Ne ionization cross section (Utterback⁸⁴).

Born calculations have been made for excitation of various states in the range n=2–13 by proton collisions^{19, 89} and by hydrogen atom collisions.⁹⁰ For the H + H* collisions the extrapolation of the available theoretical results⁹⁰ appears to agree approximately with the experimental results,⁸⁸ but since the energy is 10 mev the Born approximation would be expected to be accurate anyway.

It is interesting to note that for collisions with n=10-30 levels, the electron cross sections may peak near 0.001-0.1 ev, and the proton cross sections near 1-100 ev, so that in a hydrogen plasma the proton collisions may dominate the electron collisions for many of the upper levels.

Heavy Particle Collisions with Other Atoms

Utterback⁸⁴ has carried out experiments of He-He and He-Ne ionization at laboratory energies down to 40 $\,\mathrm{cv}$ (Fig. 15). As expected, the cross sections are very small at the lowest energies, $\sim 10^{-4}~\pi a_0^2$, and, therefore, are not competitive with electron collisions with ground states, although for highly excited He and Ne states the situation might be reversed.

There is considerable work at higher energies on collisions of $\mathrm{H^+}$, H , $\mathrm{He^+}$, $\mathrm{Ne^+}$, $\mathrm{A^+}$, $\mathrm{Kr^+}$ with the inert gases^{75, 76, 78, 82, 83, 85–87} (Fig. 16 from the paper by Gilbody and Lee gives the cross section for ionization of krypton by protons).

Appendix: Theory of Electron Collisions with Hydrogen Atoms

Most of the types of approximate theories used can be illustrated in terms of a rearrangement binary collision such as (2a). More detailed treatments of inelastic atomic collision theory can be found in the books and articles by Massey,⁶⁻⁸ Mott and Massey,⁹ Seaton,¹⁰ and Burke and Smith.¹¹

Denoting the complete set of internal coordinates (including spins) of "atom" A by a, and its state by m, a general binary collision can be expressed:

$$A(m|a) + B(n|b) \rightarrow C(m'|c) + D(n'|d)$$

The center of mass system and reduced masses M_{AB} are used in the theory, as are the known solutions for the isolated systems A, B, C, D:

$$M_{AB} = \frac{M_A M_B}{M_A + M_B}$$
 $(H_A - E_{Am}) \psi(Am | a) = 0$ (A1)

where H_A is the Hamiltonian, ψ the wave function, and E_{Am} an eigenvalue for atom A. When atom A is far from atom B, the system Hamiltonian is

$$H_{AB} = H_A + H_B + T_{AB} \tag{A2}$$

where

$$T_{AB} = -\frac{\hbar^2}{2M_{AB}} \nabla_{AB}^2 \tag{A3}$$

is the kinetic energy operator for the relative motion in the center-of-mass system, r_{AB} being the vector between the centers of mass of atoms A and B.

The scattering can then be calculated from the system wave equation

$$(H - E)\Psi = 0 \tag{A4}$$

with the appropriate boundary conditions and using appropriately symmetrized wave functions. Here H is the Hamiltonian for the interacting system,

$$H = H_{AB} + H_{AB}' = H_{CD} + H_{CD}'$$
 (A5)

where H_{AB}' , H_{CD}' are the interaction terms. The usual method of solution is to expand Ψ in terms of the complete orthonormal set of functions $\psi(Cm'|c) \psi(Dn'|d)$:

$$\Psi = \sum_{m',n'} F(m'n'|r_{CD})\psi(Cm'|c)\psi(Dn'|d) \qquad (A6)$$

which reduces the wave equation to

$$(-\nabla_{CD}^{2} - k^{2})F(m'n'|r_{CD}) = -\frac{2M_{CD}}{\hbar^{2}} \iint \psi^{*}(Cm'|c)\psi^{*}(Dn'|d)H_{CD}'\Psi d\tau_{C}d\tau_{D}$$
(A7)

$$k^2 = \frac{2M_{CD}}{\hbar^2} (E - E_{Cm'} - E_{Dn'})$$

By introducing the effective interaction

$$V(m'n'|r_{CD}|m''n'') = ff\psi^*(Cm'|c)\psi^*(Dn'|d)H_{CD}\psi(Cm''|c)\psi(Dn''|d)d\tau_Cd\tau_D$$
(A8)

the unsymmetrized formulation thus gives an infinite set (all m', n') of coupled differential equations:

$$(-\nabla_{CD}^{2} - k^{2})F(m'n'|r_{CD}) = -\frac{2M_{CD}}{\hbar^{2}} \sum_{m'',n''} V(m'n'|r_{CD}|m''n'')F(m''n''|r_{CD}) \quad (A9)$$

To simplify the discussion, we shall now restrict consideration to electron collisions with hydrogen atoms, with A = C = electron, B = D = hydrogen atom, and r_1 and r_2 the electron coordinates. Then the unsymmetrized case for the

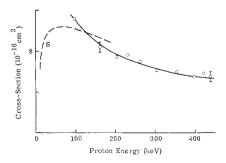


Fig. 16 Ionization of krypton by protons. S, Solov'ev et al., 86 cross section for production of electrons σ_e ; -0-, Gilbody and Lee, 74 total ionization cross section σ_+ (Gilbody and Lee⁷⁴).

electron is merely (A9) with m', m'', and the m'' summation, deleted. The symmetrized case can be derived similarly; in terms of the exchange operator W defined by

$$W(n|r_2|n')F(n'|r_2) =$$

$$\int \psi^*(n|r_1) [H - E] F(n'|r_1) d\tau_1 \psi(n'|r_2)$$
 (A10)

the exact solution is given by the infinite set (all n) of coupled integrodifferential equations

$$(-\nabla^{2} - k^{2})F^{\pm}(n'|r) = -\frac{2m}{\hbar^{2}} \sum_{n''} [V(n'|r|n'') \pm W(n'|r|n'')]F^{\pm}(n''|r) \quad (A11)$$

plus the boundary conditions. Here m is the reduced electron mass. The asymptotic solutions must be combined in the correctly symmetrized fashion. In the present case, F^+ corresponds to the electron spins antiparallel and F^- to the spins parallel. The correct inelastic cross section is then

$$\sigma(n|n') = (k_n'/k_n) \frac{1}{4} \{ |f^+|^2 + 3|f^-|^2 \}$$
 (A12)

where $\hbar k_n(\hbar k_n')$ is the incident (final) electron momentum at

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